

**Exploring the alteration of river-derived particles in
estuaries and its implication on elemental cycles:
evidence from lithium isotopes**

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I, Chunyao Liu, confirm that the work presented in this thesis is my own. Where information has been derived from other sources, I confirm that this has been indicated in the thesis.

Abstract

The estuary zone is the critical area that connects the continent to the oceans. Every year, global rivers transport billions of tonnes of continental weathering products, including both dissolved material and solid material (i.e., river-derived particles), to the ocean through estuaries. In principle, the river-derived particles can be further altered during sediment-water interaction in estuaries, such as by mineral dissolution and secondary mineral formation, similar to continental weathering processes. The alteration of river-derived particles in the estuary may influence element cycling in the ocean, the fate of alkalinity, and organic carbon burial. Although lithium (Li) isotopes are regarded as a good tracer for the carbon burial efficiency of silicate weathering, the influences of the alteration of river-derived particles in the estuary on global Li cycling have not been investigated widely. In this study, four series of interaction experiments were conducted to imitate natural estuarine processes and two natural estuaries, the Borgarfjörður estuary (Iceland) and the Amazon estuary were explored. To better distinguish the influence of different fractions (i.e., exchangeable, carbonate, oxide, clay, and residue) in the solid load, a sequential extraction method of silicate solid samples was developed. The element concentrations (e.g., Na, Ca, Mg, K, Fe, Al, and Mn) and Li isotope compositions were examined. The Li concentrations and Li isotope compositions in the dissolved load and the different fractions of the solid load indicated net uptake of Li from the dissolved load by the solids, mainly the clay fraction, with accompanying Li isotope fractionation, during the alteration of river-derived particles in estuaries. River-derived particles were estimated to uptake $\sim 1\text{--}4\text{ }\mu\text{g}$ of Li per gram, with Li isotope fractionation between solids and seawater of -17.1 to -24.0‰ . The estuarine Li uptake is likely to be a significant Li sink in the ocean with the high dissolved Li concentration in the estuarine zone likely to be the main reason for the Li uptake. Furthermore, the analysis of Li isotopes and element concentrations implied the formation of oxides and clays in estuaries, which, on the one hand, may hinder alkalinity sequestration in marine carbonates, but, on the other hand, may enhance organic carbon formation and burial.

Impact statement

This study has benefited both inside and outside of academia. First, this study improved the sequential chemical extraction method for exchangeable, carbonate, oxide, and clay fractions from silicate solids for Li isotopes, which can be widely used on the silicate solid samples in the future. It also provided a lot of data (i.e., Ca, Mg, K, Fe, Mn, and Al concentrations and Li isotopes) of fractions in reference materials, which aims with the inter-laboratory comparison. Second, this study reported Li isotope data from the Amazon estuary, one of the largest rivers in the world, for the first time, which benefits the understanding of the global Li cycle. Third, this study developed a model to estimate the estuarine Li removal flux, which could be applied to other estuaries. Fourth, this study revealed that the estuarine alteration of river-derived particles is likely related to the continental erosion rate. Thus, the factors that influence continental erosion probably also influence the alteration of river-derived particles in estuaries. Besides natural factors, such as tectonic activity, human activities also affect the flux and characteristics of river-derived particles in the estuary. For example, changes in land use (e.g., deforestation, cultivation) may increase the supply of river-derived particles, whereas dam construction can reduce the flux of particles transported into the estuary. As such, this study suggests that it is important to evaluate the influence of human activities on river-derived particles. Fifth, this study revealed that oxide and clay formation occur during the alteration of river-derived particles in estuaries, which may enhance the organic burial in the estuarine zone, whereas clay formation may hinder alkalinity burial as marine carbonate. Thus, the alteration of river-derived particles in the estuary may have important implication for carbon storage and sequestration.

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Table of Contents

Chapter 1. Introduction	23
1.1 The importance of alteration of river-derived particles in estuaries	23
1.2 Lithium and Li isotopes as promising tracers of silicate weathering	28
1.2.1 Lithium and Li isotopes background	28
1.2.2. Lithium and Li isotope behaviour during silicate weathering and its implications	32
1.2.3. The Li cycle in the modern ocean	38
1.2.4 Lithium isotopes tracing weathering regimes in geological time	41
1.2.5 Previous studies on Li and Li isotope behaviour during the alteration of river-derived particles in an estuary	43
1.3 Research aims and outline	46
1.3.1 Research aims	46
1.3.2 Research outline	46
Chapter 2. Methods.....	49
2.1 Sample collection.....	49
2.2 Reagent preparation	49
2.3 Chemical preparation for concentration and isotope analysis.....	50
2.3.1 Dissolved load samples	50
2.3.2 Solid samples	51
2.4 Elemental concentration analysis	54
2.5 Lithium isotope analysis.....	56
2.5.1 Chemical separation of lithium.....	57
2.5.2 MC-ICP-MS analysis	58
2.6 Other analysis	60
Chapter 3. Leaching method exploration	61
3.1 Introduction	61
3.2 Oxide leaching method trials.....	63
3.2.1 Materials and leaching methods	63
3.2.2 Leaching experimental trial design	66

3.2.3 Influence of temperature.....	72
3.2.4 Influence of leaching time.....	78
3.2.5 Influence of the reagent/solid ratio.....	80
3.2.6 Comparison of Tessier, weak, and strong oxide leaching methods	82
3.3 Full sequential leaching procedure	86
3.3.1 Full sequential leaching trials.....	86
3.3.2 Reproducibility and accuracy of the full sequential leaching.....	90
3.3.3 The interplay among the full sequential extractions	92
3.4 Conclusions	97
Chapter 4. Solid-water interaction experiments with salinity increasing ..	99
4.1 Introduction.....	99
4.2 Experiment design	100
4.2.1 Setup of interaction experiments	101
4.2.2 Interaction experiments and sampling	104
4.3 Results.....	106
4.3.1 Basalt-water experiments	106
4.3.2 Loess-water experiments.....	115
4.4 Discussion	116
4.4.1 Major element behaviour	116
4.4.2 Lithium concentration and isotope behaviour	127
4.5 Conclusions	134
Chapter 5. Alteration of river-derived particles in a basaltic river estuary, Borgarfjörður, Iceland	135
5.1 Introduction.....	135
5.2 Sample collection.....	138
5.3 Results.....	140
5.3.1 Dissolved load	140
5.3.2 Suspended load samples	145
5.3.3 Bedload samples	157
5.4 Discussion	165
5.4.1. Dissolved load	165
5.4.2 Suspended particles and bedload particles	166
5.4.3 Estimated Li flux from Li incorporation into sediments in the	

estuary.....	176
5.5 Conclusions	177
Chapter 6. Alteration of river-derived particles in the Amazon estuary ...	179
6.1 Introduction	179
6.2 Study area and sampling	180
6.3 Results.....	185
6.3.1 Dissolved load	185
6.3.2 Solid samples	193
6.4 Discussion	200
6.4.1 Uptake of Li by solids from the dissolved load	200
6.4.2 Retention of major cations during estuarine weathering	214
6.4.3 Mechanical sorting and chemical alteration of bulk sediments	222
6.5 Conclusions	227
Chapter 7. Synthesis and implications	229
7.1 Influence of estuarine weathering on the Li cycle	229
7.1.1 Li behaviour during estuarine weathering	229
7.1.2 Factors influencing Li behaviour during estuarine weathering	232
7.1.3 Importance of estuarine weathering for the Li cycle of the modern ocean and implications for ancient oceans	235
7.2 Influence of estuarine weathering on major element cycles and implications for the global carbon cycle	239
7.2.1 Behaviour of mobile major elements (Na, Ca, Mg, and K) and implications for ocean biogeochemistry	239
7.2.2 Behaviour of immobile elements (Fe, Mn, and Al) and implications for ocean biogeochemistry	242
7.3 Conclusions	244
Chapter 8. Conclusions and prospects	245
Bibliography	249
Appendix: Supplementary Tables	285

List of Tables

Table 2.1 The elemental concentrations of SRM 88A determined by ICP-OES in this study and previously reported.	55
Table 2.2 The elemental concentrations of SGR-1 determined by ICP-MS in this study and previously reported.....	56
Table 2.3 The procedure of cation-exchange columns for Li purification.	58
Table 3.1 Elemental composition of bulk solids.....	65
Table 3.2 List of oxide leaching method experimental trials.	68
Table 3.3 Elemental concentrations and Li isotopes of oxide leaching method experimental trials.....	70
Table 3.4 Elemental concentrations and Li isotopes of replicate samples.	87
Table 4.1 Formula of concentrated artificial seawater.	102
Table 4.2 Element concentrations and Li isotope values in fractions of the solid and the bulk solid.	112
Table 5.1 Sampling locations in the Borgarfjörður estuary.	139
Table 5.2 Data of dissolved load samples collected in 2017.	141
Table 5.3 Element concentrations and Li isotopes in leached fractions in suspended load samples collected in 2017.	148
Table 5.4 Element concentrations and Li isotopes in leached fractions and bulk solutions in bedload samples collected in 2008.	160
Table 6.1 Sampling locations in the Amazon estuary	184
Table 6.2 Chemistry and Li isotope compositions of the dissolved load samples	187
Table 6.3 Elemental concentrations and Li isotope compositions for different phases of the MUC and SPM samples	188

List of Figures

Figure 1.1 Schematic diagram of weathering.....	25
Figure 1.2 Range of $\delta^7\text{Li}$ values in natural reservoirs	31
Figure 1.3 Li isotope fractionation between different fractions in solids and the solution in low temperature experiments ($< 25\text{ }^\circ\text{C}$)	34
Figure 1.4 Lithium cycle in the modern ocean	40
Figure 1.5 Synthesis of published dissolved Li concentration and isotope data in modern estuaries.	45
Figure 2.1 Chemical extraction procedure for solid samples.	53
Figure 3.1 Elemental concentrations in the experimental trials of the Tessier oxide leaching method as a percentage of the total elemental concentrations of each bulk solid.....	73
Figure 3.2 Fe and Li concentrations and Li isotopes in oxide leachates from leaching experimental trials.	74
Figure 3.3 Li concentrations and Li isotopes in oxide leachates of SGR-1b using different reagent/solid ratios in Tessier oxide leaching experimental trials.	82
Figure 3.4 Li concentration-Li isotope diagrams and Mn-Mg-Fe ternary diagrams of oxide leaching trials of RS, RRS, and BCR-2.	85
Figure 3.5 Frequency histogram of relative standard deviations of elemental concentrations in fractions in repeated full sequential extractions.	91
Figure 3.6 Li concentrations and Li isotopes in each fraction from the repeated full sequential leaching for BCR-2, RS, Bed10, and YR.	96
Figure 4.1 Locations of natural sediments for the initial solids in the interaction experiments.	103
Figure 4.2 Dissolved major element concentrations (Ca, Mg, K, and Na) through	

time in four interaction experiments.	108
Figure 4.3 Li concentration and Li isotopes in dissolved load samples in four interaction experiments during the preconditioning stage (0–33 days), the salinity-increasing stage (33–51 days, and the first 4 days after the salinity-increasing stage (51–55 days).....	109
Figure 4.4 Li concentration and Li isotopes in dissolved load samples in four interaction experiments during the after-salinity-increasing stage (after 51 days).....	110
Figure 4.5 Element (Ca, Mg, K, Na, and Li) transfer from solid to dissolved load in four interaction experiments.....	119
Figure 4.6 Si transfer and pH variation with interaction time in four interaction experiments.	123
Figure 4.7 Mineral saturation index calculated in the two basalt-water interaction experiments from 0 to 39 days.....	126
Figure 4.8 The relationship between dissolved Li concentration at the highest salinity step and dissolved Li concentration at steady state.....	129
Figure 4.9 Lithium transfer during the salinity-increasing stage and after the salinity-increasing stage in the basalt-Li-add experiment.	132
Figure 5.1 Setting of the Borgarfjörður estuary and sampling locations.....	137
Figure 5.2 Dissolved Li concentrations and Li isotopes.	142
Figure 5.3 Dissolved concentrations of major elements (Na, Mg, K, and Ca), alkalinity, and Si.	143
Figure 5.4 Mineral saturation indices.	144
Figure 5.5 Concentrations of the major elements (Ca, Mg, K, Al, Fe, and Mn) in the different leached fractions (i.e., exchangeable, carbonate, oxide, and clay) of the suspended load samples.....	152
Figure 5.6 Li concentrations and Li isotopes in the different fractions (i.e., exchangeable, carbonate, oxide, clay, and residue) and the bulk of the	

suspended load and bedload samples.	153
Figure 5.7 Comparison of soluble elements (K, Mg, Ca, and Li) and Li isotopes between the dissolved load and the exchangeable fraction in the solid samples.	154
Figure 5.8 Major elements (Ca, Mg, K, Fe, Mn, and Al) in the bulk suspended load and bedload samples.	155
Figure 5.9 Li concentrations and Li isotopes in the bulk suspended load and bedload samples.	156
Figure 5.10 Concentrations of major elements (Ca, Mg, K, Al, Fe, and Mn) in different fractions (i.e., exchangeable, carbonate, oxide, and clay) of the bedload samples.	163
Figure 5.11 The proportion of Li in different fractions in the bedload samples.	164
Figure 5.12 Schematic of likely multiple processes operating in the Borgarfjörður estuary. Not to scale.	167
Figure 5.13 The relationship between Li isotopes and Li concentrations in the bulk suspended load and bedload samples.	171
Figure 5.14 Calculated Li isotope fractionation between the leached secondary fractions of the bedload samples and seawater.	175
Figure 6.1 Setting of the Amazon estuary and sampling locations.	183
Figure 6.2 Dissolved load Li concentrations and Li isotope compositions.	186
Figure 6.3 Elemental concentrations for different fractions of the sediment samples.	197
Figure 6.4 Lithium concentrations and isotope compositions for different fractions of solids.	198
Figure 6.5 Element concentrations in bulk solids.	199
Figure 6.6 $\delta^7\text{Li}$ values versus $1/\text{Li}$ for the different fractions of the sediment samples in the north channel transect.	204
Figure 6.7 Modelled Li isotope fractionation by sediment removal.	209

List of Figures

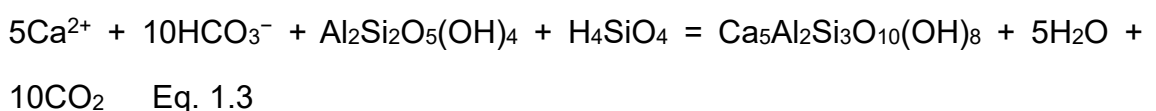
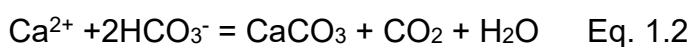
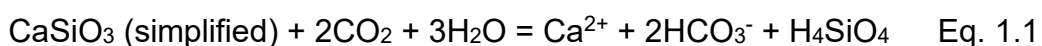
Figure 6.8 Modelled Li loss from the dissolved load through the estuary.....	213
Figure 6.9 The adsorption of cations by the exchangeable fraction.	215
Figure 6.10 The retention of cations in oxide fractions.....	216
Figure 6.11 The retention of cations in the clay fractions.	219
Figure 6.12 Stability diagrams of K-aluminosilicate and Na-aluminosilicate. ..	220
Figure 6.13 Saturation index (SI) for selected minerals in the Amazon estuary.	221
Figure 6.14 Relationships between Al, Si, and Li concentrations, and Li isotopes, of bulk sediment samples from the Amazon.	225
Figure 6.15 Relationship between bulk Al/Si ratios and BET surface area in the MUC sediment samples.....	226
Figure 6.16 SEM images for sediment samples 24MUC and 85MUC.	227
Figure 7.1 Synthesis of dissolved Li concentration and isotope data in modern estuaries.	231

Chapter 1. Introduction

1.1 The importance of alteration of river-derived particles in estuaries

Weathering is a critical process in climate stabilization and global elemental cycling (e.g., Walker et al., 1981; Berner and Berner, 1996; Gíslason et al., 2009). Weathering on the continents is widely investigated (e.g. Nesbitt and Young, 1989; White and Blum, 1995; Gaillardet et al., 1997; West et al., 2005; Gíslason et al., 2009; Bouchez et al., 2013). On the continents, weathering includes physical weathering, i.e., erosion (E), and (bio)chemical weathering (W) (Figure 1.1) (Gíslason and Oelkers, 2011; Bouchez et al., 2013). Erosion can directly produce a huge amount of particles that can be transported by rivers (i.e., suspended sediments and bedload sediments) into the ocean through estuaries (Oelkers et al., 2011, 2012). These river-derived eroded particles may be further altered in the estuary. In addition, erosion also provides the fresh materials for chemical weathering (West et al., 2005; Gíslason and Oelkers, 2011; Bouchez et al., 2013).

On the one hand, chemical weathering, and especially the hydrolysis of silicates, can consume atmospheric CO₂ and produce alkalinity, dissolved cations, and dissolved silica (Eq. 1.1) (Walker et al., 1981). If this dissolved load is transported by rivers to the ocean, and the alkalinity and cations precipitate as carbonates in the ocean (Eq. 1.2), there will be a net burial of atmospheric CO₂ into the ocean, which further influences Earth's temperature and climate (Walker et al., 1981; Berner et al., 1983).



On the other hand, secondary mineral formation (e.g., oxide and clay minerals) also tends to occur during weathering (Eq. 1.3) (Gíslason et al., 1996; Stefánsson and Gíslason, 2001; West et al., 2005). Secondary mineral formation can retain the cations dissolved from primary rocks in their exchangeable sites or structural sites, and reverts the alkalinity to CO₂ (Pogge von Strandmann et al., 2020a; Tipper et al., 2021). Thus, these cations and alkalinity cannot precipitate as carbonates in the ocean, so there is no or less net CO₂ burial (Gíslason and Oelkers, 2011; Pogge von Strandmann et al., 2020a; Tipper et al., 2021). Meanwhile, the continent-formed secondary minerals can be transported as suspended load and/or bedload sediments by rivers to the ocean through estuaries (Oelkers et al., 2011, 2012). These river-derived secondary minerals may also be further altered in the estuary. Continental weathering also provides nutrients (e.g., N, P, and Si) and organic matter to the ocean, which also plays a significant role in ocean biogeochemistry and the carbon cycle, such as through marine primary production and organic carbon burial (Mukhopadhyay et al., 2006; Galy et al., 2007; Cotrim da Cunha et al., 2007; Kennedy and Wagner, 2011; Holmes et al., 2012; Kennedy et al., 2014).

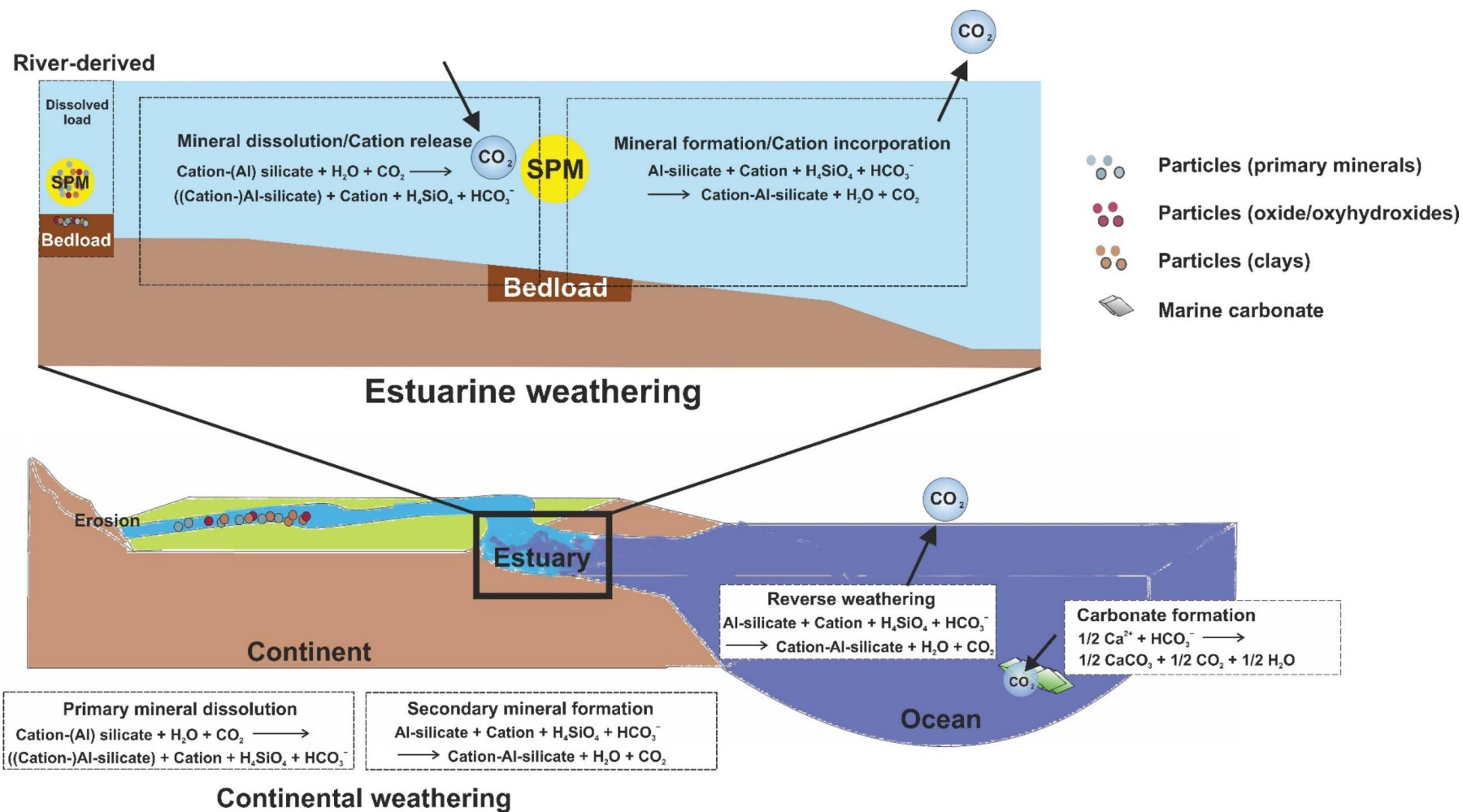


Figure 1.1 Schematic diagram of weathering.

Not to scale. SPM represents suspended particulate matter.

Continental weathering is influenced by multiple factors, such as temperature, rainfall, topography, lithology, and plants (Stallard, 1985; West et al., 2005; Gíslason and Oelkers, 2011). Generally, based on the limiting factors in the weathering zone, the weathering regime is divided into kinetically limited (i.e., weathering limited) and supply limited (i.e., transport limited) weathering regimes (West et al., 2005; Dellinger et al., 2015). A weathering area located in high-relief mountains and/or cold areas has a low weathering intensity. These weathering regimes are kinetically limited (i.e., weathering limited), in that the chemical weathering reaction is the limiting factor, and these regimes are therefore more sensitive to climatic changes. Conversely, a weathering area located on large plains and/or warm areas usually has high weathering intensity. It is supply limited (or transport limited). Here, fresh rock supply (i.e., physical erosion) is the main limiting factor of weathering because weathering is sufficiently fast to completely chemically alter all the supplied weatherable material.

The estuary zone connects the continent to the oceans via complicated multiple processes to rapidly change from a river system to a marine system (Sholkovitz, 1976; Berner and Berner, 1996; Meade, 1996). Every year, global rivers transport billions of tonnes of continental weathering products to the ocean through estuaries, including both dissolved material ($\sim 1.0\text{--}3.8 \times 10^{12}$ kg/yr) and solid material (i.e., river-derived particles) ($\sim 1.8\text{--}3.0 \times 10^{13}$ kg/yr) (Milliman and Farnsworth, 2011; Oelkers et al., 2011). The dissolved load includes dissolved cations, alkalinity, silica, nutrients, etc., and the river-derived particles include the eroded primary minerals from physical erosion and the secondary minerals formed during continental chemical weathering (Milliman and Farnsworth, 2011; Oelkers et al., 2011). The river-derived particle flux is significant as it is $\sim 5\text{--}20$ times greater than the dissolved fluxes (Meade, 1996; Milliman and Farnsworth, 2011; Oelkers et al., 2012). Furthermore, most modern river-derived particles settle out and accumulate in the estuarine zone (e.g., deltas near estuaries,

coastlines along shores, continental shelf), rather than being transported further into the deep ocean (Meade, 1996; Milliman et al., 1999; Geyer et al., 2004; McKee et al., 2004; Liu et al., 2007). The river-derived particles, especially oxide and clay particles, may settle in association with organic matter and therefore enhance organic carbon burial and influence the global carbon cycle (Kennedy and Wagner 2011, Bianchi et al., 2015). Furthermore, because of the difference in the aqueous chemistry between continents and estuaries, in principle, some of the river-derived particles may be further altered during sediment-water interaction in the estuary, which is named as ‘estuarine weathering’ here (Figure 1.1). ‘Estuarine weathering’ is used to refer to the alteration of river-derived particles in a salinity range of 0 to 35 in the estuary before the particles are buried and diagenetically altered. Theoretically, estuarine weathering, similar to continental weathering, includes both mineral dissolution causing element release and CO₂ consumption, and mineral formation causing element incorporation. Notably, if the cations are incorporated into aluminosilicates instead of carbonate, there is no carbon burial in the ocean and therefore no net atmospheric CO₂ consumption (Berner and Berner, 1996). This formation of aluminosilicates in the ocean, including in the estuary, on the continental shelf, and/or at the ocean floor, has been termed as ‘reverse weathering’ in some previous studies (Mackenzie and Garrels, 1966; Mackenzie and Kump, 1995; Krissansen-Totton and Catling, 2020). Different from the reverse weathering which is thought to be mainly controlled by the ocean fluid geochemical cycle, especially the silica (opal) cycle (Garrels, 1965; Michalopoulos and Aller, 2004; Rahman et al., 2017; Krissansen-Totton and Catling, 2020), the alteration of river-derived particles in the estuary is likely to be influenced by continental erosion and the chemical weathering regime in the catchment area (Oelkers et al., 2011). Thus, the river-derived particles may have significant effects on biogeochemical cycles in the estuarine zone, and therefore in the ocean.

Except for the most mobile major cation Na, almost all other elements, including Ca, Mg, and Li, have a greater input flux to the ocean carried by particulate material than by the dissolved load (Oelkers et al., 2011), such that particulate-dissolved interactions in the estuaries should be explored. The previous studies showed that more than 70% of the dissolved Fe, 25–45% of the dissolved Mn, and 20–50% of the dissolved Al transported by river water can be removed in estuaries, because of flocculation, complexation, and adsorption (Boyle et al., 1977; Hydes and Liss, 1977; Sholkovitz, 1978; Morris et al., 1986; Zhu et al., 2018). In contrast, dissolved Na, K, and Mg have been observed to undergo conservative mixing between river water and seawater in many estuaries (Chester, 1990; Berner and Berner, 1996; Pogge von Strandmann et al., 2008). In addition, the estuarine behaviour of trace metals, nutrients, and organic matter, and their influence on elemental fluxes, has also been explored (Sholkovitz, 1978; Chester, 1990; Benner and Opsahl, 2001; Callahan et al., 2004; Pearce et al., 2013; Jones et al., 2014; Yao et al., 2014; Jiang et al., 2019; Schneider et al., 2022; Xu et al., 2023). Most of the trace elements show non-conservative behaviour during the mixing of river water and seawater (Sholkovitz, 1978; Pearce et al., 2013; Jones et al., 2014; Schneider et al., 2022). Organic matter is likely to be buried with or by Fe, Mn, and Al flocculation in the estuary (Benner and Opsahl, 2001; Kennedy and Wagner, 2011; Kennedy et al., 2014). However, the estuarine behaviour of Li and Li isotopes, as a promising tracer of silicate weathering, has not been widely explored (Section 1.2.5).

1.2 Lithium and Li isotopes as promising tracers of silicate weathering

1.2.1 Lithium and Li isotopes background

Lithium and Li isotopes are regarded as one of the most promising tracers of silicate weathering (e.g., Kisakürek et al., 2004a; 2005; Pogge von Strandmann

et al., 2020a, 2021a). Lithium is the lightest metal element of the periodic table. It has two natural stable isotopes, ^6Li and ^7Li (Dempster, 1921; Meija et al., 2016a, b), with around 15% relative mass difference. With the development of analysis technology and methods, the Li isotope composition can be determined with sufficient accuracy and precision to be applied in many fields, especially geochemistry (Tomascak et al., 1999; Jeffcoate et al., 2004). Currently, the most popular analysis method for Li isotope compositions is using multi-collector inductively coupled plasma mass spectrometry (MC-ICP-MS), following Li purification by ion chromatography, which takes advantage of the small-sample requirement, rapid analysis, and easy operation (Tomascak et al., 1999; Nishio and Nakai, 2002; Jeffcoate et al., 2004; Choi et al., 2013; Gou et al., 2018; Liu et al., 2022). The Li isotope composition is reported as the variation of the $^7\text{Li}/^6\text{Li}$ ratio in samples to the reference material LSVEC, as shown in Eq. 1.4.

$$\delta^7\text{Li} (\text{‰}) = [(^7\text{Li}/^6\text{Li})_{\text{sample}} / (^7\text{Li}/^6\text{Li})_{\text{LSVEC}} - 1] \times 1000 \quad \text{Eq. 1.4}$$

LSVEC is the delta-zero reference material for Li isotopes, with $^7\text{Li}/^6\text{Li} = 12.17285 \pm 0.00023$, which is distributed by the International Atomic Energy Agency (IAEA) and the National Institute of Standards and Technology (NIST) (Flesch et al., 1973; Qi et al., 1997; Magna et al., 2004). Recently, LSVEC was replaced by IRMM-016, prepared by the Institute for Reference Materials and Measurements (IRMM). The Li isotopic composition of IRMM-016 is the same as LSVEC within external analytical uncertainty (Qi et al., 1997; Jeffcoate et al., 2004; Caciagli et al., 2011; Tomascak et al., 2016; Pogge von Strandmann et al., 2019a). Internal precision and long-term precision of the MC-ICP-MS method can be better than 0.3‰ (2SD) and 0.5‰ (2SD), respectively (Pogge von Strandmann et al., 2019a; Gou et al., 2020), which satisfies the requirement of applying Li isotopes in many geological process, such as to trace chemical

weathering.

Lithium concentrations and Li isotope compositions in natural reservoirs have been well investigated (Tomascak et al., 2016). Because Li is a moderately incompatible element (White, 2013), the primitive mantle (1.39 ± 0.10 $\mu\text{g/g}$, 2SD) and mid-ocean-ridge basalt (MORB) (5.5 ± 3.8 $\mu\text{g/g}$, 2SD) have lower Li concentrations than the continental crust (18 $\mu\text{g/g}$), especially the upper continental crust, with a concentration of 30.5 ± 3.6 $\mu\text{g/g}$ (Marschall et al., 2017; Pogge von Strandmann et al., 2020a). In addition, the Li isotopic composition has a narrow range in the mantle (3.5 ± 1.0 ‰, 2SD) (Figure 1.2) (Tomascak et al., 2016; Marschall et al., 2017). The $\delta^7\text{Li}$ values of most continental primary rocks vary from -10 to 10 ‰ with a mean of ~ 0 ‰ for granites and of 3 – 5 ‰ for basalts (Elliott et al., 2006; Marschall et al., 2017). However, high $\delta^7\text{Li}$ values in quartz have been reported recently, such as, 18.9 – 22.0 ‰ in quartz in granite (Zhang et al., 2021; Zhu et al., 2023) and 11.4 – 55.4 ‰ in quartz in pegmatites (Phelps and Lee, 2022). The $\delta^7\text{Li}$ values in soils and river sediments exhibit a wide range from -20.2 to 26.8 ‰ (Rudnick et al., 2004; Pogge von Strandmann et al., 2012; Tomascak et al., 2016) and from -4.3 to 12.0 ‰ (Kisakürek et al., 2005; Pogge von Strandmann et al., 2010; Tomascak et al., 2016; Weynell et al., 2021), respectively. Furthermore, the Li concentrations in carbonates and plants are orders of magnitude lower than in silicates (Kisakürek et al., 2005; Lemarchand et al., 2010; Dellinger et al., 2015; Clergue et al., 2015; Pogge von Strandmann et al., 2021a). Global rivers have a wide range of dissolved Li concentration from 2×10^{-4} to 100 $\mu\text{g/l}$ (Pogge von Strandmann et al., 2020a). The Li isotopic compositions of river water and groundwater ranges from -1 to 49 ‰ (Bottomley et al., 2003; Tomascak et al., 2016; Pogge von Strandmann et al., 2021a; Mayfield et al., 2021), which is isotopically heavier than solid materials. In the modern oceans, the Li concentration is uniform at 180 $\mu\text{g/l}$, and $\delta^7\text{Li}$ values are homogeneous at ~ 31 ‰, due to the long ocean residence time of ~ 1.2 million

years (Stoffyn-Egli and Mackenzie, 1984; Misra and Froelich, 2012; Tomascak et al., 2016; Kalderon-Asael et al., 2021).

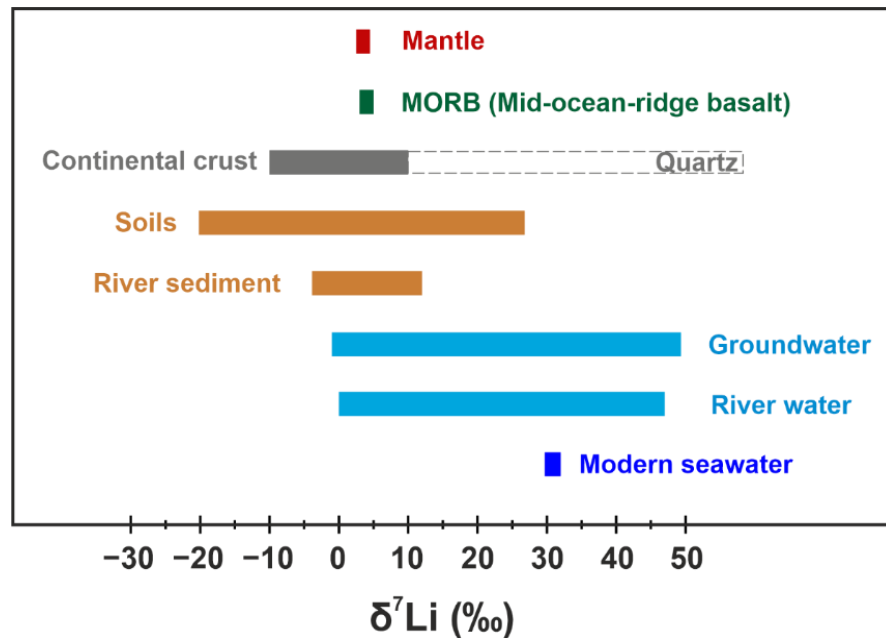


Figure 1.2 Range of $\delta^7\text{Li}$ values in natural reservoirs

This figure is modified from Figure 2 in Pogge von Strandmann et al. (2021b). The dashed column represents the quartz fractions with high $\delta^7\text{Li}$ values (Zhang J.-W. et al., 2021; Phelps and Lee, 2022; Zhu et al., 2023).

The large variations in $\delta^7\text{Li}$ values in water and solids at the Earth's surface are thought to be mainly caused by silicate weathering (Huh et al., 1998; Kiskakürek et al., 2004a; Dellinger et al., 2014; Pogge von Strandmann et al., 2020a). Although some research has shown that plant organs have different Li isotope compositions (Lemarchand et al., 2010; Li et al., 2020), and that vegetation influences Li isotope compositions in the shallow regolith (Li et al., 2020), the low Li concentrations in plants nevertheless result in less influence of plants than of silicate weathering on Li isotopes. In addition, Li isotopes are rarely affected by carbonate weathering because of the low Li concentrations in carbonates (Kiskakürek et al., 2005; Dellinger et al., 2015), and the Li isotope

composition is not directly influenced by redox changes, because Li only exists in the +1 valence state in natural environments (Kisakürek et al., 2005). Thus, Li isotopes are regarded as one of the most promising tracers of silicate weathering.

1.2.2. Lithium and Li isotope behaviour during silicate weathering and its implications

Lithium isotopes show significant fractionation during silicate weathering in the surface or near-surface environment (Huh et al., 1998; Rudnick et al., 2004; Dellinger et al., 2014; Pogge von Strandmann et al., 2017a). The Li isotope fractionation between two phases, A and B, ($\Delta^7\text{Li}_{\text{A-B}}$) is calculated in Eq. 1.5.

$$\Delta^7\text{Li}_{\text{A-B}} = \delta^7\text{Li}_{\text{A}} - \delta^7\text{Li}_{\text{B}} \quad \text{Eq. 1.5.}$$

Here, $\delta^7\text{Li}_{\text{A}}$ and $\delta^7\text{Li}_{\text{B}}$ are the Li isotope values of A and B, respectively.

Several experiments conducted under low temperature (<25 °C) show no significant Li isotopic fractionation when Li is released from primary minerals (e.g., basalt glass and forsterite, Wimpenny et al., 2010a) or rocks (e.g., basalt and microgranite, Pistiner and Henderson, 2003; basalt and granite, Li et al., 2021) under equilibrium conditions. In contrast, during mineral adsorption and mineral formation, Li isotope fractionation has been widely observed, with a preference of solids for the lighter Li isotope (i.e., ^6Li) (Vigier et al., 2008; Millot et al., 2010a; Wimpenny et al., 2015; Pogge von Strandmann et al., 2019a, 2022; Hindshaw et al., 2019; Li and Liu, 2020; Zhang X. et al., 2021). According to the stable isotope fractionation theory, the Li isotope fractionation becomes smaller with increasing temperature (Urey, 1947; Vigier et al., 2008; Li and West, 2014; Hindshaw et al., 2019). Furthermore, the degree of Li isotope fractionation is thought to be highly related to the Li sites in the secondary minerals (Chan and Hein, 2007; Vigier et al., 2008; Wimpenny et al., 2010a, b; Pogge von Strandmann et al., 2019a;

Hindshaw et al., 2019; Li et al., 2020). For the process of Li adsorption on the surface and/or in the interlayers of secondary minerals, the Li isotope fractionation is generally less than 15‰ (Figure 1.3) (Pistiner and Henderson, 2003; Vigier et al., 2008; Wimpenny et al., 2015; Hindshaw et al., 2019; Li and Liu, 2022). In contrast, Li incorporation into the secondary mineral lattice, such as Li-O-Fe bonding in secondary Fe oxides (Kim et al., 2008; Kim and Grey, 2010), octahedral sites in clays (Vigier et al., 2008; Hindshaw et al., 2019), and six-membered rings in gibbsite (Wimpenny et al., 2015), is accompanied by considerable isotope fractionation ($\Delta^7\text{Li}_{\text{secondary mineral lattice-solution}} = -10 \text{ to } -27\text{‰}$) (Figure 1.3) (Vigier et al., 2008; Wimpenny et al., 2015; Hindshaw et al., 2019; Liu et al., 2022; Pogge von Strandmann et al., 2022). Thus, it is necessary to examine the Li isotope composition in different fractions, e.g., exchangeable, oxide, and clay fractions (details in Chapter 2 and 3) (Hindshaw et al., 2018; Pogge von Strandmann et al., 2019a, 2022; Li et al., 2020; He et al., 2021; Liu et al., 2022).

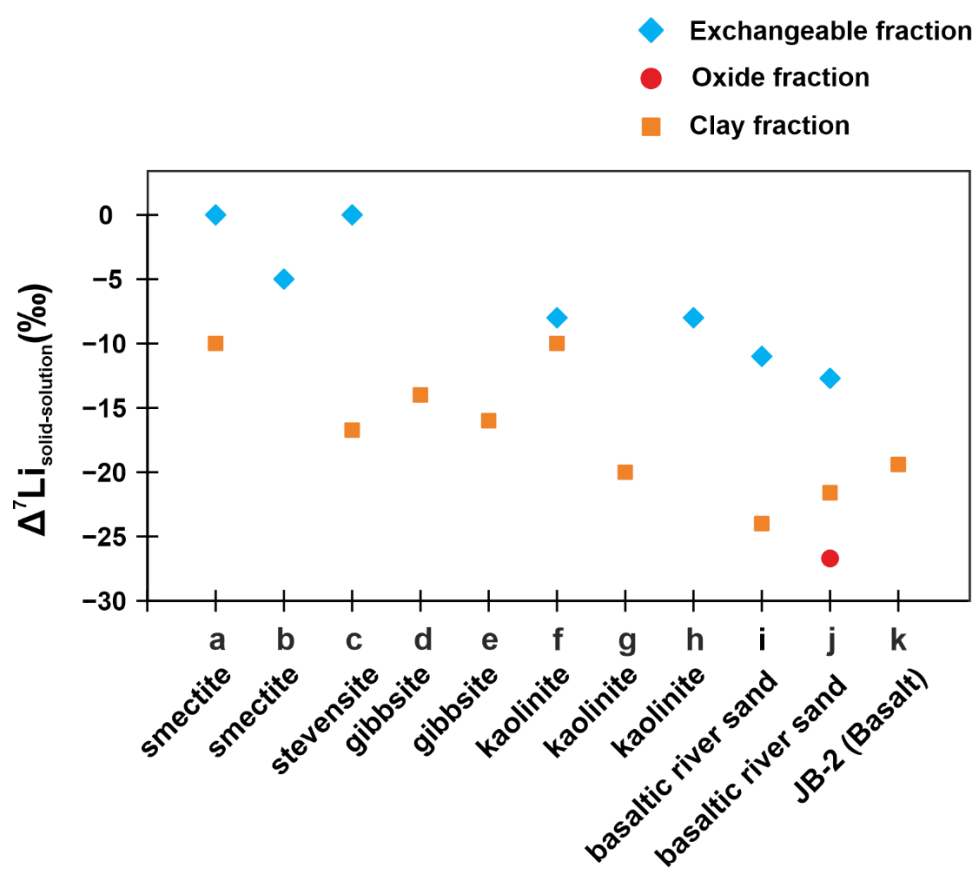


Figure 1.3 Li isotope fractionation between different fractions in solids and the solution in low temperature experiments (< 25 °C)

Data from references: a. Vigier et al. (2008); b. Li and Liu (2022); c. Hindshaw et al. (2019); d. Pistiner and Henderson (2003); e. Wimpenny et al. (2015); f. Li and Liu (2020); g. Zhang X. et al. (2021); h. Li and Liu (2022); i. Pogge von Strandmann et al. (2019a); j. Pogge von Strandmann et al. (2022); k. Millot et al. (2010a).

Lithium and Li isotopes have been widely investigated in various natural weathering profiles and river catchments on the continents, such as basaltic weathering profiles (Huh et al., 2004; Kisakürek et al., 2004b; Pogge von Strandmann et al., 2012; Liu et al., 2013; Ryu et al., 2014; Li et al., 2020), andesitic weathering profiles (Clergue et al., 2015), granitic weathering profiles (Rudnick et al., 2004; Lemarchand et al., 2010; Négrel and Millot, 2019), loess

profiles (Tsai et al., 2014; He et al., 2021), glacial rivers (Pogge von Strandmann et al., 2006; Wimpenny et al., 2010b; Hindshaw et al., 2018; Murphy et al., 2019), mountain rivers (Milot et al., 2010b; Tipper et al., 2012; Liu et al., 2015; Pogge von Strandmann and Henderson, 2015), mountain-large floodplain rivers (Wang et al., 2015; Dellinger et al., 2015; Pogge von Strandmann et al., 2017a), tropical low-relief rivers (Henchiri et al., 2016), basaltic rivers (Pogge von Strandmann et al., 2010; Liu et al., 2015), andesitic rivers (Clergue et al., 2015), granitic rivers (Lemarchand et al., 2010), loess rivers (Gou et al., 2019), carbonate rivers (Kisakürek et al., 2005), and groundwater (Pogge von Strandmann et al., 2014; Fries et al., 2019; Martin et al., 2020). Basically, these studies agree that Li yields and isotopes are controlled by silicate weathering rather than carbonate weathering (Kisakürek et al., 2005; Martin et al., 2020; Pogge von Strandmann et al., 2020a), although rainwater or evaporites have a partial influence in some weathering zones (Lemarchand et al., 2010; Wang et al., 2015; Gou et al., 2019; Fries et al., 2019; Ma et al., 2020). In addition, identical to the results from experiments, field-based studies show that there is little Li isotope fractionation during primary rock dissolution while there is significant Li isotope fractionation during secondary mineral formation, including clays and oxides (Wimpenny et al., 2010b; Lemarchand et al., 2010; Dellinger et al., 2015; Pogge von Strandmann et al., 2017a; Murphy et al., 2019).

To better quantify and model the isotopic fractionation of Li between two phases, A and B, the Li isotope fractionation factor α is applied to be the ratio of $^7\text{Li}/^6\text{Li}$ ratio in A and B (Eq. 1.6) (Hoefs, 2009). Here, for the isotopic fractionation of Li taking into secondary minerals, the fractionation factor α between secondary minerals and the dissolved load can be calculated using a Rayleigh fractionation model or an equilibrium (batch) fractionation model. Rayleigh fractionation is used to model one-way reactions with negligible back reaction, whereas equilibrium (batch) fractionation is suitable for a system with forward and back

reactions (Kendall and Doctor, 2003). In a Rayleigh model, the $\delta^7\text{Li}$ values of the remaining solution after Li isotope fractionation are given by Eq. 1.7. The factor f in the equation represents the fraction of Li remaining in solution, which ranges from 0 to 1. In addition, at the particular moment that f refers to, the $\delta^7\text{Li}$ value of the Li gained by the solid in a Rayleigh model is calculated as in Eq. 1.8. In the equilibrium (batch) fractionation system, the $\delta^7\text{Li}$ values in solution and solid are shown in Eq. 1.9 and Eq. 1.10, respectively.

$$\alpha_{\text{A-B}} = (^7\text{Li}/^6\text{Li})_{\text{A}} / (^7\text{Li}/^6\text{Li})_{\text{B}} = (\delta^7\text{Li}_{\text{A}} + 1000) / (\delta^7\text{Li}_{\text{B}} + 1000) \quad \text{Eq. 1.6}$$

Rayleigh fractionation:

$$\delta^7\text{Li}_{\text{solution}} = \delta^7\text{Li}_{\text{initialsolution}} + 1000 \times (\alpha_{\text{solid-solution}} - 1) \times \ln(f) \quad \text{Eq. 1.7}$$

$$\delta^7\text{Li}_{\text{solid}} = \delta^7\text{Li}_{\text{solution}} + \Delta^7\text{Li}_{\text{solid-solution}} \quad \text{Eq. 1.8}$$

Equilibrium (batch) fractionation:

$$\delta^7\text{Li}_{\text{solution}} = \delta^7\text{Li}_{\text{initialsolution}} + 1000 \times (\alpha_{\text{solid-solution}} - 1) \times (f - 1) \quad \text{Eq. 1.9}$$

$$\delta^7\text{Li}_{\text{solid}} = \delta^7\text{Li}_{\text{solution}} + \Delta^7\text{Li}_{\text{solid-solution}} \quad \text{Eq. 1.10}$$

Here, $\delta^7\text{Li}_{\text{initialsolution}}$ is the $\delta^7\text{Li}$ value in the initial solution (i.e., $f = 1$), and $\Delta^7\text{Li}_{\text{solid-solution}}$ is the Li isotope fractionation between solid and solution (Eq. 1.5).

Because there is little to no Li isotope fractionation during primary rock dissolution, while significant Li isotope fractionation occurs during secondary mineral formation (Wimpenny et al., 2010b; Lemarchand et al., 2010; Dellinger et al., 2015; Pogge von Strandmann et al., 2017a; Murphy et al., 2019), the dissolved $\delta^7\text{Li}$ values of river waters are thought to be controlled by the ratio of primary mineral dissolution to secondary mineral formation (Misra and Froelich, 2012; Pogge von Strandmann and Henderson, 2015; Dellinger et al., 2015). This ratio is known as the weathering congruency (Froelich and Misra, 2014; Pogge

von Strandmann and Henderson, 2015; Dellinger et al., 2015; Pogge von Strandmann et al., 2020a). Importantly, because primary mineral dissolution may eventually cause net CO₂ burial, whereas secondary mineral formation hinders net CO₂ burial (Section 1.1) (Walker et al., 1981; West et al., 2005), the weathering congruency is likely to indicate the degree of carbon burial (Pogge von Strandmann et al., 2020a).

Based on the compiled dissolved Li isotope data, there is a ‘boomerang-shape’ relationship between the weathering intensity (W/D) and the dissolved $\delta^7\text{Li}$ values (Dellinger et al., 2015; Pogge von Strandmann et al., 2020a). Weathering intensity represents the ratio of the chemical weathering rate (W) and the denudation rate (D), which is itself the sum of the chemical weathering rate (W) and the physical erosion rate (E) (Dellinger et al., 2015; Pogge von Strandmann et al., 2020a). When the weathering intensity is low (i.e., a kinetically limited weathering regime, or weathering limited), the dissolved $\delta^7\text{Li}$ values are low and the Li yield is high due to congruent weathering. As the weathering intensity increases, more Li is incorporated into secondary minerals and the dissolved Li yield decreases, while the $\delta^7\text{Li}$ values increase due to isotope fractionation during incongruent weathering. Further increases in weathering intensity result in a supply limited (or transport limited) regime. In a supply limited regime, the pre-formed secondary minerals dissolve and dissolved $\delta^7\text{Li}$ values start to decrease to low values again. Thus, dissolved Li concentrations and isotopes can indicate the silicate weathering intensity of different weathering regimes (Froelich and Misra, 2014; Dellinger et al., 2015; Pogge von Strandmann et al., 2020a). In turn, the continental weathering intensity traced by Li and Li isotopes can influence the ocean Li isotope composition through the riverine dissolved Li input (Section 1.2.3), which provides a tool for reconstructing the paleo-weathering regime using seawater Li isotope records (Section 1.2.4) (Misra and Froelich, 2012; Pogge von Strandmann et al., 2020a).

1.2.3. The Li cycle in the modern ocean

To date, in the modern ocean, there are two major Li inputs (continental input (mainly riverine dissolved load input) and hydrothermal input) and two major outputs (alteration of the (basaltic) oceanic crust (AOC) and uptake by marine aluminous authigenic clays (MAAC)) (Chan et al., 1992; Huh et al., 1998; Hathorne and James, 2006; Misra and Froelich, 2012; Li and West, 2014) (Figure 1.4). The modern riverine dissolved Li input flux is thought to be $5.6\text{--}6.9 \times 10^{10}$ g/yr (i.e., $0.8\text{--}1 \times 10^{10}$ mol/yr) (Huh et al., 1998; Misra and Froelich, 2012; Gaillardet et al., 2014), with a mean Li isotope composition of 23‰ (Huh et al., 1998; Hathorne and James, 2006; Misra and Froelich, 2012). However, these estimates are based on the Li concentration and isotope composition of river waters measured close to the coast but before estuarine areas (Huh et al., 1998). The hydrothermal Li input flux is estimated as $1.4\text{--}97.2 \times 10^{10}$ g/yr, where $\sim 4.2 \times 10^{10}$ g/yr (i.e., 0.6×10^{10} mol/yr) is the most accepted value (Chan et al., 1992, 1994, 2002; Hathorne and James, 2006), with a Li isotope composition of 6–11‰ (Chan et al., 1993; Misra and Froelich, 2012; Coogan and Dosso, 2012; Vigier and Godd  ris, 2015). However, there are still large uncertainties in the Li sink fluxes and their isotopic fractionation from seawater. The estimated AOC Li sink ranges from $1.0\text{--}14.6 \times 10^{10}$ g/yr, with fractionation ($\Delta^7\text{Li}_{\text{AOC-seawater}}$) ranging from –11 to –19‰ (Figure 1.4). The estimated MAAC Li sink ranges from $2.4\text{--}25.7 \times 10^{10}$ g/yr, with fractionation ($\Delta^7\text{Li}_{\text{MAAC-seawater}}$) ranging from –5 to –28‰ (Figure 1.4).

Similar to modern seawater, reconstructions of past seawater Li isotopes show that $\delta^7\text{Li}$ values stayed constant at 31‰ since 6 Ma (Hathorne and James, 2006; Misra and Froelich, 2012; Kalderon-Asael et al., 2021). Thus, based on the mass balance of the Li flux and Li isotope compositions in the modern ocean, a steady-state box model can be applied (Eqs. 1.11 and 1.12) (Stoffyn-Egli and Mackenzie, 1984; Chan et al., 1992; Huh et al., 1998; Hathorne and James, 2006; Misra and Froelich, 2012).

$$F_{\text{river}} + F_{\text{hydro}} = F_{\text{AOC}} + F_{\text{MAAC}} \quad \text{Eq. 1.11}$$

$$F_{\text{river}} \delta^7\text{Li}_{\text{river}} + F_{\text{hydro}} \delta^7\text{Li}_{\text{hydro}} = F_{\text{AOC}} (\Delta^7\text{Li}_{\text{AOC-sw}} + \delta^7\text{Li}_{\text{sw}}) + F_{\text{MAAC}} (\Delta^7\text{Li}_{\text{MAAC-sw}} + \delta^7\text{Li}_{\text{sw}}) \quad \text{Eq. 1.12}$$

Here, F_{river} , F_{hydro} , F_{AOC} , and F_{MAAC} are the continental input flux (mainly from rivers), hydrothermal input flux, alteration of the (basaltic) oceanic crust output flux, and marine aluminous authigenic clays (MAAC) output flux, respectively. The terms $\delta^7\text{Li}_{\text{river}}$, $\delta^7\text{Li}_{\text{hydro}}$, and $\delta^7\text{Li}_{\text{sw}}$ are the Li isotopic compositions of the continental input, hydrothermal input, and seawater, respectively. $\Delta^7\text{Li}_{\text{AOC-sw}}$ and $\Delta^7\text{Li}_{\text{MAAC-sw}}$ are the fractionation factors between the output from alteration of the (basaltic) oceanic crust and seawater and the output from marine aluminous authigenic clays (MAAC) and seawater, respectively. Although there appears to be a mass balance between Li input and Li output in the box model for the modern ocean (Hathorne and James, 2006; Misra and Froelich, 2012), more exploration of each independent Li sink is needed to decrease the large uncertainty on Li output fluxes.

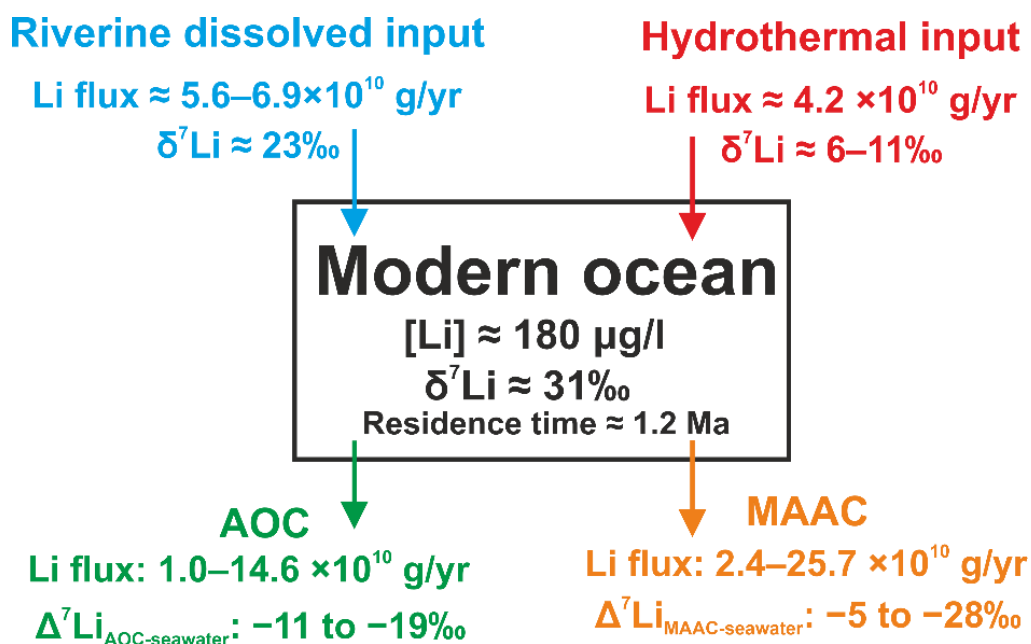


Figure 1.4 Lithium cycle in the modern ocean

The values for Li fluxes and Li isotope compositions of the riverine dissolved input and hydrothermal input are the currently most accepted values. AOC and MAAC represent sinks from the alteration of the (basaltic) oceanic crust and from marine aluminous authigenic clays. The values for the Li fluxes and Li isotope compositions of the AOC and MAAC sinks are the ranges of the published data. The details are given in Table S1.1.

1.2.4 Lithium isotopes tracing weathering regimes in geological time

Several materials are considered to be reasonable archives of seawater Li isotope compositions in the ancient ocean, such as planktonic foraminifera (Kořler et al., 2001; Hall et al., 2005; Hathorne and James, 2006; Vigier et al., 2007; Misra and Froelich, 2012), brachiopods (Pogge von Strandmann et al., 2017b; Dellinger et al., 2018; Washington et al., 2020), and marine bulk carbonates (Pogge von Strandmann et al., 2019b; Liu et al., 2023; Cao et al., 2023), although all archives may be influenced by ocean biogeochemistry, carbonate mineralogy, and diagenesis to some extent (Vigier et al., 2015; Dellinger et al., 2020; Wei et al., 2023; Chen D. et al., 2023). In contrast, it is still hard to determine the Li concentrations of paleo-seawater (Wanner et al., 2014; Vigier et al., 2015). There is no clear relationship between Li concentrations in seawater and Li/Ca ratios in archives, such as foraminifera and marine carbonates (Hathorne and James, 2006; Misra and Froelich, 2009, 2012), because the Li/Ca ratios are highly influenced by temperature (Marriott et al., 2004a, b), dissolved inorganic carbon (Hall and Chan, 2004), and diagenesis (Hall and Chan, 2004).

Because seawater Li and Li isotopes may have been out of steady-state in Earth's geological history, a dynamic ocean box model can be applied to model the Li concentrations and Li isotopes in the ocean through geological time (Eqs. 1.13 and 1.14) (Pogge von Strandmann et al., 2013, 2017b).

$$dM_{\text{Li}(\text{sw})}/dt = F_{\text{river}} + F_{\text{hydro}} - (F_{\text{AOC}} + F_{\text{MAAC}}) \quad \text{Eq. 1.13}$$

$$d(M_{\text{Li}(\text{sw})} \times \delta^7\text{Li}_{\text{sw}})/dt = F_{\text{river}} \delta^7\text{Li}_{\text{river}} + F_{\text{hydro}} \delta^7\text{Li}_{\text{hydro}} - (F_{\text{AOC}} (\Delta^7\text{Li}_{\text{AOC-sw}} + \delta^7\text{Li}_{\text{sw}}) + F_{\text{MAAC}} (\Delta^7\text{Li}_{\text{MAAC-sw}} + \delta^7\text{Li}_{\text{sw}})) \quad \text{Eq. 1.14}$$

Here, F_{river} , F_{hydro} , F_{AOC} , F_{MAAC} , $\delta^7\text{Li}_{\text{river}}$, $\delta^7\text{Li}_{\text{hydro}}$, $\delta^7\text{Li}_{\text{sw}}$, $\Delta^7\text{Li}_{\text{AOC-sw}}$, and $\Delta^7\text{Li}_{\text{MAAC-sw}}$ are defined in above (Eqs. 11 and 12). $M_{\text{Li}(\text{sw})}$ is the total number of moles of Li

in the ocean and t means time.

Recently, a Li isotope record from marine carbonates since 3 Ga shows that seawater Li isotopes were low with a value of $\sim 10\text{‰}$ during the Precambrian, and then at some time in the mid or late Palaeozoic, the seawater Li isotope values increased towards the modern value (31‰) (Kalderon-Asael et al., 2021). This transition of seawater Li isotopes in the mid/late Palaeozoic is thought to reflect changes in the carbon and silicon cycles in the ocean, and specifically the advent of a biologically-controlled Si cycle (Krissansen-Totton and Catling, 2020; Kalderon-Asael et al., 2021). Since that point, records of the seawater Li isotope composition are regarded as a tracer of continental silicate weathering in most situations (Pogge von Strandmann et al., 2013, 2017b, 2021b; Lechler et al., 2015; Sun et al., 2018; Sproson et al., 2022; Ramos et al., 2022; Qie et al., 2023), and possibly reverse weathering (Cao et al., 2022). Furthermore, the secular variation of the seawater Li isotope composition during the Cenozoic shows that $\delta^7\text{Li}$ values increased by around 9‰ over the past 60 Ma (Misra and Froelich, 2012). Around 2‰ out of the 9‰ increase in seawater Li isotope composition may stem from the cooling temperature through the Cenozoic according to stable isotope fractionation theory (Urey, 1947; Gou et al., 2019). Without considering temperature, some studies suggest that the increase was related to changes in continental erosion and chemical weathering, which could have caused a higher riverine dissolved Li input flux, and/or higher riverine dissolved $\delta^7\text{Li}$ values (Misra and Froelich, 2012; Wanner et al., 2014; Vigier and Godd ris, 2015; Caves Rugeinstein et al., 2019). In contrast, Li and West (2014) pointed out that the relative contributions of the two sinks (i.e. AOC and MAAC) in the oceans could also have changed and thereby impact on seawater $\delta^7\text{Li}$ values in the Cenozoic.

However, the effects of the alteration of river-derived particles in estuaries on the oceanic Li cycle have not been particularly considered across geological time, although some studies mentioned the influence of high river-derived particle

input loads on the past ocean Li cycle (Li and West, 2014; Pogge von Strandmann et al., 2021b).

1.2.5 Previous studies on Li and Li isotope behaviour during the alteration of river-derived particles in an estuary

Some elements (e.g., Fe, Mn, Al) have been widely explored in estuaries (Section 1.1). However, so far, only a few studies have examined Li and Li isotopes in estuaries. In general, the dissolved Li concentrations generally show conservative mixing of river water and seawater in the St. Lawrence River estuary, Canada (Stoffyn-Egli, 1982), the Scheldt River estuary, Netherlands (Stoffyn-Egli, 1982), the Mississippi River estuary (Colten and Hanor, 1984), the Gulf of Papua supplied by the Fly, Purari, and Kikori rivers (Brunskill et al., 2003), the Povoação estuary, São Miguel, Azores Archipelago (Pogge von Strandmann et al., 2008), the Kalix and Rane River estuaries, Sweden (Murphy et al., 2014), the Yangtze River estuary (Yang et al., 2021), and the Ganga estuary (Chanda et al., 2023) (Figure 1.5). The Li isotope compositions generally exhibit conservative mixing of river water and seawater in the Borgarfjörður estuary, Iceland (Pogge von Strandmann et al., 2008), Povoação, São Miguel (Pogge von Strandmann et al., 2008), and the Yangtze River estuary (Yang et al., 2021). In contrast, the dissolved Li isotope values are higher than expected for conservative mixing in the low salinity zone of the Kalix and Rane River estuaries, Sweden (Murphy et al., 2014). In addition, in the Borgarfjörður estuary, Iceland, an increase is observed in the Li concentrations and Li isotope values in bulk suspended load particles though the estuarine transect, which indicates Li removal by solids from the dissolved load with a Li isotope fractionation of around -20‰ ($\Delta^7\text{Li}_{\text{SPM-seawater}}$) (Pogge von Strandmann et al., 2008). Based on the increase in Li concentrations in the suspended load particles, the river-derived particulate flux, and the particulate residence time in the estuary, a significant Li removal flux was

estimated in the Borgarfjörður estuary (Pogge von Strandmann et al., 2008). In addition, in the Yangtze river estuary, the river-derived particles also indicate Li incorporation, especially in Fe-Mn oxyhydroxides (Yang et al., 2021, 2023). However, these previous studies on Li and Li isotopes during the alteration of river-derived particles in estuaries are not sufficient to constrain the behaviour of Li in estuaries at a global scale. Therefore, more research is needed, especially the examination of suspended and bedload solids (i.e., river-derived particles) in the estuarine zone.

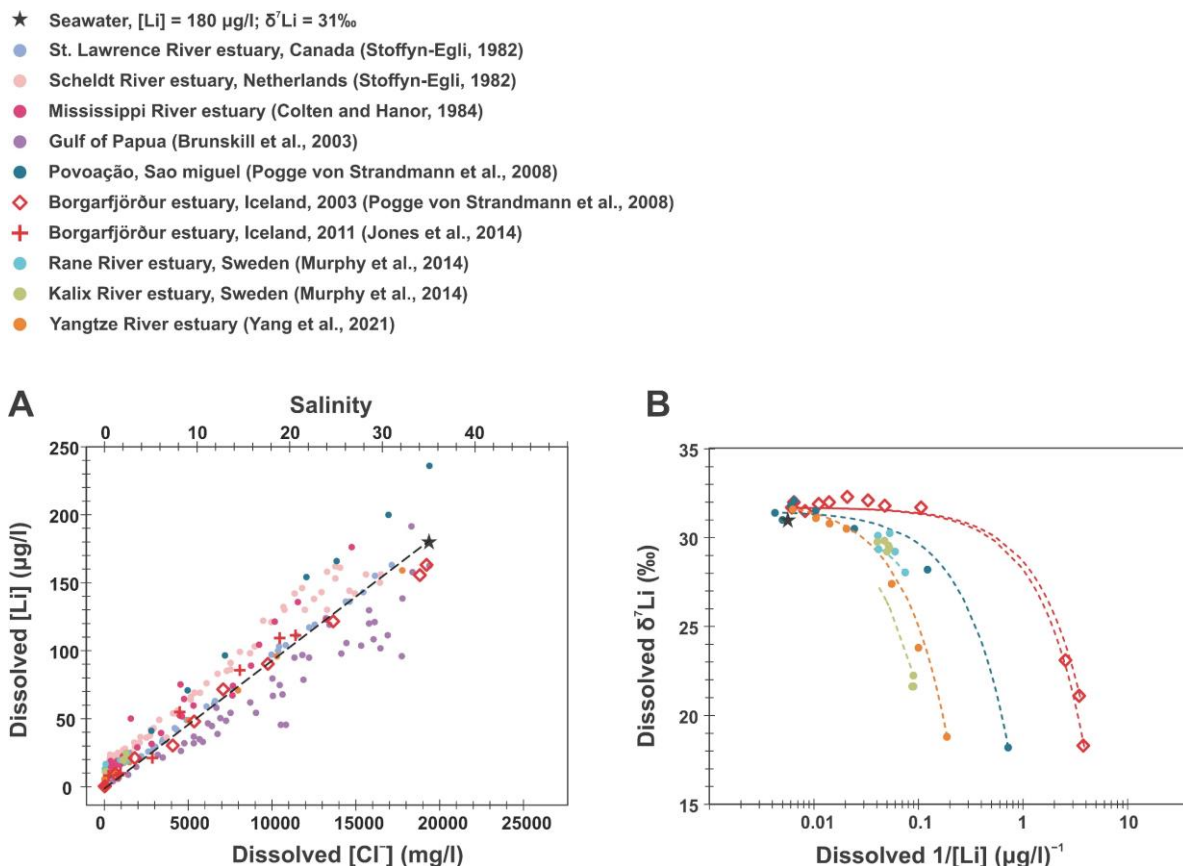


Figure 1.5 Synthesis of published dissolved Li concentration and isotope data in modern estuaries.

The data points for the St. Lawrence River estuary, the Scheldt River estuary, the Povoação estuary, and the Yangtze River estuary are based on the data of surface water samples (Stoffyn-Egli, 1982; Pogge von Strandmann et al., 2008; Yang et al., 2021). The data points for the Mississippi River estuary, the Gulf of Papua, the Kalix River, and the Rane River are re-plotted based on the figures in the references (Colten and Hanor, 1984; Brunskill et al., 2003; Murphy et al., 2014), which may cause some minor errors. In panel A, the dashed line is the linear relationship fit for all data shown. In panel B, the dashed lines are the theoretical conservative mixing lines in the corresponding estuaries.

1.3 Research aims and outline

1.3.1 Research aims

This study aims to investigate the Li and Li isotope behaviour occurring during the process of alteration of river-derived particles during estuarine weathering, and the influence of this alteration on ocean biogeochemistry and the carbon cycle. Especially, the following questions are focused on:

1) Is there any Li release or removal (with Li isotope fractionation or not) during the alteration of river-derived particles in the estuary? Which fractions (e.g., exchangeable, oxide, clay, and primary mineral residue) in the river-derived particles are involved in the alteration?

2) What are the influencing factors for Li and Li isotope behaviour during the alteration of river-derived particles in the estuary? Does the continental weathering regime influence the Li and Li isotope behaviour during the alteration of river-derived particles?

3) Is the Li release or removal flux and associated Li isotope fractionation in the estuary significant enough to modify the current estimated oceanic Li cycle, such as the riverine dissolved Li input flux and isotope composition, and/or the Li sink flux and isotope fractionation from seawater?

4) How does the alteration of river-derived particles in the estuary influence ocean biogeochemistry more broadly (e.g., Mg, Ca, and alkalinity) and the carbon cycle? Can Li and Li isotopes indicate the influence of alteration of river-derived particles in the estuary on ocean biogeochemistry and the carbon cycle?

1.3.2 Research outline

In Chapter 2, the methodology conducted in this study is described, including the analysed samples, the reagents used, the preparation of samples for analysis (especially a sequential extraction method for exchangeable, carbonate, oxide, clay fractions, and residue in solid samples), and sample analyses (especially the

elemental concentration analysis and Li isotope analysis).

In Chapter 3, first, the optimal oxide leaching methods were determined after comparison of different oxide leaching methods. Specifically, different oxide leaching methods were applied to 5 different silicate solids, and three factors were assessed in the oxide leaching trials: the leaching temperature (20 °C versus 95 °C), the leaching time, and the reagent/solid ratio. This work was published as Liu et al. (2022). Second, the reproducibility of the sequential extraction procedure for different fractions (i.e., exchangeable, carbonate, oxide, clay fractions, and residue) in solid samples was confirmed to be acceptable based on several replicate analyses, and the accuracy of elemental recovery of the full sequential leaching procedure was verified based on comparison to element concentrations in the bulk sample dissolutions.

In Chapter 4, four series of solid-water interaction experiments with gradual addition of concentrated artificial seawater were conducted to imitate estuarine processes. The main factors in these interaction experiments were the initial solid amounts and the Li concentrations in the added artificial seawater. With these main factors set as independent variables, the four series of interaction experiments were 1) basalt-Li-add experiment, 2) basalt-Li-free experiment, 3) loess-Li-add experiment, and 4) loess-Li-free experiment. Based on the elemental concentrations and the Li isotope values of the dissolved samples and different fractions of the solid samples, the transfer of elements (i.e., Na, Mg, Ca, K, and Li) and Li isotope behaviour during the interactions was assessed and discussed. In addition, based on the comparison between the four experiments, the influencing factors on the Li and Li isotope behaviour were discussed.

In Chapter 5, the Borgarfjörður estuary, a natural estuary of a small basaltic river in Iceland, was explored. This study analysed a group of bedload samples collected in 2008 and a group of dissolved load and corresponding suspended load samples collected in 2017. Compiled with previous data from samples

collected in other sampling campaigns from the same estuary, the influence of multiple processes (i.e., geochemical processes and mechanical processes) on the alteration of river-derived particles, especially the Li and Li isotope behaviour, was discussed. In addition, the Li flux related to the geochemical incorporation from the dissolved load by river-derived particles was estimated after elimination of the influence of other processes.

In Chapter 6, the Amazon estuary, a natural estuary of a large river catchment, was explored. The dissolved load samples and solid samples (i.e., the suspended load and bedload samples) from the Amazon estuary were analysed. The Li and Li isotope behaviour in the dissolved load and fractions of the solid samples were discussed, and the Li transfer flux between the dissolved load and the solids was estimated according to mass balance and an estuary model. Furthermore, the influence of geochemical processes and mechanical processes on the alteration of river-derived particles, especially Li concentrations and Li isotopes were distinguished. In addition, the behaviour of major elements, and their impact on the carbon cycle, were discussed.

In Chapter 7, the observations in the interaction experiments and natural estuarine samples were summarised and synthesised, and the influence of the alteration of river-derived particles during estuarine weathering on ocean biogeochemistry and the global carbon cycle was discussed.

Chapter 2. Methods

2.1 Sample collection

In this study, samples were obtained from four series of interaction experiments and two natural estuaries (Borgarfjörður, Iceland; Amazon, Brazil). A summary of sample collections is given below. Further details on the sampling setting are shown separately in Chapters 4 to 6.

In the interaction experiments, the two initial solids used were natural sediments from the Borgarfjörður (Iceland) and Yellow River (China) estuaries. During the experiments, there were 187 dissolved load samples and 33 solid samples collected. Further details on the samples from the interaction experiments are in Section 4.2.

In the Borgarfjörður estuary, 14 dissolved load samples and their corresponding suspended load particulate matter (SPM) were collected in July 2017. Ten bedload samples were collected in the estuary in June 2008 (Jones et al., 2014). Further details are in Section 5.2.

In the Amazon estuary, 12 dissolved load samples, 7 SPM samples, and 9 bedload samples were collected during the RV Meteor Cruise M147, process study GApr11 of the international GEOTRACES program, in April and May 2018 (Koschinsky et al., 2018). Further details are in Section 6.2.

2.2 Reagent preparation

The sample chemical preparation (Section 2.3), elemental concentration analysis (Section 2.4), isotope analysis (Section 2.5), and exploration of sequential chemical extraction (Chapter 3) were conducted in the metal-free clean laboratories of the London Geochemistry and Isotope Centre (LOGIC).

During these processes, the ultrapure water (resistivity = $18.2 \text{ M}\Omega\cdot\text{cm}$) used was produced by Merck Direct-Q® 3 (Milli-Q) or PURELAB® (Elga Veolia) systems. The nitric acid (HNO_3) was supplied as 68% *m/m* (AnalaR NORMAPUR, VWR Chemicals BDH®), and hydrochloric acid (HCl) was supplied as 32% *m/m* (AnalaR NORMAPUR, VWR Chemicals BDH®). Before use, both HNO_3 and HCl were Teflon-distilled using a DST-1000 Acid Purification System (Savillex). The sodium acetate (NaOAc) solution was quantitatively dissolved from sodium acetate powder (AnalaR, VWR Chemicals BDH®) in ultrapure water. The hydroxylamine hydrochloride (HH) solution was quantitatively dissolved from hydroxylamine hydrochloride powder (99.999% trace metals basis, Sigma-Aldrich®). The acetic acid (HOAc) was quantitatively diluted from glacial acetic acid (ROMIL-SpATM Super Purity Acids). Hydrofluoric acid (HF) was supplied as 47-51% *m/m* (ROMIL-SpATM Super Purity Acids) and perchloric acid (HClO_4) as 65-71% *m/m* (ROMIL-SpATM Super Purity Acids). The titrant and indicator in titration were 0.1 mol/l NaOH (Titripur® Sigma-Aldrich®) and Bromothymol Blue (ACS reagent, Acros Organics).

The PFA vials (Savillex) were cleaned by soaking in ~50% *v/v* HNO_3 within PYREX® standing on a hotplate (ANALAB®) at 130°C , and then by refluxing on a hotplate overnight at 130°C with ~3 ml of 6 mol/l HCl , followed by rinsing by ultrapure water. The tips (Eppendorf®) and tubes were cleaned by soaking in ~25% *v/v* HNO_3 within PYREX®, and then rinsed by ultrapure water.

2.3 Chemical preparation for concentration and isotope analysis

2.3.1 Dissolved load samples

To analyse the element concentrations by inductively coupled plasma optical emission spectroscopy (ICP-OES, Varian 720) and inductively coupled plasma mass spectrometry (ICP-MS, Agilent 7900), the dissolved load samples from the interaction experiments and natural estuaries were divided into a low-Na group

and a high-Na group according to the Na concentrations estimated using sample information (e.g., salinity). An aliquot of each sample in the low-Na group was taken and diluted by a certain amount, ranging from ~7–35×, in 2% v/v HNO₃ to match the Na concentration of ~5 mg/l in 5 ml. An aliquot of each sample in the high-Na group was taken and diluted by a certain amount, ranging from ~4–500×, to match the Na concentration of ~40 mg/l or ~80 mg/l in 5 ml.

To prepare for the chemical separation and Li isotope analysis, 0.010–5 ml of each dissolved load sample, containing ~1–15 ng Li, was taken into vials, dried down on the hotplate at 130 °C, and dissolved in 0.1 ml 0.2 mol/l titrated HCl. In addition, a certain volume of the reference material for Li isotopes (i.e., Atlantic seawater) was dried down in a PFA vial on a hotplate and dissolved in a certain volume of 0.2 mol/l titrated HCl for the chemical separation and Li isotope analysis.

2.3.2 Solid samples

To explore the different fractions within solid samples, a chemical sequential extraction procedure (Figure 2.1), modified from Tessier et al. (1979), in the order of exchangeable, carbonate, oxide, clay, and residue, was conducted. It was applied to 6 solid samples from the interaction experiments, 14 SPM samples and 10 bedload samples from the Borgarfjörður estuary, and 7 SPM samples and 9 bedload samples from the Amazon estuary. The optimal sequential extraction procedure, especially the leaching method for oxides, was tested and verified in Chapter 3. For the solid samples mentioned above, around 1–5 mg of each SPM sample from the Borgarfjörður estuary and 48–52 mg of the other solid samples were weighed into 2 ml centrifuge tubes. The exchangeable fraction was extracted using 1 mol/l NaOAc at room temperature for 1 hour with occasional agitation. To target the carbonate fraction, 1 mol/l NaOAc buffered to pH 5 by HOAc was used at room temperature for 5 hours with occasional agitation. The

oxide fraction was extracted using 0.04 mol/l HH in 25% (v/v) HOAc at room temperature for 1 hour with occasional agitation. The clay fractions were leached in 0.6 mol/l HCl at room temperature for 1 hour with occasional agitation. The clay extraction is primarily designed for examining the Li isotope composition of the secondary silicate fractions, rather than for quantitatively extracting it (Section 3.3). The ratios of the extraction reagent and targeted solid of the exchangeable, carbonate, oxide, and clay fractions are ~16 ml/g, ~16 ml/g, ~40 ml/g, and ~20 ml/g, respectively. The extracted leachate from each step was separated from the solid by centrifuging at 8200×g (relative centrifugal force) for 3 minutes in a Micro Star 12 Microcentrifuge (VWR®). Leachates (i.e., supernatants) were pipetted into pre-cleaned PFA vials, and the remaining solids were subjected to the next extraction step. The leachates in the PFA vials were dried down on a hotplate at 130 °C and dissolved in 1 ml 2% v/v HNO₃. After the extraction of these fractions, the remaining solids (i.e., residue) were totally dissolved by HNO₃ (ca. 68% *m/m*) –HF (47–51% *m/m*) –HClO₄ (65–71% *m/m*), followed by HNO₃ (ca. 68% *m/m*), and then 6 mol/l HCl in PFA vials on the hotplate at 130–140 °C. After dissolution, the solutions were dried down and dissolved in 2 ml 2% v/v HNO₃.

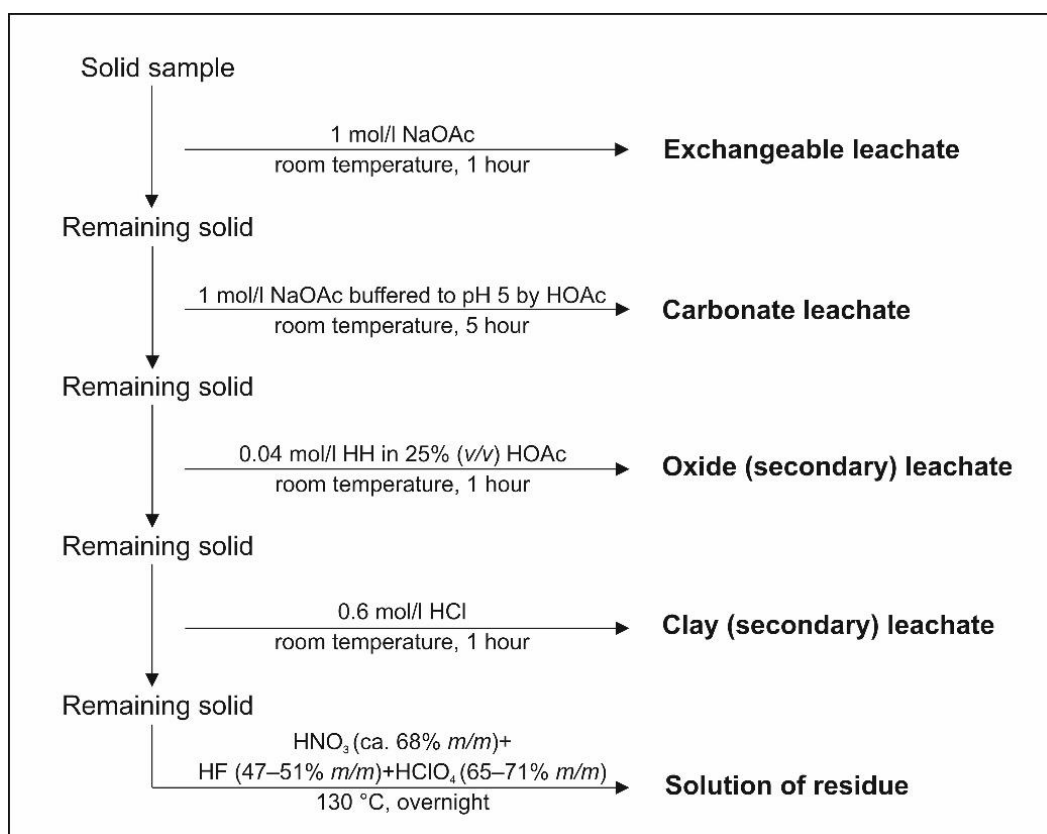


Figure 2.1 Chemical extraction procedure for solid samples.

In addition, analysis of the elemental compositions in the bulk solid samples was conducted on solid samples from the interaction experiments, bedload samples from the Borgarfjörður estuary, and SPM and bedload samples from the Amazon estuary. Around 1–50 mg of each sample was weighed into PFA vials and totally dissolved using HNO₃ (ca. 68% *m/m*) –HF (47–51% *m/m*) –HClO₄ (65–71% *m/m*), followed by HNO₃ (ca. 68% *m/m*), and then 6 mol/l HCl in PFA vials on the hotplate at 130–140 °C. After dissolution, the solutions were dried down and dissolved in 2 ml 2% *v/v* HNO₃.

An aliquot of each leachate of the exchangeable, carbonate, oxide, and clay fractions was taken and diluted by 80–200× in 2% *v/v* HNO₃ for elemental concentration analysis in several Na-matrix matched groups. An aliquot of each

dissolution of residue and bulk sample was taken and diluted 500 or 1000 times for elemental concentration analysis. Furthermore, an aliquot of each leachate and dissolution of residue, which contain ~1-20 ng Li was taken, dried down, and dissolved in 0.1 ml 0.2 mol/l titrated HCl for the chemical separation and Li isotope analysis.

To monitor the chemical extraction and bulk dissolution, the reference material USGS BCR-2 (Basalt, Columbia River) (Wilson, 1998) was treated using both the chemical extraction procedure and bulk dissolution. In addition, two samples from the Borgarfjörður estuary and a Yellow River sediment sample were repeatedly treated and analysed. The repeated full sequential extractions demonstrated fair reproducibility and accuracy (Section 3.3). The total procedural blank using the same leaching reagents was also applied to monitor the potential contamination for each batch of samples processed.

2.4 Elemental concentration analysis

The elemental concentrations of the prepared solutions, including diluted dissolved load samples, leachates of different fractions of the solids, and solutions of dissolved bulk solid samples, were analysed by ICP-OES (Varian 720) and ICP-MS (Agilent 7900) in the LOGIC laboratories.

The concentrations of Na, Mg, K, and Ca of all samples, the concentrations of Al, Mn, and Fe of the oxide leachates, clay leachates, dissolved residues, and dissolved bulk samples, and the concentrations of Si of some dissolved load samples were analysed by ICP-OES. The calibration lines for ICP-OES were constructed using a series of calibration standards made from ICP multi-element standards or ICP single-element standards, including TraceCERT® Periodic table mix 1 for ICP (Sigma-Aldrich®), Instrument Calibration Standard 2 (SPEX CertiPrep®), Ca and Na (Agilent), Li and Mg (VWR® PROLABO®), and Fe, K, and Al (PlasmaCAL, SCP SCIENCE). A standard, which is effectively closest to most

elemental concentrations of most samples, was tested every 10–20 samples as a drift monitor during each analysis batch. If the drift was larger than $\pm 5\%$, a drift correction was applied. An external standard (i.e., in-house standard solution of dissolved NBS SRM 88A) was analysed to assess accuracy and precision, and the results shown in Table 2.1 are within the recommended or published ranges (Gladney et al., 1987). The RSD of individual analyses are better than $\pm 5\%$.

Table 2.1 The elemental concentrations of SRM 88A determined by ICP-OES in this study and previously reported.

SRM 88A	Na mg/g	Mg mg/g	Al mg/g	K mg/g	Ca mg/g	Mn mg/g	Fe mg/g
This study	0.075 ± 0.006	133.558 ± 5.32	3.58 ± 0.30	1.20 ± 0.08	227.09 ± 11.68	0.224 ± 0.012	2.29 ± 0.10
References ^[1]	0.1	128.4	3.3	1.20	215.1	0.232	2.1

The uncertainty is given as the 2SD external error of 8 determinations in this study.

[1] Data are from Gladney et al. (1987), Kumar et al. (2002), and Zhang and Shields (2023).

The Li concentrations of all samples, the Al concentrations of some dissolved load samples, and the concentrations of Al, Mn, and Fe of the exchangeable and carbonate leachates were analysed by ICP-MS. During the measurements, the samples were divided into several Na-matrix groups. The calibration lines for ICP-MS were constructed using a series of calibration standards made from TraceCERT® Periodic table mix 1 for ICP (Sigma-Aldrich®) or Instrument Calibration Standard 2 (SPEX CertiPrep®). The ICP single-element standard Na (Agilent) was adopted to match the Na concentrations in different Na-matrix groups. A standard, which is effectively closest to most elemental concentrations of most samples, was tested every 10–20 samples as a drift monitor during each analysis batch. An external standard (i.e., in-house standard solution of dissolved bulk USGS SGR-1) was analysed to assess accuracy and precision, and the

results shown in Table 2.2 are within the recommended or published ranges (Gladney and Roelandts, 1988). The RSD of individual analyses are better than $\pm 5\%$.

Table 2.2 The elemental concentrations of SGR-1 determined by ICP-MS in this study and previously reported.

SGR-1	Li μg/g	Al mg/g	Mn mg/g	Fe mg/g	Sr mg/g
This study	142.91 ± 9.38 (n=20)	33.55 ± 2.80 (n=7)	0.29 ± 0.01 (n=7)	20.25 ± 2.05 (n=7)	0.44 ± 0.03 (n=7)
References ^[1]	147	34.5	0.27	21.2	0.42

The uncertainty is given as 2SD external error in this study.

[1] Data are from Gladney and Roelandts (1988).

The reported elemental concentrations in the leachates of the solid samples from the interaction experiments and natural estuaries are normalized to the total mass of leached solid according to Eq. 2.1. The composition of each element in the bulk sediment samples, termed $[X]_{\text{bulk-sum}}$, is calculated as the sum of the concentrations of that element in all fractions, with an example for Li given as Eq. 2.2. In contrast, the measured element composition in the bulk solid samples is termed $[X]_{\text{bulk-measured}}$.

$$[X] \text{ in leachate} = X \text{ mass in leachate} / \text{solid mass} = X \text{ concentration (by mass, measured)} \times \text{dilution factor} \times \text{original leachate volume} / \text{solid mass} \quad \text{Eq. 2.1}$$

$$[Li]_{\text{bulk-sum}} = [Li]_{\text{exchangeable}} + [Li]_{\text{carbonate}} + [Li]_{\text{oxide}} + [Li]_{\text{clay}} + [Li]_{\text{residue}} \quad \text{Eq. 2.2}$$

2.5 Lithium isotope analysis

The Li isotope ratios of prepared solutions, including dissolved load samples, leachates and dissolutions of solid samples, reference materials (i.e., Atlantic

seawater and leachates of BCR-2) were analysed by multi-collector inductively coupled plasma mass spectrometer (MC-ICP-MS, Nu Plasma 3) after Li purification in the LOGIC laboratories.

2.5.1 Chemical separation of lithium

The Li purification used a two cation-exchange column procedure (Pogge von Strandmann et al., 2019a). The first columns are PFA microcolumns (Savillex), filled with 3.5 mm (radius) and 8.5 cm (height) of AG[®]50W X-12 resin 200–400 mesh in 0.2 mol/l HCl. The second columns are shrink-wrapped Teflon columns filled with 1.3 mm (radius) and 5 cm (height) of AG[®]50W X-12 resin 200–400 mesh in 0.2 mol/l HCl. The column procedure is given in Table 2.3. The 0.2 mol/l HCl used in the procedure was titrated in the range of 0.200 ± 0.002 mol/l. The solution in the ‘collection’ step was collected in the vial, dried down on the hotplate, and dissolved in 1 ml 2% v/v HNO₃, as the sample solution for Li isotope analysis. To avoid Li isotope fractionation during column elution (Tomascak, 2004; Jeffcoate et al., 2004), the column yield is monitored by collecting splits of the elution before and after the Li collection bracket, which are analysed for Li content. Most of the splits have less than 0.1% of the total Li and less than 0.3% of the total Li was present in all the splits. Thus, the shift in Li isotopes caused by incomplete recovery from the columns is less than the long-term precision in Li isotopic analysis (Pogge von Strandmann et al., 2019a; Gou et al., 2020; Wilson et al., 2021). The total procedural blank samples from chemical preparation or 0.2 mol/l HCl reagent were used to monitor the procedural blank during each batch of Li purification.

Table 2.3 The procedure of cation-exchange columns for Li purification.

First column	
Preconditioning	4 ml 0.2 mol/l HCl
Load sample	0.1 ml 0.2 mol/l HCl
Elution	17.5 ml 0.2 mol/l HCl
Split pre-collection	1 ml 0.2 mol/l HCl
Collection	20 ml 0.2 mol/l HCl
Split after-collection	1 ml 0.2 mol/l HCl
Cleaning	6 mol/l HCl and ultrapure water
Second column	
Preconditioning	1 ml 0.2 mol/l HCl
Load sample	0.1 ml 0.2 mol/l HCl
Elution	4.9 ml 0.2 mol/l HCl
Split pre-collection	1 ml 0.2 mol/l HCl
Collection	12 ml 0.2 mol/l HCl
Split after-collection	1 ml 0.2 mol/l HCl
Cleaning	6 mol/l HCl and ultrapure water

2.5.2 MC-ICP-MS analysis

The Li isotope analyses used a sample-standard bracketing method. The bracketing standards for each sample solution were diluted from the Institute for Reference Materials and Measurements IRMM-016 laboratory stock by 2% v/v HNO₃ to match the Li concentration of the sample solution. The IRMM-016 has an isotopic ratio effectively identical to that of LSVEC (i.e., the delta-zero reference material for Li isotopes, Section 1.2.1) (Flesch et al., 1973; Qi et al., 1997; Jeffcoate et al., 2004; Magna et al., 2004; Pogge von Strandmann et al., 2019a).

The sample solutions and bracketing standards were taken up at a rate of ~100 µl/min into a CETAC Aridus II™ or CETAC Aridus 3 Desolvating Nebulizer system, ionized in the plasma torch, and sampled by a standard dry sampler cone (Part No. 319-646) followed by a skimmer cone that enhances sensitivity for low

mass elements (Part No. 301-020). The ^7Li and ^6Li beams were collected simultaneously by Faraday collectors H9 and L6, respectively, with $10^{11}\Omega$ resistance amplifiers. In this instance, a 5 $\mu\text{g/l}$ Li solution achieved a signal intensity of around 10 V (~ 100 pA) of $^7\text{Li}^+$. The signal intensity of background (2% v/v HNO_3) is less than 0.03 V (0.3 pA). The signal intensities of blank control samples for chemical preparation and chemical separation are less than 1% of the intensities of samples in the same batches.

Each sample ($n=1$), as well as the standards, was measured a total of 3 times with 10 ratios (50 seconds total integration time) each time. The Li isotope data are reported as the variation of the $^7\text{Li}/^6\text{Li}$ ratio in samples to the delta-zero reference LSVEC (or IRMM-016), shown in Eq. 2.3.

$$\delta^7\text{Li} (\text{‰}) = ((^7\text{Li}/^6\text{Li}_{\text{sample}})/(^7\text{Li}/^6\text{Li}_{\text{LSVEC}}) - 1) \times 1000 \quad \text{Eq. 2.3}$$

The precision of $\delta^7\text{Li}$ value for each sample (i.e., internal precision) is expressed as 2 standard deviations (2σ) of 3 determinations. The reproducibility of the repeated chemical preparation and Li isotope analyses (i.e., external precision) is expressed as 2 standard deviations (2SD). The reference material Atlantic seawater was determined in 57 analyses of 51 separate preparations, yielding a $\delta^7\text{Li}$ value of $31.09\text{‰} \pm 0.63\text{‰}$ (2SD, $n = 57$), identical to published values (Jeffcoate et al., 2004; Pogge von Strandmann et al., 2019a; Gou et al., 2020).

The bulk $\delta^7\text{Li}$ values of the solid samples were calculated based on the sum of the measured Li concentrations and isotope compositions for each step in the full leaching sequence, as shown in Eq. 2.4.

$$\delta^7\text{Li}_{\text{bulk-sum}} \times [\text{Li}]_{\text{bulk-sum}} = \delta^7\text{Li}_{\text{exchangeable}} \times [\text{Li}]_{\text{exchangeable}} + \delta^7\text{Li}_{\text{carbonate}} \times [\text{Li}]_{\text{carbonate}} + \delta^7\text{Li}_{\text{oxide}} \times [\text{Li}]_{\text{oxide}} + \delta^7\text{Li}_{\text{clay}} \times [\text{Li}]_{\text{clay}} + \delta^7\text{Li}_{\text{residue}} \times [\text{Li}]_{\text{residue}} \quad \text{Eq. 2.4}$$

2.6 Other analysis

The concentrations of F^- , Cl^- , Br^- , and SO_4^{2-} of the dissolved load samples from Borgarfjörður estuary were measured by Ion Chromatography (DIONEX-ICS3000) at Durham University. The alkalinity of the dissolved load samples from Borgarfjörður estuary was determined by titration with HCl within 6 hours of collection.

The concentrations of NO_2^- , NO_3^- and SiO_4^{4-} of dissolved load samples from the Amazon estuary were analysed by SEAL QuAAtro continuous flow auto analyser on board (Koschinsky et al., 2018). The total alkalinity of dissolved load samples from the Amazon estuary were analysed at GEOMAR (Helmholtz Centre for Ocean Research Kiel) (Koschinsky et al., 2018). The surface area of bedload samples from the Amazon estuary were determined by Nova 1200 (Quantachrome) BET Analyser at the Johannes Gutenberg University, Mainz.

The images of 3 solid samples from the interaction experiments, 2 bedload samples from the Borgarfjörður estuary, and 2 bedload samples from the Amazon estuary were obtained by Scanning Electron Microscope (SEM, JSM-6480LV) using a 7 kV accelerating voltage and around 9 mm working distance at the Department of Earth Sciences, University College London.

Chapter 3. Leaching method exploration

3.1 Introduction

The geochemical properties of Li and Li isotopes are highly dependent on the Li sites in the solid during weathering (Chapter 1) (Pistiner and Henderson, 2003; Vigier et al., 2008; Wimpenny et al., 2010a, 2015; Pogge von Strandmann et al., 2019a; Hindshaw et al., 2019; Zhang X. et al., 2021; Li et al., 2021). It is therefore important to distinguish Li that is held in different solid fractions and bonding environments.

To date, several sequential leaching methods have been applied and partly developed to extract Li from different fractions within silicate solids (Hindshaw et al., 2018; Pogge von Strandmann et al., 2019a, 2022; Li et al., 2020; He et al., 2021; Liu et al., 2022). The exchangeable Li is generally leached using sodium acetate (NaOAc) (Tessier et al., 1979; Hindshaw et al., 2018; Pogge von Strandmann et al., 2019a; Liu et al., 2022), acetic acid (HOAc) (Chan and Hein, 2007; Wimpenny et al., 2010b), or ammonium chloride (NH₄Cl) (Vigier et al., 2008; Hindshaw et al., 2019). Carbonate fractions have been leached using HOAc-buffered NaOAc or weak acid (Pogge von Strandmann et al., 2013, 2019b; He et al., 2021; Cao et al., 2023). For the Fe/Mn/Al-oxides/oxyhydroxides and clay fractions, some studies have attempted to leach the Fe/Mn/Al-oxides/oxyhydroxides and clay fractions together using HCl (Chan and Hein, 2007; Wimpenny et al., 2010b; Pogge von Strandmann et al., 2019a). These HCl leachates were regarded as leaching either oxides or clays (or some combination) depending on which is the dominant fraction in a given sample. For example, Wimpenny et al. (2010b) highlight the impact of the formation of Fe/Mn-oxides/oxyhydroxides on Li isotopic fractionation, while Pogge von Strandmann

et al., (2019a) emphasise the importance of clay formation. More importantly, some research suggests that the formation of secondary Fe/Mn-oxides/oxyhydroxides has a significant impact on Li isotopic fractionation (Vigier et al., 2008; Wimpenny et al., 2010b; Lemarchand et al., 2010; Hindshaw et al., 2018; Yang et al., 2023) and plays important roles in the global carbon cycle and climate change in terms of both silicate weathering and organic carbon burial (Hawley et al., 2017). To extract the oxides, Hindshaw et al. (2018) used 0.005 mol/l hydroxylamine hydrochloride (HH, $\text{NH}_2\text{OH}\cdot\text{HCl}$) to target the secondary oxides contained in shales, which led to significantly lighter Li isotope compositions for the oxide fractions than the corresponding bulk samples. In contrast, Li et al. (2020) used a 100 times more concentrated HH solution (0.5 mol/l) to leach Fe/Mn-oxides/oxyhydroxides within a Hawaiian soil profile, and Yang et al. (2023) used 1 mol/l HH solution to extract oxides of Yangtze River estuarine suspended sediments. Finally, the residual fraction is dissolved by strong acids, $\text{HF-HClO}_4\text{-HNO}_3\text{-HCl}$ (Tessier et al., 1979; Ryan and Langmuir, 1987; Pogge von Strandmann et al., 2019a).

As yet, the main concern for (sequential) extracting different fractions from solid samples for Li isotopes is whether these extractions successfully targeted the expected fractions or not (Pogge von Strandmann et al., 2019b; Liu et al., 2022; Cao et al., 2023). Typically, the various methods were applied in different studies, however, without additional information (such as trace element concentrations) that would enable examination and comparison. Especially the leaching methods for the oxide fraction have only been sparsely applied and the leaching reagents are more than 100 times different in concentration between studies (Hindshaw et al., 2018; Li et al., 2020; Yang et al., 2023).

This study targeted five fractions in the solids. Firstly, the exchangeable fraction refers to the cations adsorbed (exchanged) on the negatively charged external and internal surfaces of the clays (Velde 1995). Secondly, the carbonate

fraction includes the carbonate minerals, such as calcite, aragonite, and dolomite. Thirdly, the oxide fraction represents the cations incorporated into oxides and oxyhydroxides. The extraction of the oxide fraction in this study aims to target the secondary oxides, such as goethite, lepidocrocite, pyrolusite, and gibbsite (Section 3.2.3). Fourthly, the clay fraction refers to the cations incorporated into the clay lattice (Velde 1995). Fifthly, the remaining solid (i.e., residue fraction) is thought to be dominated by the primary silicate minerals.

In this chapter, different oxide leaching methods were applied to 5 different silicate solids, including a fresh basalt, two basaltic river sediments, a Yellow River sediment, and a shale, to inform recommendations for optimal oxide leaching approaches (Section 3.2) (Liu et al., 2022). Three factors were assessed in the oxide leaching trials: the leaching temperature (20 °C versus 95 °C), the leaching time, and the reagent/solid ratio. Then, to verify the full sequential leaching procedure in this study, the features of the element distribution in different fractions from repeated full sequential leaching (i.e., exchangeable, carbonate, oxide, clay, and residue) conducted on 4 different solids are discussed (Section 3.3).

3.2 Oxide leaching method trials

3.2.1 Materials and leaching methods

Five silicate solids were used as examples to compare different extraction methods of oxides from different lithological samples (i.e., fresh and weathered basalt, shale, and loess) for Li isotopes.

The first solid (i.e., RS) and second solid (i.e., RRS) are two basaltic river sand samples originally collected from the Borgarfjörður estuary in West Iceland. The RS is the solid that was used in water-rock interaction experiments by Pogge von Strandmann et al. (2019a). It mainly comprises ~55% microcrystalline material, ~19% volcanic glass, ~10% Ca feldspar, ~8% olivine, ~4% Fe-Ti oxide,

~3% K-feldspar, and a few quartz grains based on grain counting using SEM (Jones et al., 2012). The RRS is the reacted solid after these water-rock interaction experiments, during which the RS reacted with river water for around 9 months (Pogge von Strandmann et al., 2019a). There is no significant difference between RS and RRS based on XRD and FTIR analyses. However, Mg smectites as well as other secondary minerals likely formed during the interaction experiment, as indicated by element concentrations and Li isotopes (Pogge von Strandmann et al., 2019a). The RS and RRS were crushed by quartz mortar and pestle to finer than around 1 mm to avoid heterogeneity of the mineralogy between replicated leaching of each aliquot.

The third solid is the USGS reference material BCR-2 (Basalt, Columbia River) (Wilson, 1998). BCR-2 was collected from Bridal Veil Flow Quarry by the U.S Geological Survey and is an aphanitic hypocrySTALLINE basalt, characterised as andesine-trachybasalt (Flanagan, 1967). Plagioclase and pyroxenes are the dominant minerals, and it contains brown glass and iron oxides. (Hamilton, 1963; Flanagan, 1967).

The fourth solid is the USGS reference material SGR-1b (Green River Shale) (Gladney and Roelandts, 1988). SGR-1b is a lacustrine sedimentary shale, collected from part of the Mahogany Oil Shale Zone of the adjacent Piceance Creek Basin, Green River Formation, Western USA (Boak and Poole, 2015). The mineralogy of the shales near the site of SGR-1 in the Green River formation generally are ~20–35% feldspar, ~10–30% quartz, ~8–18% dolomite, and ~6–10% calcite. Clay minerals and organic matter comprise ~10–30% and ~3–10%, respectively (Boak and Poole, 2015).

The fifth solid (YR) is a sediment from the Yellow River estuary. The sediment was collected from the Ecological Tourism Area of the Yellow River Estuary (119°09'44.86" E, 37°45'32.53" N) on 6th November 2019. The sample was dried in the oven at 60 °C after collecting. Loess from the Chinese Loess Plateau

contributes more than 90% of the Yellow River sediments (Zhang et al., 1990). The sediments at the Yellow River mouth generally contain ~40% quartz, ~30% clay minerals, ~15% plagioclase, ~10% calcite, and ~7% potassium feldspar (Tian et al., 2021).

The elemental compositions of the bulk solids are given in Table 3.1.

Table 3.1 Elemental composition of bulk solids.

Sample	Fe _{total} mg/g	Mn μg/g	Al mg/g	Si mg/g	Ca mg/g	Mg mg/g	K mg/g	Li μg/g
RS	85.5	2097	78.0	n.d.	75.6	49.8	2.0	5.4
BCR-2	96.5	1520	71.4	253	50.9	21.6	14.9	~9
SGR-1	21.2	267	34.5	132	59.9	26.8	13.8	147
YR	27.2	516	63.0	n.d.	44.2	12.7	16.9	30

The elemental compositions of RS and YR are obtained from the measured elemental concentrations in the bulk dissolution in this study. The elemental composition of BCR-2 and SGR-1 are from Wilson (1998) and Gladney and Roelandts (1988), respectively.

The exploration of leaching methods was conducted in the LOGIC laboratories. The supplies of leaching reagents are described in Section 2.2. The extraction operation is similar to the operation shown in Section 2.3.2. A given mass of solids was weighed and added to centrifuge tubes, and the solid was leached using a certain volume of specific leaching reagents under specific temperature for certain hours, as designed in Section 3.2.2 (Table 3.2). The extracted leachate from each step was separated from the solid by centrifuging at 8200×g (relative centrifugal force) for 3 minutes in a Micro Star 12 Microcentrifuge (VWR®). A certain volume of leachates (i.e., supernatants) were pipetted into pre-cleaned PFA vials or removed, and the remaining solids were subjected to the next extraction step if applicable. The leachates in the PFA vials were dried down on a hotplate at 130 °C and dissolved in 1 ml 2% v/v HNO₃ for

further concentration analysis and Li isotope analysis (Sections 2.4 and 2.5). The high temperature conditions (95 °C) were created with a Pyrex water-bath on a hotplate, with a variability of 92 °C to 98 °C.

3.2.2 Leaching experimental trial design

Three different oxide leaching methods were tested (Table 3.2).

The first oxide leaching method (Tessier oxide leaching method) is based on Tessier et al. (1979). The oxide leaching reagent is 0.04 mol/l HH in 25% (v/v) HOAc. Before oxide leaching, the exchangeable fractions were removed using 1 mol/l NaOAc at room temperature for 1 hour. Based on this method, several oxide leaching experimental trials were designed to examine the influence of temperature, leaching time, and the reagent/solid ratio. For all five solid materials, around 50 mg solids were leached using 2 ml leaching reagent (i.e., a reagent/solid ratio of 40 ml/g), at both room temperature (i.e., 20±2 °C) and high temperature (i.e., 95±3 °C) for 1 hour, 3 hours, and 6 hours. For SGR-1b, one more group of leaching trials was performed with a larger reagent/solid ratio. Specifically, 12 mg to 14 mg for each solid was leached using 2 ml leaching reagent, giving a reagent/solid ratio of 143 ml/g to 167 ml/g. The leaching was replicated 3 or 4 times for each specific leaching condition.

The second leaching method (weak oxide leaching method) is based on Hindshaw et al. (2018). In this case, around 100 mg solids were leached using 0.3125 ml 0.005 mol/l HH in 2.6 mol/l HOAc (reagent/solid ratio of 3.125 ml/g) at room temperature for 1 hour. The exchangeable fractions were removed before oxide leaching as above. This leaching method was conducted on RS, RRS, BCR-2, and SGR-1b, with 4 replicates for each specific leaching condition.

The third leaching method (strong oxide leaching method) is from the Community Bureau of Reference (Rauret et al., 1999; Li et al., 2020), which recommends a stronger leaching solution of 0.5 mol/l HH in 0.05 mol/l HNO₃ (pH = 1.5). In this study, around 50 mg of each sample of RS, RRS, and BCR-2, were

leached using 2 ml strong leaching reagent at room temperature for 16 hours (reagent/solid ratio of 40 ml/g). As above, the exchangeable fractions were removed before oxide leaching. The leaching was replicated 3 times for each specific leaching condition.

Table 3.2 List of oxide leaching method experimental trials.

Leachates	Solid	reagent	reagent /solid ml/g	time hour	temperature °C	replicate samples
RS-L1	RS	0.04 mol/l HH in 25% v/v HOAc	40	1	20	4
RS-L3	RS	0.04 mol/l HH in 25% v/v HOAc	40	3	20	4
RS-L6	RS	0.04 mol/l HH in 25% v/v HOAc	40	6	20	3
RS-H1	RS	0.04 mol/l HH in 25% v/v HOAc	40	1	95	4
RS-H3	RS	0.04 mol/l HH in 25% v/v HOAc	40	3	95	4
RS-H6	RS	0.04 mol/l HH in 25% v/v HOAc	40	6	95	3
RS-W	RS	0.005 mol/l HH in 2.6 mol/l HOAc	3	1	20	4
RS-S	RS	0.5 mol/l HH in 0.05 mol/l HNO ₃ (pH = 1.5)	40	16	20	3
RRS-L1	RRS	0.04 mol/l HH in 25% v/v HOAc	40	1	20	3
RRS-L3	RRS	0.04 mol/l HH in 25% v/v HOAc	40	3	20	3
RRS-L6	RRS	0.04 mol/l HH in 25% v/v HOAc	40	6	20	3
RRS-H1	RRS	0.04 mol/l HH in 25% v/v HOAc	40	1	95	3
RRS-H3	RRS	0.04 mol/l HH in 25% v/v HOAc	40	3	95	3
RRS-H6	RRS	0.04 mol/l HH in 25% v/v HOAc	40	6	95	3
RRS-W	RRS	0.005 mol/l HH in 2.6 mol/l HOAc	3	1	20	4
RRS-S	RRS	0.5 mol/l HH in 0.05 mol/l HNO ₃ (pH = 1.5)	40	16	20	3
BCR-L1	BCR-2	0.04 mol/l HH in 25% v/v HOAc	40	1	20	4
BCR-L3	BCR-2	0.04 mol/l HH in 25% v/v HOAc	40	3	20	4
BCR-L6	BCR-2	0.04 mol/l HH in 25% v/v HOAc	40	6	20	4
BCR-H1	BCR-2	0.04 mol/l HH in 25% v/v HOAc	40	1	95	4
BCR-H3	BCR-2	0.04 mol/l HH in 25% v/v HOAc	40	3	95	4
BCR-H6	BCR-2	0.04 mol/l HH in 25% v/v HOAc	40	6	95	4

Leachates	Solid	reagent	reagent /solid ml/g	time hour	temperature °C	replicate samples
BCR-W	BCR-2	0.005 mol/l HH in 2.6 mol/l HOAc	3	1	20	4
BCR-S	BCR-2	0.5 mol/l HH in 0.05 mol/l HNO ₃ (pH = 1.5)	40	16	20	3
SGR-L1	SGR-1b	0.04 mol/l HH in 25% v/v HOAc	40	1	20	3
SGR-L3	SGR-1b	0.04 mol/l HH in 25% v/v HOAc	40	3	20	3
SGR-L6	SGR-1b	0.04 mol/l HH in 25% v/v HOAc	40	6	20	3
SGR-H1	SGR-1b	0.04 mol/l HH in 25% v/v HOAc	40	1	95	3
SGR-H3	SGR-1b	0.04 mol/l HH in 25% v/v HOAc	40	3	95	3
SGR-H6	SGR-1b	0.04 mol/l HH in 25% v/v HOAc	40	6	95	3
SGR-L1-V	SGR-1b	0.04 mol/l HH in 25% v/v HOAc	167	1	20	4
SGR-L3-V	SGR-1b	0.04 mol/l HH in 25% v/v HOAc	167	3	20	3
SGR-L6-V	SGR-1b	0.04 mol/l HH in 25% v/v HOAc	167	6	20	3
SGR-H1-V	SGR-1b	0.04 mol/l HH in 25% v/v HOAc	143	1	95	4
SGR-H3-V	SGR-1b	0.04 mol/l HH in 25% v/v HOAc	143	3	95	4
SGR-H6-V	SGR-1b	0.04 mol/l HH in 25% v/v HOAc	143	6	95	3
SGR-W	SGR-1b	0.005 mol/l HH in 2.6 mol/l HOAc	3	1	20	4
YR-L1	YR	0.04 mol/l HH in 25% v/v HOAc	40	1	20	3
YR-L3	YR	0.04 mol/l HH in 25% v/v HOAc	40	3	20	3
YR-L6	YR	0.04 mol/l HH in 25% v/v HOAc	40	6	20	3
YR-H1	YR	0.04 mol/l HH in 25% v/v HOAc	40	1	95	3
YR-H3	YR	0.04 mol/l HH in 25% v/v HOAc	40	3	95	3
YR-H6	YR	0.04 mol/l HH in 25% v/v HOAc	40	6	95	2

Table 3.3 Elemental concentrations and Li isotopes of oxide leaching method experimental trials.

Sample	Replicate samples	Elemental concentrations														$\delta^7\text{Li}$	SD
		Fe	RSD	Mn	RSD	Al	RSD	Ca	RSD	Mg	RSD	K	RSD	Li	RSD		
		mg/g		$\mu\text{g/g}$		mg/g		mg/g		mg/g		$\mu\text{g/g}$		ng/g			
RS-L1	4	1.16	5%	73.6	4%	1.22	5%	0.984	4%	0.516	6%	20.4	7%	92.0	2%	3.67	0.42
RS-L3	4	1.90	12%	84.9	6%	1.70	13%	1.61	9%	0.981	8%	32.3	6%	134	11%	3.62	0.20
RS-L6	3	2.51	4%	90.6	4%	2.03	5%	1.85	5%	1.21	4%	30.9	9%	159	3%	3.46	0.37
RS-H1	4	4.16	14%	117	9%	1.80	9%	1.36	9%	2.16	3%	37.5	6%	350	6%	-1.74	0.21
RS-H3	4	6.07	5%	147	6%	1.63	8%	1.28	8%	4.38	6%	45.7	8%	546	2%	-2.10	0.14
RS-H6	3	8.58	6%	185	3%	2.05	12%	1.62	9%	7.97	9%	46.5	7%	671	2%	-1.47	0.48
RS-W	4	0.338	36%	38.5	22%	0.362	34%	0.278	39%	0.124	41%	6.47	24%	30.0	24%	5.59	0.73
RS-S	3	5.25	7%	124	8%	3.90	8%	5.15	6%	2.98	7%	68.1	6%	396	32%	2.36	0.30
RRS-L1	3	1.30	8%	69.2	3%	1.25	8%	1.08	10%	0.542	10%	20.7	9%	123	3%	5.33	0.61
RRS-L3	3	2.02	3%	79.3	2%	1.66	4%	1.61	2%	0.943	3%	27.6	1%	146	3%	5.87	0.16
RRS-L6	3	2.79	8%	89.0	6%	2.16	7%	2.16	7%	1.36	6%	40.3	11%	277	7%	5.74	0.56
RRS-H1	3	7.05	4%	148	4%	2.49	6%	2.36	5%	5.21	4%	47.0	9%	480	6%	0.74	0.32
RRS-H3	3	9.71	3%	192	4%	2.07	10%	2.17	4%	8.98	3%	41.6	5%	699	4%	0.03	0.78
RRS-H6	3	11.9	9%	222	7%	1.91	1%	2.45	11%	12.4	9%	46.9	40%	802	10%	0.89	0.57
RRS-W	4	0.503	19%	40.1	10%	0.468	19%	0.407	17%	0.223	23%	8.27	23%	46.4	13%	9.08	0.32
RRS-S	3	6.01	13%	136	8%	4.34	11%	4.75	12%	3.78	13%	62.9	6%	312	10%	3.67	0.19
BCR-L1	4	1.26	4%	17.7	4%	0.345	10%	0.758	8%	0.0910	7%	37.7	9%	39.1	6%	-0.74	0.70
BCR-L3	4	2.04	4%	25.9	3%	0.446	10%	0.747	5%	0.138	5%	43.5	8%	52.6	5%	-1.33	0.71
BCR-L6	4	2.54	4%	31.3	5%	0.509	4%	0.699	5%	0.184	3%	42.4	4%	69.3	10%	-0.65	0.50
BCR-H1	4	5.41	9%	71.6	10%	0.556	10%	0.929	7%	0.553	11%	96.6	5%	335	9%	-0.94	0.13
BCR-H3	4	8.34	2%	119	2%	0.540	3%	0.826	2%	1.08	3%	130	3%	630	7%	-0.43	0.07
BCR-H6	4	10.7	4%	151	3%	0.727	6%	0.891	6%	1.41	4%	157	3%	798	5%	-0.42	0.05
BCR-W	4	0.653	15%	10.6	10%	0.155	7%	0.154	7%	0.0490	19%	20.2	12%	20.2	13%	-3.06	0.20

Sample	Replicate samples	Elemental concentrations															SD
		Fe	RSD	Mn	RSD	Al	RSD	Ca	RSD	Mg	RSD	K	RSD	Li	RSD	$\delta^7\text{Li}$	
		mg/g		$\mu\text{g/g}$		mg/g		mg/g		mg/g		$\mu\text{g/g}$		ng/g		‰	
BCR-S	3	4.59	2%	51.3	2%	0.801	2%	4.34	0%	0.472	4%	50.0	9%	164	6%	-1.05	0.26
SGR-L1	3	2.91	9%	59.6	11%	0.111	11%	15.8	10%	5.66	13%	29.6	15%	712	3%	20.20	0.63
SGR-L3	3	4.43	3%	95.7	4%	0.143	0%	25.1	4%	10.0	4%	33.1	12%	982	0.1%	20.19	0.38
SGR-L6	3	6.15	5%	148	6%	0.176	7%	38.1	6%	17.3	8%	35.0	36%	1500	0.6%	20.64	0.46
SGR-H1	3	7.86	3%	182	4%	0.217	5%	46.8	5%	21.7	4%	77.6	2%	2090	4%	18.88	0.60
SGR-H3	3	8.58	7%	189	7%	0.265	2%	48.3	8%	22.5	8%	105	15%	2290	4%	16.58	0.29
SGR-H6	3	8.72	8%	193	5%	0.274	7%	48.7	6%	22.9	6%	116	5%	2420	7%	15.72	0.33
SGR-L1-V	4													1470	14%	21.64	0.82
SGR-L3-V	3													1970	3%	21.38	0.49
SGR-L6-V	3													2000	7%	20.89	0.48
SGR-H1-V	4	7.98	7%	204	6%	0.304	7%	45.3	7%	21.3	5.5%	97.0	10%	2370	7%	19.20	0.63
SGR-H3-V	4	8.10	6%	190	6%	0.364	5%	41.3	6%	19.7	6.0%	163	10%	3000	6%	14.59	1.12
SGR-H6-V	3	8.27	17%	169	15%	0.444	14%	36.6	12%	17.6	14.4%	224	14%	4410	3%	11.80	0.33
SGR-W	4	0.96	4%	18.5	3%	0.0443	18%	5.15	4%	1.65	2.8%	12.1	15%	248	5%	21.23	0.63
YR-L1	3	0.25	7%	211	4%	0.172	4%	36.9	5%	0.715	8%	36.0	29%	212	5%	5.06	0.18
YR-L3	3	0.35	2%	209	3%	0.189	4%	36.1	2%	1.06	2%	33.8	11%	245	11%	4.10	0.70
YR-L6	3	0.48	3%	228	5%	0.233	1%	39.6	5%	1.44	2%	43.2	24%	277	2%	3.85	0.88
YR-H1	3	1.35	5%	237	4%	0.351	9%	38.6	5%	2.90	6%	84.6	7%	1210	2%	-5.20	0.19
YR-H3	3	2.06	2%	249	2%	0.562	5%	38.9	1%	3.22	0.5%	96.9	4%	2470	2%	-4.67	0.39
YR-H6	3	2.78	5%	267	0.1%	0.778	7%	40.6	0.2%	3.66	3%	114	15%	3700	7%	-4.89	0.20

The RSD and SD are the relative standard deviations of elemental concentrations and standard deviations of $\delta^7\text{Li}$ in the replicate 'oxide leachate'. The long-term uncertainty of seawater $\delta^7\text{Li}$ analysis using MC-ICP-MS is 0.63‰ (2SD).

3.2.3 Influence of temperature

Leaching temperature has a significant impact on the leachate compositions (Table 3.3; Figure 3.1), which may indicate that different minerals are being attacked during oxide leaching at different temperatures.

In the oxide fraction, the Fe is expected to be the major element. For all 5 solids, the Fe concentrations in the high temperature extractions is several times higher than in the room temperature extractions for the same leaching time (Figures 3.1 and 3.2). To be specific, the Fe concentration is approximately twice as high for SGR-1b at high temperature than at room temperature, while it is 3 times higher for RS, 4 times higher for BCR-2, and 5 times higher for RRS and YR at high temperature than at room temperature, respectively. Chester and Hughes (1967) also showed that 25% HOAc-acidified HH can dissolve more Fe at high temperature compared to room temperature during leaching of pelagic sediments, which they explained by the apparent targeting of clays. Similarly, the extractions generally have enriched Mn in higher temperature, by approximately a factor of 2 in RS, RRS, and SGR-1b, and by a factor of ~4 for BCR-2, compared to room temperature leaching. However, in the YR leachates, there is no significant difference in the Mn concentration between high temperature and room temperature extractions (Figure 3.1). In the high temperature extraction, the concentrations of Al, Ca, and K are either similar to, or up to twice that in room temperature extractions when other leaching variables remain constant. Most notably, high temperature extraction increases the Mg concentration even more than that of Fe. The Mg concentrations in the high temperature extractions are 1.5 to 4 times higher for SGR-1b and YR, and 4 to 10 times higher for RS, RRS, and BCR-2 than the room temperature extractions.

The high temperature leaching also causes more Li to be leached out (Figures 3.1 and 3.2). For RS, RRS, and SGR-1b, the impact of high temperature on Li is similar to its impact on Fe, leading to around 2 to 4 times more Li being leached than at room temperature. For BCR-2 and YR, the Li concentration increases even more significantly than Fe. Most interestingly, the $\delta^7\text{Li}$ values in the leachates of RS, RRS, YR, and SGR-1b at high temperature for a range of leaching times ($-1.8 \pm 0.4\text{‰}$ (SD, $n = 11$), $0.6 \pm 0.6\text{‰}$ (SD, $n = 9$), $-4.9 \pm 0.4\text{‰}$ (SD, $n = 8$), and $16.0 \pm 2.6\text{‰}$ (SD, $n = 20$, also including different reagent/solid ratios), respectively) are distinctly lower than those from the room temperature leachates ($3.6 \pm 0.3\text{‰}$ (SD, $n = 11$), $5.6 \pm 0.5\text{‰}$ (SD, $n = 9$), $4.3 \pm 0.8\text{‰}$ (SD, $n = 9$), and

20.8±0.7‰ (SD, n = 19), respectively) (Figure 3.2). In contrast, the leachates of BCR-2 do not show this difference and exhibit a narrow range of $\delta^7\text{Li}$ values between -1.3 to -0.4‰, with an average of -0.8±0.5‰ (SD, n = 24), at both room temperature and high temperature across a range of leaching times.

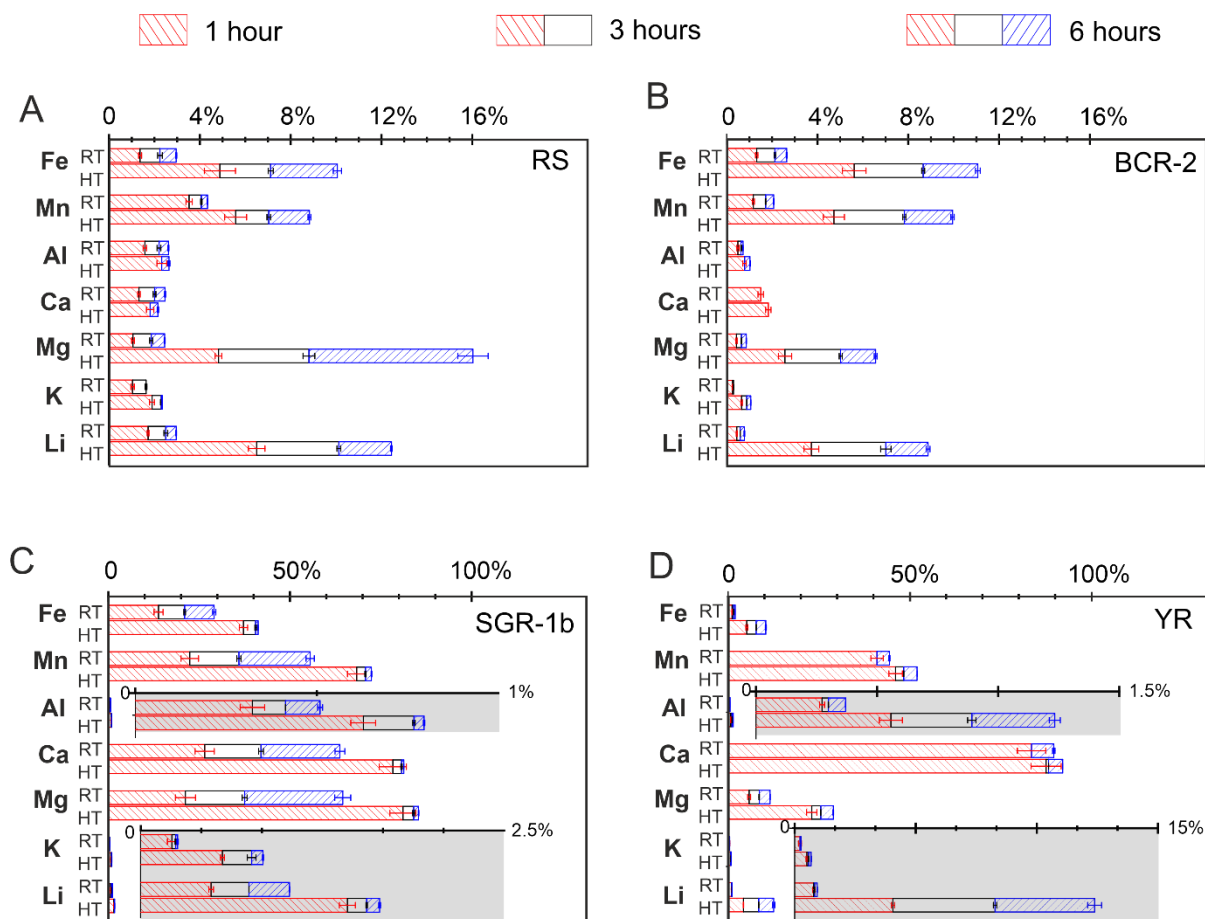


Figure 3.1 Elemental concentrations in the experimental trials of the Tessier oxide leaching method as a percentage of the total elemental concentrations of each bulk solid.

RT: room temperature (20±2°C), HT: high temperature (95±3°C). The columns with separate axes in shaded areas are magnifications of data for Al, K, and Li where required to better visualize the data. The error bar is the standard deviation of the replicated samples.

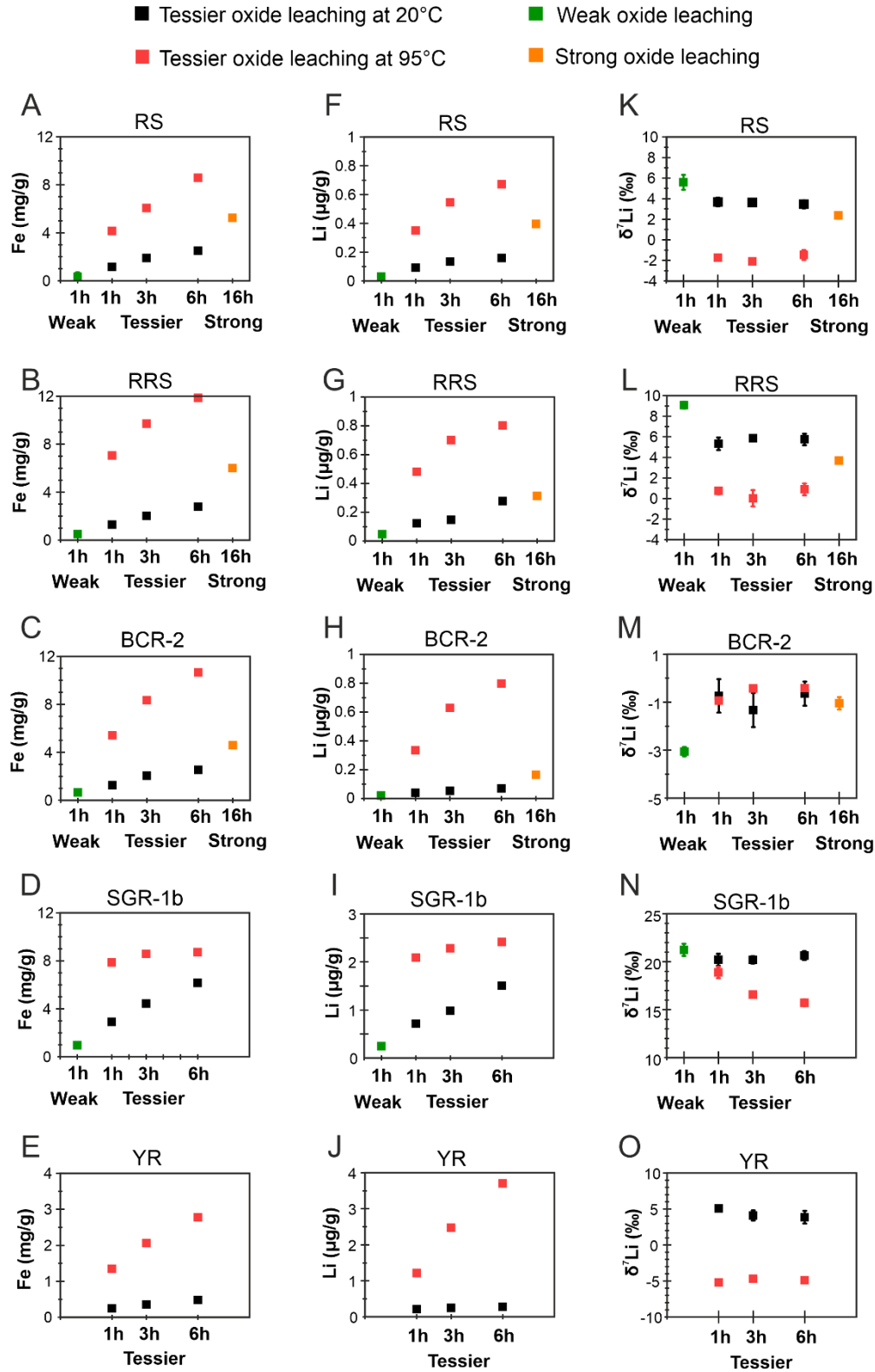


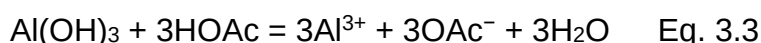
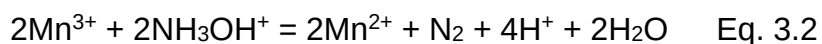
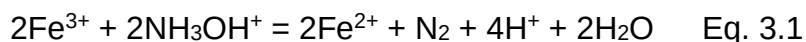
Figure 3.2 Fe and Li concentrations and Li isotopes in oxide leachates from leaching experimental trials.

See Section 3.2.2 for details of the different leaching methods. The error bars represent the standard deviation of the replicates. The absence of visible error bars means that these error bars are smaller than the symbol size.

The elemental concentration and Li isotope data together imply that the targeted minerals or fractions are different during high temperature and room temperature leaching. Basically, the expected oxide fraction in this study comprises secondary oxides, i.e., secondary Fe oxides/oxyhydroxides (e.g., goethite, lepidocrocite), secondary Mn oxides/oxyhydroxides (e.g., pyrolusite), and Al oxides/oxyhydroxides (e.g., gibbsite). However, there is no element exclusive to secondary oxides. For example, Fe in rocks generally has four forms: (i) bonded Fe in primary minerals (e.g., olivine, pyroxene) (Bigham et al., 2002; Jones et al., 2012), (ii) primary Fe oxides (e.g., Fe-Ti oxides, magnetite) (Bigham et al., 2002), (iii) secondary clays (e.g., smectites) (Velde, 1995), and (iv) secondary Fe oxides/oxyhydroxides (e.g., goethite, lepidocrocite) (Bigham et al., 2002). The Mn is preferentially incorporated into oxides/oxyhydroxides rather than into silicate secondary minerals such as clays, but it also tends to be included in carbonate and sulfide fractions (Pogge von Strandmann et al., 2019b; Dellinger et al., 2020; Lenstra et al., 2021). The most common form of Al hydroxide is gibbsite, and Al can also substitute for Fe in oxides/oxyhydroxides (Dixon and Weed, 1989; Pinney and Morgan, 2013). However, oxides/hydroxides are not the dominant fraction for Al, because Al is present at considerable levels in clays and primary minerals. Moreover, gibbsite has similar features to clays, such as a fine particle size and a capacity for the adsorption of cations (Velde, 1995; Bowles, 2021), and gibbsite can precipitate within the interlayer area of clays (Velde, 1995). It is therefore difficult to reliably distinguish gibbsite from Fe/Mn-oxides/oxyhydroxides fractions or the clay fraction. However, Ca, Mg, and K are rarely contained within secondary oxides to any significant degree, so high concentrations of those elements in an extraction targeting oxides would imply the influence of other fractions.

The reagent HH is a reducing agent, which is designed to reduce transition metals, especially Fe and Mn. Theoretically, it can reduce Fe (III) to Fe (II) and Mn (III)/(IV) to Mn (II), as shown in Eqs. 3.1 and 3.2 (Bratsch, 1989). Because both Fe(II) and Mn(II) are more soluble than in their oxidised states (Seidell, 1919; Schwertmann, 1991), these reactions enhance the leaching of oxides/oxyhydroxides. The reagent HH was used in 25% v/v HOAc (pH $\approx$ 2), leading to an acidic environment. Such an acidic environment can also play a role in leaching elements itself, such as Al as shown in Eq. 3.3. Since Al is not a transition metal, Al-oxides/oxyhydroxides are more sensitive to pH than pE (Eh),

and it has been shown that gibbsite can be dissolved in dilute NaOH or HCl in a few minutes (Hashimoto and Jackson, 1960; Hsu, 1979; Dixon and Weed, 1989). Importantly, the acidic conditions may also lead to partial leaching of other fractions, such as carbonates, clays, or other residual silicates.



It follows that temperature can affect elemental concentrations in the leachates by controlling the reductive ability of HH, the solubility of elements, and the acidity of HOAc. According to standard electrode potentials (E^0) and their temperature coefficients, both the reductive ability of HH ($\text{N}_2(\text{g}).\text{H}^+/\text{NH}_3\text{OH}^+$, $E^0 = -1.83 \text{ V}$, $dE^0/dT = -0.96 \text{ mV/K}$) and the oxidative ability of Fe^{3+} ($\text{Fe}^{3+}/\text{Fe}^{2+}$, $E^0 = 0.771 \text{ V}$, $dE^0/dT = 1.175 \text{ mV/K}$) and Mn^{3+} ($\text{Mn}^{3+}/\text{Mn}^{2+}$, $E^0 = 1.56 \text{ V}$, $dE^0/dT = 1.8 \text{ mV/K}$) increase with temperature, with an approximately linear relationship in the range of 0 to 100 °C (Bratsch, 1989). Similarly, the solubility of Fe and Mn in some aqueous solutions increases with temperature, as seen for FeCl_2 , FeCl_3 , $\text{Fe}(\text{NO}_3)_2$ and MnCl_2 (Seidell, 1919). The solubility of CaCl_2 , MgCl_2 , KCl , and LiCl also increases with temperature (Seidell, 1919).

Generally, Fe in primary minerals exists as both ferrous and ferric Fe, while most of the Fe in secondary oxides is in a ferric form (Bigham et al., 2002). In addition, mineral crystallinity is an important factor. Amorphous and poorly crystalline Fe oxides are thought to be leached more readily than crystalline Fe oxides (Chao, 1972; Gupta and Chen, 1975; Chan and Hein, 2007). So, theoretically, the order of Fe-bearing minerals expected to be leached out by HH would be secondary Fe oxide/oxyhydroxides, followed by Fe-bearing clays, primary Fe oxides, and then Fe-bearing primary silicates. Therefore, the relatively high Fe concentrations in high temperature leachates may imply dissolution of the minerals that are not explicitly targeted, such as primary oxides or clays. This hypothesis is supported by an experimental study on pyroxene dissolution by $\text{HCl-NH}_4\text{Cl-NH}_4\text{OH}$ buffer solutions, which demonstrated that higher temperatures lead to increases in dissolution rates (Oelkers and Schott, 2001). Another example is given by the dissolution of magnetite by oxalic, sulfuric, and nitric acid, whereby dissolved Fe in the leachates at 50°C is more than 10 times

greater than in the leachates at 15°C (Salmimies et al., 2011). Furthermore, the acid dissociation constant (K_a) of HOAc reaches a maximum at around 25°C (Harned and Ehlers, 1933). So, theoretically, gibbsite may be leached more readily at room temperature than at high temperature. Further, the solubility of $\text{Ca}(\text{CH}_3\text{COO})_2$ and $\text{Sr}(\text{CH}_3\text{COO})_2$ slightly decreases with temperature from 10°C to 100°C (Seidell, 1919; Apelblat, 1993). In contrast, $\text{Mg}(\text{CH}_3\text{COO})_2$ and $\text{K}(\text{CH}_3\text{COO})$ become more soluble with increasing temperature (Seidell, 1919; Apelblat, 1993). Thus, the extremely high Mg concentration in the high temperature extractions is likely due to the partial dissolution of Mg-rich clays or primary minerals. For example, the Mg concentration in the 6-hour oxide extraction of RS at high temperature represents 15% of the total Mg in the bulk RS (Figure 3.1). Hence, it appears that secondary oxides do not always dominate the leach that is nominally designed to target the oxide fraction, particularly when leaching is conducted at high temperatures.

In general, primary silicate minerals and fractions have relatively lower $\delta^7\text{Li}$ values than secondary minerals (Vigier et al., 2008; Wimpenny et al., 2015; Hindshaw et al., 2019; Li et al., 2020; Pogge von Strandmann et al., 2022). Thus, the observation of consistently lower $\delta^7\text{Li}$ values in the high temperature leachates than the room temperature leachates for all samples except BCR-2 (Figure 3.2) appears to support the idea that fractions such as igneous oxides or primary silicates, rather than only secondary oxides, are targeted at high temperatures. Since BCR-2 is a basaltic igneous rock (Wilson, 1998), its oxides are expected to be dominated by igneous oxides (Hamilton, 1963; Flanagan, 1967). The absence of any influence of temperature on the $\delta^7\text{Li}$ values of the BCR-2 leachates, which are as low as $-0.8 \pm 0.5\text{‰}$ (SD, $n = 24$), is consistent with the presence of only one primary oxide fraction that is extracted at both low and high temperatures, and suggests that igneous oxides are likely to have low $\delta^7\text{Li}$ values. The other samples are a lacustrine sedimentary oil shale (SGR-1b) and river sediments (RS, RRS, and YR), all of which will have interacted with isotopically heavy surficial fluids and can be expected to contain two types of oxides, i.e., primary igneous oxides and secondary oxides formed during chemical weathering (Pécsi, 1990; Wang et al., 2009; Jones et al., 2012; Boak and Poole, 2015; Jin et al., 2021). Correspondingly, the leachates of RS, RRS, and YR show strikingly different $\delta^7\text{Li}$ values for high temperature and room temperature leaching (Figure 3.2), consistent with derivation from predominantly

low- $\delta^7\text{Li}$ igneous oxides and high- $\delta^7\text{Li}$ sedimentary oxides, respectively. Although the $\delta^7\text{Li}$ values of SGR-1b leachates are less sensitive to temperature, they do shift towards lower values with increasing leaching time in the high temperature experiments, which is consistent with an increased contribution from isotopically light igneous oxides or other primary silicate minerals. Furthermore, the full sequential leaching results from RS, BCR-2, and YR conducted at low temperatures show that the residues, which are dominated by primary silicates, have $\delta^7\text{Li}$ values higher than in the high temperature 'oxide leachates'. Hence, the very low $\delta^7\text{Li}$ values in the high temperature leachates likely arise from the preferential dissolution of a specific primary mineral, such as pyrite, Fe-Ti oxides, or pyroxene, which can have low $\delta^7\text{Li}$ values (Tang et al., 2007; Ionov and Seitz, 2008; Penniston-Dorland et al., 2017).

3.2.4 Influence of leaching time

In general, elemental concentrations in the leachates increase with leaching time. In the extraction of RS, RRS, and BCR-2, the increase in Fe concentration with time is more significant than increases in Mn, Al, Ca, and K, but is similar to increases in the Mg concentration at room temperature, while at high temperature, Mg concentrations increase more with time than Fe (Figure 3.1). The increases in Mg concentration may imply that more Mg-rich minerals, such as from clays and/or primary silicates, are being leached out with increasing time, especially at high temperature. Therefore, the room temperature leaching has the advantage that the subsequent fractions in the leach cycle (i.e., clays and primary silicates) remain relatively unreacted. In addition, $\delta^7\text{Li}$ values in the leachates of RS, RRS, and BCR-2 are essentially constant through time, even while elemental concentrations (including Li) increase with a longer leaching time (Figure 3.2). Hence, it provides strong evidence that no significant Li isotopic fractionation occurs during leaching of oxide fractions by the reagent HH in HOAc. To be specific, neither Li re-adsorption nor Li diffusion apparently occurred to any significant extent during these leaching experimental trials, which differs from some dissolution experiments conducted on silicate rocks in weak acid in which Li isotope fractionation during diffusion was suggested to have occurred (Verney-Carron et al., 2011; Li et al., 2021). Importantly, due to the constancy of $\delta^7\text{Li}$ values through time, it is unlikely that the dominant mineral types accessed by the leachates changed significantly over time. In other words, increasing leaching

time leads to more removal of the oxide fraction, but without a significant shift between isotopically heavy secondary minerals and isotopically light primary minerals. Overall, based on the results of RS, RRS, and BCR-2, the Tessier oxide leaching method for 1 hour at room temperature is optimal, because the short leaching time is beneficial for minimizing the possible risk of leaching from primary silicate minerals or clays.

Unlike the leaching of RS, RRS, and BCR-2, the elemental concentrations in the extractions of SGR-1b and YR show some contrasting trends with leaching time. For SGR-1b, except for K, most other elements (i.e., Fe, Mn, Al, Ca, Mg, and Li) increase with leaching time at room temperature (Figure 3.1). Somewhat unexpectedly, around 64% Ca, 65% Mg, and 55% Mn out of the total amounts in the bulk solid are leached out after 6 hours at room temperature. These numbers are around 26% Ca, 21% Mg, and 22% Mn in the 1-hour room temperature extraction and around 80% Ca, 81–85% Mg, and 68–72% Mn for 1 to 6 hours leaching at high temperature. These percentages in the leachates of RS and BCR-2 are only up to 2% Ca, 16% Mg, and 10% Mn at high temperature for 6 hours. These differences are likely linked to the differences in mineralogy, and specifically the high carbonate content of SGR-1b (Hamilton, 1963; Jones et al., 2012; Boak and Poole, 2015). The BCR-2 and RS scarcely contain carbonates (Hamilton, 1963; Jones et al., 2012), but calcite and dolomite could contribute more than 6% and 8% by weight, respectively, of the bulk SGR-1b (Boak and Poole, 2015). In addition, the Mn and even Fe in SGR-1b can also be incorporated in carbonates, such as in siderite and kutnohorite (Boak and Poole, 2015). Given the acidity of the oxide leaching reagent (0.04 mol/l HH in 25% v/v HOAc, pH $\approx$ 2), it is enough to dissolve carbonates, which may therefore be included in the oxide leachates of SGR-1b because no carbonate removal step was included before the oxide leaching. However, although the elemental concentrations suggest a carbonate influence on the oxide leachates of SGR-1b, the $\delta^7\text{Li}$ values in the room temperature leachates are consistent at $20.8 \pm 0.7\text{‰}$ (SD, $n = 19$) through time (Figure 3.2). Presumably, either the Li concentrations in the carbonate are too low to influence the Li in the oxide leachates (Kisakurek et al., 2005; Dellinger et al., 2015), or the $\delta^7\text{Li}$ values of the carbonates in SGR-1b are similar to the oxides at around 20‰. At high temperature, $\delta^7\text{Li}$ values in the SGR-1b leachates decrease through time (Figure 3.2), while the concentrations of K, Al, and Li, as well as ratios such as Al/Fe and K/Fe, increase,

which points to increasing dissolution of clays or primary minerals.

For the YR leachates, the increase in Fe concentrations through time is more significant than for the other measured elements. In addition, the element concentrations in YR extractions at high temperature increase more significantly than extractions at room temperature with leaching time, especially Fe, Al, K, and Li. Notably, the concentrations of Mn and Ca in the YR oxide extractions are high and they remain relatively constant with leaching time (Figure 3.1). Around 85% Ca and 38% Mn out of the total in the bulk solids are leached out after 1 hour at room temperature, increasing only slightly to 92% Ca and 41% Mn in the 6-hour leachates, consistent with the rapid dissolution of carbonates and/or Mn oxides (Wilson et al., 2013). The Yellow River estuarine sediments contain around 10% carbonate, and most of the carbonates are calcite from the Chinese Loess Plateau (Tian et al., 2021), which appears to be readily leached. Correspondingly, $\delta^7\text{Li}$ values in the room temperature leachates slightly decrease from $5.1 \pm 0.2\text{‰}$ (SD, $n = 3$) for 1 hour to $3.8 \pm 0.9\text{‰}$ (SD, $n = 3$) for 6 hours. It therefore seems that carbonate does impact on the $\delta^7\text{Li}$ values in the oxide leachates. Thus, for solids with a relatively high carbonate content, a carbonate removal step appears to be required before oxide leaching. In contrast, $\delta^7\text{Li}$ values in the high temperature leachates of YR are consistent at $-4.9 \pm 0.4\text{‰}$ (SD, $n = 8$), although the elemental concentrations increase through time. Thus, the continuous leaching of Li perhaps stems from a particular fraction or mineral with a low $\delta^7\text{Li}$ value.

3.2.5 Influence of the reagent/solid ratio

The impact of the reagent/solid ratio was examined based on extractions for the SGR-1b. In the first group the reagent/solid ratio was 40 ml/g, and in the second group it was around 4 times higher, at 167 ml/g (room temperature) or 143 ml/g (high temperature). Comparing the Li concentrations in the low temperature extractions of the two groups shows that the second group (high reagent/solid) leaches out more Li per gram of solid than the first group (low reagent/solid) (Figure 3.3). After 1 hour, the Li concentration in the second group of extractions is approximately two times higher than in the corresponding first group extractions, which provides evidence that the amount of leaching reagent is a limiting factor for Li in the first group, and therefore Li in oxide fractions is only partly leached out. However, this scenario has the advantage that it avoids attacking other fractions. The $\delta^7\text{Li}$ values in the room temperature leachates in

the first and second groups are virtually identical at $20.3 \pm 0.5\text{‰}$ (SD, $n = 9$) and $21.3 \pm 0.6\text{‰}$ (SD, $n = 10$), respectively (Figure 3.3). This consistency in the Li isotope compositions suggests that there is no Li isotopic fractionation, and the Li is probably derived from the same fraction during leaching at room temperature from 1 to 6 hours.

For the high temperature extractions, changes in the reagent/solid ratio do not lead to significant differences in the concentrations of Fe and Mn (Table 3.3), whereas the concentrations of K, Al, and Li in second group extractions (high reagent/solid) are 1 to 2 times of that in the first group extractions (low reagent/solid). The Li concentrations are similar for the two groups after 1 hour, but become more pronounced with time (Figure 3.3). Thus, it seems that 2 ml of reagent is sufficient to extract the majority of the oxides from ~14 mg solids during leaching at high temperature. Correspondingly, the $\delta^7\text{Li}$ values in 1-hour high temperature leachates of the first and second groups are similar at $18.9 \pm 0.6\text{‰}$ (SD, $n = 3$) and $19.2 \pm 0.5\text{‰}$ (SD, $n = 3$), while in 6-hour leachates, $\delta^7\text{Li}$ values drop to $15.7 \pm 0.3\text{‰}$ (SD, $n = 3$) in the first group and $11.8 \pm 0.6\text{‰}$ (SD, $n = 3$) in the second group. Therefore, these results support the hypothesis that there is more influence by leaching of silicates (primary or secondary), which have a lower $\delta^7\text{Li}$, when there is excess leaching reagent than necessary for solely attacking the oxides.

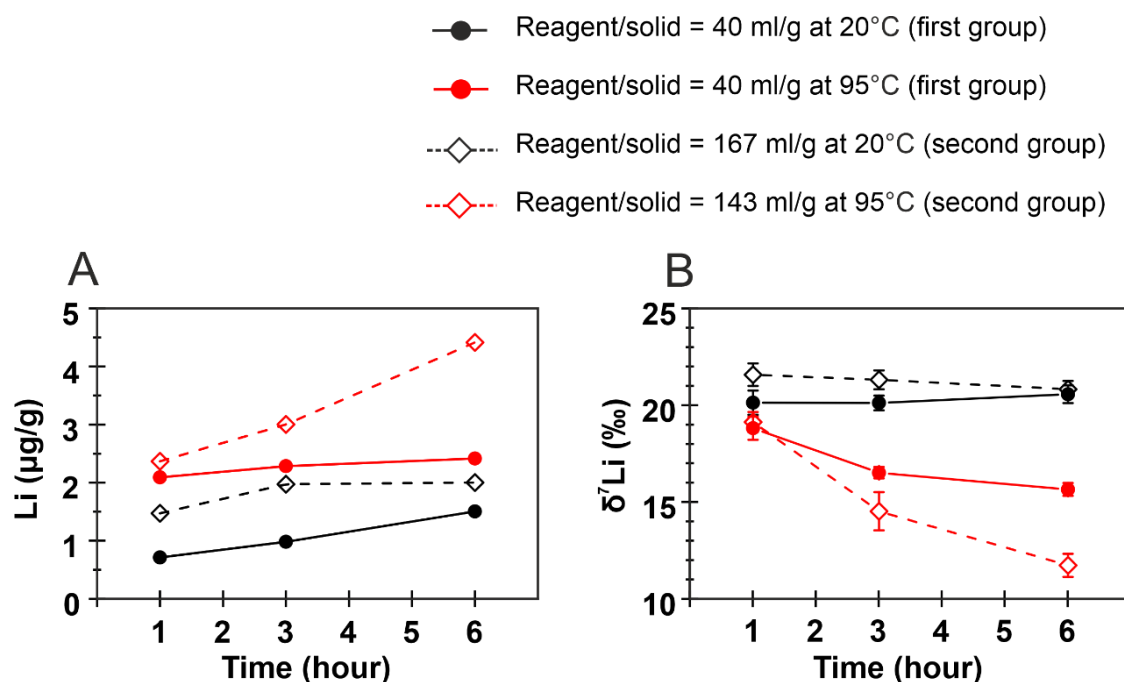


Figure 3.3 Li concentrations and Li isotopes in oxide leachates of SGR-1b using different reagent/solid ratios in Tessier oxide leaching experimental trials.

3.2.6 Comparison of Tessier, weak, and strong oxide leaching methods

Besides leaching with 0.04 mol/l HH in 25% HOAc from the method of Tessier et al. (1979), this study examined other leaching methods on the RS, RRS, BCR-2, and SGR-1b samples (Tables 3.2 and 3.3). One method is a weaker leaching method (Hindshaw et al., 2018), using 0.005 mol/l HH in 2.6 mol/l HOAc with a lower reagent/solid ratio (3.125 ml/g). Another method comprises stronger leaching (Rauret et al., 1999; Li et al., 2020), using 0.5 mol/l HH in 0.05 mol/l HNO₃ for the longer time of 16 hours. Theoretically, none of the leaching methods can exclusively extract the secondary oxides as anticipated. In practice, the most optimal approach is making sure that Li from the expected secondary oxides dominates the Li in the oxide leachates and that the different oxides could be extracted evenly to the limit. As discussed, the potential contaminants are silicates (including clays) and remaining exchangeable and carbonate fractions. The expected secondary oxides include secondary Fe/Mn-oxides/oxyhydroxides and secondary gibbsites (Al-hydroxide). Among these secondary oxides, the less-structured oxides, Mn oxides, and “pH-sensitive” oxides (i.e., gibbsite) are regarded as more readily extracted than Fe secondary oxides (Chester and

Hughes, 1967; Chao, 1972; Gupta and Chen, 1975; Dixon and Weed, 1989; Chan and Hein, 2007; Wilson et al., 2013; Pinney and Morgan, 2013; Wimpenny et al., 2015; Lenstra et al., 2021). According to the Li isotopes and element concentrations, the weak leaching method apparently contains more “readily-leached” oxides (i.e., less-structured oxides, Mn oxides, and “pH-sensitive” oxides such as gibbsite), and may be contaminated by the remaining exchangeable and carbonate fractions. In contrast, the strong leaching method probably attacks more secondary oxides, but also more unexpected silicates as well.

For RS and RRS, to a first order, the oxide leaching methods at room temperature (i.e., weak leaching, Tessier leaching at room temperature, and strong leaching) appear to follow mixing trends for Li isotopes (Figure 3.4). The weak oxide extractions have the lowest Li concentration, which is only 35% of that of the Tessier room temperature extractions, and lie at the high $\delta^7\text{Li}$ end of the mixing trend. Furthermore, the low concentrations of Fe, Mg, and Li (Figure 3.2A, B, F, and G), but high Mn/Fe and Al/Fe, in these weak oxide extractions suggest that they have a greater contribution from “readily-leached” oxides, which are considered to have higher $\delta^7\text{Li}$ values (Chan and Hein, 2007; Wimpenny et al., 2015). Meanwhile, it is notable that the remaining exchangeable and carbonate fractions of RS and RRS may also lead to the higher $\delta^7\text{Li}$ values (Pogge von Strandmann et al., 2019a), although the K/Fe and Ca/Fe in the weak leachates of RS and RRS are similar to those in the Tessier 1-hour room temperature leachates. Further, the low Mg concentrations suggest very little influence overall from silicates. Hence, the weak leachates may be dominated by “readily-leached” oxides with $\delta^7\text{Li}$ values of $5.6 \pm 0.7\text{‰}$ (SD, $n = 4$) for RS and $9.1 \pm 0.3\text{‰}$ (SD, $n = 4$) for RRS. The weak extraction, therefore, probably cannot dissolve all oxides evenly, although the weak extraction could reduce the influence of silicates.

In contrast, the strong oxide extractions lie at the high Li concentration–low $\delta^7\text{Li}$ end of the apparent mixing line, with around 3 times the Li concentration of the Tessier room temperature extractions. However, these leachates have high Fe concentrations (Figure 3.2) and high Mg/Fe ratios, which suggests a greater influence from (low $\delta^7\text{Li}$) silicates. The Mn mass fraction of the sum of masses of Fe, Mn, and Mg in the strong extractions is lower than in the weak extractions and Tessier room temperature extractions, but similar to the silicate residues

(Figure 3.4), which suggests that secondary Fe-oxides, instead of “readily-leached” oxides, dominate the oxide-derived Li in the strong leachates. Therefore, it seems that the composition of the solutions stemming from strong oxide leaching is controlled by secondary Fe-oxides, plus a degree of contamination by silicate material.

The Li concentration and $\delta^7\text{Li}$ values in the Tessier room temperature leachates lie between the weak oxide leaching and the strong oxide leaching (Figure 3.4), which suggests that the Tessier room temperature leachates consist of a mixture of both “readily-leached” oxides and secondary Fe-oxides. Although the influence of silicates on the Tessier room temperature oxide leachates cannot be excluded, their influence on these leachates is less than on the strong oxide leachates, as shown by lower Mg concentrations in the former. Furthermore, although the Li concentration in the Tessier room temperature leachates increases with time, the $\delta^7\text{Li}$ values remain constant (Figure 3.2). Hence, it is more likely that the Tessier room temperature leachates are closest to providing the composition of the “true” secondary oxide fractions, which in turn are a mixture of “readily-leached” oxides and secondary Fe-oxides, with less silicate influence.

As mentioned earlier, BCR-2 is an unweathered igneous rock, whose minerals formed at high temperatures, with little to no low-temperature secondary minerals formed at the Earth’s surface. Thus, it is to be expected that isotope fractionation between the different fractions in BCR-2 is more muted than in the other samples that have all experienced low-temperature weathering (Urey, 1947). It is supported by the consistent $\delta^7\text{Li}$ values ($-0.8 \pm 0.5\text{‰}$ (SD, $n = 27$)) in the oxide leachates by Tessier leaching and strong leaching, although the weak oxide leaching shows slightly lower $\delta^7\text{Li}$ values of $-3.1 \pm 0.2\text{‰}$ (SD, $n = 4$).

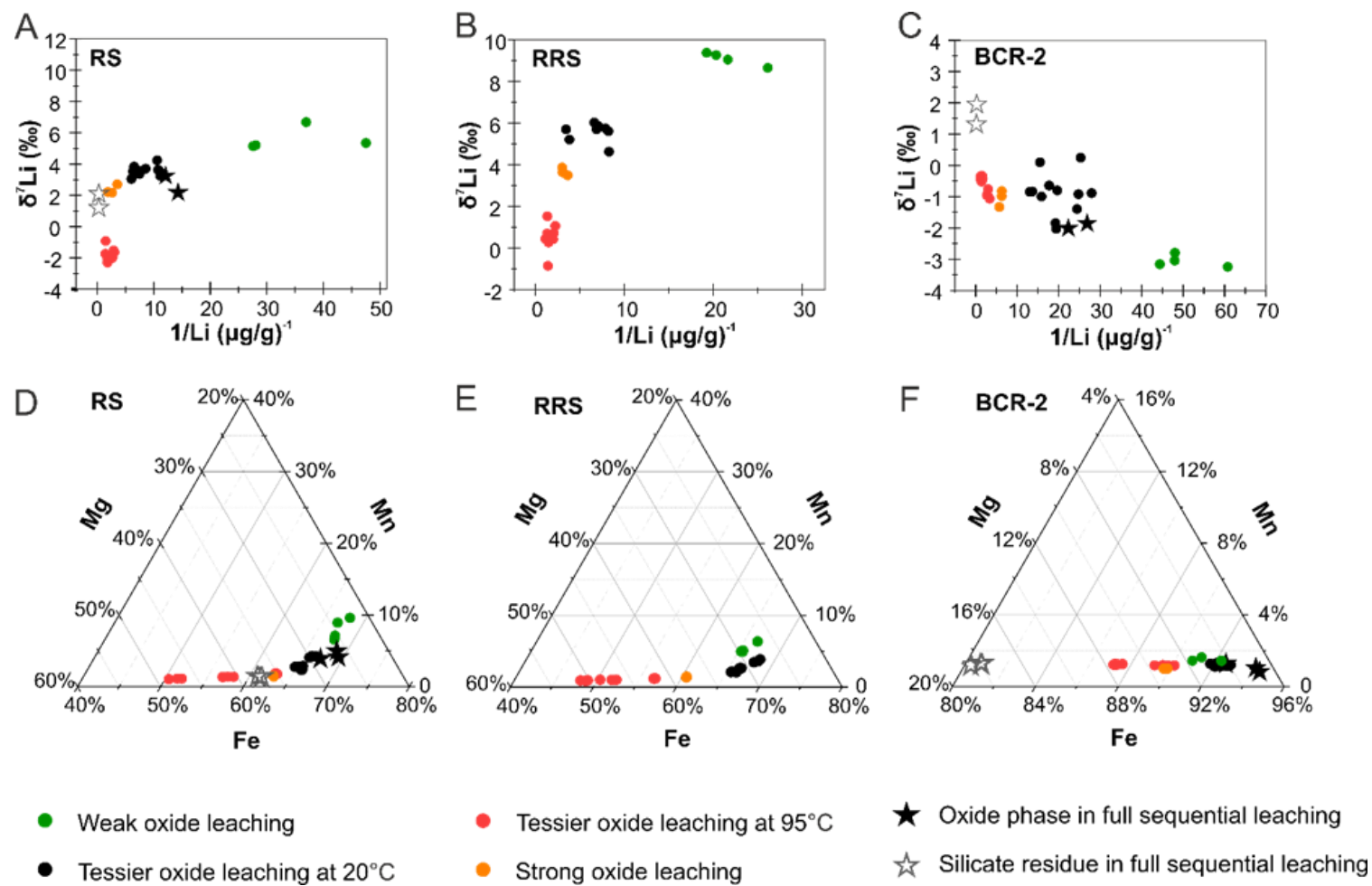


Figure 3.4 Li concentration-Li isotope diagrams and Mn-Mg-Fe ternary diagrams of oxide leaching trials of RS, RRS, and BCR-2.

3.3 Full sequential leaching procedure

3.3.1 Full sequential leaching trials

To monitor the chemical extraction and inspect the interplay among the leaching steps (i.e., exchangeable, carbonate, oxide, clay, and residue), a reference material USGS BCR-2 (Basalt, Columbia River) (Wilson, 1998), two samples (RS and Bed10) from the Borgarfjörður estuary, and the Yellow River sediment (YR) sample were repeatedly treated and analysed (Table 3.4). The BCR-2, RS, and YR were described in Section 3.2.1. The sample Bed10 is the bedload collected from the seawater endmember in the Borgarfjörður estuary in June 2008 (Jones et al., 2014) (Section 5.2). It mainly comprises ~50% microcrystalline material, ~18% volcanic glass, ~11% Ca-feldspar, ~7% olivine, ~5% Fe-Ti oxide, ~4% Calcite, ~2% K-feldspar, and ~1% quartz based on grain counting using SEM (Jones et al., 2012).

Two full sequential extractions and a bulk dissolution were applied on BCR-2, RS, and YR. In addition, one sequential extraction of RS and BCR-2 without the carbonate step was also performed. For Bed10, 4 full sequential extractions and a bulk dissolution were applied. The mass of leached Bed10 are different (50 mg, 5 mg, and 1 mg), although the reagent/solid ratio was kept constant. In contrast, all extractions of BCR-2, RS, YR were conducted on mass of 50 mg. The full sequential extraction method, elemental concentration analysis, and Li isotope analysis are described in Sections 2.3.2, 2.4, and 2.5.

Table 3.4 Elemental concentrations and Li isotopes of replicate samples.

Sample	Elemental concentration							$\delta^7\text{Li}$ ‰	2σ ‰
	Fe mg/g	Mn μg/g	Al mg/g	Ca mg/g	Mg mg/g	K mg/g	Li μg/g		
BCR-ex-1	0.0040	1.0	<0.001	0.40	0.10	0.12	0.050	3.78	0.13
BCR-ex-2	0.021	1.05	<0.001	0.42	0.11	0.14	0.029		
BCR-ex-3	0.0019	0.83	<0.001	0.32	0.10	0.14	0.019	2.81	0.26
BCR-carb-1	0.35	7.7	0.027	0.15	0.040	0.046	0.035	0.41	0.21
BCR-carb-2	0.40	11	0.04	0.15	0.040	0.042	0.028		
BCR-carb-3 (skipped)									
BCR-oxide-1	1.1	9.5	0.27	0.30	0.050	0.027	0.037	-1.86	0.19
BCR-oxide-2	0.94	10	0.25	0.23	0.048	0.033	0.027		
BCR-oxide-3	1.7	23	0.48	0.78	0.11	0.045	0.045	-2.01	0.10
BCR-clay-1	5.0	61	0.54	2.86	0.66	0.023	0.32	1.16	0.21
BCR-clay-2	3.0	33	0.44	2.32	0.39	0.023	0.18		
BCR-clay-3	3.6	44	0.40	2.4	0.51	0.025	0.21		
BCR-residue-1	93	1500	74	50	21	15	7.7	1.31	0.38
BCR-residue-2&3	91	1500	71	48	20	14	8.2	1.99	0.16
BCR-bulk-sum-1	99	1600	74	54	22	16	8.1	1.30	
BCR-bulk-sum-2	95	1500	72	51	21	15	8.4		
BCR-bulk-sum-3	96	1500	72	52	21	14	8.4		
BCR bulk measured	98	1500	75	50	22	15	8.5		
RS-ex-1	0.0055	1.8	0.0020	0.61	0.10	0.046	0.048	11.58	0.22
RS-ex-2	0.013	1.4	<0.001	0.39	0.086	0.037	0.031		
RS-ex-3	0.0018	1.1	<0.001	0.30	0.073	0.058	0.044	10.46	0.31
RS-carb-1	0.073	14	0.085	0.27	0.047	0.022	0.052	6.92	0.37
RS-carb-2	0.076	15	0.10	0.17	0.042	0.027	0.030		
RS-carb-3 (skipped)									
RS-oxide-1	0.86	51.05	0.77	0.57	0.33	0.013	0.070	2.18	0.39
RS-oxide-2	0.63	45	0.63	0.44	0.24	0.016	0.050		
RS-oxide-3	1.1	64	1.2	0.99	0.47	0.023	0.083	3.27	0.16

Sample	Elemental concentration								2σ ‰
	Fe mg/g	Mn µg/g	Al mg/g	Ca mg/g	Mg mg/g	K mg/g	Li µg/g	$\delta^7\text{Li}$ ‰	
RS-clay-1	4.2	64	3.1	2.9	1.8	0.043	0.20	2.34	0.19
RS-clay-2	2.6	42	2.2	2.1	1.2	0.02	0.13		
RS-clay-3	2.7	42	2.1	2.1	1.2	0.032	0.12	2.45	0.39
RS-residue-1	80	1900	73	77	49	2.2	4.8	2.13	0.28
RS-residue-2&3	79	2000	71	76	48	2.1	5.0	1.23	0.15
RS-bulk-sum-1	85	2000	77	81	51	2.3	5.2	2.28	
RS-bulk-sum-2	82	2100	74	79	49	2.2	5.3		
RS-bulk-sum-3	82	2100	74	79	49	2.2	5.3	1.37	
RS bulk measured	85	2100	78	76	50	2.0	5.4		
Bed10-ex-1	0.0042	0.50	<0.001	1.7	0.58	1.1	0.54	16.72	0.24
Bed10-ex-2	0.008	0.58	0.0049	1.5	0.42	0.81	0.36	16.83	0.33
Bed10-ex-5mg	0.074	2.3	0.13	6.1	0.51	0.88	0.55	15.22	0.59
Bed10-ex-1mg	0.11	2.9	0.092	4.6	0.70	0.97	0.60	16.14	0.13
Bed10-carb-1	0.072	41	0.050	25	0.59	0.20	0.56	13.67	0.15
Bed10-carb-2	0.034	10	0.028	20	0.50	0.27	0.46	13.41	0.26
Bed10-carb-5mg	0.14	41	0.13	21	0.55	0.099	0.50	12.46	0.03
Bed10-carb-1mg	0.094	33	0.045	21	0.57	0.17	0.60		
Bed10-oxide-1	0.64	35	0.46	2.0	0.25	0.026	0.45	6.61	0.21
Bed10-oxide-2	0.63	33	0.38	1.1	0.17	0.046	0.32	6.75	0.03
Bed10-oxide-5mg	0.82	33	0.58	0.85	0.28	0.019	0.49	4.35	0.11
Bed10-oxide-1mg	0.46	30	0.38	3.1	0.27	0.073	0.40		
Bed10-clay-1	5.2	53	3.1	0.84	1.5	0.08	1.7	4.77	0.14
Bed10-clay-2	3.7	39	2.9	1.8	1.1	0.074	1.6	4.24	0.14
Bed10-clay-5mg	5.6	53	3.0	2.4	1.5	0.043	1.8	4.66	0.33
Bed10-clay-1mg	3.9	37	3.0	2.4	0.97	0.035	1.6	7.17	0.33
Bed10-residue-1	98	1600	59	67	52	2.0	8.1	2.42	0.28
Bed10-residue-2	100	1500	54	70	52	2.1	8.1	2.43	0.24
Bed10-residue-5mg	90	1400	57	63	47	1.7	6.8	2.66	0.56
Bed10-residue-1mg	100	1500	59	66	54	2.0	8.0	2.51	0.29

Sample	Elemental concentration							$\delta^7\text{Li}$ ‰	2σ ‰
	Fe	Mn	Al	Ca	Mg	K	Li		
	mg/g	µg/g	mg/g	mg/g	mg/g	mg/g	µg/g		
Bed10-bulk-sum-1	100	1700	62	96	55	3.4	11	4.17	
Bed10-bulk-sum-2	110	1500	58	94	54	3.3	11	3.77	
Bed10-bulk-sum-5mg	96	1500	61	94	50	2.7	10.	4.27	
Bed10-bulk-sum-1mg	110	1600	62	97	57	3.3	11		
Bed10 bulk measured	96	1.5	66	90	57	2.9	12		
YR-ex-1	0.005	1.1	<0.001	1.2	0.20	0.10	0.13	5.23	0.05
YR-ex-2	0.010	1.1	0.0027	1.4	0.18	0.12	0.098	5.12	0.01
YR-carb-1	0.074	129	0.030	27	0.38	0.076	0.17	6.75	0.34
YR-carb-2	0.030	60	0.021	27	0.38	0.073	0.15	7.24	0.14
YR-oxide-1	0.19	62	0.10	4.7	0.43	0.034	0.11	1.39	0.09
YR-oxide-2	0.18	81	0.12	7.3	0.21	0.036	0.043	2.10	0.12
YR-clay-1	0.66	23	0.56	4.1	1.5	0.052	0.50	−1.66	0.08
YR-clay-2	0.56	30	0.58	5.4	1.7	0.052	0.36	−0.67	0.06
YR-residue-1	27	340	63	7.1	11	18	28	0.73	0.39
YR-residue-2	25	290	59	8.2	11	18	29	1.54	0.21
YR-bulk-sum-1	28	550	64	44	13	18	28	0.75	
YR-bulk-sum-2	26	470	60	50	13	19	29	1.55	
YR bulk measured	27	520	63	44	13	17	30		

2σ is the two standard deviation of measured $\delta^7\text{Li}$ values in each leachate. The 'ex' and 'carb' represent exchangeable and carbonate steps in the sequential leaching, respectively. The 'bulk measured' represents the measurements from bulk sample dissolution. The 'bulk-sum' is calculated using Eqs. 2.2 and 2.4, and therefore is without 2σ of $\delta^7\text{Li}$. The long-term uncertainty of seawater $\delta^7\text{Li}$ analysis using MC-ICP-MS is 0.63‰ (2SD).

3.3.2 Reproducibility and accuracy of the full sequential leaching

Generally, reproducibility between the repeated full sequential extractions is acceptable. Figure 3.5 shows a frequency histogram of the relative standard deviations (RSD) of the elemental concentrations (i.e., Mg, Al, K, Ca, Mn, Fe, and Li) in each fraction (i.e., exchangeable, carbonate, oxide, clay, and residue) in repeated extractions. The elements with high concentrations in the leachates show better reproducibility. For example, the relative standard deviations (RSD) of elemental concentrations (i.e., Mg, Al, K, Ca, Mn, Fe, and Li) in the residues are better than 10%, and mostly better than 5%. In contrast, the RSD of elemental concentrations in the exchangeable, carbonate, oxide, and clay fractions ranges from 1–117%, among which most RSD (94 out of 109) are better than 50%, and half of the RSD (52 out of 109) are better than 20%. Especially the Al and Fe concentrations in the exchangeable fraction show large RSD, presumably because their low concentrations make them more susceptible to slight changes in efficiency and sample heterogeneity. For BCR-2 and RS, there is one sequential extraction (out of three) for each without leaching the carbonate fraction before the oxide fraction, which results in a higher RSD in the oxide fraction. Furthermore, the elemental concentrations, especially Ca and K, in the leaching fractions of Bed10 show relatively high RSD, which may stem from the different mass (i.e., 50 mg, 5 mg, and 1 mg) of leached Bed10 in the repeated full sequential extractions. The mass of leached solid may influence the leaching efficiency, although the reagent/solid ratios were kept constant. In addition, for the bulk data, including bulk-sum and bulk-measured, the relative standard deviations (RSD) of elemental concentrations (i.e., Mg, Al, K, Ca, Mn, Fe, and Li) are better than 10%, and mostly better than 5%.

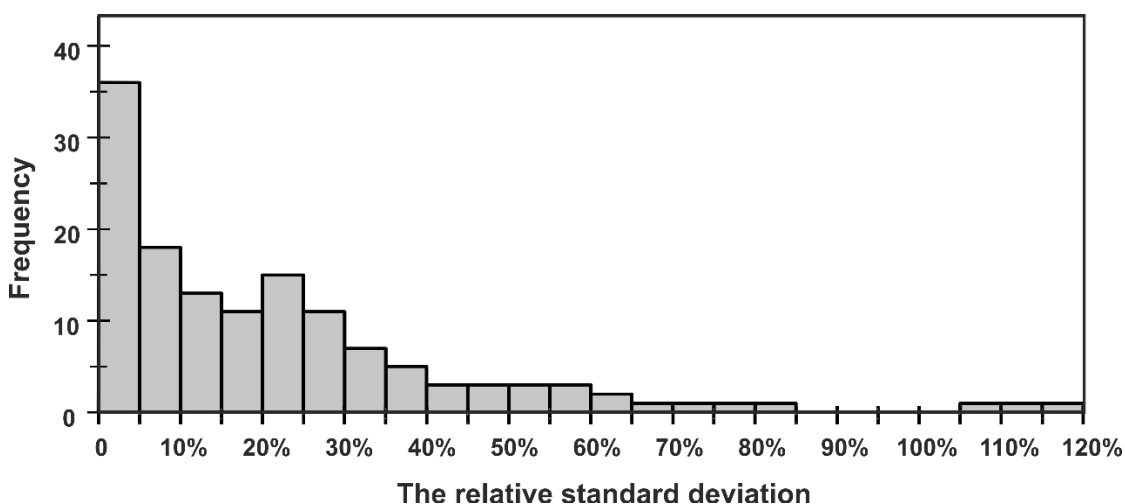


Figure 3.5 Frequency histogram of relative standard deviations of elemental concentrations in fractions in repeated full sequential extractions.

The reproducibility of $\delta^7\text{Li}$ values in the sequential leachates is examined by the standard deviations (SD) of $\delta^7\text{Li}$ in full procedural replicate samples. The SD of $\delta^7\text{Li}$ are better than 1.3‰, and most of them are better than 0.8‰, except for the $\delta^7\text{Li}$ in the oxide and clay fractions of Bed10. The oxide and clay fractions of the extractions on 5 mg and 1 mg of Bed10 show $\sim 2.5\text{‰}$ shifts from the 50 mg Bed10, perhaps because the efficiency slightly changes between different sample masses, or because the lower sample mass is more susceptible to sample heterogeneity. The long-term external reproducibility of $\delta^7\text{Li}$ values based on standards such as seawater is $\pm 0.63\text{‰}$ (2SD) in this study and fully dissolved rock reference materials is $\pm 0.5\text{‰}$ (2SD) (Pogge von Strandmann et al., 2019a; Gou et al., 2020). Thus, although the application of sequential leaching appears to slightly degrade the reproducibility of Li isotope determinations, the reproducibility of $\delta^7\text{Li}$ among replicates is fairly good overall. In addition, the uncertainty of the Li isotope determination in the replicated leachates is significantly less than the differences in the Li isotope compositions between different leachates in different solid samples from the interaction experiments (Chapter 4) and natural estuaries (Chapters 5 and 6) in this study.

The relative differences between the calculated bulk elemental concentrations in the full sequential leaching (Eq. 2.2), and the measured bulk elemental concentrations of Fe, Mn, Al, Ca, Mg, K, and Li are less than 18%, and most are less than 10%. The differences likely arise from sample heterogeneity,

because the differences are less for the homogeneous USGS reference material BCR-2 (<8%, and most <5%), than for the natural river sediments (i.e., RS, Bed10, and YR). Furthermore, the measured concentrations of Fe, Mn, Al, Ca, Mg, and K of bulk BCR-2 and the calculated sums of the elemental concentrations of different fractions (Eq. 2.2) of BCR-2 are in the range of 96–105% of the corresponding recommended elemental compositions of BCR-2 (Tables 3.1 and 3.4, Wilson, 1998). The calculated bulk $\delta^7\text{Li}$ value of BCR-2 is 1.3‰, which is slightly lower than published bulk $\delta^7\text{Li}$ values of 2.6–3.5‰ for BCR-2 (Rosner et al., 2007; Pogge von Strandmann et al., 2011, 2012, 2019a; Penniston-Dorland et al., 2012; Choi et al., 2013; Genske et al., 2014; Ryu et al., 2014; Liu et al., 2015; Bohlin et al., 2018; Liu and Li, 2019; Li et al., 2020). The calculated bulk $\delta^7\text{Li}$ values are $1.8 \pm 0.6\text{‰}$ (SD, $n = 2$) for RS and $4.1 \pm 0.3\text{‰}$ (SD, $n = 3$) for Bed10, which are within the range of published $\delta^7\text{Li}$ values (–0.2 to 9.8‰) of river sediments in the Borgarfjörður estuary, Iceland (Pogge von Strandmann et al., 2006, 2008; Vigier et al., 2008). The calculated bulk $\delta^7\text{Li}$ value for YR of $1.2 \pm 0.6\text{‰}$ is consistent with the published $\delta^7\text{Li}$ values for bulk loess from the Chinese Loess Plateau and Yellow River sediments, which range from 0.6 to 6.9‰ (Liu et al., 2007; Tsai et al., 2014; Gou et al., 2019; He et al., 2021; Xu et al., 2022). Overall, the full sequential leaching procedure demonstrates fair reproducibility and accuracy, given the procedures involved.

3.3.3 The interplay among the full sequential extractions

The key point of the full sequential leaching is to balance the influence of incidental leaching of the preceding and subsequent fractions on the fraction of interest. On the one hand, the targeted fraction cannot be entirely leached out, because no leaching method is entirely efficient, and any attempt to achieve this would lead to other fractions being attacked before the target fraction is entirely dissolved. On the other hand, the incomplete leaching of a preceding fraction may then contribute to the leachates of the following fraction in the sequence (e.g., exchangeable fractions on the carbonate fraction, or carbonates on the oxide fraction). Therefore, it is critical that the elemental composition of each fraction is examined in order to assess contributions from other fractions. Although there is no element that is exclusive for a particular fraction, some features of element concentrations were found according to the full sequential extractions of BCR-2, RS, Bed10, and YR.

For example, K, aside from the dominant residual fraction, evidently prefers the exchangeable fraction to the other fractions (i.e., carbonate, oxide, and clay) (Table 3.4). Especially, for Bed10, an estuarine sediment from saline water with very high K concentrations, its exchangeable fraction has ~30% K out of the total K in the bulk sample, and the exchangeable K probably also influences the following carbonate leachate (Table 3.4). This finding is consistent with the concept that K is more mobile and likely to be absorbed in the interlayer of clays rather than sitting in the bonded sites (Velde, 1995; Gíslason et al., 1996). Thus, K could be a useful indicator for exchangeable fractions. In contrast, Fe and Al rarely exist in the exchangeable fraction (Velde, 1995).

In general, carbonates are more prone to being leached than oxides or clay. The carbonates are rich in Ca and Mg, and sometimes Mn or even Fe may be incorporated in the carbonates (Pogge von Strandmann et al., 2019b; Dellinger et al., 2020; Lenstra et al., 2021). Therefore, if a sample contains some carbonates, it is important to separate the carbonate fraction as an individual fraction before the oxide fraction. For example, as the YR contains ~10% carbonates, the YR carbonate leachates contain more than 55% of the total Ca with Mn/Ca ratios more than 2 mg/g. Furthermore, the leaching of Bed10, which has ~5% calcite (Jones et al., 2012), shows that ~20% Ca is in the carbonate fraction, although the Mn concentration in the carbonate is low (Table 3.4). A previous study on extraction of Yellow River sediment using the Tessier method demonstrated that more Mn was contained in the carbonate fraction compared to the oxide fraction (Zhang et al., 1988). However, a different study showed that some poorly ordered Mn oxides could be dissolved more readily than carbonate (Lenstra et al., 2021). In some published studies, carbonates or calcite fossils that were targeted showed larger ranges of Mn/Ca, from around 0.1 $\mu\text{g/g}$ to 35 mg/g (Misra and Froelich, 2012; Pogge von Strandmann et al., 2013, 2019b, 2021a; Ullmann et al., 2013; Clergue et al., 2015; Bastian et al., 2018; Dellinger et al., 2020; Jin et al., 2021; Cao et al., 2022; Wei et al., 2023). The high Mn/Ca ratios could stem from Mn-carbonate formation during diagenesis and/or contamination from Mn-oxides. Moreover, if the oxide leaching of YR is conducted after removing only the exchangeable fraction and not the carbonates (Table 3.3), the leachates from the oxide step will include significantly more Ca and Mn as well as Li, likely from both carbonates and oxides. The carbonate fraction in YR is also sufficient to influence the $\delta^7\text{Li}$ values in the oxide leachates if it is not removed

before oxide leaching. Without removing carbonate, the $\delta^7\text{Li}$ value in the nominally oxide leachate is $5.1 \pm 0.2\text{‰}$ (SD, $n = 3$), while the $\delta^7\text{Li}$ value in the oxide leachate after carbonate removal is $1.7 \pm 0.5\text{‰}$ (SD, $n = 2$). In contrast, as the RS and BCR-2 rarely contain carbonate, although the element concentrations in the leachates of RS and BCR-2 indicate that oxide leaching could dissolve carbonates if they were not previously removed, the impact on $\delta^7\text{Li}$ values is less than 1‰ (Tables 3.3 and 3.4).

As discussed in Section 3.2, for the oxide fraction, Fe, Al, and Mn are expected as the major elements; however, Fe and Al are also concentrated in clays or primary silicates, and Mn may be incorporated in carbonates, clays, or primary silicates. Based on the leaching methods in this study, Fe in the oxide leachates of BCR-2, RS, Bed10, and YR only comprises $\sim 1\%$ of the Fe in the bulk solids, which is less than in the clay fractions and much less than in the silicate residue (Table 3.4). It shows that Fe is included as a significant component in clays and primary silicates, and hence is not exclusive to oxides, although the oxide fractions are only partly leached. Similarly, for BCR-2, RS, Bed10, and YR, Al in the residue comprises 95–99% of the Al in the bulk solids, while Al in the oxides comprises less 1% of bulk solids. The clay fraction contains slightly more Al, at $\sim 0.6\%$, $\sim 3\%$, $\sim 5\%$, and $\sim 1\%$ of bulk BCR-2, RS, Bed10, and YR, respectively. Here, it is noted that the HCl leach will likely not remove the clays completely because it is more designed to determine the clay composition rather than their elemental budget.

Generally, Mg indicates the dissolution of clays or primary silicates. For example, for RS and BCR-2, the Mg in clay fractions and residue comprises $\sim 2\text{--}3\%$ and $\sim 95\text{--}97\%$, respectively, of the Mg in the bulk solids. Theoretically, Mg is rarely formed as oxides in the Earth surface environment. Furthermore, although Bed10 and YR comprise $\sim 10\%$ carbonates (Yang et al., 2009; Jones et al., 2012; Wang and Jin, 2017), the carbonate leachates of Bed10 and YR only contain around $\sim 1\%$ and $\sim 3\%$ of the total Mg in the bulk solid. Thus, Mg could be regarded as a reliable indicator for clays and primary silicates during leaching, even for the samples containing carbonate, so long as there is not a large proportion of dolomite.

Among the five leached fractions, the silicate residues contain more than 94% Li of BCR-2, RS, and YR, and $\sim 70\%$ of Bed10 (Figure 3.6). The clay fraction (i.e., HCl leach) is the second richest Li reservoir in BCR-2, RS, Bed10, and YR,

comprising ~3%, ~3%, ~15%, and ~2%, respectively. Because the Li concentrations in residues are much higher than in clay fractions, and the Li concentrations in clay fractions are also much higher than in oxide fractions (~8 times higher for BCR-2, ~2 times for RS, ~4 times higher for Bed10, and ~5 times higher for YR), the $\delta^7\text{Li}$ values of the residue and clay fractions are unlikely to be significantly affected by the incomplete leaching of the preceding fractions. Thus, in this study, partial leaching, especially for oxide and clay fractions, is employed in the extraction procedure to minimize the influence of the subsequent fraction on those targeted fractions. However, generally, the Li budgets of the exchangeable, carbonate, and oxide fractions are of a similar order of magnitude (Figure 3.6). It therefore appears possible that these fractions can influence each other during sequential leaching. Thus, it is critical to analyse a suite of elemental concentrations in the leachates to monitor the interplay as discussed above. In practice, it is important to interpret the trends of Li concentrations in the leachates from a group of samples rather than a single value.

The sequential leaching indicates that the different fractions have different $\delta^7\text{Li}$ values (Figure 3.6). Generally, the exchangeable fractions have higher $\delta^7\text{Li}$ values than oxide and clay fractions, especially for the river sediments (i.e., RS, Bed10, and YR) that have been weathered. The difference supports the concept that the Li isotopic fractionation between exchangeable fractions and surface waters ($\Delta^7\text{Li}_{\text{exchangeable-solution}}$) is less than that between structural sites in secondary oxide/clay and waters ($\Delta^7\text{Li}_{\text{oxide/clay-solution}}$) (Figure 1.3) (Pistiner and Henderson, 2003; Chan and Hein, 2007; Vigier et al., 2008; Wimpenny et al., 2010b, 2015; Pogge von Strandmann et al., 2019a, 2022 Hindshaw et al., 2019; Li and Liu, 2020). The $\delta^7\text{Li}$ values in carbonate fractions of BCR-2 and RS probably represent either primary carbonate, or an influence from exchangeable and/or oxide fractions, because BCR-2 and RS only have trace amounts of carbonate. In contrast, the $\delta^7\text{Li}$ values in carbonate fractions of Bed10 and YR more likely reflect secondary carbonates, which would imply the fractionation between carbonate and the corresponding water ($\Delta^7\text{Li}_{\text{carbonate-solution}}$) is close to $\Delta^7\text{Li}_{\text{exchangeable-solution}}$, which is less than $\Delta^7\text{Li}_{\text{oxide/clay-solution}}$. The $\Delta^7\text{Li}_{\text{carbonate-solution}}$ of Bed10 and YR agree with the range of published $\Delta^7\text{Li}_{\text{carbonate-solution}}$ from 0 to ~15‰ (Marriott et al., 2004; Pogge von Strandmann et al., 2021a; Day et al., 2021; Liu et al., 2023). The Li isotope fractionation between oxide fraction and solution is shown in Table S3.1. The silicate residue fractions of five solids show relatively

lighter Li isotopic compositions than the secondary fractions (Figure 3.6). The $\delta^7\text{Li}$ values of these silicate residue fractions has a narrow range from 0.8 to 2.7‰, which is consistent with the published $\delta^7\text{Li}$ range of primary rocks (Elliott et al., 2006; Dellinger et al., 2014; Tomascak et al., 2016; Marschall et al., 2017).

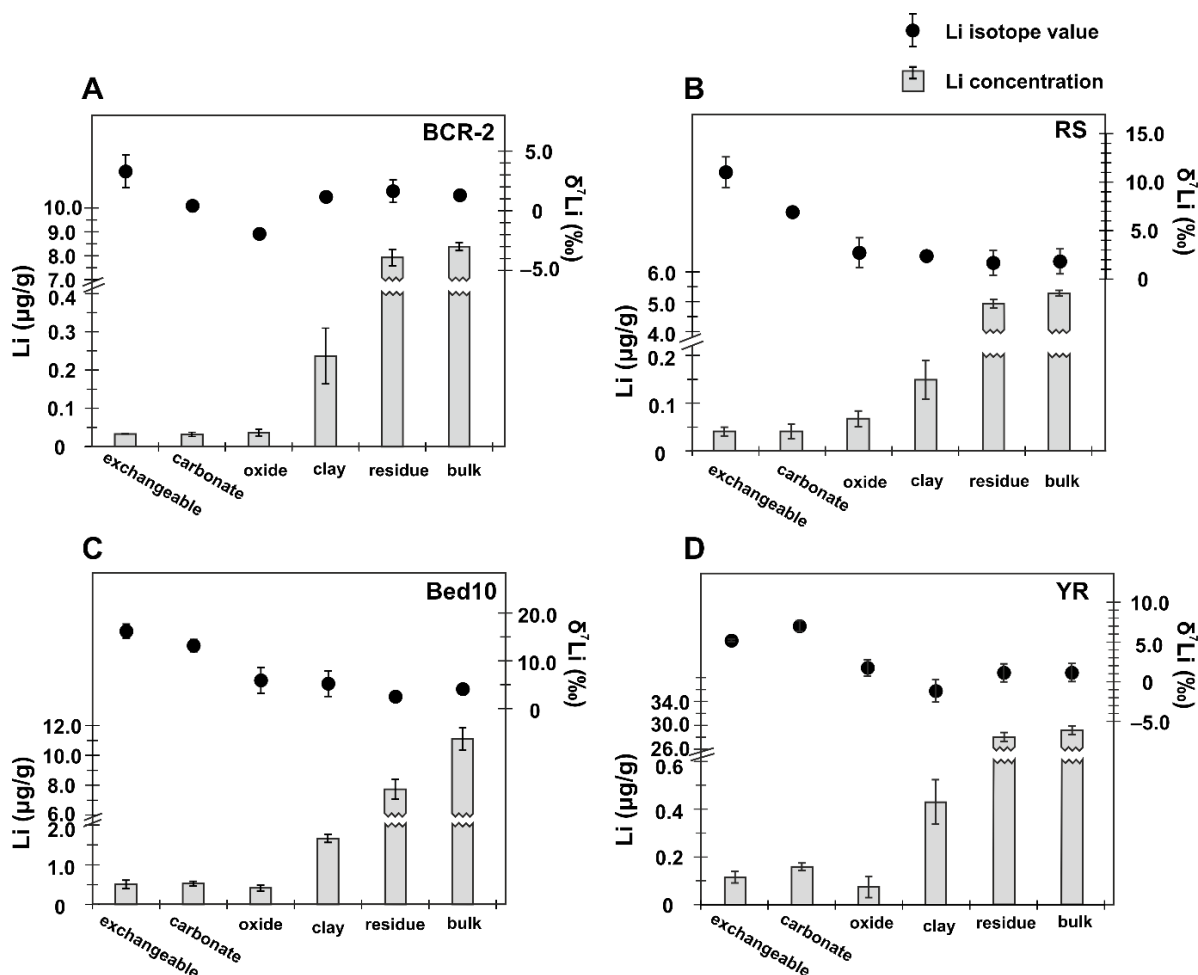


Figure 3.6 Li concentrations and Li isotopes in each fraction from the repeated full sequential leaching for BCR-2, RS, Bed10, and YR.

The bulk includes both the calculated values from full sequential leaching (Eq. 2.4) and measured bulk samples. The error bars represent the standard deviation of the replicates. No error bars are shown for the carbonate fraction of RS or the carbonate, clay, and bulk fractions of BCR-2, because of the lack of replicates for these fractions. The absence of visible error bars for other dots or columns means that these error bars are smaller than the symbol size.

3.4 Conclusions

1) Based on a series of experiments, using 0.04 mol/l HH in 25% v/v HOAc with a reagent/solid ratio of 40 ml/g at room temperature (20 ± 2 °C) for 1 h is found to be the most reliable method for selectively leaching Li isotopes from oxides. It must be noted that the applicability of the leaching method may be sensitive to the origin and composition of the bulk sediment, and it is therefore always necessary to determine the elemental composition of each leachate.

2) The results of the repeated full sequential leaching trials show that the reproducibility of element concentrations and Li isotope values is acceptable. By comparison of the measured data from full sequential leaching with the published data of the reference materials, the accuracy of element concentrations and Li isotope values acquired using sequential leaching is also shown to be acceptable.

3) According to the element concentrations in the leachates of different fractions of the solids, the K concentrations appear to be a good indicator of the exchangeable fraction. If the silicates contain more than 5% carbonate, it is necessary to remove carbonate before leaching the oxide fraction. Carbonates may also contain some Mn, meaning that Mn concentrations are not a reliable indicator of the oxide or silicate fraction. The results also suggest that more than 95% of Fe and Al can be in silicates (clays and primary minerals), rather than in oxides, which demonstrates that there are no major elements exclusively found in oxides. However, Mg appears to be a good indicator of contributions from clays and primary silicate minerals because virtually no Mg is contained in oxides. Thus, combining Mg concentrations with Fe, Mn and Al would allow the targeted fraction to better be distinguished.

Chapter 4. Solid-water interaction experiments with salinity increasing

4.1 Introduction

Solid-water interaction experiments are a useful method to explore the geochemical behaviour of elements and isotopes in different geological processes. Compared to complicated natural systems with multi-factor affected processes, solid-water interaction experiments have the advantage of isolating individual factors and quantifying the processes. To explore the Li concentration and isotope behaviour in weathering processes under Earth surface conditions, several experiments at low temperature ($<25\text{ }^{\circ}\text{C}$) have been conducted. Examples include primary mineral or rock dissolution (Pistiner and Henderson, 2003; Wimpenny et al., 2010a; Pogge von Strandmann et al., 2020b; Li et al., 2021), mineral adsorption and desorption (Pistiner and Henderson, 2003; Wimpenny et al., 2015; Li and Liu, 2020, 2022; Zhang X. et al., 2021), and secondary mineral dissolution and formation (Vigier et al., 2008; Millot et al., 2010b; Wimpenny et al., 2015; Pogge von Strandmann et al., 2019a; Hindshaw et al., 2019) (Section 1.2.2).

Because this study focuses on the estuarine area, where fresh river water and seawater rapidly mix, the main question is whether the changes in fluid geochemistry, especially the salinity and Li concentration, result in further alteration of river-derived particles. So far, to examine the influence of fluid geochemistry on Li behaviour and/or to imitate low-temperature weathering processes in the ocean, several studies conducted interaction experiments between solids and saline water (Millot et al., 2010b), high-Na solution (Hindshaw et al., 2019; Zhang X. et al., 2021; Li and Liu, 2022), or artificial seawater (Zhang X. et al., 2021). Hindshaw et al. (2019) indicated that high Na concentrations influence the Li entering interlayer sites in the Mg-rich layer and therefore can slightly decrease the Li isotope fractionation. However, the published Li isotope fractionation between minerals/solids in high-salinity fluid (5–28‰) is overall slightly larger than the fractionation between solids and fresh water (0–20‰) (Vigier et al., 2008; Millot et al., 2010b; Wimpenny et al., 2015; Pogge von

Strandmann et al., 2019a; Hindshaw et al., 2019; Zhang X. et al., 2021; Li and Liu, 2022; Yang et al., 2023). In addition, Li and Liu, (2022) showed that the Na concentration may influence the Li adsorption flux. However, no specific solid-water interaction experiment with gradually increasing salinity to imitate the process of river-derived particles passing through the estuary has been conducted.

Thus, in this chapter, four series of solid-water interaction experiments with gradual addition of concentrated artificial seawater were conducted (Section 4.2). The elemental concentrations and Li isotope values of the dissolved samples and different fractions of the solid samples were analysed (Section 4.3). Based on those results, the major element (Section 4.4.1) and Li concentration and isotope behaviour (Section 4.4.2) were examined, with a focus on their influencing factors, and the implications for quantifying fluxes and understanding the global Li cycle.

4.2 Experiment design

Four series of solid-water interaction experiments were designed and conducted in the LOGIC laboratories, with gradual addition of concentrated artificial seawater to imitate the estuarine environment, i.e., 1) basalt-Li-add experiment, 2) basalt-Li-free experiment, 3) loess-Li-add experiment, and 4) loess-Li-free experiment. Here, the solid in the basalt-water interaction experiments, i.e., 1) and 2), is a basaltic bedload sediment from the Borgarfjörður estuary, Iceland. This solid was chosen because of the rapid weathering of basalt and therefore its high contribution to weathering fluxes (Bowen, 1922; Meybeck, 1987; Gaillardet et al., 1999; Dessert et al., 2003). In addition, the basalt-water interaction experiments should provide helpful information for understanding the natural estuarine samples from the Borgarfjörður estuary (Chapter 5). The solid in the loess-water interaction experiments, i.e., 3) and 4), is a Yellow River sediment from near the Yellow River mouth. This solid was chosen to help understand the alteration of river-derived particles in the Yellow River estuary in the future. The Yellow River has the highest suspended load concentration among all large rivers (Gaillardet et al., 1999; Milliman and Farnsworth, 2011). Thus, the alteration of river-derived particles in the Yellow River estuary may exert a significant influence on the global dissolved Li flux. Furthermore, to examine the influence of dissolved Li concentrations on the Li behaviour during estuarine

processes, the Li-add experiments, i.e., 1) and 3), and Li-free experiments, i.e., 2) and 4), were designed to test the effect of the Li concentration on the weathering behaviour. There was no extra Li doping in the concentrated artificial seawater added for the Li-free experiments, whereas the extra Li doping in the concentrated artificial seawater added for Li-add experiments. Specifically, to imitate the natural mixing process in estuaries, in 1) basalt-Li-add experiment, the dissolved Li concentration was controlled as $\sim 180 \mu\text{g/l}$ when salinity at ~ 35 with doping Li in the concentrated artificial seawater.

4.2.1 Setup of interaction experiments

The basaltic bedload sediment (basalt-initial) from the Borgarfjörður estuary (Iceland) is used in the basalt-Li-add experiment and the basalt-Li-free experiment. Due to the requirement for large amount of solid material in the experiments, the basalt-initial solid was prepared by combining two natural estuarine sediments collected in 2008 from the river mouth and saline water in the Borgarfjörður estuary (Figure 4.1A) (Jones et al., 2012). The natural sediment from the river mouth accounts for 32% of the basalt-initial solid, while the natural sediment from the estuarine saline water accounts for the other 68%. The sediments from Borgarfjörður estuary generally comprise around 52% microcrystalline material, 18% volcanic glass, 10% Ca-feldspar, 8% olivine, 5% Fe-Ti oxide, 3% calcite, 2% K-feldspar, very minor quartz, and secondary minerals formed by weathering (Jones et al., 2012). The solid was crushed by quartz mortar and pestle to finer than around 1 mm diameter.

The initial solid (loess-initial) used in the loess-Li-add experiment and the loess-Li-free experiment is a Yellow River sediment. The natural sediment was collected from the Ecological Tourism Area of the Yellow River Estuary, near the river mouth, but before the estuary ($119^{\circ}09'44.86''$ E, $37^{\circ}45'32.53''$ N) on 6th November 2019 (Figure 4.1B). The loess from the Chinese Loess Plateau contributes more than 90% of the Yellow River sediments (Zhang et al., 1990). The sediments at the Yellow River mouth generally contain $\sim 40\%$ quartz, $\sim 30\%$ clay minerals, $\sim 15\%$ plagioclase, $\sim 10\%$ calcite, and $\sim 7\%$ potassium feldspar (Tian et al., 2021). The sample was dried in the oven at 60°C after collection.

The initial solutions in the experiments are tap-water from the LOGIC laboratory to obtain a natural charge balance, and this approach has been used

for several other weathering experiments (Pogge von Strandmann et al., 2019a, 2022). Concentrated artificial seawater solutions, 2.5 times that of artificial seawater (Kester et al., 1967), were added to increase the salinity of the solutions during the experiments. The artificial seawater solutions used in each experiment series were made by quantitatively dissolving NaCl (sodium chloride, >99.5%, SIGMA), KCl (potassium chloride, >99.5%, BDH), $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ (magnesium chloride hexahydrate, >99.5%, BDH), $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ (calcium chloride dihydrate, >99.5%, BDH), Na_2SO_4 (sodium sulfate anhydrous, >99.5%, Fisher chemical), and NaHCO_3 (sodium hydrogen carbonate, >99.5%, BDH) in ultrapure water (Table 4.1). The pH of the artificial seawater solutions was buffered to 8.2 by NaOH (sodium hydroxide, >99%, BDH). Lithium (Lithium plasma emission standard, BDH) was added into the artificial seawater solutions for the basalt-Li-add experiment and loess-Li-add experiment to achieve a Li concentration in the concentrated artificial seawater of $\sim 450 \mu\text{g/l}$ and $\sim 180 \mu\text{g/l}$, respectively. The element concentrations of the concentrated artificial seawater were measured using ICP-OES and ICP-MS and shown in Table S4.3 and S4.4.

Table 4.1 Formula of concentrated artificial seawater.

Experiment No.	basalt-Li-add	basalt-Li-free	loess-Li-add	loess-Li-free
NaCl	11.96 g	29.91 g	11.97 g	29.91 g
KCl	0.34 g	0.85 g	0.34 g	0.85 g
$\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$	5.41 g	13.54 g	5.41 g	13.54 g
$\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$	0.76 g	1.90 g	0.76 g	1.90 g
Na_2SO_4	2.00 g	5.01 g	2.00 g	5.01 g
NaHCO_3	0.10 g	0.25 g	-	0.25 g
Li (1000 mg/l)	90 μl	-	36 μl	-
Total volume	200 ml	500 ml	200 ml	500 ml

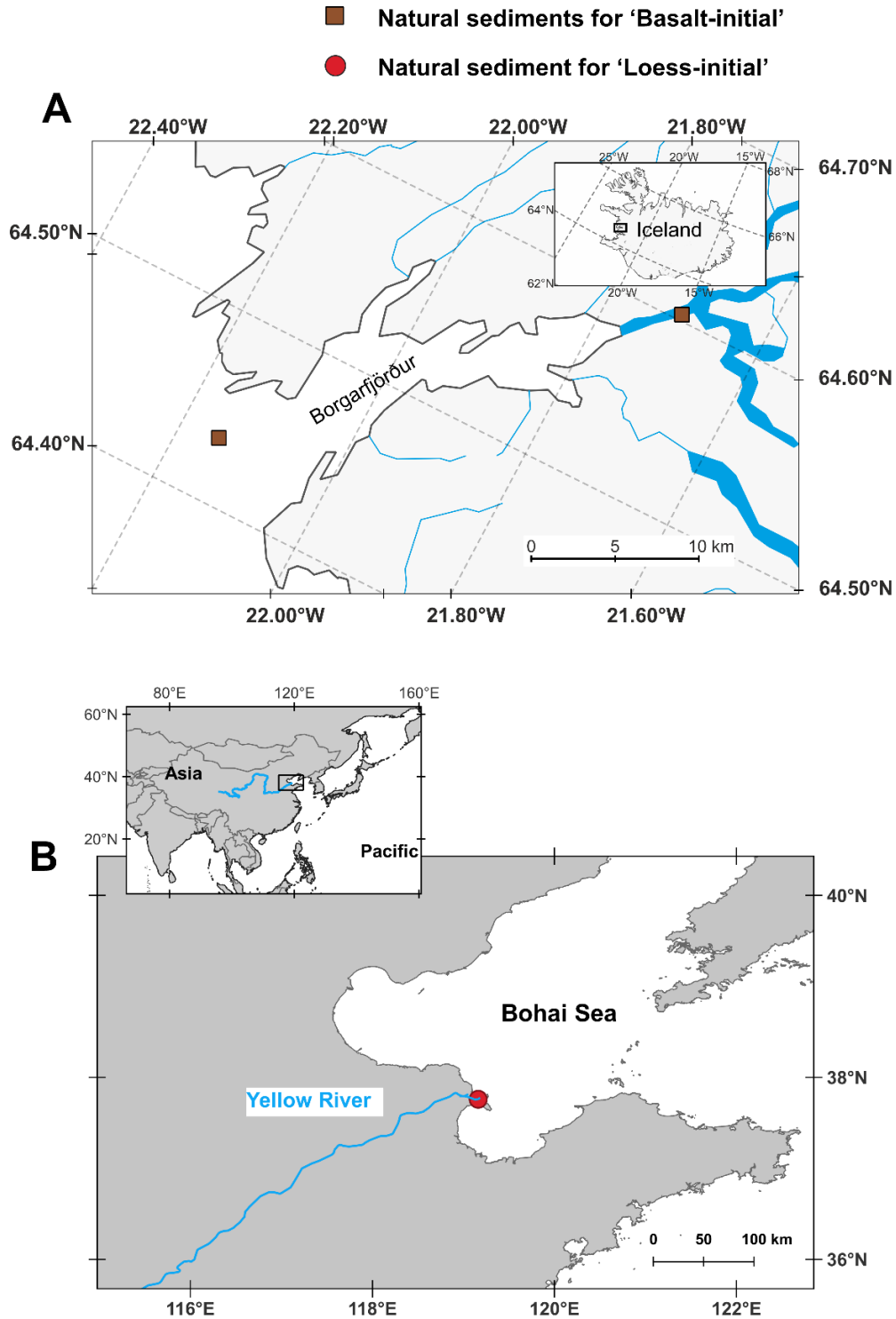


Figure 4.1 Locations of natural sediments for the initial solids in the interaction experiments.

A) Setting of the Borgarfjörður estuary. The 'basalt-initial' was prepared by combining two sediments (brown squares) from the Borgarfjörður estuary. B) Setting of the Yellow River estuary. The 'loess-initial' consists of the sediment (red dot) from the Yellow River estuary.

The initial mass ratio of water and solid was set as ~3.6. The mass of solid per mass of water in the experiment is larger than the suspended load concentrations in natural rivers (Milliman and Farnsworth, 2011), in order to better observe the influence of the solid on the dissolved load. To be specific, 1) basalt-Li-add experiment started as 103.94 g basalt-initial mixed with 374.33 g tap-water, 2) basalt-Li-free experiment started as 104.32 g basalt-initial mixed with 375.52 g tap-water, 3) loess-Li-add experiment started as 101.17 g loess-initial mixed with 364.23 g tap-water, and 4) loess-Li-free experiment started as 104.03 g loess-initial mixed with 374.53 g tap-water (Table S4.1). The interaction experiments were conducted in 1 l bottles (LDPE, NALGENE) standing in a shaking water bath (GFL® 1083) at 18–22 °C. In addition, three control experiments were conducted starting with the initial tap-water without solids (Table S4.2).

4.2.2 Interaction experiments and sampling

For each interaction experiment, three stages were sequentially conducted in one bottle: (i) preconditioning with tap-water (0–33 days), (ii) salinity-increasing stage (33–51 days), and (iii) after-salinity-increasing stage, i.e., interaction with saline water (after 51 days). The sampling list is given in Table S4.1.

In the preconditioning stage, the solids were interacted with tap-water from 0–33 days. Five dissolved load samples were collected at 2 hours, 1 day, 5 days, 11 days, and 33 days, and one solid sample was collected at 33 days from each experiment series.

Before the salinity-increasing stage, 7 µg Li (Lithium plasma emission standard, BDH) was added into the basalt-Li-free experiment and loess-Li-free experiment to increase the Li concentration in the dissolved load by ~20 µg/l (Table S4.1, S4.3, and S4.4), which was initially designed to ensure that enough Li was in the dissolved load for Li isotope analysis, because Li is normally removed from solution during interaction with rock (Pogge von Strandmann et al., 2019a). In the salinity-increasing stage (33–51 days), a calculated mass of concentrated artificial seawater solution was added to each experiment series to increase the salinity level every 3 days to 1, 2, 4, 6, 10, 20, and 35 higher than the salinity of the solution at 33 days (i.e., at the end of the preconditioning stage). Every 3 days in a salinity level is called a salinity step. Five dissolved load

samples were collected at 2 hours, 16 hours, 1 day, 2 days, and 3 days, and a solid sample was collected at the third day, in each salinity step for each experiment series.

After 51 days, the solids were left to interact with the saline water. Thirteen dissolved load samples and 2 solid samples from the loess-Li-add experiment were collected between 51–432 days, and 11 dissolved load samples and a solid sample from the other experiment series were collected between 51–529 days.

For each dissolved load sample, around 4–17 g solution was collected and filtered through 0.22 μm polyethersulfone membrane filters (Millex). The pH value for each solution was measured by a pH meter (METTLER TOLEDO) and solutions were saved for further analyses (Sections 2.3.1, 2.4, and 2.5). The solid samples from the basalt-Li-add and basalt-Li-free experiments were scooped out using plastic spoons, centrifuged to remove the solution, and then dried at 40 °C for further analyses (Sections 2.3.2, 2.4, and 2.5). It is noted that the solid sampling of the basalt-Li-add and basalt-Li-free experiments could cause heterogeneity of mineralogy or grain size. In contrast, the solid samples of the loess-Li-add and loess-Li-free experiments were collected by pouring out the muddy solution in which the loess was evenly suspended, after shaking the bottle. The solutions were then centrifuged to separate the supernatant and solid. The supernatant was added back to the interaction system, and the solid was dried at 40 °C for further analyses (Sections 2.3.1, 2.4, and 2.5). The water/solid ratios at the beginning of each salinity step were controlled in the range of 3.4–3.7, by balancing the mass of added concentrated artificial seawater solution, collected dissolved load samples, and collected solid samples (Table S4.1). In addition, the dissolved load samples were also collected from the three control experiments as a comparison.

4.3 Results

4.3.1 Basalt-water experiments

4.3.1.1 Dissolved load samples

The data for the dissolved load are shown in Table S4.3. Before increasing the salinity (0–33 days), the basalt-Li-add and basalt-Li-free experiments show similar trends (Figures 4.2 and 4.3A, C). The concentrations of Na, Ca, Mg, and K significantly increase in the first 2 hours to around 47, 1.2, 10, and 9 times of the initial concentrations, respectively. From 2 hours to 33 days, the concentrations of Mg, K, and Si slightly increase, while the Na and Ca concentrations vary. The Li concentration shows a significant increase from 5.38 µg/l to around 34.0 µg/l in the first two hours, then slightly increases to 39.2 µg/l (basalt-Li-add experiment) and 43.1 µg/l (basalt-Li-free experiment) at 5 days, and then slightly decreases to 36.0 µg/l (basalt-Li-add experiment) and 38.6 µg/l (basalt-Li-free experiment) at 33 days. However, in the first 33 days, the $\delta^7\text{Li}$ values keep increasing from 11 to ~27‰ in both the basalt-Li-add experiment and basalt-Li-free experiment.

During the salinity-increasing steps (33–51 days), there is no major difference in the concentrations of the major cations (i.e., Na, Ca, Mg, and K) between the basalt-Li-add and basalt-Li-free experiments (Figure 4.2), but the trends of Li concentration and Li isotopes are different (Figure 4.3A, C). The concentrations of Na, Ca, Mg, and K increase with adding artificial seawater. However, the variations of the concentrations of Na, Ca, Mg, and K between 5 dissolved samples collected in the same salinity step (every 3 days) is less than 3.0% (RSD). The Li concentration increases in the basalt-Li-add experiment with adding artificial seawater, but the variation between 5 dissolved samples collected in the same salinity step is less than 5% (RSD) without a clear trend. However, in the basalt-Li-free experiments, the Li concentrations generally decrease from 55.3 to 49.1 µg/l from 33–37 days, and then increase to 61.3 µg/l from 37–51 days (Figure 4.3A). Correspondingly, the $\delta^7\text{Li}$ values in the basalt-Li-free experiments increase from 24.0 to 26.8‰ in 33–36 days, are then constant in the range of 26.4–26.8‰ from 36–42 days, and decrease to 24.9‰ after 42–51 days. In contrast, in the basalt-Li-add experiments, the $\delta^7\text{Li}$ values increase

by around 0.9 to 3.0‰ in each salinity step (every 3 days), whereas the $\delta^7\text{Li}$ values initially decrease with each salinity-increasing step, because of the relatively low $\delta^7\text{Li}$ value ($\sim 11.3\text{‰}$) of the added artificial seawater (Figure 4.3C).

After increasing the salinity (after 51 days), the major cations (i.e., Na, Ca, Mg, and K) also display similar trends between the basalt-Li-add and basalt-Li-free experiments (Figure 4.2). The concentrations of Na, Ca, Mg, and K remain stable in 51–125 days, and then become higher in 125–529 days, but the overall variation in 51–529 days is less than 6.0% (RSD). Interestingly, in the basalt-Li-add experiment, the Li concentration decreases from 183–153 $\mu\text{g/l}$ in 51–125 days and remains stable at 149–158 $\mu\text{g/l}$ in 125–529 days (Figure 4.4A). Meanwhile, the $\delta^7\text{Li}$ values increase from 17.2 to 24.6‰ in 51–529 days (Figure 4.4B). In contrast, in the basalt-Li-free experiment, the Li concentration increases from 51.6 to 89.7 $\mu\text{g/l}$ in 51–197 days and then remains stable at ~ 85 $\mu\text{g/l}$, while the $\delta^7\text{Li}$ values vary slightly from 23.5 to 25.5‰ in 51–529 days.

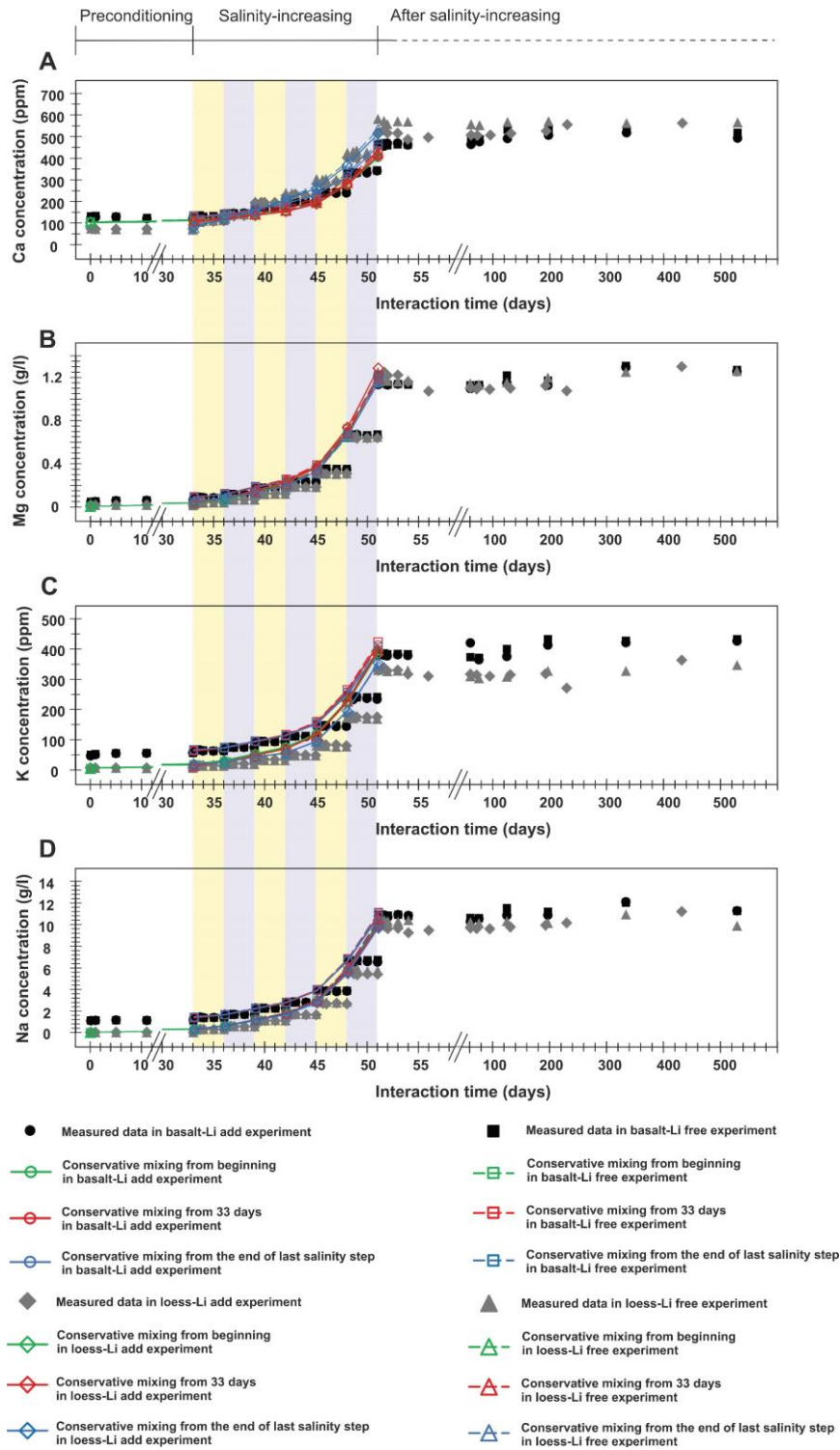


Figure 4.2 Dissolved major element concentrations (Ca, Mg, K, and Na) through time in four interaction experiments.

The x-axis is broken at 14–30 days and 60 days. The green, red, and blue points represent the conservative mixing at the beginning of each salinity step between the added artificial seawater and the tap-water at the beginning of the experiments, the solution at the end of the preconditioning stage (33 days), and the solution at the end of each previous salinity step, respectively (Tables S4.1 and S4.2). The yellow and purple shaded bars represent the salinity step every 3 days during the salinity-increasing stage.

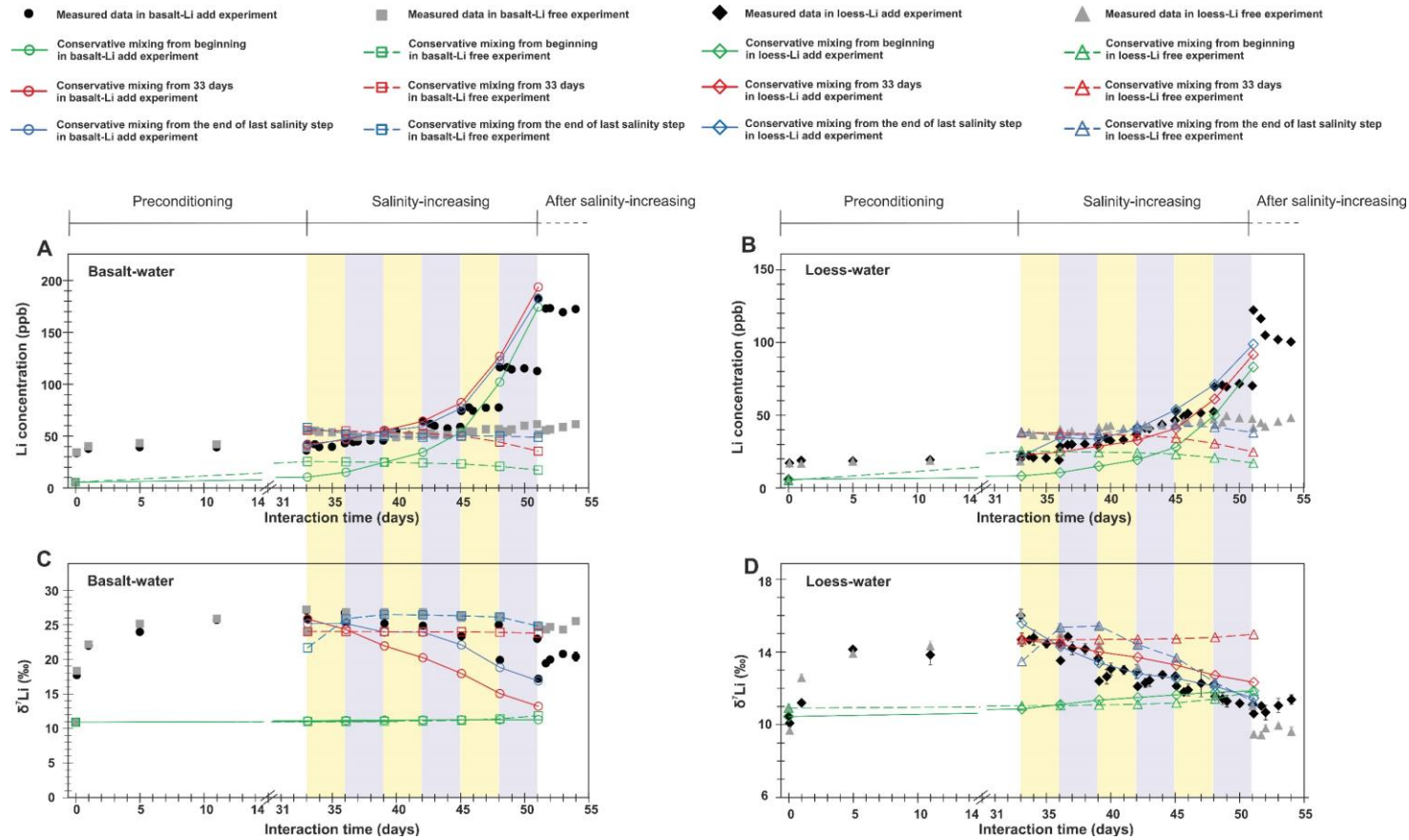


Figure 4.3 Li concentration and Li isotopes in dissolved load samples in four interaction experiments during the preconditioning stage (0–33 days), the salinity-increasing stage (33–51 days), and the first 4 days after the salinity-increasing stage (51–55 days)

The x-axis is broken from 14 to 30 days. The green, red, and blue points represent the conservative mixing at the beginning of each salinity step between the added artificial seawater and the tap-water at the beginning of the experiments, the solution at the end of the preconditioning stage (33 days), and the solution at the end of each previous salinity step, respectively (Tables S4.1 and S4.2). The error bars of the measured Li isotope values are 2σ (and are smaller than the symbol where not visible). Note the differing y-axes between panels. The yellow and purple shaded bars represent the salinity step every 3 days during the salinity-increasing stage.

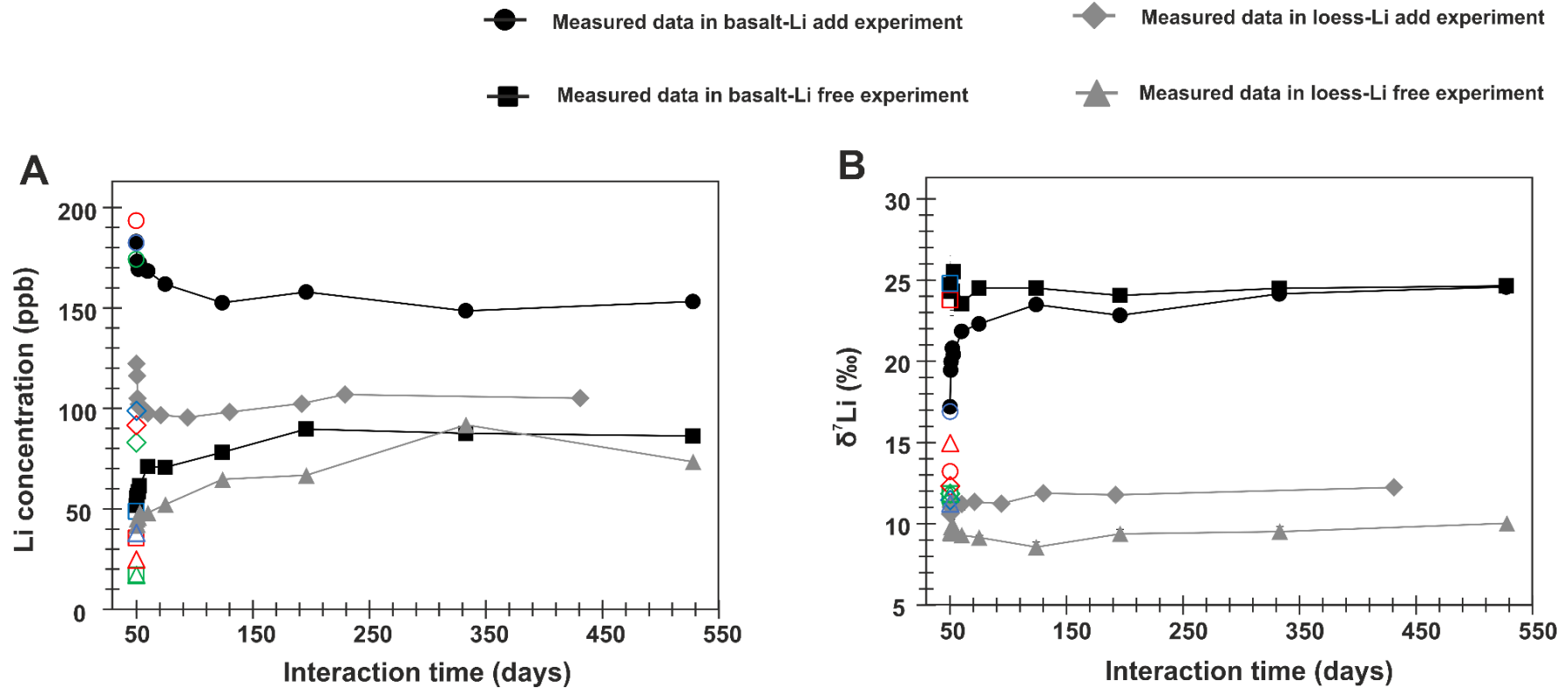


Figure 4.4 Li concentration and Li isotopes in dissolved load samples in four interaction experiments during the after-salinity-increasing stage (after 51 days).

The green, red, and blue points represent the conservative mixing at the beginning of the highest salinity step at 51 days between the added artificial seawater and the tap-water at the beginning of the experiment, the solution at the end of the preconditioning stage, and the solution at the end of the final salinity step, respectively. The error bars of the measured Li isotope values are 2σ (and are smaller than the symbol where not visible).

4.3.1.2 Solid load samples

The element concentrations and Li isotopes of the leachates of basalt-initial, basalt-Li-add-08, and basalt-Li-free-08 are given in Table 4.2. The basalt-Li-add-08 and basalt-Li-free-08 were collected at the 197th day when the elemental concentration and Li isotope values in the dissolved fraction reached stable values (Figures 4.2 and 4.4). Basically, the changes of major element concentrations in most leachates between the basalt-initial and post-interaction solids are negligible, except that $[Ca]_{\text{exchangeable}}$, $[K]_{\text{exchangeable}}$, and $[Ca]_{\text{carbonate}}$ of the post-interaction solids are lower than for the basalt-initial. In addition, the $[Li]_{\text{exchangeable}}$ values in basalt-Li-add-08 (0.21 $\mu\text{g/g}$) and basalt-Li-free-08 (0.15 $\mu\text{g/g}$) are lower than in basalt-initial (0.31 $\mu\text{g/g}$). The $\delta^7\text{Li}_{\text{exchangeable}}$ values in basalt-Li-add-08 (15.2‰) and basalt-Li-free-08 (14.5‰) are also slightly lower than in basalt-initial (16.9‰). Similarly, the $[Li]_{\text{carbonate}}$ and $\delta^7\text{Li}_{\text{carbonate}}$ in both basalt-Li-add-08 and basalt-Li-free-08 are lower than those in basalt-initial. However, for the oxide, clay, and residue fractions, the Li concentrations in the leachates or residue solution of basalt-Li-add-08 are similar to basalt-initial, but around 1.1–1.3 times the corresponding leachates or residue solution of basalt-Li-free-08. In contrast, the $\delta^7\text{Li}_{\text{clay}}$ and $\delta^7\text{Li}_{\text{residue}}$ of basalt-Li-free-08 are similar to basalt-initial, and are around 0.7–1.1‰ higher than the $\delta^7\text{Li}$ values in the corresponding leachates of basalt-Li-add-08. The $[Li]_{\text{bulk-sum}}$ (calculated using Eq. 2.2) in basalt-Li-free-08 (8.11 $\mu\text{g/g}$) is slightly less than that in basalt-Li-add-08 (8.94 $\mu\text{g/g}$) and basalt-initial (9.02 $\mu\text{g/g}$), and $\delta^7\text{Li}_{\text{bulk-sum}}$ (calculated using Eq. 2.3) of basalt-Li-add-08 (2.9‰) and basalt-Li-free-08 (3.4‰) are generally similar to basalt-initial (3.9‰).

The element concentrations of bulk solid samples (i.e., basalt-initial, basalt-Li-add-01 to 08, and basalt-Li-free-01 to 08) are given in Table 4.2. In general, for both basalt-Li-add and basalt-Li-free experiments, the concentrations of Na, Mg, K, Ca, Al, and Li decrease in the low salinity stage (~5‰), and increase in the medium and high salinity stage. In contrast, there are no obvious trends in the Fe and Mn concentrations in the experiments.

Table 4.2 Element concentrations and Li isotope values in fractions of the solid and the bulk solid.

Sample ID.	Interaction time days	Ca mg/g	Mg mg/g	K mg/g	Fe mg/g	Mn mg/g	Al mg/g	Na mg/g	Li μg/g	δ ⁷ Li ‰	2σ ‰
basalt-initial exchangeable	0	1.53	0.32	0.63	0.01	0.00	0.02		0.31	16.94	0.16
basalt-initial carbonate	0	15.7	0.32	0.12	0.02	0.01	0.03		0.31	13.69	0.10
basalt-initial oxide	0	0.59	0.11	0.03	0.47	0.05	0.34		0.21	5.52	0.06
basalt-initial clay	0	1.59	0.85	0.05	3.07	0.03	2.61		0.98	3.83	0.24
basalt-initial residue	0	72.1	50.5	2.01	95.0	1.39	58.1		7.21	2.87	0.22
basalt-initial bulk-sum	0	91.5	52.1	2.85	98.5	1.48	61.1		9.02	3.88	
basalt-Li-add-08 exchangeable	197	0.97	0.32	0.56	0.03	0.00	0.01		0.21	15.23	0.23
basalt-Li-add-08 carbonate	197	15.0	0.33	0.15	0.02	0.01	0.03		0.28	10.96	0.24
basalt-Li-add-08 oxide	197	0.79	0.11	0.03	0.40	0.05	0.33		0.19	5.58	0.14
basalt-Li-add-08 clay	197	1.68	0.87	0.05	3.12	0.03	2.55		0.98	2.70	0.01
basalt-Li-add-08 residue	197	71.9	50.4	1.94	95.8	1.40	57.2		7.27	2.16	0.00
basalt-Li-add-08 bulk-sum	197	90.3	52.00	2.74	99.3	1.49	60.1		8.94	2.89	
basalt-Li-free-08 exchangeable	197	0.89	0.30	0.50	0.01	0.00			0.15	14.52	0.22
basalt-Li-free-08 carbonate	197	12.1	0.29	0.12	0.03	0.01	0.04		0.22	11.91	0.01
basalt-Li-free-08 oxide	197	0.56	0.10	0.03	0.38	0.04	0.31		0.15	5.79	0.21
basalt-Li-free-08 clay	197	1.55	0.78	0.04	2.80	0.03	2.15		0.84	3.19	0.08
basalt-Li-free-08 residue	197	74.6	51.5	2.15	95.3	1.41	60.2		6.75	2.85	0.12
basalt-Li-free-08 bulk-sum	197	89.7	52.9	2.85	98.5	1.49	62.7		8.11	3.41	
loess-initial exchangeable	0	1.38	0.18	0.12	0.01				0.10	5.12	0.01
loess-initial carbonate	0	27.3	0.38	0.07	0.03	0.06	0.02		0.15	7.24	0.14
loess-initial oxide	0	7.29	0.21	0.04	0.18	0.08	0.12		0.04	2.10	0.12
loess-initial clay	0	5.37	1.72	0.05	0.56	0.03	0.58		0.36	-0.67	0.06
loess-initial residue	0	8.20	10.7	18.3	25.3	0.29	58.8		28.6	1.54	0.21
loess-initial bulk-sum	0	49.5	13.2	18.6	26.1	0.47	59.5		29.2	1.55	

Sample ID.	Interaction time days	Ca mg/g	Mg mg/g	K mg/g	Fe mg/g	Mn mg/g	Al mg/g	Na mg/g	Li μg/g	δ ⁷ Li ‰	2σ ‰
loess-Li-add-08 exchangeable	95	0.97	0.41	0.36	0.00	0.00	0.00		0.06	2.46	0.19
loess-Li-add-08 carbonate	95	25.9	0.34	0.11	0.02	0.06	0.01		0.10	7.89	0.08
loess-Li-add-08 oxide	95	6.08	0.22	0.03	0.16	0.07	0.07		0.04	1.77	0.11
loess-Li-add-08 clay	95	5.20	1.76	0.05	0.47	0.02	0.45		0.27	-1.02	0.12
loess-Li-add-08 residue	95	8.28	10.8	18.0	25.2	0.30	59.6		29.1	1.53	0.19
loess-Li-add-08 bulk-sum	95	46.4	13.5	18.6	25.9	0.45	60.2		29.6	1.53	
loess-Li-free-08 exchangeable	197	0.95	0.36	0.33	0.01	0.00	0.00		0.04	4.10	0.25
loess-Li-free-08 carbonate	197	25.9	0.42	0.16	0.03	0.05	0.01		0.10	7.89	0.14
loess-Li-free-08 oxide	197	6.59	0.19	0.03	0.12	0.08	0.08		0.03	2.06	0.23
loess-Li-free-08 clay	197	5.68	1.74	0.05	0.46	0.03	0.48		0.26	-0.77	0.14
loess-Li-free-08 residue	197	8.15	10.9	19.0	25.3	0.29	59.4		29.2	1.33	0.30
loess-Li-free-08 bulk-sum	197	47.2	13.6	19.6	25.9	0.45	59.9		29.6	1.34	
basalt-initial bulk-measured	0	85.6	50.0	2.50	101	1.57	68.9	17.4	9.19		
basalt-Li-add-01 bulk-measured	33	90.5	40.6	2.37	86.6	1.45	70.4	13.3	10.7		
basalt-Li-add-02 bulk-measured	36	63.2	39.7	1.95	109	1.56	51.8	10.3	8.09		
basalt-Li-add-03 bulk-measured	39	63.7	45.8	1.72	105	1.59	53.7	11.0	7.39		
basalt-Li-add-04 bulk-measured	42	69.0	46.8	1.66	106	1.52	55.6	11.6	6.58		
basalt-Li-add-05 bulk-measured	45	70.5	48.2	1.90	102	1.51	58.4	11.9	6.80		
basalt-Li-add-06 bulk-measured	48	78.1	49.2	2.28	92.8	1.49	64.9	14.0	7.86		
basalt-Li-add-07 bulk-measured	51	72.6	53.7	1.99	98.5	1.52	60.2	15.3	7.35		
basalt-Li-add-08 bulk-measured	197	84.2	52.6	2.50	101	1.56	67.3	14.7	8.60		
basalt-Li-free-01 bulk-measured	33	93.9	37.9	2.49	86.9	1.47	69.5	13.5	10.7		
basalt-Li-free-02 bulk-measured	36	71.8	49.0	2.22	97.5	1.52	60.8	12.0	6.44		
basalt-Li-free-03 bulk-measured	39	57.0	36.7	1.71	116	1.59	46.4	9.1	7.91		
basalt-Li-free-04 bulk-measured	42	69.7	54.4	1.41	98.1	1.59	57.3	11.1	7.38		
basalt-Li-free-05 bulk-measured	45	65.5	44.9	2.40	104	1.54	55.8	11.9	7.60		

Sample ID.	Interaction time days	Ca mg/g	Mg mg/g	K mg/g	Fe mg/g	Mn mg/g	Al mg/g	Na mg/g	Li μg/g	$\delta^7\text{Li}$ ‰	2σ ‰
basalt-Li-free-06 bulk-measured	48	76.3	50.9	1.79	94.5	1.56	61.0	12.7	6.98		
basalt-Li-free-07 bulk-measured	51	60.9	47.7	2.38	110	1.55	51.6	12.9	7.81		
basalt-Li-free-08 bulk-measured	197	80.7	56.5	1.97	107	1.70	64.9	13.9	8.73		
loess-initial bulk-measured	0	44.2	12.7	16.9	27.2	0.52	63.0	14.2	29.9		
loess-Li-add-01 bulk-measured	33	44.5	13.0	12.7	27.7	0.50	64.6	15.0	28.4		
loess-Li-add-02 bulk-measured	36	43.5	12.9	15.8	26.9	0.51	63.8	15.6	29.6		
loess-Li-add-03 bulk-measured	39	43.1	12.9	16.9	26.8	0.50	63.6	15.1	29.6		
loess-Li-add-04 bulk-measured	42	44.9	13.1	17.3	27.5	0.50	64.7	15.5	28.4		
loess-Li-add-05 bulk-measured	45	43.7	13.0	17.6	27.4	0.51	65.1	16.0	28.7		
loess-Li-add-06 bulk-measured	48	43.7	12.9	17.8	27.1	0.50	63.9	16.4	29.3		
loess-Li-add-07 bulk-measured	51	43.9	13.1	16.6	27.1	0.51	62.9	16.2	28.9		
loess-Li-add-08 bulk-measured	95	44.0	13.0	16.7	26.2	0.50	62.7	16.8	29.0		
loess-Li-free-01 bulk-measured	33	50.0	12.6	15.3	26.6	0.52	58.7	11.3	30.7		
loess-Li-free-02 bulk-measured	36	44.5	12.9	15.6	27.3	0.51	63.3	14.1	29.0		
loess-Li-free-03 bulk-measured	39	43.9	12.8	17.1	26.8	0.49	64.1	15.3	29.8		
loess-Li-free-04 bulk-measured	42	43.0	12.7	16.1	26.5	0.51	62.5	14.6	30.4		
loess-Li-free-05 bulk-measured	45	43.6	13.1	16.6	26.6	0.51	63.2	15.0	29.5		
loess-Li-free-06 bulk-measured	48	42.6	12.9	14.0	26.4	0.49	63.3	16.0	30.0		
loess-Li-free-07 bulk-measured	51	47.2	13.3	16.9	27.6	0.52	65.3	17.5	28.0		
loess-Li-free-08 bulk-measured	197	44.9	13.2	17.2	26.7	0.50	63.8	18.0	29.4		

2σ is the two standard deviation of each measured $\delta^7\text{Li}$ value. The long-term uncertainty of seawater $\delta^7\text{Li}$ analysis using MC-ICP-MS is 0.63‰ (2SD).

4.3.2 Loess-water experiments

4.3.2.1 Dissolved load samples

The data for the dissolved load is shown in Table S4.4. Before the salinity-increasing stage, the element concentrations in the loess-Li-add and loess-Li-free experiments are similar (Figures 4.2 and 4.3B, D). In the first two hours, the Ca concentration decreases from ~105 to ~70 mg/l, while the concentrations of Na, K, and Mg increase. From 2 hours to 33 days, the concentrations of Mg and Si slightly increase, while the Na, K, and Ca concentrations vary. The Li concentration shows a significant increase from ~6 to ~17 µg/l in first two hours, then slightly increases to 18.6 µg/l (loess-Li-add experiment) and 19.8 µg/l (loess-Li-free experiment) at 33 days. Meanwhile, in the first 33 days, the $\delta^7\text{Li}$ values increase from ~11 to ~16‰ in both loess-Li-add experiment and loess-Li-free experiment.

During the salinity-increasing steps (33–51 days), there is no major difference in the concentrations of major cations (i.e., Na, Ca, Mg, and K) between the loess-Li-add and loess-Li-free experiments (Figure 4.2). Generally, the concentrations of Na, Ca, and Mg, which are added by the artificial seawater, in the same salinity step (every 3 days) varies by less than 5.0% (RSD). In contrast, the K concentrations, despite also being added by artificial seawater, show a decrease in each salinity step (every 3 days) (Table S4.4). For Li concentrations, in both the loess-Li-add and loess-Li-free experiments, there is no clear trend among the five dissolved samples collected in each salinity step (Figure 4.3B). However, although Li is only added in the artificial seawater for the loess-Li-add experiment, the Li concentrations in both the loess-Li-add and loess-Li-free experiments show an overall increasing trend with addition of the artificial seawater step by step. Furthermore, the $\delta^7\text{Li}$ values in both experiments show a general decreasing trend from around 15 to 11‰ step by step with addition of the artificial seawater (Figure 4.3D).

After increasing the salinity (after 51 days), in both experiments, the concentrations of Mg, K, and Ca generally decrease from 51 to ~75 days and increase after ~75 days. (Figure 4.2). However, the overall variations of the concentrations of Na, Ca, Mg, and K are less than 7.0% (RSD) in both the loess-Li-add and loess-Li-free experiments. Interestingly, in the loess-Li-add

experiment, the Li concentration decreases from around 122 to 94.4 $\mu\text{g/l}$ from 51 to 95 days, and then increases to around 105 $\mu\text{g/l}$ at 432 days (Figure 4.4A). In contrast, the Li concentration in the loess-Li-free experiment keeps increasing from 41.7 to around 70 $\mu\text{g/l}$ after 51 days. In addition, $\delta^7\text{Li}$ values slightly increase from 10.6 to $\sim 11.5\text{‰}$ in the loess-Li-add experiment after 51 days (Figure 4.4B). In contrast, in the loess-Li-free experiment, $\delta^7\text{Li}$ slightly varies from 8.6 to 10.0 ‰ with no clear trend after 51 days.

4.3.2.2 Solid load samples

The element concentrations and Li isotopes of leachates of loess-initial, loess-Li-add-08 (collected in 95 days), and loess-Li-free-08 (collected in 197 days) are given in Table 4.2. In both loess-Li-add and loess-Li-free experiments, the $[\text{Mg}]_{\text{exchangeable}}$ and $[\text{K}]_{\text{exchangeable}}$ of the post interaction solids increase around 2 and 3 times than loess-initial, respectively. In contrast, the $[\text{Ca}]_{\text{exchangeable}}$, $[\text{Fe}]_{\text{oxide}}$, $[\text{Al}]_{\text{oxide}}$, $[\text{Fe}]_{\text{clay}}$, and $[\text{Al}]_{\text{clay}}$ in the post interaction solids show a decrease compared to the initial solid. In addition, the Li concentrations in the exchangeable, carbonate, oxide, and clay fractions in loess-Li-add-08 and loess-Li-free-08 are lower than the corresponding fractions in loess-initial. The $\delta^7\text{Li}_{\text{exchangeable}}$ in loess-Li-add-08 (2.5 ‰) and loess-Li-free-08 (4.1 ‰) are also lower than $\delta^7\text{Li}_{\text{exchangeable}}$ in basalt-initial (5.1 ‰). In contrast, $\delta^7\text{Li}$ values in the carbonate, oxide, and clay fractions change negligibly after the experiments, while the differences of both the Li concentrations and $\delta^7\text{Li}$ values in the residues are also negligible.

The element concentrations of bulk solid samples (i.e., loess-initial, loess-Li-add-01 to 08, and loess-Li-free-01 to 08) are given in Table 4.2. In both loess-Li-add and loess-Li-free experiments, the concentrations of Na, K, and Mg display generally increasing trends in the salinity-increasing stage. In contrast, the concentrations of Al, Fe, Mn, and Li slightly vary without clear trends.

4.4 Discussion

4.4.1 Major element behaviour

4.4.1.1 Element transfer between dissolved load and solids

In the dissolved load of these four interaction experiments, the concentrations of major elements (i.e., Na, Ca, Mg, and K) rapidly change in the first 2 hours (Tables S4.3 and S4.4), which indicates the immediate interaction between the solids and the initial solutions that are different from their natural ambient solutions. In particular, in the basalt-Li-add and basalt-Li-free experiments, the rapid release of Na, K, and Mg increases the salinity from 0.4 to ~4 in the first 2 hours (Table S4.3). In contrast, the salinity in the loess-Li-add and loess-Li-free experiments changes negligibly, although Na, Mg, and K also increase slightly. The initial basalt solid, which comprises bedload sediments from Borgarfjörður estuary (Jones et al., 2012), has already interacted with natural seawater (or at least brackish water). Therefore, the significant increase of Na, Mg, and K in both basalt experiments in the first 2 hours probably stems from the dissolution of salts and desorption of exchangeable cations. Due to the unexpected salinity increase in the first 2 hours, the actual salinity in the two basalt experiments is higher than the designed salinity in the subsequent steps.

From 2 hours to 33 days (preconditioning stage), 33 to 51 days (salinity-increasing stage), and 51 to 53 days (the first 3 days after the salinity-increasing stage), the concentrations of Na, Ca, Mg, and K show progressive linear increases with the addition of seawater, whereas there is no significant change between the five dissolved load samples collected in each salinity step (every 3 days) (Figure 4.2). However, compared to the conservative mixing expected from simply adding the artificial seawater, the dissolved load shows loss of Mg and K, and gain of Ca, which corresponds to the major element behaviour in some natural estuaries (Sayles and Mangelsdorf, 1979; Pogge von Strandmann et al., 2008; Lupker et al., 2016; Yang et al., 2021).

Here, to quantify the element behaviour, the element transfer between the dissolved and solid load in the four interaction experiments is calculated based on the dissolved elemental concentrations using Eqs. 4.1 and 4.2 (Tables S4.3 and S4.4).

$$[X]_{w\Delta(i+1)} M_{w(i)} = [X]_{w(i+1)} M_{w(i)} - [X]_{w(i)} (M_{w(i)} - M_{CASW(i)}) - [X]_{CASW(i)} M_{CASW(i)} \quad \text{Eq. 4.1}$$

$$\sum_1^i [X]_{r\Delta(i+1)} = - \sum_1^i ([X]_{w\Delta(i+1)} \times \frac{M_{w(i)}}{M_{r(i)}}) \quad \text{Eq. 4.2}$$

Here, $M_{w(i)}$ and $M_{r(i)}$ are the water mass and rock mass, respectively, that remains in the experiments after sampling the dissolved load sample i , sampling the solid sample (if done), and adding artificial seawater (if done). $M_{CASW(i)}$ and $[X]_{CASW(i)}$ are the mass and elemental concentration, respectively, of the added concentrated artificial seawater (if done). $[X]_{w(i)}$ is the measured concentration of element X in dissolved sample i , which is collected before adding artificial seawater. $[X]_{w\Delta(i+1)}$ is the loss/gain in mass of the dissolved element X caused by solid-water interaction per mass (g) of water (i.e., the changes of element concentration in the dissolved load caused by solid-water interaction) between sampling of dissolved load samples i to $i+1$. For $[X]_{w\Delta(i+1)}$, a negative value means loss, i.e., element transfer from water to solid (and vice versa for positive values). $[X]_{r\Delta(i+1)}$ is the loss/gain in mass of the element X in the solid caused by solid-water interaction per mass (g) of solid (i.e., the changes of element concentration in the solid caused by solid-water interaction) between sampling of dissolved load samples i to $i+1$. For $[X]_{r\Delta(i+1)}$, a negative value means loss, i.e., element transfer from solid to water (and vice versa for positive values). Then, $\sum_1^i [X]_{r\Delta(i+1)}$ gives the accumulated changes of element X in the solid from the start to the moment of sampling the dissolved load $i+1$ (Figure 4.5).

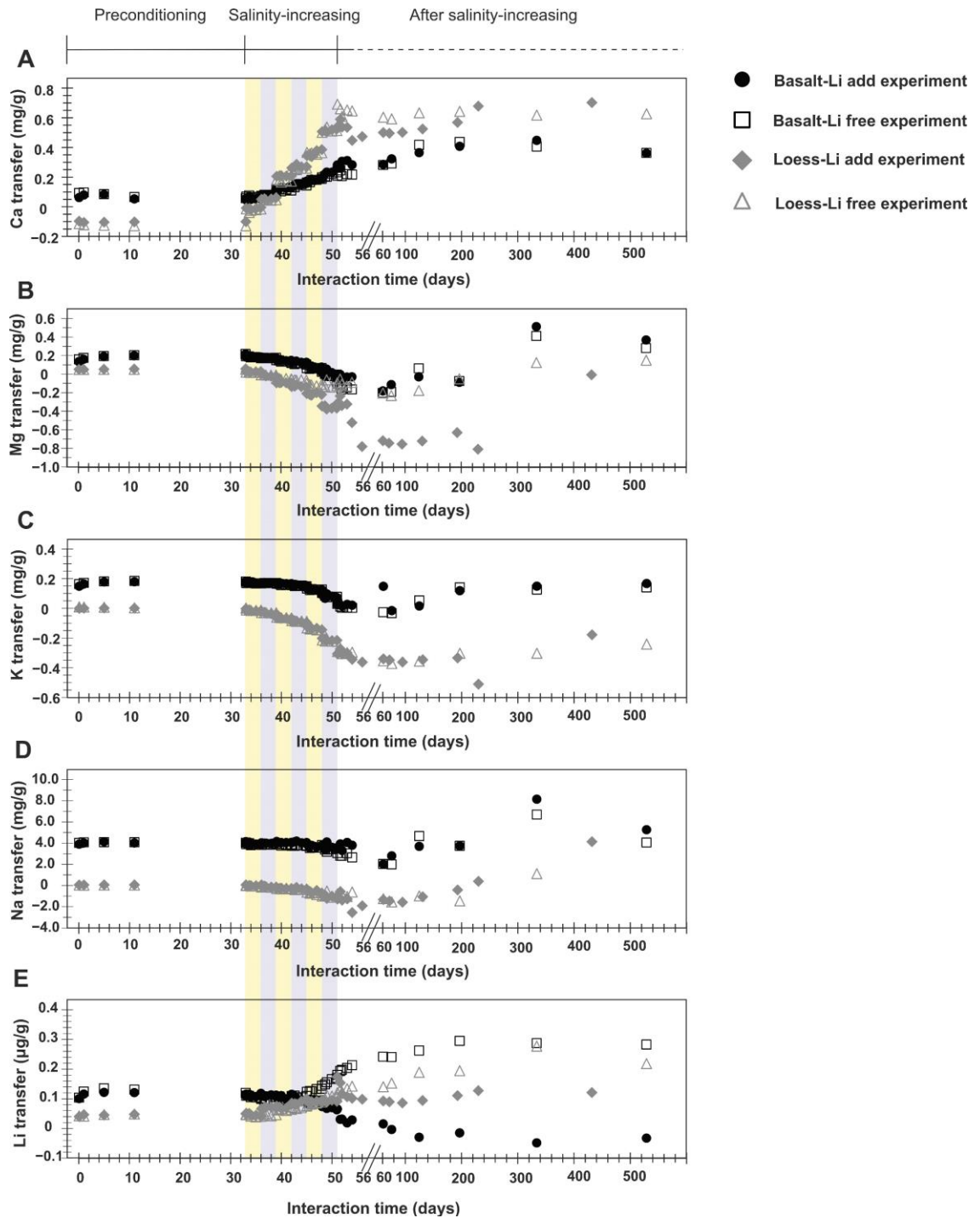


Figure 4.5 Element (Ca, Mg, K, Na, and Li) transfer from solid to dissolved load in four interaction experiments.

The element transfer is calculated based on the dissolved element concentrations using Eqs. 4.1 and 4.2. The element transfer is expressed as the mass of element per gram of solid released to the dissolved load (positive value) or uptake from the dissolved load (negative value) to achieve mass balance. The x-axis is broken at 58 days. The yellow and purple shaded bars represent the salinity step every 3 days during the salinity-increasing stage.

Basically, the major element (i.e., Ca, Mg, K, and Na) transfers show similar trends in all four experiments (Figure 4.5), which indicates that the different solid types do not control the major element behaviour during the experiments, and the different Li concentrations in the dissolved load are not significant enough to influence the major element behaviour. During the salinity-increasing stage, which is designed to imitate the natural process of solids passing through the estuary, the solids remove Na, Mg, and K from the dissolved load, while they release Ca into the dissolved load (Figure 4.5).

The element mass transfer accumulated from the sample $i = 6$ (at 33 days 2 hours) to the sample i as a proportion of the total mass of the element in the dissolved load at sample i , which is noted $X_{\Delta/w(6 \text{ to } i)}$, can also be calculated using Eq. 4.3 (Tables S4.3 and S4.4).

$$X_{\Delta/w(6 \text{ to } i)} = \frac{\sum_6^i ([X]_{w\Delta(i+1)} M_{w(i)})}{([X]_{\text{tapwater}} M_{\text{tapwater}} + \sum_0^i ([X]_{\text{CASW}(i)} M_{\text{CASW}(i)}) + \sum_0^5 ([X]_{w\Delta(i+1)} M_{w(i)}) - \sum_0^i ([X]_{w(i)} M_{\text{sampling}(i)})} \quad \text{Eq. 4.3}$$

Here, $[X]_{w\Delta(i+1)}$ is the loss/gain in mass of the dissolved element X caused by solid-water interaction per mass (g) of water (i.e., the changes of element concentration in the dissolved load caused by solid-water interaction) between sampling of dissolved load samples i to $i+1$ (Eq. 4.1). The accumulated value, $\sum_0^5 ([X]_{w\Delta(i+1)} M_{w(i)})$, is the element loss/gain in mass accumulated from the beginning to the end of the preconditioning stage. The sample collected at the end of the preconditioning stage is $i = 5$, at 33 days. The first sample collected during the salinity-increasing stage is the sixth sample ($i = 6$) at 33 days 2 hours. $M_{\text{CASW}(i)}$ and $[X]_{\text{CASW}(i)}$ are the mass and elemental concentration, respectively, of the added concentrated artificial seawater. M_{tapwater} and $[X]_{\text{tapwater}}$ are the mass and elemental concentration, respectively, of the tap-water (i.e., initial solution). $M_{w(i)}$ is the water mass that remains in the experiments after sampling the dissolved load sample i , sampling the solid sample (if done), and adding artificial seawater (if done). $M_{\text{sampling}(i)}$ is the sampling mass of the dissolved load sample i . $[X]_{w(i)}$ is the measured concentration of element X in the dissolved sample i , which is collected before adding the artificial seawater.

In the salinity-increasing stage from 33–51 days ($i = 6 \text{ to } 35$), the $Na_{\Delta/w(6 \text{ to } i)}$,

$Mg_{\Delta/w(6 \text{ to } i)}$, and $K_{\Delta/w(6 \text{ to } i)}$ are -6.0 to -0.2% , -15.2 to -5.3% , and -16.2 to -1.5% , respectively, in the two basalt experiments (Tables S4.3 and S4.4). In the two loess experiments, they are -11.0 to -0.2% , -28.6 to -8.0% , and -44.7 to -18.8% , respectively. These calculations provide strong evidence for the incorporation of Na, Mg, and K into the river-derived particles with increasing salinity. Hence, similar behaviour may be expected when riverine particles pass through natural estuaries, although dissolved Na, Mg, and K concentrations generally show conservative mixing between river water and seawater in natural estuaries (Chester, 1990; Berner and Berner, 1996; Pogge von Strandmann et al., 2008). The observed conservative mixing in natural estuarine water may result from the large seawater volume relative to rock volume, as well as high mobile element concentrations that mask the minor changes within the analytical uncertainties of element concentration determination. In contrast, the interaction experiments were conducted with water/solid ratios of ~ 3.6 g/g, which could enhance detection of the element transfer into the dissolved load. In addition, the retention of Na and K but release of Ca also supports the hypothesis that the dominant cations in the exchangeable pool within sediments shift from Ca to Na and K when the fluid is changed from river water to saline water (Sayles and Mangelsdorf, 1979; Lupker et al., 2016; Tipper et al., 2021).

The stage after the increasing-salinity (>51 days) is designed to imitate the process after the river-derived particles settle on the sea floor in the high salinity zone. In all four experiments, the solids continue removing Na, Mg, and K until around 80 days, but then release Na, Mg, and K from 80 days to the last sampling time (432 days for the loess-Li-add experiments and 529 days for the other three experiments) (Figure 4.5). In comparison, Ca continues to be released from the basalt solids until around 200 days, and is generally constant after 200 days. In the loess-Li-add experiment, Ca also continues to be released after 51 days, while, in the loess-Li-free experiment, there is no significant transfer of Ca after 51 days. The element transfer scenarios revealed in these experiments are in contrast to the retention of Mg and K in sediments in the ocean, which is attributed to authigenic clay formation (Michalopoulos and Aller, 1995; Michalopoulos et al., 2000; Santiago Ramos et al., 2018; Berg et al., 2019; Spiegel et al., 2021; Baldermann et al., 2022). The authigenic clay formation is thought of as reverse weathering and it is closely related to the dissolved silica (Si) concentration

(Garrels, 1965; Nelson et al., 1995; Mackenzie and Kump, 1995; Michalopoulos and Aller, 2004; Dunlea et al., 2017; Krause et al., 2017; Isson and Planavsky, 2018; Krissansen-Totton and Catling, 2020). Although the dissolved Si concentrations after 51 days were not determined in this study, the dissolved Si gradually decreased during the salinity-increasing stage, which probably indicates that Si was entering the solids (Figure 4.6). Hence, the lack of a continuous and sufficient supply of dissolved Si, such as that supplied in the oceans by the dissolution of biogenic Si (Wollast and De Broeu, 1971; Brady and Walther, 1989; Nelson et al., 1995; Michalopoulos and Aller, 2004; Rahman et al., 2019), may hinder the retention of Na, Mg, and K after 80 days, or even hinder the solids from retaining the Mg and K removed from the dissolved load in the previous stage.

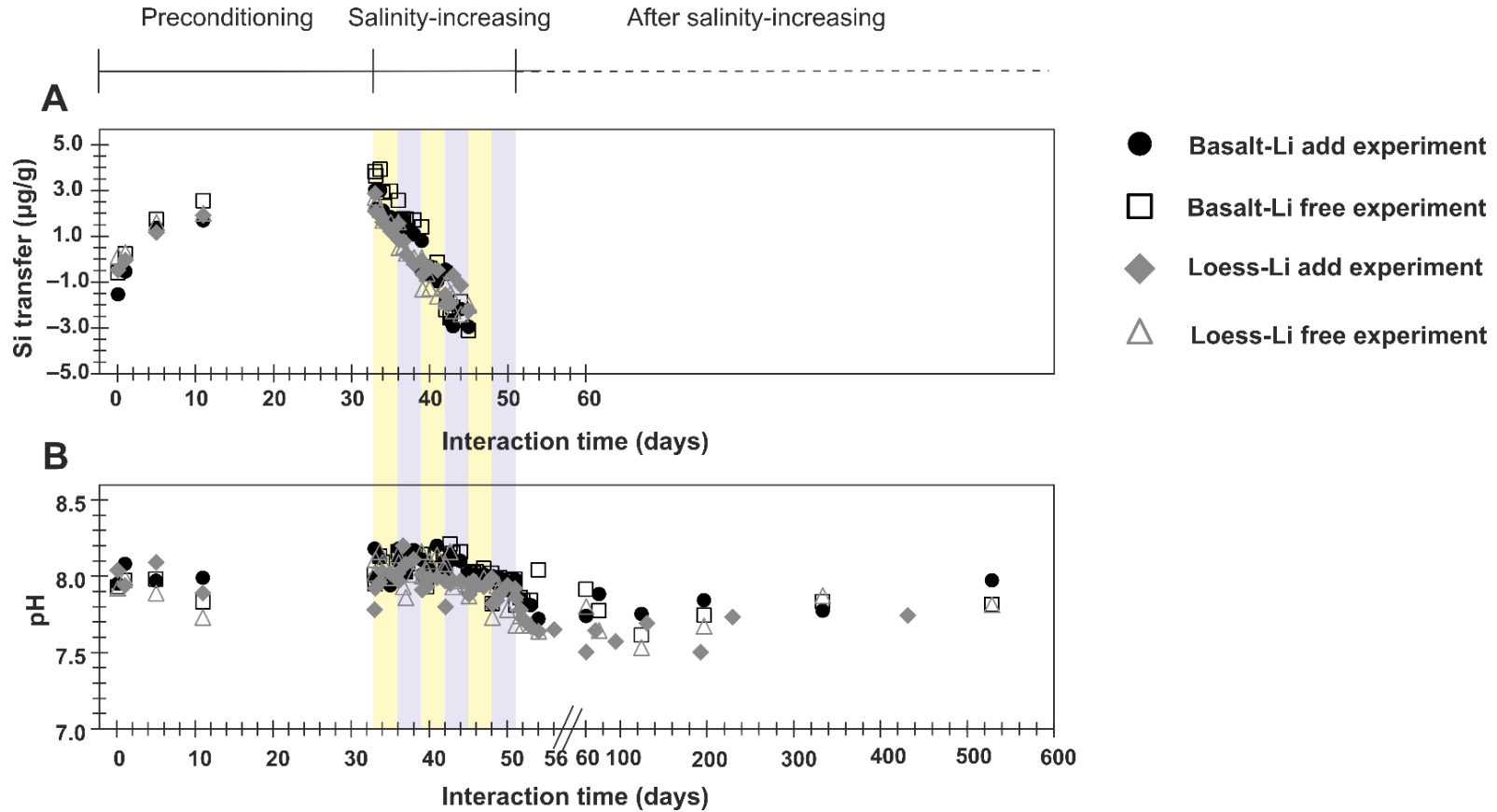


Figure 4.6 Si transfer and pH variation with interaction time in four interaction experiments.

A) Si transfer from solid to dissolved load in the four experiments. The Si transfer is calculated based on the dissolved Si concentrations using Eqs. 4.1 and 4.2. The Si transfer is expressed as the mass of Si per gram of solid released to the dissolved load (positive value) or incorporated from the dissolved load (negative value) to achieve mass balance. B) The change of pH with interaction time in the four interaction experiments. The x-axis is broken at 58 days. The yellow and purple shaded bars represent the salinity step every 3 days during the salinity-increasing stage.

4.4.1.2 Involved fractions of solids

In principle, the element concentrations in the solids should show corresponding changes that quantitatively match with the calculated element transfer. However, because of the low water/solid ratio (~ 3.6 g/g) in the experiments, the elemental budget in the bulk solid is 2–3 orders of magnitude greater than in the dissolved load, so the changes in the bulk solid caused by element transfer are negligible. For example, according to the transfer calculations based on measured concentrations up to 197 days in the dissolved load, the solid in the basalt-Li-add experiment loses 0.41 mg/g Ca and 0.14 mg/g K, and gains 0.02 mg/g Mg, and the solid in the basalt-Li-free experiment loses 0.44 mg/g Ca and 0.16 mg/g K, and gains 0.01 mg/g Mg (Figure 4.5). These transfers only correspond to $\sim 0.5\%$ for Ca, $\sim 5\%$ for K, and less than 0.1% for Mg, of the respective elemental concentrations in the bulk solids (i.e., basalt-Li-add-08 and basalt-Li-free-08). In addition, according to the transfer calculation based on the measured dissolved concentrations up to 95 days in the loess-Li-add experiment and 197 days in the loess-Li-free experiment, the solid in the loess-Li-add experiment loses 0.50 mg/g Ca, and gains 0.36 mg/g K and 0.75 mg/g Mg, and the solid in the loess-Li-free experiment loses 0.64 mg/g Ca, and gains 0.30 mg/g K and 0.04 mg/g Mg (Figure 4.5). Similarly, these transfers only represent $\sim 1.0\%$ for Ca, $1.5\text{--}2.0\%$ for K, and $0.3\text{--}5.5\%$ for Mg of the respective elemental concentrations in the bulk solids (i.e., loess-Li-add-08 and loess-Li-free-08). Hence, they are unlikely to be resolved in measurements of the bulk solid elemental concentrations, given that the analytical uncertainty of element concentrations is $\pm 5\%$ (RSD).

Furthermore, due to the sampling methods, the heterogeneity of sampling may influence the quantitative comparison of the elemental concentrations in leaching fractions (e.g., exchangeable, carbonate, oxide, clay, or residue) between the initial and post-interaction solids. In this case, the loss and/or gain of elements is difficult to quantify from the leaching data, which hinders the identification of the source and/or sink fractions for the element transfer, even though the amount of element transfer is theoretically sufficient to influence some fractions (e.g., exchangeable, carbonate, oxide, and clay). Despite those caveats, the $[\text{Ca}]_{\text{exchangeable}}$ in basalt-Li-add-08, basalt-Li-free-08, loess-Li-add-08, and loess-Li-free-08 are 0.56, 0.64, 0.41, and 0.43 mg/g, respectively, lower than in

the corresponding initial solids (Table 4.2). In addition, in the two loess experiments, the $[K]_{\text{exchangeable}}$ and $[Mg]_{\text{exchangeable}}$ in the post-interaction solids are around 0.2 mg/g lower than in the initial solid. Thus, at least, the exchangeable fraction in the solid samples generally confirms the elemental behaviour observed in the dissolved load samples. However, this observation does not mean that the exchangeable fractions are the only fraction involved in element transfer during the interaction experiments, because the high elemental concentrations in the other fractions may mask the changes.

In an alternative approach to explore the interacting fractions or minerals during the interaction experiments, the saturation index (SI) for a range of minerals was calculated using PHREEQC, based on the temperature, pH, and dissolved concentrations of Na, Ca, Mg, K, and Li (and Si and Al, if available) in the four experiments (Parkhurst and Appelo, 2013). For the two loess experiments, because of the lack of dissolved Al concentrations, the SI for aluminosilicate minerals (e.g., feldspars and clays) is unavailable. The SI of quartz in the two loess water experiments is close to 0. For the two basalt experiments, primary minerals, including albite, anorthite, and K-feldspar, are undersaturated (Figure 4.7), while the secondary mineral Ca-montmorillonite is also undersaturated. In contrast, kaolinite and K-mica are oversaturated, and the SI of gibbsite is close to 0. Thus, the mineral SI values support the alteration of primary minerals to clays and the substitution of Ca by Mg and K in the clays (Sayles and Mangelsdorf, 1979; Nesbitt and Young, 1989; Lupker et al., 2016; Tipper et al., 2021). Because concentrations of elements such as Fe, Mn, and Ti in the dissolved load samples could not be determined, the SI of Fe/Mn-oxides and some common minerals in basalts, such as pyroxene, and olivine are unavailable. However, given that, first, mafic silicates (e.g. olivine, pyroxene) are easier to weather than felsic silicates (e.g. K-feldspar, quartz) (Goldich, 1938; Schott et al., 1981; Oelkers and Schott, 2001; Oelkers et al., 2018); second, Fe-oxides likely form at a pH of ~8 (Stefánsson and Gíslason, 2001; Pogge von Strandmann et al., 2022); and, third, Fe/Mn flocculation likely occurs in brackish water (Sholkovitz, 1978; Nasrabadi et al., 2022; Khoo et al., 2022), the weathering of olivine and pyroxene to form Fe/Mn-oxide likely occurs in the experiments (Jones et al., 2012).

Besides, because the alkalinity could not be determined, the SI of the

carbonates is also unavailable. However, according to the carbonate leachates of the solid samples in the four experiments, the $[Ca]_{\text{carbonate}}$ in the post-interaction solids are slightly lower than the $[Ca]_{\text{carbonate}}$ in the corresponding initial solids, while Jones et al. (2012) also demonstrated undersaturation of carbonates in their seawater-basalt interaction experiments. Therefore, we suggest that carbonates probably tend to dissolve rather than precipitate during the interaction experiments. In contrast, natural bedload samples from the Borgarfjörður estuary imply carbonate formation in high salinity conditions (Jones et al., 2014; Chapter 5), while the Yellow River estuary samples also indicate carbonate precipitation (Cauwet and Mackenzie, 1993; Liu et al., 2014), although the Yellow River-derived solids already have a high carbonate content ($\sim 10\%$) (Tian et al., 2021). Perhaps this difference is due to the differing pH values, which are ~ 8.2 in natural estuaries, but which decrease from ~ 8.2 to ~ 7.8 during the salinity-increasing step in the interaction experiments (Figure 4.6). Alternatively, biological processes may enhance carbonate formation in the natural estuary and/or the carbonate could be reworked from other areas by tides.

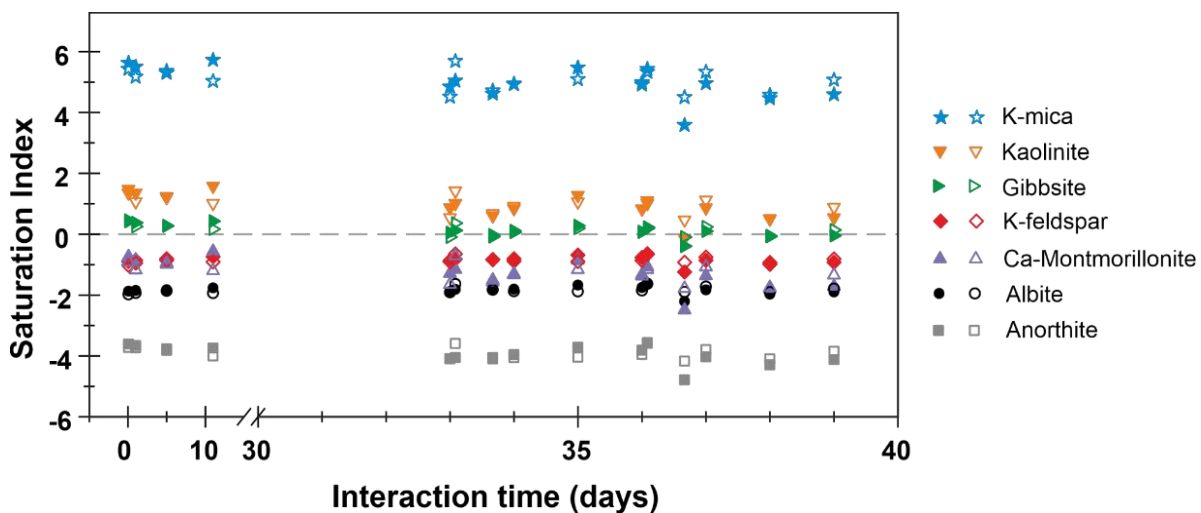


Figure 4.7 Mineral saturation index calculated in the two basalt-water interaction experiments from 0 to 39 days.

The solid symbols and open symbols represent the saturation index of the minerals in the basalt-Li-add and basalt-Li-free experiments, respectively. The x-axis is broken from 15 to 30 days.

4.4.2 Lithium concentration and isotope behaviour

4.4.2.1 Lithium concentration and isotope evolution during the preconditioning stage

During the preconditioning stage, the behaviour of Li and Li isotopes in the four experiments is similar (Figure 4.3). In the first two hours, the dissolved Li concentrations increase from ~5.5 to ~34 µg/l in the basalt experiments and from ~5.5 to ~17 µg/l in the loess experiments. This increase may indicate the rapid desorption of exchangeable cations and/or dissolution of a soluble fraction (e.g., salts) from the solids, acting to rebuild the equilibrium between solids (salts and exchangeable fraction at least, which are likely faster-reacting than other phases) and the solutions in the interaction experiments, because the initial solids had previously interacted with their different natural ambient solutions. Notably, the Li concentrations of their previous ambient solutions were ~150 µg/l for basalt-initial (Jones et al., 2014) and ~20 µg/l for loess-initial (unpublished data; Gou, personal communication), both of which are higher than the Li concentrations in the initial experimental solutions (~5.5 µg/l).

Assuming conservative mixing between the initial solution and the Li released from the solids in the first 2 hours of the experiments, the released Li isotope value is calculated to be ~19‰ in the basalt experiments and ~9‰ in the loess experiments. Meanwhile, the $\delta^7\text{Li}_{\text{exchangeable}}$ values of the basalt-initial and loess-initial solids are 16.9‰ and 5.1‰, respectively. The $\delta^7\text{Li}$ value in the previous ambient solutions of the basalt-initial and loess-initial solids are ~31‰ (Jones et al., 2014) and ~15–25‰ (unpublished data; Gou, personal communication), respectively. Thus, the released Li in the first 2 hours is probably derived from a combination of the exchangeable pool and soluble salts.

From 2 hours to 33 days, the dissolved Li concentrations slightly increase in the loess experiments. In the basalt experiments, dissolved Li concentrations slightly increase from 2 hours to 5 days and then slightly decrease from 5 days to 33 days. However, the Li isotope values continuously increase from ~18 to ~27‰ in the basalt experiments and from ~10 to ~16‰ in the loess experiments (Figure 4.3). If only dissolution or removal were occurring, it would be hard to explain the significant Li isotope increases at the same time as the slight Li concentration variations. Therefore, a two-way transfer of Li between the dissolved load and the

solids (i.e., both dissolution and incorporation) is probably occurring (Steinboefel et al., 2021).

4.4.2.2 Lithium concentration and isotope evolution with increasing salinity

During and after the salinity-increasing stage (>33 days), there is a significant difference in the Li behaviour between the Li-add and Li-free experiments, especially after 45 days at a salinity of ~10 in the basalt experiments, and after 51 days at salinity of ~35 in the loess experiments (Figures 4.3 and 4.4). The solids remove Li from the dissolved load in the Li-add experiments, while they release Li to the dissolved load in the Li-free experiments until reaching a steady state (Figure 4.4A). Meanwhile, the dissolved $\delta^7\text{Li}$ trends in the Li-add experiments and Li-free experiments also differ, especially after the salinity-increasing stage (Figure 4.4B). The $\delta^7\text{Li}$ values in the basalt-Li-free and loess-Li-free experiments remain constant after the salinity-increasing stage, which indicates a steady state. In contrast, the $\delta^7\text{Li}$ values in the Li-add experiments increase after 51 days until becoming stable at around 100 days. Again, the occurrence of only dissolution or incorporation could not explain the significant increase in Li concentrations but generally stable Li isotopes after the salinity-increasing stage in the basalt-Li-free and loess-Li-free experiments, because dissolution does not cause significant Li isotope fractionation (Pistiner and Henderson, 2003; Wimpenny et al., 2010a; Pogge von Strandmann et al., 2020a), while solid phases preferentially incorporate ^6Li during Li uptake (Vigier et al., 2008; Wimpenny et al., 2015; Pogge von Strandmann et al., 2019a; Hindshaw et al., 2019; Li and Liu, 2020; Zhang X. et al., 2021; Li and Liu, 2022) (Section 1.2.2). Thus, release and removal of Li probably occurs simultaneously throughout the experiments. The net influence of dissolution and incorporation would then depend on the dissolved Li concentrations, which is the only variable that differs between the Li-add and Li-free experiments.

Interestingly, the Li concentration at 51 days (at the maximum salinity step) and the Li concentration at the steady state in the four experiments has a linear relationship (Figure 4.8). In this case, it seems that the Li behaviour depends on the fluid geochemistry (Li and Liu, 2020), especially the Li concentration. Similarly, experiments of Li uptake by gibbsite and kaolinite also show that a high Li

concentration in the dissolved load helps enhance the solid uptake of Li (Fogg and O'Hare, 1999; Wimpenny et al., 2015; Li and Liu, 2020, 2022). Thus, the higher Li concentrations in brackish/saline water than in river water could result in greater Li removal by river-derived solids in natural estuaries (Pogge von Strandmann et al., 2008; Yang et al., 2021), and ultimately clays formed from seawater (Chan et al., 1992; Elderfield and Schultz, 1996; Zhang et al., 1998; Li and West, 2014; Andrews et al., 2020). This rapid and significant Li concentration increase could break the solid-water equilibrium in the river water and force the river-derived solids to uptake Li from the dissolved load to build a new equilibrium when passing through the estuary. Therefore, it seems possible that net Li removal by river-derived solids when passing through the estuary is a global phenomenon (Pogge von Strandmann et al., 2008; Yang et al., 2021), since the Li concentration increases with salinity in estuaries across the world (Brunskill et al., 2003; Pogge von Strandmann et al., 2008; Yang et al., 2021).

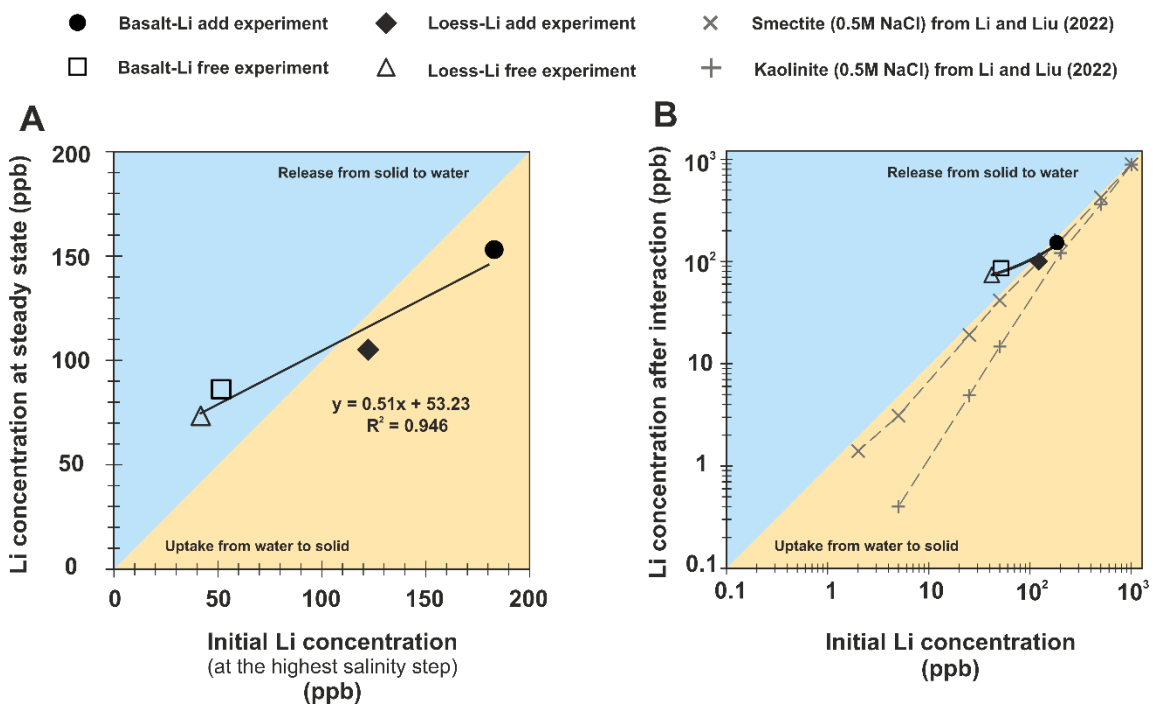


Figure 4.8 The relationship between dissolved Li concentration at the highest salinity step and dissolved Li concentration at steady state.

The yellow and blue shaded regions indicate Li uptake by the solid and Li release from the solid, respectively (the boundary is where $y = x$). In panel B, the axes are logarithmic. The grey crosses are based on the data from Li adsorption experiments in Li and Liu (2022).

After ~250 days, the dissolved Li isotopes reach constant values of ~24.5‰ in both the basalt-Li-add and basalt-Li-free experiments, with constant Li concentrations of ~150 and ~85 µg/l, respectively (Figure 4.4). The dissolved Li isotopes also reach constant values of ~12‰ in the loess-Li-add and ~9.5‰ in the loess-Li-free experiments, with constant Li concentrations of ~100 and ~70 µg/l, respectively. In this case, the transfer of Li and Li isotopes in all four experiments can be regarded as reaching steady state without net changes. Assuming that the released Li is derived from primary mineral dissolution without fractionation (Pistiner and Henderson, 2003; Wimpenny et al., 2010a), the $\delta^7\text{Li}$ values of the released Li in this steady state are estimated to be ~3.5‰ in the basalt experiments and ~1.5‰ in the loess experiments based on measured solid data (Table 4.2). In this case, the Li isotope fractionations between the dissolved load and secondary minerals during Li removal in steady state are constrained to be around -21‰, i.e., $\Delta^7\text{Li}_{\text{basalt-solution}} = \sim 3.5\text{‰} (\delta^7\text{Li}_{\text{basalt}}) - \sim 24.5\text{‰} (\delta^7\text{Li}_{\text{solution}})$, in the basalt experiments, and around -8.0 to -10.5‰, i.e., $\Delta^7\text{Li}_{\text{loess-solution}} = \sim 1.5\text{‰} (\delta^7\text{Li}_{\text{loess}}) - \sim 12\text{‰}$ or $\sim 9.5\text{‰} (\delta^7\text{Li}_{\text{solution}})$, in the loess experiments. The fractionations indicate a fractionation factor of $\alpha_{\text{basalt-solution}} \approx 0.980$ in the basalt experiments and $\alpha_{\text{loess-solution}} \approx 0.990$ in the loess experiments at steady state. These fractionations are within the published ranges of fractionation from previous laboratory experiments and natural observations (Figure 1.3) (Pistiner and Henderson, 2003; Vigier et al., 2008; Pogge von Strandmann et al., 2008, 2019a; Wimpenny et al., 2010a; Murphy et al., 2019; Hindshaw et al., 2019; Li and Liu, 2020, 2022; Zhang X. et al., 2021).

The observations of different fractionation factors in experiments with different initial solids (basalt versus loess), but similar fractionation factors in the Li-add and Li-free experiments with the same initial solid, suggest that the isotopic fractionation of Li during the uptake process at steady state depends on the solid mineralogy rather than on the initial dissolved Li concentrations (Li and Liu, 2022). The different fractionation factors at steady state in the basalt experiments and the loess experiments may stem from differences in the sites where Li is incorporated in the solids. In general, the Li isotope fractionation between solution and exchangeable sites in solids ranges from 0 to -15‰ (Pistiner and Henderson, 2003; Vigier et al., 2008; Wimpenny et al., 2015; Hindshaw et al., 2019; Pogge von Strandmann et al., 2020a; Li and Liu, 2022), while that between solution and

lattice sites in secondary minerals is larger than -10‰ and up to -28‰ (Figure 1.3) (Vigier et al., 2008; Wimpenny et al., 2015; Hindshaw et al., 2019; Pogge von Strandmann et al., 2020a; Liu et al., 2022; Yang et al., 2023). Thus, the mineralogy of river-derived particles may influence the Li isotope fractionation during the Li removal process when the particles pass through the estuary, and therefore influence the Li isotope value in global seawater (Dellinger et al., 2014); however, the time scale of mineralogy changes, and hence their influence on the ocean Li cycle via estuarine weathering, remains to be further explored.

4.4.2.3 Lithium removal flux and its implications for natural estuaries

To quantify the Li transfer flux at the salinity-increasing stage, which imitates natural estuaries, the basalt-Li-add experiment is taken as the example, because the element concentrations (i.e., Na, Ca, Mg, K, and Li) in this experiment is designed to match natural estuaries. Compared to the end of the preconditioning stage at 33 days ($i = 5$), although the Li transfer shifts between minor release (from solid to dissolved load) and minor uptake (from dissolved load to solid) from 33 to 43 days, the Li is clearly removed from the dissolved load by the solid after 43 days (salinity of 10) (Figure 4.9A, B). The proportion of the Li removed by the solids relative to the total dissolved Li ($\text{Li}_{\Delta/w(6 \text{ to } i)}$, Eq. 4.3) increases to $\sim 5\%$ at the salinity of 8 and 10, $\sim 7\%$ at a salinity of 13.5, $\sim 11\%$ at a salinity of 23, $\sim 12\%$ at a salinity of 38, and $\sim 25\%$ at steady state at a salinity of 40 (Figure 4.9C) (Table S4.5).

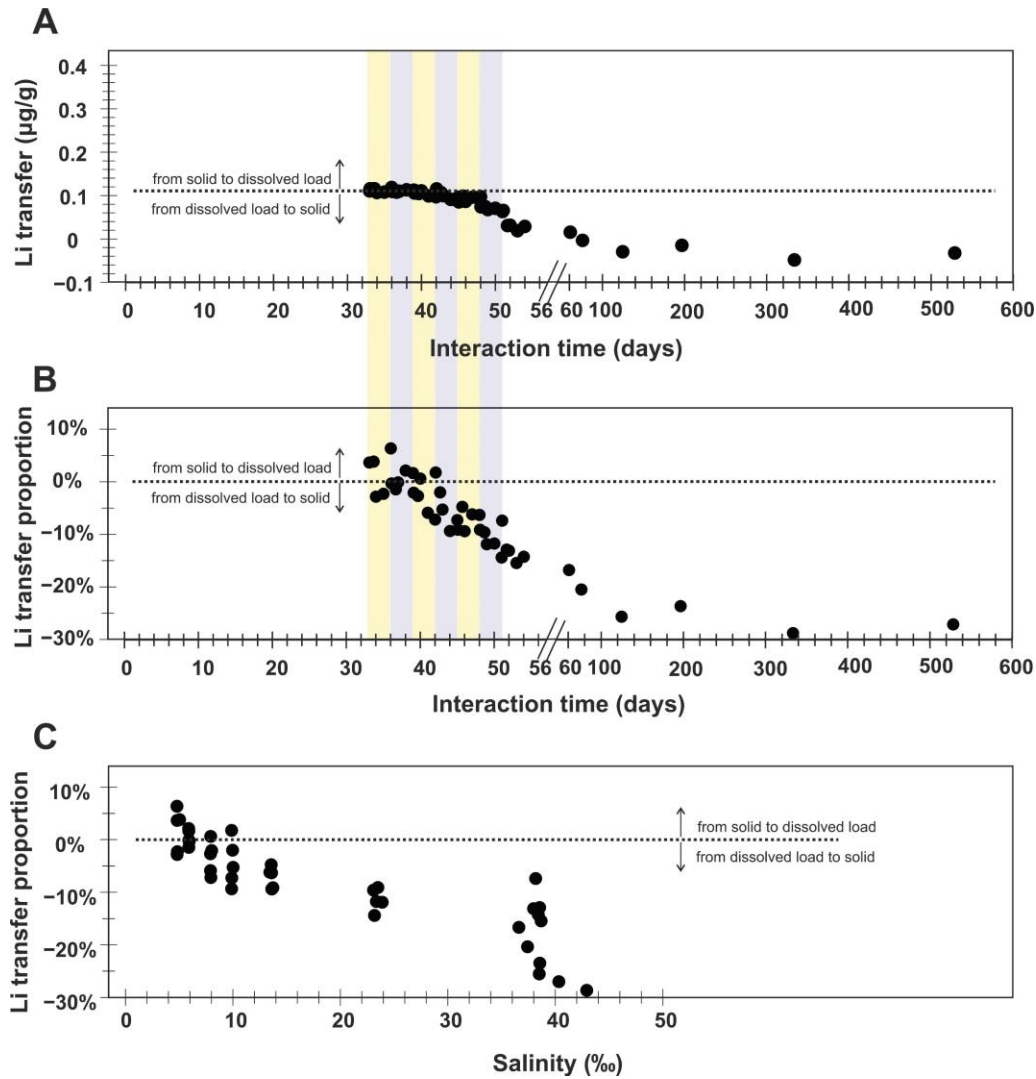


Figure 4.9 Lithium transfer during the salinity-increasing stage and after the salinity-increasing stage in the basalt-Li-add experiment.

In panel A, the ‘Li transfer’ refers to the Li transfer mass between the dissolved load and solid per gram of solid, which is calculated based on the dissolved Li concentrations using Eq. 4.1 and 4.2 (Section 4.4.1.1; Table S4.5). The Li transfer is expressed as the mass of Li per gram of solid released to the dissolved load (positive value) or incorporated from the dissolved load (negative value) to achieve mass balance. In panels B and C, the ‘Li transfer proportion’ refers to the Li mass transfer accumulated from the sample $i = 6$ (at 33 days 2 hours) to the sample i at interaction times (x-axis in panel B) as a proportion of the total mass of the Li in the dissolved load at sample i , which is noted as $Li_{\Delta/w(6 \text{ to } i)}$, and is calculated using Eq. 4.3 (Section 4.4.1.1; Table S4.5). The negative values indicate net Li loss from the dissolved load to the solid (and vice versa for positive values). In panels A and B, the x-axis is broken at 58 days and the yellow and purple shaded bars represent the salinity step every 3 days during the salinity-increasing stage. The dashed lines in panels A, B, and C represent the Li transfer at the end of the preconditioning stage, which is considered as a baseline.

Every year, the input of dissolved Li from worldwide rivers to the ocean through estuaries is $\sim 5.6 \times 10^{10}$ g Li (i.e., 8×10^9 mol), with average Li concentrations of 1.5 $\mu\text{g/l}$, which is estimated at river mouths before estuarine processes in Huh et al. (1998). If it is assumed that $\sim 12\%$ Li (value at salinity of 38) will be removed by the solids, as seen in the basalt-Li-add experiment here, then 6.8×10^9 g/yr dissolved Li riverine input will be taken up by river-derived particles when they are passing through the salinity-increasing zone in the estuary. The $\sim 12\%$ loss of Li from the dissolved load with fractionation ($\Delta^7\text{Li}_{\text{basalt-solution}}$) of -21‰ will cause the $\delta^7\text{Li}$ value of the dissolved riverine Li input to increase by $\sim 2.5\text{‰}$, based on a Rayleigh fractionation model or batch fractionation model (Eqs. 1.7, 1.8, 1.9, and 1.10) (Vigier et al., 2009; Pogge von Strandmann et al., 2019a; Murphy et al., 2019; Li et al., 2020a).

However, there are three ideal assumptions used in this estimate of the Li removal flux, which are unlikely to exist in natural estuaries. First, the rock/water ratio (272–362 g/l) in the experiments are 3 orders of magnitude higher than in typical natural estuaries, considering that the average suspended load concentration of the global river input is $\sim 0.3\text{--}0.5$ g/l (Gaillardet et al., 1999; Milliman and Farnsworth, 2011), with the highest being 26.9 g/l for the Yellow River. Second, the ratios of solid and water were controlled to be $\sim 272\text{--}296$ g/l at the start of each salinity step, whereas the suspended load concentration usually varies significantly in estuaries because of resuspension or particle settling. For example, in the Amazon estuary, the suspended load concentration is more than 10 g/l in a fluid-mud area in the low- and medium-salinity regions, while it is less than 0.5 g/l in the high-salinity area (Gibbs, 1976; Kuehl et al., 1986; Kineke et al., 1996). As such, the uneven distribution of river-derived particles may change the Li removal flux. Third, the different mineralogy of the river-derived particles needs to be considered, although the four experiments in this study imply that the net Li transfer flux mainly depends on the Li concentration in the brackish/saline water rather than on the solid mineralogy (Figure 4.8). Considering the first assumption, in the basalt-Li-add experiment, the transfer calculation shows that the solid uptakes ~ 0.15 μg Li per gram, whereas it has been shown that natural solid samples collected from the same estuary (Borgarfjörður estuary) can take up ~ 3 μg Li per gram (Chapter 5; Pogge von Strandmann et al., 2008). This difference probably implies that the dissolved load

is the limiting factor for Li removal in the experiments in this study, while the solid load is the limiting factor in the natural estuary (Section 7.1.2). Exploration of the natural samples (Chapters 5 and 6) is therefore necessary to estimate the Li removal flux more accurately.

4.5 Conclusions

Four solid-water interaction experiments with increasing salinity were conducted and their results indicate:

1) During the salinity-increasing stage, Na, Mg, and K are removed by solids from the dissolved load, while Ca is released into the dissolved load in all experiments.

2) Both the release and removal of Li probably occurs simultaneously during the interaction experiments, and a steady state is reached after around 100 days.

3) The net change of Li concentrations in the Li-add experiments and Li-free experiments is different, which depends on the dissolved Li concentrations. This finding implies that the rapidly increasing Li concentrations in natural estuarine water could result in enhanced Li removal by river-derived solids in estuaries worldwide.

4) The Li isotope fractionation between the dissolved load and the solid in the steady state is different in experiments conducted with different initial solids, i.e., around -21‰ ($\Delta^7\text{Li}_{\text{basalt-solution}}$) in basalt-water experiments and around -8.0 to -10.5‰ ($\Delta^7\text{Li}_{\text{loess-solution}}$) in loess-water experiments, but is similar in Li-add and Li-free experiments using the same initial solid. Thus, the Li isotope fractionation likely depends on the solid mineralogy rather than the fluid geochemistry, at least within the concentration ranges tested here.

5) Taking the basalt-Li-add experiment as an example to imitate the natural estuary, around 12% of the total dissolved Li mass is removed by solids in the interaction during the salinity-increasing stage, with the solids gaining $\sim 0.15 \mu\text{g}$ Li per gram. However, due to the large solid/water ratio applied in the interaction experiments, more exploration of natural estuarine samples is needed to estimate the global Li transfer flux in the process of river-derived particles passing through estuaries.

Chapter 5. Alteration of river-derived particles in a basaltic river estuary, Borgarfjörður, Iceland

5.1 Introduction

Basalt weathering plays an important role in global weathering and the carbon cycle, because of its low resistance to weathering (Bowen, 1922; Meybeck, 1987; Gaillardet et al., 1999; Dessert et al., 2003). Iceland provides an excellent natural laboratory to explore basalt weathering, because most of Iceland is covered by basaltic rocks with little vegetation, and minor anthropogenic pollution (Gíslason et al., 1996). The basaltic rocks of Iceland were formed within the last 25 Ma and the exposed basalts at the surface are younger than 14 Ma (Moorbath et al., 1968; Gíslason et al., 1996). The main types of Icelandic basalt are olivine tholeiite, olivine-free tholeiite, and porphyrite with plagioclase/pyroxene (Sæmundsson, 1979). Iceland has an oceanic boreal climate, with a mean annual temperature of 4 °C. The annual precipitation varies spatially, from ~3000 mm on the south coast, to ~1000 mm on the west coast, with less than 400 mm in the central highlands (Einarsson, 1984; Gíslason et al., 1996; Pogge von Strandmann et al., 2006). In addition, around 11% of the surface in Iceland is glaciated (Sæmundsson, 1979; Gíslason et al., 1996). The total discharge of Icelandic rivers to the ocean is ~170 km³/yr, which accounts for ~0.45% of the global river discharge, and the total particle load transported by Icelandic rivers is 0.02 to 0.025 km³/yr, which accounts for ~0.3% of the global riverine particle flux to the ocean (Gíslason et al., 1996; Pearce et al., 2010). Such an abundance of river-derived particles from a single lithology provides a good opportunity to investigate the alteration of river-derived particles in estuaries.

The Borgarfjörður estuary is located in western Iceland (Figure 5.1). The river sediment at the river mouth is composed of ~55% microcrystalline material, ~19% volcanic glass, ~11% Ca feldspar, ~8% olivine, ~4% Fe-Ti oxides, and ~3% K feldspar (Jones et al., 2012). Several studies have examined dissolved load, suspended load, and bedload samples collected in the Borgarfjörður estuary to explore the alteration of the river-derived particles using different geochemical tracers (Pogge von Strandmann et al., 2008; Pearce et al., 2010; Jones et al.,

2014). These studies suggest that river-derived particles can release elements (e.g., Mo and Sr) into the dissolved load (Pearce et al., 2010; Jones et al., 2014) or remove elements (e.g., Li) from the dissolved load in the estuary (Pogge von Strandmann et al., 2008). Based on the suspended load samples collected in 2003, Pogge von Strandmann et al. (2008) pointed out that the river-derived particles can remove $\sim 3 \mu\text{g/g}$ Li from the dissolved load in the Borgarfjörður estuary, although the dissolved load basically shows conservative mixing of Li and Li isotopes between river water and seawater. In addition to the collection of dissolved load and suspended load samples from the Borgarfjörður estuary in 2003 (Pogge von Strandmann et al., 2008; Pearce et al., 2010), a set of bedload samples was collected in 2008 (Jones et al., 2014), and two sets of dissolved load and corresponding suspended load samples were collected in 2011 and 2017 (Jones et al., 2014) (Figure 5.1).

Thus, this chapter aims to further explore the Li and Li isotope behaviour during the alteration of river-derived particles, such as, whether the Li concentrations or Li isotope compositions show a difference between the suspended load and bedload solids, and what proportions of Li are incorporated in the different fractions. In this chapter, the elemental concentrations and Li isotope ratios in the dissolved load samples collected in 2017, in different fractions of the suspended load samples collected in 2017, and in different fractions of the bedload samples collected in 2008 were analysed (Sections 5.2 and 5.3). By comparison with the samples collected in other sampling campaigns (Pogge von Strandmann et al., 2008; Jones et al., 2014), the influence of multiple processes (i.e., geochemical processes and mechanical processes) on the alteration of river-derived particles, especially the Li and Li isotope behaviour, is discussed in Sections 5.4.1 and 5.4.2. In Section 5.4.3, the Li flux of the geochemical incorporation from the dissolved load by river-derived particles is estimated after elimination of the influence of other processes.

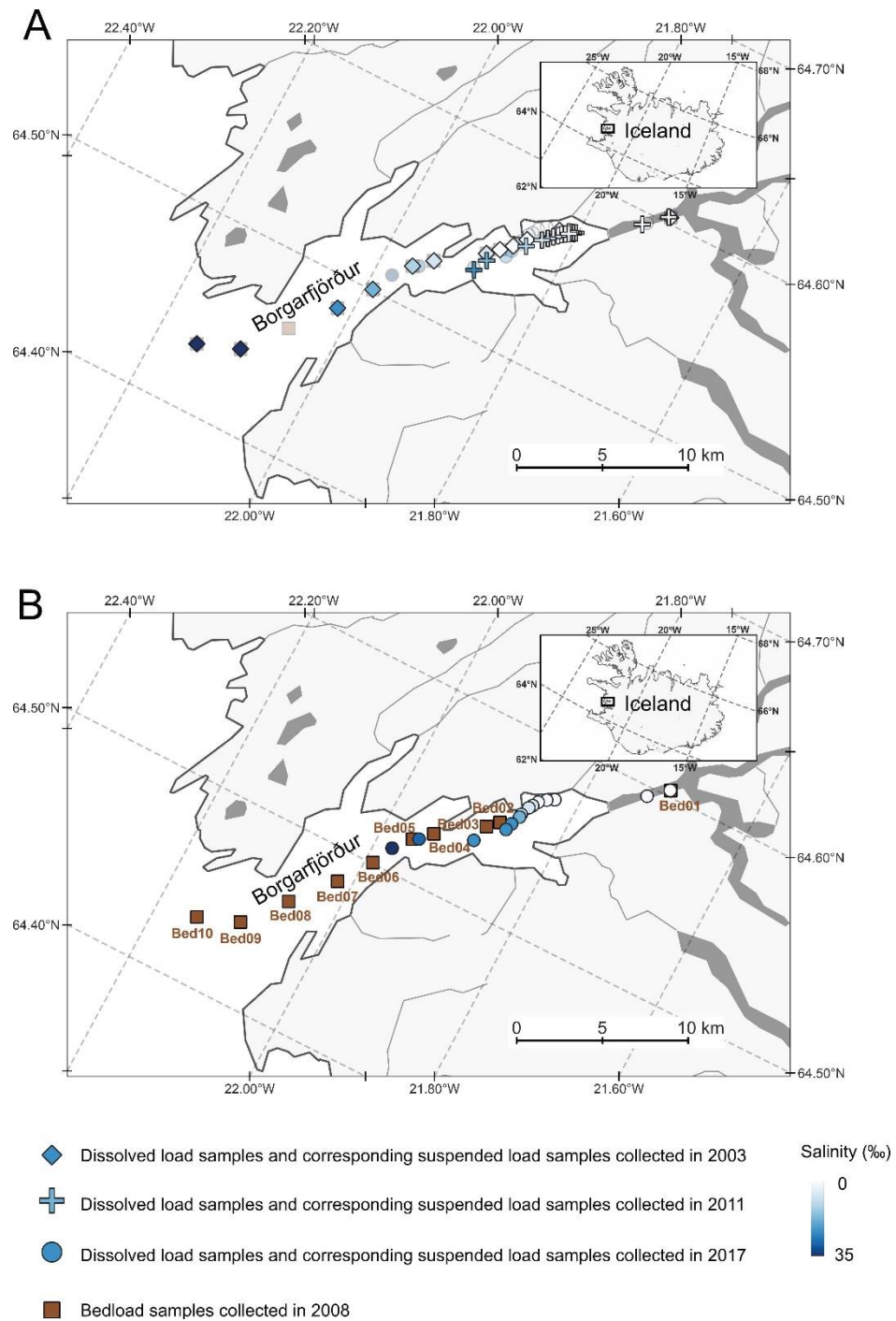


Figure 5.1 Setting of the Borgarfjörður estuary and sampling locations.

A) The locations of samples collected in 2003 (diamonds) and 2011 (crosses) (Pogge von Strandmann et al., 2008; Jones et al., 2014), with the locations of samples collected in 2008 (shaded squares) (Jones et al., 2014) and 2017 (shaded dots). B) The locations of samples analysed in this study collected in 2008 (squares) and 2017 (dots). The gradient colour in the dissolved load symbols in both panels displays the salinity, which is calculated based on dissolved Cl^- concentrations in each sample, using $\text{salinity (‰)} = 1.80655 \times \text{Cl}^- (\text{mg/g})$ (Wooster et al., 1969).

5.2 Sample collection

The Borgarfjörður estuary is over 25 km long, but it is narrow at less than 5 km wide. The depth is around 1–2 m to a distance of 5 km, and then increases to around 100 m at a distance of 10 km. The estuary is tide-dominated, and is therefore well mixed, both vertically and horizontally (Gíslason et al., 1996; Pogge von Strandmann et al., 2008; Jones et al., 2014). In July 2017, dissolved load samples (2017RW and 2017E01–2017E13) and their corresponding suspended load samples (2017SPMR and 2017SPM01–2017SPM13) were collected from a 15 km-transect from the Hvítárvellir bridge with salinity (Cl^-) increasing (Figure 5.1, Table 5.1). The water was collected at a depth of ~1 m in pre-cleaned Go-Flo bottles by boat. The temperature was analysed at each sampling location. The samples were filtered through a 0.2 μm cellulose acetate membrane filter in a Teflon mounting. The solutions after filtration were saved as dissolved load samples. Suspended particles were removed from the filter paper by ultrasonication and saved in deionised water.

A set of bedload samples (Bed01–Bed10) was collected in June 2008 (Jones et al., 2014) in locations corresponding to the previous dissolved load and suspended load sampling conducted in 2003 (Pogge von Strandmann et al., 2008). The bedload sample Bed01 was directly scooped, Bed02–07 were the top 20 cm of sediment cores, Bed08 and Bed10 were collected by a bucket dragged behind the boat, and Bed09 was grabbed using a metal claw. The samples were dried at 40 °C after collection.

The elemental concentrations and Li isotope compositions of 14 dissolved load samples, and the sequentially leached fractions of 14 suspended load samples and 10 bedload samples, were determined (Chapter 2). Importantly, the suspended load samples, which were saved in deionised water, were dried down before the extraction procedure. The pure water may dissolve cations and influence the effectiveness of the extraction procedure (Section 5.3.2).

Table 5.1 Sampling locations in the Borgarfjörður estuary.

Sample	Latitude	Longitude	SPM concentration mg/l
2017RW(SPM)	64°36.20'N	21°42.52'W	636
2017E01(SPM)	64°35.71'N	21°43.84'W	558
2017E02(SPM)	64°34.32'N	21°49.74'W	570
2017E03(SPM)	64°34.20'N	21°50.26'W	558
2017E04(SPM)	64°34.02'N	21°50.74'W	555
2017E05(SPM)	64°33.85'N	21°50.99'W	558
2017E06(SPM)	64°33.74'N	21°51.16'W	555
2017E07(SPM)	64°33.45'N	21°51.43'W	551
2017E08(SPM)	64°33.35'N	21°51.44'W	550
2017E09(SPM)	64°33.05'N	21°51.72'W	545
2017E10(SPM)	64°32.81'N	21°51.90'W	545
2017E11(SPM)	64°32.07'N	21°53.64'W	540
2017E12(SPM)	64°31.33'N	21°57.23'W	540
2017E13(SPM)	64°30.70'N	21°58.67'W	540
Bed01	64°36.20'N	21°42.48'W	
Bed02	64°32.92'N	21°52.53'W	
Bed03	64°32.62'N	21°53.27'W	
Bed04	64°31.69'N	21°56.45'W	
Bed05	64°31.24'N	21°57.65'W	
Bed06	64°30.03'N	21°59.43'W	
Bed07	64°29.02'N	22°01.07'W	
Bed08	64°27.77'N	22°03.55'W	
Bed09	64°26.52'N	22°05.96'W	
Bed10	64°26.05'N	22°08.97'W	

5.3 Results

5.3.1 Dissolved load

The dissolved load data are shown in Table 5.2. The Li concentrations in the dissolved load increase from 0.23 µg/l (salinity of 0.01) to 150.8 µg/l (salinity of 30.48), and show a linear relationship with Cl^- (Figure 5.2A). The dissolved load Li isotope values vary from 16.7–25.4‰ in the very low salinity zone (<0.1), increase to 28.7‰ (salinity of 0.38), and range from 30.1–31.8‰ at a salinity of 3.45 to 30.48 (Figure 5.2B). The concentrations of Na, Ca, Mg, K, and alkalinity also increase through the estuary (Figure 5.3). The dissolved Si concentration decreases from ~7.0 to ~1.0 mg/l (Figure 5.3).

Mineral saturation indices (SIs) are calculated using PHREEQC (Helgeson et al., 1978; Parkhurst and Appelo, 2013; Griffioen, 2017), based on the measured concentrations of Na, Ca, Mg, K, Si, Cl^- , SO_4^{2-} , and alkalinity in all dissolved samples, and the measured dissolved Al concentrations in low salinity samples (2017RW and 2017E01–04). The primary minerals, including anorthite, albite, K-feldspar, olivine, and pyroxene, are undersaturated (Figure 5.4A). In contrast, likely secondary minerals, including montmorillonite, gibbsite, and kaolinite are oversaturated at low salinity (Figure 5.4B). Furthermore, carbonates (i.e., calcite and dolomite) change from undersaturated to oversaturated at a salinity of around 17 (Figure 5.4C).

Table 5.2 Data of dissolved load samples collected in 2017.

Sample	Temperature	pH	Salinity ^[1]	Na	Ca	Mg	K	Fe	Al	Si	Cl ⁻	SO ₄ ²⁻	Alkalinity	Li	δ ⁷ Li	2σ ^[2]
	°C			mg/l	mg/l	mg/l	mg/l	mg/l	μg/l	mg/l	mg/l	mg/l	meq/l	μg/l	‰	‰
2017RW	14.2	8.30	0.01	7.42	3.34	1.34	0.37	0.050	21.8	5.41	5.16	2.07	0.50	0.23	20.40	0.40
2017E01	11.1	7.85	0.01	7.08	3.32	1.23	0.39	n.d.	29.2	6.94	4.43	2.04	0.47	0.47	16.69	0.05
2017E02	14.0	8.34	0.05	21.3	3.34	2.65	1.18	n.d.	26.2	6.67	28.9	4.97	0.53	0.65	25.39	0.40
2017E03	14.9	8.11	0.38	122	7.10	13.7	5.20	n.d.	7.91	6.06	208	31.0	0.56	2.59	28.70	0.24
2017E04	14.0	8.14	3.45	1040	42.0	127	42.7	n.d.	11.9	5.73	1909	260	0.73	17.4	31.05	0.23
2017E05	14.1	8.13	7.72	2346	91.9	288	94.5	n.d.	n.d.	4.52	4272	503	1.09	39.1	31.01	0.02
2017E06	14.3	8.16	9.05	2823	110	349	114	n.d.	n.d.	4.26	5008	575	1.01	45.6	31.44	0.03
2017E07	14.3	8.24	10.94	3503	136	433	141	n.d.	n.d.	4.90	6054	671	1.11	70.6	30.08	0.24
2017E08	13.9	8.16	17.45	5409	210	674	218	n.d.	n.d.	2.06	9660	1169	1.45	95.5	31.09	0.22
2017E09	13.3	8.20	22.76	6833	264	846	274	n.d.	n.d.	1.05	12600	1738	1.61	124	30.97	0.32
2017E10	12.9	8.18	24.84	7385	287	924	300	n.d.	n.d.	1.05	13750	1828	1.69	135	31.80	0.14
2017E11	13.2	8.21	23.56	7101	277	882	290	n.d.	n.d.	1.66	13040	1768	1.66	137	31.36	0.27
2017E12	12.3	8.24	28.49	8223	316	1006	332	n.d.	n.d.	1.06	15770	2007	2.05	142	31.41	0.29
2017E13	11.6	8.22	30.48	9289	358	1144	373	n.d.	n.d.	n.d.	16870	2097	n.d.	151	31.37	0.61

[1] The salinity is calculated based on Cl⁻ concentrations, using salinity (‰) = 1.80655 × Cl⁻ (mg/g) (Wooster et al., 1969).

[2] 2σ is the two standard deviation of each measured δ⁷Li value. The long-term uncertainty of seawater δ⁷Li analysis using MC-ICP-MS is 0.63‰ (2SD).

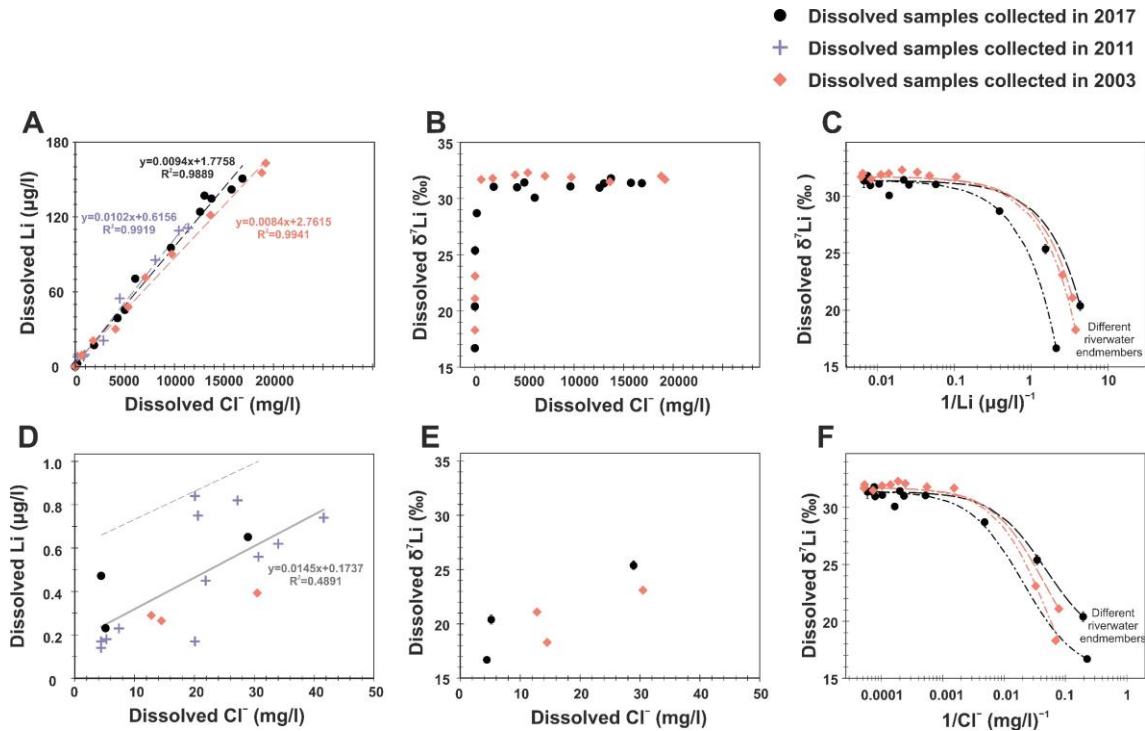


Figure 5.2 Dissolved Li concentrations and Li isotopes.

The data for samples collected in 2003 (diamonds) and 2011 (crosses) are from Pogge von Strandmann et al. (2008) and Jones et al. (2014).

A) Dissolved Li concentration through the transect. The dashed lines are the linear relationship fitting lines for different groups of samples in all salinity zones.

B) Dissolved Li isotopes through the transect.

C) Relationship between dissolved Li concentrations and Li isotopes, presented as a mixing diagram. The dashed lines are conservative mixing lines between riverwater (with different endmember values) and seawater endmembers.

D) Dissolved Li concentration in the very low salinity zone (<0.1). The grey solid line is the linear relationship fitting line for the samples in the very low salinity zone. The purple dashed line is the linear relationship fitting line for the samples in all salinity zones collected in 2011, identical to the purple dashed line in panel A. The dashed fitting lines for samples collected in 2003 and 2017 are out of the range shown in panel D.

E) Dissolved Li isotopes in the very low salinity zone (<0.1).

F) Relationship between dissolved Li isotopes and the Cl⁻ concentration, presented as a mixing diagram. The dashed lines are conservative mixing lines between river water (with different endmember values) and seawater endmembers.

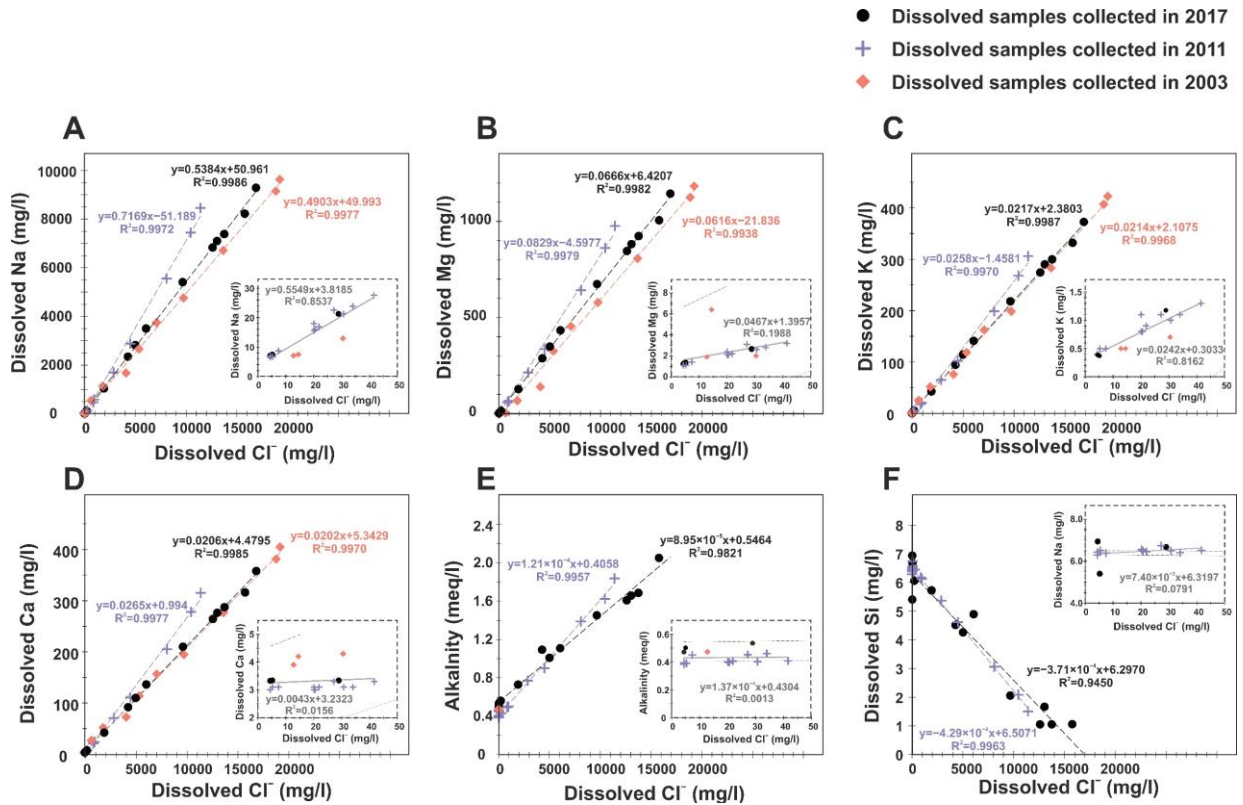


Figure 5.3 Dissolved concentrations of major elements (Na, Mg, K, and Ca), alkalinity, and Si.

The data for samples collected in 2003 (diamonds) and 2011 (crosses) are from Pogge von Strandmann et al. (2008) and Jones et al. (2014).

The dashed lines are the linear relationship fitting lines for the different groups of samples in all salinity zones. The small panel insert in each figure shows the concentrations in the very low salinity zone (<0.1). The grey solid lines in the small panels are the linear relationship fitting lines for the samples in the very low salinity zone. The dashed lines in the small panels are the linear relationship fitting lines for the samples in all salinity zones, as in the corresponding main panels. Where not visible, the dashed fitting lines in the small panels are out of the range shown on those small panels.

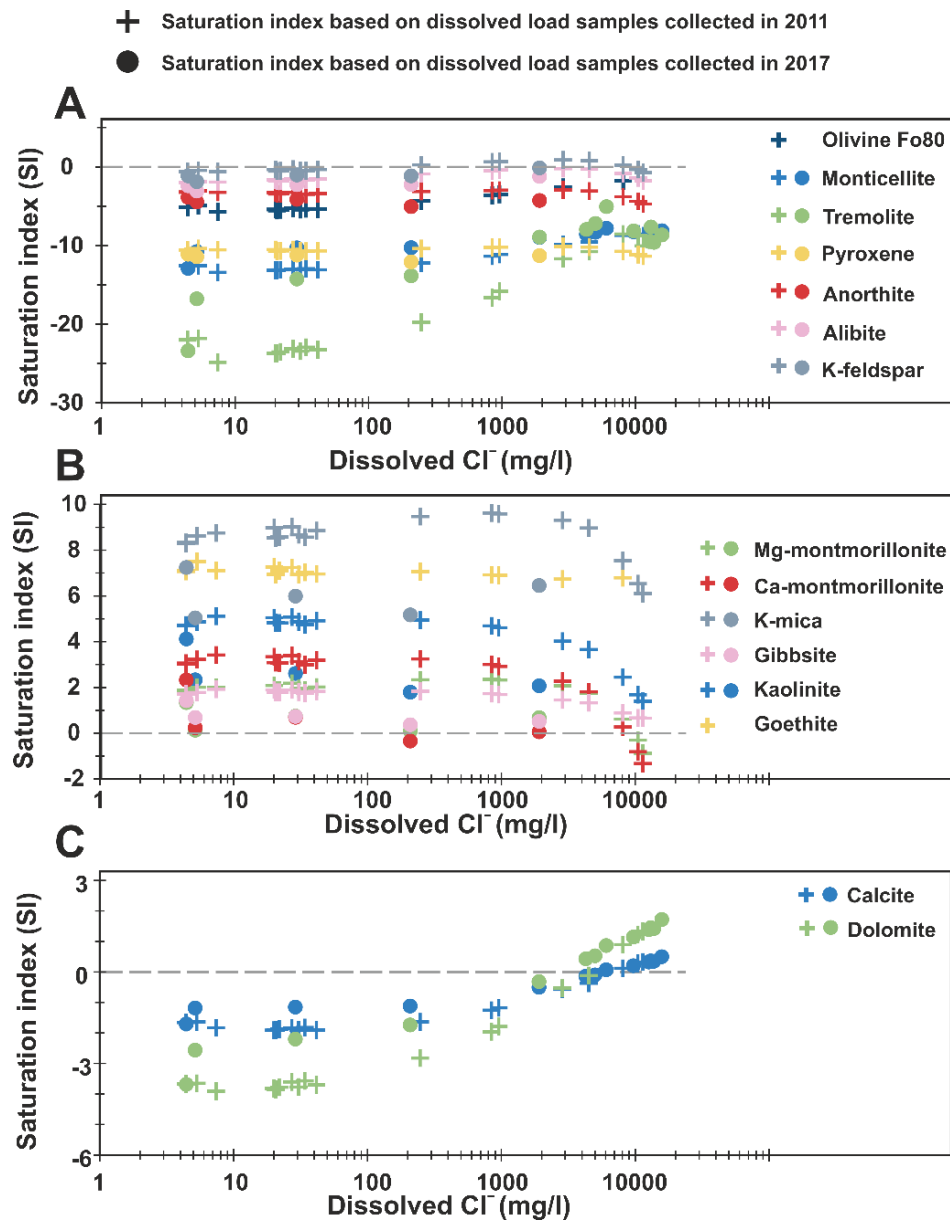


Figure 5.4 Mineral saturation indices.

The data for samples collected in 2011 (crosses) are from Jones et al. (2014). The dashed line represents a saturation index of 0.

5.3.2 Suspended load samples

The suspended load data in the different fractions are shown in Table 5.3. Notably, due to the low mass of the suspended particle material (SPM), the mass of each SPM sample (~1 mg or ~5 mg) leached in the extraction procedure is less than that of the bedload samples (Bed01–10) (~50 mg). Given that the SPM samples were stored in deionised water before drying down, this treatment may have caused some ions to be dissolved out of the fractions (e.g., exchangeable, carbonate, oxide, clay, and residue) in the SPM into the deionised water. These ions could then precipitate as soluble salts when drying down, and be contained in the 'exchangeable' fraction in the extraction procedure. Therefore, this unexpected interaction between SPM particles and deionised water may influence the effectiveness of sequential extraction procedures on the SPM samples.

In the exchangeable fraction of the SPM, there is a significant increase in the $[Ca]_{\text{exchangeable}}$, $[Mg]_{\text{exchangeable}}$, $[K]_{\text{exchangeable}}$, and $[Li]_{\text{exchangeable}}$ through the estuarine transect (Figures 5.5A–C and 5.6A). Furthermore, the proportion of Ca, Mg, K, and Li in this fraction in the bulk (i.e., $[X]_{\text{exchangeable}}/[X]_{\text{bulk-sum}}$, Eq. 2.2), increases from 2 to 57%, 1 to 72%, 18 to 89%, and 1% to 62%, respectively, from the river endmember (2017SPMR) to the corresponding sample at a dissolved salinity of 30.48 (2017SPM13). Considering that the 2017SPM particles were kept in deionised water for a long time and that the particle mass is small, the mobile elements (e.g., Na, Ca, Mg, K, and Li) in the 2017SPM samples may have been influenced by the remaining seawater during sampling, filtering, and storage as described above.

In addition, the ratios of $[K]_{\text{exchangeable}}/[Ca]_{\text{exchangeable}}$, $[K]_{\text{exchangeable}}/[Mg]_{\text{exchangeable}}$, and $[Mg]_{\text{exchangeable}}/[Ca]_{\text{exchangeable}}$ approach the ratios of K/Ca, K/Mg, and Mg/Ca in the dissolved load (Figure 5.7A–C). Similarly, $[Li]_{\text{exchangeable}}/[Ca]_{\text{exchangeable}}$, $[Li]_{\text{exchangeable}}/[Mg]_{\text{exchangeable}}$, and $[Li]_{\text{exchangeable}}/[K]_{\text{exchangeable}}$ also approach the ratios of the dissolved load (Figure 5.7D–F). Thus, the nominal exchangeable fraction begins to dominate the Li reservoir (i.e., $[Li]_{\text{exchangeable}}/[Li]_{\text{bulk-sum}}$ is 62%) in 2017SPM13 at a salinity of 31. In addition, $\delta^7\text{Li}_{\text{exchangeable}}$ values vary from 27.5 to 31.0‰, which is close to the dissolved $\delta^7\text{Li}$ values, at a salinity higher than 17.45 (Figure 5.6B). Thus, the elemental concentrations of Mg, Ca, K, and Li, as well as the $\delta^7\text{Li}$ values, in the

SPM samples, especially in the high salinity zone, appear to be significantly influenced by the sea salts.

In the carbonate fraction, $[Ca]_{\text{carbonate}}$, $[Mg]_{\text{carbonate}}$, $[K]_{\text{carbonate}}$, and $[Li]_{\text{carbonate}}$ increase from 2017SPMR to 2017SPM11 (Figures 5.5A–C and 5.6A). In addition, $\delta^7Li_{\text{carbonate}}$ shows a generally increasing trend from around 15.0–20.4‰ (2017SPM05–07) to 21.3–26.3‰ (2017SPM08–11) (Figure 5.6B). However, the $[Mn]_{\text{carbonate}}/[Ca]_{\text{carbonate}}$ and $[Al]_{\text{carbonate}}/[Ca]_{\text{carbonate}}$ of the SPM samples range from 6.6 to 85.1 mg/g and 4.9 to 51.7 mg/g, respectively. In comparison, $[Mn]_{\text{carbonate}}/[Ca]_{\text{carbonate}}$ in typical carbonate samples ranges from around 0.1 µg/g to 35 mg/g (Misra and Froelich, 2012; Pogge von Strandmann et al., 2013, 2019b, 2021a; Ullmann et al., 2013; Clergue et al., 2015; Bastian et al., 2018; Dellinger et al., 2020; Jin et al., 2021; Cao et al., 2022; Wei et al., 2023). Furthermore, the recommended $[Al]_{\text{carbonate}}/[Ca]_{\text{carbonate}}$ for a carbonate leach where δ^7Li values represent the carbonate material is less than 0.81 mg/g (i.e., 1.2 mmol/mol) (Cao et al., 2023), 0.54 mg/g (i.e., 0.8 mmol/mol) (Pogge von Strandmann et al., 2013), or even less than 0.27 mg/g (i.e., 0.4 mmol/mol) (Dellinger et al., 2020). Thus, the leached carbonate fractions of the SPM samples here are likely influenced by ions leached from other fractions (Chapter 3).

In the oxide fractions, the $[Mg]_{\text{oxide}}$, $[K]_{\text{oxide}}$, and $[Li]_{\text{oxide}}$ generally increase through the salinity transect, while the $[Ca]_{\text{oxide}}$ varies (Figures 5.5 and 5.6A). Interestingly, the $[Fe]_{\text{oxide}}/[Fe]_{\text{bulk-sum}}$ and $[Al]_{\text{oxide}}/[Al]_{\text{bulk-sum}}$ also increase through the salinity transect, although $[Fe]_{\text{oxide}}$ varies and $[Al]_{\text{oxide}}$ decreases. The $\delta^7Li_{\text{oxide}}$ of 2017SPM05–11 varies between 8.8–22.8‰ with an overall increasing trend with increasing salinity (Figure 5.6B).

In the clay fractions, the $[Fe]_{\text{clay}}$ and $[Al]_{\text{clay}}$ increase from sample 2017SPMR to 2017SPM02, and then decrease through the salinity transect, whereas the $[Mg]_{\text{clay}}$ varies (Figure 5.5). The $[Mg]_{\text{clay}}/[Fe]_{\text{clay}}$ and $[Mg]_{\text{clay}}/[Al]_{\text{clay}}$ ratios slightly decrease from 2017SPMR to 2017SPM04, and then increase, especially from 2017SPM09 to 13. The $[Li]_{\text{clay}}$ increases from 2017SPMR to 2017SPM05 and then decreases through the salinity transect (Figures 5.5 and 5.6A). In contrast, the $[Li]_{\text{clay}}/[Fe]_{\text{clay}}$ and $[Li]_{\text{clay}}/[Al]_{\text{clay}}$ ratios increase through the estuary. The δ^7Li_{clay} of 2017SPM02 to 11 varies from 6.4–11.8‰ with an overall increasing trend (Figure 5.6B).

Interestingly, the $[Ca]_{\text{residue}}$, $[Mg]_{\text{residue}}$, $[K]_{\text{residue}}$, $[Fe]_{\text{residue}}$, $[Mn]_{\text{residue}}$, and

[Al]_{residue} decrease through the salinity transect. In contrast, the [Li]_{residue} increases from 2017SPMR to 2017SPM06 but then decreases from 2017SPM06 to 13 (Figure 5.6A), although the [Li]_{residue}/[Li]_{bulk-sum} (Eq. 2.2) decreases throughout the estuarine transect. The $\delta^7\text{Li}_{\text{residue}}$ generally shows an increasing trend from 2.1 to 11.1‰ through the transect (Figure 5.6B).

The [Ca]_{bulk-sum}, [Fe]_{bulk-sum}, [Mn]_{bulk-sum}, and [Al]_{bulk-sum} for the SPM decrease through the estuary, whereas the [K]_{bulk-sum} increases (Figure 5.8). In addition, [Li]_{bulk-sum} increases from 3.9 µg/g at 2017SPMR to 9.3 µg/g at 2017SPM05, and then varies from 6.1–9.3 µg/g at 2017SPM05–13. The $\delta^7\text{Li}_{\text{bulk-sum}}$ varies from 5.4–15.8‰ with a general increasing trend from 2017SPM05–11 (Figure 5.9).

Table 5.3 Element concentrations and Li isotopes in leached fractions in suspended load samples collected in 2017.

Sample	Leached SPM mass mg	Ca mg/g	Mg mg/g	K mg/g	Fe mg/g	Mn mg/g	Al mg/g	Li µg/g	$\delta^7\text{Li}$ ‰	2σ ‰
2017SPMR exchangeable	5.1	2.16	0.31	0.30	0.01	0.02	0.02	0.03	n.d.	
2017SPM01 exchangeable	1.0	5.56	0.70	0.42	0.08	0.01	0.07	0.11	n.d.	
2017SPM02 exchangeable	5.3	3.52	1.11	0.75	0.02	0.13	0.01	0.12	n.d.	
2017SPM03 exchangeable	4.8	2.63	1.61	1.12	0.02	0.12	0.01	0.13	n.d.	
2017SPM04 exchangeable	4.5	3.58	8.18	4.27	0.04	0.13	0.03	0.80	25.58	0.16
2017SPM05 exchangeable	4.4	6.91	8.83	5.17	0.04	0.07	0.08	1.24	28.63	0.37
2017SPM06 exchangeable	5.2	6.01	4.49	2.74	0.05	0.17	0.11	0.69	23.53	0.37
2017SPM07 exchangeable	5.0	8.01	6.79	4.31	0.01	0.04	0.01	1.21	24.69	0.06
2017SPM08 exchangeable	4.6	9.19	13.7	6.83	0.01	0.02	0.01	1.81	31.03	0.41
2017SPM09 exchangeable	5.2	8.37	6.77	3.25	0.02	0.05	0.01	1.34	27.63	0.44
2017SPM10 exchangeable	5.6	8.12	12.4	5.71	0.00	0.05	0.01	1.73	29.61	0.28
2017SPM11 exchangeable	4.4	11.7	14.4	8.02	0.01	0.01	0.02	2.77	27.53	0.48
2017SPM12 exchangeable	0.8	15.7	35.4	22.7	0.35	0.02	0.08	3.63	n.d.	
2017SPM13 exchangeable	1.2	12.2	31.0	15.5	0.22	0.01	0.06	3.78	n.d.	
2017SPMR carbonate	5.1	0.56	0.04	0.04	0.01	0.01	0.01	0.02	n.d.	
2017SPM01 carbonate	1.0	1.30	0.13	0.09	0.05	0.01	0.06	0.07	n.d.	
2017SPM02 carbonate	5.3	0.65	0.12	0.15	0.01	0.06	0.01	0.07	n.d.	
2017SPM03 carbonate	4.8	0.61	0.09	0.18	0.13	0.05	0.03	0.07	n.d.	
2017SPM04 carbonate	4.5	0.63	0.26	0.43	0.02	0.04	0.02	0.15	n.d.	
2017SPM05 carbonate	4.4	3.32	0.56	0.54	0.03	0.11	0.02	0.31	20.44	0.35
2017SPM06 carbonate	5.2	2.44	0.25	0.40	0.02	0.12	0.03	0.21	15.00	0.13
2017SPM07 carbonate	5.0	5.95	0.25	0.42	0.02	0.05	0.03	0.22	17.60	0.48
2017SPM08 carbonate	4.6	3.30	1.18	0.55	0.02	0.07	0.02	0.35	24.31	0.08
2017SPM09 carbonate	5.2	2.51	1.37	0.88	0.02	0.06	0.03	0.35	21.33	0.53
2017SPM10 carbonate	5.6	3.47	3.58	1.72	0.02	0.06	0.02	0.61	26.02	0.47
2017SPM11 carbonate	4.4	11.6	2.86	1.12	0.06	0.08	0.06	0.47	26.27	0.50

Sample	Leached SPM mass mg	Ca mg/g	Mg mg/g	K mg/g	Fe mg/g	Mn mg/g	Al mg/g	Li µg/g	δ ⁷ Li ‰	2σ ‰
2017SPM12 carbonate	0.8	5.50	6.13	1.99	0.08	0.12	0.12	1.04	n.d.	
2017SPM13 carbonate	1.2	1.35	4.82	0.99	0.03	0.07	0.01	0.60	n.d.	
2017SPMR oxide	5.1	0.79	0.20	0.01	0.67	0.05	1.32	0.04	n.d.	
2017SPM01 oxide	1.0	1.27	0.25	0.04	0.94	0.07	2.07	0.11	n.d.	
2017SPM02 oxide	5.3	0.59	0.14	0.07	0.74	0.12	1.85	0.07	n.d.	
2017SPM03 oxide	4.8	0.49	0.12	0.06	0.59	0.05	1.54	0.06	n.d.	
2017SPM04 oxide	4.5	0.76	0.26	0.16	0.97	0.05	1.89	0.19	n.d.	
2017SPM05 oxide	4.4	1.32	0.54	0.30	1.44	0.15	1.85	0.40	13.38	0.23
2017SPM06 oxide	5.2	1.16	0.30	0.18	1.29	0.06	1.95	0.23	8.76	0.25
2017SPM07 oxide	5.0	0.09	0.29	0.16	1.35	0.26	1.85	0.25	10.27	0.23
2017SPM08 oxide	4.6	0.86	0.70	0.21	0.99	0.08	1.16	0.30	17.50	0.18
2017SPM09 oxide	5.2	0.95	0.30	0.22	0.55	0.01	0.75	0.29	16.66	0.24
2017SPM10 oxide	5.6	2.34	1.73	0.89	0.48	0.03	0.38	0.43	22.81	0.31
2017SPM11 oxide	4.4	0.02	1.37	0.28	1.00	0.09	0.94	0.39	18.63	0.11
2017SPM12 oxide	0.8	2.35	4.10	1.06	1.12	0.15	1.00	0.48	n.d.	
2017SPM13 oxide	1.2	0.73	2.79	0.50	0.37	0.05	0.40	0.29	n.d.	
2017SPMR clay	5.1	3.42	1.44	0.02	5.80	0.10	5.26	0.16	n.d.	
2017SPM01 clay	1.0	6.67	2.66	0.03	9.37	0.16	9.26	0.34	n.d.	
2017SPM02 clay	5.3	4.11	1.87	0.07	9.55	0.17	9.04	0.57	6.76	0.09
2017SPM03 clay	4.8	3.53	1.68	0.07	9.43	0.16	8.43	0.58	6.44	0.33
2017SPM04 clay	4.5	2.99	1.61	0.08	9.96	0.10	7.56	0.68	8.56	0.19
2017SPM05 clay	4.4	3.74	2.56	0.14	10.57	0.14	8.13	1.17	7.57	0.42
2017SPM06 clay	5.2	3.74	2.29	0.11	10.50	0.12	7.74	1.02	6.50	0.33
2017SPM07 clay	5.0	3.65	2.17	0.11	9.93	0.10	7.32	0.96	6.55	0.03
2017SPM08 clay	4.6	2.11	1.38	0.06	5.38	0.07	3.80	0.77	9.80	0.28
2017SPM09 clay	5.2	2.23	1.40	0.09	6.49	0.06	4.50	0.70	8.48	0.09
2017SPM10 clay	5.6	1.62	1.12	0.16	3.85	0.04	2.83	0.51	11.81	0.10

Sample	Leached SPM mass mg	Ca mg/g	Mg mg/g	K mg/g	Fe mg/g	Mn mg/g	Al mg/g	Li µg/g	δ ⁷ Li ‰	2σ ‰
2017SPM11 clay	4.4	2.63	1.56	0.05	5.32	0.07	3.90	0.81	9.78	0.04
2017SPM12 clay	0.8	3.90	2.16	0.09	4.90	0.07	3.36	0.83	n.d.	
2017SPM13 clay	1.2	1.61	1.11	0.00	1.20	0.02	0.92	0.38	n.d.	
2017SPMR residue	5.1	83.8	39.7	1.31	74.5	1.20	88.2	3.69	2.09	0.13
2017SPM01 residue	1.0	89.3	38.1	1.71	77.5	1.24	99.3	4.26	2.23	0.18
2017SPM02 residue	5.3	56.9	27.2	1.67	66.6	0.99	71.0	5.13	2.65	0.36
2017SPM03 residue	4.8	61.8	31.7	2.04	75.0	1.12	74.7	5.98	2.32	0.00
2017SPM04 residue	4.5	43.0	22.1	1.53	54.7	0.81	55.7	4.72	5.36	0.25
2017SPM05 residue	4.4	46.3	22.0	1.56	54.6	0.83	56.2	6.19	3.56	0.55
2017SPM06 residue	5.2	53.4	26.3	1.88	62.1	0.99	62.5	6.79	2.92	0.31
2017SPM07 residue	5.0	43.3	20.7	1.56	51.1	0.82	52.0	5.55	3.25	0.43
2017SPM08 residue	4.6	25.5	12.4	0.80	29.8	0.46	30.1	3.22	3.86	0.61
2017SPM09 residue	5.2	28.8	14.4	1.02	33.4	0.51	33.9	3.61	3.59	0.13
2017SPM10 residue	5.6	22.8	11.5	0.97	27.6	0.42	27.4	3.24	5.51	0.55
2017SPM11 residue	4.4	22.3	10.6	0.76	25.8	0.39	26.6	3.05	4.74	0.25
2017SPM12 residue	0.8	20.0	10.1	1.18	24.5	0.35	24.7	2.87	7.53	0.34
2017SPM13 residue	1.2	5.28	3.51	0.40	6.79	0.09	6.47	1.06	11.15	0.29
2017SPMR bulk-sum	5.1	90.7	41.7	1.69	81.0	1.37	94.8	3.94	n.d.	
2017SPM01 bulk-sum	1.0	104	41.9	2.30	87.9	1.49	111	4.88	n.d.	
2017SPM02 bulk-sum	5.3	65.8	30.4	2.71	76.9	1.46	81.9	5.97	n.d.	
2017SPM03 bulk-sum	4.8	69.1	35.2	3.48	85.2	1.51	84.7	6.81	n.d.	
2017SPM04 bulk-sum	4.5	51.0	32.4	6.47	65.7	1.13	65.2	6.53	n.d.	
2017SPM05 bulk-sum	4.4	61.6	34.4	7.71	66.7	1.30	66.3	9.31	8.39	
2017SPM06 bulk-sum	5.2	66.7	33.7	5.30	74.0	1.46	72.3	8.94	5.36	
2017SPM07 bulk-sum	5.0	61.0	30.2	6.55	62.4	1.27	61.2	8.19	7.41	
2017SPM08 bulk-sum	4.6	40.9	29.4	8.45	36.2	0.70	35.1	6.45	13.95	
2017SPM09 bulk-sum	5.2	42.9	24.2	5.47	40.5	0.70	39.1	6.29	10.86	

Sample	Leached SPM mass mg	Ca mg/g	Mg mg/g	K mg/g	Fe mg/g	Mn mg/g	Al mg/g	Li µg/g	$\delta^7\text{Li}$ ‰	2σ ‰
2017SPM10 bulk-sum	5.6	38.3	30.2	9.46	32.0	0.60	30.7	6.53	15.46	
2017SPM11 bulk-sum	4.4	48.2	30.8	10.2	32.2	0.64	31.5	7.50	15.78	
2017SPM12 bulk-sum	0.8	47.4	58.0	27.0	30.9	0.71	29.2	8.83	n.d.	
2017SPM13 bulk-sum	1.2	21.1	43.3	17.3	8.61	0.24	7.86	6.11	n.d.	

The nominal fractions in suspended load samples may be influenced by sea salt residue; see details in Section 5.3.2. The data for SPM bulk-sum are calculated as the sum of exchangeable, carbonate, oxide, clay fractions and residue (Eq. 2.2). n.d. means not determined.

The two standard deviation of each measured $\delta^7\text{Li}$ value is shown as 2σ . The long-term uncertainty of seawater $\delta^7\text{Li}$ analysis using MC-ICP-MS is 0.63‰ (2SD).

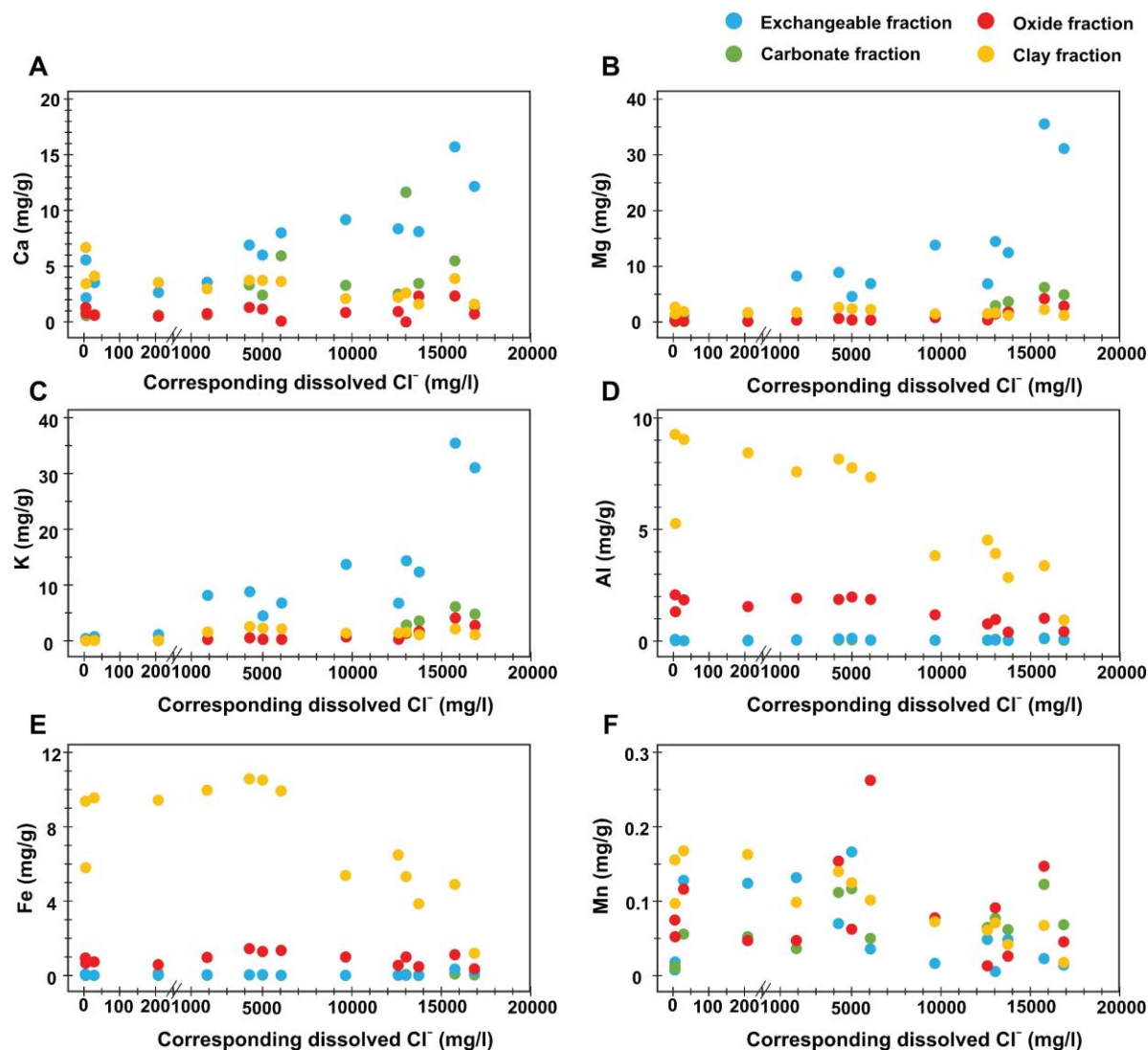


Figure 5.5 Concentrations of the major elements (Ca, Mg, K, Al, Fe, and Mn) in the different leached fractions (i.e., exchangeable, carbonate, oxide, and clay) of the suspended load samples.

The nominal fractions may be influenced by sea salt residue; see details in Section 5.3.2. The x-axis scale is broken at a Cl^- concentration of 300 to 900 mg/l.

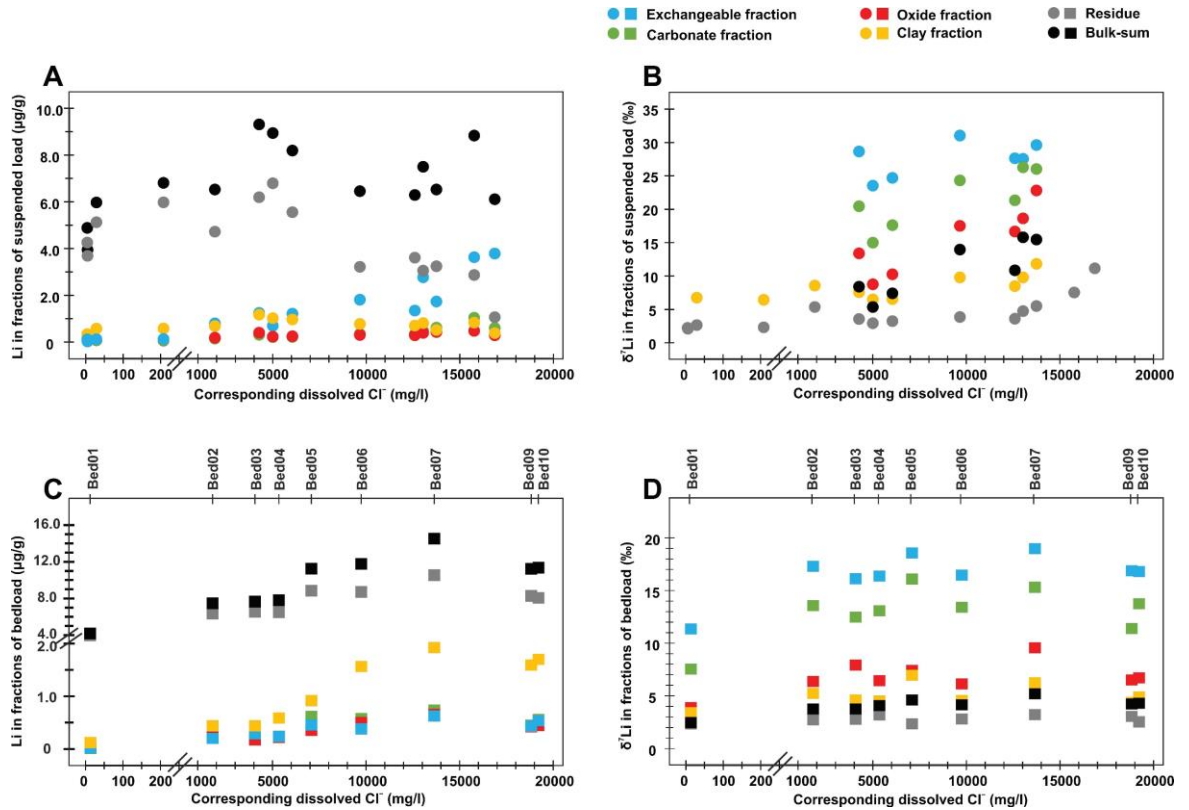


Figure 5.6 Li concentrations and Li isotopes in the different fractions (i.e., exchangeable, carbonate, oxide, clay, and residue) and the bulk of the suspended load and bedload samples.

The nominal fractions in suspended samples (in panel A and B) may be influenced by sea salt residue; see details in Section 5.3.2. The corresponding dissolved Cl⁻ concentrations of the bedload samples in panel C and D are assumed to be the same as the corresponding surface dissolved load samples collected in 2003 at the same locations (Figure 5.1). The bedload sample IDs are labelled in panel C and D. Sample Bed08 is not shown because of the lack of corresponding surface dissolved load data at the same location. The x-axis scale is broken at a Cl⁻ concentration of 300 to 900 mg/l. The y-axis in panel C is broken at a Li concentration of 2 to 4 µg/g.

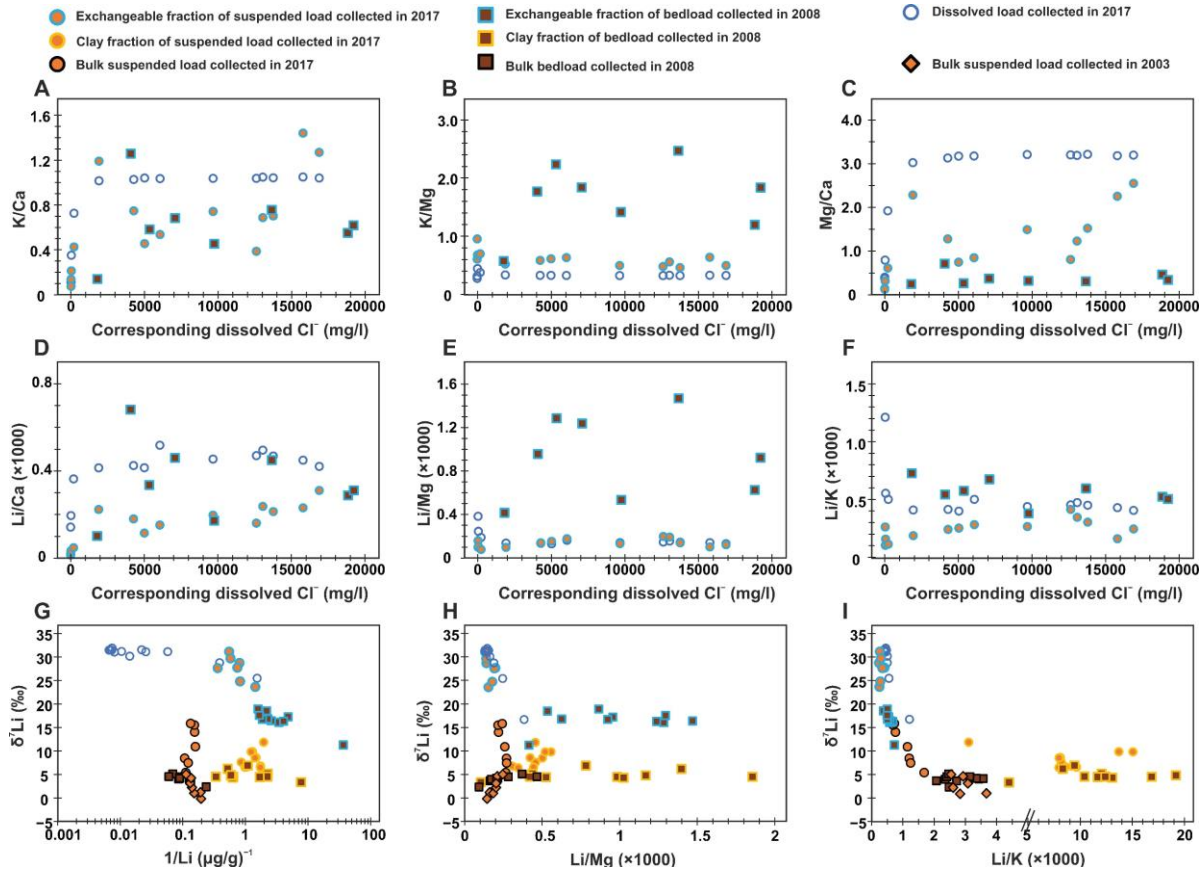


Figure 5.7 Comparison of soluble elements (K, Mg, Ca, and Li) and Li isotopes between the dissolved load and the exchangeable fraction in the solid samples.

The data for the samples collected in 2003 (diamonds) are from Pogge von Strandmann et al. (2008). The corresponding dissolved Cl^- concentrations of bedload samples in panels A–F are assumed to be the same as the surface dissolved load samples collected in 2003 at the same locations (Figure 5.1). Sample Bed08 is not shown in panels A–F because of lack of corresponding surface dissolved load at the same location.

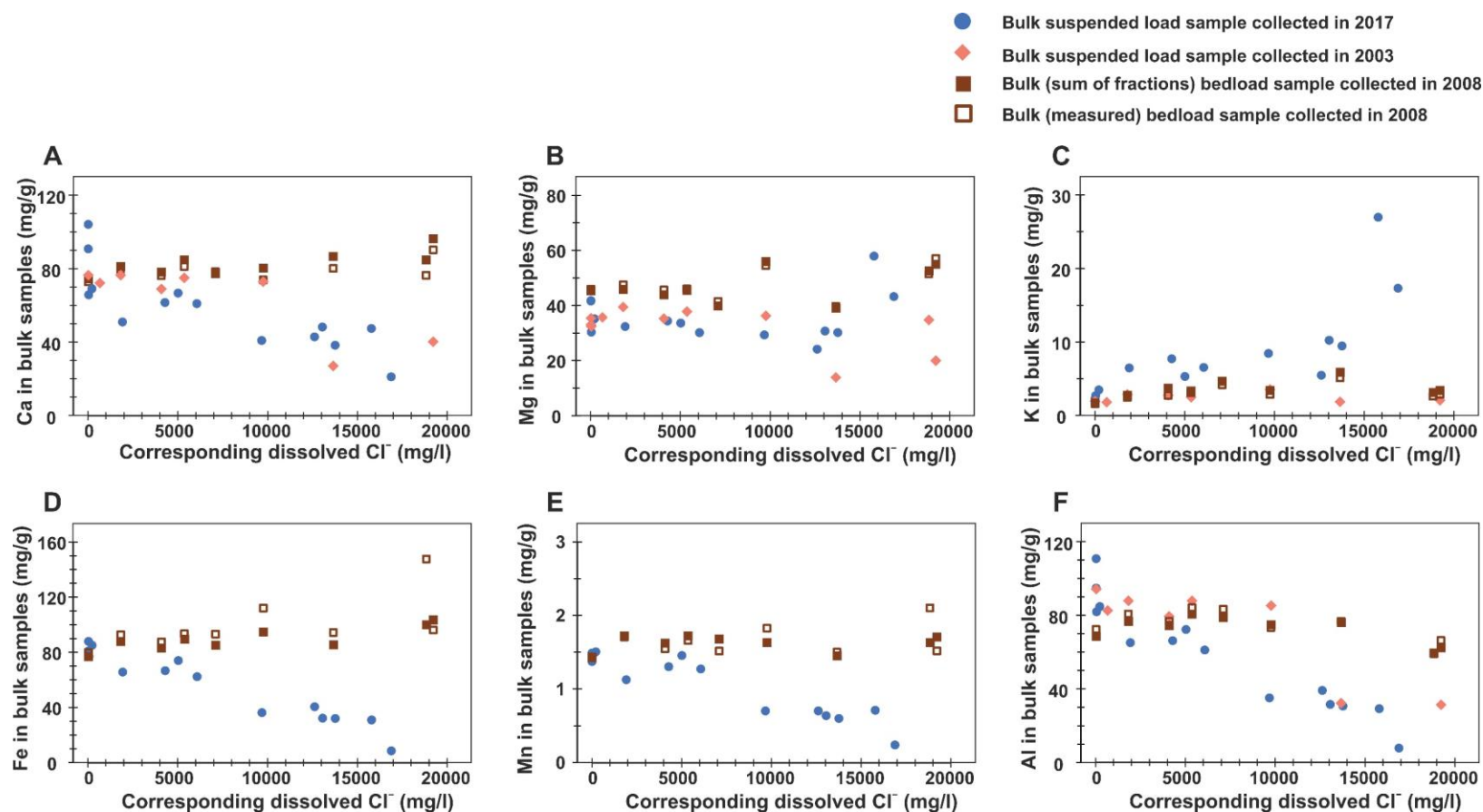


Figure 5.8 Major elements (Ca, Mg, K, Fe, Mn, and Al) in the bulk suspended load and bedload samples.

The data for samples collected in 2003 (diamonds) are from Pogge von Strandmann et al. (2008). The brown open squares represent the measured element concentrations in the bulk dissolution, and the brown solid squares represent the sum of element concentrations in the different fractions (Eq. 2.2). The corresponding dissolved Cl^- concentrations of the bedload samples are assumed to be the same as the surface dissolved load samples collected in 2003 at the same locations (Figure 5.1). Sample Bed08 is not shown because of the lack of corresponding surface dissolved load data at the same location.

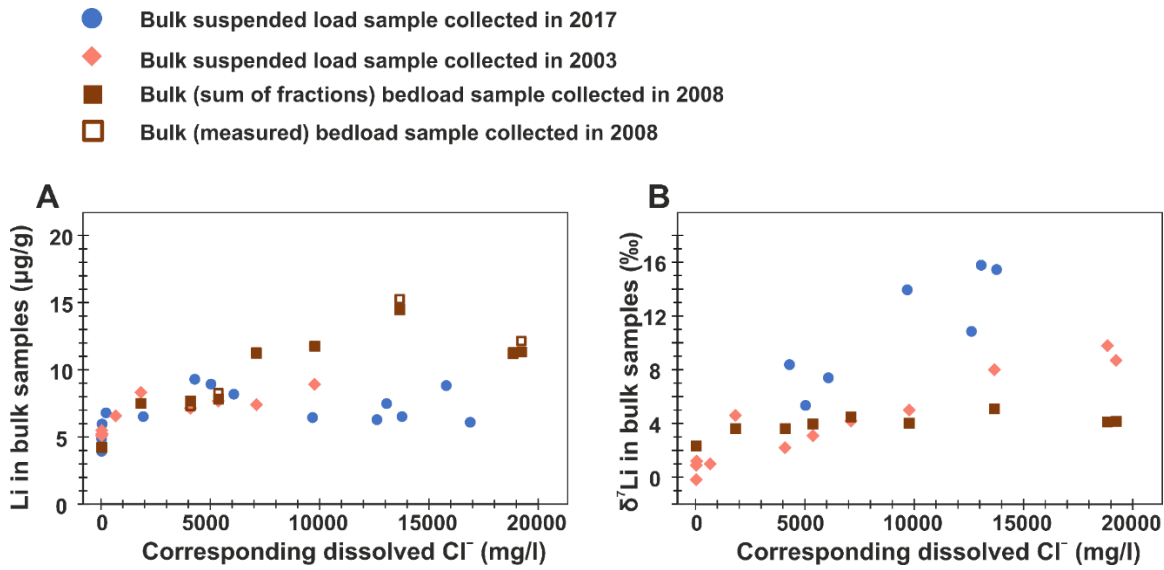


Figure 5.9 Li concentrations and Li isotopes in the bulk suspended load and bedload samples.

The data for the samples collected in 2003 (diamonds) are from Pogge von Strandmann et al. (2008). The corresponding dissolved Cl^- concentrations of the bedload samples are assumed to be the same as the surface dissolved load samples collected in 2003 at the same locations (Figure 5.1). Sample Bed08 is not shown because of the lack of corresponding surface dissolved load data at the same location. In panel A, the brown open squares represent the measured element concentrations in the bulk dissolution, and the brown solid squares represent the sum of element concentrations in the different fractions (Eq. 2.2).

5.3.3 Bedload samples

The elemental concentrations and Li isotopes in the different fractions and the bulk of the bedload samples are given in Table 5.4.

In the exchangeable fraction, aside from Na (which is added during the leaching process), Ca, Mg, and K dominate the exchangeable leachates. Generally, $[Ca]_{\text{exchangeable}}$ (0.27–2.96 mg/g), $[Mg]_{\text{exchangeable}}$ (0.07–0.86 mg/g), and $[K]_{\text{exchangeable}}$ (0.04–1.27 mg/g) show increasing, but fluctuating, trends through the estuarine transect (Figure 5.10). In contrast, the $[Fe]_{\text{exchangeable}}$, $[Mn]_{\text{exchangeable}}$, and $[Al]_{\text{exchangeable}}$ are lower than 0.01 mg/g, without clear trends. The $[Li]_{\text{exchangeable}}$ increases from 0.03 $\mu\text{g/g}$ near the river mouth (Bed01) to 0.2 $\mu\text{g/g}$ at low salinity (Bed02), then generally increases to around 0.5 $\mu\text{g/g}$ in the high salinity zone (Figure 5.6C). The $\delta^7\text{Li}_{\text{exchangeable}}$ increases from 11.3‰ near the river mouth (Bed01) to 17.2‰ at low salinity (Bed02), and then varies from 16.0‰ to 18.9‰ (Figure 5.6D).

Calcium dominates the carbonate leachates as expected, and the $[Ca]_{\text{carbonate}}$ increases from 0.35 to 24.8 mg/g in the estuary (Figure 5.10A). In the low and medium salinity zone (Bed01–Bed06), the $[Mn]_{\text{carbonate}}/[Ca]_{\text{carbonate}}$, and $[Al]_{\text{carbonate}}/[Ca]_{\text{carbonate}}$ ratios range from 0.008 to 0.15 mg/mg and 0.009 to 0.66 mg/g, respectively, which indicates the influence of a non-carbonate fraction on some of the carbonate leachates (Sections 3.3.3 and 5.3.2). In the high salinity area (Bed07–10), the $[Mn]_{\text{carbonate}}/[Ca]_{\text{carbonate}}$ and $[Al]_{\text{carbonate}}/[Ca]_{\text{carbonate}}$ ratios are lower than 3.2 $\mu\text{g/g}$ and 5.2 $\mu\text{g/g}$, respectively. The low $[Mn]_{\text{carbonate}}/[Ca]_{\text{carbonate}}$ and $[Al]_{\text{carbonate}}/[Ca]_{\text{carbonate}}$ ratios are identical to the carbonate fraction of published carbonate-dominated samples (Misra and Froelich, 2012; Pogge von Strandmann et al., 2013; Ullmann et al., 2013; Bastian et al., 2018; Washington et al., 2020; Cao et al., 2023). Correspondingly, the $[Ca]_{\text{carbonate}}/[Ca]_{\text{bulk-calculation}}$ in the bedload samples from the high salinity zone ranges from 20–26%, while in the low and medium salinity zone, the $[Ca]_{\text{carbonate}}/[Ca]_{\text{bulk-sum}}$ increases from around 0.5 to 7.7%. The $[Li]_{\text{carbonate}}$ generally increases from 0.02 to 0.86 $\mu\text{g/g}$, but decreases to around 0.5 $\mu\text{g/g}$ in the last two samples (Bed09 and Bed10) in the estuarine transect (Figure 5.6C). The $\delta^7\text{Li}_{\text{carbonate}}$ values increase from 7.4‰ near the river mouth (Bed01) to 13.5‰ at low salinity (Bed02), and then vary from 11.3‰ to 16.0‰ (Figure 5.6D).

In the oxide fraction, $[Fe]_{\text{oxide}}$ and $[Al]_{\text{oxide}}$ range from 0.58 to 1.68 mg/g and

0.46 to 1.04 mg/g, respectively, which are higher than the $[\text{Ca}]_{\text{oxide}}$ (0.13–0.72 mg/g, except Bed10), $[\text{Mg}]_{\text{oxide}}$ (0.18–0.30 mg/g), $[\text{K}]_{\text{oxide}}$ (0.01–0.21 mg/g), and also $[\text{Mn}]_{\text{oxide}}$ (13.8–163.9 $\mu\text{g/g}$) (Figure 5.10). Similar to the carbonate fraction, the $[\text{Li}]_{\text{oxide}}$ increases from 0.04 to 0.96 $\mu\text{g/g}$, but decreases to around 0.4 $\mu\text{g/g}$ in the last two samples in the transect (Figure 5.6C). The $\delta^7\text{Li}_{\text{oxide}}$ values increase from 3.8‰ near the river mouth (Bed01) to 6.3‰ at low salinity (Bed02), and then vary from 6.3‰ to 9.5‰ (Figure 5.6D).

In the clay fraction, $[\text{Fe}]_{\text{clay}}$, $[\text{Al}]_{\text{clay}}$, and $[\text{K}]_{\text{clay}}$ show clear increasing trends from 2.53 to 7.47 mg/g, 1.96 to 5.05 mg/g, and 0.03 to 0.24 mg/g, respectively, in Bed01–08, but decrease to 5.2 mg/g, 3.2 mg/g, and 0.10 mg/g in the last two samples (Figure 5.10). The $[\text{Ca}]_{\text{clay}}$ and $[\text{Mg}]_{\text{clay}}$ fluctuate slightly in the ranges from 1.83 to 3.17 mg/g (except Bed10) and 1.0 to 1.6 mg/g, respectively. The $[\text{Li}]_{\text{clay}}$ first increases from 0.13 to 2.96 $\mu\text{g/g}$ and then decreases to around 1.6–1.7 $\mu\text{g/g}$, similarly to Fe, Al, and K (Figure 5.6C). The $\delta^7\text{Li}_{\text{clay}}$ values increase from 3.3‰ near the river mouth (Bed01) to 5.1‰ at low salinity (Bed02), and then vary from 4.3‰ to 6.8‰ in the estuary.

The $[\text{Fe}]_{\text{residue}}$ and $[\text{Al}]_{\text{residue}}$ vary in a narrow range from 73.6 to 88.1 mg/g, and 66.0 to 74.1 mg/g, respectively, in Bed01–08. Then, in the last two samples, the $[\text{Fe}]_{\text{residue}}$ increases to 93.9 and 97.5 mg/g, while the $[\text{Al}]_{\text{residue}}$ decreases to 55.8 and 58.7 mg/g. The $[\text{Li}]_{\text{residue}}$ also first increases from 4.0 to 11.4 $\mu\text{g/g}$ and then decreases to around 8.0 $\mu\text{g/g}$ in the last two samples (Figure 5.6C). In contrast, the $\delta^7\text{Li}_{\text{residue}}$ values remain stable in the range from 2.2‰ to 3.1‰ throughout the estuarine transect (Figure 5.6D). Interestingly, the $[\text{Li}]_{\text{residue}}/[\text{Li}]_{\text{bulk-sum}}$ decreases from 95% to ~70% in the estuary (Figure 5.11). The contributions of some major elements (i.e., Mg, K, Fe, and Al) from the residue to the corresponding bulk samples also decrease in the low and medium salinity part of the estuary.

The calculated bulk concentrations of the elements in all fractions of the sequential extractions are calculated based on Eq. 2.2, and mostly correspond well with the measured bulk element concentrations (Figures 5.8 and 5.9). The concentrations of Ca, Na, and Fe in the bulk samples generally slightly increase in the estuary, whereas those of K and Al increase from Bed01–08 but decrease in the high salinity area (i.e., Bed09 and 10) (Figure 5.8). Similarly, the $[\text{Li}]_{\text{bulk-sum}}$ first increases from 4.23 to 16.8 $\mu\text{g/g}$ and then decreases to around 11.3 $\mu\text{g/g}$ in

the last two samples (i.e., Bed09 and 10), which is similar to the trends of Li concentrations in the oxide and clay fractions and residues (Figure 5.6C). In contrast, the $\delta^7\text{Li}_{\text{bulk-sum}}$ increases gradually from 2.3‰ to 4.5‰ in the low and medium salinity regions, and then varies in the range from 4.0 to 5.1‰ in the remainder of the estuary (Figures 5.6D and 5.9B).

Table 5.4 Element concentrations and Li isotopes in leached fractions and bulk solutions in bedload samples collected in 2008.

Sample	Corresponding dissolved Cl ⁻ concentration	Ca	Mg	K	Fe	Mn	Al	Na	Li	δ ⁷ Li	2σ
	mg/l	mg/g	mg/g	mg/g	mg/g	mg/g	mg/g	mg/g	μg/g	‰	‰
Bed01 exchangeable	12.8	0.27	0.07	0.04	0.006	0.0005	b.d.l.		0.03	11.25	0.27
Bed02 exchangeable	1808	0.31	0.22	0.38	0.005	0.0007	b.d.l.		0.21	17.21	0.22
Bed03 exchangeable	4077	0.88	0.23	0.51	0.009	0.0007	b.d.l.		0.29	16.04	0.31
Bed04 exchangeable	5353	0.54	0.20	0.37	0.006	0.0006	b.d.l.		0.25	16.27	0.12
Bed05 exchangeable	7091	2.70	0.86	1.22	0.004	0.0082	b.d.l.		0.46	18.49	0.07
Bed06 exchangeable	9750	0.86	0.26	0.65	0.003	0.0003	b.d.l.		0.39	16.37	0.28
Bed07 exchangeable	13649	2.96	0.73	1.27	0.006	0.0006	b.d.l.		0.63	18.90	0.17
Bed08 exchangeable		1.32	0.46	1.21	0.004	0.0003	b.d.l.		0.60	17.53	0.17
Bed09 exchangeable	18826	1.52	0.70	0.84	0.009	0.0009	b.d.l.		0.44	16.78	0.28
Bed10 exchangeable	19216	1.73	0.58	1.07	0.004	0.0005	b.d.l.		0.54	16.72	0.24
Bed01 carbonate	12.8	0.35	0.04	0.07	0.06	0.01	0.09		0.02	7.44	0.18
Bed02 carbonate	1808	0.21	0.15	0.11	0.09	0.03	0.14		0.25	13.49	0.20
Bed03 carbonate	4077	1.62	0.12	0.11	0.04	0.02	0.08		0.19	12.38	0.37
Bed04 carbonate	5353	0.34	0.13	0.08	0.06	0.03	0.10		0.23	13.00	0.27
Bed05 carbonate	7091	5.41	0.33	0.41	0.11	0.06	0.05		0.62	16.01	0.06
Bed06 carbonate	9750	6.16	0.33	0.18	0.08	0.05	0.10		0.58	13.33	0.39
Bed07 carbonate	13649	18.4	0.66	0.41	0.11	0.06	0.10		0.74	15.23	0.30
Bed08 carbonate		19.2	0.64	0.40	0.06	0.04	0.07		0.86	15.21	0.28
Bed09 carbonate	18826	16.7	0.64	0.21	0.07	0.04	0.09		0.46	11.30	0.29
Bed10 carbonate	19216	24.8	0.59	0.20	0.07	0.04	0.05		0.56	13.67	0.15
Bed01 oxide	12.8	0.34	0.22	0.01	0.58	0.05	0.59		0.04	3.75	0.14
Bed02 oxide	1808	0.36	0.22	0.02	0.87	0.16	0.65		0.24	6.27	0.21
Bed03 oxide	4077	0.37	0.18	0.02	0.73	0.13	0.61		0.18	7.82	0.02
Bed04 oxide	5353	0.29	0.19	0.03	0.70	0.11	0.53		0.23	6.33	0.12
Bed05 oxide	7091	0.56	0.21	0.17	1.68	0.03	1.04		0.36	7.32	0.12

Sample	Corresponding dissolved Cl ⁻ concentration	Ca	Mg	K	Fe	Mn	Al	Na	Li	δ ⁷ Li	2σ
	mg/l	mg/g	mg/g	mg/g	mg/g	mg/g	mg/g	mg/g	µg/g	‰	‰
Bed06 oxide	9750	0.44	0.25	0.05	0.96	0.06	0.62		0.50	6.02	0.28
Bed07 oxide	13649	0.13	0.27	0.21	1.05	0.08	0.96		0.66	9.47	0.17
Bed08 oxide		0.72	0.30	0.17	1.16	0.08	0.72		0.96	7.14	0.12
Bed09 oxide	18826	0.62	0.23	0.09	0.79	0.01	0.47		0.42	6.40	0.13
Bed10 oxide	19216	2.00	0.25	0.03	0.64	0.03	0.46		0.45	6.61	0.21
Bed01 clay	12.8	2.09	1.22	0.03	2.53	0.04	1.96		0.13	3.29	0.11
Bed02 clay	1808	1.83	1.01	0.04	3.23	0.04	1.87		0.44	5.11	0.19
Bed03 clay	4077	2.04	1.05	0.04	3.38	0.04	2.11		0.44	4.49	0.49
Bed04 clay	5353	2.00	1.12	0.05	3.76	0.05	2.25		0.59	4.41	0.01
Bed05 clay	7091	1.90	1.17	0.10	4.71	0.05	3.63		0.92	6.84	0.01
Bed06 clay	9750	2.17	1.59	0.09	5.71	0.06	3.35		1.56	4.45	0.29
Bed07 clay	13649	3.17	1.37	0.23	5.70	0.06	4.59		1.92	6.14	0.08
Bed08 clay		1.89	1.59	0.24	7.47	0.06	5.05		2.96	4.47	0.20
Bed09 clay	18826	1.92	1.55	0.12	5.25	0.05	3.25		1.59	4.26	0.31
Bed10 clay	19216	0.84	1.45	0.09	5.20	0.05	3.13		1.70	4.77	0.14
Bed01 residue	12.8	71.5	43.8	1.56	73.6	1.34	66.0		4.02	2.21	0.32
Bed02 residue	1808	78.3	44.2	2.21	83.6	1.49	74.1		6.36	2.60	0.02
Bed03 residue	4077	73.2	42.4	3.04	78.8	1.42	71.6		6.58	2.66	0.16
Bed04 residue	5353	81.7	43.9	2.79	84.9	1.53	77.8		6.53	3.06	0.01
Bed05 residue	7091	66.8	37.3	2.77	78.7	1.53	74.1		8.86	2.23	0.17
Bed06 residue	9750	70.7	53.6	2.45	88.1	1.47	70.7		8.72	2.68	0.19
Bed07 residue	13649	62.1	36.0	3.76	78.7	1.26	70.5		10.5	3.08	0.02
Bed08 residue		61.2	33.0	3.33	75.2	1.16	70.9		11.4	2.83	0.34
Bed09 residue	18826	63.9	49.5	1.88	93.9	1.53	55.8		8.30	2.92	0.15
Bed10 residue	19216	66.9	52.1	2.00	97.5	1.58	58.7		8.09	2.42	0.28
Bed01 bulk-sum	12.8	74.5	45.4	1.71	76.8	1.44	68.7		4.23	2.34	
Bed02 bulk-sum	1808	81.0	45.8	2.76	87.8	1.72	76.7		7.51	3.63	

Sample	Corresponding dissolved Cl ⁻ concentration	Ca	Mg	K	Fe	Mn	Al	Na	Li	δ ⁷ Li	2σ
	mg/l	mg/g	mg/g	mg/g	mg/g	mg/g	mg/g	mg/g	μg/g	‰	‰
Bed03 bulk-sum	4077	78.1	43.9	3.71	83.0	1.62	74.4		7.68	3.63	
Bed04 bulk-sum	5353	84.8	45.6	3.32	89.5	1.72	80.7		7.83	3.97	
Bed05 bulk-sum	7091	77.3	39.9	4.66	85.2	1.68	78.8		11.2	4.50	
Bed06 bulk-sum	9750	80.4	56.0	3.42	94.8	1.63	74.8		11.8	4.04	
Bed07 bulk-sum	13649	86.7	39.1	5.88	85.5	1.45	76.2		14.5	5.09	
Bed08 bulk-sum		84.3	36.0	5.34	83.9	1.34	76.7		16.8	4.53	
Bed09 bulk-sum	18826	84.7	52.7	3.14	100	1.63	59.6		11.2	4.13	
Bed10 bulk-sum	19216	96.2	55.0	3.38	103	1.71	62.3		11.3	4.17	
Bed01 bulk-measured	12.8	72.7	45.9	1.59	79.8	1.42	72.4	13.6	4.24	n.d.	
Bed02 bulk-measured	1808	79.3	47.5	2.44	92.7	1.71	80.7	17.9	7.52	n.d.	
Bed03 bulk-measured	4077	76.1	45.6	2.72	87.5	1.55	76.7	16.4	7.29	n.d.	
Bed04 bulk-measured	5353	81.1	46.0	3.09	93.4	1.66	84.0	18.6	8.26	n.d.	
Bed05 bulk-measured	7091	78.3	41.5	4.15	93.1	1.51	83.2	28.1	11.3	n.d.	
Bed06 bulk-measured	9750	73.7	54.5	2.84	112	1.83	73.4	17.1	11.7	n.d.	
Bed07 bulk-measured	13649	80.1	39.7	5.10	94.2	1.50	76.6	25.0	15.3	n.d.	
Bed08 bulk-measured		76.1	36.5	4.27	92.1	1.43	75.1	19.9	15.8	n.d.	
Bed09 bulk-measured	18826	76.3	51.5	2.61	148	2.10	59.2	22.9	11.3	n.d.	
Bed10 bulk-measured	19216	90.2	57.1	2.86	96.1	1.52	66.3	23.2	12.1	n.d.	

There are no Na concentrations for the exchangeable, carbonate, oxide, and clay fractions and residue, because sodium acetate was used as the leaching reagent. The data for Bed-bulksum are calculated as the sum of exchangeable, carbonate, oxide, and clay fractions and residue in the sequential extraction procedure (Eq. 2.2). The data for Bed bulk-measured are the measured values from the dissolution of bulk samples. n.d. means not determined. b.d.l. means below detection limit. The two standard deviation of each measured δ⁷Li value is shown as 2σ. The long-term uncertainty of seawater δ⁷Li analysis using MC-ICP-MS is 0.63‰ (2SD).

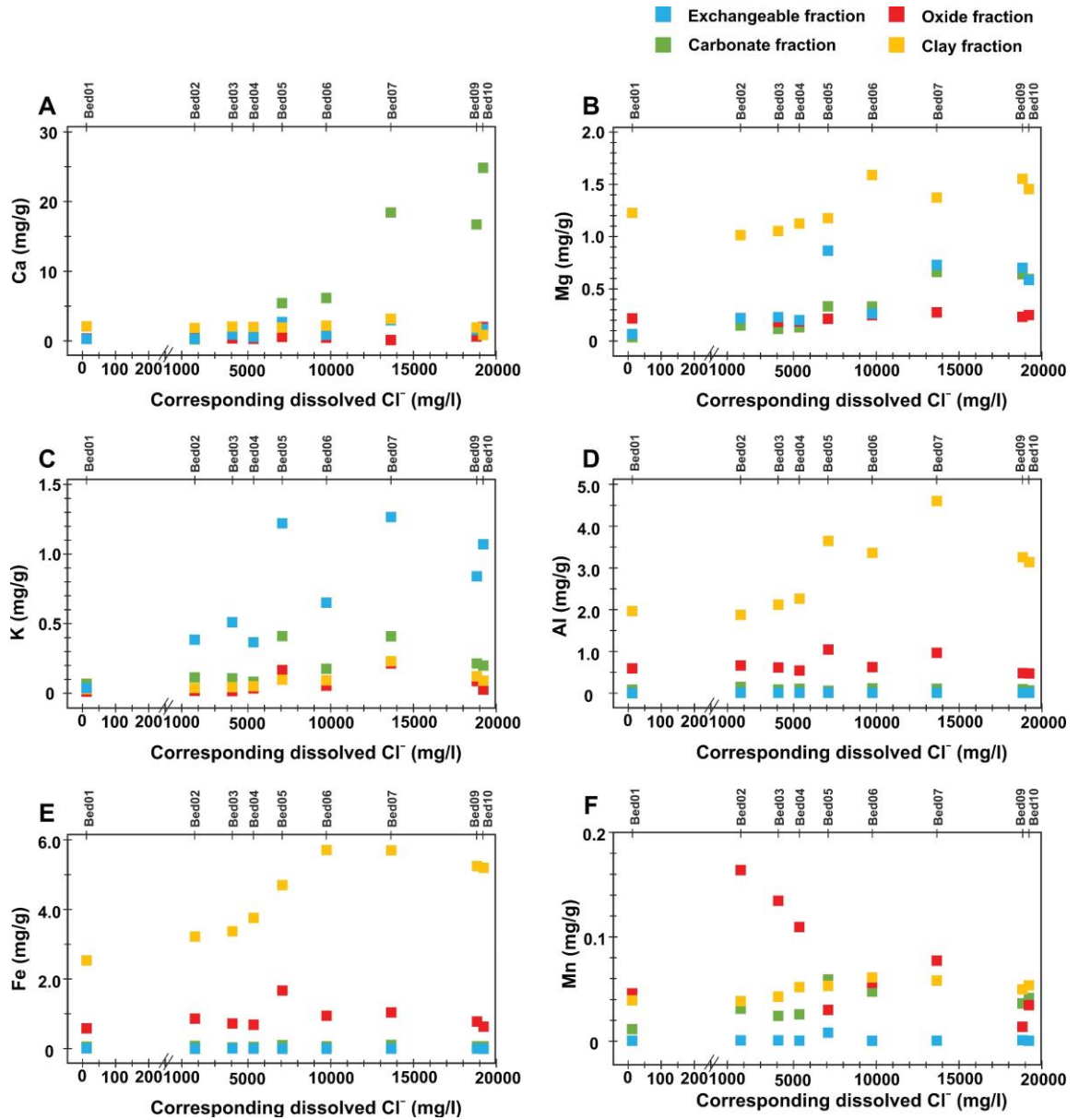


Figure 5.10 Concentrations of major elements (Ca, Mg, K, Al, Fe, and Mn) in different fractions (i.e., exchangeable, carbonate, oxide, and clay) of the bedload samples.

The nominal carbonate fraction may be influenced by leaching of other fractions; see details in Section 5.3.3. The corresponding dissolved Cl⁻ concentrations of the bedload samples are assumed to be the same as the surface dissolved load samples collected in 2003 at the same locations (Figure 5.1). The bedload sample IDs are labelled. Sample Bed08 is not shown because of the lack of corresponding surface dissolved load data at the same location. The x-axis scale is broken at a Cl⁻ concentration of 300 to 900 mg/l.

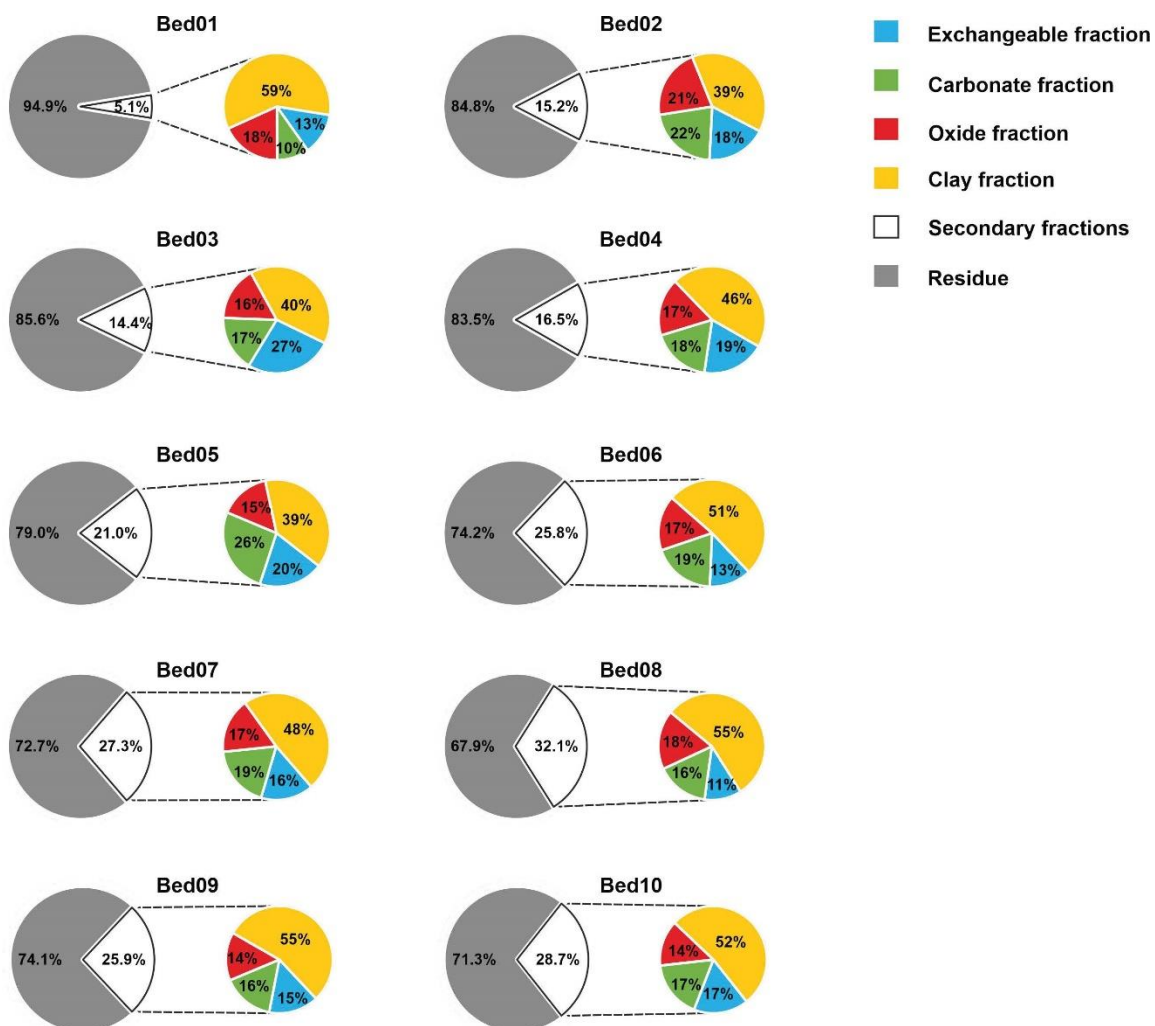


Figure 5.11 The proportion of Li in different fractions in the bedload samples.

The secondary fractions are the sum of exchangeable, carbonate, oxide, and clay fractions.

5.4 Discussion

5.4.1. Dissolved load

The dissolved Na, K, Ca, Mg, and alkalinity concentrations generally show a linear relationship with Cl^- through the transect in this study, as well as in the samples collected from the same estuary in 2003 and 2011 (Pogge von Strandmann et al., 2008; Jones et al., 2014), which indicates elemental conservative mixing between river water and seawater in the Borgarfjörður estuary (Figure 5.3). Dissolved Sr and Mo concentrations also show conservative mixing in the Borgarfjörður estuary (Pearce et al., 2010, Jones et al., 2014). However, the fitting line shows a large relative uncertainty in the dissolved element concentrations in the very low salinity zone, where the salinity is lower than 0.1 (i.e., Cl^- concentration <55.3 mg/l) at a distance of 0 to ~5–8 km from the river mouth. In the very low salinity zone, the samples from the three transects in 2003, 2013, and 2017 show conservative mixing of dissolved Na, Mg, and K between fresh water and saline water, whereas the dissolved Ca concentrations slightly vary with increasing Cl^- concentration. This fluctuating Ca may result from changes in the exchangeable fraction (Tipper et al., 2021) or from carbonate precipitation. The dissolved Si maintains a constant value at very low salinity and then decreases at medium and high salinity through the estuary transect (Figure 5.3F).

The dissolved load Li concentrations also generally show a linear relationship with Cl^- (salinity), similar to the samples collected in 2003 and 2011 (Pogge von Strandmann et al., 2008), which indicates conservative mixing of Li between river water and seawater in the Borgarfjörður estuary (Figure 5.2A). However, in the very low salinity zone (i.e., Cl^- concentration <55.3 mg/L), the Li isotope values fluctuate widely, although there is a general increasing trend with salinity (Figure 5.2D), ranging from 16.7 to 25.4‰ in this study and the data of Pogge von Strandmann et al., (2008) (Figure 5.2E). The large variability of $\delta^7\text{Li}$ values at very low salinity may result from multiple reasons. First, the Li isotope values of the riverine endmember and/or the mixing ratios between river water and saline water are influenced by varying river input and/or tidal flow (Gíslason et al., 1996). Second, the river-derived particles may release Li to, or uptake Li from, the dissolved load in the very low salinity zone in the estuary (Pogge von

Strandmann et al., 2008; Yang et al., 2021), where the suspended particle concentrations are still high (i.e., before settling out), which would lead to deviation from conservative mixing. Interestingly, the isotopic compositions of some other elements, including Sr and Mo isotopes, also fluctuate in the very low salinity zone of the Borgarfjörður estuary, and are slightly lower than the conservative mixing lines, which is thought to be due to the alteration of river-derived particles (Pearce et al., 2010; Jones et al., 2014). Furthermore, the variations of $\delta^7\text{Li}$ in the very low salinity zone lead to a large uncertainty in the $\delta^7\text{Li}$ value of the riverine endmember. Thus, the uncertainty in the estimated conservative mixing for $\delta^7\text{Li}$ values at a salinity less than 9 (i.e., Cl^- concentration <500 mg/L) is around 2‰ (Figure 5.2F). In contrast, the estimated $\delta^7\text{Li}$ values for conservative mixing at salinity >9 are identical to the $\delta^7\text{Li}$ value of seawater (i.e., ~ 31 ‰). When the uncertainties described above are considered, the measured $\delta^7\text{Li}$ values at salinity >0.1 are within the range expected for conservative mixing (Figure 5.2C, F). Thus, the dissolved $\delta^7\text{Li}$ values basically show conservative mixing in the Borgarfjörður estuary.

5.4.2 Suspended particles and bedload particles

5.4.2.1 Influence of multiple processes on solid geochemistry

Based on the bulk suspended particles (SPM) collected in 2017 in this study, the bulk SPM samples collected in 2003 (Pogge von Strandmann et al., 2008), and the bulk bedload samples collected in 2008 in this study, the trends of some elemental compositions through the Borgarfjörður estuarine transect are different between SPM samples and bedload samples (Figure 5.8). For example, the Ca, Fe, Mn, and Al concentrations in bulk SPM samples decrease with increasing salinity, whereas, for bulk bedload samples, the Ca and Fe concentrations generally increase through the estuary. In addition, the suspended sediment concentrations (SSC) in the high salinity zone are lower than in the river endmember and low salinity zone (Table 5.1). Although the mobile elements (e.g., Na, Ca, Mg, and K) in the SPM samples may have been influenced by the remaining seawater during sampling (Section 5.3.2), it is likely that not only geochemical processes (i.e., dissolution, incorporation, flocculation, and precipitation), but also mechanical processes (e.g., particle settling, saltation,

rolling) have a significant effect on the solid geochemistry in the Borgarfjörður estuary (Figure 5.12) (Thorpe et al., 2019).

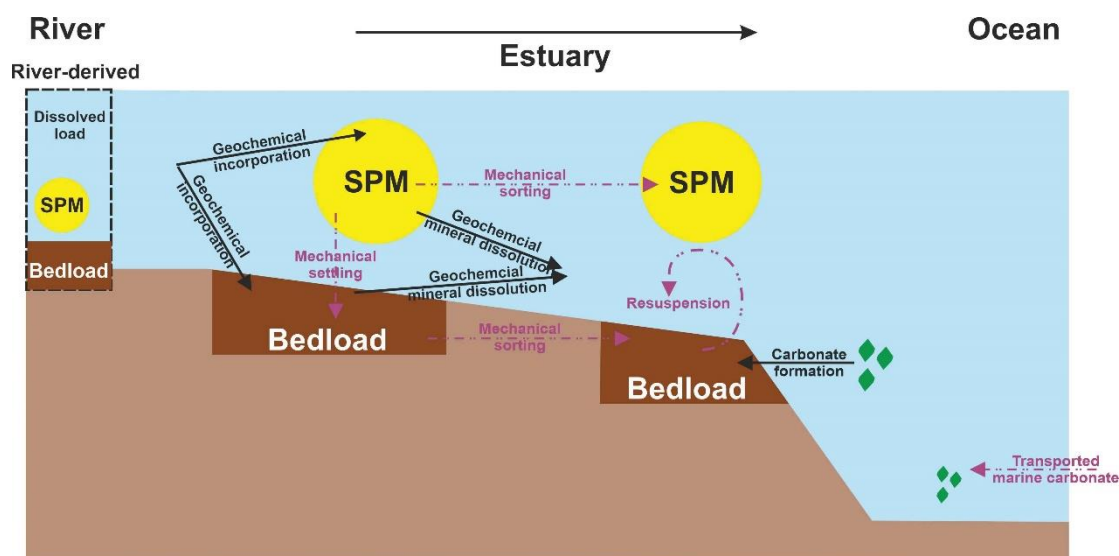


Figure 5.12 Schematic of likely multiple processes operating in the Borgarfjörður estuary. Not to scale.

For suspended particles, the main processes for removing elements are particle settling and particle dissolution, whereas the main processes for adding elements are element incorporation. In contrast, for bedload sediments, the main processes for removing elements are sediment dissolution, whereas the main processes for adding elements are particle settling from the water column, mineral precipitation, and element incorporation. The mechanical processes themselves rarely cause element transfer between the dissolved load and the solid load (i.e., suspended and bedload sediments). However, these processes may influence each other or occur together. For example, oxide and clay formation may cause more flocculation (Kennedy and Wagner 2011), flocculation can accelerate particle settling (Boyle et al., 1977; Sholkovitz et al., 1978), mineral neoformation (e.g., carbonates) can dilute the concentrations of the original minerals (e.g., silicates), and particle settling assisted by mineral density differences and bedload movement together cause mechanical sorting through the estuary (Komar, 2007).

Different minerals and therefore elements are expected to exhibit different

behaviour during these processes. During particle settling, there will be preferential settling of minerals with larger grain sizes, as well as heavy minerals (Allen, 1985; Komar, 2007; Thorpe et al., 2019). Generally, the primary minerals have a larger grain size than secondary newly-formed minerals (Velde, 1995). Furthermore, basaltic (or mafic) minerals (e.g., magnetite, ilmenite, pyroxene, olivine) tend to have higher density than granitic (or felsic) minerals (e.g., K-feldspar, quartz) (Mange and Maurer., 1992; Garzanti and Andò, 2019). Thus, the SPM data indicate loss of the major elements from basaltic minerals (e.g., Fe, Mg, Ca, and Al) (Pogge von Strandmann et al., 2008), and the bedload gains these elements by mineral settling. Notably, in addition to mechanical settling, the basaltic minerals are also readily weathered (Bowen, 1922) and can produce the related secondary minerals, including Fe-oxides and/or Al-silicates, such as smectite (Pogge von Strandmann et al., 2019a, 2022). Mineral saturation indices calculated using PHREEQC indicate that primary mineral dissolution and secondary mineral formation are thermodynamically favourable (Figure 5.4A, B). Similarly, the dissolved load samples collected from the Borgarfjörður estuary in 2011 (Jones et al., 2014) also show undersaturation of primary minerals (e.g., anorthite, albite, monticellite, pyroxene, forsterite, and olivine), and oversaturation of secondary minerals, including montmorillonite, gibbsite, and kaolinite, and also goethite (Figure 5.4A, B). Furthermore, $[\text{Fe}]_{\text{oxide}}$, $[\text{Fe}]_{\text{clay}}$, $[\text{Al}]_{\text{clay}}$, and $[\text{Mg}]_{\text{clay}}$ in the bedload samples increases, consistent with the formation of secondary minerals (Figure 5.10). The interaction experiments reported in Chapter 4 also show incorporation of Mg into solids. The flocculation of particles (e.g., Fe-oxides) may also enhance organic carbon burial and therefore influence the carbon cycle (Bianchi et al., 2018).

Whereas Fe, Al, Mg, and Ca are largely associated with basaltic minerals, K is largely associated with feldspar minerals (Bowen, 1922; Railsback, 2003). The K concentrations in the bulk SPM and bedload samples both increase through the estuarine transect (Figure 5.8C). According to the solid leaching, the $[\text{K}]_{\text{exchangeable}}$ and $[\text{K}]_{\text{exchangeable}}/[\text{K}]_{\text{bulk-sum}}$ increase in both SPM samples and bedload samples. The $[\text{K}]_{\text{clay}}$ and $[\text{K}]_{\text{clay}}/[\text{K}]_{\text{bulk-sum}}$ in the bedload samples also significantly increase, and the $[\text{K}]_{\text{residue}}/[\text{K}]_{\text{bulk-sum}}$ decreases through the estuarine transect (Figures 5.6 and 5.10). Although it is hard to exclude the influence of the remaining K in the dissolved load or in other fractions on the $[\text{K}]_{\text{exchangeable}}$ in the

SPM (Section 5.3.2), the increasing K in the solid samples, both SPM and bedload, nevertheless indicates that K is incorporated into these solids, likely in the exchangeable fraction and clay fractions. This finding is consistent with the interaction experiments in Chapter 4, a previous basalt-river water interaction experiment (Pogge von Strandmann et al., 2019a), and some other studies on natural estuaries, which also indicate the exchange of Ca by K and/or the incorporation of K into the solid load (Sayles and Mangelsdorf, 1979; Pogge von Strandmann et al., 2019a; Tipper et al., 2021; Spiegel et al., 2021; Yang et al., 2021).

Furthermore, at the highest salinity, the Al concentrations in the bulk SPM (2017SPM12 and 13) and the bulk bedload (Bed09 and 10) drop sharply (Figure 5.8), which is probably due to the dilution effect of carbonate formation, likely biogenic due to the visible shell material. The $[Ca]_{\text{carbonate}}$ increases to ~ 20 mg/g and $[Ca]_{\text{carbonate}}/[Ca]_{\text{bulk-sum}}$ reaches as high as 20% in the bedload (Bed07–10) at high salinity (Figure 5.10). In addition, the tidal flow in the Borgarfjörður estuary may transport marine carbonate from the deeper ocean into the estuary, which would be hard to distinguish geochemically from local carbonate formation. Overall, there are evidently multiple processes that influence the major element concentrations of the SPM and bedload particles in the Borgarfjörður estuary.

5.4.2.2 Li concentrations and Li isotopes in SPM particles

In different fractions of the SPM samples from 2017, the $[Li]_{\text{exchangeable}}$, $[Li]_{\text{oxide}}$, $[Li]_{\text{exchangeable}}/[Li]_{\text{bulk-sum}}$, and $[Li]_{\text{oxide}}/[Li]_{\text{bulk-sum}}$ increase through the estuary. In contrast, $[Li]_{\text{clay}}$ and $[Li]_{\text{clay}}/[Li]_{\text{bulk-sum}}$ increase from the river endmember to a salinity of ~ 8 but then decrease at higher salinities (Figure 5.6A). In addition, among the exchangeable, oxide, and clay fractions, the exchangeable fraction gradually becomes the largest reservoir of Li, making up 85% of Li in 2017SPM13. However, as discussed in Section 5.3.2, the Li concentration and δ^7Li values of the SPM samples from 2017 are likely influenced by Li acquired from the sea salts during sampling and filtering, and the interaction with deionised water (Figure 5.7). Thus, for the Li in the estuarine SPM samples collected in 2017, there is probably a mixing relationship between the Li remaining in the river-derived particles when entering the estuary, the Li incorporation from the dissolved load with fractionation in the estuarine transect, and mainly the

remaining dissolved Li during sampling. In addition, particle settling and resuspension may assist in removing the river-derived particles, thereby increasing the proportion of newly-formed secondary minerals in the SPM samples (Figure 5.12). Thus, the $\delta^7\text{Li}_{\text{bulk-sum}}$ and $[\text{Li}]_{\text{bulk-sum}}$ in the 2017SPM samples does not necessarily indicate a binary mixing trend as shown in Pogge von Strandmann et al. (2008), especially in the high salinity zone (Figure 5.13).

In contrast, because of the minor influence of remaining seawater on the SPM samples collected in 2003, those SPM samples indicate a mixing trend between the Li remaining in the river-derived particles when entering the estuary and the Li incorporation from dissolved load after Li isotope fractionation in the estuary. The empirical $\delta^7\text{Li}$ value for the incorporated Li in the Borgarfjörður estuary is $\sim 11.7\text{‰}$ (Pogge von Strandmann et al., 2008), so the fractionation between SPM and the dissolved load (i.e., seawater, $\delta^7\text{Li} = 31\text{‰}$) during Li incorporation in the estuary is constrained as $\Delta^7\text{Li}_{\text{bulkSPM-seawater}} \approx 19\text{‰}$ (i.e., fractionation factor $\alpha_{\text{bulkSPM-seawater}} \approx 0.981$) (Pogge von Strandmann et al., 2008). This value corresponds to the fractionation in the basalt-water interaction experiment (Section 4.4) and is similar to the fractionation reported for the alteration of the oceanic crust by seawater (Chan et al., 1992).

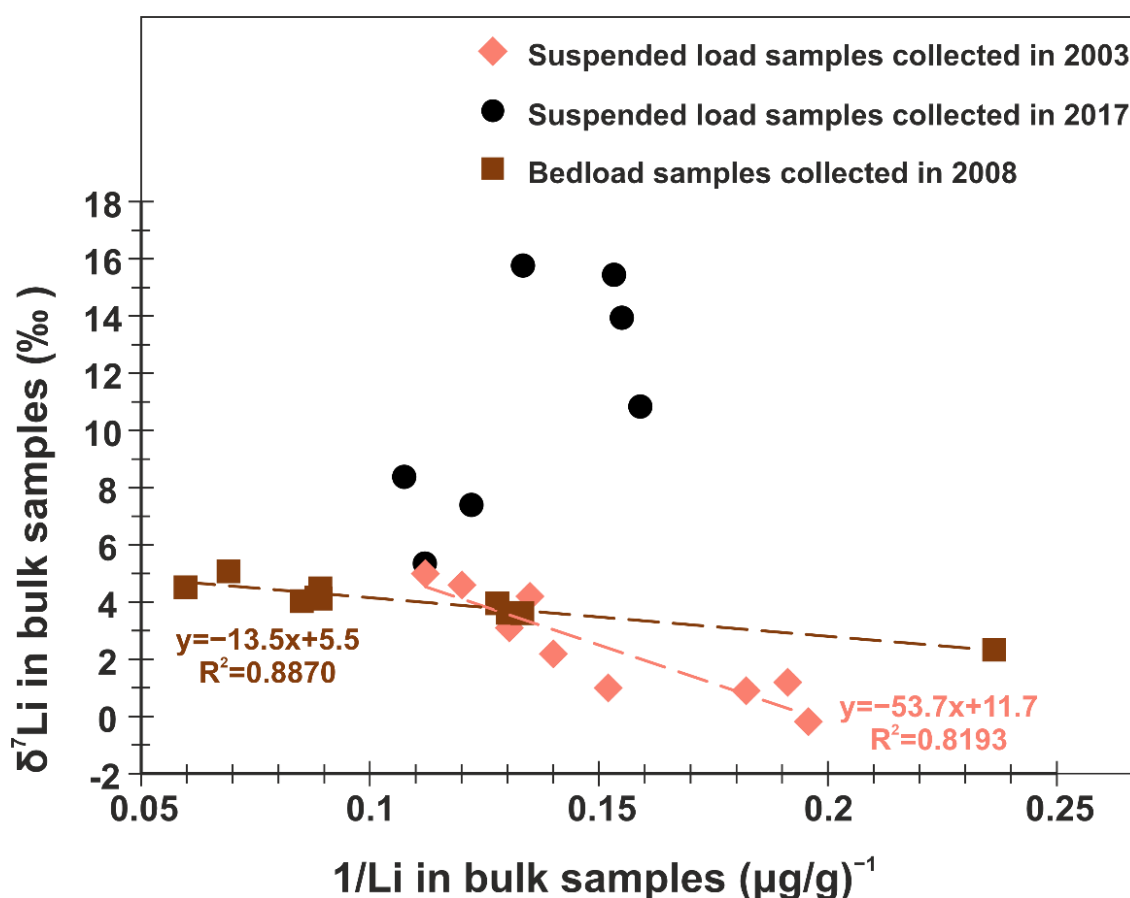


Figure 5.13 The relationship between Li isotopes and Li concentrations in the bulk suspended load and bedload samples

The dashed lines are the linear relationship fitting lines for the bulk bedload samples collected in 2008 and the bulk suspended load samples collected in 2003 (Pogge von Strandmann et al., 2008).

5.4.2.3 Li concentrations and Li isotopes in bedload particles

For bedload samples (Bed01–10) collected in 2008, the Li concentrations and Li isotope compositions of the exchangeable, oxide, and clay fractions generally show similar trends through the estuarine transect (Figure 5.6C and D). In the low salinity zone, at a distance of 0 to 8 km from the river mouth, the Li concentrations increase by around 7.5, 6.1, and 3.4 times in the exchangeable, oxide, and clay fractions, respectively. These increases indicate that secondary fractions (i.e., exchangeable, oxide, and clay fractions) in the bedload lead to a net uptake of Li, which agrees with the SPM samples in this estuary (Pogge von Strandmann et al., 2008), the SPM samples from shallow and deep depths in the Yangtze River estuary (Yang et al., 2021), the SPM and bedload samples in the Amazon estuary (Chapter 6), and the basalt-water interaction experiment in Chapter 4. Furthermore, because the Li in the secondary fractions increases 3–8 times from Bed01 to Bed02 (the low salinity samples), the Li in the secondary fractions of Bed02 becomes dominated by the Li gained in the estuarine environment. Correspondingly, the $\delta^7\text{Li}$ values increase from 11.2 to 17.2‰ in the exchangeable fraction, from 3.8 to 6.3‰ in the oxide fraction, and from 3.3 to 5.1‰ in the clay fraction (Figure 5.6D). Notably, although mineral settling from SPM samples to the bedload could also add Li to the bedload solids, mineral settling in the low salinity zone itself cannot lead to higher $\delta^7\text{Li}$ values. Thus, the increase of $\delta^7\text{Li}$ values in the low salinity zone probably indicates Li incorporation from the dissolved load with Li isotope fractionation.

In the medium and high salinity zones, at a distance of around 8 to 15 km from the river mouth, the Li concentrations generally increase by around 3–4 times in the exchangeable and oxide fractions, and 6.7 times in the clay fraction in bedload (Figure 5.6C). However, the Li isotope values only vary in a relatively narrow range from 16.0–18.9‰, 6.0–9.5‰, and 4.4–6.8‰ in the exchangeable, oxide, and clay fractions, respectively (Figure 5.6D). This variation may stem from the co-effect of geochemical and mechanical processes. Specifically, Li is incorporated from the dissolved load into the secondary fractions (i.e., newly incorporated Li), while simultaneously there is spatial mixing of secondary minerals which contain the newly incorporated Li due to resuspension (Figure 5.12). However, because of the much higher Li concentration in the secondary fractions (i.e., exchangeable, oxide, and clay) in Bed02 than Bed 01, the newly

incorporated Li in the secondary fractions in the estuarine environments with higher $\delta^7\text{Li}$ values dominates over the Li in the secondary fractions from the very low salinity region. Thus, the Li isotope fractionations during the process of Li incorporation from estuarine water into each secondary fraction of the solid are constrained as -11.7 to -14.5‰ ($\Delta^7\text{Li}_{\text{exchangeable-seawater}}$), -21.2 to -24.8‰ ($\Delta^7\text{Li}_{\text{oxide-seawater}}$), and -23.6 to -26.4‰ ($\Delta^7\text{Li}_{\text{clay-seawater}}$) (Figure 5.14A). In Figure 5.14B, the empirical $\delta^7\text{Li}$ values for the incorporated Li in the exchangeable, oxide, and clay fractions are $17.6 \pm 0.3\text{‰}$, $7.5 \pm 0.4\text{‰}$, $5.2 \pm 0.4\text{‰}$, respectively, indicating fractionation between exchangeable, oxide, and clay fractions and seawater of $-13.4 \pm 0.3\text{‰}$ ($\Delta^7\text{Li}_{\text{exchangeable-seawater}}$), $-23.5 \pm 0.4\text{‰}$ ($\Delta^7\text{Li}_{\text{oxide-seawater}}$), and $-25.8 \pm 0.4\text{‰}$ ($\Delta^7\text{Li}_{\text{clay-seawater}}$) (Figure 5.14B). These Li isotope fractionations are essentially identical between the two methods, and fit within the reported range of fractionation between different secondary fractions in the solid and dissolved load, i.e., $\Delta_{\text{exchangeable-water}} = 0$ to -15‰ and $\Delta_{\text{oxide/clay-water}} = -15$ to -28‰ , but closer to the larger fractionation end (Figure 1.3) (Pistiner and Henderson, 2003; Chan and Hein, 2007; Wimpenny et al., 2010b, a; Hindshaw et al., 2018; Pogge von Strandmann et al., 2019a, 2022; Li and Liu, 2020; Andrews et al., 2020; Liu et al., 2022; Yang et al., 2023).

Amongst the secondary fractions (i.e., exchangeable, oxide, and clay fractions), the oxide and clay fractions contribute more than 70% of the Li removal (Figure 5.11). In addition, the Li isotope fractionation ($\Delta^7\text{Li}_{\text{secondaryfractions-seawater}}$) between the combined secondary fractions (i.e., the sum of exchangeable, carbonate (influenced by other secondary fractions), oxide, and clay fractions) and seawater during the process of Li incorporation in the estuary is around -17.1 to -22.8‰ (Figure 5.14A). In Figure 5.14B, the empirical $\delta^7\text{Li}$ value for the incorporated Li in the secondary fractions (i.e., the sum of exchangeable, carbonate (influenced by other secondary fractions), oxide, and clay fractions) in the bedload is $-9.7 \pm 0.7\text{‰}$, which indicates that the fractionation between the secondary fractions and seawater ($\Delta^7\text{Li}_{\text{secondaryfractions-seawater}}$) is $-21.3 \pm 0.7\text{‰}$. This fractionation agrees with the results indicated by the SPM samples from 2003 (Pogge von Strandmann et al., 2008) and the basalt-water interaction experiments (Chapter 4). In addition, this fractionation between basaltic particles and estuarine water under relatively low temperatures of $\sim 15^\circ\text{C}$ is similar to the fractionation between basaltic oceanic crust and seawater during alteration of

oceanic crust in both experimental studies and field studies (Chan et al., 1992; Millot et al., 2010a).

At a salinity higher than 30, i.e., Bed09 and 10 which sit at more than 20 km from the river mouth, the Li concentrations in both the leached fractions and the bulk bedload samples decrease (Figure 5.6C), whereas their $\delta^7\text{Li}$ values remain relatively constant (Figure 5.6D). As discussed in Section 5.4.2.2, the $[\text{Ca}]_{\text{carbonate}}$ and $[\text{Ca}]_{\text{carbonate}}/[\text{Ca}]_{\text{bulk-sum}}$ are higher and the $[\text{Al}]_{\text{bulk-sum}}$ decreases in Bed09 and 10 (Figure 5.10). In addition, the carbonate saturation shifts from undersaturated to oversaturated in the high salinity area (Figure 5.4). Therefore, the decrease in Li concentration may be due to the increase in carbonate and therefore relative decrease in silicate abundance.

For the residue in the bedload samples, the $[\text{Li}]_{\text{residue}}$ increases from 4.0 to 11.4 $\mu\text{g/g}$ through the estuary, whereas the $[\text{Li}]_{\text{residue}}/[\text{Li}]_{\text{bulk-sum}}$ decreases from 95% in the river endmember to ~70% in the high salinity zone (Figure 5.11). In addition, the $\delta^7\text{Li}_{\text{residue}}$ is in a narrow range from 2.2 to 3.1‰, identical to the riverine endmember without any clear increase (Figure 5.6D). Thus, the main reason for the increasing $[\text{Li}]_{\text{residue}}$ appears to be mechanical sorting.

Thus, both the geochemical Li incorporation and mechanical sorting have a significant impact on Li in the bulk bedload samples. The Li incorporation enriches the Li concentrations in the secondary fractions and increases the $\delta^7\text{Li}_{\text{bulk-sum}}$ values throughout the estuarine transect, because the $\delta^7\text{Li}$ value for the Li incorporated in the secondary fractions in the estuarine environment is ~9.7‰, which is higher than for the Li transported from continents (~2‰ for bulk). In contrast, mechanical sorting of river-derived particles helps to accumulate Li through the estuary, because Li is generally enriched in finer-grained particles (Dellinger et al., 2014; Yang et al., 2021). However, mechanical sorting of river-derived particles has little effect on the $\delta^7\text{Li}_{\text{bulk-sum}}$, because the difference in $\delta^7\text{Li}$ values between the clay formed on the continents (i.e., finer riverine particles) and primary minerals (i.e., relatively coarser particles) is small, e.g., ~1‰ in Bed01, and ~2‰ in the regime with low chemical weathering intensity based on data from a global compilation (Dellinger et al., 2014).

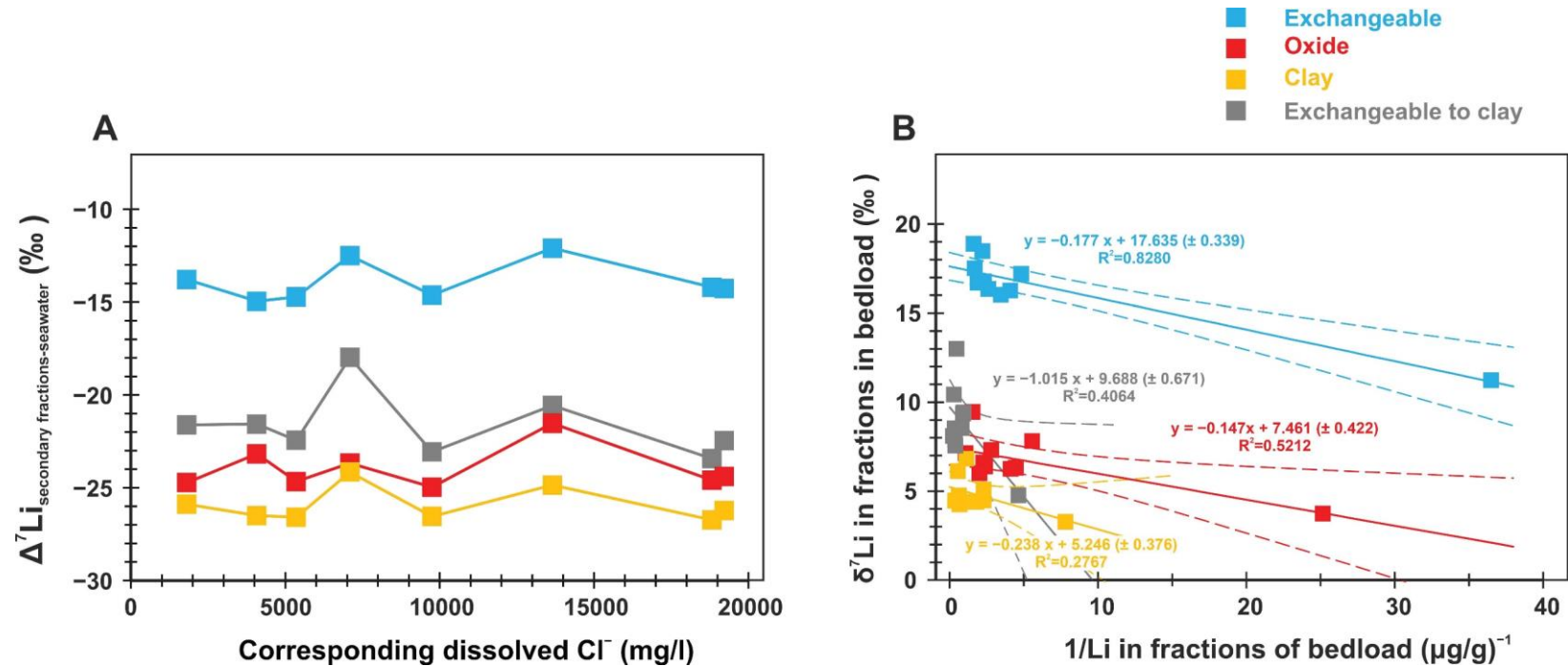


Figure 5.14 Calculated Li isotope fractionation between the leached secondary fractions of the bedload samples and seawater.

A) Li isotope fractionation between the leached secondary fractions of the bedload samples and seawater. The Li isotope value of seawater is set as 31‰. The corresponding dissolved Cl^- concentrations of the bedload samples are assumed to be the same as the surface dissolved load samples collected in 2003 at the same locations (Figure 5.1). Sample Bed08 is not shown because of a lack of corresponding surface dissolved load data at the same location. The fractionation at the river endmember (Bed01) is also not shown. The 'exchangeable to clay' represents the sum of the exchangeable, carbonate (influenced by other secondary fractions, and therefore not shown), oxide, and clay fractions.

B) $\delta^7\text{Li}$ values versus $1/[\text{Li}]$ for the leached secondary fractions of the bedload samples. The solid lines are the best-fit lines for the different fractions. The dashed lines represent the boundaries of the fits with $p < 0.05$. The 'exchangeable to clay' represents the sum of the exchangeable, carbonate (influenced by other secondary fractions), oxide, and clay fractions.

5.4.3 Estimated Li flux from Li incorporation into sediments in the estuary

Due to the multiple processes occurring in the estuary, it is hard to exclusively quantify the Li flux incorporated into the solids. However, as discussed in Section 5.4.2, the changes in Li concentrations and Li isotope compositions in the bulk SPM samples collected in 2003 and in the secondary fractions (i.e., exchangeable, oxide, and clay) of the bedload samples collected in 2008 probably stem from geochemical Li incorporation. According to the secondary fractions of the bedload samples from 2008, these secondary fractions are estimated to incorporate $\sim 1 \mu\text{g/g}$ Li in the low salinity zone, and $\sim 5 \mu\text{g/g}$ through the whole estuarine transect. Amongst the secondary fractions, the exchangeable, oxide, and clay fractions take up $\sim 15\%$, $\sim 20\%$, and $\sim 55\%$ of the Li, respectively. Notably, the Li in the nominal carbonate fraction accounts for $\sim 10\%$, but the carbonate fractions in Bed01–06 are significantly influenced by other secondary fractions. In Pogge von Strandmann et al. (2008), if it is assumed that the changes of Li concentration and Li isotopes of SPM samples in 2003 indicate mixing of the Li from the riverine system and the newly formed Li from the estuarine dissolved load after fractionation, the SPM is estimated to take up $\sim 3 \mu\text{g/g}$ Li through the estuary. Furthermore, as discussed in Section 5.4.2.3, $[\text{Li}]_{\text{bulk}}$ increases due to both solid uptake and mechanical sorting, whereas the $\delta^7\text{Li}_{\text{bulk}}$ increase is likely due to solid uptake. Thus, the influence of mechanical sorting can be eliminated by re-correcting the linear relationship between $\delta^7\text{Li}_{\text{bulk}}$ and $[\text{Li}]_{\text{bulk}}$ in the bedload samples from 2008, while assuming that the empirical Li isotope composition of newly-incorporated Li from the estuarine environment is $11.7 \pm 3.5\text{‰}$ (Pogge von Strandmann et al., 2008), i.e., the $\Delta^7\text{Li}_{\text{secondary fraction-seawater}}$ is around -20‰ (Sections 5.4.2.2 and 5.4.2.3). In this case, $\sim 1.1\text{--}3.7 \mu\text{g}$ Li is estimated to be incorporated per gram of solid during estuarine processes. In addition, although there are variations of dissolved Li concentrations and $\delta^7\text{Li}$ values at a salinity lower than 0.1, the observed dissolved Li concentrations and Li isotopes indicate a general conservative mixing between the riverine endmember and seawater. Based on the mass balance and fractionation laws, if the dissolved load lost more than $\sim 5\%$ Li into the solid fraction with a fractionation of -20‰ , the changes of dissolved Li concentration and dissolved Li isotopes would be higher than the analytical uncertainty (i.e., $\sim 5\%$ RSD for Li concentration and $\sim 1\text{‰}$ 2SD for Li isotopes). Thus, the net Li transfer from the

dissolved load to the solid load is constrained to be less than 5% of the Li mass in the dissolved load. Considering the SPM particle concentrations (Table 5.1), the net Li uptake per gram of solid should be less than 1 μg in the low salinity zone (0.1–1), less than 5 μg in the salinity range of 1–10, less than 10 μg in the salinity range of 10–20, and less than 15 μg in the salinity range of 20–35.

Overall, the solids are estimated to incorporate 1–3 $\mu\text{g/g}$ Li in the estuarine environment with fractionation factors between the dissolved load and the secondary fractions in the solids of -17.1 to -22.8‰ , similarly to the findings in Pogge von Strandmann et al. (2008). Every year, around 3.63×10^{12} g particulate material enters the Borgarfjörður estuary, so around $0.36\text{--}1.09 \times 10^7$ g/yr Li is incorporated into the solids from the dissolved load (similar to the estimate of Pogge von Strandmann et al. (2008)). It is notable that the Li that is newly incorporated by the solids is sourced from both the input of the riverine dissolved load and the seawater during mixing in this estuary. The further implications will be discussed in Chapter 7. In addition, this estimate represents the net Li transfer, because primary mineral dissolution probably also occurs (Chapter 4 and Section 5.4.2.2) (Pearce et al., 2010; Jones et al., 2014).

5.5 Conclusions

In the Borgarfjörður estuary, the dissolved load generally shows conservative mixing between river water and seawater for both Li concentrations and Li isotopes. However, both the Li concentrations and isotope values fluctuate in the very low salinity zone (<0.1), which may result from variability in the various river inputs and tidal flow and/or the alteration of river-derived particles in the estuary. The suspended and bedload samples indicate that both geochemical and mechanical processes affect the solid geochemistry. For bedload samples, the secondary fractions show strong evidence that there is Li incorporation by solids, whereas the mechanical sorting of river-derived particles probably has a greater impact on the Li concentration in the residues. Based on the secondary fractions of the bedload, the Li isotope fractionation between each secondary fraction, i.e., exchangeable, oxide, and clay fractions, and estuarine water are constrained as -11.7 to -14.5‰ ($\Delta^7\text{Li}_{\text{exchangeable-seawater}}$), -21.2 to -24.8‰ ($\Delta^7\text{Li}_{\text{oxide-seawater}}$), and -23.6 to -26.4‰ ($\Delta^7\text{Li}_{\text{clay-seawater}}$), respectively. The fractionation between all secondary fractions combined and estuarine water is around -20‰ . Furthermore,

river-derived particles are estimated to incorporate 1–3 $\mu\text{g/g}$ Li in the estuarine environment, and the proportions of uptake by the exchangeable, oxide, and clay fractions are ~15%, ~20%, and ~55%, respectively (with the remaining fraction in the nominal carbonate). Overall, around $0.36\text{--}1.09 \times 10^7$ g/yr Li in dissolved sourced from both river water and seawater is estimated to be removed into the solids in the Borgarfjörður estuary.

Chapter 6. Alteration of river-derived particles in the Amazon estuary

6.1 Introduction

The Amazon River is the largest river in the world and drains an area of around 6.3×10^6 km² in the tropics of northern South America. It discharges around 6300 km³/yr (6.3×10^{15} kg/yr) of water, representing ~20% of the global river discharge, and 1.2×10^{12} kg/yr of particles to the Atlantic Ocean, which is ~6% of the global river-derived particles (Gibbs, 1967; Milliman and Farnsworth, 2011; Dellinger et al., 2015). Thus, the alteration of river-derived particles in the Amazon estuary likely plays an important role in the global perspective.

The Amazon River originates in the Andes, converges with tributaries from the Guyana and Brazilian Shields, and runs through the Amazon floodplain, before entering the Atlantic Ocean at Para, Brazil (Gibbs, 1967). Over 95% of the particles at its river mouth are silt- and clay-sized particles, consisting of quartz, illite, kaolinite, montmorillonite, and feldspar (Gibbs, 1977; Martinelli et al., 1993). These sediments are mostly derived from the Andes, which contain low-grade uplifted Palaeozoic silicate sedimentary rocks and a few Tertiary and Quaternary sedimentary deposits (Gibbs, 1967; Dellinger et al., 2015).

The continental erosion, chemical weathering, and biogeochemistry of the Amazon river catchment have been widely explored through major elements, trace elements, REEs, and isotope systems including Li, Ni, Sr, Mo, Ba, and U (Gibbs, 1967; Stallard, 1985; Gaillardet et al., 1997; Vital and Stattegger, 2000; Dosseto et al., 2006; Bouchez et al., 2014; Dellinger et al., 2014, 2015; Charbonnier et al., 2020; Revels et al., 2021a, b). Specifically, Li isotopes in the Amazon River water are reported to be controlled by the proportion of Li that enters secondary minerals relative to that supplied from the dissolution of primary rocks, and show a 'boomerang' relationship with the ratio of chemical weathering rates to total denudation rates, where denudation comprises both chemical weathering and physical erosion rates (Dellinger et al., 2015). In addition, several studies have examined the behaviour of elements, especially the trace metals, in the processes of the river-derived particles passing through the estuary or after

the burial in Amazon estuary (Rousseau et al., 2015; Zhang et al., 2020; Spiegel et al., 2021; de Carvalho et al., 2021; Léon et al., 2022; Gledhill et al., 2022; Vosteen et al., 2022; Schneider et al., 2022; Xu et al., 2023). Most of the trace elements show non-conservative behaviour during the mixing of river water and seawater. The source and transport of organic matter in the Amazon estuary has also been investigated (Cai et al., 1988).

However, Li concentrations and Li isotopes, as apparently useful tracers of silicate weathering, have not been examined in the Amazon estuary. Thus, in this chapter, to explore the behaviour of Li concentrations and Li isotopes in the Amazon estuary, and the implications for silicate weathering and element cycles, the element concentrations and Li isotopes in the dissolved load and in different fractions of solid samples (i.e., the suspended load and bedload samples) from the Amazon estuary were analysed (Chapter 6.2 and 6.3). The Li and Li isotope behaviour in the dissolved load and fractions of the solid samples are discussed, and the flux of Li transfer between the dissolved load and solids is estimated according to mass balance and an estuary model (Chapter 6.4.1). In addition, in Chapter 6.4.2, the behaviour of major elements, and its impacts on the carbon cycle are discussed. In Chapter 6.4.3, the influence of geochemical processes and mechanical processes on the alteration of river-derived particles, especially Li concentration and Li isotopes are distinguished.

6.2 Study area and sampling

The continental shelf adjacent to the Amazon River mouth is as wide as 300 km, narrowing to 100 km towards the northwest (Figure 6.1). The inner shelf is relatively flat and smooth to about the 40 m isobath, where the shelf steepens abruptly. The outer shelf (60–100 m water depth) is again relatively flat, but it is mantled with large-scale bedforms oriented perpendicular to the shelf break (Kuehl et al., 1982). In the Amazon estuary, the Amazon River splits into the north and south channels. The Amazon estuary is located under easterly prevailing trade winds, which shift between northeasterly winds (December to June) and southeasterly winds (June to December) (Kuehl et al., 1982; Nittrouer and DeMaster, 1996). The North Brazil Current flows along the Amazon shelf towards the northwest, and is at its maximum strength in July to August and its minimum in April to May (Kuehl et al., 1982; Condie, 1991; Geyer et al., 1996). In addition,

the semi-diurnal tides near the Amazon mouth can produce a strong tidal wave, with a tidal range of up to 10 m, over the shelf and into the river mouth (Gibbs, 1976; Geyer et al., 1996; Nittrouer and DeMaster, 1996).

The freshwater from the Amazon debouches onto the shelf through the north and south channels, and mostly then mixes with seawater in the direction of offshore (Geyer et al., 1996). The bottom water salinity increases to reach 35 at around the 15 m isobath, which is ~150 km away from the river mouth. The near-surface salinity shows seasonal variations, with the surface salinity reaching 35 at ~260 km away from the river mouth during the high-discharge season, but at ~200 km from the river mouth during the low-discharge season (Geyer et al., 1996). In the alongshore direction, part of the freshwater travels northwards and forms a relatively homogenous salinity belt running parallel to the shore, with salinity increasing offshore (Geyer et al., 1996).

The riverine particles discharge through the north and south channels and most of the particles are deposited either directly offshore or alongshore on the Amazon shelf (Kuehl et al., 1986). In the offshore transects, the suspended sediment concentration near the bottom reaches a maximum of more than 0.5 g/l (Gibbs, 1976) at a distance of 100 km from the river mouth. In the alongshore area, the suspended particles can be transported northwest-wards for around 600 km (Gibbs, 1976). Notably, the North Brazil Current and tides may cause resuspension of the ocean surface sediments, and therefore create a fluid mud area (between the 10 m isobath and 20 m isobath) with suspended sediment concentrations near the bottom of >10 g/l (Kuehl et al., 1986; Kineke et al., 1996).

All water and sediment samples were collected from the Amazon estuary during RV Meteor Cruise M147, process study GApr11 of the international GEOTRACES program, in April and May 2018 (Koschinsky et al., 2018). Twelve surface water samples (i.e., dissolved load) were collected in a transect across the mixing zone between the Amazon south channel and seawater, spanning a salinity range from 0.03 to 30.75 (Figure 6.1, Table 6.1). The W56fish sample was collected by a towed fish surface water sampler and the other 11 samples were collected by a Conductivity-Temperature-Depth (CTD) rosette at depths of 2–3 m. The water samples were filtered through 0.45 µm Nucleopore filters and acidified to pH ~2 using concentrated ultrapure distilled HCl. The temperature, salinity, and pH were determined during sampling. The concentration of Cl⁻ (mg/g)

was calculated based on salinity, using $\text{salinity (‰)} = 1.80655 \times \text{Cl}^-$ (Wooster et al., 1969).

Seven suspended particulate matter (SPM) samples were obtained from material that settled during filtering of 20l CTD water samples. At GEOMAR, the SPM was rinsed into pre-cleaned containers using ultrapure water (resistivity = 18.2 MΩ cm). The excess water was removed by siphoning after the SPM had visually settled and then by centrifugation (3220×g, 30 minutes). The SPM was freeze-dried at -52 °C and homogenised before an aliquot was sent to the LOGIC laboratories. Notably, the finest particles were attached on the 0.45 μm Nucleopore filters after filtering, and were hard to remove. Therefore, the finest particles, which account for approximately 3% of the bulk SPM samples by mass, were not included in the following analyses. According to their locations, the SPM samples are divided into two groups (Figure 6.1). Five SPM samples (i.e., SPM27–31) are from a small area with medium salinity, ranging from 1.78 to 12.89, in the north channel. The other two samples (SPM8s and SPM8d) were collected from the same location near the Para River outflow, which is to the south of the Amazon river mouth, but at different water depths (16 m and 20 m, respectively).

Nine marine surface sediment samples were collected by Multi-corer (MUC) and the samples used here were the uppermost 0.5–2 cm of sediment from each core. At GEOMAR, the pore waters were removed by centrifugation (3220g, 30 minutes). The MUC samples were freeze-dried at -52 °C and homogenised before an aliquot was sent to the LOGIC laboratories. According to their locations (Figure 6.1), the MUC samples can be divided into three groups. In the first group, four samples (i.e., 24MUC, 85MUC, 117MUC, and 41MUC) lie on an offshore transect across the north outflow. The five suspended load samples (i.e., SPM27–31) are also located in this transect between 24MUC and 85MUC. In the second group, two samples (i.e., 67MUC and 73MUC) lie on an offshore transect across the southern outflow. The third group consists of four samples (i.e., 85MUC, 89MUC, 108MUC, and 93MUC) in an alongshore transect that starts on the north channel transect at 85MUC.

The elemental concentrations and Li isotope compositions of the 12 dissolved load samples, and the sequential extractions of 7 suspended load samples and 9 marine surface sediment samples, were determined (Chapter 2).

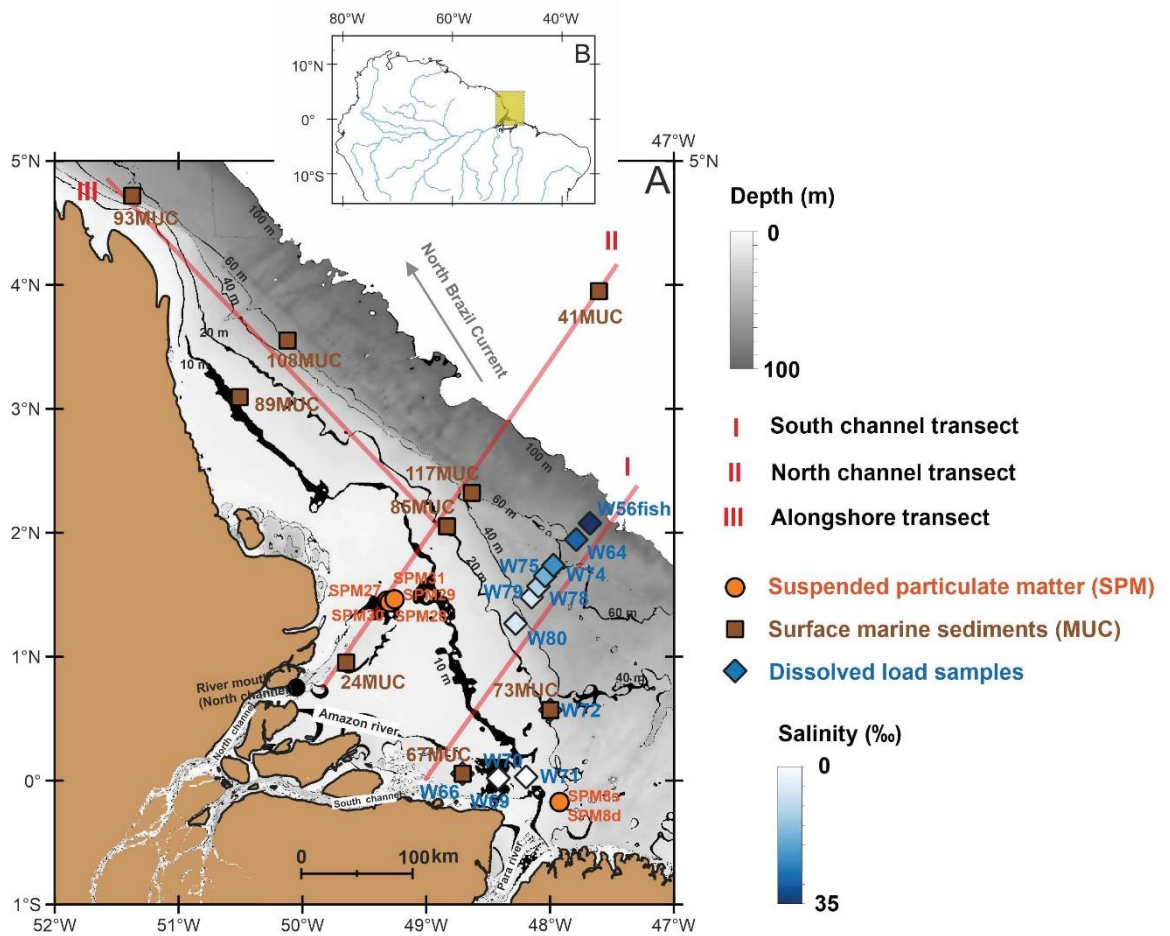


Table 6.1 Sampling locations in the Amazon estuary

Sample	Latitude	Longitude	Depth m	SPM concentration mg/l
W66	00°03.27'N	48°42.45'W	2.4	
W70	00°01.20'N	48°25.02'W	2.5	
W69	00°01.07'N	48°25.11'W	2.4	
W71	00°01.72'N	48°11.60'W	2.3	
W80	01°16.00'N	48°16.71'W	2.9	
W72	00°34.07'N	47°59.88'W	2.7	
W79	01°28.77'N	48°08.91'W	3.1	
W78	01°34.06'N	48°05.65'W	3.1	
W75	01°39.12'N	48°02.38'W	2.8	
W74	01°44.22'N	47°58.39'W	3	
W64	01°56.64'N	47°47.33'W	3.2	
W56fish	02°04.50'N	47°40.71'W	2	
SPM27	01°27.07'N	49°19.04'W	3	262.5
SPM28	01°26.26'N	49°16.85'W	3	257.4
SPM29	01°26.36'N	49°17.21'W	3	367.7
SPM30	01°26.27'N	49°17.86'W	3	588.9
SPM31	01°27.74'N	49°15.37'W	3	570.8
SPM8s	00°10.46'S	47°55.41'W	16	16.0
SPM8d	00°10.46'S	47°55.41'W	20	33.3
24MUC	00°57.11'N	49°38.86'W	23.5	
85MUC	02°03.05'N	48°49.93'W	24.9	
117MUC	02°19.25'N	48°37.90'W	42.8	
41MUC	03°56.93'N	47°36.31'W	1974.2	
89MUC	03°05.65'N	50°30.46'W	21.1	
108MUC	03°33.05'N	50°07.25'W	73.6	
93MUC	04°43.15'N	51°22.51'W	50.6	
67MUC	00°03.29'N	48°42.37'W	15.8	
73MUC	00°34.06'N	47°59.86'W	27.9	

6.3 Results

6.3.1 Dissolved load

The data from the dissolved load are shown in Table 6.2. The dissolved Li concentration increases through the Amazon estuary, displaying a linear relationship with salinity, ranging from 0.87 $\mu\text{g/l}$ (at salinity of 0.03) to 151 $\mu\text{g/l}$ (at salinity of 30.75) (Figure 6.2A). The Li isotope composition ($\delta^7\text{Li}_{\text{diss}}$) increases rapidly from 23.7‰ (at salinity of 0.03) to 31.0‰ (at salinity of 1.03), before increasing more slowly to peak at 32.8‰ (at salinity of 9.33) (Figure 6.2). Subsequently, there appear to be minor fluctuations before a slight decrease to 31.2‰ (identical to the composition of deep seawater) in the most offshore sample (at salinity of 30.75) (Figure 6.2). The concentration of major elements, such as Na, Mg, Ca, and K, also increases in a linear relationship with salinity through the estuary. The total alkalinity also increases with salinity, while the SiO_4^{4-} and NO_3^- decrease with salinity. The pH increases from 7.2 (at salinity of 0.03) to around 8.5 at medium salinity (salinity of around 6–12) and decreases to around 8.0 at high salinity.

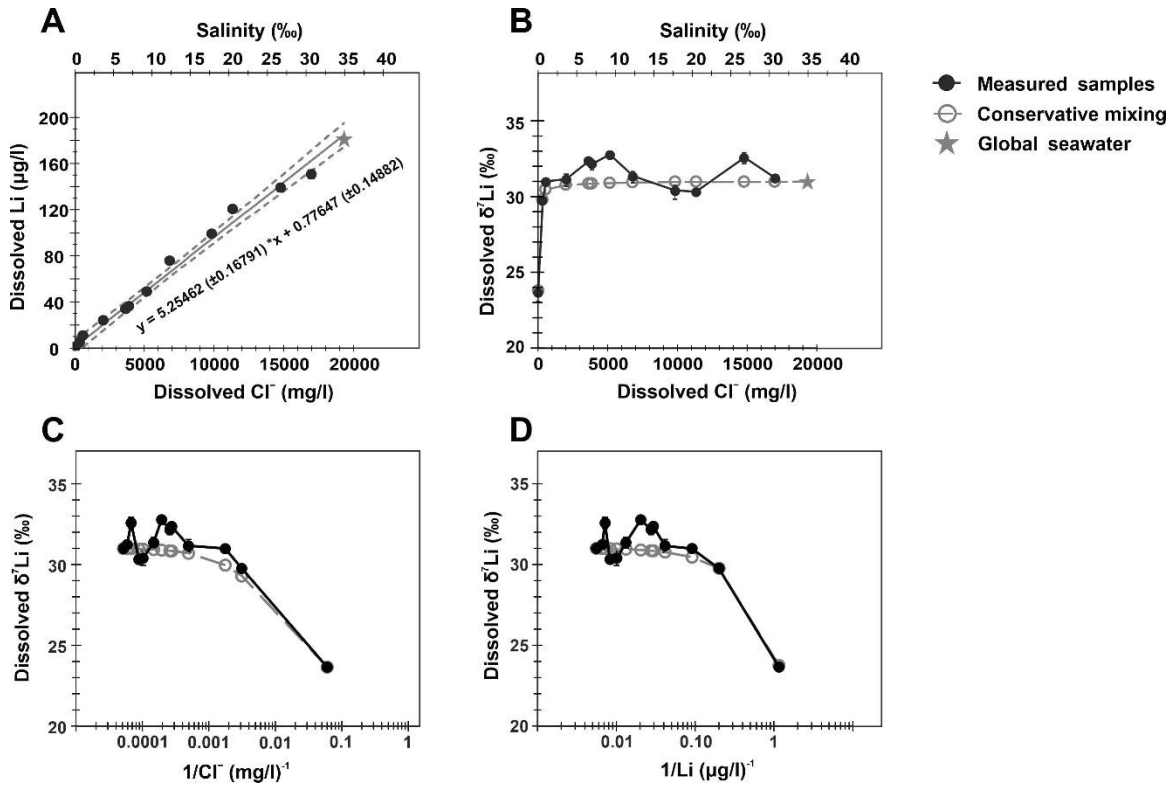


Figure 6.2 Dissolved load Li concentrations and Li isotope compositions.

In panel A, the grey line is a fit to the data and the dashed lines represent confidence levels of $p < 0.05$. The error bars for Li concentration data represent analytical uncertainty (SD). Where not visible, error bars are hidden by sample symbols. In panels B, C, and D, the dashed grey line is a conservative mixing line for Li isotopes (Section 6.4.1.1). The error bars for $\delta^7\text{Li}$ data represent analytical uncertainty (2σ); where not visible, error bars are hidden by sample symbols.

Table 6.2 Chemistry and Li isotope compositions of the dissolved load samples

Sample	Salinity	Temperature °C	pH	Na mg/l	Ca mg/l	Mg mg/l	K mg/l	Li µg/l	$\delta^7\text{Li}$ ‰	2σ ‰	Cl^- mg/l	SiO_4^{4-} µmol/l	NO_2^- µmol/l	NO_3^- µmol/l	Total alkalinity µmol/l
W66	0.03	28.3	7.23	17.3	5.95	3.06	1.63	0.87	23.65	0.29	16.6	150	0.16	12.2	388
W70	0.58	27.0	8.18	258	15.5	31.2	11.3	4.99	29.76	0.18	321	147		14.9	381
W69	1.03	27.8		413	26.7	82.5	26.2	11.0	30.99	0.19	570	141		16.0	
W71	3.67	27.5	8.20	1178	52.7	154	51.7	24.1	31.16	0.40	2032	125	0.44	12.4	576
W80	6.58	28.1	8.65	1986	84.3	256	85.6	34.0	32.37	0.09	3642	66.0	0.11	0.08	820
W72	7.01	28.2	8.53	2075	88.2	266	88.6	36.4	32.17	0.32	3880	50.6	0.30	2.03	1275
W79	9.33	28.0	8.54	2925	124	379	126	49.1	32.78	0.04	5165	67.8	0.08	0.39	1010
W78	12.31	27.9	8.47	4300	182	574	188	75.8	31.35	0.34	6814	58.3	0.11	1.61	1187
W75	17.79	27.9		5466	222	680	228	99.1	30.39	0.45	9848	44.2	0.08	0.55	
W74	20.51	28.1	8.29	6366	263	830	272	121	30.32	0.08	11353	31.0	0.11	0.31	1612
W64	26.76	28.4	8.06	8103	314	1020	333	139	32.58	0.34	14813	16.3	0.06	0.29	1867
W56fish	30.75	28.0		9320	362	1184	381	151	31.24	0.08	17021	1.30			

The two standard deviation of each measured $\delta^7\text{Li}$ value is shown as 2σ . The long-term uncertainty of seawater $\delta^7\text{Li}$ analysis using MC-ICP-MS is 0.63‰ (2SD).

Table 6.3 Elemental concentrations and Li isotope compositions for different phases of the MUC and SPM samples

Sample ID.	$\delta^7\text{Li}$ ‰	$2\sigma^{[1]}$ ‰	$\text{Li}^{[2]}$ μg/g	$\text{Ca}^{[2]}$ mg/g	$\text{Mg}^{[2]}$ mg/g	$\text{K}^{[2]}$ mg/g	$\text{Fe}^{[2]}$ mg/g	$\text{Mn}^{[2]}$ mg/g	$\text{Al}^{[2]}$ mg/g	Na mg/g	$\text{Si}^{[3]}$ mg/g
24MUC exchangeable	5.74	0.00	0.08	0.80	0.51	0.12	0.008	0.004	0.002		
SPM27 exchangeable	9.72	0.07	0.11	0.71	1.17	0.26	0.005	0.002	0.001		
SPM28 exchangeable	9.72	0.28	0.14	0.85	1.41	0.35	0.009	0.002	0.002		
SPM29 exchangeable	11.30	0.28	0.15	0.82	1.37	0.40	0.006	0.001	0.002		
SPM30 exchangeable	14.30	0.36	0.16	0.68	1.18	0.48	0.004	0.001	0.001		
SPM31 exchangeable	13.47	0.05	0.15	0.68	1.19	0.48	0.005	0.001	0.001		
85MUC exchangeable	18.45	0.26	0.31	0.81	1.39	1.15	0.003	0.003	0.002		
117MUC exchangeable	16.37	0.29	0.24	1.11	1.16	0.95	0.005	0.003	0.002		
41MUC exchangeable	17.00	0.47	0.26	1.54	1.34	1.06	0.006	0.001	0.001		
89MUC exchangeable	17.48	0.15	0.29	0.93	1.62	0.99	0.007	0.006	0.001		
108MUC exchangeable	18.56	0.07	0.31	1.19	1.81	1.17	0.004	0.004	0.001		
93MUC exchangeable	16.92	0.34	0.34	1.63	1.87	1.45	0.006	0.004	0.002		
67MUC exchangeable	2.14	0.33	0.08	2.17	0.34	0.12	0.009	0.004	0.001		
73MUC exchangeable	19.83	0.15	0.26	1.32	1.93	1.17	0.013	0.002	0.001		
SPM8s exchangeable	16.84	0.28	0.28	1.22	1.74	0.81	0.005	0.002	0.001		
SPM8d exchangeable	16.56	0.45	0.27	1.38	1.76	0.79	0.007	0.001	0.001		
24MUC carbonate ^[4]	-0.44	0.31	0.06	0.22	0.09	0.04	0.04	0.03	0.02		
SPM27 carbonate ^[4]	0.42	0.01	0.10	0.24	0.23	0.10	0.03	0.03	0.02		
SPM28 carbonate ^[4]	0.61	0.07	0.11	0.20	0.26	0.13	0.03	0.03	0.02		
SPM29 carbonate ^[4]	1.35	0.15	0.13	0.43	0.30	0.17	0.02	0.03	0.02		
SPM30 carbonate ^[4]	4.55	0.24	0.14	0.27	0.29	0.18	0.02	0.02	0.02		
SPM31 carbonate ^[4]	5.21	0.24	0.16	0.27	0.41	0.22	0.03	0.02	0.02		
85MUC carbonate ^[4]	8.21	0.20	0.38	0.34	0.53	0.43	0.08	0.09	0.03		
117MUC carbonate ^[4]	8.39	0.16	0.33	4.29	0.61	0.37	0.12	0.30	0.02		
41MUC carbonate	14.87	0.32	0.33	66.9	0.79	0.36	0.09	0.02	0.01		
89MUC carbonate ^[4]	10.05	0.31	0.32	0.39	0.55	0.37	0.02	0.09	0.02		

Sample ID.	$\delta^7\text{Li}$ ‰	$2\sigma^{[1]}$ ‰	$\text{Li}^{[2]}$ μg/g	$\text{Ca}^{[2]}$ mg/g	$\text{Mg}^{[2]}$ mg/g	$\text{K}^{[2]}$ mg/g	$\text{Fe}^{[2]}$ mg/g	$\text{Mn}^{[2]}$ mg/g	$\text{Al}^{[2]}$ mg/g	Na mg/g	$\text{Si}^{[3]}$ mg/g
108MUC carbonate ^[4]	10.40	0.37	0.36	1.26	0.66	0.46	0.05	0.24	0.02		
93MUC carbonate ^[4]	8.45	0.07	0.44	0.98	0.60	0.55	0.09	0.20	0.02		
67MUC carbonate ^[4]	-5.00	0.44	0.06	0.54	0.06	0.04	0.09	0.05	0.02		
73MUC carbonate ^[4]	10.39	0.31	0.29	1.68	0.69	0.46	0.04	0.06	0.02		
SPM8s carbonate ^[4]	6.77	0.29	0.25	0.50	0.51	0.34	0.03	0.05	0.02		
SPM8d carbonate ^[4]	6.72	0.37	0.27	0.73	0.53	0.31	0.03	0.04	0.02		
24MUC oxide	-2.82	0.10	0.05	0.10	0.02	0.01	0.47	0.17	0.08		
SPM27 oxide	0.32	0.17	0.12	0.14	0.07	0.06	0.72	0.20	0.16		
SPM28 oxide	-0.72	0.16	0.12	0.11	0.07	0.05	0.59	0.19	0.09		
SPM29 oxide	0.77	0.19	0.15	0.12	0.09	0.08	0.69	0.21	0.19		
SPM30 oxide	2.40	0.41	0.16	0.15	0.10	0.07	0.74	0.24	0.12		
SPM31 oxide	2.03	0.25	0.19	0.14	0.13	0.11	0.76	0.23	0.22		
85MUC oxide	4.39	0.29	0.33	0.12	0.16	0.13	0.95	0.03	0.11		
117MUC oxide	5.19	0.17	0.37	0.62	0.20	0.14	1.53	0.20	0.12		
41MUC oxide ^[5]	19.02	0.30	0.59	121	0.60	0.15	0.38	0.26	0.18		
89MUC oxide	4.66	0.35	0.33	0.14	0.17	0.13	0.84	0.22	0.12		
108MUC oxide	6.05	0.17	0.36	0.25	0.20	0.18	1.02	0.43	0.18		
93MUC oxide	4.72	0.04	0.37	0.20	0.18	0.18	1.14	0.21	0.11		
67MUC oxide	-6.23	0.11	0.04	0.14	0.02	0.02	0.97	0.39	0.10		
73MUC oxide	6.11	0.21	0.15	0.26	0.12	0.11	0.65	0.10	0.09		
SPM8s oxide	4.33	0.30	0.24	0.18	0.13	0.14	0.95	0.30	0.17		
SPM8d oxide	4.10	0.05	0.20	0.18	0.12	0.10	0.73	0.24	0.09		
24MUC clay	0.24	0.20	0.19	0.40	0.09	0.02	2.04	0.06	0.57		
SPM27 clay	2.84	0.21	0.42	0.33	0.22	0.05	3.39	0.11	0.94		
SPM28 clay	2.76	0.29	0.51	0.32	0.25	0.06	3.64	0.15	1.02		
SPM29 clay	3.28	0.02	0.52	0.35	0.28	0.06	3.70	0.16	1.03		
SPM30 clay	3.96	0.19	0.60	0.35	0.33	0.08	4.29	0.18	1.17		

Sample ID.	$\delta^7\text{Li}$ ‰	$2\sigma^{[1]}$ ‰	$\text{Li}^{[2]}$ μg/g	$\text{Ca}^{[2]}$ mg/g	$\text{Mg}^{[2]}$ mg/g	$\text{K}^{[2]}$ mg/g	$\text{Fe}^{[2]}$ mg/g	$\text{Mn}^{[2]}$ mg/g	$\text{Al}^{[2]}$ mg/g	Na mg/g	$\text{Si}^{[3]}$ mg/g
SPM31 clay	3.67	0.12	0.68	0.35	0.35	0.09	4.20	0.18	1.14		
85MUC clay	5.37	0.39	0.88	0.34	0.43	0.13	3.33	0.06	1.02		
117MUC clay	4.66	0.03	0.87	0.62	0.49	0.12	4.20	0.10	1.01		
41MUC clay	4.98	0.04	0.71	5.78	0.29	0.09	1.75	0.02	0.66		
89MUC clay	4.51	0.04	0.93	0.25	0.45	0.12	3.78	0.19	1.06		
108MUC clay	5.10	0.09	0.86	0.32	0.46	0.14	3.75	0.24	1.10		
93MUC clay	5.15	0.29	1.21	0.38	0.58	0.15	5.02	0.22	1.00		
67MUC clay	-0.27	0.33	0.22	0.49	0.11	0.02	4.01	0.16	0.77		
73MUC clay	4.47	0.32	0.60	0.37	0.35	0.15	4.54	0.17	1.02		
SPM8s clay	4.17	0.37	0.68	0.29	0.40	0.13	5.51	0.26	1.25		
SPM8d clay	4.12	0.39	0.65	0.35	0.40	0.14	5.02	0.28	1.19		
24MUC residue	-1.58	0.06	32.2	5.35	5.94	14.9	28.3	0.34	59.6		
SPM27 residue	-2.39	0.30	56.4	2.98	8.62	21.4	38.5	0.35	93.8		
SPM28 residue	-2.07	0.07	61.5	2.79	9.21	21.6	42.3	0.39	101		
SPM29 residue	-1.88	0.31	62.4	3.20	9.48	22.2	43.4	0.41	104		
SPM30 residue	-2.55	0.20	61.7	2.70	9.53	22.8	43.6	0.41	101		
SPM31 residue	-1.54	0.52	64.2	3.26	9.84	23.0	45.3	0.41	107		
85MUC residue	-1.99	0.23	56.3	2.98	8.64	19.1	41.8	0.37	91.1		
117MUC residue	-1.70	0.34	49.1	3.91	8.21	18.5	37.0	0.33	85.0		
41MUC residue	-1.82	0.31	31.5	2.70	4.60	6.42	21.0	0.13	47.5		
89MUC residue	-2.25	0.21	66.0	1.97	9.99	21.4	47.7	0.44	105		
108MUC residue	-2.68	0.12	61.6	2.07	9.47	19.6	46.9	0.43	98.8		
93MUC residue	-2.56	0.29	67.8	2.09	10.2	19.7	46.5	0.42	104		
67MUC residue	-1.93	0.06	42.7	5.37	7.33	17.5	34.1	0.35	75.9		
73MUC residue	-1.56	0.05	60.6	2.32	8.73	19.3	45.3	0.39	101		
SPM8s residue	-2.32	0.45	65.0	2.21	9.44	20.6	48.8	0.43	111		
SPM8d residue	-2.57	0.13	71.3	2.01	10.4	22.6	54.3	0.50	121		

Sample ID.	$\delta^7\text{Li}$ ‰	$2\sigma^{[1]}$ ‰	$\text{Li}^{[2]}$ μg/g	$\text{Ca}^{[2]}$ mg/g	$\text{Mg}^{[2]}$ mg/g	$\text{K}^{[2]}$ mg/g	$\text{Fe}^{[2]}$ mg/g	$\text{Mn}^{[2]}$ mg/g	$\text{Al}^{[2]}$ mg/g	Na mg/g	$\text{Si}^{[3]}$ mg/g
24MUC bulk-sum	-1.55		32.6	6.87	6.65	15.1	30.8	0.60	60.2		375
SPM27 bulk-sum	-2.32		57.1	4.40	10.3	21.9	42.7	0.68	95.0		334
SPM28 bulk-sum	-1.99		62.4	4.27	11.2	22.2	46.5	0.76	102		321
SPM29 bulk-sum	-1.79		63.3	4.92	11.5	22.9	47.8	0.81	106		316
SPM30 bulk-sum	-2.42		62.7	4.14	11.4	23.6	48.7	0.85	102		319
SPM31 bulk-sum	-1.42		65.6	4.70	11.9	23.9	50.3	0.84	108		312
85MUC bulk-sum	-1.67		58.2	4.60	11.1	20.9	46.2	0.55	92.3		331
117MUC bulk-sum	-1.42		50.9	10.6	10.7	20.0	42.8	0.94	86.1		335
41MUC bulk-sum	-1.00		33.4	197	7.63	8.08	23.2	0.43	48.3		269
89MUC bulk-sum	-1.98		67.9	3.67	12.8	23.1	52.4	0.94	107		312
108MUC bulk-sum	-2.34		63.5	5.09	12.6	21.6	51.7	1.34	100		318
93MUC bulk-sum	-2.22		70.2	5.29	13.4	22.1	52.8	1.05	105		312
67MUC bulk-sum	-1.92		43.1	8.71	7.86	17.7	39.2	0.95	76.8		351
73MUC bulk-sum	-1.34		61.9	5.96	11.8	21.2	50.5	0.73	102		318
SPM8s bulk-sum	-2.11		66.4	4.40	12.2	22.0	55.3	1.04	113		305
SPM8d bulk-sum	-2.38		72.7	4.65	13.2	24.0	60.1	1.06	123		291
24MUC bulk-measured			33.0	6.34	6.56	15.3	31.9	0.60	61.5	8.34	368
SPM27 bulk-measured			59.4	5.02	10.2	19.3	42.7	0.63	96.4	6.54	327
SPM28 bulk-measured			67.0	4.26	11.5	20.1	45.8	0.76	104	6.61	318
SPM29 bulk-measured											
SPM30 bulk-measured			67.5	5.08	11.2	20.2	46.6	0.77	102	6.77	318
SPM31 bulk-measured			73.8	4.86	11.8	22.1	48.7	0.82	105	7.02	312
85MUC bulk-measured			62.1	4.76	11.2	19.0	47.3	0.52	94.1	14.6	321
117MUC bulk-measured			55.5	10.2	10.8	18.6	43.4	0.91	88.2	15.5	325
89MUC bulk-measured			72.6	4.06	12.6	20.6	51.6	0.90	107	11.7	306
108MUC bulk-measured			69.7	5.20	12.7	20.0	50.8	1.25	104	16.8	306
93MUC bulk-measured			72.2	5.84	13.2	20.4	51.9	1.02	106	17.1	302

Sample ID.	$\delta^7\text{Li}$ ‰	$2\sigma^{[1]}$ ‰	Li ^[2] μg/g	Ca ^[2] mg/g	Mg ^[2] mg/g	K ^[2] mg/g	Fe ^[2] mg/g	Mn ^[2] mg/g	Al ^[2] mg/g	Na mg/g	Si ^[3] mg/g
67MUC bulk-measured			43.4	9.00	7.86	16.6	39.7	0.92	79.8	8.01	343
73MUC bulk-measured			64.8	6.22	11.9	19.7	50.2	0.70	104	17.7	306
SPM8s bulk-measured			81.2	4.72	13.3	21.6	58.1	1.08	120	10.2	290
SPM8d bulk-measured			75.5	4.39	12.4	20.7	55.3	0.92	116	6.99	299

[1] The two standard deviation of each measured $\delta^7\text{Li}$ value is shown as 2σ . The long-term uncertainty of seawater $\delta^7\text{Li}$ analysis using MC-ICP-MS is 0.63‰ (2SD).

[2] Elemental concentrations report the mass of the element in the leachate per gram of solid leached (Eq. 2.1).

[3] Si concentration in bulk sediments is calculated; see Section 6.4.3.

[4] The nominal carbonate fraction is strongly influenced by other phases; see Section 6.3.2.

[5] The oxide fraction of 41MUC is influenced by carbonates; see Section 6.3.2.

The data for 'bulk-sum' are calculated as the sum of exchangeable, carbonate, oxide, and clay fractions and residue in the sequential extraction procedure (Eq. 2.2). The data for 'bulk-measured' are the measured values from the dissolution of bulk samples.

6.3.2 Solid samples

The elemental concentrations and Li isotopes in leachates of sediments are shown in Table 6.3.

Apart from Na, which was added from the leaching reagents, the exchangeable fractions of both SPM and MUC samples are dominated by Mg, Ca, and K, whereas the Fe, Al, and Mn contents are very low (Figure 6.3). In the north channel transect, the $[Ca]_{\text{exchangeable}}$ fluctuates from 0.68 to 0.85 mg/g at low and medium salinity and increases to 1.54 mg/g at high salinity. The $[Mg]_{\text{exchangeable}}$ increases from 0.51 mg/g in the river endmember to 1.17 mg/g at low salinity, and then fluctuates from 1.16 to 1.41 mg/g at higher salinities. The $[K]_{\text{exchangeable}}$ generally increases through the transect from 0.12 to 1.06 mg/g. In the alongshore transect, $[K]_{\text{exchangeable}}$ generally remains constant, whereas $[Ca]_{\text{exchangeable}}$ and $[Mg]_{\text{exchangeable}}$ increase from 0.81 to 1.63 mg/g, and from 1.39 to 1.87 mg/g, respectively. In addition, $[Li]_{\text{exchangeable}}$ increases from 0.08 $\mu\text{g/g}$ near the mouth to around 0.15 $\mu\text{g/g}$ at low salinity, and then increases again to around 0.25 $\mu\text{g/g}$ at high salinity, while $\delta^7\text{Li}_{\text{exchangeable}}$ also increases from 5.7 to 17.0‰ through the transect of the north channel (Figure 6.4). In the alongshore transect, $[Li]_{\text{exchangeable}}$ remains constant at around 0.3 $\mu\text{g/g}$, and the $\delta^7\text{Li}_{\text{exchangeable}}$ values are within a relatively small range of 16.9–18.6‰.

Apart from the sample 41MUC, the operationally defined carbonate leachates of the other MUC and SPM samples are likely influenced by leaching of other fractions, due to their low carbonate content. The sample 41MUC contains 39.7% carbonate, based on total inorganic carbonate analysis (Spiegel et al., 2021). Its $[Ca]_{\text{carbonate}}$ is 66.9 mg/g, which is around 80 times higher than its $[Mg]_{\text{carbonate}}$, which indicates that carbonate dominates its carbonate leachates. The $[Mn]_{\text{carbonate}}/[Ca]_{\text{carbonate}}$ and $[Al]_{\text{carbonate}}/[Ca]_{\text{carbonate}}$ ratios are 0.30 mg/g and 0.13 mg/g, respectively. Furthermore, the $[Ca]_{\text{oxide}}$ of 41MUC is 120 mg/g, which is higher than its $[Ca]_{\text{carbonate}}$, indicating that the oxide leachates of 41MUC appear to be influenced by carbonates that were not fully leached in the previous step, likely because the leaching method used in this study is primarily designed for

silicate soils, sediments, and rocks. The $[\text{Li}]_{\text{carbonate}}$ of 41MUC is $0.33 \mu\text{g/g}$, which represents only approximately 1% of the Li in the bulk sample, while the $\delta^7\text{Li}_{\text{carbonate}}$ of 41MUC is 14.9‰ . In contrast, the $[\text{Mn}]_{\text{carbonate}}/[\text{Ca}]_{\text{carbonate}}$ ratios of the other sediments (except 41MUC) range from 34 to 253 mg/g , and $[\text{Al}]_{\text{carbonate}}/[\text{Ca}]_{\text{carbonate}}$ ratios range from 4 to 118 mg/g . However, the Mn/Ca ratios in leachates of carbonate-dominated samples range from $0.1 \mu\text{g/g}$ to 35 mg/g (Misra and Froelich, 2012; Pogge von Strandmann et al., 2013, 2019b, 2021a; Ullmann et al., 2013; Clergue et al., 2015; Bastian et al., 2018; Dellinger et al., 2020; Jin et al., 2021; Cao et al., 2022; Wei et al., 2023). The recommended $[\text{Al}]_{\text{carbonate}}/[\text{Ca}]_{\text{carbonate}}$ of carbonates leached for the reconstruction of past seawater Li isotopes is less than 0.81 mg/g (i.e., 1.2 mmol/mol) (Cao et al., 2023), 0.54 mg/g (i.e., 0.8 mmol/mol) (Pogge von Strandmann et al., 2013), or even less than 0.27 mg/g (i.e., 0.4 mmol/mol) (Dellinger et al., 2020). Except for 41MUC, the $\delta^7\text{Li}_{\text{carbonate}}$ values of the other sediments, which range from -5 to 10.4‰ , lie between their corresponding $\delta^7\text{Li}_{\text{exchangeable}}$ and $\delta^7\text{Li}_{\text{oxide}}$ values (Figure 6.4).

For the oxide fractions, Fe, Mn, and Al dominate the oxide leachates of the MUC and SPM samples (except 41 MUC) (Figure 6.3). In the north channel transect, $[\text{Fe}]_{\text{oxide}}$ generally increases from 0.47 to 1.53 mg/g with salinity. Meanwhile, $[\text{Fe}]_{\text{oxide}}/[\text{Fe}]_{\text{bulk}}$ fluctuates at around 1.5% from the river endmember up to medium salinity, then increases to 3.6% at a salinity of ~ 20 . In the alongshore transect, $[\text{Fe}]_{\text{oxide}}$ remains stable at around 1.0 mg/g . For $[\text{Mn}]_{\text{oxide}}$, one ocean surface sediment sample, 85MUC, located at the intersection of the north channel transect and the alongshore transect has low $[\text{Mn}]_{\text{oxide}}$ (0.03 mg/g). Except for 85MUC and 41MUC, the $[\text{Mn}]_{\text{oxide}}$ in the north transect varies in a narrow range from 0.17 to 0.24 mg/g ; these values are higher than $[\text{Mg}]_{\text{oxide}}$ and $[\text{K}]_{\text{oxide}}$ in all sediments, and higher than $[\text{Ca}]_{\text{oxide}}$ at low and medium salinity. The $[\text{Mn}]_{\text{oxide}}/[\text{Mn}]_{\text{bulk}}$ is in the range of 20 to 32.3% (except for 85MUC at 6.0% and 41MUC at 60.35%). For $[\text{Al}]_{\text{oxide}}$, the values range from 0.08 to 0.22 mg/g and do not show a clear trend with salinity in the offshore transect or with distance from the river mouth in the alongshore transect. In the north channel transect, $[\text{Li}]_{\text{oxide}}$

increases from 0.05 to 0.37 $\mu\text{g/g}$ with salinity and the $\delta^7\text{Li}_{\text{oxide}}$ values increase from -2.8‰ in the riverine endmember to 5.2‰ at a salinity of 20 (Figure 6.4). In the alongshore transect, the $[\text{Li}]_{\text{oxide}}$ generally remains stable at 0.33–0.37 $\mu\text{g/g}$ and the $\delta^7\text{Li}_{\text{oxide}}$ values range from 4.4 to 6.1‰.

In the clay fraction of most of the MUC and SPM samples (except for 41MUC), Fe and Al are the dominant cations (Figure 6.3). The clay fraction of sediment 41MUC also has a high $[\text{Ca}]_{\text{clay}}$ of 5.78 mg/g, whereas in the other samples the $[\text{Ca}]_{\text{clay}}$ is lower and stable at around 0.35 mg/g, except for slightly higher values in 117MUC (0.62 mg/g). Except for 41MUC, $[\text{Fe}]_{\text{clay}}$ increases from 2.04 to 3.39 mg/g at the start of the Amazon north channel transect, then increases slightly to 4.29 mg/g, and it fluctuates at 3.7–5.0 mg/g in the alongshore transect. For $[\text{Al}]_{\text{clay}}$, the riverine endmember of the north transect has 0.57 mg/g and it varies from 0.94 to 1.25 mg/g in the other sediments. Both $[\text{Mg}]_{\text{clay}}$ and $[\text{K}]_{\text{clay}}$ in the north channel transect increase continuously with salinity, from 0.09 to 0.49 mg/g, and from 0.02 to 0.13 mg/g, respectively. The $[\text{Li}]_{\text{clay}}$ also increases from 0.19 to 0.88 $\mu\text{g/g}$ in the north channel transect, and the $\delta^7\text{Li}_{\text{clay}}$ values generally increase from 0.2 to $\sim 5.0\text{‰}$ (Figure 6.4). In the alongshore transect, the $[\text{Li}]_{\text{clay}}$ generally remains stable at 0.88–1.21 $\mu\text{g/g}$, and the $\delta^7\text{Li}_{\text{clay}}$ ranges from 4.5 to 5.4‰.

The calculated bulk concentrations of elements in all fractions in the sequential extractions (i.e., $[\text{X}]_{\text{bulk-sum}}$) are calculated based on Eq. 2.2, most of which correspond well with the measured bulk element concentrations (Figure 6.5). Among these elements, the $[\text{Al}]_{\text{bulk-sum}}$ is highest, followed by $[\text{Fe}]_{\text{bulk-sum}}$, $[\text{K}]_{\text{bulk-sum}}$, $[\text{Mg}]_{\text{bulk-sum}}$, $[\text{Ca}]_{\text{bulk-sum}}$, and $[\text{Mn}]_{\text{bulk-sum}}$. In the north channel transect, the $[\text{Ca}]_{\text{bulk-sum}}$ is 6.87 mg/g in the river endmember, remains stable at around 4.5 mg/g at low and medium salinity, and increases to 197 mg/g in the carbonate-dominated sediment 41MUC. In contrast, in that same transect, the $[\text{Fe}]_{\text{bulk-sum}}$, $[\text{Al}]_{\text{bulk-sum}}$, $[\text{Mg}]_{\text{bulk-sum}}$, and $[\text{K}]_{\text{bulk-sum}}$ increase in the low salinity zone, and then remain relatively constant at around 1.6 times the river endmember at medium salinity, before decreasing at high salinity. The leaching residue of the sediment samples contains more than 94% of the Li in the bulk sediments, so that the

$[\text{Li}]_{\text{bulk-sum}}$ and $\delta^7\text{Li}_{\text{bulk-sum}}$ are dominated by the residue (Figures 6.4 and 6.5). In the north channel transect, $[\text{Li}]_{\text{bulk-sum}}$ is 32.6 $\mu\text{g/g}$ in the river endmember, remains stable at around 63 $\mu\text{g/g}$ at medium salinity, and decreases to 33.4 $\mu\text{g/g}$ in the offshore sediment 41MUC. Although the $[\text{Li}]_{\text{bulk-sum}}$ at medium salinity is approximately double that of the river endmember, the $\delta^7\text{Li}_{\text{bulk-sum}}$ lies in a narrow range from -2.4 to -1.0‰ for all samples without showing a clear relationship with salinity. In the alongshore transect, $[\text{Li}]_{\text{bulk-sum}}$ ranges from 58.2 to 70.2 $\mu\text{g/g}$, and $\delta^7\text{Li}_{\text{bulk-sum}}$ ranges from -2.3 to -1.7‰ .

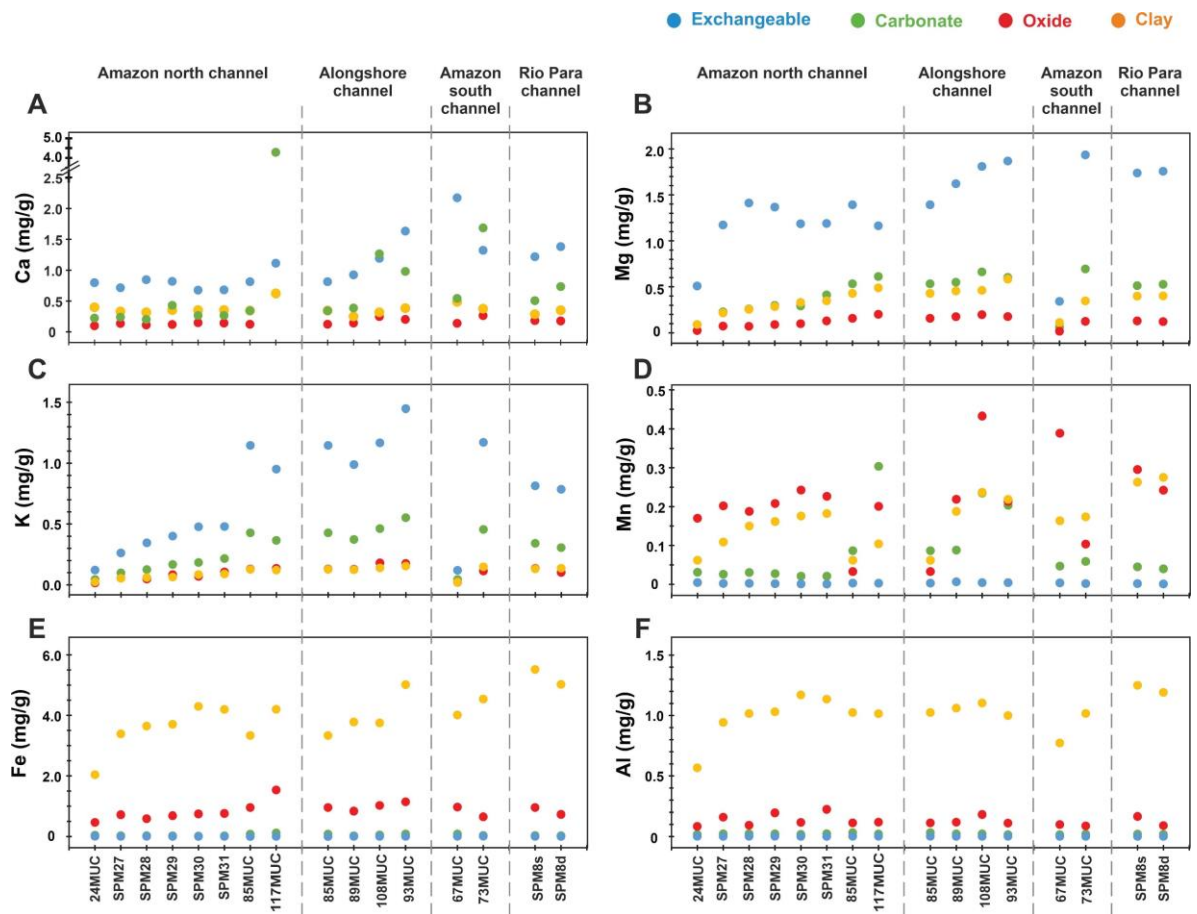


Figure 6.3 Elemental concentrations for different fractions of the sediment samples.

In panel A, the y-axis is broken from 2.5 to 4.0 mg/g. The fractions are separated based on sequential leaching, but note that the carbonate fraction is probably influenced by the leaching of fractions other than carbonate (Section 6.3.2). Also note that data from sample 41MUC are not shown.

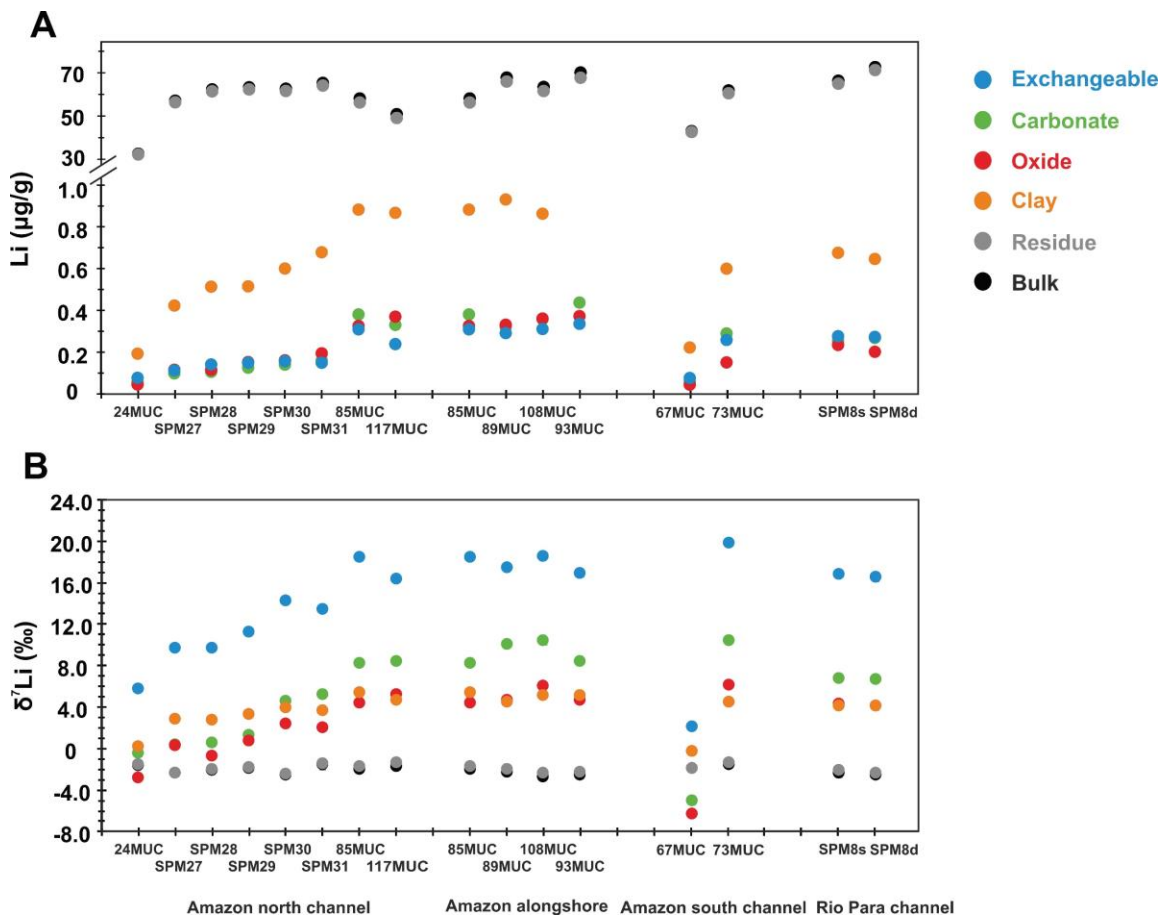


Figure 6.4 Lithium concentrations and isotope compositions for different fractions of solids.

In panel A, the Li concentration axis is broken between 1.0 and 30 µg/g. The fractions are separated based on sequential leaching, but note that the carbonate fraction is probably influenced by the leaching of fractions other than carbonate (Section 6.3.2). The data labelled 'bulk' represent the sum of all fractions (Eqs. 2.2 and 2.3). Where the black data points are not visible, they are hidden by the grey data points because of their similar values. Note that data from sample 41MUC is not shown.

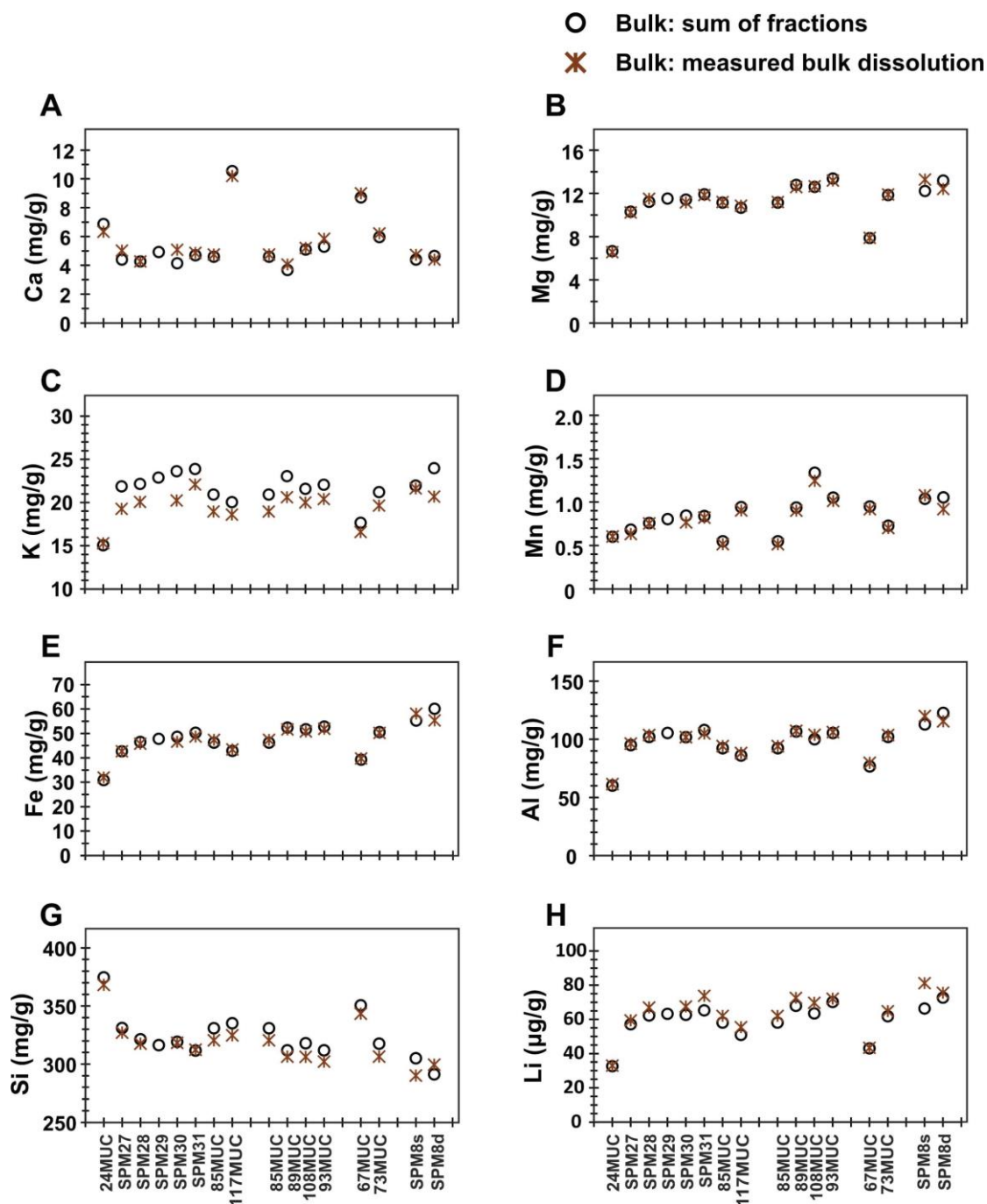


Figure 6.5 Element concentrations in bulk solids.

In panels A–F and H, the brown cross represents the measured element concentrations in the bulk dissolution, and the black circle represents the sum of element concentrations in the different fractions (Eq. 2.2). In panel G, the brown cross represents the Si calculated based on the measured concentrations of Al, Fe, K, Mg, Ca, Na, and Mn in the bulk dissolution, while the black circle represents the Si calculated based on the measured concentrations of Al, Fe, K, Mg, Ca, and Mn in the different fractions (Section 6.4.3).

6.4 Discussion

6.4.1 Uptake of Li by solids from the dissolved load

6.4.1.1 Dissolved Li during mixing of river and seawater

In the transect of the Amazon south channel, the dissolved Li concentrations of surface water samples generally lie within the conservative mixing line between river water and seawater (Figure 6.2A), which agrees with previous studies on other estuaries (Stoffyn-Egli, 1982; Colten and Hanor, 1984; Brunskill et al., 2003; Pogge von Strandmann et al., 2008; Murphy et al., 2014; Yang et al., 2021). Thus, the dissolved Li generally shows conservative behaviour in the Amazon estuary, although the measured Li concentrations of some samples deviate slightly from the precise theoretical mixing line, as also reported by previous studies (Pogge von Strandmann et al., 2008; Yang et al., 2021). The slight deviations may be analytical (i.e., analytical precision of salinity or Li concentration measurements), but are more likely due to mixing variations due to small influences of waves and/or tides, or dissolution/incorporation by particles, as discussed in Section 6.4.1.3. Based on conservative binary mixing of river water and seawater and mass balance, the theoretical conservative mixing of Li isotopes (i.e., $\delta^7\text{Li}_{\text{conservative}}$) can be calculated using Eqs. 6.1–6.6 (Figure 6.2D).

$$[\text{Li}]_{\text{measured}} = [\text{Li}]_{\text{riverwater}} \times FV_{\text{riverwater}} + [\text{Li}]_{\text{seawater}} \times FV_{\text{seawater}} \quad \text{Eq. 6.1}$$

$$FV_{\text{riverwater}} = V_{\text{riverwater}} / V_{\text{total}} = V_{\text{riverwater}} / (V_{\text{riverwater}} + V_{\text{seawater}}) \quad \text{Eq. 6.2}$$

$$FV_{\text{seawater}} = V_{\text{seawater}} / V_{\text{total}} = V_{\text{seawater}} / (V_{\text{riverwater}} + V_{\text{seawater}}) \quad \text{Eq. 6.3}$$

$$FL_{\text{riverwater}} = FV_{\text{riverwater}} \times ([\text{Li}]_{\text{riverwater}} / [\text{Li}]_{\text{measured}}) \quad \text{Eq. 6.4}$$

$$FL_{\text{seawater}} = FV_{\text{seawater}} \times ([\text{Li}]_{\text{seawater}} / [\text{Li}]_{\text{measured}}) \quad \text{Eq. 6.5}$$

$$\delta^7\text{Li}_{\text{conservative}} = \delta^7\text{Li}_{\text{riverwater}} \times FL_{\text{riverwater}} + \delta^7\text{Li}_{\text{seawater}} \times FL_{\text{seawater}} \quad \text{Eq. 6.6}$$

In those equations, $[\text{Li}]_{\text{measured}}$ is the measured Li concentration of each dissolved sample. $[\text{Li}]_{\text{seawater}}$ and $\delta^7\text{Li}_{\text{seawater}}$ represent the Li concentration (180 $\mu\text{g/l}$) and

the Li isotope composition (31.0‰) of the modern global ocean, respectively (Jeffcoate et al., 2004; Tomascak et al., 2016). $[Li]_{\text{riverwater}}$ and $\delta^7Li_{\text{riverwater}}$ are the Li concentration (0.87 $\mu\text{g/l}$) and Li isotope composition (23.7‰) of the Amazon estuarine river, based on the riverine endmember sampled at the south channel (i.e., sample W66). The Li concentrations at the river endmember (W66) are within the ranges of published Li concentrations (0.67–1.04 $\mu\text{g/l}$) near the Amazon River mouth (Huh et al., 1998; Dellinger et al., 2015), and the Li isotope values at the river endmember (W66) are similar to the lower Amazon river water of 22.1‰ (Huh et al., 1998). The $V_{\text{riverwater}}$ and V_{seawater} are the volume that the Amazon River water and seawater contributed to each sample, respectively, based on conservative mixing of Li concentrations (similar to results based on Na or Cl^- concentrations). $FV_{\text{riverwater}}$ and FV_{seawater} refer to the mass fraction of the water volume contributed by the Amazon River and seawater, respectively. The $FLi_{\text{riverwater}}$ and FLi_{seawater} refer to the mass fraction of the Li derived from the Amazon River water and seawater, respectively.

Based on the mixing calculation, the theoretical dissolved δ^7Li value increases to over 30‰ at a very low salinity of 1.03 (equivalent to sample W69) (Figure 6.2), which is due to the significantly higher Li concentration of seawater compared to river water. At a salinity of 1.03, seawater contributes around 92% of the total dissolved Li (i.e., FLi_{seawater}), although the volume of seawater only comprises around 4% of the total water volume (i.e., FV_{seawater}). At a salinity of 6.58, the theoretical conservative mixing-derived δ^7Li value reaches 30.8‰, which is within the range of modern seawater, because the seawater dominates the Li in the dissolved samples (i.e., $FLi_{\text{seawater}} > 98\%$). As shown in Figure 6.2, the measured dissolved Li isotopes ($\delta^7Li_{\text{measured}}$) lie on the mixing line in the low salinity zone, suggesting conservative mixing. However, from a salinity of 6.58–9.33, the $\delta^7Li_{\text{measured}}$ is around 1–2‰ higher than the theoretical mixing line (i.e., analytically distinct, given the long-term external error of $\pm 0.5\%$). The higher $\delta^7Li_{\text{measured}}$ may imply Li uptake by particles, although there is no significant decrease in dissolved Li concentration. At salinities higher than 10, the $\delta^7Li_{\text{measured}}$

appears consistent with conservative mixing (except for one sample with a salinity of 26.76 that shows a higher $\delta^7\text{Li}_{\text{measured}}$). In general, the high seawater Li concentrations may mask the observation of Li isotope fractionation during Li incorporation into the particles (Pogge von Strandmann et al., 2008; Murphy et al., 2014; Yang et al., 2021).

6.4.1.2 Behaviour of Li in the sediment samples

In general, both Li concentrations and $\delta^7\text{Li}$ values in the leachates of the sediment samples increase through the estuary (Figure 6.4). Furthermore, in the north channel transect, $\delta^7\text{Li}_{\text{exchangeable}}$ shows a linear relationship with $1/[\text{Li}]_{\text{exchangeable}}$, supporting the addition of Li to the exchangeable fraction and allowing the $\delta^7\text{Li}$ composition of this endmember to be calculated as $21.7 \pm 2.8\text{‰}$ (Figure 6.6). Assuming derivation from seawater, the fractionation factor ($\alpha_{\text{exchangeable-seawater}}$) between the exchangeable fraction and seawater is calculated as 0.9907 ± 0.0028 (2SD), which is similar to the fractionation factor calculated in previous experimental studies and natural settings (0.99 in Wimpenny et al., 2010b; 0.988 in Pogge von Strandmann et al., 2019a; 0.999 in Hindshaw et al., 2019; 0.992 in Li and Liu, 2020). In the alongshore transect, $[\text{Li}]_{\text{exchangeable}}$ remains constant at around $0.3 \mu\text{g/g}$, and the $\delta^7\text{Li}_{\text{exchangeable}}$ values are within a small range from 17.0 to 18.6‰ (Figure 6.6), which gives an $\alpha_{\text{exchangeable-seawater}}$ value of 0.9860 – 0.9876 , similar to the previous calculation. Overall, the consistent Li concentrations and isotope compositions in those samples may imply that the maximum amount of Li that can be adsorbed on exchangeable sites by the sediments in the Amazon plume is around $0.3 \mu\text{g Li per gram sediment}$ (i.e., $12.5 \pm 1.0 \text{ ng/m}^2$ with surface area of MUC samples at alongshore transect as $24 \pm 2.0 \text{ m}^2/\text{g}$), which is less than 0.5% of the Li in the bulk sediments.

For the oxide fraction, the $[\text{Li}]_{\text{oxide}}$ increases from 0.05 to $0.37 \mu\text{g/g}$ with salinity in the north channel transect (except for sample 41MUC), while the $\delta^7\text{Li}_{\text{oxide}}$ values also increase from -2.8 to 5.2‰ , and show a linear relationship

with $1/[Li]_{\text{oxide}}$ (Figures 6.4 and 6.6). In this case, the empirical value for the endmember is $4.4 \pm 2.0\text{‰}$, which implies that oxides take up Li from seawater with a fractionation factor ($\alpha_{\text{oxide-seawater}}$) of 0.9734 ± 0.0020 (2SD). This value is similar to that reported in some studies (Wimpenny et al., 2010b; Hindshaw et al., 2018; Pogge von Strandmann et al., 2022; Yang et al., 2023), but is a smaller value (implying greater fractionation) than reported in some other studies (Pistiner and Henderson, 2003; Chan and Hein, 2007; Li et al., 2020). To avoid a specific sample dominating the fit, a fitting line without 24MUC (the riverine endmember) is tested, giving an empirical value for $\delta^7Li_{\text{oxide}}$ of $7.1 \pm 1.8\text{‰}$, and giving an $\alpha_{\text{oxide-seawater}}$ of 0.9779 ± 0.0018 (2SD), i.e., virtually identical to the previous value. In the alongshore transect, the Li concentrations are stable at around $0.35 \mu\text{g/g}$ and δ^7Li values vary in a narrow range from 4.4 to 6.1‰ , giving an $\alpha_{\text{oxide-seawater}}$ of $0.9738\text{--}0.9754$.

Similarly, for the clay fraction, δ^7Li_{clay} and $1/[Li]_{\text{clay}}$ also have a linear relationship (Figure 6.6), with $[Li]_{\text{clay}}$ increasing from 0.20 to $0.88 \mu\text{g/g}$ in the north channel transect (except for sample 41MUC), while δ^7Li_{clay} increases from 0.2‰ to around 5.0‰ . This observation implies the uptake of Li by clays in saline water, with an empirical δ^7Li endmember of $5.7 \pm 1.0\text{‰}$, and hence a fractionation factor ($\alpha_{\text{clay-seawater}}$) between the clay fraction and seawater of 0.9747 ± 0.0010 (2SD). This fractionation factor is close to the low end (higher fractionation) of the range reported in previous studies from 0.9950 to 0.9763 (Pogge von Strandmann et al., 2008, 2020a; Andrews et al., 2020). In the alongshore transect, $[Li]_{\text{clay}}$ stabilises at around $1.0 \mu\text{g/g}$ and δ^7Li_{clay} values are from 4.5 to 5.4‰ , giving an $\alpha_{\text{clay-seawater}}$ of $0.9738\text{--}0.9747$.

Among the exchangeable, oxide, and clay fractions, the concentrations of Li retained in exchangeable and oxide fractions in the bulk sediments are similar at $0.3 \mu\text{g/g}$, which is less than the Li retained in the clay fractions ($0.7\text{--}1.0 \mu\text{g/g}$). Furthermore, given that the clay leaching method is designed to obtain the Li isotope composition of the clay fraction rather than to quantitatively leach the entire clay fractions (Chapters 2 and 3), the amount of Li removed into the clay

fraction may be underestimated in this case. Besides, based on the element concentrations in leachates, it appears that the inadvertent leaching of the clay can influence the oxide fraction. However, because of the similar $\alpha_{\text{oxide-seawater}}$ and $\alpha_{\text{clay-seawater}}$, the oxide and clay fractions can be combined. Thus, the amount of Li retained in secondary mineral lattice sites (i.e., oxide and clay) is estimated to comprise more than 90% of the total Li removal (i.e., by exchangeable, oxide, and clay) in the Amazon estuary, as also reported from weathering experiments (Pogge von Strandmann et al., 2019a). These secondary mineral lattice phases can remove Li from saline solutions with larger isotopic fractionations than the exchangeable fraction in the Amazon estuary.

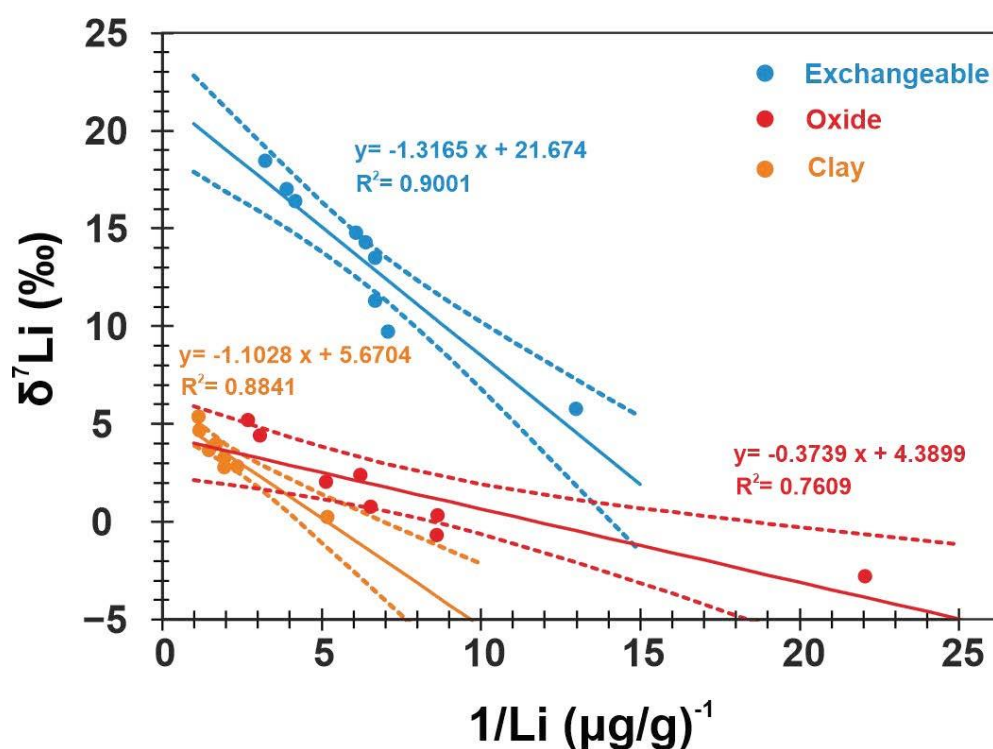


Figure 6.6 $\delta^7\text{Li}$ values versus $1/\text{Li}$ for the different fractions of the sediment samples in the north channel transect.

The solid line is the best-fit line for each fraction. The dashed lines represent the boundaries of the fits with $p < 0.05$. Data from sample 41MUC are not included for the oxide and clay fractions, because of the influence of carbonate.

6.4.1.3 Fractionation modelling of Li removal into sediments

As discussed above, the exchangeable, oxide, and clay fractions of the sediments appear to remove Li from the saline water with accompanying isotopic fractionation in the Amazon estuary, especially along the offshore transect. In the dissolved load, $[Li]_{\text{measured}}$ is indistinguishable from conservative mixing, but the $\delta^7Li_{\text{measured}}$ values are slightly higher than $\delta^7Li_{\text{conservative}}$ values, especially at medium salinity (Figure 6.2).

Here, Rayleigh models (Eq. 6.7) and batch models (Eq. 6.8) are fitted to explore the influence of sediment Li uptake from the dissolved load (Dellinger et al., 2015; Pogge von Strandmann et al., 2019a; Murphy et al., 2019; Yang et al., 2021).

$$\delta^7Li_{\text{after-removal}} = \delta^7Li_{\text{conservative}} + 1000 \times (\alpha - 1) \times \ln(f) \quad \text{Eq. 6.7}$$

$$\delta^7Li_{\text{after-removal}} = \delta^7Li_{\text{conservative}} + 1000 \times \ln(\alpha) \times (f - 1) \quad \text{Eq. 6.8}$$

$$[Li]_{\text{after-removal}} = [Li]_{\text{conservative}} \times f \quad \text{Eq. 6.9}$$

The terms $[Li]_{\text{conservative}}$ and $\delta^7Li_{\text{conservative}}$ are the Li concentration and Li isotope composition in the dissolved load calculated based on conservative mixing. Because the measured dissolved Li concentrations conform to conservative mixing, the $[Li]_{\text{conservative}}$ here is the same as $[Li]_{\text{measured}}$ in Eq. 6.1. In the model, six $[Li]_{\text{conservative}}$ points are designated as 4.99 $\mu\text{g/l}$ (sample W70), 10.99 $\mu\text{g/l}$ (sample W69), 33.96 $\mu\text{g/l}$ (sample W80), 49.10 $\mu\text{g/l}$ (sample W79), 99.11 $\mu\text{g/l}$ (sample W75), and 150.65 $\mu\text{g/l}$ (sample W56fish) (Table S6.1), based on the Li concentrations in the dissolved load in the south channel transect. The terms $[Li]_{\text{after-removal}}$ and $\delta^7Li_{\text{after-removal}}$ are the Li concentration and Li isotope composition in the dissolved load after Li removal by sediments, and α is the fractionation factor between specific sediment fractions and seawater. As outlined in Section 6.4.1.2, the leachate data indicate that $\alpha_{\text{exchangeable-seawater}}$ is approximately 0.9860–0.9935 and $\alpha_{\text{oxide/clay-seawater}}$ is approximately 0.9714–0.9757. Therefore, in the following modelling, $\alpha_{\text{exchangeable-seawater}}$ is set as 0.9900 ± 0.0050 and $\alpha_{\text{oxide-}}$

seawater and $\alpha_{\text{clay-seawater}}$ are set as 0.9750 ± 0.0050 (Table S6.1). These α values are similar to, or slighter smaller than, reported in previous studies (Pistiner and Henderson, 2003; Chan and Hein, 2007; Pogge von Strandmann et al., 2008, 2019a; Wimpenny et al., 2010a; Hindshaw et al., 2018; Li and Liu, 2022). The term f is the fraction of Li that remains in the dissolved load after removal by the sediments calculated from Eq. 6.10.

$$f = 1 - \text{SSC} \times [\text{Li}]_{\text{sediment added}} / [\text{Li}]_{\text{conservative}} \quad \text{Eq. 6.10}$$

Here, SSC is the suspended sediment concentration, and $[\text{Li}]_{\text{sediment added}}$ is the mass of Li per gram that is gained by sediments. The SSC of SPM_{27–31} ranges from 0.26 g/l to 0.59 g/l (Table 6.1). Generally, in the Amazon estuary, the SSC in the surface layer (<3 m) is greater than 0.2 g/l just off the river mouth, greater than 0.5 g/l in the mud resuspension area in the middle of the estuary, but less than 0.1 g/l towards the end of the estuary (Gibbs, 1976; Kineke et al., 1996). The average SSC in the Amazon River estuary has also been calculated as 0.19 g/l based on the Amazon River annual discharge of water and particle load (Gaillardet et al., 1999; Milliman and Farnsworth, 2011). To examine the general situation, the estimated range for SSC is 0.1–1.0 g/l in the model. Based on the data in the fractions of the solid samples (Section 6.4.1.2), $[\text{Li}]_{\text{sediment added}}$ in the exchangeable fraction is set as 0.2 and 0.3 $\mu\text{g/g}$ (Table S6.1). Because of their similar fractionation factors, the oxide and clay fractions can be combined as one fraction whose $[\text{Li}]_{\text{sediment added}}$ is set as 0.5, 1.0, 2.0, 5.0, and 10.0 $\mu\text{g/g}$. (Table S6.1).

The results of the modelling demonstrate that the Li adsorbed by the exchangeable fractions rarely affects either the $[\text{Li}]_{\text{conservative}}$ or the $\delta^7\text{Li}_{\text{conservative}}$ in the dissolved load, while the Li removed by oxides and clay fractions could increase the $\delta^7\text{Li}_{\text{conservative}}$ without significant alteration of the $[\text{Li}]_{\text{conservative}}$ in the dissolved load (Table S6.1). The exchangeable fractions achieve a maximum adsorption of $4.2 \pm 1.9\%$ of the dissolved load Li at a very low $[\text{Li}]_{\text{conservative}}$ of 5 ng/g,

and as a result the $\delta^7\text{Li}$ values in the dissolved load can only increase by $0.28 \pm 0.25\text{‰}$. At a higher salinity (higher dissolved Li concentration), the exchangeable fractions scavenge less than 3%, and generally less than 1% of the dissolved load. This relatively small amount of Li uptake leads to very little increase (less than 0.3‰) in the dissolved $\delta^7\text{Li}$ values. Thus, due to the relatively small amount of Li removal and the modest isotopic fractionation, the exchangeable fractions negligibly change the dissolved Li behaviour, and there is no discernible deviation from conservative mixing. In contrast, due to the large isotopic fractionation ($\alpha_{\text{clay/oxide-seawater}} = 0.9750 \pm 0.0050$), dissolved $\delta^7\text{Li}$ values can be increased by $2.0\text{--}3.2\text{‰}$ by oxide/clay uptake if f is 0.90 (i.e., 10% removal), and by $4.0\text{--}6.7\text{‰}$ if f is 0.80 (i.e., 20% removal). However, the observed conservative mixing for dissolved Li concentrations in the Amazon estuary provides a constraint on f , which has to remain higher than 0.95 (based on the analytical uncertainty 5% RSD of the Li concentrations). Thus, dissolved $\delta^7\text{Li}$ values could be increased by $1.0\text{--}1.5\text{‰}$ by oxide/clay uptake, when f is 0.95 (Figure 6.7A), which may explain the higher measured dissolved $\delta^7\text{Li}$ values in the medium salinity zone than those calculated based on conservative mixing.

The measured data and modelling results of dissolved Li isotopes are compared in Figure 6.7B. At very low salinity (0–0.5), there is little resolvable Li uptake by particles. At low salinity (1–7), although no significant Li isotope fractionation is observed, Li removal could be approximately 1–2%, considering approximately 0.2 g/l SSC (Gibbs, 1976) and $1\text{--}2 \mu\text{g/g} [\text{Li}]_{\text{sediment added}}$ ($\text{SSC} \times [\text{Li}]_{\text{sediment added}} = 0.2 \text{ to } 0.5$). At medium salinity (7–18), Li removal is enhanced up to 5%, linked to 0.5 g/l SSC (Gibbs, 1976) and $4\text{--}5 \mu\text{g/g} [\text{Li}]_{\text{sediment added}}$ ($\text{SSC} \times [\text{Li}]_{\text{sediment added}}$ is up to 2.5). In this case, the Li removal can elevate the dissolved $\delta^7\text{Li}_{\text{measured}}$ values by $1\text{--}2\text{‰}$ higher than $\delta^7\text{Li}_{\text{conservative}}$, without leading to a resolvable decrease in the dissolved Li concentration. The medium salinity zone is affected by resuspension of mud particles due to the tides (Kineke et al., 1996). The particles in this area show higher biogenic silica concentrations, finer grain sizes, and longer interaction times with the dissolved load (Gibbs, 1967;

DeMaster et al., 1983; Kineke et al., 1996), which likely enhances Li removal, but is not expected to affect equilibrium fractionation factors. At higher salinity (>20), due to the high dissolved Li concentrations and low SSC, particle Li uptake could only comprise a relatively small fraction, which would not cause resolvable Li isotope fractionation. Overall, for the Amazon estuary as a whole, based on the assumption that 70% of the particles are deposited in the low and medium salinity area (Kineke et al., 1996), the average $[\text{Li}]_{\text{sediment added}}$ is estimated to be 3–4 $\mu\text{g/g}$.

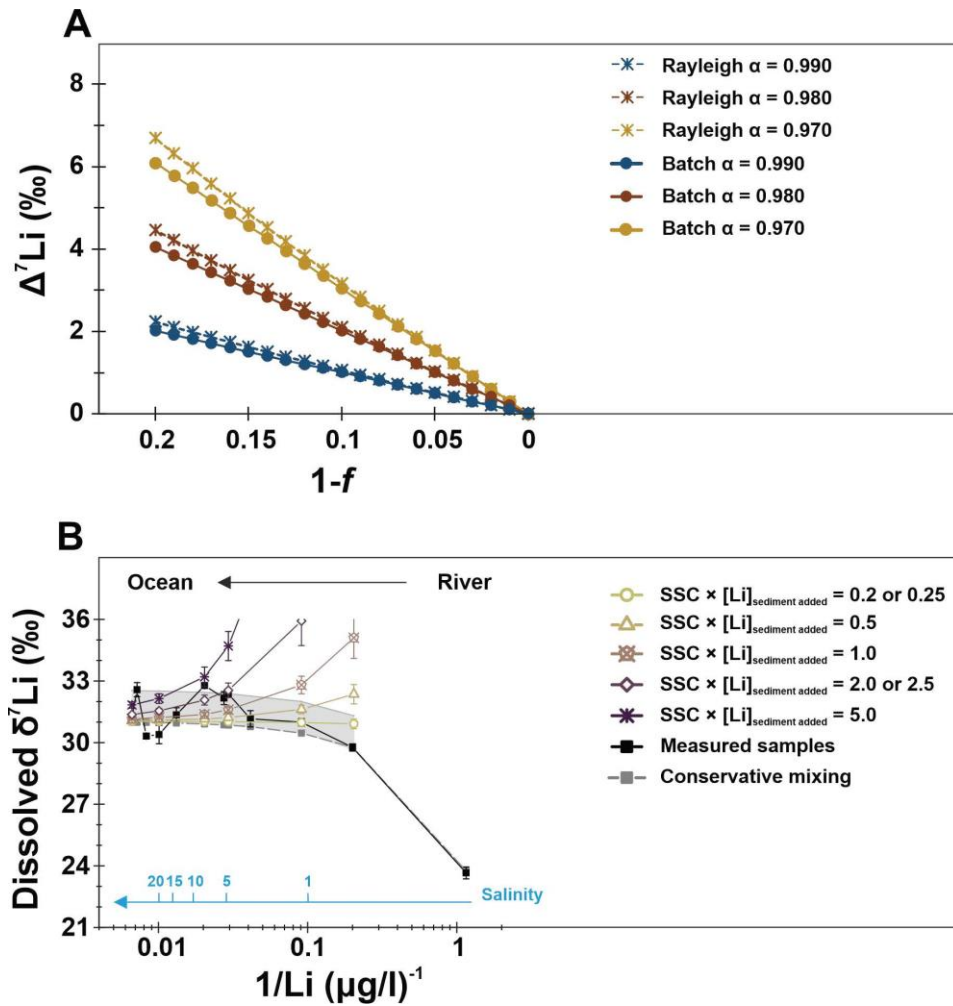


Figure 6.7 Modelled Li isotope fractionation by sediment removal

A) Modelled relationship between the fraction of Li loss and the Li isotope fractionation for the dissolved load (i.e., after Li loss compared to before Li loss in the dissolved load). The term f is the fraction of Li remaining in the dissolved load after Li uptake by sediments (Section 6.4.1.3). Curves are plotted for Rayleigh and batch models and for different fractionation factors (α).

B) Dissolved Li concentrations and Li isotope compositions for measured samples (black symbols and line) compared to a conservative mixing curve (grey dashed line) and to modelled results (coloured open symbols). The blue scale labels the corresponding salinity. The grey shaded region shows the limitation on Li loss of the dissolved Li (less than 5%) at the corresponding Li concentration. SSC is the suspended sediment concentration, and $[\text{Li}]_{\text{sediment added}}$ is the mass of Li per gram that is gained by the sediments. The uncertainty (SD) of $\delta^7\text{Li}$ for the points from the fractionation modelling stems from uncertainty in α (i.e., 0.975 ± 0.005) and the difference between Rayleigh and batch models. The modelled points in the scenario with $\text{SSC} \times [\text{Li}]_{\text{sediment added}} = 0.2$ and 0.25 are combined, as well as the scenario with $\text{SSC} \times [\text{Li}]_{\text{sediment added}} = 2.0$ and 2.5 , and their differences are included in the uncertainty.

6.4.1.4 Estimation of the Li removal flux by estuarine weathering

An estuary model is used to calculate the Li budget accumulated through the entire Amazon estuary, because the amounts of Li incorporated by the solids differs between salinity zones (Section 6.4.1.3). Here, the estuary is assumed to be at steady state, with the exchange of material (i.e., water and particles) between the river, estuary, and ocean being stable with time, and the geochemistry and particle distribution remaining constant with time. For the dissolved load in the estuary, the inputs of dissolved Li are from river water, seawater, and sediment dissolution. However, the sediment samples exhibit net Li removal from the dissolved load rather than Li input. The Li input from sediment dissolution is therefore more than offset by Li uptake by secondary minerals. In other words, the output of dissolved Li in the model is the sediment uptake.

According to the fractionation model (Section 6.4.1.3), the fraction of Li that remains in the dissolved load after sediment uptake (f) was calculated to be 1.00, 0.98, 0.95 and 0.98 at very low, low, medium, and high salinity, respectively (Table S6.2). Thus, the fraction of Li remaining in the dissolved load after sediment removal from the beginning of the Amazon estuary to the corresponding salinity point can be calculated as Σf (Eq. 6.11). Then, Σf_{river} is the fraction of Li (supplied by river water) remaining in the dissolved load (supplied by river water) after Li sediment removal accumulated from the beginning of the estuary to a given point in the estuary (Eq. 6.12). Similarly, the $\Sigma f_{\text{seawater}}$ is the fraction of Li (supplied by seawater) remaining in the dissolved load (supplied by seawater) after Li sediment removal accumulated from the beginning of the estuary to a given point in the estuary (Eq. 6.13).

$$\Sigma f = \int f \times [\text{Li}]_{\text{conservative}} dV_{\text{total}} / \int [\text{Li}]_{\text{conservative}} dV_{\text{total}} \quad \text{Eq. 6.11}$$

$$\Sigma f_{\text{river}} = \int f \times [\text{Li}]_{\text{conservative}} \times F\text{Li}_{\text{riverwater}} dV_{\text{total}} / \int [\text{Li}]_{\text{conservative}} \times F\text{Li}_{\text{riverwater}} dV_{\text{total}} \quad \text{Eq. 6.12}$$

$$\Sigma f_{\text{seawater}} = \int f \times [\text{Li}]_{\text{conservative}} \times F\text{Li}_{\text{seawater}} dV_{\text{total}} / \int [\text{Li}]_{\text{conservative}} \times F\text{Li}_{\text{seawater}} dV_{\text{total}} \quad \text{Eq. 6.13}$$

In the above equations, the terms $FL_{\text{riverwater}}$, FL_{seawater} , and V_{total} are described in the conservative mixing calculation (Section 6.4.1.1). The $[Li]_{\text{conservative}}$ here is the same as $[Li]_{\text{measured}}$ in Eq. 6.1. The Σf , Σf_{river} , and $\Sigma f_{\text{seawater}}$ are mentioned above. Here, Σf , Σf_{river} , and $\Sigma f_{\text{seawater}}$ were calculated using a rectangular numerical integration method. To increase the accuracy of the numerical integration, the $[Li]_{\text{conservative}}$ value is interpolated at every 1 $\mu\text{g/l}$ from 1 to 150 $\mu\text{g/l}$ (Table S6.2). The corresponding salinity is calculated using linear interpolation according to the $[Li]_{\text{measured}}$ between every measured samples. Based on the modelling, the Σf in the Amazon estuary is calculated as 0.96–0.98 at medium and high salinity (Figure 6.8A). Specifically, around 2–3% of the Li contributed from river water, and around 2–4% of the Li contributed from seawater, is removed by the sediments in the Amazon estuary. Therefore, the Li loss from river water in the Amazon estuary is calculated to be around $1.1\text{--}1.7 \times 10^8$ g/yr (i.e., equivalent to 2–3% of the dissolved Li flux of the Amazon River).

Meanwhile, from the sediment perspective, the average $[Li]_{\text{sediment added}}$ is estimated to be 3–4 $\mu\text{g/g}$ using the fractionation model (Section 6.4.1.3). Combined with the Amazon sediment load of around 1.2×10^{12} kg/yr (Milliman and Farnsworth, 2011), the total Li removed from the dissolved load by sediment in the Amazon estuary is estimated to be $3.6\text{--}4.8 \times 10^9$ g/yr. However, it is notable that the removed Li flux is contributed to by both river water and seawater in the estuary. The ratios of seawater-contributed Li mass and the river water-contributed Li mass are calculated using Eqs. 6.14–6.16. The volume of river water ($V_{\text{riverwater}}$) input is regarded as constant throughout the whole estuary, since it represents the integration of river discharge over a period of time, with the Amazon river water input being around 6300 km^3 per year (Milliman and Farnsworth, 2011). Assuming that the Li concentration in the river water at the river mouth also remains stable, the total riverine Li input flux remains stable. In other words, the river water input is assumed to travel through the whole estuary and to mix into the body of ocean water on the shelf (Figure 6.8C). Based on the

mixing model, the total water volume ($V_{total} = V_{riverwater}/F_{V_{riverwater}}$) and the seawater-contributed volume can be calculated, and both increase through the estuary. Thus, the mass of Li from river water and seawater can be integrated as in Eqs. 6.14 and 6.15, and their ratio is as given by Eq. 6.16 (Table S6.2).

$$ML_{riverwater} = \int [Li]_{conservative} \times FLi_{riverwater} dv_{total} \quad \text{Eq. 6.14}$$

$$ML_{seawater} = \int [Li]_{conservative} \times FLi_{seawater} dv_{total} \quad \text{Eq. 6.15}$$

$$ML_{seawater} / ML_{riverwater} = \frac{[Li]_{seawater}}{[Li]_{riverwater}} \times \left(\frac{V_{total} - V_{river}}{V_{river} \times \ln(V_{total}/V_{river})} - 1 \right) \quad \text{Eq. 6.16}$$

In the above equations, $ML_{riverwater}$ and $ML_{seawater}$ represent the mass of Li discharged by the river, and the mass of Li from seawater participating in the conservative mixing, respectively. The $[Li]_{conservative}$ here is the same as $[Li]_{measured}$ in Eq. 6.1. The terms $[Li]_{riverwater}$, $[Li]_{seawater}$, $FLi_{riverwater}$, $FLi_{seawater}$, V_{total} , $V_{riverwater}$, and $V_{seawater}$ are described in the conservative mixing calculation (Section 6.4.1.1).

Based on Eq. 6.16, the seawater-contributed Li mass is integrated as ~36 times that of the river water-contributed Li mass from the river mouth to the middle estuary (i.e., at a salinity of 9.3), ~109 times from the river mouth to a salinity of 17.8, and ~377 times from the river mouth to a salinity of 30.8 (Figure 6.8B). Because the Li removal mainly occurs from the mouth to the middle estuary, the seawater-contributed Li mass is assumed to be ~36 times that of the river water-contributed Li mass, i.e., from the river mouth to the middle estuary at a salinity of 9.3. (Figure 6.8A). In this case, around $1.0\text{--}1.3 \times 10^8$ g/yr of the Li removal by sediment is from river water, which is 1.8–2.4% of the dissolved Li discharge of the Amazon River. This estimate from the sediment perspective is broadly in agreement with the estimate from the dissolved perspective, but the small difference likely stems from the uncertainty in the SSC values and spatial distributions through the estuary. In contrast to the minimal removal of Li derived from river water, it is estimated that around $3.5\text{--}4.7 \times 10^9$ g/yr Li is removed from seawater by Amazon estuarine sediments.

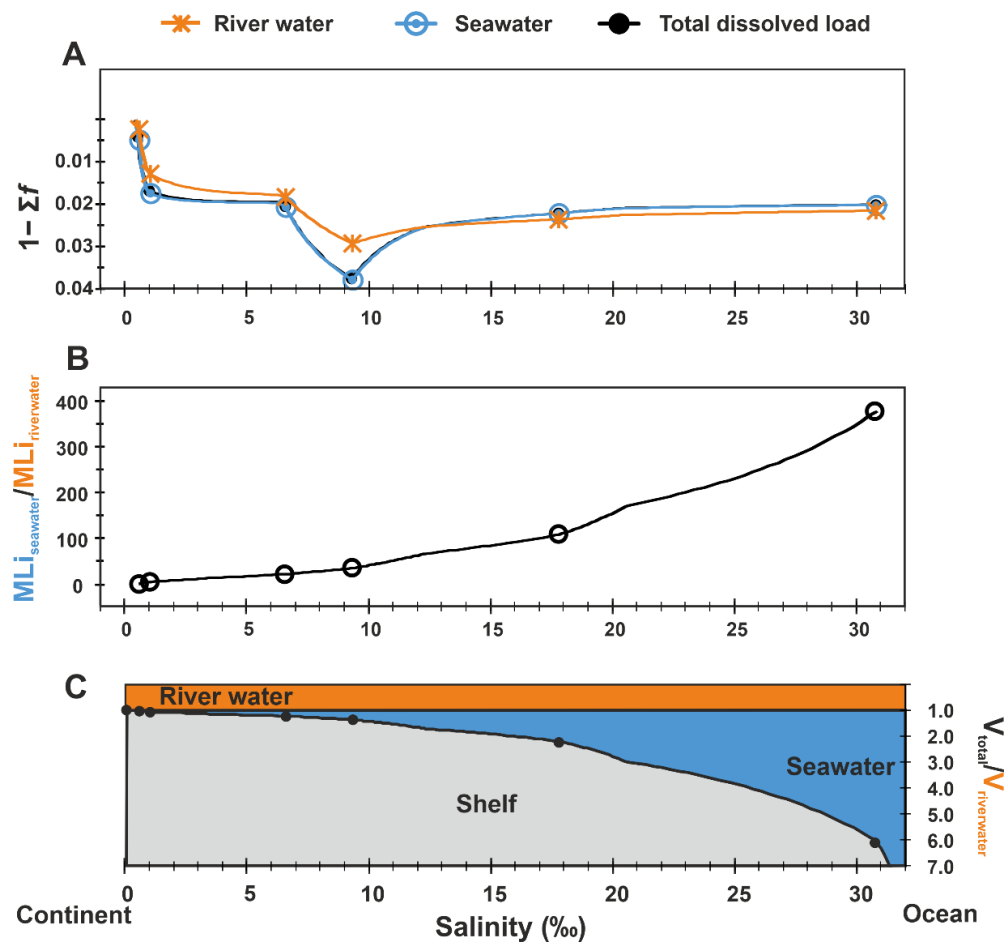


Figure 6.8 Modelled Li loss from the dissolved load through the estuary

(a) The accumulated fraction of Li loss from the dissolved load after sediment removal (i.e., from the start of the Amazon estuary to the corresponding salinity point) (Section 6.4.1.4). The black points represent Σf , which is the fraction of Li that remains in the dissolved load after Li removal by sediments accumulated to a given point in the estuary. The orange cross symbols represent Σf_{river} , which is the fraction of Li supplied by the river water that remains in the dissolved Li after Li removal by sediments accumulated to a given point in the estuary. The blue open circles represent $\Sigma f_{\text{seawater}}$, which is the fraction of Li sourced from the seawater that remains in the dissolved Li after Li removal by sediments accumulated to a given point in the estuary. (b) The ratio of dissolved load Li derived from seawater to that derived from river water through the Amazon estuary (Section 6.4.1.4). (c) The ratio of total water volume to river water volume, and a schematic diagram for river water and seawater volumes in the estuary (Section 6.4.1.4). In all panels, the lines between every points are connected based on the data at the fitting salinities. The fitting salinities are calculated by linear interpolation between two samples whose salinity and Li concentration are obtained by measurements (Section 6.4.1.4).

6.4.2 Retention of major cations during estuarine weathering

In addition to Li, several major elements, such as Na, K, Mg, and Ca, may transfer between the dissolved load and sediments during estuarine weathering, which is likely to influence ocean biogeochemistry and the carbon cycle. It is known that continental silicate weathering consumes atmospheric CO₂, if the dissolved cations and alkalinity produced during continental silicate weathering are transported into the ocean by rivers and deposited as carbonate (Berner and Berner, 1996). In contrast, if the dissolved cations and alkalinity are adsorbed and/or incorporated by aluminosilicate and/or hydroxide particles, there is no net atmospheric CO₂ consumption (Mackenzie and Kump, 1995; Berner and Berner, 1996). Thus, it is important to examine the fate of the cations, especially the Ca and Mg, which are the major cations during carbonate formation.

6.4.2.1 Exchangeable fractions

Some major elements in the riverine dissolved load, such as K, Mg, and Ca, can be attracted by the charged surfaces of sediments, especially clays (Sposito et al., 1999; Tipper et al., 2021). Although there is no direct alkalinity transfer during ion exchange (White, 2013), the adsorption of cations, especially Ca and Mg, can affect the cycle of Ca and Mg and the pH of seawater in theory, as well as affecting the charge balance of the water, and hence may influence the carbon cycle (Pogge von Strandmann et al., 2019a; Tipper et al., 2021). Notably, the exchangeable cations could return to the dissolved load during subsequent diagenesis (Higgins and Schrag, 2010), because of the rapid interaction between the exchangeable fraction and porewater (Sayles and Mangelsdorf, 1979; Lupker et al., 2016; Tipper et al., 2021).

The [Ca]_{exchangeable} in the riverine endmember from the north channel (24MUC) and south channel (67MUC) transects are 0.8 mg/g and 2.2 mg/g, respectively, while the [Ca]_{exchangeable} in the estuarine sediments varies from 0.7 to 1.5 mg/g. There is no clear relationship between [Ca]_{exchangeable} and [Li]_{exchangeable} (Figure 6.9A), while [Ca]_{exchangeable}/[Li]_{exchangeable} decreases with increasing $\delta^7\text{Li}_{\text{exchangeable}}$

(Figure 6.9B) and increasing salinity. Furthermore, $[Ca]_{\text{exchangeable}}/[Li]_{\text{exchangeable}}$ is much lower in the estuary than in the riverine endmember. Therefore, the estuarine exchangeable fraction may not be a significant sink for continent-derived Ca (Sayles and Mangelsdorf, 1979). In contrast, the Amazon estuary exchangeable fraction is likely a sink of continent-derived Mg (Sayles and Mangelsdorf, 1979). The $[Mg]_{\text{exchangeable}}$ in the estuarine sediments varies from 1.2 to 1.9 mg/g, which is higher than $[Mg]_{\text{exchangeable}}$ in the riverine endmember from the north channel (0.5 mg/g) and south channel (0.3 mg/g) (Figure 6.3). Interestingly, the $[K]_{\text{exchangeable}}/[Ca]_{\text{exchangeable}}$ and $[K]_{\text{exchangeable}}/[Mg]_{\text{exchangeable}}$ ratios in the Amazon estuarine sediments are higher than in Amazon River sediments. This difference implies that the dominant cations in the exchangeable fraction shift from Ca in the river sediments to K, as well as Na (Sayles and Mangelsdorf, 1979), in the estuarine sediments, which is also observed globally (Lupker et al., 2016; Tipper et al., 2021).

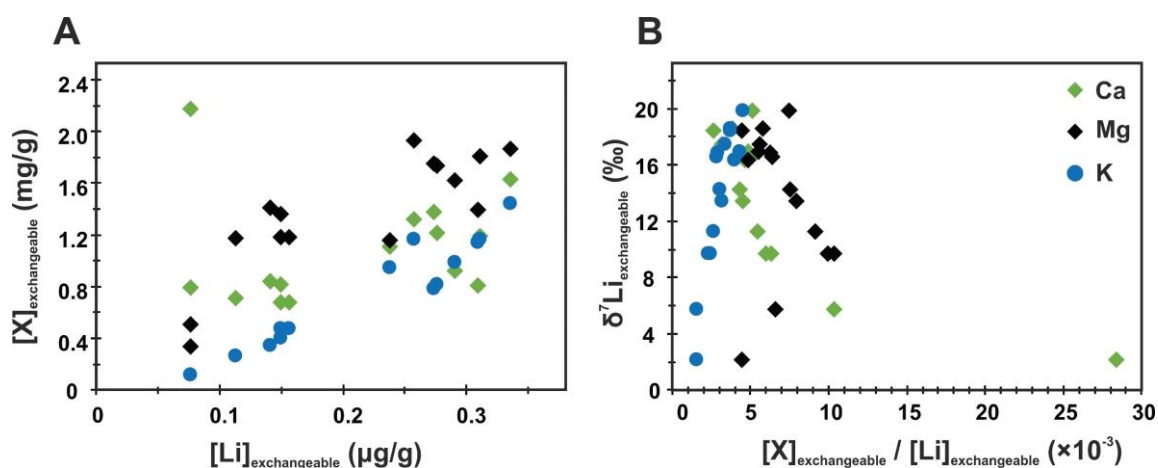


Figure 6.9 The adsorption of cations by the exchangeable fraction.

A) Trends of major element concentrations (Ca, Mg, and K) with Li concentrations in the exchangeable fraction of the sediment samples, i.e., SPM and MUC.

B) Trends of major element concentrations (Ca, Mg, and K) with Li isotope compositions in the exchangeable fraction of the sediment samples, i.e., SPM and MUC.

The element ratios are by mass.

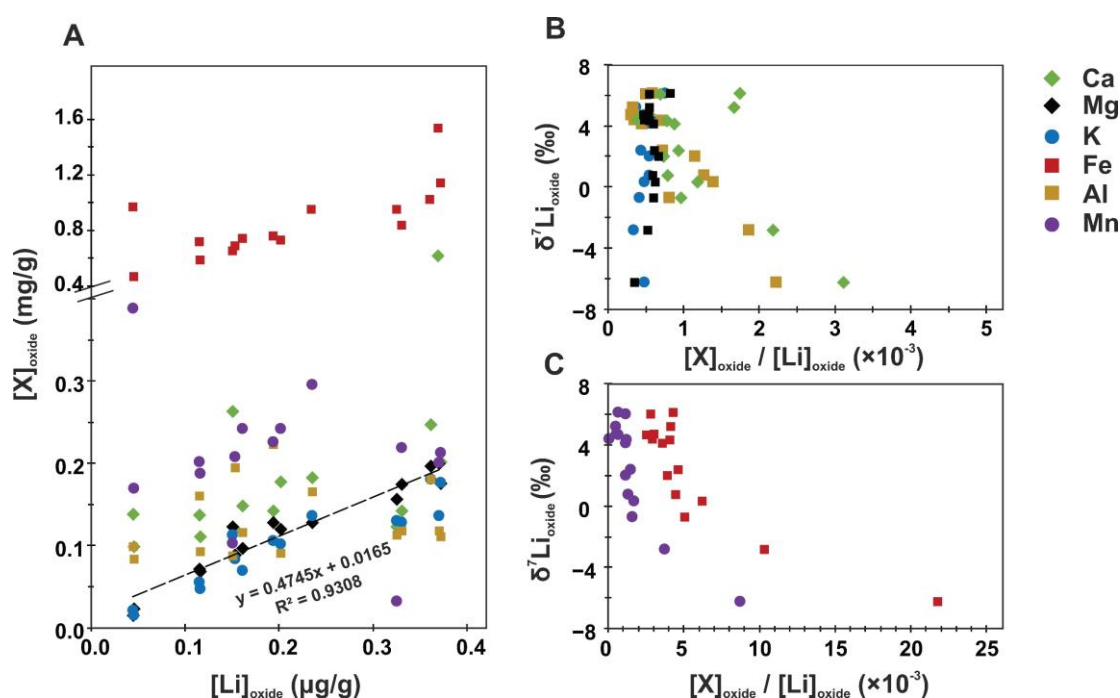


Figure 6.10 The retention of cations in oxide fractions

A) Trends of major element concentrations (Ca, Mg, K, Fe, Al, and Mn) with Li concentrations in the leached oxide fraction of the sediment samples, i.e., SPM and MUC (except for 41MUC). The black dashed line is a best-fit line for $[Mg]_{\text{oxide}}$ and $[Li]_{\text{oxide}}$.

B) Trends of Ca, Mg, K, and Al concentrations with Li isotope compositions in the leached oxide fraction of the sediment samples, i.e., SPM and MUC (except for 41MUC).

C) Trends of Fe and Mn concentrations with Li isotope compositions in the leached oxide fraction of the sediment samples, i.e., SPM and MUC (except for 41MUC).

The element ratios are by mass.

6.4.2.2 Retention of cations in oxides

Except for sample 41MUC, the $[Fe]_{\text{oxide}}$ in the other leachates shows a positive relationship with $[Li]_{\text{oxide}}$ (Figure 6.10). In contrast, $[Al]_{\text{oxide}}$ are generally constant through the estuary and do not show clear relationships with $[Li]_{\text{oxide}}$. The different trends between $[Fe]_{\text{oxide}}$ and $[Al]_{\text{oxide}}$ may imply that there is less formation of Al-oxides (i.e., gibbsite), while more formation of Fe-oxides (e.g., ferrihydrite, lepidocrocite, or goethite) through the Amazon estuary. Such a

scenario seems reasonable, because Fe removal in estuaries is regarded as highly related to flocculation (Boyle et al., 1977; Sholkovitz et al., 1978). The Fe-oxide formation and settling may enhance the burial of marine or terrestrial-derived organic carbon and therefore influence the carbon cycle (Benner and Opsahl, 2001; Callahan et al., 2004; Bianchi et al., 2018; Zhao et al., 2023).

Furthermore, $[\text{Mg}]_{\text{oxide}}$ also increases through the estuary and shows a positive linear relationship with $[\text{Li}]_{\text{oxide}}$, while the $[\text{Mg}]_{\text{oxide}}/[\text{Li}]_{\text{oxide}}$ ratio is the same as in the clay fraction (Figure 6.11). Since Mg is not the major element in oxide fraction and Amazon sediments contain more secondary clays than secondary oxides (Martinelli et al., 1993), the oxide leachates may be additionally influenced by inadvertent leaching of the clay or residue (Chapter 2). In contrast, a recent study in Yangtze River estuary stressed the importance of oxide formation for element cycles (Yang et al., 2023).

6.4.2.3 Retention of cations in clays

The element concentrations in the clay fraction indicate the retention of cations by aluminosilicate particles. Both $[\text{Mg}]_{\text{clay}}$ and $[\text{K}]_{\text{clay}}$ increase through the estuary (Figure 6.3) and have a positive relationship with both $[\text{Li}]_{\text{clay}}$ and $\delta^7\text{Li}_{\text{clay}}$ (Figure 6.11). In contrast, $[\text{Al}]_{\text{clay}}$ and $[\text{Fe}]_{\text{clay}}$ increase at low salinity but remain stable after medium salinity. Therefore, $[\text{Al}]_{\text{clay}}/[\text{Li}]_{\text{clay}}$ and $[\text{Fe}]_{\text{clay}}/[\text{Li}]_{\text{clay}}$ decrease through the estuary and display a negative relationship with $\delta^7\text{Li}_{\text{clay}}$ values (Figure 6.11). This finding indicates that the concentrations of mobile cations (e.g., Mg, K, and Li) in the clay fraction increase through the estuary, which may be caused by the changes in water composition from river to estuary. The concentrations of dissolved Mg, K, and Li in the saline water are much higher than in river water, while the dissolved Al and Fe concentrations decrease to very low levels in the low salinity zone due to flocculation in the estuary (Boyle et al., 1977; Sholkovitz, 1978). The increasing concentrations of mobile cations in the clay is also supported by mineral stability diagrams (calculated by PhreePlot, using the parameters also used in the PHREEQC calculations), which show a shift from the

kaolinite (1:1 structure clay) field in the river water to the Na/K-mica or Na/K-smectite (2:1 structure clays) fields in the estuary (Figure 6.12) (Velde, 1995). Compared to kaolinite, mica and smectite can retain more cations (e.g., Na, K, Mg, Li). Although other processes operating across the estuary transect, such as the mechanical sorting of river-derived sediments or the differential flocculation of different clays, could also lead to a shift from kaolinite to montmorillonite (Gibbs, 1967, 1977), the increased $\delta^7\text{Li}_{\text{clay}}$ values nevertheless indicate the chemical retention of cations.

Interestingly, $[\text{Mg}]_{\text{clay}}/[\text{Li}]_{\text{clay}}$ and $[\text{K}]_{\text{clay}}/[\text{Li}]_{\text{clay}}$ generally remain constant at 500 and 150, respectively, through the estuary (Figure 6.11). In the dissolved load, starting from a salinity of 0.58, the concentration ratios of Mg and Li, and of K and Li are stable at around 7300 and 2000, respectively. These data may indicate an uptake of K, Mg, and Li by the clays in equal proportions, possibly because major cations (but also Li) are present in high concentrations in the brackish/saline water, due to inflow from seawater. In this case, clays (as well as oxides) incorporate $\sim 2 \mu\text{g Li}$ for every 1 mg Mg incorporated (Figure 6.11). According to the calculations for sediment removal from the Li isotope fractionation model, the $[\text{Li}]_{\text{sediment added}}$ is around 3–4 $\mu\text{g/g}$ and the total Li removal is $3.6\text{--}4.8 \times 10^9 \text{ g/yr}$ (Section 6.4.1.3 and 6.4.1.4). Therefore, the Mg incorporated into clays in the Amazon estuary is calculated to be $1.8\text{--}2.4 \times 10^{12} \text{ g/yr}$. Furthermore, calculations using PHREEQC (Parkhurst and Appelo, 2013) show that Mg-clays, such as sepiolite, are highly supersaturated, with their saturation index (SI) increasing from around 10 to 17 at low to medium salinity and then decreasing to around 14 at high salinity (Figure 6.13). Thus, the Mg incorporated in clays during estuarine processes likely has a significant influence on the Mg cycle in the ocean (Tipper et al., 2006; Berg et al., 2019; Shalev et al., 2019), although the Mg incorporated into clays during estuarine processes could subsequently be altered during diagenesis after burial (Higgins and Schrag, 2010). In contrast, $[\text{Ca}]_{\text{clay}}$ remains relatively stable throughout the estuary (excluding the high-carbonate sample 41MUC) and $[\text{Ca}]_{\text{clay}}/[\text{Li}]_{\text{clay}}$ decreases with

increasing $\delta^7\text{Li}_{\text{clay}}$ (Figure 6.11). In addition, the calculated SI of calcite and dolomite changes from undersaturated at low salinity to supersaturated at medium salinity, which implies carbonate formation (Figure 6.13). Therefore, in the Amazon estuary, river-derived dissolved Ca is more likely to participate in carbonate formation than retention by clays.

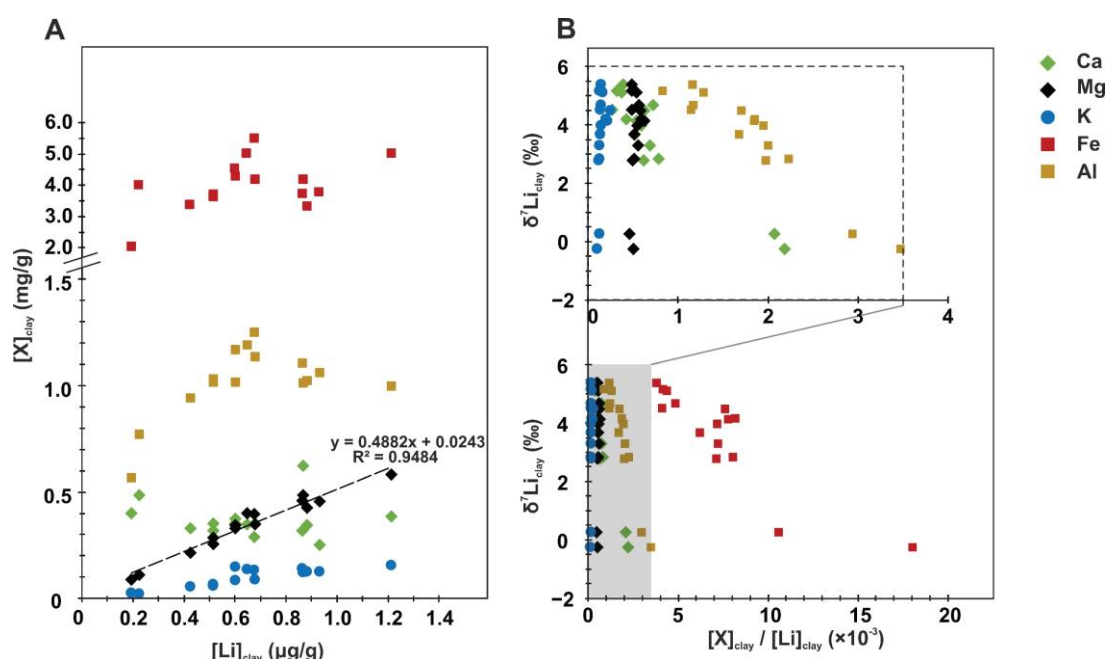


Figure 6.11 The retention of cations in the clay fractions.

A) Trends of major element concentrations (Ca, Mg, K, Fe, and Al) with Li concentrations in the leached clay fraction of the sediment samples, i.e., SPM and MUC (except for 41MUC). The black dashed line is a best-fit line for $[\text{Mg}]_{\text{clay}}$ and $[\text{Li}]_{\text{clay}}$.

B) Trends of major element concentrations (Ca, Mg, K, Fe, and Al) with Li isotope compositions in the leached clay fraction of the sediment samples, i.e., SPM and MUC (except for 41MUC). The shaded area is magnified in the inset graph surrounded by the dashed box.

The element ratios are by mass.

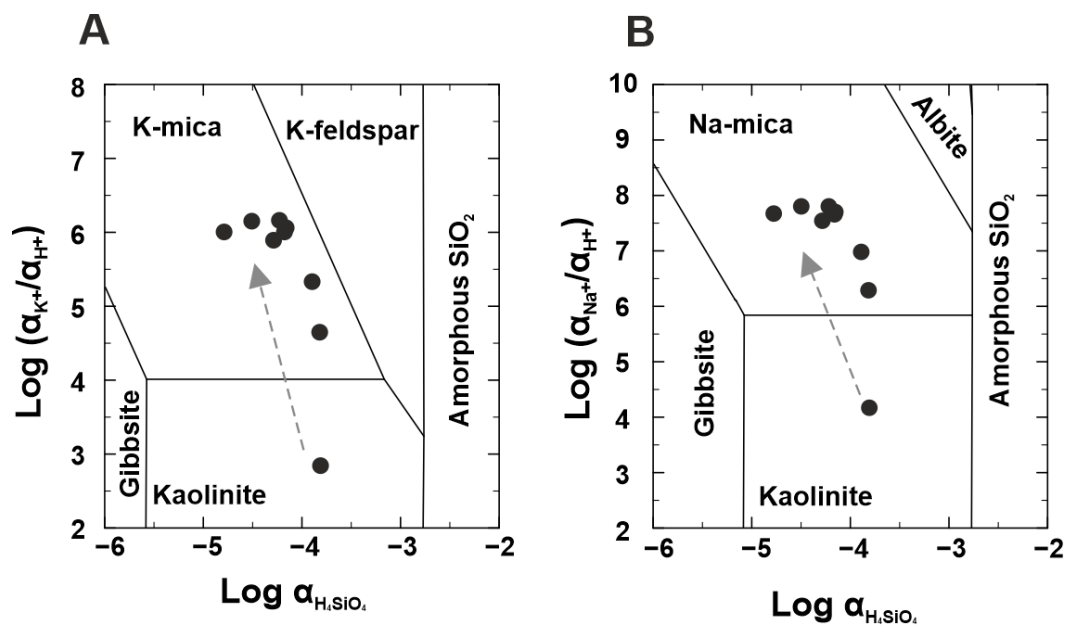


Figure 6.12 Stability diagrams of K-aluminosilicate and Na-aluminosilicate. Calculations for individual water samples are shown as black filled circles, and the grey arrows indicate the direction from river to ocean. The stability diagrams were plotted by PhreePlot (Kinniburgh and Cooper, 2011), with the database from PHREEQC (Parkhurst and Appelo, 2013) and Robie and Hemingway (1995).

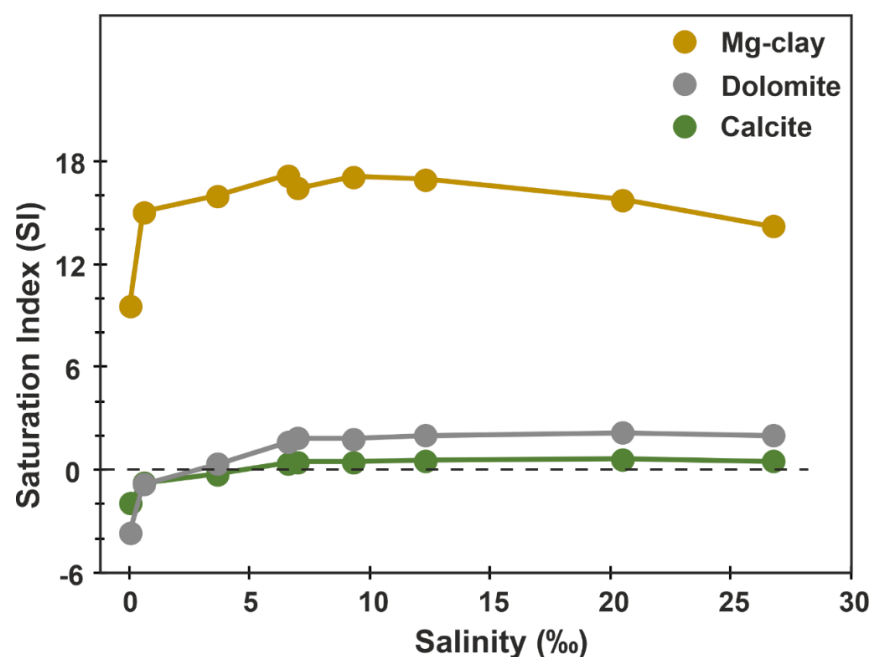


Figure 6.13 Saturation index (SI) for selected minerals in the Amazon estuary.

The saturation index (SI) was calculated based on dissolved concentrations of Na, Ca, Mg, K, Li, NO_2^- , SiO_4^{4-} , NO_3^- , Cl^- , and alkalinity, temperature, and pH using PHREEQC (Parkhurst and Appelo, 2013). The dashed black line is plotted at SI=0; lower values are undersaturated and higher values are supersaturated. The Mg-clay is sepiolite.

6.4.3 Mechanical sorting and chemical alteration of bulk sediments

The calculated bulk concentrations (i.e., $[X]_{\text{bulk-sum}}$) of Ca, Mg, K, Fe, Mn, Al, and Li in all fractions in the sequential extractions are calculated based on Eq. 2.2, most of which correspond well with the measured bulk element concentrations (i.e., $[X]_{\text{bulk-measured}}$) (Figure 6.5). Due to the addition of Na from the leaching reagent (Na-acetate), the bulk Na concentrations are not available from the sequential leaching, but the Na concentrations are measured in the bulk dissolved samples (Table 6.3). Concentration data for Si are not available from either the sequential extraction or the bulk dissolution, due to the use of HF. Therefore, the Si concentrations are calculated based on both the bulk dissolution data and the sequential extraction data. First, based on the bulk dissolution data, the Si concentrations can be approximately calculated using Eqs. 6.17 and 6.18, assuming the major elements are Al, Fe, K, Mg, Ca, Na, and Mn.

$$\text{SiO}_2 \text{ (g/g)} = 1 \text{ (g/g)} - (\text{Al}_2\text{O}_3 \text{ (g/g)} + \text{Fe}_2\text{O}_3 \text{ (g/g)} + \text{K}_2\text{O (g/g)} + \text{MgO (g/g)} + \text{CaO (g/g)} + \text{Na}_2\text{O (g/g)} + \text{MnO (g/g)}) \quad \text{Eq. 6.17}$$

$$[\text{Si}]_{\text{bulk}} \text{ (mg/g)} = 1000 \times \text{SiO}_2 \text{ (g/g)} \times \text{molar mass Si (g/mol)} / \text{molecular mass SiO}_2 \text{ (g/mol)} \quad \text{Eq. 6.18}$$

Second, based on the sequential extraction data, the Si concentrations can be approximately calculated using Eqs. 6.18 and 6.19, assuming the major elements are Al, Fe, K, Mg, Ca, and Mn.

$$\text{SiO}_2 \text{ (g/g)} = 1 \text{ (g/g)} - (\text{Al}_2\text{O}_3 \text{ (g/g)} + \text{Fe}_2\text{O}_3 \text{ (g/g)} + \text{K}_2\text{O (g/g)} + \text{MgO (g/g)} + \text{CaO (g/g)} + \text{MnO (g/g)}) \quad \text{Eq. 6.19}$$

Here, although the unavailable Na concentrations are not included, the influence of the Na₂O composition on the Si concentration calculation is negligible, because Na₂O comprises less than 2.5% of the bulk samples. The calculated $[\text{Si}]_{\text{bulk}}$ for the estuarine sediments range from 233 to 368 mg based on the measured bulk

data, and 269 to 375 mg/g based on the sequential extraction data (Figure 6.5G), which are within the range of measured Amazon River sediments further inland (Dellinger et al., 2014). In the further discussion, the $[\text{Si}]_{\text{bulk}}$ data calculated based on the sequential leaching is applied.

Based on the comparison between the suspended load samples (SPM) and the bedload samples (MUC) in the north channel transect, the bulk SPM samples have higher K, slightly higher Mg, Al, and Li, but lower Ca and Si than bulk MUC samples (Figure 6.5). In addition, the $[\text{Al}]_{\text{bulk}}/[\text{Si}]_{\text{bulk}}$ ratios of the SPM samples are generally slightly higher than the MUC samples (Figure 6.14A). This small vertical difference between the suspended samples from surface water and the bedload from deep water indicates slightly higher clay content in the suspended samples than in the bedload samples, because the Al composition in clays is generally higher than in primary silicate minerals (Velde, 1995). In addition, according to the spatially varying location of the sampling sites, the $[\text{Al}]_{\text{bulk}}/[\text{Si}]_{\text{bulk}}$ ratios of the MUC samples show significant increases from the sites close to the river mouth to the ocean in the Amazon estuary, except for sample 41MUC which is dominated by marine carbonate rather than river-derived particles. Similarly, the $[\text{Al}]_{\text{bulk}}/[\text{Si}]_{\text{bulk}}$ ratios of SPM samples also increase with increasing salinity in the dissolved load. The increase in $[\text{Al}]_{\text{bulk}}/[\text{Si}]_{\text{bulk}}$ ratios from the location near the river mouth to the ocean indicates an increase in clay content. The increasing surface area of the MUC samples also suggests an increasing clay content through the estuary (Figure 6.15).

The increase in clay content could stem from two processes: clay neoformation in the estuary (Michalopoulos and Aller, 1995; Michalopoulos et al., 2000; Pogge von Strandmann et al., 2008) and/or mechanical sorting (Gibbs, 1977), since clays have a finer particle size and hence slower settling rates than (eroded) primary grains. For the bulk samples in the Amazon estuary, there are three types of mineral compositions with different Al/Si, Li/Si, and $\delta^7\text{Li}$ characteristics. First, the primary minerals transported by the river, which have relatively low Al/Si, low Li/Si, and $\delta^7\text{Li}$ values of $\sim 0\text{--}4\text{‰}$ (Dellinger et al., 2014).

Second, the secondary minerals formed on the continent and transported by the river, which have relatively high Al/Si and low $\delta^7\text{Li}$ values of less than 0‰ (Dellinger et al., 2014). Third, the secondary minerals formed in the estuarine environment, which have relatively high Li/Al and high $\delta^7\text{Li}$ values of ~6‰ (Sections 6.4.1.2 and 6.4.2; Figures 6.6, 6.11, and 6.14B). If the increase in clay content and $[\text{Li}]_{\text{bulk}}$ was mainly caused by clay neoformation in the estuary, the $\delta^7\text{Li}_{\text{bulk}}$ should show an increasing trend towards $\delta^7\text{Li}$ formed in the estuary (i.e., ~6‰). However, the $\delta^7\text{Li}_{\text{bulk}}$ values lie in a narrow range from -2.4 to -1.3‰ through the estuary, identical to the continental riverine sediments, without a clear relationship to $[\text{Al}]_{\text{bulk-sum}}/[\text{Si}]_{\text{bulk}}$ or $[\text{Li}]_{\text{bulk-sum}}/[\text{Al}]_{\text{bulk-sum}}$ (Figures 6.14C and D). This result indicates that the increase in clay content and Li concentration in the bulk sediment is mainly caused by mechanical sorting of river-derived particles rather than clay neoformation in the Amazon estuary. Using Scanning Electron Microscope (SEM), the sample 85MUC at around 200 km away from Amazon River mouth is observed to contain more finer particles than the sample 24MUC from the river endmember in the Amazon estuary (Figure 6.16).

In contrast, during continental weathering in the Amazon catchment, as well as global large river catchments, the $\delta^7\text{Li}$ values of bulk sediments appear to decrease with increasing $[\text{Al}]/[\text{Si}]$ and $[\text{Li}]/[\text{Al}]$ (Figure 6.14B, C) (Dellinger et al., 2014; Yang et al., 2021). This relationship reflects clay neoformation during continental weathering that significantly contributes to the increasing clay content in river sediments. Hence, the amount of clays formed in the Amazon basin and the amount of eroded grains in the hinterland are much larger than the amount of clays formed directly in the estuary. The clays and eroded grains from the Amazon basin dominate the bulk estuarine sediments, which masks the potential for changes in bulk Li isotope composition during estuarine processes. Although the $\delta^7\text{Li}_{\text{bulk}}$ values in estuarine sediments do not appear to reflect estuarine weathering processes, the chemically extracted clay fractions nevertheless do provide evidence of estuarine weathering (Section 6.4.2), which indicates the value in examining the different fractions in the bulk sediment samples.

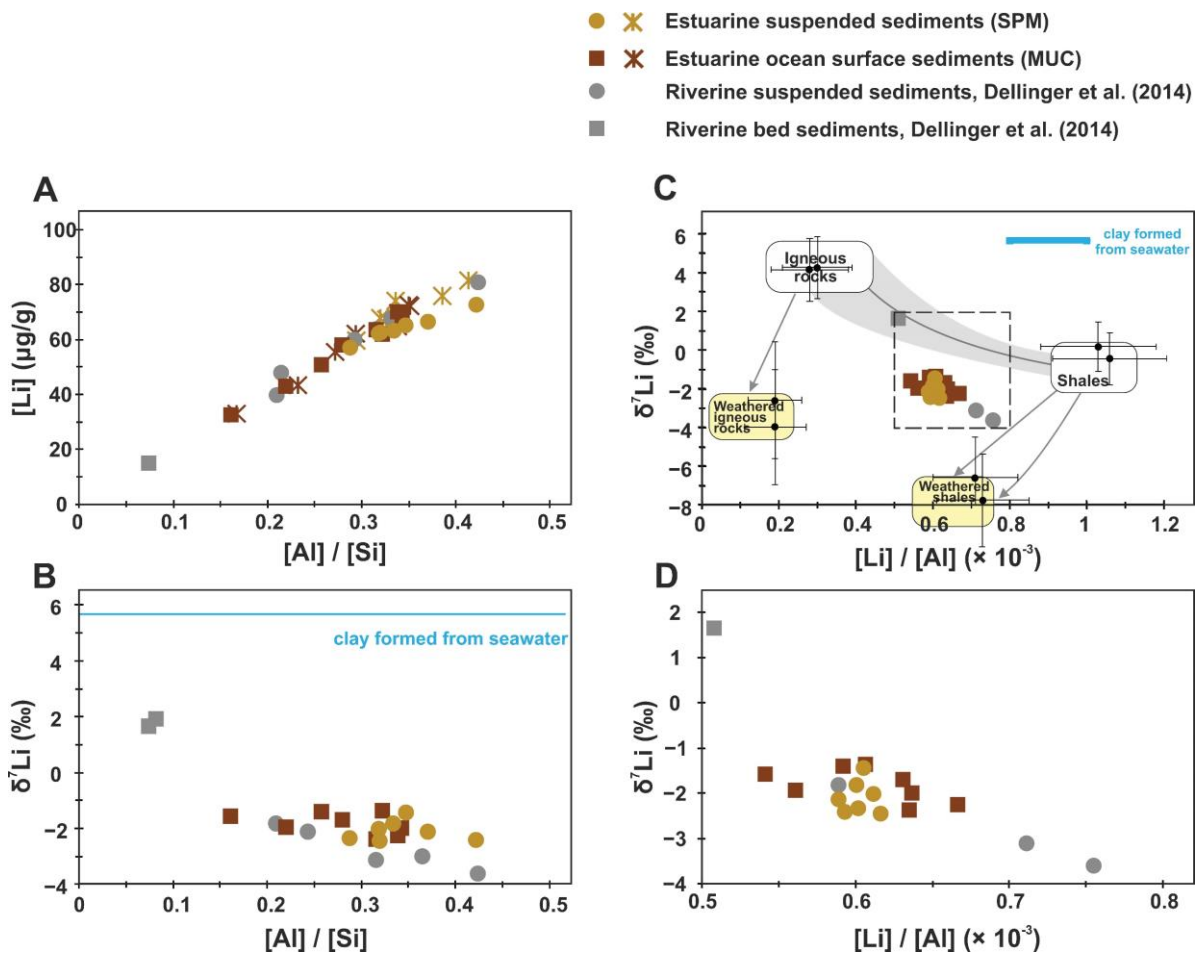


Figure 6.14 Relationships between Al, Si, and Li concentrations, and Li isotopes, of bulk sediment samples from the Amazon.

A) Relationship between Al/Si ratios and Li concentrations in bulk sediment samples, including data from this study and from Dellinger et al. (2014). The brown crosses and yellow crosses represent the Al/Si ratios calculated based on the measured element concentrations in the bulk dissolutions of the MUC and SPM samples, respectively. The brown squares and yellow dots represent the Al/Si ratios calculated based on the sum of the measured element concentrations in the different fractions of the MUC and SPM samples, respectively (Section 6.4.3).

B) Relationship between Al/Si ratios and Li isotope compositions in bulk sediment samples, including data from this study and from Dellinger et al. (2014). The blue line represents the estimated endmember composition of clays formed in seawater ($\delta^7\text{Li} = 5.7$ ‰; Figure. 6.6).

C) Relationship between Li/Al ratios and Li isotope compositions in bulk sediment samples, including data from this study and from Dellinger et al. (2014). The blue line represents the estimated endmember composition of clays formed in seawater ($\delta^7\text{Li} = 5.7$ ‰, Li/Al = 0.8–1.0). The rectangles with round corners are

the continental weathering endmembers from Dellinger et al. (2014) and the black dots with error bars are the posteriori endmembers for the Amazon River derived in the inverse mixing modelling of Dellinger et al. (2014). The grey line and shaded area represent mixtures between the igneous rock and shale endmembers, and the grey arrows represent the Li isotope fractionation trend during weathering as shown in Dellinger et al. (2014). The data in the dashed box are shown magnified in panel D.

In all cases, the element ratios are by mass. Note that data from sample 41MUC are not included.

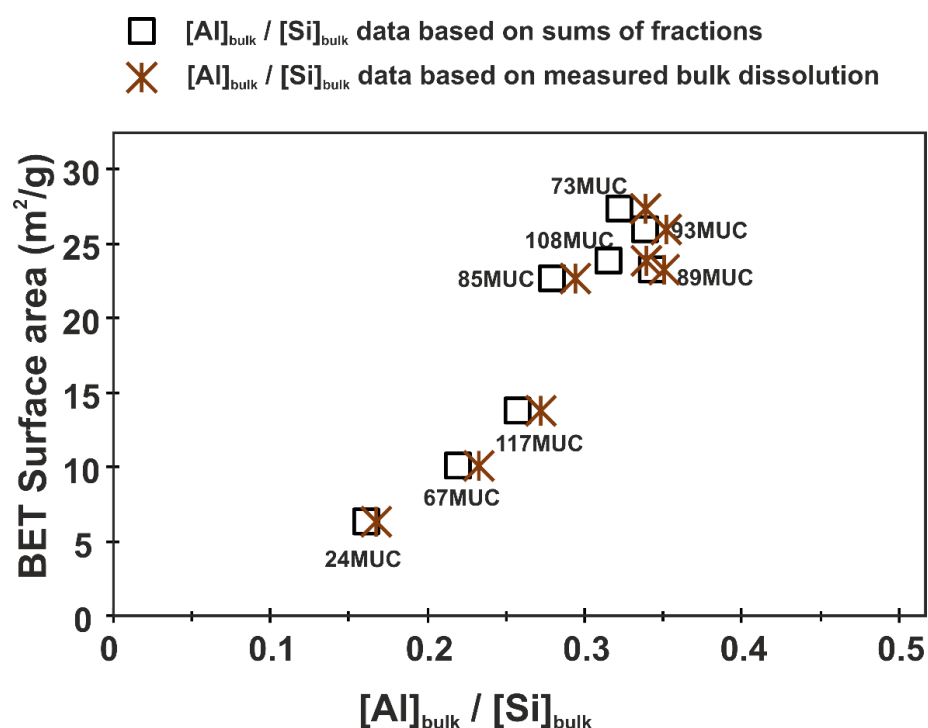


Figure 6.15 Relationship between bulk Al/Si ratios and BET surface area in the MUC sediment samples.

The brown crosses represent the Al/Si ratios calculated based on the measured element concentrations in the bulk dissolution, while the black squares represent the Al/Si ratios calculated based on the sum of the measured element concentrations in the different fractions (Section 6.4.3). Sample 41MUC is excluded because of its high carbonate content. The element ratios are by mass. The surface area of the MUC samples was determined by Nova 1200 (Quantachrome) at Johannes Gutenberg University, Mainz.

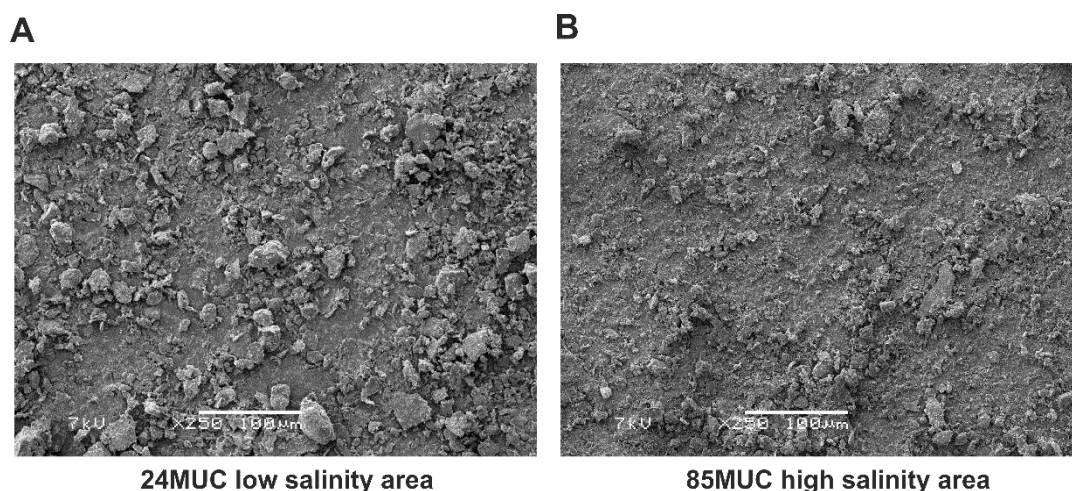


Figure 6.16 SEM images for sediment samples 24MUC and 85MUC.

A) Sample 24MUC at 50 km away from the Amazon River mouth in the estuary.
B) Sample 85MUC at ~200 km away from the Amazon River mouth in the estuary.
Samples were imaged at UCL with a Jeol JSM-6480LV high-performance Variable Pressure Analytical Scanning Electron Microscope, using a 7 kV accelerating voltage and around 9 mm working distance. The scale bars are 100 µm.

6.5 Conclusions

Lithium concentrations and isotopes from the dissolved load and different leached fractions of the suspended sediment and bedload were measured at a series of sites from the Amazon estuary. The dissolved Li concentrations generally show conservative mixing between river water and seawater in the Amazon offshore transect. In contrast, the dissolved $\delta^7\text{Li}$ values are slightly higher than the predicted values based on conservative mixing at medium salinity, indicating a sensitivity of Li isotopes to non-conservative processes, and specifically to Li removal by sediments. Although there is some contribution from adsorption onto the exchangeable fraction, the Li is mainly retained in the secondary mineral lattices, especially clays. In the Amazon estuary, the fraction of Li neo-incorporated into secondary mineral fractions is estimated to be 3–4 µg/g in the river-derived sediments, with an isotopic fractionation factor $\alpha_{\text{clay-seawater}}$

of approximately 0.975. Through the whole Amazon estuary, the river-derived sediments remove around $3.6\text{--}4.8\times 10^9$ g/yr Li from the dissolved load. Specifically, around $1.0\text{--}1.7\times 10^8$ g/yr is removed from river water, representing around 1.8–3.0% of the dissolved Li flux discharged by the Amazon River, while around $3.5\text{--}4.7\times 10^9$ g/yr Li is removed from seawater (~1–10% of the Li output flux from the ocean) by river-derived sediments in the Amazon estuary.

In addition, elements such as Mg and K show similar removal patterns to Li, and are also retained by the sediments, with an influence from exchangeable, oxide, and clay fractions. The different solution compositions of river water and seawater could be responsible for a shift in mineral stability in estuaries, thereby promote the retention of Mg, K, and Li in river-derived sediments. In particular, the retention of Mg in clays may be a significant sink in the ocean Mg budget and would reduce the CO₂ burial efficiency arising from continental chemical weathering.

Chapter 7. Synthesis and implications

7.1 Influence of estuarine weathering on the Li cycle

7.1.1 Li behaviour during estuarine weathering

In the basalt-Li-add interaction experiment (Chapter 4), the small basaltic natural estuary at Borgarfjörður, Iceland (Chapter 5), and the Amazon estuary (Chapter 6), Li shows generally similar behaviour during estuarine weathering, i.e., there is some Li removal from the dissolved load by river-derived particles.

According to the dissolved load samples, the measured Li concentrations generally show conservative mixing between fresh water (i.e., tap water or river water) and saline water (i.e., concentrated artificial seawater or seawater) (Figure 7.1A). However, in the basalt-Li-add experiment, the transfer model based on the measured dissolved Li concentrations indicates that there is Li loss from the dissolved load during the salinity-increasing stage (Figure 4.9). For dissolved Li isotopes in the Borgarfjörður estuary, there is apparently conservative mixing between river water and seawater, although the river water endmember fluctuates, whereas the basalt-Li-add experiment and the Amazon estuary show higher measured dissolved $\delta^7\text{Li}$ values than predicted by theoretical conservative mixing (Figures 4.3, 5.2, and 6.2), which indicates Li loss from the dissolved load. Furthermore, the analyses of solid samples show an increase in Li concentration and $\delta^7\text{Li}$ values in secondary fractions (i.e., exchangeable, oxide, and clay) in the suspended load and bedload samples in the Borgarfjörður and Amazon estuaries (Figures 5.6 and 6.4), which indicates Li uptake from the dissolved load by river-derived particles, especially the clay fraction.

Besides the two estuaries explored here, the dissolved Li concentration generally also shows conservative mixing between river water and seawater in the St. Lawrence River estuary, Canada (Stoffyn-Egli, 1982), the Scheldt River estuary, Netherlands (Stoffyn-Egli, 1982), the Mississippi River estuary (Colten and Hanor, 1984), the Gulf of Papua supplied by the Fly, Purari, and Kikori rivers (Brunskill et al., 2003), the estuary at Povoação, São Miguel, Azores archipelago (Pogge von Strandmann et al., 2008), the Kalix and Rane River

estuaries, Sweden (Murphy et al., 2014), the Yangtze River estuary (Yang et al., 2021), and the Ganga estuary (Chanda et al., 2023) (Figure 7.1A). The dissolved Li isotopes show generally conservative mixing of river water and seawater at Povoação, São Miguel (Pogge von Strandmann et al., 2008) and the Yangtze River estuary (Yang et al., 2021), as well as Borgarfjörður estuary, Iceland (Chapter 4, Pogge von Strandmann et al., 2008) (Figure 7.1). In contrast, the dissolved Li isotopes are higher than predicted for conservative mixing in the low-salinity zone of the Kalix and Rane River estuaries, Sweden (Murphy et al., 2014) (Figure 7.1B), similarly to the Amazon estuary (Chapter 5). In addition, river-derived particles show Li incorporation, especially by Fe-Mn oxyhydroxides in the Yangtze river estuary (Yang et al., 2021, 2023).

Furthermore, Li isotope fractionation during the process of Li removal from the dissolved load by solids has been observed in this study in the basalt-Li-add experiments, the Borgarfjörður estuary, and the Amazon estuary. The estimated Li isotope fractionation between the exchangeable, oxide, and clay fractions and seawater are similar in both the Borgarfjörður estuary and the Amazon estuary, at -6.5 to -14.5‰ ($\Delta^7\text{Li}_{\text{exchangeable-seawater}}$), -21.2 to -28.6‰ ($\Delta^7\text{Li}_{\text{oxide-seawater}}$), and -23.6 to -26.5‰ ($\Delta^7\text{Li}_{\text{clay-seawater}}$). The estimated Li isotope fractionation between the total secondary fraction (i.e., sums of exchangeable, carbonate, oxide, and clay fractions) in the basalt-Li-add experiments and the two natural estuaries is also similar at -17.1 to -24.0‰ ($\Delta^7\text{Li}_{\text{secondaryfraction-seawater}}$). These values are also consistent with a recent study showing that the Li isotope fractionation is -11.7‰ ($\Delta^7\text{Li}_{\text{exchangeable-seawater}}$) and -19.0 to -26.5‰ ($\Delta^7\text{Li}_{\text{oxide-seawater}}$) during Li uptake in the Yangtze river estuary (Yang et al., 2023).

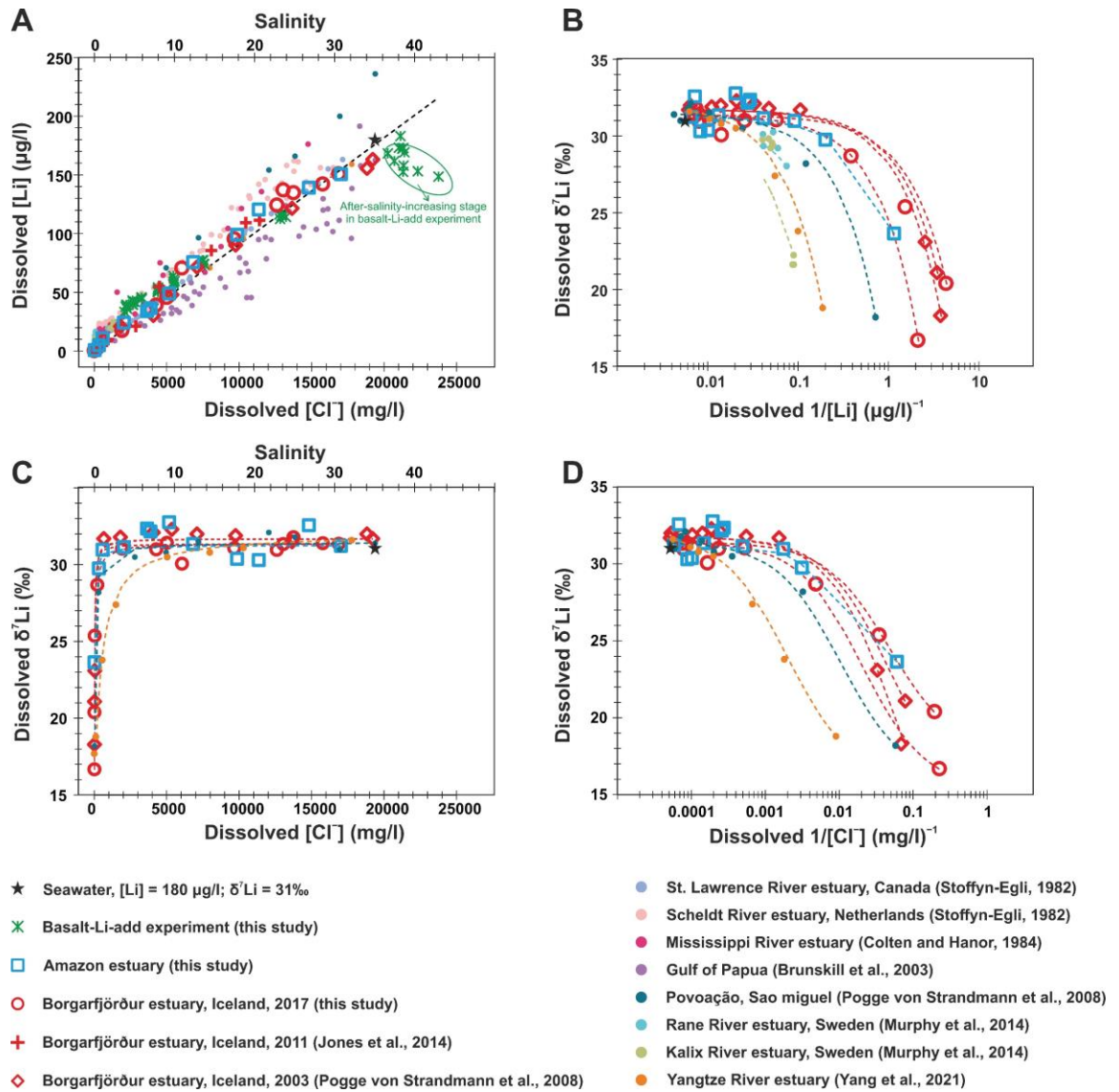


Figure 7.1 Synthesis of dissolved Li concentration and isotope data in modern estuaries.

The data for the St. Lawrence River estuary, the Scheldt River estuary, the Povoação estuary, and the Yangtze River estuary are based on the published data from surface water samples (Stoffyn-Egli, 1982; Pogge von Strandmann et al., 2008; Yang et al., 2021). The data for the Mississippi River estuary, the Gulf of Papua, the Kalix River, and the Rane River are re-plotted based on the published figures (Colten and Hanor, 1984; Brunskill et al., 2003; Murphy et al., 2014), which may cause minor errors. In panel A, the dashed line is the linear relationship fit for all data shown. In panels B, C, and D, the dashed lines are theoretical conservative mixing lines for each estuary.

7.1.2 Factors influencing Li behaviour during estuarine weathering

As discussed in Chapter 4, the different Li behaviour between the Li-free experiments and the Li-add experiments indicates that the rapid increase in Li concentration in the estuarine water is likely to be the main reason for river-derived particles removing Li from the dissolved load during estuarine weathering. The Li concentration in the modern ocean is constant at $\sim 180 \mu\text{g/l}$ (Riley and Tongudai, 1964; Fujinaga et al., 1980; Tomascak et al., 2016; Steiner et al., 2022), and much higher than in modern river water (discharge-weighted average $\sim 1.5 \mu\text{g/l}$) (Huh et al., 1998), which leads to an increase in Li concentration in all modern estuaries. Therefore, the Li uptake by river-derived particles during estuarine weathering is probably a common global phenomenon, possibly driven by an approximately constant partition coefficient of Li into particles.

Interestingly, although both the basalt-Li-add experiment and the two natural estuaries consistently show that Li is removed from the dissolved load by solids during estuarine weathering, the main evidence in the basalt-Li-add experiment for this process comes from the dissolved load data, whereas the main evidence for this process in natural estuaries comes from the solid load. This difference may stem from the different mass ratios of the solid load to the dissolved load. As discussed in Section 4.4.2.3, the rock/water ratio (272–362 g/l) in the experiments is several orders of magnitude higher than the suspended sediment concentration in the Borgarfjörður estuary (0.5–0.6 g/l), in the Amazon estuary ($< 0.5 \text{ g/l}$ in general; $\sim 10 \text{ g/l}$ in muddy areas), or in the Yangtze River estuary ($< 2.1 \text{ g/l}$) (Yang et al., 2021). Therefore, although the concentrations of the major elements (i.e., Na, Ca, Mg, and K) and Li in the basalt-Li-add experiment were designed to imitate natural estuaries, the total mass of Li in the dissolved load in the experiments is nevertheless much less than in the natural estuaries, because the water volume in the estuaries is much greater than the water volume in the experiments. According to mass balance, the Li loss from the dissolved load should be equal to the Li gain in the solids (Eqs. 7.1 and 7.2).

$$[\text{Li}]_{\text{water loss}} \times M_{\text{water}} = [\text{Li}]_{\text{sediment added}} \times M_{\text{solid}} \quad \text{Eq. 7.1}$$

$$\text{i.e., } [\text{Li}]_{\text{water loss}} = \text{SSC} \times [\text{Li}]_{\text{sediment added}} \quad \text{Eq. 7.2}$$

Here, $[\text{Li}]_{\text{water loss}}$ and $[\text{Li}]_{\text{sediment added}}$ are the decrease in Li concentration in the

dissolved load and the increase in the Li concentration in the solids, respectively. The mass of water and solids are M_{water} and M_{solid} , respectively, and SSC is the suspended sediment concentration.

Thus, in the experiments, the limiting factor for Li removal is the Li mass of the dissolved load (Section 4.4.2). The Li removal mass accounts for 12–25% of the total dissolved Li mass in the intimated saline water, whereas the Li changes in the solids represent a smaller proportion of the total Li mass in the bulk solids, which hinders the ability to determine out changes in the solids. In contrast, in modern natural estuaries, the limiting factor for Li removal during estuarine weathering is the capacity of river-derived particles to uptake Li. The Li changes are significant enough for the change in Li mass in the solids to be determined, especially when the secondary fractions are isolated. In contrast, the proportion of Li lost from the total dissolved Li mass involved in the mixing process in natural estuaries is not enough to be determined in the measurements of dissolved Li concentrations, or even in the dissolved Li isotopes in some cases. Furthermore, because the Li uptake capacity of river-derived particles is likely to be the limiting factor for the Li removal flux in natural estuaries, this flux is probably strongly related to the concentration of river-derived particles and the Li concentration that can be taken up by per gram of river-derived particles.

On the one hand, the concentration of river-derived particles (i.e., SSC) is related to the continental erosion rate (Milliman and Syvitski, 1992; Berner and Berner, 1996; Dellinger et al., 2015). Thus, higher erosion rates may increase the Li uptake flux during estuarine weathering. On the other hand, in principle, the Li concentration that can be taken up per gram of river-derived particles is probably also related to the continental chemical weathering degree of the river-derived particles. Theoretically, in a first situation, if the river-derived particles are rich in fresh primary minerals with little secondary minerals, these solids can likely be further weathered in the estuary, thus forming more secondary minerals, thereby taking up more Li per gram of solid (Dellinger et al., 2015; Pogge von Strandmann et al., 2020a). In a second situation, if the river-derived particles have already been significantly weathered on the continents, and mainly comprise secondary minerals rich in mobile elements (e.g., Mg, K, Ca, Na, Li), such as smectites, the new uptake of Li by the solids during estuarine weathering is likely to be limited (as there is probably already a significant amount of Li in the river-derived

particles). In a third situation, if the river-derived particles were weathered on the continents but mainly comprise secondary minerals that are depleted in mobile elements (e.g., Mg, K, Ca, Na, Li), such as kaolinite, then the particles could potentially take up such mobile elements and alter to smectites during estuarine weathering (Figure 6.12). In a fourth situation, if the river-derived particles are dominated by quartz, which is highly resistant to weathering, then little Li is likely to be taken up during estuarine weathering. So far, the new data and compilation from previous studies is not yet sufficient to fully test these hypotheses, but according to the continental weathering regimes, the Borgarfjörður estuary seems to represent the first situation (Chapter 5) and the Amazon estuary seems to represent the third situation (Chapter 6). In addition, the grain size and surface area of river-derived particles may also influence the Li uptake mass, which needs to be further examined.

The residence time of the particle suspended in the estuarine area or stay on the bedload surface in the estuaries area before burial and diagenesis may also influence the Li removal flux (Pogge von Strandmann et al., 2008). In principle, the particle residence time is related to the grain size of particles and mineralogy of particles influenced by continental weathering, as well as tides, waves, and topography of the estuary. However, based on the basalt-Li-add experiment, the Li uptake by the solid from the dissolved is likely to be rapid. Thus, the particle residence time may be not the limiting factor, although the more exploration is needed in the future work. In addition, it appears that the mineralogy of the river-derived particles may also influence the Li isotope fractionation during Li removal, as indicated by the difference in Li isotope fractionation between the basalt-water experiments ($\Delta^7\text{Li}_{\text{solid-seawater}} = -21\text{‰}$) and the loess-water experiments ($\Delta^7\text{Li}_{\text{solid-seawater}} = -8.0$ to -10.5‰) (Section 4.4.2).

Overall, the rapid and massive increase in the dissolved load Li concentration is the main reason for Li removal by river-derived particles from the dissolved load during estuarine weathering. Moreover, the flux of Li removal and the Li isotope fractionation during this removal are likely both related to the concentrations and characteristics of the river-derived particles. The concentration of river-derived particles is related to the continental erosion rate, whereas the characteristics of the river-derived particles are mainly related to the continental chemical weathering degree and the mineralogy of the weathering

products.

7.1.3 Importance of estuarine weathering for the Li cycle of the modern ocean and implications for ancient oceans

So far, only relatively few estuaries have been explored for their Li concentration and isotopic behaviour, which is not yet sufficient to give a comprehensive global view. In the Borgarfjörður estuary, Iceland (flux of river-derived particles $\sim 3.63 \times 10^{12}$ g/yr), the Li removal flux is estimated as $0.36\text{--}1.09 \times 10^7$ g/yr (with $1\text{--}3$ $\mu\text{g/g}$ Li uptake in the solid) in this study (Chapter 5) and $\sim 1.10 \times 10^7$ g/yr (with ~ 3 $\mu\text{g/g}$ Li uptake in the solid) in Pogge von Strandmann et al. (2008). In the Amazon estuary (flux of river-derived particles $\sim 1.2 \times 10^{15}$ g/yr, Milliman and Farnsworth, 2011), $\sim 3.6\text{--}4.8 \times 10^9$ g/yr Li is estimated to be removed during estuarine weathering, with $3\text{--}4$ $\mu\text{g/g}$ Li uptake in the solid (Chapter 6). Although the concentration of newly incorporated Li in river-derived particles in estuaries is likely to be different in different global settings, as discussed in Section 7.1.2, this concentration ranges from 1 to 4 $\mu\text{g/g}$ in the Borgarfjörður estuary and the Amazon estuary. Thus, given that the global sediment flux to the ocean is around 1.8×10^{16} g/yr (Milliman and Farnsworth, 2011), the Li removal flux into river-derived particles is estimated to be $1.8\text{--}7.2 \times 10^{10}$ g/yr ($2.6\text{--}10.3 \times 10^9$ mol/yr), by assuming the amount of removal observed in the above estuaries. However, this estimate requires verification in other rivers, especially large rivers and rivers with higher river-derived particle concentrations, such as the Ganges-Brahmaputra and Yellow River (Huh et al., 1998; Milliman and Farnsworth, 2011).

It is notable that the dissolved Li removed by river-derived particles during estuarine weathering is sourced from both rivers and seawater, because both are involved in the mixing process in estuaries. As discussed in Chapter 6, only $\sim 1.8\text{--}3.0\%$ of the river-derived dissolved Li was removed by the particles during estuarine weathering in the Amazon estuary based on the fractionation model and estuary model. In the Borgarfjörður estuary, the removal of riverine Li is constrained to be less than 5%, because of the observed conservative mixing of the Li concentrations and isotope compositions (Chapter 5). Furthermore, if it is assumed that the partitioning of Li during removal from river water and seawater ($M_{\text{Li seawater}} / M_{\text{Li riverwater}} = 377$ at salinity of 30.8) is similar to that of the Amazon estuary (Section 6.4.1.4), approximately $0.6\text{--}1.7\%$ of the riverine dissolved Li

input flux is estimated to be removed by river-derived particles in the Borgarfjörður estuary. A limited modification of riverine dissolved Li input flux and isotope composition by estuarine processes has also been observed in the Yangtze River estuary (Yang et al., 2021). Considering the similar minor modifications of riverine dissolved Li in the estuaries of the above rivers, especially the two large rivers, the Amazon River and the Yangtze River, the modification of the global riverine dissolved Li input flux by river-derived particles during estuarine weathering would be expected to be less than 5.0% of its total. However, again, this minor impact on the riverine dissolved Li input fluxes needs to be examined in other estuaries, especially for large rivers with very high SSC, such as the Yellow River (average 26.9 g/l), Indus (2.8 g/l), or Ganges-Brahmaputra (1.1 g/l) (Huh et al., 1998; Gaillardet et al., 1999; Milliman and Farnsworth, 2011).

In contrast to the relatively minor impact on the riverine dissolved Li flux, the amount of Li removed from seawater by river-derived particles is significant, due to the higher Li concentrations in seawater. Thus, ~97% of the removed Li in the Amazon estuary is sourced from seawater (Section 6.4.1.4), representing $\sim 3.5\text{--}4.7 \times 10^9$ g/yr Li removal sourced from seawater (Chapter 6). Again, more exploration in different estuaries needs to be performed to make a more accurate estimate, but the current global estimate is $1.8\text{--}7.2 \times 10^{10}$ g/yr ($2.6\text{--}10.3 \times 10^9$ mol/yr) Li removal from seawater during estuarine weathering. This Li sink before burial and diagenesis is named estuarine cation removal (ECR) here. The Li isotope fractionation from Li removal during estuarine weathering is likely to be around -17.1 to -24.0‰ ($\Delta^7\text{Li}_{\text{secondaryfraction-seawater}}$) (Section 7.1.1).

There are generally thought to be two major Li inputs (i.e., river input and hydrothermal input) and two major outputs (i.e., alteration of the (basaltic) oceanic crust (AOC) and uptake by marine aluminous authigenic clays (MAAC)) from seawater (Chan et al., 1992; Huh et al., 1998; Hathorne and James, 2006; Misra and Froelich, 2012; Li and West, 2014) (Section 1.2.3, Figure 1.4). However, there are still large uncertainties in the Li sink fluxes and their isotopic fractionation factors from seawater. The estimated AOC Li sink ranges from $1.0\text{--}14.6 \times 10^{10}$ g/yr, with isotope fractionation ($\Delta^7\text{Li}_{\text{AOC-seawater}}$) ranging from -11 to -19‰ (Seyfried et al., 1984; Stoffyn-Egli and Mackenzie, 1984; Hathorne and James, 2006; Coogan et al., 2017). The estimated MAAC Li sink is $2.4\text{--}25.7 \times 10^{10}$ g/yr,

with isotope fractionation ($\Delta^7\text{Li}_{\text{MAAC-seawater}}$) ranging from -5 to -28‰ (Stoffyn-Egli and Mackenzie, 1984; Hathorne and James, 2006; Andrews et al., 2020; Kalderon-Asael et al., 2021) (Figure 1.4). However, the ECR sink in this study, with a magnitude of approximately $1.8\text{--}7.2 \times 10^{10}$ g/yr and a fractionation factor ($\Delta^7\text{Li}_{\text{ECR-seawater}}$) of -17.1 to -24.0‰ , could make another comparatively important additional contribution to the AOC and MAAC sinks (Figure 1.4).

In the ECR sink, Li is mainly incorporated into secondary minerals, especially clays (Chapters 5 and 6). The interactive environment and the Li-bonding sites in the ECR sink are therefore theoretically similar to those involved in MAAC, and therefore the ECR sink is not a completely “new” sink, but rather a significant part of what is considered the MAAC sink. In this case, the isotope fractionation associated with ECR and MAAC sinks is similar, but larger than during AOC, whose alteration temperature is higher (Hoefs and Sywall, 1997; Huh et al., 1998; Zhang et al., 1998; Li and West, 2014; Kalderon-Asael et al., 2021) (Table S1.1). Thus, from a model perspective at least, the ECR sink can likely be considered part of the MAAC sink for three reasons: 1) the similar Li isotope fractionation mechanism; 2) the limited understanding of ECR (and also MAAC); 3) the estimated sink flux (i.e., AOC and MAAC) in the current oceanic Li cycle model has a huge uncertainty in its range, and is usually set to match the input flux (and to therefore maintain a steady-state), and the ratio of AOC to MAAC is set to fit the observed seawater Li isotope compositions.

To date, the MAAC Li sink has mainly been explored as a diagenetic process that occurs after burial or in the open ocean, including authigenic clay formation (Hoefs and Sywall, 1997; Huh et al., 1998), marine clay uptake (Seyfried et al., 1984; Elderfield and Schultz, 1996), and clay authigenesis in carbonate-rich sedimentary environments due to the presence of biogenic silica (Andrews et al., 2020). In this view, the ECR can be regarded as an additional part of the current estimated MAAC sink, especially because of the different influencing factors on ECR and the current estimated MAAC. However, because of the large uncertainty on the current estimates of the AOC and MAAC sink fluxes, and the passive response of the sink flux to the input flux in the current oceanic Li cycle models, this study emphasises the influence of the ECR Li sink rather than aiming to correct the exact value of the Li sink flux. Specifically, any changes in the Li flux from ECR, and therefore the proportion of ECR to total output fluxes (or the

proportion of ECR to MAAC, and then the proportion of MAAC to total output fluxes), may have an important impact on ocean Li isotope compositions (Li and West, 2014). Overall, this study prefers to regard the ECR flux as a part of the MAAC sink, but with different influencing factors.

As mentioned above, ECR is likely to be closely related to the continental weathering regime (Section 7.1.2). Therefore, changes in these regimes over geological history may influence not only the riverine dissolved Li input, which has been widely considered (Pogge von Strandmann et al., 2013, 2017b, 2021b; Lechler et al., 2015; Sun et al., 2018; Sproson et al., 2022; Ramos et al., 2022; Qie et al., 2023), but also the ECR sink, which would lead to a dual control on Li isotope changes in the past oceans. For example, given that the continental erosion rate is thought to have increased during the Cenozoic due to mountain uplift and glacial expansion (Hay et al., 1989; Métiévier et al., 1999; Caves Rugenstein et al., 2019), the ECR sink is likely to be much higher in the modern day than during the early Cenozoic, which could have helped contribute to the increase in seawater $\delta^7\text{Li}$ values since 63 Ma (Li and West, 2014).

Most importantly, it is notable that the discussion on ECR influences above assumes that the limiting factor in the Li uptake flux in modern estuaries is the river-derived particle flux, and it is due to the high dissolved Li concentration and massive seawater mass involved in mixing in estuaries (Eq. 7.1; Section 7.1.2). The interaction experiments in this study also indicate that the high concentration of Li in seawater may be the main reason for Li uptake by river-derived particles during estuarine weathering (Chapter 4). Thus, if the dissolved Li concentration of seawater changes through geological history, the Li behaviour in the estuary may also change, and therefore the river-derived particles may have a different influence on the ancient oceans. However, due to a lack of reliable archives or proxies to record the dissolved Li concentration in ancient oceans (Pogge von Strandmann et al., 2021a), the Li mass in the ocean usually is set as a constant value or is set to change as a constant residence time multiplied by the total input Li flux in the models applied to explore ancient weathering or reverse weathering (Pogge von Strandmann et al., 2013, 2017b, 2021b; Lechler et al., 2015; Sun et al., 2018; Kalderon-Asael et al., 2021; Sproson et al., 2022; Ramos et al., 2022; Cao et al., 2022; Qie et al., 2023). A constant seawater Li concentration through time is unlikely, because Na, Ca, Mg, and K, as the most mobile elements, are

thought to vary across Earth history (Maisonneuve, 1982; Hardie, 2003; Holland, 2005). Especially at times when the dissolved Si concentration in the oceans was sufficient to extensively form aluminosilicate secondary minerals (reverse weathering) and to rapidly remove dissolved Li from seawater (Kalderon-Asael et al., 2021; Cao et al., 2022), the Li output flux may not have been passively equal to the total input flux. The extensive removal of Li by aluminosilicates may decrease the total mass of Li in the ocean, and therefore the Li concentration of seawater. If the Li concentration of seawater is low enough, the Li flux during the alteration of river-derived particles in the estuary may even have a possibility to become a source in the ocean Li cycle, as suggested by the Li-free experiments (Figure 4.5E). Thus, it is important to further explore the Li behaviour in modern estuaries, and in particular to consider the influence of seawater Li concentrations and ECR on the seawater Li isotope composition in ancient oceanic Li cycle models.

7.2 Influence of estuarine weathering on major element cycles and implications for the global carbon cycle

7.2.1 Behaviour of mobile major elements (Na, Ca, Mg, and K) and implications for ocean biogeochemistry

The mobile major elements (i.e., Na, Ca, Mg, and K) are generally considered to exhibit conservative mixing between river water and seawater during mixing in the estuarine zone (Berner and Berner, 1996), because of the observed linear relationship between measured elemental concentrations and the Cl^- concentration (i.e., salinity) in estuarine water. However, similarly to Li, a high concentration of mobile elements may mask more subtle changes; in other words, the changes in concentration may be less than the analytical precision (i.e., 5% RSD). Furthermore, although the changes in the concentration of dissolved mobile major elements would be relatively small, the total amount of change may be significant for their elemental cycles in the ocean and may therefore also influence the global carbon cycle. This study provides some evidence that there is transfer of Na, Ca, Mg, and K between river-derived particles and the dissolved load during estuarine weathering.

Potassium concentrations are observed to be conservative in the dissolved

load in the Borgarfjörður estuary, Iceland (Figure 5.3C) and the Amazon estuary (Table 6.2). However, in interaction experiments, the transfer model based on the measured dissolved load data indicates K loss from the dissolved load into the solids in the salinity-increasing stage (Figure 4.5C). Furthermore, K concentrations increase in the secondary fractions (i.e., exchangeable, oxide, and clay) of the suspended and bedload samples in the Borgarfjörður (Figures 5.5C, 5.10C, and 5.8C) and the Amazon estuaries (Figure 6.3C), which indicates K removal from the dissolved load by river-derived particles, especially the exchangeable and clay fractions. These observations conform to the shift of the adsorbed cations from Ca to K and Na (Sayles and Mangelsdorf, 1979; Lupker et al., 2016; Tipper et al., 2021). Further, K incorporation in authigenic aluminosilicates in the ocean (i.e., reverse weathering) (Michalopoulos and Aller, 1995; Santiago Ramos et al., 2018; Spiegel et al., 2021) is an important K sink in the modern ocean (Li et al., 2022). In addition, the positive relationship between K and Li in the clay fractions in the suspended and bedload sediments from Borgarfjörður estuary and the Amazon estuary indicates a K removal flux during estuarine weathering (i.e., ECR), which may therefore also be related to the continental weathering regimes. Thus, the river-derived particles may also play a significant role in the K cycle of the ocean.

Sodium is the most mobile and conservative cation in the ocean with a residence time of ~55 Ma (Berner and Berner, 1996). The dissolved load samples in the Borgarfjörður (Figure 5.3A) and the Amazon estuaries (Table 6.2) also exhibit conservative behaviour of Na. In addition, although the transfer model in the interaction experiments indicates that Na transfers from the dissolved load to the solids in the salinity-increasing stage, perhaps due to adsorption (Sayles and Mangelsdorf, 1979; Tipper et al., 2021), the transfer is minor compared to K, Mg, and Ca (Figure 4.5). Thus, it is likely that Na behaviour in the estuary zone is mainly controlled by simple conservative mixing.

Measured Mg concentrations in the dissolved load samples from the Borgarfjörður and the Amazon estuaries also correspond to conservative mixing trends. However, the transfer model based on the measured dissolved load data indicates Mg loss from the dissolved load into solids in the salinity-increasing stage of the interaction experiments (Figure 4.5B). In addition, Mg concentrations increase in the secondary fractions of the solid samples, especially the clay

fraction of the bedload samples from the Borgarfjörður estuary (Figure 5.8B) and the exchangeable, oxide, and clay fractions in the suspended and bedload samples from the Amazon estuary (Figure 6.3B). Furthermore, there is a positive relationship between Mg and Li concentrations in the oxide and clay fractions in the solid samples from the Amazon estuary (Figure 6.10A), which indicates a Mg removal flux during estuarine weathering, which may therefore also be related to continental weathering regimes. However, the decrease in Mg concentrations in the residual fractions of the bedload samples from the Borgarfjörður estuary may indicate Mg release due to basaltic mineral dissolution, although it could also stem from a mechanical sorting effect (Section 5.4.2). Thus, more research on Mg behaviour during alteration of river-derived particles in the estuary and its influence on the Mg cycle in the ocean needs to be performed. It is important because Mg is one of the major cations that combines with alkalinity during carbonate precipitation in the ocean (Tipper et al., 2006; Arvidson et al., 2011; Berg et al., 2019; Shalev et al., 2019), so the oceanic Mg cycle has a direct influence on carbon burial.

Calcium shows generally conservative mixing in the dissolved load in both the Borgarfjörður and the Amazon estuaries, although Ca concentrations appear to fluctuate in the very low salinity zone in the Borgarfjörður estuary (Figure 5.3D). Based on the dissolved load data in the interaction experiments, the transfer model shows that Ca is released from the solids into the dissolved load (Figure 4.5A). In addition, there is no clear relationship between Ca and Li (or K and Mg) concentrations in the exchangeable, oxide, and clay fractions in the solid samples from both the Borgarfjörður and the Amazon estuary (Figures 6.9, 6.10, and 6.11). These results indicate that it is less likely for exchangeable, oxide, or clay fractions to uptake Ca during estuarine weathering. In contrast, the Ca concentrations in the carbonate fractions ($[Ca]_{\text{carbonate}}$) in the bedload solids increase by 2 orders of magnitude through the Borgarfjörður estuary transect (Figure 5.10A), and the $[Ca]_{\text{carbonate}}$ in the Amazon bedload solids (117MUC and 41MUC) in the high salinity zone are 1 to 2 magnitudes higher than the $[Ca]_{\text{carbonate}}$ in the other solids in the Amazon north transect (Table 6.3). Thus, dissolved Ca is more likely to participate in carbonate formation in estuaries, which is different from Mg that is likely to be removed by clays. These findings agree with behaviour observed in the CarbFix mineral carbonation experiment, where carbonate was

precipitated at depth in basalts, but only noticeably affected the Ca, but not Mg, behaviour (Oelkers et al., 2019; Pogge von Strandmann et al., 2019c).

Calcium is also a key major cation for carbonate precipitation in the ocean and a nutrient in the marine biosphere; therefore the Ca cycle in the ocean directly affects the carbon biogeochemical cycle (Fantle and Tipper, 2014). However, there is still uncertainty in the oceanic Ca cycle, especially the fractionation between Ca sinks and seawater, which may influence the Ca isotope composition of seawater (Zhu and Macdougall, 1998; Fantle and Tipper, 2014; Tipper et al., 2016; Chen B.-B. et al., 2023). For example, the Mg/Ca ratio in the ocean is a potential influencing factor for the Ca sinks and for the Ca fractionation between seawater and those sinks (Fantle and Tipper, 2014). Importantly, the Mg/Ca ratio of seawater may also influence the carbon cycle (Wilkinson and Algeo, 1989; Higgins and Schrag, 2012; Dunlea et al., 2017; Coogan and Dosso, 2022). Thus, the differences between the Mg and Ca behaviour during alteration of river-derived particles in estuaries likely has an impact on the carbon cycle.

7.2.2 Behaviour of immobile elements (Fe, Mn, and Al) and implications for ocean biogeochemistry

Generally, for immobile elements, more than 70% of the dissolved Fe, 25–45% of the dissolved Mn, and 20–50% of the dissolved Al transported by river water can be removed in estuaries, due to processes such as flocculation, complexation, and adsorption (Boyle et al., 1977; Sholkovitz, 1978; Sholkovitz et al., 1978; Morris et al., 1986). Correspondingly, in this study, increases in $[\text{Fe}]_{\text{oxide}}$, $[\text{Fe}]_{\text{clay}}$, $[\text{Mn}]_{\text{clay}}$, and $[\text{Al}]_{\text{clay}}$ in the bedload solids in the Borgarfjörður estuary (Figure 5.10D–F) and the Amazon estuary (Figure 6.3D–F) are observed through the salinity transects, which indicate the incorporation of Fe, Mn, and Al into the particles from the dissolved load. In addition, the decreases in Fe, Mn, and Al concentrations in the bulk suspended load in the Borgarfjörður estuary may indicate the settling of Fe, Mn and Al minerals which includes both primary minerals and secondary fractions (i.e., oxide and clay fractions), which is likely related to flocculation (Figure 5.8D–F) (Section 5.4.2.1).

On the one hand, it is known that the estuarine removal of Fe, Mn, and Al is probably combined with organic matter burial (including organic carbon) due to both physical and chemical effects (Boyle et al., 1977; Sholkovitz, 1978;

Sholkovitz et al., 1978; Morris et al., 1986). For example, the organic carbon may be directly bound to reactive Fe (Lalonde et al., 2012), and organic carbon is preserved as clay-organic nanocomposites (Kennedy and Wagner, 2011; Kennedy et al., 2014). Thus, the flux and characteristics (i.e., mineralogy, weathering degree, grain size) of river-derived particles, which is linked to continental erosion and weathering, can influence the carbon cycle through changing the fluxes of organic carbon burial (Ludwig et al., 1996; Galy et al., 2007; Hage et al., 2022). In principle, enhanced oxide and clay formation can promote organic carbon burial. On the other hand, if there is clay neoformation during estuarine weathering, the clay formation consumes not only Al and Fe, but also alkalinity and dissolved silica, with an influence that is similar to reverse weathering (Mackenzie and Kump, 1995). Specifically, the alkalinity is transferred to CO₂ during aluminosilicate formation rather than being buried as carbonate in the ocean (Isson and Planavsky, 2018). Thus, the alteration of river-derived particles is also likely to influence the inorganic carbon cycle. In principle, enhanced clay formation hinders inorganic carbon burial (Isson and Planavsky, 2018). Thus, the alteration of river-derived particles plays an opposite role to organic carbon and inorganic carbon burial in the estuary and the net effect needs to be further investigated.

More complicatedly, although a general positive relationship between [Al]_{clay} and [Li]_{clay} is observed in the bedload samples from the Borgarfjörður and Amazon north and south channel transects, [Al]_{clay} is constant in the alongshore bedload solids in the Amazon estuary, whereas [Li]_{clay} still increases (Figure 6.11). Although it is hard to exclude leaching methods and/or mechanical sorting as controlling factors, there is nevertheless a possibility that the increase in [Li]_{clay} could reflect Li incorporation into the river-derived particles, probably due to the high dissolved Li concentration, without new Si-O-Al linkages forming. In this case, the Li incorporation and associated Li isotope fractionation may change the Li isotope composition in the ocean, while the Li incorporation does not represent alkalinity consumption itself.

Overall, although there is strong evidence that Li is likely to be involved in estuarine oxide and clay formation with Li isotope fractionation (Sections 5.4.2 and 6.4.1), more exploration into the links between Li and Li isotopes as tracers and the carbon burial during estuarine processes is needed in the future.

7.3 Conclusions

The Li removal flux by river-derived particles is estimated to be $1.8\text{--}7.2 \times 10^{10}$ g/yr ($2.6\text{--}10.3 \times 10^9$ mol/yr) by assuming around 1–4 $\mu\text{g/g}$ Li removal into the solids during estuarine weathering based on the compilation of the data from this study and published data, although this estimate needs to be refined by exploring more estuaries. The estuarine Li removal is estimated to have an insignificant influence (<5%) in modifying the riverine dissolved Li input flux and isotope composition; however, it is a significant sink for dissolved Li in the modern ocean. The estuarine removal is likely to be related to the continental weathering regime (i.e., erosion and chemical weathering). Thus, changes in the continental weathering regime may directly affect the Li sink in the ocean.

Furthermore, the element concentrations and Li isotope values of natural estuarine sediments imply the formation of secondary oxide and clays in estuaries. On the one hand, clay formation may hinder inorganic carbon burial. On the other hand, oxide and clay formation within estuaries may enhance organic carbon burial because of processes such as flocculation, complexation, and adsorption. Thus, although there is strong evidence that Li is likely to be involved in oxide and clay formation with Li isotope fractionation, more exploration of the links between Li isotopes as tracers and the processes and fluxes of carbon burial during estuarine processes is needed in the future.

Chapter 8. Conclusions and prospects

To explore the alteration of river-derived particles in estuaries, especially using Li concentrations and isotopes, and the influence of this alteration on ocean biogeochemistry and the carbon cycle, first, the methodology was developed and examined (Chapters 2 and 3); second, interaction experiments were conducted to imitate the process of alteration of river-derived particles in the estuary (Chapter 4); third, the dissolved load, suspended load, and bedload samples from two estuaries were analysed to examine the alteration of river-derived particles in natural estuaries (Chapters 5 and 6); last, the observations in the interaction experiments and natural estuarine samples were summarised and the influence of the alteration of river-derived particles during estuarine weathering on ocean biogeochemistry and the carbon cycle was discussed (Chapter 7).

In Chapter 3, a sequential leaching procedure to extract the exchangeable, carbonate, oxide, and clay fractions was developed. A series of trials were conducted that explored the effects of temperature, leaching time, reagent/solid ratio, and reagent strength on extracting in particular the oxide fraction for Li isotopes. The optimised method for extracting the oxide fraction from silicates for Li isotopes is considered to be 0.04 mol/l HH in 25% v/v HOAc with a reagent/solid ratio of 40 ml/g at room temperature (20 ± 2 °C) for 1 h. In addition, the reproducibility of the sequential leaching procedure was confirmed to be acceptable based on several replicate analyses, and the accuracy of elemental recovery in the full sequential leaching procedure was verified based on comparison to the elemental concentrations measured in bulk sample dissolutions. However, it is notable that no leaching method is entirely efficient, and any operationally defined target fraction would likely contain some elements from other fractions being attacked before the target fraction is entirely dissolved. Thus, it is critical that the elemental composition of each fraction is examined to

assess any contributions from other fractions.

In Chapter 4, based on four series of solid-water interaction experiments (i.e., basalt-Li-add, basalt-Li-free, loess-Li-add, loess-Li-free experiments) with gradual addition of concentrated artificial seawater, Na, Mg, and K are observed to be removed into the solids from the dissolved load, whereas Ca is released into the dissolved load during the salinity-increasing stage of all the experiments. In addition, the net transfer flux (and potentially transfer direction) of Li likely depends on the dissolved Li concentrations in the saline water, which implies that high Li concentrations in the dissolved load may be the main reason for Li removal by solids in the natural estuaries. In contrast, the Li isotope fractionation factor likely depends on the solid mineralogy. Furthermore, taking the basalt-Li-add experiment as an example, there is net transfer of Li from the dissolved load to the solids with Li isotope fractionation during the imitated estuarine weathering.

In Chapters 5 and 6, analyses of natural samples from the small basaltic Borgarfjörður estuary, Iceland and the Amazon estuary show net transfer of Li from the dissolved load to the suspended load and bedload solids, with associated Li isotope fractionation. This removal is evidenced by the increase in Li concentrations in the secondary fractions (i.e., exchangeable, oxide, and clay fractions) in the solid samples, although the dissolved Li concentration is observed to exhibit conservative mixing of river water and seawater in both estuaries. In addition, the dissolved Li isotope composition also shows conservative mixing of river water and seawater in the Borgarfjörður estuary, whereas the dissolved Li isotope values are 1–2‰ higher than the theoretical conservative mixing values in the medium salinity zone of the Amazon estuary. The observed conservative mixing of dissolved Li concentrations in both estuaries and dissolved Li isotopes in the Borgarfjörður estuary are probably due to the high Li concentration in seawater, and the comparatively large amount of seawater involved in the estuary mixing, which can mask the Li changes in the dissolved load. After eliminating the influence of mechanical processes in the Borgarfjörður estuary, and using modelling in the Amazon estuary, the Li removal

flux is estimated to be $\sim 0.36\text{--}1.09 \times 10^7$ g/yr (with 1–3 $\mu\text{g/g}$ Li uptake in solid) in the Borgarfjörður estuary and $\sim 3.6\text{--}4.8 \times 10^9$ g/yr (with 3–4 $\mu\text{g/g}$ Li uptake in solid) in the Amazon estuary. Amongst the Li removal, most Li is incorporated into the clay fractions. In addition, the removed Li is sourced from both dissolved riverine Li, but mainly from dissolved seawater Li. The Li isotope fractionation during the process of Li removal from the dissolved load by solids is estimated to be -6.5 to -14.5‰ ($\Delta^7\text{Li}_{\text{exchangeable-seawater}}$), -21.2 to -28.6‰ ($\Delta^7\text{Li}_{\text{oxide-seawater}}$), -23.6 to -26.5‰ ($\Delta^7\text{Li}_{\text{clay-seawater}}$), and -17.1 to -24.0‰ ($\Delta^7\text{Li}_{\text{secondaryfraction-seawater}}$). Furthermore, there are also increases in K in the exchangeable and clay fractions, and increases in Mg, Fe, and Al in the clay fractions, in the bedload samples of both the Borgarfjörður and Amazon estuaries. The Mg removal flux in the Amazon estuary is estimated to be $\sim 1.8\text{--}2.4 \times 10^{12}$ g/yr, which may significantly influence the Mg cycle in the ocean.

In Chapter 7, the new data are considered in combination with a compilation of the published data from other estuaries, and the Li removal flux by river-derived particles is estimated to be $1.8\text{--}7.2 \times 10^{10}$ g/yr ($2.6\text{--}10.3 \times 10^9$ mol/yr) by assuming around 1–4 $\mu\text{g/g}$ Li removal into the solids during estuarine weathering. Notably, this estimate needs to be further tested and refined by exploring more estuaries. In addition, because the removed Li is sourced from both the riverine dissolved Li and mainly from seawater dissolved Li, the Li removal is estimated to have an insignificant influence ($<5\%$) in modifying the riverine dissolved Li input flux and isotope composition. However, the Li removal flux is a significant sink for Li from the modern ocean. Importantly, this estuarine removal is likely to be related to the continental weathering regime (i.e., erosion and chemical weathering). Thus, changes in the continental weathering regime may directly affect the Li sink in the ocean. Furthermore, estuarine weathering also removes K and Mg from the dissolved load and therefore influences the K and Mg cycles in the ocean. Especially, for Mg, as one of the major elements involved in carbonate formation and therefore the burial of inorganic carbon, the incorporation of Mg into the clay fraction in river-derived particles may hinder inorganic carbon burial and influence

the Mg/Ca ratio in the ocean. In addition, if clay formation occurs during estuarine weathering, alkalinity would be consumed and transferred to CO₂, which also hinders carbon burial. However, oxide formation and clay formation within estuaries also enhances organic carbon burial because of processes such as flocculation, complexation, and adsorption. Thus, although there is strong evidence that Li is likely to be involved in oxide and clay formation with Li isotope fractionation, more exploration of the links between Li isotopes as tracers and the processes and fluxes of carbon burial during estuarine processes is needed in the future.

In conclusion, this study revealed that Li is removed with isotopic fractionation from the dissolved load by solids, especially clay and oxide fractions, during the alteration of river-derived particles in estuaries. The rapid increase in dissolved Li concentrations is probably one of the significant reasons for Li removal by river-derived particles. The estuarine Li removal flux was estimated to be a significant Li sink in the ocean, which may influence the Li isotope composition of seawater. In addition, the estuarine Li sink is likely influenced by the continental weathering regime, especially the erosion rates. Furthermore, this study suggested a wider the importance of the alteration of river-derived particles in estuaries on ocean biogeochemistry (e.g., carbon cycle, Mg cycle, and K cycle). However, exploration of more estuaries is needed to refine the understanding of the Li behaviour during estuarine weathering in this study, in particular the understanding of the influence exerted by upstream continental weathering factors (e.g., mineralogy and weathering degree of the river-derived particles). This knowledge would also allow a more accurate and precise constraint on the Li sink flux. In addition, more work is needed to better distinguish the influence of different processes (e.g., mechanical sorting, flocculation, resuspension, clay formation, cation incorporation) on the Li and Li isotope behaviour, which would enable a better understanding of the links between Li isotope changes and the global carbon cycle.

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Appendix: Supplementary Tables

A file including supplementary tables is attached.

The supplementary tables are:

Table S1.1 Li fluxes and Li isotope compositions of input and output in modern oceanic Li cycle

Table S3.1 Li isotope fractionation between oxide fractions and solutions

Table S4.1 Sampling during interaction experiments

Table S4.2 Dissolved load in Control groups of interaction experiments and the corresponding conservative mixing calculation.

Table S4.3 Conservative mixing calculation of dissolved load in basalt-Li-add experiments and basalt-Li-free experiments.

Table S4.4 Conservative mixing calculation of dissolved load in loess-Li-add experiments and loess-Li-free experiments.

Table S4.5 Calculation of element transfer between dissolved load and solid in basalt-Li-add experiments and basalt-Li-free experiments.

Table S4.6 Calculation of element transfer between dissolved load and solid in loess-Li-add experiments and loess-Li-free experiments.

Table S6.1 Li isotope fractionation modelling in Amazon estuary

Table S6.2 Amazon estuary model