Progress towards an improved Precambrian seawater $^{87}\text{Sr}/^{86}\text{Sr}$ curve

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Abstract

The secular trend of seawater strontium isotope ratio ($^{87}\text{Sr}/^{86}\text{Sr}$) reflects changes in the relative contributions of continental versus mantle reservoirs to ocean composition, and informs global tectonic events, weathering rates and biogeochemical cycling through Earth history. However, the Precambrian seawater $^{87}\text{Sr}/^{86}\text{Sr}$ curve is known in far less detail than its Phanerozoic counterpart. For this study, we compiled 2249 strontium isotope ratios of Precambrian marine sedimentary rocks published since 2002, alongside previously compiled older data. Here we evaluate the uncertainty of all published data for constraining coeval seawater $^{87}\text{Sr}/^{86}\text{Sr}$ using four criteria (depositional environment, diagenetic alteration, age constraint and dissolution method). The resultant seawater $^{87}\text{Sr}/^{86}\text{Sr}$ curve uses mainly ‘high certainty’ data and shows an overall increasing trend from ~0.7005 at c. 3.5 Ga to ~0.7089 towards the end of the Ediacaran Period. The improved curve shows an earlier deviation of seawater $^{87}\text{Sr}/^{86}\text{Sr}$ from the contemporaneous mantle by c. 3.5 Ga, which might reflect the first significant emergence of evolved continental crust related to nascent tectonics. Additionally, the updated curve records two major rises at 2.5-2.2 Ga and 1.9-1.7 Ga in addition to a well-established event at 0.8-0.5 Ga. Despite
the relative scarcity of high-certainty data, these two increases are consistent with
enhanced continental weathering following the onset of oxidative weathering and
assembly of the supercontinent Nuna, respectively. Although confirmation of these
two events awaits more high-certainty data, Precambrian seawater $^{87}\text{Sr}/^{86}\text{Sr}$
experienced stronger oscillations and better correspondence with supercontinent
cycles than previously shown.

**Key words**

Strontium isotopes; Precambrian; Carbonates; Diagenesis; Dissolution methods;
Weathering; Supercontinent cycles
1. Introduction

Strontium isotopes are believed to be homogeneously distributed in seawater on a global scale because the residence time of Sr in the modern ocean (c.10^6 yr) is more than 1000 times longer than the ocean circulation time (Broecker and Peng, 1983; Elderfield, 1986; Hodell et al., 1990). In early studies (Brass, 1976; Faure et al., 1965; Veizer and Compston, 1974), variations in seawater $^{87}$Sr/$^{86}$Sr were tied to the weathering of different lithologies. However, since the discovery of hydrothermal exchange as a source of Sr to the ocean (Corliss et al., 1979; Spooner, 1976), the Sr isotope budget of seawater has been interpreted as a balance between more radiogenic riverine input from continental weathering and less radiogenic mantle input from mid-ocean ridges (e.g., Albarède et al., 1981; Corliss et al., 1979; Goldstein and Jacobsen, 1987; Spooner, 1976; Veizer, 1989). The strontium isotope composition of riverine input is complicated by the differential weathering of various lithologies (for example, less radiogenic, more easily weathered basalts versus highly radiogenic, less easily weathered felsic rock) and buffering by the weathering of carbonate rocks with an isotope composition close to seawater (Allègre et al., 2010; Brass, 1976; Galy and France-Lanord, 1999; Veizer and Compston, 1974). Strontium from different sources is homogenized in the ocean and incorporated into authigenic minerals, especially carbonate rocks, via substitution for calcium (McArthur, 1994). A conceptual model of the seawater Sr flux cycle is shown in Fig.1.

Strontium isotope stratigraphy (SIS) has come to be widely used in geological studies as a chemostratigraphic tool (Burke et al., 1982; Elderfield, 1986; McArthur, 1994; Veizer et al., 1999), and relies on the observation that the $^{87}$Sr/$^{86}$Sr ratio in the world’s oceans has varied over time (McArthur et al., 2012). The primary uses of SIS can be summarized as follows: 1) the numerical age of a sample with a known
$^{87}\text{Sr}/^{86}\text{Sr}$ ratio can be determined by comparison with the global seawater $^{87}\text{Sr}/^{86}\text{Sr}$ curve (McArthur, 1994; McArthur et al., 2012; 2020); 2) for a sample with known age, its $^{87}\text{Sr}/^{86}\text{Sr}$ ratio can be used to distinguish pristine from diagenetically altered samples and marine from non-marine settings (e.g., Kuznetsov et al., 2010; Stüeken et al., 2017); and 3) variations in seawater $^{87}\text{Sr}/^{86}\text{Sr}$ likely reflect long term paleo-weathering conditions and so can be used to test hypotheses of tectonic, biological, and climatic changes through Earth history (e.g., Bartley, 2001; Cawood et al., 2018; Halverson et al., 2007; Hawkesworth et al., 2016; Shields, 2007).

One of the main aims of this review is to explore the relationship between secular changes in seawater Sr isotope composition and Earth system dynamics, including weathering conditions, tectonic events and potentially also oxygenation events. It was initially believed that the seawater $^{87}\text{Sr}/^{86}\text{Sr}$ curve evolved linearly during geologic history (Wickman, 1948). This assumption was subsequently overturned when researchers realized that the strontium isotope curve oscillated with time (e.g., Burke et al., 1982; Gast, 1955; Veizer and Compston, 1976). While the Phanerozoic curve has been updated repeatedly over the years (e.g., McArthur and Howarth, 2005; McArthur et al., 2012; McArthur et al., 2020) with the abundance of datasets permitting quantification of uncertainties using LOWESS (e.g., McArthur et al., 2012, 2001), further study of the Precambrian curve, defined by only sparse datasets, has lagged behind. Shields and Veizer (2002) published a carbonate geochemistry compilation covering Precambrian time and thereby constructed a seawater strontium isotope curve using in most cases the lowest values of carbonate samples as it was suggested that diagenetic exchange would generally increase measured Sr isotope values. Although that curve is still widely used for reconstructing tectonic cyclicity over time (e.g., Cawood et al., 2018; Hawkesworth et al., 2016), many new data have
been published in the intervening two decades and it has an inadequate temporal resolution. The strontium isotope curve of seawater needs therefore to be periodically updated to keep up with new data and increasingly precise age constraints, which necessitate an updated compilation with more stringent screening.

Reconstructing the Precambrian seawater strontium isotope curve faces a number of critical difficulties such as the high potential for diagenetic alteration, greater age uncertainty, predominance of dolomite in the Precambrian, especially prior to the Neoproterozoic, etc. Moreover, different issues arise in different localities. For instance, continental margin settings, although more likely to be open marine, have generally been affected by tectonic convergence events and ocean closures, resulting in higher metamorphic grade, whereas cratonic interiors, although potentially better preserved, have less precise age constraints, and are more likely to be affected by restricted environments and alteration by meteoric fluids. SIS studies must rely on diagenetically well-preserved chemical precipitates in that post-depositional alteration could alter both chemical and isotopic compositions (Shields and Veizer, 2002).

However, well-preserved materials (low-Mg calcitic fossils; such as conodonts and articulate brachiopods) that are widely available in Phanerozoic rocks are absent in Precambrian rocks (Brand and Brenckle, 2001; Kah et al., 2001). Fine-grained bulk carbonate rocks (e.g., micrite) are often used for strontium isotope studies of Precambrian seawater, but their study requires well-honed dissolution methods and screening to obtain the least-altered values (Bailey et al., 2000; Li et al., 2011).

Additionally, other problems such as a limited amount of suitable carbonate rocks, ambiguous paleoenvironmental settings (Prokoph et al., 2008; Shields and Veizer, 200; Kuznetsov et al., 2010) also hinder Precambrian SIS studies to some degree. Nevertheless, a growing number of carefully executed studies have shown that
resolution approaching Phanerozoic levels can be achieved under ideal circumstances (e.g., Zhou et al., 2020).

The main aims of this review are:

1) To summarize the different dissolution and diagenetic screening methods used in isotopic studies of Precambrian carbonate rocks in order to demonstrate their advantages and shortcomings.

2) To update an existing Precambrian seawater strontium isotope compilation (Shields and Veizer, 2002), using publications between 2002 and 2020, and apply four criteria (depositional environment, diagenetic alteration, age constraint and dissolution method) to assign both newly and previously compiled data to one of three groups: high-certainty data; medium-certainty data; and low-certainty data. We use the most recent international geologic time scale (Strachan et al., 2020) to assign data to formal time subdivisions.

3) To discuss possible explanations for the temporal trend of the updated curve by reviewing recognizable events (supercontinent cycles, glaciations, large igneous provinces, etc.) and incorporating complementary data sets (Nd, Hf, O isotopes); to provide tests for some highly controversial topics (e.g., the onset of plate tectonics) using the improved Sr isotope curve.

2. Analytical methods

2.1 Sample types for Precambrian SIS

Low-Mg calcitic fossils, such as foraminifera, brachiopods and belemnites, and apatitic fossils, such as conodonts, are abundant in Phanerozoic marine strata. When well preserved, they tend to retain a near original seawater signal, particularly when deposited in carbonate-dominated sediment, and so are ideal materials to reconstruct the Phanerozoic seawater strontium isotope curve (e.g., McArthur et al., 2020; Veizer
et al., 1999). Because no such skeletal material is available for Precambrian SIS, bulk carbonate (e.g., Cox et al., 2016; Halverson et al., 2007) or micro-drilled primary carbonate components, such as calcite cement or homogeneous micrite (e.g., Kaufman et al., 1993; Zhou et al., 2020), are commonly used.

Recrystallization in carbonates generally leads to an increase in grain size, and so the most finely crystalline material, generally micrite, is considered to have escaped substantial diagenetic recrystallization (Kah, 2000a; Kah et al., 1999). Consequently, fine-grained carbonate components, extracted by petrographically guided micro-drilling, are generally recommended for SIS (e.g., Li et al., 2011). Early diagenetic calcite microspar cement or CMC (Zhou et al. 2020, also referred to as “Molar-tooth structure”; e.g., Fairchild et al., 1997; James et al., 1998; Shields, 2002) may also be suitable for SIS where available. CMC is characterized by uniform, equant, polygonal and tightly packed calcite crystals (Furniss et al., 1998; James et al., 1998; Pollock et al., 2006) that filled voids and cracks before deposition of much overlying sediment and before total lithification of surrounding matrix (Fairchild et al., 1997; Smith, 1968).

Non-carbonate rocks such as barite (e.g., McCulloch, 1994; Satkoski et al., 2016), gypsum or anhydrite (e.g., Kah et al., 2001) and franelite (Li et al., 2011) have also been used for strontium isotope studies. For instance, in some Archean sedimentary sequences where carbonate is scarce, barite can still be a reliable monitor for seawater Sr isotope composition as it generally has high Sr contents and resists recrystallization (Paytan et al., 1993) as long as its origin can be determined (Griffith and Paytan, 2012).

In the following discussion, we mainly focus on carbonate rocks as they are the most commonly used materials for Precambrian SIS.

2.2 Carbonate sample preparation

Significant artefacts in strontium isotope stratigraphy (SIS) studies might result from
improper sample preparation that dissolves recrystallised derivates or contaminant components, requiring a suitable dissolution method to minimise the Sr contamination from untargeted phases (McArthur, 1994). We divided dissolution methods of carbonate rocks into three main types: single-step bulk leaching method, two-step sequential leaching method, and multiple-step sequential leaching method. We further subdivided the three main types according to the acid type and reagents used for pre-leaching (ammonium acetate or acetic acid). Details and related references are provided in Table 1.

Single-step bulk leaching used to be the most common method for carbonate extraction, which is conducted by adding an acid to rock powder to dissolve carbonate minerals, while leaving insoluble detrital phases behind (e.g., Brand et al., 2012; Hall and Veizer, 1996; Kaufman and Knoll, 1995; Kupecz and Land, 1991; Miller et al., 2008). In some cases, carbonate samples are dissolved in a weak acid, such as acetic acid, which is considered to be less aggressive than a dilute strong acid, to avoid dissolution of matrix incorporated impurities (e.g., Kaufman and Knoll, 1995; Miller et al., 2008; Yoshioka et al., 2003), but in other cases, sample powders are dissolved in strong acids such as HCL and HNO₃ (e.g., Brand et al., 2012; Satkoski et al., 2017). The latter method should be avoided, especially for impure samples, because aggressive acid leaching attacks clay minerals in the rock matrix that likely contain Rb and therefore radiogenic Sr from Rb decay, leading to higher measured strontium isotope values (e.g., Bailey et al., 2000).

Pre-leaching has been emphasized as it enhances the reliability of obtained values by removing exchangeable Rb and Sr, and strips potentially-contaminating Sr from non-carbonate phases (e.g., Bailey et al., 2000). Pre-leaching has been shown to remove contaminant Sr, even from pure samples. In the experiment of Bailey et al.,
carbonate samples from Trunch and Lagerdorf were very pure (96% and 98% carbonate, respectively), but only pre-leached samples exhibited near expected seawater values. Such sequential leaching methods started already in the early 90’s and are very widely used in strontium isotope studies (Bailey et al., 2000; Bellefroid et al., 2018b; Gorokhov et al., 1995; Kupecz and Land, 1991; Liu et al., 2013; Li et al., 2011).

Based on the ten step leaching experiment of Bailey et al., (2000), later confirmed by Li et al., (2011), the commonly used two-step sequential leaching method suggests using the first leach (pre-leach process, c. 30%-40% dissolved) to remove most contaminant Sr and Rb, followed by a weak acid leach (another c. 30% dissolved) for Sr isotope analysis. This second leach has been shown to provide near primary calcite ratios, importantly leaving the sample incompletely dissolved and the solution at a neutral pH to avoid further contamination from other phases. As for the reagents used in pre-leaching, although ammonium acetate is widely used, it might be unnecessary as dilute acetic acid may remove contaminant Sr at least as effectively (e.g., Bailey et al., 2000; Li et al., 2011).

In addition to single-step bulk leaching and two-step leaching, a multiple-step leaching procedure, using acetic acid of intermediate strength, has also been tested. Although relatively complicated, this approach can improve the fidelity of measured \(^{87}\text{Sr}/^{86}\text{Sr}\) values, especially for samples with complex and heterogeneous mineralogy (Bailey et al., 2000; Bellefroid et al., 2018b; Liu et al., 2014, 2013). By measuring elemental concentrations and \(^{87}\text{Sr}/^{86}\text{Sr}\) values for all individual leaching steps, the least-contaminated fraction of each sample can be identified (Bailey et al., 2000; Bellefroid et al., 2018b).

Diverse dissolution methods utilised in the SIS studies (mainly from our new
compilation) have been summarized in Table 1.
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<tr>
<th>Type</th>
<th>Pre-leach</th>
<th>Dissolution Method</th>
<th>References</th>
<th>Comments</th>
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<tr>
<td>1. Single-bulk leaching in weak acid without pre-leaching</td>
<td>No pre-leaching</td>
<td>Aliquots of drilled powders are dissolved in weak acid (acetic acid) to avoid dissolution of clastic phases, then centrifuged to separate soluble and insoluble fractions.</td>
<td>Alvarenga et al., 2019, 2014; Bartley et al., 2001; Bekker et al., 2006, 2003b; Galindo et al., 2004; Kaufman and Knoll, 1995; Miller et al., 2008; Sawaki et al., 2010b, 2010a; Yoshioka et al., 2003; Zhang et al., 2020</td>
<td>Preferred for large datasets but lack of pre-leach increases the risk of contamination from ion exchangeable sites and secondary carbonate phases.</td>
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<tr>
<td>2. Single-bulk leaching in strong acid without pre-leaching</td>
<td>No pre-leaching</td>
<td>Powdered carbonate samples are dissolved in strong acid such as HCl and HNO₃</td>
<td>Azmy et al., 2006; Brand et al., 2012; Frauenstein et al., 2009; Nogueira et al., 2007; Satkoski et al., 2017</td>
<td>Dissolving samples in a strong acid might lead to higher $\frac{^{87}Sr}{^{86}Sr}$ by attacking more radiogenic clastic phases.</td>
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<tr>
<td>3. Two-step sequential leaching with pre-leach in ammonium acetate</td>
<td>Pre-leached in volumes of ammonium acetate to remove loosely bound Rb and Sr cations, then insoluble residues were leached in acetic acid and the subsequent insoluble residue removed by centrifugation.</td>
<td>Bartley et al., 2007; Bekker et al., 2003a; Bold et al., 2016; Cox et al., 2016; Cui et al., 2015; Gibson et al., 1999; Gorokhov et al., 1995; Halverson et al., 2007; Kochnev et al., 2018; Kuznetsov et al., 2010, 2008, 2005, 2012; Melezhik et al., 2009, 2005; Rooney et al., 2014; Semikhatov, 2002; Semikhatov et al., 2004; Thomas et al., 2004; Valladares et al., 2006</td>
<td>Effectively removes Sr contamination via pre-leach. However, same volume of acid for all samples within a given batch might lead to an acid excess for impure carbonates (Bellefroid et al., 2018b).</td>
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<tr>
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<td>Two-step sequential leaching with pre-leach in acetic acid</td>
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<td>Pre-leached in dilute acetic acid</td>
<td>After pre-leaching, samples are dissolved partially using acetic acid.</td>
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<td></td>
<td>George et al., 2019; Li et al., 2011, 2020; Ray et al., 2003; Zhou et al., 2020</td>
<td>Acetic acid pre-leach might remove contaminant Sr more effectively compared with ammonium acetate (Bailey et al., 2000; Li et al., 2011).</td>
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<th>Multiple-step sequential leaching</th>
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<td></td>
<td>Pre-leached in volumes of ammonium acetate (NH₄OAc)</td>
<td>Aliquots of powdered carbonate are pre-leached in volumes of ammonium acetate, then the insoluble residues are sequentially leached in acetic acid to identify the most pristine value.</td>
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<tr>
<td></td>
<td>Bailey et al., 2000; Bellefroid et al., 2018b; Fairchild et al., 2018; Li et al., 2020; Liu et al., 2014, 2013</td>
<td>This method is more complicated, but it is more likely to obtain an improved $^{87}$Sr/$^{86}$Sr, especially for samples with complex mineralogy and heterogeneities (ammonium acetate could be unnecessary if followed by dilute acetic acid).</td>
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Table 1. Summary of different dissolution methods of bulk carbonate rocks for strontium isotope analysis. References include the method papers and the newly compiled papers in this study.
3. Diagenetic analysis

3.1. Carbonate diagenesis

Precambrian strontium isotope stratigraphy (SIS) relies on the analysis of well-preserved marine carbonate rocks because post-depositional alteration can alter the chemical and isotope composition of carbonate rocks. Carbonate diagenesis can include dissolution and reprecipitation that affects both the mineralogy and crystal size of the original carbonate precipitate and can occur in different types of fluids such as meteoric or marine fluids (Higgins et al., 2018; Melim et al., 2004; Swart, 2015). The degree of geochemical alteration by diagenesis depends on factors such as the openness and the water-rock ratio of the diagenetic system and the stability of mineralogy (Marshall, 1992; Banner and Hanson, 1990). Open-system and high water-rock ratios generally lead to a greater loss of primary environmental signals (Marshall, 1992). When dissolution takes place in a large volume of pore water, the composition of pore fluids is little influenced by the input of dissolving materials. Thus the composition of replacement phases would be similar to pore fluids that reflect equilibrium with the diagenetic environment (Marshall, 1992; Veizer, 1983).

High-magnesium calcite and aragonite are metastable, whereas low-magnesium calcite is relatively insoluble and inherently has less potential for diagenetic exchange (Marshall, 1992; Morse and Mackenzie, 1990; Swart, 2015).

Using static limits of trace elements such as Mn or Sr to select least-altered data has been proposed (e.g., Bates and Brand, 1991; Denison et al., 1994; Montañez et al., 1996). However, it has also been argued that the static threshold inadequately parameterizes the range of diagenetic effects experienced by carbonate components (Brand, 2004; Brand et al., 2012, 2010). It is unlikely that there are any unique criteria for the robust screening of altered samples because the post-depositional history
varies from basin to basin and even from sample to sample within a basin, so using static limits ignores spatial and temporal variations in local conditions (Bartley et al., 2001; Melizhik et al., 2001; Halverson et al., 2007). Therefore, a dynamic approach defined as utilising various screening methods to examine coeval materials from individual horizons is recommended (Fig. 2), which generally includes field and petrological examinations, geochemical screening (major and trace elements, stable isotopes, and strontium isotopes) and coeval sample comparisons (e.g., Banner, 2004; Bartley et al., 2001; Brand et al., 2012; Zhou et al., 2020).

3.2. Screening methods

3.2.1. Petrographic screening

Petrographic screening investigates textural or mineralogical changes in rocks using scanning electron microscopy, X-ray diffraction, thin section examination, and cathodoluminescence techniques (McArthur, 1994 and references therein) to distinguish primary from secondary sedimentary components. Primary components such as stromatolitic laminae, micrites, syndepositional marine cement and oolitic grains are most likely to retain original isotopic signals; while secondary components such as cross-cutting veins, late-stage void filling spar and dissolution features should be avoided during sampling (e.g., Kah et al., 2012, 1999; Kaufman and Knoll, 1995). Additionally, siliciclastic material might flag diagenetic alteration because it is normally associated with increased permeability to diagenetic fluids (Kah et al., 1999).

Diagenetic recrystallization processes commonly result in coarsening of grain size or complete obliteration of primary fabrics, if diagenesis took place in the presence of a fluid phase (e.g., meteoric or deep burial fluid) very distinct in composition from seawater. By contrast, fine-grained, primary components that preserve original
textures (e.g., ooids, small-scale sedimentary structure) indicate that recrystallization might have occurred in the presence of fluids similar to the composition of seawater, which means recrystallization/diagenesis occurred synsedimentarily or during shallow burial (Gilleaudeau et al., 2018).

Cathodoluminescence study of polished thick sections provides a qualitative way of estimating alteration (Bartley et al., 2007; Frank et al., 2003; Kah et al., 1999; Kaufman and Knoll, 1995). Luminescence in carbonates is commonly activated by Mn$^{2+}$ and quenched by Fe$^{2+}$ (Hemming et al., 1989). Mn and Fe are commonly rich in meteoric and burial fluids. Thus, this technique can be used to differentiate between samples that have been altered by meteoric and burial diagenesis and samples that have not (Kaufman and Knoll, 1995). Generally, dull, uniform to patchy luminescence indicates primary components, while brightly luminescent to non-luminescent, distinct zoning indicates secondary components (Kah et al., 2012, 1999).

### 3.2.2. Geochemical screening

1) Major and trace elements

Trends in the concentration of major and trace element such as Mg, Ca, Sr, Fe, and Mn are commonly used to recognize potential alteration in suites of samples (e.g., Denison et al., 1994; Van Geldern et al., 2006; Veizer et al., 1992a, 1992b). Mn/Sr or Fe/Sr are widely used as indices of alteration, and are generally expected to be higher in diagenetically-altered samples than in coeval seawater (Banner and Hanson, 1990; Brand and Veizer, 1980; Gorokhov et al., 1995; Kaufman and Knoll, 1995). This is because the distribution coefficient of Mn and Fe in stable (hexagonal) carbonate minerals (e.g., dolomite and calcite) is much higher than Sr, so recrystallization leads to an increase in Mn/Sr and Fe/Sr ratios (Rimstidt et al., 1998). However, this general relationship is complicated by variable redox conditions, diagenetic fluids, and...
mineralogy. High Mn/Sr or Fe/Sr ratios might indicate carbonate precipitation from anoxic waters instead of diagenetic alteration because both Fe and Mn tend to revert to their more soluble reduced forms under suboxic-anoxic conditions (Bruland et al., 2014; Canfield and Thamdrup, 2009). For instance, in low-oxygen Proterozoic oceans, elevated Mn and Fe concentrations could also reflect primary seawater (Bekker et al., 2003b; Gilleaudeau and Kah, 2013; Kah et al., 2004; Kah and Bartley, 2011). Burial diagenetic phases are commonly enriched in Mn and Fe due to reducing conditions in burial fluids (Veizer, 1983), but meteoric diagenetic phases can be characterized by either enrichment or depletion of Mn and Fe due to variable redox conditions in meteoric fluids (Banner and Hanson, 1990; Brand and Veizer, 1980). Moreover, mineralogies also need to be considered. For instance, dolomite generally has a higher preference for Fe and Mn (Mazzullo, 1992) and a lower preference for Sr compared with calcite (Vahrenkamp and Swart, 1990), while some early diagenetic dolomite can also be enriched in Sr relative to Fe and Mn (Gilleaudeau et al., 2018). It is common to use Mg/Ca to quantify the relative contribution of dolomite of samples (e.g., stoichiometric dolomite is generally considered as Mg/Ca ratios of >0.6). Using Mg/Ca ratio in conjunction with Mn/Sr, Fe/Sr could indicate modification of trace elements during dolomitization.

2) Stable isotope composition

The oxygen isotopic composition ($\delta^{18}O$) of carbonate rocks is sensitive to post-depositional alteration resulting from exchange with pore water oxygen and/or recrystallisation at elevated temperatures. The original oxygen isotope composition might be retained where carbonate minerals were subject to only minor recrystallisation under low water-rock ratio conditions (<10; Banner and Hanson, 1990; Jacobsen and Kaufman, 1999). Recrystallization and neomorphism at higher
temperatures are generally expected to lower the $\delta^{18}O$ of samples (Veizer, 1983).

However, $\delta^{18}O$ composition of meteoric waters is variable, i.e., it becomes lower with decreasing temperature and increasing latitude (Bowen and Wilkinson, 2002).

Therefore, meteoric waters will often be not so different to seawater in tropical marine carbonate platform settings. Additionally, dolomitization tends to increase $\delta^{18}O$. For instance, at 25°C the estimates for $\Delta\delta^{18}O_{dolo-cal}$ (difference in $\delta^{18}O$ between coprecipitated dolomite and calcite) range from 5‰ to 9‰ (Clayton and Epstein, 1958), 4‰ to 7‰ (e.g., Degens and Epstein, 1964; Northrop and Clayton, 1966) or 2.6‰ (Vasconcelos et al., 2005). Considering the variability of $\delta^{18}O$ in different situations, it needs be used in conjunction with other parameters such as trace element or strontium isotopes to indicate diagenetic alteration.

Compared with oxygen isotopes, carbon isotope values ($\delta^{13}C$) are more resistant to overprinting during diagenetic recrystallisation owing to the higher concentration of carbon in carbonate rocks relative to diagenetic fluids (e.g., Halverson et al., 2005). Given water/rock ratios $>1000$ (Banner and Hanson, 1990), $\delta^{13}C$ values of carbonates might be altered by re-equilibration during recrystallization, whereby interactions with diagenetic fluids would generally decrease $\delta^{13}C$ values because diagenetic fluids potentially contain isotopically depleted carbon. Cross-plots of $\delta^{13}C$ against $\delta^{18}O$ values are commonly applied to identify covariation, which might indicate diagenetic alteration (Banner, 1995; Brand and Veizer, 1981). However, authigenic carbonate precipitated from sediment pore fluids that have a different composition from overlying seawater, can produce higher or lower carbonate isotope values than primary carbonate, which complicates the use of $\delta^{13}C$ in identifying diagenetic processes (e.g., Schrag et al., 2013; Sun and Turchyn, 2014; Torres et al., 2020; Zhao et al., 2016).
Mineralogical changes, e.g. recrystallization of aragonite to calcite and dolomite, affect the geochemical indices to some degree (Brand et al., 2012). For instance, an aragonite precursor may cause $\delta^{13}C$ and $\delta^{18}O$ values to shift by $+1.8\%_o$ and $+0.8\%_o$, respectively, and these signatures could be retained if recrystallisation happened in a closed system (Rubinson and Clayton, 1969; Saltzman, 2005). Dolomitization would increase $\delta^{18}O$ and decrease Ca and Sr concentrations simultaneously, leading to smaller changes to $\delta^{18}O$ values and Sr/Ca, which might erroneously imply a lesser degree of alteration (Halverson et al., 2007).

3) Strontium isotopes

The Sr isotope composition of carbonate minerals is commonly affected by diagenesis; hence $^{87}\text{Sr} / ^{86}\text{Sr}$ ratios can also be used as indicators of alteration in the case that the original Sr isotope composition is known (Gorokhov et al., 1995; Ovchinnikova et al., 1995). In general, post-depositional processes tend to increase $^{87}\text{Sr} / ^{86}\text{Sr}$ values because evolved K-bearing silicates (rich in $^{87}\text{Rb}$ and thus higher $^{87}\text{Sr} / ^{86}\text{Sr}$) release $^{87}\text{Sr}$ into interstitial fluids from where it can be incorporated into carbonate rocks during diagenetic recrystallization (e.g., Fairchild et al., 2018). Therefore, in general, the current best estimates for seawater $^{87}\text{Sr} / ^{86}\text{Sr}$ are based mainly on the least radiogenic samples within a suite of rocks (e.g., Shields and Veizer, 2002). However, fluids that are less radiogenic than contemporaneous seawater, influenced either by mafic components/juvenile silicate, hydrothermal fluids or pressure solution of older, underlying carbonate rocks, may drive carbonate $^{87}\text{Sr} / ^{86}\text{Sr}$ to lower values (e.g., Brand et al., 2010; Cui et al., 2020; Miller et al., 2008; Satkoski et al., 2017). Alternatively, deviation from seawater values might also reflect a mixture of seawater and influence from river catchments in restricted environments (Miller et al., 2008). Therefore, a combination of multiple screening methods and
appropriate leaching methods, as well as careful sample selection and well-
constrained geological context, are needed to get a robust result. Elemental and
isotopic thresholds used for diagenetic screening compiled from the literature are
shown in Table 2.

4. Rubidium contamination

The radioactive isotope of Rb, $^{87}\text{Rb}$, decays to $^{87}\text{Sr}$ over time with a decay constant
($\lambda$) of $1.42 \times 10^{-11}$ yr$^{-1}$ (Steiger and Jäger, 1977); thus, the measured $^{87}\text{Sr}/^{86}\text{Sr}$ values of
carbonate rocks increase with radioactive $^{87}\text{Rb}$ decay. Some rubidium may have been
incorporated into the carbonate minerals directly, although its large size and $1^+$ charge
precludes substantial replacement of $\text{Ca}^{2+}$ or $\text{Mg}^{2+}$ ions in the mineral lattice. Most Rb
in sedimentary rocks is incorporated in the structure of igneous minerals and their
weathering products as well as potassium-rich clay minerals, which can constitute a
substantial portion of some bulk rock samples (McArthur et al., 2012). Therefore, it is
common to carry out a correction for Rb decay to estimate the initial $^{87}\text{Sr}/^{86}\text{Sr}$ value
(e.g., Sawaki et al., 2010a; Zhou et al., 2020). However, errors in Rb correction can be
introduced because of uncertainty in the samples’ ages, especially for Precambrian
samples, and because of incongruent leaching of Rb versus Sr. Well-preserved, pure
carbonate components will not contain much Rb. Aragonite with its more open structure
could accommodate Rb more easily than calcite, but it still incorporates much more Sr,
making the Rb/Sr ratios very low and the Rb correction unnecessary (McArthur, 1994).
For bulk rock samples, initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratios may be overcorrected because clay
minerals preferentially lose $^{87}\text{Sr}$ from their lattices during diagenesis or leaching
procedures compared with the parent Rb (Shields and Veizer, 2002). A good correlation
between Rb concentration and Al concentration could demonstrate that Rb derives from
aluminosilicates; hence, sample cleaning and pre-leaching is preferable to automatic
Rb-decay correction (Gorokhov et al., 1995; Hall and Veizer, 1996; Wierzbowski et al., 2012). To avoid error caused by Rb correction in our compilation, in most cases we directly use the measured values, which, where demonstrably well preserved, must therefore represent near primary maximum constraints on contemporaneous seawater.
<table>
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<tr>
<th>Sr (ppm)</th>
<th>Mn/Sr</th>
<th>Fe/Sr</th>
<th>Mg/Ca</th>
<th>δ¹⁸OVPDB (%)</th>
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<td>MP</td>
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<tr>
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<tr>
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<td>MP</td>
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<td>Supergroup</td>
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<td>&gt; −10</td>
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</tr>
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<td>PP</td>
<td>Kuznetsov et al., 2010</td>
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<tr>
<td>-6~−12</td>
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<td>Bekker et al., 2003a, 2001; Veizer et al., 1992a, 1992b</td>
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<td>&lt; 6</td>
<td>D</td>
<td>PP</td>
<td>Kaufman and Knoll, 1995</td>
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</table>

Table 2. Elemental and isotopic thresholds used to identify suitably well preserved carbonate rock samples in the published literature. L: limestone; D: dolostone; DL: dolomitic limestone. NP: Neoproterozoic; MP: Mesoproterozoic; PP: Paleoproterozoic. Although static thresholds are widely applied in chemostratigraphic studies, they cannot be applied across different studies and need to be justified on a case-by-case basis.
5. Age constraints and data evaluation

5.1. Age constraints

Chemostratigraphic correlation (mainly carbon isotopes) is well-established for the Neoproterozoic (especially Ediacaran), in part due to relatively abundant radiometric ages (i.e., U-Pb, Pb-Pb, Re-Os etc.) and high amplitude carbon isotope fluctuations (Halverson et al., 2010; Kaufman and Knoll, 1995; Knoll et al., 1986). A well-constrained chronostratigraphic framework allows us to assign ages of Neoproterozoic samples with a greater degree of precision. We have put almost all Neoproterozoic datasets into chronostratigraphic in order to get the best-estimated ages based on and updated from the latest age models, such as those of Macdonald et al., (2013), Cox et al., (2016), Bold et al., (2016), Fairchild et al., (2018). In these age models, carbon isotope trends were used by authors to calibrate Sr isotope records to get precise relative ages. In each succession, ages were constructed either by basic thermal subsidence modelling (e.g., Halverson et al., 2002) or by linear interpolation between correlated ages by assuming a constant sedimentation rate (Cox et al., 2016; Zhou et al., 2020).

Unfortunately, the global chemostratigraphic record remains limited for earlier Proterozoic and Archean times, and stratigraphic correlation still faces many challenges. Without well-established global chronostratigraphic frameworks and age models, it is generally not possible to assign ages to earlier Proterozoic and Archean samples in the same way as for the Neoproterozoic. Therefore, we mainly use ages provided by authors (e.g., absolute dates, chemostratigraphic correlation etc.), and update them where any newly-published dating/correlation has become available. We follow Shields and Veizer, (2002), defining age uncertainties less than ±50 Ma as well-constrained, and larger than ±50 Ma as poorly constrained.
5.2. Data evaluation

Four criteria (depositional environment, preservation, age constraints and dissolution methods) are used to assign compiled data to one of high, medium and low-certainty groups (Table 3, Fig. 3). The updated strontium isotope curve of Precambrian seawater is based mainly on high-certainty data. Medium-certainty data are also included in the reconstruction for completeness but only contribute to the interpretation of the curve where high-certainty data are not available. Low-certainty data are excluded from the curve reconstruction.

Depositional environment and preservation are essential preliminary criteria for data ranking in this compilation. Samples used to reconstruct the seawater strontium isotope curve have to be deposited in an unrestricted marine environment and record the original seawater signal. Any non-marine or/and diagenetically altered samples would be rated as “low-certainty” and excluded from the curve reconstruction, whether they meet other criteria (i.e., age constraints and dissolution methods) or not.

Age constraints and dissolution methods are used to distinguish “high-certainty” from “medium-certainty” data, but not for defining “low-certainty”. A well-constrained age (age uncertainty within ±50 Ma) and appropriate dissolution method (i.e., pre-leaching and using a weak acid, see discussion in section 2.2) provide a greater degree of precision. We define samples that satisfy all four criteria (marine, well-preserved, well-constrained age, appropriate leaching method) as “high-certainty”. “Medium-certainty” data are those without well-constrained ages or appropriate leaching method, but still likely containing an original marine signal (i.e., marine environment, well-preserved). “Medium-certainty” data are included to fill some “high-certainty” data gaps in the curve construction and assist the curve interpretation.
Table 3. Summary of criteria for data certainty ranking

<table>
<thead>
<tr>
<th>Marine environment</th>
<th>Good preservation</th>
<th>Well constrained ages (less than ±50 Ma)</th>
<th>Good leaching method</th>
<th>Certainty rating</th>
</tr>
</thead>
<tbody>
<tr>
<td>Yes</td>
<td>Yes</td>
<td>Yes</td>
<td>Yes</td>
<td>High</td>
</tr>
<tr>
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<td>Not necessarily</td>
<td>Medium</td>
</tr>
<tr>
<td>Not necessarily</td>
<td>Not necessarily</td>
<td>-</td>
<td>-</td>
<td>Low</td>
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</table>

6. Compilation and curve description

6.1 Compilation

Chemostratigraphic data compilations need continual updating in order to take into account new data, improved age constraints and potentially different screening criteria. For this reason we provide all the relevant isotopic data and metadata in the supplementary materials associated with this paper.

For this study, we compiled 2249 Sr isotope ratios from Precambrian to Cambrian rocks (4000 Ma – 500 Ma) published between 2002 and 2021 from 62 published articles and 3 unpublished articles (Supplementary Material 1, 3 and Table 4). We assigned certainty criteria to all published data, including those compiled in Shields and Veizer (2002) (Supplementary Material 1, Fig. 3) and we presented data used for the curve construction, i.e., high and medium certainty data, in Supplementary Material 2 (see Table 5 for structure). All data have been normalized to a value of 0.71025 for the international isotope standard SRM NBS 987 using the reporting laboratories’ measured values over the period of analysis. In most cases, Rb-corrected data were not used in this study.

Recently, several studies have suggested updated seawater strontium isotope curves for different parts of the Precambrian (Neoproterozoic: Zhou et al., 2020, Cox et al., 2016; Mesoproterozoic: Kuznetsov et al., 2008, Kuznetsov et al., 2019;
Paleoproterozoic: Kuznetsov et al., 2021, 2010; Archean: Ravindran et al., 2020, Roerdink et al., 2021, Satkoski et al., 2017) and a SIS study from Kuznetsov et al., (2018) proposed an updated curve for the Proterozoic part. These published curves provide valuable and complementary references for the reconstruction of the Precambrian seawater $^{87}$Sr/$^{86}$Sr curve.

6.2 Fundamental descriptions of the updated curve

The updated seawater $^{87}$Sr/$^{86}$Sr curve demonstrates an overall increasing trend from ~0.7005 at c. 3.5 Ga to ≥0.7089 towards the end of the Ediacaran Period with three peaks at c. 2.2 Ga, c. 1.65 Ga and c. 0.5 Ga, respectively (Fig.4).

The Archean seawater $^{87}$Sr/$^{86}$Sr ratio appears to have deviated from the contemporaneous mantle value since at least c. 3.5 Ga (~0.7005) (McCulloch, 1994; Roerdink et al., 2021), followed by a gradual increase until the end of the Archean c. 2.5 Ga when the ratio reached ~0.702 (Kamber and Webb, 2001). In the Paleoproterozoic ocean, the $^{87}$Sr/$^{86}$Sr ratio experienced strong oscillations that increased significantly from ~0.702 at c. 2.5 Ga (Kamber and Webb, 2001) to ~0.705 at c. 2.2 Ga (Bekker et al., 2006, 2003a), followed by a drop at c. 2.1 Ga (~0.703) (Bekker et al., 2003b; Kuznetsov et al., 2010). Then, there was a rebound to another peak of ~0.7062 (Veizer and Compston, 1976) at c. 1.65 Ga before a fall to ~0.7046 (Ray et al., 2003) around the Paleoproterozoic - Mesoproterozoic boundary. The overall pattern of the Paleoproterozoic curve in this study shows similarity with that of Kuznetsov et al., (2018). However, the 2.5-2.2 Ga and 1.9-1.7 Ga parts of the curve are mainly composed of medium certainty data, so the shape, duration and acme of these rises need further confirmation once more high-certainty data become available.

The Mesoproterozoic $^{87}$Sr/$^{86}$Sr values of the new compilation exhibit modest fluctuation from ~0.7046 to ~0.7050 during c. 1.6-1.2 Ga (Gorokhov et al., 1995; Hall
and Veizer, 1996; Kuznetsov et al., 2008, 2005; Pokrovskiy and Vinogradov, 1994; Ray et al., 2003), before a modest rise to ~0.7059 (Gibson et al., 2019; Kuznetsov et al., 2019; Shields, 2002), followed by a slight decrease to ~0.7052 (Semikhatov, 2002) around the Mesoproterozoic to Neoproterozoic transition. The seawater $^{87}\text{Sr}/^{86}\text{Sr}$ curve then begins rising through multiple fluctuations from the beginning of the Neoproterozoic (~0.7052, Kuznetsov et al., 2017) until the end of the Ediacaran (~0.7089, Sawaki et al., 2010b), with several significant declines at approximately 0.92 Ga, 0.83 Ga, 0.72 Ga and 0.59 Ga respectively.
<table>
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<td>Additional relevant information</td>
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<td>Formation name occasionally including groups, members, etc.</td>
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<tr>
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<td>Name of section, borehole and/or region</td>
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<tr>
<td>Country</td>
<td>Name of country</td>
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<td>Depth in borehole</td>
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<tr>
<td>Height, m</td>
<td>Stratigraphic height in section</td>
</tr>
<tr>
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<td>100 Ma intervals or “Geons” from 0 to 37 (Hofmann, 1999)</td>
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<tr>
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<td>Age, Ma</td>
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<td>Source: data</td>
<td>Literature reference for isotopic data (see appendix)</td>
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<td>Source: age</td>
<td>Literature references for age constraints</td>
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<td>Dating technique, e.g., U-Pb single zircon, biostratigraphy, correlations</td>
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<td>Calcium concentration in carbonate phase, weight%</td>
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<td>(\delta^{13}C_{\text{other}}) PDB</td>
<td>Carbon isotope composition of other carbonate minerals, (%_{\text{PDB}})</td>
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Table 4. Structure of Precambrian strontium isotope database version 2021 (a). This version includes 249 newly-compiled data of this study and previous compilation of Shields and Veizer, (2002), whereby the structure is inherited from the PMCID (Precambrian marine carbonate isotope database) version 1.1 (a) of Shields and Veizer, (2002), but adding detailed comments and certainty rating.
Table 5. Structure of Precambrian strontium isotope database version 2021 (b). This version shows data used for reconstruction of Precambrian seawater $^{87}$Sr/$^{86}$Sr curve, which includes high and medium certainty data from both this study and Shields and Veizer (2002).

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<td>Ages of samples, all samples ages are up to data</td>
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<td>Literature reference for isotopic data (see supplementary material 3)</td>
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</tr>
<tr>
<td>Rating (medium-certainty)</td>
<td>Marine environment, least altered, poor age constraints or/and inappropriate leaching method (no-preleaching, using strong acids)</td>
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<td>High and medium certainty data from this study</td>
</tr>
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<td>Old data</td>
<td>High and medium certainty data from PMCID of Shields and Veizer (2002)</td>
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7. Discussion on the updated $^{87}$Sr/$^{86}$Sr curve of Precambrian seawater

Continental chemical weathering exports cations to the ocean and so is one of the key processes influencing not only the evolution of seawater $^{87}$Sr/$^{86}$Sr but also the long-term carbon cycle and climate through the consumption of atmospheric CO$_2$ (Berner, 2003; Berner et al., 1983; Walker et al., 1981). Rb preferentially accumulates in granitic melts due to the relative incompatibility of Rb compared with Sr, resulting in Rb enrichment (high Rb/Sr ratios, thus high $^{87}$Sr) in the continental crust and Rb depletion (low Rb/Sr ratios, thus low $^{87}$Sr) in the residual mantle and oceanic crust.

Secular changes of $^{87}$Sr/$^{86}$Sr in the ocean record the relative importance of radiogenic strontium derived from continental crust versus unradiogenic strontium derived from hydrothermal alteration of oceanic crust and so could track the long-term changes in Earth’s subaerial weathering. Sr isotope ratios in seawater are affected not only by changes in the rates of continental weathering versus sea-floor spreading (normally associated with supercontinent cycles) but also by changes in the $^{87}$Sr/$^{86}$Sr composition of rocks undergoing weathering (generally associated with emplacement of large igneous provinces, crust reworking etc.), which has an intimate association with Earth system dynamics.

Here we show our updated Sr isotope curve against the background of zircon abundance and the supercontinent cycle (Fig. 5A), incorporating also Nd, Hf and O isotopes (Fig. 5B) and a compilation of collective sizes of large igneous provinces (LIPs; Fig. 5C). Peaks in U-Pb zircon crystallisation ages are linked to the amalgamation stages of the supercontinent cycle (Bradley, 2011; Condie, 2004; Condie et al., 2011; Rino et al., 2004). These peaks have been suggested also to have been a consequence of a preservation bias inherent in the supercontinent cycle, whereby high volumes of magma are generated along subduction zones, but the
preservation potential of crust generated in collisional orogens is greater (Cawood et al., 2013; Condie et al., 2011; Hawkesworth et al., 2009). The zircon / supercontinent record provides important clues to interpreting secular Sr isotope changes. Supercontinent assembly is thought to be associated with tectonic collision and uplift, resulting in higher erosion rates and therefore an increase in seawater $^{87}\text{Sr}/^{86}\text{Sr}$. Conversely, rifting and opening of new basins during supercontinent fragmentation might increase input of less radiogenic hydrothermal fluxes into the ocean, driving down seawater $^{87}\text{Sr}/^{86}\text{Sr}$ (Asmerom et al., 1991; Kaufman et al., 1993; Raymo et al., 1988). However, input fluxes are not always primary controls for marine Sr isotope records, sources of Sr (older and radiogenic crust versus juvenile crust) undergoing continental weathering could also be controlling factors (Bartley et al., 2001; Bataille et al., 2017; Halverson et al., 2007).

Isotopic proxies such as εHf and δ$^{18}$O in zircons and εNd in whole-rock sediments and granitoids, and the emplacement of large igneous provinces could reflect types of rocks (lithologies) undergoing weathering. εHf and εNd values express the relative deviation of $^{176}\text{Hf}/^{177}\text{Hf}$ and $^{143}\text{Nd}/^{144}\text{Nd}$ ratios of a sample from the contemporaneous chondritic uniform reservoir (CHUR) respectively (White, 2015). εHf values in zircons and εNd in whole-rock sediments and granitoids record the degree to which the magma contains the juvenile mantle (high values) versus the reworked crust (low values) (Condie and Aster, 2013). Mantle-derived magmas have relatively low δ$^{18}$O (5.3±0.3‰; Valley, 2003), whereas magmas that include a contribution from sedimentary rocks have elevated δ$^{18}$O because rocks that have experienced a sedimentary cycle or low-grade hydrothermal alteration will have experienced isotopic exchange with water at low temperatures (c. 7–25‰; Eiler, 2001). Thus, elevated δ$^{18}$O values in zircon are proposed as a ‘fingerprint’ for the generation of
felsic igneous rocks (Hawkesworth et al., 2010). Increasing $\varepsilon_{\text{Hf}}$ and $\varepsilon_{\text{Nd}}$ values, and decreasing $\delta^{18}\text{O}$ values with time reflect more significant input of juvenile crust with unradiogenic Sr isotope ratios; conversely, decreasing $\varepsilon_{\text{Hf}}$ and $\varepsilon_{\text{Nd}}$ values, and high $\delta^{18}\text{O}$ values reflect reworking of older crust with high Sr isotope ratios (Belousova et al., 2010; Collins et al., 2011; Condie and Aster, 2013).

Large igneous provinces represent large volumes (>0.1Mkm$^3$; frequently above>1Mkm$^3$) of mafic lavas, typically in less than a few million years (Bryan and Ernst, 2008; Coffin and Eldholm, 1994; Ernst and Ernst, 2014). LIP (or continental flood basalt) weathering plays an important role in regulating seawater $^{87}\text{Sr}/^{86}\text{Sr}$ and global climate due to ~5-10 times greater weatherability of basalts than felsic continental crust (White and Brantley, 1995). Rapid chemical weathering of LIPs delivers unradiogenic Sr into the ocean, leading to a decrease in marine $^{87}\text{Sr}/^{86}\text{Sr}$ and CO$_2$ drawdown (Cox et al., 2016; Dessert et al., 2001). The importance of basalt weathering is especially noted for the early-middle Neoproterozoic and Phanerozoic fluctuations in seawater $^{87}\text{Sr}/^{86}\text{Sr}$ (Bataille et al., 2017; Cox et al., 2016; Gemon et al., 2016; Godderis et al., 2003; Jagoutz et al., 2016; Prokoph et al., 2013). For instance, major strontium isotope falls in the middle Neoproterozoic and middle-late Ordovician were suggested to have been due to enhanced volcanic weathering that potentially triggered the Sturtian and late Ordovician glaciations (Cox et al., 2016; Shields et al., 2003; Young et al., 2009). It is worth noting that evolving palaeogeography is another potential control over seawater $^{87}\text{Sr}/^{86}\text{Sr}$. Continental lithologies and global climatic zonation vary spatially; thus, ongoing continental drift would lead to changes in the average $^{87}\text{Sr}/^{86}\text{Sr}$ signature of continental runoff and thus of the ocean (Goddéris et al., 2017).

In this section, we will discuss possible explanations for the temporal trend of the
updated seawater Sr isotope curve combining recognizable events and complementary data sets, and will propose plausible hypotheses for some highly controversial topics (e.g., onset of plate tectonics) using this improved curve.

7.1. Archean (4.0-2.5 Ga)

Plate tectonics is a defining characteristic of the modern Earth System that involves a globally linked system of lateral motion of rigid surface plates with lithosphere formed at mid-ocean ridges and consumed in subduction zones. When and whether modern style plate tectonics operated during the Archean remain topics of considerable debate and rigorous research (Brown et al., 2020; Cawood et al., 2018, 2006; Dhuime et al., 2015, 2012; Ernst et al., 2016; Greber et al., 2017; Griffin et al., 2014; Harrison et al., 2008; Hawkesworth et al., 2017, 2010, 2020; Hopkins et al., 2008; Keller and Harrison, 2020; Komiya et al., 1999; Kröner and Layer, 1992; Lipp et al., 2021; Moyen et al., 2006; Nutman et al., 2002; Smithies et al., 2007; Stern, 2018; M. Tang et al., 2016; Taylor and McLennan, 1985; Van Kranendonk, 2010; Van Kranendonk et al., 2007; Windley et al., 2021). Many authors have suggested that plate tectonics commenced during Meso- to Neoarchean times, around 3.2–2.5 Ga (e.g., Brown et al., 2020; Cawood et al., 2018; Dhuime et al., 2015; Hawkesworth et al., 2020, 2017; Tang et al., 2016; Taylor and McLennan, 1985). However, a contrasting view supports an earlier onset of plate tectonic before 3.5 Ga and as early as the Hadean (e.g., Greber et al., 2017; Harrison et al., 2008; Keller and Harrison, 2020; Lipp et al., 2021; Windley et al., 2021). Others argue that modern style plate tectonics began only in the Neoproterozoic Era (Stern, 2018). A detailed discussion on different hypotheses of plate tectonics lies outside the scope of this review, but the updated seawater Sr isotope curve may provide an additional viewpoint from which to appreciate the debate.
The Earth’s crust was originally mafic but eventually evolved into two compositionally distinct components: thin, dense, silica-poor oceanic crust and thicker, buoyant, silica-rich continental crust. This dichotomy is generally accepted as maintained by plate tectonics. Thus changes in upper-crust composition (development of felsic crust) are suggested to be a piece of geological evidence for plate tectonic commencement (Greber et al., 2017; Lipp et al., 2021; Tang et al., 2016; Windley et al., 2021). Due to the higher Rb/Sr (higher $^{87}$Sr) in silica-rich continental crust than oceanic crust, deviation of seawater Sr isotopes from the contemporaneous mantle has been related to the emergence and weathering of evolved continental crust (Flament et al., 2013). The modelled Sr isotope evolution in the depleted mantle (Fig. 6) shows a linear increase to the present-day value of c. 0.7026 with a constant Rb/Sr ratio of ~0.016 (Workman and Hart, 2005). The compilation of Shields and Veizer (2002) indicated that the seawater $^{87}$Sr/$^{86}$Sr curve might have deviated from the predicted value for mantle evolution before c. 2.5 Ga and as early as ~2.9 Ga (Fig. 6). Our updated compilation, however, shows an earlier deflection before c. 3.5 Ga, after considering data from recent studies such as Roerdink et al., (2021), Ravindran et al., (2020) and Satkoski et al., (2017, 2016). The emerging Sr isotope curve implies that the onset of continental weathering of more evolved crust began before 3.5 Ga and could even have begun as early as 3.7 Ga (Roerdink et al., 2021). The early deviation of the seawater $^{87}$Sr/$^{86}$Sr curve might provide support for the earlier crustal differentiation and plate tectonics onset model (before 3.5 Ga). However, it is challenging to discern the role of continental weathering this far back in time, based solely on Sr isotopes, because early continental crust, while differentiated, would have had little time to grow more $^{87}$Sr and would remain isotopically very similar to the mantle for over a billion years. Therefore, the leverage of continental weathering to
modify seawater composition was much reduced in the Archean such that relatively small changes, once verified, can be considered significant.

Titanium (Ti) isotope composition in shale is an alternative way to constrain the chemical composition of the continental crust exposed to weathering. The $^{49}$Ti/$^{47}$Ti ratio (expressed as $\delta^{49}$Ti; part per mil deviation of the $^{49}$Ti/$^{47}$Ti ratio in a sample from that of the Origins Laboratory Ti reference material) is associated with SiO$_2$ concentration because during fractional crystallization, light Ti is preferentially incorporated in Fe-Ti oxides (Millet et al., 2016). For instance, mafic rocks and komatiites have near bulk silicate Earth values [+0.005 ± 0.005 (‰), 95% c.i], while $\delta^{49}$Ti in evolved rocks has a higher value of +0.6‰ (at SiO$_2$ concentration of 75%; Greber et al., 2017). Although the Ti concentration of mafic rocks is much higher than that of felsic rocks, Greber et al. (2017) shows that the average $\delta^{49}$Ti value of shales is almost constant and always higher than that of basalt and komatiites during the past 3.5 Ga, indicating that emergent crust was likely dominated by felsic (silica-rich) rocks as far back as 3.5 Ga. The gradual increase of $^{87}$Sr/$^{86}$Sr ratios in Paleoarchean seawater also coincides with the widespread occurrence of granitoid-rich crust in the western Dharwar, Kaapvaal and Pilbara cratons and the presence of detrital deposits with felsic sources (Hessler and Lowe, 2006), suggesting that the marine Sr budget started to be dominated by crustal-derived, more radiogenic materials (Ravindran et al., 2020).

Plate tectonics would eventually produce supercontinents, thicken the lithosphere and increase crustal reworking (Cawood et al., 2013; Flament et al., 2013; Hawkesworth et al., 2016; Spencer et al., 2014). The subsequent assembly of the first putative supercontinent Kenorland at c. 2.7-2.6 Ga (Williams et al., 1991; Bleeker, 2003) produced collisional orogens that were susceptible to subaerial weathering, potentially
increasing further the flux of radiogenic $^{87}\text{Sr}$ to the ocean during the Neoarchean.

7.2. Proterozoic (2.5-0.54 Ga)

7.2.1. Paleoproterozoic (2.5-1.6 Ga)

The Paleoproterozoic Era is marked by a substantial increase in the oxygen content of the atmosphere at c. 2.4-2.3 Ga (e.g., Bekker et al., 2004; Bekker and Holland, 2012; Canfield et al., 2013; Holland, 2002; Karhu and Holland, 1996; Poulton et al., 2021; Rye and Holland, 1998; Walker et al., 1983); widespread glaciation (e.g., Barley et al., 2005; Kopp et al., 2005; Young, 1991), the Earth’s largest positive carbon isotope excursion (Baker and Fallick, 1989; Martin et al., 2013; Melezhik et al., 2005; Schidlowski et al., 1975); the oldest microfossils diagnostic of cyanobacteria and eukaryotes (Hofmann, 1976; Javaux et al., 2013; Javaux and Lepot, 2018; Knoll et al., 2006; Knoll and Golubic, 1992) and sustained plate tectonics (e.g., Cawood et al., 2018; Hawkesworth et al., 2020; Taylor and McLennan, 1985).

The Paleoproterozoic seawater $^{87}\text{Sr}/^{86}\text{Sr}$ curve appears to have oscillated markedly with two increases at 2.5-2.2 Ga and 1.9-1.7 Ga, respectively. Although the first dramatic increase of $^{87}\text{Sr}/^{86}\text{Sr}$ from 2.5 Ga to 2.2 Ga is relatively poorly constrained, it coincides with important Earth System events, such as the first accumulation of atmospheric $\text{O}_2$ (the Great Oxidation Episode or GOE; Poulton et al., 2021) and a series of extensive glaciations (c. 2.45-2.22 Ga). Contributing factors to the rise in seawater $^{87}\text{Sr}/^{86}\text{Sr}$ include: 1) a decrease in mantle input flux; 2) an increase in the Sr isotopic composition of rocks undergoing weathering; and 3) an increase in continental weathering flux. However, the interval 2.5-2.2 Ga corresponds to a relative low in the zircon age abundance record and sits in a quiet transition before a period of widespread magmatism and rifting, related in part to the breakup of Kenorland at 2.2-2.1 Ga. An increase in the Sr isotope composition of rocks
undergoing weathering is plausible, as more felsic crust might have been produced during this period (Dhuime et al., 2015; Lee et al., 2016). However, there is no obvious evidence from Hf, Nd and O isotopes (Fig. 5B), so it might not be a primary control for such a dramatic Sr isotope rise. We therefore consider a role for an enhanced chemical weathering rate, probably driven by several possible factors, such as increased emergence of continental crust (e.g., Flament et al., 2013), maximised mineral surface area during glaciations (Hallet et al., 1996; Koppes and Montgomery, 2009) and oxidative weathering of pyrite (producing sulfuric acid) during the GOE (Bekker and Holland, 2012; Bachan and Kump, 2015; Torres et al., 2014).

A thickened lithosphere and largely emergent low-latitude continental crust during the early Proterozoic (c. 2.5 Ga) likely increased the surface area exposed to weathering (Flament et al., 2013; Lee et al., 2016), potentially contributing to the dramatic increase of seawater $^{87}$Sr/$^{86}$Sr at ~2.5 Ga. Modelled evolution of P concentrations in Earth’s emerged crust through time by Greber et al., (2017) shows a 50% increase in the concentration of P (from 0.10 to 0.15 wt% P$_2$O$_5$) across the Archean-Proterozoic boundary (2.5 Ga), which could be a result of enhanced continental weathering during this period. As a major limit to biological productivity over geological time scales (Lenton and Watson, 2004; Tyrrell, 1999), an increase in the flux of P from chemical weathering could have led to an expansion of oxygenic photosynthesis and therefore a rise in atmospheric O$_2$ at c.2.4 Ga (Fig. 5D).

As for the Sr isotope peak at ~2.3-2.2 Ga, the onset of pyrite weathering (producing sulfuric acid) (Bekker and Holland, 2012; Torres et al., 2017, 2014) may have contributed significantly to the rise to values as high as ~0.705 (Bekker et al., 2006, 2003a). The generation of sulfuric acid (H$_2$SO$_4$) from pyrite weathering would have decreased the pH of soil and groundwater, inducing the dissolution of rocks and
minerals, including apatite, and giving rise to further chemical weathering through net production of CO\textsubscript{2} (Guidry and Mackenzie, 2003; Konhauser et al., 2011; Torres et al., 2017). Additionally, glacial flour could have maximised the surface area exposed to weathering (Anderson, 2007; Hallet et al., 1996; Herman et al., 2013; Koppes and Montgomery, 2009). Therefore, we propose that increased sulfuric acid and largely exposed reactive surface area during glaciation might have resulted in an increased radiogenic Sr flux from the continent.

Afterwards, a sharp $\frac{^{87}\text{Sr}}{^{86}\text{Sr}}$ fall between c. 2.2 Ga to c. 2.1 Ga might be attributed to an increased flux of less radiogenic strontium from mid-ocean ridges and rift volcanism, associated with the final breakup of the Kenorland at 2.2-2.1 Ga (Aspler and Chiarenzelli, 1998; Wanke and Melezhik, 2005), as well as a decreased flux of more radiogenic riverine strontium due to peneplanation of Kenorland. The subsequent second sharp rise of $\frac{^{87}\text{Sr}}{^{86}\text{Sr}}$ ratios after c. 2.0-1.9 Ga, reaching a peak at c. 1.7 Ga, is concurrent with the amalgamation of the supercontinent Nuna (Fig. 5A) and was likely related to global-scale collisional events (Bradley, 2011; Zhao et al., 2004, 2002). It has long been proposed that tectonic-related uplift could facilitate erosion and chemical weathering (e.g., Raymo et al., 1988; Ruddiman and Prell, 1997), thus, increasing the continental Sr flux into the ocean. Moreover, the low $\epsilon$Hf values of detrital zircons, low Nd isotope ratios in whole-rock sediments and granitoids and zircon $\delta^{18}$O values during this period imply a contribution from reworked crust with presumably higher $\frac{^{87}\text{Sr}}{^{86}\text{Sr}}$ ratios (Condie and Aster, 2013; Hawkesworth et al., 2016; Cawood et al., 2018). The following drop of $\frac{^{87}\text{Sr}}{^{86}\text{Sr}}$ ratios to around 0.7046 at c. 1.6 Ga occurred at the transition from the Paleoproterozoic Era to the Mesoproterozoic Era, implying an increased input of unradiogenic sources, possibly related to the onset of a partial breakup of Nuna (Anderson, 1983; Rogers...
Simultaneously, εHf and εNd values both show an increasing trend, coupled with decreasing zircon δ¹⁸O values, probably indicating a gradual transition from reworked crust to more juvenile crust during this period (Fig. 5B).

7.2.2. Mesoproterozoic (1.6 Ga-1.0 Ga)

The middle portion of the Proterozoic Eon (1.8 to 0.85 Ga) is characterised by its relative environmental, evolutionary, and lithospheric stability (e.g., Cawood and Hawkesworth, 2014) with a paucity of passive margins (Bradley, 2008), absence of glaciation (Bradley, 2011) and muted variability in the geochemical record (e.g., Bartley and Kah, 2004; Brasier and Lindsay, 1998; Buick et al., 1995; Shields, 2007). However, following further detailed studies conducted in recent years, more and more mysteries of this so-called “Boring Billion” have been revealed in terms of eukaryotic evolution (e.g., Adam et al., 2017; Butterfield, 2000; Butterfield et al., 1990; Javaux et al., 2001; Knoll, 2014, 1994; Lamb et al., 2009; Miao et al., 2019; Shi et al., 2017; Tang et al., 2020; Zhang et al., 2018b; Zhu et al., 2016), global tectonic reorganisations (Anderson, 1983; Condie, 2020; Evans and Mitchell, 2011; Huang et al., 2019; Rogers and Santosh, 2002; Zhao et al., 2004), surface O₂ dynamics (e.g., Diamond et al., 2018; Gilleaudeau and Kah, 2015; Johnston et al., 2005; Kah et al., 2001, 1999; Kah and Bartley, 2011; Liu et al., 2021) and possible carbon isotope excursions (e.g., Bartley et al., 2001; Kah et al., 1999; Knoll et al., 1995; Zhang et al., 2016).

The updated strontium isotope curve for Mesoproterozoic seawater shows relatively low values (~0.7045-0.705) with only muted variability between 1.6 Ga-1.2 Ga. The low $^{87}$Sr/$^{86}$Sr ratios are concurrent with the fragmentation of the supercontinent Nuna, which began at c. 1.6 Ga with continental rifting and anorogenic
magmatism until its final breakup at about 1.2 Ga with widespread emplacement of mafic dike swarms (Anderson and Arthur, 1983; Rogers and Santosh, 2002; Zhao et al., 2004). The above-zero $\varepsilon$Hf and $\varepsilon$Nd curves and low $\delta^{18}$O (Fig. 5B), alongside previous studies, indicate that this period was under the influence of considerable amounts of juvenile mantle-derived rocks and associated hydrothermal systems (Condie and Aster, 2013; Hawkesworth et al., 2016; Semikhatov, 2002). Additionally, 1.6-1.2 Ga also witnessed the emplacement of several large igneous provinces (Fig. 5C), such as the ~1267 Ma Mackenzie LIP, ~1385 Ma Mashak LIP (and other coeval LIPs) and ~1501 Kuonamka LIP etc. (Ernst and Youbi, 2017). The low marine $^{87}$Sr/$^{86}$Sr ratios during this period, together with evidence from complementary datasets ($\varepsilon$Hf, $\varepsilon$Nd and $\delta^{18}$O, LIPs) suggest that a significant juvenile crust was likely involved in mountain building, and continental weathering was dominated by juvenile less radiogenic crust over ancient, more radiogenic continental crust. A subsequent increase of $^{87}$Sr/$^{86}$Sr since c. 1.2 Ga towards the end of the Mesoproterozoic coincides with amalgamation of the supercontinent Rodinia (Spencer et al., 2013). Weathering conditions during this period were less-constrained previously, but enhanced chemical weathering towards the end of the Mesoproterozoic Era has been proposed recently by Gibson et al., (2019), who related a rise in $^{87}$Sr/$^{86}$Sr at ca. 1050 Ma to weathering of Grenville-aged orogens (linked to amalgamation of supercontinent Rodinia). However, in our compilation (Fig. 5A), the incremental rise of $^{87}$Sr/$^{86}$Sr during assembly of Rodinia contrasts with the sharp increase during the earlier assembly of Nuna and later assembly of Gondwana, which might indicate that the weathering of materials with relatively low $^{87}$Sr/$^{86}$Sr ratios may have predominated even during periods of uplift and erosion. Semikhatov (2002) proposed several possible reasons, such as juvenile magmatism, an extremely arid
climate, or the paleogeographic lock-up of continental runoff, whereby collisional
orogens at continental margins represented barriers for the terrestrial material
transported by rivers. The first reason seems plausible considering the overall high
juvenile crust production, which is marked by relatively radiogenic Nd and Hf isotope
signatures, and LIPs such as the c. 1005 Ma Sette Daban event (Ernst and Youbi,
2017).

7.2.3. Neoproterozoic (1.0 Ga-0.54 Ga)

The Neoproterozoic Era is characterised by climatic vicissitudes, including two
prolonged global glaciations during the Cryogenian Period and short-lived, regional
ice ages during the Ediacaran Period (e.g., Hoffman et al., 2017; Young et al., 2015
and references therein), biological radiations (e.g., Narbonne, 2005; Xiao and
Laflamme, 2009), the eruption of large igneous provinces (LIPs) (e.g., Cox et al.,
2016; Ernst and Youbi, 2017), oscillations of carbon isotopes (e.g., Halverson et al.,
2005; Rothman et al., 2003), ocean oxygenation events (e.g., Shields-Zhou and Och,
2011) and tectonic reorganization including fragmentation of the supercontinent
Rodinia and subsequent assembly of Gondwana (e.g., Condie and Puetz, 2019;
Merdith et al., 2017).

A sustained increase in continental weathering rate was believed to be a major
contributing factor driving increased $^{87}$Sr/$^{86}$Sr ratios in Neoproterozoic seawater
(Shields, 2007). However, Halverson et al., (2010) pointed out that some notable
trends superimposed on the long term “base-level shift” of marine $^{87}$Sr/$^{86}$Sr values,
such as the decline prior to Cryogenian glaciation, could tentatively be assigned to the
weathering of widespread flood basalts. Coincidently, Bataille et al., (2017) found
that $^{87}$Sr/$^{86}$Sr changes in igneous rocks were generally well correlated with changes to
seawater $^{87}$Sr/$^{86}$Sr over the last 1.0 Ga, which indicates that the isotope composition of
weathering input might have played an important role in shaping the seawater 
$^{87}\text{Sr}/^{86}\text{Sr}$ curve during this period. Additionally, many researchers have also proposed
a critical role for large igneous provinces (LIPs) in determining seawater $^{87}\text{Sr}/^{86}\text{Sr}$
ratios due to the higher weatherability of basalt (e.g., Cox et al., 2016). Enhanced
silicate weathering of unradiogenic, low latitude LIPs likely led to steep dips in the
strontium isotope curve. For instance, the falls of $^{87}\text{Sr}/^{86}\text{Sr}$ ratios at 0.92 Ga, 0.83 Ga,
0.72 Ga could have resulted from the weathering of the Dashigou, Guibei and
Franklin LIPs, respectively (Ernst and Youbi, 2017; Zhou et al., 2020). Accelerated
uptake of CO$_2$ via LIP weathering might outweigh the climatic effects of CO$_2$
degassing, triggering glaciations, such as the Sturtian glaciation (Cox et al., 2016;
Ernst and Youbi, 2017; Rooney et al., 2014). Conversely, continental drift (changing
palaeogeography) might diminish LIP weathering, allowing seawater $^{87}\text{Sr}/^{86}\text{Sr}$ to rise
again. For instance, numerical models suggest the southward drift of the Franklin
LIPs outside the original tropical convergence zone (Li et al., 2013), decreasing its
contribution to total Sr flux of continental silicate weathering from 4.5% at 720 Ma to
2.5% at 680 Ma and 635 Ma, which could be a potential reason for the rise of
$^{87}\text{Sr}/^{86}\text{Sr}$ after 635 Ma (Goddéris et al., 2017).
The relatively low values of $^{87}\text{Sr}/^{86}\text{Sr}$ (c.0.7055-0.7060) during 0.95-0.85 Ga
coincided with the tenure of the supercontinent Rodinia (Bradley, 2011). Evidenced
by the increasing values of $\varepsilon\text{Hf}$ and $\varepsilon\text{Nd}$, the low strontium isotope values during this
period might reflect input of less radiogenic strontium from basalt and andesite from
surrounding volcanic arcs (Goddéris et al., 2017) during an interval of low relief and
high continentality. The subsequent sharp rise of strontium isotope ratios from 0.85
Ga to the end of Precambrian encompasses the breakup of the supercontinent Rodinia
at c.0.8-0.65 Ga (Condie and Puetz, 2019) and the assembly of Gondwana at c. 0.6-
0.5 Ga (Cawood and Buchan, 2007; Merdith et al., 2017). During breakup, the old and radiogenic continental interiors might have been uplifted, exposed and rapidly weathered, giving rise to an overall increase in ocean \(^{87}\text{Sr}/^{86}\text{Sr}\), interrupted by several eruptive events (Goddéris et al., 2017; Halverson et al., 2007; Zhou et al., 2020). Simultaneously, the \(\varepsilon\text{Hf}\) and \(\varepsilon\text{Nd}\) curves start showing a decreasing trend, which indicates that the crustal production began shifting to an advancing external phase, where the reworked components with higher \(^{87}\text{Sr}/^{86}\text{Sr}\) values exceeded juvenile components with lower \(^{87}\text{Sr}/^{86}\text{Sr}\) ratios (Condie and Aster, 2013). Afterwards, the onset of Gondwana assembly produced widespread collisional orogens and generated highly pulverised bedrocks by physical weathering, thereby promoting rapid chemical weathering (Ruddiman et al., 1997). Abrupt increases in \(^{87}\text{Sr}/^{86}\text{Sr}\) follow both the Sturtian and Marinoan glaciations may relate to enhanced chemical weathering of freshly exposed rock surfaces beneath a CO\(_2\)-rich atmosphere (e.g., Cox et al., 2016). Such increases in weathering efficiency will eventually draw down carbon dioxide levels, bringing weathering rates back down again. Alternatively, Shields et al., (2019) proposed that a genuine rise of continental weathering rates without lowering CO\(_2\) if uplift and erosion events led to enhanced evaporite sulfate weathering, which if coupled with pyrite burial/organic carbon oxidation could maintain CO\(_2\) forcing of chemical weathering. Continent-continent collisions might also deliver the radiogenic isotope signal of the largely-reworked crust into the ocean, given the sharp decreases in \(\varepsilon\text{Hf}\) and \(\varepsilon\text{Nd}\) as well as the rise of \(\delta^{18}\text{O}\) values from c. 0.85 Ga to c. 0.55 Ga.

8. Linking the updated Sr isotope record to supercontinental cycles

Tectonic processes are the major influence on Sr fluxes to the ocean and the updated seawater \(^{87}\text{Sr}/^{86}\text{Sr}\) curve shows both stronger oscillations and better correspondence
with tectonic events than had previously been shown (Shields and Veizer, 2002) (Fig. 5A; Fig. 6). In particular, supercontinent cycles, which have in the interim become more evident in zircon abundance, s-type granite, metamorphic grade and zircon isotopic records, show more convincing covariation with seawater $^{87}\text{Sr}/^{86}\text{Sr}$ throughout the Proterozoic as well as the already established Phanerozoic Eon.

In the new curve, in most cases, rising $^{87}\text{Sr}/^{86}\text{Sr}$ rises coincide with proposed times of supercontinent amalgamation; and $^{87}\text{Sr}/^{86}\text{Sr}$ falls accompany times of high continentality / supercontinent tenure and initial breakup. For instance, the assembly stages of supercontinent Kenorland (postulated), Nuna and Gondwana all correspond to increases in the Sr isotope curve, while their tenure and rifting coincide with lower points in the curve (Fig. 5A). It was suggested that supercontinent amalgamation enhances continental weathering of uplifted terrains and increased input of radiogenic Sr flux to the ocean, while supercontinent breakup is associated with ocean ridge activity, rift-related magmatism and sea-level rise, leading to increased input of relatively unradiogenic Sr flux to the ocean and low seawater $^{87}\text{Sr}/^{86}\text{Sr}$ values (e.g., Asmerom et al., 1991; Raymo et al., 1988; Veizer et al., 1989). It is worth noting that the updated Sr isotope curve reaches peaks after zircon abundance peaks related to supercontinent assembly. For example, for Nuna the Sr isotope peak at c. 1.7 Ga follows a zircon abundance peak at c. 1.87 Ga and for Gondwana the c. 500 Ma acme follows a peak at c. 600 Ma, which corresponds to rapid erosion of particularly high “supermountains” as evidenced by the high production rate of S-type granites (Brown and Johnson, 2019; Zhu et al., 2020). Orogeny may lead to higher seawater Sr isotope ratio, not through chemical weathering, which is related to outgassing of carbon dioxide, but to physical weathering, and desorption of Sr from fine-grained suspended sediment carried by rivers, in which case Sr isotopes can act more as an erosional proxy than...
merely chemical weathering (Oelkers et al., 2012). The extreme continental weathering
during assembly of Nuna and Gondwana may have triggered the increased input of bio-
essential materials to the ocean, fuelling the evolution and radiations of early euksaryotes
(late Paleoproterozoic; e.g., Javaux et al., 2018) and animals (Neoproterozoic-
Cambrian; e.g., Xiao and Laflamme, 2019), respectively (Fig. 5D).

One possible exception relates to the assembly and breakup of Rodinia and Pangaeas. Seawater $^{87}\text{Sr}/^{86}\text{Sr}$ values only experienced a modest increase during Rodinia amalgamation and even a fall during Pangaea assembly, while their breakups were associated with increases in the seawater Sr curve. Contrasting with the pronounced negative $\varepsilon$Hf and $\varepsilon$Nd values during assembly of Nuna and Gondwana, Hf and Nd isotope values are anomalously radiogenic (above the value of the chondritic uniform reservoir) during the time of Rodinia and Pangaea amalgamation (Fig. 5B), which possibly indicates the predominant production and weathering of unradiogenic juvenile crust (Condie and Aster, 2013; Spencer et al., 2013). Halverson et al., (2007) suggested that supercontinent assembly might shift rainfall away from radiogenic continental interiors to unradiogenic juvenile crust on the edges of continents, resulting in lower seawater $^{87}\text{Sr}/^{86}\text{Sr}$; while supercontinental break-up could shift rainfall to older and uplifted continental interiors, leading to an increase of seawater $^{87}\text{Sr}/^{86}\text{Sr}$. Therefore, compared with other periods, during Rodinia and Pangaea assembly and breakup, seawater Sr isotope values might be more controlled by compositional changes of Sr sources undergoing weathering. Alternatively, Wang et al., (2021) presented the concept of “megacontinent” as a geodynamic precursor and a large subset of the next supercontinent. They suggested that the supercontinent Pangea was preceded by the formation of “megacontinent” Gondwana that was formed by an assembly of multiple continents and represented ~70% size of the Pangea. It is likely that supercontinent
amalgamation had less influence on global erosion rates than the preceding formation of its megacontinent, therefore resulting in the relatively low values of seawater Sr isotopes during Pangea amalgamation stage compared with the Gondwana assembly stage.

9. Conclusions

1) 2249 strontium isotope data points have been compiled from Precambrian marine carbonate rocks, from 62 publications and 3 unpublished materials over the past 18 years, and added to the previous seawater $^{87}\text{Sr}/^{86}\text{Sr}$ database by Shields and Veizer (2002). Four criteria (depositional environment, preservation, age constraints and dissolution methods) have been used to assign values to one of high, medium and low certainty groups.

2) After reviewing and summarizing diagenetic screening methods, a dynamic approach that generally includes field and petrological examinations, geochemical screening (major and trace elements, stable isotopes, and strontium isotopes) and coeval sample comparisons is recommended.

3) A range of analytical methods have been compared. In conclusion, pre-leaching of samples is essential because it removes Sr contamination from clay-associated ions and secondary carbonate overgrowths, thus enhancing the reliability of obtained values and potentially lessen the need for major Rb-decay correction. Aggressive acid leaching should be avoided as it attacks clay minerals in the rock matrix, thus contaminating original carbonate strontium isotope values.

4) An updated strontium isotope curve of Precambrian seawater has been generated based mainly on high-certainty data from the updated compilation. Compared with the previous version (Shields and Veizer, 2002), this updated curve exhibits relatively high-amplitude fluctuations that correspond to proposed
supercontinental cycles (wherein $^{87}$Sr/$^{86}$Sr rises accompany supercontinent amalgamation; and $^{87}$Sr/$^{86}$Sr falls accompany supercontinent breakup).

5) Several hypotheses have been proposed based on the improved Sr isotope curve. For instance, an earlier deflection of seawater $^{87}$Sr/$^{86}$Sr from the contemporaneous mantle at $\sim$3.5 Ga might support the earlier onset of plate tectonics. Two sharp rises in the new curve at 2.5-2.2 Ga and 1.9-1.7 Ga, with uncertainties, indicate elevated continental weathering before and during the Great Oxygenation Event and the assembly of supercontinent Nuna, respectively.

6) Significant data gaps still exist in the Neoarchean, late Paleoproterozoic and Mesoproterozoic, requiring further work. More high-certainty data are needed to test the hypotheses proposed in this study, especially during the periods of 2.5-2.2 Ga and 1.9-1.7 Ga.

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Appendix A: Supplementary data

Supplementary material 1. Precambrian strontium isotope database version 2021 (a).

Supplementary material 2. Precambrian strontium isotope database version 2021 (b).

Supplementary material 3: Reference lists for Precambrian strontium isotope database version 2021 (a).
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Fig. 1. Conceptual model of the seawater Sr fluxes cycle. Major sources of seawater Sr budget include radiogenic river runoff (F_{RR}) and unradiogenic hydrothermal input (F_{H}). River runoff (F_{RR}) can be divided into chemical weathering of silicate minerals (F_{RRS}) and dissolution of marine sediments (F_{RRC}). Other (minor) Sr seawater sources include ground water runout (F_{GW}), diagenetic reflux of Sr from recrystallization of sediments and buried pore water (F_{DIA}). At steady state, sources of seawater Sr are counteracted by removal of Sr via marine sediment burial (F_{SEDB}) and oceanic crust -seawater interaction (F_{OC}). Solid lines represent major Sr fluxes, and dash lines represent minor Sr fluxes. Boxes show reservoirs and arrows show fluxes.
Fig. 2. A recommended procedure for selecting the least altered $^{87}\text{Sr}/^{86}\text{Sr}$ data for SIS (Strontium isotope stratigraphy).
Fig. 3. Certainty and quantity distribution of samples from the Neoproterozoic to Archean. A) Data certainty versus eras. NP: Neoproterozoic, MP: Mesoproterozoic, PP: Paleoproterozoic, A: Archean. The Neoproterozoic has the most abundant high-certainty data. Low-certainty data occupy the largest proportions for all four periods. B) Quantity distribution of data from 500 Ma to 4000 Ma. Neoproterozoic era has relatively abundant datasets, but the Neoarchean, late Paleoproterozoic and Mesoproterozoic have relatively sparse datasets.
Fig. 4. The updated seawater $^{87}$Sr/$^{86}$Sr curve with zoom-in image of the Neoproterozoic era. A) An updated strontium isotope curve of seawater. The Precambrian part is updated from this study, and the Phanerozoic part is from McArthur et al., (2020). B) A zoom-in image of Neoproterozoic strontium isotope curve from Fig.4A. The Neoproterozoic part is composed of well age constrained data in the high and medium certainty groups. The curve is updated from Zhou et al., (2020).
Fig. 5. An overview of the updated strontium isotope curve in the context of Earth systems evolution. A) The updated strontium isotope curve from this study couples zircon records from Voice et al., (2011) and supercontinental cycles. Periods of the supercontinent assembly are from Hawkesworth et al., (2016) and supercontinent breakups from Bradley, (2011); Condie, (2014); Condie and Puetz, (2019); Zhao et al., (2004). B) The black curve shows compilation of ~3300 δ18O analyses of zircon...
versus U-Pb age from recent sediments (Spencer et al., 2014). Green and brown lines represent median value of εHf for detrital zircons, εNd for whole-rock sediments and granitoids respectively (Condie et al., 2013). C) Vertical blue bars denote major glaciations during Earth’s history (Young et al., 2019). Red bars show updated compilation of collective size of Large Igneous Provinces (LIPs) based on Ernst (2014), Ernst and Youbi (2017), and an updated compilation at http://www.largeigneousprovinces.org/. The δ¹³C record throughout Earth history is compiled from Bekker et al., (2016), Hoffman and Lamothe, (2019) and Och and Shields-Zhou (2012). D) Schematic histories of atmospheric O₂ is from Catling and Zahnle (2020), which marks three major oxygenation events: GOE (Great Oxygenation Event), NOE (Neoproterozoic Oxygenation Event), and DOE (Devonian Oxygenation Event). Horizontal red bars shows evolution of life within the biosphere (Knoll and Nowak, 2017; Lenton et al., 2012).
Fig. 6. A comparison of updated Precambrian seawater $^{87}\text{Sr}/^{86}\text{Sr}$ curve from this study with that from Shields and Veizer (2002). The updated curve shows an earlier deviation from contemporaneous mantle and a stronger fluctuation than the curve from Shields and Veizer (2002). The depleted mantle evolution curve is from Workman and Hart (2005).