Strontium isotope stratigraphy of the Cretaceous

John M. McArthur* and Richard J. Howarth
Earth Sciences, University College London, Gower Street, London WC1E 6BT
*Correspondence: j.mcarthur@ucl.ac.uk

Abstract: This contribution outlines the methodology of strontium isotope stratigraphy, and reviews the information that underpins the calibration curve of marine $^{87}\text{Sr} / ^{86}\text{Sr}$ against time for the Cretaceous.

When marine minerals, such as calcite, aragonite, gypsum, barite or apatite, precipitate from seawater they incorporate into their structure some of the strontium (Sr) dissolved in seawater. That Sr records the $^{87}\text{Sr} / ^{86}\text{Sr}$ value of dissolved Sr at the time of incorporation. As the $^{87}\text{Sr} / ^{86}\text{Sr}$ of Sr in the oceans has varied through Cretaceous time (Fig. 1), the numerical age of a marine mineral can be found by comparing its $^{87}\text{Sr} / ^{86}\text{Sr}$ to the calibration curve, i.e. Figure 1, either in its graphical or tabular form. The tabular form is termed LOWESS 7 and is available from the senior author and from ResearchGate.

Values of $^{87}\text{Sr} / ^{86}\text{Sr}$ can also be used to correlate different sections by comparing their profiles of $^{87}\text{Sr} / ^{86}\text{Sr}$ against stratigraphic level (Fig. 2); levels correlate if they have the same $^{87}\text{Sr} / ^{86}\text{Sr}$ value. The Sr-isotope ratio can be thought of as a proxy for the Sr-isotope fractionation (Thirlwall 1991) and brought to a common reference isotope ratio by a double-spike technique (Veizer et al. 1984). The isotopes of Sr fractionate in nature, but they also fractionate both during sample processing (to separate Sr from the sample matrix by ion-exchange chromatography) and during the mass-spectrometric analysis of Sr. In order to remove the fractionation arising during processing and measurement, isotopic ratios are corrected for that fractionation (Thirlwall 1991) and brought to a common basis of 0.1194 for the $^{87}\text{Sr} / ^{86}\text{Sr}$ ratio. This process removes any natural fractionation of the isotopes that had occurred in nature. It is possible to measure the real $^{87}\text{Sr} / ^{86}\text{Sr}$ of a sample, but the process involves a double-spike and two measurements on the same sample, so is seldom done; see Krabbenhöft et al. (2009) and Vollstaedt et al. (2014) for details.

What is $^{87}\text{Sr} / ^{86}\text{Sr}$’?

Measurements of $^{87}\text{Sr} / ^{86}\text{Sr}$ of Sr in a sample are not measurements of the isotopic ratios of $^{87}\text{Sr}$ to $^{86}\text{Sr}$ in the sample; they are measurements of $^{87}\text{Sr} / ^{86}\text{Sr}$ in the sample after adjustment of the ratio so that the sample’s $^{87}\text{Sr} / ^{86}\text{Sr}$ is 0.1194 (Thirlwall 1991). To explain, the isotopes of Sr fractionate in nature, but they also fractionate both during sample processing (to separate Sr from the sample matrix by ion-exchange chromatography) and during the mass-spectrometric analysis of Sr. In order to remove the fractionation arising during processing and measurement, isotopic ratios are corrected for that fractionation (Thirlwall 1991) and brought to a common basis of 0.1194 for the $^{86}\text{Sr} / ^{88}\text{Sr}$ ratio. This process removes any natural fractionation of the isotopes that had occurred in nature. It is possible to measure the real $^{87}\text{Sr} / ^{86}\text{Sr}$ of a sample, but the process involves a double-spike and two measurements on the same sample, so is seldom done; see Krabbenhöft et al. (2009) and Vollstaedt et al. (2014) for details.

The shape of the curve

The calibration curve in Figure 1 shows considerable sinuosity. Explanations of that sinuosity are beyond the remit of this article, so brief comments only on the matter are in order. The major variations (e.g. the late Aptian minimum) have been traditionally viewed as responses to changes in the flux and $^{87}\text{Sr} / ^{86}\text{Sr}$ of three sources of Sr to the ocean: that from continental weathering (rivers and submarine
groundwater discharge), with an $^{87}\text{Sr}/^{86}\text{Sr}$ around 0.710 (averaged globally; Peucker-Ehrenbrink and Fiske 2019); that from hydrothermal discharges at mid-ocean ridges (Spooner 1976 and many subsequent publications), which typically inputs to the ocean Sr with a $^{87}\text{Sr}/^{86}\text{Sr}$ of around 0.704 (Diehl and Bach 2023); that from carbonates deposited on the seafloor, and buried beneath it, that lose Sr to pore water (and, ultimately, seawater) during recrystallization, contributing Sr with a ratio that depends on the average age of that carbonate. This last flux is typically viewed as a minor influence. The magnitude of these fluxes, and their $^{87}\text{Sr}/^{86}\text{Sr}$ values, will have varied through time, thus causing the fluctuations in marine $^{87}\text{Sr}/^{86}\text{Sr}$ seen in Figure 1.

The minor variations in the shape of the calibration curve, for example, the upward convexity of the Valanginian part of the curve, and the changes in gradient of the curve at the Coniacian–Santonian and the Campanian–Maastrichtian boundaries, may be real or may be artefacts of the age models used to construct the curve, perhaps because those age models do not adequately account for changes in sedimentation rate (cf. Fig. 3). Resolving such issues requires profiling $^{87}\text{Sr}/^{86}\text{Sr}$ through many more sections than has presently been done.

**Age models**

Calibration curves (e.g. Fig. 1) are made by assigning age models to trends of $^{87}\text{Sr}/^{86}\text{Sr}$ through rock sections. Age models need to be calibrated to an evolving geological timescale; here the primary calibration is to the numerical ages assigned to age/stage boundaries in the timescale of Gradstein et al. (2020, GTS2020 hereafter). Internal scaling between those boundaries is based mostly on zone boundaries in GTS2020, with alternative scaling for a few intervals that are detailed in the text.

Some principles that can guide the conversion of profiles of $^{87}\text{Sr}/^{86}\text{Sr}$ through rock into profiles of $^{87}\text{Sr}/^{86}\text{Sr}$ through time are outlined in Figure 3. Most of the Cretaceous calibration curve (Fig. 1) has been derived from sediments of nearshore settings and epeiric seas, which are commonly replete with condensed sections and hiatuses. The
incompleteness of such stratigraphic records makes difficult the conversion of trends of $^{87}\text{Sr}/^{86}\text{Sr}$ against stratigraphic level ($\Delta R/\Delta L$, which is what is measured) into trends of $^{87}\text{Sr}/^{86}\text{Sr}$ against time ($\Delta R/\Delta t$, which is what is desired), so the process requires close attention to the difference between rock and time (e.g. Ager 1973, 1993; Sadler 1981; Barefoot et al. 2023; and references therein). Rock and time are sometimes confused: for example, a sudden increase in the slope of a profile of $^{87}\text{Sr}/^{86}\text{Sr}$ against stratigraphic level through a rock section has been described as a change to a more rapid rate of change of $^{87}\text{Sr}/^{86}\text{Sr}$, thereby implying a faster $\Delta R/\Delta t$, when the changes expresses nothing more than a decrease in sedimentation rate (Figs 2 and 3).

A robust calibration curve of $^{87}\text{Sr}/^{86}\text{Sr}$ against stratigraphic level through a rock section has been described as a change to a more rapid rate of change of $^{87}\text{Sr}/^{86}\text{Sr}$, thereby implying a faster $\Delta R/\Delta t$, when the changes expresses nothing more than a decrease in sedimentation rate (Figs 2 and 3). A robust calibration curve of $^{87}\text{Sr}/^{86}\text{Sr}$ against stratigraphic level through a rock section has been described as a change to a more rapid rate of change of $^{87}\text{Sr}/^{86}\text{Sr}$, thereby implying a faster $\Delta R/\Delta t$, when the changes expresses nothing more than a decrease in sedimentation rate (Figs 2 and 3).

Plainly wrong, because the commonly episodic deposition and variable rates of sedimentation in such environments is frequently overlooked (Ager 1973, 1993; Sadler 1981; Barefoot et al. 2023; see also Pearce et al. 2020 for a local study of changing sedimentation rates through time in the Chalk of the UK). The difficulty of incorporating such matters into cyclostratigraphic analysis is illustrated by, for example, the fact that cyclostratigraphic durations of the Albian range from $\approx 7.2$ Myr (Leandro et al. 2022) through $\approx 9.4$ (Charbonnier et al. 2023) to 13.42 Myr (Huang et al. 2010).

The best way to ameliorate the shortcomings of age models underpinning SIS is to profile $^{87}\text{Sr}/^{86}\text{Sr}$ against stratigraphic level through sections from widely separated locations. The one which gives the smoothest trend through the rock section is likely to be the one which best approximates the trend of $^{87}\text{Sr}/^{86}\text{Sr}$ through time.

**Legacy data**

It is often difficult to update legacy data for $^{87}\text{Sr}/^{86}\text{Sr}$ to evolving biostratigraphies and an evolving timescale. The ratification of GSSPs for 9 of the 12 Stages

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**Fig. 2.** Correlation with $^{87}\text{Sr}/^{86}\text{Sr}$. Levels in marine sections anywhere in the world correlate when they have the same $^{87}\text{Sr}/^{86}\text{Sr}$, provided the $^{87}\text{Sr}/^{86}\text{Sr}$ are measured accurately, corrected for interlaboratory bias, and obtained on well-preserved samples.
of the Cretaceous (the Berriasian, Valanginian and Aptian apart) has helped to stabilize some biostratigraphic nomenclature. Nevertheless, updating calibration curves is made difficult by continuing revision of zonal hierarchies, changes to fossil names, new fossil discoveries that force boundaries to move (usually) down in a section, and redemptions of biostratigraphic boundaries. As an example, Reboulet et al. (2023) propose using ammonites as a boundary marker for the base of the Valanginian rather than the commonly used calpionelids and setting the boundary 7 m lower than previously accepted. As another example, the base of the Campanian has traditionally been set at the last occurrence of the crinoid Marsupites testudinarius (Gale et al. 1995), at which level the value of $^{87}\text{Sr}/^{86}\text{Sr}$ given by those authors was $0.707473 \pm 0.000005$ (2 s.e.). That boundary definition, and its $^{87}\text{Sr}/^{86}\text{Sr}$ value, are no longer relevant as the base of the Campanian is now set at the base of magnetic polarity Chron C33r (Gale et al. 2023), which causes a problem for SIS as none of the sections profiled for $^{87}\text{Sr}/^{86}\text{Sr}$ has a useful magnetic record (but see the later section on the Campanian). The curve presented

![Diagram](image_url)

**Fig. 3.** The effect of changes in sedimentation rate on profiles of $^{87}\text{Sr}/^{86}\text{Sr}$ through a rock section. Rates of change of $^{87}\text{Sr}/^{86}\text{Sr}$ with stratigraphic level ($\Delta R/\Delta L$) must not be confused with rates of change of $^{87}\text{Sr}/^{86}\text{Sr}$ with time ($\Delta R/\Delta t$).
in Figure 1 therefore represents only the authors’ best efforts to accommodate such changes, and to deal with sometimes conflicting data, which occasionally involves a subjective choice, e.g. whether to constrain the Albian trend in $^{87}$Sr/$^{86}$Sr by using the in ocheramid data of Bralower et al. (1997) or the data of Denison et al. (2003).

Accuracy and precision of analysis

Using SIS to obtain reliable numerical ages, or to accomplish good biostratigraphic correlation, requires that close attention is paid to the accuracy and precision of analysis for $^{87}$Sr/$^{86}$Sr. The best modern instrumentation, used together with replicate analysis in order to reduce the standard error of the mean, allows $^{87}$Sr/$^{86}$Sr to be measured today to a precision no better than ± 0.000001. The accuracy is unlikely to be better than ± 0.000004 owing to interlaboratory bias (Hildreth and Henderson 1971; McArthur 1994; McArthur et al. 2020b), a matter explained below.

Analysis of $^{87}$Sr/$^{86}$Sr is done after extraction from the sample of the target Sr and purification of the Sr by ion-exchange chromatography. Traces of Rb may survive the purification process and be present during the measurement process. Rubidium has two isotopes, $^{85}$Rb and $^{87}$Rb, the latter indistinguishable from $^{86}$Sr during conventional mass spectrometry. Correction is thus needed for this isobaric interference (see Thirlwall 1991 for the procedure for TIMS analysis). As an alternative possible during TIMS analysis, data acquisition for Sr can be delayed until all the Rb has been lost from the sample (Zaky et al. 2019), as analysis involves evaporating the purified sample at temperatures around 1400°C, during which Rb evaporates much faster than does Sr.

In order to have comparable measurements of $^{87}$Sr/$^{86}$Sr between laboratories, measurement bias between them (interlaboratory bias) must be corrected for. Data must be adjusted (i.e. normalized) to an accepted value for the same standard, which is analysed in each laboratory. Two standards in common use are NIST987 (also termed SRM987), an SrCO$_3$ powder available from the National Institute of Standards and Technology, USA, with a value of 0.710248, and EN-1, a giant clam from Enewetak Atoll, distributed by the US Geological Survey, with a value recommended here of 0.709174 (Table 1); all data used in this work are normalized to these relative values. An older standard, a SrCO$_3$ made by Eimer and Amend Company of New York (Hildreth and Henderson 1971) has a value of 0.708022 ± 0.000004 (2 s.e., n = 34; Jones et al. 1994b) relative to 0.710248 for NIST(SRM)987. The E&A standard is not widely available. The use of IAPSO North Atlantic seawater as a standard is not recommended as it is stored in glass (risking contamination) and recent data (Mokadem et al. 2015; reinterpreted in fig. 7.6 of McArthur et al. 2020b) hints that open-ocean seawater is not uniform in its $^{87}$Sr/$^{86}$Sr composition. A modern coral, JCp-1, primarily used as a standard for Sr/Ca measurements, is occasionally used to represent modern marine $^{87}$Sr/$^{86}$Sr. It was distributed by the Geological Survey of Japan but is no longer exported from Japan. Finally, an alternative to EN-1 is to use modern shells from open-ocean environments away from rivers. This route requires checking for non-marine influences on $^{87}$Sr/$^{86}$Sr. For example, use of oysters, which can live in brackish environments, is not recommended unless the provenance is known definitively to be fully marine (see the next section for details).

Interlaboratory bias is supposedly corrected for by measuring $^{87}$Sr/$^{86}$Sr in a standard, calculating the difference between measured and accepted values, and then adding that difference to all data (e.g. if a laboratory reports 0.710258 for SRM987, then −0.000010 should be added to all data that lab produces). In theory, which standard is used should not matter. Unfortunately, the differences between the values of standards (i.e. the $^{87}$Sr/$^{86}$Sr of SRM987 minus the $^{87}$Sr/$^{86}$Sr of EN-1 or similar) are not the same for every laboratory (Hildreth and Henderson 1971; McArthur 1994; Table 1): data for a laboratory that normalizes data to SRM(NIST)987 may therefore differ systematically from data obtained in a laboratory that normalizes data to EN-1 or an equivalent.

The standard used should be that which has an $^{87}$Sr/$^{86}$Sr value that is closest to the values being measured. On that basis, use of E&A would be best for many deep-time studies because, of all available standards, its $^{87}$Sr/$^{86}$Sr is nearer to the values measured in marine minerals. Unfortunately, E&A is not widely available, so normalization to EN-1 or an equivalent is the usual alternative even though all Cretaceous values of $^{87}$Sr/$^{86}$Sr are well below its value of 0.709174.

As an example of the effect of interlaboratory bias, Figure 4 compares two trends in $^{87}$Sr/$^{86}$Sr through Maastrichtian time. One trend is based on McArthur and Howarth (2004). The other trend is based on Huber et al. (2008), updated from MacLeod et al. (2003) for sediments from ODP cores from Blake Nose. Both trends are given to the same (outdated) timescale of Gradstein et al. (2004). During the Maastrichtian, $\Delta R/\Delta t$ was only +0.000020 per Myr. The trend through the data of MacLeod et al. (2003) is around 0.000018 higher than, but parallel to, the calibration curve of McArthur and Howarth (2004). The difference can be ascribed to interlaboratory bias. Were data from MacLeod et al. (2003) used to derive numerical age from Figure 1 without correction for that bias (i.e. without subtraction of
0.000018 from their data), the error in a predicted age would be 0.9 Myr.

Few of the analyses used for the construction of the calibration curve in Figure 1 attained precision below ±0.000015, as do few of the analyses used by other authors for dating by SIS. If SIS is to realize its full potential to date and correlate marine sediments, the calibration curve shown in Figure 1 needs to be reconstructed from scratch, using the best modern instrumentation and samples from well-documented and stable sites where $^{87}\text{Sr}/^{86}\text{Sr}$ values can be tied directly to place-in-section, so that changing biostratigraphies can be accommodated.

### Homogeneity of marine $^{87}\text{Sr}/^{86}\text{Sr}$

SIS is based on the assumption that the oceans have always been homogeneous with respect to $^{87}\text{Sr}/^{86}\text{Sr}$. The degree to which this was true depends on the accuracy with which $^{87}\text{Sr}/^{86}\text{Sr}$ is measured. As rivers, submarine groundwater discharge, and mid-ocean-ridge hydrothermal plumes, have $^{87}\text{Sr}/^{86}\text{Sr}$ different from that of open-ocean seawater, any mix will have an $^{87}\text{Sr}/^{86}\text{Sr}$ reflecting the relative proportions of that mix. Such mixing was modelled or discussed by, inter alia, Ingram and Sloan (1992), Andersson et al. (1992), McArthur et al. (1994, 2020b), Bryant et al. (1995), Kuznetsov et al. (2012), El Meknassi et al. (2018) and Zaky et al. (2019); Kuznetsov et al. (2012) demonstrate particularly well the departures from 0.709174 of $^{87}\text{Sr}/^{86}\text{Sr}$ in samples from closed and semi-closed basins, such as the Sea of Azov.

The problem posed by riverine influences increases as the accuracy and precision of measurement of $^{87}\text{Sr}/^{86}\text{Sr}$ increases (Fig. 5). At the best

### Table 1. Values of $^{87}\text{Sr}/^{86}\text{Sr}$ in EN-1, seawater and modern marine biogenic carbonate. All values adjusted to a value of 0.710 248 for SRM(NIST)987.

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**Recommended value** 0.709 174

5. Long-term average, Bochum University
6. Study average for Zaky et al. (2019)
7. Mean of samples <31 ka
8. Mean of samples <50 ka
9. Ages by radiocarbon, mean of samples <30 ka
10. Mean of samples <25 ka
18. Mean of samples <44 ka, ODP Site 758A
21. Modern biogenic carbonate, unrestricted Atlantic and Pacific coasts; 31 analyses of 31 samples
23. Extrapolated to 0 mbsf
24. For five-year period
Fig. 4. The effect of interlaboratory bias on numerical ages derived by SIS. The pink trend (for clarity, shown without data) is the \(^{87}\text{Sr}/^{86}\text{Sr}\) calibration curve of McArthur and Howarth (2004). The blue trend, with data points, is the preferred trend of Huber et al. (2008) through the data of MacLeod et al. (2003) for ODP cores from Blake Nose. Both trends are to the timescale of Gradstein et al. (2004). Compared to the pink calibration curve, the blue trend is higher by 0.000 018. See the text for an interpretation of the difference in \(^{87}\text{Sr}/^{86}\text{Sr}\) between the trends.

attainable precision of \(\pm 0.000001\), 87% of modern rivers can alter the \(^{87}\text{Sr}/^{86}\text{Sr}\) of seawater at a dilution of 15%, i.e. from a salinity 35 psu to one of 30 psu (Fig. 5): at a precision of \(\pm 0.0000020\), typical of many analyses, as many as 10% can do so. Whilst such non-marine influences pose a problem for SIS, the problem may be over-emphasized because it is not always clear what part of the range of \(^{87}\text{Sr}/^{86}\text{Sr}\) for modern marine Sr in some reports arises from real heterogeneity and what arise from artefacts of preservation, analysis, or normalization.

When using SIS, non-marine influences should be looked for palaeontologically. When that is not diagnostic, such influences might be detectable by analysing specimens from both benthic and planktic environments from a single stratigraphic level, or multiple specimens of the same species from a single stratigraphic level. If variation in measured values of \(^{87}\text{Sr}/^{86}\text{Sr}\) is greater than analytical precision, either non-marine influences or imperfect preservation is indicated (on the latter, see later).

Samples for SIS

Samples analysed for SIS in the Cretaceous are usually belemnites and brachiopods as these are common in Cretaceous sediments and often preserve their original signals well, albeit only in resistant parts of the fossil. Notwithstanding that, most well-preserved marine precipitates will serve, e.g. gypsum, apatite (conodonts, shark teeth), barite and carbonate cements. Care is needed when dating gypsum (and anhydrite) as freshwater influences may have been strong in evaporites and lead to erroneous dates: Denison et al. (1998) and Denison and Peryt (2009) discuss and illustrate the problem well. Biogenic phosphate (e.g. shark teeth) tends to be altered diagenetically (Martin and Scher 2004) and seldom gives accurate results for SIS, although it often yields approximate ages that are, nevertheless, useful. Analysing bulk carbonate sediment risks contamination from Sr derived from diagenetic andlastic phases, thus skewing the result. Contamination from clastics often increases \(^{87}\text{Sr}/^{86}\text{Sr}\) in samples from continental settings and decreases \(^{87}\text{Sr}/^{86}\text{Sr}\) in samples from settings with mantle affinity (e.g. back-arc basins).

Where analysis of bulk sediment is the only option, it should be used only on samples that contain little detrital material. The meaning of the term ‘little’ needs to be decided on a case-by-case basis, but more than 2% detrital material is likely to create contamination from non-target phases of a magnitude that exceeds analytical uncertainty. The likelihood of getting good data from whole-rock analysis is hypothesized here to be inversely proportional to the degree of lithification of a sample. Ways to minimize, but not eliminate, contamination when analysing bulk sediment are given in Bailey et al. (2000) and McArthur et al. (2020b). In brief, use gentle dissolution methods, such as 90% acetic acid, and use a serial leaching process to remove as much contaminant as possible and target the most unaltered part of the sample.

Sample preservation

Use of SIS requires well-preserved samples and that, in turn, requires assessment of the quality of preservation of the material analysed (usually biogenic calcite). Samples are typically described in published works as ‘well preserved’. Whether they are so is often debatable. The term ‘well-preserved’ is subjective and interpreted differently by palaeontologists and geochemists. Here, the term ‘well preserved’ means that samples retain their original \(^{87}\text{Sr}/^{86}\text{Sr}\) value. Multiple criteria exist for assessing preservational state. Most commonly used is the content of Sr, Fe and Mn (Brand and Veizer 1980, 1981; Veizer 1989; Podlaha et al. 1998; amongst others) but for reservations on the use of Fe and Mn, see Jones et al. (1994a, b). The concentration of Ba in calcite may signal alteration if present at concentrations >10 ppm (Li et al. 2021); the advantage of Ba
over Mn and Fe is that Ba is not redox-sensitive. Cathodoluminescence is excellent at assessing alteration in calcite (Marshall 1988 and many later papers on this topic), but it is not foolproof as some modern biogenic carbonate (presumably unaltered) shows luminescence (Barbin et al. 1991). Another excellent method is visual inspection, in both hand specimens and as fragmented samples under the binocular microscope (Fig. 6), and as polished and/or thin section (Li et al. 2021; fig. 7.8 of McArthur et al. 2020b). For calcite, visual inspection and cathodoluminescence are better than trace-element analysis as they are more sensitive to small degrees of alteration. For aragonite, scanning electron microscopy is often used but is not diagnostic unless used at magnifications of at least 20,000, since that degree of magnification is needed to see variable thickness in nacre layers, and overgrowths on nacre plates (Fig. 6g, h).

An excellent test of preservation is to compare the precisions, as standard deviations, of sample data, replicate data on individual samples and standards run with samples (e.g. Jones et al. 1994b). Neither the precision of replicates of a single sample, nor the precision (of detrended) sample data, should be greater than the precision of analysis of the data as judged by multiple analysis of standards. As an example, Jones et al. (1994b) provided 28 analyses of 12 belemnites from a single bedding plane; only one sample departed from the mean value of all analyses by more than analytical uncertainty (± 0.000025, 2.s.d.), so only one sample could be considered altered (Fig. 7a). As another example, McArthur et al. (2004) provided 32 analyses, with a precision of ± 0.000015 (2.s.d.; incorrectly reported as 2 s.e. in that paper), for 15 belemnites from 2.4 m of the Valanginian Polyptichytes Beds of Speeton, UK. The data show no overall trend (i.e. \( \Delta R/\Delta L = 0 \); Fig. 7b) and residuals about a line of linear regression are \( \leq +0.000014 \), with all but one being \( \leq +0.000010 \). On this basis, the samples were well preserved.

Corrections for \( ^{87}\text{Rb} \) decay

The incorporation of marine Sr into a mineral is accompanied by the incorporation of marine Rb. Atoms of \( ^{87}\text{Rb} \) decay to \( ^{86}\text{Sr} \) and so can alter the \( ^{87}\text{Sr}/^{86}\text{Sr} \) of a mineral, potentially leading to a false age derived from SIS. Whether correction is needed depends on the Sr/Rb of the sample and its age.

From theory, for Cretaceous samples, correction for Rb decay is needed only if the precision sought is \( \leq 0.000001 \) and Sr/Rb is less than 7000 (for a more detailed discussion of this topic, see table 7.2 of McArthur et al. 2020b). How likely is it that Sr/Rb mass ratios \( <7000 \) will be encountered in...
samples for SIS? Data for Rb in calcite are uncommon: Kiel et al. (2014) report concentrations of Rb <0.03 ppm (Sr/Rb $\approx$ 10 000) in Cretaceous specimens of the rhynchonellid brachiopod Peregrinella, whilst McArthur et al. (2000) report Rb concentrations typically <0.1 ppm in Toarcian belemnite calcite (Sr/Rb >15 000). Given such sparse data, we additionally use a proxy argument to evaluate the likelihood of a Rb problem affecting Cretaceous samples. The size of the Rb$^+$ ion is larger than the size of the Ca$^{2+}$ ion (161 v. 112 pm at CN = 8; Speight 2017) so aragonite, in which the cation site...
is larger than in calcite, should incorporate more Rb than does calcite. Yet Sr/Rb in aragonite is >9000 in coralline aragonite (Allison 1996) and >49 000 in inorganic marine aragonite (Oyanagi et al. 2021). From all of the above, Sr/Rb mass ratios are unlikely to occur in Cretaceous carbonates used for SIS. Information is lacking on the Rb content of gypsum, anhydrite, barite or biogenic apatite, so analysis for Rb would be wise when dating such materials by SIS.

Notes on the calibration curve (Fig. 1)

Berriasian, 143.1 ± 0.6

No formal GSSP has been fixed for the base of the Berriasian Stage (ICS 2023). The base of the Stage is here set at the level set in GTS2020, which is at the level of the first appearance of the calpionellid Calpionella alpina, a level approximately in the middle of magnetochron M19n.2n. The numerical age assigned in GTS2020 is 143.1 Ma. The level correlates to the middle of the Berriasella jacobi ammonite Zone in western Tethys (GTS2020, fig. 27.9). The equivalent level on the Russian Platform is the base of the Craspedites milkovensis Sz. of the Craspedites nodiger ammonite Zone (upper Volgian; Wierzbowski et al. 2017). The base of the Berriasian has an $^{87}\text{Sr}/^{86}\text{Sr}$ of 0.707190 ± 0.000003 (2 s.e., n = 23) as defined by analysis of belemnites from the Boreal Realm (Kuznetsov et al. 2017), with minor contributing data from belemnites from southeastern France (McArthur et al. 2007). Upwards from the base of the Berriasian, $^{87}\text{Sr}/^{86}\text{Sr}$ appears to increase more or less linearly with time to the base of the Valanginian (Fig. 1).
Valanginian, 137.7 ± 0.5

No GSSP has been fixed for the base of the Valanginian Stage (ICS 2023). In view of that, the Tethyan base of the Valanginian is set here at the base of the ‘Thurmanniceras’ pertransiens ammonite Zone at Vergol, in SW France (Kenjo et al. 2021), which is a candidate section and placement for the Valanginian GSSP (Reboulet et al. 2023). Owing to new finds of ammonites in sections at Vergol, the base set by Kenjo et al. (2021) is around 7 m lower than that recognized in the 87Sr/86Sr curve for the Valanginian given in McArthur et al. (2007). The new boundary profile at Vergol for 87Sr/86Sr is shown in Figure 8. The new boundary value is 0.707289 ± 0.000004 (2 s.e., n = 12), which is 0.000005 less than the value given in McArthur et al. (2007, 2020b). The base of the Boreal Valanginian (Ryazanian-Valanginian boundary) appears to be fixed by the data of Möller et al. (2015) at 0.707293 ± 0.000003 (2 s.e., n = 14).

Fig. 8. Profile of 87Sr/86Sr through the Berriasian/Valanginian boundary section at Vergol, SE France. All samples are from the Vergol section. Source: litholog courtesy of S. Reboulet.

Hauterivian, 132.6 ± 0.6

The GSSP for the Hauterivian Stage is placed at the base of Bed 189 in the La Charce section of southeastern France (Mutterlose et al. 2021). This level marks the first occurrence of the ammonite genus Acanthodiscus which, in southeastern France, is the base of the Acanthodiscus radiatus ammonite

The Valanginian part of the calibration curve (Fig. 1) is based on the data of Möller et al. (2015). The age model used is based on numerical ages of ammonite zones and subzones in the Vocontian Basin of southeastern France (McArthur et al. 2007). The age model used is based on numerical ages of ammonite zones and subzones given in GTS2020: these, in turn, are based on the cyclostratigraphy of Martinez et al. (2013, 2015) for the limestone-marls alternations of the Vocontian Basin, southeastern France where, through the Valanginian and Hauterivian, age is approximately linearly related to stratigraphic level (Fig. 9). In the uppermost Valanginian, ΔR/Δt decreases in the middle Late Valanginian to essentially zero before increasing again across the Valanginian–Hauterivian boundary and continuing to increase through the Hauterivian. It remains to be seen if these Late Valanginian changes in ΔR/Δt are artefacts of an incorrect age model arising from changing rates of sedimentation, or whether they are real. The plot of 87Sr/86Sr against level shown for the Valanginian in Möller et al. (2015, their fig. 2; see also McArthur et al. 2016, fig. 9 and discussion) suggests that a more linear trend might be more appropriate; however, the data of the former for the Upper Valanginian are sparse so that interpretation is uncertain.

Fig. 9. Numerical ages of ammonite zones and subzones from GTS2020 plotted against stratigraphic level for the composite section for the Vocontian Basin, S.E. France, given in McArthur et al. (2007).
Zone. No profile exists of $^{87}\text{Sr}/^{86}\text{Sr}$ through the section at La Charce. The Valanginian–Hauterivian boundary profile of McArthur et al. (2007) is based on belemnites from Vergel and Angles, both also in southeastern France. Correlation of those sections to La Charce yields a value for the Valanginian–Hauterivian boundary of 0.707383 using the data of McArthur et al. (2007), with the 2 s.e. recalculated here to be $\pm 0.000002$ ($n = 9$).

In the UK, the lowest Hauterivian strata of the Speeton Clay is the Endemoceras ambylogonium ammonite Zone, which marks the base of the Boreal Hauterivian (fig. 27.9 in GTS2020). The mean $^{87}\text{Sr}/^{86}\text{Sr}$ value of three measurements on belemnites from this zone is 0.707381 $\pm 0.0000002$ (range of three values; McArthur et al. 2004). The value of $^{87}\text{Sr}/^{86}\text{Sr}$ confirms that deposition of Hauterivian sediment at Speeton began in the earliest Hauterivian on a phosphatic remanié surface of Valanginian age (Rawson 1971). The $^{87}\text{Sr}/^{86}\text{Sr}$ values of belemnites from 2.4 m of the 3.8 m of the Boreal Valanginian sediments (most of the Polyptychites Beds, Fig. 7b) underlying the remanié surface is 0.707337 $\pm 0.000002$ (2.s.e., $n = 32$). That ratio correlates to the boundary of the bioselelense/campylotoxus Szs of the B. Campylotoxus Zone of the Tethyan Vocontian Basin (McArthur et al. 2007); the zonation of the Vocontian Basin has since been revised (Reboulet et al. 2023).

**Barremian, 126.5 $\pm 0.7$**

The GSSP for the Barremian Stage is in the process of final approval but will be in Bed 171 in the section at Río Argos near Caravaca, Murcia Province, Spain at the first appearance of the Tethyan ammonite Taveraidiscus hugii (ICS 2023). No useful $^{87}\text{Sr}/^{86}\text{Sr}$ data exist for the section but extrapolation from sparse $^{87}\text{Sr}/^{86}\text{Sr}$ values for uppermost Hauterivian belemnites in correlative equivalents in the Tethyan Vocontian Basin (data in McArthur et al. 2007) suggest that the base of the T. hugii zone in Tethys has an $^{87}\text{Sr}/^{86}\text{Sr}$ value of 0.707474 $\pm 0.000010$ (2 s.e., $n = 6$). The belemnite $^{87}\text{Sr}/^{86}\text{Sr}$ data of Bodin et al. (2015) for the Tethyan Vocontian Basin, predicts a value of 0.707472 $\pm 0.000005$ (2 s.e., $n = 19$) for the base of the Barremian. The base of the Tethyan T. hugii ammonite Zone equates to the base of the Boreal Paracrioceras rarocinctum ammonite Zone (GTS2020). In the Boreal record of $^{87}\text{Sr}/^{86}\text{Sr}$, based on belemnites from the Speeton Clay, Yorkshire, UK (data of McArthur et al. 2004), the base of the P. rarocinctum Zone, and so the base of the Boreal Barremian, has an $^{87}\text{Sr}/^{86}\text{Sr}$ value of 0.707475 $\pm 0.000001$ (2 s.e., $n = 16$).

A detailed record of $^{87}\text{Sr}/^{86}\text{Sr}$ through Barremian time was given in McArthur et al. (2004) for the Boreal Realm and was based on the Speeton Clay. That record formed the basis of the Barremian part of the Sr-isotope calibration curve in McArthur et al. (2020b; LOWESS 6). The numerous hiatuses in the Speeton Clay section, and the variable sedimentation rate through it, suggest that a better basis for a calibration curve for the Barremian is the sparser data of Bodin et al. (2015) for the Vocontian Basin, where sedimentation appears less interrupted, so the Barremian in Figure 1, and in the LOWESS 7 fit, was prepared on that basis.

The stratigraphic position of the Barremian maximum in $^{87}\text{Sr}/^{86}\text{Sr}$ is, however, poorly defined in the data of Bodin et al. (2015). At Speeton, for which data are more abundant, the maximum $^{87}\text{Sr}/^{86}\text{Sr}$ of 0.707485 $\pm 0.000003$ (2 s.e. $n = 8$) occurs in the *Paracrioceras elegans* ammonite Zone which, according to figure 27.9 of GTS2020, correlates to the Tethyan ammonite zone of Moutoniceras moutonianum, with bounding ages for both of 124.4 and 124.8. Accordingly, LOWESS 7 has the Barremian maximum of 0.707485 at 124.8 Ma.

**Aptian, 121.4 $\pm 0.6$, and Albian, 113.2 $\pm 0.3$**

No GSSP for the Aptian Stage has been agreed (ICS 2023) but the base of magnetic anomaly M0r is typically used as a marker level for the base of the Stage (e.g. GTS2020). This level is around 0.2 Myr later than the first appearance of the ammonite Deshayesites oglanensis (GTS2020). The GSSP for the Albian Stage is set at 0.4 m above the base of the Niveau Kilian bed (a laminated shale) in the Vocontian Basin at Col de Pré-Guittard, Department Drôme, in southeastern France (Kennedy et al. 2017).

The trend of $^{87}\text{Sr}/^{86}\text{Sr}$ through the Aptian and Albian is based on four datasets. The first, that of Bodin et al. (2015) for belemnites from the Vocontian Basin, southeastern France, is calibrated by ammonite zones and is mostly for the Aptian. The second, that of Bralower et al. (1997) for inoceramid data for ODP Site 51, is calibrated to microfossil datums and it is mostly for the Albian. Here, the data of Bralower et al. (1997) are revised to the age model for Site 511 given by Dummann et al. (2020). The third is that of Jenkyns et al. (1995) for atoll carbonates from the Mid-Pacific Mountains (notably Resolution Gouyet), for which age control is based on SIS because of a lack of age-diagnostic fossils; this dataset is used simply to provide qualitative confirmation of the trends from the other two sets of data. The last is that of Burla et al. (2009) for the Luz Section (Algarve Basin, Portugal) with weak biostratigraphic control but which confirms a late Aptian minimum, the level and $^{87}\text{Sr}/^{86}\text{Sr}$ value of which is probably not obscured by a hiatus between the
Lower and Upper Luz Marls because the minimum $^{87}\text{Sr}/^{86}\text{Sr}$ is within analytical uncertainty of the minimum value seen in other sections (discussed below). Sparse $^{87}\text{Sr}/^{86}\text{Sr}$ data, at two levels close to the Aptian–Albian boundary, given in Kennedy et al. (2000), are from multiple localities and difficult to place within the stratigraphic framework used here, so are not used.

The $^{87}\text{Sr}/^{86}\text{Sr}$ value for the base of the Aptian is around 0.707436 based on the data of Bodin et al. (2015). In the section at Cresmina (Lusitanian Basin, Portugal), a value of 0.707446 ± 0.000005 (2 s.e., $n = 14$) can be derived for the base of the Aptian from the data of Burla et al. (2009).

The base of the Albian has a value around 0.707227 based on the sparse Albian data of Bodin et al. (2015) and the more numerous data of Bralower et al. (1997).

In the Aptian–Albian interval, $^{87}\text{Sr}/^{86}\text{Sr}$ declines through the Aptian to a minimum in the latest Aptian, and an increase through the early Albian (Fig. 1). The minimum $^{87}\text{Sr}/^{86}\text{Sr}$ value recorded by Burla et al. (2009) is 0.707179 ± 0.000013 (2 s.e., $n = 3$). The minimum $^{87}\text{Sr}/^{86}\text{Sr}$ recorded by Bralower et al. (1997), defined by two samples, is between 0.707211 and 0.707213, both with measurement uncertainty of ±0.00 0 025, whilst the minimum recorded by Bodin et al. (2015) is 0.707193 ± 0.000009 (2 s.e., $n = 6$). The biostratigraphic level of the latest Aptian minimum in $^{87}\text{Sr}/^{86}\text{Sr}$ differs between Bralower et al. (1997) and Bodin et al. (2015). In Bodin et al. (2015), from their figure 5, the minimum occurs between the Jacob Level and the higher Kilian Level, in the Hypacanthoplites jacobi ammonite Zone, around 35% up from its base (their fig. 5). According to Herrle and Mutterlose (2003, their fig. 5) this is within the lower part of nannofossil Zone NC8A of Roth (1978). In Bralower et al. (1997) the minimum occurs in the middle of nannofossil Zone NC7C, the zone underlying NC8A and a level approximately 20% of the way up from the base in the Ticinella bejaouaensis foraminiferal Zone (now termed the Paraticinella rohri Zone; Ando et al. 2016). Correlated to the Vocontian Basin, that level is ≈ 40 m below the Jacob Level and in the H. nolani ammonite Zone (see fig. 5 of Herrle and Mutterlose 2003), the zone immediately underlying the H. jacobi ammonite Zone.

The minimum in $^{87}\text{Sr}/^{86}\text{Sr}$ must be synchronous, so the different biostratigraphic positions of the minima show either diachronieity of the fossil datums used to calibrate the curves, or the fact that the minima are too poorly defined stratigraphically for their positions to be compared properly. As differences are small and systematic between the numerical ages of the age boundaries for the Aptian used in Bralower et al. (1997; 99.0, 112.2 Ma) and in GTS2020 (100.5, 113.2 Ma), these differing numerical ages cannot account for the mismatch. Evidently, much remains to be clarified with respect to the $^{87}\text{Sr}/^{86}\text{Sr}$ across the latest Aptian–earliest Albian interval.

Turning to wider issues of the temporal calibration of $^{87}\text{Sr}/^{86}\text{Sr}$ through Aptian and Albian time, the Aptian interval in Figure 1 is based on the sparse dataset of Bodin et al. (2015), calibrated to the ammonite zonation of the Vocontian Basin, southeastern France. Updating their trends of $^{87}\text{Sr}/^{86}\text{Sr}$ against time is made difficult by the unsettled nature of the ammonite zonations for the interval (Reboulet et al. 2018; Szives et al. 2023). Here we use the ammonite zones of GTS2020 (see their fig. 27.9) but adjust the numerical ages of a few zone boundaries in order to minimize an inflection in the late Aptian $^{87}\text{Sr}/^{86}\text{Sr}$ trend. Table 2 provides the numerical ages of the zone bases both those in GTS2020 and those of our new scale.

The biggest difference between numerical ages used here and those used in GTS2020 concerns the duration of the zone of Acanthohoplites nolani, which reduces from 2.4 Myr in duration in GTS2020 to 1.0 Myr here. Support for the shorter duration comes from the fact that, in GTS2020, the duration of the A. nolani ammonite Zone correlates to the lower 70% of the Paraticinelli rohri foraminiferal Zone. The duration of the P. rohri Zone is given as 3.5 Myr in GTS2020 but as 1.3 Myr in Leandro et al. (2022), based on cyclostratigraphic analysis of the Poggio le Guaine core, and 1.1 Myr in Charbonnier et al. (2023) based on cyclostratigraphic analysis of the marl-limestone alternations in the Vocontian Basin. Although these cyclostratigraphic estimates differ by 17% (and cyclostratigraphic analysis of sedimentary rocks often give rise to concern), both give shorter durations than GTS2020, so our shortening of the nolani Zone seems acceptable.

To ensure that the late Aptian minimum in $^{87}\text{Sr}/^{86}\text{Sr}$ given in the works of Bodin et al. (2015) and Bralower et al. (1997) coincide, the data of Bralower have also been reduced by 0.000018, which is the difference between the $^{87}\text{Sr}/^{86}\text{Sr}$ values of the minimum defined by each dataset. This adjustment is made on the assumption that the difference reflects either a diagenetic effect on the data of Bralower et al. (1997) or unnoticed interlaboratory bias, rather than the stratigraphic mismatch noted earlier.

Cenomanian, 100.5

The GSSP for the Cenomanian Stage is set at 36 m below the top of the Marnes Bleues Formation at Mont Risou, east of Rosans, Haute-Alpes, France. That level coincides with the first appearance of the planktonic foraminifera Rotalipora globotruncanoides Sigal, 1948 (Kennedy et al. 2004). There is no profile of $^{87}\text{Sr}/^{86}\text{Sr}$ through that section.
The curve of $^{87}$Sr/$^{40}$Sr through time for the Cenomanian is based on sparse data, so is indicative only. The foraminiferal data of Bralower et al. (1997) for the interval scatter a good deal and include no reliable Cenomanian data from Site 511, a site that helped define the Albian trend. Cenomanian data for the Trunch borehole, based on macrofossil fragments augmented by analysis of pre-leached bulk sediment, are too few, and the sediments too condensed, for meaningful interpretation, but appear to show values decreasing upsection through the Cenomanian-Turonian boundary (Fig. 10). The value of $^{87}$Sr/$^{40}$Sr at the base of the Cenomanian section in Trunch is around 0.707 490 for a sample from the Paradoxica Bed (Neostlingoceras carcitanensis ammonite Subzone of the Martelliceras mantelli Zone; Pearce et al. 2020) and approximates the value for the Albian–Cenomanian boundary, which is set at the base of the *N. carcitanensis* Sz.

In the US Western Interior, sparse data for pycnodonts, inoceramids and ammonites, through the Cenomanian (McArthur et al. 1994), suggest that there was little change in $^{87}$Sr/$^{40}$Sr through that interval, with a decrease into the Turonian starting in the very latest Cenomanian. The base of the Cenomanian is placed at the base of the *Neogastropilites haasi* ammonite Zone and a single value for a specimen of *Texigrypha* in the overlying zone of *Neogastropilites cornutus* has an $^{87}$Sr/$^{40}$Sr value of 0.707400 ± 0.000015 (McArthur et al. 1994). The Cenomanian–Turonian boundary interval is poorly defined; for a discussion, see Yobo et al. (2021) and Ando et al. (2009).

**Turonian, 93.9 Ma**

The GSSP for the Turonian Stage is at the base of Bed 86 of the Bridge Creek Limestone Member of the Greenhorn Limestone Formation at a road-cut west of Pueblo, Colorado, USA and coincides with the first occurrence of the ammonite *Watinoceras devonense* (Kennedy et al. 2005). There is no $^{87}$Sr/$^{86}$Sr profile through the GSSP section. In the US Western Interior, the value for $^{87}$Sr/$^{86}$Sr for the base of the Turonian (of the *Watinoceras devonense* Zone) is 0.707377 ± 0.000006 (2 s.e., n = 10; Fig. 11). In the Trunch borehole, the base of the Turonian is placed at 500.2 mbgl (Pearce et al. 2020) and the value of $^{87}$Sr/$^{86}$Sr at that level, based on macrofossil debris moderated by pre-leached bulk Chalk, is around 0.707450; that is, higher than appears to be the case for the US Western Interior if these levels are indeed the same age and the samples in the Trunch borehole have not been elevated by diagensis.

The Cenomanian–Lower Turonian interval of the Trunch section contains numerous hardgrounds and erosion surfaces (Pearce et al. 2020) and the age model for the borehole (Pearce et al. 2020) shows a pronounced change in sedimentation rate somewhere in the uppermost Turonian–lowest Cenomanian, between 460 m and 500 mbgl. Where that change occurs is not defined well, but the $^{87}$Sr/$^{86}$Sr profile through the interval (Fig. 10) suggests that it might occur around 495 mbgl. There is no obvious lithological expression of such a change in the lithological log given in Pearce et al. (2020). The data for

<table>
<thead>
<tr>
<th>Stage/age</th>
<th>Ammonite zone</th>
<th>GTS2020 Fig. 27.9 (Ma)</th>
<th>Duration (Myr)</th>
<th>This work (Ma)</th>
<th>Duration (Myr)</th>
<th>Difference in duration (Myr)</th>
</tr>
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<tbody>
<tr>
<td>Albian</td>
<td><em>Douvilleiceras mammillatum</em></td>
<td>110.87</td>
<td>1.17</td>
<td>110.87</td>
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<td>1.00</td>
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<td>0.75</td>
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<td>120.40</td>
<td>1.25</td>
<td>-0.40</td>
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<td>0.60</td>
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</table>
the Sr-isotope profile shown in Figure 10 scatter more than the precision of the analysis and the data are not numerous, so the $^{87}\text{Sr}/^{86}\text{Sr}$ profile in Figure 10(b) should be viewed as preliminary. Nevertheless, Figure 10 gives an idea of what might be achieved in defining levels at which sedimentation rate changes occur should more and better $^{87}\text{Sr}/^{86}\text{Sr}$ data become available.

The curve of $^{87}\text{Sr}/^{86}\text{Sr}$ against time for the Turonian is based mostly on sparse data for ammonites and inoceramids from the US Western Interior (data of McArthur et al. 1994); those samples could be positioned only to zonal level. Previous trends of $^{87}\text{Sr}/^{86}\text{Sr}$ through time (e.g. McArthur et al. 2020b) gave to samples a numerical age equal to the base of the zone in which the sample occurred. Here, the mid-point of the zone is used, with ages being interpolated between the ages for zone boundaries given in GTS2020. The difference this change makes to prediction of age is typically <0.5 Ma and is shown in Figure 11, where the trend through Turonian time of $^{87}\text{Sr}/^{86}\text{Sr}$ derived is compared to the trend given in McArthur et al. (2020b).

Values of $^{87}\text{Sr}/^{86}\text{Sr}$ decline through the early Turonian to a minimum in the latest Turonian before increasing again to the Turonian–Coniacian boundary. The $^{87}\text{Sr}/^{86}\text{Sr}$ value for the Turonian minimum in the US Western Interior is poorly defined by three analyses of a single inoceramid (0.707292, 0.707293, 0.707309) from the S. whitfieldi ammonite Zone (Table 3; McArthur et al. 1994). Lower values
of $0.707280 \pm 0.000003$ (2 s.e., $n = 12$) are found for macrofossils from the Whisky Bay Formation of James Ross Island, Antarctica (Table 3), which is of Turonian age (Fig. 2 of Crane et al. 2006). Furthermore, Steuber (2001) recorded values for Turonian rudists of $0.707286$ and $0.707289$ (Table 3) from two sites near Salzburg, Austria. These two sets of data show either that the minimum recorded in the US Western Interior is too high by around $0.000013$ (cf. analytical uncertainty of $\pm 0.000015$) because unnoticed diagenetic alteration has increased $^{87}$Sr/$^{86}$Sr in the ineramid from the $S$. *whiffielfi* Zone, or that the minimum lies in the unsampled latest three Turonian ammonite zones of the US Western Interior ($S$. *mariasensis*, *P*. *gernani* and $S$. *nigricollensis*; Table 3). Here, it is assumed that the minimum occurs in the $S$. *whiffielfi* Zone and is $0.707280$. Clearly, the Turonian calibration curve, as with most of the Cretaceous curve, needs improvement.

**Coniacian, 89.4 \pm 0.2**

The GSSP for the Coniacian Stage is defined by the ineramid bivalve species *Cremonoceras deformis erectus* (Walaszczyk et al. 2022), which appears in Bed 46 of the section at Salzgitter–Salder in eastern Lower Saxony, Germany. There is no profile of $^{87}$Sr/$^{86}$Sr through the section.

The curve of $^{87}$Sr/$^{86}$Sr through time for the Coniacian is based on sparse data from the US Western Interior and data from the Trunch borehole (McArthur et al. 1993a, 1994). The base of the $C$. *d. erectus* Zone in the US Western Interior coincides with the base of the *Scaphites preventicosus* ammonite Zone (Cobban et al. 2006). The $^{87}$Sr/$^{86}$Sr value of that level is $0.707314 \pm 0.00002$ (2 s.e., $n = 14$). In the Trunch borehole, $C$. *d. erectus* has not been found (Pearce et al. 2020), but those authors place the base of the Coniacian at 429.9 mbgl based on a C-isotope correlation. The lowest level in the Coniacian of the Trunch borehole for which good $^{87}$Sr/$^{86}$Sr data are available is 427 mbgl. Extrapolating the $^{87}$Sr/$^{86}$Sr trend to 429.9 mbgl gives a value of $0.707319 \pm 0.000004$ (2 s.e., $n = 8$) based on a reinterpretation of data in McArthur et al. (1993a). A lower value of $0.707293 \pm 0.000006$ (2 s.e.) is predicted by LOWESS 7 because of the need to accommodate a late Turonian minimum (see Turonian section). Further work is required to define the base Coniacian value more closely.

**Santonian, 85.7 \pm 0.2**

The GSSP for the Santonian Stage is at 94.4 m in the eastern border of the ‘Cantera de Margas’ quarry, Olazagutia, Navarra, N. Spain at the first occurrence (FO) of the ineramid bivalve *Platyceramus undulatoplicatus* (Lamolda et al. 2014). There is no record of $^{87}$Sr/$^{86}$Sr through that section.

The base of the Santonian in the English Chalk of the Trunch borehole is at 372.5 mbgl (Lamolda et al. 2014; Pearce et al. 2020). That level is 5.5 m lower than given in McArthur et al. (1993a). The value of $^{87}$Sr/$^{86}$Sr at 372.5 m is $0.707397 \pm 0.000002$ (2 s.e., $n = 14$). The base of the Santonian in the US Western Interior is 80% up in the *Scaphites depressus* ammonite Zone (Walaszczyk and Cobban 2007; fig. 27.9 of GTS2020), with an $^{87}$Sr/$^{86}$Sr value of $0.707418 \pm 0.000002$ (2 s.e., $n = 6$) based on the sparse data in McArthur et al. (1994).

The curve for the Santonian is based on the US Western Interior, plus sparse data for the English Chalk and the Chalk of Germany (McArthur et al. 1993a, b, 1994), all updated to the GTS2020 timescale.

**Campanian, 83.7 \pm 0.5**

The GSSP for the Campanian Stage is at the base of magnetic polarity Chron C33r, which occurs at 221.5 m in the Bottaccione Gorge section at Gubbio, Umbria–Marche Basin, Italy (Gale et al. 2023). No good record of $^{87}$Sr/$^{86}$Sr exists for the section. The $^{87}$Sr/$^{86}$Sr curve for the interval (Fig. 1) is based on belemnites and pre-leached bulk Chalk from Kronsmoor and Lägerdorf, northern Germany (McArthur et al. 1993b) and the assumption of a constant sedimentation rate through the sections sampled. The data of McArthur et al. (1993b) were revised for GTS2020 and here by removing a 7 m gap, assumed by those authors to be present between the top of the exposed section at Lägerdorf and the base of the exposed section in Kronsmoor,
following a demonstration that the gap did not exist (Voigt and Schönfeld 2010), and by expanding the section from Flint 93 to Flint 100 by 7.8 m to allow for a thickness in that interval apparently being greater than in previous lithological logs (Voigt and Schönfeld 2010).

In the US Western Interior, the base of the Campanian has been traditionally set at the base of the *Scaphites Leei* III ammonite Zone (Cobban et al. 2006) or some 20% up from the base (fig. 27.9 in GTS2020). The base of the zone has an $^{87}$Sr/$^{86}$Sr value of $0.707454 \pm 0.000002$ (2 s.e., $n = 6$) based on the data of McArthur et al. (1994); the value for the base of the overlying zone of *Scaphites hippocrepis I* is 0.707465. Thibault et al. (2016; their figs 9 and 10) correlate the base of the *S. leei* III Zone to the level of the last occurrence of the crinoid *Marssonites testudinarius* in the English Chalk.

In the English Chalk, the traditional placement of the base of the Campanian has been the last

<table>
<thead>
<tr>
<th>U.S. Western Interior</th>
<th>Ammonite Zonation (Cobban et al. 2006)</th>
<th>Type</th>
<th>Numeric age, GTS2020</th>
<th>$^{87}$Sr/$^{86}$Sr $\pm$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coniacian (Base)</td>
<td><em>Scaphites preventricosus</em></td>
<td>Inoceramid calcite</td>
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<td>0.707334 15</td>
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<td><em>Pycnodont</em> calcite</td>
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<td>0.707310 15</td>
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<td>Turonian</td>
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<td><em>Ostrea</em> calcite</td>
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<td>0.707352 15</td>
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<td><em>Vescoceras birchbyi</em></td>
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<tr>
<td>Turonian</td>
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<tr>
<td>Turonian (Base)</td>
<td><em>Watinoceras devonense</em></td>
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</table>

<table>
<thead>
<tr>
<th>Steuber (2001) Salzburg</th>
<th>Sample</th>
<th>Type</th>
<th>$^{87}$Sr/$^{86}$Sr $\pm$</th>
</tr>
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<tbody>
<tr>
<td>Turonian</td>
<td>NW24-1, St. Gilgen-Billroth</td>
<td>Rudist calcite</td>
<td>0.707292 8</td>
</tr>
<tr>
<td>Turonian</td>
<td>NW24-3, St. Gilgen-Billroth</td>
<td>Rudist calcite</td>
<td>0.707284 8</td>
</tr>
<tr>
<td>Turonian</td>
<td>NW18-1, St. Gilgen, Wolfgangsee</td>
<td>Rudist calcite</td>
<td>0.707281 8</td>
</tr>
<tr>
<td>Turonian</td>
<td>NW18-2, St. Gilgen, Wolfgangsee</td>
<td>Rudist calcite</td>
<td>0.707290 8</td>
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</tbody>
</table>

<table>
<thead>
<tr>
<th>James Ross Island, Antarctica</th>
<th>Sample</th>
<th>Type</th>
<th>Level, m</th>
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<td>Oyster</td>
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<td>421.5–461.5</td>
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<td>0.707278 9</td>
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<td>DJ 1456.200</td>
<td>Belemnite</td>
<td>392</td>
<td>0.707278 10</td>
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<tr>
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<td>DJ 1456.200</td>
<td>Belemnite</td>
<td>392</td>
<td>0.707280 10</td>
</tr>
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<td>Belemnite</td>
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<td>DJ 1456188-192</td>
<td>Oyster</td>
<td>392</td>
<td>0.707273 10</td>
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<td>0.707273 10</td>
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<td>Oyster</td>
<td>383.5–414</td>
<td>0.707278 9</td>
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<td>DJ 1456.159</td>
<td>Oyster</td>
<td>383.5–414</td>
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<td>Oyster</td>
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<td>Oyster</td>
<td>383.5–414</td>
<td>0.707280 9</td>
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</table>

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<thead>
<tr>
<th>Cretaceous SIS</th>
<th>Sample</th>
<th>Type</th>
<th>$^{87}$Sr/$^{86}$Sr $\pm$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Turonian</td>
<td>NW24-1, St. Gilgen-Billroth</td>
<td>Rudist calcite</td>
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</tr>
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<td>Rudist calcite</td>
<td>0.707290 8</td>
</tr>
</tbody>
</table>

Mean 0.707280 2 s.e. 0.000003

Table 3. Turonian values of $^{87}$Sr/$^{86}$Sr. Values from the US Western Interior (McArthur et al. 1994), the Brandy Bay Member of the Whisky Bay Fm., James Ross Island, Antarctica, and Salzburg, Austria (from table 2 of Steuber 2001). For the stratigraphic levels of Antarctica samples, see Crame et al. (2006).
occurrence of the crinoid *Marsupites testudinarius* (e.g. discussion in *Gale et al.* 2023). The \({^{87}\text{Sr}}/{^{86}\text{Sr}}\) value for that level in the Chalk of the Trunch Borehole (307.4 mbgl; *Pearce et al.* 2020) is 0.707477 + 0.000001 (2 s.e., \(n = 30\)) based on reinterpretation of the data of *McArthur et al.* (1993a). The base of Chron 33r is suggested by *Jarvis et al.* (2023) to occur at 294 mbgl in the Trunch borehole; that level has an \({^{87}\text{Sr}}/{^{86}\text{Sr}}\) value of 0.707490 ± 0.000004 (\(n = 34\)). *Montgomery et al.* (1998) place the base of Chron 33r in the lower part of the *Gonioteuthis granulata/Socialis unicerinca Zone*. In the Trunch borehole, that level (assumed to be 20% up in the zone) has an \({^{87}\text{Sr}}/{^{86}\text{Sr}}\) value of 0.707450 ± 0.000001 (2 s.e., \(n = 30\)).

In the Chalk of Germany at Lägerdorf, the traditional placement of the base of the Campanian has been the base of the *Gonioteuthis granulataquadrata* belemnite Zone (*Schulz et al.* 1984; *Schönfeld et al.* 1996), for which the value of \({^{87}\text{Sr}}/{^{86}\text{Sr}}\) is 0.707460 ± 0.000001 (2 s.e., \(n = 16\)), based on a reinterpretation of the data of *McArthur et al.* (1993b). According to *Jarvis et al.* (2023, fig. 14), the base of Chron 33r should be some 20 m higher and at the base of the *Offaster pilula* Zone in Lägerdorf. This level coincides with a prominent market horizon, marl M1, and has an \({^{87}\text{Sr}}/{^{86}\text{Sr}}\) value of 0.707482 ± 0.000001 (2 s.e., \(n = 16\)). At Lägerdorf, *Thibault et al.* (2016, their fig. 5) appear to place the boundary (base of Chron 33r) within the lowermost part of the *Offaster pilula* Zone, so the base of Chron 33r in Lägerdorf on that placement would have a value greater than 0.707482. If the level of Chron 33r in the English Chalk given by *Montgomery et al.* (1998) is correlated biostratigraphically to be 20% up in the *U. socialis* Zone of Lägerdorf, the level would be around 16 m below that for which \({^{87}\text{Sr}}/{^{86}\text{Sr}}\) data exist; the \({^{87}\text{Sr}}/{^{86}\text{Sr}}\) value for that level can be estimated by extrapolation to be around 0.707430.

The values of boundaries given above provide guidance in correlating boundary levels from place to place. Given the increased understanding of all aspects of SIS gained over the past few decades, and the refinement of the stratigraphy of the Chalk of Germany in that period, it is clear that dedicated profiling anew of \({^{87}\text{Sr}}/{^{86}\text{Sr}}\) across the Santonian–Campanian boundary (or any other boundary), using analysis of macrofossils and the most modern instrumentation, would prove more than capable of resolving the discrepancies alluded to above. Until then, we can interpret only the data to hand, and in doing so have retained in LOWESS 7 the traditional placements of the base of the Campanian in the Chalk of northwestern Europe until further work definitively establishes the level of the base of Chron 33r in sections suitable for defining \({^{87}\text{Sr}}/{^{86}\text{Sr}}\) of the boundary.

### Maastrichtian (72.2 ± 0.2) and the Maastrichtian–Danian Boundary, 66.04

The GSSP for the Maastrichtian Stage is defined as a mean position of 12 fossil datums at Tercis les Bains, in southwestern France (*Odin and Lamaurelle* 2001). No \({^{87}\text{Sr}}/{^{86}\text{Sr}}\) profile exists for the section.

The most detailed boundary profile of \({^{87}\text{Sr}}/{^{86}\text{Sr}}\) is that of *McArthur et al.* (1995b) for belemnites and pre-leached bulk Chalk from Kronsmoor, northern Germany. Correlations from the GSSP place the base of the Maastrichtian in Kronsmoor either 14 m above the prominent stratigraphic marker bed labelled Flint 600 (see fig. 4 of *Voigt and Schönfeld* 2010) or 12.5 m above Flint 600 at the level of marl mB609 (see fig. 2 of *Wilmsen et al.* 2019). The latter is within a few metres of the base of the *Belemnella obtusa* belemnite Zone, which is taken in GTS 2020 as the base of the Maastrichtian. The \({^{87}\text{Sr}}/{^{86}\text{Sr}}\) values are 0.707744 ± 0.000002 (2 s.e., \(n = 21\)) for the 12.5 m level and 0.707746 ± 0.000002 (2 s.e., \(n = 21\)) for the 14 m level. In *Voigt et al.* (2012) and in GTS2020, the boundary correlates to the uppermost *Baculites eliasti* ammonite Zone of the US Western Interior, which has an \({^{87}\text{Sr}}/{^{86}\text{Sr}}\) value of 0.707739, based on extrapolation from adjacent zones of the data of *McArthur et al.* (1994).

In the borehole at Trunch, the base of the Maastrichtian was set around a level 61 mbgl by *Wood et al.* (1994). That level has an \({^{87}\text{Sr}}/{^{86}\text{Sr}}\) value of 0.707729 ± 0.000005 (2 s.e., \(n = 9\)). According to *Voigt et al.* (2012), C-isotope stratigraphy shows that the base of the Maastrichtian is not present in the borehole; nevertheless, their figure 5 suggests that, were it present, it would be around 40 mbgl, a level 7 m above the highest sample analysed. The 40 m level would, by extrapolation, have an \({^{87}\text{Sr}}/{^{86}\text{Sr}}\) value of 0.707758 ± 0.000005 (2 s.e., \(n = 9\)).

Updating the Maastrichtian curve of \({^{87}\text{Sr}}/{^{86}\text{Sr}}\) against time for Figure 1 used the \({^{87}\text{Sr}}/{^{86}\text{Sr}}\) data of *Barrera et al.* (1997) for DSDP Site 463 fitted to the age model of *Li and Keller* (1999), plus the data from *Sugarman et al.* (1995) from the Atlantic coastal plain of New Jersey, USA, and (for the lower Maastrichtian) data from *McArthur et al.* (1993b) from the German Chalk at Kronsmoor. The trend so defined has a value of 0.707744 ± 0.000003 (95% CI) for the base of the Maastrichtian.

The value for \({^{87}\text{Sr}}/{^{86}\text{Sr}}\) at the base of the Danian is fixed by the data of *McArthur et al.* (1998) for the Maastrichtian–Danian boundary as being 0.707830 ± 0.000006 (2 s.e., \(n = 76\)) based on macrofossil debris from sections on Seymour Island, Antarctica (0.707832 ± 0.000005; 2 s.e., \(n = 43\)) and pre-leached bulk Chalk from Kjølby Gaard and Nye Kløv, Denmark (0.707828 ± 0.000003; 2 s.e., \(n = 33\)). The boundary in neither section is marked by any anomaly in \({^{87}\text{Sr}}/{^{86}\text{Sr}}\).
Competing interests The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Author contributions JMM: conceptualization (equal), data curation (lead), formal analysis (equal), investigation (lead), project administration (lead), writing – original draft (lead), writing – review & editing (lead); RJH: formal analysis (equal), writing – original draft (supporting).

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Data availability The Phanerozoic Sr-isotope curve, LOWESS 7, which includes the updated Cretaceous Sr-isotope curve, is available on ResearchGate and from JM McArthur via e-mail at j.mcarthur@ucl.ac.uk

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