

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

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8 **Abstract**

9 The secular trend of seawater strontium isotope ratio ($^{87}\text{Sr}/^{86}\text{Sr}$) reflects changes in
10 the relative contributions of continental versus mantle reservoirs to ocean
11 composition, and informs global tectonic events, weathering rates and biogeochemical
12 cycling through Earth history. However, the Precambrian seawater $^{87}\text{Sr}/^{86}\text{Sr}$ curve is
13 known in far less detail than its Phanerozoic counterpart. For this study, we compiled
14 2249 strontium isotope ratios of Precambrian marine sedimentary rocks published
15 since 2002, alongside previously compiled older data. Here we evaluate the
16 uncertainty of all published data for constraining coeval seawater $^{87}\text{Sr}/^{86}\text{Sr}$ using four
17 criteria (depositional environment, diagenetic alteration, age constraint and
18 dissolution method). The resultant seawater $^{87}\text{Sr}/^{86}\text{Sr}$ curve uses mainly ‘high
19 certainty’ data and shows an overall increasing trend from ~ 0.7005 at c. 3.5 Ga to
20 ≥ 0.7089 towards the end of the Ediacaran Period. The improved curve shows an
21 earlier deviation of seawater $^{87}\text{Sr}/^{86}\text{Sr}$ from the contemporaneous mantle by c. 3.5 Ga,
22 which might reflect the first significant emergence of evolved continental crust related
23 to nascent tectonics. Additionally, the updated curve records two major rises at 2.5-
24 2.2 Ga and 1.9-1.7 Ga in addition to a well-established event at 0.8-0.5 Ga. Despite

25 the relative scarcity of high-certainty data, these two increases are consistent with
26 enhanced continental weathering following the onset of oxidative weathering and
27 assembly of the supercontinent Nuna, respectively. Although confirmation of these
28 two events awaits more high-certainty data, Precambrian seawater $^{87}\text{Sr}/^{86}\text{Sr}$
29 experienced stronger oscillations and better correspondence with supercontinent
30 cycles than previously shown.

31 **Key words**

32 Strontium isotopes; Precambrian; Carbonates; Diagenesis; Dissolution methods;
33 Weathering; Supercontinent cycles

34 **1. Introduction**

35 Strontium isotopes are believed to be homogeneously distributed in seawater on a
36 global scale because the residence time of Sr in the modern ocean (c.10⁶ yr) is more
37 than 1000 times longer than the ocean circulation time (Broecker and Peng, 1983;
38 Elderfield, 1986; Hodell et al., 1990). In early studies (Brass, 1976; Faure et al., 1965;
39 Veizer and Compston, 1974), variations in seawater ⁸⁷Sr/⁸⁶Sr were tied to the
40 weathering of different lithologies. However, since the discovery of hydrothermal
41 exchange as a source of Sr to the ocean (Corliss et al., 1979; Spooner, 1976), the Sr
42 isotope budget of seawater has been interpreted as a balance between more radiogenic
43 riverine input from continental weathering and less radiogenic mantle input from mid-
44 ocean ridges (e.g., Albarède et al., 1981; Corliss et al., 1979; Goldstein and Jacobsen,
45 1987; Spooner, 1976; Veizer, 1989). The strontium isotope composition of riverine
46 input is complicated by the differential weathering of various lithologies (for example,
47 less radiogenic, more easily weathered basalts versus highly radiogenic, less easily
48 weathered felsic rock) and buffering by the weathering of carbonate rocks with an
49 isotope composition close to seawater (Allègre et al., 2010; Brass, 1976; Galy and
50 France-Lanord, 1999; Veizer and Compston, 1974). Strontium from different sources
51 is homogenized in the ocean and incorporated into authigenic minerals, especially
52 carbonate rocks, via substitution for calcium (McArthur, 1994). A conceptual model
53 of the seawater Sr flux cycle is shown in **Fig.1**.

54 Strontium isotope stratigraphy (SIS) has come to be widely used in geological
55 studies as a chemostratigraphic tool (Burke et al., 1982; Elderfield, 1986; McArthur,
56 1994; Veizer et al., 1999), and relies on the observation that the ⁸⁷Sr/⁸⁶Sr ratio in the
57 world's oceans has varied over time (McArthur et al., 2012). The primary uses of SIS
58 can be summarized as follows: 1) the numerical age of a sample with a known

59 $^{87}\text{Sr}/^{86}\text{Sr}$ ratio can be determined by comparison with the global seawater $^{87}\text{Sr}/^{86}\text{Sr}$
60 curve (McArthur, 1994; McArthur et al., 2012; 2020); 2) for a sample with known
61 age, its $^{87}\text{Sr}/^{86}\text{Sr}$ ratio can be used to distinguish pristine from diagenetically altered
62 samples and marine from non-marine settings (e.g., Kuznetsov et al., 2010; Stüeken et
63 al., 2017); and 3) variations in seawater $^{87}\text{Sr}/^{86}\text{Sr}$ likely reflect long term paleo-
64 weathering conditions and so can be used to test hypotheses of tectonic, biological,
65 and climatic changes through Earth history (e.g., Bartley, 2001; Cawood et al., 2018;
66 Halverson et al., 2007; Hawkesworth et al., 2016; Shields, 2007).

67 One of the main aims of this review is to explore the relationship between secular
68 changes in seawater Sr isotope composition and Earth system dynamics, including
69 weathering conditions, tectonic events and potentially also oxygenation events. It was
70 initially believed that the seawater $^{87}\text{Sr}/^{86}\text{Sr}$ curve evolved linearly during geologic
71 history (Wickman, 1948). This assumption was subsequently overturned when
72 researchers realized that the strontium isotope curve oscillated with time (e.g., Burke
73 et al., 1982; Gast, 1955; Veizer and Compston, 1976). While the Phanerozoic curve
74 has been updated repeatedly over the years (e.g., McArthur and Howarth, 2005;
75 McArthur et al., 2012; McArthur et al., 2020) with the abundance of datasets
76 permitting quantification of uncertainties using LOWESS (e.g., McArthur et al., 2012,
77 2001), further study of the Precambrian curve, defined by only sparse datasets, has
78 lagged behind. Shields and Veizer (2002) published a carbonate geochemistry
79 compilation covering Precambrian time and thereby constructed a seawater strontium
80 isotope curve using in most cases the lowest values of carbonate samples as it was
81 suggested that diagenetic exchange would generally increase measured Sr isotope
82 values. Although that curve is still widely used for reconstructing tectonic cyclicality
83 over time (e.g., Cawood et al., 2018; Hawkesworth et al., 2016), many new data have

84 been published in the intervening two decades and it has an inadequate temporal
85 resolution. The strontium isotope curve of seawater needs therefore to be periodically
86 updated to keep up with new data and increasingly precise age constraints, which
87 necessitate an updated compilation with more stringent screening.

88 Reconstructing the Precambrian seawater strontium isotope curve faces a number
89 of critical difficulties such as the high potential for diagenetic alteration, greater age
90 uncertainty, predominance of dolomite in the Precambrian, especially prior to the
91 Neoproterozoic, etc. Moreover, different issues arise in different localities. For
92 instance, continental margin settings, although more likely to be open marine, have
93 generally been affected by tectonic convergence events and ocean closures, resulting
94 in higher metamorphic grade, whereas cratonic interiors, although potentially better
95 preserved, have less precise age constraints, and are more likely to be affected by
96 restricted environments and alteration by meteoric fluids. SIS studies must rely on
97 diagenetically well-preserved chemical precipitates in that post-depositional alteration
98 could alter both chemical and isotopic compositions (Shields and Veizer, 2002).
99 However, well-preserved materials (low-Mg calcitic fossils; such as conodonts and
100 articulate brachiopods) that are widely available in Phanerozoic rocks are absent in
101 Precambrian rocks (Brand and Brenckle, 2001; Kah et al., 2001). Fine-grained bulk
102 carbonate rocks (e.g., micrite) are often used for strontium isotope studies of
103 Precambrian seawater, but their study requires well-honed dissolution methods and
104 screening to obtain the least-altered values (Bailey et al., 2000; Li et al., 2011).
105 Additionally, other problems such as a limited amount of suitable carbonate rocks,
106 ambiguous paleoenvironmental settings (Prokoph et al., 2008; Shields and Veizer,
107 200; Kuznetsov et al., 2010) also hinder Precambrian SIS studies to some degree.
108 Nevertheless, a growing number of carefully executed studies have shown that

109 resolution approaching Phanerozoic levels can be achieved under ideal circumstances
110 (e.g., Zhou et al., 2020).

111 The main aims of this review are:

- 112 1) To summarize the different dissolution and diagenetic screening methods used
113 in isotopic studies of Precambrian carbonate rocks in order to demonstrate
114 their advantages and shortcomings.
- 115 2) To update an existing Precambrian seawater strontium isotope compilation
116 (Shields and Veizer, 2002), using publications between 2002 and 2020, and
117 apply four criteria (depositional environment, diagenetic alteration, age
118 constraint and dissolution method) to assign both newly and previously
119 compiled data to one of three groups: high-certainty data; medium-certainty
120 data; and low-certainty data. We use the most recent international geologic
121 time scale (Strachan et al., 2020) to assign data to formal time subdivisions.
- 122 3) To discuss possible explanations for the temporal trend of the updated curve
123 by reviewing recognizable events (supercontinent cycles, glaciations, large
124 igneous provinces, etc.) and incorporating complementary data sets (Nd, Hf, O
125 isotopes); to provide tests for some highly controversial topics (e.g., the onset
126 of plate tectonics) using the improved Sr isotope curve.

127 **2. Analytical methods**

128 2.1 Sample types for Precambrian SIS

129 Low-Mg calcitic fossils, such as foraminifera, brachiopods and belemnites, and
130 apatitic fossils, such as conodonts, are abundant in Phanerozoic marine strata. When
131 well preserved, they tend to retain a near original seawater signal, particularly when
132 deposited in carbonate-dominated sediment, and so are ideal materials to reconstruct
133 the Phanerozoic seawater strontium isotope curve (e.g., McArthur et al., 2020; Veizer

134 et al., 1999). Because no such skeletal material is available for Precambrian SIS, bulk
135 carbonate (e.g., Cox et al., 2016; Halverson et al., 2007) or micro-drilled primary
136 carbonate components, such as calcite cement or homogeneous micrite (e.g., Kaufman
137 et al., 1993; Zhou et al., 2020), are commonly used.

138 Recrystallization in carbonates generally leads to an increase in grain size, and so
139 the most finely crystalline material, generally micrite, is considered to have escaped
140 substantial diagenetic recrystallization (Kah, 2000a; Kah et al., 1999). Consequently,
141 fine-grained carbonate components, extracted by petrographically guided micro-
142 drilling, are generally recommended for SIS (e.g., Li et al., 2011). Early diagenetic
143 calcite microspar cement or CMC (Zhou et al. 2020, also referred to as “Molar-tooth
144 structure”; e.g., Fairchild et al., 1997; James et al., 1998; Shields, 2002) may also be
145 suitable for SIS where available. CMC is characterized by uniform, equant, polygonal
146 and tightly packed calcite crystals (Furniss et al., 1998; James et al., 1998; Pollock et
147 al., 2006) that filled voids and cracks before deposition of much overlying sediment
148 and before total lithification of surrounding matrix (Fairchild et al., 1997; Smith, 1968).
149 Non-carbonate rocks such as barite (e.g., McCulloch, 1994; Satkoski et al., 2016),
150 gypsum or anhydrite (e.g., Kah et al., 2001) and francolite (Li et al., 2011) have also
151 been used for strontium isotope studies. For instance, in some Archean sedimentary
152 sequences where carbonate is scarce, barite can still be a reliable monitor for seawater
153 Sr isotope composition as it generally has high Sr contents and resists recrystallization
154 (Paytan et al., 1993) as long as its origin can be determined (Griffith and Paytan, 2012).
155 In the following discussion, we mainly focus on carbonate rocks as they are the most
156 commonly used materials for Precambrian SIS.

157 2.2 Carbonate sample preparation

158 Significant artefacts in strontium isotope stratigraphy (SIS) studies might result from

159 improper sample preparation that dissolves recrystallised derivatives or contaminant
160 components, requiring a suitable dissolution method to minimise the Sr contamination
161 from untargeted phases (McArthur, 1994). We divided dissolution methods of
162 carbonate rocks into three main types: single-step bulk leaching method, two-step
163 sequential leaching method, and multiple-step sequential leaching method. We further
164 subdivided the three main types according to the acid type and reagents used for pre-
165 leaching (ammonium acetate or acetic acid). Details and related references are provided
166 in **Table 1**.

167 Single-step bulk leaching used to be the most common method for carbonate
168 extraction, which is conducted by adding an acid to rock powder to dissolve carbonate
169 minerals, while leaving insoluble detrital phases behind (e.g., Brand et al., 2012; Hall
170 and Veizer, 1996; Kaufman and Knoll, 1995; Kupecz and Land, 1991; Miller et al.,
171 2008). In some cases, carbonate samples are dissolved in a weak acid, such as acetic
172 acid, which is considered to be less aggressive than a dilute strong acid, to avoid
173 dissolution of matrix incorporated impurities (e.g., Kaufman and Knoll, 1995; Miller
174 et al., 2008; Yoshioka et al., 2003), but in other cases, sample powders are dissolved
175 in strong acids such as HCL and HNO₃ (e.g., Brand et al., 2012; Satkoski et al., 2017).
176 The latter method should be avoided, especially for impure samples, because
177 aggressive acid leaching attacks clay minerals in the rock matrix that likely contain
178 Rb and therefore radiogenic Sr from Rb decay, leading to higher measured strontium
179 isotope values (e.g., Bailey et al., 2000).

180 Pre-leaching has been emphasized as it enhances the reliability of obtained values
181 by removing exchangeable Rb and Sr, and strips potentially-contaminating Sr from
182 non-carbonate phases (e.g., Bailey et al., 2000). Pre-leaching has been shown to
183 remove contaminant Sr, even from pure samples. In the experiment of Bailey et al.,

184 (2000), carbonate samples from Trunch and Lagerdorf were very pure (96% and 98%
185 carbonate, respectively), but only pre-leached samples exhibited near expected
186 seawater values. Such sequential leaching methods started already in the early 90's
187 and are very widely used in strontium isotope studies (Bailey et al., 2000; Bellefroid
188 et al., 2018b; Gorokhov et al., 1995; Kupecz and Land, 1991; Liu et al., 2013; Li et
189 al., 2011).

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

200 In addition to single-step bulk leaching and two-step leaching, a multiple-step
201 leaching procedure, using acetic acid of intermediate strength, has also been tested.
202 Although relatively complicated, this approach can improve the fidelity of measured
203 $^{87}\text{Sr}/^{86}\text{Sr}$ values, especially for samples with complex and heterogeneous mineralogy
204 (Bailey et al., 2000; Bellefroid et al., 2018b; Liu et al., 2014, 2013). By measuring
205 elemental concentrations and $^{87}\text{Sr}/^{86}\text{Sr}$ values for all individual leaching steps, the
206 least-contaminated fraction of each sample can be identified (Bailey et al., 2000;
207 Bellefroid et al., 2018b).

208 Diverse dissolution methods utilised in the SIS studies (mainly from our new

209 compilation) have been summarized in **Table 1**.

Type	Pre-leach	Dissolution Method	References	Comments
1. Single-bulk leaching in weak acid without pre-leaching	No pre-leaching	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.	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	Preferred for large datasets but lack of pre-leach increases the risk of contamination from ion exchangeable sites and secondary carbonate phases.
2. Single-bulk leaching in strong acid without pre-leaching	No pre-leaching	Powdered carbonate samples are dissolved in strong acid such as HCL and HNO ₃	Azmy et al., 2006; Brand et al., 2012; Frauenstein et al., 2009; Nogueira et al., 2007; Satkoski et al., 2017	Dissolving samples in a strong acid might lead to higher ⁸⁷ Sr/ ⁸⁶ Sr by attacking more radiogenic clastic phases.
3. Two-step sequential leaching with pre-leach in ammonium acetate	Pre-leached in aqueous ammonium acetate (NH ₄ OAc)	Aliquots of powdered carbonate are 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.	Bartley et al., 2007; Bekker et al., 2003a; Bold et al., 2016; Cox et al., 2016; Cui et al., 2015; Gibson et al., 2019; 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	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).

4. Two-step sequential leaching with pre-leach in acetic acid	Pre-leached in dilute acetic acid	After pre-leaching, samples are dissolved partially using acetic acid.	George et al., 2019; Li et al., 2011, 2020; Ray et al., 2003; Zhou et al., 2020	Acetic acid pre-leach might remove contaminant Sr more effectively compared with ammonium acetate (Bailey et al., 2000; Li et al., 2011).
5. Multiple-step sequential leaching	Pre-leached in volumes of ammonium acetate (NH ₄ OAc)	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.	Bailey et al., 2000; Bellefroid et al., 2018b; Fairchild et al., 2018; Li et al., 2020; Liu et al., 2014, 2013	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)

210 **Table 1.** Summary of different dissolution methods of bulk carbonate rocks for strontium isotope analysis. References include the method papers and the newly compiled
211 papers in this study.

212 **3. Diagenetic analysis**

213 *3.1. Carbonate diagenesis*

214 Precambrian strontium isotope stratigraphy (SIS) relies on the analysis of well-
215 preserved marine carbonate rocks because post-depositional alteration can alter the
216 chemical and isotope composition of carbonate rocks. Carbonate diagenesis can
217 include dissolution and reprecipitation that affects both the mineralogy and crystal
218 size of the original carbonate precipitate and can occur in different types of fluids
219 such as meteoric or marine fluids (Higgins et al., 2018; Melim et al., 2004; Swart,
220 2015). The degree of geochemical alteration by diagenesis depends on factors such as
221 the openness and the water-rock ratio of the diagenetic system and the stability of
222 mineralogy (Marshall, 1992; Banner and Hanson, 1990). Open-system and high
223 water-rock ratios generally lead to a greater loss of primary environmental signals
224 (Marshall, 1992). When dissolution takes place in a large volume of pore water, the
225 composition of pore fluids is little influenced by the input of dissolving materials.
226 Thus the composition of replacement phases would be similar to pore fluids that
227 reflect equilibrium with the diagenetic environment (Marshall, 1992; Veizer, 1983).
228 High-magnesium calcite and aragonite are metastable, whereas low-magnesium
229 calcite is relatively insoluble and inherently has less potential for diagenetic exchange
230 (Marshall, 1992; Morse and Mackenzie, 1990; Swart, 2015).

231 Using static limits of trace elements such as Mn or Sr to select least-altered data
232 has been proposed (e.g., Bates and Brand, 1991; Denison et al., 1994; Montañez et al.,
233 1996). However, it has also been argued that the static threshold inadequately
234 parameterizes the range of diagenetic effects experienced by carbonate components
235 (Brand, 2004; Brand et al., 2012, 2010). It is unlikely that there are any unique criteria
236 for the robust screening of altered samples because the post-depositional history

237 varies from basin to basin and even from sample to sample within a basin, so using
238 static limits ignores spatial and temporal variations in local conditions (Bartley et al.,
239 2001; Melizhik et al., 2001; Halverson et al., 2007). Therefore, a dynamic approach
240 defined as utilising various screening methods to examine coeval materials from
241 individual horizons is recommended (**Fig. 2**), which generally includes field and
242 petrological examinations, geochemical screening (major and trace elements, stable
243 isotopes, and strontium isotopes) and coeval sample comparisons (e.g., Banner, 2004;
244 Bartley et al., 2001; Brand et al., 2012; Zhou et al., 2020)

245 *3.2. Screening methods*

246 *3.2.1. Petrographic screening*

247 Petrographic screening investigates textural or mineralogical changes in rocks
248 using scanning electron microscopy, X-ray diffraction, thin section examination, and
249 cathodoluminescence techniques (McArthur, 1994 and references therein) to
250 distinguish primary from secondary sedimentary components. Primary components
251 such as stromatolitic laminae, micrites, syndepositional marine cement and oolitic
252 grains are most likely to retain original isotopic signals; while secondary components
253 such as cross-cutting veins, late-stage void filling spar and dissolution features should
254 be avoided during sampling (e.g., Kah et al., 2012, 1999; Kaufman and Knoll, 1995).
255 Additionally, siliciclastic material might flag diagenetic alteration because it is
256 normally associated with increased permeability to diagenetic fluids (Kah et al.,
257 1999).

258 Diagenetic recrystallization processes commonly result in coarsening of grain size
259 or complete obliteration of primary fabrics, if diagenesis took place in the presence of
260 a fluid phase (e.g., meteoric or deep burial fluid) very distinct in composition from
261 seawater. By contrast, fine-grained, primary components that preserve original

262 textures (e.g., ooids, small-scale sedimentary structure) indicate that recrystallization
263 might have occurred in the presence of fluids similar to the composition of seawater,
264 which means recrystallization/diagenesis occurred syngeneitically or during shallow
265 burial (Gilleaudeau et al., 2018).

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

275 3.2.2. Geochemical screening

276 1) Major and trace elements

277 Trends in the concentration of major and trace element such as Mg, Ca, Sr, Fe, and
278 Mn are commonly used to recognize potential alteration in suites of samples (e.g.,
279 Denison et al., 1994; Van Geldern et al., 2006; Veizer et al., 1992a, 1992b). Mn/Sr or
280 Fe/Sr are widely used as indices of alteration, and are generally expected to be higher
281 in diagenetically-altered samples than in coeval seawater (Banner and Hanson, 1990;
282 Brand and Veizer, 1980; Gorokhov et al., 1995; Kaufman and Knoll, 1995). This is
283 because the distribution coefficient of Mn and Fe in stable (hexagonal) carbonate
284 minerals (e.g., dolomite and calcite) is much higher than Sr, so recrystallization leads
285 to an increase in Mn/Sr and Fe/Sr ratios (Rimstidt et al., 1998). However, this general
286 relationship is complicated by variable redox conditions, diagenetic fluids, and

287 mineralogy. High Mn/Sr or Fe/Sr ratios might indicate carbonate precipitation from
288 anoxic waters instead of diagenetic alteration because both Fe and Mn tend to revert
289 to their more soluble reduced forms under suboxic-anoxic conditions (Bruland et al.,
290 2014; Canfield and Thamdrup, 2009). For instance, in low-oxygen Proterozoic
291 oceans, elevated Mn and Fe concentrations could also reflect primary seawater
292 (Bekker et al., 2003b; Gilleaudeau and Kah, 2013; Kah et al., 2004; Kah and Bartley,
293 2011). Burial diagenetic phases are commonly enriched in Mn and Fe due to reducing
294 conditions in burial fluids (Veizer, 1983), but meteoric diagenetic phases can be
295 characterized by either enrichment or depletion of Mn and Fe due to variable redox
296 conditions in meteoric fluids (Banner and Hanson, 1990; Brand and Veizer, 1980).
297 Moreover, mineralogies also need to be considered. For instance, dolomite generally
298 has a higher preference for Fe and Mn (Mazzullo, 1992) and a lower preference for Sr
299 compared with calcite (Vahrenkamp and Swart, 1990), while some early diagenetic
300 dolomite can also be enriched in Sr relative to Fe and Mn (Gilleaudeau et al., 2018). It
301 is common to use Mg/Ca to quantify the relative contribution of dolomite of samples
302 (e.g., stoichiometric dolomite is generally considered as Mg/Ca ratios of >0.6). Using
303 Mg/Ca ratio in conjunction with Mn/Sr, Fe/Sr could indicate modification of trace
304 elements during dolomitization.

305 2) Stable isotope composition

306 The oxygen isotopic composition ($\delta^{18}\text{O}$) of carbonate rocks is sensitive to post-
307 depositional alteration resulting from exchange with pore water oxygen and/or
308 recrystallisation at elevated temperatures. The original oxygen isotope composition
309 might be retained where carbonate minerals were subject to only minor
310 recrystallisation under low water-rock ratio conditions (<10; Banner and Hanson,
311 1990; Jacobsen and Kaufman, 1999). Recrystallization and neomorphism at higher

312 temperatures are generally expected to lower the $\delta^{18}\text{O}$ of samples (Veizer, 1983).
313 However, $\delta^{18}\text{O}$ composition of meteoric waters is variable, i.e., it becomes lower with
314 decreasing temperature and increasing latitude (Bowen and Wilkinson, 2002).
315 Therefore, meteoric waters will often be not so different to seawater in tropical marine
316 carbonate platform settings. Additionally, dolomitization tends to increase $\delta^{18}\text{O}$. For
317 instance, at 25°C the estimates for $\Delta\delta^{18}\text{O}_{\text{dolo-cal}}$ (difference in $\delta^{18}\text{O}$ between
318 coprecipitated dolomite and calcite) range from 5‰ to 9‰ (Clayton and Epstein,
319 1958), 4‰ to 7‰ (e.g., Degens and Epstein, 1964; Northrop and Clayton, 1966) or
320 2.6‰ (Vasconcelos et al., 2005). Considering the variability of $\delta^{18}\text{O}$ in different
321 situations, it needs be used in conjunction with other parameters such as trace element
322 or strontium isotopes to indicate diagenetic alteration.

323 Compared with oxygen isotopes, carbon isotope values ($\delta^{13}\text{C}$) are more resistant to
324 overprinting during diagenetic recrystallisation owing to the higher concentration of
325 carbon in carbonate rocks relative to diagenetic fluids (e.g., Halverson et al., 2005).
326 Given water/rock ratios >1000 (Banner and Hanson, 1990), $\delta^{13}\text{C}$ values of carbonates
327 might be altered by re-equilibration during recrystallization, whereby interactions
328 with diagenetic fluids would generally decrease $\delta^{13}\text{C}$ values because diagenetic fluids
329 potentially contain isotopically depleted carbon. Cross-plots of $\delta^{13}\text{C}$ against $\delta^{18}\text{O}$
330 values are commonly applied to identify covariation, which might indicate diagenetic
331 alteration (Banner, 1995; Brand and Veizer, 1981). However, authigenic carbonate
332 precipitated from sediment pore fluids that have a different composition from
333 overlying seawater, can produce higher or lower carbonate isotope values than
334 primary carbonate, which complicates the use of $\delta^{13}\text{C}$ in identifying diagenetic
335 processes (e.g., Schrag et al., 2013; Sun and Turchyn, 2014; Torres et al., 2020; Zhao
336 et al., 2016)

337 Mineralogical changes, e.g. recrystallization of aragonite to calcite and dolomite,
338 affect the geochemical indices to some degree (Brand et al., 2012). For instance, an
339 aragonite precursor may cause $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values to shift by +1.8‰ and +0.8‰,
340 respectively, and these signatures could be retained if recrystallisation happened in a
341 closed system (Rubinson and Clayton, 1969; Saltzman, 2005). Dolomitization would
342 increase $\delta^{18}\text{O}$ and decrease Ca and Sr concentrations simultaneously, leading to
343 smaller changes to $\delta^{18}\text{O}$ values and Sr/Ca, which might erroneously imply a lesser
344 degree of alteration (Halverson et al., 2007).

345 3) Strontium isotopes

346 The Sr isotope composition of carbonate minerals is commonly affected by
347 diagenesis; hence $^{87}\text{Sr}/^{86}\text{Sr}$ ratios can also be used as indicators of alteration in the
348 case that the original Sr isotope composition is known (Gorokhov et al., 1995;
349 Ovchinnikova et al., 1995). In general, post-depositional processes tend to increase
350 $^{87}\text{Sr}/^{86}\text{Sr}$ values because evolved K-bearing silicates (rich in ^{87}Rb and thus higher
351 $^{87}\text{Sr}/^{86}\text{Sr}$) release ^{87}Sr into interstitial fluids from where it can be incorporated into
352 carbonate rocks during diagenetic recrystallization (e.g., Fairchild et al., 2018).
353 Therefore, in general, the current best estimates for seawater $^{87}\text{Sr}/^{86}\text{Sr}$ are based
354 mainly on the least radiogenic samples within a suite of rocks (e.g., Shields and
355 Veizer, 2002). However, fluids that are less radiogenic than contemporaneous
356 seawater, influenced either by mafic components/juvenile silicate, hydrothermal fluids
357 or pressure solution of older, underlying carbonate rocks, may drive carbonate
358 $^{87}\text{Sr}/^{86}\text{Sr}$ to lower values (e.g., Brand et al., 2010; Cui et al., 2020; Miller et al., 2008;
359 Satkoski et al., 2017). Alternatively, deviation from seawater values might also reflect
360 a mixture of seawater and influence from river catchments in restricted environments
361 (Miller et al., 2008). Therefore, a combination of multiple screening methods and

362 appropriate leaching methods, as well as careful sample selection and well-
363 constrained geological context, are needed to get a robust result. Elemental and
364 isotopic thresholds used for diagenetic screening compiled from the literature are
365 shown in **Table 2**.

366 **4. Rubidium contamination**

367 The radioactive isotope of Rb, ^{87}Rb , decays to ^{87}Sr over time with a decay constant
368 (λ) of $1.42 \times 10^{-11} \text{ yr}^{-1}$ (Steiger and Jäger, 1977); thus, the measured $^{87}\text{Sr}/^{86}\text{Sr}$ values of
369 carbonate rocks increase with radioactive ^{87}Rb decay. Some rubidium may have been
370 incorporated into the carbonate minerals directly, although its large size and 1^+ charge
371 precludes substantial replacement of Ca^{2+} or Mg^{2+} ions in the mineral lattice. Most Rb
372 in sedimentary rocks is incorporated in the structure of igneous minerals and their
373 weathering products as well as potassium-rich clay minerals, which can constitute a
374 substantial portion of some bulk rock samples (McArthur et al., 2012). Therefore, it is
375 common to carry out a correction for Rb decay to estimate the initial $^{87}\text{Sr}/^{86}\text{Sr}$ value
376 (e.g., Sawaki et al., 2010a; Zhou et al., 2020). However, errors in Rb correction can be
377 introduced because of uncertainty in the samples' ages, especially for Precambrian
378 samples, and because of incongruent leaching of Rb versus Sr. Well-preserved, pure
379 carbonate components will not contain much Rb. Aragonite with its more open structure
380 could accommodate Rb more easily than calcite, but it still incorporates much more Sr,
381 making the Rb/Sr ratios very low and the Rb correction unnecessary (McArthur, 1994).
382 For bulk rock samples, initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratios may be overcorrected because clay
383 minerals preferentially lose ^{87}Sr from their lattices during diagenesis or leaching
384 procedures compared with the parent Rb (Shields and Veizer, 2002). A good correlation
385 between Rb concentration and Al concentration could demonstrate that Rb derives from
386 aluminosilicates; hence, sample cleaning and pre-leaching is preferable to automatic

387 Rb-decay correction (Gorokhov et al., 1995; Hall and Veizer, 1996; Wierzbowski et al.,
388 2012). To avoid error caused by Rb correction in our compilation, in most cases we
389 directly use the measured values, which, where demonstrably well preserved, must
390 therefore represent near primary maximum constraints on contemporaneous seawater.

Sr (ppm)	Mn/Sr	Fe/Sr	Mg/Ca	$\delta^{18}\text{O}_{\text{VPDB}}$ (‰)	Sample	Era	Reference
	< 5	< 10			L	NP	Kochnev et al., 2018
	< 0.2		< 0.01		L	NP	Galindo et al., 2004
	≤ 4	≤ 10			L	NP	Kuznetsov et al., 2006
	< 0.2	< 5.0			L	NP	Kuznetsov et al., 2005
	< 0.1				L	NP	Melezhik et al., 2009
				-5~-11	L	NP	Miller et al., 2009
	< 0.2			> -8		NP	Yoshioka et al., 2003
> 400	< 1		< 0.1		L	NP	Gibson et al., 2019
> 500	< 0.1		< 0.01		L	NP	Cox et al., 2016
> 500					L	NP	Bold et al., 2016
≥ 200	≤ 0.5		< 0.01		L	NP	Zhou et al., 2020
>1000	<0.6				L	NP	Thomas et al., 2004
	<1 (mostly <0.5)		<0.4 (mostly <0.02)	-5~ -11	L/DL	NP	Halverson et al., 2007

	< 10	< 40			D	NP	Kochnev et al., 2018
	≤ 6	≤ 15			D	NP	Kuznetsov et al., 2006
	≤ 1.2	≤ 3.0	≥ 0.608		D	NP	Kuznetsov et al., 2003b
> 400	< 0.45				D	NP	Alvarenga et al., 2014
	<3		>-11		D/L	NP	Kaufman et al., 1993
>50	< 5		> -10		D	NP	Zhang et al., 2020
	< 0.2	< 5.0	< 0.02	> -10	L	MP	Gorokhov et al., 1995; Kuznetsov et al., 1997; 2008, 2006, 2003a, 2003b; Semikhatov, 2002; Semikhatov et al., 2004;
	< 1.5				L	MP	Bartley et al., 2001
			-6~-9			MP	Bartley et al., 2007
	<1				L	MP	Derry et al., 1992; George et al., 2019

< 3.0	> -10	D	MP	Bartley et al., 2001
< 0.2		L	PP	Kuznetsov et al., 2010
< 2.0		D	PP	Kuznetsov et al., 2010
	-6~-12	D	PP	Bekker et al., 2003a, 2001; Veizer et al., 1992a, 1992b
< 6		D	PP	Kaufman and Knoll, 1995

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

394 **5. Age constraints and data evaluation**

395 *5.1. Age constraints*

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

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

419 5.2. *Data evaluation*

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

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

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

Marine environment	Good preservation	Well constrained ages (less than ± 50 Ma)	Good leaching method	Certainty rating
Yes	Yes	Yes	Yes	High
Yes	Yes	Not necessarily	Not necessarily	Medium
Not necessarily	Not necessarily	-	-	Low

443 **Table 3.** Summary of criteria for data certainty ranking

444 **6. Compilation and curve description**

445 *6.1 Compilation*

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

450 For this study, we compiled 2249 Sr isotope ratios from Precambrian to Cambrian
451 rocks (4000 Ma – 500 Ma) published between 2002 and 2021 from 62 published
452 articles and 3 unpublished articles (**Supplementary Material 1, 3 and Table 4**). We
453 assigned certainty criteria to all published data, including those compiled in Shields
454 and Veizer (2002) (**Supplementary Material 1, Fig. 3**) and we presented data used
455 for the curve construction, i.e., high and medium certainty data, in **Supplementary**
456 **Material 2 (see Table 5 for structure)**. All data have been normalized to a value of
457 0.71025 for the international isotope standard SRM NBS 987 using the reporting
458 laboratories' measured values over the period of analysis. In most cases, Rb-corrected
459 data were not used in this study.

460 Recently, several studies have suggested updated seawater strontium isotope
461 curves for different parts of the Precambrian (Neoproterozoic: Zhou et al., 2020, Cox
462 et al., 2016; Mesoproterozoic: Kuznetsov et al., 2008, Kuznetsov et al., 2019;

463 Paleoproterozoic: Kuznetsov et al., 2021, 2010; Archean: Ravindran et al., 2020,
464 Roerdink et al., 2021, Satkoski et al., 2017) and a SIS study from Kuznetsov et al.,
465 (2018) proposed an updated curve for the Proterozoic part. These published curves
466 provide valuable and complementary references for the reconstruction of the
467 Precambrian seawater $^{87}\text{Sr}/^{86}\text{Sr}$ curve.

468 *6.2 Fundamental descriptions of the updated curve*

469 The updated seawater $^{87}\text{Sr}/^{86}\text{Sr}$ curve demonstrates an overall increasing trend from
470 ~ 0.7005 at c. 3.5 Ga to ≥ 0.7089 towards the end of the Ediacaran Period with three
471 peaks at c. 2.2 Ga, c. 1.65 Ga and c. 0.5 Ga, respectively (**Fig.4**).

472 The Archean seawater $^{87}\text{Sr}/^{86}\text{Sr}$ ratio appears to have deviated from the
473 contemporaneous mantle value since at least c. 3.5 Ga (~ 0.7005) (McCulloch, 1994;
474 Roerdink et al., 2021), followed by a gradual increase until the end of the Archean c.
475 2.5 Ga when the ratio reached ~ 0.702 (Kamber and Webb, 2001). In the
476 Paleoproterozoic ocean, the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio experienced strong oscillations that
477 increased significantly from ~ 0.702 at c. 2.5 Ga (Kamber and Webb, 2001) to ~ 0.705
478 at c. 2.2 Ga (Bekker et al., 2006, 2003a), followed by a drop at c. 2.1 Ga (~ 0.703)
479 (Bekker et al., 2003b; Kuznetsov et al., 2010). Then, there was a rebound to another
480 peak of ~ 0.7062 (Veizer and Compston, 1976) at c. 1.65 Ga before a fall to ~ 0.7046
481 (Ray et al., 2003) around the Paleoproterozoic - Mesoproterozoic boundary. The
482 overall pattern of the Paleoproterozoic curve in this study shows similarity with that
483 of Kuznetsov et al., (2018). However, the 2.5-2.2 Ga and 1.9-1.7 Ga parts of the curve
484 are mainly composed of medium certainty data, so the shape, duration and acme of
485 these rises need further confirmation once more high-certainty data become available.
486 The Mesoproterozoic $^{87}\text{Sr}/^{86}\text{Sr}$ values of the new compilation exhibit modest
487 fluctuation from ~ 0.7046 to ~ 0.7050 during c. 1.6-1.2 Ga (Gorokhov et al., 1995; Hall

488 and Veizer, 1996; Kuznetsov et al., 2008, 2005; Pokrovskiy and Vinogradov, 1994;
489 Ray et al., 2003), before a modest rise to ~0.7059 (Gibson et al., 2019; Kuznetsov et
490 al., 2019; Shields, 2002), followed by a slight decrease to ~0.7052 (Semikhatov,
491 2002) around the Mesoproterozoic to Neoproterozoic transition. The seawater
492 $^{87}\text{Sr}/^{86}\text{Sr}$ curve then begins rising through multiple fluctuations from the beginning of
493 the Neoproterozoic (~0.7052, Kuznetsov et al., 2017) until the end of the Ediacaran
494 (~0.7089, Sawaki et al., 2010b), with several significant declines at approximately
495 0.92 Ga, 0.83 Ga, 0.72 Ga and 0.59 Ga respectively.

Column name	Content of Column
Sample ID number	Unique sample number taken from original publication
Sample description	Additional relevant information
Formation	Formation name occasionally including groups, members, etc.
Location	Name of section, borehole and/or region
Country	Name of country
Depth, m	Depth in borehole
Height, m	Stratigraphic height in section
Mineral	C, calcite; D, dolomite; A, anhydrite; B, barite; M, magnesite; P, phosphorite; H, halite
Era	A, Archean; PP, Paleoproterozoic; MP, Mesoproterozoic; NP, Neoproterozoic
Interval	Eras subdivision from Eoarchean to Neoproterozoic
Geon	100 Ma intervals or “Geons” from 0 to 37 (Hofmann, 1999)
Age, Ma	Well-constrained ages (less than ± 50 Ma)
Age, Ma	Poorly constrained ages (greater than ± 50 Ma)
Uncertainty, Ma	Published age constraints
Source: data	Literature reference for isotopic data (see appendix)
Source: age	Literature references for age constraints
Dating technique	Dating technique, e.g., U-Pb single zircon, biostratigraphy, correlations
Fe, ppm	Iron concentration in carbonate phase, ppm
Mg/Ca	Mg/Ca ratio of carbonate phase
Mg, ppm	Magnesium concentration in carbonate phase, ppm
Ca, wt %	Calcium concentration in carbonate phase, weight%
Mn, ppm	Manganese concentration in carbonate phase, ppm
Sr, ppm	Strontium concentration in carbonate phase, ppm
$\delta^{13}\text{C}_{\text{calcite}}$ PDB	Carbon isotope composition of calcite, ‰ PDB
$\delta^{13}\text{C}_{\text{dolomite}}$ PDB	Carbon isotope composition of dolomite, ‰ PDB
$\delta^{13}\text{C}_{\text{others}}$ PDB	Carbon isotope composition of other carbonate minerals, ‰ PDB

$\delta^{18}\text{O}_{\text{calcite}}$ PDB	Oxygen isotope composition of calcite, ‰ PDB
$\delta^{18}\text{O}_{\text{dolomite}}$ PDB	Oxygen isotope composition of dolomite, ‰ PDB
$\delta^{18}\text{O}_{\text{others}}$ PDB	Oxygen isotope composition of other carbonate minerals, ‰ PDB
$^{87}\text{Sr}/^{86}\text{Sr}_{\text{measured}}$	Reported strontium isotope composition of carbonate phase
$^{87}\text{Sr}/^{86}\text{Sr}_{\text{initial}}$	Strontium isotope composition of carbonate phase after Rb correction
$^{87}\text{Sr}/^{86}\text{Sr}_{\text{norm.}}$	$^{87}\text{Sr}/^{86}\text{Sr}$ normalised to SRM NBS 987 = 0.71025
Rb, ppm	Rubidium concentration in carbonate phase, ppm
Comments	Comments on data in four aspects (depositional environment, diagenetic alteration, age constraints and leaching approach)
Rating (high-certainty)	Marine environment, least altered, well age constraints, appropriate leaching method (pre-leached, weak acids)
Rating (medium-certainty)	Marine environment, least altered, poor age constraints or/and inappropriate leaching method (no-preleaching, using strong acids)
Rating (low-certainty)	Non-marine or/and diagenetic altered

496 **Table 4.** Structure of Precambrian strontium isotope database version 2021 (a). This version includes
497 2249 newly-compiled data of this study and previous compilation of Shields and Veizer, (2002),
498 whereby the structure is inherited from the PMCID (Precambrian marine carbonate isotope database)
499 version 1.1 (a) of Shields and Veizer, (2002), but adding detailed comments and certainty rating.

Column name	Content of Column
Sample ID number	Unique sample number taken from original publication
Formation	Formation name occasionally including groups, members, etc.
Country	Name of country
Era	A, Archean; PP, Paleoproterzoic; MP, Mesoproterozoic; NP, Neoproterozoic
Interval	Eras subdivision from Eoarchean to Neoproterozoic
Age, Ma	Ages of samples, all samples ages are up to data
Source: data	Literature reference for isotopic data (see supplementary material 3)
$^{87}\text{Sr}/^{86}\text{Sr}_{\text{norm.}}$	$^{87}\text{Sr}/^{86}\text{Sr}$ normalised to SRM NBS 987 = 0.71025
Rating (high-certainty)	Marine environment, least altered, well age constraints, appropriate leaching method (pre-leached, weak acids)
Rating (medium-certainty)	Marine environment, least altered, poor age constraints or/and inappropriate leaching method (no-preleaching, using strong acids)
New data	High and medium certainty data from this study
Old data	High and medium certainty data from PMCID of Shields and Veizer (2002)

500 **Table 5.** Structure of Precambrian strontium isotope database version 2021 (b). This version shows data
501 used for reconstruction of Precambrian seawater $^{87}\text{Sr}/^{86}\text{Sr}$ curve, which includes high and medium
502 certainty data from both this study and Shields and Veizer (2002).

503 7. Discussion on the updated $^{87}\text{Sr}/^{86}\text{Sr}$ curve of Precambrian seawater

504 Continental chemical weathering exports cations to the ocean and so is one of the
505 key processes influencing not only the evolution of seawater $^{87}\text{Sr}/^{86}\text{Sr}$ but also the
506 long-term carbon cycle and climate through the consumption of atmospheric CO_2
507 (Berner, 2003; Berner et al., 1983; Walker et al., 1981). Rb preferentially accumulates
508 in granitic melts due to the relative incompatibility of Rb compared with Sr, resulting
509 in Rb enrichment (high Rb/Sr ratios, thus high ^{87}Sr) in the continental crust and Rb
510 depletion (low Rb/Sr ratios, thus low ^{87}Sr) in the residual mantle and oceanic crust.
511 Secular changes of $^{87}\text{Sr}/^{86}\text{Sr}$ in the ocean record the relative importance of radiogenic
512 strontium derived from continental crust versus unradiogenic strontium derived from
513 hydrothermal alteration of oceanic crust and so could track the long-term changes in
514 Earth's subaerial weathering. Sr isotope ratios in seawater are affected not only by
515 changes in the rates of continental weathering versus sea-floor spreading (normally
516 associated with supercontinent cycles) but also by changes in the $^{87}\text{Sr}/^{86}\text{Sr}$
517 composition of rocks undergoing weathering (generally associated with emplacement
518 of large igneous provinces, crust reworking etc.), which has an intimate association
519 with Earth system dynamics.

520 Here we show our updated Sr isotope curve against the background of zircon
521 abundance and the supercontinent cycle (**Fig. 5A**), incorporating also Nd, Hf and O
522 isotopes (**Fig. 5B**) and a compilation of collective sizes of large igneous provinces
523 (LIPs; **Fig. 5C**). Peaks in U-Pb zircon crystallisation ages are linked to the
524 amalgamation stages of the supercontinent cycle (Bradley, 2011; Condie, 2004;
525 Condie et al., 2011; Rino et al., 2004). These peaks have been suggested also to have
526 been a consequence of a preservation bias inherent in the supercontinent cycle,
527 whereby high volumes of magma are generated along subduction zones, but the

528 preservation potential of crust generated in collisional orogens is greater (Cawood et
529 al., 2013; Condie et al., 2011; Hawkesworth et al., 2009). The zircon / supercontinent
530 record provides important clues to interpreting secular Sr isotope changes.
531 Supercontinent assembly is thought to be associated with tectonic collision and uplift,
532 resulting in higher erosion rates and therefore an increase in seawater $^{87}\text{Sr}/^{86}\text{Sr}$.
533 Conversely, rifting and opening of new basins during supercontinent fragmentation
534 might increase input of less radiogenic hydrothermal fluxes into the ocean, driving
535 down seawater $^{87}\text{Sr}/^{86}\text{Sr}$ (Asmerom et al., 1991; Kaufman et al., 1993; Raymo et al.,
536 1988). However, input fluxes are not always primary controls for marine Sr isotope
537 records, sources of Sr (older and radiogenic crust versus juvenile crust) undergoing
538 continental weathering could also be controlling factors (Bartley et al., 2001; Bataille
539 et al., 2017; Halverson et al., 2007).

540 Isotopic proxies such as ϵHf and $\delta^{18}\text{O}$ in zircons and ϵNd in whole-rock sediments
541 and granitoids, and the emplacement of large igneous provinces could reflect types of
542 rocks (lithologies) undergoing weathering. ϵHf and ϵNd values express the relative
543 deviation of $^{176}\text{Hf}/^{177}\text{Hf}$ and $^{143}\text{Nd}/^{144}\text{Nd}$ ratios of a sample from the contemporaneous
544 chondritic uniform reservoir (CHUR) respectively (White, 2015). ϵHf values in
545 zircons and ϵNd in whole-rock sediments and granitoids record the degree to which
546 the magma contains the juvenile mantle (high values) versus the reworked crust (low
547 values) (Condie and Aster, 2013). Mantle-derived magmas have relatively low $\delta^{18}\text{O}$
548 ($5.3\pm 0.3\text{‰}$; Valley, 2003), whereas magmas that include a contribution from
549 sedimentary rocks have elevated $\delta^{18}\text{O}$ because rocks that have experienced a
550 sedimentary cycle or low-grade hydrothermal alteration will have experienced
551 isotopic exchange with water at low temperatures (c. 7–25‰; Eiler, 2001). Thus,
552 elevated $\delta^{18}\text{O}$ values in zircon are proposed as a ‘fingerprint’ for the generation of

553 felsic igneous rocks (Hawkesworth et al., 2010). Increasing ϵ_{Hf} and ϵ_{Nd} values, and
554 decreasing $\delta^{18}\text{O}$ values with time reflect more significant input of juvenile crust with
555 unradiogenic Sr isotope ratios; conversely, decreasing ϵ_{Hf} and ϵ_{Nd} values, and high
556 $\delta^{18}\text{O}$ values reflect reworking of older crust with high Sr isotope ratios (Belousova et
557 al., 2010; Collins et al., 2011; Condie and Aster, 2013).

558 Large igneous provinces represent large volumes ($>0.1\text{Mkm}^3$; frequently
559 above $>1\text{Mkm}^3$) of mafic lavas, typically in less than a few million years (Bryan and
560 Ernst, 2008; Coffin and Eldholm, 1994; Ernst and Ernst, 2014). LIP (or continental
561 flood basalt) weathering plays an important role in regulating seawater $^{87}\text{Sr}/^{86}\text{Sr}$ and
562 global climate due to $\sim 5\text{-}10$ times greater weatherability of basalts than felsic
563 continental crust (White and Brantley, 1995). Rapid chemical weathering of LIPs
564 delivers unradiogenic Sr into the ocean, leading to a decrease in marine $^{87}\text{Sr}/^{86}\text{Sr}$ and
565 CO_2 drawdown (Cox et al., 2016; Dessert et al., 2001). The importance of basalt
566 weathering is especially noted for the early-middle Neoproterozoic and Phanerozoic
567 fluctuations in seawater $^{87}\text{Sr}/^{86}\text{Sr}$ (Bataille et al., 2017; Cox et al., 2016; Gernon et al.,
568 2016; Godderis et al., 2003; Jagoutz et al., 2016; Prokoph et al., 2013). For instance,
569 major strontium isotope falls in the middle Neoproterozoic and middle-late Ordovician
570 were suggested to have been due to enhanced volcanic weathering that potentially
571 triggered the Sturtian and late Ordovician glaciations (Cox et al., 2016; Shields et al.,
572 2003; Young et al., 2009). It is worth noting that evolving palaeogeography is another
573 potential control over seawater $^{87}\text{Sr}/^{86}\text{Sr}$. Continental lithologies and global climatic
574 zonation vary spatially; thus, ongoing continental drift would lead to changes in the
575 average $^{87}\text{Sr}/^{86}\text{Sr}$ signature of continental runoff and thus of the ocean (Godd ris et al.,
576 2017).

577 In this section, we will discuss possible explanations for the temporal trend of the

578 updated seawater Sr isotope curve combining recognizable events and complementary
579 data sets, and will propose plausible hypotheses for some highly controversial topics
580 (e.g., onset of plate tectonics) using this improved curve.

581 *7.1. Archean (4.0-2.5 Ga)*

582 Plate tectonics is a defining characteristic of the modern Earth System that
583 involves a globally linked system of lateral motion of rigid surface plates with
584 lithosphere formed at mid-ocean ridges and consumed in subduction zones. When and
585 whether modern style plate tectonics operated during the Archean remain topics of
586 considerable debate and rigorous research (Brown et al., 2020; Cawood et al., 2018,
587 2006; Dhuime et al., 2015, 2012; Ernst et al., 2016; Greber et al., 2017; Griffin et al.,
588 2014; Harrison et al., 2008; Hawkesworth et al., 2017, 2010, 2020; Hopkins et al.,
589 2008; Keller and Harrison, 2020; Komiya et al., 1999; Kröner and Layer, 1992; Lipp
590 et al., 2021; Moyen et al., 2006; Nutman et al., 2002; Smithies et al., 2007; Stern,
591 2018; M. Tang et al., 2016; Taylor and McLennan, 1985; Van Kranendonk, 2010;
592 Van Kranendonk et al., 2007; Windley et al., 2021). Many authors have suggested
593 that plate tectonics commenced during Meso- to Neoproterozoic times, around 3.2–2.5
594 Ga (e.g., Brown et al., 2020; Cawood et al., 2018; Dhuime et al., 2015; Hawkesworth
595 et al., 2020, 2017; Tang et al., 2016; Taylor and McLennan, 1985). However, a
596 contrasting view supports an earlier onset of plate tectonic before 3.5 Ga and as early
597 as the Hadean (e.g., Greber et al., 2017; Harrison et al., 2008; Keller and Harrison,
598 2020; Lipp et al., 2021; Windley et al., 2021). Others argue that modern style plate
599 tectonics began only in the Neoproterozoic Era (Stern, 2018). A detailed discussion
600 on different hypotheses of plate tectonics lies outside the scope of this review, but the
601 updated seawater Sr isotope curve may provide an additional viewpoint from which to
602 appreciate the debate.

603 The Earth's crust was originally mafic but eventually evolved into two
604 compositionally distinct components: thin, dense, silica-poor oceanic crust and
605 thicker, buoyant, silica-rich continental crust. This dichotomy is generally accepted as
606 maintained by plate tectonics. Thus changes in upper-crust composition (development
607 of felsic crust) are suggested to be a piece of geological evidence for plate tectonic
608 commencement (Greber et al., 2017; Lipp et al., 2021; Tang et al., 2016; Windley et
609 al., 2021). Due to the higher Rb/Sr (higher ^{87}Sr) in silica-rich continental crust than
610 oceanic crust, deviation of seawater Sr isotopes from the contemporaneous mantle has
611 been related to the emergence and weathering of evolved continental crust (Flament et
612 al., 2013). The modelled Sr isotope evolution in the depleted mantle (**Fig. 6**) shows a
613 linear increase to the present-day value of c. 0.7026 with a constant Rb/Sr ratio of
614 ~ 0.016 (Workman and Hart, 2005). The compilation of Shields and Veizer (2002)
615 indicated that the seawater $^{87}\text{Sr}/^{86}\text{Sr}$ curve might have deviated from the predicted
616 value for mantle evolution before c. 2.5 Ga and as early as ~ 2.9 Ga (**Fig. 6**). Our
617 updated compilation, however, shows an earlier deflection before c. 3.5 Ga, after
618 considering data from recent studies such as Roerdink et al., (2021), Ravindran et al.,
619 (2020) and Satkoski et al., (2017, 2016). The emerging Sr isotope curve implies that
620 the onset of continental weathering of more evolved crust began before 3.5 Ga and
621 could even have begun as early as 3.7 Ga (Roerdink et al., 2021). The early deviation
622 of the seawater $^{87}\text{Sr}/^{86}\text{Sr}$ curve might provide support for the earlier crustal
623 differentiation and plate tectonics onset model (before 3.5 Ga). However, it is
624 challenging to discern the role of continental weathering this far back in time, based
625 solely on Sr isotopes, because early continental crust, while differentiated, would have
626 had little time to grow more ^{87}Sr and would remain isotopically very similar to the
627 mantle for over a billion years. Therefore, the leverage of continental weathering to

628 modify seawater composition was much reduced in the Archean such that relatively
629 small changes, once verified, can be considered significant.

630 Titanium (Ti) isotope composition in shale is an alternative way to constrain the
631 chemical composition of the continental crust exposed to weathering. The $^{49}\text{Ti}/^{47}\text{Ti}$
632 ratio (expressed as $\delta^{49}\text{Ti}$; part per mil deviation of the $^{49}\text{Ti}/^{47}\text{Ti}$ ratio in a sample from
633 that of the Origins Laboratory Ti reference material) is associated with SiO_2
634 concentration because during fractional crystallization, light Ti is preferentially
635 incorporated in Fe-Ti oxides (Millet et al., 2016). For instance, mafic rocks and
636 komatiites have near bulk silicate Earth values [$+0.005 \pm 0.005$ (‰), 95% c.i.], while
637 $\delta^{49}\text{Ti}$ in evolved rocks has a higher value of +0.6‰ (at SiO_2 concentration of 75%;
638 Greber et al., 2017). Although the Ti concentration of mafic rocks is much higher than
639 that of felsic rocks, Greber et al. (2017) shows that the average $\delta^{49}\text{Ti}$ value of shales is
640 almost constant and always higher than that of basalt and komatiites during the past
641 3.5 Ga, indicating that emergent crust was likely dominated by felsic (silica-rich)
642 rocks as far back as 3.5 Ga. The gradual increase of $^{87}\text{Sr}/^{86}\text{Sr}$ ratios in Paleoarchean
643 seawater also coincides with the widespread occurrence of granitoid-rich crust in the
644 western Dharwar, Kaapvaal and Pilbara cratons and the presence of detrital deposits
645 with felsic sources (Hessler and Lowe, 2006), suggesting that the marine Sr budget
646 started to be dominated by crustal-derived, more radiogenic materials (Ravindran et
647 al., 2020).

648 Plate tectonics would eventually produce supercontinents, thicken the lithosphere
649 and increase crustal reworking (Cawood et al., 2013; Flament et al., 2013;
650 Hawkesworth et al., 2016; Spencer et al., 2014). The subsequent assembly of the first
651 putative supercontinent Kenorland at c. 2.7-2.6 Ga (Williams et al., 1991; Bleeker, 2003)
652 produced collisional orogens that were susceptible to subaerial weathering, potentially

653 increasing further the flux of radiogenic ^{87}Sr to the ocean during the Neoproterozoic.

654 7.2. Proterozoic (2.5-0.54 Ga)

655 7.2.1. Paleoproterozoic (2.5-1.6 Ga)

656 The Paleoproterozoic Era is marked by a substantial increase in the oxygen content
657 of the atmosphere at c. 2.4-2.3 Ga (e.g., Bekker et al., 2004; Bekker and Holland,
658 2012; Canfield et al., 2013; Holland, 2002; Karhu and Holland, 1996; Poulton et al.,
659 2021; Rye and Holland, 1998; Walker et al., 1983); widespread glaciations (e.g.,
660 Barley et al., 2005; Kopp et al., 2005; Young, 1991), the Earth's largest positive
661 carbon isotope excursion (Baker and Fallick, 1989; Martin et al., 2013; Melezhik et
662 al., 2005; Schidlowski et al., 1975); the oldest microfossils diagnostic of
663 cyanobacteria and eukaryotes (Hofmann, 1976; Javaux et al., 2013; Javaux and Lepot,
664 2018; Knoll et al., 2006; Knoll and Golubic, 1992) and sustained plate tectonics (e.g.,
665 Cawood et al., 2018; Hawkesworth et al., 2020; Taylor and McLennan, 1985).

666 The Paleoproterozoic seawater $^{87}\text{Sr}/^{86}\text{Sr}$ curve appears to have oscillated markedly
667 with two increases at 2.5-2.2 Ga and 1.9-1.7 Ga, respectively. Although the first
668 dramatic increase of $^{87}\text{Sr}/^{86}\text{Sr}$ from 2.5 Ga to 2.2 Ga is relatively poorly constrained, it
669 coincides with important Earth System events, such as the first accumulation of
670 atmospheric O_2 (the Great Oxidation Episode or GOE; Poulton et al., 2021) and a
671 series of extensive glaciations (c. 2.45-2.22 Ga). Contributing factors to the rise in
672 seawater $^{87}\text{Sr}/^{86}\text{Sr}$ include: 1) a decrease in mantle input flux; 2) an increase in the Sr
673 isotopic composition of rocks undergoing weathering; and 3) an increase in
674 continental weathering flux. However, the interval 2.5-2.2 Ga corresponds to a
675 relative low in the zircon age abundance record and sits in a quiet transition before a
676 period of widespread magmatism and rifting, related in part to the breakup of
677 Kenorland at 2.2-2.1 Ga. An increase in the Sr isotope composition of rocks

678 undergoing weathering is plausible, as more felsic crust might have been produced
679 during this period (Dhuime et al., 2015; Lee et al., 2016). However, there is no
680 obvious evidence from Hf, Nd and O isotopes (**Fig. 5B**), so it might not be a primary
681 control for such a dramatic Sr isotope rise. We therefore consider a role for an
682 enhanced chemical weathering rate, probably driven by several possible factors, such
683 as increased emergence of continental crust (e.g., Flament et al., 2013), maximised
684 mineral surface area during glaciations (Hallet et al., 1996; Koppes and Montgomery,
685 2009) and oxidative weathering of pyrite (producing sulfuric acid) during the GOE
686 (Bekker and Holland, 2012; Bachan and Kump, 2015; Torres et al., 2014).

687 A thickened lithosphere and largely emergent low-latitude continental crust during
688 the early Proterozoic (c. 2.5 Ga) likely increased the surface area exposed to
689 weathering (Flament et al., 2013; Lee et al., 2016), potentially contributing to the
690 dramatic increase of seawater $^{87}\text{Sr}/^{86}\text{Sr}$ at ~2.5 Ga. Modelled evolution of P
691 concentrations in Earth's emerged crust through time by Greber et al., (2017) shows a
692 50% increase in the concentration of P (from 0.10 to 0.15 wt% P_2O_5) across the
693 Archean- Proterozoic boundary (2.5 Ga), which could be a result of enhanced
694 continental weathering during this period. As a major limit to biological productivity
695 over geological time scales (Lenton and Watson, 2004; Tyrrell, 1999), an increase in
696 the flux of P from chemical weathering could have led to an expansion of oxygenic
697 photosynthesis and therefore a rise in atmospheric O_2 at c.2.4 Ga (**Fig. 5D**).

698 As for the Sr isotope peak at ~2.3-2.2 Ga, the onset of pyrite weathering
699 (producing sulfuric acid) (Bekker and Holland, 2012; Torres et al., 2017, 2014) may
700 have contributed significantly to the rise to values as high as ~0.705 (Bekker et al.,
701 2006, 2003a). The generation of sulfuric acid (H_2SO_4) from pyrite weathering would
702 have decreased the pH of soil and groundwater, inducing the dissolution of rocks and

703 minerals, including apatite, and giving rise to further chemical weathering through net
704 production of CO₂ (Guidry and Mackenzie, 2003; Konhauser et al., 2011; Torres et
705 al., 2017). Additionally, glacial flour could have maximised the surface area exposed
706 to weathering (Anderson, 2007; Hallet et al., 1996; Herman et al., 2013; Koppes and
707 Montgomery, 2009). Therefore, we propose that increased sulfuric acid and largely
708 exposed reactive surface area during glaciation might have resulted in an increased
709 radiogenic Sr flux from the continent.

710 Afterwards, a sharp ⁸⁷Sr/⁸⁶Sr fall between c. 2.2 Ga to c. 2.1 Ga might be attributed
711 to an increased flux of less radiogenic strontium from mid-ocean ridges and rift
712 volcanism, associated with the final breakup of the Kenorland at 2.2-2.1 Ga (Aspler
713 and Chiarenzelli, 1998; Wanke and Melezhik, 2005), as well as a decreased flux of
714 more radiogenic riverine strontium due to peneplanation of Kenorland. The
715 subsequent second sharp rise of ⁸⁷Sr/⁸⁶Sr ratios after c. 2.0-1.9 Ga, reaching a peak at
716 c. 1.7 Ga, is concurrent with the amalgamation of the supercontinent Nuna (**Fig. 5A**)
717 and was likely related to global-scale collisional events (Bradley, 2011; Zhao et al.,
718 2004, 2002). It has long been proposed that tectonic-related uplift could facilitate
719 erosion and chemical weathering (e.g., Raymo et al., 1988; Ruddiman and Prell,
720 1997), thus, increasing the continental Sr flux into the ocean. Moreover, the low ε_{Hf}
721 values of detrital zircons, low Nd isotope ratios in whole-rock sediments and
722 granitoids and zircon δ¹⁸O values during this period imply a contribution from
723 reworked crust with presumably higher ⁸⁷Sr/⁸⁶Sr ratios (Condie and Aster, 2013;
724 Hawkesworth et al., 2016; Cawood et al., 2018). The following drop of ⁸⁷Sr/⁸⁶Sr ratios
725 to around 0.7046 at c. 1.6 Ga occurred at the transition from the Paleoproterozoic Era
726 to the Mesoproterozoic Era, implying an increased input of unradiogenic sources,
727 possibly related to the onset of a partial breakup of Nuna (Anderson, 1983; Rogers

728 and Santosh, 2002; Zhao et al., 2004). Simultaneously, ϵ_{Hf} and ϵ_{Nd} values both show
729 an increasing trend, coupled with decreasing zircon $\delta^{18}\text{O}$ values, probably indicating a
730 gradual transition from reworked crust to more juvenile crust during this period (**Fig.**
731 **5B**).

732 *7.2.2. Mesoproterozoic (1.6 Ga-1.0 Ga)*

733 The middle portion of the Proterozoic Eon (1.8 to 0.85 Ga) is characterised by its
734 relative environmental, evolutionary, and lithospheric stability (e.g., Cawood and
735 Hawkesworth, 2014) with a paucity of passive margins (Bradley, 2008), absence of
736 glaciation (Bradley, 2011) and muted variability in the geochemical record (e.g.,
737 Bartley and Kah, 2004; Brasier and Lindsay, 1998; Buick et al., 1995; Shields, 2007).
738 However, following further detailed studies conducted in recent years, more and more
739 mysteries of this so-called “Boring Billion” have been revealed in terms of eukaryotic
740 evolution (e.g., Adam et al., 2017; Butterfield, 2000; Butterfield et al., 1990; Javaux
741 et al., 2001; Knoll, 2014, 1994; Lamb et al., 2009; Miao et al., 2019; Shi et al., 2017;
742 Tang et al., 2020; Zhang et al., 2018b; Zhu et al., 2016), global tectonic
743 reorganisations (Anderson, 1983; Condie, 2020; Evans and Mitchell, 2011; Huang et
744 al., 2019; Rogers and Santosh, 2002; Zhao et al., 2004), surface O_2 dynamics (e.g.,
745 Diamond et al., 2018; Gilleaudeau and Kah, 2015; Johnston et al., 2005; Kah et al.,
746 2001, 1999; Kah and Bartley, 2011; Liu et al., 2021) and possible carbon isotope
747 excursions (e.g., Bartley et al., 2001; Kah et al., 1999; Knoll et al., 1995; Zhang et al.,
748 2016)

749 The updated strontium isotope curve for Mesoproterozoic seawater shows
750 relatively low values (~ 0.7045 - 0.705) with only muted variability between 1.6 Ga-
751 1.2 Ga. The low $^{87}\text{Sr}/^{86}\text{Sr}$ ratios are concurrent with the fragmentation of the
752 supercontinent Nuna, which began at c. 1.6 Ga with continental rifting and anorogenic

753 magmatism until its final breakup at about 1.2 Ga with widespread emplacement of
754 mafic dike swarms (Anderson and Arthur, 1983; Rogers and Santosh, 2002; Zhao et
755 al., 2004). The above-zero ϵHf and ϵNd curves and low $\delta^{18}\text{O}$ (**Fig. 5B**), alongside
756 previous studies, indicate that this period was under the influence of considerable
757 amounts of juvenile mantle-derived rocks and associated hydrothermal systems
758 (Condie and Aster, 2013; Hawkesworth et al., 2016; Semikhatov, 2002). Additionally,
759 1.6-1.2 Ga also witnessed the emplacement of several large igneous provinces (**Fig.**
760 **5C**), such as the ~1267 Ma Mackenzie LIP, ~1385 Ma Mashak LIP (and other coeval
761 LIPs) and ~1501 Kuonamka LIP etc. (Ernst and Youbi, 2017). The low marine
762 $^{87}\text{Sr}/^{86}\text{Sr}$ ratios during this period, together with evidence from complementary
763 datasets (ϵHf , ϵNd and $\delta^{18}\text{O}$, LIPs) suggest that a significant juvenile crust was likely
764 involved in mountain building, and continental weathering was dominated by juvenile
765 less radiogenic crust over ancient, more radiogenic continental crust.

766 A subsequent increase of $^{87}\text{Sr}/^{86}\text{Sr}$ since c. 1.2 Ga towards the end of the
767 Mesoproterozoic coincides with amalgamation of the supercontinent Rodinia
768 (Spencer et al., 2013). Weathering conditions during this period were less-constrained
769 previously, but enhanced chemical weathering towards the end of the
770 Mesoproterozoic Era has been proposed recently by Gibson et al., (2019), who related
771 a rise in $^{87}\text{Sr}/^{86}\text{Sr}$ at ca. 1050 Ma to weathering of Grenville-aged orogens (linked to
772 amalgamation of supercontinent Rodinia). However, in our compilation (**Fig. 5A**), the
773 incremental rise of $^{87}\text{Sr}/^{86}\text{Sr}$ during assembly of Rodinia contrasts with the sharp
774 increase during the earlier assembly of Nuna and later assembly of Gondwana, which
775 might indicate that the weathering of materials with relatively low $^{87}\text{Sr}/^{86}\text{Sr}$ ratios may
776 have predominated even during periods of uplift and erosion. Semikhatov (2002)
777 proposed several possible reasons, such as juvenile magmatism, an extremely arid

778 climate, or the paleogeographic lock-up of continental runoff, whereby collisional
779 orogens at continental margins represented barriers for the terrestrial material
780 transported by rivers. The first reason seems plausible considering the overall high
781 juvenile crust production, which is marked by relatively radiogenic Nd and Hf isotope
782 signatures, and LIPs such as the c. 1005 Ma Sette Daban event (Ernst and Youbi,
783 2017).

784 *7.2.3. Neoproterozoic (1.0 Ga-0.54 Ga)*

785 The Neoproterozoic Era is characterised by climatic vicissitudes, including two
786 prolonged global glaciations during the Cryogenian Period and short-lived, regional
787 ice ages during the Ediacaran Period (e.g., Hoffman et al., 2017; Young et al., 2015
788 and references therein), biological radiations (e.g., Narbonne, 2005; Xiao and
789 Laflamme, 2009), the eruption of large igneous provinces (LIPs) (e.g., Cox et al.,
790 2016; Ernst and Youbi, 2017), oscillations of carbon isotopes (e.g., Halverson et al.,
791 2005; Rothman et al., 2003), ocean oxygenation events (e.g., Shields-Zhou and Och,
792 2011) and tectonic reorganization including fragmentation of the supercontinent
793 Rodinia and subsequent assembly of Gondwana (e.g., Condie and Puetz, 2019;
794 Merdith et al., 2017).

795 A sustained increase in continental weathering rate was believed to be a major
796 contributing factor driving increased $^{87}\text{Sr}/^{86}\text{Sr}$ ratios in Neoproterozoic seawater
797 (Shields, 2007). However, Halverson et al., (2010) pointed out that some notable
798 trends superimposed on the long term “base-level shift” of marine $^{87}\text{Sr}/^{86}\text{Sr}$ values,
799 such as the decline prior to Cryogenian glaciation, could tentatively be assigned to the
800 weathering of widespread flood basalts. Coincidentally, Bataille et al., (2017) found
801 that $^{87}\text{Sr}/^{86}\text{Sr}$ changes in igneous rocks were generally well correlated with changes to
802 seawater $^{87}\text{Sr}/^{86}\text{Sr}$ over the last 1.0 Ga, which indicates that the isotope composition of

803 weathering input might have played an important role in shaping the seawater
804 $^{87}\text{Sr}/^{86}\text{Sr}$ curve during this period. Additionally, many researchers have also proposed
805 a critical role for large igneous provinces (LIPs) in determining seawater $^{87}\text{Sr}/^{86}\text{Sr}$
806 ratios due to the higher weatherability of basalt (e.g., Cox et al., 2016). Enhanced
807 silicate weathering of unradiogenic, low latitude LIPs likely led to steep dips in the
808 strontium isotope curve. For instance, the falls of $^{87}\text{Sr}/^{86}\text{Sr}$ ratios at 0.92 Ga, 0.83 Ga,
809 0.72 Ga could have resulted from the weathering of the Dashigou, Guibei and
810 Franklin LIPs, respectively (Ernst and Youbi, 2017; Zhou et al., 2020). Accelerated
811 uptake of CO_2 via LIP weathering might outweigh the climatic effects of CO_2
812 degassing, triggering glaciations, such as the Sturtian glaciation (Cox et al., 2016;
813 Ernst and Youbi, 2017; Rooney et al., 2014). Conversely, continental drift (changing
814 palaeogeography) might diminish LIP weathering, allowing seawater $^{87}\text{Sr}/^{86}\text{Sr}$ to rise
815 again. For instance, numerical models suggest the southward drift of the Franklin
816 LIPs outside the original tropical convergence zone (Li et al., 2013), decreasing its
817 contribution to total Sr flux of continental silicate weathering from 4.5% at 720 Ma to
818 2.5% at 680 Ma and 635 Ma, which could be a potential reason for the rise of
819 $^{87}\text{Sr}/^{86}\text{Sr}$ after 635 Ma (Goddéris et al., 2017).

820 The relatively low values of $^{87}\text{Sr}/^{86}\text{Sr}$ (c.0.7055-0.7060) during 0.95-0.85 Ga
821 coincided with the tenure of the supercontinent Rodinia (Bradley, 2011). Evidenced
822 by the increasing values of ϵHf and ϵNd , the low strontium isotope values during this
823 period might reflect input of less radiogenic strontium from basalt and andesite from
824 surrounding volcanic arcs (Goddéris et al., 2017) during an interval of low relief and
825 high continentality. The subsequent sharp rise of strontium isotope ratios from 0.85
826 Ga to the end of Precambrian encompasses the breakup of the supercontinent Rodinia
827 at c.0.8-0.65 Ga (Condie and Puetz, 2019) and the assembly of Gondwana at c. 0.6-

828 0.5 Ga (Cawood and Buchan, 2007; Merdith et al., 2017). During breakup, the old and
829 radiogenic continental interiors might have been uplifted, exposed and rapidly
830 weathered, giving rise to an overall increase in ocean $^{87}\text{Sr}/^{86}\text{Sr}$, interrupted by several
831 eruptive events (Godd ris et al., 2017; Halverson et al., 2007; Zhou et al., 2020).
832 Simultaneously, the ϵHf and ϵNd curves start showing a decreasing trend, which
833 indicates that the crustal production began shifting to an advancing external phase,
834 where the reworked components with higher $^{87}\text{Sr}/^{86}\text{Sr}$ values exceeded juvenile
835 components with lower $^{87}\text{Sr}/^{86}\text{Sr}$ ratios (Condie and Aster, 2013). Afterwards, the
836 onset of Gondwana assembly produced widespread collisional orogens and generated
837 highly pulverised bedrocks by physical weathering, thereby promoting rapid
838 chemical weathering (Ruddiman et al., 1997). Abrupt increases in $^{87}\text{Sr}/^{86}\text{Sr}$ follow
839 both the Sturtian and Marinoan glaciations may relate to enhanced chemical
840 weathering of freshly exposed rock surfaces beneath a CO_2 -rich atmosphere (e.g., Cox
841 et al., 2016). Such increases in weathering efficiency will eventually draw down
842 carbon dioxide levels, bringing weathering rates back down again. Alternatively,
843 Shields et al., (2019) proposed that a genuine rise of continental weathering rates
844 without lowering CO_2 if uplift and erosion events led to enhanced evaporite sulfate
845 weathering, which if coupled with pyrite burial/organic carbon oxidation could
846 maintain CO_2 forcing of chemical weathering. Continent-continent collisions might
847 also deliver the radiogenic isotope signal of the largely-reworked crust into the ocean,
848 given the sharp decreases in ϵHf and ϵNd as well as the rise of $\delta^{18}\text{O}$ values from c.
849 0.85 Ga to c. 0.55 Ga.

850 **8. Linking the updated Sr isotope record to supercontinental cycles**

851 Tectonic processes are the major influence on Sr fluxes to the ocean and the updated
852 seawater $^{87}\text{Sr}/^{86}\text{Sr}$ curve shows both stronger oscillations and better correspondence

853 with tectonic events than had previously been shown (Shields and Veizer, 2002) (**Fig.**
854 **5A; Fig. 6**). In particular, supercontinent cycles, which have in the interim become
855 more evident in zircon abundance, s-type granite, metamorphic grade and zircon
856 isotopic records, show more convincing covariation with seawater $^{87}\text{Sr}/^{86}\text{Sr}$ throughout
857 the Proterozoic as well as the already established Phanerozoic Eon.

858 In the new curve, in most cases, rising $^{87}\text{Sr}/^{86}\text{Sr}$ rises coincide with proposed times
859 of supercontinent amalgamation; and $^{87}\text{Sr}/^{86}\text{Sr}$ falls accompany times of high
860 continentality / supercontinent tenure and initial breakup. For instance, the assembly
861 stages of supercontinent Kenorland (postulated), Nuna and Gondwana all correspond
862 to increases in the Sr isotope curve, while their tenure and rifting coincide with lower
863 points in the curve (**Fig. 5A**). It was suggested that supercontinent amalgamation
864 enhances continental weathering of uplifted terrains and increased input of radiogenic
865 Sr flux to the ocean, while supercontinent breakup is associated with ocean ridge
866 activity, rift-related magmatism and sea-level rise, leading to increased input of
867 relatively unradiogenic Sr flux to the ocean and low seawater $^{87}\text{Sr}/^{86}\text{Sr}$ values (e.g.,
868 Asmerom et al., 1991; Raymo et al., 1988; Veizer et al., 1989). It is worth noting that
869 the updated Sr isotope curve reaches peaks after zircon abundance peaks related to
870 supercontinent assembly. For example, for Nuna the Sr isotope peak at c. 1.7 Ga follows
871 a zircon abundance peak at c. 1.87 Ga and for Gondwana the c. 500 Ma acme follows
872 a peak at c. 600 Ma, which corresponds to rapid erosion of particularly high
873 “supermountains” as evidenced by the high production rate of S-type granites (Brown
874 and Johnson, 2019; Zhu et al., 2020). Orogeny may lead to higher seawater Sr isotope
875 ratio, not through chemical weathering, which is related to outgassing of carbon dioxide,
876 but to physical weathering, and desorption of Sr from fine-grained suspended sediment
877 carried by rivers, in which case Sr isotopes can act more as an erosional proxy than

878 merely chemical weathering (Oelkers et al., 2012). The extreme continental weathering
879 during assembly of Nuna and Gondwana may have triggered the increased input of bio-
880 essential materials to the ocean, fuelling the evolution and radiations of early eukaryotes
881 (late Paleoproterozoic; e.g., Javaux et al., 2018) and animals (Neoproterozoic-
882 Cambrian; e.g., Xiao and Laflamme, 2019), respectively (**Fig. 5D**).

883 One possible exception relates to the assembly and breakup of Rodinia and Pangaea.
884 Seawater $^{87}\text{Sr}/^{86}\text{Sr}$ values only experienced a modest increase during Rodinia
885 amalgamation and even a fall during Pangaea assembly, while their breakups were
886 associated with increases in the seawater Sr curve. Contrasting with the pronounced
887 negative ϵHf and ϵNd values during assembly of Nuna and Gondwana, Hf and Nd
888 isotope values are anomalously radiogenic (above the value of the chondritic uniform
889 reservoir) during the time of Rodinia and Pangaea amalgamation (**Fig. 5B**), which
890 possibly indicates the predominant production and weathering of unradiogenic juvenile
891 crust (Condie and Aster, 2013; Spencer et al., 2013). Halverson et al., (2007) suggested
892 that supercontinent assembly might shift rainfall away from radiogenic continental
893 interiors to unradiogenic juvenile crust on the edges of continents, resulting in lower
894 seawater $^{87}\text{Sr}/^{86}\text{Sr}$; while supercontinental break-up could shift rainfall to older and
895 uplifted continental interiors, leading to an increase of seawater $^{87}\text{Sr}/^{86}\text{Sr}$. Therefore,
896 compared with other periods, during Rodinia and Pangaea assembly and breakup,
897 seawater Sr isotope values might be more controlled by compositional changes of Sr
898 sources undergoing weathering. Alternatively, Wang et al., (2021) presented the
899 concept of “megacontinent” as a geodynamic precursor and a large subset of the next
900 supercontinent. They suggested that the supercontinent Pangea was preceded by the
901 formation of “megacontinent” Gondwana that was formed by an assembly of multiple
902 continents and represented ~70% size of the Pangea. It is likely that supercontinent

903 amalgamation had less influence on global erosion rates than the preceding formation
904 of its megacontinent, therefore resulting in the relatively low values of seawater Sr
905 isotopes during Pangea amalgamation stage compared with the Gondwana assembly
906 stage.

907 **9. Conclusions**

908 1) 2249 strontium isotope data points have been compiled from Precambrian
909 marine carbonate rocks, from 62 publications and 3 unpublished materials over the past
910 18 years, and added to the previous seawater $^{87}\text{Sr}/^{86}\text{Sr}$ database by Shields and Veizer
911 (2002). Four criteria (depositional environment, preservation, age constraints and
912 dissolution methods) have been used to assign values to one of high, medium and low
913 certainty groups.

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

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

924 4) An updated strontium isotope curve of Precambrian seawater has been
925 generated based mainly on high-certainty data from the updated compilation.
926 Compared with the previous version (Shields and Veizer, 2002), this updated curve
927 exhibits relatively high-amplitude fluctuations that correspond to proposed

928 supercontinental cycles (wherein $^{87}\text{Sr}/^{86}\text{Sr}$ rises accompany supercontinent
929 amalgamation; and $^{87}\text{Sr}/^{86}\text{Sr}$ falls accompany supercontinent breakup).

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

936 6) Significant data gaps still exist in the Neoproterozoic, late Paleoproterozoic and
937 Mesoproterozoic, requiring further work. More high-certainty data are needed to test
938 the hypotheses proposed in this study, especially during the periods of 2.5-2.2 Ga and
939 1.9-1.7 Ga.

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946 **Appendix A: Supplementary data**

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

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

949 Supplementary material 3: Reference lists for Precambrian strontium isotope database

950 version 2021 (a).

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Figures

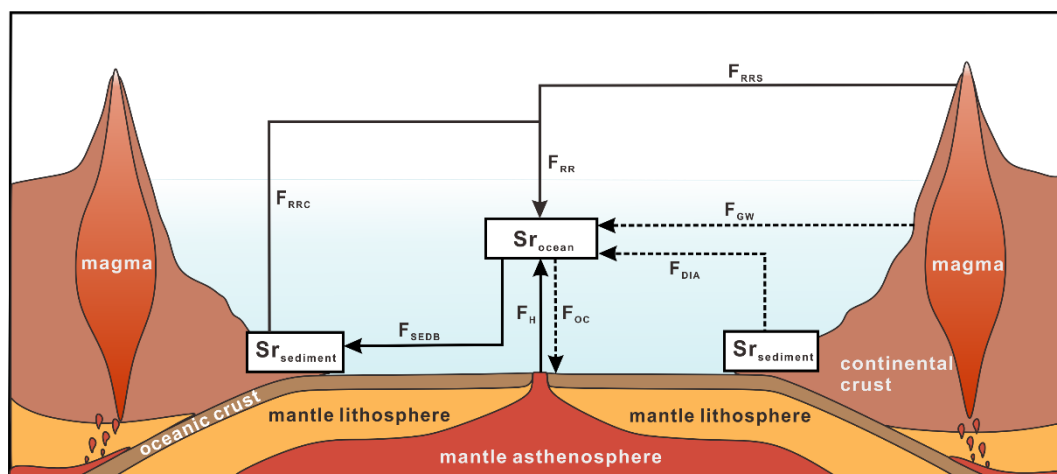


Fig. 1. Conceptual model of the seawater Sr fluxes cycle. Major sources of seawater Sr budget include radiogenic river runoff (F_{RR}) and unradiogenic hydrothermal input (F_H). River runoff (F_{RR}) can be divided into chemical weathering of silicate minerals (F_{RRS}) and dissolution of marine sediments (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_{SEDDB}) 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.

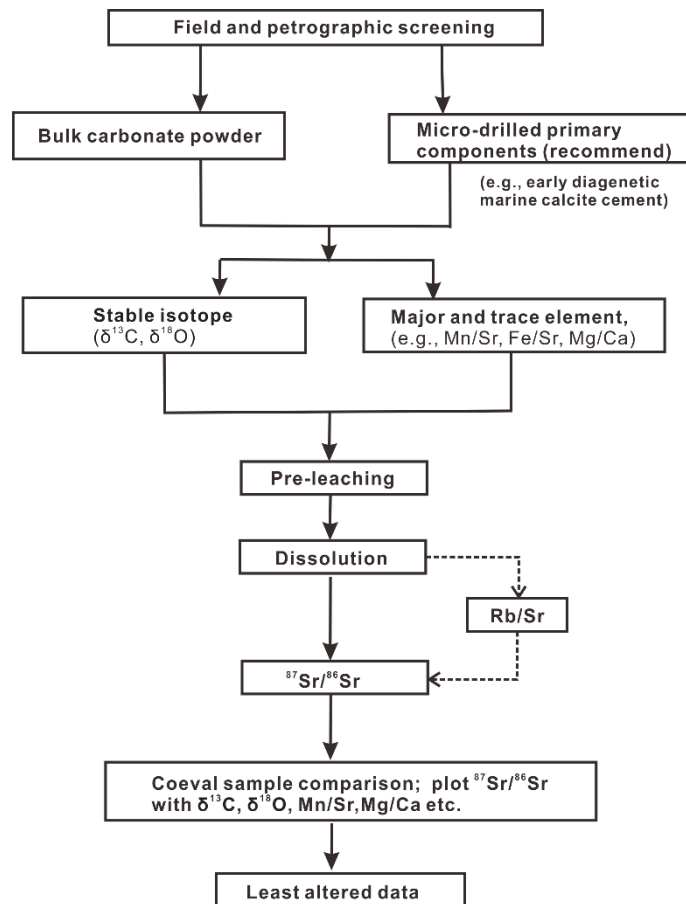


Fig.2. A recommended procedure for selecting the least altered $^{87}\text{Sr}/^{86}\text{Sr}$ data for SIS (Strontium isotope stratigraphy).

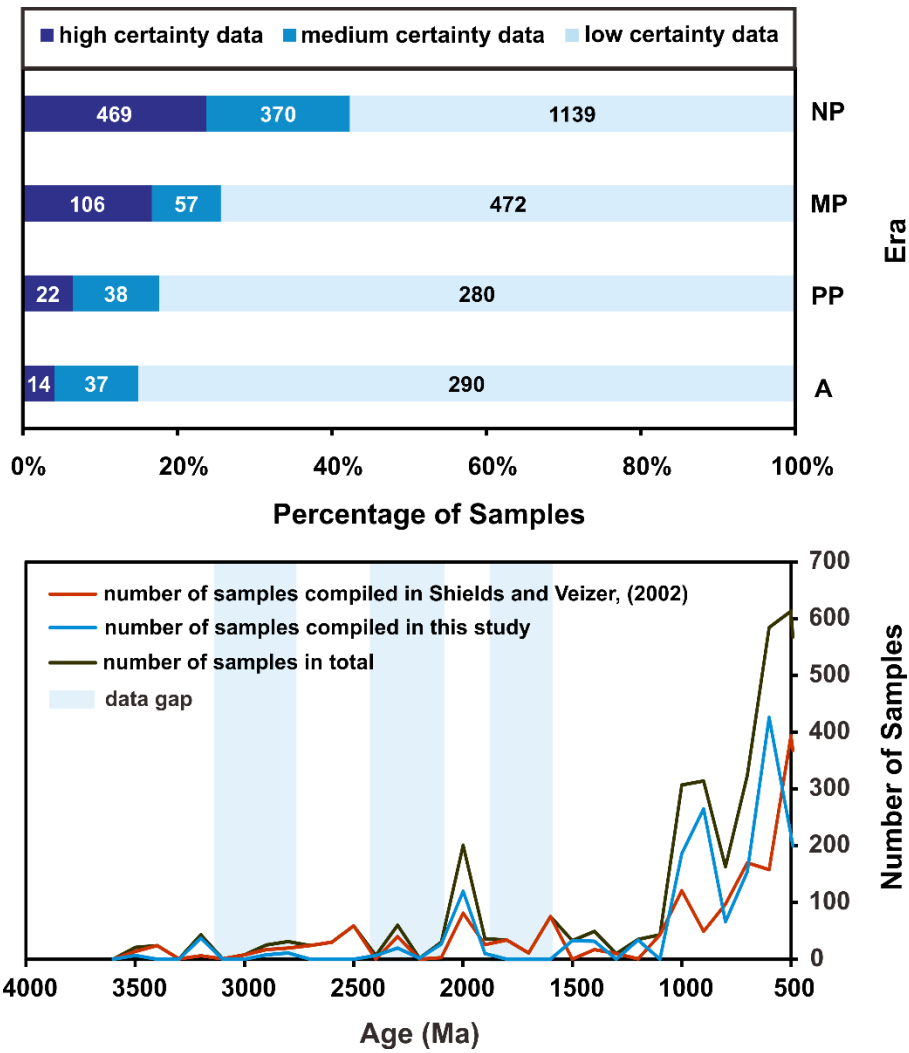


Fig. 3. Certainty and quantity distribution of samples from the Neoproterozoic to Archean. A) Data certainty versus eras. NP: Neoproterozoic, MP: Mesoproterozoic, PP: Paleoproterozoic, A: Archean. The Neoproterozoic has the most abundant high-certainty data. Low-certainty data occupy the largest proportions for all four periods. B) Quantity distribution of data from 500 Ma to 4000 Ma. Neoproterozoic era has relatively abundant datasets, but the Neoproterozoic, late Paleoproterozoic and Mesoproterozoic have relatively sparse datasets.

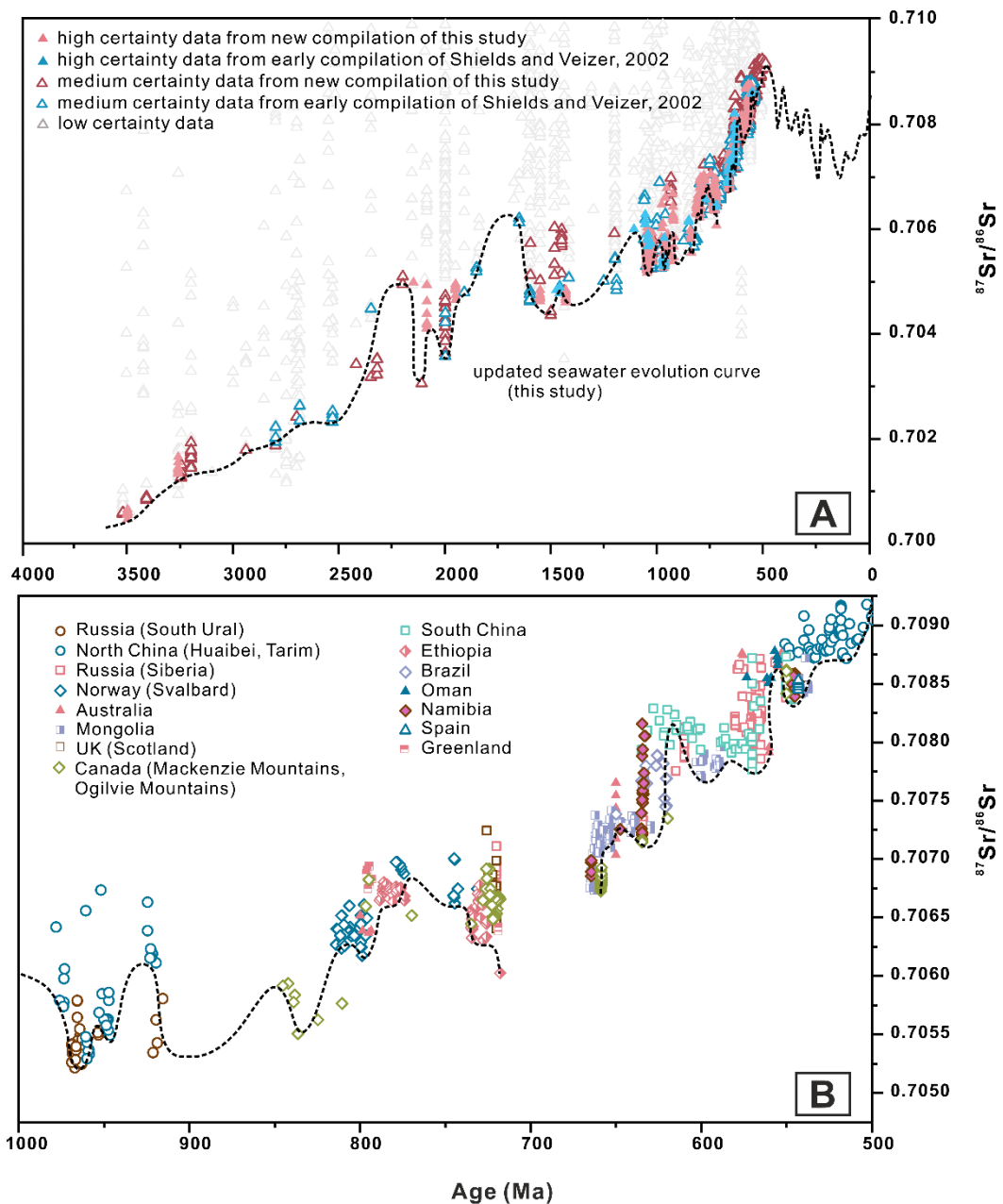


Fig. 4. The updated seawater $^{87}\text{Sr}/^{86}\text{Sr}$ curve with zoom-in image of the Neoproterozoic era. A) An updated strontium isotope curve of seawater. The Precambrian part is updated from this study, and the Phanerozoic part is from McArthur et al., (2020). B) A zoom-in image of Neoproterozoic 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).

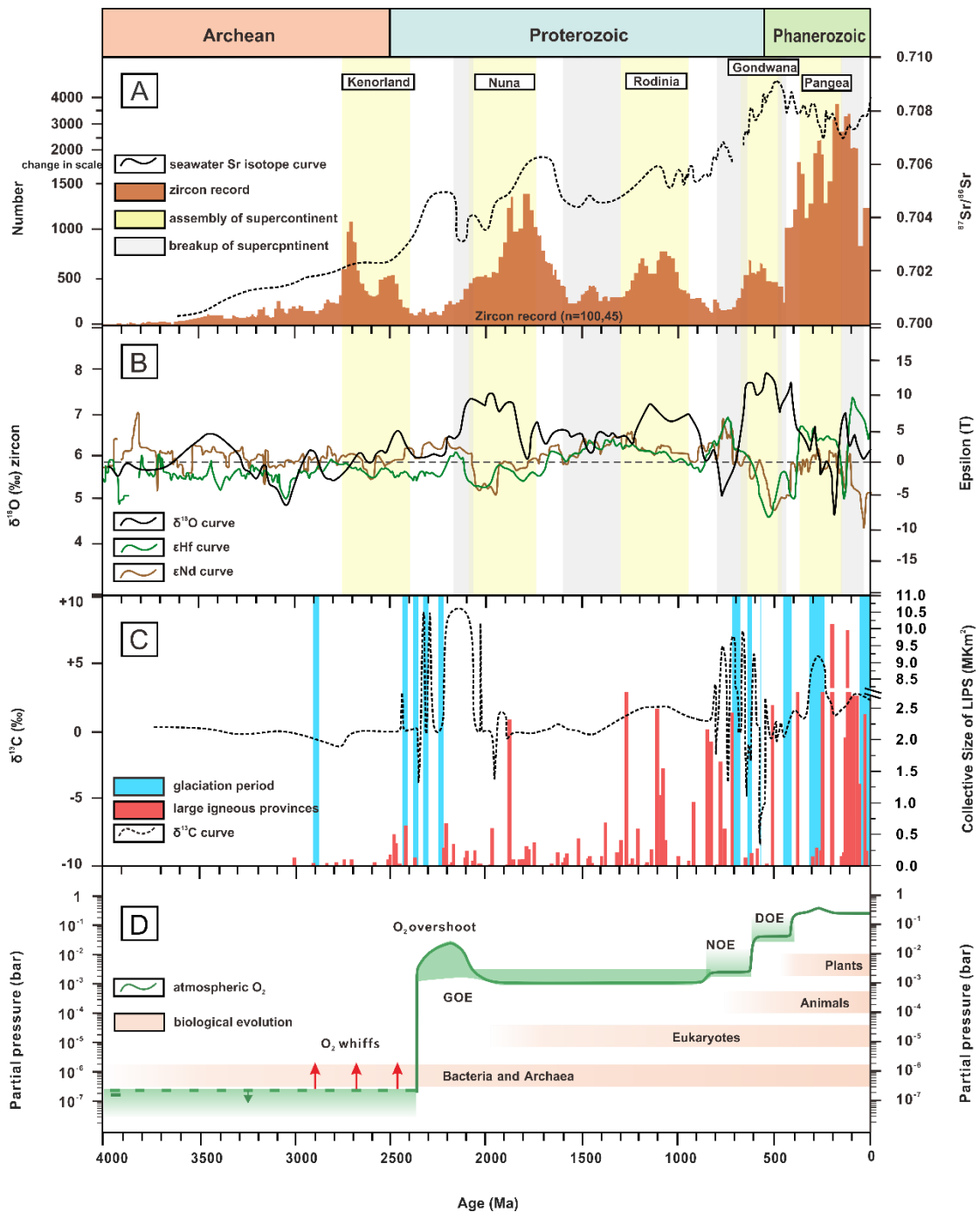


Fig. 5. An overview of the updated strontium isotope curve in the context of Earth systems evolution. A) The updated strontium isotope curve from this study couples zircon records from Voice et al., (2011) and supercontinental cycles. Periods of the supercontinent assembly are from Hawkesworth et al., (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 $\delta^{18}\text{O}$ analyses of zircon

versus U-Pb age from recent sediments (Spencer et al., 2014). Green and brown lines represent median value of ϵ_{Hf} for detrital zircons, ϵ_{Nd} 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 $\delta^{13}\text{C}$ 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 O_2 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).

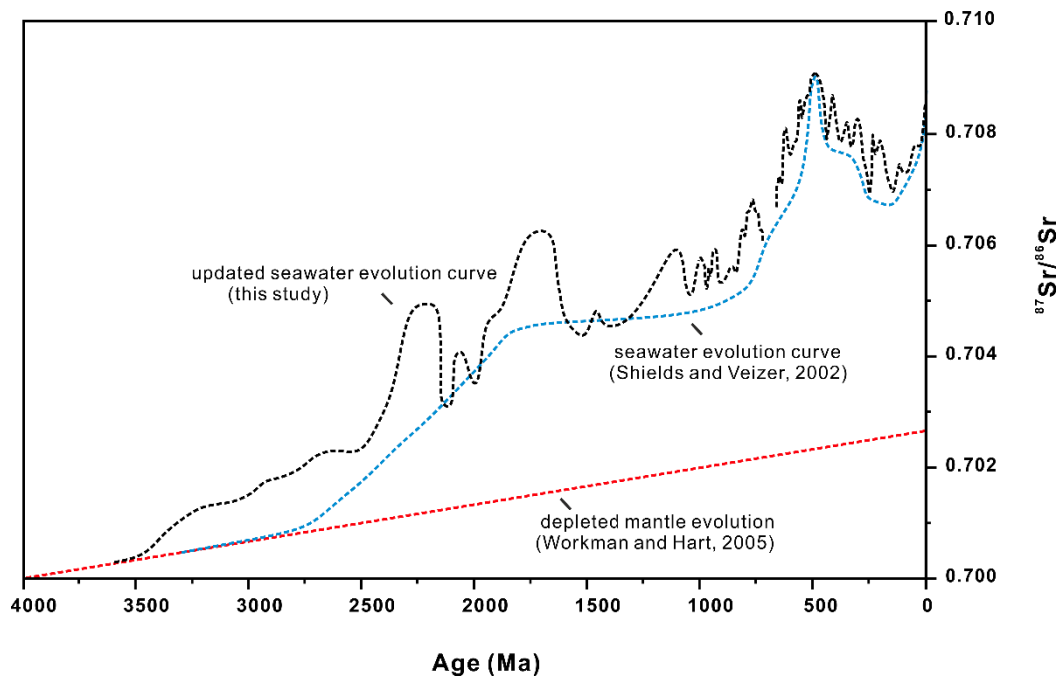


Fig.6. A comparison of updated Precambrian seawater $^{87}\text{Sr}/^{86}\text{Sr}$ curve from this study with that from Shields and Veizer (2002). The updated curve shows an earlier deviation from contemporaneous mantle and a stronger fluctuation than the curve from Shields and Veizer (2002). The depleted mantle evolution curve is from Workman and Hart (2005).