

Interactive comment on “A normalised seawater strontium isotope curve and the Neoproterozoic-Cambrian chemical weathering event” by G. A. Shields

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Received and published: 4 April 2007

Reply to review by Bernhard Peucker-Ehrenbrink of “A normalised seawater strontium isotope curve and the Neoproterozoic-Cambrian chemical weathering event” by Graham A. Shields (eEarth 2, 69-84, 2007)

By Graham A. Shields

At the outset I would like to thank Dr Peucker-Ehrenbrink for his constructive comments. They will not only be helpful in improving the manuscript but also in progressing this fascinating debate over the implications of the seawater Sr isotope curve for chemical weathering. Here I endeavour to address his challenging questions and comments in the same constructive light.

The first summary paragraph of his review looks at the similarities between my normalised Sr isotope curve and those of previous studies. The published contributions of Jacobsen and coauthors are the only ones to my knowledge to consider normalisation of the seawater Sr isotope curve to the changing isotopic composition of ocean sources (Jacobsen, 1988; Asmerom et al., 1991; Kaufman et al., 1993). The omission of these citations was an oversight on my part which needs to be rectified in any revised version of the manuscript. The pioneering study of Jacobsen (1988) and related studies (Asmerom et al., 1991; Kaufman et al., 1993) used the marine Nd isotope record to constrain both riverine eNd and riverine eSr systematics, using an approximately linear relationship between these latter two parameters which was outlined in Goldstein and Jacobsen (1987). Therefore, their published curves were the first to ‘normalise’ the seawater Sr isotope curve not against the evolving $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of the Bulk Earth but also against changes in the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of river input. However, this approach appears to have been overlooked by subsequent workers in the field of Earth System modeling (Berner and Rye, 1992; Francois and Walker, 1992; Berner, 2004).

The curve of global erosion rate (Sr flux to the oceans) obtained by Jacobsen (1988) for the period 700–0 Ma and Asmerom et al. (1991) from 850–0 Ma are indeed similar to the curve produced by my normalisation (Fig. 1b). Importantly, their results show no evidence for a step-wise jump in erosion rates across the Proterozoic-Phanerozoic transition (cf. Derry, 2006; Kennedy et al., 2006) and this is mirrored in my assessment. However, there are some differences. In similar fashion to Veizer et al. (1983), Asmerom et al. (1991) outline an extraordinarily high hydrothermal flux at 830 Ma with erosion versus hydrothermal influence as low as 10% of the modern value. In addition, the Jacobsen (1988) study considers modern erosion rates to be the highest of all time. Both these findings can be explained differently when the changing isotopic composition of carbonate rocks undergoing weathering is taken into consideration. When the buffering effects of carbonate weathering on seawater $^{87}\text{Sr}/^{86}\text{Sr}$ are considered, the relative hydrothermal influence at 830 Ma is no greater than that during the mid-Paleozoic, while the modern peak in erosion rates appears less pronounced than that

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during the Cambrian period. This latter finding seems reasonable considering 1) the evidence for colossal mountain building during the Neoproterozoic-Cambrian interval (e.g. Jacobsen, 1988; Squire et al., 2006) and 2) the requirement that CO₂ drawdown due to weathering match outgassing rates, which were at least as high or higher in the past. Therefore, there are significant differences between the present study and the preceding studies cited in the review.

In regard to quantification (addressing reviewer's last comment), Jacobsen (1988)'s method could also be applied to the new seawater ⁸⁷Sr/⁸⁶Sr curve in the present study. However, a number of possibly unjustifiable assumption need to be made. Firstly, there are very few Nd isotope data for the crucial interval of most concern; the Neoproterozoic-Cambrian interval. In order for the average riverine eNd to be established, many marine eNd values from all of the world's paleo-oceans need to be averaged, which requires far more data than is currently available. For example, modern oceans exhibit a range of average eNd values between -12 and -3, which is too great to be of use in constraining the integrated average eSr of all global rivers. Newer marine eNd data are indeed available for the early Cambrian Period and Early Paleozoic (e.g. Felitsyn et al., 2002; Wright et al., 2002) and could possibly be used to reconstruct riverine eSr. Felitsyn et al. (2002) constrain the average eNd value of the Early Cambrian (530-510 Ma) to -8, which is similar to the constraints of Keto and Jacobsen (1987; 1988) used in Jacobsen (1988) and subsequent publications (e.g. Asmerom et al., 1991), and so would not greatly change the conclusions of those studies or the major trend in my figure 1b. Secondly, the assumption that average seawater eNd is equal to average riverine eNd, assumes an equivalence of fluxes across a wide range of isotopic compositions, and is only broadly demonstrated in the study of Goldstein and Jacobsen (1987) as the relevant fields barely overlap. I am unaware of the current state of this field, and will endeavour to find newer data on this subject. Thirdly, more recent estimates of riverine ⁸⁷Sr/⁸⁶Sr input (currently 0.7124 as opposed to 0.7101 in 1987) and average marine eNd do not fit the linear correlation (eSr in rivers = -6.44.eNd in rivers + 31.2) of Goldstein and Jacobsen (1987).

Jacobsen (1988) considers the Pan-African orogeny of continent-continent collision to have been responsible for the rise in seawater $^{87}\text{Sr}/^{86}\text{Sr}$ and this early mention of this connection will be mentioned in any revised manuscript.

The reviewer's main problem is that I have greatly simplified the silicate riverine source, while "justifiably" complicating the picture by dividing the riverine component into carbonate and silicate weathering components and I accept the point. If nothing else comes of this contribution, I think it necessary to point out that the carbonate and silicate weathering components need to be treated separately when looking back at the paleo-seawater curve. The reasons for this are 1) that the carbonate component is likely always to be much younger and less radiogenic than the silicate component; 2) carbonate rocks more easily soluble and exceptionally Sr-rich; the idealized isotopic composition of carbonates has evolved predictably through time; and 4) carbonate weathering is less susceptible to changes in erosion rate as carbonate rocks undergo acidic dissolution underground as well as on the Earth's surface (Berner, 2004), thus buffering seawater $^{87}\text{Sr}/^{86}\text{Sr}$ during periods of low erosion and supercontinent existence. Nevertheless, although the carbonate component is the dominant Sr-bearing component in rivers, the isotopic composition of the silicate component is certainly more variable and so changes in the age and origin of material undergoing weathering may have exerted an inordinate influence on seawater $^{87}\text{Sr}/^{86}\text{Sr}$ trends as pointed out in the review. For the first-order trend of the Phanerozoic seawater Sr isotope curve to have been caused by changes to the isotopic composition of the riverine silicate input, the $^{87}\text{Sr}/^{86}\text{Sr}$ of silicate minerals undergoing weathering would need to have been significantly higher than today during the Cambrian Period (>0.720) because of the lower $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of the hydrothermal and carbonate weathering components at that time. Similarly, the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of silicate minerals undergoing weathering must have been considerably lower than today during the mid-Paleozoic. Initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratios for shales (Goldstein, 1988) are consistently lower than 0.720 throughout the Phanerozoic shale record, and average 0.715 during the Cambrian Period of elevated seawater $^{87}\text{Sr}/^{86}\text{Sr}$, which is consistent with the RRS curve in Figure

1. This coincidence will be mentioned now in any revised text. Of course, more data are required to settle this issue, and there are almost certainly more recent data relevant to this question. Certainly, more discussion on this topic can be added to the paper, including discussion of the possibility that the first-order trends are also composition-dependent using the above constraints as a thread. In this regard, I note that Bluth and Kump (1991) consider the strong possibility that the distribution of rock-types is largely monotonic with apparent trends towards decreasing shield area exposed to weathering caused by the greater resistance to erosion of old shield lithologies.

Reviewer: I would therefore add a fifth factor to the author's list of potential drivers of variations in the marine Sr isotope record (page 75 lines 20-25): fluctuating Sr isotope composition of the continental runoff. If the author had made allowance for such variations it is unclear to me whether the conclusions were the same.

Author: I am unclear as to the meaning of the reviewer here. Surely, this is covered under point 1 of the list. This is clearly one of the possibilities mentioned in the text, but is dismissed as the major influencing factor because of the correlation of the Sr isotope peak with global tectonics (CO₂ outgassing rates should be discussed in this context in any revised version), the seawater sulphur isotope record and terrestrial biotic evolution. Even if my arguments are not accepted, the normalized curve in figure 1b (relative influence of continental weathering on ocean composition) can still be interpreted as reflecting changing isotopic composition of runoff or a combination of such changes with an increased weathering flux.

Reviewer: However, the conclusion reached at the end of the paragraph (page 73, lines 1-3; if RRS Sr isotope composition is constant the major features of the normalized curve are preserved) is true only if the RRS and RR curves are monotonically increasing.

Author: If RRS is kept constant, it cannot at the same time be increasing as the reviewer states above so this is perhaps a typo. The point here is that if RRS is held

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constant, then RR will still increase monotonically because 1) RRC is increasing in response to increasing seawater $87\text{Sr}/86\text{Sr}$ and 2) RRC exerts a considerable influence on RR. I agree though with the overall thrust of these comments that the alternative possibility of non-ideal RRS needs to be stated more clearly.

Additional points by Peucker-Ehrenbrink: 1) Reviewer: While Rowley (2002) found little significant variations in ocean crust production, other investigators disagree with his interpretation. A recent Eos (86, 37, 335, 2005) report on a meeting on seafloor spreading, sea level, and ocean chemistry changes summarizes the state of the art. Two recent papers reconstruct rates that are different than those calculated by Rowley for the past 50 Myr for which the data is most reliable (Cogne & Humler, 2006; Conrad & Lithgow-Bertelloni, 2007). I think the statement in the introduction needs to reflect the uncertain nature of this important flux in the geologic past, particularly prior to 50 Ma.

Author: Cogné & Humler (2006) do indeed come to different conclusions to Rowley (2002) over relatively short-time scales; however, one of their main conclusions was that “the average rate of spreading [has been] constant since [about] 125 Ma”. Their study will now be cited in the text. The Conrad and Lithgow-Bertelloni (2007) study also draws attention to relatively short-term changes in seafloor-spreading rates, but estimated variations lie within a quite narrow range of +/- 20% which cannot explain first- or even second-order changes in seawater $87\text{Sr}/86\text{Sr}$ on their own. The lack of direct constraints on seafloor spreading rates prior to 180 Ma will be expressly stated in any revised text.

2) Reviewer: The role of land plants in silicate weathering is not as firmly established as the author states (page 74, lines 23-25), because the effects of increased soil pCO_2 , production of organic acids, and water retention have to be balanced against the slope stabilizing effect of a vegetation cover. As there is a significant positive correlation between physical erosion and chemical weathering (Gaillardet et al., 1999) it is not clear to me that lack of vegetation corresponds to less silicate weathering (see Drever,

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1994; Boucot & Gray, 2001).

Author: That vascular plants increased weathering efficiency seems to me to be self evident, and plenty of good reason for this are given in the literature (e.g. Berner, 2004). There seems to be little dispute in the literature that plants accelerate weathering. Drever (1994) concluded that the direct effect on the weathering of silicate rocks was “probably less than an order or magnitude” but with indirect physical and geographic effects being of even greater significance. Likewise, Boucot and Gray (2001)’s comprehensive review of pre-vascular land plants and bacteria does not dispute the acceleratory effect that land biota exerts on weathering rates. They do dispute, however, that the evolution of vascular (tracheophyte) land plants had as great an effect as generally accepted. On page 79, Boucot and Gray state that “each new innovation in the microbial soil community resulted in greater biotic enhancement of weathering, culminating in the rhizosphere”. It seems fairly certain that those authors would agree to the general assertion that the Proterozoic-Phanerozoic interval of eukaryotic innovation (Heckman et al., 2001; Yuan et al., 2005) would have led to major increases in the efficiency of chemical weathering as stated in the text and literature (e.g. Lenton and Watson, 2004; Kennedy et al., 2006). With regard to the Devonian ‘green revolution’, the roots of vascular plants clearly reach deeper than bryophytes, lichens and fungi. Simply by virtue of their more rapid growth and sheer size, vascular plants aid in both physical and chemical weathering (Berner, 2004). The quantitative effect of trees, relative to mosses and lichens, on rates of weathering has been estimated in field experiments (e.g. Moulton et al., 2001), showing an acceleration of weathering of at least 3x over non-tracheophytes (Berner et al., 2003; Berner, 2004).

3) Reviewer: The average detrital silicate component in modern rivers of 0.7178±0.0014 (Bickle, 1994) is identical to the GLOSS average of 0.7173 (Plank & Langmuir, 1998), but the spread is very large (0.703 to 0.77), leaving open the possibility (and I think likelihood) of significant variations through the Phanerozoic. It is important to stress that silicate weathering delivers radiogenic as well as unradiogenic

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(e.g., Iceland) Sr to the oceans.

Author: I think that this is a valid point and this large spread will now be explicitly referred to in any new version of the text. At present though there are few options available to constrain changes to the isotopic composition of this flux. Previous work suggests that the Sr isotopic composition of the globally integrated detrital erosion flux may not have changed greatly or even increased slightly throughout the Phanerozoic (Goldstein, 1988). The Plank and Langmuir (1998) value is now also cited in the text.

4) Reviewer: The link between Sr and P is not only dependent on P input from rivers, but also on atmospheric inputs (presently ~6-33% of the river input, but potentially more important during drier “super-continent” periods), and intra-oceanic recycling (pages 77-78). I do not think we know the workings of the P cycle in the geologic past well enough to link enhanced P preservation unequivocally to enhanced chemical weathering on the continents (e.g. review by Benitez-Nelson, 2000).

Author: The link between Sr and P is weaker in the case of atmospheric inputs because only a small fraction of detrital wind-blown material will be soluble in seawater. Very little is yet known about windblown P, but it is conceivable that a large proportion derives from soil materials anyway. This last statement is undoubtedly true; however, the Proterozoic-Phanerozoic global acme in phosphorite deposition was clearly anomalous by the standards of Earth history, as was the approximately contemporaneous deposition of black shales worldwide preserving soft-bodied animal parts in anoxic basins across the world. Combined with the uniquely high seawater $\delta^{34}\text{S}$ values of this time, the argument would appear to be quite strong that there is a connection with continental weathering of nutrients.

5) Reviewer: The paleogeographic arguments made on page 76 (lines 16-30) should include variations in continental runoff (e.g. Tardy et al., 1989; Donnadieu et al., 2006) that may have led to changes in the flux of Sr, though the correlation between runoff and Sr flux hasn't been established.

Author: The Donnadiou et al. (2006) study will now be added to the text and runoff used as an additional argument for connections between supercontinent break-up and elevated rates of weathering.

Author: Finally, Peucker-Ehrenbrink mentions that although important, carbonate weathering alone cannot cause seawater $87\text{Sr}/86\text{Sr}$ to increase. This is true. However, decreases in carbonate relative to silicate weathering rates (by terrestrial biota innovations, pCO_2 changes or supercontinent disintegration) diminish the buffering effect that carbonate weathering exerts on seawater $87\text{Sr}/86\text{Sr}$, thus allowing seawater $87\text{Sr}/86\text{Sr}$ to rise more rapidly and reach higher values, and changing the baseline for future seawater $87\text{Sr}/86\text{Sr}$ changes. This possibility could be added to any new version of the text.

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