

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

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Godderis makes three points in his review which I will briefly address here before amending my contribution accordingly.

Firstly, Godderis is correct to state that the isotopic ratios of continental and silicate rocks being weathered did not evolve linearly through time. In this regard, my normalised curve is only meant to be a basis for discussion rather than a complete interpretation. This point was already partly addressed in my response to Peucker-Ehrenbrinck, although Godderis mentions in addition that the $^{87}\text{Sr}/^{86}\text{Sr}$ of the carbonate component is also likely to have undergone a more complex evolution, citing the example of the Himalayan marbles, which are considerably more radiogenic than their

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sedimentary precursors. This point is an important one, and it would certainly be more realistic to divide up the carbonate weathering component still further by separating sedimentary from metamorphic carbonate rocks. I wonder whether this has been done at least for the present? This point and the studies mentioned by Godderis need clearly to be cited in any future version. The assumption made by most authors, including myself, is that the integrated $87\text{Sr}/86\text{Sr}$ composition of carbonates undergoing weathering today is a weighted average of past seawater $87\text{Sr}/86\text{Sr}$ (weighted towards the more recent Phanerozoic sedimentary record), i.e. approximately 0.708. I know of no better estimate at present for this parameter although this value must be an underestimate because carbonate minerals incorporate radiogenic Sr during recrystallisation either during diagenesis or metamorphism. However, as the Himalayan marble example shows, the genuine value would inevitably be higher than 0.708, thus implying an even greater relative contribution from carbonate weathering to seawater! This point was already made in the paper and further emphasises the importance of constraining the effects of changing carbonate weathering fluxes on seawater $87\text{Sr}/86\text{Sr}$. With regard to the Cenozoic rise in seawater $87\text{Sr}/86\text{Sr}$, I concede that the jury is out. However, my paper deals primarily with first-order shifts over much longer time intervals than are relevant to the Himalayan orogen. It seems to me unlikely that relatively short-lived collisional episodes can cause first-order trends in seawater $87\text{Sr}/86\text{Sr}$ (although they can affect the base-line curve - see comment below). Comparison of the Himalayan example with other such events from the geological record such as the late Palaeozoic collision to form the Ural Mountains during a time of low seawater $87\text{Sr}/86\text{Sr}$ suggest that such events may only be of secondary importance. In any new version of the manuscript, I propose to discuss the Cenozoic example, citing the studies mentioned by Godderis, and compare briefly the effects of the Himalayan collision with the effects of similar collisional events in Earth history.

On a related issue, because the Himalayan orogen does indeed increase seawater $87\text{Sr}/86\text{Sr}$ and thus raises the isotopic composition of the future carbonate weathering component to seawater, such events can indeed contribute to trends in the baseline

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seawater $87\text{Sr}/86\text{Sr}$ value. This can be seen in the shift in the $87\text{Sr}/86\text{Sr}$ baseline between the Proterozoic (0.704) and the Phanerozoic (0.707), both of which correspond to the estimated $87\text{Sr}/86\text{Sr}$ ratio of the carbonate weathering component during those parts of Earth history, respectively.

The second point in Godderis' review concerns the current debate over the impact of vegetation on continental weathering. Berner (2004) supports the thesis that vascular land plants are more efficient at drawing down atmospheric CO_2 through chemical weathering than non-vascular land plants such as bryophytes, lichen or bacteria alone. Both reviewers, however, find themselves at odds with this and my interpretation. According to the current paradigm (Berner), the introduction of land plants helped to decrease atmospheric CO_2 levels by increasing weathering efficiency; however, overall silicate weathering rates are ultimately constrained by CO_2 outgassing rates and so this need not have impacted seawater $87\text{Sr}/86\text{Sr}$. By contrast, land colonisation during the late Neoproterozoic and Cambrian was accompanied by a significant long-term rise in seawater $87\text{Sr}/86\text{Sr}$. The major factor in increasing overall chemical weathering rates at this time was probably not greater weathering efficiency, but instead rising outgassing rates resulting from metamorphism and collisional tectonics. This aspect was mentioned only briefly in the original version, but will be expanded upon in any future version as it needs emphasising. On a more general note, although I fully accept the complexities of regional weathering dynamics and their controls, about which I am hardly competent to comment, it is clear that silicate weathering efficiency must have increased over geological time if we are to accept the general paradigm that atmospheric $p\text{CO}_2$ has decreased throughout Earth history. This is because the weathering CO_2 sink needs to balance out the outgassing source, while this sink clearly requires greater efficiency at lower $p\text{CO}_2$ than at higher $p\text{CO}_2$. It appears plausible to me that CO_2 -sequestration strategies, evolved during times of CO_2 crisis, such as the mid-Neoproterozoic-Cambrian (lichen and land plants), mid-Palaeozoic (vascular land plants) and Cenozoic (C-4 plants), helped to enhance weathering efficiency during such times. Subsequently, these strategies would have led to higher overall weathering

rates during times of greater CO₂ outgassing, such as during major tectonic upheaval such as during the late Neoproterozoic and Cambrian. In this way, they helped to limit the upper limits of atmospheric CO₂ to ever lower levels.

The third point is mirrored by a comment of mine that is already in the paper but can be expanded upon. That is to say, if weathering increases then the river sulphur flux from weathered pyrite will also increase thus helping to lower seawater d₃₄S. However, neither the weathering nor the volcanogenic S flux provides sulphur with a d₃₄S value anywhere close to seawater during times of high d₃₄S such as the Cambrian Period. Therefore, seawater d₃₄S does not reflect a mixture of the different sources of S but is largely controlled by the fractionation of S isotopes during biogenic sulphate reduction. Although peaks in seawater d₃₄S could conceivably be produced by decreasing the weathering flux but increasing isotopic fractionation during times of high d₃₄S there is no evidence for this. High d₃₄S during periods of tectonic upheaval such as during the Cambrian Period of high ⁸⁷Sr/⁸⁶Sr, and low d₃₄S during periods of supercontinent existence such as during the Permian Period of low ⁸⁷Sr/⁸⁶Sr, argue for a systematic relationship between S and erosion, which is not directly related to pyrite weathering as suggested by Godderis because this would lead to the opposite relationship, e.g. low d₃₄S during the Cambrian Period of high erosion, for instance. Instead, it appears to me more plausible that the high d₃₄S values of the Cambrian were caused by a relative acme in pyrite burial (relative to the influence of volcanogenic and mantle S input). I agree wholeheartedly though that more modelling needs to be done of the S cycle to constrain its influences further. This will also help us in our quest to explain the Sr cycle!

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