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Non-uniqueness and interpretation of the seawater $^{87}Sr/^{86}Sr$ curve

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Abstract

Variations in the seawater $^{87}Sr/^{86}Sr$ curve through time can be caused by fluctuations in the strontium flux or variations in the isotopic ratio from at least six different sources and sinks. Thus, 12 or more parameters control each single measurement although widely accepted assumptions allow this to be reduced to typically six unknowns. Interpreting the causes of time-variation in the seawater $^{87}Sr/^{86}Sr$ curve is therefore hampered by inherent non-uniqueness. However, this problem is under-constrained rather than unconstrained. As a result, whilst there are an infinite number of possible interpretations, these all come from a few families of very similar solutions. Using this insight, it is possible to find solutions having the smallest possible variations in source flux or source $^{87}Sr/^{86}Sr$ ratio. Thus, lower-bounds can be placed upon the source variations responsible for the observed fluctuations in the seawater $^{87}Sr/^{86}Sr$ curve. When applied to the evolution of the Early Jurassic $^{87}Sr/^{86}Sr$ seawater curve, this approach demonstrates that a short-lived Toarcian event is genuine since it is present in all models, regardless of the values chosen for the unknown source fluxes and unknown source isotope ratios. However, the variations in strontium flux or isotopic ratio necessary to explain the Toarcian event may be significantly smaller than would be predicted assuming modern values for the unknown parameters.

1. Introduction

Interpretation of the variation in the seawater strontium isotope ratio with time is important in many studies of the ancient Earth system (e.g., Brass, 1976; Hodell et al., 1989, 1990, 1991; Berner and Rye, 1992; Françoise and Walker, 1992; Veizer et al., 1997, 1999; Pálfy and Smith, 2000; Jones and Jenkyns, 2001; Wallmann, 2001). However, a fundamental difficulty is that this ratio is controlled by a large number of time-varying factors and so a unique interpretation is not possible. However, it is not true to say that this problem is completely unconstrained. Although, there are an infinite number of ways to interpret the data, all solutions have properties in common and, as we show in this paper, it is possible to find the minimum variation in any given parameter that could have produced the observed seawater strontium isotope curve.

The application of strontium isotope ($^{87}Sr/^{86}Sr$) stratigraphy to the geological record has been extensive. Most of these studies have focused on the more recent past, particularly the Cenozoic (DePaolo and Ingram, 1985; Koepnick et al., 1985; Palmer and Elderfield, 1985; Clemens et al., 1993; Sugarman et al., 1997; Martin et al., 1999). However, over the past decade many studies have looked in particular at the Cretaceous period (McArthur et al., 1992, 1993, 1994; McLaughlin et al., 1995; Jenkyns et al., 1995; Bralower et al., 1997; Crame et al., 1999), which has been made possible with the recovery of well-preserved carbonate and microfossils from ODP cores. An increasing number of studies recently have been aimed at constructing the Jurassic portion of this curve (Koepnick et al., 1990; Jones, 1992; Jones et al., 1994a,b; Podlaha et al., 1998; McArthur et al., 2000; Hesselbo et al., 2002; Jenkyns et al., 2002; Price and Gröcke, 2002; Gröcke et al., 2003; Hall et al., 2004).

The seawater $^{87}Sr/^{86}Sr$ curve has therefore been reasonably well reconstructed but interpretation of the results is hampered by non-uniqueness, i.e., there is more than one

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sequence of events capable of reproducing the observed isotope variations. The under-determined nature of this problem is well illustrated by Françoise and Walker (1992) who discuss six different sources and sinks for strontium, namely:

1. Weathering of old igneous rocks ($^{87}Sr/^{86}Sr \sim 0.718$).
2. Weathering of young igneous rocks ($^{87}Sr/^{86}Sr \sim 0.705$).
3. Weathering of sedimentary rocks ($^{87}Sr/^{86}Sr \sim 0.708$).
4. Fluid exchange between the ocean and seafloor hydrothermal systems ($^{87}Sr/^{86}Sr \sim 0.703$).
5. Alteration of buried sediments by diagenetic fluids and expulsion of these into the oceans ($^{87}Sr/^{86}Sr \sim 0.708$).
6. Incorporation of oceanic strontium into carbonate sediments.

Each of these sources and sinks has an associated time-varying flux and time-varying isotope ratio and hence, for each moment in time, there are at least a dozen unknown factors and only a single measurement (i.e., the palaeo-seawater $^{87}Sr/^{86}Sr$ value).

There are several possible strategies for resolving this difficulty although none are completely satisfactory:

1. Many of the individual fluxes can be grouped together into a single flux. In particular, many authors group all of the weathering fluxes into a single riverine flux with a time-varying $^{87}Sr/^{86}Sr$ value controlled by the relative contributions of the three weathering-related sources (e.g., Palmer and Elderfield, 1985; Françoise and Walker, 1992; Jones and Jenkyns, 2001). We will also use this tactic in this paper.
2. The strontium isotope system can be assumed to be close to equilibrium at all times (Hodell et al., 1989; Berner and Rye, 1992). This implies that the sources and sinks balance, i.e., there is an additional constraint. In this paper, we will assume that a balance between sources and sinks occurs but only when fluxes are averaged over time periods long compared to the strontium residence time in the oceans. Thus, we allow the system to be out of equilibrium on short time scales.
3. Some of the unknown parameters can be linked to other, hopefully better-constrained processes, for example the weathering rate (and hence, the riverene flux) can be related to atmospheric CO_2 concentrations (e.g., Françoise and Walker, 1992; Wallmann, 2001). Although this is a very useful strategy, we will not use similar constraints here.
4. Educated guesses can be made concerning some of the unknown parameters, for example, present-day values can be assumed (Hodell et al., 1990). Alternatively, a number of solutions can be produced using educated guesses about likely ranges of controlling parameters (Jones and Jenkyns, 2001). We adopt a similar strategy in this paper except that we aim to investigate all possible solutions given such ranges rather than just a few examples.

These assumptions restrict the range of solutions but leave an infinite number of solutions within that range. The key new factor in our approach is that we find an approximate general form for all possible solutions to the problem. It is then a simple matter to find a specific solution having the smallest possible parameter variation with time. Thus, we can calculate lower-bounds for the time-variations in fluxes and/or isotope ratios. In addition, because we know how all solutions are related to each other, we can confidently extend conclusions based upon a single solution to the set of all solutions. In other words, this is mathematically much more rigorous than the frequently used approach of guessing reasonable values for the unknown parameters and then hoping, without real justification, that firm conclusions can be extrapolated from this one case (or even a limited range of cases).

2. The Early Jurassic seawater strontium isotope curve

The dataset we use (Fig. 1) is based upon a compilation given by Jenkyns et al. (2002). The stratigraphic resolution of these data is generally better than one ammonite subzone (i.e., about 200 kyr) and, in places, is constrained by intense sampling of belemnites giving it a resolution as high as 40 kyr. However, McArthur et al. (2000) have suggested that portions of the curve may have significantly greater time uncertainties, perhaps as great as 0.25 Myr.

In this paper, we concentrate upon a specific event in the Jurassic, namely a sharp rise in the seawater $^{87}Sr/^{86}Sr$ value at around 182 Ma. This rise has been discussed by Pálfy and Smith (2000) who note that it coincides with the emplacement of a large igneous province in Gondwana (Ferrar–Karoo). This event coincides with a minor extinction event and the global distribution of organic-rich black shales associated with the Toarcian oceanic anoxic event (see Jenkyns et al., 2002). Pálfy and Smith (2000) explain these events through an abrupt and short-lived increase in weathering rate resulting from volcanically enhanced greenhouse warming. However, it is possible that the observed rise in the $^{87}Sr/^{86}Sr$ curve results from long-term, gradual changes in conditions rather than from a short, sharp event. The methods developed here allow us to put lower-bounds, on the change in weathering rates, etc., necessary to produce the observed rise in the $^{87}Sr/^{86}Sr$ curve thus allowing us to eliminate this ‘‘null hypothesis.’’

3. Preprocessing of the data

The application of strontium isotope ($^{87}Sr/^{86}Sr$) stratigraphy to the geological record becomes more straightforward if a representative smooth curve is constructed through the raw data. Many different methods can be used to generate such a curve (e.g., LOWESS, McArthur et al. (2001)), but the smooth curve in Fig. 1 was generated by fitting a linear regression through successive groups of 29 points (i.e., 14 points either side of a central point).