

Radiogenic isotopes and rare earth elements as tracers in the oceans

H. Elderfield
Department of Earth Sciences
University of Cambridge, England

ABSTRACT

The rare earth elements and $^{87}\text{Sr}/^{86}\text{Sr}$ and $^{143}\text{Nd}/^{144}\text{Nd}$ ratios can be used as source and reactivity tracers to provide information on mantle and crustal sources of elements to the oceans and on their participation in marine geochemical cycling.

INTRODUCTION

It is fundamental to marine geochemistry to know the contributions made to the composition of sea water by the two major sources of elements (continental and oceanic crust) and to understand the processes that facilitate the passage of elements through and within the oceans. Studies of the marine geochemistry of radiogenic isotopes and rare earth elements (REE) offer an important insight to these fundamental problems. The REE have been used extensively for studying the origin of marine deposits (e.g. Bender et al. 1971; Piper 1974; Elderfield et al. 1981), but, until recently, only limited data were available on their concentrations and distributions in sea water (Goldberg et al. 1963; Hogdahl et al. 1968). Some studies of marine radiogenic isotope geochemistry had been carried out (e.g. Chow and Patterson 1962; Dasch 1969; Peterman et al. 1970; Hawkesworth and Elderfield 1978) but the potential of radiogenic isotope studies in oceanography is only now being realized (e.g. Piepgras and Wasserburg 1983).

Some of the early work also considered the use of REE and radiogenic isotopes in

palaeo-oceanography. The most substantial contribution has been that of assessing variations in the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of sea water through time (Peterman et al. 1970; Viezer and Compston 1974; Brass 1976; Spooner 1967). Work using rare earths (Fryer 1977) was based on extreme assumptions which have been shown to be invalid (Graf 1978).

BASIC PRINCIPLES

The rare earth elements

The usefulness of the REE in studies of marine geochemistry can be recognised from their chemical properties. They are an extremely coherent group (predominantly sharing the 3+ oxidation state, they exhibit systematically decreasing ionic radii with increasing atomic number and share the same outer electronic configuration); yet important subtleties are imposed upon this broad picture of chemical similarity: two of the REE exhibit dual oxidation states in the natural environment (Ce as 3+ and 4+; Eu as 2+ and 3+) and there is a monotonic variation in the stabilities of REE complexes within the series.

Their intrinsic chemical coherence pre-

vents *extensive* fractionation of one rare earth from another, and so their relative abundances give some indication of the nature of their ultimate source. The relative amounts of the REE differ in continental rocks and in oceanic crust, producing characteristic "REE patterns"¹⁾ for different source materials. The patterns shown by sea waters reflect the mixing of REE from each source plus the impact of fractionation processes by which the REE are removed from sea water into authigenic phases. The power of REE studies is that the subtleties of their chemistry can be exploited to understand such fractionation processes. The multiple oxidation states of Ce and Eu provide a means of understanding redox related reactions. For example, the most common REE pattern for sea water shows a negative Ce anomaly, reflecting oxidation of cerium in sea water and fractionation from the other REE. Differences in stability constants of light (e.g. La) and heavy (e.g. Yb) rare earths can be used to understand particle scavenging processes in the oceans. For example, the REE pattern for sea water normalized against average continental rocks shows a depletion in the light REE because the weaker stabilities of their complexes with ligands in sea water lead to greater reactivity and removal from sea water than for the heavy REE.

Radiogenic isotopes

Whilst the reactivities of elements often can be inferred from the form of their distributions within the oceans, the contributions from different sources are, however, extremely difficult to recognize except in regions close to inputs (e.g. Mn in hydrothermal plumes). The REE are exceptional in

this respect because of the use of REE patterns.

It is in view of this difficulty in evaluating sources from elemental analyses that radiogenic isotope studies offer such great promise. The method relies on the observation that the continental crust has developed with significant fractionation of Rb/Sr, Sm/Nd and U/Pb relative to ocean crust. Rb, Sm and U all have long-lived ($t_{1/2} \sim 10^9 - 10^{11}$ yrs) isotopes that decay to ^{87}Sr , ^{143}Nd and ^{207}Pb and ^{206}Pb , respectively. Therefore, it follows that the isotopic compositions of Sr ($^{87}\text{Sr}/^{86}\text{Sr}$), Nd ($^{143}\text{Nd}/^{144}\text{Nd}$) and Pb ($^{207}\text{Pb}/^{204}\text{Pb}$, $^{206}\text{Pb}/^{204}\text{Pb}$) can be used to determine the relative importance of the different sources. The impact of the sources for each element on ocean chemistry is affected by its reactivity in sea water. The bonus of the method is that these three elements span a wide range in oceanic reactivities, from 10^6 yrs residence time for Sr to $10^0 - 10^2$ yrs for Pb. Thus, their degrees of isotopic homogeneity in the oceans differ substantially allowing consideration of the ultimate sources of elements dispersed widely in the oceans and also of local input and mixing effects in individual ocean basins.

SUMMARY OF RESULTS

Rare earth elements and Nd isotopes in sea water

An understanding of the marine cycles of elements has been gained from several approaches such as calculating residence times of elements as guides to their reactivity, by measuring radioactive isotopes in sea water to compute scavenging rates of metals, from direct flux measurements of elements and isotopes using sediment traps, from accumulation rates of metals in oceanic sediments. However, our understanding of ocean chemistry has undergone a "quantum leap" (Bruland 1983) in the last 8 years because of the successful measurements of

¹⁾ To smoothe out natural odd-even effects of REE abundance it is usual to normalize to a standard (shale, chondrite) on an element-by-element basis and plot the concentration ratios on a logarithmic scale as a function of atomic number.

vertical concentration profiles in sea water of a number of trace elements. Significant technical advances have revealed that many elements show wide but "oceanographically consistent" (Boyle et al. 1977) variations in concentrations (often at much lower levels than previously thought) that may be interpreted to give direct evidence of geochemical cycles within the oceans.

In recent work, the first complete sets of REE profiles and REE patterns for nine rare earths (La, Ce, Nd, Sm, Eu, Gd, Dy, Er, Yb) in sea water, in the Atlantic (Elderfield and Greaves 1982) and Pacific (Klinkhammer et al. 1983) oceans have been produced. Depth gradients of the REE demonstrate that they are involved in both active scavenging and regeneration within the oceans, the light REE more susceptible to scavenging and the heavy REE more susceptible to regeneration. The results constrain the residence times of the REE to about 400 years (shorter for the light REE and longer for the heavy REE). This is an important conclusion because the residence times are shorter than the ocean mixing times, and this means that REE patterns in sea water retain a signal related to their sources. Indeed, it has been possible to demonstrate that Mediterranean outflow water in the Atlantic has a very distinct REE pattern and can be distinguished from adjacent waters (Elderfield and Greaves 1982). De Baar et al. (1983) have also reported REE profiles for the Atlantic, supporting the ideas expressed by Elderfield and Greaves (1982) and adding important new data for the elements Pr, Tb, Ho, Tm and Lu.

Complementary work on Nd isotopes in ocean waters has shown that different ocean basins are characterized by different $^{143}\text{Nd}/^{144}\text{Nd}$ ratios (Piepgras and Wassenburg 1980) and that Mediterranean water flowing into the Atlantic has a distinct Nd isotopic composition (Piepgras and Wassenburg 1983). Thus, the REE and Nd isotope

studies show compatible results and each strengthens the conclusion of the other.

Another approach has been to measure $^{143}\text{Nd}/^{144}\text{Nd}$ in sea water by proxy using biogenic carbonate from core top samples. Results have shown that the Atlantic is not isotopically homogeneous for Nd but that distinct Nd isotope "provinces" exist within the ocean that correlate with provinces of Pb and aluminosilicate Sr (Palmer and Elderfield 1985a).

Sr/Ca and $^{87}\text{Sr}/^{86}\text{Sr}$ ratios

Because of its long oceanic residence time, there is no observable variability in the isotopic composition of Sr in sea water, apart from in regions very close to its sources. Similarly, variations in the concentrations of Sr (Sr/salinity or Sr/Ca) are small (see Brass and Turekian 1972). Therefore, most interest has centred on an evaluation of the factors that define the abundance and isotopic composition of Sr in sea water and the extent to which these have varied through time.

The dominant source of Sr to the oceans is rivers and the only major sink is calcium carbonate (Brass 1976). The Ca in limestones also comes from rivers plus a significant amount from hydrothermal activity (Edmond et al. 1981). Therefore, it would seem possible to investigate the competition between river and hydrothermal fluxes and see how they have varied through time from examination of the Sr/Ca ratios of marine carbonates. (In fact, a significant source of Sr to sea water is from carbonate diagenesis, but this can easily be corrected for.) This has been done in a very careful study by Graham et al. (1982) which showed that there have been small but significant changes in Sr/Ca ratios at certain times, for example since the middle Miocene. Unfortunately, it is not possible to unequivocally interpret the data because the Sr/Ca ratio also is related to basin/shelf fractionation. Calcium carbonate deposited

on shelves as aragonite contains much more Sr than that deposited in ocean basins as calcite.

However, factors involving mass fluxes out of sea water are not important if the isotopic composition of Sr is considered. The $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of present-day sea water is close to 0.7092 and is defined by the mixing of Sr from three sources: a) hydrothermal (mantle) Sr. Although there is no Sr mass transfer at ocean ridges, Sr isotopic exchange does occur (Albarede et al. 1981; Elderfield and Greaves 1981). Sea water enters mid-ocean-ridge hydrothermal systems with a $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of 0.7092 but leaves the systems with ratios of 0.703–0.704. b) limestone Sr. Strontium is added to the oceans from weathering of uplifted limestones and as a consequence of marine diagenesis of carbonates. In both cases, the effect is to recycle sea water Sr and thus buffer otherwise extreme variations from a) and c). The recycling of limestones has a mass half time of the order of 100 million years (possibly shorter) which therefore recycles 100 myr old sea water. Sr released by carbonate diagenesis has an isotopic composition equivalent to that of 20 myr old sea water. c) continental crust Sr. This has an average ratio of about 0.716. This is mixed with limestone Sr such that river water has a $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of approximately 0.711.

An oceanic mass balance for Sr isotopes can be constructed and although there is some uncertainty about the magnitude of isotopic exchange at ocean ridges it is possible to conclude that both hydrothermal exchange and carbonate recycling are dominant factors in defining the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of sea water. However, the fluctuations in this ratio through time (see Burke et al. 1982) appear to be caused by variations in the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of Sr derived from silicate weathering (Palmer and Elderfield 1985b).

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