NEODYMIUM, STRONTIUM, OXYGEN AND HYDROGEN ISOTOPE COMPOSITIONS OF WATERS IN PRESENT AND PAST OCEANS: A REVIEW

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Knowledge of the isotopic compositions of trace elements dissolved in present and ancient sea waters is important for the following reasons.

1) Sea water integrates dissolved elements from continents, which are supplied by rivers, ground waters, terrigenous sediment particles, hydrothermal activities in oceans, submarine weathering of the oceanic crust, and diagenesis of sediments. As the isotopic compositions of some of the dissolved elements in these different sources are sufficiently varied, the isotopic signatures of the analyzed elements in the sea water may provide insight to the inventory of the elements present in sea water.

2) Any intra-oceanic variation in the isotopic compositions

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may provide clues to the presence of major current systems within ocean basins.

3) Erosional history of the continent may be further understood from information on temporal variations in the isotopic compositions.

4) Quantification of isotopic composition of se water through geologic time is important for utilization of the time-trend isotopic change in problems of stratigraphy, origin of subsurface waters, water-rock interactions, and paleothermometry.

In this review article, we discuss only about the isotope compositions of Sr, Nd, O and H of present-day and ancient sea waters. Discussions on other isotopes such as S and C, have been given elsewhere in this book.

RECENT SEA WATER

Strontium Isotopes

Strontium occurs as a trace element in sea water with concentrations of about 7-8 mg/l. The residence time of Sr in the ocean is about 5×10^6 yrs, which is much longer than one cycle mixing time (about 10^3 yrs) of ocean waters. The $^{87}Sr/^{86}Sr$ ratio of present-day sea water is considered to be nearly uniform at about 0.70922 $\pm$ 0.00002 (Elderfield, 1986). But the uniformity in the Sr isotopic composition should be viewed with caution, as several studies have shown that small but measurable differences in the Sr isotopic values can exist for waters in different parts of oceans (Veizer, this volume). For example, ocean waters close to areas of hydrothermal activities have been found to have much lower values than the one frequently quoted in the literature (Albarède et al., 1981; Clauer and Olafsson, 1981). Submarine thermal spring waters from sea bed of the Florida continental shelf about 45 km south-southwest of Ft. Meyers, Florida, were found to contain 12.9 mg/l Sr with an $^{87}Sr/^{86}Sr$ ratio of 0.70858 $\pm$ 0.00004 (Clauer, unpublished data). Similarly, the Sr isotopic value of some present-day shallow

coastal marine waters have been found to deviate from the presumed uniform marine Sr isotopic value: the Sr isotopic values of bay waters can be different from the norm, as noted by Aberg and Wickman (1987) in their study of waters from the Bothnian Bay of the Baltic Sea which yielded $^{87}Sr/^{86}Sr$ ratios between 0.70935 and 0.70951. Some studies of ancient marine sulfate deposits have also underscored differences in the Sr isotopic compositions of these minerals from their presumed contemporary marine waters, suggesting potential atypical Sr isotopic compositions for ocean water in restricted circulation basins adjacent to continents (Clauer, 1981; Burke et al., 1982; Chaudhuri and Clauer, this volume).

The balance of the sea water $^{87}Sr/^{86}Sr$ ratio was initially thought to be governed largely by the continental weathering which is dominated by fluvial inputs of Sr derived from silicate and marine carbonate rocks (Brass, 1976). Recognition of the alteration of oceanic crust at mid-oceanic ridge areas emphasized the importance of the oceanic hydrothermal activities as a factor governing the Sr isotopic composition of sea water (Clauer, 1976; Spooner, 1976). Strontium isotopic studies of interstitial waters in marine carbonate sediments also established that diagenetic flux of Sr from the carbonate sediments could have some bearing on the Sr isotopic budget of sea water (Elderfield and Gieskes, 1982). Runout or ground water can be an additional source of Sr which can augment the influence of continental Sr flux in the mass balance of the isotopic composition of Sr in sea water (Chaudhuri and Clauer, 1986). Assuming a steady-state condition for Sr in the ocean, Chaudhuri and Clauer presented the following equation for the Sr isotopic mass balance of the modern sea:

$$Sr_{rw}R_{rw} + Sr_{gw}R_{gw} + Sr_{dc}R_{dc} + Sr_{ob}R_{ob} = (Sr_{rw} + Sr_{gw} + Sr_{dc} + Sr_{ob})\ R_{sw}$$

where Sr_{rw} = flux of river Sr (2.21×10^{12} gy^{-1}), R_{rw} = isotope composition of river water (0.7111), Sr_{gw} = flux of ground water Sr (2.10×10^{12} gy^{-1}), R_{gw} = isotope composition of ground water (0.7110), Sr_{dc} = flux of diagenetic carbonate Sr (0.48×10^{12} gy^{-1}), R_{dc} = isotope composition of diagenetic carbonate (0.7084), Sr_{ob} = flux of oceanic basalt Sr (1.26×10^{12} gy^{-1}), R_{ob} = isotope composition of oceanic basalt (0.7029), and R_{sw} = isotope composition of modern sea water

(0.7092). Opinions are still divided as to the magnitude of influence between the crustal and the mantle sources of Sr on the Sr isotopic composition of sea water, as significant differences exist in the various estimates of the isotopic compositions and fluxes of the sources of Sr to the oceans (Veizer, 1989; Palmer and Edmond, 1989). Estimates of axial hydrothermal flux of Sr have ranged between 0.42×10^{12} and 1.36×10^{12} gy^{-1}.

Neodymium Isotopes

Both Nd and Sm occur as trace constituents in sea water respectively with average concentrations of about 2.6×10^{-6} mg/l and 0.5×10^{-6} mg/l. The Sm/Nd ratio of sea water is about 0.20, which is about the same as that of average crustal rocks or of average river suspended load. The residence time of Nd is still in question, as the estimates have ranged from about 300 to 7,100 years (Faure, 1986; Goldstein and Jacobsen, 1988).

The knowledge of the Nd isotopic compositions of ocean waters has come from measurements made either on the waters or on sediments precipitated from these waters, such as Mn nodules, phosphate and carbonate sediments, and others (Piepgras et al., 1979; Piepgras and Wasserburg, 1980, 1982; O'Nions et al., 1978; Clauer et al., 1984; Shaw and Wasserburg, 1985; Grandjean et al., 1987, Stille and Fischer, 1990; Stille et al., 1991, 1992). These results have shown that the major ocean basins differ in their Nd isotopic compositions. For example, the ϵ_{Nd} isotopic values of Atlantic Ocean waters are about -12 ± 2, that of Pacific Ocean waters are about -3 ± 2, and that of Indian Ocean waters are about -8 ± 2. Even within a single ocean basin, measurable differences exist in the Nd isotopic values of the waters. The Nd isotopic differences among the basins or within a basin reflect the differences in the isotopic compositions of the sources of Nd in the sea waters. The high negative ϵ_{Nd} values in general reflect contributions of Nd largely from continental sources, as the present-day oceanic basalts have an average ϵ_{Nd} value of about +10. The difference in the Nd isotopic compositions between Pacific and Atlantic ocean waters, the former being less negative than the latter, can be attributed to relati-

vely young continental crusts surrounding the Pacific Ocean and its increased oceanic volcanic activities which produce rocks with elevated $_{Nd}$ values and the dominance of old continental rocks surrounding the Atlantic Ocean basin.

Any differences in the ϵ_{Nd} values of waters within a basin or between basins can be used to study the origins and exchange between different water masses, which has been demonstrated by Piepgras and Wasserburg (1982). These authors found that the Nd isotopic composition of sea water at the Drake Passage (South America) was between that of Pacific and Atlantic ocean waters, and they calculated that about 70% of Atlantic sea water is involved in the Antarctic Circumpolar Currents. Piepgras and Wasserburg (1980, 1982, 1983) also observed from investigations of water columns in the Atlantic Ocean, the Pacific Ocean, and the Saragasso Sea that the source of REE in the surface water of each ocean is distinct from that of the respective deep waters (Fig. 1). Their studies suggested that the isotopic data may be used to reconstruct circulation patterns and mixing mechanisms within the oceans.

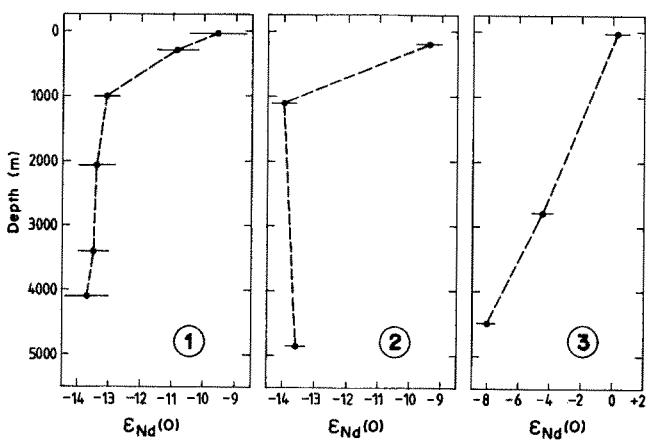

Figure 1: $\epsilon_{Nd}(0)$ as a function of depth in ocean water of Sargasso Sea (1), northwestern Atlantic Ocean (2), and southcentral Pacific Ocean (3) (modified from Piepgras and Wasserburg, 1983)

The Nd isotopic analyses can potentially be useful means of studying basinal flows. This has been demonstrated by Piepgras and Wasserburg (1983) who used the Nd isotopic analyses to study the flows of the water masses into and out of the Mediterranean Sea.

They observed that the Mediterranean outflow causes a shift of more than 2 in the ϵ_{Nd}d value toward more radiogenic Nd at a depth of about 1000 m. The core of the Mediterranean outflow corresponds to an ϵ_{Nd} value of -9.8, whereas the overlying and the underlying waters have $_{Nd}$ values of about -12. The eastern part of the North Atlantic Ocean and the Mediterranean Sea have significantly different Nd isotopic compositions. Based on mass balance calculations, these authors estimated an ϵ_{Nd} value of -6 for the Mediterranean Sea, which agrees well with the value of -7 for biogenic carbonates previously analyzed by Elderfield and Greaves (1982).

The ϵ_{Nd} values of the Mediterranean sea waters are between the more radiogenic values for waters of the Pacific Ocean and the less radiogenic values for waters of the Indian and the Atlantic oceans. Frost et al. (1986) suggested that the Nd isotopic compositions of Mediterranean sea waters probably reflect an influence of the particulate-Nd input rather than of the dissolved-Nd input to the basin. This is in agreement with the results of Elderfield and Greaves (1982) who observed that the surface water layers of the Atlantic Ocean are enriched in REE which led them to suggest the enrichment due to dissolution of the particulate materials delivered to the ocean basin. The idea of dissolution of particles is far from clear, as the enrichment in REE of surface waters is not everywhere evident. For example, Piepgras and Wasserburg (1983) noted Sm and Nd concentrations to increase with increasing nutrient concentrations (PO_4, NO_3, etc.) from surface downward. They suggested that these increases in the elemental contents with depth are induced by progressive increase in the dissolution of particles in the process of settling in deep oceans. Atlantic ocean waters from depths greater than 1000 m have been found with low ϵ_{Nd} values between -13 and -14, as compared to surface waters having ϵ_{Nd} values between -9 and -10. The source of this non-radiogenic Nd component in the bottom water has not yet been clearly identified. Piepgras and Wasserburg (1983) suggested that the low $^{143}Nd/^{144}Nd$ ratios for the deep waters in the Atlantic Ocean are the result of either run-off from Precambrian shields of North America and Asia into the Arctic Ocean by bottom current transport, or REE injection from old components in the deep sea sediments into the overlying water column.

Hydrogen and Oxygen Isotopes

Ocean waters, having their δD and $\delta^{18}O$ values close to zero, are to a small degree spatially varied in their H and O isotope compositions. For example, the $\delta^{18}O$ values of surface waters in large parts of the Atlantic and the Pacific oceans range from about +1.5 to -1.0 per mil. The ^{18}O concentrations also vary with depth, as Craig and Gordon (1965) have shown in their study of Indian Ocean waters pointing to measurable decrease in the concentrations of the heavy isotopes within the upper 1-1.5 km depth, below which the concentration remains unchanged. The average $\delta^{18}O$ contents of deep ocean waters among major basins are varied, ranging from about +0.12 per mil for the North Atlantic, to about -0.17 to -0.21 for the Pacific, to about -0.45 for the Antarctic (Craig and Gordon, 1965). These variations are related to evaporation, precipitation, addition of river water, freezing and melting of ice, and mixing of different water masses.

The H and O isotopic compositions of surface waters of major oceans are approximately linearly related due primarily to the combined effects of evaporation of the surface waters and precipitation of atmospheric moisture. Craig (1965) gave the following relationship for the surface waters of some major oceans:

$$\delta D = m\, \delta^{18}O$$

where m is equal to 7.5 for the North Pacific Ocean, 6.5 for the North Atlantic Ocean, and 6.0 for the Red Sea.

The H and O isotopic variations of waters in restricted or semi-enclosed seas can be significantly different from that in large open oceans. For example, the Gulf of Aqaba is about 180 km long and 14 km wide with average depth of about 800 m and connects to the Red Sea with inflow of surface water and outlow beneath the surface from and into the Red Sea. The surface waters of the Gulf of Aqaba have $\delta^{18}O$ values ranging from +2.0 to +2.5 per mil, as compared to Red Sea surface waters having $\delta^{18}O$ values of generally less than +1.8 (Anati and Gat, 1989). The $\delta^{18}O$ concentration increa-

ses to a δ-value of about 2.95 per mil at depth of about 150 m from the surface. Anati and Gat explain such high isotopic values for waters in the Gulf of Aqaba in terms of evaporation exceeding precipitation and runoff in an arid climate.

ISOTOPIC COMPOSITIONS OF OCEAN WATER THROUGH GEOLOGIC TIME

The chemical and isotopic composition of ocean water is mainly controlled by three fluxes, the riverine, the ground water and the hydrothermal input. Mountain building processes, changes in the configuration of the continents, climatic variations, increasing and decreasing subaquatic, hydrothermal activities and changes in the degree of alteration of continental and oceanic crust during the different geologic epochs caused the oscillations of isotopic compositions in sea water with time.

Secular Variation of Strontium Isotopes

The trend of variation in the $^{87}Sr/^{86}Sr$ ratios with time shows a significant shift to a more radiogenic value from Archean to Proterozoic time at about 2.5 Ga, suggesting major influence of run-off influx of radiogenic ^{87}Sr from newly evolved continents with recycling history that is coupled with decreased influx of mantle Sr to the oceans. In a very broad sense, the sea water $^{87}Sr/^{86}Sr$ ratio increased progressively through the Proterozoic and the Phanerozoic. Details about variations in the $^{87}Sr/^{86}Sr$ ratios of sea water during the Proterozoic suffer from lack of data with good stratigraphic control. But the data from sea water during the Phanerozoic show, generally speaking, progressive decrease in the $^{87}Sr/^{86}Sr$ ratios during the Paleozoic which is followed by an increasing trend in the ratio during the Mesozoic and the Cenozoic. Many prominent short-period fluctuations in the $^{87}Sr/^{86}Sr$ ratios have been noted, and these have been explained in terms of the balance between continental Sr input by run-off and run-out and mantle Sr

input by oceanic hydrothermal activities.

For more detailed discussions of the secular variation of Sr isotopes, we refer to the companion paper by Veizer in this volume.

Secular Variation of Neodymium Isotopes

The secular variation of Nd isotopes in sea water is poorly known for several reasons.

1) Isotopic homogenization has not been attained between the water masses of different oceans. Therefore, in establishing the secular variation of Nd isotopes, changes in the configuration of the continents and resulting changes of the oceanic basins have to be considered. Even within water columns of present-day oceans large Nd isotopic variations have been observed (see above). Therefore, only samples coming from similar depositional environments (deep sea, shallow water, etc.) might yield a coherent picture of the secular variation. Also, knowledge of the streaming conditions, of the co-circulations, between the different water masses is of immense importance for the sampling and the interpretation of the isotope data. This has been discussed by Stille (1992) showing that during the past 80 Ma at some specific epochs the Nd isotopic composition of the Atlantic ocean water was much more controlled by changing circulation patterns between the North Atlantic and the Tethys oceans, and by the water masses coming from the Indian and Pacific oceans, than by river fluxes from surrounding continental areas.

2) Different materials such as metalliferous sediments, Fe-Mn ores, carbonate fossils, marine phosphates, authigenic argillites, clay fractions and glauconites have been used to estimate the Nd isotopic variation in ancient ocean waters. All of these components might have integrated the Nd and Sr isotopic composition of sea water, but formed in different environments and depths of the ocean and consequently integrated Nd isotopic compositions typical (or peculiar) to the broad environments in which they formed. A common evidence for reliable record of isotopic signatures of ancient sea water is given by phosphate minerals being strongly enriched in Nd and Sr. Conodonts are especially well suited for such isotopic

studies because they can be precisely dated biostratigraphically. Although metalliferous sediments and Fe-Mn ores integrate the Nd isotopic composition of sea water, chemical exchanges over tens of millions of years potentially render them to have typical sea water isotopic compositions (Clauer et al., 1984). Carbonates only contain small amounts of Nd and therefore their Nd isotopic compositions are suspect because they can have been influenced by diagenesis. Authigenic argillites, clay fractions and glauconites can be suitable for the derivation of the sea water Nd isotopic composition, but in many cases it is difficult to exclude contamination by inherited Nd coming from detritus.
These factors are limiting the precise derivation of the Nd secular variation. Nevertheless, for the use of any sedimentary material, one controlling factor has to be systematically considered: to ensure no diagenetic effects or inheritance modified the Nd isotopic compositions of the analyzed samples. One assurance of the choice of appropriate materials is to ensure that the Sr isotopic composition of the materials is identical to that of the contemporaneous sea water.

Nd isotopic variations in the Precambrian sea water

To constrain the secular variation in Precambrian sea water only a very small data base is available, which is founded mainly on information from banded iron formations (BIF) presumably of marine origin from chemical precipitation in the Precambrian oceans (Miller and O'Nions, 1985; Jacobsen and Pimentel-Klose, 1988a, 1988b). Therefore, they are expected to have incorporated the Nd isotopic composition of sea water at the time of their formation. The analyzed samples came from geographically widely different places of the world: Urucum (Bolivia-Brazilia), Sokoman (Labrador), Gunflint (Canada), Hammersly and Cleaverville (Australia), Vermillion and Beartooth (USA), Bjornevann (Norway), Michipicoten (Canada), Fig Tree (South Africa). The data are compiled in figure 2. Also included are data from some presumably authigenic clay materials from the Gunflint BIF, which define a time of diagenesis approximating close to the time of sedimentation, with an isochron age of 2.08 $\pm$ 0.25 Ga (Stille and Clauer, 1986) and some data on phosphorites (Bros, 1992) which formed about 2.04 $\pm$ 0.79 Ga ago within the Francevillian sedimentary basin, Gabon (Bros et al.,

1992).

The data define a huge field with Nd isotopic variations of up to 6 epsilon units for a single BIF. This range of variation is comparable with that of present-day sea water in a single oceanic basin. A trend of increasing $_{Nd}$ values with age is observable. This trend might indicate that the early Precambrian sea water was dominated by a much larger mantle component due to hydrothermal activity than the sea water of the late Precambrian or Phanerozoic. This observation is supported by Sr isotope data (Veizer et al., 1983). Therefore, Jacobsen and Pimentel-Klose (1988a) "argue for a dominantly hydrothermal source (with depleted mantle-like ϵ_{Nd} values) of rare earth elements in BIF's older than 2.0 Ga".

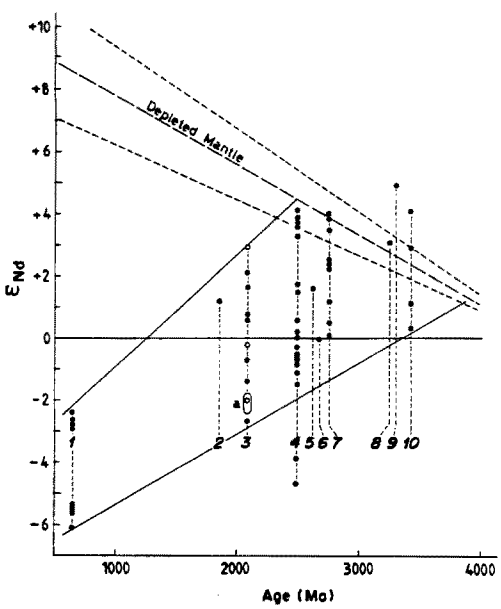

Figure 2: Nd isotopic variations in Precambrian sea water. The initial Nd values are plotted vs. the stratigraphic ages of the samples. Filled circles stand for Banded Iron Formations of Urucum (1), Sokoman (2), Gunflint (3), Hamersley (4), Vermillion (5), Bjornevann (6), Michipicoten (7), Beartooth (8), Cleaverville (9), and Fig Tree (10). Open circles stand for phosphates of Gabon (3). Authigenic clays from Gunflint Banded Formation are in the area (3a). Data are from Miller and O'Nions (1985), Stille and Clauer (1986), Jacobsen and Pimentel-Klose (1988a and b), and Bros (1992)

These authors, however, ignored the partly significantly negative ϵ_{Nd} values of the Hamersley BIF and the Gunflint BIF.

Argillites and a chlorite fraction (<2μm) of the Gunflint BIF define an isochron initial ratio of ϵ_{Nd} = -2.06 at 2.04 Ga, and Stille and Clauer (1986) suggested that the initial ratio of the isochron corresponds to the Nd isotopic composition of sea water some 2.04 Ga ago. Phosphorite sequences from the Francevillian sedimentary series in Gabon support the existence of crustal-like Nd in sea water at that time. These phosphorites show ϵ_{Nd} values ranging between +3 and -2. Therefore, similar to Miller and O'Nions (1985), we suggest that dominantly mantle sources can be discarded for the post-Archean sea water. However, because of the similarity of Nd isotopic composition in the mantle and crustal reservoirs during the Archean we cannot exclude that the Nd budget of the Archean sea water was influenced by mantle sources. The observed large variation of the Nd isotopic composition in the Precambrian sea water may be caused by: (a) post-depositional mobilization of Sm and Nd, (b) presence of mantle and crustal detritus in the investigated samples, (c) existence of different basins which have not been connected with eachother, and (d) different depositional environments and water depths in which the sediments formed.

Nd isotopic variations in the Phanerozoic sea water

Paleozoic - The Paleozoic sea water shows large variations in Nd isotopic compositions with ϵ_{Nd} values ranging from -3 to -20 (Fig. 3). For the time span between 400 Ma and 550 Ma, two different paleo-geography dependent evolutionary trends of ϵ_{Nd} values have been discovered (Keto and Jacobsen, 1987). These authors studied phosphatic brachiopods and conodont fossils from Europe, North America and the Southeastern US and observed that the samples coming from North America are generally much less radiogenic in Nd isotopic composition (ϵ_{Nd} from -10 to -20) than the samples coming from Europe and the southeastern United States (ϵ_{Nd} from -5 to -9). The ϵ_{Nd} values found for the samples from Europe and southeastern United States are identical to those defined earlier by Hooker et al. (1981) for the Iapetus Ocean. Therefore, Keto and Jacobsen (1987) inferred two ocean basins between North America and Baltica separated by an island and/or shoal circulation barrier, the smaller Iapetus Ocean having ϵ_{Nd} values ranging between -5 and -9 and the larger, coeval Pacific-Panthalassa Ocean with ϵ_{Nd} values ranging between -10 to -20. In the Late Ordovician to Silurian

(400-440 Ma) the two evolutionary Nd variation trends join each other. It is the time of the Taconic orogeny in North America when the Iapetus ocean closed again. At the end of the Paleozoic 300 Ma to 250 Ma ago the Nd isotopic composition of sea water strongly increases toward more radiogenic values (ϵ_{Nd} from -3 to -5) pointing to increasingly important volcanic activities and new generation of subduction zones around the Pacific/Panthalassa ocean.

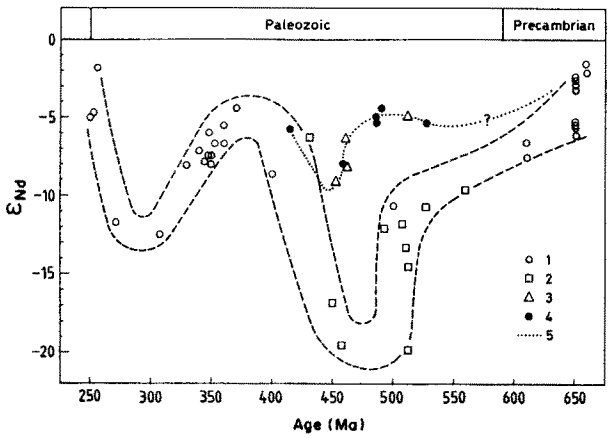

Figure 3: Nd isotopic variation in the Paleozoic sea water. Initial Nd values of mainly phosphates are plotted vs. their stratigraphic ages. Symbols 1 and 2 are for North American samples; 3 is for samples from southeastern United States; 4 is for European samples. The general dashed trend represents the Nd isotopic evolution in the Pacific-Panthalassa Ocean and the dotted line represents the Nd isotopic evolution in the Iapetus Ocean. Data are from Hooker et al. (1981), Shaw and Wasserburg (1985), Keto and Jacobsen (1987), and Banner et al. (1988)

Mesozoic and Cenozoic - This time span comprises the formation of the present-day oceans and therefore is of largest paleoceanographic interest to see the different evolutionary trends of Nd isotopic compositions in the Pacific, the Indian-Tethys-Mediterranean Sea and in the North and South Atlantic (Fig. 4); the variation being to some extent dependent on the communications between these oceans. During the past 220 Ma, the Nd isotopic composition in the Pacific increased with ϵ_{Nd} values ranging from -10 to -7 some 220 Ma ago and present-day values ranging between -1 and -4. The early Tethys sea water had Nd isotopic signatures identical to that of the Pacific, indicating that some 200 to 180 Ma ago Pacific sea

water entered in the rift zones of the newly forming Tethys basin. However, continental runoff draining into the rift became more and more important as indicated by the decreasing ϵ_{Nd} values. No data are available for the early Atlantic ocean. At about 100 Ma ago a broad seaway existed between the Tethys and North Atlantic oceans. Therefore, at this time Tethys and Atlantic sea water must have had the same Nd isotopic composition. In the time span between 70 Ma and present-day the Tethys and Atlantic sea water evolved isotopically in different ways. This isotopic decoupling might be caused by the slowly closing of the Tethys seaway.

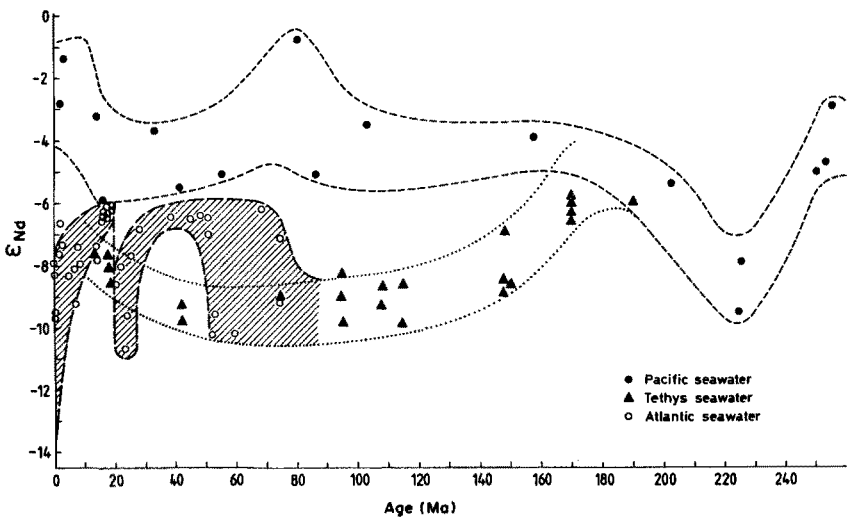

Figure 4: Nd isotopic variation in the Mesozoic and Cenozoic sea water of Pacific, Tethys, and Atlantic oceans. Data are from Piepgras and Wasserburg (1980), Chyi et al. (1984), Shaw and Wasserburg (1985), Staudigel et al. (1985), Grandjean et al. (1987), Keto and Jacobsen (1988), Stille et al. (1989), Stille and Fisher (1990), Steinmann et al. (1991), Stille et al. (1991, 1992), and Stille (1992)

A striking feature in the isotopic variation of the Atlantic sea water is that the Nd isotopic composition changed abruptly twice during the past 70 m.y. but not the Sr isotopic composition (see companion paper by Veizer, this volume) in the time span between 70 Ma and 35 Ma, the Sr isotopic composition of seawater only slightly increased, yet the Nd isotopic composition changed strongly toward more radiogenic values. A similar, even more abrupt change occurred at about 20 Ma. Stille (1992), who described these

isotopic variations for the first time, suggests that these changes in Nd isotopic compositions without accompanying changes in Sr isotopic compositions reflect mixing of different water masses rather than changes in runoff due to orogeny. The author relates these variations to major changes in the configuration of the continents, which produced changes in the ocean-water circulation patterns within the Atlantic and changes in the communication of the Atlantic with other oceans.

With the opening of the South Atlantic and the northward drift of India, a broad seaway developped ca. 100 to 80 Ma which allowed westward-traveling currents of the Pacific Ocean to cross into the Indian Ocean and finally enter into the basins of the South Atlantic and later the North Atlantic. Pacific sea water with a more radiogenic Nd isotopic composition (ϵ_{Nd} -5 to -2) began to mix with first the South and then the North Atlantic sea waters. This mixing resulted in an increase of the Nd isotopic composition in the Atlantic seawater. It lasted approximately 40 m.y., reflecting the period of the progressive northward shift of the South-Atlantic-North Atlantic boundary and the continous widening of the passage between the South and North Atlantic. When Australia separated from Antarctica ca. 45 Ma ago, the current pattern in the Indian and Atlantic oceans changed again. The influx of Pacific currents into the South Atlantic must have diminished with the northward drift of Australia and its collision with Indonesia during middle Miocene time. The diminishing influx of Pacific sea water has caused the Nd isotopic composition to evolve back toward more crustal values.

At 25-20 Ma, major changes in the oceanic circulation occurred again, triggered mainly by the opening of the Drake passage and the formation of the deep circum-Antarctic currents. Antarctic Bottom Water (ABW) and Pacific sea water were able to enter the Atlantic Ocean. The new admixture of more radiogenic Pacific sea water (ϵ_{Nd} -6 to -3) and ABW resulted in a very rapid increase of the Nd isotopic composition in the Atlantic at about 20 Ma. The data imply that the Atlantic and Pacific oceans had strong co-circulations during the early Miocene.

Hydrogen and Oxygen Isotopic Secular Variations

There is a great controversy regarding the H and O isotopic composition of ocean water through geologic time. The role of Pleistocene glaciation on the H and O isotopic composition of the ocean is widely recognized, although the magnitude of this effect is uncertain. Craig (1965) calculated that the mean δD and $\delta^{18}O$ values of the ocean could be -0.6 and -5 per mil, respectively, if all the continental glaciers were to melt. The mean δD and $\delta^{18}O$ values of the ocean during the time of maximum glaciation during the Pleistocene epoch would have increased from present values by 1.0 and 7.4 per mil, respectively (see Emiliani and Shackleton, 1974, and Williams et al., 1981 for data and discussions).

There are two contrasting views on the H and O isotopic composition of ocean water through geologic time. The first view is based on the isotopic compositions of marine sediments, including cherts, carbonates, phosphates and glauconites (Weber, 1965; Perry and Tan, 1972; Knauth and Lowe, 1978; Shemesh et al., 1983; Veizer et al., 1986) that suggest that the $\delta^{18}O$ value of ocean water has increased monotonically at a rate of about 5 per mil per billion years. Taylor (1977), on the other hand, concluded that ocean water must have been relatively uniform in δD and $\delta^{18}O$ values during the past 2.5 billion years. Taylor's conclusion is based on the fact that granites affected by meteoric-hydrothermal waters have similar isotopic characteristcs over this time span.

Studies of the $\delta^{18}O$ values of the oceanic crust by Muehlenbachs and Clayton (1976) and Gregory and Taylor (1981) have also led to the conclusion that the $\delta^{18}O$ values of ancient oceans have been relatively constant. Material balance calculations based on the processes that deplete ocean water in ^{18}O (low temperature submarine weathering and sedimentation) and enrich it in ^{18}O (high-temperature hydrothermal alteration of the oceanic crust and the cycling of chemically bound water from the mantle) showed that the $\delta^{18}O$ of the ocean water probably has been held constant at about zero at least since the Cretaceous period. The $\delta^{18}O$-buffering of the ocean at about 0 per mil is also indicated by the patterns

of $\delta^{18}O$ distribution in greenschist metabasalts on the modern ocean floor (Muelenbachs and Clayton, 1976), in Cretaceous ophiolitic sections (Gregory and Taylor, 1981) and in the Archean greenstones (Smith et al., 1984).

Assuming an isotopically buffered ocean water, there are two possible explanations for the generalized lowering of $\delta^{18}O$ values of marine sediments with increasing age. The first is based on increased post depositional isotopic exchange with isotopically light meteoric water. The second, used to explain the variations in the $\delta^{18}O$ values of chert (Knauth and Lowe, 1978) and of coexisting chert-phosphate pairs (Karhu and Epstein, 1986), is based on warmer oceanic (>60°C for Precambrian) temperatures. There are objections to these required high temperatures, and the fundamental question of whether the isotopic composition of ocean water has changed significantly over geologic time remains unresolved (for more discussion and references see Veizer et al., 1986; Muelenbachs, 1986; Wadleigh and Veizer, 1992; and Knauth, this volume).

CONCLUSIONS

The sea water $^{87}Sr/^{86}Sr$ ratio increased progressively through the Proterozoic and the Phanerozoic pointing to the increasing influence of run-off influx of radiogenic ^{87}Sr from newly evolved continents with recycling history and coupled with decreased influx of mantle Sr to the oceans.

The many prominent short-period fluctuations in the $^{87}Sr/^{86}Sr$ ratios can be explained in terms of the balance between continental Sr input by run-off and run-out and mantle Sr input by oceanic hydrothermal activities.

The $^{143}Nd/^{144}Nd$ ratio of the Proterozoic and Phanerozoic sea water indicate that dominantly mantle sources can be excluded for post-Archean sea water. In contrast to Sr, however, the secular variation of Nd in sea water is not only controlled by varying

proportions of mantle and crustal influx. The residence time of Nd in sea water being much shorter than that of Sr and the time necessary to mix the oceans causes the Nd to be poorly mixed not only among major oceanic basins but also within each basin. Therefore, short periods of fluctuations in the Nd isotopic composition can be induced not only by strong changes of the relative erosion rates of very young and very old crustal material, the input of Nd during times of high hydrothermal activities but also by changes in the paleo-currents or in the communication paths between paleo-oceans.

The phenomenon of significantly different Nd isotopic compositions in the water masses of the recently formed oceans has proved to be useful for potential applications to paleoceanographic reconstructions. This phenomenon also implies that coherent pictures of the Nd secular variation can only be attained by comparing samples comming from similar depositional environments of one specific oceanic basin.

Modern open ocean waters have very limited range of H and O isotopic compositions, mostly close to zero for the δD and $\delta^{18}O$ values. Waters in restricted or semi-closed marginal ocean basins have been found with $\delta^{18}O$ values as high as about +3, which is related to excess evaporation and runoff in arid climate.

Maximum glaciation during the Pleistocene epoch might have caused the increase in mean δD and $\delta^{18}O$ values by about 1.0 and 7.4, respectively, from the present values. Opinions about the stable isotope composition of ocean waters during much of the geologic time are split between monotonous increase in the $\delta^{18}O$ value by about 5 per mil per billion years and relatively uniform during the past 2.5 billion years.

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