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THE δ^{18}O RECORD OF PHANEROZOIC ABIOTIC MARINE CALCITE CEMENTS

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Abstract. Monomineralic, abiotic marine cements formed in low-latitude Phanerozoic reefs provide the direction and amplitude of secular variation of δ^{13}C and δ^{18}O in marine calcite and defines two end member compositions — 580 to 360 my (-7 to –5 ‰ $\delta^{18}O_{PDB}$) and 360 to present (-3 to 0 ‰ $\delta^{18}O_{PDB}$). Sampling of the Devono-Carboniferous transition (375-320 my) at several global sites reveals a rapid change in carbonate isotopic compositions. Bracketed within Fammenian to Early Visean-aged strata, a 7 to 15 my time interval, this shift corresponds to a 2 ‰ offset in mean δ^{13}C and 3-4 ‰ offset in δ^{18}O. The abruptness of such change, and its overall correlation with variations in $^{87}Sr/^{86}Sr$, δ^{34}S, δ^{13}C, and Li/Al ratios in marine sediments suggests a primary offset in marine water composition.

Introduction

Numerous studies have demonstrated that the history of the Phanerozoic ocean is one of dynamic chemical exchange among hydrospheric, lithospheric and atmospheric reservoirs (Perry and Tan, 1972; Brass, 1976; Veizer et al., 1980; Claypool et al., 1980; Holser, 1984; Popp et al., 1986; Veizer et al., 1986). Variation in ocean chemistry is recorded in changes in carbon, sulfur, and strontium isotopic compositions preserved in authigenic sedimentary minerals. A record of ^{18}O variation has, however, emerged slowly due to the difficulty of extracting a primary oxygen isotopic record. Unlike other tracers, oxygen can be strongly fractionated during precipitation and most marine phases have a propensity for alteration during diagenesis which can result in primary compositions being modified or lost. Thus, the magnitude of secular variation in δ^{18}O of the paleocean has remained controversial, and a dichotomy has developed between arguing either for the constancy or inconstancy of paleocean oxygen isotopic composition (Veizer et al., 1986; Kahru and Epstein, 1986).

The Record of δ^{18}O Variation

Long Term Variation: The Phanerozoic

During the last decade, an increasing volume of data on secular variation of δ^{18}O has emerged from a variety of marine authigenic minerals including carbonates, phosphates and cherts (Given and Lohmann, 1985; Popp et al., 1986; Luz et al., 1984; Shemesh et al., 1983; Kahru and Epstein, 1986; Veizer et al., 1986). Taken individually or together, these data define a pattern of variable oxygen isotopic composition exhibiting an overall trend of depleted δ^{18}O values for the early Phanerozoic followed by enriched values during middle and late Phanerozoic time.

The most extensive δ^{18}O record has been obtained from carbonates, reflecting their abundance, their uniform occurrence throughout the Phanerozoic, and the excellent control on their environmental distribution. At present, two compatible yet distinct components are actively used to document long-term secular variations in δ^{18}O, brachiopods and abiotic marine cements. Recognition of diagenetic overprints through textural and chemical alterations allows for primary compositions to be determined (Given and Lohmann, 1985;Popp et al., 1986; Veizer et al. 1986). The overall agreement of records of secular trends suggests that either may be employed to define patterns of δ^{18}O variation.

Primary marine δ^{18}O values for marine calcites, which formed in shallow, low-latitude, reefal limestones, range from –6.5 to –0.5 ‰ (Figure 1). By focusing on a very specific marine shelf-margin facies, it has been possible to limit variation induced by environmental factors such as latitudinal temperature gradients and local changes in salinity. From these data, it is clear that although variation is present throughout the Phanerozoic the principal change in δ^{18}O occurs during the Devono-Carboniferous transition and is accompanied by an offset in mean δ^{13}C values. Importantly, this δ^{18}O event is exhibited in marine cements (Lohmann, 1987), in brachiopods, (Popp et al., 1986; Veizer et al., 1986), and phosphates (Shemesh et al., 1983; Luz et al., 1984).

Short Term Variation: the Devono-Carboniferous Transition

In a study of the Devono-Carboniferous sequence of Belgium and Ireland (Dunn, 1988) documented the timing of δ^{18}O and δ^{13}C change. Analyses concentrated on marine cements in reefal deposits, ranging in age from early Frasnian to early Visean. Isotopic analyses utilized a microsampling approach to document compositional heterogeneity in partially altered carbonates (Given and Lohmann, 1985). Diagenetic trends were identified which reflect compositional variation ranging from partially altered to unaltered values.

When all data from the Devonian sequence of Belgium are plotted together, an extreme range in δ^{18}O and δ^{13}C is observed (Figure 2A). However, when examined in a stratigraphic context (Figure 2B), δ^{13}C values vary systematically with age, and analyses of time-equivalent, geographically-separated sites exhibit nearly identical shifts

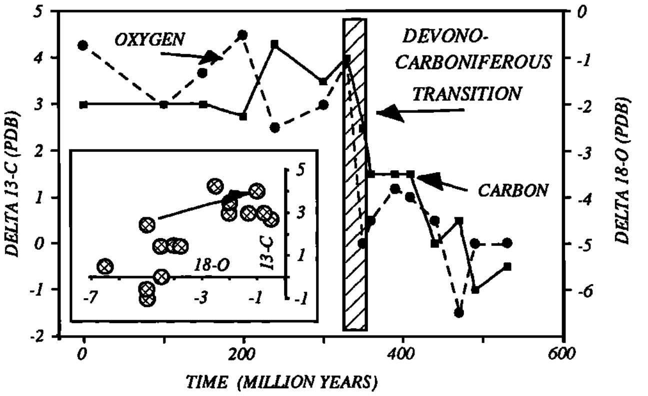

FIG. 1. Secular variation of δ^{18}O in abiotic marine carbonates. The most significant variation is the enrichment in both δ^{18}O and δ^{13}C at the Devono-Carboniferous transition.

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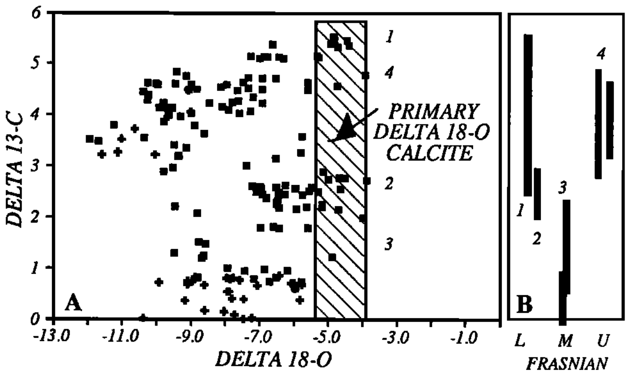

FIG. 2. A – $\delta^{18}O$ and $\delta^{13}C$ variation of Frasnian-aged marine cement, Dinant Synclinorium, Belgium. B – When examined relative to stratigraphic age $\delta^{13}C$ values vary systematically. Analyses from time-equivalent reefs define distinct alteration trends which converge to a common range of $\delta^{18}O$ of –6 to –4.5‰. (Data from Dunn, 1988)

in $\delta^{13}C$ composition with time. This record, defined by diagenetic trends of variable $\delta^{18}O$ and relatively invariant $\delta^{13}C$, is interpreted to reflect primary secular shifts in the $\delta^{13}C$ composition of Frasnian marine waters which range in composition from +1 to +5.5 ‰ $\delta^{13}C$.

When individual diagenetic trends are examined, the most enriched $\delta^{18}O$ values converge to a common range of between –5 to –4 ‰. Such values are typical of late Devonian marine cements analyzed from other global sites. These include Frasnian and Fammenian reefs of the Canning Basin, Australia (Hurley, 1988: -5.2 $\delta^{18}O$ and +2.5 $\delta^{13}C$) and Frasnian reefs of the Alberta Basin, Canada (Carpenter and Lohmann, 1987: -5.0 $\delta^{18}O$ and +2.5 $\delta^{13}C$). Moreover, these values coincide with the range of $\delta^{18}O$ values measured in low magnesium calcite brachiopods (Veizer et al., 1986; Popp et al., 1986).

Identical methods were employed for analysis of marine cements from Tournasian and Visean-aged Waulsortian reefs of Southwestern Ireland (Figure 3). In these reefs, isotopic values converge to a composition of –2 to –1 ‰ $\delta^{18}O$ and +4 ‰ $\delta^{13}C$. Comparable values have been observed for time equivalent, Osagean-aged (Visean) shelf carbonates and marine cements of North America (Meyers and Lohmann, 1985).

Two principal features should be noted in these data. 1) Isotopic compositions of marine carbonates are apparently recording a phenomenon of global scale; and, 2) Variability of $\delta^{13}C$ is markedly different in Devonian cements relative to Carboniferous cements. Secular variation of $\delta^{13}C$ during the Late Devonian exhibits a range of 5 ‰ on a time scale of 10^6 years. In contrast, variation is not discernable throughout the entire sequence of Carboniferous-aged reefs which span a time range of approximately 20 my. Thus, the geological phenomenon which offsets the mean $\delta^{18}O$ and $\delta^{13}C$ values of marine carbonate may have simultaneously affected the factors which control the variability of $\delta^{13}C$. Clearly, these patterns of variation suggest a dynamic period in Earth history during Devonian times followed by relative quiescence in the Carboniferous.

Interpretation of Phanerozoic Variations in $\delta^{18}O$

To account for $\delta^{18}O$ variations of marine minerals, two opposing scenarios are possible. In the first, the shift directly reflects a change in the $\delta^{18}O$ composition of sea water in response to the changes in global-scale geologic processes during the Phanerozoic. In light of mass balance constraints, such processes could relate to pulses in either tectonism or seafloor spreading which, in turn, might modify the mass transfer of ^{18}O between lithosphere and hydrosphere reservoirs of oxygen (Veizer et al., 1986; Walker and Lohmann, this issue).

Alternatively, these shifts in $\delta^{18}O$ of carbonate from the Devonian to the Carboniferous would require a decrease in Earth surface temperature from 60°C to 30°C. Even higher temperatures have been postulated for the Precambrian and early Phanerozoic, ranging from 75 to 120°C (Kahru and Epstein,1986, fig. 8). While such thermal pulses in Phanerozoic surface water temperatures are certainly possible, Veizer et al. (1986) summarize the numerous problems of elevating the temperature of Phanerozoic marine waters. These include the incompatability of large scale glaciation with "hot" world oceans, the preferential precipitation of gypsum rather than anhydrite in Phanerozoic evaporites, and the upper temperature limit constrained by the viability of biological metabolic functions and the decomposition temperature of essential organic compounds. Clearly, thermal variations of the magnitude implied by the range of isotopic compositions preserved in marine carbonates are inconsistent with a variety of independent geologic and paleontologic data.

Additional complications arise when the magnitude of the $\delta^{18}O$ change is examined within the context of variation expected from glacial versus non-glacial paleoclimates. For example, estimates of the effect of ice volume on marine water composition have been deduced from numerous studies of Cenozoic sequences (Matthews and Poore, 1980). From these, the magnitude of $\delta^{18}O$ change for seawater accompanying the transition from an "ice-free" to "ice full" glaciated world can account for only about 1.6 ‰ of the observed variation. Thus, a greater than 2 ‰ discrepancy remains for the observed change in marine carbonate values from Devonian to Carboniferous times. Moreover, the lack of shifts of comparable magnitude and similar absolute values during post-Devonian times argues against an ice volume effect as the sole control on the $\delta^{18}O$ composition of seawater.

Other Factors Controlling the $\delta^{18}O$ of Seawater

While geological and biological considerations undermine the hypothesis for major temperature variations of the paleocean, at least for the Phanerozoic, mass balance calculations of ^{18}O fluxes place limits on the ability of the ocean to modify its isotopic composition (Muehlenbachs and Clayton, 1976; Holland, 1984; Walker and Lohmann, this issue). Specifically, to change the $\delta^{18}O$ composition of marine water, isotopic exchange and flux of ^{18}O must take place between the lithosphere and hydrosphere. For example, weathering of silicate rocks at low temperatures preferentially enriches alteration products in ^{18}O while

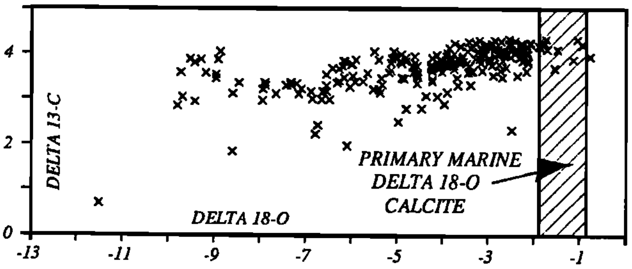

FIG. 3. Isotopic variation of Tournasian and early Visean marine cements, Ireland. Diagenetic alteration trends suggest a primary marine composition of –1 to –2 ‰ $\delta^{18}O$ and +4 ‰ $\delta^{13}C$. (Data from Dunn, 1988)

depleting reactive waters. Conversely, water-rock reaction at high temperatures, associated with MOR hydrothermal activity, provides for ^{18}O exchange with minimal fractionation. Isotopically enriched igneous rocks (+6 ‰ SMOW) become depleted and reactive waters become enriched approaching the isotopic composition of the average silicate rock materials.

Within this context, analysis of Cretaceous basalts suggests that ^{18}O flux related to low and high temperature weathering regimes were dynamically balanced. These data support an overall mass balance which may effectively buffer the isotopic composition of marine water (Muehlenbachs and Clayton, 1976).

Using a similar mass balance approach, Holland (1984) re-estimated continental, submarine (low T) and hydrothermal (high T) fluxes of ^{18}O. His results indicate that increases in spreading rate relative to present day rates would have a negligible effect on ocean $\delta^{18}O$ with an upper limit of +1 ‰. In contrast, decreasing rates of spreading would manifest themselves in an increasing dominance of Low T continental flux with a decrease in $\delta^{18}O$ to a lower limit of −10 ‰.

Importantly, the mass flux model of Holland (1984) does not allow for the effect of changing the relative dominance of hydrothermal alteration (High T) to submarine weathering (Low T); it assumes that both are proportional to rate of seafloor spreading. While data of Alt et al. (1986) suggest that such a balance exists at present, this does not preclude an imbalance from occurring during periods of the Phanerozoic. Within the context of an unbalanced model, secular variation in $\delta^{18}O$-carbonate (Figure 1) may reflect long term variations in the dominance of high temperature hydrothermal versus low temperature submarine and continental weathering. Such a model may be supported by evaluating patterns of variation of other isotopic and elemental tracers.

Long-term Variation in Other Geochemical Tracers

It has been well documented that first order changes in $^{87}Sr/^{86}Sr$ of marine water correspond to changing dominance by either continental or mantle fluxes (Brass, 1976). Although punctuated by excursions toward more radiogenic values, perturbations inferred to record episodes of tectonic uplift and/or increased continental weathering (Holland, 1984; Brass, 1976), the long term $^{87}Sr/^{86}Sr$ trend from Cambrian through Permian implies an increasing dominance of mantle contribution to oceanic Sr (Figure 4).

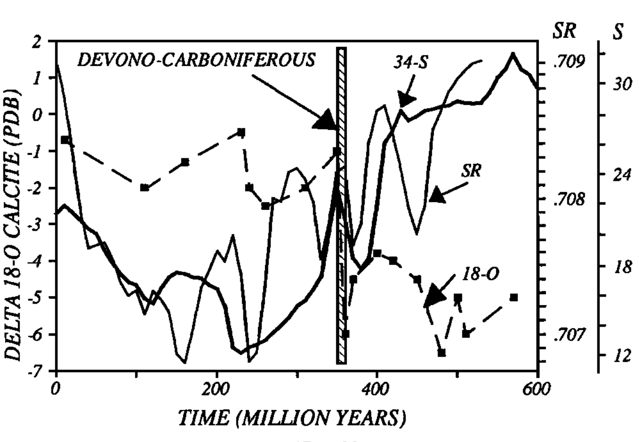

FIG. 4. Secular variation in $^{87}Sr/^{86}Sr$ of marine carbonate and $\delta^{34}S$ of marine sulfate decrease from early to middle Phanerozoic times.

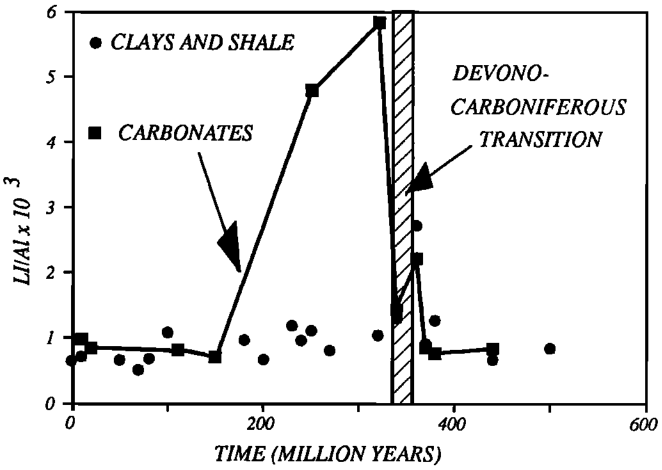

FIG. 5. Secular variation of Li/Al in marine carbonates (Ronov et al., 1970).

Interestingly, the overall variation of $^{87}Sr/^{86}Sr$ is matched by a comparable long term trend in $\delta^{34}S$, which may also reflect contributions of isotopically-light, mantle-derived sulfur (Holland, 1984; Walker, 1985). Although this proposition does not preclude control by the oxidation-reduction, exogenic cycle for carbon and sulfur (Garrels and Lerman, 1981; Veizer et al., 1980), it suggests that the flux of reduced sulfur to the ocean via hydrothermal circulation at spreading centers may lead to compensatory shifts in the average $\delta^{13}C$ composition of marine carbon. This offset would occur in response to oxidation of the exhalative reduced sulfur, resulting in anoxic marine bottom waters which in turn would stimulate the burial of organic carbon (Walker, 1985).

Secular variation in the abundance of lithium associated with carbonates and shales provides additional insight into the temperatures of exchange with oceanic lithosphere. Holland (1984) notes that in response to high temperature alteration of igneous rocks, Li is preferentially enriched in the fluid phase. In the case of seawater-basalt interactions, hydrothermal solutions remove Li from basalts and enrich sea water. This is in contrast to low temperature weathering, whereby Li, along with K, are progressively enriched in alteration products. Thus, periods dominated by high temperature alteration of MOR basalts should be recorded by relative highs in the concentration of Li in authigenic sediments. Data of Ronov et al. (1970) exhibit a significant increase in Li/Al ratios for carbonates during the Devonian through Permian time interval (Figure 5). The coincidence with the depleted trend in $^{87}Sr/^{86}Sr$ suggests that while ocean Sr chemistry was dominated by a net mantle flux, high T hydrothermal alteration dominated low T submarine weathering. Such a relationship is consistent with the setting necessary to enhance the net $\delta^{18}O$ flux toward more enriched values for seawater.

Conclusions

The empirical record of $\delta^{18}O$ variation of abiotic marine carbonates demonstrates a primary offset in composition at the Devono-Carboniferous transition. It is unlikely that this results from a change in paleotemperature, but rather is most compatible with modification of the $\delta^{18}O$ of seawater. While the geologic event which resulted in this offset remains speculative, the process must manifest in an isotope flux between silicate rock materials and seawater. The coincidence of depleted $^{87}Sr/^{86}Sr$ with depleted $\delta^{34}S$ during the Permian implies that these tracers may be coupled to a common geologic process and record an increased mantle contribution to the paleocean. Moreover, the mid-Phanerozoic perturbation in Li/Al of carbonate suggests dominance by high temperature exchange reactions relative to low temperature weathering of coeval oceanic and continental crust.

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