

FOUR BILLION YEARS OF EVOLUTION FROM SEAWATER ISOTOPE RECORD

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Summary

A new generation of $^{87}\text{Sr}/^{86}\text{Sr}$, $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ curves for Precambrian and Phanerozoic seawater, based on several thousand stratigraphically well defined and well preserved samples, results in much better constrained secular trends. All first order isotope trends over billions of years, including $\delta^{34}\text{S}$ but not $\delta^{18}\text{O}$, can be generated by a model driven by two variables, exponential decline of mantle heat dissipation combined with a delayed growth of continental crust. This scenario generates also oxygenation of the ocean/atmosphere system around the Archean/Proterozoic transition without resorting to a need for biological innovation.

For the Phanerozoic, the oxygen isotope signal exhibits a long-term increase of $\delta^{18}\text{O}$ from a mean value of about - 8 ‰ (PDB) in the Cambrian to a present mean value of about 0 ‰ (PDB). Superimposed on the general trend are shorter term oscillations with their apexes coincident with cold episodes and glaciations. The carbon isotope signal shows a similar climb during the Paleozoic, an inflexion in the Permian, followed by an abrupt drop and subsequent fluctuations around the modern value. The means of the observed isotope signals for $^{87}\text{Sr}/^{86}\text{Sr}$, $\delta^{18}\text{O}$, $\delta^{13}\text{C}$ and the less complete $\delta^{34}\text{S}$ (sulfate) are strongly interrelated at any geologically reasonable (1 to 40 Ma) time resolution. Factor analysis indicates that the system is driven by three factors. On geological timescales (≥ 1 Ma), we are dealing with a unified exogenic (litho-, hydro-, atmo-, biosphere) system driven by tectonics via its control of (bio)geochemical cycles.

Introduction

One of the fundamental issues that are essential for understanding the evolution of this planet is the timing of continent formation. The two end-member alternatives are an instantaneous "big bang" generation of continents due to large scale differentiation of the Earth in nascent stages of its evolution (Armstrong 1968), as opposed to the more gradual growth, with the major phase of continental formation some 2 to 3 Ga ago (Veizer and Jansen 1979; Taylor and McLennan 1985). The issue is of importance not only for understanding the evolution of the solid earth, its magmatic and metamorphic complexes, sediments and mineral deposits, but also of the ocean/atmosphere system and life. The chemistry of the ocean is dominated by two principal fluxes, the meteoric hydrologic cycle ("river" flux) and the hydrothermal oceanic flux, principally at mid-oceanic ridges ("mantle" flux). These two fluxes during geologic history were likely proportional to the size of the continents and to the mantle heat flow flux, respectively. Although the rate and the magnitude of the mantle heat flow on the early Earth is still disputed, there is a consensus that it had to decline exponentially in the course of geologic history. For an "instantaneous" differentiation model, a near-modern steady-state of the above two fluxes would have been established already on the young Earth, as would be the chemistry of the ocean and the dynamics of biogeochemical cycles. In contrast, the model of delayed continental growth predicts that the

early ocean chemistry would have to be dominated by the "mantle" flux, with subsequent transition to "river"-dominated oceans (Veizer et al., 1982). These authors argued qualitatively that such an evolution could generate not only most of the first order isotopic patterns observed in ancient chemical sediments (hence oceans), but also explain the apparent oxygenation of the ocean/atmosphere system in the early Proterozoic, and the temporal succession of sediments and mineral deposits. Thus, a single mechanism could account for a plethora of experimental observations. They also suggested that, on geological time scales, it was the global tectonic evolution, and not life (e.g. Gaia of Lovelock 1979), that controlled and generated the evolutionary pattern of exogenic chemical and biogeochemical cycles. Quantitative modelling of the above scenarios represents the major topic of this presentation.

Seawater isotope signals: 10^9 year time scale

A numerical model that couples carbon-sulfur-strontium and atmospheric oxygen cycles (Godd  ris and Veizer in press) is used here to explore the impact of continental growth on the long term ($\geq 10^8$ years) evolution of the isotopic composition of seawater. Three growth scenarios are tested: "big bang" generation of continents shortly after the accretion of the Earth, and two more gradual scenarios, with a major growth episode around the Archean-Proterozoic boundary. The corresponding $^{87}\text{Sr}/^{86}\text{Sr}$, $\delta^{34}\text{S}$ and $\delta^{13}\text{C}$ of seawater, and the sizes of the respective crustal sedimentary reservoirs, are calculated for each scenario, and compared to the available data. The gradual continental growth scenarios yield a better fit to the existing $^{87}\text{Sr}/^{86}\text{Sr}$, $\delta^{34}\text{S}$ and $\delta^{13}\text{C}$ isotope data for ancient seawater than does the "big bang" model. These scenarios also generate a progressive oxygenation of the ocean/atmosphere system, with a large $p\text{O}_2$ rise coincident with (and due to) the major continental growth event around the Archean-Proterozoic transition, in accord with the geologic record that indicates a major oxidation event in the early Proterozoic. The advancing oxygenation of the planetary exogenic system may therefore be a consequence of tectonic evolution, rather than of biological innovations, such as the photosystem 2. The latter may have predated considerably the impact of oxygenation visible in the geologic record. The model also generates a strong climatic cooling around the Archean-Proterozoic transition, coincident with the first glaciation of global extent in the early Proterozoic. In contrast to the above isotope systematics, the model does not approximate well experimental observations of large $\delta^{18}\text{O}$ variations at 10^8 year time scales (see the Phanerozoic below). The reason for this discrepancy may depend on the model structure that permits large variations in the oxygen isotopic composition of seawater only on time scales of 10^9 years.

Seawater isotope signals: Phanerozoic

The proposition that exogenic (bio)geochemical cycles are, on geological time scales, controlled by tectonics is strongly

supported by the new isotopic databases for Phanerozoic oceans (Veizer et al. 1999). A total of 2128 calcitic and phosphatic shells, mainly brachiopods with some conodonts and belemnites, were measured for their $\delta^{18}\text{O}$, $\delta^{13}\text{C}$ and $^{87}\text{Sr}/^{86}\text{Sr}$ values. The data set covers the Cambrian to Cretaceous time interval. Where possible, these samples were collected at high temporal resolution, up to 0.7 Ma (1 biozone), from the stratotype sections of all continents but Antarctica and from many sedimentary basins. Paleogeographically, the samples are mostly from paleotropical domains. The SEM, petrography, cathodoluminescence and trace element results of the studied calcitic shells and the CAI data of the phosphatic shells are consistent with an excellent preservation of the ultrastructure of the analyzed material. These datasets are complemented by extensive literature compilations of Phanerozoic low-Mg calcitic, aragonitic and phosphatic isotope data for analogous skeletons. The oxygen isotope signal exhibits a long-term increase of $\delta^{18}\text{O}$ from a mean value of about - 8 ‰ (PDB) in the Cambrian to a present mean value of about 0 ‰ (PDB). The carbon isotope signal shows a similar climb during the Paleozoic, an inflexion in the Permian, followed by an abrupt drop and subsequent fluctuations around the modern value. The $^{87}\text{Sr}/^{86}\text{Sr}$ ratios differ from the earlier published curves in their greater detail and in less dispersion of the data. The means of the observed isotope signals for $^{87}\text{Sr}/^{86}\text{Sr}$, $\delta^{18}\text{O}$, $\delta^{13}\text{C}$ and the less complete $\delta^{34}\text{S}$ (sulfate) are strongly interrelated at any geologically reasonable (1 to 40 Ma) time resolution. All correlations are valid at the 95 % level of confidence, with most valid at the 99 % level. Factor analysis indicates that the $^{87}\text{Sr}/^{86}\text{Sr}$, $\delta^{18}\text{O}$, $\delta^{13}\text{C}$ and $\delta^{34}\text{S}$ isotope systems are driven by three factors, all related to tectonic forcing.

Superimposed on the general Phanerozoic trends are higher order oscillations. For oxygen isotopes, these oscillations yield a good correlation with icehouse/greenhouse episodes as established by sedimentological criteria (Frakes et al. 1992). The oxygen isotope data suggest $\geq 8^\circ\text{C}$ tropical sea surface temperature differences between the apexes of greenhouse and icehouse modes and $\geq 4^\circ\text{C}$ for the superimposed stadials and interstadials. The ultimate cause(s) of such large planetary temperature oscillations are not known, but the resulting climate variability was modulated more likely by the water cycle than by its carbon counterpart. In this scenario, the atmospheric CO_2 levels on geological time scales are a consequence of, and contributing factor to, climatic change, but probably not the leading modulating agent.

Conclusions

The first order secular trends for isotopic composition of ancient seawater are consistent with a tectonically driven model that assumes a delayed generation of the bulk of continental crust at about the Archean-Proterozoic transition. This model can generate the 10^9 year trends for $^{87}\text{Sr}/^{86}\text{Sr}$, $\delta^{13}\text{C}$ and $^{34}\text{S}/^{32}\text{S}$, but not yet for $\delta^{18}\text{O}$. In addition, the model generates oxygenation of the ocean-atmosphere system coincident with the major phase of continent formation.

The covariance of the above isotopic trends during the Phanerozoic (resolution of 10^7 - 10^8 years) supports the notion that the terrestrial exogenic system is a unified entity driven mostly by tectonic forcing. Higher order oscillations, particularly for oxygen isotopes, nevertheless reflect the superimposed climatic variations,

with tropical temperature differences at icehouse/greenhouse modes considerably in excess of values generated by present day GCM models.

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