

SULFUR ISOTOPES AND EARTH'S BIOGEOCHEMICAL EVOLUTION

STRAUSS, HARALD, Geologisch-Paläontologisches Institut und Museum, Westfälische Wilhelms-Universität Münster, Münster, Germany.

Summary

The element sulfur participates in long-term, geological and short-term, biological processes and, thus, represents a key element for understanding earth's biogeochemical evolution. These processes are associated with sometimes substantial changes in the isotopic composition of oxidized or reduced sulfur present in the atmosphere, hydrosphere, biosphere, and lithosphere. Marine sedimentary rocks provide a record of these signals and, thus, can document the evolution of the global sulfur cycle.

The sulfur isotopic composition of seawater witnessed substantial secular variations during the past 800 million years as evident from a new, high-resolution temporal record of $\delta^{34}\text{S}$, based on the analysis of structurally substituted sulfate in stratigraphically well constrained biogenic carbonates. Additional data were derived from trace sulfate in inorganic carbonates or phosphorites. The record is further supplemented by $\delta^{34}\text{S}$ data obtained from marine barite.

Discrete biological and environmental signals are reflected in the isotopic composition of reduced sedimentary sulfur. These suggest temporal changes in the mode of biological sulfur cycling in response to changes of environmental parameters. The latter include the availability of metabolizable organic matter and/or sulfate, and/or prevailing redox conditions in the sedimentary environment.

Introduction

Seawater sulfate represents the central reservoir within the modern sulfur cycle. Input into the reservoir is largely twofold, through riverine transport of sulfate derived from continental weathering of sulfate and sulfide minerals, and from the mantle at mid-ocean ridges. Both inputs comprise a specific and different isotopic composition resulting in a mixture for the resulting dissolved seawater sulfate. The final signature will depend – in part – on the proportions of both inputs. The most important output functions are the deposition of evaporitic sulfate minerals and the bacterial reduction of sulfate to hydrogen sulfide. The latter is generally fixed in the sediment, most frequently in the form of iron sulfides. While the pure precipitation of evaporitic sulfate minerals is not associated with any substantial change in $\delta^{34}\text{S}$, a significant isotope effect generally accompanies the process of bacterial sulfate reduction.

The sedimentary sulfur cycle reflects changing redox conditions in the sedimentary realm. These changes can be monitored through the isotopic composition of seawater sulfate. Modeling of this temporal record and correlation with the appropriate isotope records of carbon, oxygen and strontium substantiates our understanding of the exogenic cycle on earth. In accordance with the pronounced isotope effect associated with the bacterial reduction of seawater sulfate, mass balance considerations for the global sulfur cycle have generally been expressed as changes in the deposition of reduced sulfur resulting from bacterial sulfate reduction.

The isotopic composition of reduced sedimentary sulfur, notably iron sulfides or organically bound sulfur, can provide important information with respect to type and effectiveness of diverse biologically controlled processes in the sedimentary environment. In principle, these are reduction of sulfate, oxidation of sulfide and disproportionation of intermediate sulfur species. All processes are accompanied by discrete displacements of the sulfur isotopic composition between educt and product, which is characteristic of the appropriate biological process as well as the influence of surrounding environmental parameters. Among others, these include the availability of an appropriate organic substrate.

The isotopic composition of seawater through time

A temporal record for $\delta^{34}\text{S}$ of seawater sulfate is documented by data which were largely derived from structurally substituted sulfate contained in stratigraphically well constrained biogenic carbonates and inorganic precipitates. Supplementary data for the Neoproterozoic stem from marine evaporite deposits. The Cenozoic is also documented by sulfur isotope data recently presented by Paytan et al. (1998). With respect to time resolution, this record strongly contrasts previously available data sets derived from marine evaporitic sulfates (e.g. Claypool et al. 1980), which were much more susceptible to erosion and, thus, resulted in a rather fragmentary documentation of the temporal evolution in $\delta^{34}\text{S}$.

Seawater sulfate witnessed substantial secular variations in $\delta^{34}\text{S}$ during the past 800 million years, with strongly ^{34}S enriched values in the terminal Neoproterozoic and early Paleozoic and ^{34}S depleted minimum values in the Permian. While this overall temporal evolution had been already documented in the evaporite based record (e.g. Claypool et al. 1980), much more detail and internal structure of the sulfur isotope curve is discernible from the new data.

During the terminal Neoproterozoic, pre-Sturtian (>725 Ma) evaporites display an isotopic composition around +20 ‰. Post-glacial units are characterized by strongly ^{34}S enriched values of +30 to +35 ‰, as currently documented for the post-Varanger or post-Marinoan glacial interval (i.e. <600 Ma) and inferred for the post-Sturtian (<725 Ma).

Substantially more detail is provided for the Phanerozoic sulfur isotope record which is largely based on structurally substituted sulfate from biogenic carbonates. While including all previously documented temporal changes based on marine evaporites, numerous new secular variations in ^{34}S on different time scales can be observed which were undetected before as a consequence of the fragmentary nature of the evaporite based record.

The isotopic composition of sedimentary sulfides

Biologically driven processes within the sedimentary sulfur cycle are associated with sometimes substantial sulfur isotope effects. The most prominent process, judged on its importance in modern marine environments, is bacterial sulfate reduction (e.g. Jørgensen 1982). This reaction favors the transfer of ^{32}S over ^{34}S and causes a depletion in ^{34}S in the resulting hydrogen sulfide which can potentially be substantial. A temporal record for this reaction is provided by the isotopic composition of (biogenic) iron sulfides. This record displays substantial variation, both in respect to the distribution of $\delta^{34}\text{S}$ values over the past 800 million years as well as for any individual time segment or even stratigraphic unit. These latter ranges can attain a total spread in $\delta^{34}\text{S}$ of up to 75 ‰. This clearly demonstrates the importance of additional factors affecting the isotopic composition apart from the entirely physiological part. Environmental parameters like the availability of sulfate, metabolizable organic matter and reactive iron strongly affect the process of bacterial sulfate reduction and its traces in the sediment, both as far as the presence and isotopic composition of sedimentary sulfides are concerned.

The temporal record of $\delta^{34}\text{S}$ can be analysed through an assessment of minimum and maximum values as well as the isotopic difference between seawater sulfate as primary sulfur source and iron sulfide as reaction product. Although marked by significant variability, the temporal distribution of the minimum isotope values (i.e. those displaying the largest isotope fractionation when compared to parental seawater sulfate) somewhat parallels the distribution of the sulfate record. This can best be evaluated by observing a fairly constant maximum isotope fractionation around 50 ‰ during the entire Phanerozoic. Somewhat more variable conditions appear to be characteristic of the Neoproterozoic which displays some of the largest isotopic variability per time unit. Again, a distinct pattern appears to characterize the pre-Sturtian, the post-Sturtian, and the post-Varanger or post-Marinoan time interval.

Maximum sulfur isotope values for sedimentary sulfides (i.e. those displaying the smallest isotope fractionation between parental sulfate and resulting biogenic sulfide) document a different situation. The Neoproterozoic and early Paleozoic display maximum $\delta^{34}\text{S}$ values which generally exceed the value for coeval seawater. This pattern changes in the Devonian and remains fairly uniform thereafter.

The minimum sulfide sulfur isotope values are interpreted to record the net isotope effect associated with biological fractionation. As stated above, bacterial sulfate reduction is regarded as prime process in the sedimentary environment. Compared to experimental data, the apparent displacement between sulfate and sulfide as recorded in the iron sulfides is too large, and internal sulfur cycling and disproportionation has been invoked to explain these observations (Canfield and Teske 1996).

The sometimes extreme variability in $\delta^{34}\text{S}$, particularly the strongly ^{34}S enriched values, are interpreted to record a different influence related to environmental parameters. Bacterial sulfate reduction continues in the diagenetic environment until either the organic substrate or dissolved sulfate becomes limited. Thus, sedimentary sulfides reflect an entire range of diagenetic conditions which can be expressed by highly variable isotopic compositions. Sulfate limitation in particular results in progressively more ^{34}S enriched values of later diagenetic phases in accordance with Rayleigh fractionation mechanisms. The observed variability is interpreted to reflect the temporal evolution of a diagenetic system with early as well as late phases.

Additional influence on the process of bacterial sulfate reduction results from the availability of metabolizable organic matter. The maximum $\delta^{34}\text{S}$ value for sedimentary sulfide decreases in the Devonian, although time resolution of the current database is fairly crude (e.g. Strauss 1999). This change coincides with the rapid evolution and growing importance of land plants. Presumably, this has resulted in an increase of terrigenous organic detritus delivered into the near-shore marine environments. As terrestrial organic matter is less easily metabolizable than purely marine organic material (Lyons and Gaudette 1979), this should have affected the effectiveness of bacterial sulfate reduction. It should be noted that similar conclusions were drawn from an observed change in the sulfur-to-carbon-ratio between early and late Paleozoic (Raiswell and Berner 1986).

Conclusions

The sulfur isotopic composition of sedimentary sulfur species provides important information in respect to the biogeochemical evolution on earth. This pertains to the identification of relevant processes as well as the reconstruction of temporal pattern of evolution. Prime prerequisites are a sufficient time resolution and a clear separation of biological versus environmental signals.

Acknowledgements

Research has been supported financially by the Deutsche Forschungsgemeinschaft. This study represents a contribution to the Earth System Evolution Program of the Canadian Institute for Advanced Research (Toronto) and to IGCP Project No. 386.

References

- Canfield, D.E. and Teske, A., 1996. Late Proterozoic rise in atmospheric oxygen concentration inferred from phylogenetic and sulphur-isotope studies. *Nature*, 382: 127-132.
- Claypool, G.E., Holser, W.T., Kaplan, I.R., Sakai, H., Zak, I., 1980. The age curves of sulfur and oxygen isotopes in marine sulfate and their mutual interpretation. *Chem. Geol.*, 28: 190-260.
- Jørgensen, B.B., 1982. Mineralization of organic matter in the sea bed – the role of sulphate reduction. *Nature*, 296: 643-645.
- Lyons, W.B. and Gaudette, M.E., 1979. Sulfate reduction and the nature of organic matter in estuarine sediments. *Org. Geochem.*, 1: 151-155.
- Paytan, A., Kastner, M., Campbell, D., Thiemens, M.H., 1998. Sulfur isotopic composition of Cenozoic seawater sulfate. *Science*, 282: 1459-1462.
- Raiswell, R. and Berner, R.A., 1986. Pyrite and organic matter in Phanerozoic normal marine shales. *Geochim. Cosmochim. Acta*, 50: 1967-1976.
- Strauss, H., 1999. Geological evolution from isotope proxy signals – sulfur. *Chem. Geol.*, 161: 89-101.