High activity of sulphate-reducing bacteria in Archaean and Proterozoic oceans and an early development of the Phanerozoic-style sulphur cycles

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Pyrite crystals in Precambrian sedimentary rocks are characterized by $\delta^{34}S$ values around 0‰. Two different models have been suggested to explain these sulphur isotope data: sulphide formation in sulphate-poor ocean (Cameron, 1982; Canfield and Teske, 1996); sulphide formation by extensive microbial sulphate reduction in sulphate-rich ocean (Ohmoto *et al.*, 1993). Changes in the sulphate content of the past oceans were likely to have been directly related to the oxygen level in the atmosphere, because sulphate is a product of oxic weathering of sulphide minerals on continents, as well as of weathering of anhydride. The surface environments (temperature, redox state) of the Precambrian Earth can be constrained by examining whether pyrites in Precambrian sedimentary rocks were formed in sulphate-rich or sulphate-poor oceans. For that purpose, micro-analyses of sulphur isotopes were performed on large numbers of single grains of pyrite crystals in the Archaean and Proterozoic sedimentary rocks.

Results and discussions

A total of 369 micro-analyses were performed using a Nd-YAG laser microprobe method on shales from the 2.7 to 2.5 Ga formations in the Hamersley Range, Australia, the 2.7 Ga formations in the Abitibi greenstone belt, Canada, and the 3.4 to 3.2 Ga formations in the Barberton greenstone belt, S. Africa. Pyrite crystals in shales from each formation are found to exhibit large $\delta^{34}S$ variations: −2.5‰ to +8.5‰ for the 3.4−3.2 Ga Barberton samples; −4.4‰ to +7.0‰ for the 2.7 Ga Abitibi samples; +0.4‰ to +10.2‰ for the 2.7 Ga Hamersley (Jeerinah Fm.) samples; and −6.3‰ to +11.8‰ for the 2.5 Ga Hamersley (Mt. McRae Shale) samples. Remarkable features of the analytical results are large $\delta^{34}S$ variations (up to 10‰) within small scales, such as a 2 mm^2 area on a bedding plane or a 5 cm^3 rock chip, of samples from the Barberton and Hamersley districts, and systematic zonings of $\delta^{34}S$ values in pyrite nodules from the Abitibi district.

The characteristics of $\delta^{34}S$ frequency patterns (the range, mean, and skewness) of pyrite grains in the examined samples suggest that: (1) most pyrites in the Archaean shales were formed by microbial reduction of seawater sulphate; and (2) the positive shift of $\delta^{34}S$ of seawater sulphate from 0‰ had already begun by 3.4 Ga due to the preferential fractionation of ^{32}S into sedimentary sulphides by biological processes. $\delta^{34}S$ values of coeval seawater sulphate can also be estimated from the $\delta^{34}S_{(py)}$ frequency patterns. The results of this study suggest that $\delta^{34}S$ values of seawater sulphate increased from +2‰ at 3.4 Ga to +5‰ at 2.7 Ga and to +10‰ at 2.5 Ga. The kinetic isotope effects (Δ) associated with the microbial sulphate reduction appear to have generally increased with time: the maximum Δ values were about 6‰ at 3.4 Ga, about 12‰ at 2.7 Ga, and about 20‰ at 2.5 Ga. Because the kinetic isotopic effects larger than about 5‰ were observed in laboratory systems with sulphate contents greater than ~10 mM, the above Δ values suggest that the normal Archaean seawater already contained more than ~1/3 of sulphate content of modern seawater. This suggestion further implies that the Archaean atmosphere was already oxygen rich.

Heavy sulphur isotope values (more than +25‰) and variable $\delta^{34}S$ values were found by the laser microprobe method for sedimentary pyrites in the Precambrian/Cambrian boundary (0.54 Ga) section of the Chapel Island Formation, Newfoundland, Canada. The kinetic isotope effects during the formation of these pyrites were very small, less than 5‰, and comparative to those for the Archaean sedimentary sulphides. The lithology and the sulphur isotopic characteristics of the Chapel Island samples suggest that the sediments accumulated in an evaporating basin with an oxic seawater. The moderate concentrations of $S_{(py)}$ and the extremely low contents of $C_{(org)}$ in the Chapel Island samples indicate that the organic matter trapped in the sediments were nearly completely metabolized by sulphate-reducing bacteria during early diagenesis of the sediments. The abundance of highly metabolizable organic matter can explain the small kinetic isotopic effects accompanying bacterial sulphate reduction. Therefore, the environmental conditions for the 3.4 Ga Barberton shales may have been similar to those for the 0.54 Ga Chapel Island Formation.

Summary and conclusions

Since at least 3.4 Ga, the oceans appear to have been sulphate-rich, sulphate-reducing bacteria have been actively forming sedimentary pyrite, and the modern-style of sulphur cycles have been operated. The smaller kinetic isotope effects associated with bacterial sulphate reduction in Archaean oceans were probably due to higher rates of the activity of sulphate-reducing bacteria. Generally warmer climate and higher availability of digestible organic matter in Archaean oceans, compared to modern ones, were probably the causative factors for the higher activity of sulphate-reducing bacteria.

References

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