The Neoproterozoic sedimentary sulphur cycle: evidence from the isotopic composition of marine evaporites and sedimentary pyrite

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Introduction

The Neoproterozoic and its transition into the Cambrian was a time of major geological, evolutionary and geochemical changes. Geological key features include the break-up of the supercontinent(s) (i.e. Smith *et al.* 1981), low-latitude glaciations (Kirschvink 1992), deposition of iron-formations (Klein & Beukes 1992) and evaporites (Zharkov 1984). Evolutionary features include extinction and radiation events (i.e. Brasier 1979, 1982). Geochemical changes include secular variations of the global carbon, sulphur and strontium isotope records (i.e. Derry *et al.* 1992, Strauss 1993, Kaufman *et al.* 1993, Kaufman & Knoll 1994).

Constraints regarding the Neoproterozoic sedimentary sulphur cycle and its isotopic characteristics can be derived from marine evaporite deposits as tracers for past seawater composition and sedimentary pyrite, reflecting the activity of sulphate reducing bacteria. Results will be presented from a recent worldwide survey of more than 250 Neoproterozoic and early Cambrian samples (evaporites, carbonates, clastic sediments) with respect to their sulphur geochemistry and isotopic composition. In addition, relevant literature data have been compiled.

Results

Sulphur isotope data for several Neoproterozoic and early Cambrian evaporites from Australia, Canada, India, Iran and Russia indicate a transition from values around +20 ‰ to values of +30 to +35 ‰ (CDT) at around 600 Ma before present. These strongly positive sulphur isotope values are also characteristic of early Cambrian marine sulphates, representing the most ³⁴S-enriched compositions during all of Earth's history.

Sedimentary pyrite of Neoproterozoic age displays highly variable δ^{34} S-values between -30 ‰ and +55 ‰. Frequently, the total range of

observed isotope values within a single stratigraphic unit exceeds 50 % (with a maximum of 73 % for the Precambrian/Cambrian transition in the Lesser Himalaya, Deb *et al.* 1994). These ³⁴Senriched values for pyrite are even more positive than values for coeval sea water sulphate.

Discussion

Sulphur isotope data from marine sulphate deposits of Neoproterozoic and early Cambrian age allow the reconstruction of a sulphur isotope age curve for this time interval with a time resolution of 100 to 150 Ma. It shows fairly constant isotopic compositions close to +20 ‰ for most of the time, followed by a pronounced increase in 34 S to values around +30 ‰ for the Vendian. This trend continues into the Cambrian. The precise stratigraphic level of this steep increase is not documented in any massive evaporite deposit. However, a stratigraphic position can be obtained due to the fact that all deposits characterized by these very positive δ^{34} S-values are younger than the last Neoproterozic glacials, the Varanger glaciation. This allows correlation with the carbonate carbon isotope curve for this time interval. The variable isotope values for sedimentary pyrite reflect their formation via bacterial sulphate reduction. Correlation of petrographic observations regarding diagenesis and pyrite formation with the geochemical results for these sedimentary sulphides indicate the continuous evolution of their isotopic composition along the line of a Rayleigh fractionation process. Earliest diagenetic, framboidal pyrite is characterized by isotopically light (³⁴S-depleted) sulphur, whereas later diagenetic phases, concretions and overgrowth display in part strongly ³⁴S-enriched sulphur isotope values. These observations can best be explained by bacterial sulphate reduction and formation of sedimentary pyrite under sulphate-limiting conditions.

Conclusions

Key features characterizing the Neoproterozoic sedimentary sulphur cycle include a significant change in the isotopic composition of marine sulphate at around 600 Ma and highly variable δ^{34} S-values for sedimentary pyrite reflecting bacterial sulphate reduction under sulphate-limiting conditions.

Acknowledgements

Support of this work through the Deutsche Forschungsgemeinschaft (Grant Ve 112/1-1/1-2) is gratefully acknowledged.

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