

## Dynamic ocean chemistry around the Marinoan glaciation – Isotopic evidence from cap carbonates

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Hurtgen et al. (2002) suggested that the oceanic sulfate pool would become strongly enriched in <sup>34</sup>S during the Neoproterozoic snowball Earth due to continuous bacterial sulfate reduction and lack of supply of S from continental weathering. Overturn of this deep ocean with high  $\delta^{34}\text{S}_{\text{sulfate}}$  would have caused a large positive excursion in the  $\delta^{34}\text{S}$  of CAS (carbonate-associated sulfate) in cap carbonates.

Comparable large positive excursions in  $\delta^{34}\text{S}_{\text{sulfate}}$ , more than 25‰, occur in the Doushantuo cap carbonates following the Marinoan glaciation as shallow-water platform facies on the Yangtze Block. Yet,  $\delta^{34}\text{S}$  for CAS from the deep-water cap carbonates of the Jinjiadong Formation do not support the Hurtgen et al. (2002) model. Significantly different from the Doushantuo Formation, CAS from carbonate of the Jinjiadong section has lower  $\delta^{34}\text{S}$  and  $\delta^{18}\text{O}$  values: 11.2 to 19.7‰ with an average of 14.9 ‰ for S and 5.0 to 8.0‰ with an average 6.6‰ for O, whereas the  $\delta^{34}\text{S}$  and  $\delta^{18}\text{O}$  values from the Doushantuo cap carbonates fall mostly between 25 to 45‰ and 12 to 18‰ respectively. In the Jinjiadong cap carbonates, the  $\delta^{34}\text{S}$  values for pyrite range from 6.1 to 22.9‰ with an average of 14.8‰.

Comparable  $\delta^{34}\text{S}$  values for CAS and pyrite suggest two possibilities: 1) the pyrite was formed through bacterial sulfate reduction but at very low sulfate concentration; or/and 2) the sulfate originated from reoxidation of bacterially derived H<sub>2</sub>S. A negative correlation between carbonate  $\delta^{13}\text{C}$  and CAS  $\delta^{34}\text{S}$  supports that BSR probably happened in a stagnant ocean. However, the relatively uniform S and O isotope data for CAS imply that the deep-water, representing coeval ocean water, may have had of  $\delta^{34}\text{S}$  values at 15‰ and  $\delta^{18}\text{O}$  values around 7‰, rather than the high  $\delta^{34}\text{S}$  values described by Hurtgen et al. (2002). Therefore, a dynamic model is proposed to interpret short-term variations in S, C, and O isotopes of global ocean water following the Marinoan glaciation.

### Reference

Hurtgen M.T., Arthur M.A., Suits N.S., Kaufmann A.J., (2002), *Earth Planet. Sci. Lett.* 203, 413-429.

## Iron isotope constraints on the Archean and Paleoproterozoic ocean redox state

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The response of the ocean redox state to the rise of atmospheric oxygen by ca. 2.3 Ga ago is poorly constrained although deposition of BIFs until ca. 1.8 Ga suggests at least episodic deep ocean anoxia during the Paleoproterozoic. Since Fe, along with C and S, are coupled with and maintain the redox state of the surface environment, Fe seawater concentration and isotopic composition were likely affected by the change in the redox state of the atmosphere. We will present a study of Fe isotope composition of sedimentary sulfides over geological time and provide evidence for a change in the ocean Fe cycle at the same time as atmospheric redox state changed.

We analyzed Fe isotope compositions of ~ 150 pyrites from 20 black shale units, specifically focusing on Late Archean to Paleoproterozoic time.  $\delta^{56}\text{Fe}$  values of handpicked sulfides were obtained using a Neptune MC-ICPMS at WHOI and are reported relative to IRMM-14 with an external precision of 0.1‰ at 2 $\sigma$  level.

The emerged general pattern of Fe isotope record allows dividing the Earth's history into three stages which are strikingly similar to the stages defined by the  $\delta^{34}\text{S}$  and  $\Delta^{33}\text{S}$  as well as other indicators of the redox state of the atmosphere and ocean. (1) Stage 1 (>2.8 to 2.3 Ga) is characterized by highly variable and negative  $\delta^{56}\text{Fe}$  values of pyrite (down to -3.5‰) that are interpreted to reflect the reservoir effects during partial oxidation of hydrothermally-derived Fe(II) and precipitation of Fe-oxides. (2) Stage 2 (2.3 to ~1.6 Ga) is characterized by  $\delta^{56}\text{Fe}$  values ranging from -0.3 to 1.2‰ that might be related to the increased effect of sulfide precipitation in a redox-stratified ocean. (3) Stage 3, from 1.6 Ga through the Phanerozoic, is characterized by sedimentary pyrite having a limited range of  $\delta^{56}\text{Fe}$  variations (less than 0.5‰ around igneous value at ~0‰) reflecting the establishment of an Fe-poor oxygenated ocean.