

Enhanced primary productivity in the aftermath of the rise of atmospheric oxygen

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Carbonates from ~2.3-2.1 Ga have markedly positive carbon isotope values, commonly reaching +10‰. If these values capture the primary composition of marine dissolved inorganic carbon, this event, referred to as the Lomagundi excursion, represents the most severe and long-lived perturbation of the Earth's global carbon cycle and may reflect greatly enhanced organic carbon burial. Other researchers attribute these values to widespread methanogenesis within the sediments, possibly linked more broadly with Earth's redox evolution. We have found that there is a narrow range of moderate $\delta^{34}\text{S}$ values from carbonate-associated sulfate (CAS) of Lomagundi age, which is inconsistent with carbonate formation in the methanic zone. Instead, CAS $\delta^{34}\text{S}$ values that closely match those from coeval sulfate evaporites suggest that the carbonates record primary seawater signals and that C-S isotope systematics can be used to track the global C and S cycles.

In the falling limb of the carbon isotope excursion there is an up-section increase in the $\delta^{34}\text{S}$ of CAS. We propose that this enigmatic relationship reflects a decrease in the extent of spatially widespread environments with nearly quantitative sulfate reduction. When sediment organic carbon loading was high, and therefore not limiting for bacterial sulfate reduction, H_2S production and burial would be expected to have little net effect on the $\delta^{34}\text{S}$ value of seawater sulfate. In this light, the inverse relationship between carbonate-C and CAS-S isotopes can be understood in terms of varying extents of sediment organic matter delivery. The Lomagundi excursion appears to be linked with high levels of sediment organic matter loading rather than methane-related overprints.

The oxidation state of magmas from melt inclusions and olivine hosts

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Debate continues on the extent to which the oxidation state of magmas reflects the oxidation state of the mantle vs. confounding processes in the crust, such as degassing, crystal fractionation or diffusive exchange. Part of the debate stems from complexities that plague one approach over another, or from measurements in degassed, evolved volcanic rocks. Here we circumvent both of these issues by examining several heterovalent elements in undegassed melt inclusions, with examples from pyroclastic samples from the Aleutian volcanic arc and Basin and Range. One method is based on the sulfur content of magmas at sulfide saturation [1], which increases exponentially as a function of $f\text{O}_2$ due to the addition of sulfate species to the melt. Least degassed melt inclusions from both regions vary strongly in their sulfur content, from 1200 to 5000 ppm total sulfur, placing lower limits on $f\text{O}_2$ of FMQ to FMQ+1.8, respectively. Total sulfur is a particularly robust measure of high- $f\text{O}_2$, given that it is difficult to envision crustal processes that lead to increases in the sulfur content of a magma; it also avoids the artifacts associated with measuring sulfur species directly in glasses [2]. In the same samples, we have also measured the vanadium concentrations in the olivine population and melt inclusions or host basalts in order to calculate the ol/liq partition coefficient of V, which decreases strongly with increasing $f\text{O}_2$ [3, 4]. The V-based estimates of $f\text{O}_2$ are concordant with the sulfide saturation model, and also consistent with the high $\text{Fe}^{3+}/\text{Fe}_T$ (~30%) measured by micro-XANES [5] in the most sulfur-rich Aleutian melt inclusions. Within each dataset, $f\text{O}_2$ correlates not with H_2O , but with La/Sm and other source features of the magmas. The concordancy of the different redox-sensitive species, the primitive nature of some of the melt inclusions (i. e., in Fo_{86-90} olivines), and the correlation with incompatible trace element ratios all point to intrinsic variations in $f\text{O}_2$ of the primary melts, and not late-stage modification.

[1] Jugo (2009) *Geology*; [2] Metrich, *et al.* (2009) *GCA*; [3] Canil (2002) *EPSL*; [4] Mallmann & O'Neill (2009) *J.Pet.* [5] Kelley and Cottrell (2009) *Science*.