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Sulfur and oxygen isotopic compositions of early Cambrian phosphorites from Lesser Himalaya: Constraints on the diagenetic frame work

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Early Cambrian phosphogenesis is a widely recorded event and has been related to major perturbations in the biogeochemical cycling of phosphorous during this time interval. However, the mechanism of formation of early Cambrian phosphate has remained equivocal owing to the absence of comparable modern marine counterparts. We have studied sulfur and oxygen isotopic compositions of structural sulfate in francolite (carbonate fluorapatite) and associated pyrite from a suite of samples collected from Lower Tal Formation, Lesser Himalaya, India. A shallow marine depositional setup has been suggested. In the present work an attempt has been made to constrain the diagenetic framework for the francolite precipitation.

Structural sulfate concentrations of francolite in the studied samples vary from 0.07 to 0.3%. The $\delta^{34}S_{SO4}$ data range from 21 to 30‰ and most values are significantly less than what have been recorded [1] from other early Cambrian phosphorites (30‰ and above). This would suggest incorporation of depleted sulfate formed by oxidation of H_2S at the sediment water interface into francolite lattice at the time of its precipitation. Had francolite been precipitated in an anoxic sulfate reducing zone the structural sulfate would have recorded enriched sulfur isotopic composition compared to the contemporary sea water sulfate. The preliminary $\delta^{18}O_{so4}$ data range from 8.1 to 13.2‰ and apparently do not indicate significant residual oxygen enrichment through sulfate reduction or disproportionation. In contrast the $\delta^{34}S$ of pyrite associated with the phosphorites shows a large distribution (-29 to 34‰), suggesting typically a late diagenetic S isotopic enrichment due to sulfate limitation through bacterial mediation and possibly anaerobic methane oxidation. Based on earlier studies [2] on $\delta^{13}C$ of Tal phosphorite and the present work we suggest that the crystallisation of francolite possibly took place in a suboxic condition and was followed by pyritisation when the francolite layer encounterd the zone of sulfate reduction.

References

[1] Shields et al. (1999) *JGSL.* **156,** 943-955.
[2] Mazumdar, A and Banerjee, D.M (2001) *Chem. Geol.* **175**, 5-15.

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Seawater sulfur isotope fluctuations in the Cretaceous

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The exogenic sulfur (S) cycle in tightly coupled with many other geochemical cycles including carbon, phosphorus, iron, strontium and oxygen. We present a high-resolution, precise, S isotope curve for seawater sulfate for the Cretaceous. The overall record indicates isotope values more depleted in ^{34}S during the Cretaceous compared with the past 45 million years, most likely as a result of extensive volcanic activity. Superimposed on this background value are two excursions towards less positive $\delta^{34}S$ values, one between 120-105 Ma and the other between 95-80Ma. These excursions represent periods of significantly lower burial rates of reduced S (pyrite), probably as a result of a shift in the location of organic C burial to either terrestrial settings where sulfate availability is limiting sulfate reduction or open-ocean settings where iron availability may be limiting pyrite formation. These data imply a non steady state of the oceanic S system and variability in atmospheric oxygen partial pressure.