

# Phosphorites as tracers of 2.0 Gyr old ocean chemistry and oxygenation

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Sedimentary phosphorites contain francolite (carbonate fluorapatite) as the major mineral phase. The open structure of francolite acts as a chemical sponge, facilitating numerous substitutions of trace elements and oxyanion complexes. Francolite is known to incorporate sulphate in proportion to its concentration in ambient pore fluids. By correlating francolite-bound sulphate with  $\delta^{34}\text{S}$  (in combination with REE,  $\delta^{13}\text{C}$ ,  $\text{FeS}_2$  content), the effects of sulphate reduction and sulphide reoxidation at the redox interface on sulphate concentrations can be constrained. This allows us to extrapolate back to primary francolite sulphate levels, and by comparison with recent phosphorite to coeval ocean sulphate concentrations.

The Jhamarkotra Phosphorite is the oldest known marine (and non BIF associated) sedimentary apatite deposit. Formed predominantly under open shelf conditions, marine phosphorites are likely to be suitable for reconstructing ancient seawater chemistry. High  $\delta^{13}\text{C}_{\text{carb}}$  values in 2.0 Gyr old dolostones from the same formation were interpreted to reflect changes in biological activity and elevated rates of organic carbon burial [1]. Such circumstances can lead to a rise in atmospheric oxygen levels, as postulated to have occurred after ca. 2.3 Ga [2], possibly related to a tectonically driven rise in chemical weathering rates at that time [3]. Such oxygenation events in early Earth history likely increased not only atmospheric and seawater  $\text{O}_2$  levels but also the concentrations of oxyanions, such as sulphate in seawater. Evaluation of the francolite sulphate concentration in Jhamarkotra phosphorites will allow us to determine the seawater sulphate levels and provide direct evidence for Earth's surface oxygenation in the Late Paleoproterozoic.

## References

- [1] Sreenivas B., Das Sharma S., Kumar B., Patil D.J., Roy A.B., Srinivasan R. (2001) *Precamb. Res.* **106**, 277-290.
- [2] Bekker et al. (2004) *Nature* **427**, 117-120.
- [3] Shields, G.A. (2006) *Science*, submitted.