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Development of a global sulfidic ocean at ~1.84 Ga: Evidence from Fe-S systematics in the Rove Formation, Ontario

S.W. POULTON[1], D.E. CANFIELD[1] AND P. FRALICK[2]

[1] Danish Center for Earth System Science, Institute of Biology, University of Southern Denmark, 5230 Odense M, Denmark (s.poulton@biology.sdu.dk; dec@biology.sdu.dk)
[2] Department of Geology, Lakehead University, Thunder Bay, Ontario, Canada (pfralick@lackheadu.ca)

The cessation of banded iron formation (BIF) deposition at approximately 1.8-1.9 Ga has traditionally been explained by oxygenation of oceanic deep waters, with resultant precipitation of Fe(II) as ferric oxides. An alternative hypothesis suggests that increasing sulfate availability stimulated bacterial sulfate reduction, leading to euxinic conditions and the removal of Fe(II) in the form of pyrite [1]. In this contribution we explore Fe-S systematics in the 1.84 Ga Animike Group, Ontario. This sequence records a transition from the Gunflint iron formation into the overlying shales of the Rove Formation, and represents the final stages of BIF deposition in a global ocean setting. The sediments show enrichments in 'highly reactive' iron (iron oxides + siderite + pyrite) throughout the sequence, implying deposition beneath an anoxic water column. Thus the global cessation of BIF deposition at this time did not apparently occur due to oxygenation of oceanic deep waters. Furthermore, a comparison of pyrite Fe/total Fe profiles with (oxide + siderite Fe)/total Fe profiles demonstrates a clear transition from an Fe(II)-rich water column, through a transitional stage, into an upper zone of persistant sulfidic conditions. The transitional stage appears to represent the initial pulses of sulfide into the water column (either from the deposited sediments or due to water column sulfate reduction). Supporting evidence for these observations comes from sulfur isotope profiles. The lower stages display a wide range in pyrite S isotope values, consistent with those commonly seen during diagenetic pyrite formation. Towards the top of the sequence the pyrite S isotope signal becomes less variable, consistent with isotopic signatures commonly evident in euxinic settings, and additionally becomes markedly heavier (approaching a likely seawater composition of 20-25‰). Thus these sediments appear to record the almost complete reduction of water column sulfate to sulfide. We conclude that the initial pulses of sulfide into the water column resulted in the rapid removal of Fe(II) in the form of pyrite, leading to the termination of BIF deposition and ultimately the development of a sulfidic global ocean.

References

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Theoretical estimates of equilibrium $^{18}O/^{16}O$ fractionation between phosphate minerals and water

E.A. SCHAUBLE[1] AND H.P. SCHWARCZ[2]

[1] UCLA, Los Angeles, CA, USA (schauble@ess.ucla.edu)
[2] McMaster University, Hamilton, ON, Canada (schwarcz@mcmaster.ca)

Oxygen isotope measurements of biogenic and inorganic phosphate minerals have been extensively used in studies of ancient climates and environments. At low temperatures, aqueous phosphate approaches isotopic equilibrium with water very slowly unless exchange-catalyzing biological enzymes are present, suggesting that phosphate oxygen-isotope measurements may provide evidence of ancient or extraterrestrial biological activity [1]. Both uses of phosphate oxygen-isotope measurements require accurate knowledge of the equilibrium fractionation between phosphate and water at low temperatures, but the size and temperature sensitivity of these fractionations are still somewhat uncertain.

In the present study, equilibrium $^{18}O/^{16}O$ fractionations between phosphate minerals (e.g., xenotime and $LuPO_4$) and water are calculated theoretically using the standard thermodynamic approach of Urey (1947). To perform this type of calculation it is necessary to know the vibrational spectra of pure ^{18}O- and ^{16}O-substituted crystals. Here *ab initio* and empirical force-field models are used to calculate vibrational frequencies, because the vibrational spectra of ^{18}O-substituted phosphates have not been measured. *Ab initio* force fields are determined using density functional theory; comparison with measurements on natural (^{16}O-dominated) phosphates suggests accuracies of several per mil in calculated isotopic fractionation factors at room temperature.

The calculated oxygen isotope fractionation between xenotime (YPO_4) and water is 33‰ at 0ºC, and declines by about 0.25‰/ºC to 27‰ at 25ºC, and more slowly to 12‰ at 120ºC. This result is within 2‰ of the fractionation between the xenotime analogue $LuPO_4$ and water calculated using an empirical force field. Close agreement between *ab initio* and empirical force-field results suggests that both are reasonably accurate. Calculated xenotime-water and $LuPO_4$-water fractionations are within the range of measured $[PO_4]^{3-}_{aq.}$-water fractionations [2], suggesting that there is little fractionation between aqueous phosphate and xenotime. The present results are in disagreement with previously published semi-theoretical calculations [3], which predict that xenotime will have $^{18}O/^{16}O$ ratios > 38‰ higher than water at 25ºC.

References

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