Fe-S systematics in the 1.88 Ga Virginia Formation: Implications for the chemical evolution of the Proterozoic ocean

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The cessation of 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 (Canfield, 1998). In this contribution we explore Fe-S systematics in the 1.88 Ga Virginia Formation, N. Minnesota. These shales were deposited during the final stages of BIF deposition and thus may potentially record information relating to the evolution of ocean chemistry during this important transitional period.

Highly reactive:total Fe ratios are low (0.03-0.28), consistent with those found in modern and ancient marine sediments deposited beneath either oxygenated bottom waters or anoxic waters with relatively high clastic fluxes (Poulton and Raiswell, 2002). However, the application of a new extraction procedure suggests enrichments in both siderite Fe (up to 6.3 wt%) and magnetite Fe (up to 0.55 wt%), implying deposition beneath an anoxic, Fe(II)-rich water column. Sulfur isotope compositions vary within the sequence, but preliminary data suggest three distinct groups; 1. Siderite-poor sediments with $\delta^{34}S$ of 5.7 ± 1.8‰, 2. Siderite-rich, pyrite-poor sediments with $\delta^{34}S$ of 0.0 ± 5.3‰, and 3. Siderite-rich, pyrite-rich sediments with $\delta^{34}S$ of 26.5 ± 8.8‰. Thus isotopic compositions are generally quite ^{34}S-enriched compared to a likely seawater composition of 20-25‰, and are relatively uniform between each sediment group. On the basis of the above observations we suggest that these sediments may record the early stages of a transition from an anoxic Fe(II)-rich ocean to a sulfidic ocean. This transition apparently occurred in phases, whereby periodically seawater sulfate was extensively reduced to sulfide. This sulfide was initially removed from solution by reaction with water column Fe(II). Persistent sulfidic conditions were likely established later, when ambient dissolved Fe(II) concentrations were sufficiently reduced by reaction with sulfide and when sulfide production rates exceeded Fe(II) delivery rates.

References

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Constraining actinides migration in soils using activity ratios

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Atmospheric fallout of nuclear weapon test that most occurred in the fifties and in the sixties involved activation products isotopes such as ^{238}Pu (half-life = 87.7 y), ^{239}Pu (half-life = 24 131 y), ^{240}Pu (half-life = 6 537 y), ^{241}Pu (half-life = 14.4 y) as well as radiogenic ^{241}Am (half-life = 432 y) daughter product of ^{241}Pu. Thus atmospheric source terme was well characterized from activity ratios. For example, $^{241}Am/^{239}Pu+^{240}Pu$ ratios measured in the air and in rain has allowed to estimate residence time of radioactive dust in the atmosphere, after each nuclear shots.

As a consequence soils are nowadays the largest environmental reservoir of transuranic elements. In soil, ^{241}Am originates from atmospheric fallout and from *in situ* decaying ^{241}Pu. Thus from a theoretical point of view soil Am/Pu ratios are time dependent and yield the age of Pu deposition onto soil. Therefore soil Am/Pu ratio provides unique opportunity to trace the behaviour of transuranic elements in soil, to check if $^{241}Am/^{239+240}Pu$ and $^{241}Pu/^{239+240}Pu$ ratios are time dependant or if Am/Pu chemical fractionation occurred.

We studied soils from high altitude catchments (French Alps and Vosges mountains) where strong radioactive fallout are due to large precipitation amount. Soils exhibit two distinct Am/Pu ratios :

- ratios close to the theoretical signature expected from atmospheric reservoir characterize "reference soils"

- anomalous soils exhibit lower Am/Pu ratios than expected. Despite such low daughter activity, $^{241}Pu/^{239+240}Pu$ ratios of those soils are consistent with primary atmospheric fallout ratio. In this case Am/Pu ratios trace Am and/or Pu migration in soils. Assuming Pu is immobile with respect to Am, we calculated that anomalous ratios are consistent with migration of 25-40% of Am inventory. Transuranic elements migrations will be further characterized from soil/water interface chemical properties.