Sulfidic organic-rich shales in the Archean low-sulfate ocean: Evidence for transient oxygenated conditions, enhanced volcanism, or low sedimentation rates?

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One of the main motivations to study sedimentary sulfides and sulfates was to constrain seawater sulfate level in the past. Fractionation in $\delta^{34}S$ values between sulfate (or its proxies) and sulfide has been used to address this question. While late Neoproterozoic and younger sediments show S isotope fractionations larger than 45‰, fractionations are much smaller in sediments older than 2.3 Ga, deposited before the rise of atmospheric oxygen. This temporal trend has been related to low seawater sulfate content due to the lack of oxidative weathering under the anoxic atmosphere.

Organic-rich sulfidic shales deposited in association with mantle plume breakout events and BIFs are common in the Archean sedimentary record starting at ca. 2.74 Ga. Three mechanisms could have contributed to their formation: 1) transient, gradual, or local oxidized conditions; 2) giant volcanic eruptions loading atmosphere with SO_2 and increasing delivery of sulfate and S^0 aerosols to the ocean; and 3) low sedimentation rates under which sulfate could diffuse into sediments and be reduced in sediments building sufficient H_2S level in porewaters to form pre-compaction diagenetic sulfide nodules.

The ca. 2.7 Ga Manjeri Formation of the Belingwe Greenstone Belt in Zimbabwe contains organic-rich shales stratigraphically above BIF and structurally below a several kilometers thick mafic-ultramafic volcanic succession. Pyrite nodules and layers in these shales have a large range of negative and positive $\delta^{34}S$ values, consistent with previous studies (e.g. Grassineau *et al.* 2006), but also a large range of stratigraphically highly variable positive and negative $\Delta^{33}S$ values, indicating that photochemically fractionated S was delivered from an anoxic atmosphere rather than from continents by oxidative continental weathering. Multiple S isotope data indicate a complex microbial community living in the Manjeri basin including sulfate-reducing and S^0-disproportionating bacteria. We infer that low sedimentation rates coupled with high atmospheric S flux during mantle plume breakout events might explain the origin of sulfidic organic-rich shales in the Archean anoxic low-sulfate ocean.

Deep circulation and upward migration of brines in the St. Lawrence Lowlands (Qc, Canada) traced by noble gases

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Hypersaline brines (120 to 340 g/L) associated with gas accumulations have been found in the St. Lawrence Lowlands, Eastern Canada. They are hosted by fractured sedimentary rocks of the lower and intermediate parts (Potsdam, Beekmantown and Trenton groups) of an autochthonous platform sequence of Cambrian-Ordovician age overlying a Grenvillian metamorphic basement. Normal faulting related to the St-Lawrence rift affects these rocks units. The brines are either Na-Ca-Cl or Ca-Na-Cl type. Na vs Cl ratios of the brines are identical to fluids circulating in crystalline rocks of the Canadian Precambrian Shield. Stable isotopes (δH, $\delta^{18}O$) and $^{87}Sr/^{86}Sr$ suggest water-rock interactions between evaporated seawater and silicates, possibly from the Grenvillian basement.

Noble gas isotopes are good tracers of fluid circulation through the crust. Eight gas and brine wells were sampled near Trois-Rivières, 100 km to the north-east of Montréal, Québec. The $^{3}He/^{4}He$ (0.07 - 0.25 R/R_A), $^{20}Ne/^{22}Ne$ (9.8 - 10.5), $^{21}Ne/^{22}Ne$ (0.029 - 0.067), $^{40}Ar/^{36}Ar$ (288 - 2424) and $^{129}Xe/^{130}Xe$ (6.431 – 6.611) ratios all suggest a mixing between three noble gas components: the atmosphere, the crust and about 3-12% of mantle. Relations between atmospheric, radiogenic and mantle-derived gases indicate that components are transported by advection by brines.

The occurrence of a deep-seated noble gas component suggests that the brines circulated deeper in the basement before migrating upward in the sedimentary rock reservoirs, possibly through normal faults related to the St. Lawrence rift. The mantle anomaly could be linked to a tectonically-driven magmatic episode related to rifting or rift fault reactivation between 450 and 150Ma, or related to Cretaceous Monteregian magmatism at ca, 120 Ma. The subsequent ageing of this initial magmatic input would translate into an increasingly radiogenic noble gas component.