

Al solubility in SiO₂-H₂O fluids at 800-1000°C, 5-20 kbar: Evidence for Al/Si complexing

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Low solubility of Al in pure H₂O to high *P* and *T* [1] nominally supports the assumption that Al is immobile in environments such as the lower crust, upper mantle and subduction zones. However, veins with Al-rich minerals found in the same settings imply significant Al mobility. SiO₂ is among the most abundant solutes in vein fluids, and it has been suggested that SiO₂-Al₂O₃ complexing leads to elevated Al solubility [2]. To investigate this hypothesis we studied (1) the solubility of corundum in fluids of varying initial SiO₂/H₂O ratios at 800°C, 10 and 15 kbar, (2) the effect of *P* on corundum solubility at fixed SiO₂/H₂O ratio, and (3) the effect of temperature on the solubility of corundum at 15 kbar and quartz (qz) saturation. Synthetic corundum, natural high-purity qz, and ultrapure H₂O were equilibrated using hydrothermal piston-cylinder methods [3]. Initial SiO₂ concentrations were varied between zero and qz saturation. Solubility was determined by the weight loss from the corundum crystals. The solubility of Al in pure H₂O was 0.0028 molal, consistent with previous work. At 800°C, 10 kbar, the concentration of Al increases with increasing dissolved SiO₂, to a maximum of 0.0152 molal at qz saturation. The increase in Al concentration with increasing Si requires Al-Si complexing, consistent with recent predictions of Al-Si oligomerization in high *P-T* fluids [2]. At constant SiO₂ molality, Al solubility rises with increasing *P*. At 15 kbar and qz saturation, Al molality is described by the equation $m_{Al} = 5.84 \times 10^{-9} e^{0.01957P}$. At 950°C, 15 kbar, the concentration of AlO_{1.5} is equal to 2.14 weight percent. The Al in these experiments will also decrease the hydrothermal melting point of quartz. These results suggest that Al-Si complexing is a simple mechanism for enhancing Al solubility in metamorphic settings.

[1] P. Tropper & C.E. Manning (2007) *Chem. Geol.* **240**, 54–60. [2] C.E. Manning (2007) *Geofluids* **7**, 258–269. [3] C.E. Manning & S.L. Boettcher (1994) *Am. Mineral.* **79**, 1153–1158.

Late Archean oceanic redox fluctuations revealed by iron speciation in the 2.73Ga old Tumbiana Formation

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Recent chemostratigraphic studies (C, N, S isotopes) of the 2.73Ga old Tumbiana sedimentary formation (Hamersley basin, Australia) revealed microbial metabolisms thriving on oxidized species of N (nitrate) and S (sulfate), thus arguing for 'local' oxygen-rich paleoenvironmental conditions during deposition of the sediments. However, the recognition of substantial Mass Independent Fractionation of Sulfur indicate that the atmospheric (and oceanic) oxygen levels were rather low (<10⁻⁵ PAL) during that time. In order to better characterize respective water column redox conditions we report high resolution iron speciation data.

Fe_{carb} (siderite or dolomite-ankerite), Fe_{ox} (ferrihydrite, goethite and hematite), Fe_{mag} (magnetite), Fe_{PRS} (chlorite, glauconite and biotite) and Fe_{py} (pyrite) were measured in mudstones, stromatolitic carbonates and siltstones from the PDP-1 diamond drill core, using an established sequential extraction protocol. Stromatolites show high Fe_{HR}/Fe_T (0.31) and low Fe_{py}/Fe_{HR} (0.18) arguing for depositional conditions beneath an anoxic ferruginous water column. Variations in Fe_{HR} within stromatolites result from differences in Fe_{carb} rather than Fe_{py} being consistent with sulfate reduction with reactive Fe in excess of dissolved H₂S. Mudstones show lower Fe_{HR}/Fe_T (0.15) and Fe_{py}/Fe_{HR} (0.05) with Fe_{ox} and Fe_{mag} providing high proportions of Fe_{HR} in the mudstones, averaging 6.2 and 38.3 wt.%, respectively. This suggests transient oxic conditions during the deposition of mudstones. Tumbiana siltstones yield a wide range of Fe_{HR}/Fe_T ratios from 0.09 to 0.51. Fe_{py}/Fe_T are also variable, with a low average of 0.07 which might reflect detrital iron input from terrestrial sources. Some horizons within the siltstone with high Fe_{mag} (>45.8 wt.%) also support temporarily oxidizing water column conditions.

Accordingly, we propose that the 2.73Ga old Tumbiana Formation was deposited from an anoxic ferruginous water column that was temporarily oxidizing with respect to iron reinforcing the idea that first whiffs of oxygen might have occurred in the surface ocean before the 2.4Ga GOE.