

Progress in the establishment of a new Infrared calibration for the SiO₂-system

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Conventionally used Infrared (IR) calibrations (Paterson, 1982; Libowitzky & Rossman, 1997) for the quantification of water in solids are established on hydrous minerals and glasses with several wt% water. These calibrations are based on a negative correlation between the IR absorption coefficient for water and the mean wavenumber of the corresponding OH pattern. The correlation reflects the dependence of the OH band position on the corresponding O-H...O distances and thereby the magnitude of the dipole momentum which is proportional to the band intensity. It has been observed that these calibrations can not be applied to nominally anhydrous minerals (NAMs) (Rossman, 2006). Up to now the ultimate cause remains completely unclear.

To learn more about absorption coefficients in NAMs and their potential dependence on structure and chemistry we synthesized SiO₂ polymorphs with specific isolated hydroxyl point defects, e.g. quartz, coesite and stishovite with B³⁺+H⁺=Si⁴⁺ and/or Al³⁺+H⁺=Si⁴⁺ substitutions. Experiments were performed with water in excess in piston cylinder and multi-anvil presses. Single crystal IR spectra reveal the presence of hydroxyl groups in all our samples and enable us to propose new OH incorporation models. Furthermore, IR spectra demonstrate that we successfully managed to separate generally complicated OH band patterns as e.g. observed in natural quartz and synthetic coesite samples. We quantified sample water contents of both natural samples and our synthesis products by applying broad-beam proton-proton-scattering (Reichart *et al.* 2004) and Raman spectroscopy (Thomas *et al.*, 2006).

We present new material-specific correlations and resultant single calibration constants for the SiO₂ polymorphs. It turns out that the magnitude of absorption coefficients within one structure type is independent of the liable OH point defect and therewith the wavenumber of the observed band position but in contrast varies with the structure itself. Similar results concerning an intra-structural constancy of the integral molar absorption coefficient have been shown before for feldspars (Johnson & Rossman, 2003).

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Multiple Sulfur and Carbon isotopic chemostratigraphy of the 2.73 Ga carbonated Tumbiana formation, new insights for the Fortescue excursion

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In order to bring further insights into the environmental conditions prevailing during the δ¹³C negative Fortescue Excursion attributed to an increase in methanotrophic biomass, we carried out a detailed carbon (¹²C, ¹³C) and multiple sulfur (³²S, ³³S, ³⁴S) isotopic study through the entire pristine core drilled from the 2.7 Ga Tumbiana Formation (Pilbara Drilling Project; Van Kranendonk *et al.*, 2006).

Organic δ¹³C_{PDB} values vary markedly at meter scale and display a bimodal distribution with two maxima at -43 and -28‰. This isotopic record, together with petrological and other geochemical evidence, cannot be explained by secondary processes including diagenesis or metamorphism and argues for the occurrence of two distinct pools of biomass likely produced by different metabolic pathways, photosynthesis and methanotrophy. δ³⁴S_{CDT} values of sedimentary pyrite vary from -5.8 to 2.7‰ (average -0.5‰). Lithologically independent heterogeneities (at centimeter scale) in isotopic composition (>5‰), sulfur content and S/C ratio are best interpreted by coexisting microbial sulfate reduction and sulfur oxidation metabolisms. Sedimentary pyrite display Mass Independent Fractionation with Δ³³S_{CDT} anomalies ranging between -0.24 and 1.64 ‰ (average 0.46 ‰) and correlating positively with the ¹²C enrichment of organic matter. This suggests that the sulfur components derived from photochemically-processed volcanic gases and delivered to the Tumbiana sediments were ultimately involved in the metabolic activity of sulfur processors.

Our results suggest that at least four different types of metabolism operating under various redox conditions were present in the Tumbiana paleo-environment and we propose that the δ¹³C negative Fortescue Excursion reflects methane assimilation by a consortium of organisms including Anaerobic Oxidation of Methane Archea and Sulfate Reduction Bacteria in anoxic time of the Tumbiana basin.

Reference

Van Kranendonk M. J., Philippot P., and Lepot K. (2006), *Western Australia Geological Survey, Record 2006/14*, 25p.