

Raman spectroscopic study on the Cr⁶⁺ speciation in aqueous fluids at elevated P and T

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In oxidizing environments, chromium is hexavalent. There is a considerable number of Cr⁶⁺ minerals, which are almost exclusively chromates. Chromium(VI) is much more mobile than Cr³⁺ due to the higher solubility of Cr⁶⁺ in aqueous fluids. Chromium(VI) equilibria in aqueous solutions have been studied at ambient P and T, e.g. as function of pH and total Cr⁶⁺ concentration [1]. Here, we report first results on changes in the aqueous Cr⁶⁺ speciation with pressure and temperature.

We recorded Raman spectra of an H₂O + 11.7 wt% K₂Cr₂O₇ fluid and a D₂O + 19 wt% K₂Cr₂O₇ fluid up to 1.6 GPa and 400 °C using a hydrothermal diamond-anvil cell [2] and quartz as pressure sensor [3]. The Raman spectra reflect mostly the chromate [CrO₄]²⁻ – dichromate [Cr₂O₇]²⁻ equilibrium. The normalized integrated intensities of the stretching bands of [Cr₂O₇]²⁻ tend to decrease and that of [CrO₄]²⁻ to increase slightly with pressure. The ratio of the integrated intensity of these bands does not change significantly with temperature. The formation of [CrO₄]²⁻ is strongly suppressed in the D₂O fluid, but this has no effect on the observed behavior of the [Cr₂O₇]²⁻ and [CrO₄]²⁻ species with pressure and temperature.

In both experiments, a new band at 260–290 cm⁻¹ appears in the spectra at temperatures above 200 °C. The intensity of this broad band shows no distinct dependence on pressure, but increases strongly at 300 and 400 °C, which is coupled with a decrease in the intensity of bands assigned to chromate and dichromate bending modes. This suggests the formation of another Cr-species in the fluid. In analogy to Raman bands of phosphate [4] and sulfate [5] in aqueous solutions, the new band is tentatively assigned to a restricted translation mode from Cr–O⁻HOH or Cr–O⁻DOD and may thus result from hydrated chromate or dichromate ions in the solution at elevated temperatures. This interpretation is supported by the observed band shift by about 20 cm⁻¹ to lower wavenumbers in the experiment using D₂O, which indicates an involvement of hydrogen or deuterium in the species.

[1] Ramsey *et al.* (2001) *Corros Sci.* **43**, 1557-1572. [2] Bassett *et al.* (1993) *Rev. Sci. Instrum.* **64**, 2340-2345. [3] Schmidt & Ziemann (2000) *Am. Mineral.* **85**, 1725-1734. [4] Rudolph & Irmer (2007) *Appl. Spectrosc.* **61**, 1312-1327. [5] Rudolph (2010) *J. Solution. Chem.* **39**, 1039-1059.

Geochemistry across the Frasnian / Famennian Boundary, Hongguleleng Formation, Xinjiang Province, China

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The Hongguleleng Formation has yielded a very diverse Famennian shallow marine community and records the rebound from the Frasnian–Famennian (F/F) extinction event in a highly fossiliferous shallow marine setting associated with a Devonian oceanic island arc complex. Faunas from the Hongguleleng demonstrate that the rebound from the F/F extinction event happened much more rapidly than previously thought and suggest that central Asia may have acted as a refugium. This study uses a multiproxy geochemical approach to put constraints on environmental changes, which occurred at the F/F boundary (Late Devonian) within the Hongguleleng Formation. Recent conodont studies place the F/F boundary approximately three meters above the base of the Hongguleleng Formation, giving us an opportunity to conduct detailed geochemical and sedimentological studies across the boundary in a unique setting (oceanic island arc complex) in a part of the world which has a paucity of data at this interval. Changes in the detrital flux were evaluated by examining variations in mineral composition and diagnostic elemental ratios. The hydrothermal and volcanic influence on sedimentation was estimated using Al/(Al+Fe+Mn) and Zr/Al₂O₃ proxies. The input of nutrients was determined by excess P₂O₅ and Ba. The degree of anoxia during deposition was constrained by the V/Cr ratio and the concentration of redox sensitive metals in the sediment.

Samples were collected from the basal six meters of shale and limestone in the Hongguleleng Formation and the upper one meter of shale and volcanoclastic sandstone in the underlying Zhulumute Formation. This interval also spans the *linguiformis* / *triangularis* conodont zone boundary which forms the F/F boundary. Although the Kellwasser event is not recognizable in outcrop by evidence of black shale, it can be recognized geochemically as series of dysoxic and anoxic events that span three meters of section below the boundary. The same interval also shows high levels of biological productivity based on excess Ba and P₂O₅ proxies. The upper limestone surfaces in this interval often have large concentrations of brachiopods. In contrast, limestones and shales in the lower Famennian show oxidic to slightly dysoxic conditions. Pulses of volcanoclastic and hydrothermal components to detrital sedimentation are common throughout the interval and are recognized by mineralogy and Al/(Al+Fe+Mn) and Zr/Al₂O₃.

The analysis of multiple geochemical proxies allows us to confirm the presence of the Kellwasser event in the open oceanic part of Paleotethys. The tectonic setting of the Hongguleleng Formation is in contrast to the sections previously studied, which were located near Laurussia, Gondwana, Siberia, and the South China plate. We plan additional studies of C, O and Sr isotopes in the near future to further refine our model of changing climatic and oceanographic conditions in the Hongguleleng Formation.