

XAS studies of the geometric transitions of Co(II) species in chloride brines from 25°C to 150°C

STACEY BORG^{1*}, WEIHUA LIU¹, DENIS TESTEMALE²,
AND JOËL BRUGGER³

¹CSIRO Exploration & Mining, Australia

(*correspondence: Stacey.Borg@csiro.au)

²Institut Néel, Département MCMF, France

³South Australian Museum and The University of Adelaide, Australia

Aqueous Co(II) chloride complexes play an important role in cobalt transport and deposition in hydrothermal ore-forming systems as well as in industrial ore processing. Despite this, the nature and thermodynamic properties of the aqueous Co(II) chloride complexes in hypersaline brines at elevated temperature are poorly understood.

This study examined the octahedral-tetrahedral transition of Co(II) chloride complexes as a function of temperature and Cl concentration, with the aim to derive formation constants for the tetrahedral complex CoCl_4^{2-} . Co K-edge fluorescence XANES spectra were collected for solutions containing 0-5 m NaCl at 25 and 150°C, at ANBF beamline 20B (Photon Factory, Japan) using a titanium hydrothermal cell developed by the authors. The systematic changes in the XANES spectra qualitatively indicate that the contribution of tetrahedral species (i.e., CoCl_4^{2-}) increases with an increase in chloride concentration and/or temperature. The measured XANES spectra are also compared with theoretical XANES calculations.

Formation constants for the tetrahedral complex CoCl_4^{2-} have been retrieved from the measured XANES spectra at 150°C. Together with the properties available at lower temperatures, thermodynamic properties for cobalt chloride complexes are extrapolated to 300°C, and future experiments will aim to obtain measurements at temperatures up to 600°C.

Inclusions and crown-like chrome spinel in chromites from the Oman ophiolite: Evidence for hydrous MORB melts in the mantle-crust transition zone

A. Y. BORISOVA^{1,2*}, G. CEULENEER³, S. ARAI⁴,
F. BÉJINA¹, B. A. BAZYLEV⁵ AND M. POLVÉ¹

¹LMTG, 31400 Toulouse, France

(*correspondence: borisova@lmtg.obs-mip.fr)

²MGU, 119991 Moscow, Russia

³DTP, 31400 Toulouse, France

(Georges.Ceuleneer@ntp.obs-mip.fr)

⁴Kanazawa University, 920-1192 Kakuma, Japan

⁵GEOKHI, 119991 Moscow, Russia

We evidenced primary melt inclusions in chromites of podiform and stratiform chromitites in the Cretaceous Oman ophiolite. Post-entrapment processes transformed the hydrous melt into daughter phases like pargasites, aspidolites, enstatites and chromites. The daughter phase compositions imply that the host chromite crystallized from basaltic melt similar to those of mid-ocean ridge (MORB) with 2 wt % TiO_2 , 15 wt % Al_2O_3 , 9 wt % CaO , and 4 wt % Na_2O , except for a much higher H_2O content (~4 wt %). Crystal inclusions of euhedral pigeonite, forsterite, augite, bytownite, and anhedral pargasite suggest that the chromite crystallized from a hydrous melt at pressures below 2 kbar. A crystallization temperature (T) of $1100 \pm 50^\circ\text{C}$ and a diffusion closure temperature (T_c) of $980 \pm 20^\circ\text{C}$ are estimated for chromite based on olivine - liquid [1] and olivine - spinel [2] equilibria.

The "crown-like" structures identified in chromite are inferred to be formed as daughter chromite with high *cr*- and low *mg*-numbers due to fractional crystallization (~20%) from the entrapped melt. Compositional profiles in chromite adjacent to the melt inclusions are similar to those in olivine corresponding to partial re-equilibration of up to ~25% in the hypothesis of instant cooling [3]. The concentration profiles imply that the chromites underwent rapid cooling (of the order of a few hours) from T to T_c . The MORB melt crystallized at reduced $f_{\text{O}_2} = 10^{-11 \pm 2}$ bar and became saturated in aqueous fluid; this fluid saturation, leading to rapid cooling of the chromitite magma, is the proposed model for the investigated chromitite genesis in the MOHO mantle-crust transition zone.

[1] Almeev *et al.* (2007) *Am. Mineral.* **92**, 670-674.

[2] Ballhaus *et al.* (1991) *Contrib. Mineral. Petrol.* **107**, 27-

40. [3] Danyushevsky *et al.* (2002) *J. Petrol.* **43**, 1651-1671.