



	Experiment title: Impact of chloride on the fate of cadmium in hydrothermal fluids and vapors: an in situ XAFS spectroscopy study	Experiment number: MA 443
Beamline: BM30B	Date of experiment: from: 28 November 2007 to: 04 December 2007	Date of report: 31 August 2008
Shifts: 18	Local contact(s): Dr. Jean-Louis Hazemann (hazemann@grenoble.cnrs.fr)	<i>Received at ESRF:</i>
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Report:

Experimental. The local atomic structure around cadmium in nitrate and chloride aqueous solutions was studied by XAFS spectroscopy at the Cd K-edge (26.7 keV) at temperatures 20 – 450°C and pressures 1 – 600 bar using an X-ray cell developed at the Institut Néel (Testemale et al., 2005). XAFS spectra of Cd aqueous solutions were collected in both transmission and fluorescence mode at BM30B beamline (FAME).

Results from the nitrate system. Two nitrate solutions were examined: 0.10m Cd(NO₃)₂ – 0.10m HNO₃ and 0.01m Cd(NO₃)₂ – 0.20m HNO₃ (where m denotes the number of moles of each solute per kg of water) at T = 20-300°C and P = 600 bar. Results from EXAFS spectra show that in the first atomic shell Cd is coordinated by 6 oxygen atoms at 2.28±0.02 Å with no detectable change with increasing temperature. These structural data are consistent with the octahedral Cd(H₂O)₆²⁺ cation in solution. At T ≥ 300°C, however, precipitation of CdO from solution is observed likely due to the enhanced Cd²⁺ hydrolysis.

Results from the chloride system. Six Cl-bearing solutions were studied in the system CdCl₂-HCl-NaCl-H₂O with 0.04m, 0.77m, 0.12m, 2.30m, 2.55m and 5.23m of total chloride concentration. Two kinds of runs were performed: as a function of temperature (20-450°C) at 600 bar and as a function of pressure (600-268 bar) at 400°C (for 0.04m Cl solution).

Although EXAFS modeling shows that single scattering (SS) from O is much weaker than that from Cl in the first coordination shell of Cd, the inclusion of oxygen in the model for all spectra improves the fit significantly. Neither more distant signals from beyond-the-first atomic shells around Cd, nor multiple scattering evens could be detected within the spectral resolution.

EXAFS spectra modeling shows that at ambient temperature in all solutions the dominant Cd aqueous species are octahedral CdCl_n(H₂O)_{6-n} complexes containing from 1 Cl + 5 O (water molecules) in the 1st atomic shell at the lowest Cl concentration (0.04m) to 4 Cl + 2 O at the highest Cl concentration (5.23m). The Cd-Cl and Cd-O distances at ambient temperature were found to be 2.48±0.03 Å and 2.33±0.03 Å, respectively. With increasing temperature, these octahedral-like species transform to tetrahedral-like as shown by changes in XANES spectra with increasing T, and confirmed by EXAFS modeling (Fig. 1). At the same Cl concentration, the Cd-O distance does not change within errors with increasing temperature at least to 450°C (not shown), whereas the Cd-Cl distance systematically decreases (Fig. 2). At the same T, Cd-O distance remains the same, whereas the Cd-Cl distance increases with increasing chloride concentration; for example, at 450°C Cd-Cl distance changes from 2.40±0.02 Å at 0.04m Cl to 2.46±0.02 Å at 5.23m Cl (Fig. 2). At a given T, with increasing mCl, oxygen atoms in the first atomic cell are progressively replaced by chlorine atoms (Fig. 3). This increase of the number of Cl atoms with mCl confirms our solubility data (Bazarkina, PhD thesis in prep.) and existing thermodynamic predictions (e.g., Sverjensky et al., 1997), indicating that CdCl₂ and CdCl₃ are likely to be the dominant species in the whole Cl range.

Our single experiment at 400°C as a function of P (~density of fluid) shows that with decreasing P from 600 to 268 bar there is no significant change in XAFS and XANES spectra. In the whole density range

(0.6-0.2 g/cm³) Cd is coordinated by 2.5±0.5 Cl atoms at 2.41±0.02Å and 2.5±0.5 O atoms at 2.33±0.03Å. These data are consistent with the formation of the neutral CdCl₂ complex hydrated by ~2 water molecules.

The solvation by water molecules of Cd chloride complexes at supercritical conditions may have important consequences for the Cd transport by hydrothermal fluids and volcanic vapors. Possible structural differences in the solvation between Cd and Zn aqueous complexes may probably explain the increase of Cd/Zn ratio in the low-density volcanic gases in comparison with dense hydrothermal brines at high T (Rubin, 1997).

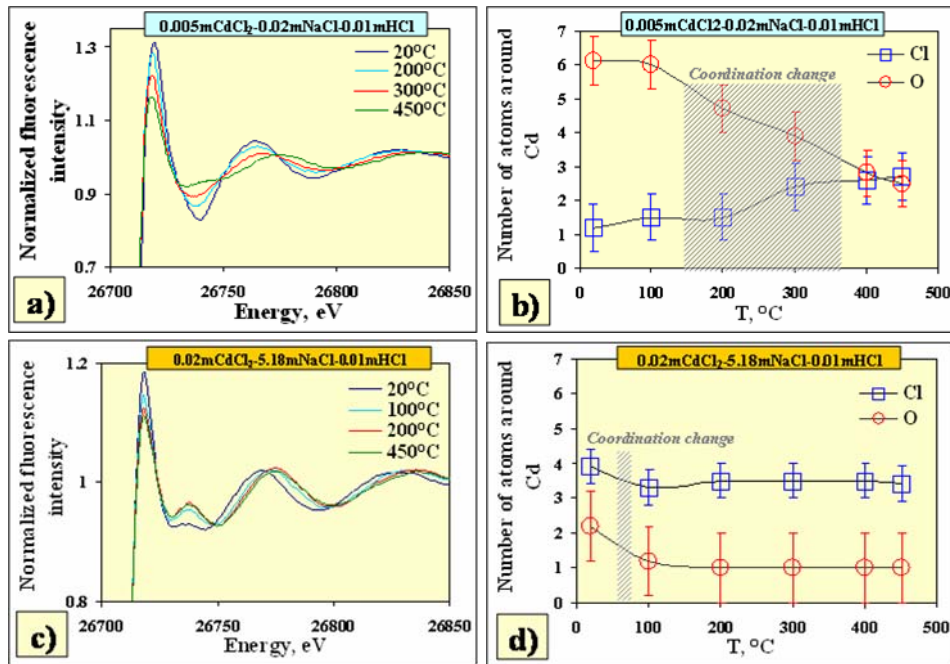


Fig 1. Evolution of XANES spectra (a, c) and the number of Cl and O (b, d) as a function of T for the lowest (0.04m) and highest (5.23m) Cl concentrations investigated.

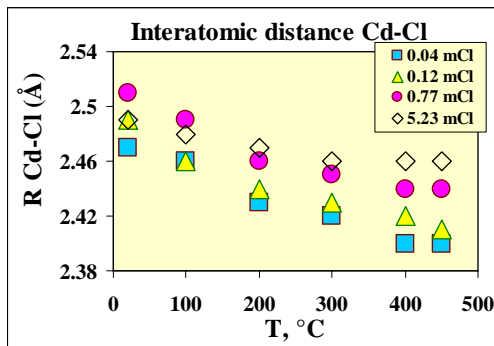


Fig 2. Cd-Cl interatomic distances in the first atomic shell as a function of temperature and mCl.

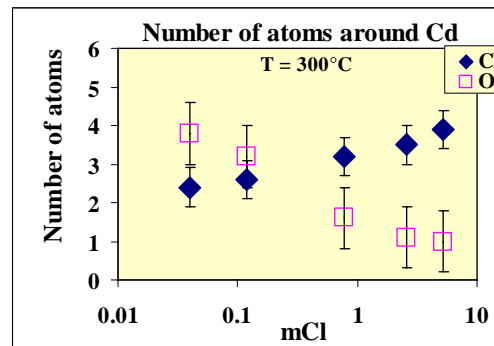


Fig 3. The number of Cl and O around Cd in the first atomic shell as a function of mCl at 400°C and 600 bar.

Conclusions and perspectives. This first in situ measurement of the structures and stoichiometries of Cd species will be indispensable for the interpretation of our solubility data of CdO and CdS minerals (Bazarkina, PhD thesis in prep.) to derive the thermodynamic properties of the dominant Cd-Cl-H₂O complexes in hydrothermal brines and vapors. Knowledge of the dominant aqueous complexes at the atomic scale will improve our understanding of Cd and similar metals (Zn, Cu, Hg) behavior in high T-P ore-forming fluids and volcanic gases, and could potentially be used in metal extraction and ore treatment technologies.

References.

- Bazarkina E.F. Transport of base metals (Zn, Cd, Cu) by hydrothermal/volcanic vapors and fluids: experimental approach and physical-chemical modeling. PhD thesis (in preparation).
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