


Experiment title:

Zinc transport by hydrothermal fluids and vapors

Experiment
number:

ES 253

Beamline: BM30B	Date of experiment: from: 02 February 2015 to: 10 February 2015	Date of report: 06 April 2017
Shifts: 18	Local contact(s): Dr. Jean-Louis Hazemann (jean-louis.hazemann@neel.cnrs.fr)	<i>Received at ESRF:</i>

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Report:

Experimental. The local atomic structure around zinc in aqueous solutions and ZnS solubility was studied by XAS spectroscopy at the Zn K-edge (9.66 keV) at temperatures 20 – 520°C and pressure 600 and 185 bar. The spectra of Zn aqueous solutions were collected in both transmission and fluorescence mode at BM30B beamline (FAME) using an X-ray cell developed at the Institut Néel (Testemale et al., 2005). Eight successful experiments were performed, including 1 run in Zn-bearing nitrate solution, 3 runs in Zn-bearing chloride solutions, 1 vapor-liquid partitioning run in ZnCl₂-HCl-H₂O system, and 3 ZnS solubility runs (2 in NaCl-HCl and 1 in Na₂S₂O₃ solution). In addition, 7 Zn solids were measured at ambient *T-P* as standards.

Results from the nitrate system. XANES spectra of 0.015*m* Zn(NO₃)₂ – 0.32*m* HNO₃ (where *m* is molality) at 30°C is very close to that of solid Zn(NO₃)₂·6H₂O, where Zn is coordinated by 6 oxygen atoms in the first coordination shell (Ferrari, 1967). Results from EXAFS modeling confirms $N_{O} = 6.0 \pm 1.0$ around Zn at $R_{Zn-O} = 2.08 \pm 0.01$ Å. These structural data are consistent with the octahedral Zn(H₂O)₆²⁺ cation in solution. With heating up to 200°C, R_{Zn-O} decreases down to 2.05 ± 0.01 Å, the coordination number does not change within error. At higher *T* precipitation of Zn from solution is observed likely due to hydrolysis of Zn, similarly with the cations of other metals (e.g., Cd and Pd, Bazarkina et al., 2010; 2014).

Results from the chloride system. Six Cl-bearing systems were analyzed: three ZnCl₂-NaCl-H₂O solutions with 0.020, 0.34, and 11.2*m* of total Cl concentration at 30-520°C and 600 bar, two HCl-NaCl-H₂O solutions with 0.014 and 0.87*m* of total Cl in equilibrium with ZnS at 600 bar (solubility runs) and one 0.0008*m* ZnCl₂ – 0.0011*m* HCl-H₂O solution at 400-366°C and 600 bar (single phase fluid) and 185 bar (vapor phase at vapor-liquid equilibrium).

At 30°C, solutions with low Cl concentration (0.02-0.3*m* Cl) have the XANES spectra very close to that in nitrate solution, indicating that the dominant Zn species is the same. The EXAFS modeling confirms that Zn is surrounded by 6 O atoms, i.e. the octahedral Zn(H₂O)₆²⁺ cation is the dominant Zn species. This is in agreement with available thermodynamic data. At high Cl concentration (11.2*m* Cl), the XANES spectrum is very different from those in nitrate and low Cl concentration solutions, this spectra is shifted by 1.9 eV to lower energy and has a typical tetrahedral shape. According to EXAFS modeling, Zn is surrounded by 4 Cl atoms at 2.27 ± 0.01 Å. These data confirms results of previous XAS studies; the tetrahedral ZnCl₄²⁻ is the single dominant species at such high Cl concentration at 30°C.

With increasing *T* spectra of all Cl-bearing solutions becomes “tetrahedral-like” (e.g., 350°C, Fig. 1). Thus in solutions with low Cl concentration Zn coordination changes from octahedral to tetrahedral between 100 and 200°C. The spectra of 11.2*m* Cl solution demonstrates very close XANES and EXAFS up to 460°C. Weak changes are observed at 520°C, it may corresponds to appearance of other species such as ZnCl₃(H₂O)⁻, the fracture of such complexes similar with ZnCl₄²⁻ may reach up to 50%. To quantify more accurately their fracture more spectroscopic data at high Cl concentration (2-10*m*) and high *T* are required. The approximate speciation

model for 0.9m Cl solution at 350°C is shown in Figure 1. Our new spectroscopic data indicate that the role of ZnCl_4^{2-} complex at such moderate Cl concentrations at T above 200°C was overestimated by recent studies (e.g., Akinfiev and Tagirov, 2014; Mei et al., 2015).

Our single experiment at 366-400°C as a function of P (or fluid density) shows that with vapor-liquid phase separation with P decreasing from 600 to 185 bar, the XANES spectrum of the vapor phase remains very close to those obtained in other solutions with low Cl concentration (i.e., 0.03m) at 300-450°C. These observations allow to suppose the formation of the neutral ZnCl_2 complex hydrated by ~ 2 water molecules at low Cl concentrations at high T at all P (i.e. at all densities). The primary treatment of ZnS solubility measured in solutions with 0.014m and 0.87m Cl indicate that previous studies have overestimated stability of ZnCl_4^{2-} complex, but underestimated ZnS solubility at 1.0m Cl (e.g., Akinfiev and Tagirov, 2014; Mei et al., 2015).

Results from the S-rich system. Dissolved Zn concentration and Zn aqueous environment were measured in 2.1m $\text{Na}_2\text{S}_2\text{O}_3$ solution in equilibrium with ZnS(s) at 345°C and 460°C. At T above 200°C the thiosulfate becomes unstable and decomposes to SO_4^{2-} , $\text{H}_2\text{S}^0(\text{aq})/\text{HS}^-$ and other intermediate-valence S species (Pokrovski&Dubessy, 2015). The solubility of ZnS measured in such solution at 345°C measured after 2.5h is 0.0022m which is 1 and 2 orders of magnitude below than thermodynamic predictions of Akinfiev and Tagirov (2014) and Mei et al. (2016), correspondingly. The XANES spectra of this solution is compared with those of octahedral $\text{Zn}(\text{H}_2\text{O})_6^{2+}$ and tetrahedral ZnCl_4^{2-} species in Figure 2. The XANES spectra of Zn in such S-rich solution is E shifted by 0.8eV to lower energy and has the lower amplitude of the first XANES peak. This may indicate the species with the new structure. According to EXAFS modeling, in this solution Zn is surrounded by 3.5 S atoms at $2.33\pm 0.01\text{\AA}$. Due to the fact that hydrosulfide HS^- is one on the major S species in our solution at 345°C, the question is open to assign this Zn species to the trigonal planar $\text{Zn}(\text{HS})_3^-$ (Mei et al., 2016) or tetrahedral $\text{Zn}(\text{HS})_4^{2-}$. Further measurements in H_2S -bearing reduced solutions at high T - P are required to test these hypothesis. At 460°C ZnS solubility is far below 10^{-4}m , the decrease of ZnS solubility may result from S precipitation at such T - P .

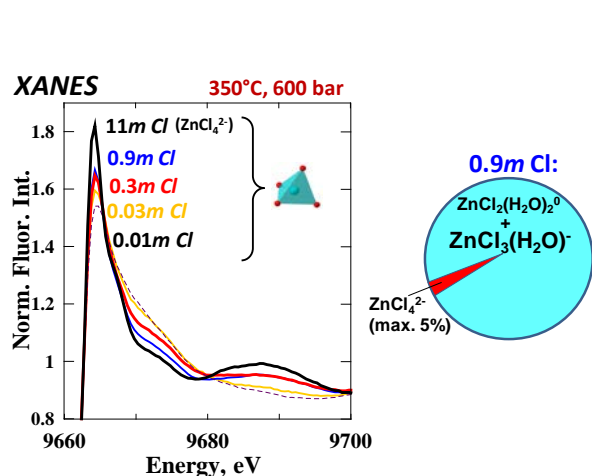


Fig 1. XANES spectra of tetrahedral Zn-Cl- H_2O complexes in hydrothermal fluids at 350°C and 600bar and speciation model for 0.9m Cl solution.

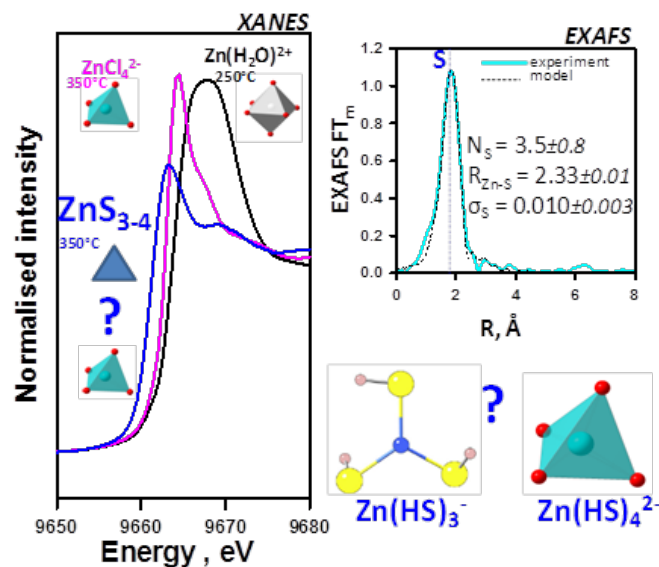


Fig 2. The XANES spectra of Zn species at high T - P and the EXAFS modeling of Zn complex dominant in SO_4 - H_2S solution.

Conclusions and perspectives. Our measurements on Zn aqueous complexes in Cl- and S-bearing fluids have shown that the available in literature thermodynamic data are too uncertain to be used for quantitative modeling of Zn transport. The new data on Zn species will be indispensable for the revised thermodynamic database creation and the interpretation of Cd/Zn variations in natural hydrothermal ores (Bazarkina, PhD). Knowledge of the dominant aqueous complexes at the atomic scale will improve our understanding of Zn and other base metals (Cu, Pb, Fe) behavior in high T - P ore-forming fluids and volcanic gases, and could potentially be used in metal extraction and ore treatment technologies.

References.

Akinfiev and Tagirov (2014) *Geochem. Int.* **52**, 197; Bazarkina E.F. (2009) PhD thesis, Toulouse; Bazarkina E.F. et al. (2010) *Chem. Geol.* **276**, 1; Bazarkina E.F. et al. (2014) *GCA* **146**, 107; Ferrari et al (1967) *Acta Cryst.* **22**, 240 ; Mei et al. (2015) *GCA* **150**, 265 ; Mei et al. (2016) *GCA* **179**, 32 ; Pokrovski&Dubessy (2015) *EPSL* **411**, 298 ; Testemale D. et al. (2005) *Rev. Sci. Instrum.* **76**, 43905.