TRANSITION METALS IN HYPERSALINE SOLUTIONS: EXPERIMENTS AND NUMERICAL MODELLING

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INTRODUCTION

Hypersaline brines form a significant proportion of present-day surface water in semi-arid environments. Understanding metal transport in hypersaline brines is important for predicting the dispersion of metals around ore deposits, and hence for ranking geochemical anomalies in the regolith in terms of their prospectivity. It is also required to model element mobility in salinity-affected drainage systems. Moreover, the transport of metals in hypersaline brines (>> 1 molal salt) over a wide range of temperatures (25° C to > 550° C) played a fundamental role in the formation of many Cu, Au, Pb and Zn ore deposits. Despite this, the nature and stability of the aqueous complexes of trace metals in hypersaline brines are poorly understood.

The study of metal speciation in hypersaline brines is limited by several theoretical and practical factors. On the one hand, activity-composition relationships for trace elements in hypersaline solutions are poorly understood (e.g., Helgeson & Kirkham 1974), which renders the quantitative interpretation of the data difficult. On the other hand, most traditional experimental techniques are difficult to apply to these systems. For example, high solubilities limit the use of solubility experiments to relatively low salt concentrations (e.g., Liu *et al.* 2001), while potentiometric experiments are limited to relatively dilute solutions.

We are investigating the use of X-ray absorption spectroscopy (XAS) and ultra-violet—visible—near-infra-red (UV-Vis-NIR) spectrophotometry to understand the speciation of metals such as Cu and Fe in highly saline solutions. Specifically, we explore the use of UV spectrophotometric and synchrotron XAS experiments to identify important aqueous complexes of Fe and Cu forming over a wide range of chloride concentrations (up to 15 molal) and temperatures (25-250°C). The new experimental data are combined with existing information to provide thermodynamic properties for metal-chloride complexes covering the whole range of chloride activities found in nature. These properties can be used for modelling metal speciation and transport in surface, ground and hydrothermal waters. Furthermore, an understanding of the speciation of metals is necessary to understand the bio-availability and sorption/desorption behaviour.

COPPER(I)

Copper can act as both a micro-nutrient or a toxin (mainly as Cu(I)) in surface and groundwater. Moreover, understanding its behaviour in the regolith is important for designing effective soil sampling and data processing strategies in geochemical prospecting. Copper exists in two main oxidation states in near-surface solutions: Cu(I); and Cu(II). Cu(II) is highly soluble and mobile as the distorted octahedral Cu(II) hexa-aquo complex $[Cu(H_2O)_6]^{2+}$. Its mobility is also promoted by the formation of octahedral, tetrahedral, and possibility trigonal dipyramidal chloro-complexes at very high salt concentrations (Brugger *et al.* 2001). Cu(I) on the other hand is virtually insoluble in pure water, but formation of stable aqueous Cu(I) chloro-complexes will increase its solubility in saline groundwater. Thus Cu(I) is an important form of copper in groundwater, and is the main form of copper in most hydrothermal solutions.

Liu *et al.* (2001, 2002) suggested that linear CuCl(OH₂)_(aq) and CuCl₂⁻ predominate at lower salinity, and tetrahedral Cu(OH₂)Cl₃²⁻ and CuCl₄³⁻ are the dominant species at high salt concentrations at temperatures ranging from 25 °C to in excess of 200 °C. The two linear complexes were characterised by Fulton *et al.* (2000), who measured the Extended X-ray Absorption Fine Structure (EXAFS) spectra of Cu(I)-chloride solutions up to 325 °C and 2 molal HCl + NaCl. At the relatively low salt concentration of their experiment, Fulton *et al.* (2000) found no evidence for higher-order complexes, in agreement with the results of Liu *et al.* (2001).

X-ray absorption near-edge spectroscopy (XANES) is sensitive to the oxidation state of the metal, coordination geometry of the complex, and the nature of the ligands. XANES spectra of Cu(I)-bearing LiCl solutions change systematically with increasing salt concentration (Figure 1). This indicates a change in the metal-Cl-H₂O coordination. Comparison with spectra taken for solids in which Cu(I) exists in known

coordination (Kau *et al.* 1987) suggests that at high salinity the coordination of Cu(I) changes from linear to tetrahedral or, possibly, trigonal planar. EXAFS refinements show an increase in the number of Cl ligands with increasingly saline solutions, but suggest that only 3 chloride ions surround the Cu(I) atom. This result is in contradiction with the model proposed by Liu *et al.* 2002).

The cause of this discrepancy may reside in:

- Erroneous assumption in the interpretation of UV spectroscopic experiments by Liu *et al.* (2002), resulting in erroneous speciation. Liu *et al.* (2002) assumed that the UV-Vis spectra they collected followed the Beer-Lambert law. However, deviations from the Beer-Lambert law arise due to changing complex-solvent interaction (e.g., Clifford & Crawford 1966) with increasing salt concentration for a particular complex.
- Problems linked to the strong absorption of the x-rays by the chloride-rich solutions.

These difficulties illustrate the complexity of working with highly saline solutions, and the need for multiple analytical techniques to obtain a reliable and accurate model. If a species like CuCl₃²⁻ really is the dominant form of Cu(I) in highly saline brines (>30 wt. % salt), this raises interesting questions as this complex is rare in solids, contrary to CuCl₄³⁻,



Figure 1: Comparison of CuK α XANES spectra for solutions and compounds (data from Fulton *et al.* 2000 and Kau *et al.* 1987) at room temperature. Note that the spectrum for Cu(I) in the acidic 15 m LiCl solution is similar to that of the tetrahedral complex Cu(I)S₄. The two spectra for Cu(I) in LiCl solutions were recorded at the Australian National Beamline Facility at Tsukuba, Japan, and has a lower resolution than the literature data.

which appears in many coordination compounds. Resolving this uncertainty will help us to establish spectroscopic techniques for the study of highly saline systems, and also some fundamental understanding about the chemistry of metals in such solutions. We are planning to conduct more XANES and EXAFS work at the European Synchrotron Research Facility in Grenoble, collecting spectra at higher resolution and with dramatically improved statistics.

IRON(III)

Fe is an essential oligo-element controlling biomass in surface and ground waters (e.g., Millero *et al.* 1995). Fe is also an important element in major and accessory minerals found in hydrothermal ore deposits that form over conditions ranging from diagenetic to exhalative to magmatic hydrothermal. Fe exists in minerals as Fe(II) (e.g., pyrite), Fe(III) (e.g., hematite) or in mixed valence states (e.g., magnetite). Fe(III) is poorly soluble in groundwater, except where the pH becomes highly acidic (<3), but similar to Cu(I), Fe(III) is readily soluble in brines due to formation of Fe(III)-chloro complexes. Fe(III) is an important catalyst of inorganic and organically mediated geochemical processes, for example in acid mine drainage situations (Peiffer & Stubert 1999).

In acidic aqueous solution, Fe(III) exists as the hexaaquo complex, $[Fe(OH_2)_6]^{3+}$, an ion with octahedral geometry (e.g., Harris *et al.* 1997). As the chloride concentration is increased, substitution of H₂O ligands by Cl⁻ ions results in the formation of a number of Fe(III)-chloro complexes. At sufficiently high chloride concentration, Raman and EXAFS studies indicate that the geometry of the complex changes from octahedral to tetrahedral (Apted *et al.* 1985, Murata *et al.* 1989). Spectrophotometric studies of ferrous chloride complexes indicate similar octahedral to tetrahedral transition at high salinity (Susak & Crerar 1985, Zhao & Pan 2001).

Despite numerous studies on the nature and stability of ferric chloride complexes conducted using a variety of techniques, the speciation and standard thermodynamic properties of ferric chloride complexes in hypersaline solutions and at elevated temperatures are still poorly understood. A few studies have reported formation constants of $FeCl_2^+$ and $FeCl_{3(aq)}$, but they are in poor agreement. Only two studies provided equilibrium constants for aqueous FeCl₄ at 25°C (Gamlen & Jordan 1953, Marcus 1960), although a Raman study by Murata et al. (1989) suggested that tetrahedral $FeCl_4^$ predominates at 300°C in solutions with chloride concentration greater than 3 m. Recently, Tagirov et al. (2000) reported standard state thermodynamic properties of FeCl²⁺ from 25°C to 90°C measured using a nonisothermal electrochemical technique, however, no thermodynamic properties for higher chloro complexes, i.e., FeCl_{3(aq)} and FeCl₄, are available.

We collected UV-Vis electronic, XANES and EXAFS spectra for Fe(III) in acidic (pH \leq 1) LiCl solutions containing up to 15 molal salt and at temperatures of 25°C to 90°C. Qualitative interpretation of the UV-Vis spectra shows that FeCl²⁺, FeCl₂⁺, FeCl_{3(aq)} and FeCl₄ were present in the experimental solutions. As chloride concentrations increase, higher ligand number complexes become important with FeCl₄ predominating in solutions containing more than 10 m at 25°C. This result is confirmed by the XANES spectra (Figure 2). The octahedral to tetrahedral transition is indicated by the shift of the edge towards lower energy, due to an apparent increase of the intensity of the 1s->4s transition (Figure 2a, b). The octahedral to tetrahedral transition occurs at lower salt concentration as temperature increases, indicating higher stability of tetrahedral complexes at elevated temperature (Figure 2).



Figure 2: XANES spectra of Fe(III) chloride solutions measured at the Australian National Beamline Facility at Tsukuba, Japan, at 25°C and 90°C in acidic LiCl solution (0.1 to 15.1 m). (a) XANES spectra, with labelling of the different electronic transitions seen in the spectrum. (b) First derivative of the XANES spectra, showing the systematic edge shift towards low energy with increasing salt concentration and temperature.

The room temperature formation constants for three ferric chloride complexes (FeCl₂⁺, FeCl_{3(aq)} and FeCl₄⁻) determined from the UV data are generally in good agreement with previous studies. Based on the experimental data generated from this and previous studies, the formation constants for ferric chloride complexes were extrapolated up to 300°C using the density model equation of Anderson *et al.* (1991). ρ_w refers to density (g/cm³) of pure water at temperature (*T*) in Kelvin:

$$\log K_{\text{Fe}^{+++}+2\text{CI}^-=\text{FeCI}_{3}^+} = -\frac{1}{2.303} \left(3.3456 - \frac{2121.0}{T} + \frac{54359 \ln \rho_w}{T} \right)$$
$$\log K_{\text{Fe}^{+++}+3\text{CI}^-=\text{FeCI}_{3(aq)}} = -\frac{1}{2.303} \left(14.930 - \frac{4724.0}{T} + \frac{84870 \ln \rho_w}{T} \right)$$
$$\log K_{\text{Fe}^{+++}+4\text{CI}^-=\text{FeCI}_{4}^-} = -\frac{1}{2.303} \left(21.458 - \frac{5247.7}{T} + \frac{94873 \ln \rho_w}{T} \right)$$

The effect of the new properties is illustrated in Figure 3, in which the solubility of hematite in acidic brines as a function of temperature is illustrated. As previous models did not take into account tetrahedral species (e.g., Tagirov *et al.* 2000), they fail to predict correctly the strong increase in hematite solubility resulting from the high stability of these complexes at elevated temperature (Figure 3a, b).

CONCLUSIONS

This study reveals that tetrahedral chloride complexes play important roles in transport of transition metal in hypersaline solutions. This study also shows that XAS is an excellent technique to study the speciation of transition metals in hypersaline solutions, when used in conjunction with other techniques. Further work is required to refine the interpretation of spectroscopic data of metals in highly saline solutions. As we accumulate knowledge about behaviour of well-studied metal ions, we also establish the basis required for exploring the activity-composition relationships in brines, using trace metals to probe the structure of the solution and the activity of the chloride ions.

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Figure 3: Comparison of the predicted solubility of hematite in acidic brines as a function of temperature using the new speciation model and Tagirov et al. (2000)'s model. (a) predicted solubility, (b) distribution of Fe(III) species for the model presented in this study.

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