Fluid speciation controls of redox-sensitive non-traditional stable isotope systems

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Introduction

The study of Ohmoto (1972) on the sulfur isotope system demonstrated that mass-balance among reduced and oxidized solution species potentially exerts a strong control on the isotopic composition of hydrothermal sulphide ore minerals. In the present study, we extend this approach to redox-sensitive non-traditional stable isotope systems. Significant isotopic fractionation occurs between reduced and oxidized solution species (~3 to 12 ‰), with the heavy isotope being enriched in the oxidized species. Since the stable isotope composition of a precipitated mineral is close to that of its equivalent solution species (Asael et al., 2009), isotopic compositions are therefore a function of redox-sensitive thermo-chemical parameters.

Methodology

Reactions and equilibrium constants among the different solution species in the studied isotopic systems (Cu, Mo and Cr) were calculated with the Geochemist's Workbench 4.04 software. All calculations were made at a standard state pressure of 1 atm and temperature of 25°C. The effect of pressure on the fluid speciation calculations in the range relevant for sedimentary and hydrothermal processes is negligible. Eh-pH phase diagrams were calculated with Matlab software to give the stable solution complexes and contour diagrams of the species relative abundance and their isotopic composition.

The set of reactions and equilibrium constants for the Cu-Cl system

1. $CuCl_3^{-2} \leftrightarrow CuCl^+ + e^- + 2Cl^-$ .... $\log K_{Cu1} = -7.843$
2. $CuOH^+ + Cl^- + H^+ \leftrightarrow CuCl^+ + H_2O$ .... $\log K_{Cu2} = 6.670$
3. $CuCl_3^{-2} + H_2O \leftrightarrow CuOH^+ + e^- + 3Cl^- + H^+$ .... $\log K_{Cu3} = -14.513$

The set of reactions and equilibrium constants for the Mo-S system

1. $SO_4^{-2} + 10 \cdot H^+ + 8 \cdot e^- \leftrightarrow H_2S_{(aq)} + 4 \cdot H_2O$ .... $\log K_{S1} = 40.609$
2. $SO_4^{-2} + 8 \cdot e^- + 9 \cdot H^+ \leftrightarrow HS^- + 4 \cdot H_2O$ .... $\log K_{S2} = 33.659$
3. $H_2S_{(aq)} \leftrightarrow HS^- + H^+$ .... $\log K_{S3} = -6.950$
4. $H_2S_{(aq)} + 4 \cdot H_2O \leftrightarrow HSO_4^- + 8 \cdot e^- + 9 \cdot H^+$ .... $\log K_{S4} = -38.616$
5. $MoO_4^{-2} + 4 \cdot H_2S \leftrightarrow MoS_4^{-2} + 4H_2O$ .... $\log K_{Mo} = 24.206*$

*taken from Erickson & Helz, 2000

The set of reactions and equilibrium constants for the Cr system

1. $CrO_4^{-2} + H^+ \leftrightarrow HCrO_4^-$ .... $\log K_{Cr1} = 6.523$
2. $CrO_4^{-2} + 7 \cdot H^+ + 3 \cdot e^- \leftrightarrow CrOH^{++} + 3 \cdot H_2O$ .... $\log K_{Cr2} = 69.018$
3. $CrO_4^{-2} + 6 \cdot H^+ + 3 \cdot e^- \leftrightarrow Cr(OH)_2^+ + 2 \cdot H_2O$ .... $\log K_{Cr3} = 62.285$
4. $CrO_4^{-2} + 5 \cdot H^+ + 3 \cdot e^- \leftrightarrow Cr(OH)_3 + H_2O$ .... $\log K_{Cr4} = 54.832$
5. $CrO_4^{-2} + 4 \cdot H^+ + 3 \cdot e^- \leftrightarrow Cr(OH)_4^-$ .... $\log K_{Cr5} = 45.469$
6. $CrO_4^{-2} + e^- \leftrightarrow CrO_4^{-2}$ .... $\log K_{Cr6} = 1.760$
7. $CrO_4^{-2} + 8 \cdot H^+ + 3 \cdot e^- \leftrightarrow Cr^{+++} + 4 \cdot H_2O$ .... $\log K_{Cr7} = 72.820$

Redox couple A – B	Δ(A – B) [‰]	Source
Cu(II) – Cu(I)	≈ 3 ‰	Asael et al., 2006; Ehrlich et al., 2004; Mathur et al., 2005
MoO_4^{-2} – MoS_4^{-2}	≈ 4.5 ‰	Tossell, 2005
Cr(VI) – Cr(IV)	3.4 ± 0.1 ‰	Ellis et al., 2002

References
Asael, D. et al., 2006. 16th Annual V M Goldschmidt Conference. Pergamon-Elsevier Science Ltd, Melbourne, AUSTRALIA, pp. A23-A23.
Asael, D., Matthews, A., Oszczepalski, S., Bar-Matthews, M. and Halicz, L., 2009. Chemical Geology: In press, doi: 10.1016/jchemgeo.2009.01.015 (2009).
Ehrlich, S. et al., 2004. Chemical Geology, 209: 259- 269.
Ellis, A.S., Johnson, T.M. and Bullen, T.D., 2002. Science, 295(5562): 2060-2062.
Erickson, B.E. and Helz, G.R., 2000. Geochimica et Cosmochimica Acta, 64(7): 1149-1158.
Mathur, R. et al., 2005. Geochimica et Cosmochimica Acta, 69(22): 5233-5246.
Ohmoto, H., 1972. Economic Geology, 67(5): 551-578.
Tossell, J.A., 2005. Geochimica et Cosmochimica Acta, 69(12): 2981-2993.

A. Cu speciation with contours of relative abundance

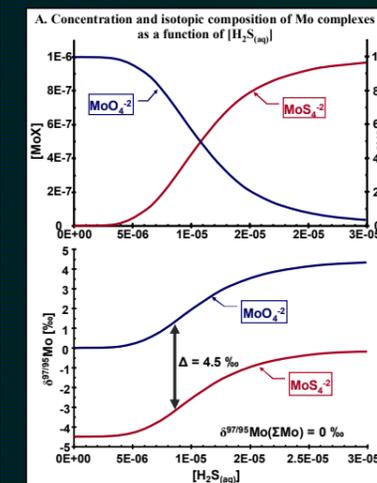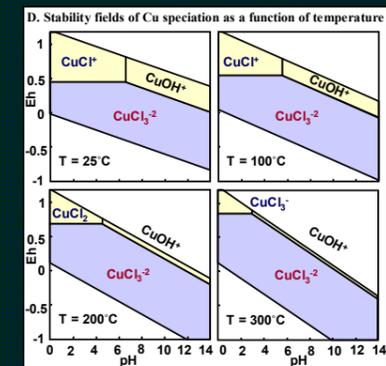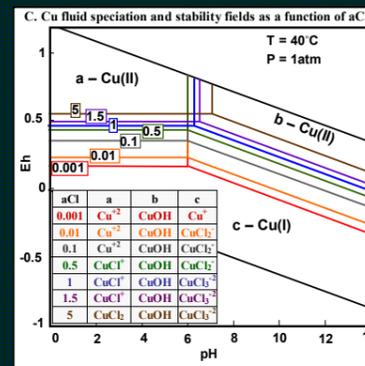B. Cu isotopic composition of the Cu-Cl complexes
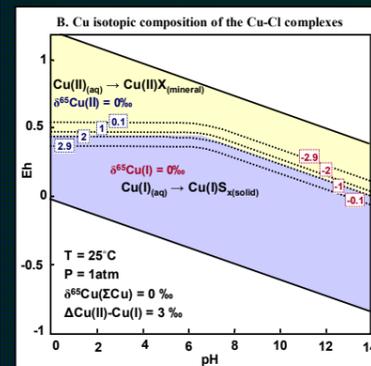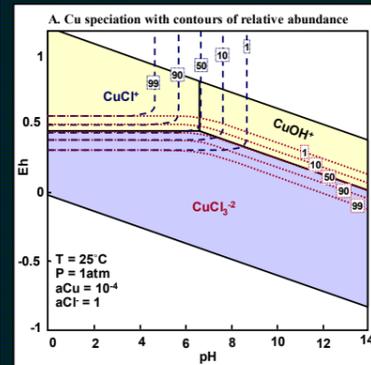
- The Cu isotopic composition of a precipitated Cu(I)-sulphide mineral reflects that of the stable Cu(I) solution species, which in turn, depends on the molar ratio between the stable Cu(II) and the Cu(I) complexes in solution. This molar ratio is a function of Eh, pH, T and chloride activity (aCl⁻) (Fig. A and B).

- The size of the stability field of Cu(I) complexes increases with the chloride activity. Consequently, in natural systems with high chloride activity, the Cu isotopic composition of Cu(I) sulphide will tend to be close to that of the bulk source solution (Fig. C).

- The dominance of the Cu(I) complexes increases with temperature. At temperatures typical of hydrothermal systems (T>200°C) the Cu(I) complexes dominate almost all of the water stability field and redox fractionations are unlikely to occur. This observation may explain the uniform isotopic compositions measured in high temperature environments (Fig. D).
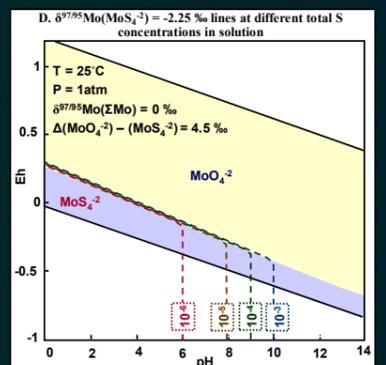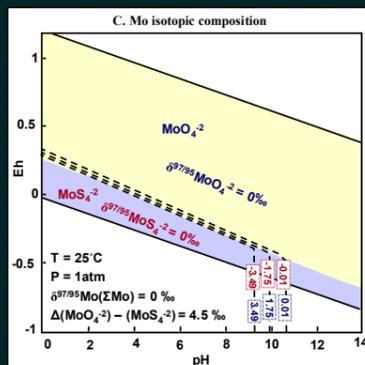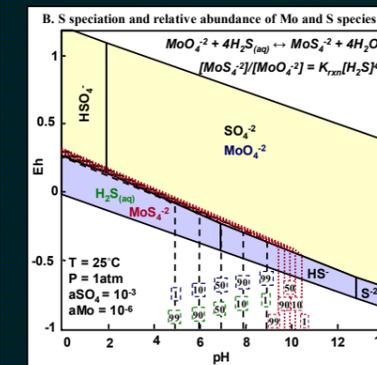
- This approach is general. For example, the isotopic composition of Cu(II) minerals will reflect that of Cu(II) solution species (Fig. A and B).


C. Cu fluid speciation and stability fields as a function of aCl

D. Stability fields of Cu speciation as a function of temperature

A. Concentration and isotopic composition of Mo complexes as a function of [H₂S(aq)]

- The transition between MoO_4^{-2} and MoS_4^{-2} occurs via the following reaction: $MoO_4^{-2} + 4 \cdot H_2S_{(aq)} \leftrightarrow MoS_4^{-2} + 4 \cdot H_2O$. The molar ratio between MoO_4^{-2} and MoS_4^- and hence their Mo isotopic composition, is strongly dependant on the $H_2S_{(aq)}$ concentration according to the equation: $[MoS_4^{-2}]/[MoO_4^{-2}] = K_{rxn}[H_2S]^4$ (Fig. A).

- The redox transition between SO_4^{-2} and H_2S occurs in a narrow range of H_2S concentrations (from about 2E-5 to 5E-5 molar). Under these conditions the two Mo complexes will coexist in solution and hence Mo isotopic fractionation will be observed (Figs. A, B and C).

- Fractionations are likely to occur between MoO_4^{-2} and MoS_4^{-2} during the transition from H_2S to HS^-. The location of the transition between MoO_4^{-2} and MoS_4^{-2} is sensitive to the total S in solution (Fig. D).

B. S speciation and relative abundance of Mo and S species

C. Mo isotopic composition

D. δ⁹⁷/⁹⁵Mo(MoS₄⁻²) = -2.25 ‰ lines at different total S concentrations in solution

Cr(VI)	Cr(III)
Toxic, apparently carcinogenic	Essential nutrient at proper concentrations
Highly soluble and mobile	Low solubility, tend to adsorb and precipitate
Commonly appears in solution as $CrOH_{(0-4)}$	Commonly appears in solution as $HCrO_4^-$ and CrO_4^{-2}

A. Cr speciation

B. Cr isotopic composition
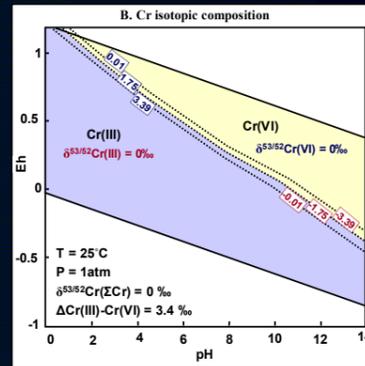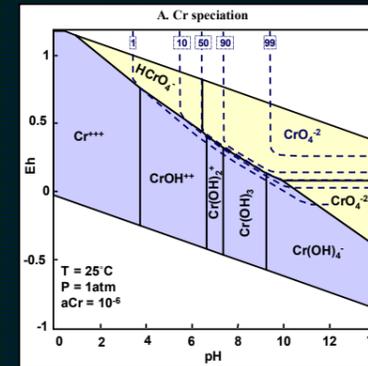
- The Cr isotopic composition of Cr (III) solid phases depends on the molar ratio between the Cr(VI) and the Cr(III) complexes in solution, which in turn, is a function of thermo-chemical parameters such as Eh, pH, T and activity of other ions in the solution.

- More reducing conditions imply a Cr(III) solid phase with Cr isotopic composition closer to that of the source and more efficient removal of Cr from the solution.

- Evaluating the extent of Cr contamination. As conditions become more oxidizing, a larger portion of the Cr is in the form of the soluble and mobile Cr(VI) complexes, and contaminations may be wider spread. Simultaneously, the isotopic composition of the precipitated Cr(III) phases will be lighter.

Summary

- The isotopic composition of the solid phases reflects the isotopic composition of the solution species, and the isotopic composition of the solution species depends on its relative amount in solution, which in turn is a function of redox conditions, and thermodynamic parameters such as T and concentrations of the oxidized and reduced ionic species.

- It is shown that the fluid speciation approach can contribute for the understanding and modeling of many processes involving non-traditional stable isotope systems. Potential applications may include tracing the thermo-chemical conditions of precipitation and absorption, locate the redox boundary of water bodies and evaluating the spreading of contaminations and their removal.

- For natural environments where several redox fractionation factors may exist (abiogenic, biogenic, multiple oxidation states), the main challenge will be to determine net redox fractionation before using this approach. However, if the natural thermo-chemical conditions are known, this approach can be used to evaluate the net fractionation and hence the quantitative relationships among the different processes.