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 sulfide 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 isotopes being enriched in the oxidized species. Since the stable isotopic 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.

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-Cr system

1. CuCl3-2 + e- = Cu+ + 3Cl- logK_{CuCl3} = 7.434
2. Cu(OH)2+ + 3Cl- = Cu+ + 3Cl- + H2O logK_{Cu(OH)2} = 6.670
3. CuCl2- + H2O = Cu(OH)+ + 2Cl- + H+ logK_{CuCl2} = 14.513

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

1. SO42- + 8H+ + 2Cl- = 2H2S(aq) + 4MoO4(aq) logK_{SO4} = 40.689
2. SO42- + 4H+ + 3e- = 2H2O + MoO4(aq) logK_{SO4} = 36.639
3. HS- = HS- + H+ logK_{HS} = 6.950
4. HS- + 4H2O = SO42- + 4H+ + 3e- logK_{HS} = 36.616
5. MoO4-2 + 4H2O = MoS4-2 + 8H+ + 2e- logK_{MoO4} = 24.606

The set of reactions and equilibrium constants for the Cr system

1. CrOH++ = Cr(OH)+ + H+ logK_{CrOH} = 6.323
2. Cr(OH)+ = Cr+ + H2O logK_{CrOH} = 6.010
3. Cr+ + 3H+ = CrOH+ + 2H2O logK_{Cr} = 6.225
4. Cr+ + 3HS- = CrOH+ + H2O logK_{Cr} = 54.832
5. Cr+ + 3H2O = Cr(OH)3 + 3H+ logK_{Cr} = 45.469
6. Cr+ + 3H+ = CrOH2+ logK_{Cr} = 1.760
7. Cr+ + 3HS- = CrOH2+ + 3H+ logK_{Cr} = 72.820

The Cu isotopic composition of a precipitated Cu(I)-sulphide mineral reflects that of the stable Cu(II) 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) sulphides 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 above 25°C, the Cu isotopic composition of a precipitated Cu(I)-sulphide mineral will tend to be close to that of the bulk source solution (Fig. C).

The approach is general. For example, the isotopic composition of Cu(II) minerals will reflect that of Cu(I) solution species (Fig. A and B).

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