Solubility of iron-bearing minerals in supercritical NaCl (KCl)-rich acid solutions

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Natural evidences and experimental studies on aqueous iron geochemistry show that this metal is transported in hydrothermal and metamorphic solutions mostly as ferrous-chloride species. Numerous experimental studies on ferrous-chloride complexation demonstrated that Fe^{2+} and $FeCl^+$ species dominate hydrothermal iron transport at temperatures to 250°C. At higher temperatures $FeCl_2^0$ is favoured over $FeCl^+$ and considered to be the predominant iron species also in supercritical solutions. However, thermodynamic properties for $FeCl_2^0$ were derived from experimental data obtained only at t <350°C (Ohmoto *et al.*, 1994; Heinrich and Seward, 1990), without NaCl (KCl) (Chou and Eugster, 1977; Boctor *et al.*, 1980; Korzhinskiy, 1987) or in the systems with complex mineral association (Hemley *et al.*, 1992; Fein *et al.*, 1992).

The influence of high concentrations of alkaline and alkaline-earth metal chlorides in hydrothermal fluids on iron solubility is not yet quantified. This study, therefore, focuses on the determination of Fe(II) speciation in NaCl (KCl) -rich acid metamorphic solutions, typical for scarn environments.

Solubility of ferberite ($FeWO_4$) + tungstite (WO_3) (*FT*) and hematite (α-Fe_2O_3) + magnetite (Fe_3O_4) (*HM*) mineral assemblages has been measured at 500–700°C, 1–2 kbar in NaCl (KCl) solutions (0–4 m) with HCl^0 fugacity buffered by Ag-AgCl + *HM* mineral association. α-Fe_2O_3, Fe_3O_4, and WO_4 'Pure for Analysis' reagents were used. $FeWO_4$ was hydrothermally synthesized at 600°C, 2 kbar from a mixture of FeO and WO_3, in Pt-ampoule. Solids were checked with X-ray diffraction analysis.

A set of up to 15 hermetically closed Pt ampoules was used for each experiment. All but two of these ampoules were loaded with Ag-AgCl, *FT* or *HM* solid buffers and HCl+NaCl (KCl) solution. Two ampoules containing Ag-AgCl mixture and HCl solution were included into each experiment. All ampoules were placed in a large open stainless steel container together with *HM* buffer. This container was placed into sealed steel autoclave connected to a

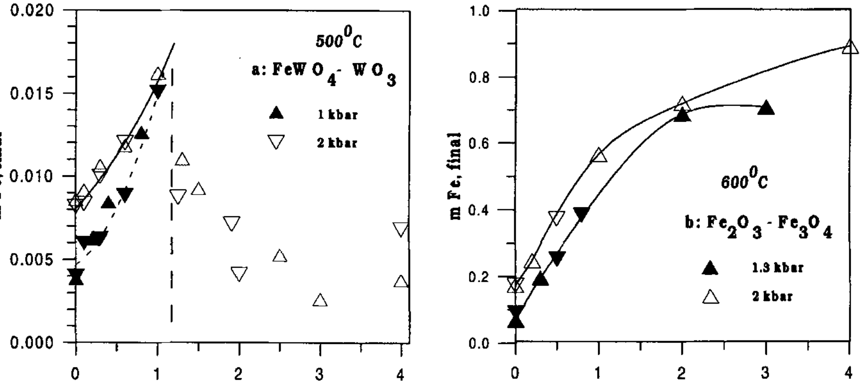

FIG. 1. Solubility of iron as a function of NaCl concentration at 500 (a) and 600°C (b).

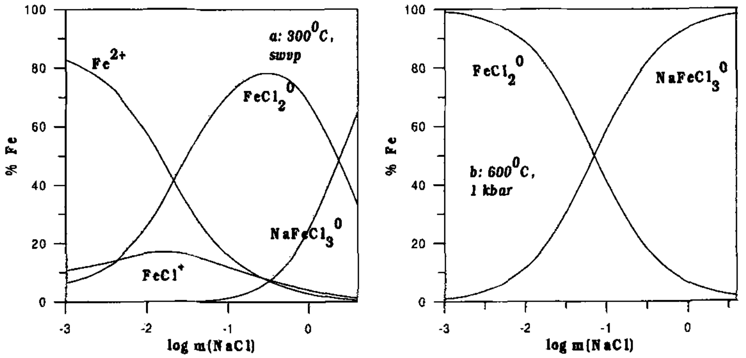

FIG. 2. Aqueous iron speciation as a function of NaCl concentration at 300 (a) and 600°C(b).

pressure line. Pressure in autoclave was maintained to ± 10 bar and temperature ± 5°C. Run durations were 14-30 days. After water quenching, the ampoules were opened, solutions extracted, diluted, acidified (except those from ampoules without Fe-minerals), filtered and the total aqueous iron concentration was measured by flame AAS. pH values were measured in ampoules which did not contained Fe-minerals.

Experimental data at 500 and 600°C as a function of NaCl concentration are plotted in Fig. 1a and b. Solubility of *FM* buffer increases with NaCl concentration. Figure 1a, however, demonstrates a reproducible breakup in solubility curve around NaCl concentration of 1.1m. The decrease in solubility at 500°C at higher NaCl content is proportional to solid/fluid ratio and run duration, which may be explained by the formation of Na-Fe-W-O-Cl complex solids. *FT* mineral assemblage was also found to be unstable at all studied NaCl concentrations at 600°C. Consequently, solubility data for *FT* buffer at NaCl concentration >1.1m at 500°C and all data at 600°C were discarded. Only data for *HM* buffer were used at 600°C. Solubility of *HM* buffer increases with NaCl concentration as shown in Fig. 1b for 600°C, 1.3–2 kbar. No breakup was obserwed in this system.

Increase in iron solubility in NaCl (KCl) solutions may be attributed to the formation of $NaFeCl_3^0$ ($KFeCl_3^0$) species according to reactions (M-L. Pascal, personal communication):

$$FeCl^0_{2(aq)} + NaCl^0{}_{(aq)} = NaFeCl^0_{3\,(aq)} \qquad (1)$$

or

$$FeCl^0_{2(aq)} + KCl^0{}_{(aq)} = KFeCl^0_{3\,(aq)} \qquad (2)$$

In our experimental system, $FeCl_2^0$ activity was controlled by reactions

$$FeWO_{4(s)} + 2HCl^0{}_{(aq)} = FeCl^0_{2(aq)} + WO_{3\,(s)} + H_2O_{(l)} \qquad (3)$$

or

$$Fe_3O_{4(s)} + 2HCl^0{}_{(aq)} = FeCl^0_{2(aq)} + Fe_2O_{3\,(s)} + H_2O_{(l)} \qquad (4)$$

Using thermodynamic properties of HCl^0 from Tagirov *et al.* (1997) and those for other aqueous species from SUPCRT92 (Johnson, 1992), the molal thermodynamic constants of the reactions (1) and (2) were claculated from experimental solubility data for solutions with $m(NaCl) \leqslant 2$. At 500°C, 1 and 2 kbar, and 600°C, 1.3 and 2 kbar log $K_{(1)}$ values were found to be 0.68 ± 0.17, 0.30 ± 0.15, 0.89 ± 0.10, and 0.69 ± 0.15, respectively. At 500°C, 2 kbar log $K_{(2)}$ value was calculated 0.34 ± 0.15.

To estimate the importance of $NaFeCl_3^0$ species as a function of T and P in natural fluids, experimental values of log $K_{(1)}$ were extrapolated using Ryzhenko-Bryzgalin electrostatic model of association. Stability constants of $FeCl^+$ complex derived from data and those of $FeCl_2^0$ from Chou and Eugster (1977), Boctor (1980), Korzhinskiy (1987) and of Heinrich, and Seward (1990) were used. Calculated Fe speciation diagrams are presented in Fig. 2a,b. These calculations suggest that $NaFeCl_3^0$ species becomes predominant even at 300°C in solutions with m(NaCl)> 2.2 (Fig. 2a) and at 350°C at m(NaCl) > 0.7. The role of this complex in hydrothermal transport of iron increases with temperature and decrease with pressure.

Acknowledgements

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