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$_2^+$ is favoured over FeCl$^-$ and considered to be the predominant iron species also in supercritical solutions. However, thermodynamic properties for FeCl$_2^+$ 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 ($\alpha$-Fe$_2$O$_3$) + magnetite (Fe$_3$O$_4$) (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. $\alpha$-Fe$_2$O$_3$, Fe$_3$O$_4$, 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
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 1.1 m. The decrease in solubility at 500°C at higher NaCl content is proportional to solid/liquid ratio and run duration, which may be explained by the formation of Na-Fe-W-O-CI 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 >1.1 m 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 observed in this system.

Increase in iron solubility in NaCl (KCl) solutions may be attributed to the formation of NaFeCl₃ (KFeCl₃) species according to reactions (M.-L. Pascal, personal communication):

\[ \text{FeCl}_2^{0(aq)} + \text{NaCl}^{0(aq)} = \text{NaFeCl}_3^{0(aq)} \] (1)

or

\[ \text{FeCl}_2^{0(aq)} + \text{KCl}^{0(aq)} = \text{KFeCl}_3^{0(aq)} \] (2)

In our experimental system, FeCl₃ activity was controlled by reactions

\[ \text{FeWO}_{4(s)} + 2\text{HCl}^0_{(aq)} = \text{FeCl}_2^{0(aq)} + \text{WO}_3^{(s)} + \text{H}_2\text{O}(l) \] (3)

or

\[ \text{Fe}_3\text{O}_4(s) + 2\text{HCl}^0_{(aq)} = 3\text{FeCl}^{0(aq)} + \text{Fe}_2\text{O}_3^{(s)} + \text{H}_2\text{O}(l) \] (4)

Using thermodynamic properties of HCl⁰ 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 calculated from experimental solubility data for solutions with \( m(\text{NaCl}) \leq 2 \). 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 NaFeCl₃ 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 FeCl³⁻ complex derived from data and those of FeCl₂⁻ 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 NaFeCl₃ species becomes predominant even at 300°C in solutions with \( m(\text{NaCl}) \geq 2.2 \) (Fig. 2a) and at 350°C at \( m(\text{NaCl}) > 0.7 \). The role of this complex in hydrothermal transport of iron increases with temperature and decrease with pressure.

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