THE STABILITY OF ILVAITE AND COMPUTATION OF ASSOCIATED PHASE DIAGRAMS FOR THE Ca-Fe-Si-O-H±C SYSTEM

J. Delgado-Martín

E.T.S. Ingenieros de Caminos, Canales y Puerto. Universidade da Coruña.Campus de Elviña s/n; 15192, La Coruña, Spain

INTRODUCTION

Stability relationships among phases of the Ca-Fe-Si-O-H (±C) system are important to understand the evolution of many skarn ore deposits. It is generally accepted that, within that chemical system, the thermodynamic data and parameters needed to construct accurate phase diagrams are reasonably well known for a number of important end-member mineral phases (i.e. hedenbergite, andradite, grunerite, quartz, magnetite, calcite). However, this is not the case of ferroactinolite and ilvaite, which are two key phases in order to depict comprehensive phase diagrams amenable of use in Al-Mg-poor skarn systems and other more exotic rock types.

Actinolitic amphiboles are common in nature but pure ferroactinolitic compositions are rare due to the fact that most of the common rocks contain additional components. Deviations from ideal stoichiometry usually imply the substitution of variable amounts of Fe^{2+} , Ca and Si by Mn, Mg, Al and Fe^{3+} in the 4 and 6-fold coordinated sites coupled with OH substitutions by F⁻, Cl⁻ or O²⁻ and the partial filling of the A-sites by big cations (Na, K). On the other hand, the mixed-valence iron-calcium sorosilicate ilvaite is a rare mineral although it has been described in a great diversity of geological environments (i.e. iron-rich skarns, the metalliferous sediments of the Red Sea, in low temperature voids and veins, serpentinites, as alteration product of mafic dykes, in blueschist facies rocks and in metarodingites).

The purpose of this contribution is to present a preliminary assessment relative to the theoretical stability field of ilvaite relative to the mineral phases typically associated and to discuss the effect of changes in the unit activity of the pure end members.

SOURCES AND DATA

It is beyond the scope of this contribution to introduce the details of the retrieval of thermodynamic data and only a brief summary of the most significant points will be addressed here. Our calculations were performed using the internally consistent thermodynamic database of Berman (1988) with the aid of the Ge0-Calc software. Berman's original database was enlarged to embrace some extra relevant minerals, which were not originally included. Hence, we derived thermodynamic data for andradite, hedenbergite, ilvaite and ferroactinolite from selected sources and published experiments (Table 1). In



Figure 1: P-T phase diagram for the CaO-FeO-SiO₂-H₂O system. The shaded grey zones include the stability field of ilvaite for different values of ferroactinolite activity. For the rest of mineral phases, activity is equal to unity. Aluminum silicate boundaries are shown for reference. Symbols for mineral phases according to Kretz (1983)

the case of hedenbergite and andradite, we used the reversals reported by Moecher and Chou (1990). For grunerite we used the data reported in Lattard and Evans (1992) without further modifications as far as they are compatible with the data contained in the Ge0-Calc databases.

In the case of ferroactinolite, we took into account the experiments by Ernst (1966), using the data and parameters already published (Delgado et al., 1996). It is worth noting that, within the range of uncertainty, this data is readily comparable with the data and experiments presented by Jenkins and Bozhilov (2003) relative to the re-investigation of the stability and thermodynamic properties of ferroactinolite. For ilvaite, although many published contributions deal with is crystallochemistry and chrystallophysics, only a few experimental works concerning its stability are available. Hence, we used the reversals reported by Gustafson (1974) and Ghazi-Bayat et al. (1987) to constrain the thermodynamic data of ilvaite.

In order to compare the results of the theoretical stability field of ilvaite with a filed case, we used data and observations derived from earlier studies on ilvaitebearing skarns from the central Pyrenees (Delgado, 1993).

Parameter	Andradite	Ferroactinolite	Hedenbergite	Ilvaite
$\Delta_{\rm f} {\rm H^o} ({\rm J \ mol^{-1}})$	-5761985.8	-10518042.6	-2837802.5	-3695605.5
$\Delta_{\rm f} {\rm G}^{\rm o} ({\rm J mol}^{-1})$	-5419000.0	9839000.0	-2674300.0	-3440000.0
S° (J mol-1 K-1)	316.4	685.1	173.59	291.5
Vº (J bar-1)	13.167	28.260	6.785	10.016
k _o (J mol ⁻¹ K ⁻¹)	569.7558	1321.15758	353.31148	682.79138
k1 (J mol-1 K-1)	-1441.440	-8966.454	-3106.646	-8787.112
k ₂ (J mol ⁻¹ K ⁻¹)	-22441040.802	-21705844.286	2047911.742	30183568.71
k3 (J mol-1 K-1)	3146543781.0	3236159154.0	-563018581.0	-5666432624.0
v ₁ x10 ⁵ (bar ⁻¹)	2.07252500	2.84	2.796487	1.801543
v ₂ x10 ⁵ (bar ⁻¹)	0.000561	0.0	0.0	0.001152
v ₃ x10 ⁵ (K ⁻¹)	-0.06539136	-0.15	-0.17457	-0.06838
v ₄ x10 ⁸ (K ⁻¹)	0.0001635	0.0	0.00151	0.000024

Table 1: Selected thermodynamic data in Ge0-Calc format.

RESULTS AND DISCUSSION

Phase diagrams for the Ca-Fe-Si-O-H system were constructed assuming unit activity for magnetite, quartz (alpha and beta), hedenbergite, wollastonite and calcite. Further, unit activity was also used for fayalite and ferrosilite. The activities of ilvaite and ferroactinolite were set to one although a sensitivity analysis was conduced with ferroactinolite in order to evaluate the effect of lowering its activity on the stability field of ilvaite (Fig. 1).

According to our computed phase diagram, the stable reactions bounding the minimum stability of ilvaite are three:

$32 \alpha Q + 34 Ilv = 4 And + 11 Fact + 13 Mt + 6 H_2O$	R1
8 αQ + 14 Ilv = Gru + 14 Hd + 7 Mt + 6 H ₂ O	R2
$4 \alpha O + 6 Ilv = Fact + 4 Hd + 3 Mt + 2 H_2O$	R3

It is interesting to observe that, in the pure system –unit activity for all the mineral phases– the minimum T and P for ilvaite stability is around 2.0 kbar and 440 °C but when the activity of ferroactinolite is lowered to 0.6, the minimum stability of ilvaite rises to more than 3.0 kbar



Figure 2: P-T phase diagram of the CaO-FeO-SiO₂-H₂O-CO₂ system, for a X_{CO2} of 0.01 and 0.02 and unit activity for all the solid phases. Bold lines bound the stability field of ilvaite within the given P-T window. Symbols for mineral phases according to Kretz (1983)

and 470 °C. On the other hand, when considering the coupled effect of reducing the activities of ferroactinolite and ilvaite, the stability of the latter mineral drops to 2 kbar whilst temperature remains very close to 480 °C. Therefore, small changes in the chemical composition of ilvaite and ferroactinolite turn out to be of major importance when considering its barometric and, to a much lesser extent, its thermal stability. That suggests that ilvaite is not a likely stable phase in systems where pressure is sensibly lower than 2 kbar or when the chemical composition of the accompanying mineral phases deviate from the pure composition. In fact, ilvaite compositions have been quite often reported to be very close to that of the ideal end member, with Mn, Mg, and Al as the most significant replacements.

In order to take into account the effect of carbon as an additional component sixth component of the system we need to specify the CO_2 content of the fluid phase. Addition of CO_2 to the system shrinks the stability field of ilvaite. It is worth noting that, in the water-rich edge of the H₂O-CO₂ binary ilvaite displays a high sensitivity with respect to minor changes in the CO_2 content. Thus, in the case of pure end-member minerals and for a X_{CO2} range from 0.005 to 0.02, the minimum stability of ilvaite locates around 2 kbar and 450 to 475 °C. These are nearly identical conditions to the carbon-free system. However, the stability field of ilvaite collapses to a significantly smaller area attending to the different response of reactions to variations in the CO_2 content (Figure 2).

The stability field of ilvaite in the P-T window illustrated by figure 2 is bounded by a series of stable reactions, three of which are common to the carbon-free system (R1, R2 & R3). Two additional reactions involving calcite constrain the lower thermal stability of ilvaite:

$14 \text{ Cc} + 3 \text{ Gru} + 7 \text{ Mt} + 4 \alpha \text{Q} + 4\text{H}_2\text{O} = 14 \text{ Ilv} + 14 \text{ CO}_2$	R4
$4 \text{ Cc} + 3 \text{ Fact} + 5 \text{ Mt} + 2 \text{ H}_2\text{O} = 4 \alpha \text{Q} + 10 \text{ Ilv} + 4 \text{ CO}_2$	R5

The calculation of the phase diagram depicted in figure 2 encompasses a correction for non-ideality of Kerrick and Jacobs (1981) for the system CO_2 -H₂O but do not take into account the effects of NaCl. According to Bowers and Helgeson (1983) fugacity coefficients for CO_2 at high temperatures and pressures are consistently greater in NaCl-CO₂-H₂O solutions than in the equivalent NaCl-free



Figure 3: Hematite-magnetite buffer normalized $\log fO_2$ vs. temperature diagram showing the stability field of relevant minerals in skarn systems. Total pressure is 3 kbar and X_{CO2} equals 0.01. NNO and QFM stand for the nickel-bunsenite and quartz-fayalite-magnetite oxygen buffers. Symbols for mineral phases according to Kretz (1983)

solutions, and this effect tends to overestimate the mole fraction of CO_2 . Therefore, according to these preliminary results, it seems reasonable that ilvaite should be expected to form in the presence of a fluid of rather low CO_2 contents and for temperatures and pressures in excess of 450 °C and 2 kbar.

Oxygen fugacity is a dominant variable when considering mineral reactions in skarn systems. Figure 3 is a $logfO_2$ vs. temperature diagram where the relevant reactions have been normalized with respect the hematite-magnetite oxygen buffer. Reactions include redox-sensitive minerals (hedenbergite, andradite, ilvaite, ferroactinolite, grunerite, and magnetite) in addition to quartz, calcite, and wollastonite and have been computed for a total pressure of 3 kbar and X_{CO2} of 0.01.

The breakdown reactions of andradite/hedenbergite plus magnetite to form ilvaite can be expressed as

 $\begin{array}{l} 36 \ \text{IIv} + 11 \ \text{O}_2 = 12 \ \text{Andr} + 28 \ \text{Mt} + 36 \ \alpha \text{Qz} + 18 \ \text{H}_2 \text{O} \\ 12 \ \text{IIv} + \text{O}_2 = 12 \ \text{Hd} + 8 \ \text{Mt} + 6 \ \text{H}_2 \text{O} \\ \end{array} \begin{array}{l} \text{R6} \\ \text{R7} \end{array}$

and the destabilization of ilvaite to lower temperatures and oxygen fugacities would occur according to:

3 Fact + Mt + O_2 = 12 α Qz + 6 Ilv	R8
3 Fact + Gru + 2 Hd + 2 $O_2 = 20 \alpha Qz + 8 Ilv$	R9
28 Hd + 8 Gru + 7 O_2 + 6 H ₂ O = 64 α Qz + 28 Ilv	R10

In general, the stability of ilvaite overlaps an oxygen fugacity field located between the nickel-bunsenite (NNO) and quartz-fayalite-magnetite (QFM) buffers. It is worth noting, however, that there exists a narrow stability area above the NNO buffer at low temperatures what suggests that the presence of ilvaite under relatively oxidized conditions is not likely but can not be discarded.

As an example of its applicability, the phase diagrams computed were adapted to the specific conditions prevailing along the formation of a selected Ca-Fe-rich skarn system in the central Pyrenees. According to electron microprobe analyses, unit activity was assigned to magnetite, quartz, hedenbergite, and calcite. The activities of ferroactinolite (~0.5) and ilvaite (~0.85) were corrected assuming an ideal ionic model. Finally, an X_{CO2} value of 0.005 was fixed attending to fluid inclusions and stable isotope constrains.

Mineral assemblages and textural relationships indicate that hedenbergite and hedenbergite + magnetite constituted one of the earliest mineral assemblages. The scarcity of andradite-rich garnets suggest that at the early stages of skarn evolution oxygen fugacity was not higher than half a log unit from the NNO buffer or lower than the QFM buffer. Ilvaite was formed later, as the breakdown product of the previous hedenbergite + magnetite assemblage, as described by reaction R7. The latest mineral assemblage observed in the skarns is formed by magnetite, quartz, and calcite. Under the prescribed conditions, that assemblage would have formed at temperatures below 400 °C.

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