

GRAND-DAUGHTER MINERALS IN FLUID INCLUSIONS: A COMBINED RAMAN AND MICROTHERMOTRIC STUDY OF PYROXENE-FERROPYROSMAHITE EQUILIBIUM IN SALINE FE-RICH INCLUSIONS

KODĚRA, P.¹, MURPHY, P. J.², RANKIN, A. H.²

¹Geological Survey of the Slovak Republic, Mlynská dolina 1, Bratislava, 817 04, Slovakia.

²School of Earth Sciences and Geography, Kingston University, Kingston-upon-Thames, Surrey, KT1 2EE, UK.

E-mail: koder@gsrr.sk

Introduction

A wide variety of minerals are reported from fluid inclusions from a range of geological environments. In many cases they dissolve on heating and can be inferred as direct crystallisation products of the enclosed fluid (true "daughter minerals"). In other instances, especially when they fail to show any signs of dissolution, they may be interpreted as captive mineral phases (sometimes referred to as "step-daughter minerals"). During the course of an investigation of Fe-rich saline inclusions from granodiorite associated with Fe-skarn from a locality in Slovakia we have observed and studied the retrograde transformation of one Fe-rich mineral to another. This represents the evidence for another class of solid phases in inclusions referred here to as "grand-daughter minerals". The transformation described below (pyroxene = ferropyrosmalite) can drastically alter the composition of associated fluid, and, unless it is recognised, it may lead to misinterpretation of fluid inclusion chemistry, including metal and silica solubilities.

Ferropyrosmalite and its identification

Ferropyrosmalite is the iron-rich end-member of the phyllosilicate pyrosmalite series $(\text{Fe,Mn})_8\text{Si}_6\text{O}_{15}(\text{OH,Cl})_{10}$. The recognition of ferropyrosmalite as a daughter mineral in fluid inclusions is relatively rare, but in the absence of Raman spectroscopic analyses it may be mistaken for one of a range of possible hydrated iron-chlorides. Their optical properties are similar, and during microprobe analyses, incorporation of silica from the host mineral may confuse the identification. Ferropyrosmalite has been reported as a common daughter mineral in multiphase fluid inclusions from Cu-Au-Co and Pb-Zn-Ag deposits in the Cloncurry District, NW Queensland (e.g. Dong & Pollard 1997), and in inclusions in granodiorite associated with Fe-skarn mineralisation from the Banská Štiavnica district in Slovakia (Koděra et al., 2000), which have been also used in the present study.

Identification of ferropyrosmalite in fluid inclusions is based on a combination of Raman microspectroscopy and characteristic microthermometric behaviour. The Raman spectrum for ferropyrosmalite has strong bands at 615 and 1022 cm^{-1} with additional Raman bands in the O-H stretching region at 3551, 3579, and 3627 cm^{-1} (Dong, Pollard, 1997; Koděra et al., 2003). Optically, ferropyrosmalite has very high relief, a green-yellow colour, prismatic to oval (rarely xenomorphic) shape and in most cases it appears to be anisotropic. Dissolution of ferropyrosmalite occurs around 465°C ($\pm 35^\circ\text{C}$) and is often accompanied by the precipitation and/or growth of a new insoluble phase.

Inclusions containing ferropyrosmalite in this study showed variable liquid-vapour homogenisation temperatures, ranging from 186 up to above 598°C (the upper temperature limit of the heating-freezing stage) as well as variable halite dissolution temperatures, ranging from 320 up to 546°C. The dissolution of ferropyrosmalite, accompanied by the precipitation of a new phase, occurred in the range 372-546°C, but most often in a narrow range 460-490°C. The new phase was stable upon further heating and subsequent cooling, although in one inclusion the new phase clearly dissolved at 545°C.

Clinopyroxene and its identification

Dissolution of ferropyrosmalite, accompanied by growth of the new mineral phase during heating, has been studied by Raman spectroscopy in several fluid inclusions where the presence of ferropyrosmalite was confirmed by Raman analyses before heating. After the heating run, analysis of the new phase showed that the Raman bands due to OH bonding of ferropyrosmalite around 3500 cm^{-1} have disappeared, and the bands at low frequency now occur at 662 and 1011 cm^{-1} . There is also a minor band around 376-382 cm^{-1} . All these bands are very similar to those for hedenbergite (strong peaks at 666 and 1014 and moderate at 323, 358, 390 cm^{-1}), identified elsewhere within the samples from this deposit.

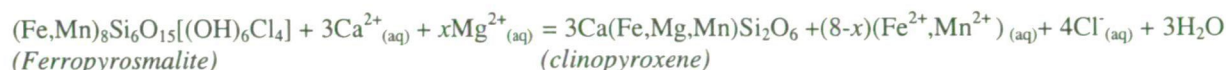
Note, that clinopyroxene was never identified in fluid inclusions that had not previously been heated, which suggests that these crystals had formed at the expense of ferropyrosmalite during heating. Presumably due to kinetic constraints the new phase was stable at room temperature in most cases, despite forming small single crystals, which were sometimes less than 2-3 μm in size. However, in one relatively small inclusion (<10 μm) the ferropyrosmalite-clinopyroxene transformation appeared to be reversible, as upon localised heating by the Raman laser, clinopyroxene developed back at the expense of ferropyrosmalite. Clinopyroxenes identified within endoskarnised samples can be classified as hedenbergite with variable proportions of diopside and very minor johansenite components ($\text{Hd}_{63-70}, \text{Jo}_{0-1.6}$) (Koděra 2000).

SEM-EDX microprobe analyses

In order to confirm the evidence from Raman analyses, semi-quantitative SEM-EDX microprobe analyses of exposed mineral phases in opened inclusions were performed. The analyses were conducted on all solid phases within the opened inclusions on samples both unheated and previously heated to 500°C. The relative proportions of Cl, Ca(+Mg) and Fe(+Mn) detected showed that the solid phases after heating are significantly richer in Ca(+Mg) than in unheated samples. This is clearly consistent with the Raman evidence which indicated the dissolution of ferropyrrosmalite $[(\text{Fe},\text{Mn})_8\text{Si}_6\text{O}_{15}(\text{OH},\text{Cl})_{10}]$ and the formation of clinopyroxene $[\text{Ca}(\text{Fe},\text{Mg},\text{Mn})\text{Si}_2\text{O}_6]$. Analyses of ferropyrrosmalite showed a minor manganese component ($\text{Fe}/(\text{Fe}+\text{Mn}) > 85\%$). These are very similar to the data of Vaughan (1986) who gave an $\text{Fe}/(\text{Fe}+\text{Mn})$ composition for ferropyrrosmalite of 92%. Analyses of clinopyroxene showed relatively variable proportions of Fe, Mg and Mn, with far the most dominant hedenbergite component (Fe^{2+}). These compositions are comparable to clinopyroxenes from the endoskarn samples analysed by Koděra (2000).

Discussion and conclusions

Both Raman and microprobe analyses indicate that the phase change observed on heating represents the breakdown of ferropyrrosmalite and the formation of clinopyroxene. The following equilibrium reaction for this transformation is suggested:



where $\text{Fe} \gg \text{Mn}$ in the ferropyrrosmalite, $x \leq 3$, and the amounts of Mg^{2+} , Fe^{2+} and Mn^{2+} involved will depend on the composition of both ferropyrrosmalite and clinopyroxene. The equations assume that all of the silica involved in the reaction is contained within the ferropyrrosmalite and pyroxene and that the contribution from the host quartz is negligible. This reaction also suggests that a significant amount of Fe^{+2} and Cl^- are released to the solution upon dissolution of ferropyrrosmalite. This is in agreement with published experimental data, which show relatively high concentrations of iron and high solubilities of iron chlorides in magmatic fluids at elevated temperatures (Whitney et al., 1985). Note that estimates of the Fe, Cl and Si contents and solubilities in such systems based on daughter mineralogy (e.g., Kwak et al., 1986) can lead to significant degrees of uncertainty, if ferropyrrosmalite is misidentified as a simple Fe-chloride.

The observation of this transformation on heating strongly suggests that the original high temperature mineral phase in the inclusion was clinopyroxene, which underwent a retrograde reaction with the inclusion brine on cooling, to form ferropyrrosmalite. The retrograde reaction of clinopyroxene to form ferropyrrosmalite had been recognised by previous workers (e.g., Vaughan, 1986) but this is the first recognition of the reaction occurring within fluid inclusions after entrapment. Silicate daughter minerals such as clinopyroxene are rarely reported in fluid inclusions, although they are common in many of the environments from which fluid inclusions are studied. The occurrence of similar retrograde reactions involving other common silicates (e.g., feldspars) within fluid inclusions may explain why they are so rarely seen as captive or daughter phases.

Given recognition of retrograde reactions between the minerals and fluid within an inclusion, it cannot be assumed that the daughter mineral assemblage observed at room temperature is the same after microthermometric heating as it was before. While simple chloride minerals dissolve on heating and re-precipitate on cooling, silicate daughter minerals may undergo more complex reactions and, in the case discussed here, sluggish kinetics may prevent them from returning to the original equilibrium assemblage. Any analyses such as Raman or SEM-EDX should be carried out before or, ideally, both before and after heating.

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