Retrograde mineral reactions in saline fluid inclusions: The transformation ferropyrosmalite ↔ clinopyroxene

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ABSTRACT

Evidence is presented for retrograde reaction of silicate minerals with saline brine inside fluid inclusions during post-entrapment cooling. Ferropyrosmalite \([(\text{Fe},\text{Mn})_8\text{Si}_6\text{O}_{15}(\text{OH},\text{Cl})_{10}, \text{where Fe}>>\text{Mn}]\) has previously been interpreted as a daughter mineral in saline inclusions in magmatic quartz from altered granodiorite associated with the Vyhne-Klokočů Fe-skarn deposit of Slovakia. Based on combined Raman spectroscopic, microthermometric, and SEM-EDX techniques this phase is shown to react, on heating above 450 °C with a Ca-enriched saline inclusion fluid, to form clinopyroxene. This suggests that clinopyroxene was originally present in the inclusions at high temperature, and then underwent retrograde reaction with the saline fluid, on cooling, to form ferropyrosmalite. In its simplest form, the equilibrium reaction for this transformation is:

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\begin{align*}
\text{Fe}_8\text{Si}_6\text{O}_{15}\{(\text{OH})_6\text{Cl}_4\} + 3\text{Ca}^{2+}_{(aq)} & = 3\text{CaFeSi}_2\text{O}_6 + 5\text{Fe}^{2+}_{(aq)} + 4\text{Cl}^–_{(aq)} + 3\text{H}_2\text{O} \\
(\text{ferropyrosmalite}) & \quad (\text{hedenbergite})
\end{align*}
\]

In practice, the reaction is complicated by the presence of Mn and Mg. The resulting “daughter” mineral assemblage observed at room temperature is actually a low-temperature equilibrium assemblage very different to that originally present at high temperature.

Although silicate daughter minerals such as clinopyroxene are rarely, if ever, described in fluid inclusions, they may have originally been present but underwent similar retrograde reactions. Ferropyrosmalite itself is likely to be frequently overlooked, as in the absence of Raman spectroscopic analyses it may be mistaken for one of a range of possible hydrated iron-chloride minerals. Improved Raman spectra for ferropyrosmalite are presented which will make future identification easier.

Failure to recognize intra-inclusion retrograde reactions such as this may lead to misinterpretation of fluid inclusion chemistry, including metal and silica solubilities.

INTRODUCTION

Identification of daughter or captive minerals in fluid inclusions can provide useful insights to the chemistry of ancient hydrothermal fluids. The most commonly reported daughter minerals are alkali metal chlorides, sulfates, and carbonates (Roedder 1984). In recent years, however, with the development of laser Raman microspectroscopy, a number of more unusual daughter minerals have been positively identified (Burke 2001). Surprisingly, silicate daughter minerals, even in saline fluid inclusions in quartz from high temperature environments, are rarely reported. The Fe-Mn-hydrated silicate ferropyrosmalite is an exception (e.g., Dong and Pollard 1997; Kodeřa et al. 1998b), and it is apparent from more recent studies that this phase is much more common in high temperature, Fe-rich hydrothermal environments than previously recognized.

In a previous study of inclusions in quartz from granodiorite associated with Fe-skarns from a location in Slovakia, ferropyrosmalite was interpreted as a common daughter mineral (Kodeřa et al. 1998b) which underwent characteristic dissolution and growth of a new mineral phase on heating. In this study we identify this new mineral phase as clinopyroxene. We present evidence to suggest that an original clinopyroxene daughter or trapped mineral phase underwent retrograde reaction with a saline multi-component fluid to form the “daughter” mineral ferropyrosmalite within the inclusion. The identification of this retrograde reaction has important implications in fluid inclusion studies not only where daughter minerals are used as indicators of bulk fluid composition, but also when studying clinopyroxene-hosted fluid inclusions. In the wider context, it is possible that similar reactions involving other silicate daughter phases might also occur and thus could explain some of the unusual heating behaviors sometimes reported for daughter minerals in inclusions from other environments (Roedder 1984).

FERROPYROSMALITE

Ferropyrosmalite is the iron-rich end-member of the phyllisolicite pyrosmalite series \((\text{Fe},\text{Mn})_8\text{Si}_6\text{O}_{15}(\text{OH},\text{Cl})_{10}\). Generally, minerals of the pyrosmalite series are related to metamorphism and are associated with Fe- and Mn-rich silicate...