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

**PETER KODĚRA,* PAMELA J. MURPHY, AND ANDREW H. RANKIN†**

Centre for Earth and Environmental Science Research, School of Earth Sciences and Geography, Kingston University, Penrhyn Road, Kingston-upon-Thames, Surrey, KT1 2EE, U.K.

## ABSTRACT

Evidence is presented for retrograde reaction of silicate minerals with saline brine inside fluid inclusions during post-entrapment cooling. Ferropyrosmalite [$(Fe,Mn)_8Si_6O_{15}(OH,Cl)_{10}$, where Fe>>Mn] has previously been interpreted as a daughter mineral in saline inclusions in magmatic quartz from altered granodiorite associated with the Vyhne-Klokoč 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:

$$\underset{\text{(ferropyrosmalite)}}{Fe_8Si_6O_{15}[(OH)_6Cl_4]} + 3Ca^{2+}_{(aq)} = \underset{\text{(hedenbergite)}}{3CaFeSi_2O_6} + 5Fe^{2+}_{(aq)} + 4Cl^{-}_{(aq)} + 3H_2O$$

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.