IDENTIFICATION OF SOME FE-BEARING DAUGHTER MINERALS IN FLUID INCLUSIONS USING RAMAN SPECTROSCOPY

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Introduction

Hydrothermal, high temperature fluids related to acid to intermediate intrusives are often hypersaline (up to 80 wt % total dissolved salts) and particularly rich in Fe (up to 45 wt % $FeCl_2$). Associated fluid inclusions usually contain Fe-bearing minerals but these are only rarely identified, except for simple Fe oxides, such as magnetite and hematite. Other Fe-bearing phases remain unidentified but are generally thought to be hydrated Fe chlorides or mixed Fe-K chlorides, based on their optical properties and semiquantitative SEM data from opened inclusions. Laser Raman Microspectroscopy, though unsuitable for some simple chlorides (such as NaCl), is particularly useful for the *in situ* identification of more complex daughter minerals, providing an important insight into Fe-contents, total salinity and redox state of the trapped fluid.

Raman spectra of hydrated chlorides & OH-bearing minerals

The essential features of Raman spectra of hydrated chlorides and OH-bearing minerals are the water bending and stretching bands and molecular OH bands. The number of OH peaks, their position and relative intensities vary from mineral to mineral and are controlled by the types and number of crystallographically equivalent sites of OH groups and the types of cation occupancies around OH sites, as well as the probabilities of these occupancies.

Concerning salt hydrates, published Raman spectra exist for hydrohalite ($NaCl.2H_2O$), antarcticite ($CaCl_2.6H_2O$), $MgCl_2.6H_2O$, $MgCl_2.12H_2O$, $FeCl_3.6H_2O$, $KCl.MgCl_2.6H_2O$ and $LiCl.5H_2O$ (Dubessy et al., 1982,1992), with major OH bands within the range 3300-3550 cm^{-1} (mainly <3450 cm^{-1}). The band widths are significantly narrower at low temperatures than at high temperatures, allowing better resolution of the closely spaced peaks.

The OH stretches within hydroxyl groups in a crystal lattice are narrow even at room temperature. OH peaks within simple hydroxides occur in a very narrow range 3566-3578 cm^{-1} and within phyllosilicates in a relatively broader range ~3550-3700 cm^{-1} (Lutz et al., 1994; Wang et al., 2002).

Raman spectra of Fe-bearing hydrates

As the Raman spectra of most Fe-bearing hydrated chlorides have never been reported, we attempted to record these spectra using synthetic compounds, both at room temperature and at low temperature (-180°C) and over the frequency range 100 to 4000 cm^{-1} and a time interval of 30-300 seconds (table 1).

$Fe^{+3}Cl_3.6H_2O$ is yellow. It is stable in saturated water solutions at room temperature, but forms a series of $Fe^{+3}Cl_3$ compounds with varying degrees of hydration (Kroschwitz & Howe-Grant, 1995) on drying. The Raman spectra showed several very strong sharp peaks at low wavenumbers, probably corresponding to lattice vibration, in contrast to weak peaks in the O-H spectral region. Compared to the spectra published by Dubessy et al. (1982) there is a difference in the location of one peak (3271 vs. 3321 cm^{-1}), probably due to orientation effects.

Erythrosiderite ($K_2Fe^{+3}Cl_5.H_2O$) was prepared from a saturated solution with dissolved $Fe^{+3}Cl_3.6H_2O$ and KCl that has been subsequently evaporated and the precipitated red crystals have been identified using quantitative SEM analyses. The Raman spectra showed again strong peaks at low wavenumbers in contrast to weak peaks in the O-H spectral region.

$Fe^{+2}Cl_2.4H_2O$ is pale to bluish green, stable in saturated water solutions at room temperature. Below 12.3°C hexahydrate is stable, while dihydrate and monohydrate occur at >75°C and >150-160°C, respectively (Kroschwitz & Howe-Grant, 1995). Its Raman spectra showed several weak peaks at low wavenumbers, in contrast to very strong peaks in the O-H stretching spectral region.

Table 1: Raman frequencies (in cm^{-1}) for Fe^{+3} and Fe^{+2} hydrates recorded at -180°C determined in this study. Strong peaks are highlighted in bold.

FeCl₃.6H₂O	K₂FeCl₅.H₂O	FeCl₂.4H₂O	FeCl₂.2H₂O
	174	178	
		194	
		217	
	231		
243			
259			
305	**304**		
		340	
			377
	402		
424			
			598
		618	
	1588		
			1621
1635		1634	
		1658	
			2192
	2205		
3004			
			3175
		3216	3221
3271			
	3337		
	3381	**3377**	
			3392
		3415	
3421			
		3431	**3428**
3534			

Synthesis of $Fe^{+2}Cl_2.2H_2O$ was attempted in two ways: by slow heating of $Fe^{+2}Cl_2.4H_2O$ crystals (recrystallisation occurred > ~50 °C) and by evaporation of saturated solution at 100°C resulting in precipitation of transparent to reddish, needle-shaped crystals. In both cases the same type of Raman spectrum have been recorded.

Attempts were made to synthesise mixed Fe^{+2}-K hydrated chlorides from a solution with dissolved $Fe^{+2}Cl_2.4H_2O$ and KCl. Evaporation produced sylvite, erythrosiderite, $Fe^{+2}Cl_2.4H_2O$ and a yellow to orange, needle-shaped hydrate, possibly douglasite ($K_2Fe^{+2}Cl_4.2H_2O$). On evaporation to dryness the hydrate subsequently unmixed into sylvite and a brown-coloured solution (oxidation of Fe^{+2} to Fe^{+3}). The resulting Raman spectra of this hydrate were much affected by this decomposition.

Spectra of daughter minerals in fluid inclusions

The experimentally derived spectra, together with other published reference spectra, were used to identify the Fe-daughters present in inclusions in samples from four districts, each related to different types of hydrothermal mineralization.

Fluid inclusion studies on the *Hodruša granodiorite related to Fe-skarn (Slovakia),* showed Raman spectra typical of hydrates but the exact position of peaks did not match with any of the experimentally determined spectrum of hydrates. However, SEM-EDX results and the absence of sylvite in these inclusions indicate the presence of both Fe and K in their structures, possibly present in variable ratios. These daughters were yellow-green, anisotropic with high relief and showed two modes of dissolution temperatures (~112 and ~130°C). Raman spectroscopy determined here also a common presence of OH bearing daughter minerals, typically with sharp OH peaks both at room and low temperatures. Based on published spectra they have been identified as biotite and ferropyrosmalite [$Fe_8Si_6O_{15}(OH,Cl)_{10}$], respectively, and an unknown, isotropic, green-yellow mineral with high relief, dissolving in the range from 324 to 465°C (sharp peak at 3449 cm^{-1} in addition to two smaller peaks at 385 and 199 cm^{-1}) - perhaps hibbingite [$Fe_2(OH)_3Cl$].

Raman spectroscopic study of inclusions in quartz from the *Chorloque Sn-porphyry (Bolivia)* detected two types of hydrates. Compared to the experimentally determined spectra, the first type can be identified as $FeCl_2.2H_2O$. The second, with a greenish colour, is probably a Fe-K hydrate with an unknown K-Fe ratio. Furthermore, the spectrum of the unknown OH-bearing daughter mineral, apparent in the Slovakian sample (hibbingite?), was also recorded in the Chorloque inclusions

Raman spectroscopic study of inclusions in topaz from the *Mole Granite related to W-Mo-Sn in silexite (Australia)* detected two hydrates, showing distinctive spectra. Limited data does not allow a positive identification. However, their optical properties (green colour, anisotropy) indicate the presence of Fe-K hydrates.

A preliminary Raman spectroscopic study of inclusions in quartz from the *Dartmoor Granite related Sn-W-Fe veins (UK)* failed to detect any hydrates. However, the spectra of the same unknown OH-bearing daughter mineral, as detected in the Slovakian and Bolivian samples (hibbingite?), were also recorded here.

Conclusions

Hydrated Fe^{+2} and Fe^{+3} chlorides and erythrosiderite show characteristic, but previously unpublished, Raman bands, which can be used to identify certain Fe-Cl-daughter minerals. Of particular note is the fact that ferrous and ferric chloride hydrate species differ substantially in their Raman spectra.

The presence of *simple* ferrous chloride hydrates as daughter minerals in fluid inclusions appears to be more rare than previously expected, while no evidence has been found for the presence of ferric hydrates. This is not surprising, as data obtained from experiments suggest that ferrous iron is the dominant species in natural hydrothermal solutions, whereas ferric species generally occur in abnormal oxidised solutions (e.g. Kwak et al, 1986). Mixed Fe^{+2}-K chloride hydrates are probably more common, while the Fe/K ration can probably largely differ, depending on the fluid composition and temperature of $FeCl_2$ saturation. The present study also demonstrates the common presence of an OH- and Fe-bearing daughter mineral, whose identity, at present, remains speculative (hibbingite?).

Acknowledgement

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