Raman spectroscopic investigations of fluoride minerals with the general formula $NaX[AlF_6] \cdot H_2O$

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Thomsenolite and pachnolite, both $NaCa[AlF_6] \cdot H_2O$, as well as ralstonite, $NaMg[Al(F,OH)_6] \cdot H_2O$, are typical minerals derived from the alteration of cryolite. Type locality and till now locality for the best crystals each is the famous cryolite deposit Ivigtut, Greenland.

Crystals of all three minerals as well as cryolite for comparison have been investigated by means of micro Raman spectroscopy. The identity of all samples has been proven by electron probe micro-analysis (EMPA) and X-ray diffraction (XRD).

Raman spectra of all three minerals are contained in the Rruff database, but show very few details especially in the hydrogen stretching region which is determinative for easy distinguishing these three minerals. The Raman spectra of the three minerals in the range 200–1000 cm^{-1} are similar but well distinguishable and compare well with the simpler spectrum of cryolite.

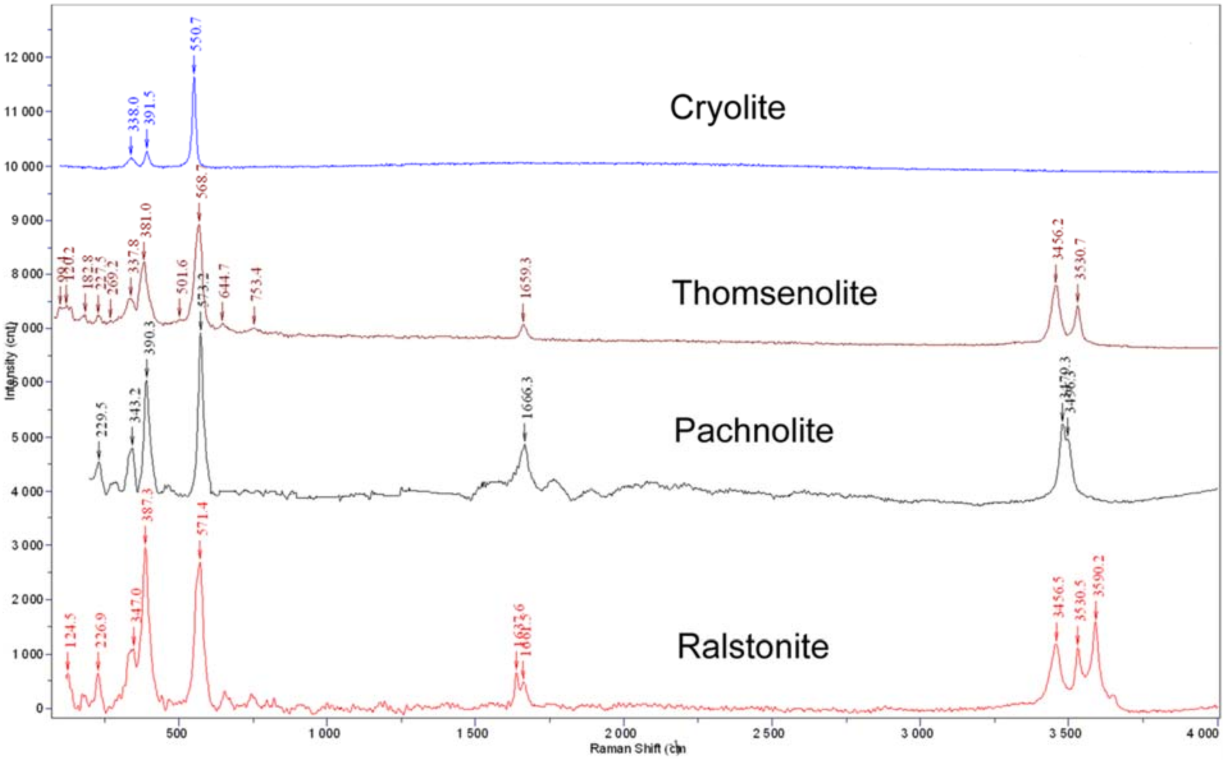

Fig 1. *Raman spectra of (from above) cryolite, thomsenolite, pachnolite and ralstonite.*

In the hydroxyl stretching region between 3000 and 3800 cm^{-1} ralstonite shows the most complex spectrum in this region with three well defined bands at 3456, 3530 and 3590 cm^{-1} respectively. Thomsenolite displays only two bands which are almost identical to the first two bands of ralstonite with 3456 and 3530 cm^{-1}. These two bands are interpreted as the hydrogen stretching vibrations of molecular water, whereas the third band of the ralstonite spectrum at 3590 cm^{-1} is attributed to the hydrogen stretching vibrations of the hydrogen group which is partially replacing fluorine in ralstonite.

Pachnolite shows two bands at 3479 and 3496 cm^{-1} similar to those of the chemical identic thomsenolite. But whereas there is a gap between the two bands of 75 cm^{-1} in the thomsenolite spectrum, the gap in the pachnolite spectrum is only 17 cm^{-1}. If we consider both bands as a doublet the center of the doublet is identical within a failure of ±3 cm^{-1}.

The case is the same for the first two bands of ralstonite. That means that in all three minerals there are two different environments of H_2O, which are nearly identical in pachnolite and considerably different in thomsenolite and ralstonite. In the case of thomsenolite and pachnolite this is consistent with the structure determination of thomsenolite and pachnolite by Adhikesavalu et al. (1985).

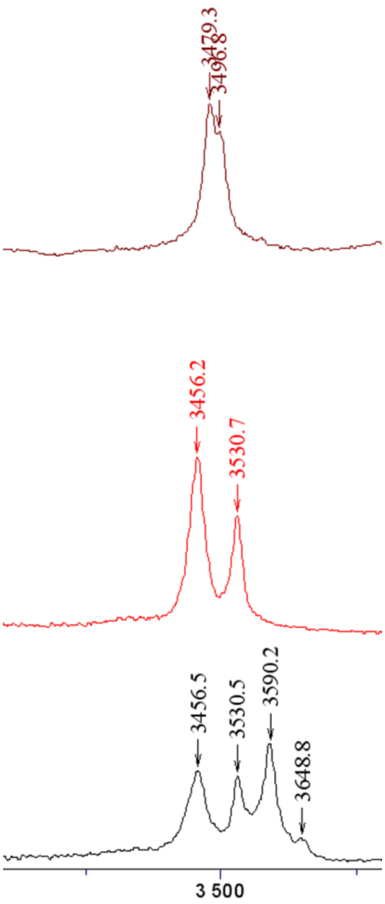

Fig 2. *The hydrogen stretching region of (from above) pachnolite, thomsenolite and ralstonite.*

Conclusion

Micro Raman spectroscopy is an easy tool to distinguish the cryolite derived minerals thomsenolite, pachnolite and Ralstonit. Especially in the hydrogen stretching region all three minerals show significant easy to recognize differences.

Reference:

Adhikesavalu D, Cameron TS, Knop O (1985) Thomsenolite, NaCa[AlF$_6$] · H_2O: hydrogen bonding and comparison with pachnolite. Can J Chem 63:3322–3327