Is 4500 cm-1 Water Proven to be OH (Hydroxyl) Water?

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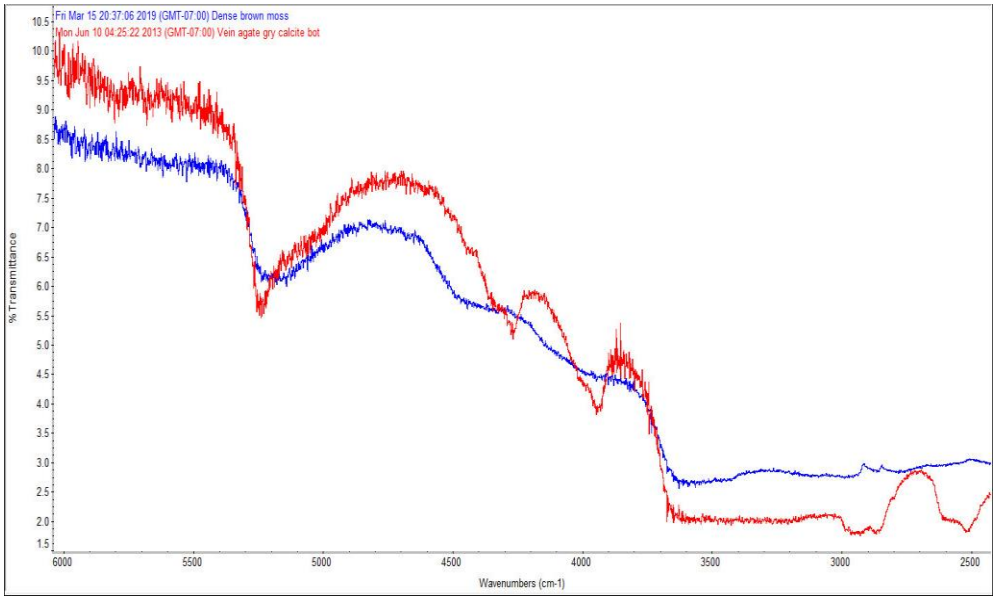
If we look at a paper studying quartz water, we find papers like Courdier and Doukhan (1991, American Mineralogist, Vol. 75, Pp. 361-369) to tell us all about finding water in rocks comparing a 5200 cm-1 band and 4500 cm-1 band. At 4000 cm-1, they cut off the spectrum, typical in all papers seen so far studying this water region. 5200 is free water, and 4500 is stated as OH hydroxy water, accurate by calibration of others to 2% water. End of story, right?

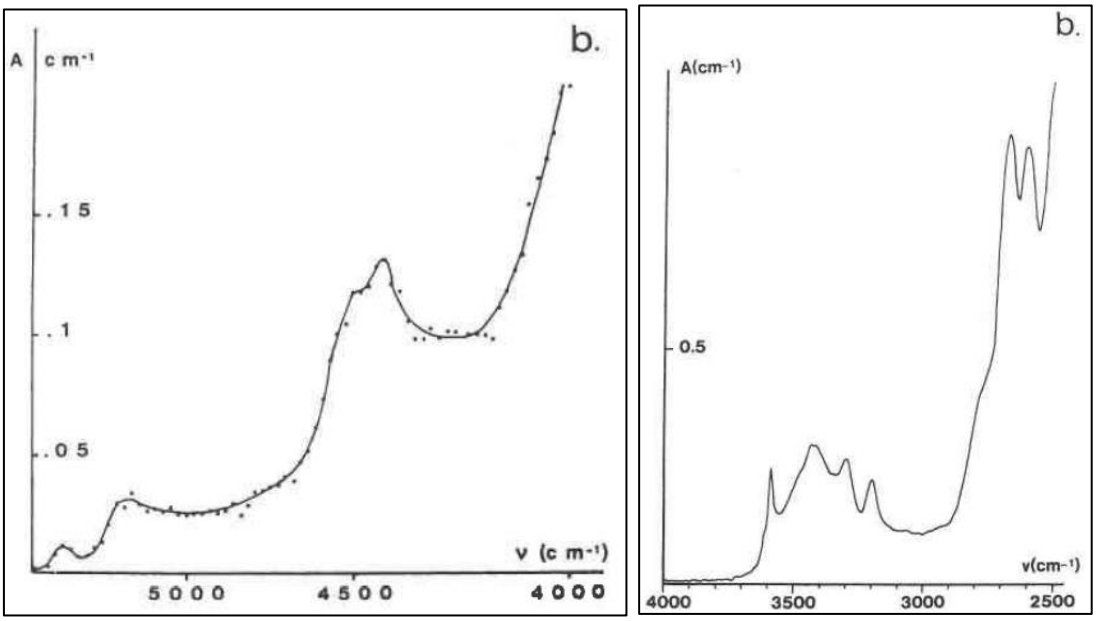
Well, there is a little problem. There is no such thing as a lone 4500 cm-1 band. If it occurs, it is only found with a 4000 cm-1 band, which is always cut off and ignored. Let us zoom out with our own data and take a look as shown below.



Blue spectrum, moss agate on the moss inclusion structure. Red spectrum, is calcite in a vein agate.

In the figure above, both have the 4500/4000 cm-1 doublet. No other mineral than calcite is linked to the sharp bands in red. The blue spectrum rolls do not occur in agate banding without inclusions. One can presume just as easily as OH water for 4500cm-1 is that shallow rolls represent trace parts-per-million carbonate in quartz. That would be a doublet of CaOH water.

Here is an example on the water bands studied from the paper cited:



Example of Courdier and Doukhan (1991) paper on water studied in synthetic quartz. Left is their figure 3b. Right is their figure 8b.

The 4000 cm-1 part of the 4500/4000 cm-1 doublet it erased in their figure shown above. This provides credence to the paper author's citation of a long history of these bands that 5200cm-1 is free water and 4500cm-1 is claimed to be OH hydroxyl water. However, if calcite is not present, the 4500/4000cm-1 doublet is not found for sharp bands. There is no such thing as just at 4500cm-1 band unless you are above 4500cm-1 looking for clay doublets. The authors show this 4500/4000 cm-1 doublet in their Figure 14, trying to sum up the peaks to simulate them with mathematical peak summation, but the 4000cm-1 peak is never used in any paper of this type to study water percentage in a rock or mineral.

The authors then study 3600-2500 cm-1 water bands in detail, showing spectra while providing no exact band positions, instead the 2500cm-1 bands are ignored entirely. An example is shown on the right figure above. Well, they show a doublet just above 2500 cm-1, that the author compares to his master bands of carbonate water with 2529cm-1 as the marker for calcite. There is a left band to compare to their doublet, but in reflectance infrared it is usually a ledge roll that is broad and hard to locate within 10cm so the author does not key on that second band. The author has never seen and thus considered those bands to be anything other than in the carbonate group, whose exact position shifts with the specific carbonate species.

Keep in mind, in the study of these lab grown quartz specimens, pure water is never used. There is always a cation solvent added such as NaOH, sodium hydroxide, which they mention, while they don't know exactly how their crystals obtained from others were specifically produced.

Conclusion:

4500cm-1 water is CaOH water, not free hydroxyl water. As such, it is found in carbonates. Carbonates in quartz rocks occurs all the time, particularly volcanic agates. A weak doublet is either low calcite concentration, or caliche (hard water scale). The author's mineral water region model is based on the observation of no clear OH hydroxyl water at all above 3600 cm-1. It is all cation-OH bound water or free water.