Do Infrared Mineral Fundamental Bands Sum to Make Water Bands (Overtone Theory)?

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The Christiansen trough is the dominant reflectance minima in a mineral infrared spectrum. It is described in the literature that at higher wavenumbers is the water region where only water troughs are found. The author can show that there are four kinds of water found in infrared—free water, surface adsorbed water vapor, site defect/caged water, and mineralogically bound water. The last we are discussing here that is made up of cation-hydroxyl water units, where the cation comes from the host mineral.

At lower wavenumbers, basic vibrational units of the mineral occur and so this is called the fundamental region. A stalwart, bedrock tenet of infrared theory is that fundamental band frequencies sum to make water bands. The author proposes this is trivially, provably false, and that spectra of minerals have water bands all the time with no identifiable fundamental bands that was supposed to make them. This is very common for clay water in minerals. That is, the water region is about two orders of magnitude higher sensitivity to water and water-cation complexes than is the fundamental region. We are on the hunt to debunk another junk theory of infrared, so here is a case study example.

Chinese writing stone has a quartz matrix with tabular clusters of feldspar crystals contained within it. In the first spectrum below, we see that the matrix is dominated by quartz and albite. There is another amorphous, bland roll in the 1100 cm-1 region, but no way to identify it. One thing is clear is that this is not epidote which is a loud spectral vibrator with many sharp peaks. With the quartz and albite all the other bands are accounted for.

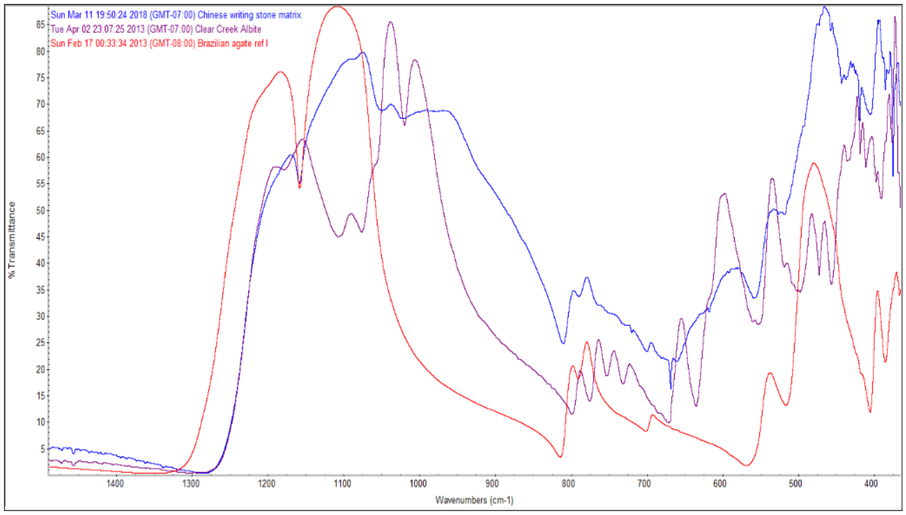
Then we roam down to the water region and zoom in. This has the classical epidote doublet, which is compared to a reference epidote crystal. The huge archive of the author has no other mineral found thus far in 10 years with this doublet, or something close.

This specimen has quartz and albite fundamental bands, which cannot sum to make epidote water bands. That doesn't even make rational sense how this could occur. What has happened in this specimen is that the epidote is so trace, it produces no identifiable fundamental epidote bands, but does produce epidote water bands. This occurs a lot with epidote, typically with serpentine rocks that have epidote water. Yet, the whole basis of overtone theory is that we can pick a bunch of fundamental bands, note their frequencies, sum then, and hunt for water overtones at that summed, predicted location. This works best for authors smart enough to get noisy minerals like the borosilicates with a huge number of bands so they can fiddle around with supercomputers to sum all conceivable combinations to claim matches to water bands, assuming huge errors of 200 cm or more is called an accurate model to you. It is considered an accurate model in mineralogy even though overtone theory has many big problems such as this case example points out.

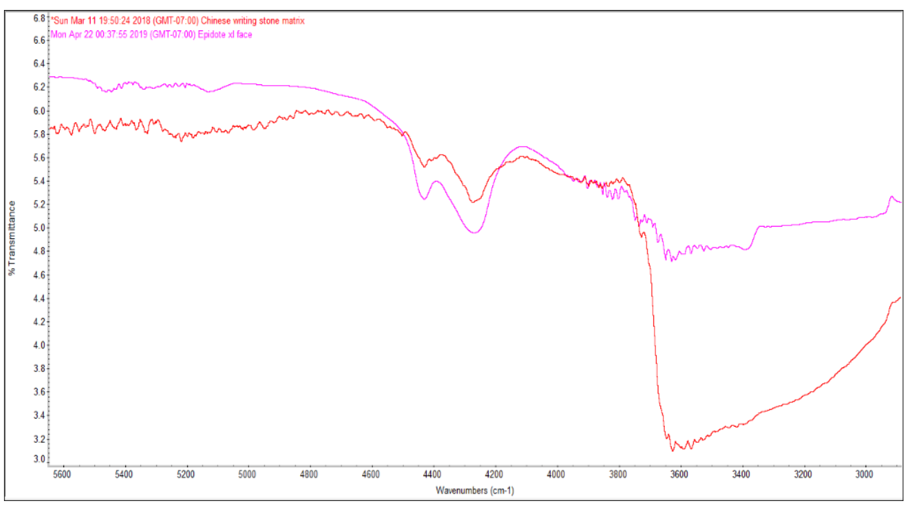
This leads to disastrous conclusions of unwary authors like the gentlemen (Anbalagen, et al, 2009) who studied sanidine and then concluded all of its water was sanidine water, when competent study and a much, much better archive shows they found dickite and celadonite clays. Oh well, now they contaminated our literature with false sanidine feldspar water bands to be repeated forever. Sanidine is a common feldspar found in volcanic rocks, and so is celadonite. That is, they found a common mutual source heritage, but not a common mineral in the water. Is there feldspar water? No.

In addition to that, detailed statistical study of trend relationships shows that **THE ENTIRE SPECTRUM OF A MINERAL IS THE WATER REGION**, and that the **FUNDAMENTAL REGION IS A SUBSET OF THE WATER REGION**. This means that there isn't always another place at higher wavenumbers for overtones of water to be predicted. Water bands can also be next to fundamental bands, and hence, cannot be summed with mid-infrared bands. As an example, look for 1271 cm^{-1} for water that is commonly in a mineral fundamental region. If you cannot see it, flip to grazing angle reflectance where the peaks approach square waves and the peak rolls don't obscure this band. Far infrared minerals such as anatase and brookite have their fundamental region shifted to low enough wavenumbers, the band is easy to see there also.

This is not to be confused with repeats (overtones) of water bands in the water region. This is found all the time. Fundamental bands don't sum to source water bands, but water bands can repeat throughout the water region. This is probably where the urban myth about overtone formation started.

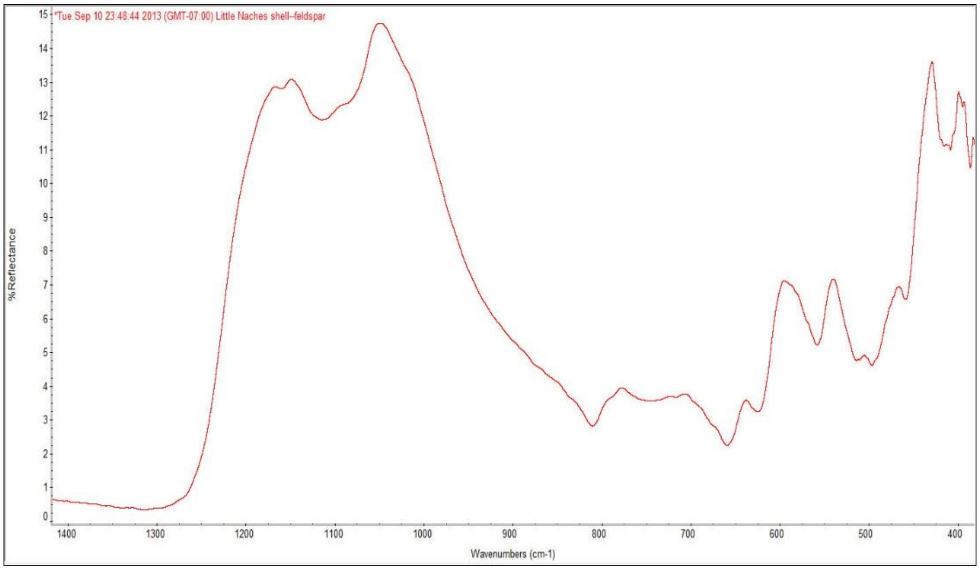


Chinese writing stone matrix with quartz and feldspar. The rock is not from China, it is from a San Gabriel Mtns., CA pegmatite. It is common with pegmatite tourmaline-bearing bodies. The name refers to the feldspar inclusions that look like Chinese characters with the interlocking albite blades.

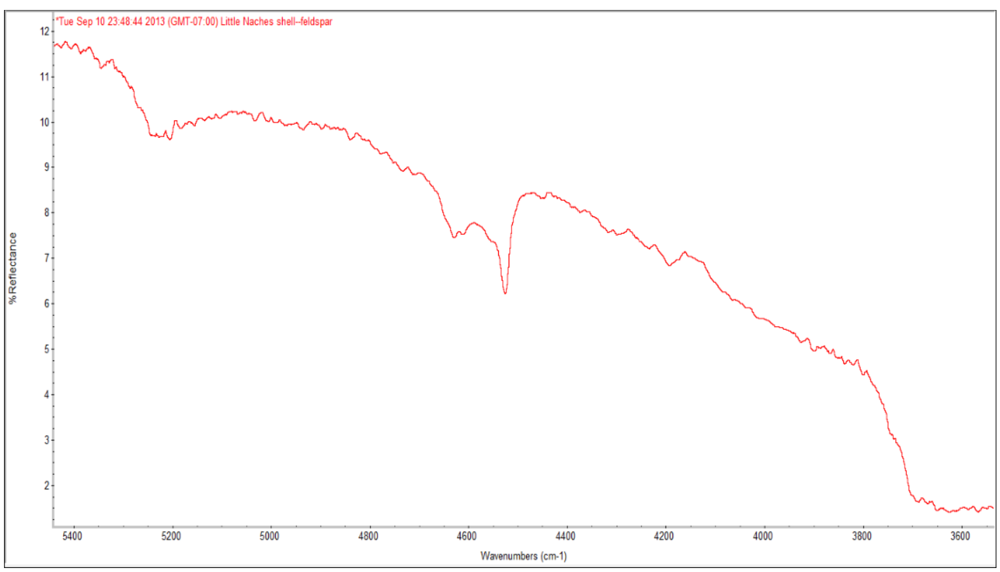


This Chinese writing stone has epidote water in the 4400 cm^{-1} region. 3600 cm^{-1} has generic free water rolls. The sample is compared to an epidote crystal from a famous locale in Maine.

Here is a common example of rhyolite alteration with weathering that produces the rhyolite quartz-orthoclase combination, and kaolinite water. There are no fundamental region bands to sum as an overtone for the kaolinite water.



Little Naches, OR geode shell showing quartz and orthoclase.



The Little Naches, OR geode shell showing kaolinite water in the 4500 cm^{-1} region.