

## Stability of hydrogen sites and hydrogen bonding in humite group minerals

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Natural humite group minerals (norbergite, chondrodite, humite, clinohumite) generally contain both F and OH in the structures, but F-free phases (chondrodite-OH, clinohumite-OH) can be stabilized under high pressures. If these minerals contain Ti, OH content is reduced by a substitution of  $\text{TiO}_2 = \text{Mg}(\text{OH})_2$ . Many structural refinements of both natural and synthetic humite group minerals are conducted to date. In term of hydrogen environments, two H sites (H1 and H2) are reported for chondrodite-OH and clinohumite-OH with 50% occupancies. If H1 site is fully occupied, short H1-H1 distance is realized in the structure, and it is generally thought that such configuration is less stable. On the other hand, in natural minerals containing F and Ti, only H1 site has been reported. Based on classical energy calculations (Abbott et al., AmMin, 1989), it was suggested that H2 site is more stable, and is further stabilized in F- or Ti-containing systems. This is contrary to the observations. In order to clarify this issue, and further understand stability of H1 and H2 sites in relation with hydrogen bondings in the humite group, first-principles calculations of the humite groups are conducted. The calculations include F- and Ti-containing systems too.

For the calculations, Quantum-Espresso package is used, and PAW potentials with GGA (pbesol-kjpaw\_psl) were used. First, structural models are constructed, and then the structures are optimized, and enthalpies of the systems are obtained. NMR parameters are also calculated. Chemical shift of proton provides a measure of hydrogen bonding. For all calculations, single unit cell was used, except Ti-containing system (chondrodite) where a 1x2x1 supercell was used.

For F- and Ti-free systems, when fully occupied H1 site and fully occupied H2 site are compared, H1 site was more stable energetically. This rather surprising result can be explained by elongated H1-H1 distance, whereas almost no hydrogen bonding in H2 site. When H1 and H2 sites are occupied 50% each, significant energy reduction was obtained by forming O-H1...O-H2 (... means hydrogen bonding) configuration. This configuration has lowest energy because H1-H1 repulsion no longer exists, and O-H1...O now forms straight hydrogen bonding. Therefore, for F- and Ti-free systems, the structures with both H1 and H2 sites half occupied are most stable as observed.

For natural minerals, OH contents are generally below 50%. As a result, O-H1...O configuration will not be realized in such systems. Therefore, solely occupied H1 or H2 sites should be compared. Our calculations reveal that in all humite minerals, H1 site is always more stable than H2. Note that short H1-H1 repulsion is no longer important in this system. Therefore, H1 is further stabilized. For Ti-containing systems, oxygens coordinating to Ti are underbonding state, and will behave as hydrogen acceptor. H1 site forms stronger hydrogen bonding with this hydrogen acceptor, where as H2 site can not, further stabilizing H1 site. Our calculations are fully consistent with the observed structures in F- or Ti-containing systems.

The present calculations reveals that hydrogen prefers H1 site, but when occupancy exceeds 50%, H1-H1 repulsion forces hydrogen to occupy less stable H2 site. Similar situation is known for topaz-F(OH), and can be interpreted similarly. Present study demonstrated that hydrogen bonding has strong influence on structural stability of humite group minerals.

Keywords: humite group, hydrogen bonding, First-principles calculation, crystal structure, hydrogen site, topaz-OH