

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

Influence of framework and extra-framework cations substitutions on the zeolite structure:
Single crystal X-ray diffraction analysis of analcime and wairakite solid solutions[(Ca_{0.5x}
Na_{1-x})AlSi₂O₆·H₂O]

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Zeolite is generally composed of Si/AlO₄ three-dimensional framework structure with interconnected cages and open channels. Cations and water molecules occupy the extra-framework space in the structure. Because the extra-framework cations can be substituted with different charged cations, consequently the Si/Al distribution in the framework is reordered to maintain its charge balance. The diversity of chemical composition caused by the coupled substitution gives the evidence of an effect of temperature, pressure and chemical potential on the mineral formation. Therefore, investigating the relationship between structural change and chemical composition may provide the clues to understanding the condition of rock forming processes at the near surface environment. The study aimed to clarify the structural change associated with chemical composition in a solid solution between analcime (NaAlSi₂O₆·H₂O) and wairakite (Ca_{0.5}AlSi₂O₆·H₂O). Single crystals with compositions between analcime and wairakite were synthesized by hydrothermal method. Aluminium sulfate, sodium metasilicate nonahydrate, and some calcium reagents gelled with distilled water were heated for 24 - 48 hours at 150 - 250 °C. The hydrothermally synthesized crystalline materials were analyzed by scanning electron microscope (SEM), electron probe micro-analyser (EPMA), and powder and single-crystal X-ray diffraction analyses. SEM images showed that the grown single crystals exhibited an euhedral trapezohedron shape ranging 100 - 200µm in size. From the EPMA analysis, we succeeded to synthesis the continuous solid solution exhibiting the chemical composition up to Ca/(Na+Ca) = 10 mol%. However, starting material with high Ca/Na ratio lead to yield fine products such as calcite and calcium sulfate. These by-productions inhibited the crystallization in the solid solution on the high Ca/Na side. Structure refinements based on the single-crystal X-ray diffraction data exhibited that crystal structures with the cubic Iad kept approximately unchanged with increase of Ca content in spite of the variation of Si/Al distribution in the framework. Lattice parameter a was monotonously increased from 13.713 (1) Å to 13.741 (1) Å as a function of Ca concentration. The contraction of the 6-membered oxygen rings was closely associated with exchanged Ca cations and reordered framework Si/Al cations. This study indicates that a geometry of micro-porous zeolite structure known as a molecular sieve is significantly influenced by the substitution of extra-framework cations followed by reordering of framework cations.

Keywords: zeolite, single crystal X-ray diffraction analysis

Mafic intrusion from Cape Nonamai, Shakotan Peninsula, Hokkaido

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Late Miocene doleritic intrusions are discussed from a petrological point of view. The intrusion consists of massive zone and layered zone. The massive zone is characterized by primitive olivine basalt, and the layered zone has more than 4 dolerite layers, which was originated by fractional crystallization from the mafic magma.

Keywords: fractional crystallization, dolerite, mafic intrusion