Report for the Joint Use/Research of the Institute for Planetary Materials, Okayama University for FY2024

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Category: ☑International Joint Research ☐General Joint Research ☐Joint Use of Facility ☐Workshop

Name of the research project: structural order-disorder in prehnite

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Research report:

The mineral prehnite (nominally Ca2Al2Si3O10(OH)2) is a hydrous aluminosilicate common in low grade metamorphic rocks, and knowledge of its thermodynamic properties and structure is important to calculations of pressure/temperature relationships in oceanic subduction complexes. Its structure is unique, with Si and 50% of Al cations in tetrahedral sites with either 4 or 2 neighboring tetrahedra, and OH groups associated with AlO6 octahedra. Previous studies, and 'conventional wisdom', suggest that SiO4 and AlO4 tetrahedra should alternate with strict ordering, but some details of the structure, notably the interaction of H+ with tetrahedral groups and the chance of residual disorder, remain unresolved,

resulting in incomplete understanding of any resulting configurational entropy (Rose and Bird 1987; Stebbins 1992; Sugiyama et al. 2021).

The two-dimensional (2D) and double-resonance NMR (Nuclear Magnetic Resonance) methods for observation of local structural environments of H, Al, and Si, which have been pioneered for aluminosilicate minerals by Dr. Xue of IPM, present a unique and powerful approach to learning about short-range structural details of prehnite, in particular for quantifying interactions of H+ with Al3+ and Si4+ cations and structural order-disorder (Xue et al. 2006; Xue and Kanzaki 2009; Stebbins and Xue 2014; Xue and Kanzaki 2024) . These results should be useful in resolving issues concerning configurational entropy, which in the past have lead to discrepancies between calculated high pressure/temperature phase equilibria.

During this fiscal year, Xue performed careful 1D 1H MAS NMR, 29Si MAS NMR and 1H-29Si CPMAS NMR measurements with and without proton decoupling, and 2D 1H-29Si HETCOR measurements on four prehnite samples supplied by Prof. Stebbins (two natural samples and two synthetic samples, which were also

studied by Stebbins 1992), as well as first-principles calculations of prehnite with different space groups and with and without Si-Al disorder. It was found that the 1H-29Si CPMAS NMR spectra with proton decoupling yield much better resolution than single-pulse 29Si MAS NMR spectra as were done in an earlier study (Stebbins 1992). These data clearly revealed the presence of Si in both Q2 sites with 2Si0Al next-nearest neighbors (NNN) and Q2 sites with 0Si2Al NNN, in addition to Q2 sites with 1Si1Al NNN, as are expected for a fully ordered structure, for all samples. For the two synthetic samples, significantly greater proportions of Q2 sites with 2Si0Al and 0Si2Al NNN were detected, and peaks of Si in Q4 sites with 3Si1Al NNN, in addition to Q4 sites with 2Si2Al NNN as are expected for strict alternating Si/Al distribution within the Q4 chains, were also observed, suggesting the presence of Al-O-Al and Si-O-Si linkages in the Q4 chains (i.e., the breakage of the Al avoidance principle). The occurrence of the additional Q2 sites, but not additional Q4 sites, beyond those expected for an ordered structure of prehnite, for the two natural samples could be a result of constrained Si-Al disorder in Q4 sites (under the constraint of alternating Si/Al within a given chain), chain disorders (due to displacement of Q4 chains while maintaining alternating Si/Al within a given chain), or Si/Al disorder associated

with domain boundaries. The greater abundances of extra Q2 sites and additional Q4 sites associated with Si-Al short-range disorder within the Q4 chains indicate greater structural disorder and thus higher configurational entropies for the synthetic prehnite samples than natural samples, likely due to failure to attain equilibrium in the synthesis experiments. These results may explain the previously reported discrepancies in the phase boundaries determined experimentally and those calculated thermodynamically (Rose and Bird 1987). The observed 1H and 29Si NMR chemical shifts were well reproduced by first-principles calculations.

References

Liou, J.G. 1971. Synthesis and stability relations of prehnite, Ca2Al2Si2O10(OH)2. Am. Min. 56, 507-531.

Perkins, D. and Westrum, E.F. 1980. The thermodynamic properties and phase relations of some minerals in the system CaO-Al2O3-SiO2-H2O. Geochim. Cosmochim. Acta, 44, 61-84.

Rose, N.M. and Bird, D.K. 1987. Prehnite-epidote phase relations in the Nodre Aputiteq and Kruuse Fjord layered gabbros, East Greenland. J. Petrol. 28, 1193-1218.

Stebbins, J.F. 1992. Nuclear magnetic resonance spectroscopy of geological materials. MRS Bull., 27, 45-52.

Stebbins, J.F. and Xue, X. 2014. NMR spectroscopy of inorganic Earth materials. In: Henderson, G.S., Neuville, D. and Downs, R.T. (eds): Spectroscopic Methods in Mineralogy and Materials Sciences,

Mineralogical Society of America, Reviews in Mineralogy and Geochemistry, 78, 605-653.

Sugiyama, K., Kawamata, T. and Kuribayashi, T. 2021. Structure refinement of prehnite from Passaic Countu, New Jersey, USA. J. Min. Petrol. Sci. 116, 272-276.

Xue, X., Kanzaki, M., Fukui, H., Ito, E. and Hashimoto, T. 2006. Cation order and hydrogen bonding of high-pressure phases in the Al2O3-SiO2-H2O system: An NMR and Raman study. Am. Min. 91, 850-861.

Xue, X. and Kanzaki, M. 2009. Proton distribution and hydrogen bonding in crystalline and glassy hydrous silicates and related inorganic materials: Insights from high-resolution solid-state nuclear magnetic resonance spectroscopy. J. Am. Ceram. Soc. 92, 2803-2830.

Xue, X. and Kanzaki, M. 2024. Correlation between Si-Al disorder and hydrogen-bonding distance variation in ussingite (Na2AlSi3O8OH) revealed by 1D and 2D multi-nuclear NMR and first-principles calculation. Am. Mineral. 109(5), 858-871.