

Enthalpy of formation of katoite $\text{Ca}_3\text{Al}_2[(\text{OH})_4]_3$: Energetics of the hydrogarnet substitution

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ABSTRACT

The silicon-free end member of the hydrogrossular solid solution series, katoite $\text{Ca}_3\text{Al}_2[(\text{OH})_4]_3$, was synthesized in a solid-media, piston-cylinder apparatus. The enthalpy of formation from the component oxides was measured by high-temperature oxide melt calorimetry and found to be $\Delta H_f = -255.6 \pm 12.2$ kJ/mol; the resulting enthalpy of formation from the elements is $\Delta H_f = -555.5 \pm 16.4$ kJ/mol. From this value, enthalpies for breakdown reactions of hydrogrossular were calculated and the relative energetic stability of katoite evaluated.

INTRODUCTION

To quantitatively assess the presence of water in the earth's interior, it is useful to investigate the structure, energetics, and phase relations of either hydrous minerals or nominally anhydrous minerals that can incorporate water. The garnet group, specifically the hydrogrossular series $\text{Ca}_3\text{Al}_2[\text{SiO}_4]_3$ - $\text{Ca}_3\text{Al}_2[(\text{OH})_4]_3$, can accommodate large quantities of water. Furthermore, garnets also are stable to pressures found in the Earth's mantle. The substitution of four hydroxyl groups for one silicate tetrahedral unit accounts for a complete solid solution series, where the fully hydrated end-member contains 28.79 wt% water. In natural garnets, the extent of substitution depends strongly on the overall composition, in particular on the large divalent cation in the dodecahedral site. For magnesium garnets, the relatively small Mg^{2+} ion (0.67 Å) results in the substitution of only 50 to 100 ppm water (Aines and Rossman 1984), whereas in natural calcium garnets with the larger Ca^{2+} (0.99 Å), substitution of up to 20 wt% has been reported (O'Neill et al. 1993). Knittle et al. (1992) showed the existence of intermediate hydrogrossular with 50% katoite component (14 wt% water) up to 25 GPa at low temperature.

The substitution $[\text{SiO}_4]^{4-} = [(\text{OH})_4]^{4-}$ also has been observed in nominally anhydrous minerals, such as quartz, where it may play a role as precursor for fluid inclusions (see Purton et al. 1992). This observation justifies expectations that the mechanism of the hydrogarnet substitution may be important for water-bearing, high-pressure phases with tetrahedrally coordinated silicon that are yet unknown.

The energy associated with this particular substitution of water for silica could be deduced if accurate phase equilibrium data for the dehydration of hydrogarnet

were available. Previous research has focused on equation-of-state data and on high-pressure, high-temperature dynamic properties (see for example, Rossman and Aines 1991; Olijnyk et al. 1991; Knittle et al. 1992; Lager and von Dreele 1996). A direct determination of the thermochemical properties of intermediate hydrogrossular garnets and of the fully hydrated end-member, katoite, is lacking.

The only work directly addressing the energy associated with the reaction



has been a numerical simulation published by Wright et al. (1994). Using empirical pairwise interaction potentials and minimizing positional parameters, the energy of the "hydrogarnet defect" $[\text{V}_{\text{Si}}(\text{OH})_4]$ in an anhydrous $[\text{SiO}_4]$ lattice was calculated to be 148.6 eV, relative to infinitely separated ions. This value neglects any vibrational contribution. From this defect energy, the energy of the hydration reaction



was determined to be +1.02 eV, or 98.4 kJ/mol. The present calorimetric study was done to provide an experimental constraint for the energy of this reaction.

EXPERIMENTAL METHODS

The silicon-free end member of the hydrogrossular solid solution series, katoite $\text{Ca}_3\text{Al}_2[(\text{OH})_4]_3$, was synthesized at 500 °C and 2.0 GPa in a piston-cylinder apparatus. The starting material was an oxide mix obtained by sintering together stoichiometric proportions of Al_2O_3 and CaCO_3 at 1500 °C. The starting material was sealed in a gold capsule with excess water and held at target conditions for ten days. Puncturing the capsule after the synthesis experiment showed the presence of excess water and

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TABLE 1. Details of calorimetric experiment

mass (mg)	ΔH_{dsol} (J/g)	ΔH_{dsol} (kJ/mol)
4.88	1931.30	730.580
4.63	2034.20	769.507
4.62	2000.88	756.903
4.82	2007.52	759.415
5.93	1992.29	753.655
5.04	1958.57	740.897
4.24	2069.17	782.737
4.39	1988.05	752.051
5.50	1949.39	737.426
4.89 ± 0.36	1992.37 ± 28.57	753.7 ± 10.8

thereby confirmed that during the experiment $P_{\text{H}_2\text{O}} = P_{\text{total}}$. The reaction product was verified by X-ray diffraction and electron microprobe analysis. The lattice parameter of 12.564(2) Å compares reasonably well with the value of 12.573 Å recorded in the JCPDS powder diffraction file. The composition determined from microprobe analysis is 26.60 ± 0.44 wt% Al₂O₃ and 44.44 ± 1.57 wt% CaO. Water was calculated by difference to be 28.95 ± 1.57 wt%. These values, too, compare well with the theoretical composition of 26.95 wt% Al₂O₃, 44.47 wt% CaO and 28.57 wt% water.

Enthalpies of drop-solution were determined by high-temperature oxide melt calorimetry with lead borate as calorimetric solvent (see Navrotsky 1997, for a review). A series of samples, 5 mg each, was dropped from room temperature into the solvent at 969.90 ± 0.05 K. The samples were introduced into the calorimeter quickly; decomposition prior to contact with the solvent did not occur. The calorimeter was purged with argon gas during the measurement to flush out water generated by the decomposition reaction. Earlier experiments conducted in our laboratory showed that the energy of interaction of water with the solvent is zero if the atmosphere in the calorimeter is flushed with an inert gas (Navrotsky et al. 1994). A low flow rate of 15 cm³/min was chosen so that the evolved water could thermally equilibrate with the calorimeter prior to being flushed out. Results of the measurements are detailed in Table 1. The enthalpy of formation was calculated by the thermodynamic cycle shown in Table 2.

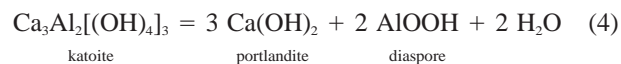
RESULTS AND DISCUSSION

The enthalpy of formation of katoite at 298 K has been determined to be $\Delta H_f = -255.6 \pm 12.2$ kJ/mol for the reaction

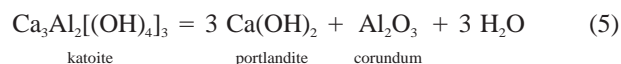


Liquid water was chosen as the reference state for H₂O. This value can be used to verify the enthalpy of the substitution reaction (2) as determined by Wright et al. (1994). The difference in enthalpies of formation of katoite and of anhydrous grossular normalized to one mole [SiO₄] is 29.4 kJ/mol, or 0.30 eV. This energy is even less endothermic than the value calculated by Wright et al. (1994) as 1.02 eV, or 98.4 kJ/mol and, therefore, indicates a greater stability of the hydrogarnet "defect" than previously suggested. Simple ionic models commonly overestimate energy differences. It may be that hydrogen bonding, which was not accounted for, causes the discrepancy. A partial charge model would presumably give a result more in accord with the experiment.

Energies of decomposition of katoite to other hydrated phases in the CaO-Al₂O₃-H₂O system can be used as indicators for the relative energetic stability of katoite; for example:



(with $\Delta H = 20.5 \pm 31.4$ kJ/mol; $\Delta V = 25.05$ cm³)



(with $\Delta H = 60.1 \pm 18.8$ kJ/mol; $\Delta V = 29.68$ cm³).

Enthalpies of formation for portlandite, diaspore, and corundum were taken from Robie and Hemingway (1995). These positive enthalpies of decomposition at 25 °C with H₂O as liquid clearly indicate favorable energetics for the hydrogarnet substitution relative to the formation of layered hydroxyl-bearing phases. Because katoite is also denser than these decomposition products, it should be further stabilized by pressure.

From these data, katoite appears to be thermodynamically stable at atmospheric conditions, which is consistent with the observation of katoite and intermediate hydrogarnets as weathering products on silica-poor rocks. From

TABLE 2. Thermodynamic cycle to calculate the enthalpy of formation of katoite

Ca ₃ Al ₂ [(OH) ₄] ₃ (s, 298 K) = solution (973 K)	$\Delta H_{\text{dsol, katoite}} = 753.7 \pm 10.8$ kJ/mol*
Al ₂ O ₃ (s, 298 K) = solution (973 K)	$\Delta H_{\text{dsol, Al}_2\text{O}_3} = 108.0 \pm 1.0$ kJ/mol*
CaCO ₃ (s, 298 K) = solution (973 K)	$\Delta H_{\text{dsol, cc}} = 194.1 \pm 1.8$ kJ/mol*
CO ₂ (v, 298 K) = CO ₂ (v, 973 K)	$\Delta H_{\text{heat, CO}_2} = 32.2$ kJ/mol†
H ₂ O (l, 298 K) = H ₂ O (v, 973 K)	$\Delta H_{\text{heat, water}} = 69.0$ kJ/mol†
3·CaCO ₃ + Al ₂ O ₃ + 6·H ₂ O = Ca ₃ Al ₂ [(OH) ₄] ₃ + 3·CO ₂	$\Delta H_f, \text{katoite} = -\Delta H_{\text{dsol, katoite}} + \Delta H_{\text{dsol, Al}_2\text{O}_3} + 3 \cdot (\Delta H_{\text{dsol, cc}} + \Delta H_{f, \text{cc}} - \Delta H_{\text{heat, CO}_2}) + 6 \cdot \Delta H_{\text{heat, water}}$
$\Delta H_f, \text{katoite} = -255.6 \pm 12.2$ kJ/mol	(formation from the oxides)
$\Delta H_f, \text{katoite} = -5551.5 \pm 16.4$ kJ/mol	(formation from the elements)

* This study; dsol = "drop solution."

† Heat content calculated from Robie and Hemingway (1995); enthalpy of formation for calcite from Robie and Hemingway (1995) $\Delta H_{f, \text{cc}} = -178.77$ kJ/mol.

structural work it can be concluded that the water incorporated in garnets persists at least up to 24 GPa at room temperature (Knittle et al. 1992). The extended pressure stability range and the small energy cost of substituting $(\text{OH})_4$ for $[\text{SiO}_4]$ is an indication that hydrogarnet, or at least this particular substitution mechanism, has significant potential to accommodate water in the Earth's interior.

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