

## Thermochemistry of a synthetic Na-Mg-rich triple-chain silicate: Determination of thermodynamic variables

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### ABSTRACT

An understanding of the thermodynamics of triple-chain silicate phases can offer insight into their formation in nature. Because the more common Mg triple-chain silicates have not yet been synthesized, this study focused on the Na-analogue to clinojimthompsonite (Na-cjt), which forms readily in a laboratory setting. Synthetic Na-cjt was characterized using electron microscopy and microanalysis, thermogravimetric analysis, infrared spectroscopy, and loss on ignition to determine its water content. The results of these studies indicated a formula for Na-cjt of  $\text{Na}_{3.74}\text{Mg}_{8.13}\text{Si}_{12}\text{O}_{32.00}(\text{OH})_4 \cdot 1.40\text{H}_2\text{O}$ , although there was substantial uncertainty ( $\pm 13\%$ ) associated with the total water (OH + H<sub>2</sub>O) content. A series of experimental reversals was performed over a temperature range of 350–650 °C and a pressure range of 0.1–1 GPa for the reaction between Na-cjt and a double-chain silicate. In the pressure range of 0.2–0.5 GPa, this reaction has the stoichiometry  $\text{Na}_{3.74}\text{Mg}_{8.13}\text{Si}_{12}\text{O}_{32.00}(\text{OH})_4 \cdot 1.40\text{H}_2\text{O}$  (Na-cjt) = 1.5  $\text{Na}_{2.49}\text{Mg}_{5.42}\text{Si}_8\text{O}_{21.34}(\text{OH})_{2.66}$  (Na-Mg amph) + 1.40 H<sub>2</sub>O. The equilibrium boundary reaches a maximum temperature near 550 °C at 0.4 GPa, continuing to lower temperatures above this pressure. The third-law entropy and enthalpy of formation of both Na-cjt and the associated Na-Mg amphibole were measured using adiabatic and oxide-melt solution calorimetry, respectively. Calculating the equilibrium boundary for the reaction using the calorimetrically determined values does not produce the same boundary found through the experimental reversals. The discrepancy was attributed to water variability in Na-cjt with pressure. This variability and its effect on Na-cjt's thermodynamic values can be expressed by the following equations that, for simplicity, indicate the total water content (OH + H<sub>2</sub>O) as moles of H<sub>2</sub>O in Na-cjt over the range of 0.1 to 1.0 GPa:

$$v_{\text{H}_2\text{O}} \text{ (moles of H}_2\text{O in Na}_{3.74}\text{Mg}_{8.13}\text{Si}_{12}\text{O}_{30.60} \cdot v_{\text{H}_2\text{O}}) = 11.06 + 28.36P - 5.25P^2 - 29.01P^{0.5} \text{ (} P \text{ in GPa)}$$

$$\Delta H_f^\circ \text{ of Na}_{3.74}\text{Mg}_{8.13}\text{Si}_{12}\text{O}_{30.60} \cdot v_{\text{H}_2\text{O}} \text{ (kJ/mol)} = -295.5v_{\text{H}_2\text{O}, \text{Na-cjt}} - 17408.8$$

$$S^\circ \text{ of Na}_{3.74}\text{Mg}_{8.13}\text{Si}_{12}\text{O}_{30.60} \cdot v_{\text{H}_2\text{O}} \text{ [J/(K}\cdot\text{mol)}] = 43.4v_{\text{H}_2\text{O}, \text{Na-cjt}} + 756.5$$

$$V \text{ of Na}_{3.74}\text{Mg}_{8.13}\text{Si}_{12}\text{O}_{30.60} \cdot v_{\text{H}_2\text{O}} \text{ [J/(bar}\cdot\text{mol)}] = 1.46v_{\text{H}_2\text{O}, \text{Na-cjt}} + 36.90$$

where the entropy does not include any contributions from configurational mixing. If one includes configurational entropy contributions from cation and vacancy disorder in the triple-chain silicate and amphibole, one obtains  $S^\circ$  and  $\Delta H_f^\circ$  for Na-cjt of 919.2 J/(K·mol) and –18417.6 kJ/mol, respectively, and  $S^\circ$  and  $\Delta H_f^\circ$  for Na-Mg amphibole of 650.9 J/(K·mol) and –11919.7 kJ/mol, respectively.

**Keywords:** Triple-chain silicate, Na-clinojimthompsonite, thermochemistry, calorimetry