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ABSTRACT

The solubilities of analcime and clinoptilolite were determined in dilute, weakly alkaline, aqueous solutions below 300 °C and at vapor-saturated pressures. Analcimes used in this study were from Mont St. Hilaire, Quebec (an₁, Si/Al = 2.02) and Wikieup, Arizona (an₂, Si/Al = 2.55); clinoptilolite samples were from Castle Creek, Idaho (Si/Al = 4.50). The effects of alkali content (Na,K) on clinoptilolite solubility were determined by using cation-exchanged varieties of the Castle Creek material (cp₁, cp₂). In neutral to weakly alkaline solutions, the dominant solubility-controlling reactions of these zeolites are

\[
\text{NaAlSi}_5\text{O}_{12}\cdot\text{H}_2\text{O}(\text{an}) + 5\text{H}_2\text{O}(l) \leftrightarrow \text{Na}^+ + \text{Al(OH)}_2^- + 2\text{Si(OH)}_4(aq),
\]

\[
\text{Na}_{0.85}\text{Al}_{1.15}\text{Si}_{2.00}\text{O}_{7.85}\cdot\text{H}_2\text{O}(\text{an}) + 5\text{H}_2\text{O}(l) \leftrightarrow 0.85\text{Na}^+ + 0.85\text{Al(OH)}_2^- + 2.15\text{Si(OH)}_4(aq),
\]

\[
\text{Na}_{1.1}\text{Al}_{1.1}\text{Si}_{4.9}\text{O}_{12}\cdot3.5\text{H}_2\text{O}(\text{cp}) + 8.5\text{H}_2\text{O}(l) \leftrightarrow 1.1\text{Na}^+ + 1.1\text{Al(OH)}_2^- + 4.9\text{Si(OH)}_4(aq),
\]

and

\[
\text{K}_{1.1}\text{Al}_{1.1}\text{Si}_{4.9}\text{O}_{12}\cdot2.7\text{H}_2\text{O}(\text{cp}) + 9.3\text{H}_2\text{O}(l) \leftrightarrow 1.1\text{K}^+ + 1.1\text{Al(OH)}_2^- + 4.9\text{Si(OH)}_4(aq).
\]

The logarithm of the equilibrium constants of these reactions were fitted to the function: \(\log K = A + BT + C/T + D \log T\). At 25 °C, \(\log K_{25}\) values for the Mont St. Hilaire analcime, Wikieup analcime, Na-clinoptilolite, and K-clinoptilolite are −16.1, −15.0, −26.5, and −28.1, respectively. These data were combined with the thermodynamic properties of the aqueous (aq) species \(\text{Si(OH)}_4\), \(\text{Al(OH)}_2^−\), Na⁺, K⁺, and liquid water (l) to determine standard Gibbs free energies of formation as a function of temperature. Values of \(\Delta G_f^\circ\) at 25 °C and 1 bar for the Mont St. Hilaire analcime and Wikieup analcime are −3089.2 and −3044.4 kJ/mol, respectively. The \(\Delta G_f^\circ\) values for hydrous Na-clinoptilolite and K-clinoptilolite, respectively, are −6267.9 and −6107.4 kJ/mol at 25 °C and 1 bar. The solubility data reported here, and results obtained from previous calorimetric studies, indicate that the aluminosilicate frameworks of analcime and clinoptilolite are stabilized by an increase in Al content.

INTRODUCTION

Zeolites are widespread authigenic aluminosilicates that form during water-rock interactions below roughly 300 °C and 2 kbars. The predominant geologic settings where zeolites form (Hay 1978) are (1) deep-sea pelagic sediments (e.g., Kastner and Stonecipher 1978; Gingele and Schulz 1993), (2) near-surface environments where alkaline meteoric waters interact with volcanic rocks (e.g., Sheppard and Gude 1969; Sourdam and Sheppard 1978), (3) geothermal regions (e.g., Kristmannsdottir and Tomasson 1978), and (4) under low-grade metamorphic conditions (e.g., Iijima and Utada 1966).

Analcime and clinoptilolite are common in all of these zeolite-forming environments and are among the most abundant zeolites in nature (e.g., Gottardi and Galli 1985). The prevalence of analcime and clinoptilolite in the rhyolitic tuffs at Yucca Mountain, Nevada, a potential repository for high-level radioactive wastes, has recently stimulated research on their physico-chemical properties (e.g., Bish 1984; Bowers and Burns 1990; Pabalan 1994; Gunter et al. 1994; Murphy et al. 1996; Carey and Bish 1996). Clinoptilolite at Yucca Mountain is particularly important because of its hydration/dehydration behavior, its potential to breakdown to analcime, and its cation-exchange properties and potential for immobilizing radionuclide cations, such as Cs and Np. The precipitation of these zeolites directly affects the permeability of volcanics and sediments because of their normal distribution as fracture fillings so that an understanding of their stability is an important factor in evaluating the permeabilities of their host rocks. However, predicting the extent of diagenetic and low-grade metamorphic reactions of zeolites and other clay minerals has been impeded by insufficient