Trona at extreme conditions: A pollutant-sequestering material at high pressures and low temperatures

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ABSTRACT

Single-crystal X-ray diffraction of trona, Na3COHCO3·2H2O, was measured between 100 and 340 K at ambient pressures, and the infrared and Raman spectra of this material characterized to ~25 GPa. The thermal expansion of trona is greatest in the b direction, which is due to a particularly large expansion of the long Na2-O2 bonds within the sodium septahedron in the trona structure. This crystallographic direction is associated with the distance between neighboring carbonate groups and neighboring water molecules within the structure. The dimensions of the carbonate group undergo no systematic changes over this temperature range, and the disordered hydrogen atom within the structure does not order at temperatures down to 100 K. Thus, detailed changes in the geometry of the sodium polyhedra primarily modulate the response of trona to decreases in temperature. The infrared and Raman spectra undergo discontinuous and reversible changes at ~7 and ~14.5 GPa: the former of these phase transitions is likely associated with a shift primarily in the sodium-oxygen polyhedra, while the latter also involves shifts in bonding of the carbonate groups. New assignments are suggested for portions of the vibrational spectrum based on the high-pressure results. Resonance effects between different vibrational modes are observed, including the observation of a transmission maximum associated with a resonant interaction between the carbonate symmetric stretching vibration and a broad mode at similar frequencies. The behavior of trona under extreme conditions is useful for understanding CO2-vapor-saturated alkali-rich systems, and late-stage peralkaline magmatic processes and, in its usage as both a sorbent and scrubber of SO2 and CO2 in flue gasses and lignite coals.

Keywords: Trona, high pressure, low temperature, single-crystal diffraction, vibrational spectroscopy

INTRODUCTION

Trona, Na3COHCO3·2H2O, is a non-marine evaporite mineral that, from the perspective of its chemical formula, contains the unusual combination of both a carbonate and bicarbonate anion. It has environmental importance as a product of carbon sequestration of flue gasses (Yoo et al. 2013; Ficicilar and Dogu 2006) and in its utilization in sulfur removal from both flue gasses and lignite coals (Kong and Wood 2010; Su et al. 2011; Sutcu and Eker 2013). Additional uses of trona include as a food additive (Nielsen 1999; Ekosse 2010), and as a common source of soda ash, which is a significant economic commodity because of its applications in manufacturing glass, chemicals, paper, detergents, and textiles. Trona is also observed as a phase within deteriorating concrete (Figg et al. 1976). Hence, the properties of trona at differing conditions of pressure and temperature can provide insights into the interplay between the structure and stability of this phase. From a crystal chemical viewpoint, trona is of interest as a carbonated phase that contains both water and hydroxyl units, and hence may provide insights into how water and carbonate ions interact within a single phase: indeed, its response to pressure may provide insight into the structural changes undergone by salt-bearing carbon-rich aqueous fluids and/or hydrated carbonatitic magmas under compression.

Trona has also been found in magmatic environments: Markl and Baumgartner (2002) show that trona can be formed by autometasomatic reactions of late-magmatic fluids or melts (or supercritical fluid-melt mixtures), with earlier crystallized rocks within the same plutonic complex, or by large-scale vapor unmixing in the very final stages of magmatism. Furthermore, Liu and Fleet (2009) have found that trona’s thermal stability is markedly enhanced by pressures of only a few tenths of a GPa: at ambient pressure, trona begins to decompose at ~340 K, but Liu and Fleet (2009) observed it to be stable up to 848 K at 0.21 GPa in equilibrium with CO2-rich vapor. Thus, understanding the behavior of trona under extreme conditions is useful for understanding late-stage peralkaline magmatic processes, and CO2-vapor-saturated alkali-rich systems.

Brown et al. (1949) first determined the crystal structure of trona using single-crystal X-ray diffraction. Bacon and Curry (1956) refined the structure with two-dimensional single-crystal neutron diffraction, and suggested that the H atom in the symmetric (HC3O4)3− anion is disordered. This disordering of the hydrogen generates a sharing of the hydrogen atom between the carbonate units, and hence produces the mixed carbonate/bicarbonate character of these anion groups. Candlin (1956)