Natrolite is not a “soda-stone” anymore: Structural study of alkali (Li$^+$), alkaline-earth (Ca$^{2+}$, Sr$^{2+}$, Ba$^{2+}$) and heavy metal (Cd$^{2+}$, Pb$^{2+}$, Ag$^+$) cation-exchanged natrolites

YONGJAE LEE,* DONGHOON SEOUNG, AND YONGMOON LEE

Department of Earth System Sciences, Yonsei University, Seoul 120-749, Korea

ABSTRACT

We report here the preparation and structural models of alkaline-earth (Ca$^{2+}$, Sr$^{2+}$, Ba$^{2+}$) and heavy metal (Cd$^{2+}$, Pb$^{2+}$, Ag$^+$) cation-exchanged natrolites at ambient conditions and compare them to the alkali (Li$^+$, Na$^+$, K$^+$, Rb$^+$, Cs$^+$) cation forms. The latter two groups all crystallize in the orthorhombic $Fdd2$ symmetry as the natural sodium natrolite, whereas the alkaline earth analogues are all found in the monoclinic $Cc$ symmetry as scolecite, the natural calcium counterpart. We find the existence of a universal linear relationship between the unit-cell volume and the non-framework cation radius in natrolite. The rotation angles of the fibrous chain units are distributed between 25.5° (Li-form) and 2.9° (Cs-form) to show its inverse proportionality to the non-framework cation radius and the channel opening area. We also propose a possible threshold in the cation radius that dictates the distribution pattern of the non-framework cations and water molecules in the ordered and disordered fashions in natrolite.

Keywords: Natrolite, ion exchange, crystal chemistry, Rietveld refinement

INTRODUCTION

Natrolite (Na$_{16}$Al$_8$Si$_{24}$O$_{80}$·16H$_2$O), named after a “soda-stone” (Klaproth 1803), is one of the naturally occurring zeolites known for composition near the pure sodium end-member (Alberti et al. 1982; Ross et al. 1992). Although there exist natural calcium analogues, mesolite (Na$_{13}$Ca$_3$Al$_{16}$Si$_{24}$O$_{80}$·21.3H$_2$O), and scolecite (Ca$_8$Al$_{16}$Si$_{24}$O$_{80}$·24H$_2$O) (Alberti et al. 1982), direct calcium substitution is highly limited to establish any solid-solution relationships between these polymorphs, and no other cation forms have been reported to occur naturally in any meaningful compositional alteration (Meneghinello et al. 1999). Natrolite framework is composed of $T$-$O$$_8$ building units formed from linking two Al and three Si-tetrahedra (Meier 1960; Taylor et al. 1933). These units are then connected along the c-axis to form the so-called natrolite chains. Further polymerization of these chains via Al-O-Si linkages leads to the formation of the helical 8-ring channels along the c-axis. Sodium cations and water molecules are tightly held to the framework in the six- and fourfold coordination environments, respectively, by forming cross-linked zigzag chains along the helical 8-ring channels (Artioli et al. 1984). This well-ordered distribution of sodium cations and water molecules is suspected to be related to the poor water mobility and cation exchange capacity of the natural natrolite. Accordingly, it has only been possible to employ high-temperature melt exchange to substitute the sodium cations with smaller monovalent cations such as Li$^+$ or larger NH$_4^+$, which led to unit-cell volume contractions by ca. 5% for the partially Li-exchanged natrolite or by ca. 4% for the anhydrous NH$_4^+$-natrolite (Baur et al. 1990; Stuckenschmidt et al. 1992). For the substitution of larger monovalent cations, Baur and Yamazaki reported two conflicting structural models on the fully K-exchanged natrolites (Baur et al. 1990; Yamazaki et al. 1987). We have recently reported a method to prepare a series of alkali metal substituted natrolites (K-, Rb-, and Cs-natrolites) and demonstrated that the modification of the ordered cation-water distribution induced by the sodium-to-potassium cation substitution is the key parameter for further cation exchange to produce Rb- and Cs-forms (Lee et al. 2010). Unlike those previously reported models, we found that the potassium cations and water molecules are statistically distributed at different sites from those for the sodium cations and water molecules in the original natrolite. Such a disordered distribution persisted to the Rb- and Cs-forms, and the helical channels converted to progressively more circular shapes as the cation size increases. Thereafter, we have been successful in preparing three alkaline-earth cation forms of natrolites, some heavy metal cation forms, and a fully Li-exchanged natrolite from the potassium natrolite. Here we report for the first time the structures of fully Ca$^{2+}$-, Sr$^{2+}$-, Cd$^{2+}$-, Pb$^{2+}$-, Ag$^+$-, and Li$^+$-exchanged natrolites at ambient conditions and compare them to the previously established alkali (Na$^+$, K$^+$, Rb$^+$, Cs$^+$) cation-forms.

EXPERIMENTAL METHODS

The starting material, K-natrolite (K-NAT), was prepared using a 4 M KNO$_3$ (ACS reagent grade from Sigma-Aldrich) solution and a ground mineral natrolite (ideally Na$_{16}$Al$_8$Si$_{24}$O$_{80}$·16H$_2$O, San Juan, Argentina, from OBG International) in a 100:1 weight ratio. The mixture was stirred at 80 °C by minimizing the loss of water content in a closed system. After 24 h, the solid was separated from the solution by centrifugal method. The dried powder was used for the second and third exchange cycles in the same conditions. The final product was air dried, and from the elemental analysis (Jarrell-Ash Polyscan 61E Inductively Coupled Plasma), over 99% K-exchange was confirmed (Lee et al. 2010). Further cation-exchange...