Dehydration of the natural zeolite goosecreekite CaAl$_2$Si$_6$O$_{16}$·5H$_2$O upon stepwise heating: A single-crystal and powder X-ray study

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ABSTRACT

The zeolite mineral goosecreekite CaAl$_2$Si$_6$O$_{16}$·5H$_2$O has been structurally investigated between 25 and 600 °C to monitor structural modifications upon partial dehydration. Temperature-dependent in situ powder and single-crystal X-ray techniques were combined with TG/DTA experiments. Goosecreekite has a porous framework structure with well-ordered Si,Al distribution. In its natural form extraframework Ca is seven-coordinated. Up to ca. 100 °C, 1 H$_2$O molecule is expelled reducing the Ca coordination from 7 to 6 accompanied by very minor changes of the tetrahedral framework. Depending on humidity and equilibration time a second structural change begins between 150 and 250 °C due to loss of additional 2.8 H$_2$O pfu. The space group $P_2_1$ is maintained but the $c$ axis doubles and the structure is highly twinned. This new phase may be interpreted with a disordered model having two different framework topologies: one with the original T-O-T linkage and a second one with broken T-O-T links. Starting at ca. 300 °C, another 1.2 H$_2$O are lost and this new orthorhombic, strongly contracted phase of $P2_12_12_1$ symmetry has five-coordinated Ca. The X-ray powder signal of the orthorhombic phase persists up to 600 °C, but the structure becomes increasingly X-ray amorphous until complete destruction at 675 °C. A single crystal ($P2_1$ phase with doubled $c$ axis) partly dehydrated at 200 °C recovers the structure of natural goosecreekite under ambient conditions. Similar rehydration occurs after one month under ambient humidity for a powder sample of the orthorhombic $P2_12_12_1$ phase produced by heating of goosecreekite to 325 °C.

Keywords: Zeolite, goosecreekite, dehydration, crystallography

INTRODUCTION

Some zeolites have been known to undergo structural modifications with dehydration to varying degrees. Many of these structural changes are reversible upon rehydration. Furthermore, upon “almost” complete dehydration due to heat treatment, several zeolite frameworks break down to X-ray amorphous products. The latter behavior has recently been quantified (Cruciani 2006) by the stability index (SI), which ranges between 1 (breakdown <350 °C) and 5 (breakdown >800 °C). Among natural zeolites, those with Ca as dominant extraframework cation are of special interest because breaking of T-O-T links, leading to modified framework topology, has been observed with progressive dehydration for heulandite-Ca (Alberti et al. 1983) and stellerite (Alberti et al. 1978, 2006). This behavior is not limited to zeolites but has also been found for microporous 11 Å tobermorite (Merlino et al. 2001), which is an important hydrous calcium silicate in Portland cements. The relatively high-ionic potential Z/r (Z: nominal charge; r: ionic radius) of extraframework Ca is believed to be one of the factors responsible for framework rupture (e.g., Alberti and Vezzalini 1983; Cruciani 2006). On the other hand, the type of the framework structure also plays an important role (Armbruster 2010). The maximum thermal stability of Ca-rich natural zeolites or their tendency to undergo topological changes depends on the Ca coordination after loss of H$_2$O originally contributing to the Ca coordination. As an example: under ambient conditions chabazite-Ca has Ca coordinated to framework O and extraframework H$_2$O. However, even if all H$_2$O is expelled, the complex chabazite cage allows Ca to migrate to alternative sites satisfying bonding requirements of Ca. For this reason, the structure has high thermal stability (Zema et al. 2008). If in a partially dehydrated zeolite structure Ca cannot find bonding partners among framework O belonging to SiO$_4$ and AlO$_4$ tetrahedra, the framework will either locally rupture (breaking T-O-T links) to satisfy Ca charge balance (e.g., in stellerite and heulandites-Ca) or the framework will entirely collapse as found for laumontite, which becomes amorphous at ca. 350 °C (Ståhl et al. 1996).

There are three natural zeolites with the stoichiometric formula of CaAl$_2$Si$_6$O$_{16}$·nH$_2$O – epistilbite (5.33 H$_2$O), yugawaralite (4 H$_2$O), and goosecreekite (5 H$_2$O). The former two zeolites undergo severe framework distortion upon heating and accompanying dehydration at high temperatures (Cruciani et al. 2003; Alberti et al. 1996) and become X-ray amorphous above ca. 520 °C. Thus, Cruciani (2006) rated them with SI = 3.

Epistilbite undergoes three episodes of water loss: at ca. 97, 197, and 300 °C. Due to H$_2$O loss, Ca-coordination decreases below 6, resulting in a phase transition at 300 °C associated with severe structural distortion. The tetrahedral framework remains stable up to ca. 530 °C (Cruciani et al. 2003).