Topotactic transformation and dehydration of the zeolite gismondine to a novel Ca feldspar structure

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ABSTRACT

Temperature-dependent single-crystal X-ray data were collected on gismondine (GIS) Ca₄(Al₆Si₄O₁₄)·18H₂O from Rio Pian del Foco, Genova province, Italy, in steps of 25 °C up to 600 °C. At room temperature, gismondine has space group P2₁/c with a = 10.0214(1), b = 10.5997(1), c = 9.8327(1) Å, β = 92.363(1)°, V = 1043.58(2) Å³. This structure remained stable up to 50 °C. The dehydration behavior then divided into two different pathways depending on the sample. In the more frequent path I, the LT P2₁2₁2₁ structure (phase B) Ca₄(Al₆Si₄O₁₂)·12H₂O [a = 13.6801(8), b = 10.4670(6), c = 13.8667(9) Å, V = 1985.6(2) Å³] formed at 75 °C. The orthorhombic structure has a doubled volume relative to the monoclinic room-temperature structure. At 150 °C the HT P2₁2₁2₁ structure (phase C) with 8 H₂O pfu [a = 13.9014(12), b = 8.9469(8), c = 13.9697(14) Å, V = 1737.5(3) Å³] occurred. This phase C has strongly compressed elliptical channels with Ca ions bonding to adjacent walls. At high temperature (300 °C), the quality of the diffraction pattern in path I further degraded and became inclusive.

In path II the diffraction patterns were of considerably higher quality and at 75 °C the phase LT I2/a with 16 H₂O pfu [a = 9.790(2), b = 10.437(2), c = 9.790(2) Å, β = 90.97(3)°, V = 1000.1(4) Å³] formed, changing at 150 °C to HT I2/a [at 225 °C: a = 9.434(4), b = 9.044(2) c = 9.695(2), β = 89.04(1)°, V = 827.0(4) Å³] with 4 H₂O. Above 250 °C the HT I2/a structure topotactically transformed by a reconstructive mechanism to a triclinic CT Ca feldspar structure [a = 8.152(5), b = 12.917(5), c = 7.126(4) Å, α = 93.26(3), β = 116.37(6), γ = 88.72(5)°, V = 671.2(7) Å³], which does not follow Loewenstein’s (1954) rule, as the framework has ordered corner-linked AlO₄ tetrahedra. As a consequence of the GIS to Ca feldspar transformation T-O bonds within four-membered rings break and reconnect to a new framework type. The HT I2/a structure with strongly twisted double crankshaft chains acts as precursor for the feldspar formation without an intermediate X-ray amorphous phase usually found after complete dehydration of most natural zeolites.

This study reports for the first time a low-temperature topotactic transformation from gismondine to Ca feldspar and explains the highly unusual occurrence of ordered Al-O-Al clusters in this feldspar structure.

Keywords: Zeolite, gismondine, dehydration, crystal structure, Ca feldspar, Loewenstein’s rule

INTRODUCTION

There are four natural zeolite species with corresponding tetrahedral framework topology (framework type GIS): gismondine Ca₄(Al₆Si₄O₁₄)·18H₂O, garrisonite Ca₃Na(Al₆Si₄O₁₄)·14H₂O, gobbinsite Na₉Ca(Al₆Si₄O₁₂)·12H₂O, and amicite Na₉K₄(Al₆Si₄O₁₂)·10H₂O (Coombs et al. 1997; Armbruster and Gunther 2001). The topology of the GIS framework is tetragonal, space group I₄/amd. The lowering of the symmetry in minerals with GIS framework is due to Si,Al order and ordered incorporation of channel occupants.

The structure of gismondine at room temperature is monoclinic space group P2₁/c with a = 10.02, b = 10.61, c = 9.84 Å, β = 92.4°. In this setting a and c correspond to the a axes of the tetragonal GIS framework. Alternating SiO₄ and AlO₄ tetrahedra build four-membered rings connected to double-crankshafts that run parallel to the a and c axes. These are linked so that eight-membered channels run parallel to these axes as well. Large, ovoid cavities are formed at the intersection of the channels. These cavities are occupied by extraneous framework Ca ions bonded to two framework O atoms on one side of the cavity, and four H₂O molecules on the opposite side. In general, one H₂O site is split, resulting in variable Ca coordination. Gismondine has the same Ca:Al:Si ratio of 1:2:2 as anorthite.

Before the gismondine structure had been solved, Smith and Rinaldi (1962), with later revisions by Smith (1968), classified framework structures formed by four- and eightfold rings. They distinguished two ways how chains built by four-membered rings of UUDD type can be crosslinked. The UUDD nomenclature (Smith and Rinaldi 1962) indicates that within the four-membered rings two adjacent tetrahedra point upward (U) and the other two downward (D). The two different connections lead either (1) to a flexible framework or (2) to an inflexible framework...