

## 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**)  $\text{Ca}_4(\text{Al}_8\text{Si}_8\text{O}_{32})\cdot 18\text{H}_2\text{O}$  from Rio Pian del Foco, Genova province, Italy, in steps of 25 °C up to 600 °C. At room temperature, gismondine has space group  $P2_1/c$  with  $a = 10.0214(1)$ ,  $b = 10.5997(1)$ ,  $c = 9.8327(1)$  Å,  $\beta = 92.363(1)^\circ$ ,  $V = 1043.58(2)$  Å<sup>3</sup>. 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  $P2_12_12_1$  structure (phase B)  $\text{Ca}_4(\text{Al}_8\text{Si}_8\text{O}_{32})\cdot 12\text{H}_2\text{O}$  [ $a = 13.6801(8)$ ,  $b = 10.4670(6)$ ,  $c = 13.8667(9)$  Å,  $V = 1985.6(2)$  Å<sup>3</sup>] formed at 75 °C. The orthorhombic structure has a doubled volume relative to the monoclinic room-temperature structure. At 150 °C the HT  $P2_12_12_1$  structure (phase C) with 8 H<sub>2</sub>O pfu [ $a = 13.9014(12)$ ,  $b = 8.9469(8)$ ,  $c = 13.9697(14)$  Å,  $V = 1737.5(3)$  Å<sup>3</sup>] 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 H<sub>2</sub>O pfu [ $a = 9.790(2)$ ,  $b = 10.437(2)$ ,  $c = 9.790(2)$  Å,  $\beta = 90.97(3)^\circ$ ,  $V = 1000.1(4)$  Å<sup>3</sup>] formed, changing at 150 °C to HT  $I2/a$  [at 225 °C:  $a = 9.434(4)$ ,  $b = 9.044(2)$ ,  $c = 9.695(2)$ ,  $\beta = 89.04(1)^\circ$ ,  $V = 827.0(4)$  Å<sup>3</sup>] with 4 H<sub>2</sub>O. Above 250 °C the HT  $I2/a$  structure topotactically transformed by a reconstructive mechanism to a triclinic  $C\bar{1}$  Ca feldspar structure [ $a = 8.152(5)$ ,  $b = 12.917(5)$ ,  $c = 7.126(4)$  Å,  $\alpha = 93.26(3)$ ,  $\beta = 116.37(6)$ ,  $\gamma = 88.72(5)^\circ$ ,  $V = 671.2(7)$  Å<sup>3</sup>], which does not follow Loewenstein's (1954) rule, as the framework has ordered corner-linked  $\text{AlO}_4$  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