# Dehydration of the natural zeolite goosecreekite CaAl<sub>2</sub>Si<sub>6</sub>O<sub>16</sub>·5H<sub>2</sub>O upon stepwise heating: A single-crystal and powder X-ray study

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# ABSTRACT

The zeolite mineral goosecreekite CaAl<sub>2</sub>Si<sub>6</sub>O<sub>16</sub>·5H<sub>2</sub>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<sub>2</sub>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<sub>2</sub>O pfu. The space group  $P2_1$  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<sub>2</sub>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 and Vezzalini 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

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undergo topological changes depends on the Ca coordination after loss of H<sub>2</sub>O originally contributing to the Ca coordination. As an example: under ambient conditions chabazite-Ca has Ca coordinated to framework O and extraframework H<sub>2</sub>O. However, even if all H<sub>2</sub>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<sub>4</sub> and AlO<sub>4</sub> 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<sub>2</sub>Si<sub>6</sub>O<sub>16</sub>·nH<sub>2</sub>O – epistilbite (5.33 H<sub>2</sub>O), yugawaralite (4 H<sub>2</sub>O), and goosecreekite (5 H<sub>2</sub>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<sub>2</sub>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).

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Seven H<sub>2</sub>O sites are present in yugawaralite, of which only two are fully occupied. Alberti et al. (1996) applied single-crystal X-ray methods to study the structural behavior of yugawaralite upon heating to 250 °C. Even after loss of 80% H<sub>2</sub>O the topology of the framework did not change. Yugawaralite undergoes a phase transition at ca. 420 °C (from *Pc* to *Pn*) accompanied by severe structural distortions and remains stable up to 530 °C (Artioli et al. 2001).

There are no temperature-dependent structural studies for goosecreekite available, but published differential thermal analysis (DTA) and differential thermo-gravimetry (DTG) data suggest a complex dehydration behavior (Apte 1998; Henry et al. 2008).

Goosecreekite CaAl<sub>2</sub>Si<sub>6</sub>O<sub>16</sub>·5H<sub>2</sub>O, monoclinic space group  $P2_1$ , is a natural zeolite that was first described by Dunn et al. (1980) and named after the type locality in Goose Creek quarry, Loudoun County, Virginia. The structure was further characterized by crystal structure determination (Rouse and Peacor1986). Samples from Loudoun County occur in vugs in altered seams that cut diabase (Dunn et al. 1980). Additional localities of goosecreekite are the Jalgaon Quarries, Maharashtra, India, in the Deccan Volcanic Province (Apte 1998).

The framework of goosecreekite (framework type GOO) consists of completely ordered  $SiO_4$  and  $AlO_4$  tetrahedra. The tetrahedra form eight-membered rings that are highly deformed creating channels that are parallel to the **a** axis. These channels are intersected by two additional eight-member channels parallel to the **b** axis (in a zigzag manner) and the **c** axis. Calcium is seven coordinated and is located at the intersection of the channels and bonds to two framework O and five H<sub>2</sub>O molecules (Rouse and Peacor 1986) as seen in Figure 1. Natural goosecreekite at ambient conditions has 15 wt% H<sub>2</sub>O.

Previous structural studies of goosecreekite have been limited to single-crystal measurements at ambient conditions (Dunn et al. 1980; Rouse and Peacor 1986), powder X-ray diffraction (Dunn et al. 1980; Apte 1998; Lewis et al. 2006; Henry et al. 2008), powder neutron diffraction (Henry et al. 2008), Raman spectroscopy (Lewis et al. 2006), thermo-gravimetric analysis, differential thermo-dilatometry (DTD), differential thermal analysis (DTA), thermodilation (TD) (Apte 1998), as well as computer simulation (Almora-Barrios et al. 2001; Lewis et al. 2006; Ruiz-Salvador et al. 2007).

The purpose of this study is to further characterize the structure and behavior of goosecreekite using single-crystal and powder X-ray diffraction (XRD) conjoined with step-wise dehydration to elevated temperatures and thermo-gravimetry (TG)/DTA analysis.

#### **EXPERIMENTAL METHODS**

Samples of goosecreekite used in this study originated from two sources: the type locality in Loudoun County, Virginia, U.S.A. (kindly provided by the Smithsonian Institution, sample NMNH 148274) and Jalgaon Quarries Maharashtra, India. Samples from India were compositionally analyzed on a JEOL JXA8200 electron microprobe for Al (anorthite), Si (orthoclase), Cl (scapolite), Na (albite), K (orthoclase), Mg (forsterite), Ca (anorthite), F (phlogopite), Fe (almandine), Ba (barite), Sr (carbonate), and Cr (eskolaite). Operating conditions for 14 analyses were 15 kV accelerating voltage, 20 nA beam current, and a 30 µm spot size.

#### Single-crystal XRD

Single-crystal XRD was carried out on a Bruker APEX II diffractometer with  $MoK\alpha$  (0.71073 Å) X-ray radiation with 50 kV and 40 mA X-ray power. Samples



**FIGURE 1.** Crystal structure of goosecreekite measured at -100 °C viewed down the **a** axis. SiO<sub>4</sub> and AlO<sub>4</sub> tetrahedra are labeled. Extraframework Ca ions are the large, black spheres and bond to framework oxygen and H<sub>2</sub>O molecules (small, black spheres).

from both Loudoun County and Jalgaon Quarries were mounted in open 0.2 mm diameter quartz glass capillaries and heated in 25 °C increments to 225 °C under a constant dry nitrogen stream using an Oxford Cryostream Plus 700 Series. Samples of both localities were held at temperature for times ranging from 30 min to 5 h, and then quenched to -100 °C for data acquisition. Capillaries were net sealed after quenching. Due to the comparable structures of samples from both localities, measurements above 225 °C were carried out on the Jalgaon Quarries samples only (the prefixes "IG" on sample names indicates Indian goosecreekite). The Loudoun sample was first measured at room temperature, then at -100 °C for comparison.

Samples were then heated to 50, 100, 175, 200, and 225 °C and held at temperature for 1.5 h, quenched to -100 °C and measured with a 10 s frame exposure time. The procedure for the Jalgaon sample up to 225 °C was the same as for the Loudoun sample, but additionally the sample was heated in 25 °C increments from 250 to 425 °C under a dry N2 stream, and again held at temperature for 1.5 h. Data acquisition was performed (in situ) at elevated temperatures to avoid crystal loss or destruction due to strain when quenching to low temperature. CCD data were integrated and an empirical absorption-corrected was applied using the Apex2 v. 2009-11.0 software package (Bruker 2009). The structure was refined with SHELXTL Version 2008/4 (Bruker 2008) using the structural model of Rouse and Peacor (1986) and neutral atom scattering factors as starting values. Operating conditions are summarized in Table 1. In general anisotropic atomic displacement parameters (adp) were refined for fully occupied sites. An exception represents the monoclinic phase with doubled c axis. In this case, the adp's of a few O sites converged to non-positive definite values due to correlation problems and low data quality (twinning). Such O sites were refined with isotropic displacement parameters.

#### Powder XRD

Samples of Jalgaon Quarries goosecreekite were ground to a fine powder in acetone and dried. Measurements were made with a PANalytical X'Pert Pro MPD  $\theta$ – $\theta$  diffractometer with Ni-filtered 1.6 kW CuK $\alpha$  radiation. A 0.25° antiscatter slit and a 0.125° divergence slit were in the primary path and a 0.125° antiscatter slit in the diffracted beam path. Conditions include a step-size of 0.008°/step and a measurement time of 57 s/step. Sample rotation was 30 rpm. Samples were heated using an Anton Paar HTK 1200 heating-chamber in 25 °C steps up to 700 °C and held at temperature for 30 min and measured. No cover gas was used, therefore the sample was in contact to room humidity. Powder diffraction data were recorded from 10 to 60 °20. Data were refined using Pawley refinement in Topas-Academic v. 4.1 (Coelho 2007).

# TG/DTA analysis

TG/DTA was conducted at the Institute of Mineralogy and Petrography, University of Innsbruck, with a Setaram Setsys Evolution 2400 instrument using samples from Jalgaon Quarries, India. Samples of ca. 18 mg were previously ground to a fine powder in acetone and placed into a 100  $\mu$ L corundum crucible. All runs were conducted under a dry helium atmosphere. Between 25 and 600 °C three different heating rates of 2, 5, and 10 °C/min were used with a gas flow rate of 20 mL/min. Samples were heated and then cooled to room temperature at the same rate.

## RESULTS

# Electron microprobe analyses

The type locality sample from Loudoun (Virginia) has not been analyzed in this study because compositional data are available from Dunn et al. (1980) indicating CaAl<sub>2</sub>Si<sub>6</sub>O<sub>16</sub>·5H<sub>2</sub>O stoichiometry.

The composition of Jalgaon goosecreekite was stoichiometrically consistent with the ideal chemical formula with minor amounts of F and Na (0.035 and 0.035 apfu, respectively). The polished topography of the samples in carbon-coated thin sections noticeably deteriorated under vacuum alone.

## Single-crystal XRD

In contrast to the Loudoun sample, which had relatively little twinning, most crystals from Jalgaon were highly twinned [001,010,100]. The structures of both goosecreekite samples show identical frameworks and corresponding channel occupants. Three dehydration steps could be separated between 25 and 425 °C based on discontinuities of temperature dependence of cell dimensions and symmetry. Starting at room-temperature goosecreekite has space group  $P2_1$ . According to the Flack parameter the acentric crystals from Loudoun show merohedral twinning by the inversion operation, but samples of the Jalgaon goosecreekite selected for structure analysis were not twinned. Coordinates and displacement parameters are summarized in Tables 2-5<sup>1</sup>. Up to 100 °C, 1 H<sub>2</sub>O pfu (W3) is released without influence on symmetry and cell setting. Corresponding atomic coordinates and displacement parameters are given in Tables 6 and 71 for measurement at 150 °C. This first dehydration step reduces the extraframework Ca coordination from seven (two framework O atoms plus five H2O molecules) to six (two

TABLE 1	• C	Operating	condi	itions a	nd refi	nement	results	from	the si	ingle-	crysta	I XRD	study	⁄ on a E	Bruker	Smart /	APEXII (	CCD	diffractometer	

	IG_GOOSb_RT	IG_HT100	IG_Heating_150	IG_HT_200	IG_HT_425	IG_HT_Month_25
Temperature °C (heated to)	25	25	150	200	425	25
Temperature °C (measured at)	25	-100	-100	-100	425	25
Crystal size (mm)	$0.15\times0.10\times0.08$	0.17  imes 0.11  imes 0.08	0.17  imes 0.11  imes 0.08	0.17  imes 0.11  imes 0.08	$0.17 \times 0.11 \times 0.08$	$0.17 \times 0.11 \times 0.08$
Number of frames	2029	1492	1499	1492	1412	1493
Space group	P21	P21	P21	P21	P212121	P21
Cell dimension (Å) a	7.2976(2)	7.2840(2)	7.2799(2)	7.2226(2)	11.7294(3)	7.2989(2)
Cell dimension (Å) b	17.3987(5)	17.1073(4)	17.0244(4)	16.3708(5)	16.2598(4)	17.3509(4)
Cell dimension (Å) c	7.4310(2)	7.4639(2)	7.4707(2)	14.2624(4)	8.1950(2)	7.4288(2)
Cell volume (Å <sup>3</sup> )	908.83(4)	890.95(4)	885.26(4)	1651.76(8)	1562.93(7)	905.46(4)
β (°)	105.5810(10)	106.6770(10)	107.0370(10)	101.630(2)	90.00	105.7550(10)
Z	2	2	2	4	4	2
Reflections collected	13847	13 407	13114	14054	21 409	8610
Max. 20	63.93	64.64	65.19	46.89	61.15	47.26
Index range	$-10 \le h \le 10$	$-10 \le h \le 10$	–11 ≤ <i>h</i> ≤ 10	$-8 \le h \le 8$	–15 ≤ <i>h</i> ≤ 16	$-7 \le h \le 8$
	$-24 \le k \le 25$	–25 ≤ <i>k</i> ≤ 25	$-25 \le k \le 24$	–18 ≤ <i>k</i> ≤ 18	–23 ≤ <i>k</i> ≤ 21	–19 ≤ <i>k</i> ≤ 19
	–11 ≤ / ≤ 11	–11 ≤ / ≤ 9	-11 ≤ <i>l</i> ≤ 10	−15 ≤ <i>l</i> ≤ 15	−11 ≤ <i>l</i> ≤ 11	$-8 \le l \le 8$
Unique reflections	5668	6050	5909	4819	4773	2667
Reflections > $2\sigma(l)$	5360	5517	5487	4634	3846	2561
R <sub>int</sub>	0.0353	0.0397	0.0339	0.0573	0.0697	0.0290
R <sub>σ</sub>	0.0464	0.0597	0.0497	0.0640	0.0549	0.0319
Number of least-squares parameters	271	273	263	483	237	271
GooF	1.358	1.129	1.121	1.207	1.045	1.111
$R1, I > 2\sigma(I)$	0.0377	0.0422	0.0359	0.0902	0.0377	0.0337
R1 , all data	0.0403	0.0475	0.0397	0.0926	0.054	0.0356
wR2 (on F <sup>2</sup> )	0.0996	0.1149	0.0965	0.2208	0.0917	0.0877
$\Delta \rho_{min} (-e/Å^3)$	–0.46 (0.51 Å	–0.48 (0.57 Å	–0.62 (0.60 Å	–0.93 (0.75 Å	–0.34 (1.54 Å	–0.39 (0.60 Å
	from W6)	from Si3)	from Si3)	from O9)	from O3)	from W4)
Δρ <sub>max</sub> (e/ų)	1.14 (0.78 Å	1.94 (2.10 Å	0.61 (0.93 Å	1.15 (0.65 Å	0.41 (0.95 Å	0.63 (1.03 Å
	from Ca1)	from W4)	from O9)	from O7B)	from Ca1B)	from W3)

Notes: Operating conditions for all samples were MoKα (0.71073 Å) X-ray radiation with a generator power of 50 kV and 40 mA. Sample to detector distance was 4.95 cm.

framework O atoms plus four H<sub>2</sub>O molecules; Fig. 2). The second dehydration step beginning at 175 °C is associated with a relative volume reduction of ca. 7%. At the same time, the c axis doubles and the orientation of the unit-cell changes. The most obvious modification to the new cell is the change of the  $\beta$  angle to a value of ca. 101.5°, whereas  $\beta$  was 107° at 150 °C immediately before the doubling of the c axis. This new doublec phase is highly twinned. In addition, there occur either two different structural varieties simultaneously or domains of the first variety are randomly intergrown with domains of the second one. Thus, in the latter case the new phase is highly disordered. Varieties 1 and 2 occur in a 1:1 ratio and have different tetrahedral framework topologies. Variety 1 will be called "no flip" because the connectivity of the tetrahedra is the same as the one of the room-temperature phase (Fig. 3). Variety 2 is named "flipped" because the bonds between two tetrahedra (Al2 and Si1) break and the tetrahedra flip into the channels (Fig. 4). These "flipped" tetrahedra have one terminated apex, which bonds to Ca. Corresponding structural data are presented in Tables 8 and 91.

At 300 °C, goosecreekite became orthorhombic with space group  $P2_12_12_1$ . The acentric crystals were untwinned. The structure recovers to the same tetrahedral topology as found under ambient conditions (Fig. 5). The flipped domains disappear. The orthorhombic modification is strongly contracted reducing the relative volume by another 4.7% relative to the  $P2_1$  structure at 225 °C. One low occupied H<sub>2</sub>O site (W2) remains stable up to 375 °C, causing some Ca to be six coordinated by one bond to H<sub>2</sub>O and five bonds to framework O. With increasing temperature the unit-cell volume decreases between 300 and 425 °C. This is associated with loss of relict H<sub>2</sub>O coordinated to Ca. In the orthorhombic modification at the highest temperature, Ca is coordinated to five framework O. Atomic coordinates and displacement parameters of the P212121 modification are summarized in Tables 10 and 111. Calcium oxygen distances, including framework oxygen and H2O molecules, for all structure refinements are listed in Table 121. CIF data is also on deposit1.

Goosecreekite will recover from the structural changes due to dehydration. A single crystal [GOOS2b, original cell parameters a = 7.2990(3), b = 17.4141(8), c = 7.4427(3) Å,  $\beta = 105.578(2)^\circ$ , V = 911.26(7) Å<sup>3</sup>] heated up to 200 °C and left at ambient conditions for one month (IG\_HT\_Month\_25 in Table 1) rehydrated and resumed the original cell parameters when remeasured [a = 7.2910(1), b = 17.3675(3), c = 7.4380(1) Å,  $\beta = 105.685(1)^\circ$ , V = 906.78(2) Å<sup>3</sup>]. All five H<sub>2</sub>O molecules were regained, restoring the Ca to its original sevenfold coordination and the structure rearranged to  $P2_1$  space group with the original setting.

#### Powder XRD

Initial cell dimensions, shown in Table 13, were recorded at 25 °C (Fig. 6). Loss of one  $H_2O$  up to 100 °C appears as a smooth process. Unlike single-crystal goosecreekite under a dry



**FIGURE 2.** Crystal structure of goosecreekite held at 150 °C, measured at -100 °C. Calcium (large black spheres) is sixfold coordinated and has one H<sub>2</sub>O (small black spheres) less than goosecreekite in Figure 1.



**FIGURE 3.** Variety I ("no flip") of goosecreekite held at 200 °C and measured at -100 °C projected along **a**. Shading as in Figures 1 and 2, with the addition of the patterned tetrahedra in the "no-flip" position that differ in varieties I and II (striped tetrahedra). H<sub>2</sub>O molecules and Ca1 are labeled, Ca1b is unlabeled.



**FIGURE 4.** Variety II ("flip") of goosecreekite held at 200 °C and measured at -100 °C projected along **a**. Shading and labeling as in Figure 3, with arrows indicating the "flip" position.

<sup>&</sup>lt;sup>1</sup> Deposit item AM-11-032, Tables 2–12 and CIF. Deposit items are available two ways: For a paper copy contact the Business Office of the Mineralogical Society of America (see inside front cover of recent issue) for price information. For an electronic copy visit the MSA web site at http://www.minsocam.org, go to the *American Mineralogist* Contents, find the table of contents for the specific volume/ issue wanted, and then click on the deposit link there.



FIGURE 5. Crystal structure of goosecreekite at 425 °C. Calcium (black spheres) bonds only to framework O.

nitrogen stream, the powdered sample undergoes the first change in cell dimensions at ca. 225 °C when the *c* axis doubles (Table 13; Fig. 6). At 225 °C, there are two phases present: the original (IG\_Heating2a) and the doubled *c* axis (IG\_Heating2b, Table 13). The mixture of the two phases persists until at ca. 300 °C when the orthorhombic structure becomes apparent (IG\_Heating2c; Table 13; Fig. 6). The X-ray powder pattern characteristic of the orthorhombic structure remains resolvable up to 550 °C and the signal persists up to ca. 600 °C. Upon further heating, the pattern becomes increasingly X-ray amorphous until complete

#### TABLE 13. Summary of powder XRD results

destruction at ca. 675 °C. A powdered sample previously heated to 325 °C (orthorhombic  $P2_12_12_1$  space group) and allowed to sit at ambient conditions rehydrated within one month to its original structure.

# TG/DTA

TG indicates a loss of 1.06 wt% H<sub>2</sub>O between 25 and 150 °C associated with a broad endothermic DTA effect. Approximately 8 wt% H<sub>2</sub>O are released between 150 and 310 °C accompanied by a strong, well-defined endothermic DTA signal setting in at about 200 °C. An additional dehydration step occurs between 310 and 600 °C associated with further loss of ca. 3.4 wt% corresponding to approximately 1 H<sub>2</sub>O pfu. This latter dehydration is also accompanied with an endothermic DTA effect starting at ca. 300 °C. The total mass lost during the 25 to 600 °C heating excursion sums up to 12.76 wt% H<sub>2</sub>O (Figs. 7 and 8). For the fastest heating rate (10 °C/min), water loss and associated phase transitions occur at slightly higher temperature; ca. 50 °C higher compared to the 2 °C/min heating rate (Fig. 9).

# DISCUSSION

Goosecreekite undergoes three transitions related to water loss. Our room-temperature structure is in full agreement with the results of Rouse and Peacor (1986) yielding the well-established GOO framework of space group  $P2_1$  with sevenfold-coordinated Ca formed by two bonds to O of the tetrahedral framework and five bonds to extraframework H<sub>2</sub>O.

	IG-Heating2	IG_Heating2a	IG_Heating2b	IG_Heating2c	IG_Heating2_above500
T (measured at)	25	225	225	425	550
Space group	P21	P21	P21	P212121	P212121
Cell dimension (Å) a	7.301(1)	7.337(1)	7.238(1)	11.739(1)	11.754(2)
Cell dimension (Å) b	17.390(1)	17.183(2)	16.525(2)	16.269(1)	16.271(1)
Cell dimension (Å) c	7.443(1)	7.450(1)	14.319(2)	8.200(1)	8.205(1)
β (°)	105.68 (1)	106.90 (9)	101.85 (1)	90.00	90.00
Cell volume (Å <sup>3</sup> )	909.82 (3)	898.66 (16)	1676.2 (3)	1566.04(17)	1569.2 (4)
GooF	0.948	1.064	1.064	0.970	1.172
R <sub>wp</sub>	7.677	8.381	8.381	7.381	9.462



#TG/% ∆ Mass: -1,06 % W3 -6 A Mass' -8 28 % W1 W4 W5 -8 10 A Mass: -3.42 % W2 12 100 200 300 400 500 600 Sample temperature/°C

**FIGURE 6.** Powder XRD patterns for goosecreekite at 25, 150, and 275 °C (after doubling of the *c* axis) and 425 °C (after cell has transformed from monoclinic to orthorhombic).

**FIGURE 7.** Weight curve and calculated mass loss of the goosecreekite with a heating rate of 5 °C/min and a rinsing gas flow of 100 mL/min with a heating path of 25–600–25 °C. Mass and corresponding water molecules lost are indicated in each stage of dehydration.



FIGURE 8. Heat flow signal (DTA) of goosecreekite at a heating rate of 5 °C/min and a gas flow of 100 mL/min with a heating path of 25-600-25 °C.



FIGURE 9. Weight curves and calculated mass loss of the goosecreekite at different heating rates of 2 °C/min (small dash), 5 °C/min (large dash), and 10 °C/min (solid) with a gas flow of 20 mL/min with a heating path of 25–600–25 °C.

# The partly dehydrated P21 phase with 4 H2O pfu

The first dehydration step starts slightly above room temperature (25 °C) and is associated with a decrease of extraframework Ca coordination from seven to six but this first step of H<sub>2</sub>O loss has only little effect on the structure. At ca. 100 °C, the W3 site becomes empty. DTA/TG experiments on powders display only a loss of 1.06 wt% H<sub>2</sub>O between 25 and 150 °C, which is significantly below ca. 3 wt% corresponding to 1 H<sub>2</sub>O pfu. We assume that H<sub>2</sub>O loss already started under ambient conditions during acetone drying and equilibrating the powder under dry He atmosphere. This assumption is in line with the observation that after DTA/TG heat-excursion up to 600 °C only 12.76 wt% H<sub>2</sub>O were expelled, whereas Dunn et al. (1980) reported 15 wt% H<sub>2</sub>O, which corresponds to 5 H<sub>2</sub>O. The room-temperature singlecrystal structure refinement also confirms 5 H<sub>2</sub>O pfu, whereas a data set measured under dry nitrogen atmosphere at -100 °C revealed only 4.15 H<sub>2</sub>O pfu, indicating the weak bonding and easy stripping of the first H<sub>2</sub>O molecule under dry conditions.

The powder diffraction data (collected under ambient humidity) yield a 1.7% decrease in unit-cell volume due to loss of one H<sub>2</sub>O between 25 °C (V = 909.8 Å<sup>3</sup>) and 100 °C (V = 894.7 Å<sup>3</sup>).

# The partly dehydrated $P2_1$ phase with doubled *c* axis and ca. 1.2 H<sub>2</sub>O pfu

The second dehydration step starts at ca. 175 °C (under dry conditions) and is associated with a strongly endothermic reaction caused by loss of ca. 2.8 H<sub>2</sub>O pfu (Fig. 8). Single-crystal X-ray structure refinements of crystals quenched to -100 °C indicate doubling of the c axis and complicated twinning, allowing only poor refinement quality. Under ambient moisture (X-ray powder data) the phase transition is shifted to ca. 200 °C, and the new partly dehydrated phase is strongly contracted as evidenced by a relative volume contraction of 6.9% (Fig. 10). The new phase also crystallizes in P21 space group and has two symmetrically independent eight-membered ring channels running parallel to a occupied by Ca1 and Ca1B. The channels are rather oblate parallel to b, due to extraframework Ca bonding to opposing channel walls. The structure shows two topological varieties occurring in a 1:1 ratio named "no-flip" and "flipped." The no-flip variety has the same structural topology as the natural goosecreekite, whereas the flip-variety has broken T-O-T bonds at O6B and the tetrahedra Si1B and Al2B flip toward the open channels with the unconnected tetrahedral apex bonding to Ca1B. Thus, the framework becomes interrupted and we assume that the non-linked tetrahedral apices of Si1 and Al2 are hydroxylated. Flipping of tetrahedra only occurs in the channel characterized by the suffix "B," whereas the other channel remains topologically intact. Thus, 50% flipped tetrahedra (Si1B and Al2B) indicate that 25% of Ca has a topological environment that differs from the remaining Ca sites.

The reaction enabling broken T-O-T links may be written as  $O^{2-} + H_2O \leftrightarrow 2$  (OH)<sup>-</sup>. Similar examples with interrupted frameworks among natural zeolites are partheite and maricopaite (e.g.,



FIGURE 10. Normalized cell volume vs. temperature based on powder XRD data. In the case of mixed phases (shaded areas), only the volume from the newest phase is used. Approximate stages of water loss are shown by the corresponding labels. Error bars are less than data point size. Data points between 300 and 350 °C are approximate due to an inability to resolve the mixture of phases.

Armbruster and Gunter 2001). The Ca1 site in the goosecreekite structure with doubled c axis is coordinated by four framework O and two additional H<sub>2</sub>O molecules (W1: fully occupied and W4 ca. <sup>1</sup>/<sub>2</sub> occupied). Ca1B is hydrated by W5 and W2. W5 has occupancy of 0.36 and W2 of 0.52 (sample heated at 200 °C and quenched to -100 °C for data collection). However, Ca1B is additionally coordinated by the hydroxylated apices of the flipped tetrahedra. W5 and OCF (the hydroxylated apex of the flipped Al2 tetrahedron) are only 1.2 Å apart. In addition, W2 and W5 are only separated by 2.25 Å excluding simultaneous occupation. Thus, there is strong evidence that the deficit of H2O coordinating Ca1B is balanced by flipping Al2 and Si1 tetrahedra with one unconnected apex toward the channel, enabling sixfold Ca1B coordination by four framework O and two hydroxylated tetrahedral apices. Based on site occupancy refinements, which were carried out with fixed atomic displacement parameters for partly occupied H<sub>2</sub>O sites, goosecreekite at 200 °C has ca. 1.25  $H_2O$ . Thus, 2.75  $H_2O$  were expelled from the 4  $H_2O$  structure to form the new partly dehydrated variety. The value of 2.75 H<sub>2</sub>O pfu is in excellent agreement with TG results indicating a loss of 2.8 H<sub>2</sub>O pfu.

In most examples known to us, e.g., stellerite (Alberti et al. 1978; Arletti et al. 2006), heulandite-Ca (Alberti and Vezzalini 1983; Khobaer et al. 2008), and Cd-exchanged heulandite (Döbelin and Armbruster 2003), a modification of tetrahedral topology upon dehydration, accompanied by breaking of T-O-T links leads to uninterrupted frameworks. This means that "flipped" tetrahedra newly connect to other flipped tetrahedra establishing a new T-O-T link. Thus the partly dehydrated goosecreekite phase is one of the few examples where terminate, hydroxylated tetrahedra are formed. A similar case is exemplified by strongly dehydrated Sr-dominant zeolite brewsterite (Sacerdoti et al. 2000). The reduced quality of the structure refinement of this intermediate goosecreekite phase is due to the random overlap of "flipped" and "no-flip" varities. In case of the "flipped" variety, not only do flipped tetrahedra occur at a new position but the whole surrounding is also influenced by slight positional shifts. These minor secondary changes could not be separated and the remaining structure is represented as an unresolved average of two varieties. We have compared the calculated powder pattern of the partly dehydrated  $P2_1$  structure with doubled c axis (measured after quenching to -100 °C) with the observed powder pattern recorded between 200 and 275 °C. The good agreement of the diffraction patterns suggests that the quenched structure has the same characteristics as the one at high temperature, i.e., the quenching process does not alter the structure.

The reason for doubling the **c** axis upon dehydration is probably related to local strain imposed by severe distortions in T-O-T angles due to the oblate shape of the channel inlets. This strain builds up within the short periodicity along **c** of the original (room-temperature) structure and becomes partially relaxed by the repetition of the structural unit with a slightly different distortion leading to the doubling of the **c** axis. This second unit (Tables 8 and 9) is emphasized by the suffix "B." In addition, the intimate twinning observed in the diffraction pattern is also strain related as there are two possibilities how the original channel cross-section may distort in the variety with doubled **c** axis. An important building block of the goosecreekite framework is a branched, strongly folded unit of four edge-sharing four-rings of TO<sub>4</sub> tetrahedra (Fig. 11). Structural strain in individual fourrings of this unit is translated into bending of the entire building block and vice versa. The walls of the channel cross-section are formed, with exception of the Si6-O10-Si2 component, by fourrings belonging to the edge-sharing unit described above (Fig. 12). Thus any channel distortion influences strain in the fourrings. For electrostatic reasons the softest link in the fourrings is an AlO<sub>4</sub> tetrahedron. If strain exceeds a certain limit an Al-O-Si link will rupture. However, temperature-dependent distortions in T-O-T angles in the various goosecreekite dehydration phases (Table 14) do not provide a convincing argument why specifi-



**FIGURE 11.** Schematic representation of an important building block of the goosecreekite framework: A branched, strongly folded unit of four edge-sharing four-rings of  $TO_4$  tetrahedra. The center of each four-ring edge represents an O site, corners are tetrahedrally coordinated sites. Corresponding T-O-T angles of the various goosecreekite phases are summarized in Table 14.



**FIGURE 12.** An eight-membered ring built by  $TO_4$  tetrahedra forms the cross-section of channels running parallel to **a**. With exception of Si2-O10-Si6 all T-O-T links are part of the edge-sharing four-rings shown in Figure 11.

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TABLE 14. T-O-T angles (°) for goosecreekite and various partly dehydrated varieties

Т-О-Т	RT	150 °C dehvd	200 °C B/A*	425 °C						
T-O-T link	c part of the c	trongly folded u	init of four edge-sh	aring						
four-rings of TO, tetrahedra (Fig. 11)										
Si6-014-Si4	144 8(2)	136 6(2)	128(1) 131 2(7)	122 1(2)						
Si6_016_Si5	156 0(2)	152.0(2)	120(1) 151.2(7)	122.1(2)						
	140.2(2)	132.9(2)	140.0(0) 139.0(9)	142 6(2)						
AI2 012 CI2	149.2(2)	132.1(2)	149.0(0) 130.9(0)	142.0(2)						
AIZ-012-513	142.5(2)	136.0(2)	152(2) 126.2(7)	130.1(2)						
Al2-06-Si1	138.3(2)	143.2(2)	158(2) 138.5(7)	137.2(2)						
Si3-011-Si5	144.4(2)	147.0(2)	134.4(8) 138.2(7)	133.3(2)						
Si5-O5-Si1	138.3(2)	137.1(1)	130.1(8) 134.9(7)	136.3(2)						
Si1-O1-Al1	135.8(2)	137.2(1)	149(2) 146.2(7)	136.7(2)						
Al1-O4-Si4	142.7(2)	141.8(2)	142.5(7) 135.3(8)	148.8(2)						
Si4-013-Al2	138.4(2)	140.4(2)	134.1(8) 155.0(9)	143.9(2)						
Si3-O8-Si2	147.6(2)	145.6(2)	145.3(8) 138.3(7)	137.5(2)						
Si3-O3-Al1	137.6(1)	134.4(1)	125.7(7) 142.6(9)	132.3(2)						
Si2-O9-Si4	138.9(2)	141.4(2)	130.3(7) 144.0(9)	132.4(2)						
Mean	143.0	140.4	139.9 140.7	135.7						

T-O-T links not part of the strongly folded unit of four edge-sharing four-rings of TO, tetrahedra									
Si2-O2-Al1	147.7(2)	143.3(1)	142.0(8) 132.7(7)	131.7(2)					
Si1-07-Si6	143.7(2)	137.1(2)	137(1) 134.1(7)	130.9(2)					

Si6-O10-Si2 152.1(2) 153.1(2) 153.1(9) 160(1) 156.2(2) Note: A\* corresponds to the structural fragment without ruptured T-O-T links (atom coordinates in Tables 8-91 without suffix), B represents the structural fragment with ca. 50% ruptured Al2-O6-Si1 links (atom coordinates in Tables 8-91 with suffix B). T-O-T angles are only given for the original goosecreekite tetrahedral framework and not for the ruptured variety.

cally the Si1B-O6B-Al2B link ruptures. In summary, flipped tetrahedra are an additional way of strain reduction. Doubling the c axis and twinning are long-range effects, whereas flipped tetrahedra seem to occur randomly at certain positions and represent short-range strain compensation.

## The dehydrated orthorhombic P212121 phase

Starting at ca. 300 °C, another 1.2 H<sub>2</sub>O pfu are set free (TG; Fig. 7) associated with a volume reduction of additional 6.5% (powder XRD). The endothermic reaction (DTA; Fig. 8) leads to an orthorhombic modification, space group  $P2_12_12_1$ , of the goosecreekite tetrahedral framework. This is the maximum symmetry of a GOO framework with CaAl<sub>2</sub>Si<sub>6</sub>O<sub>16</sub> composition and completely ordered arrangement of Si and Al tetrahedra. For a random Si,Al distribution, the symmetry could be as high as C222<sub>1</sub>. The orthorhombic structure has a different setting compared to the previous partly dehydrated varieties. Monoclinic a becomes [101] in the orthorhombic cell. The topology of the framework is the same as the one of the natural goosecreekite structure (Fig. 5). Thus, the hydroxylated flipped tetrahedra of the intermediate monoclinic structure flipped back to their original setting: 2 (OH)<sup>-</sup>  $\rightarrow$  O<sup>2-</sup> + H<sub>2</sub>O, which provides 0.25 H<sub>2</sub>O pfu (based on 1 Ca). In addition, the orthorhombic structure is essentially anhydrous. Very minor H<sub>2</sub>O (up to ca. 0.2 pfu) cannot be excluded as data were collected at high temperature and dynamic behavior of H2O prevents proper localization and quantification. Nevertheless, there is good agreement between H<sub>2</sub>O loss measured by TG and H<sub>2</sub>O determined by site occupancy refinement in the corresponding structures. Calcium in the orthorhombic structure is strongly disordered with one major site of 80% occupancy with positions of minor occupancy very close by (within 1.5 Å). Probably due to dynamic behavior, only ca. 95% of Ca could be located. All located Ca sites are five coordinated by framework O. The major Ca position nestles in a pocket close to the channel wall to obtain maximum O coordination.

Another consequence of orthorhombic symmetry is a different denotation for Al1 and Al2. Corresponding labels already existed for the Al sites in the structure of fully hydrated natural goosecreekite and its partly dehydrated monoclinic varieties. In the orthorhombic phase Al1(ortho) and Al2(ortho) represent symmetrically equivalent mixtures of Al1(mono) and Al2(mono) of the monoclinic phases (Fig. 5). In particular, in projections along [101] of the orthorhombic phase, which correspond to projections along a of the monoclinic phase, All and Al2 tetrahedra alternate along the projection direction. In the monoclinic phases these tetrahedra are either of the Al1 or Al2 type.

# The effect of dehydration

The overall volume decrease of goosecreekite between 25 and 425 °C amounts to 14%. The average T-O-T bond angles decrease with increasing temperature and dehydration; 143.0° (natural goosecreekite measured at -100 °C), 140.4° (dehydrated at 150 °C, measured at -100 °C), 140.7° (dehydrated at 200°C and measured at -100 °C, no-flip variety), 139.9° (dehydrated at 200 °C and measured at -100 °C, flip variety) and 135.7° (dehydrated and measured at 425 °C). As dehydration progresses, Ca loses coordinating H<sub>2</sub>O and increases the number of bonds with framework O. The loss of H<sub>2</sub>O in the channels as bonding partners for Ca causes strain on the framework and initiates the structural transitions, as well as partial breaking of T-O-T bonds in the framework and twinning.

Powder XRD measurements are consistent with both the TG/ DTA data and single-crystal XRD data albeit transitions occur at slightly higher temperatures because no dry cover gas has been used for powder XRD. In addition, samples were held at constant temperature for only 30 min before data collection began. This did not allow for the samples to equilibrate, which resulted in ranges in temperature where two phases were present: between 300 and 325 °C and between 225 and 250 °C. The defined stages of water loss are clearly visible by volume discontinuities when temperature vs. volume is plotted (Fig. 10). The TG data curve in Figure 9 demonstrates the heating rate dependence. Faster heating rates shift the weight loss curve to higher temperatures; increasing the rate from 2 to 10 °C/min shifts the curve up to 30 °C higher.

Stepwise dehydration of goosecreekite has shown that while the structure of the framework may be altered with increasing water loss, it is recoverable when exposed to atmospheric conditions that allow the structure to rehydrate. This has been verified by a single crystal previously partly dehydrated at 200 °C (P21 phase with double c axis) and a powder dehydrated at 325 °C (P2<sub>1</sub>2<sub>1</sub>2<sub>1</sub> phase). Above 600 °C, goosecreekite transforms into an X-ray amorphous product.

Cruciani et al. (2003) summarized that the main trigger for structural collapse in Ca zeolites is when the coordination of Ca falls below six. In goosecreekite, Ca remains six coordinated throughout the first structural transition leading to a strongly contracted structure and becomes five coordinated in the completely dehydrated orthorhombic phase. Rather, it is the bonding of the Ca to the framework O that causes stress to be applied to the framework topology and eventual breakage. The initial structural change in the "flip" and "no-flip" varieties at 175 °C is likely due to the need for additional bonding partners for Ca. With increased temperature and H<sub>2</sub>O loss, these flipped tetrahedra become also unstable due to their hydroxylated character [2 (OH)<sup>-</sup>  $\rightarrow$  O<sup>2-</sup> + H<sub>2</sub>O↑] and the topology is reverted to its original form in the anhydrous orthorhombic phase.

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