

Terranovaite from Antarctica: A new 'pentasil' zeolite

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ABSTRACT

A new high-silica zeolite, terranovaite, was recently found in cavities of Ferrar dolerites at Mt. Adamson (Northern Victoria Land, Antarctica). The mineral $[(\text{Na}_{4.2}\text{K}_{0.2}\text{Mg}_{0.2}\text{Ca}_{3.7})_{\Sigma 8.3}(\text{Al}_{12.3}\text{Si}_{67.7})_{\Sigma 80.0}\text{O}_{160} \cdot > 29 \text{H}_2\text{O}]$ occurs as globular masses that flake off in transparent lamellae; it has a vitreous luster, white streak, {010} perfect cleavage, and {001} distinct parting. The observed density is $2.13 \pm 0.02 \text{ g/cm}^3$. Optically, it is biaxial positive, with $2V = 65^\circ$, $\alpha = 1.476$, $\beta = 1.478$, $\gamma = 1.483$ (all ± 0.002). The orientation is $X = c$, $Y = a$, and $Z = b$. Terranovaite is orthorhombic with $a = 9.747(1)$, $b = 23.880(2)$, $c = 20.068(2) \text{ \AA}$ and topological symmetry $Cmcm$. The strongest powder X-ray diffraction lines are (d (Å), I , hkl): 11.94,40,020; 10.16,65,021,002; 9.04,33,110; 3.79,100,025,240; 3.61,40,153. Terranovaite topology, hitherto unknown in either natural or synthetic zeolites, is characterized by the presence of pentasil chains and of a two-dimensional ten-membered ring channel system. The mineral was named terranovaite after the Italian Antarctic Station at Terranova Bay, Antarctica.

INTRODUCTION

Jurassic Ferrar dolerites of Mt. Adamson, Northern Victoria Land, Antarctica, have become a very rich source of zeolitic species. Besides the finding of rare zeolites, such as tschernichite and boggsite (Galli et al. 1995), two new phases have been discovered; the first, gottardiite, the natural counterpart of the synthetic zeolite NU-87, was described by Galli et al. (1996), and Alberti et al. (1996) have determined its crystal structure. Here we describe the second, terranovaite, a new five-membered ring (pentasil) zeolite with a topology hitherto unknown in either natural or synthetic materials. The mineral has been named terranovaite for the name of the Italian Antarctic Station at Terranova Bay, where the Italian geologists collected the zeolite-bearing rocks. The new mineral and the name have received the approval of the I.M.A. Commission on New Minerals and Mineral Names. Holotype material was deposited in the Museo di Storia Naturale e del Territorio, University of Pisa, Italy (catalog no. 15520). The IZA Structure Commission has approved the new topology with IUPAC name TER.

The complete characterization of terranovaite was made very difficult by the extreme paucity of the available rock samples and by the rarity of the mineral.

OCCURRENCE

Mt. Adamson, Northern Victoria Land, Antarctica, consists of a crystalline basement (Paleozoic granites) overlaid by a 35 m thick layer of sandstone (Beacon sediments), capped by about 450 m of basaltic rocks (Ferrar

dolerites). Lenses of sandstone varying in size and thickness are repeatedly interbedded in the basaltic rock. During field work carried out in the austral summer 1990-91, as part of the Italian Antarctic Research Program (PNRA), some Ferrar dolerite samples were collected along the Mt. Adamson ridge in a small area not covered by snow.

X-ray fluorescence analysis (Galli et al. 1996) places this volcanic rock in the field of the basaltic andesites of the T.A.S. diagram (Le Bas et al. 1986). The texture varies from hyalophitic to medium-grained ophitic. The phenocrysts are Ca-rich plagioclase, pyroxene (both often zoned and twinned), and rare olivine crystals. The groundmass consists of microcrysts of Ca-rich plagioclase, clinopyroxene, relict olivine, interstitial glass, and opaque minerals (iron titanium oxides) as microlites.

The rock samples are characterized by the presence of many vesicles and cavities, whose abundance and size are variable in the samples collected. The walls of the cavities are always covered by a thin layer of disordered Fe-rich smectite, varying in color from pale yellow to dark orange. The Fe-rich smectite crystallization preceded that of zeolites and the other neogenic minerals.

The zeolites identified are, in order of abundance, mordenite, heulandite, erionite, phillipsite, stilbite, levyne, epistilbite, tschernichite, boggsite, gottardiite, ferrierite, and cowlesite (Vezzalini et al. 1994; Galli et al. 1995, 1996). The presence of so many five-membered ring zeolites in this area is noteworthy. The other neogenic minerals present in the cavities are quartz, cristobalite, apophyllite, gypsum, and calcite.

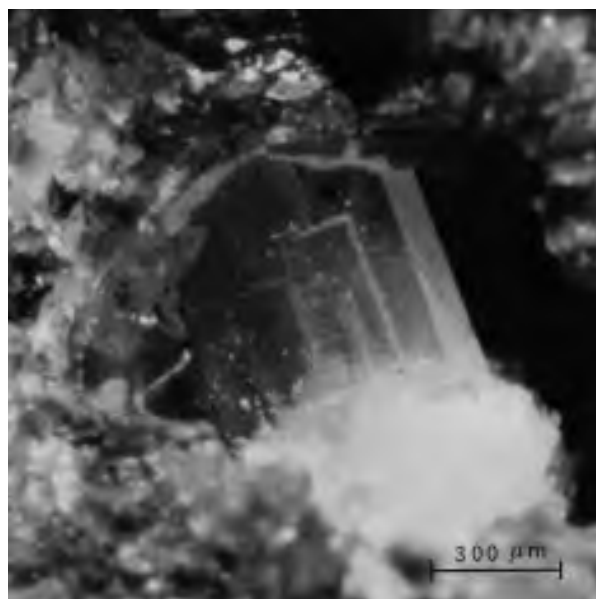


FIGURE 1. Terranovaite from Mt. Adamson (photo by V. Casodi).

Terranovaite is very rare and was found in only one of the Ferrar dolerite samples collected. The specimen is from the SW crest, just under the summit of Mt. Adamson (Lat. 73°56' S, Long. 162° 56' E).

APPEARANCE AND PHYSICAL PROPERTIES

Terranovaite has been found in only three small cavities, up to 3 mm across. In two of these the mineral occurs in transparent globular masses, closely associated with heulandite, from which it is barely distinguishable. The two zeolites completely fill the cavities, and their habit is molded by the rough layer of yellowish smectite below. The only sample of terranovaite with crystalline habit occurs in the third cavity (Fig. 1). In this case it rests on a globular aggregate of small prismatic crystals, from transparent to milky, of an unknown zeolitic species. A drusy group of tschernichite crystals is present in the same geode; these crystals are similar to those referred to as "small" by Boggs et al. (1993) and Galli et al. (1995).

Terranovaite appears as a tabular, transparent, bluish crystal, measuring $0.7 \times 0.6 \times 0.2$ mm, with dominant {010} and less developed {001} pinacoids and terminated by a {110} prism. Some smaller crystals have grown on the main pinacoid.

The streak is white. No fluorescent effects were observed under either long- or short-wavelength ultraviolet radiation. Owing to the small size of the crystals it was impossible to determine their hardness. Terranovaite is brittle, with irregular fracture, and exhibits perfect {010} cleavage and distinct {001} parting. The measured density is 2.13 ± 0.02 g/cm³, determined by sinking in heavy liquid (sodium polytungstate). Calculations using the

TABLE 1. Chemical analysis and unit-cell content (on the basis of 160 O atoms) of terranovaite

Oxide	Wt%*	Atoms per unit cell	
SiO ₂	73.02 ± 1.45	Si	67.73
Al ₂ O ₃	11.25 ± 0.92	Al	12.30
Fe ₂ O ₃	tr.	Fe ³⁺	—
MgO	0.14 ± 0.15	Mg	0.19
CaO	3.72 ± 0.39	Ca	3.70
SrO	tr.	Sr	—
BaO	tr.	Ba	—
Na ₂ O	2.33 ± 0.59	Na	4.19
K ₂ O	0.20 ± 0.06	K	0.24
		O	160
H ₂ O**	9.34	H ₂ O	28.90
R†	0.85		
M/D‡	1.14		
E%	0.8§		

* Electron microprobe analysis: mean of 10 point-analyses and standard deviation. tr. = less than the detection limit at 99% of confidence (Donovan, 1995).

** H₂O content calculated by difference to 100.

† R = Si/(Si + Al).

‡ M = Na + K; D = Mg + Ca.

§ Passaglia (1970).

TABLE 2. X-ray powder diffraction data for terranovaite

<i>l</i>	<i>d</i> _{meas}	<i>d</i> _{calc}	<i>hkl</i>	<i>l</i>	<i>d</i> _{meas}	<i>d</i> _{calc}	<i>hkl</i>	<i>l</i>	<i>d</i> _{meas}
40	11.94	11.94	020			2.901	313	6	1.957
65	10.16	{10.26 10.03	021 002	13	2.881	{2.881 2.861	332 082	5 5	{1.938 1.878
33	9.04	9.02	110			2.743	333	5	1.862
29	8.23	8.23	111	12	2.733	{2.732 2.726	117 083	6 5	{1.837 1.810
29	7.69	7.68	022			2.627	264	5	1.771
28	6.71	6.71	112	12	2.615	{2.600 2.565	137 084	6 5	{1.733 1.715
28	6.16	6.17	130			2.564	066	4	1.696
28	5.89	{5.97 5.89 5.84	040 131 023	12	2.564	{2.561 2.560	190 315	5 5	{1.644 1.636
23	5.36	5.37	113			2.504	008	5	1.636
28	5.12	5.13	042	14	2.504	{2.504 2.493	246 353	4 3	{1.605 1.574
24	4.86	4.87	200			2.455	028	4	1.550
22	4.39	{4.38 4.38	114 202	11	2.450	{2.445 2.388	265 0.10.0	4 7	{1.505 1.482
27	4.18	4.19	151			2.388	420	5	1.470
24	4.13	4.12	222			2.382	157	4	1.457
21	3.97	3.98	060	9	2.382	{2.388 2.379	283 283	3 3	{1.422 1.422
100	3.79	{3.80 3.78	025 240			2.314	048	3	1.413
40	3.61	3.61	153	8	2.314	2.313	048	3	1.413
24	3.53	3.53	242	8	2.297	2.291	372	2	1.391
22	3.42	3.42	063	7	2.286	2.283	247	2	1.386
22	3.33	{3.34 3.33	006 045	8	2.207	{2.219 2.201	373 242	4 2	{1.359 1.347
17	3.28	3.26	243	7	2.141	{2.141 2.138	317 443	2 2	{1.335 1.302
16	3.24	{3.22 3.22 3.22	026 170 310	10	2.048	{2.052 2.044 2.042	425 391 2.10.3	3 3 3	{1.281 1.266 1.247
24	3.10	{3.12 3.08	064 260	10	2.017	{2.020 2.013	1.11.3 392	2 2	{1.225 1.201
27	3.03	{3.02 3.01	244 330	9	2.002	{2.007 1.999	0.0.10 229	3 2	{1.184 1.172
14	2.964	{2.975 2.953	331 081						

Notes: Gandolfi camera (114.6 mm diameter, Ni-filtered CuK α radiation); angular and densitometer measurements by AS/880 microphotometer (Officina Elettrotecnica di Tenno, Italy); units of measure for *d* are Å; indexing with unit-cell parameters from single-crystal data.

TABLE 3. Atomic coordinates, occupancy, and displacement factors for terranovaite

Atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	Occ.	B^*_{eq} (Å ²)
T1	0	0.4524(1)	0.3281(1)	1.0	1.01
T2	0	0.5440(1)	0.4396(1)	1.0	1.18
T3	0.7919(1)	0.3604(1)	0.3728(1)	1.0	1.28
T4	0.7917(1)	0.6392(1)	0.4694(1)	1.0	1.13
T5	0	0.1806(1)	0.4414(1)	1.0	1.07
T6	0	0.7321(1)	0.4365(1)	1.0	1.01
T7	0	0.2697(1)	0.3272(1)	1.0	1.15
T8	0	0.8252(1)	0.3289(1)	1.0	1.02
O1	0	0.4692(4)	¼	1.0	3.41
O2	0	0.5113(3)	0.3679(3)	1.0	3.97
O3	0.1367(5)	0.4160(2)	0.3453(2)	1.0	3.74
O4	0	½	½	1.0	5.66
O5	0.8630(4)	0.5836(2)	0.4415(3)	1.0	3.97
O6	0.1958(5)	0.3583(2)	0.4512(2)	1.0	5.04
O7	0.6325(4)	0.3623(2)	0.3488(2)	1.0	3.16
O8	0.8661(4)	0.3057(2)	0.3415(2)	1.0	3.47
O9	0.3663(3)	0.6374(1)	0.4453(2)	1.0	2.34
O10	0.8655(4)	0.6932(2)	0.4377(2)	1.0	3.03
O11	0	0.2124(2)	0.3685(2)	1.0	2.93
O12	0	0.7751(2)	0.4970(3)	1.0	3.09
O13	0	0.7648(2)	0.3656(3)	1.0	2.39
O14	0	0.2515(3)	¼	1.0	3.28
O15	0	0.8123(4)	¼	1.0	4.01
X1	0	0.0458(3)	0.4442(4)	0.47(1)	0.7(1)
X2	0	0.0403(4)	¼	0.72(1)	1.6(2)
X3	0.3578(12)	0.4603(5)	¼	0.98(2)	9.2(3)
X4	0.1457(12)	0.0399(5)	0.3495(5)	0.74(1)	9.5
X5	0	0.6982(12)	¼	0.56(2)	9.5
X6	0	0.9509(9)	0.4405(10)	0.56(2)	9.5
X7	0.9089(21)	0.1288(9)	¼	0.56(2)	9.5
X8	0.3519(22)	0.4804(8)	0.4598(8)	0.37(1)	8.2(5)
X9	0	0.9651(12)	0.3547(13)	0.26(1)	4.1(6)
X10	0	0.5972(14)	¼	0.56(2)	11.8(9)
X11	0.3056(24)	0.1983(10)	¼	0.48(2)	9.5
X12	0.1901(40)	0.0815(16)	0.1907(18)	0.20(1)	8.7(9)

* $B^*_{eq} = \frac{2}{3}\pi^2(U_{11} + U_{22} + U_{33})$; B^*_{iso} for all extraframework sites.

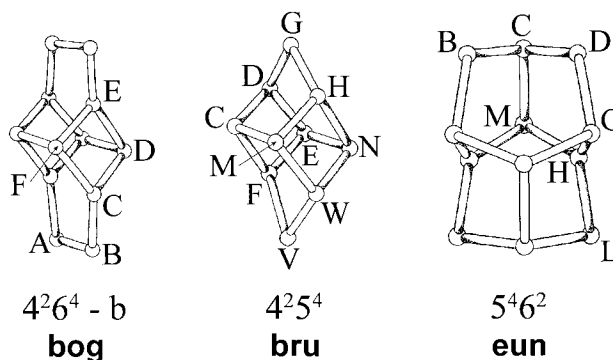
Gladstone-Dale relationship and the constants reported by Mandarino (1981) indicate a compatibility index (1-Kp/Kc) = -0.022 (excellent) obtained for measured density and chemical data reported in Table 1. On the universal stage, in parallel sodium light ($\lambda = 589$ nm), terranovaite is biaxial positive, with $2V_{meas} = 65(5)^\circ$ and $2V_{calc} = 65^\circ$. The refractive indices are $\alpha = 1.476(2)$, $\beta = 1.478(2)$, $\gamma = 1.483(3)$ with optical orientation $X = c$, $Y = a$, and $Z = b$.

CHEMICAL COMPOSITION

The chemical analyses were performed with an ARL-SEM-Q electron microprobe operating in wavelength-dispersive mode at 15 kV, with a 10 nA sample current. The standards used were natural albite (Si, Al, Na), microcline

TABLE 4. Terranovaite framework interatomic distances (Å)

T1-O1	1.617(3)	T2-O2	1.636(6)	T3-O3	1.597(4)	T4-O5	1.600(4)
T1-O2	1.618(6)	T2-O4	1.605(2)	T3-O6	1.579(4)	T4-O6	1.599(4)
T1-O3 × 2	1.628(4)	T2-O5 × 2	1.636(4)	T3-O7	1.628(4)	T4-O9	1.615(3)
mean	1.623	mean	1.628	T3-O8	1.620(4)	T4-O10	1.607(4)
T5-O9 × 2	1.664(3)	T6-O10 × 2	1.608(4)	mean	1.606	mean	1.605
T5-O11	1.648(5)	T6-O12	1.588(6)	T7-O8 × 2	1.588(4)	T8-O7 × 2	1.616(4)
T5-O12	1.627(6)	T6-O13	1.624(5)	T7-O11	1.600(5)	T8-O13	1.618(5)
mean	1.651	mean	1.607	T7-O14	1.610(3)	T8-O15	1.613(2)
				mean	1.597	mean	1.616

**FIGURE 2.** Polyhedral subunits present in terranovaite.

(K), paracelsian (Ba), synthetic An₇₀ glass (Ca), Sr-containing anorthite (Sr), P140 olivine (Fe), and DI85-JD15 (Mg). Data acquisition and processing utilized the PROBE program (Donovan 1995). To reduce ion mobility and H₂O loss, which commonly occur in zeolites, a beam diameter of 40 μ m was used. A total of ten point analyses were performed on three crystals and averaged. The analytical results are summarized in Table 1, together with the chemical formula based on 160 O atoms, the number of framework O atoms in the unit cell according to the structure analysis. The very low balance error (Passaglia 1970) E = + 0.8%, supports the reliability of the chemical analysis. The variability in the chemical data, although obtained on few point analyses, suggests some compositional variability for different crystals of terranovaite. The Si/Al ratio of (5.5) is worth noting; it is among the highest found of the natural pentasil zeolites. The monovalent extra-framework cations (4.43 a.p.f.u.) prevail slightly over the divalent cations (3.89 a.p.f.u.).

The H₂O content could not be directly determined because of the very small amount of material available; the value reported in Table 1 (9.34%) is therefore determined by difference to 100. Assuming this H₂O content, we obtained a calculated density of 1.98 g/cm³, a rather low value when compared with the measured density (2.13 g/cm³). To obtain a calculated density of 2.13 g/cm³ it is necessary to assume an H₂O content of about 15.50%, which is certainly a more typical value for a zeolite, such as terranovaite, with a high Si/Al ratio and wide channels (as discussed below). The empirical formula of terranovaite is thus (Na_{4.2}K_{0.2}Mg_{0.2}Ca_{3.7})_{Σ8.3}(Al_{12.3}Si_{67.7})_{Σ80.0}O₁₆₀ · >

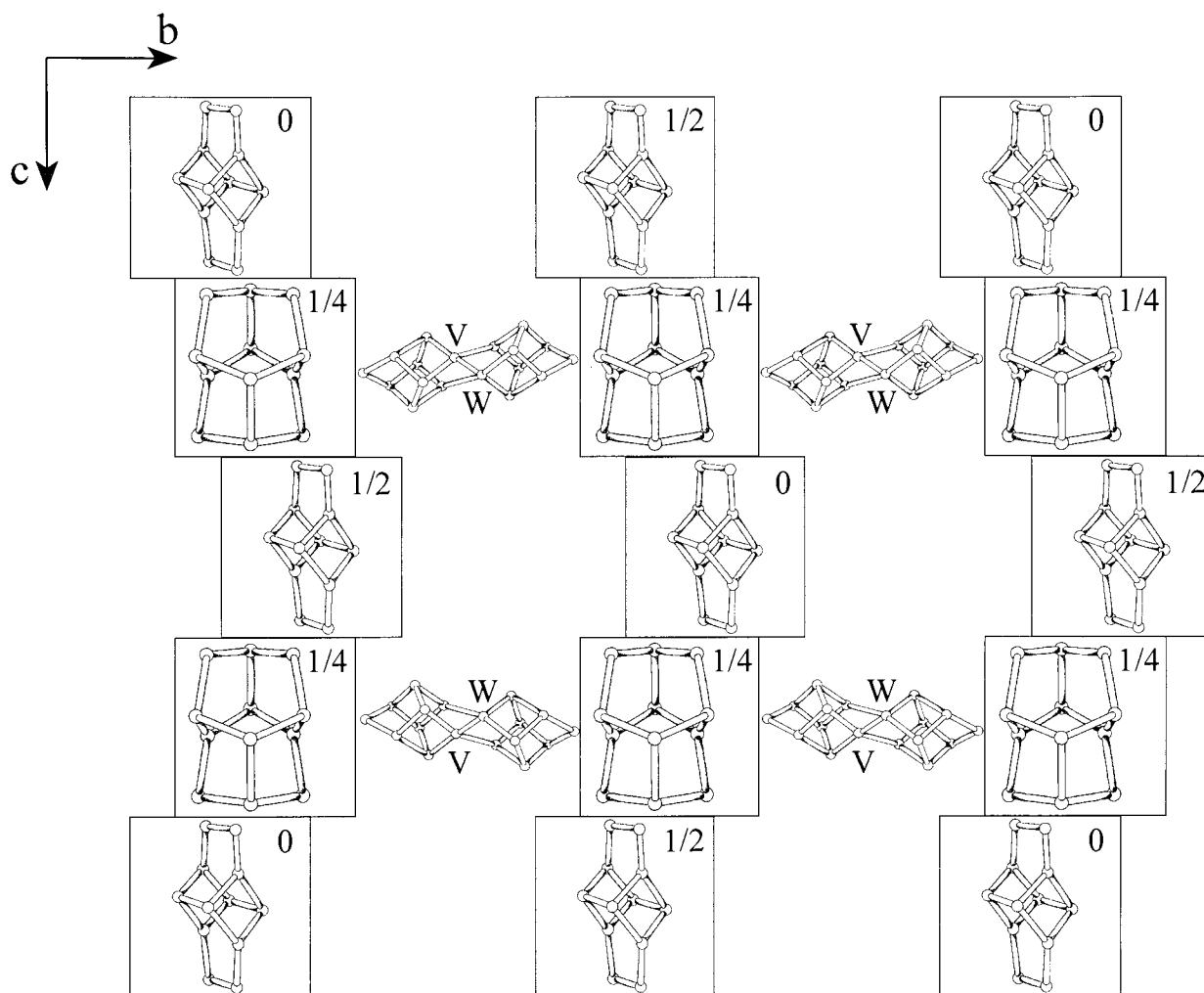


FIGURE 3. Schematic projection along [100] of the terranovaite framework. Each square represents a chain parallel to [100]; the fractions in the squares indicate the height, along a , of the center of gravity of the bog and eun units. V and W of the bru units (corresponding to T2 of Table 1) are the tetrahedra that bridge the sheets.

29 H₂O. The simplified formula is NaCaAl₃Si₁₇O₄₀ · > 7 H₂O, $Z = 4$.

X-RAY CRYSTALLOGRAPHY

Powder data

The X-ray powder diffraction pattern of terranovaite, reported in Table 2, was obtained using a Gandolfi camera (diameter 114.6 mm) with CuK α radiation and Pb(NO₃)₂ as an internal standard. The angular and densitometer measurements of the Gandolfi pattern were obtained with the AS/880 System (Officina Elettrotecnica di Tenno). Indexing was obtained with unit-cell parameters from a single-crystal data.

Structure analysis

A platy single crystal, measuring 0.38 mm along a , 0.09 mm along b , and 0.13 mm along c , was used in the structural analysis. Rotating [100], Weissenberg ($hk0$) and pre-

cession ($hk0$) and ($h0l$) photographs indicated an orthorhombic symmetry with $a = 9.73$, $b = 23.85$, $c = 20.04$ Å. The crystal was then mounted on a Siemens four-circle diffractometer using a rotating anode X-ray generator (MoK α radiation). Refinement of unit-cell parameters using 37 diffractions confirmed the orthogonal symmetry with $a = 9.747(1)$, $b = 23.880(2)$, $c = 20.068(2)$ Å.

A total of 8533 intensities were collected in the range $2^\circ < \theta < 32^\circ$, (ω scan) and then merged to yield 4376 independent reflections. Of these, 2849 reflections with $I > 5\sigma$, were used in the structure determination and refinement. Systematic extinctions were consistent with space groups $Cmcm$, $C2cm$, $Cmc2_1$.

Direct methods, using SHELX-86 (Sheldrick 1986), gave an initial model that was refined using a combination of three-dimensional electron density synthesis and full-matrix least-squares techniques (SHELX-76, Sheldrick 1976). X-ray intensity data were corrected for Lorentz and polar-

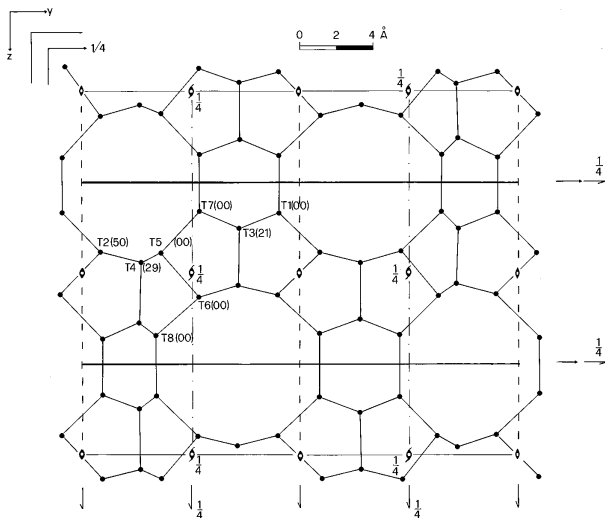


FIGURE 4. Projection of the terranovaite net onto the bc plane.

ization effects. An absorption correction was performed using the DIFABS method proposed by Walker and Stuart (1983). No extinction correction was applied. Atomic scattering factors for neutral atoms were used; a scattering curve for $\text{Si}_{0.85}\text{-Al}_{0.15}$ was used for T atoms and an O curve for all extra-framework sites. At the end of structure refinement in space group $Cmcm$ (framework atoms were refined with anisotropic displacement parameters and extra-framework atoms with isotropic ones), the R and R_w discrepancy factors were 7.1% and 6.8%, respectively.

The topological symmetry of the framework is $Cmcm$. However, the presence of a framework O atom on an inversion center, with unfavorable T-O-T angles of 180° , suggests a lower symmetry (Alberti 1986). The strong anisotropy of the thermal ellipsoids of the O on the inversion center and of the other framework atoms lying on the mirror plane orthogonal to $[100]$ (with the largest axis along the direction $[100]$), led us to perform a refinement in space group $C2cm$. The discrepancy factor R_w reduced to 5.9%. Consequently, according to the Hamilton test (Hamilton 1965), and on the basis of the R_w fac-

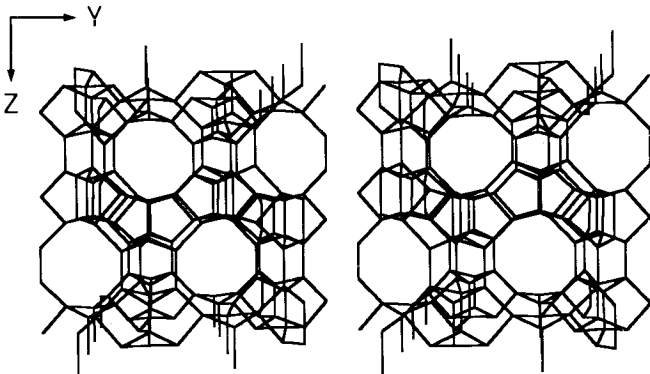


FIGURE 5. Stereoscopic view of terranovaite along $[100]$.

tors, the space group $C2cm$ is more probable (99.9%) than $Cmcm$. However, this test must be accepted with caution when there is a situation of "inverse overlap" between all the pairs of atoms in the non-centrosymmetric space group (Parthasarathy et al. 1969; Alberti 1972), as in the case of terranovaite. Moreover, a strongly pseudocentric symmetry is evident in the $C2cm$ refinement. The positional and displacement parameters reported in Table 3 are from the structure refinement in the centric $Cmcm$ space group, even though the real symmetry is probably $C2cm$. Table 4 reports the framework interatomic distances. Bond distances, angles, and anisotropic displacement factors are reported in Table 5.¹ The list of observed and calculated structure factors is reported in Table 6.¹

Different polyhedral building units (Fig. 2) are present in the framework of terranovaite: the 4^26^4 unit (referred to as 4^26^4 -b, bog, after Smith 1989) found in laumontite and boggsite; the 4^25^4 unit (bru), present in boggsite, heulandite group zeolites, and synthetic SSZ-23 and SSZ-33; the 5^46^2 unit (eun) found in boggsite, gottardiite, and synthetic EU-1.

The terranovaite net can be described by two different chains, both developing along $[100]$. The first is constructed of bog units, which share the AB edges (Fig. 2). The second chain is made of eun units, which share the DG, GH, and HL edges. The two chains share the BC and CD edges of the bog and eun units thus forming wavy impermeable sheets parallel to (010) (Fig. 3). The sheets are linked along $[010]$ through pairs of tetrahedra. As a result, couples of bru units, which share the VW edge (Figs. 2 and 3), are formed. Each bru unit shares a four-membered ring (CDEF in Fig. 2) with a bog unit and five-membered rings with two adjacent eun units, (DGHMC) and (DGHNE), respectively. A cluster of one bog sandwiched by two bru and four eun units can be identified in the terranovaite framework. A cluster of the same units is also present in boggsite. However, in terranovaite this cluster has $2mm$ symmetry (with the diad parallel to $[010]$), whereas in boggsite the symmetry of the cluster is $2/m$ (with an inversion center at the center of the bog unit).

A two-dimensional channel system parallel to the (010) plane is present in the terranovaite framework. Straight ten-membered-ring channels run along $[100]$ (Figs. 4 and 5) and $[001]$ (Figs. 6 and 7); the channel dimensions are about $5.5 \times 5.1 \text{ \AA}$ and $7.0 \times 4.3 \text{ \AA}$, respectively. The net of terranovaite projected onto the bc plane (Fig. 4) is equivalent to that of many other pentasil zeolites (ferrierite, boggsite, ZSM-5, ZSM-11, theta 1), whereas the net projected onto the ab plane is equivalent to that of AlPO_4 -41 (Kirchner and Bennett 1994).

The mean T-O distance (Table 4) for seven of the eight

¹ A copy of Tables 5 and 6 may be ordered as Document AM-97-635 from the Business Office, Mineralogical Society of America, 1015 Eighteenth Street NW, Suite 601, Washington, DC 20036, U.S.A. Please remit \$5.00 in advance for the microfiche.

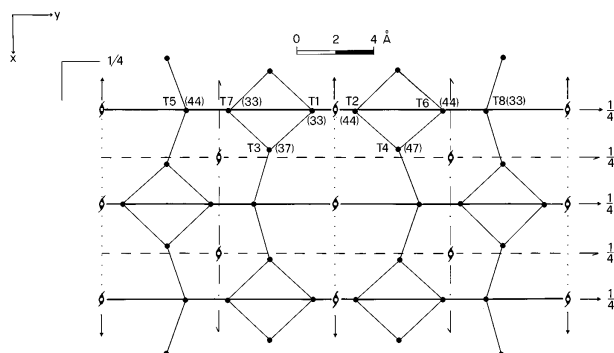


FIGURE 6. Projection of the terranovaite net onto the *ab* plane.

independent tetrahedra varies in the range 1.597–1.628 Å. Only T5 has a notably larger mean T-O distance (1.651 Å), which may suggest a preferential occupancy by Al in this latter site.

Twelve extra-framework sites have been localized; all show weak, broad, and ill-defined peaks at distances from the framework O atoms greater than 2.7 Å [except X1-O9 = 2.55(1) Å], suggesting that only a weak interaction must exist between aluminosilicate framework and extra-framework atoms. As a consequence, any attempt to locate Na, Ca, and H₂O molecules was unsuccessful, as is frequently the case in the structure refinements of zeolites with wide channels and large cages [e.g., faujasite (Bergerhoff et al. 1958), boggsite (Pluth and Smith 1990), and gottardiite (Alberti et al. 1996)]. Overall, structure refinement affords 438 electrons for the extra-framework sites, compared with the 358 electrons afforded by the chemical formula, assuming the H₂O content determined by difference to 100. However, because the H₂O content is probably underestimated, as stated above, the latter value is certainly too low. The number of electrons based on an H₂O content of 15.50% (as deduced from the observed density) is 539, which is a more reasonable value considering that the crystal structure refinement of zeolites characterized by a strong disorder in the extra-framework sites, such as terranovaite, usually gives a total electron number lower than the true one. Therefore, we think that an H₂O content of 15.50%, which corresponds to 51.45 H₂O in the formula, is a more reasonable value for terranovaite.

CONCLUSIONS

Zeolites containing a high proportion of five-membered rings of tetrahedra in the framework are widely used in heterogeneous catalysis; they include synthetic ZSM-5, ZSM-11, beta, theta-1, NU-87, the synthetic counterparts of natural mordenite and ferrierite, and the natural zeolite clinoptilolite. Recently, new natural pentasil zeolites have been found either with a new topology, e.g., boggsite (Pluth and Smith 1990), or with the same topology as that of known synthetic materials, e.g., tschernichite-

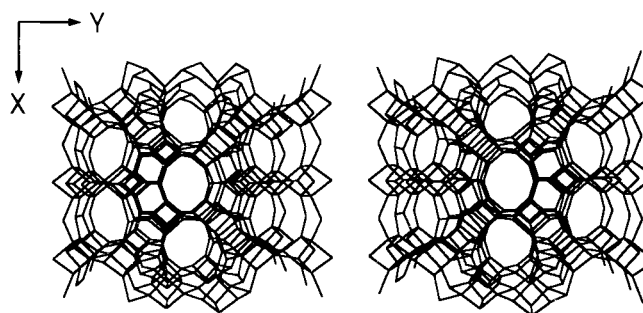


FIGURE 7. Stereoscopic view of terranovaite along [001].

↔beta (Smith et al. 1991) and gottardiite↔NU-87 (Alberti et al. 1996).

It is noteworthy that almost all the pentasil natural zeolites are present at Mt. Adamson; two, boggsite and tschernichite (Galli et al. 1995), are very rare and two, gottardiite (Galli et al. 1996) and terranovaite, have been found for the first time. Accurate structure refinements performed on boggsite (Pluth and Smith 1990), gottardiite (Alberti et al. 1996), and terranovaite (all high-silica zeolites) have revealed a strong disorder in the extra-framework cations and H₂O molecule distribution and very large atomic displacement parameters for the framework atoms. These peculiarities indicate that somewhat special conditions were involved in the crystallization of these zeolites, such as rapid cooling during crystal growth. If these conditions could be identified, a way of synthesizing these phases, which are potentially useful as molecular sieves and catalysts, might be found.

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