

Tschernichite, a new zeolite from Goble, Columbia County, Oregon

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ABSTRACT

The new zeolite tschernichite occurs as 0.1–10 mm, colorless to white, steep tetragonal dipyramids commonly showing the forms {302} and {001} as drusy linings, radiating hemispherical groups, and single and twinned crystals in small vesicles in dense Eocene basalt near Goble, Columbia County, Oregon, where it has formed through the action of local hydrothermal activity. Associated minerals include copper, calcite, smectite, boggsite, okenite, mordenite, quartz (chalcedony), heulandite, apophyllite, levyne, offretite, erionite, chabazite, aragonite, opal, analcime, and thomsonite (in approximate order of crystallization). The mineral is tetragonal, possible space group $P4/mmm$, with $a = 12.880(2)$, and $c = 25.020(5)$ Å. A relationship with zeolite beta suggests that tschernichite may consist of an intergrowth of an enantiomorphic pair in the tetragonal space groups $P4_122$ and $P4_222$ and a triclinic polymorph with space group $P\bar{1}$. The strongest lines of the X-ray powder diffraction pattern are d (Å), I , hkl : 12.52,10,002; 11.63,32,101; 4.22,14,301; 4.03,100,311; 3.569,13,320; 3.156,16,315; 3.062,15,226; 2.730,10,334; 2.114,16,602. The Mohs hardness is $4\frac{1}{2}$, and there are a conchoidal fracture and no observable cleavage. The optical properties are uniaxial (-), $\epsilon = 1.484(1)$, $\omega = 1.483(1)$. Tschernichite shows no to a pale yellow fluorescence under both long- and short-wavelength ultraviolet radiation. Electron microprobe analyses show variation in the Si/Al ratio from about 3/1 to 3.7/1. Representative analyses give empirical formulas ranging from $(\text{Ca}_{0.97}\text{Na}_{0.05}\text{Mg}_{0.08})(\text{Si}_{5.95}\text{Al}_{2.00}\text{Fe}_{0.02})\text{O}_{16}7.96\text{H}_2\text{O}$ for the crystals with low Si contents to $(\text{Ca}_{0.73}\text{Na}_{0.11}\text{K}_{0.02}\text{Mg}_{0.00})(\text{Si}_{6.33}\text{Al}_{1.69}\text{Fe}_{0.02})\text{O}_{16}3.98\text{H}_2\text{O}$ for the highest Si contents.

INTRODUCTION

A few specimens of tschernichite were first found by Rudy W. Tschernich at the Goble location in 1972. At that time, they were thought to be possibly apophyllite with an unusual habit. In 1985 they were shown to R.C.B., and it was realized that they were not apophyllite because of the lack of cleavage. Preliminary X-ray diffraction studies indicated that the material was probably a new zeolite, and work was started on its characterization. At the same time, attempts were made to locate more material at the locality, since only six small specimens were available for characterization. Collecting in 1987–1988 eventually turned up considerably more material, as well as a second new zeolite, boggsite (Howard et al., 1990), which occurs in close association with tschernichite. Tschernichite (pronounced Cher-nich-ite) is named after Rudy W. Tschernich of Snohomish, Washington, in recognition of his original discovery of the material, as well

as his extensive studies of the zeolite occurrences and associations in the Pacific Northwest.

The new mineral tschernichite has been approved by the Commission on New Minerals and Mineral Names, I.M.A., and type specimens have been deposited at the National Museum of Natural History, Smithsonian Institution, Washington, DC.

OCCURRENCE

Tschernichite is found on the top of a small projection of basalt located above a cliff along Goble Creek, on the south side of the Neer Road, approximately 50 m west of the junction with Highway 30, 0.2 km north of Goble, Columbia County, Oregon (latitude $46^{\circ}1'13.1''\text{N}$, longitude $122^{\circ}52'39.6''\text{W}$). This area was mapped by Wilkinson et al. (1946) as the late Eocene Goble Volcanic Series, which consists of porphyritic basalt flows, pyroclastics, and minor amounts of sediments. This area is overlain

by 300 m of Oligocene sediments and Miocene Columbia River basalt. Drilling shows the Goble Volcanics to be the basement rock, extending to over 1520 m below the surface (Wilkinson et al., 1946).

The tschernichite-bearing flow is composed of 0.6–2 m of basal flow breccia, covered by a meter of highly vesicular basalt containing large, elongated, flattened gas cavities, which decrease in size and number toward the fine-grained nearly nonvesicular center of the flow. The top of the flow has been removed by erosion. Tschernichite is found only in a small area, 3 m by 2 m wide and 1 m thick, which represents a transition zone between the fine-grained, dense central portion of the flow and the highly vesicular basal portion of the same flow.

Zeolites are abundant in the vesicular portions of the basalt flows and flow breccia in the vicinity of Goble Creek. A description of the rock-forming minerals and occurrence and zonation of these zeolites can be found in Howard et al. (1990).

The intensity of rock alteration, amount and size of vesicles, and abundance of zeolites decrease toward the massive center of the flow. Black to dark green clay is more abundant. Drusy heulandite is scarce, and zeolites are found only in a few cavities. Larger tschernichite crystals are found near the rims of the joint blocks of basalt. The tschernichite is often covered with okenite, analcime, levyne, offretite, erionite, opal, and chabazite, which are usually altered to white formless masses. Unaltered radial elongated prisms of heulandite, spheres of mordenite, and quartz are also present. Less commonly, cavities in the rim of the joint blocks contain colorless transparent analcime, levyne, and, rarely, blue thomsonite.

In a small localized portion of the dense rock, near the central portion of the flow, where alteration is at a minimum, the rock is very fine grained and nearly nonvesicular. Drusy tschernichite is present in nearly every cavity, occasionally accompanied by a single boggsite hemisphere. The very center of the flow contains vesicles with only tiny smooth tschernichite hemispheres scattered on otherwise bare clay, or with a total absence of any zeolites or clay.

The sequence of crystallization at Goble has been determined from studies of thousands of specimens. The crystallization of boggsite and tschernichite represent an early hydrothermal phase that predates the more widespread zeolitization in the area, which commenced with the crystallization of drusy heulandite. In the tschernichite-bearing rock, thin sheets of native copper or small mounds of calcite occasionally formed on the walls of some vesicles, followed by up to seven thin layers of dark green Fe-rich smectite, alternating with light green Fe- and Ca-rich smectite, both of which become black after exposure to air. Tschernichite was the first zeolite to crystallize, forming tiny, smooth, colorless hemispheres 0.1–0.5 mm in size, widely scattered on the clay lining in nearly all the tiny vesicles. Boggsite usually formed a single, fine-grained, colorless, radial hemisphere, 0.5–1.5 mm in diameter, in only a few of the cavities. Both tschernich-

ite and boggsite continued to grow, the single hemispheres of boggsite becoming enlarged and tschernichite forming larger divergent crystals extending from the initial smooth hemispheres until the vesicle was completely lined. The two minerals do not occur on each other.

Toward the end of crystallization, both tschernichite and boggsite were partly dissolved. Rarely, small dark green Fe-rich smectite spheres crystallized on the surface of both boggsite and tschernichite. Renewed crystallization of both boggsite and tschernichite then enclosed the clay.

Following crystallization of tschernichite and boggsite, sparse cream-colored spheres of chalcedony formed, followed by heulandite, apophyllite, levyne, chabazite, calcite, aragonite, or opal. In the adjacent rock, which contains larger scattered tschernichite crystals without boggsite, a more complex crystallization sequence occurs (in order of formation): native copper, smectite, okenite, tschernichite, okenite, opal, mordenite, okenite, levyne, offretite, erionite, heulandite, opal and analcime, okenite, and chabazite, followed by alteration of all the low-silica species (okenite, levyne, offretite, chabazite, analcime) to chalky white masses.

A second hydrothermal phase (drusy heulandite), which is widespread in the breccia, and highly vesicular basalt are found in vesicles near the rims of some joint blocks overgrown on the tschernichite, boggsite, and altered white masses of the first phase.

A possible control on the occurrence of the zeolites with higher Si contents, tschernichite and boggsite, in the denser parts of the flows may be an increase in the pH of the fluids during alteration of the volcanic glass and formation of the zeolites due to the restriction of fluid flow through the denser parts of the flows (W. S. Wise, personal communication). A higher pH would tend to produce solutions with higher silica contents, leading to the crystallization of silica-rich zeolites from these solutions. This is consistent with the smaller silica content in the larger tschernichite crystals, which occur in the outer, less dense parts of the flows.

PHYSICAL PROPERTIES

Tschernichite is colorless to white, transparent to translucent, with a vitreous luster and a white streak. The centers of the larger colorless crystals are commonly milky white because of the many small fluid inclusions. Tschernichite shows no to a very pale yellow fluorescence under both long- and short-wavelength ultraviolet radiation. The fluorescence is slightly brighter under short-wavelength ultraviolet radiation. Tschernichite is brittle, with a conchoidal fracture, and does not exhibit any observable cleavage. The Mohs hardness is 4½. The measured density is 2.02(1) g/cm³, determined by flotation in a methylene iodide and acetone solution. This is slightly less than the calculated density of 2.12 g/cm³, most probably because of the presence of fluid inclusions.

The compatibility indices (Mandarino, 1981), calculated using the composition of the larger crystals (Analysis

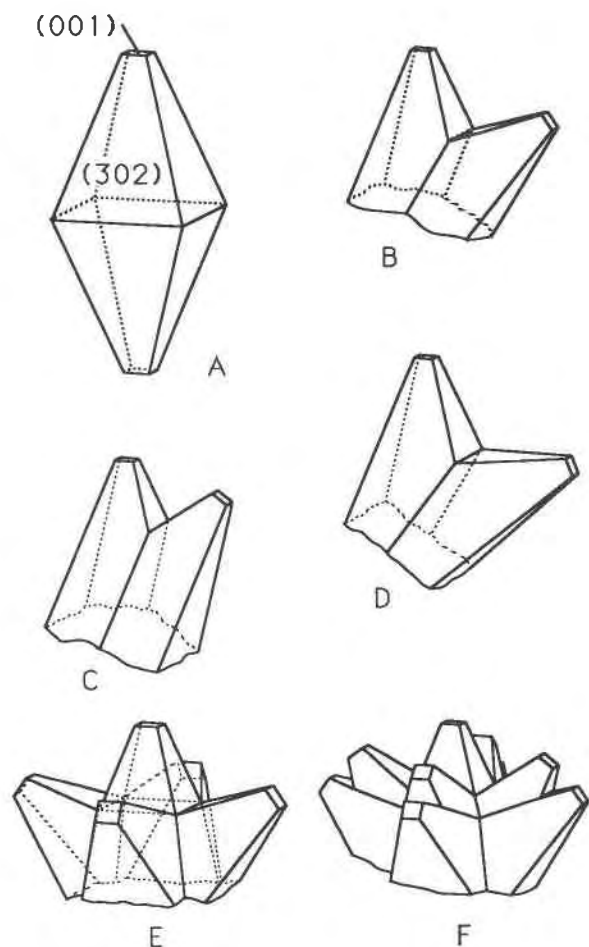


Fig. 1. Crystal drawings of tschernichite. (A) Untwinned crystal, (B) twinning on the plane $\{101\}$, (C) twinning on $\{302\}$, and (D) twinning on $\{304\}$, (E) multiple twinning on $\{101\}$, (F) multiple twinning on both $\{101\}$ and $\{302\}$.

1) and the measured and calculated densities, are 0.0052 and 0.0531, respectively, which indicate superior to good compatibility among density, indices of refraction, and chemical composition.

OPTICAL PROPERTIES

Tschernichite was studied optically using a spindle stage and a Na-line interference filter ($\lambda = 5893 \text{ \AA}$) according to the methods of Bloss (1981). Tschernichite is uniaxial (–) with $\omega = 1.484(1)$ and $\epsilon = 1.483(1)$ and very low birefringence. Almost all crystals of tschernichite show somewhat wavy extinction and are not strictly uniaxial. Thin sections cut to be perpendicular to (100) show areas of parallel extinction, as well as apparent twin lamellae perpendicular to (001), which show inclined extinction. These relationships indicate that the symmetry of tschernichite may be lower than tetragonal, as is also indicated by the relationship to zeolite beta (Treacy and Newsam, 1988; Smith et al., 1991).

MORPHOLOGICAL CRYSTALLOGRAPHY

Tschernichite occurs as steep tetragonal dipyrramids $\{302\}$, normally terminated by a small basal pinacoid $\{001\}$ (Fig. 1A). Three other minor dipyrramids, $\{104\}$, $\{101\}$, and $\{502\}$, have been observed on a few crystals. Tschernichite is commonly twinned by reflection on $\{101\}$, $\{302\}$, and $\{304\}$ (Fig. 1B, 1C, and 1D). Multiple twinning involving both twin planes often occurs, resulting in complex ball-like groups (Fig. 1E and 1F). This twinning, as well as possible twinning on other $\{h0l\}$ planes, contributes to the formation of hemispherical tschernichite groups. Single crystals of tschernichite range in size from $<0.1 \text{ mm}$ to 1 cm rarely. Most crystals are $<3 \text{ mm}$ in length. Aggregates of tschernichite occur as $0.1\text{--}0.5 \text{ mm}$ smooth hemispherical groups $0.1\text{--}0.5 \text{ mm}$ in size, drusy linings of crystals of $0.1\text{--}0.5 \text{ mm}$, radiating groups of crystals of $0.2\text{--}3 \text{ mm}$ showing distinct dipyramid terminations, and larger single crystals of $1\text{--}10 \text{ mm}$ and twinned aggregates. The c axis of tschernichite is oriented radially from the center of the hemispherical aggregates.

X-RAY CRYSTALLOGRAPHY

Powder X-ray diffraction studies of tschernichite were carried out using a Picker diffractometer, $\text{CuK}\alpha$ radiation ($\lambda = 1.54178 \text{ \AA}$), and annealed synthetic fluorite ($a = 5.459 \text{ \AA}$) as an internal standard. The powder X-ray diffraction data are shown in Table 1. Least-squares refinement of the powder data yielded $a = 12.880(2) \text{ \AA}$ and $c = 25.020(5) \text{ \AA}$, based on a tetragonal cell. Attempts to determine the space group, using several crystals and Weissenberg photography by R. C. Boggs, were unsuccessful because of the poor quality of the photographs, which show diffuseness along the c axis, as well as imperfect reflection profiles and overlapping patterns of diffraction spots from different domains. Attempts (J. V. Smith and Subrata Ghose, personal communication) to determine the space group using four-circle goniometers were also unsuccessful. The poor quality of the single-crystal data appears to be due to mosaic structure, stacking faults perpendicular to the c axis, and possibly the presence of domains of differing symmetry (see optical properties section). The morphological data imply that the point group is $4/m2/m2/m$. Possible space groups based on the indexing of the X-ray powder data are $P422$, $P42_12$, $P4mm$, $P42m$, $P42_1m$, $P4m2$, and $P4/mmm$. The most probable space group is $P4/mmm$, if one assumes that the inferred point group is correct. The structure of tschernichite, based on work by Smith et al. (1991), is that of the zeolite beta of Treacy and Newsam (1988), which consists of an intergrowth of an enantiomorphic pair having the tetragonal space groups $P4_122$ and $P4_222$, with $a = 12.447(5) \text{ \AA}$ and $c = 26.56(1) \text{ \AA}$ (polymorph A), and a triclinic polymorph (B) with space group $P\bar{1}$, with $a \approx b = 12.4 \text{ \AA}$, $c = 14.5 \text{ \AA}$; $\alpha \approx \beta = 73^\circ$, and $\gamma \approx 90^\circ$. This structure is based on the comparison of the powder pattern of tschernichite with a calculated powder pattern

TABLE 1. X-ray powder diffraction data for tschernichite

hkl	d_{obs}	d_{calc}	hkl
2	26.0	25.02	001
10	12.5	12.51	002
32	11.6	11.45	101
7	6.24	6.25	004
2	5.63	5.63	104
2	4.97	5.00	005
2	4.74	4.74	213
2	4.45	4.48	221
14	4.22	4.23	301
1	4.12	4.17	006
100	4.03	{ 4.07 4.02	{ 310 311
4	3.971	3.967	106
6	3.708	3.681	224
2	3.651	3.659	313
13	3.569	3.572	320
7	3.500	3.500	206
5	3.333	3.327	117
16	3.156	3.158	315
15	3.062	3.075	226
7	2.990	2.991	306
1	2.950	2.950	332
2	2.818	2.813	208
10	2.730	2.731	334
2	2.617	2.616	424
5	2.527	{ 2.527 2.526	{ 327 510
3	2.439	{ 2.454 2.417	{ 336 513
1	2.300	2.299	523
2	2.220	{ 2.234 2.210	{ 524 418
2	2.191	{ 2.193 2.192	{ 2,2,10 436
2	2.164	2.162	3,3,10
16	2.114	{ 2.116 2.116	{ 602 2,1,11
1	2.079	2.079	603
1	2.064	2.063	517
1	2.002	{ 2.005 2.000	{ 541 429
1	1.9035	1.9035	1,0,13
2	1.8693	1.8695	519
1	1.8142	{ 1.8167 1.8131	{ 551 529
2	1.7802	{ 1.7816 1.7795	{ 641 553
1	1.6845	1.6845	619
3	1.6634	1.6636	2,2,14
1	1.5831	{ 1.5847 1.5846 1.5808	{ 742 5,3,11 803
1	1.5298	{ 1.5309 1.5287 1.5236	{ 5,1,13 737 559
3	1.5227	1.5232	6,3,10
3	1.5164	1.5162	5,3,12
2	1.4807	1.4811	4,0,15
1	1.4650	1.4655	834
1	1.4584	{ 1.4587 1.4585	{ 658 747
1	1.3947	{ 1.3951 1.3948	{ 904 761

for an approximately 50-50 mixture of polymorphs A and B of zeolite beta. The presence of the triclinic polymorph can account for the twin lamella, with inclined extinction observed in thin-section.

COMPOSITION

Analyses were performed at both the University of Chicago, using a Cameca SX-50 electron microprobe op-

TABLE 2. Chemical analytical data for tschernichite

	1*	2**	3*
SiO ₂	54.09	59.78-65.11	65.77
Al ₂ O ₃	15.43	14.61-15.23	14.44
CaO	8.27	6.58-7.82	6.58
FeO†	0.26	0.00-1.04	n.d.
MgO	0.51	0.00-0.17	n.d.
Na ₂ O	0.22	0.00-0.91	0.00
K ₂ O	n.d.	0.00-0.24	0.06
H ₂ O‡	22.7	12.26-15.53	13.15
Total	101.48	100.00-100.00	100.00

Note: Values are in weight percent.

* Analysis performed at Eastern Washington University.

** Range of compositions based on analyses performed at University of Chicago and Eastern Washington University.

† Fe_{tot} as Fe₂O₃.

‡ H₂O by difference for all but Analysis 1.

erating at 15 kV and 2-nA sample current and an energy-dispersive detector, and at Eastern Washington University, using an ARL-EMX SM electron microprobe operating at 15 kV and 10-nA sample current and an Ortec energy-dispersive detector. The standards used were An₇₀ glass (Na,Al,Si,Ca), microcline (K) from Asbestos, Quebec, and manganese hortonolite (Fe,Mg) at the University of Chicago, and albite (Na,Al,Si), microcline (K), anorthite (Ca), hematite (Fe), and fayalite (Mg) at Eastern Washington University. Because of possible ion mobility and H₂O loss, a beam diameter of 50 μm was used. H₂O was determined by weight loss on heating of a 14-mg sample of the larger crystals to 800 °C in a Pt crucible. The analyses are shown in Table 2. Analysis 1 is of the larger individual crystals, whereas the other analyses are of the smaller drusy crystals. The smaller crystals show a higher silica content than the larger crystals, probably as a result of differing conditions during their formation (see occurrence section).

These analyses give an empirical formula (on the basis of 16 framework O atoms) ranging from (Ca_{0.97}Na_{0.05}Mg_{0.08})(Si_{5.95}Al_{2.00}Fe_{0.02})O₁₆·7.96H₂O for the larger crystals to (Ca_{0.73}Na_{0.11}K_{0.02}Mg_{0.00})(Si_{6.33}Al_{1.69}Fe_{0.02})O₁₆·3.98H₂O for the most silica-rich drusy crystals. The H₂O content is probably low for the smaller, more silica-rich crystals because it was not possible to determine the H₂O content directly. The data do suggest, however, that the silica-rich crystals probably have a slightly lower H₂O than do the silica-poor crystals, possibly because of the presence of fewer H₂O molecules coordinating the smaller number of cations. This gives a simplified formula of (Ca,Na,K,Mg)_{1.1}Si₆Al₂O₁₆·8H₂O for the crystals with the lowest Si content and (Ca,Na,K,Mg)_{0.95}Si_{6.33}Al_{1.67}O₁₆·4H₂O for the crystals with the highest Si content. The Si/Al ratio of tschernichite ranges from about 3/1 to 3.7/1, with z = 8 for all of the above formulas.

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REFERENCES CITED

- Bloss, F.D. (1981) *The spindle stage: Principles and practices*, 340 p. Cambridge University Press, New York.
- Howard, D.G., Tschernich, R.W., Smith, J.V., and Klein, G.L. (1990) Boggsite, a new high silica zeolite from Goble, Columbia County, Oregon. *American Mineralogist*, 75, 1200–1204.
- Mandarino, J.A. (1981) The Gladstone-Dale relationship. IV. The compatibility concept and its application. *Canadian Mineralogist*, 19, 441–450.
- Smith, J.V., Pluth, J.J., Boggs, R.C., and Howard, D.G. (1991) Tschernichite, the mineral analogue of zeolite beta. *Journal of the Chemical Society, Chemical Communications*, 363–364.
- Treacy, M.M., and Newsam, J.M. (1988) Two new three-dimensional twelve-ring zeolite frameworks of which zeolite beta is a disordered intergrowth. *Nature*, 322, 249–251.
- Wilkinson, W.D., Lowry, W.D., and Baldwin, E.M. (1946) *Geology of the St. Helens Quadrangle, Oregon*. Oregon State Department of Geology and Mineral Industries Bulletin, 31, 39 p.

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ERRATUM

Octahedral excess mixing properties in biotite: A working model with applications to geobarometry and geothermometry, by A. E. Patiño Douce, A. D. Johnston, and J. M. Rice (v. 78, p. 113–131). The calculated loci of the QFM buffer at 7, 10, and 13 kbar shown in Figure 1 of Patiño Douce et al. (1993) are in error. The correct loci (calculated with standard-state thermodynamic properties from Berman, 1988) are shown here in Figure 1 (numbers on curves indicate pressure in kilobars). This error in no way affects any of the derivations or conclusions of Patiño Douce et al. (1993) regarding mixing properties in biotite. In particular, estimation of Fe^{3+} contents in biotite relies on f_{O_2} values in the experimental charges, which were estimated from Reaction 1 (and shown by symbols in Fig. 1), and these values are not affected. The only statement that must be modified is that regarding the redox conditions in NaCl-based piston-cylinder cell assemblies, which are now shown to be at or below QFM and not 2 log units above QFM, as asserted in Patiño Douce et al. (1993).

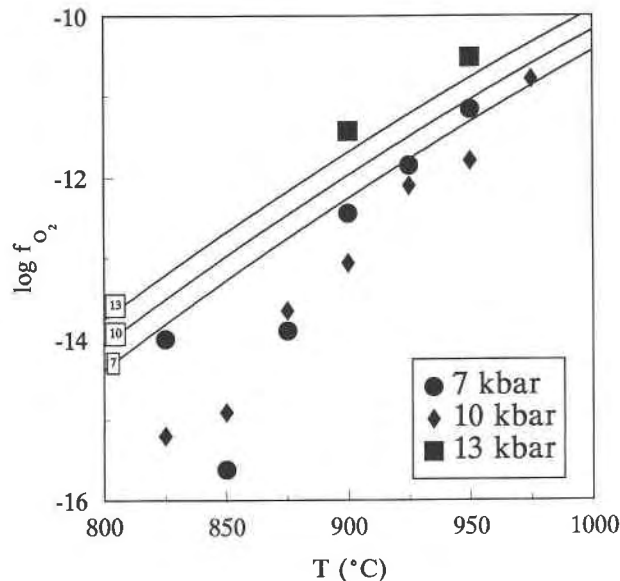


Fig. 1. The f_{O_2} values in experiments (symbols) estimated from garnet compositions.