American Mineralogist, Volume 74, pages 676–684, 1989

# Geigerite, the Mn analogue of chudobaite: Its description and crystal structure

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## ABSTRACT

Geigerite, a new manganese arsenate mineral, was found in the abandoned manganese ore mines near Falotta, Oberhalbstein (Canton of Grisons, Switzerland). From the structure determination and from microprobe analysis, the following formula was derived: $Mn_5(H_2O)_8(AsO_3OH)_2(AsO_4)_2 \cdot 2H_2O$. The mineral is triclinic, space group $P\bar{1}$, with $a$ = 7.944(1), $b$ = 10.691(1), $c$ = 6.770(1) Å, $\alpha$ = 80.97(1), $\beta$ = 84.20(1), $\gamma$ = 81.85(1)°, $V$ = 560.3(1) Å$^3$, and Z = 1. Density is 3.05(10) (meas.) and 3.00 g/cm$^3$ (calc.). The eight strongest lines of the powder-diffraction pattern are ($d_{obs}$ in Å, ($hkl$), $I/I_0$): 10.45,(010),100; 3.051,(01$\bar{2}$),24; 3.507,(201),21; 3.340,(002,220),20; 3.011,(022),17; 2.786,(230),14; 7.85,(100),13; and 4.89,($\bar{1}$01),12. Geigerite forms platy, partly triangular crystals of rose-red color up to 0.5 mm in length. They are flattened on (010) and have a perfect cleavage along this direction. The luster is vitreous to pearly and the streak is white. Microhardness VHN is 105–115 kg/mm$^2$, corresponding to a Mohs hardness of about 3. The mineral is optically biaxial negative with $\alpha$ = 1.601(2), $\beta$ = 1.630(2), and $\gamma$ = 1.660(2) for 589 nm; $2V_{obs}$ is large, $2V_{calc}$ = 89°. The pleochroism is weak, from colorless to rose-red, and absorption is $Z > Y \simeq X$.

As for other rare manganese and arsenate minerals at Falotta (brandtite, sarkinite, tilasite, manganberzeliite, grischunite, etc.), the formation of geigerite is closely related to Alpine metamorphism, by which the pre-Alpine manganese ores in the radiolarites became transformed and partly remobilized. From examining the crystal-structure data and the chemical formula, geigerite is found to be the Mn equivalent of chudobaite.

The crystal structure was solved by direct methods and refined using 2567 independent reflections measured by a single-crystal X-ray diffractometer. The final $R$ index is 0.028 for all the observed data. The structure contains an equal number of $AsO_4$ and $AsO_3OH$ ions sharing corners with octahedra centered on Mn atoms; some analogy with huréaulite can be observed, but no cavities containing acid H are present; one water molecule is not directly linked to any metal atom. A remarkable structural feature of geigerite is the presence of a complicated network of hydrogen bonds, whose number exceeds the number of the H atoms.

## INTRODUCTION

The old manganese mines in the Oberhalbstein region (Canton of Grisons, Switzerland), abandoned since World War II, have attracted the interest of local mineral collectors since the early 1970s. Among the materials found at the locality Falotta by the so-called "Strahler," a number of rare and uncommon minerals such as tilasite, sarkinite, manganberzeliite, and brandtite have been identified in addition to some completely new species such as grischunite (Graeser et al., 1984; Bianchi et al., 1987) and geigerite (this paper). The existence of the latter species was discovered when the rose-red color of an unknown mineral on samples from Falotta attracted the attention of the finder, Walter Cabalzar, who sent the mineral to one of us (S.G.) for closer inspection. The Långban mineral bergslagite, published as a new mineral by Hansen et al. (1984), was observed and studied simultaneously and independently by us on samples from Falotta. Two additional new Mn minerals are still under investigation. Geigerite is named for Dr. Thomas Geiger, Wiesendangen, Switzerland, who studied Falotta manganese ores in his 1948 doctoral thesis. Type material is deposited at the Natural History Museum, Basel, and at the Miner-

0003–004X/89/0506–0676$02.00

Fig. 1. Geigerite from Falotta. Typical triangular crystals with well-developed {010} faces and a perfect cleavage along this face. A second cleavage is indicated parallel to the *c* axis (see Fig. 2). The length of the scale units is 10 µm.

alogical Institute, University of Basel. The mineral and the name geigerite have been accepted by the Commission on New Minerals and Mineral Names, IMA prior to publication.

## OPTICAL AND PHYSICAL PROPERTIES

The new mineral covers the rock in minute crystals, rarely exceeding 0.5 mm in length, on areas of the order of 1 cm$^2$. The color is very faint, and isolated single crystals appear almost colorless. The crystals are platy on {010}, with striation parallel to the *c* axis, and have a perfect cleavage parallel to {010} (Figs. 1–2). The morphology appears clearly triclinic. During the investigation, another type of geigerite was observed, that consisting of massive, fine-grained to fibrous aggregates up to 1 cm in length.

Geigerite crystals are completely transparent under the polarizing microscope, with weak pleochroism in thicker fragments. Some specimens have a milky translucent aspect, presumably owing to an alteration process. Optical properties were determined only on fresh, transparent material. The optical orientation was derived from a crystal previously studied by single-crystal X-ray work. Optical and physical data of geigerite are given in Table 1.

The mineral is extremely brittle and quite soft. Microhardness was determined by a Leitz Durimet microscope. The VHN values, in the range of 105–115 kg/mm$^2$, correspond to a Mohs hardness of about 3.

The density was measured for geigerite aggregates using heavy liquids. The sample used was checked for purity by means of Gandolfi X-ray photographs. The considerable uncertainty range of the determination might be due to the aggregate form and is perhaps a consequence of intergrowth with small amounts of other minerals. Notwithstanding this, the agreement with the corresponding calculated value (see Table 1) is quite satisfactory.

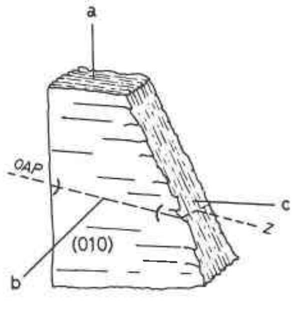

Fig. 2. An idealized sketch of a geigerite crystal showing the optical orientation.

## CHEMICAL COMPOSITION

The preparation of geigerite material for microprobe work was quite difficult because of its brittleness and perfect cleavage. From preliminary qualitative determinations by an EDS probe on a scanning electron microscope (SEM laboratory, Geological Institute, Basel), it became obvious that geigerite was a manganese arsenic oxide mineral.

A small sample of the mineral was studied on a Perkin-Elmer 883-IR spectrophotometer. The resulting infrared spectrum (Fig. 3) yielded the following main absorption maxima (in cm$^{-1}$, transmittance in percent): 3428 (27.6), 1643 (74.5), 824 (27.6), 714 (61.1), 400 (48.3), and 370 (47.3). This is typical of an arsenate mineral with a dominant vibration at 824 cm$^{-1}$. The vibrations at 3428 and 1643 cm$^{-1}$ prove the presence of water, and the intensity of the vibration at 1643 cm$^{-1}$ indicates that it is present mainly as $H_2O$ rather than as OH groups.

The final quantitative determinations were performed on an ARL microprobe. The following materials were used as standards: scorodite, stranskiite, olivenite, and synthetic $AlAsO_4$ (for $As_2O_5$); manganite, metallic Mn, and pyroxmangite (for Mn); and wollastonite (for Ca). As the small amount of material did not permit using analytical methods other than the electron microprobe and IR spectroscopy, $H_2O$ had to be calculated by difference. From

**TABLE 1.** Optical and physical properties of geigerite

| | |
|---|---|
| Biaxial, negative | (all data for 589 nm) |
| $\alpha = 1.601(2)$ | $2V_{obs}$ = large |
| $\beta = 1.630(2)$ | $2V_{calc} = 89°$ |
| $\gamma = 1.660(2)$ | Pleochroism: very weak, colorless to rose-red |
| $\Delta = 0.059$ | Absorption: $Z > Y \simeq X$ |
| Orientation: $X \simeq b$, $Y \simeq a$, $Z \simeq c$. | |
| on {010}: $Z \wedge c = 15°$, | $X$ almost normal to {010} |
| on {100}: $Z \wedge c = 6°$ | |
| Color: rose-red | Streak: white |
| Luster: vitreous to pearly | Nonfluorescent |
| Hardness: VHN$_{(25)}$ 105 kg/mm$^2$<br>VHN$_{(50)}$) 115 kg/mm$^2$ | |
| Cleavage: perfect on {010} | |
| Density (meas.): 3.05(10) g/cm$^3$ (heavy liquids) | |
| Density (calc.): 3.00 g/cm$^3$ | |

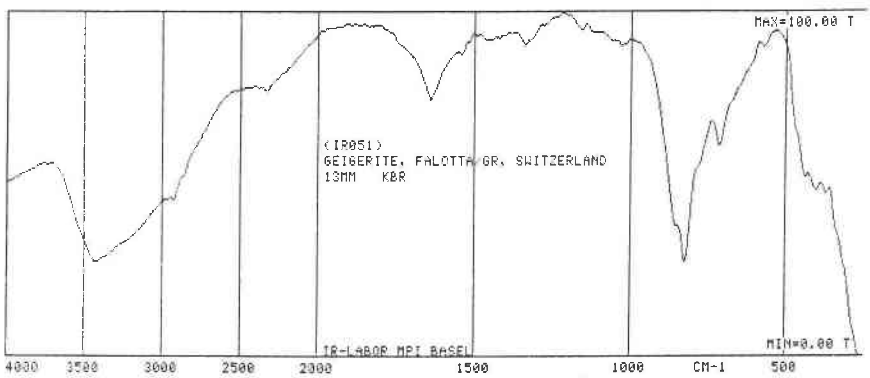

Fig. 3. Infrared spectrum of geigerite. The dominant absorption maximum at 824 cm$^{-1}$ is characteristic of an arsenate mineral. Two other maxima (at 3428 and 1643 cm$^{-1}$) prove the presence of $H_2O$.

the large number of analyses performed on geigerite crystals, five are compiled in Table 2. A previous calculation of the mineral formula from the analytical data without the help of structural information caused considerable difficulties, as it was not possible to derive a proper formula either for a $Mn^{2+}$ arsenate or for a $Mn^{3+}$ arsenate. Because the presence of arsenate groups was confirmed by the IR study, we tried to achieve a balanced mineral formula by assuming a $Mn^{2+}/Mn^{3+}$ ratio of 3/1. This procedure turned out to be in error, as proved by subsequent structure determination (see below). From the structural data, it became evident that a balanced formula could be achieved by introduction of an acid $AsO_3OH$ group instead of varying the Mn valence.

## X-RAY POWDER DATA

The powder-diffraction data for geigerite from Falotta led to the conclusion that the mineral was new because they were not identifiable with any known mineral species; they are reported in Table 3. Unit-cell parameters, determined from Weissenberg and precession photographs and refined by fit to the powder data are also reported in Table 3; from these parameters the triclinic symmetry of the mineral is evident. From the unit-cell parameters and the compilation of arsenate mineral data (Strunz, 1977), a possible relationship to the mineral chudobaite, described by Strunz (1960), appeared possible; this relationship was fully confirmed by structure determination (see below).

**Table 2.** Chemical analyses (wt%) of geigerite from Falotta

| | 1 | 2 | 3 | 4 | 5 | 6 | 7 |
|---|---|---|---|---|---|---|---|
| CaO | 0.14 | 0.12 | 0.11 | 0.13 | 0.08 | — | — |
| MnO | 39.86 | 39.74 | 39.36 | 40.44 | 39.17 | 30.55 | 35.04 |
| $Mn_2O_3$ | — | — | — | — | — | 11.33 | — |
| $As_2O_5$ | 50.20 | 50.57 | 49.38 | 50.56 | 49.87 | 49.50 | 45.51 |
| $H_2O$ | (9.80) | (9.57) | (11.15) | (8.87) | (10.88) | 8.62 | 19.55 |

*Note:* Columns 1–5, individual analyses of geigerite; 6, $Mn^{2+}_{4.5}Mn^{3+}_{1.5}$-$(AsO_4)_{4.5}\cdot5H_2O$ (original interpretation); 7, $Mn_5(H_2O)_8(AsO_3OH)_2(AsO_4)_2\cdot2H_2O$ (from structure).

## OCCURRENCE AND PARAGENESIS OF GEIGERITE

Geigerite is found in small vugs in the Mn-bearing radiolarites in the Oberhalbstein region, Canton of Grisons, associated by other manganese arsenate minerals such as brandtite, sarkinite, grischunite, bergslagite, manganberzeliite, etc. Just as for grischunite, another manganese arsenate recently discovered in the same locality (Graeser et al., 1984), and for numerous other minerals, geigerite represents a product of Alpine metamorphism of primary, pre-Alpine manganese ores (braunite, psilomelane). Greenschist-facies metamorphism of the manganese ores in radiolarites produced a considerable number of uncommon manganese and/or arsenate minerals by remobilization of the primary manganese ores and reaction with abundant As in the surrounding sedi-

**Table 3.** X-ray powder diffraction data for geigerite

| *h* | *k* | *l* | $d_{obs}$ | $d_{calc}$ | $I/I_0$ |
|---|---|---|---|---|---|
| 0 | 1 | 0 | 10.45 | 10.45 | 100 |
| 1 | 0 | 0 | 7.85 | 7.85 | 13 |
| 1 | −1 | 0 | 5.94 | 5.93 | 3 |
| 0 | 1 | −1 | 5.28 | 5.29 | 7 |
| 1 | 0 | −1 | 4.89 | 4.898 | 12 |
| 1 | 1 | −1 | 4.41 | 4.392 | 4 |
| 2 | 0 | 0 | 3.92 | 3.925 | 9 |
| 2 | 1 | 0 | 3.837 | 3.838 | 9 |
| 2 | 0 | 1 | 3.507 | 3.503 | 21 |
| 0 | 0 | 2 | 3.340 | 3.333 | 20 |
| 2 | 2 | 0 | | 3.349 | |
| 1 | 0 | 2 | 3.158 | 3.157 | 4 |
| 0 | 1 | −2 | 3.051 | 3.052 | 24 |
| 0 | 2 | 2 | 3.011 | 3.011 | 17 |
| 2 | −2 | 0 | 2.961 | 2.963 | 6 |
| 1 | −3 | −1 | 2.866 | 2.874 | 8 |
| 2 | 3 | 0 | 2.786 | 2.787 | 14 |
| 1 | −2 | −2 | 2.691 | 2.686 | 9 |
| 2 | 0 | −2 | 2.448 | 2.449 | 7 |
| 1 | −2 | −3 | 2.015 | 2.016 | 5 |
| 3 | −3 | 0 | 1.9755 | 1.9752 | 5 |
| 3 | −1 | 3 | 1.6844 | 1.6839 | 5 |

*Note:* Debye-Scherrer camera, Mn-filtered Fe*Kα* radiation. Intensities determined by densitometer. Indexing based on parameters refined from powder data: $a = 7.952$, $b = 10.664$, $c = 6.767$ Å, $\alpha = 81.15$, $\beta = 84.42$, $\gamma = 81.96°$.

**TABLE 4.** Unit-cell data for geigerite and chudobaite

| | Geigerite triclinic $P\bar{1}$ | Chudobaite triclinic $P\bar{1}$ |
|---|---|---|
| $a$ (Å) | 7.944(1) | 7.797(9) |
| $b$ (Å) | 10.691(1) | 10.485(5) |
| $c$ (Å) | 6.770(1) | 6.616(3) |
| $\alpha$ (°) | 80.97(1) | 80.53(1) |
| $\beta$ (°) | 84.20(1) | 84.23(10) |
| $\gamma$ (°) | 81.85(1) | 82.12(10) |
| Z | 1 | 1 |
| $V$ (Å$^3$) | 560.3(1) | 526.8(10) |
| | $Mn_5(H_2O)_8(AsO_3OH)_2(AsO_4)_2 \cdot 2H_2O$ | $(Mg,Zn)_5(H_2O)_8(AsO_3OH)_2(AsO_4)_2 \cdot 2H_2O$ |

ments, as is consistent with ore concentrations on active ocean ridges (Boström and Valdes, 1969).

## DETERMINATION OF THE STRUCTURE

From a fragment of a crystal measuring about 125 × 100 × 40 μm, a new determination of the unit-cell dimensions was performed, using a Nonius CAD-4 diffractometer. The final results have been refined from reflections with 2$\theta$ around 50°, using Mo$K\alpha$ radiation ($\lambda$ = 0.71069 Å); they are slightly different from the original data and are reported in Table 4. The Laue symmetry of the reciprocal lattice is $\bar{1}$ ($C_i$), and no systematic extinctions are present. The existence of a center of symmetry was proved by solution of the crystal structure, and the space group is therefore $P\bar{1}$.

Of 2567 independent reflections that were collected using the CAD-4 diffractometer, 2102 for which $I > \sigma(I)$ were used in the refinement. Owing to a marked irregularity of the shape of the crystal fragment, an empirical absorption correction was introduced, using the method of Walker and Stuart (1983). The structure was solved by direct methods using the MULTAN package (Germain et al., 1971; Main, 1977). From the $E$-map, all peaks corresponding to the heavier atoms (excluding water oxygen atoms) were easily identified. The remaining oxygen atoms and all the H atoms were located from a difference-Fourier map.

The refinement was carried out by least-squares, using weights equal to $4I/\sigma^2(I)$. The variance of each reflection, $\sigma^2(I)$, was assigned according to the formula $\sigma^2(I) = \sigma^2_{c.s.}(I) + 0.0004I^2$, where $\sigma^2_{c.s.}$ is the variance derived from the counting statistics. The atomic form factors for neutral atoms were taken from Cromer and Waber (1965), and the anomalous dispersion corrections $\Delta f'$ and $\Delta f''$ were taken from Cromer (1965). A secondary extinction coefficient (1.6 × $10^{-7}$) was derived from the least-squares refinement.

The refinement converged at an $R$ index of 0.030 for all the observed reflections (the weighted $R$ index was 0.031). After inclusion of all the H atoms in the structure-factor calculations, a difference-Fourier synthesis revealed an additional peak of about 0.6 e/Å$^3$ near the oxygen atom O(9). This peak (here called H*) is located at (0.141, 0.834, 0.584) and gives bond distances and angles in reasonable agreement with a water H atom (O-H = 0.75 Å; H-O-H ranging from 86° to 121°). The most reasonable interpretation is that there is substantial disorder of the H atom associated with the water oxygen O(9), a point that causes no surprise in view of the extensive disorder of the H atoms in ice and many hydrated salts.

Besides the disordered H atom, the highest residuals are of the order of 0.6 e/Å$^3$ and may correspond to the "lone pairs" of some oxygen atoms. The final $R$ index is 0.028 for all the observed reflections, and the weighted $R$ is 0.029. The final list of observed and calculated structure factors is reported in Table 4A.[1] The atomic coordinates and the equivalent isotropic thermal parameters are given in Table 5; the anisotropic thermal parameters are shown in Table 6. A projection of the structure along the $c$* axis is shown in Figure 4, and the packing of polyhedra along $c$* and $a$ is shown in Figures 5–6. The programs ORTEP-II (Johnson, 1976) and STRUPLO'84 (Fischer, 1984) were used, respectively, to prepare these diagrams.

The bond distances and angles geigerite are reported in Table 7; the estimated standard deviation for the M–O distances is about 0.003 Å, and that for the bond angles is about 0.1°. Such standard deviations derive from the residuals and the inverse matrix of the least-squares normal equations; no correction for systematic errors due to thermal libration was made. The latter might result in bond-length estimates that are systematically shorter by about 0.005 Å. The standard deviation for the H–O bond lengths is about 0.06 Å, and that for the angles about 6°.

## STRUCTURE DESCRIPTION

Of the two independent arsenate ions in geigerite, one is an acid $AsO_3OH$ group. The As–OH bond (1.751 Å) is considerably longer than the As–O bonds (average: 1.681 Å). Such values are in good agreement with the averages (1.739 and 1.674 Å, respectively) of Ferraris (1970). The As(2)–O(7) bond, which belongs to a normal $AsO_4$ group, is also markedly longer than the other As–O bonds. This effect is due to a strong hydrogen bond to O(1) (see below). Within each arsenate group, all the other bond distances are remarkably constant, which implies a virtual

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[1] A copy of Table 4A may be ordered as Document AM-89-408 from the Business Office, Mineralogical Society of America, 1625 I Street, N.W., Suite 414, Washington, D.C. 20006, U.S.A. Please remit $5.00 in advance for the microfiche.

**TABLE 5.** Final atomic coordinates and equivalent isotropic thermal parameters (Å$^2$) in geigerite

| | $x$ | $y$ | $z$ | $U_{eq}$ |
|---|---|---|---|---|
| As(1) | 0.36967(5) | 0.36543(4) | 0.40344(6) | 0.0086(1) |
| As(2) | −0.03902(5) | 0.33350(4) | −0.07716(6) | 0.0068(1) |
| M(1) | 0.00000 | 0.00000 | 0.00000 | 0.0141(2) |
| M(2) | 0.08271(8) | 0.59557(6) | 0.59920(9) | 0.0101(2) |
| M(3) | 0.36170(7) | 0.43412(6) | −0.10853(9) | 0.0100(2) |
| O(1) | 0.1860(3) | 0.3051(3) | 0.3571(4) | 0.0135(8) |
| O(2) | 0.5037(3) | 0.2372(3) | 0.4864(4) | 0.0151(9) |
| O(3) | 0.4383(3) | 0.4425(3) | 0.1821(4) | 0.0124(8) |
| O(4) | 0.3152(3) | 0.4618(3) | 0.5776(4) | 0.0111(8) |
| O(5) | −0.1173(3) | 0.1969(3) | −0.0900(5) | 0.0132(8) |
| O(6) | −0.0480(3) | 0.4268(3) | −0.3016(4) | 0.0107(8) |
| O(7) | 0.1677(3) | 0.3012(3) | −0.0190(4) | 0.0111(8) |
| O(8) | −0.1525(3) | 0.4094(3) | 0.1035(4) | 0.0115(8) |
| O(9) | 0.1579(4) | 0.7851(3) | 0.5152(5) | 0.0186(9) |
| O(10) | 0.5324(4) | 0.2478(3) | −0.1198(5) | 0.0181(9) |
| O(11) | 0.0863(4) | 0.0436(3) | 0.2751(5) | 0.027(1) |
| O(12) | 0.2321(4) | 0.0620(3) | −0.1616(6) | 0.036(1) |
| O(13) | 0.5542(5) | −0.0647(4) | −0.2428(6) | 0.044(1) |
| H(1)* | 0.179(9) | 0.310(7) | 0.211(11) | 0.09(3) |
| H(91)* | 0.270(7) | 0.778(6) | 0.543(9) | 0.07(2) |
| H(92)* | 0.125(7) | 0.805(6) | 0.375(9) | 0.10(3) |
| H(101)* | 0.527(9) | 0.227(8) | −0.234(10) | 0.10(3) |
| H(102)* | 0.636(9) | 0.230(7) | −0.111(9) | 0.05(2) |
| H(111)* | 0.032(7) | 0.074(6) | 0.371(11) | 0.05(2) |
| H(112)* | 0.186(7) | 0.056(6) | 0.274(8) | 0.05(2) |
| H(121)* | 0.333(9) | 0.033(7) | −0.191(10) | 0.11(3) |
| H(122)* | 0.241(7) | 0.137(6) | −0.146(9) | 0.05(2) |
| H(131)* | 0.528(8) | −0.104(6) | −0.320(8) | 0.07(2) |
| H(132)* | 0.554(16) | −0.138(11) | −0.127(21) | 0.33(8) |

*Note:* Atoms marked with * were refined isotropically. The equivalent isotropic temperature factors are defined as $U_{eq} = [\beta_{11}\alpha^2 + \cdots + 2\beta_{23}bc(\cos\alpha)]/6\pi^2$.

independence from external influences, with the exception of hydrogen bonding. Although this observation is at the limit of significance, considering the standard deviation, it suggests good accuracy of our results. The three shorter bonds in the $AsO_3OH$ ion are definitely shorter than the three shorter bonds in the $AsO_4$ group. This is in agreement with bond-strength theory. The average of the four As–O bond lengths is nearly the same (1.691 vs. 1.689 Å, respectively) for the two groups, and the difference might not be significant.

The three independent Mn atoms are each linked to six oxygen atoms in an essentially regular octahedral coordination. The average Mn–O distance is 2.186 Å, compared to the average of 2.21 Å reported in the literature for $Mn^{2+}$ (e.g., the *International Tables for X-ray Crystallography,* MacGillavry and Rieck, 1968). This virtually excludes the presence of Mn in the 3+ oxidation state. If the concept of "bond strength" as defined by Pauling is used and the bond strengths are estimated according to Brown and Wu (1976), their sums to the cations in the

**TABLE 6.** Anisotropic thermal parameters (Å$^2$) in geigerite

| | $U_{11}$ | $U_{22}$ | $U_{33}$ | $U_{12}$ | $U_{13}$ | $U_{23}$ |
|---|---|---|---|---|---|---|
| As(1) | 0.0085(2) | 0.0098(2) | 0.0076(2) | −0.0015(2) | −0.0004(2) | −0.0011(1) |
| As(2) | 0.0072(2) | 0.0061(2) | 0.0073(2) | −0.0008(2) | −0.0007(1) | −0.0008(1) |
| M(1) | 0.0150(4) | 0.0093(4) | 0.0176(4) | −0.0006(3) | −0.0021(4) | −0.0011(4) |
| M(2) | 0.0106(2) | 0.0102(3) | 0.0094(3) | −0.0011(2) | −0.0007(2) | −0.0018(2) |
| M(3) | 0.0095(2) | 0.0117(3) | 0.0090(3) | −0.0018(2) | −0.0010(2) | −0.0014(2) |
| O(1) | 0.009(1) | 0.017(1) | 0.016(1) | −0.003(1) | −0.003(1) | −0.002(1) |
| O(2) | 0.013(1) | 0.012(1) | 0.019(1) | 0.003(1) | −0.006(1) | 0.001(1) |
| O(3) | 0.013(1) | 0.016(1) | 0.008(1) | −0.006(1) | 0.000(1) | 0.002(1) |
| O(4) | 0.012(1) | 0.013(1) | 0.009(1) | −0.001(1) | −0.002(1) | −0.003(1) |
| O(5) | 0.012(1) | 0.007(1) | 0.021(1) | −0.004(1) | −0.003(1) | −0.001(1) |
| O(6) | 0.015(1) | 0.010(1) | 0.007(1) | −0.004(1) | −0.004(1) | 0.001(1) |
| O(7) | 0.008(1) | 0.012(1) | 0.013(1) | −0.002(1) | −0.004(1) | 0.001(1) |
| O(8) | 0.011(1) | 0.012(1) | 0.011(1) | 0.002(1) | 0.001(1) | −0.003(1) |
| O(9) | 0.015(1) | 0.020(2) | 0.020(2) | −0.004(1) | −0.002(1) | 0.001(1) |
| O(10) | 0.014(1) | 0.019(2) | 0.021(2) | 0.001(1) | −0.002(1) | −0.005(1) |
| O(11) | 0.032(2) | 0.026(2) | 0.026(2) | −0.008(1) | −0.004(1) | −0.009(1) |
| O(12) | 0.024(2) | 0.020(2) | 0.061(3) | −0.006(1) | 0.017(2) | −0.008(2) |
| O(13) | 0.032(2) | 0.041(2) | 0.067(2) | 0.004(2) | −0.012(2) | −0.033(2) |

*Note:* Thermal parameters are of the form $\exp[-2\pi^2(U_{11}a^{*2}h^2 + \cdots + 2U_{23}a^*b^*hk]$.

**Table 7.** Bond distances (Å) and angles (°) in geigerite

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | **As(1)O$_3$(OH) tetrahedron** | | | | | **As(2)O$_4$ tetrahedron** | | | |
| As(1)–O(1) | 1.752(3) | 1.740* | | | As(2)–O(7) | 1.702(2) | 1.699* | | |
| –O(3) | 1.672(3) | 1.675* | | | –O(8) | 1.688(2) | 1.684* | | |
| –O(4) | 1.671(3) | 1.671* | | | –O(5) | 1.684(3) | 1.680* | | |
| –O(2) | 1.671(3) | 1.669* | | | –O(6) | 1.683(2) | 1.679* | | |
| mean | 1.691 | 1.689* | | | mean | 1.689 | 1.686* | | |
| | | | Angle at As(1) | | | | | Angle at As(2) | |
| O(1)–O(2) | 2.719(3) | 2.699* | 105.2(1) | 104.7* | O(5)–O(6) | 2.742(3) | 2.739* | 109.0(1) | 109.3* |
| O(1)–O(3) | 2.719(4) | 2.709* | 105.1(1) | 105.0* | O(5)–O(7) | 2.776(4) | 2.761* | 110.1(1) | 109.6* |
| O(1)–O(4) | 2.770(4) | 2.777* | 108.1(1) | 109.0* | O(5)–O(8) | 2.764(4) | 2.759* | 110.1(1) | 110.2* |
| O(2)–O(3) | 2.794(3) | 2.798* | 113.3(1) | 113.6* | O(6)–O(7) | 2.757(3) | 2.747* | 109.0(1) | 108.9* |
| O(2)–O(4) | 2.766(4) | 2.751* | 111.7(1) | 110.9* | O(6)–O(8) | 2.769(3) | 2.767* | 110.4(1) | 110.7* |
| O(3)–O(4) | 2.785(4) | 2.792* | 112.8(1) | 113.1* | O(7)–O(8) | 2.745(3) | 2.739* | 108.2(1) | 108.2* |
| O(1)–H(1) | 1.02(7) | | | | | | | | |
| As–O–H | | | 110(4) | | | | | | |
| | **M(1) octahedron** | | | | | **M(2) octahedron** | | | |
| M(1)–O(5)$^{A}$(× 2) | 2.197(2) | 2.119* | | | M(2)–O(1) | 2.258(2) | 2.169* | | |
| –O(11) (× 2) | 2.186(3) | 2.075* | | | –O(6) | 2.190(3) | 2.091* | | |
| –O(12) (× 2) | 2.179(3) | 2.068* | | | –O(4)$^{C}$ | 2.177(2) | 2.092* | | |
| mean | 2.196 | 2.087* | | | –O(9) | 2.168(3) | 2.062* | | |
| | | | | | –O(8)$^{D}$ | 2.132(3) | 2.051* | | |
| | | | | | –O(6′)$^{C}$ | 2.116(3) | 2.043* | | |
| | | | | | mean | 2.173 | 2.085* | | |
| | | | Angle at M(1) | | | | | Angle at M(2) | |
| O(5)–O(11) | 3.000(5) | 2.905* | 86.4(1) | 87.7* | O(1)–O(6) | 2.901(4) | 2.792* | 81.4(1) | 81.9* |
| O(5)–O(11)$^{B}$ | 3.193(4) | 3.024* | 93.5(1) | 92.3* | O(1)–O(6′) | 3.143(4) | 3.006* | 91.8(1) | 91.0* |
| O(5)–O(12) | 3.215(4) | 3.037* | 94.5(1) | 93.0* | O(1)–O(8) | 3.302(3) | 3.195* | 97.5(1) | 98.4* |
| O(5)–O(12)$^{B}$ | 2.972(4) | 2.882* | 85.6(1) | 87.0* | O(1)–O(9) | 3.024(4) | 2.881* | 86.2(1) | 85.8* |
| O(11)–O(12) | 3.051(5) | 2.898* | 88.7(1) | 88.8* | O(4)–O(6) | 2.967(3) | 2.887* | 87.4(1) | 87.7* |
| O(11)–O(12)$^{B}$ | 3.120(5) | 2.960* | 91.3(1) | 91.2* | O(4)–O(6′) | 2.977(3) | 2.899* | 86.0(1) | 88.6* |
| | | | | | O(4)–O(8) | 2.844(4) | 2.703* | 82.6(1) | 81.4* |
| | **M(3) octahedron** | | | | O(4)–O(9) | 3.480(4) | 3.287* | 106.4(1) | 104.6* |
| M(3)–O(10)$^{E}$ | 2.252(3) | 2.158* | | | O(6)–O(6′) | 2.976(5) | 2.801* | 87.4(1) | 85.3* |
| –O(7)$^{C}$ | 2.219(3) | 2.148* | | | O(6′)–O(9) | 3.135(4) | 3.010* | 94.1(1) | 94.3* |
| –O(8)$^{E}$ | 2.186(2) | 2.114* | | | O(8)–O(9) | 3.051(4) | 2.919* | 90.4(1) | 90.4* |
| –O(3′)$^{F}$ | 2.177(3) | 2.091* | | | | | | | |
| –O(4) | 2.161(3) | 2.073* | | | | | | | |
| –O(3)$^{E}$ | 2.136(3) | 2.044* | | | | | | | |
| mean | 2.189 | 2.105* | | | | | | | |
| | | | Angle at M(3) | | | | | | |
| O(3)–O(3′) | 2.730(5) | 2.599* | 78.5(1) | 77.9* | | | | | |
| O(3)–O(7) | 3.303(4) | 3.184* | 98.6(1) | 98.8* | | | | | |
| O(3)–O(8) | 3.210(3) | 3.095* | 95.9(1) | 96.2* | | | | | |
| O(3)–O(10) | 3.107(4) | 2.978* | 90.1(1) | 90.2* | | | | | |
| O(3′)–O(4) | 3.043(4) | 2.948* | 89.1(1) | 90.1* | | | | | |
| O(3′)–O(8) | 3.219(3) | 3.188* | 95.1(1) | 98.6* | | | | | |
| O(3′)–O(10) | 3.309(4) | 3.123* | 96.7(1) | 94.6* | | | | | |
| O(4)–O(7) | 3.198(3) | 3.078* | 93.8(1) | 93.6* | | | | | |
| O(4)–O(8) | 2.844(4) | 2.073* | 81.7(1) | 80.4* | | | | | |
| O(4)–O(10) | 3.245(3) | 3.140* | 94.7(1) | 95.8* | | | | | |
| O(7)–O(8) | 3.044(4) | 2.739* | 87.4(1) | 87.1* | | | | | |
| O(7)–O(10) | 2.905(3) | 2.764* | 81.0(1) | 79.9* | | | | | |

*Note:* Symmetry transformations are (A) $x - 1, y, z$; (B) $-x, -y, -z$; (C) $1 - x, -y, 1 - z$; (D) $1 - x, -y, -z$; (E) $x, y, 1 + z$; (F) $1 - x, 1 - y, 1 - z$. Esd's are in parentheses.

* Corresponding distances and angles for chudobaite.

structure are remarkably close to a value of 2. They range, in fact, from 1.96 to 2.09. This also confirms the existence of Mn in the 2+ oxidation state, exclusively.

Hydrogen bond O···O distances are given in Table 8. All the H atoms in the structure are involved in hydrogen bonding, and such bonds range from 2.572 to 3.154 Å in length. Still longer distances (3.264 to 3.373 Å, or more), whose geometry is compatible with hydrogen bonds, are present, but they are at the limit between true hydrogen bonds and normal nonbonded O···O contacts. For this reason, they are not reported in Table 8.

Of the hydrogen bonds in this structure, O(1)–O(7) is particularly strong, being 2.572 Å. This shortness is not exceptional in acid compounds, and here the donor is the acid H of the AsO$_3$OH group. The angle O–H···O is large (174°), in agreement with previous observations for strong hydrogen bonds (Hamilton, 1962; Pedersen, 1974; Brown, 1976). The effect of such a strong hydrogen bond joining the two crystallographically independent arsenate ions is quite evident also in the normal AsO$_4$ group: the As(2)–O(7) distance (1.702 Å) is significantly longer than the average of the other As(2)–O distances, in agreement with similar observations (see, for instance, Donnay and Allmann, 1970). No statistical distribution of the hydrogen

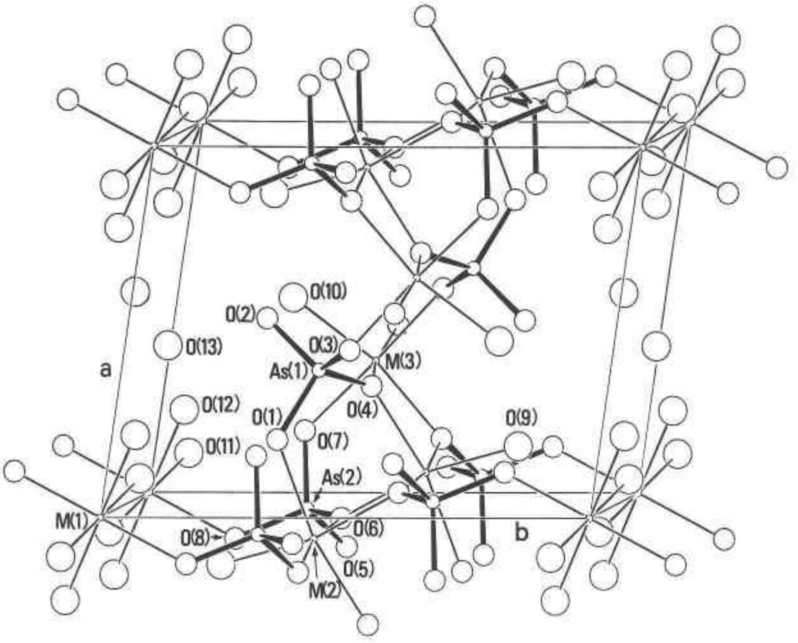

Fig. 4. The geigerite structure, as seen along the $c^*$ axis.

between O(1) and O(7) is observed, since no minor peak is found close to O(7) in the final difference-Fourier map. Therefore the "acid" and the "normal" arsenate groups are quite independent in the crystal structure.

Another remarkable feature of geigerite is the presence of a particular network of hydrogen bonds, whose number exceeds the number of H atoms present. In fact, all the hydrogen bonds longer than 2.80 Å are multiple [with the only exception of O(13) as donor], and the list of multiplicities would substantially increase if the O···O contacts from 3.2 to 3.4 Å were considered. According to many authors, such hydrogen bonds are called bifurcated, but Chiari and Ferraris (1982) consider bifurcated hydrogen bonds to be only those in which the two bonds have comparable strength. The additional weak bonds are called second weak contacts. In geigerite, all the longest bonds involve weak contacts of this kind, and the only bifurcated bonds in the strict sense might be, for instance, the ones concerning H(92). Therefore, it seems that hydrogen-bonding capability can be exhausted by making a single strong bond, or two weak ones, or a moderately strong bond plus a very weak one. This is in agreement with recent observations (Brown, 1976; Chiari and Ferraris, 1982). There is also agreement with the electrostatic explanation of the hydrogen bond, if the effect of induced charge is taken into account.

Some O···O hydrogen bonds can take place statistically through different atoms. For instance, the O(9)–O(11)

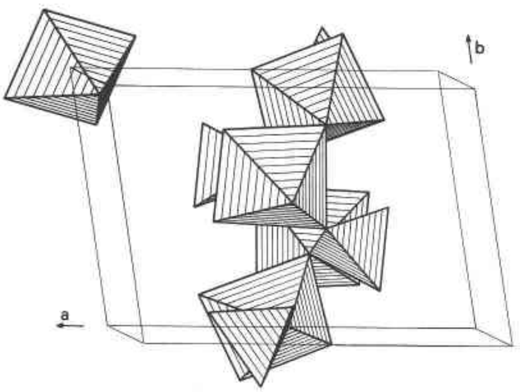

Fig. 5. Polyhedra in the geigerite structure, as seen along the $c^*$ axis.

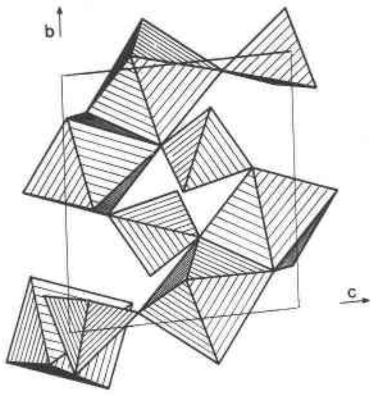

Fig. 6. Polyhedra in the geigerite structure, as seen along the $a$ axis.

**TABLE 8.** Hydrogen bond distances (Å) and angles (°) in geigerite

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| O(1)–O(7)$^{A}$ | 2.572(4) | 2.535* | O(1)–H(1) | 1.02(8) | H···O(7) | 1.55(8) | 174(7) |
| O(9)–O(2)$^{B}$ | 2.664(4) | 2.647* | O(9)–H(91) | 0.92(6) | H···O(2) | 1.78(6) | 162(6) |
| O(10)–O(2)$^{C}$ | 2.720(5) | 2.664* | O(10)–H(101) | 0.85(7) | H···O(2) | 1.90(7) | 162(8) |
| O(12)–O(13)$^{A}$ | 2.766(5) | 2.756* | O(12)–H(121) | 0.84(7) | H···O(13) | 1.94(7) | 169(7) |
| O(13)–O(2)$^{D}$ | 2.772(6) | 2.744* | O(13)–H(131) | 0.78(7) | H···O(2) | 2.00(7) | 167(6) |
| O(10)–O(5)$^{E}$ | 2.780(4) | 2.797* | O(10)–H(102) | 0.83(7) | H···O(5) | 1.96(7) | 177(8) |
| O(12)–O(7)$^{A}$ | 2.835(5) | 2.824* | O(12)–H(122) | 0.84(6) | H···O(7) | 2.06(6) | 153(5) |
| O(11)–O(13)$^{D}$ | 2.880(5) | 2.880* | O(11)–H(112) | 0.82(6) | H···O(13) | 2.06(6) | 171(6) |
| O(11)–O(9)$^{F}$ | 2.895(5) | 2.886* | O(11)–H(111) | 0.82(7) | H···O(9) | 2.15(6) | 150(7) |
| O(9)–O(11) | | | O(9)–H* | 0.74(14) | H···O(11) | 2.29(12) | 139(13) |
| O(9)–O(5)$^{G}$ | 2.902(5) | 2.852* | O(9)–H(92) | 0.99(6) | H···O(5) | 1.94(6) | 163(5) |
| O(12)–O(5)$^{A}$ | 2.972(4) | 2.882* | O(12)–H(122) | 0.84(6) | H···O(5) | 2.83(5) | 91(4) |
| O(13)–O(10)$^{D}$ | 2.978(5) | 2.926* | O(13)–H(132) | 1.02(12) | H···O(10) | 2.00(12) | 159(10) |
| O(9)–O(11)$^{H}$ | 2.989(4) | 3.011* | O(9)–H(92) | 0.99(6) | H···O(11) | 2.52(6) | 109(4) |
| O(11)–O(12)$^{A}$ | 3.051(5) | 2.898* | O(11)–H(112) | 0.82(6) | H···O(12) | 2.93(6) | 91(4) |
| O(9)–O(6)$^{G}$ | 3.135(5) | 3.010* | O(9)–H(92) | 0.99(6) | H···O(6) | 2.76(6) | 103(4) |
| O(11)–O(1)$^{A}$ | 3.154(5) | 3.147* | O(11)–H(111) | 0.82(7) | H···O(1) | 2.89(6) | 101(5) |
| O(11)–O(1) | | | O(11)–H(112) | 0.82(6) | H···O(1) | 2.81(6) | 108(4) |

*Note:* Symmetry transformations are (A) *x*, *y*, *z*; (B) 1 − *x*, 1 − *y*, 1 − *z*; (C) *x*, *y*, *z* − 1; (D) 1 − *x*, −*y*, −*z*; (E) *x* + 1, *y*, *z*; (F) −*x*, 1 − *y*, 1 − *z*; (G) −*x*, 1 − *y*, −*z*; (H) *x*, 1 + *y*, *z*. Esd's are in parentheses.

* Corresponding O–O distances in chudobaite.

bond can alternatively use either O(9) or O(11) as donors (see Table 8). The residual peak in the difference-Fourier map (mentioned as H* in Table 8) is very probably due to a disordered distribution of the H atoms arouond O(9), a situation that is similar to that in ice. In other cases [such as O(11)···O(1)] the same hydrogen bond can take place using two different H atoms; however, the distance is so large that we are at the limit between true bonds and weak contacts.

## RELATIONSHIP TO OTHER MINERALS

Apart from an excess of water, geigerite might be considered to be essentially the arsenate equivalent of the well-known phosphate huréaulite, $Mn_5(H_2O)_4(PO_3OH)_2(PO_4)_2$. In this mineral (Moore and Araki, 1973), all the water molecules are bonded to the metal, and no zeolitic water molecules are present. In spite of a much larger water content, only one (independent) molecule in geigerite is not bonded to metal atoms, i.e., the one including O(13), which can be called zeolitic. For this reason, the geigerite formula can best be written as $Mn_5(H_2O)_8(AsO_3OH)_2(AsO_4)_2 \cdot 2H_2O$. Unlike huréaulite, the oxygen atom of the OH group in the $AsO_3OH$ ion is bonded to a Mn atom [Mn(2)].

As with huréaulite, the possibility of having empty cavities (Moore and Araki, 1973) in the structure was examined. For this purpose, the program OPEC (Gavezzotti, 1983) was used. A single cavity was indeed found centered at $x = 0.2$, $y = 0.2$, $z = 0.7$, which is about 2.3 Å away from the nearest oxygen atoms and 1.8 Å away from the nearest H atom. However, whereas in huréaulite the acid H seems to be associated with this cavity, here all the H atoms that are near to the cavity are water hydrogens. No similarity between the two structures in this respect is therefore evident.

Such a cavity might be, at least in principle, a good "hiding place" for some extraneous cations; however, no peak in the final difference synthesis occurs in the cavity, and even the presence of light elements such as Li or Be should be revealed under these conditions. Therefore, any residual uncertainty about the chemical formula can be ruled out.

A thorough inspection of all the data concerning natural arsenates reveals a close connection of geigerite with the very rare species chudobaite. Although Strunz (1960) gave the formula of chudobaite as $(Na,K,Ca)(Mg,Zn,Mn)_2H(AsO_4)_2 \cdot 4H_2O$, a revised formula, $(Mg,Zn)_5H_2(AsO_4)_4 \cdot 10H_2O$, was proposed by Dorner and Weber (1976), who determined the structure of the mineral. The latter can be rewritten as $(Mg,Zn)_5(H_2O)_8(AsO_3OH)_2(AsO_4)_2 \cdot 2H_2O$, in excellent agreement with our proposed formula for geigerite. In view of the similarity of the ionic radii of $Mn^{2+}$ and $Mg^{2+}$, an isotypic relationship between the two minerals is very likely to exist. The unit cell for chudobaite reported by Dorner and Weber can be transformed into an equivalent one with $a = 7.797$, $b = 10.485$, $c = 6.616$ Å, $\alpha = 80.53°$, $\beta = 84.23°$, and $\gamma = 82.12°$ (the transformation matrix of coordinates is (−100/010/0−11), in close agreement with the unit cell of geigerite (see Table 4). The structural work by Dorner and Weber on chudobaite was critized by Fleischer (1977), apparently on the basis that the original analysis (and formula) given by Strunz (1960) showed the presence of nonnegligible amounts of Na, K, and Ca, whereas they are absent in the new formula. However, the very low value of the final discrepancy factor *R* (2.4%) and the number of collected data (2682 reflections) leave little doubt about the validity of the structure and of the new formula. The analogy with the geigerite structure, which was solved by us independently, is another point in favor of the results. Moreover (see above), no residual peak corresponding to possible neutralization of the acid H atom by alkali metals or alkaline earths is evident in the final difference-Fourier map of geigerite.

Although we consider Fleischer's criticism of the work of Dorner and Weber (1976) to be excessive, the results reported by those authors are not entirely satisfactory. In particular, the published coordinates do not lead to an acceptable geometry, and no bond lengths and angles are given. Some outright errors are evident: for instance, by comparison with geigerite, we found that all the minus signs (where needed) in the atomic coordinates are omitted. Starting from the isotypic relationship of the two crystal structures, it was possible to correct all the coordinates of chudobaite. They are reported in Table 2A (see footnote 1), referred to the new unit cell proposed by us. By using the corrected coordinates, the bond lengths and angles in chudobaite become reasonable and close to the corresponding ones in geigerite. For instance, the acid $AsO_3OH$ group is linked to the normal $AsO_4$ group by a very strong hydrogen bond (2.535 Å), which is even stronger than in geigerite.

The other bond lengths and angles for chudobaite are reported in Table 7, next to the corresponding values for geigerite. Such a comparison is interesting and useful, especially because no list of bond distances and angles is reported in the paper by Dorner and Weber. As one might expect, the similarity is striking in the geometry of the arsenate groups, whereas the metal–oxygen distances of chudobaite (average 2.092 Å) are smaller than those of geigerite. The average M–O distance reported in the literature (see, for instance, the *International Tables for X-Ray Crystallography,* MacGillavry and Rieck, 1968) is 2.07 (or 2.10 Å) for sixfold-coordinated Mg, or 2.10 Å for Zn. This is in excellent agreement with Dorner and Weber's structure and explains the difference with geigerite. The decrease in the unit-cell parameters and in the metal–oxygen bonds on going from geigerite to chudobaite is also an indirect proof of the analytical results and of the consequent nonidentity between the two species.

## ACKNOWLEDGMENTS

Walter Cabalzar, Chur (Canton of Grisons), sent us the original samples for the inspection and kindly provided us with the material requested for the study. Preliminary investigations of the mineral were carried out in the SEM laboratory, Geological Institute, University of Basel (Operator M. Düggelin). Help and advice from the chairman of the Commission on New Minerals and Mineral Names, J. A. Mandarino, is gratefully acknowledged.

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MANUSCRIPT RECEIVED JUNE 6, 1988
MANUSCRIPT ACCEPTED JANUARY 9, 1989