

Crystal structure of grischunite

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ABSTRACT

The crystal structure of grischunite ($a = 12.855$, $b = 13.487$, $c = 12.047$ Å, space group $Pcab$, $Z = 4$) has been determined and refined to $R = 0.036$ using 2393 reflections. The structure consists of insular AsO_4 groups, which are joined by octahedral oxygen-coordination polyhedra around (Mn^{2+}, Fe^{3+}) and Na^+ , and by irregular oxygen-coordination polyhedra of order eight around Ca^{2+} . The determination of the structure leads to a new formula for the mineral, $NaCa_2Mn_4(Mn_{0.5}^{2+}, Fe_{0.5}^{3+})_2(H_2O)_2(AsO_4)_6$, and grischunite is therefore an aquated arsenate. The agreement of the new formula with the chemical analysis is superior for the AsO_4 groups (average 1.684 Å) to the previous $(Ca, Na)(Mn^{2+}, Fe^{3+})_2(AsO_4)_2$. All the bond lengths involving M(1) and M(2) are in accord with typical values. Around the M atoms with octahedral coordination, the M–O bond distances range between 2.089 and 2.391 Å, but around M(2) with an average M(2)–O of 2.090 Å, the range is between 2.013 and 2.134 Å. These latter values suggest a substitution by Fe^{3+} for about 50% of Mn^{2+} ; the presence of significant amounts of vacancies (\square) is suggested in the Na^+ position ($x_{Na} = 0.730$, $x_{Ca} = 0.126$, $x_{\square} = 0.144$, where x is the fractional occupancy by each species).

INTRODUCTION

In recent years, a considerable number of rare arsenates have been discovered in the old manganese mine at Falotta, Graubünden, Switzerland (Graeser and Stalder, 1976; Graeser et al., 1978; Hansen and Fälth, 1984; Hansen et al., 1984). Many of these species are similar or identical to the “classic” Långban- or Franklin-type minerals. However, others seem to be unique to the locality. Among these, grischunite was the first to be discovered and studied in detail (Graeser et al., 1984). However, owing to the paucity of available material, the chemical composition could not be fully ascertained, and the compatibility index with respect to the Gladstone-Dale relationship (Mandarino, 1981) was poor. In this respect, the question of the oxidation states of Fe and Mn in the mineral and of the possible presence of water had to be settled. Professor Graeser, from the University and Natural History Museum of Basel, kindly brought these problems to our attention and supplied us with a good crystal from the holotype material, whose quality permitted a precise structural study.

DETERMINATION OF THE STRUCTURE

From a crystal fragment measuring about $50 \times 100 \times 150$ μm , a new determination of the unit-cell dimensions was performed by mounting it on a Nonius CAD-4 diffractometer. The final results [$a = 12.855(2)$, $b =$

$13.487(2)$, $c = 12.047(1)$ Å] have been determined and refined from 24 reflections with 2θ around 50° , using $MoK\alpha$ radiation ($\lambda = 0.71069$ Å). They are similar to the corresponding values reported by Graeser et al. (1984). The Laue symmetry is mmm , and extinctions are present for $0kl$ ($l \neq 2n + 1$), $h0l$ ($h \neq 2n + 1$), and $hk0$ ($k \neq 2n + 1$), thereby confirming the previous determination of the space group as $Pcab$ (D_{2h}^{12}).

Of 2393 independent reflections, which were collected on the Nonius diffractometer, 1739 for which $I > \sigma(I)$ were used in the refinement. Since the crystal was rather irregular in shape and owing to the great risk of damage by grinding it into a sphere, an empirical absorption correction was applied using the procedure of Walker and Stuart (1983). The structure was solved by direct methods, using the program MULTAN (Main, 1977), and all peaks corresponding to the heavier atoms were easily identified from the E map. The refinement was conducted by least-squares, and the final weights were $4|F_o|^2/\sigma^2(|F_o|^2)$. The variance of each reflection, $\sigma^2(I)$, was assigned according to the formula $\sigma^2(I) = \sigma_{cs}^2(I) + (0.03I)^2$, where σ_{cs}^2 is the variance as derived from counting statistics. Atomic form factors corresponding to neutral atoms were taken from Cromer and Waber (1965), and anomalous dispersion corrections, $\Delta f'$ and $\Delta f''$, from Cromer (1965).

The final R index for the observed reflections is 0.036, and the discrepancy factor among the F_o values of crystallographically equivalent reflections is 0.038. The latter value confirms the validity of Walker and Stuart's absorption correction. The only flaw might be a systematic

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TABLE 1. Atomic coordinates and equivalent isotropic thermal parameters

| | x | y | z | B* (Å ²) |
|-------|------------|------------|------------|----------------------|
| As(1) | 0.38647(5) | 0.30184(5) | 0.22290(5) | 0.48(1) |
| As(2) | 0.10259(5) | 0.44276(5) | 0.24941(6) | 0.50(1) |
| As(3) | 0.27068(5) | 0.12342(5) | 0.46957(5) | 0.60(1) |
| M(1) | 0.14943(8) | 0.20588(8) | 0.22049(8) | 0.72(2) |
| M(2) | 0.33363(9) | 0.04294(8) | 0.21900(8) | 0.93(2) |
| M(3) | 0.02378(9) | 0.26978(8) | 0.45401(8) | 0.99(2) |
| Ca | 0.2626(1) | 0.3725(1) | 0.4908(1) | 0.62(2) |
| Na | 0.000 | 0.000 | 0.000 | 1.89(9) |
| O(1) | 0.4999(4) | 0.2697(4) | 0.2827(3) | 0.73(9) |
| O(2) | 0.4065(4) | 0.3429(4) | 0.0935(4) | 0.97(9) |
| O(3) | 0.3140(4) | 0.1989(4) | 0.2119(4) | 1.23(9) |
| O(4) | 0.3297(4) | 0.3864(4) | 0.3055(4) | 0.89(9) |
| O(5) | 0.1704(4) | 0.5489(4) | 0.2539(5) | 1.29(9) |
| O(6) | 0.1608(4) | 0.3581(4) | 0.1684(4) | 0.70(9) |
| O(7) | 0.0929(4) | 0.4040(4) | 0.3807(4) | 0.76(9) |
| O(8) | -0.0114(4) | 0.4684(4) | 0.1873(4) | 1.4(1) |
| O(9) | 0.1908(4) | 0.2105(3) | 0.4139(4) | 0.90(9) |
| O(10) | 0.3632(4) | 0.1906(4) | 0.5373(4) | 1.3(1) |
| O(11) | 0.2020(4) | 0.0433(4) | 0.5480(4) | 1.4(1) |
| O(12) | 0.3414(5) | 0.0493(4) | 0.3857(4) | 2.2(1) |
| O(13) | -0.0257(4) | 0.1177(4) | 0.4843(4) | 1.09(9) |
| H(1) | 0.031 | 0.090 | 0.555 | |
| H(2) | -0.008 | 0.078 | 0.424 | |

* The equivalent isotropic thermal parameters is defined as $B = 4/3(\Sigma B_{ij}a_i a_j)$.

decrease of all the temperature factors relative to their physically significant counterparts, but this is of marginal importance for the objective of our investigation.

In the last stage of the refinement, both temperature factors and peaks on the Fourier synthesis indicated a substantial difference in the atomic content for three positions. These had been assigned initially to Ca, replaced in part by Na according to the formula $(Ca^{2+}, Na^+)(Mn^{2+}, Fe^{3+})_2(AsO_4)_2$, which had been originally proposed for the mineral by Graeser et al. (1984). Our results indicate a prevalence of Na over Ca at the origin, whereas two other sites equivalent by symmetry are essentially filled by Ca atoms; the structure is therefore essentially ordered with respect to this substitution.

Of the three crystallographically nonequivalent sites containing transition metals in octahedral coordination with oxygen, M(2) has shorter distances to the adjacent oxygen atoms (average 2.090 Å) than either M(1) or M(3) (averages 2.189 and 2.230 Å, respectively). Since the average distance for $^{VI}Mn^{2+}-O$ is 2.21 Å, and the $^{VI}Fe^{3+}-O$ distance is 2.01 Å (MacGillavry and Rieck, 1968), this suggests a partial substitution by Fe^{3+} for Mn^{2+} , principally in the M(2) position. This substitution by Fe^{3+} for about one-half of the Mn^{2+} in the M(2) position is necessary for balancing the substitution for one-third of the Ca^{2+} by Na^+ ; it is also suggested by bond-strength considerations.

The final atomic coordinates and their standard deviations are reported in Table 1, together with the "equivalent" isotropic temperature factors. The anisotropic factors, which have been assigned to all non-H atoms in the refinement, are given in Table 2. Projections along [001] of the crystal structure are shown in Figures 1 and 2.

TABLE 2. Anisotropic thermal parameters ($\times 10^3$) for grischunite

| | B_{11} | B_{22} | B_{33} | B_{12} | B_{13} | B_{23} |
|-------|----------|----------|----------|----------|----------|----------|
| As(1) | 58(3) | 91(4) | 71(3) | -11(7) | -04(6) | -25(6) |
| As(2) | 95(3) | 61(3) | 73(3) | 31(7) | -29(7) | -04(6) |
| As(3) | 95(4) | 57(3) | 132(4) | -08(7) | -71(7) | -05(7) |
| M(1) | 80(5) | 89(5) | 167(6) | 02(1) | 05(1) | 02(1) |
| M(2) | 129(6) | 127(6) | 171(6) | 02(1) | -02(1) | -02(1) |
| M(3) | 187(6) | 141(6) | 118(6) | -15(1) | -01(1) | -03(1) |
| Ca | 89(7) | 121(6) | 65(7) | -09(1) | -1(1) | 06(1) |
| Na | 14(3) | 33(3) | 40(3) | 07(4) | -12(5) | 52(5) |
| O(1) | 02(2) | 20(3) | 11(3) | -03(5) | -09(5) | 05(5) |
| O(2) | 17(3) | 20(3) | 07(3) | 06(5) | 06(5) | -01(5) |
| O(3) | 10(3) | 13(3) | 36(3) | -15(5) | -06(5) | -03(6) |
| O(4) | 10(3) | 19(3) | 10(3) | 02(5) | 08(5) | -11(5) |
| O(5) | 30(3) | 06(3) | 25(3) | -07(6) | 04(7) | 09(5) |
| O(6) | 15(3) | 07(3) | 11(3) | 06(5) | 02(5) | -06(5) |
| O(7) | 20(3) | 07(3) | 07(3) | -04(5) | 08(5) | 01(4) |
| O(8) | 15(3) | 30(3) | 19(3) | 20(6) | -11(6) | 02(6) |
| O(9) | 14(3) | 08(3) | 21(3) | 11(5) | 02(5) | -02(5) |
| O(10) | 15(3) | 22(3) | 19(3) | -26(5) | -01(5) | -11(6) |
| O(11) | 22(3) | 05(3) | 39(4) | -12(5) | -25(6) | 20(5) |
| O(12) | 40(4) | 30(3) | 30(4) | 48(6) | -39(6) | -42(6) |
| O(13) | 22(3) | 09(2) | 20(3) | 01(6) | 10(6) | 08(5) |

Note: The form of the anisotropic thermal parameter is $\exp(-B_{11}h^2 - B_{22}k^2 - B_{33}l^2 - B_{12}hk - B_{13}hl - B_{23}kl)$.

The standard deviation in the M-O distances (with M being a Mn, Ca, or As atom) is about 0.005 Å on the basis of residuals and the normal-equation matrix in the final least-squares cycle; for the O-M-O angles, it is about 0.15°. The effect of thermal libration on such distances is substantially greater than their estimated standard deviation, since it amounts to about 0.01 Å; however, no corrections can be applied for lack of a suitable model. Bond lengths and angles are reported in Table 3. Observed and calculated structure factors are given in Table 4.¹

The H atoms of the water molecule have been approximately located in a final difference-Fourier map. The peak heights on the map are 1.2 and 1.1 e Å⁻³, respectively.

DISCUSSION

In the structure of grischunite, three independent arsenate groups occur in the asymmetric unit, and they deviate only slightly from each other and from the "usual" arsenate conformation. The average As-O distance is 1.684 Å; the corresponding average for this distance in several other mineral structure types is identical (Ferraris, 1970). Since the As-OH distance is significantly longer (average 1.739 Å), this excludes the presence of AsO_4OH groups in our crystal.

Around the M(1) ion, the situation corresponds to a regular octahedral coordination; a similar situation, with shorter bonds, is also observed for the M(2) site, which contains M^{2+} and Fe^{3+} in almost equal proportions. For M(3), the coordination is still octahedral, but less regular. The deviation of O-M-O bond angles from the ideal val-

¹ To obtain a copy of Table 4, order Document AM-87-351 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.

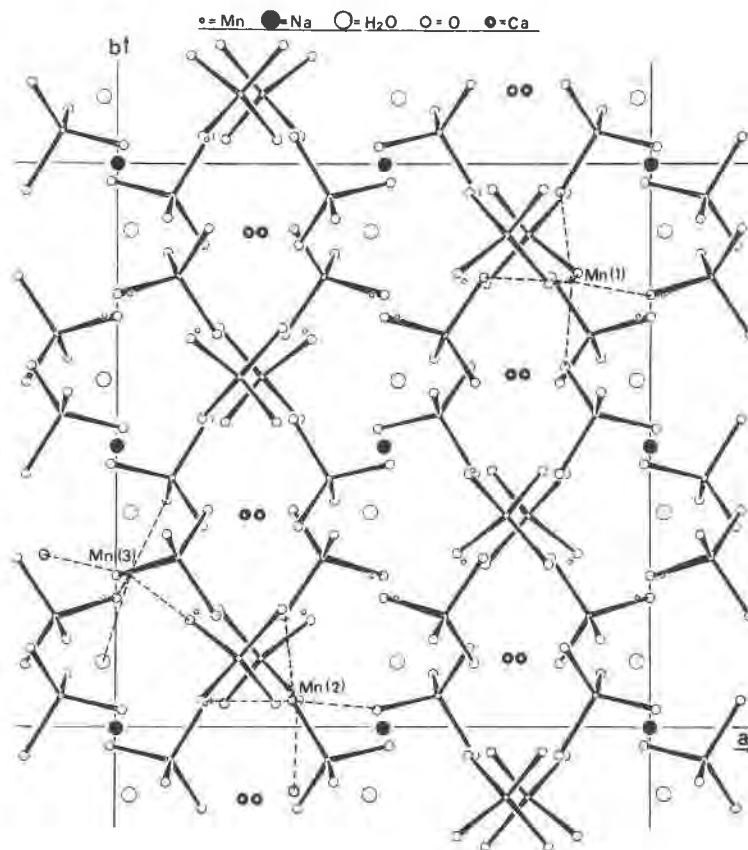


Fig. 1. Projection along c of the grischunitite structure.

ue may reach 25° (Table 3). For the Na ion, the coordination may still be described as essentially octahedral, but the arrangement of oxygen atoms around the metal ion is more irregular. For Ca^{2+} , the central ion is surrounded by eight oxygens, and the average Ca–O distance is 2.548 \AA , which is slightly larger than the reported average (2.47 \AA) in the *International Tables* (MacGillavry and Rieck, 1968). In addition, the average Na–O distance (2.503 \AA) is longer than the average (2.44 \AA). The unusually high value of the temperature factor ($B_{\text{eq}} = 1.89 \text{ \AA}^2$ vs. an average value of 0.7 \AA^2 for all the other metal atoms and 1.14 \AA^2 for oxygen atoms) suggests partial occupancy of the Na^+ site. This is in agreement with the chemical analysis, which shows a marked deficiency in Na^+ with respect to the “ideal” formula $\text{NaCa}_2\text{Mn}_3^+(\text{Mn}_{0.5}^{2+}, \text{Fe}_{0.5}^{3+})\text{(H}_2\text{O)}_2(\text{AsO}_4)_6$ (Table 5). The presence of vacancies in the alkali position appears to be a common phenomenon in phosphates of Fe, Mn, Ca, and Na, an example being alluaudite (Moore, 1971), where the leaching of alkalis is balanced by an increase in the oxidation state of Fe and Mn.

An attempt to refine the site occupancy of Na^+ together with the isotropic temperature factor yielded a contradictory result with no physical meaning owing to the strong correlation between these parameters. Another attempt

was made by constraining the temperature factor to be equivalent to the average for M atoms (0.88 \AA^2) and by refining the occupancy factor for Ca at this site in solid solution with Na whose occupancy, x_{Na} , was calculated

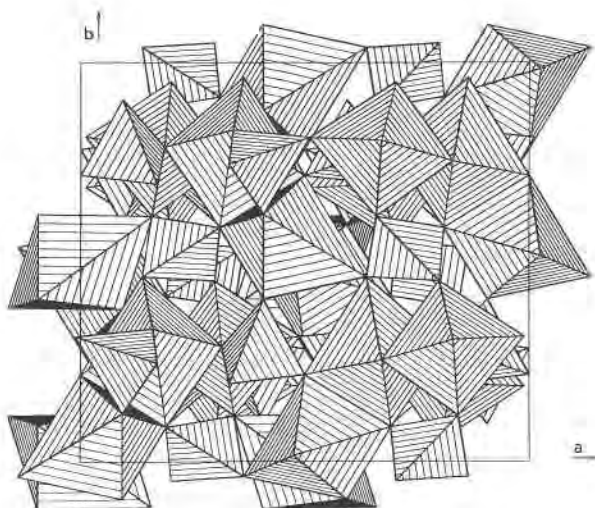


Fig. 2. Projection along c of the polyhedra arrangement in the grischunitite structure.

TABLE 5. Analytical chemical results (wt%) for grischunite compared to those of the structural analysis

| | (1) | (2) | (3) | (4) |
|--------------------------------|--------|--------|--------|--------|
| Na ₂ O | 1.74 | 1.78 | 2.38 | 1.74 |
| CaO | 9.05 | 9.19 | 8.61 | 8.91 |
| TiO ₂ | 0.08 | — | — | — |
| Fe ₂ O ₃ | 5.00 | 5.12 | 6.13 | 6.20 |
| MnO | 27.51 | 28.28 | 27.22 | 27.30 |
| As ₂ O ₅ | 54.55 | 55.64 | 52.91 | 53.08 |
| H ₂ O | 2.07 | — | 2.76 | 2.77 |
| Total | 100.00 | 100.00 | 100.00 | 100.00 |

Note: Columns are (1) average of chemical analyses by Graeser et al. (1984) (the water content is given here as the difference between 100 wt% and Graeser's total); (2) interpretation based on the chemical formula in Graeser et al. (1984); (3) calculated composition from the ideal crystallographic formula $\text{NaCa}_x\text{Mn}_2^{2+}(\text{Mn}_{0.5}^{\text{Fe}_{0.5}}\text{Fe}_{0.5}^{\text{Mn}})_2(\text{H}_2\text{O})_2(\text{AsO}_4)_6$; (4) calculated composition assuming $x_{\text{Na}} = 0.730$, $x_{\text{Ca}} = 0.126$, $x_{\square} = 0.144$.

to conform to the chemical analysis. Since the total occupancy of the Na⁺ site is $x = x_{\text{Na}} + x_{\text{Ca}} + x_{\square} = 1$, where x_{\square} is the fraction of vacancies, and $x_{\text{Na}} = 0.730$, we found by this refinement $x_{\text{Ca}} = 0.121$ and $x_{\square} = 0.144$. From these results, if we assume the charge to be balanced only by oxidation of Fe²⁺ to Fe³⁺, the composition in the fourth column of Table 5 can be deduced. After this refinement, no significant shifts of estimated structure factors were noticed with respect to the situation with the "ideal" formula. Using these new data, the compatibility index with respect to the Gladstone-Dale relationship can be defined as "excellent" (Mandarino, 1981; Graeser, 1987).

If bond strengths are estimated according to Brown and Wu (1976), the sum around the cations in the structure is in good agreement with the ion charges that are pertinent to our structural model. In fact, the sums for M(1) and M(3) are 2.06 and 1.85, respectively; and for the Ca and Na atoms they are 1.78 and 0.99, respectively. If the empirical coefficients that are intermediate between Fe³⁺ and Mn²⁺ are assumed, then the sum for M(2) is 2.52, in excellent agreement with an approximately equal mixture of these ions.

In view of their similar ionic radii, some degree of mutual substitution of Ca²⁺, Mn²⁺, and Na⁺ might be expected. For instance, a partial substitution with Na⁺ might explain the relatively long Ca–O distance, and/or the corresponding relatively low value of the bond-valence sums for Ca or M(3), and the irregular coordination around M(3). However, this should involve a corresponding substitution of Na⁺ by more Ca²⁺ than the value reported above. The temperature factor of Ca²⁺, which is definitely lower than average, militates against extensive substitution by Na⁺. Rather, it may indicate a possible substitution by Mn²⁺, but this contradicts the relatively large value of the Ca–O mean distance. In conclusion, the data that seem to point to significant substitutions of this kind are all contradictory, with the exception of the informa-

tion regarding the Na position, as discussed above. This gives qualitative evidence for the likely fit of our model to the experimental data. A possible ordering of Fe³⁺ and Mn²⁺ in the M(2) position cannot be excluded a priori on the basis of X-ray diffraction only, since the scattering factors of these two ions are practically identical. A neutron-diffraction study might reveal either a lowering of symmetry or a doubling of a unit-cell parameter.

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