*American Mineralogist, Volume 66, pages 428-431, 1981*

# The crystal structure of a Mexican axinite

J. STEVEN SWINNEA, HUGO STEINFINK

*Materials Science Laboratories, Department of Chemical Engineering*
*The University of Texas at Austin, Austin, Texas 78712*

L. E. RENDON-DIAZMIRON

*Instituto de Investigaciones en Materials UNAM*
*Ciudad Universitaria, D.F. Mexico*

and S. ENCISO DE LA VEGA

*Instituto de Geologia UNAM*
*Ciudad Universitaria, D.F. Mexico*

**Abstract**

A new occurrence of axinite and its chemical composition is reported. A three-dimensional X-ray diffraction structure analysis was carried out using 3124 observed structure amplitudes. The refinement converged to $R = 0.019$, $wR = 0.030$. The $Mg^{2+}$, $Mn^{2+}$, and $Fe^{2+}$ ions occupy the distorted "Fe" octahedral site; the bond distances and angles are essentially unchanged from those reported by Takéuchi *et al.* (1974).

The crystal chemistry and structure of axinites have received extensive attention, and correlations have been derived between their physical properties and chemical composition [Lumpkin and Ribbe (1979), Takéuchi *et al.* (1974)]. Axinite has not been previously reported from Mexico, and we describe such a location, the crystal structure of the mineral, and comment on its cation distribution.

The location is in the Vinagrillos hills about 8 km east of Mapimi, in the state of Durango, in an old lead–silver–zinc mining district known as "Ojuela." The specimens were picked from a deposit on the north side of the highway connecting Bermejillo and Mapimi (103°47′W, 25°52′N). The axinite occurs as concretions in rounded to irregular shapes, ranging up to 20 cm in diameter. Less common is the occurrence of the mineral in 5 cm thick bands and lenses. The crystals are honey brown to brown, and the best crystals develop towards the interior of concretion zones. The rock is vesicular with open spaces varying from 2 to 4 mm. The crystal size varies from about 0.1 mm to 1.5 mm. The host rock is limestone or fine sandstone of marine origin and is part of the Caracol formation, Coniacian age (late Cretaceous). The area shows an early tertiary intensive igneous activity with the main system consisting of dacite and latite intrusive bodies. The geology of this part of Mexico has been described by Clemons and McLeroy (1965).

The chemical analysis (Table 1) gives the chemical formula $(Ti_{0.01}K_{0.044}Na_{0.13}Mn_{0.26}Fe_{1.10}Mg_{0.37})Ca_{3.90}(Al_{3.56}Fe_{0.18})(OH)_{1.96}B_{1.96}Si_8O_{29.34}$. The oxygen deficiency of 0.66 is probably within the experimental error of the analysis; the alkali metal ions and $TiO_2$ may represent small amounts of admixed impurities.

An amber crystal of about triangular cross-section having sides of 0.4 mm and 0.2 mm was used for oscillation, Weissenberg, and precession X-ray diffraction photographs to determine unit-cell parameters and space group. The preliminary data agreed with those previously published. The crystal was transferred to a Syntex $P2_1$ single-crystal diffractometer and X-ray diffraction data to a value of $2\theta = 60°$ were collected, using Mo$K\alpha$ radiation monochromatized with a graphite crystal. The data and lattice constants were determined at −35°C. A least-squares refinement of 60 reflections whose $2\theta$ values were precisely determined in the range $25° \leq 2\theta \leq 30°$ yielded the lattice parameters: $a = 7.1437(4)$, $b =$

0003–004X/81/0304–0428$02.00

Table 1. Chemical analysis of axinite from Durango, Mexico

| | Weight % | | Weight % |
|---|---|---|---|
| $SiO_2$ | 43.14 | $B_2O_3$ | 6.12 |
| $Al_2O_3$ | 16.70 | MnO | 1.66 |
| CaO | 19.76 | $Na_2O$ | 0.36 |
| MgO | 1.34 | $K_2O$ | 0.23 |
| FeO | 7.12 | $TiO_2$ | 0.10 |
| $Fe_2O_3$ | 1.28 | ZnO | 0.04 |
| | | $H_2O^+$ | 1.56 |

9.1898(6), $c$ = 8.9529(4)Å, $\alpha$ = 91.857(6)°, $\beta$ = 98.188(5)°, $\gamma$ = 77.359(4)°, $P\bar{1}$. The intensities were corrected for Lorentz, polarization, and absorption using $\mu_l$ = 28.62 $cm^{-1}$. The absorption correction ranged from 0.54–0.62. Estimated errors of the intensities were calculated from

$$\sigma^2(F^2) = S\sqrt{I_p + 1/R^2(I_{B1} + I_{B2})},$$

where $I_p$ = number of counts accumulated during scan of peak, $I_{B1}$ = background counts on low $2\theta$ side, $I_{B2}$ = background on high $2\theta$ side collected for a time equal to that on the low $2\theta$ side, S = speed of scan in deg/min, and R = ratio of total background time/scan time.

The positional parameters given by Takéuchi *et al.* (1974) were used as starting parameters in a least-squares refinement for the structure, and it quickly refined to $R$ = 0.032 and $wR$ = 0.061 for 3124 observed amplitudes, using anisotropic temperature factors except for H and an extinction correction of $2.66 \times 10^{-6}$. The hydrogen atom was located from a difference electron density map. The refinement was based on the assignment of unity for the occupancy factors for Al and Fe in their respective crystallographic sites. The difference electron density map and the temperature factors indicated that Al(1) and Fe site occupancies were not quite correct. The $\Delta\rho$ map showed positive density with a peak of 0.4 $e^-Å^{-3}$ at the Al(1) position and a negative density of 1.75 $e^-Å^{-3}$ at the Fe site. A refinement on only the occupancy and temperature factors for these two atoms converged to 1.025(3) for the Al(1) site and 0.8734(15) for Fe, and $R$ dropped to 0.023 and $wR$ to 0.035. As a control, the occupancy and temperature factors for Al(2) were also refined. The temperature factors remained unchanged and the occupancy factor converged to 0.994(3). A least-squares refinement was then carried out, in which all 243 parameters were varied and convergence was obtained after two cycles. The final $R$ = 0.019 and $wR$ = 0.030 for 3124 reflections. The scattering factors were for the neutral atoms Ca, Fe, Si, Al, B, O, H (International Tables, 1974, p. 71, 148). Ca and Fe were corrected for the real and imaginary components of dispersion (Int. Tables, 1974). The final parameters are shown in Table 2 and compared with those reported by Takéuchi *et al.* (1974). The agreement is excellent, although our standard deviations are about an order of magnitude smaller than those previously reported. Table 3 lists the $F_o$ and $F_c$ amplitudes.[1] Table 4 contains bond distances, with the values obtained by Takéuchi *et al.* (1974) also shown for comparison; bond angles are not shown but they are also in excellent agreement.

The occupancy factor 0.859 for the Fe site implies that an average scattering power of 22.3 electrons is present at that site. The deviations from unity for the Al sites are barely significant and the sum for both sites is essentially 2. Thus the Al sites can be considered fully occupied and the deficiency shown in the formula based on the chemical analysis may be due to experimental error in the $Al_2O_3$ determination. This deficiency in $Al_2O_3$ would also account for the 0.66 deficiency in O. A small amount of $Fe^{3+}$ may be in the Al(1) site. However, we believe that the $Fe_2O_3$ reported in the chemical analysis may be due to the oxidation of $Fe^{2+}$ during analysis and that all of the Fe, Mg, and Mn are in the Fe site. Such an assignment leads to an effective scattering of 23.2 electrons, in excellent agreement with the X-ray result. The chemical formula based on our structural results is $(Fe,Mg,Mn)_2Ca_4Al_4B_2Si_8O_{30}(OH)_2$. The calculated density based on this formula is 3.288 g/$cm^3$; a density of 3.24 g/$cm^3$ was measured by displacement in benzene.

The structure reported by Takéuchi *et al.* (1974) is consistent with our results. The crystal structure has remained invariant even though the Mg–Fe–Mn content of our sample differs from theirs (Lumpkin and Ribbe 1979, Table 2, specimen 35).

[1] To obtain a copy of this table, order Document AM-81-153 from the Business Office, Mineralogical Society of America, 2000 Florida Avenue, N.W., Washington, DC 20009. Please remit $1.00 in advance for the microfiche.

Table 2. Axinite. Positional parameters (x $10^4$) and anisotropic thermal vibrations* (x $10^5$). Standard deviations are in parentheses. Parameters reported by Takéuchi *et al.* are shown below those obtained in this refinement

| Atom | x | y | z | $\beta_{11}$ | $\beta_{22}$ | $\beta_{33}$ | $\beta_{12}$ | $\beta_{13}$ | $\beta_{23}$ |
|---|---|---|---|---|---|---|---|---|---|
| Fe** | 7677.0(.4) | 5914.5(.3) | 1126.4(.3) | 210(6) | 245(4) | 196(4) | -68(3) | 7(3) | 59(2) |
| | 7687 (5) | 5904 (5) | 1120 (5) | 215(8) | 261(5) | 153(5) | -126(5) | -2(5) | 113(5) |
| Ca 1 | 7465.1(.5) | 3481.6(.4) | 3949.3(.4) | 234(6) | 147(4) | 191(4) | -40(3) | -30(4) | 28(3) |
| | 7465 (6) | 3480 (6) | 3956 (6) | 281(10) | 75(6) | 129(6) | -27(6) | -95(6) | 82(5) |
| Ca 2 | 1829.4(.5) | 1004.4(.4) | 837.1(.4) | 364(6) | 185(4) | 182(4) | -93(4) | -77(4) | 47(3) |
| | 1831 (6) | 1006 (6) | 837 (6) | 286(10) | 130(6) | 114(6) | -167(6) | -242(6) | 107(5) |
| Si 1 | 2104.9(.6) | 4498.6(.5) | 2337.3(.5) | 202(8) | 100(5) | 110(5) | -43(5) | -13(5) | 7(4) |
| | 2120 (8) | 4502 (8) | 2356 (8) | 114(13) | 57(8) | 44(8) | -76(8) | -64(8) | 9(6) |
| Si 2 | 2189.1(.6) | 2746.1(.5) | 5231.7(.5) | 149(8) | 99(5) | 107(5) | -41(5) | -5(5) | 3(4) |
| | 2189 (8) | 2748 (8) | 5242 (8) | 91(13) | 45(7) | 41(8) | -49(8) | -38(8) | 6(6) |
| Si 3 | 6987.4(.6) | 2566.8(.5) | 114.8(.5) | 200(8) | 163(5) | 100(5) | -20(5) | 5(5) | 16(4) |
| | 6995 (8) | 2553 (8) | 112 (8) | 142(13) | 66(8) | 12(8) | -28(8) | -39(8) | 18(6) |
| Si 4 | 6415.4(.6) | 190.7(.5) | 2304.2(.5) | 163(8) | 113(5) | 103(5) | -46(5) | 11(5) | -0(4) |
| | 6413 (8) | 189 (8) | 2304 (8) | 85(13) | 68(8) | 55(8) | -88(8) | 7(8) | -2(6) |
| Al 1+ | 526.3(.7) | 8005.3(.5) | 2540.5(.5) | 153(10) | 94(6) | 92(6) | -41(5) | 1(5) | 2(4) |
| | 529 (9) | 8009 (9) | 2543 (9) | 115(15) | 53(8) | 17(8) | -21(8) | -20(8) | 40(7) |
| Al 2++ | 3518.1(.7) | 9359.9(.5) | 4210.6(.5) | 135(10) | 89(6) | 91(6) | -47(5) | -11(5) | -8(4) |
| | 3520 (9) | 9362 (9) | 4212 (9) | 113(15) | 63(9) | 56(9) | -124(9) | -38(9) | -8(7) |
| B | 4615 (2) | 6344 (2) | 2870 (2) | 177(28) | 125(18) | 138(18) | -13(18) | -15(18) | 2(14) |
| | 4619 (33) | 6346 (31) | 2860 (31) | 171(49) | 69(29) | 20(29) | 73(31) | -48(30) | -18(23) |
| 01 | 533 (2) | 6031 (1) | 1900 (1) | 294(21) | 122(12) | 206(13) | -42(13) | -16(13) | 2(10) |
| | 564 (23) | 6033 (22) | 1897 (22) | 320(38) | 101(22) | 121(22) | -59(23) | -42(23) | -11(17) |
| 02 | 2317 (1) | 3388 (1) | 949 (1) | 446(23) | 187(15) | 215(14) | -74(14) | 23(14) | -41(10) |
| | 2333 (24) | 3386 (23) | 982 (22) | 414(40) | 115(22) | 137(23) | -51(24) | 60(24) | -52(18) |
| 03 | 4188 (2) | 4869 (1) | 3119 (1) | 250(21) | 145(12) | 210(13) | -82(13) | -35(13) | 30(10) |
| | 4202 (23) | 4864 (22) | 3135 (22) | 248(37) | 129(22) | 140(22) | -265(23) | -200(23) | 28(17) |
| 04 | 1356 (2) | 3716 (1) | 3692 (1) | 353(22) | 299(14) | 194(13) | -106(14) | -22(14) | 141(11) |
| | 1357 (24) | 3739 (25) | 3713 (23) | 316(40) | 288(25) | 144(23) | -242(26) | -111(24) | 229(19) |
| 05 | 213 (2) | 2425 (1) | 5639 (1) | 225(20) | 203(13) | 150(12) | -80(13) | 21(13) | 29(10) |
| | 218 (22) | 2419 (23) | 5638 (22) | 121(35) | 188(25) | 91(22) | -87(23) | 37(22) | 74(17) |
| 06 | 3265 (2) | 3803 (1) | 6448 (1) | 171(20) | 160(12) | 202(13) | 39(13) | -43(13) | -37(10) |
| | 3261 (22) | 3791 (22) | 6455 (22) | 131(35) | 103(21) | 131(22) | -72(22) | -60(22) | -62(17) |
| 07 | 3810 (2) | 1275 (1) | 4958 (1) | 205(20) | 119(12) | 174(13) | -36(12) | 16(13) | -25(10) |
| | 3802 (22) | 1274 (21) | 4956 (22) | 164(35) | 59(21) | 152(22) | -69(22) | -15(23) | -37(17) |
| 08 | 5347 (2) | 3437 (1) | 8769 (1) | 281(21) | 199(13) | 135(13) | -18(13) | 33(13) | 30(10) |
| | 5371 (23) | 3433 (23) | 8773 (21) | 360(39) | 146(22) | 47(21) | 18(24) | 52(23) | 114(17) |
| 09 | 8762 (2) | 1554 (1) | 9337 (1) | 255(21) | 172(12) | 151(13) | -22(13) | 29(13) | 5(10) |
| | 8759 (22) | 1543 (22) | 9334 (21) | 198(36) | 120(21) | 89(22) | 151(22) | 6(23) | -7(17) |
| 010 | 7683 (2) | 3680 (1) | 1386 (1) | 401(22) | 213(13) | 182(13) | -63(14) | 16(14) | -21(10) |
| | 7693 (25) | 3655 (24) | 1394 (23) | 431(40) | 204(24) | 112(23) | -198(25) | -43(24) | -121(18) |
| 011 | 6038 (2) | 1348 (1) | 874 (1) | 380(22) | 246(13) | 206(13) | -102(14) | 12(14) | 93(10) |
| | 6037 (24) | 1348 (24) | 863 (23) | 404(41) | 240(24) | 123(23) | -256(26) | 70(25) | 155(19) |
| 012 | 4360 (2) | 9813 (1) | 2442 (1) | 265(21) | 180(13) | 151(12) | -84(13) | 20(13) | 17(10) |
| | 4359 (22) | 9817 (22) | 2442 (22) | 191(36) | 127(22) | 121(22) | -167(23) | 20(23) | 44(17) |
| 013 | 7211 (2) | 995 (1) | 3847 (1) | 259(21) | 167(12) | 144(13) | -86(13) | 14(13) | -10(10) |
| | 7204 (23) | 998 (22) | 3842 (22) | 266(37) | 186(23) | 67(21) | -243(24) | -62(23) | -21(18) |
| 014 | 7937 (2) | 8740 (1) | 1775 (1) | 223(21) | 192(13) | 178(13) | -32(13) | 4(13) | -31(10) |
| | 7943 (22) | 8735 (23) | 1783 (23) | 169(37) | 159(22) | 159(23) | 39(23) | 19(23) | -12(18) |
| 015 | 3251 (2) | 7461 (1) | 3546 (1) | 198(20) | 134(12) | 148(12) | -49(12) | 20(12) | -33(10) |
| | 3256 (22) | 7464 (21) | 3545 (21) | 131(34) | 75(21) | 102(21) | -57(22) | 25(22) | -85(17) |
| 016 | 968 (2) | 9955 (1) | 3223 (1) | 220(21) | 161(13) | 174(13) | -41(13) | 53(13) | -38(10) |
| | 968 (21) | 9954 (22) | 3232 (21) | 70(34) | 133(22) | 111(22) | -3(22) | 15(22) | -55(17) |
| H | 9895 (39) | 9604 (31) | 6299 (31) | 2·37(.57) | | | | | |
| | 23 (669) | 9697 (671) | 6259 (670) | | | | | | |

* The temperature factor is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.
** The occupancy factor is 0.859(1).
\+ The occupancy factor is 1.013(3).
++ The occupancy factor is 0.983(3).

Table 4. Bond distances in Å for axinite

| | | this work | Takéuchi | | | this work | Takéuchi | | | this work | Takéuchi |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Fe | 01 | 2.084 | 2.105 | Si 1 | 01 | 1.618 | 1.615 | Al 1 | 01 | 1.885 | 1.887 |
| | 02 | 1.986 | 2.009 | | 02 | 1.586 | 1.581 | | 05 | 1.864 | 1.864 |
| | 06 | 2.354 | 2.357 | | 03 | 1.653 | 1.652 | | 09 | 1.905 | 1.906 |
| | 08 | 2.127 | 2.154 | | 04 | 1.638 | 1.636 | | 014 | 1.863 | 1.861 |
| | 010 | 2.074 | 2.090 | | | | | | 015 | 1.989 | 1.992 |
| | 014 | 2.683 | 2.693 | Si 2 | 04 | 1.632 | 1.634 | | 016 | 1.951 | 1.951 |
| | | | | | 05 | 1.597 | 1.594 | | | | |
| Ca 1 | 03 | 2.434 | 2.424 | | 06 | 1.656 | 1.648 | Al 2 | 07 | 1.907 | 1.904 |
| | 05 | 2.345 | 2.348 | | 07 | 1.613 | 1.616 | | 07 | 1.917 | 1.924 |
| | 06 | 2.463 | 2.478 | | | | | | 012 | 1.862 | 1.863 |
| | 010 | 2.338 | 2.336 | Si 3 | 08 | 1.648 | 1.642 | | 013 | 1.943 | 1.945 |
| | 013 | 2.329 | 2.329 | | 09 | 1.629 | 1.624 | | 015 | 1.866 | 1.869 |
| | 015 | 2.586 | 2.584 | | 010 | 1.605 | 1.608 | | 016 | 1.881 | 1.882 |
| | | | | | 011 | 1.641 | 1.632 | | | | |
| Ca 2 | 02 | 2.290 | 2.293 | | | | | B | 03 | 1.484(2) | 1.492(5) |
| | 09 | 2.475 | 2.469 | Si 4 | 011 | 1.646 | 1.654 | | 06 | 1.529(2) | 1.534(5) |
| | 09 | 2.363 | 2.369 | | 012 | 1.603 | 1.603 | | 08 | 1.492(2) | 1.485(5) |
| | 012 | 2.243 | 2.242 | | 013 | 1.635 | 1.635 | | 015 | 1.436(2) | 1.440(5) |
| | 014 | 2.391 | 2.397 | | 014 | 1.629 | 1.634 | | | | |
| | 016 | 2.577 | 2.586 | | | | | H | 016 | 0.826(28) | ≈ 0.9 |

* *Standard deviations of bond lengths for Si-O, Al-O, Fe-O and Ca-O are 0.001Å for this work and 0.003A for Takéuchi's structure. Values are given in parentheses for B-O and H-O.*

## Acknowledgment

H. S. gratefully acknowledges the research support of the R. A. Welch Foundation, Houston, Texas. We thank Angel Rodriguez and Anastasio Lozano, Instituto de Geologia UNAM, for the chemical analysis.

## References

Clemons, R. E. and McLeroy, D. F. (1965) Hoja Torreón 13R-I(1) Universidad Autónoma de México, Carta Geológica de México, Serie de 1:100,000.

International Tables for X-Ray Crystallography, 1974, Vol. IV. Kynoch Press, Birmingham, England.

Lumpkin, G. R. and Ribbe, P. H. (1979) Chemistry and physical properties of axinites. American Mineralogist, 64, 635–645.

Takéuchi, Y., Ozawa, T., Ito, T., Araki, T., Zoltai, T., and Finney, J. J. (1974) The $B_2Si_8O_{30}$ groups of tetrahedra in axinite and comments on the deformation of Si tetrahedra in silicates. Zeitschrift für Kristallographie, 140, 289–312.

*Manuscript received, July 21, 1980;*
*accepted for publication, October 23, 1980.*