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The crystal structure of a Mexican axinite

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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 2θ values were precisely determined in the range $25° \leq 2\theta \leq 30°$ yielded the lattice parameters: $a = 7.1437(4)$, $b =$

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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, α = 91.857(6)°, β = 98.188(5)°, γ = 77.359(4)°, $P\bar{1}$. The intensities were corrected for Lorentz, polarization, and absorption using μ_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 2θ side, I_{B2} = background on high 2θ side collected for a time equal to that on the low 2θ 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 2.66×10^{-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	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{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(13)	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(23)	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 0.003Å for Takéuchi's structure. Values are given in parentheses for B-O and H-O.*

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