SHORTER COMMUNICATIONS

THE STRUCTURE OF KEHOEITE

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INTRODUCTION

It is now known that the sample of kehoeite which McConnell (1964) examined by the x-ray powder diffraction method contained small quantities of impurities, which contributed to a few spurious intensities of diffraction maxima. Nevertheless, the analogies obtained among kehoeite, analcime and pollucite appear to be qualitatively correct, although quantitatively somewhat inaccurate. That is, the structure appears to be attributable to space group *Ia3d*, but the cube edge *(a)* of the unit cell is now found to be somewhat smaller than previously estimated.

Through the courtesy of John S. White, Jr., of the U.S. National Museum, a small sample of purified kehoeite became available in 1969 and additional diffraction patterns were obtained. White had removed from the crude material both sphalerite and quartz by use of heavy liquids, but reported (by letter) that he was unsuccessful in obtaining a satisfactory powder diffraction pattern from the lightest of three fractions. Thus an implication arose that kehoeite might be amorphous.

EXPERIMENTAL

In Table 1 are given the data obtained in 1969 for an exposure of 12 hours to filtered copper radiation (30 kv, 20 ma., and with $d = 114.6$ mm) of White's sample (lightest fraction). Lines numbered 1, 4 and 8 strongly suggest the presence of gypsum, having relative intensities of 5, 10 and 6, respectively (to the base 10). There could be contributions of gypsum also with respect to lines 9, 11 and 16, but the relative intensities of these lines are best explained on the basis of an analcime-like structure with $a = 13.45$Å, with the exception of line 16.

It also becomes apparent that the reflection (420) was in part the result of contamination by sphalerite on comparison of data obtained

TABLE 1. OBSERVED AND CALCULATED INTENSITIES FOR KEHOEITE

		Kehoeite					Calculated Intensities				Observed Intensities			
		1964		1969							Pollucite	Analcime		
	hkl	*d*	*I*	*d*	*I*	d_{calc}	α	β	γ	δ		(1955) Coombs	(1952) McConnell	Interpretations
1	[111]	7.63	3	7.61	5	7.77	--	--	--	--	--	--	--	Gyp 7.7(5)
2	211	5.68	3	--		5.49	8	20	7	13	2	8	9	Keh
3	220	4.85	1	--		4.76	11	21	11	15	3	4	4	Keh
4	[310]	4.28	5	4.28	9	4.25	0	0	0	0	--	--	--	Gyp 4.29(10)
5	[222]	3.91	1	--		3.88	0	0	0	0	--	--	--	?
6	321	3.49	3	3.50	2	3.59	2	<1	1	1	4	2	2	Keh
7	400	3.35	10	3.35	10	3.36	100	100	100	100	10	10	10	Keh
8	420	3.13	10	3.121	3	3.008	<1	0	0	<1	--	--	--	Gyp 3.06(6), Sph 3.12(10)
9	332	2.96	1	2.969	7	2.868	56	67	49	54	8	8	7	Gyp 2.87(6) + Keh
10	422	2.816	2	2.802	1	2.746	4	7	3	6	--	2	2	Keh
11	431	2.708	3	2.702	2	2.638	10	12	9	10	2	5	3	Gyp 2.68(5) + Keh
12	521	--		2.450	1	2.456	<1	<1	<1	1	--	5	3	Keh
13	440	--		2.391	<1	2.378	12	9	14	9	6	3	2	Keh
14	531	--		2.284	1	2.274	--	--	--	---	--	--	--	?
15	532	2.223	2	2.210	4	2.182	22	26	21	23	4	4	3	Keh
	611						<1	<1	<1	<1				
16	541	2.078	1	2.081	<1	2.075	1	1	<1	1	--	<1	1	Gyp 2.07(5)
17	631	1.993	2	1.985	<1	1.983	<1	0	0	1+	1+	1	1	? Keh
18	543	1.916	7	1.909	6	1.902	<1	<1	0	<1	--	<1	--	Sph 1.912(5)
19	640	1.916	7	1.909	6	1.865	10	15	9	12	2	5	4	Keh
20	552	1.816	2	1.816	3	1.830	3	4	3	3	5	4	3	Keh
	633						8	10	7	8				
	721						5	5	5	6				
21	-	1.749	1	1.752	<1		--	--	--	--	--	--	--	Sph 1.764(6)
22	732					1.708	19	19	19	18	7	6	5	
	800	1.669	1	1.673	1	1.681	10	12	9	11	2	3	2	Keh
23	741	1.633	6	1.631	4	1.656	4	4	3	4	1+	4	3	Keh
24	831	--		1.541	3	1.564	5	6	4	5	2+	3		Keh
	752					1.523	4	3	4	3	2+	--		
25	763	--		1.376	4	1.386	5	6	5	5	3+	4		Keh
	932						<1	1	0	<1				
26	10,1,1	--		--		1.338	5	6	4	4	4	4		?
	772						7	8	8	9				
27	10,3,1	--					4	4	4	3				
	952			1.289	<1	1.282	<1	<1	<1	<1	3	1		Keh
	765						1	1	1	1				
28	871	--		1.243	1	1.249	4	4	4	5	2	2		Keh
29	10,5,1	--		1.197	1	1.198	5	6	4	5	3+	3		Keh
	963						1	1	<1	1				

in 1964 *vs.* 1969, and there appears to have been also a contribution to (543).

Nevertheless, comparisons with pollucite (Fleischer & Ksanda 1940) and with analcime (McConnell 1952; Coombs 1955) show moderately good agreement in intensities, with the exceptions already noted. All spacings which show a calculated intensity of greater than 3 (base 100) are shown in Table 1, provided they are greater than 1.197Å. One notes that (10,1,1) or (772), however, was not found despite comparatively high calculated intensities.

COMPOSITION

Headden (1893) analyzed a white powder from the Merritt mine, Galena, South Dakota, which had a specific gravity of 2.34 (at 15°C) and was readily and completely soluble in concentrated KOH and also in dilute HCl, HNO_3 and H_2SO_4. It showed 1.76% of insoluble material — probably quartz — after subtraction of which yields:

H_2O	P_2O_5	SO_3	ZnO	CaO
31.60	27.13	0.51	11.75	2.75

MgO	Al_2O_3	Fe_2O_3
0.08	25.29	0.79

It is noteworthy that evolution of hydrogen sulphide was not reported, thereby eliminating sphalerite, but not gypsum. Accordingly, the "washed and air-dried material" might have contained 1.25% gypsum if all SO_3 is alloted to this mineral.

According to Headden the air-dried material lost 14.2% between 105 - 110°C, but merely 3.34% of water between 115-120°. The remainder, about 13.8% (after reduction for 1.25% of gypsum), appears to be held more firmly, as though it were a part of the framework structure of a zeolite.

We conclude, therefore, that the structural formula for kehoeite is $Zn_{5.5}Ca_{2.5}[Al_{16}P_{16}(H_3)_{16}]$ $O_{96}\cdot24H_2O$ and this gives
$\rho = 1.66\ (3404)/2433 = 2.32$
which is considered satisfactory agreement with 2.34 (Headden's determination at 15°).

STRUCTURE

In considering the structural analogy with analcime and pollucite, four possible choices exist:

α — Atomic parameters of Newnham (1967) for pollucite; *b* sites contain Zn 5.5 and Ca 2.5 atoms plus 8 molecules of water; *c* sites are randomly occupied by 16 water molecules; *g* sites contain Al, P, and H_3; *h* sites contain the framework oxygens. (Sites are those designated in *International Tables for X-ray Crystallography.*)

β — Same as α except that all 24 water molecules occur in *c* sites.

γ — This model assumes the atomic parameters of Calleri & Ferraris (1964) for analcime but has the site occupancy of model α.

δ — Same as γ except site occupancy is the same as model β.

The calculated intensities are shown to the base of 100 in Table 1, obtained through use of ORFLS, a FORTRAN program by Busing et al. (1963), and scattering factors from the *International Tables for X-Ray Crystallography*. It was not possible to refine the parameters for oxygens, however, and this leads to indecision among the four possible structures (α, β, γ and δ). Although there are specific differences, particularly for (332), nevertheless, there is probable interference of gypsum.

Kehoeite appears to be an isotype of analcime, is isometric or nearly so, and has a cube edge of approximately 13.45Å. In the absence of supplementary information on the chemical composition, its structural formula seems to be $Zn_{5.5}Ca_{2.5}[Al_{16}P_{16}(H_3)_{16}]O_{96}\cdot24H_2O$.

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