

A zinc phosphate analogue of analcime: kehoeite

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Summary. Kehoeite, a hydrated zinc aluminate-phosphate, produces an X-ray powder diffraction pattern with interplanar spacings similar to those of analcime, viséite, and pollucite. The diffraction maxima appear to be compatible with a cubic (or pseudocubic) lattice with a 13.7 Å. It is concluded that kehoeite is essentially isostructural with analcime and that its framework is composed of linked tetrahedra: $(\text{AlO}_2)^-$, $(\text{H}_3\text{O}_2)^-$, and $(\text{PO}_2)^+$, as was found to be the case for viséite, which contains (SiO_2) in addition. Calculations of the density, the number of oxygens in the unit cell, and the chemical composition are consistent with the structural formula $\text{Zn}_{5.5}\text{Ca}_{2.5}(\text{H}_2\text{O})_{32}[\text{Al}_{16}\text{P}_{16}(\text{H}_3)_{16}]\text{O}_{96}$.

DURING the investigation of the setting (hardening) process of dental cements, the question of the nature of certain zinc phosphates has necessarily arisen. One such mineral substance also contains appreciable aluminium and minor amounts of calcium. Despite the fact that these two elements occur only as minor components in dental cements, it seemed desirable to devote a small amount of time to the investigation of kehoeite, a mineral described by Headden in 1893.

In view of the writer's investigation of viséite (McConnell, 1952), it is not particularly surprising to discover another phosphate with the analcime-type structure, but kehoeite is of interest because silica is virtually absent in this mineral, whereas viséite contains appreciable silicon in addition to phosphorus and aluminium within the structural framework. Also the principal large cation is zinc, rather than sodium (analcime), caesium (pollucite), or calcium (viséite).

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Physical properties. As would be expected among a group of minerals that are essentially isostructural, there are certain similarities among the physical properties (see table I). All are soluble in hydrochloric acid, but the fusibilities are $2\frac{1}{2}$ for analcime and viséite and 6 or above for kehoeite and pollucite. The hardness of kehoeite cannot be determined because of its microcrystalline nature.

TABLE I. Comparisons of X-ray powder diffraction data for spacings > 1.62 (filtered Cu radiation ($\lambda = 1.5418$), camera diameter 114.59 mm), and of other physical properties

<i>hkl</i>	$d_{(\text{calc})}$ for $a = 13.70 \text{ \AA}$	Analcime*		Viséite*		Kehoeite		Pollucite†	
		$d_{(\text{expt})}$	<i>I</i>	$d_{(\text{expt})}$	<i>I</i>	$d_{(\text{expt})}$	<i>I</i>	$d_{(\text{expt})}$	<i>I</i>
111	7.91	—	—	—	—	7.63	3	—	—
211	5.59	5.57	9	5.68	4	5.68	3	—	—
220	4.84	4.87	4	4.98	1	4.85	1	—	—
310	4.33	—	—	—	—	4.28	5	—	—
222	3.955	—	—	—	—	3.91	1	—	—
321	3.661	3.66	2	—	—	3.49	3	3.68	6
400	3.425	3.42	10	3.46	5	3.35	10	3.44	10
330, 411	3.229	—	—	—	—	3.13	10	—	—
332	2.921	2.915	7	2.92	10	2.96	1	2.94	8
422	2.796	2.800	2	—	—	2.816	2	—	—
431, 510	2.687	2.690	3	—	—	2.708	3	2.69	2
521	2.501	2.505	3	—	—	—	—	2.49	2
440	2.422	2.430	2	—	—	—	—	2.42	6
532, 611	2.223	2.222	3	2.20	2	2.223	2	2.22	5
620	2.166	2.171	1	—	—	—	—	—	—
541	2.114	2.122	1	2.11	< 1	2.078	1	—	—
631	2.020	2.023	1	2.014	< 1	1.993	2	2.02	4
444	1.977	—	—	—	—	—	—	1.98	2
543, 550, 710	1.937	—	—	—	—	1.916	7	—	—
640	1.900	1.903	4	1.886	3	—	—	1.90	1
552, 633, 721	1.864	1.870	3	—	—	—	—	1.87	5
642	1.831	—	—	—	—	1.816	2	—	—
651, 732	1.740	1.746	5	1.740	6	1.749	1	1.74	6
800	1.731	1.719	2	—	—	—	—	1.71	4
554, 741, 811	1.686	1.692	3	—	—	—	—	1.69	1
644, 820	1.661	1.668	1	—	—	1.669	1	—	—
653	1.637	—	—	—	—	1.633	6	1.64	1
660, 822	1.615	1.622	1	—	—	—	—	—	—
Cell edge (Å)		13.71		13.65		13.7		13.74	
Sp. gr.		2.2-2.3		2.2		2.34		2.90	
Refr. index		1.48-1.49		1.53		1.52-1.54		1.51-1.53	
Optical character		Isotropic or nearly so		Isotropic		Isotropic		Isotropic	

Cell contents: Analcime $\text{Na}_{16}[(\text{Al}_{16}\text{Si}_{32})\text{O}_{96}] \cdot 16\text{H}_2\text{O}$
 Viséite* $\text{Ca}_{10}\text{Na}_2[(\text{Al}_{20}\text{Si}_6\text{P}_{10}(\text{H}_3)_{12})\text{O}_{96}] \cdot 16\text{H}_2\text{O}$
 Kehoeite $\text{Zn}_{54}\text{Ca}_{24}[(\text{Al}_{16}\text{P}_{16}(\text{H}_3)_{16})\text{O}_{96}] \cdot 32\text{H}_2\text{O}$ (this work)
 Pollucite‡ $(\text{Cs}, \text{Na})_{16}[(\text{Al}_{16}\text{Si}_{32})\text{O}_{96}] \cdot < 16\text{H}_2\text{O}$

* Data from McConnell, 1952.

† Data from Strunz, 1936.

‡ Strunz, Min. Tabellen, 1957.

Crystallographic data. In table I comparisons are given for the X-ray powder diffraction maxima of kehoeite, analcime, viséite, and pollucite. The data for pollucite are those given by Strunz (1936); for viséite and

analcime the data are those previously given (McConnell, 1952). All reflections of kehoeite are obtainable from a cubic (or pseudocubic) array with $a = 13.7 \text{ \AA}$.

Numerous differences in intensities arise, as might be expected in view of appreciable differences in the orbital electron configurations of the large cations. The atomic numbers are: 11, 20, 30, and 55 for Na, Ca,

TABLE II. Chemical composition of kehoeite

	Headden's analysis	Recalculated analysis*	Theoretical composition†
ZnO	11.64	12.6	12.6
CaO	2.70	2.9	4.0
Al ₂ O ₃	24.84	27.0	23.0
P ₂ O ₅	26.76	29.1	32.0
H ₂ O	31.06	(28.4)	28.4
Others‡	3.12	—	—
	<u>100.12</u>	<u>100.0</u>	<u>100.0</u>

* Assuming 32 molecules of water in addition to the $(\text{H}_3\text{O}_2)^-$ of the structural framework.

† Composition of $\text{Zn}_{5.5}\text{Ca}_{2.5}[(\text{Al}_{16}\text{P}_{16}(\text{H}_3)_{16})\text{O}_{96}].32 \text{ H}_2\text{O}$.

‡ Others: MgO 0.08, Fe₂O₃ 0.78, SO₃ 0.50, insoluble 1.76 % and a trace of Cl.

|| Consideration of SO₃ would relatively decrease P₂O₅ and increase Al₂O₃ or H₂O or both.

Zn, and Cs, respectively. With the exception of (H_3) , the scattering abilities of the framework cations (Al, P, and Si) are similar.

Crystallochemical data. The specimen examined in this investigation was obtained from the U.S. National Museum and bears the number R-5652. It is almost certainly representative of the material originally analysed by Headden (1893), according to Switzer (1963). The analysis is shown in table II, where it is compared with the results obtained from crystallochemical calculations.

Direct calculation of the number of oxygen atoms (from the unit-cell volume, the specific gravity, and the chemical analysis (McConnell, 1954)) yields 133, approximately 4% greater than the assumed correct number, 128 per unit cell. This result suggests that Headden's determination of the specific gravity might be slightly too high, but the amount of available material precluded a re-determination.

Assuming the specific gravity to be 2.3, it becomes necessary to assign 32 molecules of water to the structure in addition to the 24 H₂O that enter into the structural framework in the form of (H_3) , actually

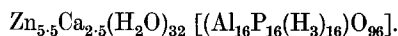
$(\text{H}_3\text{O}_2)^-$ groups analogous with $(\text{AlO}_2)^-$, $(\text{SiO}_2)^0$, and $(\text{PO}_2)^+$. These 32 molecules of water can be distributed in either of the following ways:

		Structure of Taylor (1930)	Structure of Náray-Szabó (1938)
Theoretical Na positions (analcime)	24	16
Number containing Zn,Ca (kehoeite)	8	8
Number containing H_2O (kehoeite)	16	8
Number of H_2O positions (analcime)	16	24
Number containing H_2O (kehoeite)	16	24

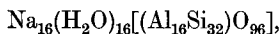
It is apparent that both proposed structures are capable of accommodating the 32 molecules of water and, as for viséite, the data for kehoeite are hardly adequate to resolve the differences between the structures proposed for analcime by Taylor (1930, 1938) and by Náray-Szabó (1938*a*, 1938*b*).

Calculation of the density for the constituents in the last column of table II yields 2.29, whereas Headden's experimental value is 2.34.

Conclusions. Consideration of all of the physical and chemical data permits the tentative conclusion that the structural formula for kehoeite is:



This formula is comparable with the structural formula for analcime:



which is presumed to have 8 vacant positions, equivalent either to the Na positions (Taylor) or to the positions for water molecules (Náray-Szabó).

As was found in the case of viséite, when the central cation is missing the number of protons associated with a group of four tetrahedral oxygens is 3 rather than 4. In orthosilicates and orthophosphates such substitutions involve 4 protons associated with each 4 oxygens. Substitution of 4 protons for S of (SO_4) groups recently has been discovered in ettringite (McConnell and Murdoch, 1962).

It is not concluded that kehoeite has the body-centred cubic structure of analcime, or even that the true symmetry is cubic. Nevertheless, kehoeite is *isotropic* and its other physical properties are similar to those of analcime (table I). If there is ordering among the zinc and calcium atoms, a likely possibility, the true symmetry might be hexagonal, tetragonal, or possibly even non-orthogonal. In this connexion it should be remembered that analcime is often merely pseudocubic (Beattie, 1954, and Coombs, 1955).

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