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A HYDROTHERMALLY SYNTHESIZED IRON ANALOG OF POLLUCITE—ITS STRUCTURE AND SIGNIFICANCE

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ABSTRACT

Hydrothermal studies of the system cesium hydroxide—silica—water in iron liners have revealed several phases, one of which is an iron analog of the mineral pollucite. Crystal structure, optical data, and other physical and chemical properties of this new material are compared with those of natural pollucite. The substitution of Fe^{3+} for Al^{3+} in the crystal structure has permitted the assignment of the cubic space group *Ia3d* for the iron analog. It is probable that the structure of natural pollucite is also based on the same cubic group.

INTRODUCTION

The substitution of Al^{3+} for Si^{4+} in tetrahedral coordination with oxygen makes possible a large number of silicate compounds, generally called aluminosilicates, which could not otherwise form. As a result, extensive literature is available concerning the properties, occurrence, stability relations, synthesis, etc. of the aluminosilicates.

It also appears possible to substitute Fe^{3+} for Si^{4+} in tetrahedral coordination with oxygen. However, published data on these materials is relatively limited. Faust (1936) and Roedder (1952) have studied systems of the general group, alkali oxide—iron oxide—silica from melts. Veres *et al.* (1955), Ostrovskiĭ (1957), Wones (1959) and Wones and Appleman (1962) have studied hydrothermal systems containing silica, iron oxide, and potassium hydroxide. They note the formation of an iron-bearing mica which Wones calls "ferri-annite" and potassium iron feldspars.

During studies in this laboratory of the general system alkali hydroxide—silica—water in iron liners, several iron-bearing phases were observed which have not been previously reported. Available chemical and *x*-ray data indicate that these compounds contain iron, in tetrahedral coordination with oxygen, within the silicate lattice in the positions occupied by aluminum in the aluminosilicate structures. This is of interest because the *x*-ray atomic scattering factors for iron and silicon are significantly different, while those of aluminum and silicon are not; hence the assignment of space group and determination of atomic positions may be accomplished more precisely for those silicates which contain iron in tetrahedral coordination than for those which contain aluminum.

An example of this difficulty was discussed by Náray-Szabó (1938) for the cesium aluminosilicate, pollucite. The preparation of an iron analog of pollucite should aid in study of its crystal structure. The purpose of this paper is to describe the synthesis of such an iron analog, to compare its physical and chemical properties to natural pollucite, and to relate its internal atomic structure, which may be determined with reasonable confidence, to that of pollucite, which was previously uncertain.

HYDROTHERMAL SYNTHESIS

The cesium iron silicate described here was synthesized hydrothermally in an autoclave which has been described previously (Kopp *et al.*, 1961). Conditions producing the best crystallized material were:

Seeds and nutrient	Quartz
Solvent	CsOH (0.5 *N*)
Partial fill	75% (est)
Temperature	
Seed region	412±2° C.
Nutrition region	427±2° C.
Pressure	1700 bars (est)
Liner	Cold-rolled low-carbon steel, 1-in. OD, $\frac{7}{8}$-in. ID
Baffle	90% closure, convex upward
Length of run	11 days

The partial fill and pressure data are estimated, based on the amount of solvent recovered, because of difficulties encountered in welding the fill-hole closure. The cesium iron silicate was obtained in two additional experiments, although the material was not as well crystallized or as abundant.

Crystals of the cesium iron silicate appeared in the upper, cooler region of the liner on the liner wall, on the seeds and seed supports, and were particular abundant on the upper end cap. Subhedral crystals were developed because of the manner of growth on the wires and wall. However, the dominant cubic and octahedral forms present indicated a cubic symmetry. As will be discussed in detail later, the material is primarily isotropic, but a surface material (which does not appear to alter the external form) is birefringent (Fig. 1). Fine-grained quench products which formed were easily removed from the crystal surfaces and therefore are not involved.

PHYSICAL AND CHEMICAL DATA

Some of the chemical and physical properties of the cesium iron silicate are compared (Table 1) with a sample of natural pollucite from Buckfield, Maine (catalog No. C-2361, Smithsonian Institute).

A pure $Cs_2O \cdot Fe_2O_3 \cdot 4SiO_2$ should contain 16.4% Fe; 38.8% Cs; and 16.5% Si. Chemical analysis of approximately 85 mg of the iron analog showed: 12% Fe; 34% Cs; 18% Si; and 1.5% H_2O (weight loss at 110°

C). This analysis is high in silicon relative to cesium and iron. The sample selected for analysis included the birefringent surface material, which may contain a greater percentage of silicon than the core material. Also, according to Winchell and Winchell (1951), pollucite analyses often are high in silicon relative to cesium and aluminum. The silicon ion may replace an aluminum ion and a cesium ion, thus maintaining electrical neutrality.

TABLE 1. COMPARISON OF NATURAL POLLUCITE WITH THE IRON ANALOG

Property	Natural Pollucite[1]	Iron Analog[2]
Color	Colorless	Pinkish to reddish brown
Hardness	6.5	Approx 4–5
Density		
Pycnometer	2.95$_3$	3.5$_5$
X-ray (computed)	Varies with Na content—2.95 for about 5 wt % $Na_2\cdot H_2O$	3.553
Chemical Composition (pure)	$Cs_2O\cdot Al_2O_3\cdot 4SiO_2$[3]	$Cs_2O\cdot Fe_2O_3\cdot 4SiO_2$[4]
Optical	Isotropic $n=1.520\pm0.002$	Isotropic $n=1.572\pm0.002$
Magnetism	Not magnetic	Slightly magnetic

[1] Properties determined for Smithsonian Institute Sample No. C-2361.

[2] ORNL Hydrothermal Run No. 63.

[3] Barrer and McCallum (1951) indicate that most natural pollucites have the general formula: $(Cs_xNa_{1-x})_2O\cdot Al_2O_3\cdot 4SiO_2\cdot 2(1-x)H_2O$.

[4] The ideal formula presented is based primarily on x-ray similarity to pollucite.

Spectrographic analysis (Table 2) was made of each of these materials to determine general sample purity and whether the pollucite contained appreciable sodium or iron.

OPTICAL EXAMINATION

Petrographic examination indicates that the bulk of the material is isotropic with $n=1.572\pm0.002$, but that the crystals are enclosed within a birefringent material (Fig. 1). That the birefringent material appears to be related to the isotropic material is supported by the following observations:

1. One of the indices of refraction is equal to that of the isotropic material. The line of demarcation between the isotropic and birefringent regions is not sharp when viewed at 430×. In addition, bands and wedge-shaped regions of the weakly birefringent material are occasionally observed within the isotropic phase.

TABLE 2. COMPARISON OF SPECTROGRAPHIC ANALYSES OF NATURAL POLLUCITE AND THE IRON ANALOG[1]

Element	Pollucite (wt. %)	Iron Analog (wt %)
Al	5	< 0.05
Ca	< 0.05	0.02
Cs	> 5	> 5
Fe	< 0.02	5
K	0.1	0.03
Na	2	0.01
Rb	0.5	0.2
Si	>10	>10

[1] Values reported are visual estimates taken from a standard plate and using a common graphite matrix. Values are to be interpreted as approximations only; actual values will generally deviate by no more than a factor of 2.

2. Although the birefringent material seems to be somewhat "fibrous," groups of pseudofibers which are at acute angles to each other will often go to extinction simultaneously under crossed Nicols.

3. The external faces appear to have cubic symmetry even though the encasing material is anisotropic. In other ways, the two materials appear dissimilar:

1. The most obvious difference is the anisotropic nature of the material which surrounds the isotropic core. The highest index of refraction coincides with the isotropic portion, while the lowest index of refraction is $n = 1.564 \pm 0.002$.
2. The birefringent material is colorless, while the isotropic material is pinkish to pinkish brown.
3. The birefringent material is most prominent on the exterior of the crystal.

The change from isotropic to anisotropic character in this material might be related to a change in iron content, iron valence state, water content, etc. Birefringence has been observed in many natural, normally isometric silicates of the garnet, feldspathoid, and zeolite families. The causes for this are not always obvious. Several suggestions concerning the reasons for birefringence in natural and synthetic analcites have been given by Taylor (1930) and Yoder and Weir (1960). These reasons include internal lattice strain connected with water content, retained lattice strain induced by compression, etc. Also, it has been noted (Lefever *et al.*, 1960) that banding in yttrium iron garnets is related to the presence of a second phase which could not be resolved with the optical microscope.

X-RAY STUDIES

The best evidence that an iron analog has been prepared under hydrothermal conditions is obtained by comparing *x*-ray data for the new material with that for natural pollucite. Debye-Scherrer, rotation, Weissenberg, and precession films were obtained from the iron analog. In addi-

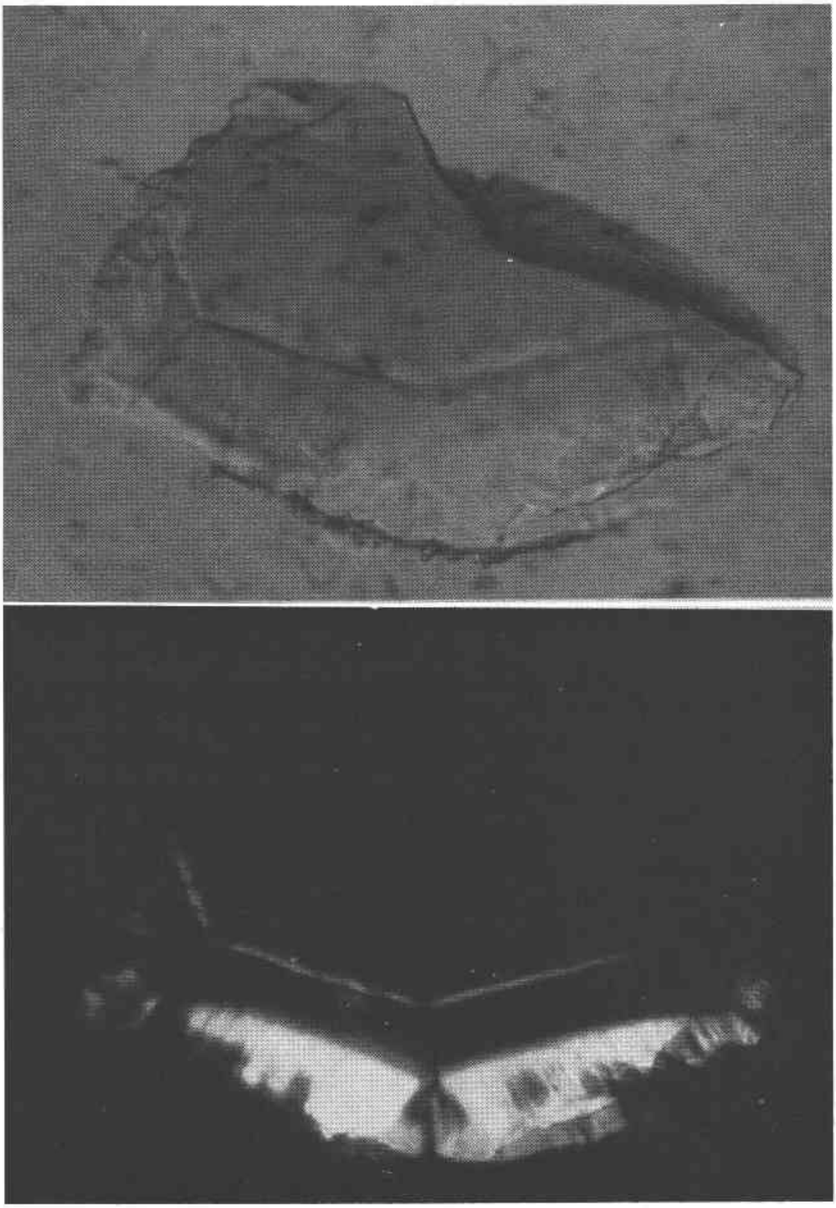

FIG. 1. Crystal fragment with (a) (upper) ordinary light and (b) (lower) crossed Nicols. Note birefringent cap and also narrow birefringent band within isotropic material.

TABLE 3. COMPARISON OF *x*-RAY DIFFRACTION PATTERNS OF NATURAL POLLUCITE AND THE IRON ANALOG

Pollucite		(hk*l*)	Iron Analog	
d(Å)	I		d(Å)	I
5.55	w	211	5.55	m
4.818	w	220	4.827	vw
3.652	s	321	3.648	s
3.421	vs	400	3.414	vs
3.048	vw	420	3.057	vw
2.907	vs	332	2.910	s
2.674	w	431	2.674	m
2.492	w	521	2.493	m
2.406	s	440	2.414	s
2.211	m	532	2.217	ms
2.007	mw	631	2.014	m
1.970	mw	444	1.970	m
1.886	w	640	—	—
1.855	s	721	1.860	s
1.731	s	651	1.736	s
1.705	m	800	1.711	w
1.679	w	741	—	—
1.630	w	653	1.635	vvw
$a=13.63\pm0.03$ Å			$a=13.66\pm0.03$ Å	

Debye-Scherrer camera, Cu radiation, Ni filter ($\lambda=1.5418$ Å).
w=weak, m=moderate, s=strong, v=very.

tion, Debye-Scherrer films were taken of the natural pollucite supplied by the Smithsonian Institute. In all cases Cu K_α radiation ($\lambda=1.5418$ Å) was used. Spacings obtained from the pollucite and the iron analog are compared in Table 3. The Debye-Scherrer data were indexed with the aid of single-crystal photographs taken of an isotropic crystal fragment.

DISCUSSION OF STRUCTURE AND CONCLUSIONS

The lattice dimensions, apparent crystal symmetry, and diffracted *x*-ray intensity distribution of the cesium iron silicate indicate isomorphism with pollucite ($CsAlSi_2O_6$), which was described by Náray-Szabó (1938) as a variation of the analcite ($NaAlSi_2O_6\cdot H_2O$) structure as described by Taylor (1930). In pollucite, which is apparently cubic ($a=13.66$ Å), the large cesium ions were found occupying the 16(*b*) positions of the space group *Ia3d* which are considered the water molecule sites in analcite. It was suggested by Náray-Szabó that the true symmetry of pollucite could be tetragonal (space group $D_{20}4h$, $I4_1/acd$), as all the

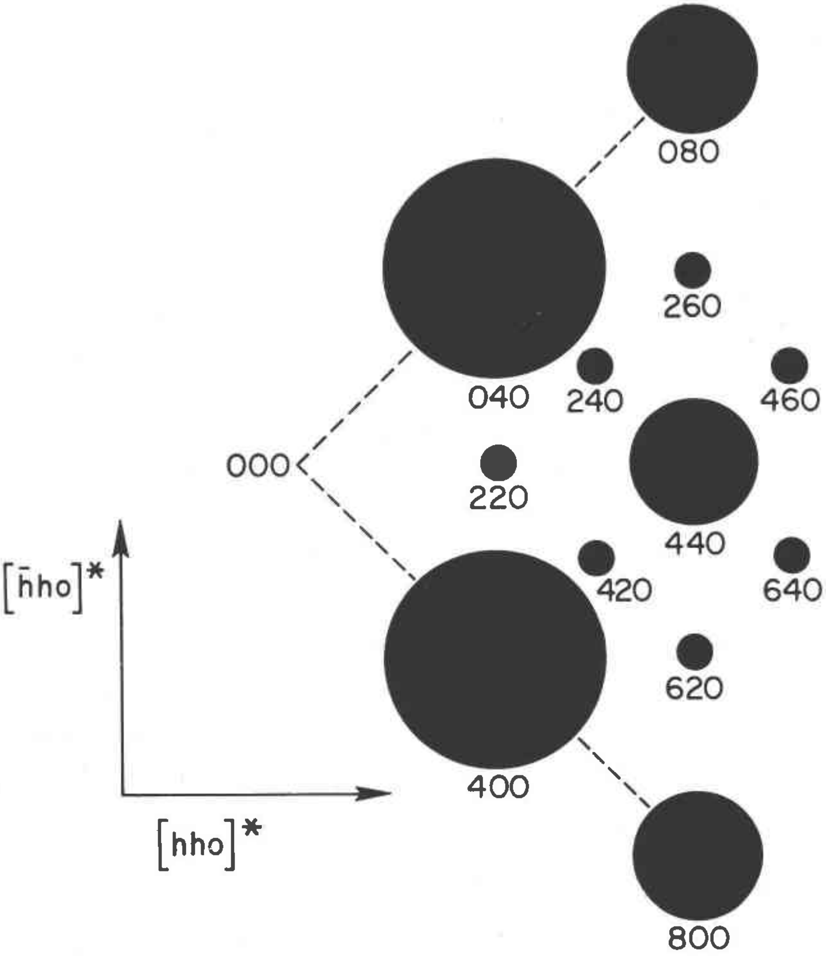

Fig. 2a. Representation of the intensity distribution on the (*hkO*) precession film.

observed *x*-ray diffraction intensities are adequately explained on this basis. However, the tetragonal symmetry requires ordering of the aluminum and silicon atoms, as opposed to the disordered arrangement proposed for the analcite-like structure based on *Ia3d*.

The synthesis of the cesium iron silicate, with its substitution of iron for aluminum, should give the difference in x-ray scattering power necessary to distinguish between order or disorder in the iron and silicon atom sites. The observed single-crystal diffraction data from the cesium iron silicate were compared with structure factors computed from the following atom distributions:

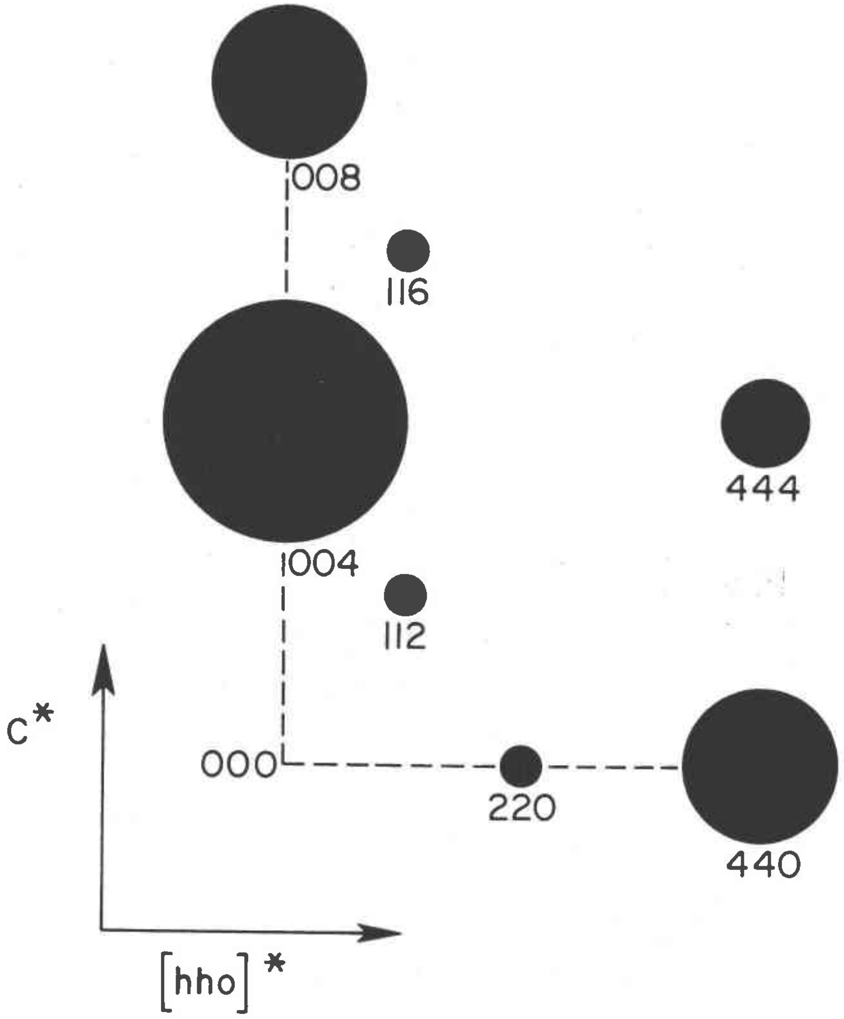

FIG. 2b. Representation of the intensity distribution on the (*hhl*) precession film.

(I) Space Group *Ia3d*

16 Cs^+ in 16(b): $\frac{1}{8}, \frac{1}{8}, \frac{1}{8}$; etc.

$\left.\begin{array}{l}16\ Fe^{3+}\\ 32\ Si^{4+}\end{array}\right\}$ in 48(g); $x, \frac{1}{4}-x, \frac{1}{8}$; etc. ($x=0.661$)

96 O^{2-} in 96(h): x, y, z; etc. ($x=0.111, y=0.131, z=0.722$)

(II) Space Group *I*4_1/*acd*

16 Cs^+ in 16(f): $x, x, \frac{1}{4}$; etc. ($x=0.125$)

16 Fe^{3+} in 16(f): $x, x, \frac{1}{4}$; etc. ($x=0.339$)

32 Si^{4+} in 32(g): x, y, z; etc. ($x=0.125, y=0.411, z=0.224$)

32 O_I^{2-} in 32(g): x, y, z; etc. ($x=0.119$, $y=0.111$, $z=0.653$)
32 O_{II}^{2-} in 32(g): ($x=0.131$, $y=0.472$, $z=0.736$)
32 O_{III}^{2-} in 32(g): ($x=0.278$, $y=0.139$, $z=0.756$)

The atom parameters for both the above distributions correspond to those suggested for pollucite by Náray-Szabó. Form factors taken from the *Internationale Tabellen* and an arbitrary temperature factor B=0 were used in the calculations.

Comparisons of calculated structure factors with observed intensity distributions were made in critical regions of the reciprocal lattice (see Table 4). Of special interest were such reflections as the 200, 020, and 002, all of which should be absent in the cubic space group *Ia3d*, while only the 002 reflection should be absent in the tetragonal space group $I4_1/acd$. It should be noted that these reflections would remain diagnostic even if the supposed single crystal were actually composed of submicroscopic tetragonal domains each with its c-axis oriented along one of the cubic cell

TABLE 4. COMPARISON OF CALCULATED STRUCTURE FACTORS FOR ATOM DISTRIBUTIONS I AND II WITH VISUALLY OBSERVED INTENSITIES OF SOME CRITICAL REFLECTIONS FROM SINGLE CRYSTAL PHOTOGRAPHS

hkl	$F_{calc(I)}$	$F_{calc(II)}$	I_{obs}
200	0	83	Not observable
002	0	0	Not observable
211	75	32	Weak
112	75	168	
220	70	94	Very weak
202	70	49	
400	1496	1479	Very strong
004	1496	1599	
411	0	83	Not observable
420	82	28	Weak
402	82	66	
204	82	134	
600	0	140	Not observable
006	0	0	
611	156	142	Medium weak
116	156	135	

edges. In this case, intensities proportional to $\frac{1}{3}[F^2\ (200)+F^2\ (020)+F^2\ (002)]=\frac{2}{3}\ F^2\ (200)$ should appear at each reflection position.

Figures 2a and 2b are representations of the intensity distributions on *hkO* and *hhl* precession films from an optically isotropic crystal of the cesium iron silicate. Together with the numerical results given in Table 4, these figures clearly show that the observed intensities are compatible only with the disordered cubic structure (I). Since the radius of the Fe^{3+} ion is greater than that of the Al^{3+} ion, there should be a stronger tendency for ordering to occur in the cesium iron silicate. For this reason it seems highly probable that the structure of pollucite involves random occupation of tetrahedral centers and is therefore cubic.

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