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Florenskyite, FeTiP, a new phosphide from the Kaidun meteorite

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ABSTRACT

Florenskyite is a new phosphide species from the Kaidun chondritic meteorite, which fell in South Yemen in 1980. Kaidun is a unique chondritic breccia containing a huge variety of fragments of different chondritic types. Florenskyite was found as four dispersed grains with a maximum dimension of 14 μm within a single mass of Fe-rich serpentine within one Kaidun clast. Florenskyite is associated with submicrometer-sized grains of pentlandite and small (up to 1.5 μm in width) laths of a still uncharacterized Fe-Cr phosphide. Florenskyite is creamy white in reflected light, and its luster is metallic. The average of three electron microprobe analyses gave (wt%) Fe 40.52, Ti 30.08, Ni 5.47, Cr 0.93, V 0.91, Co 0.60, P 21.69, Si 0.59, sum 100.79, corresponding to $Fe_{1.01}(Ti_{0.87}Ni_{0.13}Cr_{0.03}V_{0.02}Co_{0.01})_{1.06}(P_{0.97}Si_{0.03})$. Single-crystal structure analysis was performed on florenskyite using a Laue pattern collected from a multiple crystal by in-situ synchrotron X-ray diffraction. Florenskyite crystallizes in the space group *Pnma*, and has the anti-$PbCl_2$ structure. Previously determined cell constants of synthetic material [a = 6.007(1), b = 3.602(1), c = 6.897(1) Å] were used in the single-crystal data reduction. We used the POWD12 program to calculate a powder XRD pattern; the 5 most intense reflections are d = 2.301 (I = 100), 2.188 (88), 2.307 (47), 1.938 (45), and 1.801 Å (45). Florenskyite is only the fourth phosphide to be described from nature. Its paragenesis may be unique, and may be due to melting of a mineral assemblage including Fe-Ni metal, schreibersite, daubreelite, osbornite, or heideite and subsequent crystallization of phosphides from the melt.

INTRODUCTION

The Kaidun meteorite is a highly heterogeneous meteoritic breccia containing an unprecedented variety of fragments of different chondritic types (CR, CM, CI, R, EH, EL; these are classes of carbonaceous, Rumaruti, and enstatite chondrites) as well as other clasts which show unique mineralogical features (Brandstaetter et al. 1996; Clayton et al. 1994; Ivanov 1989; Ivanov et al. 1986; Zolensky et al. 1996). Kaidun is the Franklin Furnace of the meteorite world. This meteorite (842 g total mass) was recovered immediately after its observed fall in South Yemen in 1980; therefore formation of terrestrial minerals within the meteorite (due to hydration, oxidation, hydrolysis, etc.) is basically precluded. The new mineral florenskyite was found in a single polished section of Kaidun (section no. 53.10) among the twenty examined; we do not know how common it may be within the meteorite; it may well be unique.

Three natural, well-defined phosphides are known today as minerals. Schreibersite, $(Fe,Ni)_3P$, is a typical accessory mineral in most iron and many stony meteorites. Barringerite, $(Fe,Ni)_2P$, was found at first in the Ollague pallasite (Buseck 1969) and later in the Y-793274 lunar meteorite (Brandstaetter et al. 1991). Both minerals are also found on Earth, and both are characterized by high variations in Fe/Ni ratio and usually by low trace element contents. Perryite, $(Ni,Fe)_8(Si,P)_3$, contains essential P substituting for Si in tetrahedral coordination. One more Fe-Cr rich phosphide phase (~Fe_5CrP_3) was reported in the ALH85085 meteorite (Kimura and El Goresy 1989; Zanda 1992), but has not received detailed examination. Thus, florenskyite is the fourth well-defined phosphide to be described from nature.

The mineral is named for Cyrill P. Florensky (1915–1982), Russian geochemist, who is one of founders of planetology (Colleagues in the Laboratory of Comparative Planetology, 1985). The new mineral and the name have been approved by the Commission on New Minerals and Mineral Names of the IMA. The type (and sole) polished section containing florenskyite is deposited at the Meteorite Curation Facility, NASA Johnson Space Center, Houston, Texas, U.S.A.

OCCURRENCE

The Kaidun clast (no. 53.10) containing florenskyite measures approximately 4 mm × 3 mm, and consists of extremely brecciated carbonaceous and enstatite chondrite material, showing various degrees of asteroidal alteration (Fig. 1). Among these fragments are two rounded phyllosilicate masses of similar

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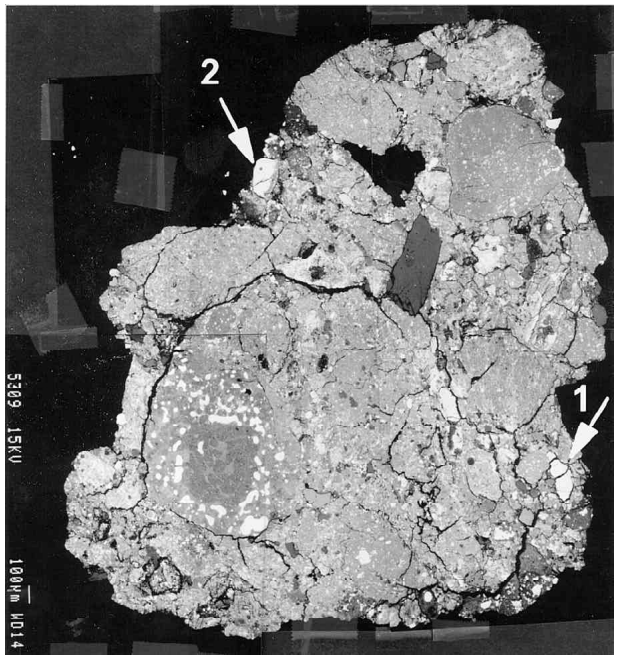

FIGURE 1. Backscattered electron image of the entire polished section no. 53.10 of the Kaidun meteorite, with the serpentine masses (1 and 2) indicated by arrows. The longest dimension of the section measures 3.5 mm.

mineralogy (masses 1 and 2, measuring 90 µm × 190 µm and 300 µm × 90 µm, respectively). Both masses contain numerous laths of Fe-Cr phosphides measuring up to 1.0–1.5 µm in width and up to 5 µm in length. The laths often form extended chains up to 100 µm in length.

Four dispersed anhedral to subhedral grains of florenskyite with a maximum dimension of 14 µm were discovered in phyllosilicate mass 1 (Fig. 2). The most euhedral grain is lozenge shaped, measuring 12 µm × 4 µm. Florenskyite in reflected light is creamy white and the luster is metallic. The small grain size of florenskyite prevented the accurate measurement of some physical and optical properties of the mineral, including reflectivity and density. The structure of synthetic FeTiP has been determined by Rundqvist and Nawapong (1966), but physical and optical properties have not been reported.

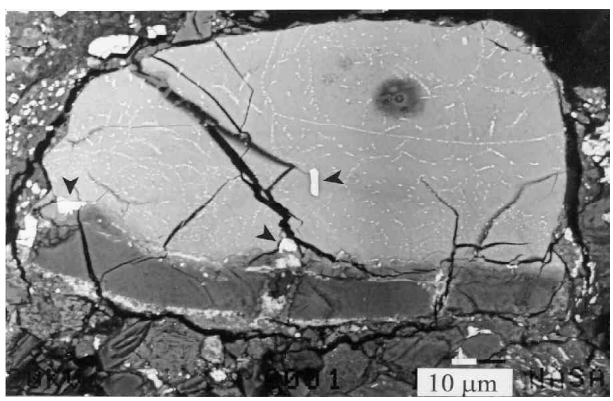

FIGURE 2. Backscattered electron image of the serpentine mass containing florenskyite grains (arrow). The florenskyite grain in the center is the one used for single-crystal XRD data collection.

CHEMICAL COMPOSITION

We attempted to analyze all phases within the two phyllosilicate masses using Cameca CAMEBAX microprobes (at NASA JSC and at the Vernadsky Institute) operated at 15 kV with a beam current ~30 nA and a focused beam diameter of ~3 µm. ZAF corrections were applied to the analytical results. Both natural minerals and synthetic compounds were used as standards. We used phosphide standards for P, Fe, and Ni (schreibersite), but resorted to metal standards for the other elements.

High-quality analyses were obtained only for florenskyite and for the host phyllosilicate; the adjacent Fe-Cr phosphides were too fine-grained to provide adequate results. Accordingly, the compositions of these Fe-Cr phosphides were calculated by subtracting from multiphase microprobe analyses the matrix compositions measured from immediately adjacent regions. Average compositions of the phyllosilicate matrix and of the enclosed phosphides are in Tables 1 and 2.

The bulk compositions of the phyllosilicate matrix (Table 1), its low analytic totals, and comparison with other Kaidun samples indicate that the matrix consists of an Fe-rich serpentine-mineral phase. High S and Ni contents are due to the presence of micrometer- to submicrometer-sized sulfide grains, probably pentlandite. Pentlandite is ubiquitous within aqueously altered clasts in Kaidun (Zolensky et al. 1996).

The average composition of florenskyite from Kaidun (Table 2, average of 3 analyses) can be approximated by the formula $Fe_{1.01}(Ti_{0.87}Ni_{0.13}Cr_{0.03}V_{0.02}Co_{0.01})_{1.06}(P_{0.97}Si_{0.03})$, which is very close to the ideal formula FeTiP. Cations were grouped in the proposed formula based upon analogies to the stoichiometry of other phosphides. We assumed that P+Si sums to 1, due to their preference for tetrahedral coordination, as in perryite.

The chemical compositions of two Fe-Cr rich phosphides (Table 2, last two lines) occurring as small laths in the mass matrix can be recalculated to $(Fe,Ni,Co)_{4.8}(Cr,V)_{0.8}(P,Si)_3$ and $(Fe,Ni,Co)_{4.1}(Cr,Ti,V)_{1.8}(P,Si)_3$. The ideal formulas for these phosphides should be $(Fe,Ni,Co)_5(Cr,V)(P,Si)_3$ and $(Fe,Ni,Co)_4(Cr,Ti,V)_2(P,Si)_3$, respectively. Thus, the composition of the first phosphide is close to that of the phosphide found in the ALH85085 chondrite (Kimura and El Goresy 1989; Zanda 1992), whereas that of the second has not been reported previously. Unfortunately, available data are inadequate to permit further discussion.

CRYSTAL STRUCTURE

As enumerated by Rundqvist and Nawapong (1966), there are a whole raft of $M^IM^{II}P$ compounds (including FeTip, with the anti-$PbCl_2$ structure), none of which were known from nature. Rundqvist and Nawapong (1996) determined the structure of the related compound FeZrP, and synthesized related compounds, including FeTiP, but did not refine its structure. Unit cell FeTiP parameters are a = 6.007 (1), b = 3.602 (1), c =

TABLE 1. Composition (wt%) of the phyllosilicate matrix from Kaidun sample no. 53.10

	SiO_2	Al_2O_3	Cr_2O_3	FeO	NiO	CoO	MgO	Na_2O	P_2O_5	S	Total
Mass 1*	18.06	1.07	0.81	37.31	9.23	1.53	2.65	1.14	0.40	6.76	78.96
Mass 2†	11.34	0.51	4.94	41.11	7.05	1.48	2.30	2.65	0.64	6.87	78.89

Notes: TiO_2, CaO, and V_2O_5 contents < 0.1wt% in both masses. Florenskyite occurs in mass 2.
* Average of 24 analyses.
† Average of 34 analyses.

TABLE 2. Composition of phosphides in Kaidun sample no. 53.10

Fe	Ni	Co	Ti	Cr	V	P	Si	Total
				wt%				
40.51	5.02	0.54	31.38	0.60	0.57	21.98	0.63	101.23*
41.90	5.36	0.60	27.74	1.21	1.31	21.80	0.53	100.45*
39.15	6.02	0.66	31.12	0.99	0.84	21.29	0.62	100.69*
40.52	5.47	0.60	30.08	0.93	0.91	21.69	0.59	100.79†
59	7	1	<1	9	2	21	2	101‡
50	4	1	3	17	2	21	1	100‖
				atoms§				
0.99	0.12	0.01	0.89	0.02	0.01	0.97	0.03*	
1.04	0.13	0.01	0.80	0.03	0.04	0.97	0.03*	
0.99	0.14	0.02	0.92	0.03	0.02	0.97	0.03*	
1.01	0.13	0.01	0.87	0.03	0.02	0.97	0.03†	
4.3	0.5	<0.1	–	0.7	0.2	2.7	0.3‡	
3.8	0.3	<0.1	0.3	1.4	0.2	2.8	0.2‖	

* Florenskyite, individual analyses.
† Florenskyite, average of analyses 1–3.
‡ Fe-Cr phosphides from mass 1 (Table 1), average of 3 analyses, after matrix subtraction.
‖ Fe-Cr phosphides from mass 2 (Table 1), average of 4 analyses, after matrix subtraction.
§ Calculated on the basis: (P+Si) = 1 for Florenskyite and (P+Si) = 3 for the Fe-Cr phosphides.

6.897 (1) Å, space group *Pnma*, and $Z = 4$.

Given the fact that the available crystals of florenskyite were a few microns in size, and that we could find only four crystals, conventional XRD is insufficient for structure refinements. We therefore resorted to in-situ single-crystal Laue diffraction work using synchrotron radiation at beamline 4B of the Photon Factory, Institute of Materials Structure Science, Tsukuba. Because of the long exposure time needed for data collection (sometimes running into hours for a single exposure), the micro-sample must be kept completely stationary with respect to the incident X-ray beam during data collection. In this experiment, a micro-pinhole collimator was used to constrain the incident X-ray beam to a diameter of 1.6 μm, and a Laue camera with an incident slit system to reduce background was developed employing an imaging plate as a detector. [The imaging plate (IP; Fuji Co., LTD.) is a two-dimensional detector, coated by storage phosphors, with high sensitivity and sufficient linearity for a wide range of intensities.] These procedures are described in detail by Ohsumi et al. (1994).

The florenskyite grains were analyzed in the thin section. The small beam diameter permitted us to locate the best region of the florenskyite crystal for data collection. However, the best spot (in the best crystal) showed the presence of 4 domains in nearly the same orientation (Fig. 3).

Indexing of the reflections was complicated by the use of polychromatic X-radiation. Therefore, we first assigned indices to Laue spots by a trial-and-error method comparing observed and calculated interplanar angles of the crystal, starting from the structure determined by Rundqvist and Nawapong (1966) for FeZrP. In general, unit-cell parameters and indices can be obtained by an axial ratio calculated from the positions of Laue spots on the IP and *d*-spacings determined by energy analysis of a few Laue spots with a solid state detector installed in the Laue camera. In this case, we had to start from the unit-cell parameters reported for synthetic FeTiP reported by Rundqvist and Nawapong (1966), and then calculate everything else. We were unable to refine the assumed cell constants further.

The special feature of our software is that the intensities of Laue spots, resulting from superposition of several Bragg reflections, are used as observed values in the least-squares refinement of the structure. The Laue pattern was obtained by 10 minute exposures with the ring current of 391 mA under the ring operation of 2.5 GeV. We used 54 reflections for data reduction and refinement of the crystal structure. The final atomic positions are given in Table 3, and the *R* factor is 0.014. Thus, florenskyite has the anti-$PbCl_2$ structure, and is isostructural with FeZrP. All atoms are in the *4c* special positions. The available data permitted us to only refine the six positional parameters (*x* and *z* for the three sites).

Starting from this model, we used the POWD12 program to calculate the powder XRD pattern, in Table 4. The five most intense reflections are at $d = 2.301$ (I = 100), 2.188 (88), 2.307 (47), 1.938 (45), and 1.801 Å (45).

DISCUSSION

Florenskyite occurs in a mass of Fe-rich serpentine, whose composition is very similar to the observed products of aqueous alteration of Fe-Ni metal in other highly altered lithologies in Kaidun (Ivanov et al. 1993). Recent work indicates that serpentine in chondrites has resulted from aqueous reactions on undifferentiated asteroids (Zolensky and McSween 1988; Zolensky et al. 1997; Krot et al. 1998). The precursor material for the serpentine in this particular Kaidun lithology plausibly included olivine, pyroxene, Fe-Ni metal containing schreibersite, and sulfides; such a mineral assemblage is common to many unaltered chondritic meteorites. In most altered chondrites this lithology is typically replaced by phyllosilicates dotted with sulfides and phosphates. The unusual feature of the Kaidun lithology is the presence of Fe-Ti-Ni-Cr phosphides rather than Ca phosphates.

The regular distribution of the Fe-Cr phosphide laths in the host serpentine masses suggests that they formed by exsolution,

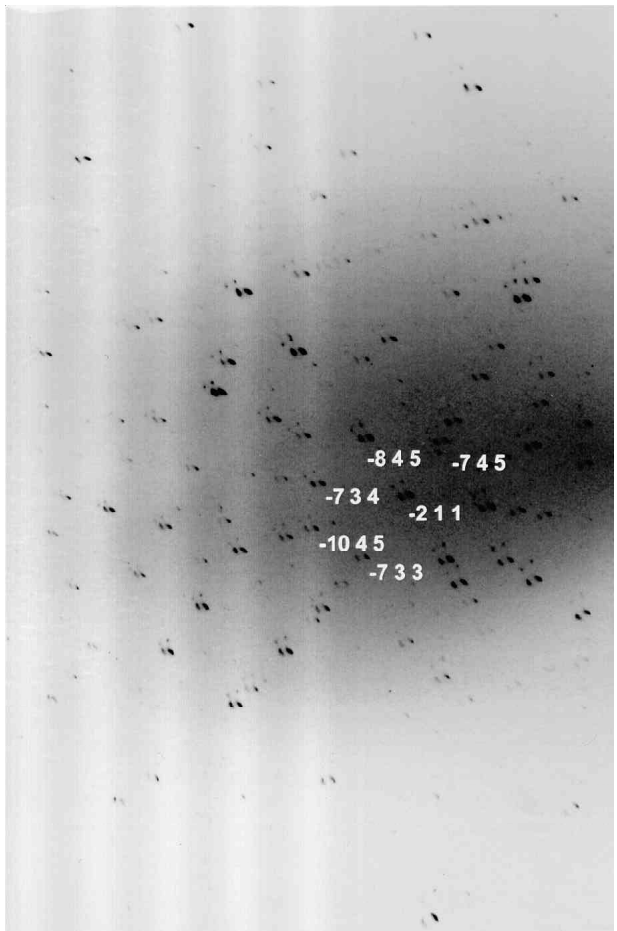

FIGURE 3. The best Laue pattern obtained from the best quality florenskyite crystal. Each reflection consists of four spots, indicating that the crystal has domain structure. A few reflections have been indexed.

TABLE 3. Fractional atomic coordinates for florenskyite

Atom	Site	*x*/*a*	*y*/*b*	*z*/*c*
Fe	4c	0.144 (1)	0.25	0.562 (2)
Ti	4c	0.025 (1)	0.25	0.176 (1)
P	4c	0.766 (3)	0.25	0.621 (3)

Notes: Site populations: Ti = $Ti_{0.87}Ni_{0.13}Cr_{0.03}V_{0.02}Co_{0.01}$; P = $P_{0.97}Si_{0.03}$.

TABLE 4. Calculated XRD pattern for FeTiP

2θ	*d* (Calc)	*h*	*k*	*l*	*I*(Calc)
19.58	4.530	1	0	1	13
25.81	3.449	0	0	2	3
29.85	2.991	1	0	2	1
31.71	2.819	1	1	1	10
39.01	2.307	2	1	0	47
39.12	2.301	1	1	2	100
39.77	2.265	2	0	2	16
41.23	2.188	2	1	1	88
42.05	2.147	1	0	3	31
46.84	1.938	0	1	3	45
47.23	1.923	3	0	1	34
47.38	1.917	2	1	2	11
49.37	1.844	1	1	3	22
49.92	1.826	2	0	3	12
50.64	1.801	0	2	0	45
52.83	1.732	3	0	2	17
53.07	1.724	0	0	4	4
54.01	1.696	3	1	1	9
54.81	1.674	1	2	1	1
55.39	1.657	1	0	4	4
56.46	1.628	2	1	3	5
61.35	1.510	3	0	3	2
63.33	1.467	4	0	1	2
66.25	1.410	2	2	2	5
67.87	1.380	1	2	3	11
68.04	1.377	4	0	2	6
69.06	1.359	4	1	1	4
69.91	1.344	1	0	5	4
71.75	1.314	3	2	1	15
73.45	1.288	0	1	5	5
73.59	1.286	4	1	2	3
73.86	1.282	2	2	3	6
75.83	1.254	2	0	5	5
76.21	1.248	3	2	2	10
76.41	1.245	0	2	4	2
77.68	1.228	3	1	4	18
78.34	1.220	1	2	4	2
81.18	1.184	2	1	5	3
83.48	1.157	3	2	3	1
85.24	1.138	4	2	1	1
85.53	1.135	5	0	2	1
85.72	1.132	4	0	4	2
86.04	1.129	1	0	6	4
86.48	1.124	5	1	1	12
87.41	1.115	2	3	0	38
87.47	1.114	1	3	2	6
88.84	1.100	2	3	1	7
89.53	1.094	4	2	2	4

Notes: Cu*K*α radiation; reflections with $I > 1$.

possibly during cooling of material enriched in Cr and P. The homogeneous distribution of the laths in both masses further suggests homogeneity in Cr and P of the precursors. A similar situation is observed for Ti in mass 2, in which Ti-bearing Fe-Cr phosphide but no florenskyite can be found. Kaidun contains enstatite chondrite lithologies displaying varying degrees of aqueous alteration. The formation of such precursors could be explained as a result of remelting of a mineral assemblage including Fe-Ni metal, schreibersite, daubreelite ($FeCr_2S_4$), osbornite (TiN), and/or heideite [$(Fe,Cr)(Ti,Fe)_2S_4$]. Partial loss of volatile components such as S or N could have accompanied the hypothesized melting. Florenskyite could have formed as a result of cooling and crystallization of a melted precursor consisting mainly of Fe-Ni metal enriched in P, Ti, and Cr, and the presence of florenskyite solely in phyllosilicate mass 1 could be due to an original heterogeneity in Ti of the precursor.

These phosphide-containing masses then experienced aqueous alteration on the parent asteroid, which resulted in complete alteration of the metal matrix and production of the serpentine. Ti-Cr rich phosphides should have been stable during such alteration.

It is also possible that the phosphides formed during aqueous alteration. However, artificial FeTiP has been synthesized only during melting experiments, at low oxygen fugacity, and there is no evidence that a hydrothermal genesis is reasonable. Further investigation of the Kaidun chondrite and enstatite chondrites may shed additional light on the paragenesis of florenskyite.

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