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MINERALS AND PARAGENESES OF MINERALS

Rare Earth and Strontium Aluminophosphates from the Vol–Vym Ridge of the Middle Timan

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Abstract—The genesis and primary source of the well-known diamond placers in the Umba–Pizhma region of Timan still remain unclear. Diamonds are not associated with the typical index minerals of the ultramafic assemblage. Epigenetic rare earth aluminophosphates (florencite, goyazite, etc.) occur as individual grains or supergene coatings on the diamonds' surfaces without any relation to the primary diamond assemblage. They are often observed over syngenetic metal films on the diamond crystals' surfaces. These minerals also occur as secondary inclusions in pores of leucoxene from the Pizhma deposit, as well as in Brazilian carbonados. Owing to their typomorphic features, aluminophosphates may be used as the secondary index minerals of the diamonds.

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INTRODUCTION

Aluminophosphates–sulfates are widespread supergene minerals in the Middle Timan occurrences. They were found on the diamond surface from the Ichet'yu occurrence (Makeev and Makeev, 2000; Makeev and Dudar, 2001), in a bauxite-bearing mantle of weathering after feldspathic metasomatic rocks (Shvetsova et al., 1989), as tiny inclusions in leucoxene grains from the Pizhma deposit, and in the recent alluvium of the Sredny and Levy Kyvvozh and Belaya Kedva rivers in the Vol–Vym Ridge (Bitkov, 1992). The supergene low-temperature and low-pressure processes in the weathered rocks or placers are responsible for the formation of these rare earth minerals.

No classical indicators of diamonds from the ultramafic assemblage (high-Cr pyrope, high-Cr chromite, and picroilmenite) were found in the well-known Ichet'yu diamond occurrence. At the same time, the index minerals of the eclogitic assemblage (pyrope–almandine, Mn-ilmenite, rutile, etc.), along with the relatively light carbon isotopic composition of the diamonds (Makeev and Makeev, 2003), indicate that mantle eclogites were a source of the local diamonds. The insufficient and ambiguous data on the index minerals of the diamonds from the Middle Timan occurrences have not yet led to the discovery of the primary sources and compel us to make an additional attempt to search for the nontraditional mineralogical criteria of the diamond resource potential.

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The objects of this study are aluminophosphates sampled from the Middle Devonian ore-bearing red beds of the Pizhma titanium deposit, diamond-bearing conglobreccia from the Middle Devonian Ichet'yu occurrence, and recent alluvium in the Umba River valley (Fig. 1).

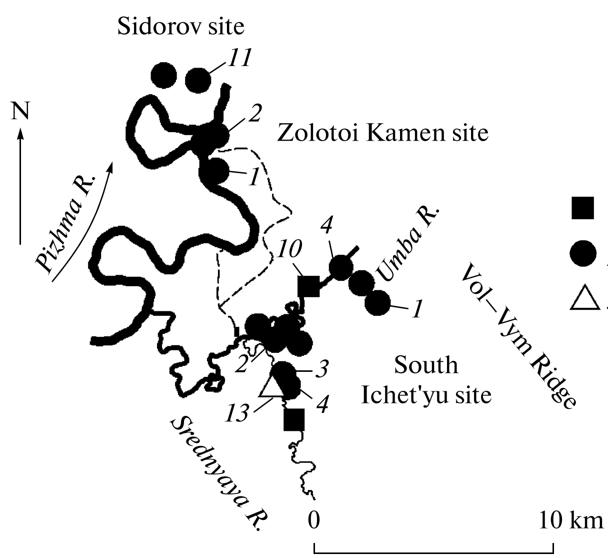

Fig. 1. Location of the samples and the occurrence frequency of the aluminophisphates in the Pizhma Depression. (*1*) Alluvium, (*2*) conglobreccia at the Ichet'yu occurrence, (*3*) sandstone of the Ti-bearing sequence from the Pizhma deposit. The numerals indicate the number of florencite grains in a 10-kg sample.

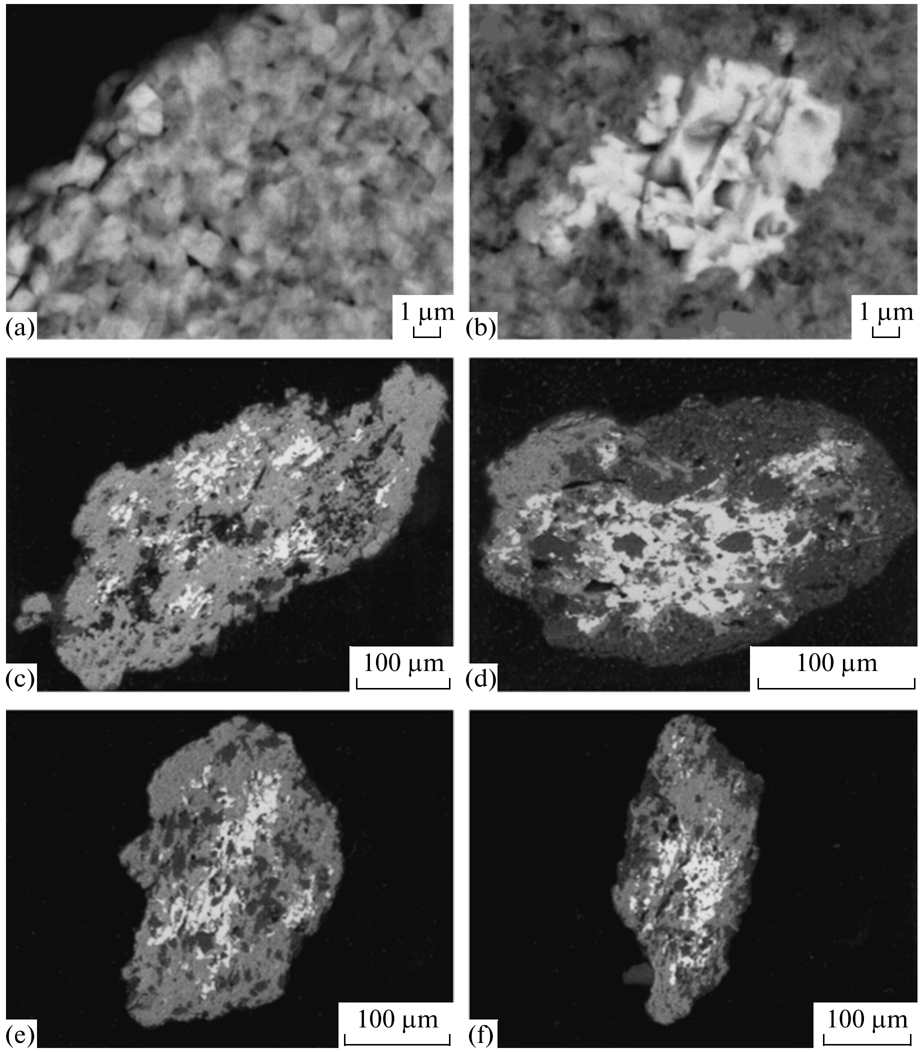

Fig. 2. SEM images of florencite: (a) polycrystalline structure of an aluminophosphate grain, the Ichet'yu occurrence; (b) pyrite inclusion in florencite, the Ichet'yu occurrence, (c–f) polished preparations of florencite in the ore from the Pizhma deposit. The monazite relics are light, the florencite is gray, and the quartz inclusions are dark.

The grain morphology and chemical composition of the aluminophosphates, the coatings thereon, and the inclusions therein were studied using a JSM-6400 SEM/EDS.

DESCRIPTION OF THE MINERALS

The florencite from the Pizhma titanium deposit is mostly red due to the inclusions of finely dispersed hematite. As monazite, the aluminophosphate grains no larger than 0.5 mm in size are characterized by their cookie morphology (Fig. 2) and an uneven surface as a result of nonuniform dissolution. Occasionally, microcrystals are observed on the grain surface as products of probable recrystallization. The XRD examination showed the holocrystalline structure of the florencite and made it possible to identify inclusions therein. The florencite contains numerous inclusions of relict monazite, ilmenite $(Fe_{0.8}Mn_{0.13})TiO_3$, rutile, quartz, pyrite, mica, and hematite (Figs. 2c–2f). The florencite is enriched in REE and contains up to 1.3 wt % ThO_2 (Table 1).

The aluminophosphates from the Ichet'yu occurrence vary in color from yellow-brown and orange to spotty gray-green. Usually, they occur as rounded grains up to 5 mm in size. The large grains were found together with relatively large grains of other accessory minerals from the heavy concentrate. The grains are polycrystalline (Fig. 2a) and reveal zonal coloration with a dark gray surface and a yellow-orange inner part (Fig. 3). The typomorphic feature of some Ichet'yu aluminophosphates is coatings of newly formed white goyazite $SrAl_3[(P,S)]O_4]_2(OH)_6$ or jarosite

Table 1. Chemical composition (wt %) of the aluminophosphates from the Vol–Vym Ridge of the Middle Timan

Grain number	Al_2O_3	P_2O_5	SO_3	CaO	Fe_2O_3	As_2O_3	SrO	BaO	La_2O_3	Ce_2O_3	Pr_2O_3	Nd_2O_3	Sm_2O_3	Gd_2O_3	ThO_2	Total
Cores of aluminophosphates from the Umba River alluvium, the Vol–Vym Ridge																
UM 127/50	26.52	21.50	1.12	1.67	2.19	0	7.89	4.58	2.68	4.21	0	0.97	0	0	0	73.32
UM 127/58	35.22	22.23	10.28	1.62	0.33	0	13.80	0.26	1.90	3.95	0	1.30	0	0	0	90.87
UM 127/59	26.31	22.48	1.62	3.61	1.24	0	4.93	0	0.52	4.31	0	1.70	0	0	0	66.70
UM 127/60	33.46	24.58	6.52	1.75	0.94	0	16.55	0	0.97	2.20	0	0.80	0	0	0	87.78
Surfaces of aluminophosphates from the Ichet'yu diamond occurrence																
V-5/20	29.71	20.46	2.12	1.90	0.51	2.80	6.05	0.99	9.42	3.29	0.82	1.98	0.16	0	0	80.21
UM-3/30	29.88	19.46	3.38	1.49	0.45	3.03	7.10	1.04	7.21	4.70	1.63	3.01	0	0	0	82.33
UM-3/31	30.22	18.31	3.39	1.63	0.25	3.98	6.71	0.75	8.26	4.47	0.95	1.58	0.05	0	0	80.55
ZK-6/30	27.46	17.39	4.76	1.41	0.88	2.61	6.40	0.64	5.80	2.19	0.99	2.30	0.11	0	0	72.92
K100-2/40	33.72	22.98	5.29	1.89	1.05	0	10.77	1.69	2.95	2.54	0.29	1.90	0.37	0	0	
Cores of aluminophosphates from the Ichet'yu diamond occurrence																
K100-2/26	25.55	18.96	4.39	2.37	0.88	0	6.06	0	4.45	0.14	0.47	1.93	0	0	0	65.21
K100-2/27	28.87	22.06	3.73	1.26	0.21	0	7.80	0	1.12	4.25	0.90	3.85	0.49	0.56	0	75.10
K100-2/29	28.65	21.21	3.60	1.00	1.08	0	7.45	0	0.00	2.58	0.59	4.72	2.09	1.67	0	74.65
UM-3/21	27.96	16.25	5.78	1.37	0	5.91	8.44	0	9.63	1.84	0.73	1.60	0	0	0	79.50
UM-3/22	29.78	20.37	3.32	2.10	0.37	3.52	7.29	0	6.59	3.23	0.25	1.85	0	0	0	78.67
SU-1/22	29.90	19.59	5.77	1.38	0.24	1.07	9.86	0	4.73	3.61	0.84	2.36	0	0	0	79.35
Cores of aluminophosphates from the Pizhma titanium deposit																
K100-8/64	26.01	22.04	0.82	1.92	2.60	0	2.49	0	7.22	9.75	0.47	1.75	0.27	0	0.71	76.06
K100-8/66	24.77	19.64	1.20	1.65	2.12	0	3.22	0	7.65	8.39	0.49	1.33	0	0	0.96	71.43
K100-8/67	28.06	24.77	0.43	0.77	1.18	0	3.70	0	5.94	10.74	0.68	4.11	0	0	0.03	80.38
K100-8/23	32.03	19.44	11.24	1.64	0.51	0	15.45	0	1.06	2.46	0	0.86	0	0	0	84.67
K100-8/27	27.92	23.94	0.45	0.91	1.33	0	2.63	0	6.23	12.49	1.50	4.67	0	0	0.27	82.31
K100-8/28	27.79	24.31	0.2S	1.17	1.44	0	4.74	0	6.34	11.33	1.16	2.76	0	0	0.34	81.64
K100-8/57	26.08	23.03	0.45	0.81	1.46	0	4.49	0	7.08	10.68	0.60	2.26	0	0	0.23	77.16
K100-8/58	23.82	19.98	0.68	1.51	2.17	0	3.32	0	5.19	9.98	0.91	3.48	0	0	0.64	71.65
K100-8/69	26.72	22.24	1.07	1.68	2.17	0	3.72	0	6.31	10.79	0.48	2.21	0.22	0	0.48	78.09
K100-8/60	29.58	23.10	1.22	2.19	4.30	0	4.29	0	5.67	7.53	0.47	1.13	0	0	1.32	80.78
K100-8/63	27.53	23.62	0.34	1.38	0.99	0	1.78	0	6.50	12.59	0.89	4.02	0.11	0	0.36	80.08

Note: The low sum is compensated by the crystallization water and the OH group.

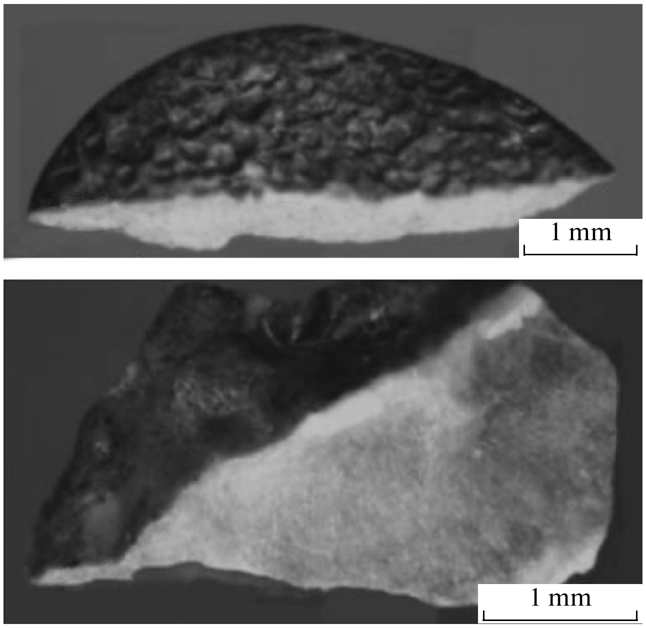

Fig. 3. Morphology, internal structure, and zoning of florencite grains from the diamond-bearing conglobreccia at the Ichet'yu occurrence.

$K_2Fe_6(SO_4)_4(OH)_{12}$. The florencite from the Ichet'yu diamond occurrence contains sporadic relics of monazite $(Ce_{0.46}La_{0.27}Nd_{0.15}Pr_{0.06}Th_{0.04}Sm_{0.02})PO_4$ and inclusions of quartz, Th-phosphate, mica, pyrite $Fe(S_{1.95-1.98}As_{0.02-0.05})_2$ (Fig. 2b), zircon $(Zr_{0.98}Hf_{0.02})SiO_4$, and xenotime $(Y_{0.80}Dy_{0.06}Er_{0.06}Gd_{0.05}Yb_{0.03})PO_4$. The florencite is characterized by almost equal REE and Sr contents and is enriched in BaO (0.8–1.7 wt %) on the surface and in Gd_2O_3 (0.6–1.7 wt %) in the cores (Table 1).

The grains from the Umba River alluvium are well rounded, gray from the surface, and up to 0.6 mm in size. They contain only hematite inclusions and are similar in this respect to the aluminophosphates from the red beds of the Pizhma deposit. Their composition is characterized by elevated SrO and BaO contents (Table 1). Some typomorphic features of the aluminophosphates (the grain morphology, size, and hematite inclusions) from the Umba River alluvium coincide with those from the Ti-bearing red sandstones. This implies that the Pizhma sandstones could have been a source of the alluvial grains. Because of their fragility, the aluminophosphates are ill-preserved in black sand and, as leucoxene, are identified in heavy concentrates at a distance no farther than 1 km from the primary source.

The unit-cell parameters (Å) of the aluminophosphates from (1) the titanium ore of the Pizhma deposit, (2) the Ichet'yu occurrence, and (3) the Umba River alluvium were calculated on the basis of the constant coefficient method: (1) $a = 6.995 \pm 0.013$, $c = 16.31 \pm 0.14$; (2) $a = 6.95 \pm 0.02$, $c = 16.\ 31 \pm 0.17$; (3) $a = 6.992 \pm 0.008$, $c = 16.35 \pm 0.05$. The unit-cell parameters of the florencite from the studied objects

Table 2. Chemical composition (wt %) of monazite relics in the florencite cores from the Pizhma titanium deposit

Analysis number	P_2O_5	CaO	La_2O_3	Ce_2O_3	Pr_2O_3	Nd_2O_3	Sm_2O_3	ThO_2	Total
K100-8/64	33,43	0.32	24.51	31.46	0.86	6.21	0.87	1.72	99.58
K100-8/64	27.76	0.45	23.49	32,06	2.66	7.61	1.08	1.64	96.74
K100-8/64	31.52	0.42	23.85	30.30	2.52	8.03	0	0.93	97.58
K100-8/64	29.21	0.17	27.75	31.02	1.43	7.64	0.03	0.39	97.64
K100-8/66	29.18	0.38	18.51	35.25	3.75	10.52	0	1.78	99.37
K100-8/66	29.63	0.24	19.18	36.09	3.57	10.55	0	0.65	99.92
K100-8/67	29.95	0.22	18.19	33.83	3.95	10.06	1.28	1.51	98.99
K100-8/67	29.66	0.24	19.98	34.35	3.46	9.89	1.33	0	98.90
K100-8/27	34.77	0,55	18.01	31.63	2.91	9.01	0	1.01	97.90
K100-8/57	26.02	0.35	16.11	35.94	4.25	12.82	0	1.51	97.02
K100-8/59	32.76	0.31	15.20	33.25	2.51	11.47	2.06	0.84	98.39
K100-8/59	31.02	0.11	15.61	33.89	3.35	11.53	1.27	0.82	97.60
K100-8/60	31.31	0.26	12.85	34.64	2.90	14.77	0	0.84	97.57
K100-8/63	31.66	0.19	10.47	34.51	2.93	16.59	0	1.03	97.38

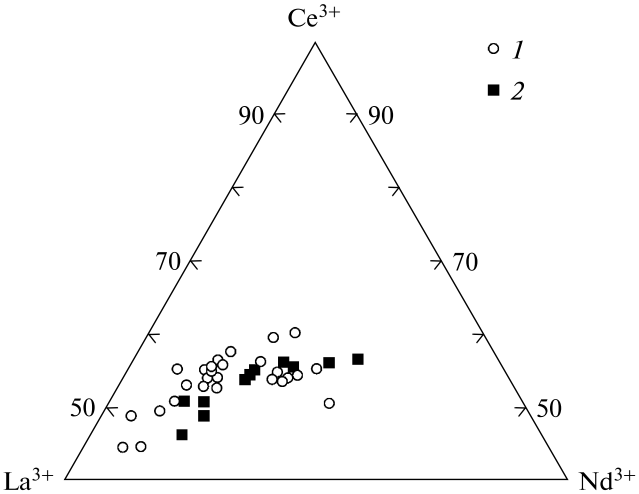

Fig. 4. Ce, La, and Nd contents in (*1*) aluminophosphates and (*2*) monazite relics from the red beds of the Pizhma deposit.

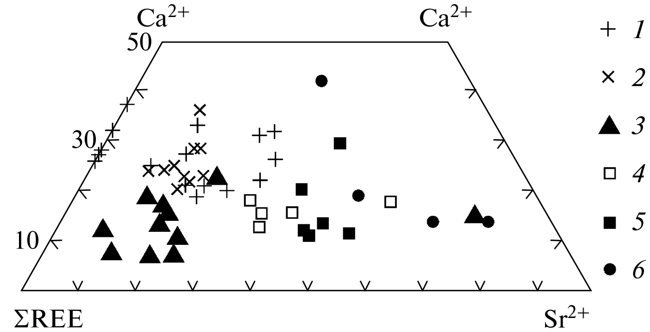

Fig. 5. Total REE, Ca^{2+}, and Sr^{2+} contents in the aluminophosphates from the Pizhma Depression. (*1*) Films on the diamond surface from the south part of the Ichet'yu occurrence; (*2*) florencite films on diamonds from the Zolotoi Kamen' and Sidorov sites of the Ichet'yu occurrence; (*3*) florencite from the Ti-bearing red beds at the Pizhma deposit; (*4*–*5*) florencite from the Ichet'yu occurrence: (*4*) the core and (*5*) surface; (*6*) recent alluvium in the Umba River valley, the Vol–Vym Ridge.

are similar (within the accuracy limits) in line with the small deviations in their composition (Table 1).

The replacement of monazite with florencite is indicated by monazite relics in cores of florencite grains from the Pizhma deposit (Fig. 2; Table 2) and by the relict tiny particles identified with an electron microscope on the surface of the aluminophosphate from the Ichet'yu occurrence. The florencite inherits relative amounts of REE (Ce, La, Nd) from the monazite (Fig. 4). The total REE, Ca^{2+}, and Sr^{2+} contents in the aluminophosphate from the Pizhma Depression correspond to the continuous florencite–goyazite isomorphic series (Fig. 5). The florencite enriched in REE from the sandstone of the Pizhma titanium deposit and the coatings on the diamond crystals clearly differs from the large florencite–goyazite grains enriched in Sr from the Ichet'yu conglobreccia and the goyazite from the black sand of the Umba River alluvium.

DISCUSSION AND CONCLUSIONS

REE- and Sr-aluminophosphates (florencite, goyazite, etc.) in association with diamonds (Makeev and Makeev, 2000; Chaikovsky, 2003) as supergene coatings over the diamonds' surfaces and above metal films (Fig. 6) on the diamond crystals (Makeev and Dudar, 2001), as well as secondary inclusions in pores of carbonado (Makeev et al., 2002) and leucoxene, may be used as secondary index minerals of diamonds not only in the Middle Timan. The poor preservation of the aluminophosphates in the alluvium and their limited spreading make it possible to find the primary source by panning.

The Middle Timan diamonds with blue cathodoluminescence (N3 centers) various in intensity also reveal yellow-green luminescence (H4 and H3 centers) as spots at the surface 10 to 600 μm across (Makeev and Dudar, 2001). Some of these spots coincide with green radiation pigment spots visible on the diamond crystals' surface or with dislocation bands. It can be suggested that these are radioactive traces of Th-bearing monazite and florencite, which coexisted with diamonds in the Ichet'yu conglobreccia for a hundred million years.

The monazite and florencite developed after this mineral are readily dissolved in water creating the preconditions for the hydrogeochemical exploration of placer diamond occurrences and their primary sources (Makeev and Bryanchaninova, 2006). Contrasting REE and Al–Fe–Mn anomalies in the water are

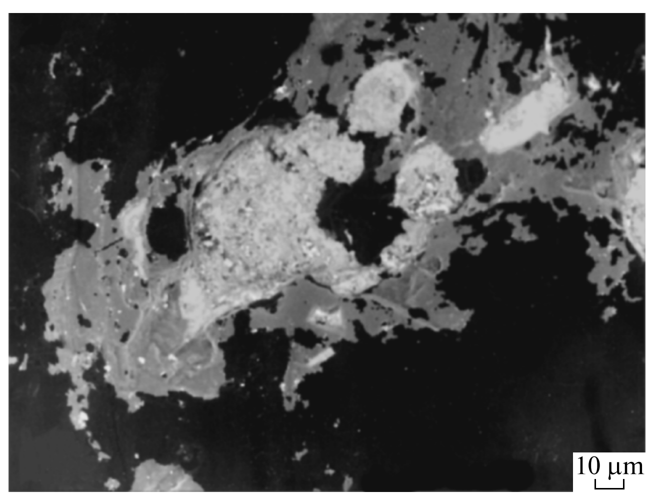

Fig. 6. Florencite coatings (white) over the gold–palladium film (gray) on diamond from the Ichet'yu occurrence.

detectable at a distance of 0.5–1.0 km from diamond occurrences.

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