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Barite and Carbonate-apatite constituting Fossil Dinosaur Bone in Sandstone from Berivotra, Madagascar*

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Introduction

In 1975 the author participated the paleontological survey team of Madagascar headed by Dr. Kazuo ASAMA, Director of Department of Geology, National Science Museum, Tokyo, Japan. During the excavation of dinosaur fossil at Berivotra located about 50 km southeast of Majunga, the author collected some barite crystals in association with fragments of dinosaur bone from an unconsolidated sandstone according to the informations of the members of previous team in 1973.

Here the mineralogical properties of the barite are reported together with the results of some mineralogical studies on a dinosaur bone.

The author is greatly indebted to Dr. Akira KATO, Department of Geology, National Science Museum, for his useful comments and critical reading of the manuscript. His sincere thanks are also subjected to Dr. Tokiko TIBA, Department of Geology, National Science Museum, for her wet chemical analysis of dinosaur bone.

Barite

The topographic and stratigraphic details of barite and dinosaur-bearing beds have been reported by OBATA and KANIE (1977). Barite is found in an unconsolidated, cross-bedded quartzose sandstone. Rarely it occurs as discrete crystals, but usually as rosette-like aggregates of interpenetrated tabular crystals. The individual crystal reaching 3 cm in diameter and 5 mm thick displays hexagonal plate formed by a(100), m(210) and c(001) (Figs. 1 and 2).

The microscopical observation, however, discloses the crystals to be mimetic ones composed of subparallel aggregate with common [001] zone (Fig. 3). The crystal always includes a few subround quartz and alkali feldspar grains less than 0.8 mm across, and sometimes fragments of dinosaur bone.

Barite is gray white in color and translucent with a vitreous luster. MOHS' hardness is about 3. Density measured by Berman microbalance is 4.47 g/cm^3. Perfect cleavage along {001} is observed. It is colorless in thin section and optically biaxial positive with 2V about 40°. Refractive indices are: $\alpha=1.636(2)$, $\beta=1.638(2)$,

* Contribution to the Paleontology of Madagascar XII.

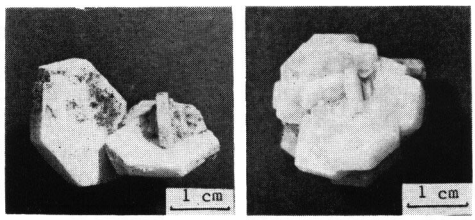

Fig. 1. Crystal group of barite.

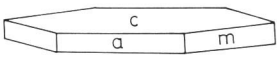

Fig. 2. Crystal form of barite.

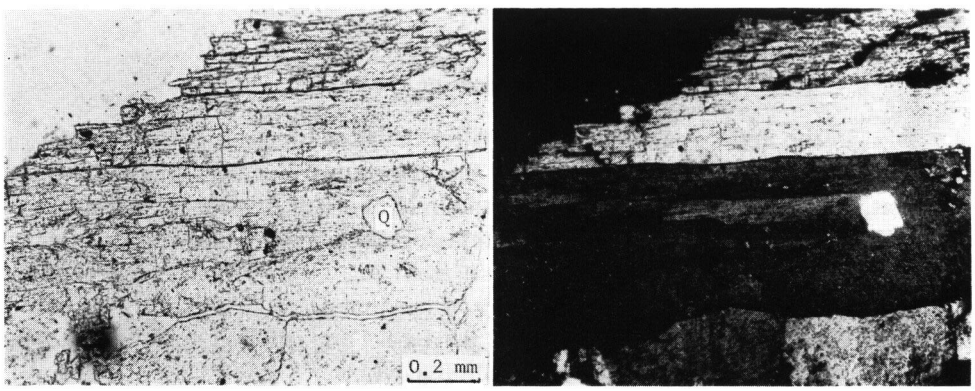

Fig. 3. Photomicrographs of barite. Left; one polar, right; crossed polars. Q: quartz sand grain.

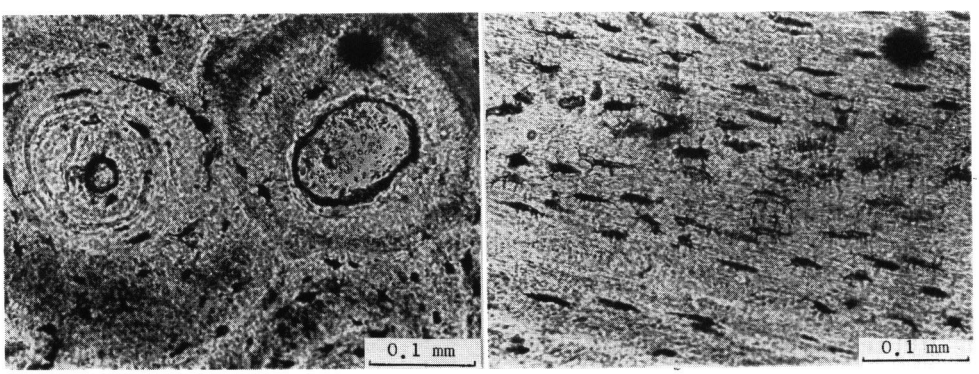

Fig. 4. Photomicrographs of fossil dinosaur bone. Left; transverse section, right; vertical section.

$\gamma=1.648(2)$ by the immersion method.

X-ray powder diffraction pattern obtained by the diffractometer method using Ni-filtered Cu radiation is given in Table 1. The unit cell parameters calculated from the indexing are: $a_0=8.874(6)$, $b_0=5.452(2)$, $c_0=7.152(2)$ Å, which are very close to those of barite from Durham, England (COLVILLE and STANDHAMMER, 1967), or nearly pure $BaSO_4$.

Table 1. X-ray powder diffraction pattern of barite.

hkl	$d_{calc.}$	$d_{obs.}$	I	hkl	$d_{calc.}$	$d_{obs.}$	I
200	4.44	4.44	12	004	1.788	1.788	10
011	4.34	4.35	18	123	1.759	1.757	10
111	3.895	3.897	35	313	1.757		
201	3.769	3.770	5	131	1.727	1.726	4
002	3.576	3.576	48	230	1.682	1.679	10
210	3.442	3.445	100	421	1.673	1.673	20
102	3.317	3.321	60	231	1.637	1.637	6
211	3.101	3.101	80	132	1.594	1.593	8
112	2.834	2.834	30	323	1.534	1.534	15
020	2.726	2.727	45	124	1.474	1.474	10
212	2.480	2.478	12	521	1.456	1.456	5
220	2.322	2.321	18	503	1.423	1.424	12
103	2.302	2.304	8	430	1.406	1.406	6
302	2.279	2.281	5	611	1.400	1.400	5
221	2.209	2.209	25	015	1.384	1.384	8
113	2.121	2.120	70	040	1.363	1.363	5
401	2.119			414	1.349	1.350	4
122	2.106	2.105	55	215	1.321	1.320	8
312	2.103			333	1.298	1.298	8
410	2.055	2.055	20	142	1.261	1.261	10
321	1.930	1.931	8	711	1.217	1.217	5
303	1.857	1.857	12	006	1.192	1.129	10

Dinosaur bone

The studied dinosaur bone has been collected from the barite-bearing bed. It is about $4 \times 2 \times 5$ cm in size and too fragmental to decide the species and part. It is pale brown in color and subresinous in luster on fracture surfaces. The hardness is slightly lower than fluorapatite. Density measured by Berman microbalance is 2.92 g/cm^3.

In the transverse and vertical sections of bone the Haversian canals, lamellae, lacunae and canaliculi are observed (Fig. 4). The Haversian canals are about 0.2 to 0.01 mm in diameter. The essential constituents of bone are mainly composed of carbonate-apatite. After macerating a piece of bone in dilute HCl the lamellae stripped off as transparent films remain unsolved. Under the microscope the thin film has a reticular structure and is made up of very slender fibers. A reddish brown substance replacing lacunae and canaliculi is seen and composed of aggregate of very minute anisotropic material.

Measurements of the optical properties of carbonate-apatite is difficult due to the cylindrical aggregate of curved thin tabular crystals. Measured refractive indices by the immersion method are $n_{max.}=1.61$, $n_{min.}=1.60$, respectively. These values correspond to those of an intermediate member of the carbonate-hydroxylapatite and carbonate-fluorapatite series.

The result of wet chemical analysis given in Table 2 leads to $Ca_5[(PO_4)_{2.43}(CO_3OH)_{0.40}]_{2.83}(OH)$ as the empirical formula of carbonate-apatite after deduction of SiO_2 as quartz, and of Fe_2O_3 and a part of H_2O as "limonite".

Table 2. Chemical analysis of carbonate-apatite constituting fossil dinosaur bone. Analyst: T. TIBA.

	SiO_2	Fe_2O_3	CaO	P_2O_5	CO_2	H_2O^+	H_2O^-	Total
wt.%	0.06	1.03	55.46	34.13	3.50	5.05	0.61	99.84

X-ray powder diffraction pattern of carbonate-apatite obtained by the diffractometer method using Ni-filtered Cu radiation is given in Table 3. The unit cell parameters calculated by the indexing are: $a_0=9.356(4)$, $c_0=6.890(4)$ Å, which are included within the variation ranges of carbonate-apatites (MACLELLAN and LEHR, 1967; LE GEROS *et al.*, 1967; BROPHY and NASH, 1968). If the substitution of fluorine for hydroxyl is not considered, the unit cell parameters of carbonate-bearing apatite group minerals are characterized by the decreasing a_0 and increasing c_0 in accordance with the substitution of CO_3(or CO_3OH) for PO_4. This fact leads to the easier discrimination of carbonate-bearing apatites which have X-ray powder diffraction patterns including overlapped diffraction peaks (211) and (112) in general, from ordinary carbonate-free apatites which have separated diffraction peaks with above indices.

If CO_3(or CO_3OH) content is considered as fixed, the substitution of fluorine for hydroxyl yields a decrease of a_0 with a small change of c_0 (Table 4). Since a_0 of the present material is admittedly smaller than the estimated value from the CO_3 content,

Table 3. X-ray powder diffraction pattern of carbonate-apatite.

hkl	$d_{calc.}$	$d_{obs.}$	I	hkl	$d_{calc.}$	$d_{obs.}$	I
100	8.10	8.22	8	203	1.998	1.998	10
101	5.25	5.26	5	222	1.934	1.933	30
110	4.68	4.67	5	312	1.882	1.881	20
200	4.05	4.06	10	213	1.837	1.838	35
111	3.869	3.870	10	321	1.794	1.794	20
201	3.491	3.450	35b	410	1.767	1.766	20
002	3.445			402	1.745	1.746	18
102	3.170	3.171	15	004	1.723	1.723	20
210	3.061	3.060	20	322	1.635	1.636	8
211	2.797	2.794	100b	501	1.577	1.575	5b
112	2.774			412	1.572		
300	2.699	2.699	50	420	1.530	1.529	8
202	2.624	2.624	25	214	1.501	1.499	8b
301	2.513	2.513	10	421	1.494		
212	2.288	2.285	12	502	1.466	1.466	15
310	2.246	2.245	25	304	1.452	1.451	15
311	2.135	2.135	15	511	1.423	1.423	10
113	2.061	2.062	12				

Table 4. Relationship of a_0 and c_0 to CO_2 and F wt.% of carbonate-apatites.

CO_2 wt.%	F wt.%	a_0	c_0	Authors
0.4	0	(9.462)	(6.878)	1
2.70	3.89	9.346	6.887	2
3.50	nd	9.356	6.890	3
3.51	0.44	9.419	6.886	2
3.7	0	(9.439)	(6.886)	1
7.3	0	(9.372)	(6.905)	1
11.0	0	(9.351)	(6.915)	1
14.7	0	(9.312)	(6.922)	1

1; Le Geros et al., 1967. ( ): numerically read on diagram.
2; Brophy and Nash, 1968.
3; This study.

the presence of fluorine can be estimated without qualitative analysis.

Conclusion

It is very common that the cavities of spongy portion and the Haversian canals of petrified bone are filled with such secondary minerals as quartz, opal, calcite and barite. The present material, however, remains porous except that the cavities in the peripheral part are filled with sand. This suggests no precipitation of secondary minerals in dinosaur bone during its burial stage. In the other word this means that the formation of euhedral barite crystals had not been held in sandstone. The barite had, therefore, settled as pebble together with fossil bone after the crystallization somewhere. It is highly probable that the barite might have been formed at the bottom of lake where hotwater inflow and its evaporation were repeated periodically. In the same time dinosaur and other reptiles had lived near the lake.

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