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Characterization of natural apatite

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Drilled cores of natural apatite were crushed and ground to the required mesh size. The apatite crystals, picked out from under a binocular microscope, were characterized by electron microscopy, chemical analysis, X-ray diffraction and infrared studies. It was confirmed that calcium hydroxylapatite also crystallizes in nature under alkaline ultramafic rock-forming conditions.

1. Introduction

Calcium hydroxylapatite $3Ca_3(PO_4)_2 \cdot Ca(OH)_2$, the principal inorganic constituent [1] of animal bones and teeth, is also synthesized in nature under the geological conditions, as in animal bodies. A series of cationic and anionic isomorphous substitutions [2] take place in the apatite crystal lattice in nature, of which the principal ones noticed are replacement of Ca^{2+} by Sr^{2+}, Y^{3+}, La^{3+} etc., and PO_4^{3-} by CO_3^{2-}. The $Ca^{2+} \rightleftharpoons Sr^{2+}$ exchange [3–5] and $PO_4^{3-} \rightleftharpoons CO_3^{2-}$ exchange [6] have already been investigated. The present study was undertaken to determine whether calcium hydroxylapatite is produced in nature under alkaline ultramafic rock-forming condition, and if cationic and anionic substitutions also take place under these conditions. Details on natural apatite are reported.

2. Sample preparation

The apatite–magnetite rock cores, recovered from the mineralized zone of Sung Valley [7], were crushed and ground to powder of 80 mesh size. The magnetic fraction was separated by combing repeatedly using a bar magnet and butter paper. The non-magnetic fraction was washed with distilled water, air dried and subjected to heavy liquid separation by bromoform (specific gravity 2.85–2.90 at 20 °C). The heavy fraction thus obtained was subjected to isodynamic magnetic separation with the forward slope of the magnet at 20°, side slope at 10°–15°, current 0.8 A and a vibration rate of 57 Hz. The separated fractions were run repeatedly to obtain maximum purity. Finally, the apatite crystals were picked up under the bionocular microscope by mounting the separated fractions on a glass slide. The separated crystal samples were then used for SEM, chemical analysis, X-ray diffraction (XRD) and infrared studies. In addition, thin sections of the apatite–magnetite rock and grain-mounted slides of the respective samples were studied under a petrological microscope.

3. Results and discussion

3.1. Petrological studies

The euhedral apatite and magnetite crystals had developed in nature and formed "apatite–magnetite rock" (Fig. 1) in the geological area under investigation. The euhedral apatite crystals are shown in Fig. 2. Hexagonal-shaped apatite crystals were also observed (Fig. 3), with "zircon" ($ZrSiO_4$) inclusions. Fig. 4 shows a magnified view of a euhedral zircon crystal. Calcite ($CaCO_3$) is also identified with the apatite.

3.2. Chemical analysis

The weight percentages of P_2O_5, CaO, MgO, Na_2O, K_2O, Fe_2O_3 (Table I) in the samples were analysed by conventional wet-chemical methods [8–10]. Trace elements (Table II copper, lead, zinc, nickel, cobalt, cadmium, silver, manganese, lithium, strontium and rubidium) were analysed by atomic absorption spectrophotometry, and gallium, antimony, bismuth, tin, molybdenum, tungsten, germanium, indium, tantalum, barium, titanium, vanadium, chromium, lanthanum, yttrium, scandium, niobium, zinc and beryllium, by emission spectrography.

A perusal of the analytical results obtained so far from the present study reveals significantly high values of sodium, strontium, lanthanum and yttrium in apatite. This may be attributed to the isomorphous substitution of Ca^{2+} (0.106 nm) from the calcium hydroxylapatite crystal lattice by elements with close ionic radii such as Na^{+}(0.106 nm), Sr^{2+}(0.127 nm), Y^{3+}(0.106 nm), La^{3+}(0.122 nm). The elements Zn^{2+}(0.083 nm), Mg^{2+}(0.078 nm), Ni^{2+}(0.078 nm), Co^{2+}(0.082 nm), Mn^{2+}(0.091 nm), etc., which have

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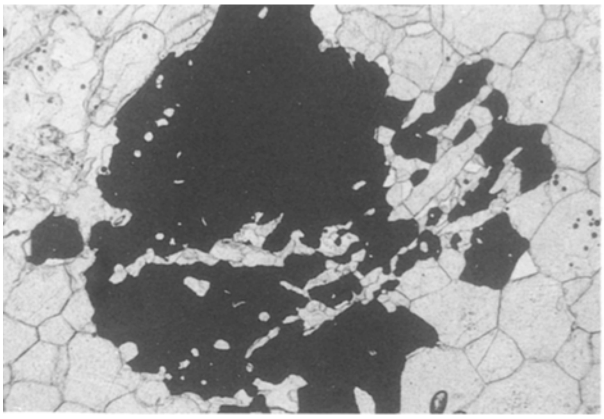

Figure 1 Thin section of apatite–magnetite rock showing "apatite" and "magnetite" crystal (× 31.25, under plane polarized light).

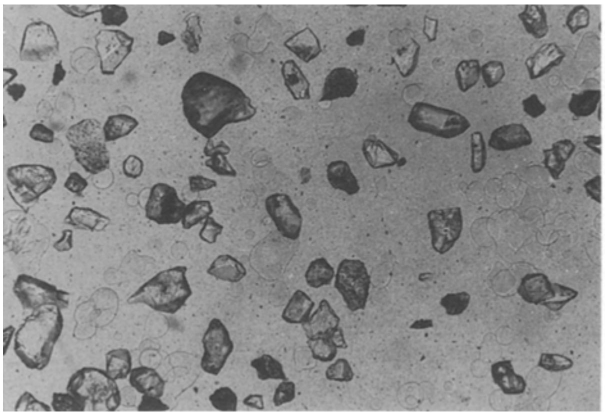

Figure 2 Separated fraction of apatite showing euhedral crystals of apatite with some magnetite (× 500, under plane polarized light).

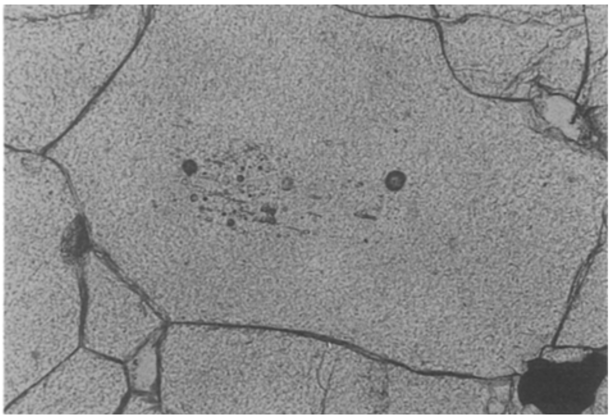

Figure 3 Thin section showing hexagonal apatite crystals with inclusions of shedded zircon (× 78.75, under plane polarized light).

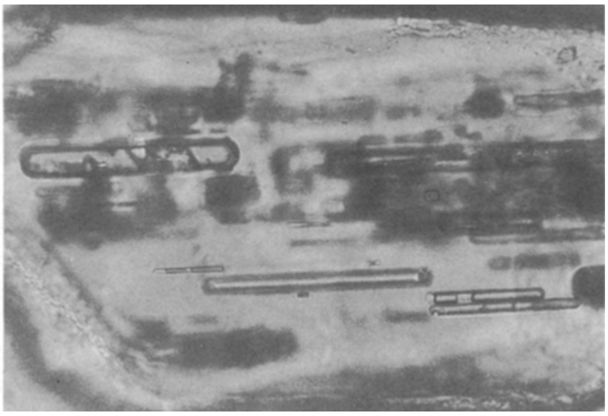

Figure 4 Thin section showing needle-shaped zircon crystals in apatite (× 500, under plane polarized light).

TABLE I Results of chemical analysis (wt %) of the apatite fraction (major constituents)

Serial no.	Sample	P_2O_5	CaO	MgO	Na_2O	K_2O	Fe_2O_3
1.	AP–21	36.94	63.73	0.30	0.17	0.036	Nf[a]
2.	SVP–7/67(AP)	35.92	60.37	1.69	0.21	0.012	0.279
3.	SVP–12/22(AP)	37.46	59.55	0.14	0.16	0.039	0.6515
4.	SVP–12/29(AP)	36.43	60.59	0.17	0.19	0.015	0.667
5.	SVP–12/13(AP)	36.43	60.59	0.72	0.15	0.02	0.124
6.	SVP–12/17(AP)	37.97	61.64	0.06	0.18	0.009	0.373
7.	SVP–20/22(AP)	30.39	60.92	2.37	0.16	0.03	0.0125
8.	SVP–12/25(AP)	37.46	59.55	0.08	0.20	0.009	0.034
9.	SVP–12/26(AP)	35.92	60.59	0.15	0.20	0.009	0.544
10.	SVP–12/18(AP)	35.92	59.55	0.17	0.19	0.009	0.6514

[a] Nf = not found.

ionic radii close to those of Fe^{2+}(0.083 nm), while Cr^{3+}(0.064 nm), Ti^{4+}(0.064 nm), V^{3+}(0.065 nm), Ti^{3+}(0.069 nm), etc., have ionic radii close to that of Fe^{3+}(0.067 nm) [11]. Therefore, these elements are interrelated between themselves, but not with the apatite crystal. The above results are related to the associated magnetic fraction only. The analytical data for zirconium (Table II) obtained with apatite are due to the zircon ($ZrSiO_4$) crystal inclusion (Fig. 4) in the apatite crystal. The results showing trace elements potassium, copper, barium and niobium may be due to the geological matrix.

3.3. X-ray data

The samples were subjected to X-ray diffraction analysis by powder method and the results for the lattice parameters *a* and *c* are shown in Table III. The plane constants (*d* nm) of the samples were compared with those reported by the JCPDS Card 9-432 [12, 13].

TABLE II Results of chemical analysis (p.p.m.) of the minor constituents of apatite fraction

Serial no.	Sample	Cu	Zn	Mn	Ba	Sr	Ti	La	Y	Nb	Zr
1.	AP–21	Nf[a]	10	170	300	800	Nf[a]	900	300	Nf[a]	200
2.	SVP–7/67(AP)	30	80	460	250	680	120	800	200	20	200
3.	SVP–12/22(AP)	20	30	270	100	680	Nf[a]	700	120	Nf[a]	> 1000
4.	SVP–12/29(AP)	30	55	450	250	640	100	800	200	20	100
5.	SVP–12/13(AP)	20	30	210	< 10	700	Nf[a]	400	150	Nf[a]	> 1000
6.	SVP–12/17(AP)	40	75	490	250	660	100	800	200	10	300
7.	SVP–20/22(AP)	Nf[a]	40	420	10	1290	Nf[a]	500	120	< 10	1000
8.	SVP–12/25(AP)	20	50	400	250	640	100	700	200	20	100
9.	SVP–12/26(AP)	30	40	440	100	680	20	800	200	Nf[a]	300
10.	SVP–12/18(AP)	30	60	440	250	640	100	800	200	20	200

[a] Nf = not found. Nf = Pb, Ni, Co, Cd, Ga, Sn, Mo, V, Cr, Sc, As, Ag, Sb, Bi, W, Ge, In, Ta, Be, Li, and Rb.

TABLE III Chemical and X-ray analysis of apatite from Sung Valley, Meghalaya, India

Serial no.	Sample	P (wt%)	Total calcium obtained (wt%)	Calcium in apatite (wt%)	Calcium in calcite (wt%)	Total Na + Sr + Y + La content in apatite (wt%)	H_2O (wt%)	a (nm)	c (nm)	Unit cell volume (10^{-3} nm^3) $(\frac{3}{2})^{1/2} a^2 c$
1.	AP–21	16.12	45.55	34.42	10.78	0.3390	1.44	0.943 19	0.688 3	530.2663
2.	SVP–7/67(AP)	15.67	43.15	33.46	9.69	0.3270	1.48	0.940 58	0.688	527.1058
3.	SVP–12/22(AP)	16.35	42.56	34.99	7.57	0.2675	1.46	0.936 07	0.682 77	518.11
4.	SVP–12/29(AP)	15.89	43.30	33.97	9.33	0.3030	1.43	0.940 10	0.682 59	522.443
5.	SVP–12/13(AP)	15.89	43.30	34.03	9.27	0.2375	1.41	0.937 68	0.687 67	523.609
6.	SVP–12/17(AP)	16.57	44.05	35.43	8.62	0.3005	1.51	0.936 11	0.687 78	522
7.	SVP–20/22(AP)	13.26	43.54	29.28	14.26	0.3110	1.19	0.940 10	0.685 47	524.646
8.	SVP–12/25(AP)	16.35	42.56	34.96	7.60	0.3040	1.42	0.936 69	0.688 02	522.77
9.	SVP–12/26(AP)	15.67	43.30	33.47	9.83	0.3180	1.50	0.935 97	0.688	521.9516
10.	SVP–12/18(AP)	15.67	42.56	33.48	9.08	0.3090	1.46	0.939 38	0.685	523.9148
	$Ca_{10}(PO_4)_6(OH)_2$[b]	18.70	–	40.00	–	–	–	0.9418	0.687	527.70

[a] H_2O represents OH ion present in apatite crystal lattice.
[b] Data for synthetic calcium hydroxylapatite from [16].

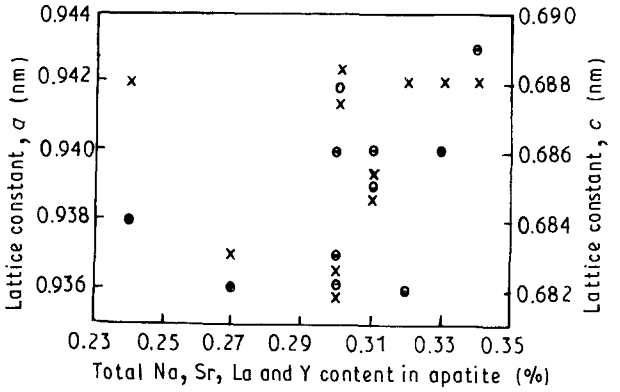

Figure 5 Dependence of lattice parameters (○) a and (×) c of apatite on the isomorphous substitution for the calcium ion by Na, Sr, La, Y, etc.

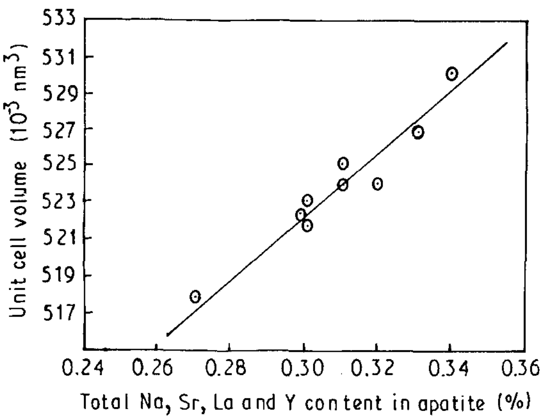

Figure 6 Dependence of unit cell volume of apatite on the isomorphous substitution for the calcium ion by Na, Sr, La, Y, etc.

The X-ray data are in close agreement with the reported synthetic calcium hydroxylapatite $Ca_{10}(PO_4)_6(OH)_2$ [14–16]. The negligible deviations of lattice parameters a and c may be due to the isomorphous substitutions for the Ca^{2+} ion by elements with similar ionic radii such as Sr^{2+}, Y^{3+}, Na^+, La^{3+}, etc., in the apatite crystal lattice. This also confirms the observations from the chemical analysis data. Unsystematic deviations of the lattice parameters (Fig. 5) may be because of the multi-elemental substitutions for the calcium ion. The deviation of the unit cell volume (Fig. 6) with isomorphous substitution is proportional to the amount of substituents. Similar investigations have been made for fluorapatite and chlorapatite, but no encouraging results were obtained. Calcite ($CaCO_3$) association with apatite was also confirmed through the X-ray diffraction studies.

3.4. Infra-red data

The strong peak at 3516 cm^{-1} confirms the presence of OH ions in the apatite crystal lattice. This band is due to the characteristic O–H stretching mode of the hydroxyl ion vibration in the crystal [17, 18]. The presence of OH ions was also confirmed by the chemical analysis data (Table III). The strong and medium absorption peaks at 1040, 1093, 733, 692 cm^{-1}, etc., confirm the presence of the "Tetrahedral orthophosphate ion" (PO_4^{3-})in the apatite crystal lattice [16, 19–21].

4. Conclusion

It has been established that the "Sung Valley apatite" in Meghalaya, India, is calcium hydroxylapatite with the chemical formula $Ca_{10}(PO_4)_6(OH)_2$ and partial isomorphous substitution for calcium ions in the crystal lattice.

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