

## ***The sources of phosphorus for the phosphatic rocks in the Toyoma Formation, Northeastern Japan***

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### **Abstract**

The apatite in the phosphatic rocks of the Toyoma Formation is carbonate fluorapatite highly enriched in Ce and Y. The Ce and Y enrichment of the apatite suggests that the source of phosphorus is biogenic phosphate mineral debris such as fish bones, teeth and scales rather than phosphorus-bearing organic matter. The spatially and stratigraphically limited distribution of the phosphatic rocks in the formation is in accord with this view.

### **Introduction**

Nodules and thin beds of phosphatic and carbonate rocks have been known to occur in the black shale of the Toyoma Formation, which is the uppermost part of the Paleozoic strata in the South Kitakami belt, northeastern Japan. It has been clarified that the phosphatic rocks and the carbonate rocks in the Toyoma Formation are diagenetic in origin (Morikiyo et al., 1994; Morikiyo and Matsunaga, 2001). The sources of phosphorus in the phosphatic rocks may be organic matter, ferric hydrous oxides, an iron phosphate mineral (vivianite), or biogenic calcium phosphate particles deposited on the sea floor. The phosphorus-bearing organic matter and iron phosphate mineral are decomposed by microbial sulfate reduction to release phosphate ions (mainly  $\text{HPO}_4^{2-}$  at  $\text{pH}=8$ ) into the sediment pore water (Koyama, 1980). Thus the organic matter and iron phosphate mineral are possible candidates for the sources of apatite in the phosphatic rocks. On the other hand, Suess (1981) has stated that dissolution of biogenic phosphate mineral debris (fish bones, teeth and scales) is a mechanism for remineralization of phosphate. In this paper, the source of phosphorus of the phosphatic rocks in the Toyoma Formation is deduced mainly from the chemical characteristics of apatite.

The Toyoma Formation is widely distributed in the Utatsu district, Miyagi prefecture. The samples studied were taken from the surface exposures at the coast of the district.

### Mineralogy of apatite

The apatite in the phosphatic rocks of the Toyoma Formation is carbonate fluorapatite. The carbonate fluorapatite was identified by X-ray diffraction and chemical analysis. Using alpha quartz as an internal standard, interplanar spacings were measured; the most prominent are shown in Table 1. These and their relative intensities are in close agreement with ASTM 15-876 data for fluorapatite and the data of Price and Calvert (1978). CO<sub>2</sub> weight percent of the fluorapatite was estimated by an X-ray peak pair method developed by Gulbrandsen (1970). The equation is as follows:  $y = 23.6341 - 14.7361x$ , where  $y$  is CO<sub>2</sub> weight percent and  $x = \Delta 2\theta[(004) - (410)]$ . The results are shown in Table 2. CO<sub>2</sub> content of the fluorapatite from the Toyoma Formation ranges from 0.5 to 4.0 % by weight. The CO<sub>2</sub> content of the apatite is almost similar to that of marine carbonate fluorapatite from the Phosphoria Formation of

Table 1 Internal spacings of the carbonate fluorapatite from the Toyoma Formation.

Phosphatic nodules 042901 SP-4		A-type rock UP-4A		Fluorapatite, syn ASTM 15-876	
d(Å)	I/I <sub>1</sub>	d(Å)	I/I <sub>1</sub>	d(Å)	I/I <sub>1</sub>
3.44	44	3.44	43	3.442	40
2.79	100	2.80	100	2.800	100
				2.772	55
2.70	53	2.71	61	2.702	60
2.63	25	2.62	28	2.624	30
2.24	30	2.25	23	2.250	20
		1.937	26	1.937	25
1.838	21	1.838	28	1.837	30
1.765	5	1.768	8	1.771	14
1.746	8	1.746	7	1.748	14
1.722	5	1.725	7	1.722	16

Table 2 CO<sub>2</sub> content of the carbonate fluorapatite.

Rock type	Sample No.	$\Delta 2\theta$	CO <sub>2</sub> wt. %
N	042901-SP2	1.33	4.04
N	042901-SP4	1.47	1.97
A	042902-SP3a	1.56	0.65
A	UP-4A	1.42	2.71
A	OP-4A	1.57	0.50

$\Delta 2\theta$  represents the difference between (004) and (410) peaks for CuK  $\alpha$  radiation.

western U.S., Florida, Morocco, and Peru (Manheim and Gulbrandsen, 1979). Thus it is proper to designate the mineral as carbonate fluorapatite.

The  $P_2O_5$  and F contents of the four rock types of the Toyoma Formation were measured by Kanisawa and Ehiro (1986). The data points for the rocks, in spite of their wide range, fall in a positive straight line in the F versus  $P_2O_5$  diagram (Fig.6 of Kanisawa and Ehiro, 1986). The inclination of the regression line,  $F/P_2O_5=0.09$ , agrees well with the stoichiometry of fluorapatite. This fact clearly indicates that  $P_2O_5$  and F in the phosphatic and carbonate rocks of the Toyoma Formation are entirely fixed in fluorapatite.

### Trace element concentration

The trace element concentrations of the phosphatic and carbonate rocks from the Toyoma Formation have been reported by Kanisawa et al., (1985). The data are reproduced in Table 3. The phosphatic nodules and A-type rock are found to be remarkably enriched in Ce and Y. Phosphatic nodules have Ce and Y concentrations of 956 and 837 ppm, respectively, and A-type rock has concentrations of 534 and 692 ppm, respectively. Phosphatic rocks of the Toyoma Formation have a Ce concentration 4-35 times higher, and a Y concentration 3-170 times higher, than modern phosphatic nodules off of Namibia (Price and Calvert, 1978). Phosphorites from elsewhere in the world do not have REE values so different from the Namibian phosphatic nodules (Kolodny, 1981), so phosphatic rocks of the Toyoma Formation have a distinctive characteristic. The black shale and C-type (carbonate rock) of the Toyoma Formation do not show any enrichment in Ce and Y. Thus, it is concluded without doubt that the

Table 3 Trace-element concentrations (in ppm) of the phosphatic and carbonate rocks from the Toyoma Formation.

Rock type	BS	BS	N	A	B	C
Sample No.	T-41	T-66	UP-59A	OP-3	UP-4	UP-56
Ba	324	482	190	119	227	246
Ce	36.1	74.4	956	534	23.6	16.3
Co	20.8	12.7	5.9	12.6	15.8	3.0
Cr	70.2	51.4	42.9	34.1	41.4	3.6
Cs	3.39	9.55	-	-	4.22	0.50
Nb	6.1	14.1	4.4	4.0	3.7	1.2
Ni	49.1	27.9	18.7	28.9	26.0	2.1
Rb	67.0	120	27.3	24.3	60.4	14.8
Sc	16.9	12.4	7.9	4.3	14.7	4.0
Sr	215	112	1003	770	439	323
Y	25.7	35.1	837	692	18.1	13.9
Zn	78	79	74	83	43	33
Zr	120	196	75.7	85.7	167	22.8

Data from Kanisawa et al. (1985).

Ce and Y in the phosphatic rocks are accommodated in fluorapatite.

### Discussion

Several workers have reported that ichthyoliths recovered from sediments were highly enriched in REE (Arrhenius et al., 1957; Bernat, 1975; Dymond and Eklund, 1978; Wright et al., 1984; Elderfield and Pagett, 1986). If such REE-enriched biogenic apatite debris are dissolved in anaerobic pore water during early stage of diagenesis (i.e., Stage 1 of Morikiyo et al., 1994), then not only phosphorus but also REE concentrations of pore water must be raised. With the progress of oxidation of organic matter by sulfate ion, another phosphorus, contained in organic matter, is liberated into pore water. Further addition of  $\text{HPO}_4^{2-}$  to anaerobic pore water as a result of sulfate reduction may bring about the precipitation apatite, which is rich in Ce and Y. This is thought to have occurred at Stage 2 of Morikiyo et al., (1994).

Precipitation of Ce and Y enriched apatite within sediments from pore water having exactly the same composition as sea water during diagenesis seems to be unlikely. Because REE concentrations of sea water are extremely low, (for example, Ce: 1ng/liter, Krauskopf, 1979), the small-volume pore water of sea water origin cannot provide sufficient amounts of Ce and Y needed for the apatite in the Toyoma Formation. On the other hand, since Nd concentration of ichthyoliths is equivalent to one million liters of sea water per gram of ichthyoliths (Elderfield and Pagett, 1986), ichthyoliths are candidates for the sources of the Ce- and Y-enriched apatite. High concentrations of Ce and Y in the diagenetic phosphatic rocks of the Toyoma Formation strongly suggest that Ce, Y, and also phosphorus, were derived from biogenic phosphate mineral debris which had undergone Ce and Y enrichment at the bottom of the sea.

Phosphatic rocks have not been found throughout the horizons of the Toyoma Formation. The occurrence seems to be spatially and stratigraphically restricted. This means that sediments originally rich in phosphorus were deposited in certain areas of the Toyoma sedimentary basin. The limited distribution of the phosphatic rocks also supports the view that the source of phosphorus in the phosphatic rocks was biogenic phosphate mineral debris rather than phosphorus-bearing organic matter.

### Conclusions

The apatite in the phosphatic rocks in the Toyoma Formation is carbonate fluorapatite with high concentrations of Ce and Y. The occurrence of the phosphatic rocks is spatially and stratigraphically restricted. These suggest that the sources of phosphorus for the apatite are biogenic phosphate mineral debris such as fish bones, teeth and scales buried in sediments, rather than phosphorus liberated by the oxidation of organic matter.

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