A STUDY ON MONAZITE FROM THE EBISU MINE, GIFU PREFECTURE

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ABSTRACT

Monazite from the Ebisu mine, Gifu Prefecture has been studied. The monazite from Ebisu is of yellowish or dark brown colour, with sp. gr.: 5,20. The result of chemical analysis of the sample is as follows: P_2O_5 26.81, SiO_2 2,24, Al_2O_3 0.36, ThO_2 4.51, U_3O_8 0.21, Ce_2O_3 24.58, $La_2 \cdot O_3$ etc, 38.51, Fe_2O_3 0.48, CaO 0.86, PbO 0.02_6, ig. loss 0.91, total 99.49% Monazites from Ratnapura, Ceylon and Minas Geraias, Brazil are also analysed for comparison. The relationships between the cell dimensions, the relative abundances of rare earths and the ThO_2 content are discussed. The chemical age of the Ebisu monazite is 108 m.y., while its thorium lead age on the basis of mass-spectrometric data is fifty million years, in accordance with the geological evidence.

Introduction

Neagi district, Gifu Prefecture, is one of the most famous localities of radioactive minerals in Japan. Recently the writer studied monazite from the Ebisu mine in the district, applying mass spectroscopic method and determined its absolute age.

The ages of several radioactive minerals from Japan have been determined by the chemical method, which is simply based on the ratio of total lead to uranium plus thorium in a mineral. This ratio will not give reliable age unless severe prerequisites are satisfied.

Occurrence

The Ebisu mine, Wada, Hirukawa village, Ena county, Gifu Prefecture, is situated about 14 kilometers north of the Oi railway station,

Chuo Line. The mine is worked for wolfram and arsenic. The geology of the district has already been reported by H. Shibata[9]. According to him, the geology of the district consists of quartz porphyry, granite porphyry, biotite granite and Palaeozoic formations. A granite mass, which contains numerous drusy pegmatites and has been specified as Naegi type by him, intruded and silicified the quartz porphyry. Its age is considered to be of late Cretaceous. The ore deposits of the Ebisu mine are composed of several pneumatolytic quartz veins accompanied by greisen in the quartz porphyry or in the granite. The ore minerals are wolframite, scheelite, molybdenite, bismuth minerals, arsenopyrite, etc. Monazite is found as small disseminated grains with the modes of occurrence of the following three types: the first, in quartz vein comprising wolframite and bismuth minerals; the second, in greisen containing topaz and micas; and the last, in the silicified country rock. It is of interest that a considerable quantity of monazite occurs in such modes as those and that similar cases have been revealed in several localities in Japan.

Physical properties

Monazite from the Ebisu mine seldom shows crystal faces. It is yellowish to dark brown in colour with white streak. The hardness is 5, and specific gravity, determined by the pycnometer method, is 5.20 at 18°C. The indices of refraction are α 1.790, β 1.791, and γ 1.840; and $(+)2V=10°$.

Chemical analysis

The monazite sample was prepared from the wolframite concentrate which was kindly offered by the Ebisu Mining Company through the courtesy of Prof. N. Katayama. About 50 kg. of the wolframite concentrate was sized into three fractions, that is 60–80, 80–110 and 110–170 mesh. From each of them, monazite was concentrated first with a magnetic separator. The monazite concentrate thus prepared was purified by hand picking under the binocular microscope. The purified

sample was analysed chemically.

Monazite from Ratunapura, Ceylon and from Minas Geraias, Brazil were also analysed for the sake of comparison.

Spectroscopic analyses revealed that the samples did not contain noticeable amount of element other than those chemically analysed.

The outline of the procedure of a quantitative analysis applied to the samples is as follows:

About 1 g. of the material was decomposed with about 10 ml. of boiling concentrated sulphuric acid for 30 min. After cooling, the decomposite was poured into 100 ml. of 2 per cent. sulphuric acid solu-

Table 1. Chemical analyses of monazites from Ebisu,
Ratnapura and Minas Geraias

	1	1a	1b	2	2a	2b	3	3a	3b
P_2O_5	26.81%	3.640		26.84%	3.591		28.57%	3.739	
SiO_2	2.24	0.336	4.640	2.46	0.390	4.075	1.18	0.177	4.121
Al_2O_3	0.36	0.070		0.43	0.076		1.08	0.205	
ThO_2	4.51	0.165		14.52	0.532		5.37	0.186	
U_3O_8	0.21	0.008		0.32	0.010		tr.		
Ce_2O_3	24.58	1.452		22.95	1.330		28.43	1.609	
La_2O_3 etc.	38.51	2.149	3.962	30.56	1.369	3.981	32.49	1.894	4.017
Fe_2O_3	0.48	0.058		0.93	0.116		2.88	0.334	
CaO	0.86	0.130		0.82	0.123		0.02	0.003	
PbO	0.026	0.000		0.20	0.001		0.09	0.000	
Ig. loss	0.91			0.35			0.46		
Total	99.49%			100.37%			100.57%		

[Analysis by T. Kato (1957)]

1   Monazite from the Ebisu mine, Gifu Pref.
2   Monazite fyom Ratnapura, Ceylon.
3   Monazite from Minas Geraias, Brazil.
    a and b are molecu;ar ratios and molecular proportions, reepectively
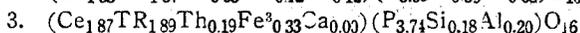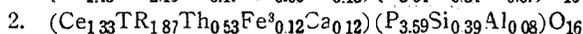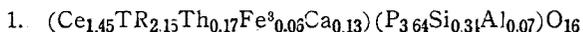
Chemical formula:
   1. $(Ce_{1.45}TR_{2.15}Th_{0.17}Fe^3{}_{0.06}Ca_{0.13})(P_{3.64}Si_{0.31}Al_{0.07})O_{16}$
   2. $(Ce_{1.33}TR_{1.87}Th_{0.53}Fe^3{}_{0.12}Ca_{0.12})(P_{3.59}Si_{0.39}Al_{0.08})O_{16}$
   3. $(Ce_{1.87}TR_{1.89}Th_{0.19}Fe^3{}_{0.33}Ca_{0.00})(P_{3.74}Si_{0.18}Al_{0.20})O_{16}$
        TR = Total rare earths except cerium.

tion. The SiO_2 was determined from the residue. The volume of the filtrate was adjusted to 250 ml. The 25 ml. portion was used to determine phosphorus, the 50 ml. portion to titrate cerium by ammonium ferrous sulfate and potassium permanganate after oxidizing cerrous to ceric ion by ammonium persulfate, and the 100 ml. portion to separate rare earths and thorium by oxalic acid and ammonium hydroxide, and

Table 2. Chemical analyses of monazites and huttonite

	1	2	3	4	5	2
Ce_2O_3	21.08%	27.77%	22.03%	19.44%	31.90%	
La_2O_3 etc.	31.27	28.15	38.57	23.24	28.00	2.6%
Y_2O_3 etc.	3.53	3.01			0.46	
ThO_2	11.08	6.49	5.53	8.52	10.22	76.6
U_3O_8	0.42	—	0.44		(0.37)	nil.
SiO_2	2.98	2.64	3.07	10.81	0.90	19.7
Fe_2O_3	0.66	1.33	1.52	nd.	1.50	1.2
P_2O_5	27.52	29.10	26.41	20.42	26.82	trace
H_2O^+	0.56	0.64	1.38	1.64	0.46	nil.
CaO	0.52	0.47	0.00	nd.	0.20	nil.
Al_2O_3	0.80	0.75	0.00	nd.	0.17	nil.
MgO	0.37	0.08	0.00	nd.	—	nil.
PbO	—	—	—	nd.	—	—
Total	100.69%	100.43%	100.39%		101.00%	100.1%
Sp. Gr.		5.11	5.0495			7.1

1. Monazite from Ishikawa, Fukushima Prefecture. Analysis by U. Shibata and K. Kimura (1921).
2. Monazite from Kuchinokura, Nara Pref. Analysis by T. Higami (1944).
3. Monazite from Kotogé, Fukuoka Pref. Analysis by T. Iimori (1936).
4. Monazite sand from Naegi, Gifu Pref. Analysis by U. Shibata and K. Kimura (1921).
5. Monazite from Travancore, Ceylon. Analysis by Johnstone (1914).
6. Huttonite from South Westland, New Zealand. Analysis by Hutton (1951).[2]

on the rare earths filtrate, iron, aluminium, calcium and manganese were determined.

In Table 1 are listed the results of the analyses of the monazites and in Table 2, some previous data for comparison.

X-ray fluorometric analysis

Semi-quantitative X-ray flluorometric analysis was carried out on the rare earths oxides which had been chemically separated from the monazite samples. The results recalculated on the basis of the sum of the intensities of CeLα and NdLα to be equal to 69.1 are shown in Table 3[4].

In reference to abundance, the rare earths in the monazites listed in Table 3 may be devided into three groups; the most abundant group comprising Sc and Y, the lanthanons with even atomic number, and the lanthanons with odd number.

Table 3. X-ray fluorometric data of monazite

Atom. No.	X-ray line	1 India	2 Ceylon	3 Thai	4 Ebisu	5 Ishikawa
57	LaLα_1	10	11	6	8	8
58	CeLα_1	45	33	38	38	28
59	PrLα_1	15	13	10	8	10
60	NdLα_1	24	25	25	23	21
62	SmLα_1	23	24	23	20	24
63	EuLα_1	9	8	11	11	10
64	GdLα_1	32	27	31	26	33
65	TbLα_1	6	5	7	7	7
66	DyLα_1	66	60	44	25	66
67	HoLα_1	8	10	15	18	25
68	ErLα_1	8	3	6	7	16
69	TuLα_2	6	5	9	7	8
70	YbLα_1	17	9	12	11	13
71	LuLα^1	9	5	6	4	8

Norelco spectrographic equipment, Target Mo, 40 kV, 15 mA. Analysing crystal LiF, line intensities were determined by the automatic scanning-recording method.

It is generally accepted that a Z-even lanthanons is always more abundant than Z-odd lanthanons of adjacent atomic number, and present data are in accordance with general trends.

The relative intensities of the $L\alpha_1$ lines of the individual rare earth-elements in the five monazite samples have been plotted against the content of thoria in Fig. 1.
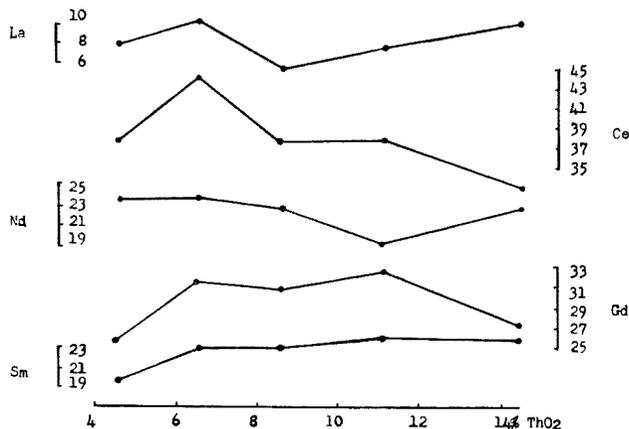
Fig. 1. Relative abundances of rare-earths in monazite.

Recently, Murata et al (1957)[4] analysed spectroscopically the rare earths in twenty-six monazite samples and showed that the contents of La and Ce increase together, and those of Nd, Sm, Gd and Y decrease concomitantly, while Pr remains nearly constant.

The data obtained by the present study do not necessarily follow their results as is obvious in Fig. 1.

X-ray examination

The X-ray powder patterns of monazites are compared in Tables 4-1 and 4-2 with that of huttonite.

Usually in monazite some thorium and a little uranium are present replacing cerium-lanthanum group elements. The increase in cation charge by the replacement is compensated for by the relevant replacement of phosphorus by silicon. The coupling replacement may

result in a solid solution series between monazite and huttonite, which have the same space group and the analogous crystal structure as monazite.

Although the cell dimensions of huttonite are very close to those of monazite, it is expected that there is systematic variation in them from monazite to huttonite.

On the other hand, Karkhanavara and Shankar (1944) and Ueda (1955)[13] proved by the X-ray powder method that some specimens of monazite were slightly metamict and lattice distension had taken place.

By using the spacings for powder lines which were calibrated by lead nitrate, the unit-cell dimensions of the raw specimen and the ignited specimen have been computed and the results are summarized in Table 5. The variation diagram of the cell dimensions versus ThO_2 content is illustrated in Fig. 2.
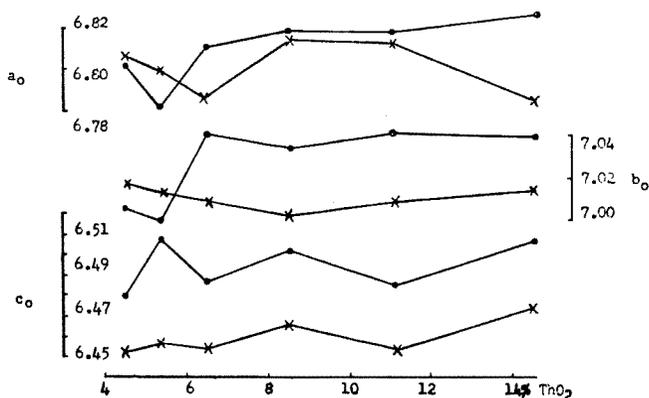
Fig. 2. Cell dimensions of monazite.

Contrary to the expectation, there is no systematic relationship between the cell dimensions and the thorium content of monazite. This may be attributable to the following facts. (1) The differences in cell dimensions between monazite and huttonite are too small to visualize the effect of the variation in thorium content. (2) In addition to the variation of thorium content, there is a complicated compositional variation in monazite.

Table 4-1. X-ray powder data of monazite and huttonite

hkl	1 monazite Ebisu			2 monazite Ishikawa			3 monazite Ceylon			4 monazite Brazil		
	d(Å)	d(Å)+	I	d(Å)	d(Å)+	I	d(Å)	d(Å)+	I	d(Å)	d(Å)+	I
10ī	5.25	5.20	10		5.19			5.23			5.23	
110	4.82	4.80	8	4.84	4.83	5		4.82		4.82	4.82	5
011	4.70	4.68	14	4.68	4.66	8	4.70	4.66	8	4.70	4.69	8
11ī	4.17	4.18	22	4.18	4.23	13	4.20	4.17	28	4.17	4.19	ī6
10ī		4.08		4.05	4.05	5	4.05			4.09	4.10	
111 020	3.51	3.51	30	3.50	3.51	25	3.52	3.51	36	3.51	3.52	16
200	3.30	3.30	60	3.34	3.31	20	3.30	3.30	50	3.34	3.30	20
120	3.09	3.09	100	3.09	3.09	100	3.10	3.09	100	3.10	3.10	100
210	2.98	2.986	22	2.996	2.988	10	2.996	2.987	20	2.994	2.987	12
012	2.877	2.827	45	2.877	2.864	80	2.877	2.864	53	2.873	2.866	80
20$\bar{2}$	2.611	2.624	11	2.609	2.628	8	2.611	2.59f	20	2.605	2.598	11
112	2.446	2.443	12	2.450	2.435	8	2.448	2.455	17	2.448	2.442	10
220	2.004	2.399	5	2.409	2.397	5	2.412		16		2.401	
931	2.198	2.191	30	29185	2.186	8	2.195	2.188	28	2.194	2.187	11
10$\bar{3}$ 31ī	2.141	2.140	32	2.141	2.140	15	2.152	2.140	25	2.147	2.138	20
221		2.128		2.116	2.116	13	2.137		23	2.128		10
212	1.965	1.924	30	1.963	1.963	6	1.966	1.967	17	1.967	1.961	20
301		1.925		1.934	1.925	7				1.940	1.936	14
23ī	1.899	1.896	10	1.897	1.892	10	1.905	1.903	14		1.898	
103 032	1.877	1.866	15	1.875	1.877 1.870	10	1.870	1.373 1.869	28	1.875	1.874 1.868	20
320	1.876	1.860	15	1.861		5					1.861	
023		1.797			1.803		1.807	1.797	5	1.398		
222 040	1.768	1.765 1.753	10	1.762	1.758	12	1.759	1.755	5	1.763	1.756	6
132	1.743	1.737	16	1.745	1.738	11	1.743	1.739	10	1.742	1.742	14
321 140	1.692	1.689	10	1.693	1.688	8	1.688	1.693	17	1.694	1.694	4
123 400							1.663		5			

'Norelco' X-ray diffractometer. CuKα/Ni. 4-I-8 slit 1°, 0.006″, 1. Speed 1′/min. (partly 2′/min.) Scale factor 4′, Multiplier 1. Time constant 8 sec. d(Å) and I are the spacings and intensities for the raw specimen, respectively. d(Å)+ are the spacings for the ignited specimen.

Since the effect of ignition on the cell dimensions is very slight, the monazite from Ebisu may be considered to be almost free from metamictization.

The contents of uranium, thorium and lead in the monazite from the Ebisu mine, Gifu Presecture were determined chemically as follows;

Table 4-2.   X-ray powder data of monazite and huttonite

(hkl)	1 monazite Thai			2 monazite India			3 nuttonite	
	d(Å)	d(Å)+	I	d(Å)	d(Å)+	I	d(Å)	I
10ī		5.17		5.22	5.28	12	5.29	3
100		4.81		4.80	4.76	17		
011	4.70	4.68	12	4.80	4.67	17	4.71	5
11ī	4.19	4.18	30	4.18	4.18	27	4.23	6
101		4.08			4.10		4.08	4
111							3.53	4
020	3.51	3.51	65	3.52	3.51	36	3.49	1
200	3.30	3.30	60	3.29	3.30	70	3.29	6
120	3.10	3.09	100	3.09	3.08	100	3.09	8
210		2.981	40		2.966	15	2.98	3
012	2.872	2.864	55	2.873	2.852	30	2.89	7
20̄2	2.614	2.597	25	2.605	2.597	11	2.65	3
112	2.449	2.443	27	2.448	2.444	12	2.44	1
220	2.	2.399			2.393			
031	2.190	2.183	25	2.195	2.190	22	2.19	4
103	2.151		30	2.144		22		
31ī		2.137			2.144		2.156	2
221							2.110	3
212	1.970	1.967	30	1.973	1.967	12	1.953	4
301		1.945			1.949			
23ī		1.892			1.895		1.893	3
103		1.889			1.872			
032	1.863	1.866	35	1.868	1.663	22		
320							1.859	5
023		1.800			1.796			
222		1.767			1.768			
040	1.756	1.759	25	1.759		14	1.749	4
132	1.-47	1.742	25	1.743	1.741	17		
321	1.694	1.691	20	1.694	1.677	12		
140							1.692	4
123								
400							1.646	2

'Norelco' X-ray diffractometer. CuKα/Ni. 30 kV. 15 mA. 4-1-8 silt 1°, 0.006″, 1. Speed 1′/min. (partly 2′/min.) Scale factor 4′, Multiplier 1. Time constant 8 sec.

Thorium and uranium were determined by the gravimetric method. Hexamine was used to separate thorium from rare earths. Uranium was precipitated as uranyl-phophate. Lead was determined by the colorimetric method by use of dithizone.

Lead was isolated from the sample by extracting it into dithizone. In order to determine the isotopic composition of the lead, following two methods were taken: 1) The extracted lead was converted

Table 5. Cell dimensions of monazite

	1 Ebisu	2 Ishikawa	3 Ceylon	4 Brazil	5 Thai	6 India	7 Huttonite
raw specimen							
a_0	6.820Å	6.820	6.843	6.782	6.813	6.820	6.80
b_0	7.003Å	7.040	7.041	6.920	7.030	7.039	6.96
c_0	6.480Å	6.485	6.506	6.508	6.503	6.485	6.54
β	103°39′	103°47′	103°43′	103°45′	103°47′	104°00′	104.9°
Vol.	299.6Å	302.5	304.4	296.7	302.6	302.5	299
ThO_2	4.51%	11.25	14.52	5.37	8.50	6.54	76.6
after ignition							
a_0	6.806A	6.819	6.793	6.800	6.787	6.819	
b_0	7.016Å	7.006	7.015	7.013	7.002	7.005	
c_0	6.452Å	6.454	6.472	6.455	6.469	6.454	
β	103°34′	103°41′	103°44′	103°43′	103°46′	103°52′	
Vol.	295.1Å³	298.9	298.9	299.0	298.0	299.6	

through lead iodide to tetramethyl lead by a reaction with Grignard solution[8]. 2) The extracted lead was converted through lead iodide to lead chloride. The products thus obtained were introduced in the mass spectrometer. The isotopic abundances were calculated after necessary corrections had been made. The obtained data are shown in Table 6.

The crude age read from graphs of Wickman's family[14] is 108 m. y. which is considerably higher than the probable age.

Table 6. Monazite from Ebisu

Th: 3.97%, U: 0.18%, Pb: 0.024%

Lead isotope	Pb^{204}	Pb^{206}	Pb^{207}	Pb^{208}
Isotopic constitution (moles)	1.9	48	41	100
Common lead″	1.4	25.7	20.8	51.5
Radiogenic lead (p.p.m.)	0	20	1	112
Age in 10^7 y.	$\dfrac{U^{238}/Pb^{206}}{8}$		$\dfrac{Th/Pb^{208}}{5}$	

″ Average ratio determined on the common lead by the writer.

The isotopic constitution of the lead in Table 6 is stated in proportions relative to Pb^{208} taken as 100.

From the geochemical point of view, it is expected that lead, apart from radiogenic lead, would be only of trace amount in monazite. Assuming that all of Pb^{204} is derived from common lead, the corresponding proportions of Pb^{206}, Pb^{207} and Pb^{208} were subtracted. Of the four isotopic ratio ages, the actinium lead age and the lead leod age are not reliable owing to the extremely small content of Pb^{207}. The remaining two ages, the thorium lead age and the uranium lead age, are rather similar, but, of the two ages, the thorium lead age is more accurate because the thorium contained in the monazite is of considerably large amount while the uranium is of very small amount.

Recently, Tilton et al. (1957)[10] reported the results of four isotopically controlled age determinations on monazites and of acid washing experiments and discussed the cause of the discordant age. However it was impossible to apply their procedure to the present data, because the age of the Ebisu monazite is too young.

Summary and discussion

The monazite from the Ebisu mine occurs in greisen and pneumatolytic quartz veins, and is chemically characterized in the thorium content which is lower than the usual monazite of pegmatitic origin. X-ray fluorometric analysis revealed that the relative abundance of rare earths is in accordance with the general tendency.

Since the effect of ignition on the cell dimension is very slight, the material used may be recognized to be almost free from metamictization. Besides, the material had been prepared from the wolframite concentrate which had been obtained from the ores mined at a stope far below the water level. Hence, it is suitable for the age determination.

The most reliable age obtained from the Th/Pb^{208} ratio, and revealed to be about fifty million years, corresponds to the earliest Tertiary or the latest Cretaceous age, which is acceptable from the geological point of view as well.

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