BARITE IN THE ROSEKI FROM THE TOCHIHARA MINE, HYOGO PREFECTURE

by

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INTRODUCTION

The roseki deposits are extensively distributed in Chugoku district, and these have been investigated geologically and mineralogically by many workers. The ores are essentially composed of pyrophyllite, kaolinite, dickite, diaspor and corundum etc., and highly aluminous in general, showing the pretty high refractoriness.

Recently, M. Kimura¹⁾ and T. Ando²⁾ have studied these deposits. During the study on the mineral components of roseki, the authors have found the white vitreous mineral in the roseki from the Tochi-hara mine, Hyogo Prefecture. By optical, chemical, and X-ray studies, we have identified the mineral as barite. Barite occurs commonly in connection with metallic ores, especially "black

Fig. 1. Tochi-hara roseki mine

ore" in Japan. So, it is interesting on occurrence that the mineral is closely associated with the kaolin minerals in roseki.

The alunite and roseki deposits^{3),4)} being very similar to this deposit have been found near this mine, but the association with barite has not been reported yet.

OCCURRENCE

The Tochi-hara mine lies in Tochi-hara, Okawachi-machi, Kanzaki-gun, Hyogo Prefecture.

The rocks near the mine mainly consist of Tertiary bed, alternating strata of sandstone and shale, and volcanic rocks, such as liparite and quartz-porphyry, covered unconformably the alternations.

The ore deposits are chiefly developed in liparite in massive and lenticular forms by epithermal solution, and the kaolinitization and chloritization caused by the ascending solution works upon some mother rocks. Especially, liparite in the neighbourhood of ore deposits is almost altered except quartz in phenocryst. Each ore body among deposits is relatively small; and the prevailing strike is N 60°W~EW and the dip is generally 5°-10°N.

The ores are chiefly classified in following types by essential minerals.

- (1) Alunite and kaolinite
- (2) Kaolinite, dickite and sericite
- (3) Kaolinite and dickite bearing barite

As barite appears, sericite is scarcely found in the ore. Mostly, the ores are white or grayish white, and compact, but although some of them often give the clayey feature, those give tolerably high refractoriness (SK No. 28~32 as shown in Table 4) as well as compact ores. The respective relation among these types mentioned above is not so distinct on the genesis.

Alunite outcrops in small lenticular forms at upper part of the gate of Tunnel No. 1. Barite are found in the ores at south side let down Tunnel No. 3, and the deposits occur in lenticular bodies, 1.5~2 meters in thickness and about 10 meters in longer diameter

between altered liparites.

The ores are consisted of aggregations of fine kaolin minerals and barite included in phenocryst-like, being almost colorless or grayish white and showing glassy luster. The mineral forms idiomorphic crystal in tubular or short prismatic shapes.

MICROSCOPIC OBSERVATION

Under the microscope, the crystals show idiomorphic or hypidiomorphic shapes being lamellar (0.1–1.0 milli-meters in length), colorless and transparent. Optical characters of the mineral is shown in Table 1.

Table 1. Optical properties of barite from Tochiara

Refractive index	α	1.636
" "	γ	1.648
Double refraction	$\gamma - \alpha$	0.012
Pleochroism	Y	Deep yellow

CHEMICAL ANALYSIS

The specimens prepared for the analysis were carefully separated from coarsely crushed ores by picking up with pincette under the magnifier. The chemical analysis data of the mineral are shown in table 2. The results are very similar to the theoretical values of barite. A little quantity of SiO_2 , Al_2O_3 , Fe_2O_3 , CaO and H_2O is considered to be the components of kaolin minerals adhered to the specimens as impurities.

Fig. 2. X-ray Spectrograms of barite and roseki from Tochiara Mine.

Table 2 Chemical components of barite from Tochiyara

	(1)	(2)
BaO	63.27	57.45
SrO	n. d.	5.28
SO ₃	33.66	33.91
SiO ₂	1.52	0.63
Al ₂ O ₃	1.28	
Fe ₂ O ₃	0.26	
CaO	0.26	
MgO	—	
H ₂ O(+)	0.44	
H ₂ O(-)	0.22	
In Sol.	0.39	
Total	101.30	97.27

Fig. 3. D. T. A. curves of roseki from Tochiyara mine

Table 3-1 X-ray data calculated from the spectrogram

d ⁽¹⁾ (Å)		d ⁽²⁾ (Å)		d ⁽³⁾ (Å)	
I		I		I	
4.32	5	4.27	4	4.35	0.20
4.22	2				
3.89	7	3.82	4	3.89	0.25
3.76	2				
3.55	9	3.55	4	3.57	0.10
3.42	22	3.42	8	3.44	0.63
3.30	11	3.30	6	3.31	0.35
3.09	14	3.08	8	3.10	0.63
3.01	1				
2.82	7	2.84	5	2.83	0.40
2.72	7	2.72	5	2.72	0.45
2.47	2	2.47	2	2.47	0.15
2.34	1	2.33	6	2.31	0.10
2.31	3				
2.27	1	2.28	2	2.20	0.15
2.20	3	2.21	4	2.10	1.00
2.11	12	2.11	10	2.04	0.10
2.05	3	2.06	4	1.92	0.05
1.931	1	1.93	2	1.85	0.15
1.853	3	1.86	5	1.74	0.08
1.753	1	1.75	4	1.67	0.15
1.679	2	1.68	5	1.63	0.08
1.668	3				
1.635	1	1.64	4	1.58	0.10
1.588	1	1.591	4	1.52	0.25
1.531	2				
1.474	1	1.480	6	1.465	0.07
1.423	2	1.426	4	1.420	0.20
1.401	1	1.403	6		

(1) Barite from Tochiyara (2) Barite quoted from Tables Pour La
 Détermination des Minéraux au Moyen des Rayons par Carbois Torre de
 Assuncao et Julio Garrido Lisbonne 1953 (3) Barite quoted from
 Chemical Analysis on X-ray Reflection by K. Kubo and S. Kato.

As shown in the specimen (2) in table 2, a little of strontia, about 5.28%, is present and this value works out at about 9.35% for strontium sulphate (celestite).

X-RAY SPECTROGRAMS

X-ray spectrograms showing in Fig 2 have been carried out with

Table 3-2 X-ray data calculated from the spectrograms

B₁ and B₂ Roseki clay

C₄ Roseki bearing barite

B ₁ (gray)		B ₂ (white)		C ₄	
d (A)	I	d (A)	I	d (A)	I
10.1	15	10.13	14		
7.15	22	7.17	11	7.15	85
5.02	10	5.05	10		
4.70	13			4.70	5
4.48	7	4.47	7	4.43	5
4.00	14	4.00	5	4.35	5
3.56	7	3.58	11	4.26	3
3.35	18	3.34	19	4.125	5
3.22	6	3.20	5	3.98	16 dias.
3.13	5			3.89	5 barite
3.06	6	3.07	7	3.57	81
3.01	4			3.42	15 D. B.
2.93	4	2.95	3	3.30	7
2.87	5	2.86	4	3.09	6 B.
2.80	4	2.81	3	2.72	5 B.
2.71	6			2.63	1
2.56	9	2.57	9	2.56	3
2.51	5	2.51	3	2.51	3
2.42	5	2.45	2	2.38	9
2.39	5	2.39	3	2.35	9
2.35	7			2.32	7 D.dias.
2.31	9	2.32	3		
2.21	5	2.20	1	2.20	2
2.07	10	2.08	4	2.11	7 barite
2.00	9	2.01	8	2.07	10 dias
1.979	3			1.975	4
1.916	3			1.853	1
1.815	3			1.785	1
1.789	2				
1.750	2				
1.714	3	1.717	1		
1.665	3	1.670	1	1.668	2
1.651	4			1.651	4
1.633	8	1.635	4	1.630	1 dias.
1.609	3				
1.571	3			1.554	1
1.545	2				
1.522	2	1.522	1		
1.495	3	1.499	4	1.485	2
1.480	5	1.482	1		
				1.431	2

"Norelco", at 30 kV, 15 mA, scanning speed $2^\circ/\text{min}$, time constant 4 seconds, scale factor 8 and multiplier 1.0; employing Ni-filtered copper radiation. The X-ray data calculated from these spectrograms are given in Table 3.

As shown in Fig. 3, there are the strong peaks at about $3.42 \text{ \AA}$, $3.09 \text{ \AA}$ and $2.11 \text{ \AA}$. Such three peaks are characteristic and are seemed to be very available for the determination of barite. Also other peaks are very much similar to those of other typical data. Although the presence of celestite was suggested from chemical data, it has not been recognized by the X-ray spectrogram, for the reflection peaks of two minerals are contiguously situated each other.

X-RAY AND THERMAL PROPERTIES OF THE "ROSEKI"

Furthermore, the X-ray and thermal properties of roseki from this mine have been compared to each other. The specimen bearing barite has been confirmed to be composed of kaolinite, dickite and diaspor by the optical observation, X-ray and thermal analyses. Sericite is not observed in this specimen.

The reflection peaks giving strong intensities at about $3.98 \text{ \AA}$, $2.31 \text{ \AA}$, $2.07 \text{ \AA}$ and $1.630 \text{ \AA}$ are characteristic for diaspor. In general, the specimens from the mine are essentially consisted of kaolin minerals and sericite, and often include a pretty quantity of diaspor as accessories. The differential thermal analysis curves reveal the following characters.

(1) The initial endothermic peaks (a) ($100\sim 200^\circ\text{C}$) are very weak or negligible.

(2) The second endothermic peaks (b) between 500°C and 700°C are generally strong and conspicuous.

Some curves have respectively shown the endothermic peaks in the region of $500^\circ\sim 600^\circ\text{C}$ and $600^\circ\sim 700^\circ\text{C}$. The lower temperature peaks (b_1) ($500^\circ\sim 600^\circ\text{C}$) are approximately symmetric, being sharp, and moreover these peaks show the values in the region of $1.0\sim 2.5$ for the slope ratio. The higher temperature peaks (b_2) ($600^\circ\sim 700^\circ\text{C}$) are manifestly asymmetric, and these show the slow approach to the maximum peak temperature and the rapid return to

the base line.

(3) The exothermic peaks appear pronouncedly between 900° and 1000°C, and are generally sharp, but some are very weak or negligible.

The b_2 peaks caused by the endothermic behaviours very resemble to that of typical dickite worked by P.F Kerr and J.L. Kulp⁵⁾, and also the b_1 peaks having the small values for the slope ratio are distinctly considered to be resulted from the decomposition of kaolinite as mentioned by L. Bramo etc⁶⁾.

It may be understood in addition to the X-ray data that the endothermic peaks at about 600°C, being broad in general, are mostly caused by the dehydration of sericite. As given by T. Sudo and K. Nagasawa etc.⁷⁾, the main endothermic peak temperature for sericite generally ranges between 600° and 620°C, but that for dickite extends in the region of 650°C–700°C. So this peak temperature difference may be able to discriminate dickite from sericite on the differential thermal curves in some degree. It is seemed to result from the diminution of exothermic reaction caused by sericite and highly aluminous minerals⁸⁾ that the exothermic peaks (c) are weak and broad, notwithstanding that kaolinite and dickite are included in the specimens.

The thermobalance curves for roseki are shown in Fig. 4. The

Fig. 4. Thermobalance curves for roseki

Table 4 Refractoriness of the roseki from Tochiara

specimen		S. K. Number
A ₁	Collected from Tunnel No. 1	30 $\frac{1}{2}$
A ₂	" "	" "
A ₃	" "	28 $\frac{1}{2}$
A ₄		30
A ₅		32
B ₁	" Tunnel No. 2	28 $\frac{1}{2}$
B ₂	" "	31 $\frac{1}{2}$
C ₁	" Tunnel No. 3	20
C ₂	" "	31
C ₃	" "	28
C ₄	" "	31

curves are recorded with the heating rate of about 3°C per minute.

These curves well illustrate the thermal properties and are more available in the combination of differential thermal analysis curves. The dehydration occurs distinctly at two stages in the region of 480°~580°C and 620°~680°C for these specimens. The region of such dehydration temperature well corresponds to the peak temperature in differential thermal curves respectively. The lower temperature loss is mostly due to the decomposition of kaolinite and the higher dehydration temperature will get to conjecture the decomposition of dickite having more highly crystallized structure than kaolinite.

SUMMARY

Barite including a little of strontia has been found in roseki from the mine, and it is not seemed to be associated with sericite from the experiments. The roseki from the mine is mostly composed of kaolinite, dickite and sericite, and is often accompanied with diaspor as accessories.

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REFERENCES

- 1) Kimura, M., On the Mitsuishi Roseki (in Japanese), Jour. Geol. Soc. Japan, **57**, 499~508, 1951.
- 2) Ando, T., Studies on the Roseki and the related hydrothermal alteration in Chugoku region, Japan, report, Geol. Survey Japan, **147**, 1952.
- 3) Iwao, S., Alunite deposit (in Japanese), Chigaku Zasshi, **624**, 75~83, 1941.
- 4) Sonobe, R., Alunite and Roseki deposits (In Japanese), Science of non-metallic ore deposits, Chap. 2.
- 5) Kerr, P. F. and Kulp, J. L., Multiple differential thermal analysis, Amer. Min., **33**, 387~419, 1948.
- 6) Bramo, L., Cady, J. G., Hendricks, S. B. and Swerdlow, M., Characterization of kaolin minerals, Soil Sci., 273~287, **73**, 1952.
- 7) Sudo, T., Nakazawa, K., Amafuji, M., Kimura, M., Honda, S., Muto, T. and Tanemura, M., Studies on differential thermal analysis curves of Japanese clay minerals : Geol. Soc. Japan. Jour. **58**, 115~130, 1952.
- 8) Keller, W. D. and Westcott, J. F., Differential thermal analyses of some Missouri fire clays, Jour. Am. Cer. Soc., **31**, 100~105, 1948.