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18. MINERALOGICAL STUDIES ON LEVYNE AND ERIONITE FROM JAPAN

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Abstract

Levynes and erionite from three Japanese localities are described to show their compositional variations reflected by their lattice constants and refractive indices. The material from Chojabaru, Iki Island contains 8.41 wt.% Na_2O placing it as the sodium dominant analogue of levyne, $(Na_2, Ca)Al_2Si_4O_{12}\cdot nH_2O$.

Introduction

Although levyne and erionite are rather rare zeolites, they have been recently found at three localities in Japan, Chojabaru, Nagasaki Prefecture, Kawaziri, Yamaguchi Prefecture, and Kuroiwa, Niigata Prefecture. Their chemical analyses extend the range of compositional variation of levyne due to substitution of Ca by Na_2 over the known range presented by Feoktistov *et al.* (1971) without any crystallographic break, confirming the existence of the isomorphous Na dominant analogue of levyne, $(Na_2, Ca)Al_2Si_4O_{12}\cdot 6H_2O$.

In this paper the mineralogical descriptions of these zeolites are presented with special reference to the variations of chemical composition, lattice constants and optical properties.

Mode of occurrence

Levyne and erionite from Chojabaru occur in amygdales of a basaltic tuff breccia of Miocene age with intimate association of some other zeolites including chabazite, stilbite, phillipsite, natrolite and thomsonite (Shimazu and Mizota, 1972).

The Kawaziri levyne associates intimately with erionite, chabazite, thomsonite, phillipsite, heulandite and stilbite in many round to subround white amygdales of 1 to 3 cm across contained in a brownish red altered basalt lava flow. In the amygdales are also found large amounts of calcite and montmorillonite with minor amounts of manganoan calcite, aragonite and halloysite.

In druses of several to ten cm across found in andesite dyke at Kuroiwa, levyne is found with diopside, garnet, wollastonite, calcite and amethyst accompaning some other zeolites and hydrous calcium silicates such as chabasite, natrolite, apophyllite, epistilbite, heulandite, analcime and gyrolite. Richterite is also found in other druses devoid of levyne. This uncommon assemblage is considered to be the product of skarnization of calcareous xenoliths in the andesite dyke intrucing Miocene calcareous sediments and subsequent hydrothermal effects to it.

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Morphology

Levyne from Kuroiwa has a hexagonal tabular habit flattened to *c*-axis and the largest one reaches 10 mm. across. Most of the crystals show interpenetrating twin. They are transparent and colourless with vitreous luster. The observed faces are *c*(0001), *r*$(10\bar{1}2)$ and *s*$(01\bar{1}1)$. The interfacial angles measured by one-circle optical goniometer are as follows:

	obs.	calc.	Haidinger*
$c \wedge r = (0001) \wedge (10\bar{1}2)$	43°11′	44°33′	$43°58\frac{3}{4}$′
$c \wedge s = (0001) \wedge (01\bar{1}1)$	61°43′	63°04′	62°37′.

The calculated figures were obtained from the lattice constants measured by x-ray powder diffraction method. The nomenclature of *c*(0001), *r*$(10\bar{1}1)$ and *s*$(02\bar{2}1)$ were taken from the work of HAIDINGER*(1828) and their indices were converted to match the unit cell data here employed, because the old axial ratio is the half of the present one. The errors for observation were mainly due to their dispersed reflection images resulting from the minute twinning, which forms uneven crystal faces. A representative figure of twinned crystals is given in Fig. 1. The Kuroiwa levyne is morphologically very similar to that from Antrim, Ireland reported by STRUNZ (1956).

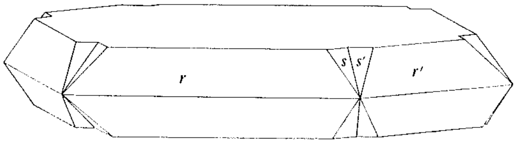

Fig. 1. Morphology of twinned levyne from Kuroiwa.

Levyne from Kawaziri has the same hexagonal tabular shape as the material from Kuroiwa, but the development of polysynthetic twinning forms deep striations on its prisms, and its interfacial angles could not be measured.

Levyne from Chojabaru does not show any euhedral form and only its basal cleavage is observed.

The crystals of erionite from Chojabaru are fibrous with about 1 mm in average length. Occassionally the columnar aggregates of fibers are found.

Microscopic observations and optical properties

The crystals of levyne have hexagonal shape tabular to *c*-axis with about 0.05 mm in width, and in many cases penetrating twinning relations were observed. Erionite is associated intimately at Chojabaru and Kawaziri, but not found in Kuroiwa. Erionite is epitaxially intergrown with levyne in general (Fig. 2).

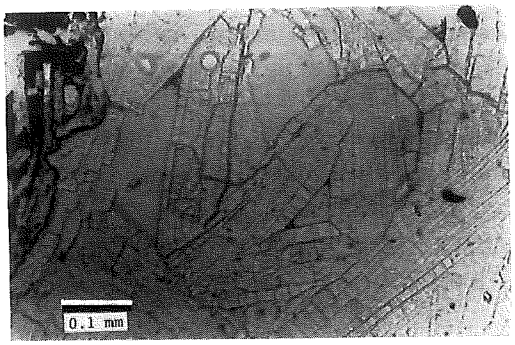

Fig. 2. Photomicrograph of levyne and erionite from Kawaziri, one Micol.

Levyne is uniaxial negative and shows very low birefringence. The refractive indices of three levynes varies to reflect their compositional variations among which Al-Si and Ca-(Na_2, K_2) substitutions seem to be significant except variations of water content. Erionite from Chojabaru is uniaxial positive with $\varepsilon = 1.467$ and fibers are elongated parallell to *c*.

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* Dana's "The System of Mineralogy", 6th Ed. 595 (1914)

Chemical compositions

Their chemical compositions were surveyed by means of electron probe microanalyser (Shimazu EMX–2) employing the following standard materials;

Standard materials analysed	Elements
analcime from Maze	Na, Si
glass of anorthite composition	Ca, Al
glass of diopside composition	Mg
adularia of unknown source	K.

The correction for E.P.M.A. data was due to BENCE and ALBEE(1968) method. The accelerating voltage of electron beam was 15 KV and integrating time of x-ray intensity measurements was for 4 seconds, not to give rise to the decomposition of zeolites. The specimens available were so small in amounts that the water contents were not quantitatively measured but estimated as the difference. In order of its preliminary correction for oxygens, the H_2O contents were fixed throughout the calculation procedures. The total of metal oxides after corrections of three cycles were almost same as initial figures. The water contents, thus estimated, were smaller by 3 to 4 percent in comparison with those of levynes appeared in the paper of FEOKTISTOV *et al.* (1971). The reason for this difference may be due to the partial dehydration by electron bombardment under to a high vaccum condition at least in part. The chemical compositions of levyne and erionite from Chojabaru reported by SHIMAZU and MIZOTA (1972) contained some errors owing to the compositional ambiguity of standard materials employed at that time. Erionite from Maze, Niigata Prefecture, Japan, used by them as the standard material had been assumed to be lower content of alumina (Al_2O_3=15.24%, HARADA, *et al.*, 1967), but it was not the same specimen analyzed by HARADA *et al.* On the other hand KAWAHARA *et al.* (1967) gave the alumina content of erionite from Maze to be 23.48%.

The final chemical composition of their anhydrous part after correction were listed in Table 2 with atomic ratio based on O=12.

Table 1. Optical properties for levynes and erionite

Levyne	uniaxial (−) Chojabaru	Kuroiwa	Kawaziri
ω	1.481	1.487	1.504
Erionite	uniaxial (+) Chojabaru		
ε	1.467 ($\varepsilon \doteqdot \omega$)		

Table 2. Partial chemical analyses of levynes and erionite

	Levyne			Erionite Chojabaru
	Chojabaru	Kawaziri	Kuroiwa	
	wt. %	wt. %	wt. %	wt. %
SiO_2	49.7	48.1	51.8	52.1
Al_2O_3	22.8	24.4	20.5	20.7
Na_2O	8.41	2.07	2.29	7.20
K_2O	1.27	0.71	0.03	3.34
CaO	3.51	10.6	8.88	1.21
MgO	0.22	0.09	0.09	0.33
Total	85.91	85.97	83.59	84.88
[H_2O]	(14.09)	(14.03)	(16.41)	(15.12)
Cations (oxygen=12 in anhydrous parts)				
Si	3.91	3.77	4.10	4.12
Al	2.11	2.25	1.91	1.93
Na	1.24	0.314	0.315	1.11
K	0.128	0.071	0.003	0.338
Ca	0.296	0.890	0.753	0.103
Mg	0.026	0.01	0.01	0.039
[H_2O]	(3.70)	(3.67)	(4.33)	(3.99)
Z	9	9	9	6

Empirical formulae:

Chojabaru levyne
$((Na_2)_{0.62}Ca_{0.30}(K_2)_{0.06}Mg_{0.03})_{1.01}[Al_{2.11}Si_{3.91}O_{12}]\cdot 3.70H_2O$

Kawaziri levyne
$(Ca_{0.89}(Na_2)_{0.16}(K_2)_{0.04}Mg_{0.01})_{1.10}[Al_{2.25}Si_{3.77}O_{12}]\cdot 3.67H_2O$

Kuroiwa levyne
$(Ca_{0.75}(Na_2)_{0.16}(K_2)_{0.00}Mg_{0.01})_{0.92}[Al_{1.91}Si_{4.10}O_{12}]\cdot 4.33H_2O$

Chojabaru erionite
$((Na_2)_{0.56}(K_2)_{0.17}Ca_{0.10}Mg_{0.04})_{0.87}[Al_{1.93}Si_{4.12}O_{12}]\cdot 3.99H_2O$.

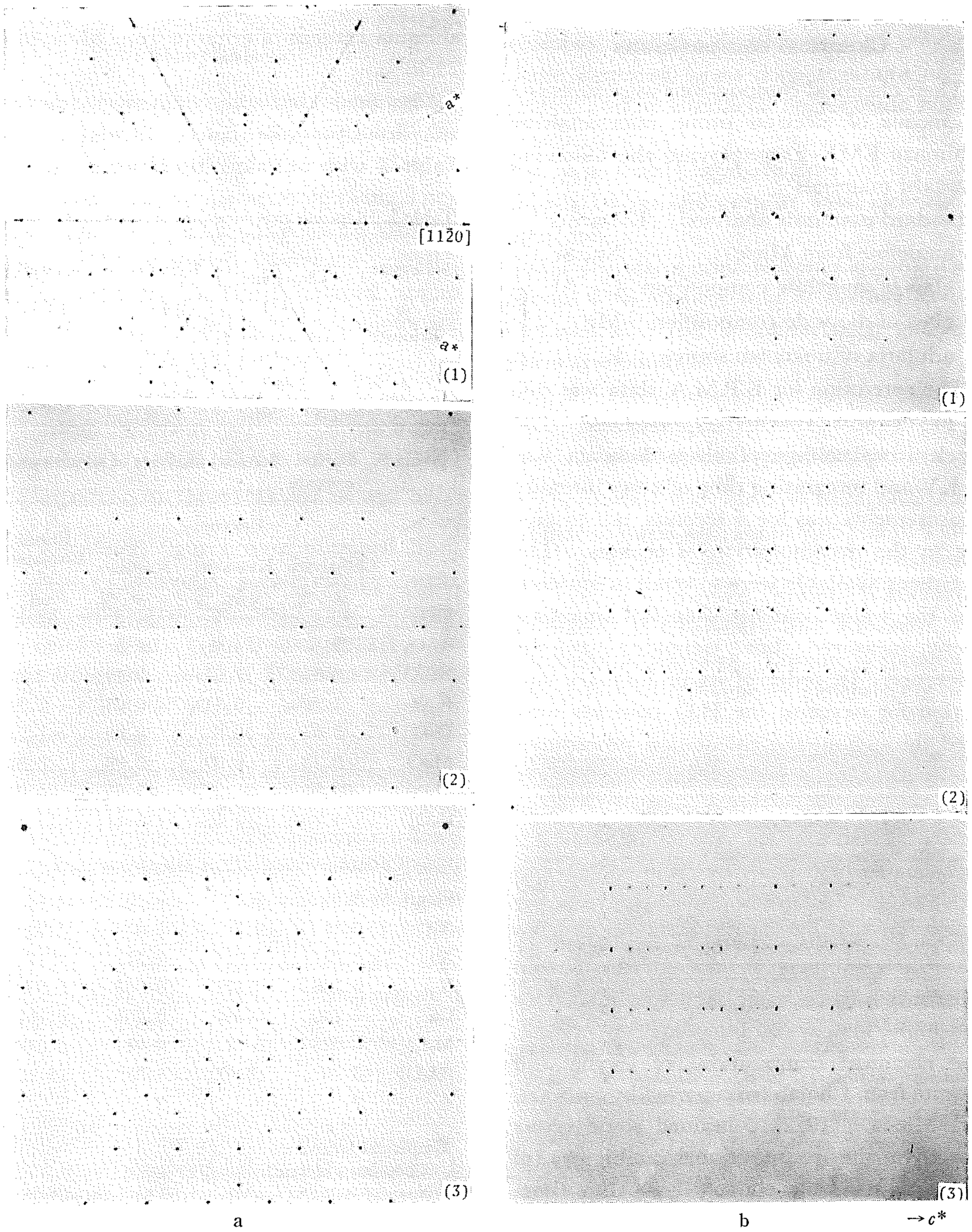

Fig. 3. X-ray precession photographs of levynes.
a: hk0 plane, $\mu=30°$, CoKα.
(1): single crystal of Kuroiwa levyne
(2): Kawaziri with weak diffraction spots of erionite included
(3): Chojabaru with relatively strong erionite spots
b: upper layer of *hkl* reciprocal plane, $\zeta=0.078$, $\mu=30°$, CoKα.
(1): single crystal pattern of Kuroiwa levyne
(2): and (3): twinned levyne and erionite diffraction pattern from Kawaziri and Chojabaru, respectively.

Levyne from Chojabaru has the highest Na_2O content of those hitherto reported, showing it to have the composition $(Na_2, Ca)(Al_2Si_4O_{12})\cdot 6H_2O$ with $Na_2 > Ca$.

X-ray studies

Because of the extreme difficulties to prepare pure materials, a part of x-ray single and powder studies was made on the mixture of levyne and erionite as given below:

Minerals	Localities	Methods of X-ray studies	
		X-ray single (precession)	X-ray powder
Levyne	Chojabaru	mixture (Figs. 3a–3, 3b–3) twinned. Spots splitting	mixture (Table 3)
	Kuroiwa	pure (Figs. 3a–1, 3b–1)	"pure" (Table 3)
	Kawaziri	mixture (Figs. 3a–2, 3b–2) twinned. Spots splitting	"pure" (Table 3)
Erionite	Chojabaru		mixture (Table 5)

The lattice constants of three levynes and one erionite are tabulated in Table 4 to show the systematic variations of *a* and *c* according to Ca-Na_2 substitution. Since the appearances of diffraction spectra of these levynes obey the same extinction rule corresponding to R$\bar{3}$m, it is highly plausible that there is no crystallographic break among them. The extinction rule of erionite from Chojabaru satisfies that of $P6_3/mmc$ hitherto assigned to erionite.

Table 3. X-ray powder data for levynes

h k l	Chojabaru		Kuroiwa		Kawaziri		
	d(obs). Å	I	*d* (obs.) Å	I	*d* (obs.) Å	I	*d* (calc.) Å
1 0 1	10.32	23	10.35	10	10.35	16	10.32
0 1 2	8.13	53	8.12	30	8.17	60	8.15
0 0 3	7.53	46*	7.51	5	7.68	14	7.68
1 1 0	6.65	100*	6.69	12	6.68	17	6.67
2 0 2	5.18	30	5.16	25	5.17	44	5.16
0 1 5	4.225	70	4.227	25	4.276	61	4.278
1 2 2	4.098	100	4.080	100	4.080	100	4.080
3 0 0	3.859	30*	3.856	15	3.851	36	3.848
0 0 6	3.777	43*	3.782	3			3.839
2 0 5	3.576	20*	3.567	12	3.601	7	3.601
2 1 4	3.474	30	3.461	12	3.477	25	3.478
3 0 3	3.451	10			3.441	10	3.440
2 2 0	3.335	25*	3.340	15	3.333	20	3.333
1 0 7	3.122	53*	3.123	15	3.163	15	3.164
3 1 2	3.103	20	3.089	12	3.086	27	3.085
4 0 1	2.880	50*	2.867	5	2.861	21	2.864
1 3 4	2.815	94*	2.800	60	2.799	100	2.798
3 0 6	2.699	30*	2.696	3	2.716	10	2.718
2 1 7	2.605	37	2.600	13	2.627	34	2.627
2 3 2					2.581	5	2.581
4 1 0	2.534	23*	2.522	11	2.519	17	2.519
0 4 5					2.446	3	2.446
1 4 3	2.403	20	2.394	6	2.397	11b	2.394
0 5 1	2.278	2	2.278	2	2.295	9	2.297
3 3 0	2.230	10	2.225	6	2.222	14	2.222
2 4 1	2.202	12*	2.171	3	2.173	2b	2.172
3 3 3	2.144	10	2.113	4	2.130	12	2.134
1 4 6					2.109	4	2.106
5 0 5					2.064	6	2.064
2 4 4					2.040	3	2.040

* Intensities may be affected by contaminating erionite.
Cu/Ni radiation. Diffractometer method.
Calibrated by silicon as internal standard.

Discussion and conclusion

Feoktistov *et al.* (1971) gave the chemical formula of levyne from Tolstomysovsk Sill, USSR as:

$Na_{0.711}\ Ca_{0.701}\ Fe_{0.049}\ Al_{1.997}\ Si_{3.939}\ O_{12}\ 4.62\ H_2O$, or $((Na_2)_{0.356}\ Ca_{0.701})_{1.057}\ (Fe_{0.049}\ Al_{1.997})_{2.046}\ Si_{3.939}\ O_{12}\ 4.62\ H_2O$, specifying it to be richest in Na_2O content than hitherto reported. But the appearance of levyne from Chojabaru shows the possibility that the range of substitution of Ca by Na_2 in this mineral reaches to the Na analogue $Na_2[Al_2Si_4O_{12}]\cdot nH_2O$. K content of the Chojabaru specimen is relatively high ($K_2O = 1.27$ wt.%) suggesting that the considerable amount of K^+ can also replace

Table 4. Unit cell constants of levypes and erionites

Mineral	Locality	Powder diffractometer		Precession camera	
		aÅ	cÅ	aÅ	cÅ
Levyne	Chojabaru	13.380(5)	22.684(9)	13.39(3)	22.64(4)
	Kuroiwa	13.350(5)	22.759(9)	13.35(3)	22.74(4)
	Kawaziri	13.330(5)	23.033(9)	13.33(3)	22.98(4)
Erionite	Chojabaru	13.311(5)	15.143(6)	13.31(3)	15.18(3)
	Kawaziri			13.33(3)	15.16(3)

Table 5. X-ray powder data for erionite from Chojabaru

d (obs.) Å	I	*d* (calc.) Å	*h*	*k*	*l*
11.57	100	11.52	1	0	0
9.21	15	9.17	1	0	1
7.62	13	7.57	0	0	2
6.66	90	6.66	1	1	0
6.36	4	6.33	1	0	2
5.77	13	5.76	2	0	0
5.40	5	5.39	2	0	1
4.64b	9	4.62	1	0	3
4.36	80	4.36	2	1	0
4.192	5	4.187	2	1	1
3.843	45	3.843	3	0	0
3.783	67	3.786	0	0	4
3.609	26	3.597	1	0	4
3.328	32	3.328	2	2	0
3.304s	5	3.298	2	1	3
3.199	19	3.197	3	1	0
3.173s	5	3.164	2	0	4
3.130	20	3.128	3	1	1
2.945	11	2.945	3	1	2
2.880	69	2.882	4	0	0
2.865s	20	2.858	2	1	4
2.831	58	2.831	4	0	1
2.694	14	2.693	4	0	2
2.514	22	2.516	4	1	0
2.498s	10	2.499	2	2	4
2.219	15	2.219	3	3	0
2.129	18	2.129	3	3	2
2.097	4	2.094	5	0	3
1.900	4	1.899	4	0	6
1.881	2	1.880	4	3	1
1.8456	9	1.8459	5	2	0
1.7840	12	1.7842	4	3	3
1.6637	19	1.6639	4	4	0
1.5942	7				

b: broad peak, s: shoulder peak. Cu/Ni radiation. Diffractometer method. Calibrated by silicon as internal standard.

Ca^{++}(or Na^+). The highest K_2O content was $K_2O = 1.61$ wt.% in the specimen from Iceland (FEOKTISTOV *et al.*, ditto). The $Ca(Na_2, K_2)$ substitution is almost maintained within the range of reliability of chemical analysis on the three specimens of the present work. SHEPPARD and GUDE (1969) reported that erionite is generally alkali-rich in the substitution between Ca and (Na_2, K_2) and has a $Si/(Al+Fe^{+3})$ ratio of 2.92 to 3.78. They also mentioned that erionite occurred generally in such a silicic rock as rhyolitic welded tuff at Durkee, Oregon, except for the erionite in altered basalt at Maze, Niigata, Japan. Erionites from Chojabaru and Kawaziri, Japan, are found in altered basaltic tuff breccia and in altered basalt lava, respectively, that is, at all of the three localities in Japan erionites are found in basic rock.

Erionite from Chojabaru has a Si/Al ratio of 2.14 which is considerably small with respect to the figures given by SHEPPARD and GUDE (1969). But the data in Table 2 show the deficiency of the total of alkalis and alkali-earths, because the (Ca, Mg)-(Na_2, K_2) substitution is not maintained over the reliability of analysis which may be caused by the error of analysis.

The space groups of levyne and erionites do not change throughout composition ranges here presented and are $R\bar{3}m$ and $P6_3/mmc$, respectively.

The orientation relations between them

from Chojabaru and Kawaziri are determined by x-ray single crystal method. The *a* and *c* axis of levyne are parallel to *a* and *c* axis of erionite as described by SHIMAZU and MIZOTA (1972).

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The HITAC 8350 computer of Computer Center of Niigata University was used for the calculation of unit cell constants and d-values of levyne and erionite.

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日本産レビ沸石とエリオン沸石の鉱物学的研究

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（要　旨）

日本で最初見出されたレビ沸石と，エリオン沸石について，それらの化学組成，格子定数，屈折率の間の関係等について研究をおこなった．

これらの沸石鉱物は，比較的産出が希であり。レビ沸石は，日本では，1972年長崎県壱岐島長者原から島津によりはじめて発見された．その後，1973年山口県川尻から渋谷が，新潟県黒岩より竹下が見出した．これらのレビ沸石の化学組成を比較すると，長者原産のものが Na_2O 8.41, K_2O 1.27 wt.% と，これまで報告されているレビ沸石の中で，もっともアルカリに富んでいる．レビ沸石構造に対して Ca—Na(K) 置換を考えると，長者原産のものは，今まで見出されたものの中で Na 端成分にもっとも近い組成をもっていることになる．

長者原，川尻のレビ沸石は，エリオン沸石と密接に共生しており，レビ沸石の (001) 面上に，*c* 軸に伸長したエリオン沸石が垂直に密生している．しかし黒岩産の

レビ沸石は，エリオン沸石と共生していない．また，川尻および長者原産レビ沸石は，スピネル双晶式の*c*軸60°回転双晶をひんぱんにくりかえしているが，黒岩産レビ沸石は，双晶が比較的少なく，単結晶のX線写真が得られる場合もある．黒岩産レビ沸石は，比較的塩基性の安山岩質貫入岩中の石灰質堆積岩のゼノリスが変質して生じたスカルン鉱物をともなうめずらしい産状を示している．

格子定数，屈折率の値は，化学組成と一定の相関関係をもつと考えられる．

地名	
Chojabaru	長者原
Kawaziri	川尻
Kuroiwa	黒岩