Carbon and oxygen isotopic compositions of hydrothermal rhodochrosites from Oe, Inakuraishi and Jokoku mines, Hokkaido, Japan

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Abstract—Carbon and oxygen isotope abundances were determined for hydrothermal rhodochrosites from Oe, Inakuraishi and Jokoku mines. The isotopic ratios of pale pink rhodochrosites from Oe and Inakuraishi are in the narrow ranges from -7.5 to -9.5 ‰ in $\delta^{13}\text{C}_{\text{PDB}}$ and 2.0 to 7.0 ‰ in $\delta^{18}\text{O}_{\text{SMOW}}$. $\delta^{18}\text{O}$ values of compact brown rhodochrosites from Oe and of large red rhodochrosite crystals from Inakuraishi spread in a range higher than that of pale pink ones. The isotopic ratios of the Jokoku rhodochrosites are in the ranges from -2.5 to -7.5 ‰ in $\delta^{13}\text{C}$ and from 7.0 to 15.0 ‰ in $\delta^{18}\text{O}$.

Pale pink rhodochrosites from Oe and Inakuraishi were derived from homogeneous hydrothermal solutions which were probably meteoric in origin. Some amounts of compact brown rhodochrosites from Oe and of large red rhodochrosite crystals from Inakuraishi were precipitated possibly from remaining hydrothermal solutions which might have exchanged oxygen isotopes with host silicates. The higher $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values of the Jokoku rhodochrosites are probably due to contamination with limestone. Homogeneous distribution of the isotopic ratios suggests that limestone was dissolved somewhere and the solution was brought to Jokoku mine.

INTRODUCTION

Genesis and nature of hydrothermal ore deposits have been studied by many methods. As to the identification of source materials, determinations of carbon and oxygen isotopic ratios of carbonates are most decisive. GARLICK and EPSTEIN (1966) and RYE (1966) reported the isotopic ratios of hydrothermal carbonates from Butte, Montana and Providencia, Mexico, respectively. OHMOTO and RYE (1970) studied Bluebell mine, British Columbia and determined the carbon and oxygen isotopic ratios of calcites at their different mineralogical stages. Those data, however, are not sufficient to discuss fully the origin of hydrothermal carbonates. Calcite is the common

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mineral of carbonates. This mineral, however, occurs generally as accessory minerals and localizes only partially in ore veins, and collection of systematic samples is difficult. In addition its isotopic ratios may be changed secondarily by meteoric water.

Rhodochrosite is the only one mineral for industrial use among hydrothermal carbonates, and occurs as large veins and massive ores. Therefore, detailed field observation and systematic sample collections of rhodochrosite along veins are possible. The isotopic ratios of rhodochrosite would not be changed secondarily by meteoric water, because the recrystallization of rhodochrosite always results in Mn (IV) compounds under sedimentary conditions. The isotopic data can be discussed in detail on genesis of hydrothermal carbonates without regard to the isotopic change since they formed. This paper is intended to discuss the distribution of carbon and oxygen isotopic ratios of rhodochrosites in Oe, Inakuraishi and Jokoku mines, Hokkaido, Japan with respect to their genesis.

GEOLOGICAL SETTINGS

Many rhodochrosites, and several dolomites and calcites were systematically collected from various points of Oe, Inakuraishi and Jokoku mines, Hokkaido, Japan. Their localities belong to so called "green tuff area of Miocene". Outlines of these mines are introduced in this chapter.

Oe (KOSEKI, 1954) Numerous manganese, copper, lead and zinc ore veins occur in altered liparitic tuff breccia or tuff and also in propylite. The region consists of green tuff breccia and black shale of Miocene and liparite flows. Miocene sediments are intruded by quartz diorite, two-pyroxene andesite and hornblende-bearing pyroxene andesite. Main veins along the strike faults generally trend about N50°W ~ N80°W and dips steeply southwest. Ores have brecciated or banded structures and consist mainly of quartz, rhodochrosite, sphalerite, galena, pyrite, chalcopyrite, barite and small amounts of tetrahedrite and argentite. Majority of the rhodochrosites are microcrystalline and pale pink in color. Compact brown rhodochrosites occur near druses.

Inakuraishi (ASAHI and MATSUMURA, 1954) This mine is located 5 km to the west of Oe mine. This region is mainly composed of liparitic rock, propylite, propylitic agglomerates and two-pyroxene andesite. The manganese deposits occur in propylite in which distinct chloritization, silicification and argillization are remarkably recognized around these deposits. Ore minerals are mainly rhodochrosite accompanied by quartz and calcite. In places ore contain alabandite, pyrite, sphalerite, galena, chalcopyrite and argentite with small amounts of pyragirite. The Inakuraishi rhodochrosites are mainly divided into large red crystals and small pink crystals. MIYAZAWA *et al.* (1964) suggested on the basis of the decrepitation temperatures that the crystallization temperatures were from 160 to 130°C for large red crystals and from 180 to 150°C

for small pink ones.

Jokoku (NISHIO, 1966) The ore deposits are of epithermal veins of Miocene age, consisting chiefly of rhodochrosite with minor amounts of sphalerite and galena. Main veins occur in a wide shear zone which forms a boundary between Paleozoic slate and Tertiary andesitic breccia. Several veins have been found branching out in the andesitic breccia. Ores consist mainly of quartz, rhodochrosite, sphalerite, galena, pyrite, dolomite, chalcopyrite and small amounts of pyargirite. Calcium carbonate is being precipitated from hot spring water of about 37°C and pH 6.7.

ANALYTICAL METHOD

Samples were ground to less than 200 meshes, and treated with 100% phosphoric acid in vacuum according to McCREA (1950). The reaction time was 5 days for rhodochrosite, 3 days for dolomite and 1 hr for calcite. The carbon dioxide evolved was purified and analyzed with a Nier type mass spectrometer modified by McKINNEY *et al.* (1950). The results of oxygen and carbon analyses are expressed as permil deviation of the $^{18}\text{O}/^{16}\text{O}$ and $^{13}\text{C}/^{12}\text{C}$ ratios from those in the standard substances, respectively:

$$\delta (\text{‰}) = \left(\frac{R_{\text{sample}}}{R_{\text{standard}}} - 1 \right) \times 1000$$

where R is $^{18}\text{O}/^{16}\text{O}$ or $^{13}\text{C}/^{12}\text{C}$ for samples and standard. In this paper, the oxygen standard is SMOW (Standard Mean Ocean Water) (CRAIG, 1961), and the carbon standard is the PDB carbonate standard (*Belemnite* from the Pee Dee formation of South Carolina) (CRAIG, 1957). All results were corrected for ^{17}O as described by CRAIG (1957). The data for dolomite and rhodochrosite were further added +0.82 and -0.08‰ respectively for correction of the kinetic fractionation on the phosphoric reaction (SHARMA and CLAYTON, 1965). The analytical error of $\delta^{13}\text{C}$ or $\delta^{18}\text{O}$ values is $\pm 0.2\text{‰}$.

RESULTS AND DISCUSSION

Carbon and oxygen isotopic ratios of rhodochrosites from Oe, Inakuraishi and Jokoku mines

The carbon and oxygen isotopic ratios of the studied rhodochrosites are shown in Figs. 1 to 3. The data are listed in Appendix. The Oe rhodochrosites are divided into two groups on the basis of their mineralogical features. Rhodochrosites of the first group are microcrystalline and pale pink in color, and occur largely in the main veins. Their isotopic ratios are distributed in a range from -7.5 to -9.5‰ in $\delta^{13}\text{C}$ and from 2.0 to 7.0‰ in $\delta^{18}\text{O}$ (Fig. 1). The other rhodochrosites are compact and brown in color, and occur mostly near druses. Their oxygen isotopic ratios spread in a range wider than that of the first group. The carbon and oxygen isotopic ratios of

Fig.1. $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values of rhodochrosites from Oe mine. ● - pale pink rhodochrosites, ○ - compact and brown rhodochrosites.

pale pink rhodochrosites from various point in the mine show only small variations.

The carbon and oxygen isotopic compositions of the Inakuraishi rhodochrosites distributed in a range similar to that of the Oe rhodochrosites (Fig.2). The Inakuraishi rhodochrosites are also divided into two groups on the basis of their mineralogical

Fig.2. $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values of rhodochrosites and calcites from Inakuraishi mine. ● - pale pink rhodochrosites, ○ - red rhodochrosites, ⊙ - brown rhodochrosites, X - calcites.

features. The isotopic ratios of the first group which consists of small pale pink crystals of rhodochrosite are similar to those of pale pink rhodochrosites from Oe. The second group which consists of large red crystals of rhodochrosite is similar in $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ to compact brown rhodochrosites from Oe. While the brown rhodochrosites occur near druses on a small scale as described above, the red rhodochrosites occur in main veins on a large scale. The isotopic ratios of hydrothermal calcites from Inakuraishi are from -8.06 to -8.78‰ in $\delta^{13}\text{C}$ and from 0.32 to -0.24‰ in $\delta^{18}\text{O}$. They are obviously low in $\delta^{18}\text{O}$ in comparison with those of rhodochrosites.

Fig.3. $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values of rhodochrosites and dolomites from Jokoku mine. ● - rhodochrosite, ○ - dolomites, ◐ - mixtures of dolomite and rhodochrosite.

The isotopic ratios of the Jokoku rhodochrosites are higher in $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ than those of rhodochrosites from Oe and Inakuraishi (Fig.3). $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values of dolomites which are disseminated in wall rocks are shown by open circles in Fig.3. They are high in $\delta^{13}\text{C}$ and similar in $\delta^{18}\text{O}$ in comparison with those of the Jokoku rhodochrosites. Mixed samples of rhodochrosite and dolomite show intermediate $\delta^{13}\text{C}$ values. Calcium carbonate which is being precipitated from hot springs in the mine has $\delta^{13}\text{C}$ values from 1 to 3‰ and $\delta^{18}\text{O}$ values from 17 to 19‰. (listed in Appendix).

Comparison with other hydrothermal carbonates Isotopic compositions of studied rhodochrosites are compared with those of other hydrothermal carbonates and CO_2 in geothermal areas. Fractionation factors for carbon and oxygen isotopes between rhodochrosite and calcite and between rhodochrosite and CO_2 are required for the comparison. The oxygen isotopic fractionation between calcite and water and

the carbon isotopic fractionation between calcite and CO_2 were studied by BOTTINGA (1968). The oxygen isotopic fractionation between rhodochrosite and calcite at 240°C was determined by O'NEIL *et al.* (1969). The carbon isotopic fractionation has never been reported. The carbon and oxygen isotopic fractionations between rhodochrosite and calcite were calculated by a simplified theoretical method which was proposed by O'NEIL *et al.* (1969). The oxygen isotopic fractionation calculated was normalized by the experimental value. The isotopic fractionations thus estimated are shown in Fig.4. As shown in Fig.4, the carbon and oxygen isotopic fractionations are probably less than 1‰ at hydrothermal temperatures.

OHMOTO and RYE (1970) studied on Bluebell mine, and determined carbon and oxygen isotopic ratios of calcites at their different mineralogical stages. The carbon isotopic ratios of the calcites were relatively uniform and similar to those of carbonatites. They, therefore, suggested that most of the carbon might have been juvenile in origin. The oxygen isotopic ratios spread in a wide range from 9 to -10‰ . The wide spread in $\delta^{18}\text{O}$ values is probably due to combined effect of many factors, *e.g.* crystallization temperature, interaction between hydrothermal solution and host silicates and recrystallization. The isotopic range of the Oe and Inakuraishi rhodochro-

Fig.4. Isotopic fractionation factors for carbon (C) and oxygen (O) isotopes between rhodochrosite and calcite. (O : after O'NEIL *et al.* 1969, C : calculated theoretically)

sites is smaller than that of the Bluebell calcites. The isotopic ratios of hydrothermal rhodochrosites probably can be easily discussed in comparison with those of calcites, as described above.

CRAIG (1953) determined carbon isotopic ratios of CO_2 from Yellowstone thermal area and found that the $\delta^{13}\text{C}$ values are from -1.1 to -6.4‰ (av. -2.8‰). HULSTON and MCCABE (1962) determined carbon isotopic ratios of CO_2 from gas and hot spring samples from the North Island, New Zealand, and found that the $\delta^{13}\text{C}$ values are mostly from 0 to -7‰ . $\delta^{13}\text{C}$ values of CO_2 from geothermal areas are generally included in a range from 0 to -7‰ , and the range is higher than that of juvenile CO_2 .

(-4 to 8‰) (SUWA *et al.*, 1969). CRAIG (1953) and HULSTON and McCABE (1962) concluded that the carbon in geothermal gases has been derived largely from limestone and to a small extent from sedimentary organic matter. Their studies suggest that carbon in hydrothermal solution is easily contaminated by limestone. The carbon isotopic ratios of the Oe and Inakuraishi rhodochrosites are lower than those of CO_2 in geothermal gases, and those of the Jokoku rhodochrosites are generally similar.

Source of hydrothermal solution On the basis of fractionation factors for oxygen isotopes between rhodochrosite and water, and for carbon isotopes between rhodochrosite and CO_2 , $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values of rhodochrosite can be estimated from $\delta^{13}\text{C}$ value of CO_2 and $\delta^{18}\text{O}$ value of water. Assuming that hydrothermal solution is composed of juvenile CO_2 ($\delta^{13}\text{C} = -6 \pm 2\text{‰}$, SUWA *et al.*, 1969) and magmatic water ($\delta^{18}\text{O} = 8 \pm 1\text{‰}$, RYE and O'NEIL, 1968), the isotope ratios of the rhodochrosite are estimated to be in the range from -2 to -5‰ in $\delta^{13}\text{C}$ and from 18 to 23‰ in $\delta^{18}\text{O}$ at temperatures from 180 to 130°C (the temperatures are estimated from decrepitation data by MIYAZAWA *et al.* 1964). YOSHIMURA (1967) suggested on the basis of the mineralogical studies that the Oe, Inakuraishi and Jokoku rhodochrosites were precipitated from residual solutions of magma. If this is accepted, the oxygen and carbon isotopic ratios of rhodochrosites should be in the range from 18 to 23‰ and from -2 to -5‰ , respectively, since the isotopic ratios of the residual solution are probably

Fig.5. Schematic diagram of isotopic compositions for rhodochrosites from Oe, Inakuraishi and Jokoku mines. I - pale pink rhodochrosites from Oe and Inakuraishi, II - brown rhodochrosites from Oe and Inakuraishi and red rhodochrosites from Inakuraishi, III - rhodochrosites from Jokoku, IV - recent marine carbonates, IV + V - limestones.

similar to those of magmatic ones. But the isotopic ratios of the Oe rhodochrosites are low in $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ in comparison with the estimated values. Hydrothermal solution of Oe must have been derived from CO_2 of lower $\delta^{13}\text{C}$ and water of lower $\delta^{18}\text{O}$ than those of magmatic ones. As shown in Fig.1 a linear relation holds between the carbon and oxygen isotopic ratios of pale pink rhodochrosites from Oe. Since this linear relation is consistent with the theoretically derived relation under temperature variation, this suggests that the isotopic variations of pale pink rhodochrosites are mainly due to changes in temperatures of ore deposition. Therefore, the oxygen and carbon isotopic compositions in the hydrothermal solution are considered to be similar in time and space during ore deposition. The oxygen isotopic ratios from 2 to 7‰ are independent of localities in the mine, and this span of ratios is found in individual specimens having brecciated or banded structures. Brecciated or banded structures of ores indicate that the ores are mixtures of minerals crystallized at some different periods. These facts suggest that homogeneous hydrothermal solution repeatedly flowed into the mine. $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values of the Oe rhodochrosites can be explained by the assumption that the rhodochrosites were precipitated in equilibrium with meteoric water of $-8 \pm 2\text{‰}$ in $\delta^{18}\text{O}$ and CO_2 of $-10 \pm 2\text{‰}$ in $\delta^{13}\text{C}$ dissolved in meteoric water at temperatures from 180 to 130°C. Small pale pink crystals of rhodochrosite from Inakuraishi were derived probably by a similar mechanism.

$\delta^{18}\text{O}$ values of compact brown rhodochrosites from Oe and large red crystals of rhodochrosite from Inakuraishi spread in a range higher than that of pale pink ones. This suggests that some of them were precipitated probably from remaining hydrothermal solution which might have exchanged oxygen isotopes with host silicate minerals, yielding higher $\delta^{18}\text{O}$ values. Low $\delta^{18}\text{O}$ values of calcites from Inakuraishi indicate that calcites were crystallized probably at higher temperatures.

$\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values of the Jokoku rhodochrosites are higher than those of rhodochrosites from Oe and Inakuraishi. This comparison is schematically shown in Fig.5 with the isotopic range of limestone. Jokoku mine is situated in a shear zone which formed at the boundary between Paleozoic slate and Tertiary andesitic breccia. Small bodies of limestone lie in the Paleozoic slate. The presence of sedimentary carbonates in the Jokoku ore bodies has been controversial. NISHIO (1966) suggested on the basis of chemical compositions of the "sedimentary carbonates" that sedimentary carbonates remained in the mine. YOSHIMURA (1967) suggested that they were derived by so called carbonitization. The higher isotopic ratios of the Jokoku rhodochrosites are probably due to contamination from limestone. Although the isotopic ratios lie in the range between those of limestone and those of the Oe rhodochrosites, the range is rather narrow and homogeneous throughout the mine. This suggests that limestone was dissolved somewhere, mixed with hydrothermal solution and the solution was brought to this mine. If limestone is involved in the mine and its CO_2 is added to the hydrothermal solutions, $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values of rhodochrosites should be scat-

tered in a range between those of limestone and those of hydrothermal carbonates. The "sedimentary carbonates" after NISHIO (1966) were realized by X-ray analysis to be mixtures of dolomite and small amounts of rhodochrosite, and are similar in $\delta^{18}\text{O}$ and slightly high in $\delta^{13}\text{C}$ in comparison with the Jokoku rhodochrosites. They are considered to have been derived from hydrothermal solution, and not to be of sedimentary origin.

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APPENDIX

$\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ values of hydrothermal rhodochrosites from Oe,
Inakuraishi and Jokoku mines

Sample No.	Locality* ¹	$\delta^{18}\text{O}_{\text{SMOW}}$, ‰	$\delta^{13}\text{C}_{\text{PDB}}$, ‰
<i>Oe mine</i>			
700e01	–150SL E 1	3.30	–8.87
700e02	–100L E17	4.87	–8.20
700e03	–150L E17	3.32	–9.21
700e04	–150L E19	3.51	–8.80
700e04'	"	3.12	–8.60
700e07	–150L W18	3.71	–9.07
700e08	–150L W12	5.23	–8.03
700e08'1	"	6.03	–7.60
700e08'2	"	5.92	–7.97
700e091	–200L W12	2.25	–9.50
700e092	"	9.05	–7.74
700e10	–200L W14	6.67	–8.22
700e11	–200L W15	6.56	–7.87
700e12	–200L W16	4.21	–8.62
700e13	–200L W16	4.77	–8.57
700e14	–200L W17	4.89	–9.18
700e15	–200L E4	5.08	–8.29
700e15'1	"	5.19	–8.07
700e15'2	"	4.48	–8.49
700e15'3	"	3.56	–8.97
700e161	–200L E0	6.32	–7.94
700e162	"	4.61	–6.85
700e16'	"	6.17	–8.07
700e17	–40L E19	4.93	–8.39
700e18	–100SL E17	5.88	–7.77
700e19	–100SL E15	2.68	–9.11

Continued on the next page

Sample No.	Locality*1	$\delta^{18}\text{O}_{\text{SMOW}}$, ‰	$\delta^{13}\text{C}_{\text{PDB}}$, ‰
700e20	-100SL E14	4.48	-8.81
700e20'	"	4.04	-8.90
700e21	-100SL E13	2.44	-8.69
700e22	-100L E15	5.75	-8.28
700e23	-100L E7	9.72	-7.07
700e241	-100L E6	8.20	-7.68
700e242	"	7.37	-7.12
700e243	"	4.42	-8.62
<i>Inakuraishi mine</i>			
70In02	4L 100m	8.58	-8.29
70In03	4L 410m	8.41	-7.70
70In041	4L 420m	3.15	-8.91
70In05	4L 500m	2.94	-8.39
70In06	"	8.77	-7.27
70In07	4L 1700m	2.97	-9.53
70In08	4L 940m	4.50	-8.53
70In09	4L 1400m	6.03	-7.73
70In10	4L 1420m	4.55	-7.63
70In111*2	4L 1600m	-0.24	-8.06
70In112	"	7.37	-6.32
70In122	4L 1745m	3.04	-9.52
70In123	"	1.88	-9.57
70In124*2	"	-0.05	-8.56
70In125	"	8.06	-8.31
70In126	"	4.41	-8.04
70In127	"	8.22	-7.41
70In128	"	8.60	-8.13
70In131	4L 1960m	3.08	-9.36
70In132*2	"	0.32	-8.78
70In14	8L W380m	9.31	-9.01
70In14'	"	7.20	-8.29
<i>Jokoku mine</i>			
70Kk02	150SL #10	12.22	-5.60
70Kk04*3	230L	9.12	-3.42
70Kk05*3	230L	14.36	-3.90
70Kk06*3	230L	7.04	-6.85
70Kk07*3	230L	14.54	-2.47
70Kk08	180L #17	10.55	-6.84
70Kk10	180L #7	9.70	-5.62
70Kk11	"	11.05	-4.61
70Kk12	150L #9	11.99	-4.49
70Kk14	"	13.25	-5.24
70Kk15*4	120L #13	13.60	-3.11
70Kk15'1	"	13.51	-4.70
70Kk15'2	"	13.39	-4.25
70Kk16*4	"	9.49	-3.02
70Kk17	"	12.23	-5.26
70Kk18	120L #16	13.26	-5.72
70Kk20	"	10.23	-6.18
70Kk22	80L #10	13.34	-5.69
70Kk23	80L #13	12.06	-5.25
70Kk241*4	"	11.07	-3.99
70Kk242*4	"	12.16	-3.72

Continued on the next page

Sample No.	Locality ^{*1}		$\delta^{18}\text{O}_{\text{SMOW}}$, ‰	$\delta^{13}\text{C}_{\text{PDB}}$, ‰
70Kk251	80L	#15	12.33	-5.16
70Kk252	"	"	13.25	-5.54
70Kk26 ^{*5}	50L	#22	17.42	0.93
70Kk281 ^{*5}	50L	#23	18.92	2.66
70Kk29 ^{*5}	50L	#22	17.96	2.49
70Kk30 ^{*5}	50L	#26	17.86	2.90
70Kk31	80L	#21	9.42	-6.55
70Kk33	"	"	10.98	-5.13
70Kk34	80L	#29	12.53	-6.34
70Kk35	"	"	11.50	-7.54
70Kk37	80L	#30	12.08	-4.98
70Kk38	80L	#30	10.67	-6.34
70Kk39	50L	#21	11.46	-6.17
70Kk41	"	"	9.75	-5.82
70Kk42	50L	#23	9.48	-5.79
70Kk43	"	"	12.01	-2.63
70Kk44 ^{*3}	-10L	#15	13.04	-5.19
70Kk461 ^{*3}	-10L	#13	12.26	-4.26
70Kk462 ^{*3}	"	"	10.29	-4.63
70Kk471 ^{*3}	-10L	#20	12.73	-4.20
70Kk472 ^{*3}	"	"	12.08	-5.09
70Kk49 ^{*3}	-10L	#22	10.80	-6.67
70Kk52 ^{*3}	50L	#17	11.72	-5.32
70Kk53 ^{*3}	"	"	13.67	-5.73

*1 : Localities are shown as the names called by their mines.

*2 : Samples from hydrothermal calcite veins in Inakuraishi mine.

*3 : Mixed samples of dolomite and rhodochrosite.

*4 : Samples of dolomite disseminated in wall rocks.

*5 : Calcium carbonates precipitated from hot springs in Jokoku mine.