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MAGNESIAN KUTNAHORITE FROM RYÛJIMA MINE, JAPAN

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ABSTRACT

Magnesian kutnahorite from the Ryûjima mine, Nagano Prefecture was formed principally as fissure fillings. The major vein minerals were deposited during a single period of mineralization in three stages: quartz, rhodochrosite and finally magnesian kutnahorite. The chemical analysis of magnesian kutnahorite gave the following molar percentages: $CaCO_3$ 48.53, $MgCO_3$ 24.80, $FeCO_3$ 1.76, $MnCO_3$ 24.91; while that of rhodochrosite gave $CaCO_3$ 3.06, $MgCO_3$ 3.69, $FeCO_3$ 3.95, $MnCO_3$ 89.30. The tie line joining coexisting magnesian kutnahorite and rhodochrosite from the mine is consistent with experimentally determined subsolidus relations in the system $CaCO_3$-$MgCO_3$-$MnCO_3$. From the chemical analysis of the minerals, the equilibrium between rhodochrosite, magnesian kutnahorite and solution can be approximately written in the form:

$$2MnCO_3 + Ca^{2+} + 1/2Mg^{2+} = Ca(Mn_{0.5}Mg_{0.5})(CO_3)_2 + 3/2Mn^{2+}$$

Filling temperatures of fluid inclusions and other considerations show that the early minerals formed at the higher temperatures in hydrothermal ore deposits. Precipitation of rhodochrosite from hydrothermal solution, and of magnesian kutnahorite in the last stage, were due to 1) decrease in temperature of hydrothermal solution; 2) decrease in the value of $(a^{L}_{Mn^{2+}})^{3/2}/(a^{L}_{Ca^{2+}})\cdot(a^{L}_{Mg^{2+}})^{1/2}$ in hydrothermal solution; or both.

INTRODUCTION

The name kutnahorite was proposed for a member of the dolomite group with Mn>Mg or Fe (Palache, Berman and Frondel, 1951). However, the existence of kutnahorite as a valid member of the dolomite group was established by Frondel and Bauer (1955). The occurrences of kutnahorite have been recorded from Franklin, New Jersey (Frondel *et al.*, 1955), Kutná Hora, Czechoslovakia (Bukowský, 1901; Frondel *et al.*, 1955; Trdlička, 1963), Chvaletice, Czechoslovakia (Žák, 1949; Frondel *et al.*, 1955) and Providencia, Mexico (Bodine, 1963).

This article presents the mode of occurrence of magnesian kutnahorite from the Ryûjima mine and discusses the genesis of the mineral in the ore deposits.

OCCURRENCE

The Ryûjima mine (lat. 36°10′42″N.; long. 138°47′19″E.) is about 15 km west-southwest of Matsumoto City, Nagano Prefecture. The sedimentary rocks in the mining area consist mainly of slate, thin-bedded chert and sandstone which are regarded as of Permian age. The regional strike of the sedimentary rocks is northeast throughout most of the area. In the vicinity of the mine the sedimentary rocks dip moderately northwest. A few narrow dikes of porphyrite, from 3 to 6 m wide, were intruded into the sedimentary rocks. The dikes strike northwest and dip steeply. Manganese veins are mainly found in the dikes and sedimentary rocks. These veins, about 3 m maximum wide, strike northwest or west and dip steeply. They are 160 m long and extended to depths more than 75 m. The veins are displaced by a normal fault striking N.85°E. and dipping 45°N. The ores have been mined for high-grade rhodochrosite.

The veins were formed principally as fissure fillings. Cavities, crustification, symmetrical banding and cockade structure are common in these veins. They generally show symmetrical banding; beginning with the wall rock itself and proceeding inward toward the center of a vein,

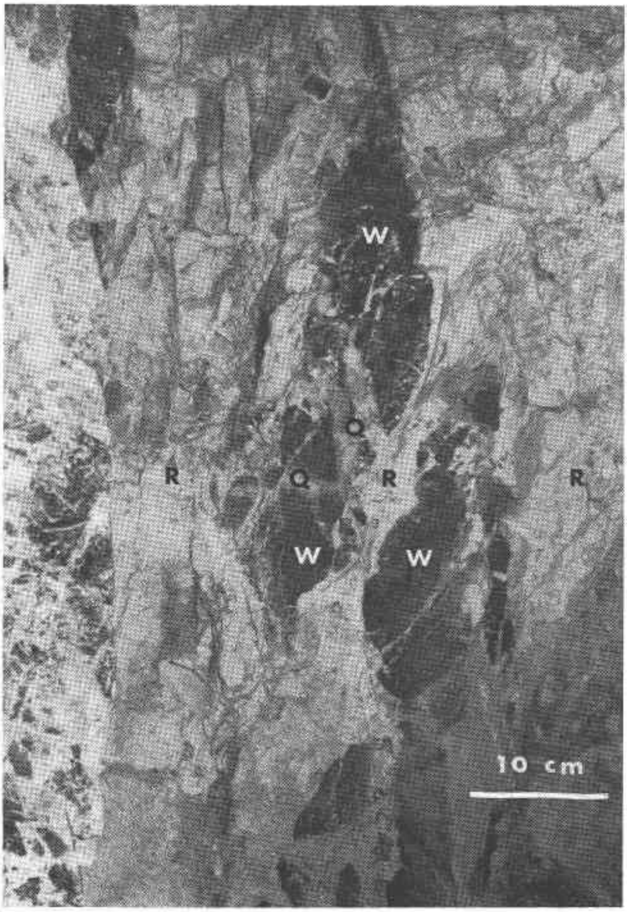

FIG. 1. A wall rock fragment (W) with stringers of quartz (Q) is surrounded by rhodochrosite (R). Ryûjima mine.

one finds successively three bands: quartz, rhodochrosite and magnesian kutnahorite. However, the quartz band may be absent in some places. These bands are from a few centimeters to a few meters wide.

In some localities wall rock fragments are pyritized and cut by centimeter-thin stringers of quartz. In other localities broken fragments of the wall rock are surrounded by a cockade growth of quartz. Quartz is commonly associated with a small amount of pyrite; in cavities it forms euhedral crystals on which euhedral crystals of rhodochrosite are superposed.

In some places wall rock fragments or those with thin stringers of quartz are surrounded by rhodochrosite (Fig. 1). Therefore, the mineralization of quartz and of rhodochrosite were separated by fault movement. This fact corresponds to the local absence of the quartz band in the symmetrical banding of the veins. Rhodochrosite is commonly associated with small amounts of galena, sphalerite and tetrahedrite. These opaque minerals occur in narrow bands parallel to the walls. Rhodochrosite forms network veinlets in altered wall rocks; in cavities it forms euhedral crystals on which euhedral crystals of magnesian kutnahorite are superposed.

The magnesian kutnahorite band is in the center of the veins. Fragments of the rhodochrosite band, quartz band and wall rocks have not been observed in the magnesian kutnahorite band (Fig. 2). However, the branching magnesian kutnahorite bands that follow subparallel fractures in the rhodochrosite band are found in some places (Fig. 2). The boundaries between the rhodochrosite and magnesian kutnahorite bands are sharp (Fig. 2). However, under the microscope it is revealed that rhodochrosite near the boundaries was partly replaced by magnesian kutnahorite (Fig. 3). Magnesian kutnahorite is commonly associated with small amounts of pyrite and arsenopyrite.

PHYSICAL AND OPTICAL PROPERTIES

Magnesian kutnahorite has perfect $\{10\bar{1}1\}$ cleavage; however, rupture takes place by subconchoidal fracture. The mineral is brittle; its hardness is 3-$\frac{1}{2}$–4. The specific gravity, 3.00, is slightly lower than the value 3.05 calculated from $CaCO_3$, $MgCO_3$, $FeCO_3$ and $MnCO_3$ end-members taken in the ratio of the analysis (Table 2). Individual crystals of magnesian kutnahorite are white to pale pink color, translucent and have a vitreous luster. The powder and streak of the compact material are white. Magnesian kutnahorite is colorless in transmitted light. It is uniaxial negative with $\omega = 1.710 \pm 0.003$, $\epsilon = 1.519 \pm 0.003$. These indices of refraction we remeasured in immersion media and they agree closely with those calculated from the end-members.

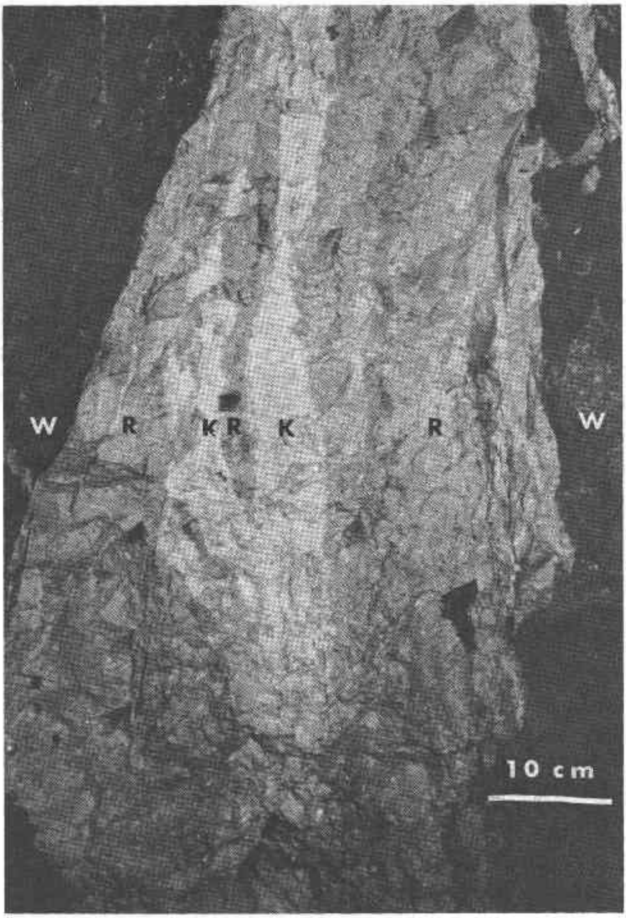

FIG. 2. Mode of occurrence of magnesian kutnahorite (K), rhodochrosite (R) and the wall rock (W). Ryûjima mine.

X-RAY DIFFRACTION DATA

The chemically analyzed magnesian kutnahorite sample (No. R8) was finely ground and prepared as a smear mount on a glass slide. Finely ground reagent grade silicon was added to the smear mount as an internal standard. X-ray powder patterns were run on a Philips X-ray diffractometer using CuK$_\alpha$ radiation and Ni filter at 1/8°/min scan rate from 90° to 15°2θ. Peak positions were measured at the estimated center line of the top 1/3 of each peak.

A least-squares unit-cell refinement using only single well-indexed lines was processed at the Mineralogical Institute, University of Tokyo

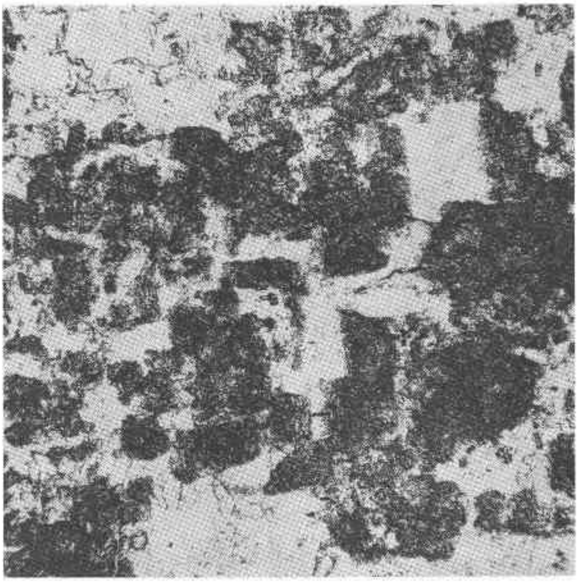

FIG. 3. (×96) Rhodochrosite (dark grains) partly replaced by magnesian kutnahorite (pale grains). Polarizer only. Ryûjima mine.

by H. Horiuchi and F. Okamura by the fixed index program. The unit-cell parameters of magnesian kutnahorite obtained by this refinement are $a=4.8438\pm0.0008$, $c=16.196\pm0.004$ Å. The unit-cell parameters agree closely with those calculated from the end-members. The spacings calculated from these refined unit-cell parameters and observed spacings for magnesian kutnahorite are compared with those of kutnahorite from Franklin, New Jersey (Frondel *et al.*, 1955) in Table 1. The superstructure reflections observed in magnesian kutnahorite are (00.3), (01.5), (10.7), (00.9), (02.7), (20.11), (03.9) and (30.9), indexed on the basis of the hexagonal unit-cell.

DIFFERENTIAL THERMAL ANALYSIS

Samples of magnesian kutnahorite were analyzed in a Mitamura apparatus using Pt-Pt,Rh thermocouples, α-alumina calcined at 1000°C as inert material, with a rate of heating of 10°C/min in an air atmosphere. For the DTA study 0.5 g of pure sample were ground to −200 mesh. The curve obtained (Fig. 4) shows endothermic peaks at 707°, 804° and 923°C. It closely resembles the DTA curves of kutnahorite described by Frondel *et al.* (1955) and Trdlička (1963) and of ankerite described by Beck (1950) and Kulp, Kent and Kerr (1951).

TABLE 1. X-RAY DIFFRACTION DATA FOR MAGNESIAN KUTNAHORITE FROM FROM RYÛJIMA MINE AND KUTNAHORITE FROM FRANKLIN, NEW JERSEY

$hk\cdot l$	$h_rk_rl_r$	Magnesian kutnahorite Ryûjima Mine, Nagano Pref.			Kutnahorite, Franklin New Jersey	
		d(calc) Å	d(*obs*) Å	I/I_0	d(obs) Å	I/I_0
00.3	111	5.399	5.411	1	—	—
10.1	100	4.061	—	—	4.268	5
01.2	110	3.725	3.731	8	3.753	20
10.4	211	2.913	2.914	100	2.935	100
00.6	222	2.699	2.701	2	2.730	5
01.5	221	2.564	2.564	1	2.593	4
11.0	$10\bar{1}$	2.422	2.423	5	2.437	14
11.3	210	2.210	2.209	10	2.225	19
02.1	$11\bar{1}$	2.080	—	—	2.095	4
20.2	200	2.030	2.031	6	—	—
10.7	322	2.026			2.043	19
02.4	220	1.862	1.862	3	1.876	9
01.8	332	1.823	1.823	9	1.837	27
11.6	321	1.803	1.804	11	—	—
00.9	333	1.800	1.800	10	1.814	31
20.5	311	1.761	—	—	—	—
21.1	$20\bar{1}$	1.578	1.578	2	1.588	6
12.2	$21\bar{1}$	1.556	1.556	4	1.566	4
02.7	331	1.554			1.540	3
10.10	433	1.511	1.512	1	—	—
21.4	310	1.476	1.477	3	1.486	7
20.8	422	1.457	1.457	2	1.469	3
11.9	432	1.444	1.445	2	1.465	3
12.5	320	1.424	—	—	1.409	5
03.0	$11\bar{2}$	1.398	1.398	2	—	—
01.11	443	1.389	—	—	—	—
30.3	300	1.354	—	—	—	—
03.3	$22\bar{1}$					
00.12	444	1.350	—	—	1.363	5
21.7	421	1.308	1.309	1	—	—
02.10	442	1.2819	1.2816	1	1.294	3
12.8	431	1.2483	—	—	1.258	4
30.6	411	1.2416	—	—	—	—
03.6	330					
22.0	$20\bar{2}$	1.2110	1.2071	1	—	—
20.11	533	1.2051			1.189	4
10.13	544	1.1943	—	—	—	—
22.3	$31\bar{1}$	1.1816	1.1799	2	—	—
11.12	543	1.1790			—	—

TABLE 1—(*Continued*)

$hk \cdot l$	$h_r k_r l_r$	Magnesian kutnahorite, Ryûjima Mine, Nagano Pref.			Kutnahorite, Franklin New Jersey	
		d(calc) Å	d(obs) Å	I/I_0	d(obs) Å	I/I_0
13.1	$21\bar{2}$	1.1605	—	—	—	—
31.2	$30\bar{1}$	1.1516	1.1524	1	—	—
21.10	532	1.1330	1.1328	2	1.145 1.141	4 4
13.4	$32\bar{1}$	1.1182	1.1176	3	1.126	5
01.14	554	1.1153			—	—
22.6	420	1.1049	—	—	—	—
03.9	441	1.1042	1.1043	2	—	—
30.9	522					
31.5	410	1.0950	—	—	—	—

CHEMICAL ANALYSIS

As pointed out by Sims and Barton (1961) and Barton, Bethke and Toulmin (1963), "surface equilibrium" between hydrothermal solution and the surface of growing crystals may have played an important role in the formation of hydrothermal deposits. Therefore, the chemical composition of magnesian kutnahorite and rhodochrosite from the Ryûjima mine may vary from one growth zone to the next. Thus, the chemical analysis of the minerals may be regarded as an average value of zoned crystals. This suggestion is supported by the broader diffraction lines of magnesian kutnahorite and rhodochrosite compared with those of quartz and silicon.

A chemical analysis of magnesian kutnahorite, made on the same material (sample No· R8) used for optical and X-ray study, is given in Table 2. The material was crushed to −200 mesh and was separated from the fines by settling in distilled water. After a pass through the Frantz isodynamic separator, final purification was achieved by handpicking under the binocular microscope. Approximately 0.3 gm were submitted for analysis. The purity of the sample was checked optically and with X-ray diffraction. Magnesian kutna-

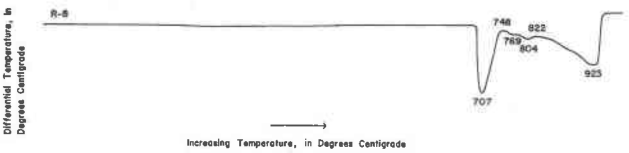

FIG. 4. Differential-thermal-analysis curve of magnesian kutnahorite from Ryûjima mine

horite was mechanically separated almost completely from its associated impurities, which are chiefly pyrite and arsenopyrite.

The chemical analysis was carried out by M. Ichikuni of Tokyo Metropolitan University and partly by Y. Matsui of Okayama University. A solution of the sample in hydrochloric acid was analyzed for calcium by EDTA titration and by the Hitachi model FPU-2A flame-photometer, for magnesium by the Jarrell-Ash model AA-1 atomic absorption spectrophotometer, for iron concentration colorimetrically with 1, 10-phenanthroline, and for manganese colorimetrically as permanganate. Another sample was mixed with calcined silica gel and heated at 700°C for 5 min to release carbon dioxide, then determined in ascarite.

A chemical analysis of rhodochrosite (sample No. R1-1) from the Ryûjima mine is reported in Table 2. The material used for chemical analysis was found on X-raying to contain approximately 1 percent magnesian kutnahorite. The methods used in the analysis are almost the same as those described in the previous section. It is uniaxial negative with $\omega = 1.812 \pm 0.003$, $\epsilon = 1.592 \pm 0.003$. The unit-cell parameters of rhodochrosite are $a = 4.7693 \pm 0.0007$, $c = 15.654 \pm 0.007$ Å. The indices of of refraction and unit-cell parameters agree closely with those calculated from the end-members.

TABLE 2. CHEMICAL ANALYSIS OF CARBONATES FROM RYÛJIMA MINE

Magnesian kutnahorite					Rhodochrosite				
	Weight percent	Numbers of ions on the basis of 6(O)				Weight percent	Numbers of ions on the basis of 6(O)		
CaO	27.10	Ca	0.964	1.99	CaO	1.51	Ca	0.062	2.01
MgO	9.96	Mg	0.493		MgO	1.31	Mg	0.074	
FeO	1.26	Fe	0.035		FeO	2.50	Fe	0.080	
MnO	17.59	Mn	0.495		MnO	55.77	Mn	1.798	
CO_2	44.28	C	2.007		CO_2	38.35	C	1.993	
	100.19					99.44			

M. Ichikuni, analyst.

For the convenience of separation of rhodochrosite, chemically analyzed material was not taken from the boundary of magnesian kutnahorite and rhodochrosite bands. However, two coexisting minerals from the boundary (sample No. R8) gave the following indices of refraction and unit-cell parameters: $\omega = 1.712 \pm 0.003$, $\epsilon = 1.523 \pm 0.003$, $a = 4.8481 \pm 0.0006$, $c = 16.199 \pm 0.004$ Å for magnesian kutnahorite; $\omega = 1.806 \pm 0.003$, $\epsilon = 1.591 \pm 0.003$, $a = 4.7692 \pm 0.0008$, $c = 15.600 \pm 0.008$ Å for rhodochrosite. These data agree with those of chemically analyzed minerals already described. Therefore, the chemical compositions of coexisting magnesian kutnahorite and rhodochrosite are approximately expressed by those of chemically analyzed two minerals shown in Table 2.

SUBSOLIDUS RELATIONS IN THE SYSTEM $CaCO_3$-$MgCO_3$-$MnCO_3$ AT LOWER TEMPERATURES

The system $CaCO_3$-$MgCO_3$-$MnCO_3$ was studied at temperatures of 500°, 600°, 700° and 800°C and 10 kb total pressure by Goldsmith and Graf (1960). Three phase triangles in the system at 500°, 600°, 700° and 800°C are superimposed in Fig. 5. The tie line joining chemically analyzed magnesian kutnahorite and rhodochrosite from the Ryûjima mine is plotted in the same figure. The $FeCO_3$ content of both phases is negligible.

Filling-temperatures of fluid inclusions in quartz and rhodochrosite were studied. Filling temperatures in quartz range from 230° to 260°C, while in rhodochrosite on which magnesian kutnahorite is superposed they are approximately 200°C. Therefore, the tie line joining the two minerals in Fig. 5 is at approximately 200°C. Since the Mn-rich corner of the three phase triangle in the system moves in the direction of the $MnCO_3$ corner as temperature decreases, and since the side of the triangle opposite this corner is little affected by temperature except for increasing length, the position of the tie line is consistent with experimentally determined subsolidus relations in the system $CaCO_3$-$MgCO_3$-$MnCO_3$.

GENETIC CONSIDERATIONS

The ore deposits of the Ryûjima mine were formed principally as fissure fillings after the consolidation of porphyrite magma. The major vein minerals were deposited during a single period of mineralization in three stages: quartz, rhodochrosite and finally magnesian kutnahorite. The quartz and rhodochrosite stages were separated by fault movement. These vein minerals were deposited from hydrothermal solutions originated during the igneous activity from which porphyrite magma was derived.

From the chemical analysis of magnesian kutnahorite and rhodochrosite, the chemical composition of these minerals is approximately expressed in the forms, $Ca(Mn_{0.5}Mg_{0.5})(CO_3)_2$,$MnCO_3$, respectively. Thus the equilibrium between rhodochrosite, magnesian kutnahorite and solution can be written in the form.

$$2MnCO_3 + Ca^{2+} + 1/2Mg^{2+} = Ca(Mn_{0.5}Mg_{0.5})(CO_3)_2 + 3/2Mn^{2+}$$

In the temperature range of formation of the Ryûjima mine, if the solid

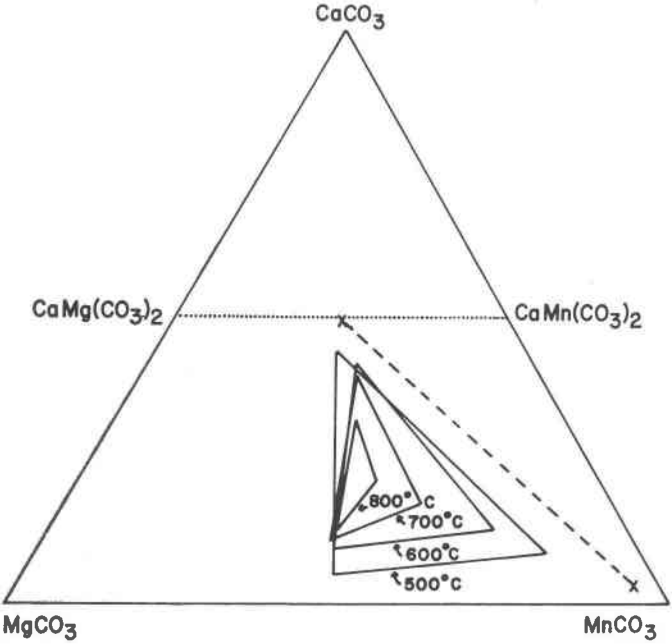

FIG. 5. The three-phase triangles for temperatures of 500°, 600°, 700° and 800°C at 10 kilobars total pressure in the system $CaCO_3$-$MgCO_3$-$MnCO_3$ (Goldsmith and Graf, 1960). The tie line joining magnesian kutnahorite and rhodochrosite from Ryûjima mine is indicated by a dashed line.

solution of Ca^{2+} and Mg^{2+} in rhodochrosite and Ca^{2+}, Mg^{2+} and Mn^{2+} in magnesian kutnahorite is small, the equilibrium constant, K, for this reaction is written in the form:

$$K = \frac{(a^{L}_{Mn^{2+}})^{3/2}}{(a^{L}_{Ca^{2+}}) \cdot (a^{L}_{Mg^{2+}})^{1/2}}$$

where $a^{L}_{Mn^{2+}}$, $a^{L}_{Ca^{2+}}$ and $a^{L}_{Mg^{2+}}$ denote the activity of Mn^{2+}, Ca^{2+} and Mg^{2+} in solution. Filling temperatures of fluid inclusions already described and other considerations show that early minerals formed at the higher temperatures in hydrothermal ore deposits. Precipitation of rhodochrosite from hydrothermal solution, and of magnesian kutnahorite in the last stage, were due to 1) decrease in temperature of hydrothermal solution; 2) decrease in the value of

$$(a^{L}_{Mn^{2+}})^{3/2} / a(^{L}_{Ca^{2+}}) \cdot (a^{L}_{Mg^{2+}})^{1/2}$$

in hydrothermal solution; or both.

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