

The Presence of Essential CO_3^{2-} in Rosenhahnite from Engyoji, Kochi City, Japan

By

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Abstract—Rosenhahnite from Engyoji, Kochi City, Japan, is proved to contain essential CO_3^{2-} after the combination of energy dispersive X-ray spectrochemical and wet chemical analyses, which gave SiO_2 49.63, FeO 0.42, CaO 45.48, H_2O 3.59, CO_2 1.60, total 100.72%, yielding the empirical formula $(\text{Ca}_{2.96}\text{Fe}_{0.02})_{\Sigma 2.98}\text{Si}_{3.02}\text{O}_8((\text{OH})_{1.46}\text{O}_{0.16}(\text{CO}_3)_{0.13})$ on the basis of total cation=6 and the ideal formula $\text{Ca}_3\text{Si}_3\text{O}_8((\text{OH})_{2-4x}\text{O}_x(\text{CO}_3)_x)$.

The material occurs as a vein mineral in greenstone fragments enclosed within serpentinite mass involved in Kurosegawa Tectonic Melange Zone. The veins consist of prehnite, rosenhahnite and xonotlite, cut pectolite veins, and are intersected by xonotlite veins. The mineral association is similar to that of the original locality, Russian River, California, U.S.A.

Introduction

The original description on rosenhahnite by PABST *et al.* (1967) referred to the conclusion of experimental work of FISTORIUS (1963), who firstly described the artificial analogue of this mineral synthesized under higher pressure condition and regarded as a high pressure polymorph of xonotlite, or else a compound with the formula $\text{CaSiO}_3 \cdot n\text{H}_2\text{O}$ where $1 > n > 0.2$. In 1975 DUNN reported the second occurrence in a trap rock from North Carolina and paid attention to the associated zeolite-bearing assemblage. LEACH and RODGERS (1977) considered that the formation requires strain after describing the occurrence in New Zealand.

The first rosenhahnite in Japan occurs in an entirely different mode of occurrence from those of known ones, that is, it is found in a limestone-contaminated granitic rock composed of microcline and clinopyroxene accompanied by gehlenite skarn from Kushiro, Hiroshima Prefecture (HENMI *et al.*, 1982). The authors pointed out the compositional deviation from the ideal formula due to the small amount of MnO up to 0.54% in weight.

The present rosenhahnite is the second occurrence in Japan and the mineral association is similar to that of the original locality. But the chemical analysis disclosed the presence of CO_2 as its essential constituent as well as the lesser content of H_2O than the theoretical figure derived from the originally supposed ideal formula $\text{Ca}_3\text{Si}_3\text{O}_8(\text{OH})_2$, which has been crystallographically validated by WAN *et al.* (1977). The presence of CO_2 in rosenhahnite had been given in the original analysis (PABST

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et al., 1967), but the authors had ascribed it to the contamination calcite. The possibility of essential CO_3^{2-} in the original rosenhahnite is here discussed.

Occurrence

The presence of various xenoliths in ultrabasic rocks distributed in the northward of Kochi city with E–W trend is reported by MARUYAMA (1981). They are located within Kurosegawa Tectonic Melange Zone and quarried at many places including those around Engyoji, Kochi City (Fig. 1). The xenoliths are rich in petrographic diversity, i.e., rodingite, granitic rocks, sandstone, mudstone, chert, amphibolite, schists and greenstone, and some schists are jadeite-bearing.

Rosenhahnite is found as veins cutting greenstone fragments enclosed in serpentinite in a quarry at Engyoji operated by Tanaka Olivine Mining Company. Although it was found in a dump, there is no doubt that fragments appeared during the mining works in the quarry. The fragments comprising veins of studied rosenhahnite has a greenish grey massive and homogeneous appearance. It is intersected by white veins of pectolite, of prehnite-rosenhahnite-xonotlite, and of xonotlite in the order of formation and they have no regularity in trend.

The pectolite veins are apparently monominerallic and composed of fibers developed parallel to the walls. The width is less than a centimeter. The prehnite-rosenhahnite-xonotlite veins are more clear than the previous one due to the dominance

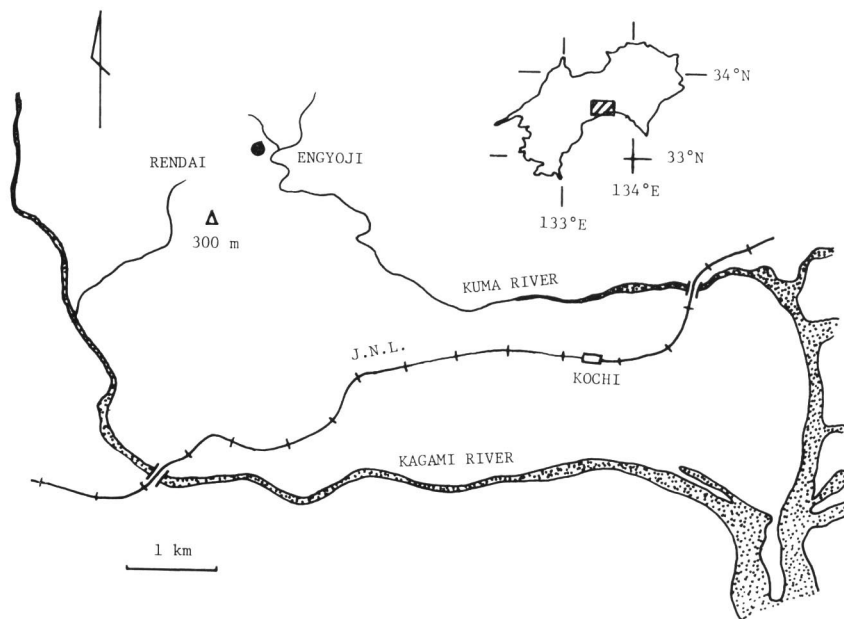


Fig. 1. The index map of the locality.

of clearer crystals of rosenhahnite. In the well-developed parts reaching more than 8 millimeters wide, they are rimmed by thin aggregate of prehnite, then filled with aggregates of thin tabular rosenhahnite crystals of more than 5 millimeters long, and the crystals are interstitially filled with opaque white powdery xonotlite, which grades into monominerallic veins cutting rosenhahnite.

Under the microscope, the greenstone consists of fine-grained aggregates of non-oriented actinolitic amphibole, epidote, leucoxene, and chlorite in the order of abundance. Besides them are aggregates of stilpnomelane forming monominerallic aggregates of a millimeter order. Actinolitic amphibole is not acicular but slender in outline with average dimensions 0.1×0.02 millimeter. It is pleochroic from very pale yellowish green to yellowish green through greenish blue. The maximum extinction angle is 22° for Z' . Epidote has a rectangular or rhombic outline and nearly colourless, occurring as isolated grains of 0.0n millimeter order. Leucoxene has a sharp outline in some grains and forms aggregates composed of a few grains, which are of 0.n millimeter order. Chlorite is an accessory interstitial filling of above mentioned minerals except for stilpnomelane. It has bluish green colour and very low birefringence with positive elongation.

Pectolite veins are monominerallic and composed of fine-grained rim and coarser-grained center where well-developed. Prehnite-rosenhahnite-xonotlite veins have the rim of prehnite composed of radially grown tablets of 0.n to 0.0n millimeter order

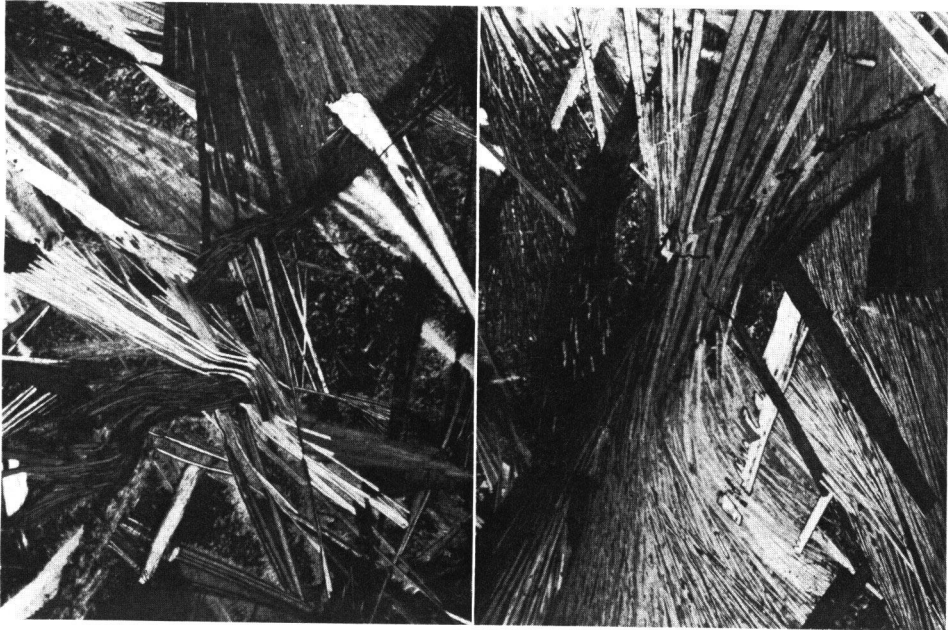


Fig. 2. The subparallel aggregate of tabular rosenhahnite crystals flattened to $\{010\}$. Left: crinkled tablets with interstitial xonotlite. View, approx. 3.6×4.8 mm. Right: intersected tablets by xonotlite veins. View, approx. 1.5×2.9 mm.

or individual crystals with undulatory extinction of X' perpendicular to the walls. Rosenhahnite occurs as subparallel aggregates of thin tablets with dominant $\{001\}$ (Fig. 2). Occasionally crinkled tablets are found. Near the center of vein the tablets are interstitially filled with xonotlite composed of very fine fiber aggregates, which grades into minute veins cutting rosenhahnite, as visually realized. Grain size of individual xonotlite fibers is of 0.0n millimeter order or less and no regularity is found in the mode of aggregate except for the parts cutting rosenhahnite with sharp wall, where fibers are more or less perpendicular to the walls. It is worth mentioning that neither veins nor xenolith fragments contain carbonates, although minor aragonite veins are found in ultrabasic rocks. This excludes the possibility of contamination of CaCO_3 in the examined material.

Physical Properties

As compared with the original data in Table 1, the present rosenhahnite had nearly same physical properties with it except for the lack of fluorescence under ultra-violet light. The colour of powder of the present rosenhahnite looks white than pure white owing to the presence of a blue hue.

Chemical Analysis

The combination of the energy dispersive X-ray spectrochemical analysis for the elements with atomic number more than 11 employing the instrument of Link Co. Ltd. and ordinary wet one including H_2O analysis by the Karl Fischer method and CO_2 analysis by the method of KONISHI (1950/51) on binocular-pure material gave

Table 1. Physical and optical properties of rosenhahnites.

	Engyoji	Russian River
Colour	white	colourless to buff
Luster	vitreous	vitreous
H. (Mohs)	$4\frac{1}{2}$ –5	$4\frac{1}{2}$ –5
Density (g/cm^3)	2.90 (calc.)	2.905 (calc.) 2.89 (meas.)
Cleavage*	$\{010\}$, perfect $\{100\}$, $\{001\}$, good	$\{010\}$, perfect $\{001\}$, good
Habit	tabular	tabular to prismatic
Fluorescence	none	yellowish green (short wave)
$2V(-)$	65°	$64(4)^\circ$
α	1.624(2)	1.625(2)
β	1.640(2)	1.640(2)
γ	1.646(2)	1.646(2)

* orientation is taken in accordance with that in JCPDS Card. Transformation matrix is 100/001/010.

the result demonstrated in Table 2. The empirical formula calculated on the basis of total cation=6 is: (Ca_{2.96}Fe_{0.02})_{Σ2.98}Si_{3.02}O₈((OH)_{1.45}O_{0.17}(CO₃)_{0.13}). The ideal formula of the present rosenhahnite is Ca₃Si₃O₈((OH)_{2-4x}O_x(CO₃)_x) where x about 0.15. It is worthy of note that the total number of oxygen atom in the larger parentheses is 2.

Table 2. Chemical analysis of rosenhahnite from Engyoji, Kochi City, Japan (analysts: K. YOKOYAMA (for SiO₂, FeO and CaO) and T. TIBA (for H₂O and CO₂)).

	wt. %	Recast to 100%	Molecular quotient	Metal number	Cation number (Σ cat.=6)
SiO ₂	49.63	49.28	0.8202	0.8202	3.02
FeO	0.42	0.42	0.0058	0.0058	0.02
CaO	45.48	45.15	0.8051	0.8051	2.96
H ₂ O	3.59	3.56	0.1976	0.3952	1.45
CO ₂	1.60	1.59	0.0361	0.0361	0.13
Total	100.72	100.00			

Empirical formula: (Ca_{2.96}Fe_{0.02})_{Σ2.98}Si_{3.02}O₈((OH)_{1.45}O_{0.17}(CO₃)_{0.13})

Table 3. X-ray powder diffraction pattern of rosenhahnites.

1.		2.		hkl	1.		2.		hkl
d(Å)	I	d(Å)	I		d(Å)	I	d(Å)	I	
8.84	5	9.00	$\frac{1}{2}$	001	2.408	9	2.409	$\frac{1}{2}$	21 $\bar{3}$
6.86	3	6.91	$\frac{1}{2}$	100	2.390	5			$\bar{1}$ 13
5.81	7	5.847	1	$\bar{1}$ 01	2.357	5	2.355	2	0 $\bar{1}$ 4
5.11	2			101	2.314	11	2.316	$\frac{1}{2}$	221
4.57	5	4.590	$\frac{1}{2}$	11 $\bar{1}$	2.285	30	2.295	10	2 $\bar{2}$ 2
4.45	2	4.471	$\frac{1}{4}$	002	2.253	13	2.252	14	031
3.990	7	3.994	$\frac{1}{2}$	$\bar{1}$ 02	2.217	6			2 $\bar{1}$ 3
3.630	3	3.642	$\frac{1}{2}$	$\bar{1}$ 12	2.200	17	2.206	9	22 $\bar{4}$
3.541	2			111	2.184	13	2.188	3	311
3.431	30	3.437	15	200	2.166	20	2.168	4	1 $\bar{1}$ 4, 11 $\bar{3}$
3.357	30	3.361	10	201	2.125	5	2.126	1b	12 $\bar{4}$
3.199	75	3.206	100	020	2.121	6			22 $\bar{3}$
3.112	21	3.118	$\frac{1}{4}$	0 $\bar{1}$ 3	2.094	5	2.094		0 $\bar{3}$ 3
3.065	25	3.070	$\frac{1}{2}$	201	2.071	5	2.075	1b	312
3.038	65	3.052	10	2 $\bar{1}$ 1	2.066	3			124
2.963	100	2.978	50	003	2.044	3	2.047	$\frac{1}{2}$	222
2.926	2			$\bar{1}$ 13	2.000	3	2.004	$\frac{1}{2}$	221
2.916	7			202	1.992	5	1.997	1	204
2.883	13	2.888	4	122, 210	1.972	5	1.975	$\frac{1}{2}$	231
2.828	2	2.831	1	12 $\bar{2}$	1.943	3	1.945	$\frac{1}{2}$	303
2.770	40	2.774	13	21 $\bar{2}$	1.931	6	1.932	$\frac{1}{4}$	302
2.740	2	2.741	$\frac{1}{2}$	021	1.925	4	1.927	1	311
2.681	2			$\bar{1}$ 21	1.884	25	1.887	7	021, 030
2.659	30	2.662	7	023	1.859	8	1.862	1	2 $\bar{1}$ 4
2.557	9	2.557	3	202	1.834	8			025
2.547	6			212	1.830	9	1.833	$\frac{1}{4}$	32 $\bar{1}$
2.495	3			$\bar{1}$ 23	1.824	20	1.827	6	232

1. Rosenhahnite. Russian River, California, U.S.A. Cu radiation. Guinier camera method. JCPDS Card No. 29-378.
2. Rosenhahnite. Engyoji, Kochi City, Japan. Cu/Ni radiation. Diffractometer method.

The minor difference in the number of O and (CO₃) in the formula comes from the fluctuation of (Ca+Fe) and Si from the ideal number 3.

X-Ray Powder Study

The X-ray powder diffraction pattern of the present rosenhahnite is compared with that of the material from the original locality appeared in JCPDS Card No. 29-379 (Table 3). The present pattern has (020) diffraction of enhanced intensity owing to the thin tabular nature of crystal or the perfect cleavage along {010}. The unit cell parameters calculated from the indexing after the reference to the JCPDS Card are: $a=6.962(3)$, $b=6.814(4)$, $c=9.52(1)\text{\AA}$, $\alpha=108.6(1)^\circ$, $\beta=95.8(1)^\circ$, $\gamma=95.0(2)^\circ$, $Z=2$. Minor differences from the JCPDS data are reflected by most of d-values especially those in the higher angle region.

Discussion

Although the present identification is based on the similarity to the original material in rough chemical composition, X-ray powder diffraction pattern, optical and some physical properties, the chemical analysis has proved the presence of essential CO₂ and lower (OH) content than hitherto considered.

It will be certain that rosenhahnite has a stability field in the high pressure condition seeing from the denser atomic arrangement (WAN *et al.*, 1977). However, as already referred to, the occurrence in druses of a trap rock (DUNN, 1975) and in skarn (HENMI *et al.*, 1982) indicate the formation under lower pressure and high temperature conditions, respectively. The find of essential CO₃²⁻ in the present rosenhahnite may account for the stable formation out of the condition outlined by the synthetic works of PISTORIUS (1963) apart from the real substantial identity of his "high pressure polymorph of xonotlite" with natural rosenhahnite. It is necessary to know the precise chemical compositions of his synthetic products to see if CO₂-free synthetic rosenhahnite is really producible or not.

The original authors of rosenhahnite had already found the content of CO₂ as high as 1.3% in weight (PABST *et al.*, 1967), but they ascribed it to the amixed calcite after the reference to the presence of calcite in the associated minerals. If all the CO₂ in the original analysis is put into rosenhahnite, the revised formula is (Ca_{2.95}Na_{0.03}Ba_{0.02}Mg_{0.01}Fe_{0.01})_{Σ3.02}Si_{2.98}O₈((OH)_{1.60}O_{0.07}(CO₃)_{0.11}), which is accounted by the newly advocated ideal formula with x about 0.1, and indicates the possible variation of CO₂ content in rosenhahnite after the comparison with the present analysis with CO₂ 1.60% in weight. This interpretation may lead to the suggestion that the range of formation of rosenhahnite must be considered with respect to the variation of CO₂ pressure. The other available chemical analyses of rosenhahnites from the other sources (Table 4) do not refer to CO₂ but use the expression of ignition loss in most cases, which may involve CO₂ besides H₂O.

Table 4. Chemical analyses of rosenhahnites.

	1.	2.	3.	4.	5.	6.
SiO ₂	48.61	47.60	47.16	48.49	49.63	49.03
Al ₂ O ₃	0.06	0.08	0.01			
FeO	0.19	0.09	0.01	0.03	0.42	
MnO	0.006	0.40	0.04	0.54		
MgO	0.10	0.05		0.05		
CaO	44.83	44.74	48.7	46.02	45.48	45.76
BaO	0.77	0.03	0.01			
SrO	0.03					
Na ₂ O	0.21		0.03	0.01		
K ₂ O	nil	0.02	0.01	0.01		
B ₂ O ₃	0.001					
H ₂ O	3.9	4.80	(4.92)	(4.86)	3.59	3.53
CO ₂	1.3				1.60	1.68
Total	100.00	97.81	100.00	100.00	100.72	100.00

1. Russian River, California, U.S.A. PABST *et al.* (1967). Recast to 100%. Figure of H₂O is from ignition loss minus CO₂.
2. Durham, North Carolina, U.S.A. DUNN (1975).
3. Wairere, New Zealand. LEACH and RODGERS (1977). () indicates the calculated figure using the formula Ca₃Si₃O₈(OH)₂.
4. Kushiro, Hiroshima Prefecture, Japan. HENMI *et al.* (1982). H₂O content is by difference.
5. Engyoji, Kochi city, Japan. The present study.
6. Theoretical Ca₃Si₃O₈((OH)_{1.44}O_{0.14}(CO₃)_{0.14}).

Among silicate minerals known to date the substitution of CO₃ for 2(OH) has not been established. For example, the treatment of chemical analyses of some scapolites with higher H₂O(+) contents do not consider the substitution of CO₃ for OH but make a separate handling (DEER, HOWIE and ZUSSMAN, 1963). The present case serves to establish a new type of substitution of CO₃ for 2(OH) in silicates.

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References

- DEER, W. A., R. A. HOWIE & J. ZUSSMAN, 1963. Rock-forming Minerals. Vol. 4. Framework Silicates. pp. 321–337. Longmans, London.
- DUNN, P. J., 1975. Rosenhahnite, a second occurrence with the zeolites of the Durham quarry, Durham, Wake County, North Carolina. *Miner. Rec.*, **6**: 300–301.

- KONISHI, Y., 1950/51. A new method for determining carbonates mainly in alkali products. *Rept. Res. Lab. Asahi Glass Co.*, **1**: 355–369. (In Japanese.)
- PABST, A., E. B. GROSS & J. T. ALFORS, 1967. Rosenhahnite, a new hydrous calcium silicate, from Mendocino County, California. *Amer. Mineral.*, **52**: 336–351.
- PISTORIUS, C. W. F. T., 1963. Thermal decomposition of portlandite and xonotlite to high pressure and temperatures. *Amer. Jour. Sci.*, **216**: 79–87.
- HENMI, C., I. KUSACHI & K. HENMI, 1982. Rosenhahnite from Kushiro, Tojo-cho, Hiroshima Prefecture. *Abstr. Autumn Meeting of Japan Assoc. Mineral. Petrol. Econ. Geol., Miner. Soc. Japan, and Soc. Mining Geol. Japan* at Tsukuba: 154. (In Japanese.)
- LEACH, T. M. & K. A. RODGERS, 1977. Rosenhahnite $\text{Ca}_3\text{Si}_3\text{O}_8(\text{OH})_2$ —a further occurrence. *Miner. Mag.*, **41**: 394–395.
- MARUYAMA, S., 1981. The Kurosegawa melange zone in the Ino district to the north of Kochi city, central Shikoku. *Jour. Geol. Soc. Japan*, **87**: 569–583.
- WAN, Che'ng, S. GHOSE & G. V. GIBBS, 1977. Rosenhahnite, $\text{Ca}_3\text{Si}_3\text{O}_8(\text{OH})_2$; Crystal structure and the stereochemical configuration of the hydroxylated trisilicate group, $(\text{Si}_3\text{O}_8(\text{OH})_2)$. *Amer. Mineral.*, **62**: 503–512.