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Wadalite, rustumite, and spurrite from La Negra mine, Queretaro, Mexico.

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Abstract: Wadalite, rustumite, and spurrite-rare calc-silicates-occur in skarns formed by Tertiary diorite intrusion into Upper Jurrassic to Lower Cretaceous limestone at La Negra mine, Queretaro, Mexico. Wadalite and rustumite occur zonally in the rock mainly composed of spurrite. They are associated with hydrogrossular, andradite, calcite, and magnetite in main and occur as fine grains less than 200 μm in size. Spurrite occurs as an aggregate of comparatively large irregular crystals up to 3 mm.

Wadalite is colorless and optically isotropic with the refractive index, $n=1.708$. Optical properties of wadalite is so similar to hydrogrossular that it is difficult to tell the former from the latter. $D_{calc}=$ 3.066 g/cm. The electron microprobe analyses of wadalite yield an empirical chemical formula, $Ca_{5.99}(Al_{3.35}Si_{2.70}Mg_{0.63}Fe^{3+}{}_{0.25})_{\Sigma 6.93}O_{16}Cl_{2.93}$, or ideally $Ca_6(Al,Si,Mg,Fe^{3+})_7O_{16}Cl_3$ on the basis of O=16. The crystal is cubic with the space group $I43d$, the cell dimension $a=12.014(1)$ Å and $V=1734(1)$ Å^3, and $Z=4$. Wadalite in this study is richer in Mg and lower in $(Al+Fe^{3+}+Mg)/Si$ ratio than that of the original description.

Rustumite is translucent to white. It is optically biaxial negative with $\alpha=1.641$, $\beta=1.646$, $\gamma=1.651$, and $\gamma-\alpha=0.010$. $D_{meas}=2.85$ and $D_{calc}=3.017$ g/cm^3. The microprobe analyses of rustumite yield an empirical formula, $Ca_{9.97}Si_{5.00}O_{18}(Cl_{1.56}(OH)_{2.44})_{\Sigma 4.00}\cdot 0.26H_2O$, or ideally $Ca_{10}Si_5O_{18}(Cl,OH)_4$ on the basis of O=18 and Cl+OH=4. The space group is $C2/c$ and the cell dimensions are $a=7.625(1)$, $b=18.576(2)$, $c=15.519(1)$ Å, $\beta=103.75(1)°$, and $V=2135(1)$ Å^3. $Z=4$.

Spurrite is bluish gray. It is optically biaxial negative with $\alpha=1.641$, $\beta=1.670$, $\gamma=1.678$, and $\gamma-\alpha=0.037$. $D_{meas}=2.94$, $D_{calc}=2.882$ g/cm^3. The wet chemical analysis of spurrite yields an empirical formula $Ca_{4.97}(Si_{1.95}Al_{0.05})_{\Sigma 2.00}(C_{0.87}B_{0.16})_{\Sigma 1.03}O_{11}$, or ideally $Ca_5(SiO_4)_2(C,B)O_3$ on the basis of O=11. The space group is $P2_1/a$ and cell dimensions are $a=10.472(2)$, $b=6.724(1)$, $c=14.174(6)$ Å, $\beta=101.31(3)°$, and $V=978.7(3)$ Å^3. This spurrite contains a small amount of boron which replaces the carbon in the CO_3 equilateral triangles in the structure.

1. Introduction

A hand specimen of a spurrite rock was taken from skarns at La Negra mine, Queretaro, Mexico by one of the authors, Takeda, during his studies on metal mines in Mexico. We found wadalite and rustumite -rare calc-silicates-in the hand specimen of the spurrite.

Wadalite, a calcium chloride alumino-silicate, was discovered in a skarn xenolith of Tertiary volcanics at Koriyama, Fukushima Prefecture, Japan (Bunno *et al.*, 1983) . The crystal structure was determined by Tsukimura *et al.* (1993) using a single crystal of the composition of $(Ca_{5.88}Mg_{0.23})(Al_{4.26}Fe_{0.46})Si_{2.00}O_{15.68}Cl_{2.64}$ or ideally $Ca_6Al_5Si_2O_{16}Cl_3$. The results show the space group $I43d$, the cell dimension $a=12.001(2)$ Å, and forming a framework of $(Al,Si)O_4$ tetrahedra in the structure.

Rustumite was firstly found at Kilchoan, Scotland (Agrell, 1965) , and secondly in Afghanistan (*JCPDS* card 29-314, 1979) . Agrell described the chemical composition of rustumite as $Ca_4Si_2O_7(OH)_2$. However, Howie and Ilyukhin (1977) determined the crystal structure and gave another ideal formula $Ca_{10}(Si_2O_7)_2SiO_4Cl_2(OH)_2$ that contains Cl to some extent replacing OH. The symmetry of the crystal is monoclinic $C2/c$ and its cell dimensions are $a=7.62$, $b=18.55$, $c=15.51$ Å, and $\beta=104.33°$.

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Keywords: wadalite, rustumite, spurrite, calc-silicate, skarn, Mexico

Spurrite, $Ca_5(SiO_4)_2CO_3$, is known at several localities such as the Kilchoan (Agrell, 1965); the Christmas Mountains, Texas (Joesten, 1974); Kushiro, Hiroshima Prefecture, Japan (Kusachi *et al.*, 1971); and Fuka, Okayama Prefecture Japan (Kusachi, 1975). According to Smith *et al.* (1960), the space group is $P2_1/a$, the cell dimensions are $a=10.49$, $b=6.705$, $c=14.16$ Å, and $\beta=101.3°$, and the structure consists of isolated SiO_4 tetrahedra and CO_3 equilateral triangles linked together by Ca atoms.

Mineralogical properties of these minerals are described in this paper and the discussion is focused especially into wadalite.

2. Occurrence

La Negra mine is located at about 2,000 m above the sea level, northeast of Queretaro in central Mexico, about 200 km north of Mexico City, approximately at latitude 20°50'N, longitude 99°30'W (Fig. 1). The mine works for silver, zinc, lead and copper. Upper Jurassic to Lower Cretaceous limestones occur in this area. They were thermally metamorphosed by intrusion of Tertiary diorite forming the skarn of 10 to 300 m wide and more than 1 km long. The ore deposit occurs along the boundary between the skarn and the limestone. Ore minerals are sphalerite, galena, chalcopyrite, arsenopyrite, pyrrhotite, pyrite, hessite, and native silver. The skarn is composed mainly of Ca-garnet, diopside, wollastonite, and spurrite.

The hand specimen in this study is composed mainly of spurrite. It contains two contact bands of rustumite and wadalite / rustumite of each 0.5 - 1cm wide. The former is the aggregate of mainly rustumite and the latter is associated with hydrogrossular, andradite, calcite, magnetite, perovskite, and other minerals in small amounts.

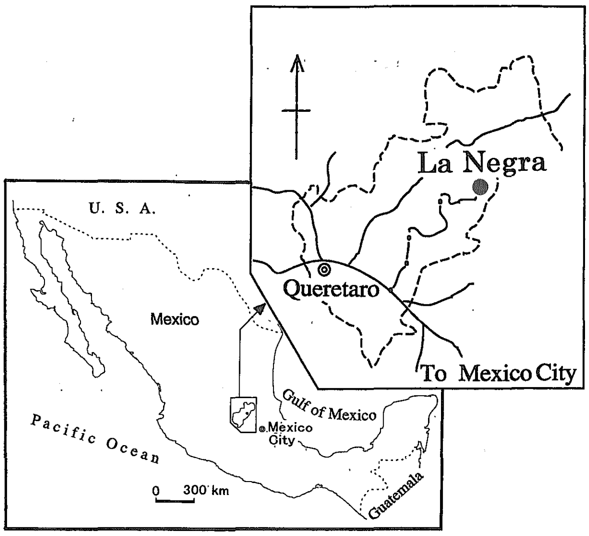

Fig. 1 Location of La Negra mine.

3. Wadalite

3.1 Physical and optical properties

Wadalite occurs as granular crystals less than 200 μm in size. The calculated density for the average chemistry from the cell volume described below is 3.066 g/cm^3. It is colorless and isotropic in thin section. The refractive index is $n=1.708$ with white light.

Wadalite is closely associated with hydrogrossular. It is usually difficult to distinguish from each other because they are similar in optical properties. However, the boundary between them is observable in the thin section under plane light as shown in a photomicrograph in Fig. 2(a). A back-scattered electron (BSE) image in Fig. 2(b) shows that wadalite is clearly brighter than hydrogrossular, because wadalite contains comparatively heavier atoms of Cl and Fe than those of hydrogrossular as described later. Most grains of wadalite are rimmed by hydrogrossular as shown in these figures. This may indicate that the wadalite was replaced secondarily by hydrogrossular. In the BSE images, brightness is slightly changed in a crystal of wadalite due to the chemical heterogeneity.

3.2 Chemical analyses

Wadalite was analyzed with a JEOL electron microprobe JXA-733 by the wavelength dispersion mode (WDX). Thirteen microprobe analyses were divided into two groups on reflective intensities of electron. One group corresponds to the brighter parts of BSE images and the other to the darker parts. The results of the analyses are listed in Tables 1 and 2, respectively. The corresponding empirical formula are given on the basis of O=16. The average empirical formula for the brighter parts is

$Ca_{6.01}(Al_{3.32}Si_{2.65}Mg_{0.61}Fe^{3+}_{0.34})_{\Sigma 6.92}O_{16}Cl_{2.90}$

and for the darker parts

$Ca_{5.96}(Al_{3.29}Si_{2.76}Mg_{0.66}Fe^{3+}_{0.14})_{\Sigma 6.95}O_{16}Cl_{2.96}$.

Both formulas give the average of

$Ca_{5.99}(Al_{3.35}Si_{2.70}Mg_{0.63}Fe^{3+}_{0.25})_{\Sigma 6.93}O_{16}Cl_{2.93}$.

Comparing Tables 1 and 2, it is notable that the brighter parts are more enriched in iron than the darker parts.

3.3 X-ray studies

A prismatic single crystal of 0.070 × 0.075 × 0.180 mm was selected for single crystal X-ray studies. A Rigaku AFC-5 four circle diffractometer and an oscillation camera equipped with it were used for determination of the symmetry and cell dimensions of the crystal. Oscillation photographs around three crystallographic axes and conventional intensity measurements showed that the space group is $I\bar{4}3d$ that is the same as reported by Tsukimura *et al.* (1993). Cell dimensions were determined using 14

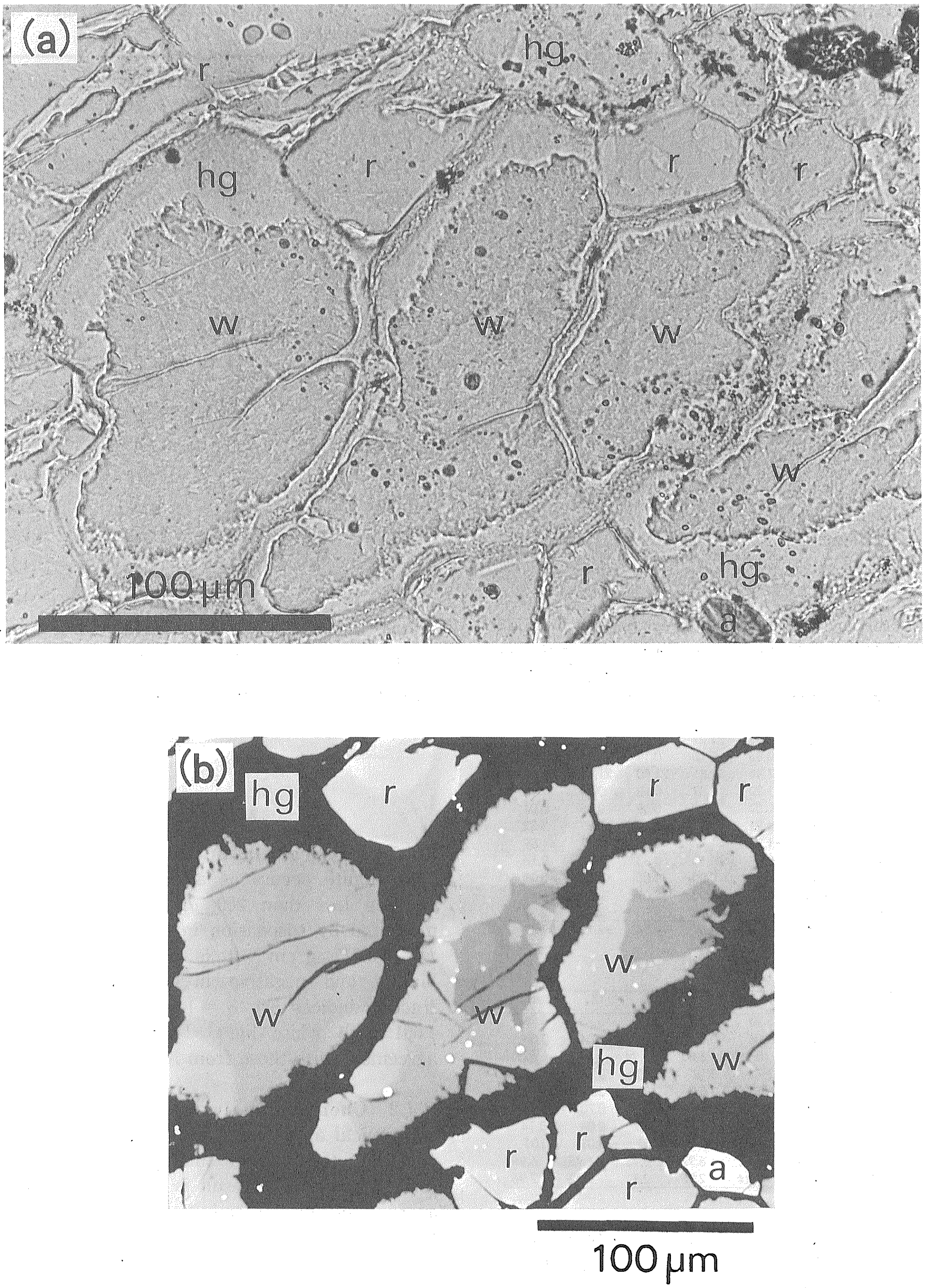

Fig. 2 (a) Photomicrograph of the thin section of wadalite and other constituent minerals under the open nicols.
(b) Back-scattered electron image of the wadalite corresponding top image. Abbreviations for minerals: w: wadalite, hg: hydrogrossular, r: rustumite, a: andradite.

Table 1 Chemical analyses of the marginal parts of wadalite crystals from La Negra. (position: the brighter area in back-scattered electron image in Fig. 1)

	1	2	3	4	5 (wt. %)	6	7	Mean
SiO_2	19.83	19.70	19.58	20.72	19.68	19.79	19.79	19.87
TiO_2	0.19	0.14	0.15	0.19	0.16	0.14	0.16	0.16
Al_2O_3	21.15	20.98	21.77	19.50	21.49	21.12	21.52	21.08
Fe_2O_3	3.49	3.46	3.03	3.53	3.52	3.39	3.09	3.36
MnO	0.00	0.02	0.01	0.03	0.03	0.06	0.06	0.03
MgO	2.97	3.12	2.84	3.62	2.91	3.11	2.88	3.06
CaO	42.25	42.59	42.10	41.75	41.89	41.74	41.95	42.04
Na_2O	0.04	0.03	0.06	0.06	0.03	0.01	0.07	0.04
K_2O	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Cl	13.35	13.47	13.51	12.12	12.41	12.34	12.50	12.81
$-(O)(=Cl_2)$	-3.01	-3.04	-3.05	-2.73	-2.80	-2.79	-2.82	-2.89
Total	100.26	100.47	100.00	98.79	99.32	98.91	99.20	99.56

Atomic proportions on the basis of O=16.

	1	2	3	4	5	6	7	Mean
Ca	6.05	6.11	6.05	5.96	5.97	5.97	5.99	6.01
Na	0.01	0.01	0.01	0.01	0.01	0.00	0.02	0.01
Σ	6.06	6.12	6.06	5.97	5.98	5.97	6.01	6.02
Al	3.33	3.31	3.44	3.06	3.37	3.32	3.38	3.32
Si	2.65	2.64	2.63	2.76	2.62	2.64	2.64	2.65
Mg	0.59	0.62	0.57	0.72	0.58	0.62	0.57	0.61
Fe^{3+}	0.35	0.35	0.31	0.35	0.35	0.34	0.31	0.34
Ti	0.01	0.01	0.01	0.02	0.02	0.01	0.01	0.02
Σ	6.93	6.93	6.96	6.91	6.94	6.93	6.92	6.94
Cl	3.02	3.06	3.07	2.74	2.79	2.79	2.82	2.90

Table 2 Chemical analyses of the inner parts of wadalite crystals from La Negra. (position: the darker area in back-scattered electron image in Fig. 1)

	8	9	10	11 (wt. %)	12	13	Mean
SiO_2	18.23	19.02	23.87	21.29	21.38	21.16	20.83
TiO_2	0.04	0.03	0.05	0.10	0.11	0.21	0.09
Al_2O_3	25.10	24.50	17.44	19.85	21.80	21.47	21.69
Fe_2O_3	1.77	1.85	1.20	2.37	0.58	0.64	1.40
MnO	0.01	0.00	0.04	0.08	0.09	0.05	0.04
MgO	1.96	2.25	4.91	3.82	3.43	3.52	3.32
CaO	41.45	42.89	41.97	41.77	41.38	41.91	41.89
Na_2O	0.04	0.02	0.27	0.11	0.33	0.19	0.16
K_2O	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Cl	14.02	12.64	13.18	13.08	12.97	12.97	13.14
$-(O)(=Cl_2)$	−3.16	−2.85	−2.97	−2.95	−2.93	−2.93	−2.97
Total	99.46	100.35	99.96	99.52	99.14	99.19	99.59

Atomic proportions on the basis of O=16.

	8	9	10	11	12	13	Mean
Ca	6.00	6.02	5.93	5.97	5.86	5.95	5.96
Na	0.01	0.01	0.06	0.03	0.08	0.04	0.04
Σ	6.01	6.03	5.99	6.00	5.94	5.99	6.00
Al	4.00	3.78	2.71	3.12	3.40	3.36	3.39
Si	2.46	2.49	3.15	2.84	2.83	2.81	2.76
Mg	0.40	0.44	0.96	0.76	0.68	0.70	0.66
Fe^{3+}	0.18	0.18	0.12	0.24	0.06	0.06	0.14
Ti	0.00	0.00	0.01	0.01	0.01	0.02	0.01
Σ	7.04	6.89	6.95	6.97	6.98	6.95	6.96
Cl	3.21	2.81	2.94	2.95	2.91	2.92	2.96

reflections in the range of $46° < 2\theta < 61°$ with graphite-monochromated Mo $K\alpha$ radiation. Obtained cell dimension of 12.014(1) Å is close to the 12.001(2) Å by Tsukimura *et al.* (1993). The X-ray diffraction data calculated from the single crystal intensities are listed in Table 3. The crystal and optical data of wadalite are summarized in Table 4 together with the data of rustumite and spurrite.

Table 3 X-ray diffraction data for wadalite from La Negra.

d_{calc}	I	hkl	d_{calc}	I	hkl
4.903 Å	16	211	1.360 Å	2	752
4.246	2	220	1.343	5	840
3.210	12	321	1.310	10	842
3.003	42	400	1.280	4	664
2.686	100	420	1.266	3	930+
2.561	6	332	1.213	4	941+
2.452	39	422	1.178	2	10, 20
2.355	18	510+	1.167	2	943+
2.193	17	521	1.145	2	765+
2.060	4	530	1.115	9	864+
1.948	7	532+	1.096	4	10, 42
1.771	2	631	1.087	3	954+
1.733	12	444	1.070	3	11, 21+
1.698	5	710+	1.062	4	880
1.665	25	640	1.053	2	970
1.634	5	552	1.038	2	12, 20
1.525	3	651+	.9741	3	10, 64+
1.501	7	800	.9322	2	11, 63+
1.478	6	741	.9053	3	12, 44
1.396	5	743+	.8952	5	10, 84+

4. Rustumite

4.1 Physical and optical properties

Rustumite occurs as aggregates of fine tabular crystals less than 200 μm in size. The density measured by suspension in CCl_4 is 2.85 g/cm^3 and D_{calc}=3.017 g/cm^3. It is colorless with optically biaxial and negative in thin sections. The refractive indices are $\alpha = 1.641$, $\beta = 1.646$, and $\gamma = 1.651$ with white light. These data are in good agreement with those from Kilchoan (Agrell, 1965).

4.2 Chemical analyses

Chemical analyses of rustumite were also carried out using the electron microprobe analyzer as described above. The result is shown in Table 5. The average formula on the basis of O=18 and Cl+OH=4 is

$Ca_{9.97}Si_{5.00}O_{18}(Cl_{1.56}(OH)_{2.44})_{\Sigma 4} \cdot 0.26H_2O$,

which is approximately expressed by

$Ca_{10}Si_5O_{18}(Cl_{1.56}(OH)_{2.44})_{\Sigma 4}$.

The formula is similar to the ideal one, $Ca_{10}Si_5O_{18}Cl_2(OH)_2$, expected by Howie and Ilyukhin (1977), although the chlorine is significantly depleted in the studied minerals.

Table 4 Crystal data with physical and optical properties of wadalite, rustumite, and spurrite.

Mineral Locality	wadalite La Negra[1)]	wadalite Koriyama[2)]	rustumite La Negra[1)]	rustumite Kilchoan[3)]	spurrite La Negra[1)]	spurrite Scawt Hill[4)]
Chemical formula	$Ca_{6.0}(Al_{3.4}Si_{2.7}$-$Mg_{0.6}Fe^{3+}{}_{0.3})_{\Sigma 7.0}$-$O_{16}Cl_{2.9}$	$(Ca_{6.0}Mg_{0.2})_{\Sigma 6.2}$-$(Al_{4.4}Si_{2.0}Fe_{0.5})_{\Sigma 6.9}$-$O_{16}Cl_{2.7}$	$Ca_{10.0}Si_{5.0}O_{18}$-$(Cl_{1.6}(OH)_{2.4})_{\Sigma 4}$-$\cdot 0.3H_2O$	$Ca_{10}Si_5O_{18}Cl_2$-$(OH)_2$	$Ca_{5.0}(SiO_4)_2$-$(C_{0.87}B_{0.16})O_3$	$Ca_5(SiO_4)_2CO_3$
Crystal system	cubic	cubic	monoclinic	monoclinic	monoclinic	monoclinic
Space group	$I\bar{4}3d$	$I\bar{4}3d$	$C2/c$	$C2/c$	$P2_1/a$	$P2_1/a$
Cell dimensions (a, b, c: Å, β: °, V: Å^3)	a = 12.014(1)	a = 12.001(2)	a = 7.625(1)	a = 7.62(5)	a = 10.472(2)	a = 10.49(1)
			b = 18.576(2)	b = 18.55(5)	b = 6.724(1)	b = 6.705(3)
			c = 15.519(1)	c = 15.51(5)	c = 14.174(6)	c = 14.16(1)
			β = 103.75(1)	β = 104.3(2)	β = 101.31(3)	β = 101.3(1)
	V = 1734(1)	V = 1729(1)	V = 2135(1)	V = 2124	V = 978.7(3)	V = 976
	Z = 4	Z = 4	Z = 4	Z = 4	Z = 4	Z = 4
Density (g/cm^3)		D_{meas} = 3.01	D_{meas} = 2.85	D_{meas} = 2.86	D_{meas} = 2.94	
Refractive index	D_{calc} = 3.066	D_{calc} = 3.056	D_{calc} = 3.017	D_{calc} = 2.921	D_{calc} = 2.882	D_{calc} = 3.025
	n = 1.708		α = 1.641	α = 1.640	α = 1.641	α = 1.638[5)]
			β = 1.646		β = 1.670	β = 1.672
			γ = 1.651	γ = 1.651	γ = 1.678	γ = 1.678
			$\gamma - \alpha$ = 0.010	$\gamma - \alpha$ = 0.011	$\gamma - \alpha$ = 0.037	$\gamma - \alpha$ = 0.040

1) present study, 2) Tsukimura *et al.* (1993), 3) Howie and Ilyukhin (1977) for chemical formula and space group, and Agrell (1965) for the other data, 4) Smith *et al.* (1960), 5) Kusachi *et al.* (1971) for refractive indices of spurrite from Kushiro.

Table 5 Chemical analyses of rustumite from La Negra.

	1	2	3	4	Mean
			(wt. %)		
SiO_2	32.48	32.14	32.25	32.45	32.33
TiO_2	0.02	0.00	0.00	0.00	0.00
Al_2O_3	0.01	0.01	0.00	0.00	0.00
FeO	0.12	0.02	0.04	0.09	0.07
MnO	0.00	0.00	0.07	0.00	0.02
MgO	0.04	0.09	0.07	0.05	0.06
CaO	60.13	59.89	60.04	59.94	60.00
Na_2O	0.00	0.01	0.00	0.00	0.00
K_2O	0.00	0.00	0.00	0.00	0.00
Cl	6.03	5.76	6.24	6.05	6.02
$-(O)(=Cl_2)$	−1.36	−1.30	−1.41	−1.37	−1.36
Total	97.47	96.62	97.30	97.21	97.15
H_2O*	2.53	3.38	2.70	2.79	2.85

Atomic proportions on the basis of O=18 and Cl+OH=4.

	1	2	3	4	Mean
Ca	9.94	9.98	9.97	9.94	9.97
Mg	0.01	0.02	0.02	0.01	0.02
Fe^{2+}	0.02	0.00	0.01	0.01	0.01
Σ	9.97	10.00	10.00	9.96	10.00
Si	5.01	5.00	5.00	5.02	5.00
Cl	1.58	1.52	1.64	1.58	1.56
OH	2.42	2.48	2.36	2.42	2.44
Σ	4.00	4.00	4.00	4.00	4.00
H_2O	0.09	0.51	0.22	0.23	0.26

*Excess water assumed in the data reduction by Bence & Albee's correction method.

Table 6 X-ray diffraction data for rustumite from La Negra.

d_{meas}	I	hkl	d_{calc}
7.89 Å	3	021	7.91 Å
7.55	3	002	7.54
6.85	6	$\bar{1}11$+	6.86
4.53	2	$\bar{1}13$	4.57
4.34	4	131+	4.35
3.770	3	004	3.769
3.690	2	113	3.688
3.424	6	$\bar{2}22$+	3.428
3.409	6	043	3.410
3.200	13	221	3.204
3.185	15	$\bar{2}23$+	3.185
3.094	58	060	3.096
3.033	100	061+	3.033
2.927	6	044	2.926
2.897	22	222+	2.897
2.873	30	$\bar{2}24$+	2.876
2.743	8	$\bar{1}35$+	2.742
2.632	24	063	2.636
2.549	7	242+	2.549
2.527	19	045+	2.529
2.512	14	006	2.512
2.373	7	204+	2.374
2.314	6	$\bar{2}45$+	2.314
2.294	20	081+	2.295
2.160	3	065	2.160
2.024	2	$\bar{2}65$	2.022
1.984	6	$\bar{2}81$	1.983
1.966	5	$\bar{2}82$+	1.965
1.952	6	$\bar{1}92$+	1.953
1.919	17	281+	1.920
1.906	27	$\bar{4}02$+	1.906
1.844	6	226+	1.844
1.769	12	067	1.768

4.3 X-ray studies

X-ray single crystal experiments are carried out in the same way as those described above. The observed extinction rules were consistent with the space group $C2/c$ by Howie and Ilyukhin (1977). The cell dimensions are a=7.625(1), b= 18.576(2), c= 15.519(1) Å, and β=103.75(1)° determined from 22 reflections in the range of 45°<2θ<55° with Mo Ka radiation. They are also in good agreement with a=7.62(5), b=18.55(5), c= 15.51(5) Å, and β=104°20'(10') by Agrell(1965). The X-ray powder diffraction data were obtained by a Rigaku RAD-γA X-ray diffractometer using graphite-monochromated Cu $K\alpha$ radiation. The data are listed in Table 6.

5. Spurrite

5.1 Physical and optical properties

Spurrite occurs as aggregates of comparatively large irregular crystals up to 3 mm. The density is D_{meas}=2.94 g/cm³ by suspension method in CCl_4. D_{calc}=2.882 g/cm³. It is bluish gray, and colorless with biaxial and negative in the thin section. The refractive indices are α=1.641, β=1.670, and γ=1.678 with white light. They are in good agreement with those from Kushiro, Japan (Kusachi *et al.*, 1971).

Table 7 Chemical analysis and number of ions for spurrite from La Negra.

SiO_2	25.84 wt. %	Ca	4.97	
TiO_2	0.04	Na	0.02	5.00
Al_2O_3	0.55	Mg	0.01	
Fe_2O_3	0.01	Si	1.95	
FeO	0.02	Al	0.05	2.03
MnO	0.02	P	0.03	
MgO	0.09	C	0.87	1.03
CaO	61.22	B	0.16	
Na_2O	0.14			
K_2O	0.04	(basis: O=11)		
P_2O_5	0.39			
CO_2	8.49			
B_2O_3	1.21			
$H_2O(+)$	1.10			
$H_2O(-)$	0.59			
Total	99.82			

Table 8 X-ray diffraction data for spurrite from La Negra.

d_{meas}	I	hkl	d_{calc}	d_{meas}	I	hkl	d_{calc}
6.94 Å	73	002	6.95 Å	2.617 Å	42	312 $40\bar{1}$	2.629 2.618 Å
6.05	24	011	6.05	2.460	10	$40\bar{3}$ 214	2.459 2.463
5.14	25	200 $20\bar{1}$	5.13 5.14	2.440	13	401	2.440
5.02	7	111	5.03	2.419	14	$32\bar{1}$	2.420
4.64	42	003	4.63	2.313	14	006	2.316
3.816	48	$20\bar{3}$ 013	3.834 3.815	2.258	26	$31\bar{5}$ $32\bar{3}$	2.261 2.261
3.786	34	$11\bar{3}$	3.781	2.211	14	031	2.213
3.472	52	004	3.475	2.189	42	016 130	2.190 2.190
3.394	9	113	3.401	2.177	34	322 $13\bar{1}$	2.177 2.177
3.361	14	020	3.362	2.149	15	412 131	2.149 2.149
3.193	26	120 $20\bar{4}$	3.195 3.182	2.133	9	032	2.133
3.098	27	$11\bar{4}$ $01\bar{4}$	3.109 3.087	2.117	17	314	2.116
3.035	31	310 022	3.050 3.026	2.101	9	$40\bar{5}$	2.103
2.990	10	$31\bar{2}$	2.992	2.021	26	$31\bar{6}$ 323	2.023 2.020
2.876	15	311 $21\bar{4}$	2.876 2.876	1.986	35	413 007	1.986 1.986
2.817	5	114 $22\bar{1}$	2.824 2.816	1.949	7	133	1.949
2.778	7	$31\bar{3}$	2.781	1.939	9	$11\bar{7}$	1.939
2.719	86	023	2.721	1.906	56	026 017	1.908 1.904
2.705	100	$22\bar{2}$	2.710	1.893	29	315 $42\bar{4}$	1.896 1.893
2.670	82	$20\bar{5}$	2.674	1.881	27	422 225	1.880 1.879
2.648	66	204	2.647	1.858	10	324	1.858

5.2 Chemical analyses

Chemical analysis was carried out by the wet method. The result is shown in Table 7. The empirical formula on the based of O=11 is
$Ca_{4.97}(Si_{1.95}Al_{0.05})_{\Sigma 2.00}(C_{0.87}B_{0.16})_{\Sigma 1.03}O_{11}$.
The characteristic of this spurrite is the presence of a small amount of boron replacing carbon atoms.

5.3 X-ray studies

The cell dimensions were measured as a = 10.472(2), b = 6.724(1), c = 14.174(6) Å, and β = 101.31(3)° by the X-ray single crystal method using 16 reflections in the range of 55°<2θ<60° with Mo Ka radiation. They are in good agreement with a=10.49, b=6.705, c=14.16 Å, and β=101.3° by Smith *et al.* (1960). The results are listed in Table 8.

6. Discussion

The crystal structure of wadalite has two kinds of cation sites: octahedral and tetrahedral sites (Tsukimura, *et al.*, 1993). The formula of wadalite can be expressed simply as $A_6T_7O_{16}Cl_3$, where A shows the octahedral sites occupied by Ca and T shows the tetrahedral sites for small cations of Al^{3+},Si^{4+}, and Fe^{3+}. Mg commonly occurs in octahedral sites in silicates. We, however, consider that Mg in wadalite may occupy T-sites, because the formula for wadalite from La Negra on the basis of O=16 and Mg in T-sites,
$Ca_{5.99}(Al_{3.35}Si_{2.70}Mg_{0.63}Fe^{3+}_{0.25})_{\Sigma 6.93}O_{16}Cl_{2.93}$, is closely consistent with $A_6T_7O_{16}Cl_3$. On the other hand, Tsukimura, *et al.* (1993) assumed Mg may occupy the octahedral sites as shown in the formula of ($Ca_{5.88}$

$Mg_{0.23})(Al_{4.26}Fe_{0.46})Si_{2.00}O_{15.68}Cl_{2.64}$ (basis: Si=2). Their formula, however, can be transformed into $Ca_{6.00}(Al_{4.35}Si_{2.04}Fe_{0.47}Mg_{0.23})_{\Sigma 7.09}O_{16}Cl_{2.69}$ on the basis of O=16 and Mg in T-sites. The latter formula is also consistent with $A_6T_7O_{16}Cl_3$. Therefore Mg in wadalite may occupy the tetrahedral sites and the formula of $Ca_6(Al,Si,Fe^{3+},Mg)_7O_{16}Cl_3$ is more feasible in natural occurrences. The other examples of Mg in the tetrahedral sites are known in structures of akermanite, $Ca_2MgSi_2O_7$(Kimata and Ii, 1981) and spinel, $MgAl_2O_4$ (Zorina and Kvitka, 1969) that are the minerals at higher temperatures.

In accordance with increase of Mg^{2+} in wadalite, $Al^{3+}(+Fe^{3+})$ is replaced for Si^{4+} in the tetrahedral sites to keep the charge balance. As the result, the increase of Mg^{2+} yields the low ratio of $(Al+Fe^{3+}+Mg)/Si$. Mg contents in wadalite from La Negra change from 0.40 to 0.96 (av. 0.63) in the formulas shown in Tables 1 and 2. The corresponding $(Al+Fe^{3+}+Mg)/Si$ ratios are 1.84 to 1.22 (av. 1.57). On the other hand the Mg content and the ratio of wadalite from Koriyama is 0.23 and 2.48, respectively. Thus wadalite from La Negra is richer in Mg and lower in $(Al+Fe^{3+}+Mg)/Si$ ratio. Theoretically the maximum content of Mg with the formula of wadalite can reach $Ca_6(Si_{4.5}Mg_{2.5})_{\Sigma 7}O_{16}Cl_3$.

Aoki *et al.*(1986) synthesized wadalite in the system of Ca-Al-Si-O-Cl by a hydrothermal method. A single phase of wadalite of $Ca_6Al_5Si_2\text{-}O_{16}Cl_3$ was synthesized under 500-700°C and 1,000 atmospheric pressure. They also obtained crystals of wadalite under the condition of 850-1000°C by a silica tube method. The syntheses confirmed that wadalite is stable at higher temperatures and high chlorine concentration in the system.

The obtained experimental formula of rustumite, $Ca_{10}Si_5O_{18}Cl_{1.56}(OH)_{2.44}$, supports the ideal formula, $Ca_{10}Si_5O_{18}Cl_2(OH)_2$, expected by Howie and Ilyukhin (1977). It means rustumite is a chlorine-bearing mineral as well as wadalite. Thus the existence of these minerals suggests high chlorine concentration in forming scarns.

Spurrite from La Negra contains small but significant amount of boron. Judging from the obtained chemical formula, boron is exchangeable with carbon and will form BO_3 equilateral triangles in the structure.

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メキシコ，ケレタロ州，ラネグラ鉱山産の和田石，ラスタマイト，スパーライト

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要　旨

希産Caケイ酸塩鉱物の和田石，ラスタマイト，スパーライトをメキシコ，ケレタロ州，ラネグラ鉱山周辺のスカルンから発見した．和田石とラスタマイトは，スパーライトを主とする岩石中にあり，ハイドログロシュラー，アンドラダイト，方解石，磁鉄鉱などとともに帯状に配列している．鏡下では和田石とラスタマイトの粒径は200 μm以下，スパーライトは3 mmまでの比較的大きな不定形の結晶として観察される．

和田石は無色で光学的に等方性，屈折率はn=1.708．光学的にハイドログロシュラーと類似していて，鏡下でこれら鉱物を識別することが難しい．密度は，$D_{calc}=3.066$ g/cm^3．X線マイクロプローブ分析では，実験式はO=16を基準として，$Ca_{5.99}(Al_{3.35}Si_{2.70}Mg_{0.63}Fe^{3+}{}_{0.25})_{\Sigma 6.93}O_{16}Cl_{2.93}$，理想式は$Ca_6(Al, Si, Mg, Fe^{3+})_7O_{16}Cl_3$である．今回の和田石はこれまで報告されている本邦郡山産よりMgを多く含み，$(Al+Fe^{3+}+Mg)/Si$比が小さいのが特徴．結晶は等軸晶系に属し，空間群$I\bar{4}3d$，格子定数a=12.014(1)Å，V=1734(1)Å^3，単位格子中の分子数Z=4．

ラスタマイトは透明または白色，光学的に二軸性負，屈折率はα=1.641，β=1.646，γ=1.651である．$\gamma-\alpha$=0.010．密度は$D_{meas}=2.85$ g/cm^3，$D_{calc}=3.017$ g/cm^{3}である．X線マイクロプローブ分析で，実験式はO=18，Cl+OH=4を基準として，$Ca_{9.97}Si_{5.00}O_{18}(Cl_{1.56}(OH)_{2.44})_{\Sigma 4.00}$，理想式は$Ca_{10}Si_5O_{18}(Cl,OH)_4$．分析結果により，これまで予測されていたClの存在を確認した．空間群$C2/c$，格子定数a=7.625(1)，b=18.576(2)，c=15.519(1)Å，β=103.75(1)°，V=2135(1)Å^3，Z=4．

スパーライトは帯青灰色，光学的に二軸性負，屈折率はα=1.641，β=1.670，γ=1.678，$\gamma-\alpha$=0.037．密度は$D_{meas}=2.94$ g/cm^3，$D_{calc}=2.882$ g/cm^3．化学分析は湿式法により行い，実験式はO=11を基準として，$Ca_{4.97}(Si_{1.95}Al_{0.05})_{\Sigma 2.00}(C_{0.87}B_{0.16})_{\Sigma 1.03}O_{11}$，理想式は$Ca_5(SiO_4)_2(C,B)O_3$．少量のBがCを置換していることが特徴．空間群$P2_1/a$，格子定数$a$=10.472(2)，$b$=6.724(1)，$c$=14.174(6)Å，$\beta$=101.31(3)°，$V$=978.7(3)Å^3，$Z$=4．