

The Mineralogical Implication of Barium and Strontium Silicates

By

Satoshi MATSUBARA

Department of Geology, National Science Museum, Tokyo

Abstract Nagashimalite ($\text{Ba}_4(\text{V}^{3+}, \text{Ti})_4[(\text{O}, \text{OH})_2|\text{Cl}|\text{Si}_3\text{B}_2\text{O}_{27}]$, orthorhombic, *Pmmn*) suzukiite ($\text{Ba}_2\text{V}_2^{3+}[\text{O}_2|\text{Si}_4\text{O}_{12}]$, orthorhombic, *Amam*), orthoericssonite*, a barian roscoelite, kinoshitalite, cymrite, celsian, slawsonite*, banalsite*, and stronalsite ($\text{SrNa}_2[\text{Al}_4\text{Si}_4\text{O}_{16}]$, orthorhombic, *Ibam*) were discovered in metamorphosed bedded manganese ore deposits and metamorphosed xenoliths in ultrabasic rocks in Japan after the author's field and laboratory works with the predictions for the geneses of barium and strontium silicate minerals. Among them, those with the chemical formula etc. are new minerals and those asterisked are new finds in Japan.

In order to interpret the mineral parageneses, the crystal structures of barium and strontium silicate minerals were scrutinized, leading to recognition of two major substitutional types. One includes so-called "quasi-layer silicate" structure and the framework structure, enabling the barium-strontium substitution. The other does framework structure excluding the substitution. The former has the coordination number around barium atoms to be 7 to 10 and the mean Ba-O, OH, H_2O distance to be under 2.87 Å, whereas the latter does the coordination number 10 to 13 and the distance over 2.94 Å.

The characteristics of barium-strontium substitution account well for the mineral parageneses, that is, 1) suzukiite-nagashimalite, 2) banalsite-cymrite-celsian, and 3) slawsonite-celsian-cymrite, where strontium substitutes barium preferentially in the first-named minerals in 1) and 2) groups and no mutual substitutions seen in all of 3) group minerals. The third case indicates the incompleteness of slawsonite-paracelsian solid solution despite their isomorphic relation.

The associated elements with barium and strontium in their silicate minerals were predicted. They are Ti, Fe, Mn, and Cl from the structural characteristics and Mn, B, V, Na, and REE from the chemical viewpoint in the geneses. Practically, an order of such elements as Ti, Na, Al, Fe, Ca, B, Mn, REE, Cl, V, P, Mg, K, Nb, Li, Be, F, Zn, Pb, Zr and Sn given by the order of frequency of appearance per mineral species corresponds to the surmised one.

Consequently, the prediction realized two major genetic groups of barium and strontium silicate minerals, i. e., 1) later stage products of deep-seated alkalic magma or their metamorphic equivalents, and 2) constituents of metamorphosed bedded manganese ores.

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Foreword

One of the most important sources of barium and strontium silicate minerals in Japan is bedded manganese ore deposits which occur in sedimentary or metamorphic rocks and the author has mineralogically investigated. The importance has now been clearly evidenced through the discoveries of some new and rare minerals including barium and strontium, such as nagashimalite, suzukiite, kinoshitalite, orthoericssonite and banalsite. Also the author has been favoured by the find of slawsonite and stronalsite near Kochi City, Shikoku, where the occurrence of celsian and cymrite are also realized.

Besides the author's field works covering above minerals, he studied the crystal structures of orthoericssonite and nagashimalite, reporting new findings of novel structural units such as Fe^{3+}O_5 tetragonal pyramid and $\text{Si}_5\text{B}_2\text{O}_{27}$ borosilicate in group their structures.

The present paper describes the results of a comprehensive survey of (1) the crystal structures of silicates containing barium and strontium as major constituent cations, (2) elemental association in those structures, (3) the mode of occurrence of barium and strontium silicate minerals. In particular, detailed descriptions have been made of the mode of occurrence and paragenetic minerals of ten mineral species which include orthoericssonite, nagashimalite, suzukiite, a barian roscoelite, kinoshitalite, cymrite, celsian, slawsonite and stronalsite. Based on these results and descriptions, this paper discusses the crystallochemical characteristics as well as genesis of this specific group of silicate minerals.

I. Crystallochemical Characteristics of Barium and Strontium in Silicate Minerals and the Elemental Association Therein

Sixty-three mineral species have been described to date in barium and strontium silicate minerals (see Appendix). They include 2 nesosilicates, 14 sorosilicates, 21 cyclosilicates, 9 inosilicates, 8 phyllosilicates and 9 tectosilicates; the structures of some of them are not clearly established.

1. Barium

The examples of nesosilicate minerals containing barium as their essential constituents are very few. Two confirmed examples are cappelenite and garrelsitite in which $[\text{SiO}_4]$ tetrahedra are connected with $[\text{B}_6\text{O}_{18}]$ ring (SHEN & MOORE, 1984) and a complex polyborate radical $[\text{B}_5\text{O}_{12}]$ (GHOSE *et al.*, 1976), respectively. Therefore, these minerals

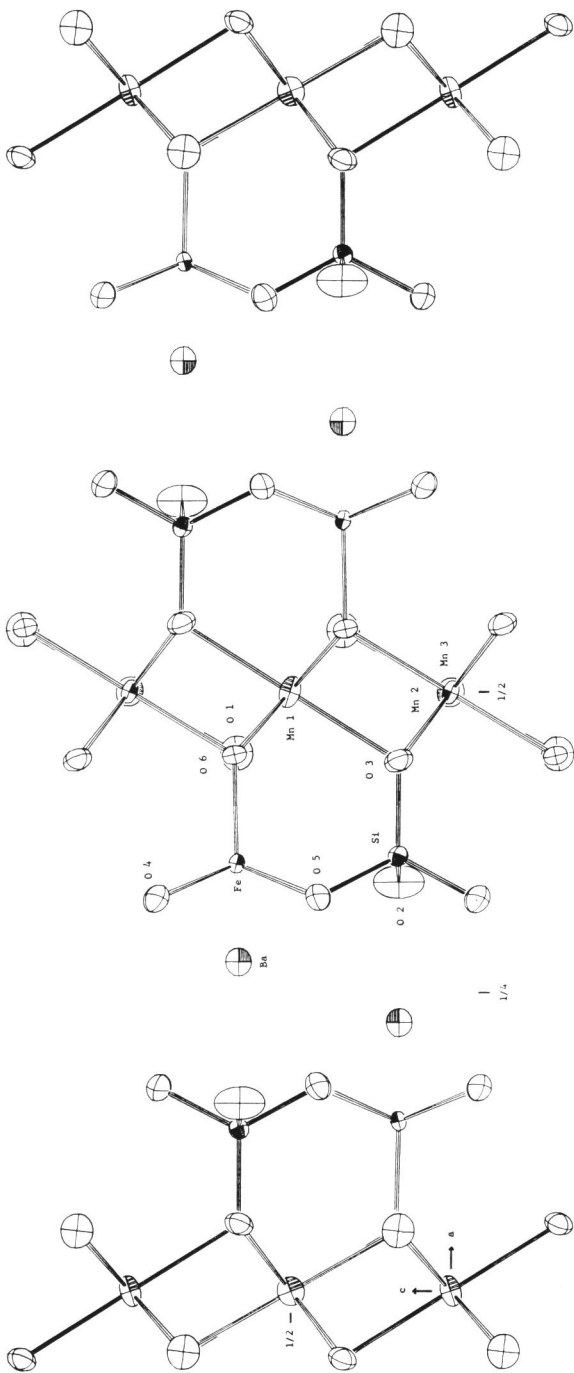


Fig. 1a

Fig. 1. Projections of the orthoericssonite structure, a: Along the *b* axis, b: Stereographic drawing viewed along *c*, c: $\text{Si}_2\text{O}_7\text{-Fe}^{3+}\text{O}_3$ sheet.

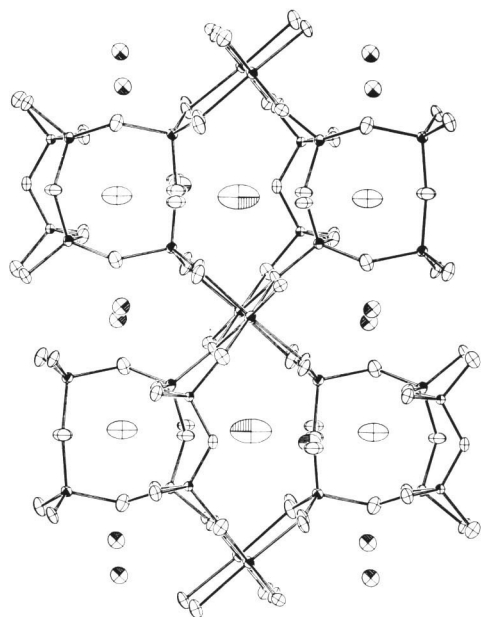
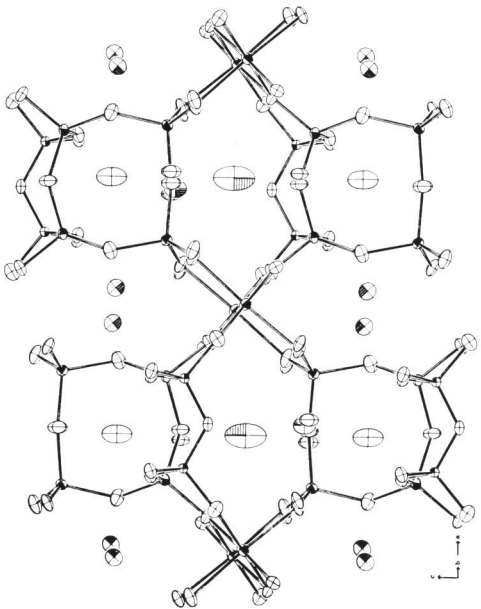


Fig. 1b



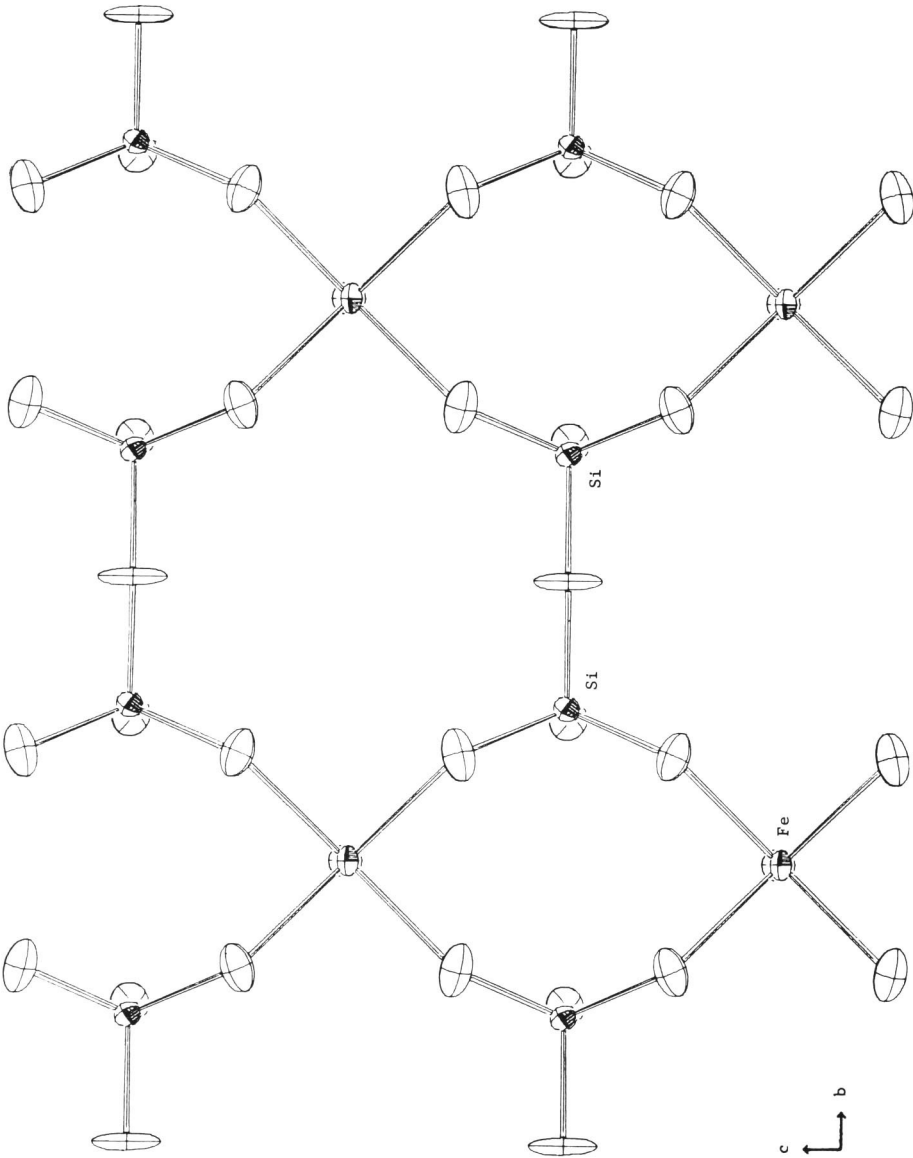


Fig. 1c

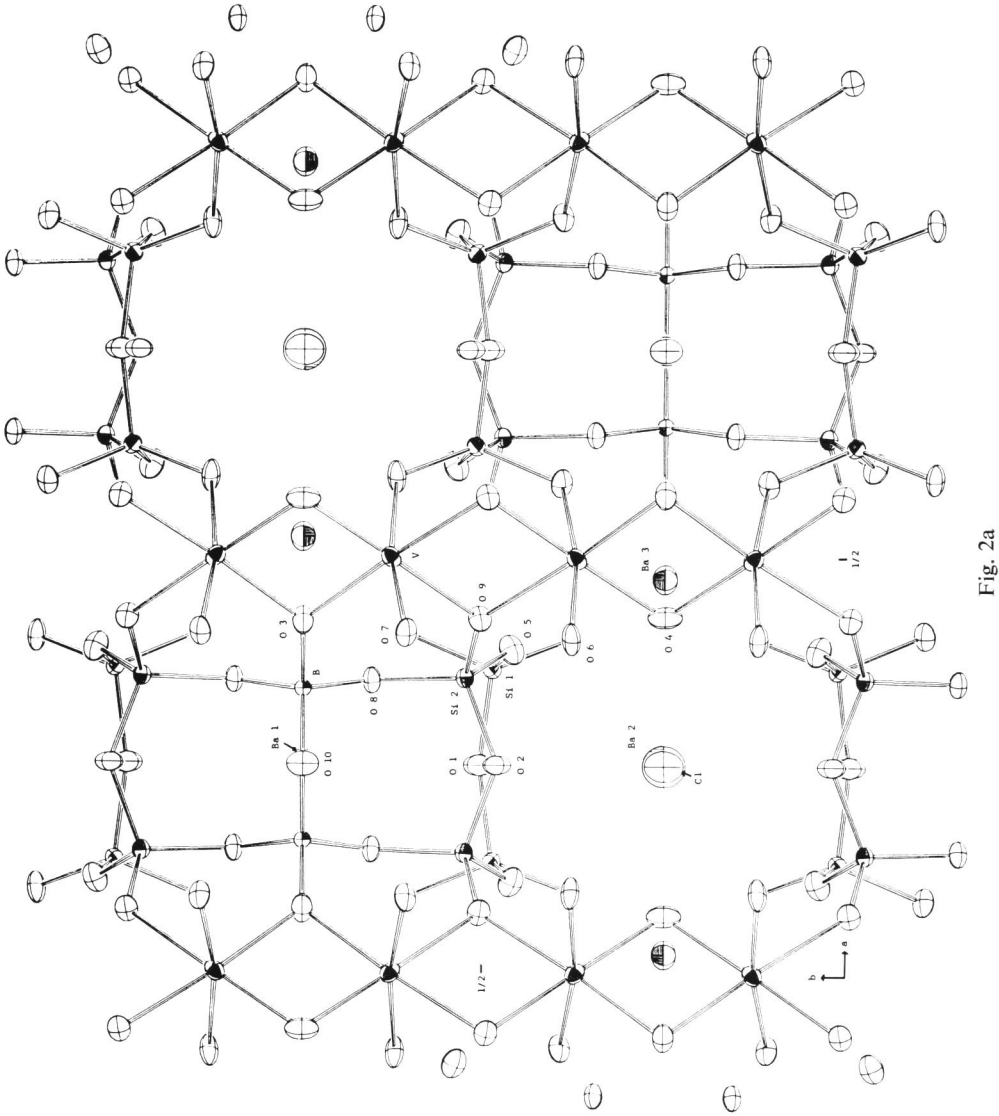
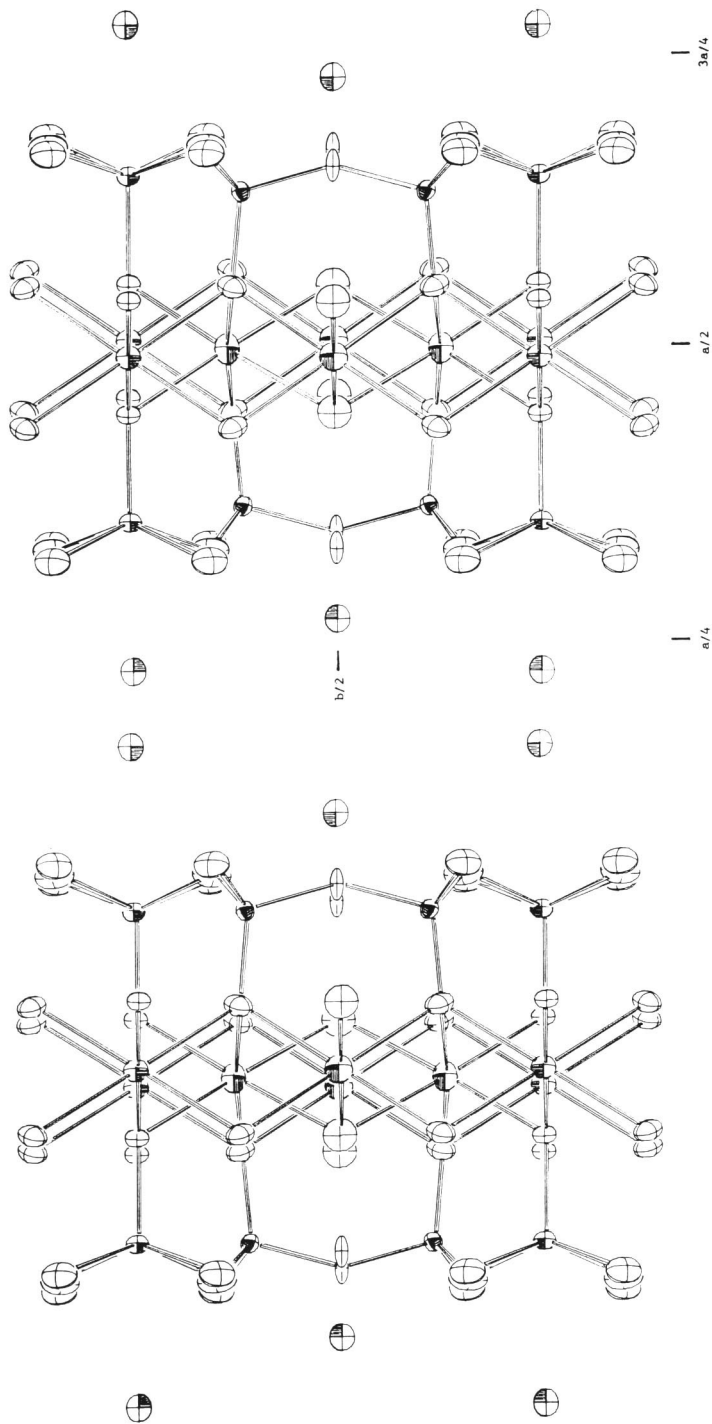


Fig. 2a

Fig. 2. Projections of the nagashimalite structure, a: Along the *c* axis, b: Stereographic drawing veiwed along *b*.



are silicoborates rather than silicates. The presence of barium partially replacing calcium in uranophene is suggested by FRONDEL (1958), though not quantitatively determined. But, the natural occurrence of nesosilicate containing barium seems possible, since MASSE and DURIF (1973) synthesized $\text{Ba}_2\text{Zr}_2(\text{SiO}_4)_3$, which is isomorphic with langbeinite, $\text{K}_2\text{Mg}_2(\text{SO}_4)_3$, or containing isolated SiO_4 . That compound corresponds to a low SiO_2 derivative of bazirite, $\text{BaZrSi}_3\text{O}_9$, which has the same Ba/Zr ratio as above compound.

Barium in sorosilicate minerals is not uncommon. All of them contain cations with coordination number 4, 5 or 6 (other than silicon). In these silicates, a partial substitution of strontium for barium is possible as seen in lamprophyllite group minerals, orthoericssonite and yoshimuraite (PENG & CHANG, 1965; MATSUBARA & NAGASHIMA, 1975; WATANABE *et al.*, 1961).

In the structure of orthoericssonite (MATSUBARA, 1980a) is a quasi-layer sheet composed of Si_2O_7 sorosilicate radicals and Fe^{3+}O_5 square pyramids and this sheet alternates with the sheet of MnO_6 octahedra. The site of barium atoms are definitely favoured under a rather severe dimensional restriction, which exclusively prefers the lodging of strontium only in place of barium (Fig. 1-a, b, c). Lamprophyllite and yoshimuraite have the structures fundamentally similar to orthoericssonite, and the sites for barium allow the vicarious entrance of strontium and potassium (WOODROW, 1964; TAKÉUCHI & HAGA, 1971, 1978). In these respects they are crystallochemically similar to such phyllosilicates as micas. The mode of linking of cation polyhedra with Si_2O_7 group makes it possible to classify quasi-layer silicates into three groups composed of six subgroup (MATSUBARA, 1980a).

Cyclosilicate minerals of barium occupy important portion in the mineralogy of barium silicates in number. It is worth mentioning that some of them contain chlorine as essential constituents. Chlorine atom is located in a large open space formed among the linkage of 4-, 8- and 12-membered silicate rings, implying its non-vicarious nature to OH but occupation of a definite atomic site. Except for anandite, all the known chlorine-bearing silicates belong to cyclosilicate. Among barium cyclosilicates, the members of taramellite series and tienshanite include essential boron. In the former boron is tetrahedrally coordinated to form a borosilicate radical and in the latter it is triangularly coordinated to form a separate unit out of silicate framework. As a member of taramellite series, nagashimalite is structurally composed of Si_4O_{12} ring silicate groups, VO_6 octahedral chains, B_2O_7 double tetrahedra groups and three non-equivalent barium polyhedra (Fig. 2-a, b) (MATSUBARA, 1980b). The two Si_4O_{12} are connected by B_2O_7 double tetrahedra and form a new type of borosilicate radical $\text{Si}_8\text{B}_2\text{O}_{27}$ (Fig. 3). Therefore, the framework of nagashimalite is more rigid than those of quasi-layer silicates of barium and the dimensional restriction around the site of barium is too severe to accomodate any cation other than barium. This situation accounts for the absence of any vicarious cation for barium in the actual cases of the taramellite series.

The examples of presence of barium in inosilicate minerals are rather few in single

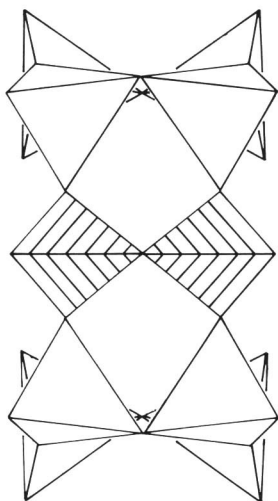


Fig. 3. The configuration of $[\text{Si}_8\text{B}_2\text{O}_{27}]$ borosilicate group of tetrahedra projected down the c axis, borate tetrahedra being ruled.

or double chain silicates. In joesmithite, a part of lead is replaced by barium. Also, there is a ribbon-like chain silicate framework in krauskopfite and synthetic barium silicates ($\text{Ba}_4\text{Si}_6\text{O}_{18}$, $\text{Ba}_5\text{Si}_8\text{O}_{21}$, $\text{Ba}_6\text{Si}_{10}\text{O}_{28}$) (KATSCHER & LIEBAU, 1969), which are not known as a mineral to date.

Although barium is seen in some phyllosilicates with a mica type Si_4O_{10} unit, there are some peculiar sheets like Si_4O_{10} in sanbornite and $\text{Ba}_4\text{Si}_{20}\text{O}_{56}$ in leucosphenite. It is worth mentioning that there are no clay minerals including barium as essential constituents. Many interpretations are possible. Most of original minerals serving as parental phases to clay minerals are feldspars or feldspathoids in which minor barium may be present. It so, the barium is to take a different behaviour from the essential constituents in these minerals, i.e., calcium and potassium, all of which enter clay minerals of common occurrence. Thus, barium is extracted from those minerals and not fixed but removed away from the site of argillization, unless the products of argillization comprise any phases capable of fixing barium, such as the alunite series of mineral. There are peculiar phyllosilicates in which silicate framework includes no unshared oxygen atom, that is, $\text{Al}_2\text{Si}_2\text{O}_8$ in cymrite (DRITS *et al.*, 1975). Although the same framework is known in synthetic hexagonal $\text{BaAl}_2\text{Si}_2\text{O}_8$ (TAKÉUCHI, 1958), cymrite is the unique example of natural material with such an unusual phyllosilicate unit.

In tectosilicate minerals, there are some barium silicates isotypic to known minerals; e.g., celsian to orthoclase and paracelsian to slawsonite. In the cancrinite series of minerals, the unique member containing barium as essential cation is wenkite which has a structure slightly different from those of the members of this series. That is, there are two cationic sites with larger coordination number. In zeolite, there are two

species with barium as their essential constituents: edingtonite and harmotome. Although the former is placed as a member of natrolite group (STRUNZ, 1970) according to the presence of compositionally same unit, $\text{Al}_2\text{Si}_3\text{O}_{10}$, the shape of framework is different from that of natrolite and its relatives, all of which do not accept any barium, though there are some thomsonites containing considerable amounts of strontium (EFIMOV *et al.*, 1966). The geochemical behaviours of strontium and barium are different under such a lower temperature and silica-poorer condition. Edingtonite is generally found in the products of such a low silica circumstance as feldspathoids are formed (GRICE & GAULT, 1981), except for one unusually calcium-rich or calcium-dominant "edingtonite" from Podol'skoye deposit, southern Urals (ISMAGILOV, 1977), where it is accompanied by quartz. While, harmotome has a structure and cell dimensions similar to those of phillipsite and chabazite. The last named one can be readily converted into the barium analogue through cation exchange (PASSAGLIA, 1978).

2. Strontium

The silicate minerals containing strontium as their essential constituents are not common. Representative minerals: (sorosilicates) lamprophyllite, ortholamprophyllite and strontio-chevkinite; (cyclosilicates) strontio-joaquinite and strontio-orthojoaquinite; (inosilicates) nordite, ohmilite and haradaite, and (tectosilicates) slawsonite, stronalsite and brewsterite. A partial substitution of barium and/or calcium for strontium in the silicates here discussed is recognized in barytolamprophyllite, orthoericssonite, yoshimuraite, bario-orthojoaquinite, traskite and suzukiite.

Almost strontium atoms are 9-, 10- or 11-coordinated and sandwiched by quasi-silicate sheets (TAKÉUCHI & JOSWIG, 1967) as seen in the lamprophyllite group minerals, orthoericssonite, yoshimuraite, haradaite and suzukiite. In the joaquinite group minerals, 9-coordinated strontium and 11-coordinated barium are also sandwiched by the sheets formed by four Si_4O_{12} rings and TiO_6 octahedron (DOWTY, 1975). The structure of ohmilite involves three different strontium atoms possessing 9-, 8- and 8-coordination, respectively (MIZOTA *et al.*, 1973, 1983). The coordination polyhedra for strontium capable of substituting for calcium in nordite and traskite are less distorted, that is, slightly twisted cube (8-coordination) and trigonal prism (6-coordination), respectively (BAKAKIN *et al.*, 1970; MALINOVSKII *et al.*, 1976).

Strontium in phyllosilicates is not known except very small amount in cymrite. The tectosilicates include three species with strontium as their essential constituents: slawsonite, stronalsite and brewsterite. A part of strontium in slawsonite and brewsterite is capable of being substituted by calcium and barium. In zeolites, there are some examples of strontium varieties for thomsonite, chabazite, heulandite and laumontite. Especially, the first three species can include up to 6.58 wt. % of SrO (EFIMOV, 1966; WEIBEL, 1963; MILLER & GHENT, 1973; LUCCHETTI *et al.*, 1982 etc.).

3. The characteristics of the Ba-Sr substitution and the coordination polyhedra of Ba and their dependance on the observed mineral parageneses

The discussion of the crystal structures of barium and strontium silicate minerals

Table 1. The characteristics of the Ba-Sr substitution and the coordination polyhedra of Ba.

substitutional type					non substitutional type		
	coordination number		mean distance (Å)			coordination number	mean distance (Å)
	Ba	Sr	Ba	Sr		Ba	Ba
orthoericssonite (Ba ₇₀ Sr ₃₀)	10		2.84		nagashimalite	13	3.09
						11	3.12
						11	2.94
joaquinite (REE ₇₀ Sr ₂₁)		9		2.62	joaquinite	11	2.95
haradaite		11		2.79			
					anandite	13	3.14
					cymrite	12	3.09
						12	3.09
						12	3.12
						12	3.11
paracelsian	7		2.80		celsian	10	2.97
slawsonite		7		2.63			
banalsite	10		2.87				
brewsterite (Sr ₈₈ Ba ₃₄)		9		2.79	harmotome	12	3.05

leads to recognition of two major substitutional types. One includes so-called “quasi-layer silicate” structure and the three-dimensional framework structure, enabling the barium-strontium substitution. The other does the three-dimensional framework structure excluding the substitution (Table 1.) The former has the coordination number around barium atoms to be 7 to 10 and the mean Ba-O, OH, H₂O distance to be under 2.87Å, whereas the latter does the coordination number 10 to 13 and the distance over 2.94Å.

The characteristics of barium-strontium substitution account well for the mineral parageneses, that is, 1) suzukiite-nagashimalite in manganese ores from the Mogurazawa mine, 2) banalsite-cymrite-celsian in country rocks of manganese ore deposit from the Shiromaru mine, and 3) slawsonite-celsian-cymrite in metamorphosed basic rocks from Sarusaka, where strontium substitutes barium preferentially in the first-named minerals in 1) and 2) groups and no mutual substitution is seen in all of 3) group minerals. The third case indicates the incompleteness of slawsonite-paracelsian solid solution despite their isomorphic relation.

4. The elemental association in barium and strontium silicates

The associated elements with barium and strontium in their silicate minerals are predicted from the geochemical and crystallochemical standpoints. They are assembled at the site of formation, and inclusive of Mn, B, V, Na and REE from ge-

netical viewpoint, and Ti, Fe, Mn and Cl are particularly accommodated in their crystal structures through crystallization from crystallochemical viewpoint. Practically, an order of such elements as Ti, Na, Al, Fe, Ca, B, Mn, REE, Cl, V, P, Mg, K, Nb, Li, Be, F, Zn, Pb, Zr and Sn given by the order of frequency of appearance per barium and strontium silicates corresponds to the surmised one. This section is to consider their geological, geochemical and crystallochemical backgrounds related to the formation of the minerals by referring to some representative elements with higher degree of frequency.

(1) Boron

Among seven barium silicate minerals containing boron as their essential constituents, leucosphenite is here considered to demonstrate its geochemical peculiarity.

At Ohmi, Niigata Prefecture, Japan and Mt. St. Hilaire, Quebec, Canada, leucosphenite occurs as a latest product in druses, and is the unique boron-bearing mineral in these localities. This mineral has higher SiO_2 content despite its appearance in mineral assemblages devoid of any silica-saturated or oversaturated minerals. Since the amount of mineral leucosphenite is so small in these localities, such requirement as to the formation may be allowed.

Leucosphenite is found in entirely different mode of occurrence, i.e., in nepheline syenite pegmatite (Mt. St. Hilaire), albitite (Ohmi) and hyperalkaline sedimentary rock (Green River Formation), the last of which is a very low temperature and low pressure condition. The participation of boron to silicate framework of the type $\text{B}_4\text{Si}_{20}\text{O}_{56}$ is favoured by such a physical condition, together with rather or really alkaline environment, as inferable from the co-existence with alkali-bearing minerals, e.g., nepheline and albite at Mt. St. Hilaire, albite and magnesioriebeckite at Ohmi and some sodium carbonates and reedmergnerite in argillaceous rock of Green River Formation.

Also the chemical composition of leucosphenite is close to that of tienshanite, which contains Mn^{2+} in addition. Since tienshanite is also found in alkali pegmatite, leucosphenite may represent a Mn^{2+} -free derivative of tienshanite. In relation to this interpretation, it is worth mentioning that tienshanite is the unique mineral containing Mn^{2+} as the essential constituent in the described assemblage.

In metamorphosed bedded manganese ore deposits in Japan, the concentration of boron gives rise to the formation of borosilicates represented by manganaxinite or tizenite in silica-rich condition and of some borates in silica-poor condition (KATO & MATSUBARA, 1980a). The source of boron is at least owing to two different processes: (1) magmatic concentration in the latest stage of igneous rock formation, and (2) chemical process accompanied by the concentration of manganese. The possibility of combination of barium with boron is expected under the condition where two cases, (1) barium in manganese deposit side is combined with boron supplied from the igneous rock side, and (2) barium and boron contained within manganese ore deposit react in each, are probable. The case of nagashimalite corresponds to the latter, where the extreme scarcity of aluminium and calcium is considered to have impeded the formation of manganaxinite despite the excess of SiO_2 in the assemblage. The occurrence

of suzukiite in the same assemblage suggests that still there was a room to admit the excess of boron, because the components of nagashimalite can be derived from that of suzukiite after the addition of boron, minor chlorine, titanium and H_2O .

(2) Sodium

Barium and strontium silicate minerals including sodium as one of their essential constituents should be separated by the degree of affinity to aluminium, i.e., quasi-layer silicates, banalsite and stronalsite. The first members are liable to exclude aluminium whereas the other contain tetrahedral aluminium as its essential constituents (The crystallochemical consideration of quasi-layer silicate minerals in general has been given elsewhere (MATSUBARA, 1980a)). It is worth mentioning that this separation corresponds to the mode of occurrence. Sodium-bearing quasi-layer silicate minerals of barium and strontium are exclusively found in alkali pegmatite or allied rocks, whereas banalsite is found in metamorphosed bedded manganese ore deposit under low-silica condition. The chemical composition of banalsite corresponds to one celsian molecule plus two potassium-free nepheline molecules. Seeing from the mode of occurrence of banalsite at the Shiromaru mine, Tokyo, the formation was favoured under a low-silica condition, as reflected by the assemblage. In this locality, the association of celsian (or cymrite) plus albite is considered to correspond the high-silica derivative of banalsite.

Generally, both of barium and strontium do not take the same atomic site as sodium, and no extensive substitution relations are found between sodium and barium or strontium in significant concentrations. In this respect, sodium ion is dissimilar to potassium, which is sometimes vicarious to barium as seen in hyalophane.

(3) Aluminium

Aluminium in barium and strontium silicate minerals in general takes tetrahedral or tetrahedral plus octahedral coordinations in same structures with the one exceptional case of balipholite in which aluminium occurs in octahedra. The tetrahedron formed by oxygen atoms about aluminium tends to form a framework together with tetrahedra about silicon, and therefore, tectosilicates include as many as ten examples of mineral species containing barium and strontium.

Although the fundamental structure of the aluminosilicate frameworks of these minerals is essentially identical, barium and strontium silicates are liable to have different atomic arrangements when they coexist under a definite geological condition. For example, at Sarusaka, Kochi Prefecture, slawsonite coexists with celsian and cymrite, the latter possibly being somewhat younger than slawsonite. These three minerals have different frameworks, though all of them have the degree of highest polymerization. One of the best evidence is also found in the mineral assemblage from Sarusaka, where grossular-clinopyroxene-chlorite rock is intersected by veinlets of celsian mantled by grossular. Both of them are very close to the theoretical composition after the X-ray powder diffraction studies, giving unit cell parameters very close to the ideal values of pure synthetic analogues. This evidence suggests that no substitution relations exist between calcium and barium under the condition producing

this assemblage.

(4) Calcium

The vicarious relations between calcium-strontium and calcium-barium are prevailing seen in such carbonate minerals as those belonging to aragonite series in which intermediate members between aragonite, strontianite, and witherite occur so frequently together with the participation of cerussite molecule. Also, the isomorphic strontium and barium analogues of calcium minerals are known in apatite series, such as strontium apatite for fluorapatite and alforsite for chlorapatite.

However, in case of silicate minerals, the calcium analogues of isomorphic barium and strontium minerals are rather uncommon. The examples are a calcium-bearing edingtonite, and small amounts of calcium-replacing barium and strontium in barytolamprophyllite, barium in traskite and strontium in nordite. In all cases, the degree of substitution is not so prominent. Although the intermediate members are unknown, there are a couple of calcium silicates structurally similar to their barium analogue in brittle micas, clintonite to kinoshitalite. The former contains some octahedral aluminium as its essential constituents, whereas it is generally poor in known analyses of the latter.

In case of feldspars, the crystallochemical difference between calcium and strontium or barium is obvious. For example, strontium analogue of anorthite is known only as a synthetic product formed under at temperature condition at least higher than 1400°C (SORRELL, 1962). No triclinic barium analogue of anorthite is known. Likewise, no calcium analogues with celsian or slawsonite structures are found, although the latter can involve some vicarious calcium for strontium up to Sr:Ca=87:13 (GRIFFEN *et al.*, 1977).

Accordingly, at the circumstances where the silicates of calcium, strontium and barium are formed, the geochemical or crystallochemical behaviours of calcium must have been discrete from those of strontium and barium. On the contrary, under the condition (such as in oxidation zones of certain metallic ore deposits and carbonatites) where the formation of anhydrous simple carbonates is possible, the behaviours of these elements have many common points allowing the vicarious substitution relations among them.

(5) Titanium

Among the cations capable of being associated with strontium and barium in silicate minerals, titanium has the highest frequency of appearance. Under ordinary igneous and metamorphic rocks without any significant concentration of barium and strontium, titanium is present in the forms of such accessory minerals as sphene, ilmenite series minerals, spinel or spinelloids, biotite and andradite. But, if the concentration of barium or strontium takes place where titanium is concentrated, titanium is used to form silicate minerals containing barium or strontium, and, therefore, occurrences of the above-mentioned minerals such as sphene and others are rare. This may be responsible for the peculiar crystallochemical nature of titanium, i.e., polyhedra TiO_5 or TiO_6 are capable of sewing up silicate groups to produce sheet-like structure

units. Barium, strontium or certain ionic groups can easily be accommodated between the sheet-like units to form crystal structures.

(8) Ferrous and ferric iron

The combination of ferric iron with barium and strontium in silicate minerals is always accompanied by the other cations, the most prevailing ionic species being titanium, which has substitution relation with ferric iron, though complete substitution couple has not been known. In contrast to the case of ordinary mafic minerals, ferrous iron in barium and strontium silicate minerals is replaced by magnesium or divalent manganese ions with difficulty except for such a few cases as seen in bafertisite.

In barium and strontium silicate minerals, the ferric iron in substitution relation to titanium is generally in five-coordinated state as in yoshimuraite, ericssonite and orthoericssonite. Also, ferrous iron in joaquinite group minerals are in five-coordinated state. The other ferrous and ferric iron in barium and strontium silicate minerals are in octahedrally coordinated except for ferrous iron in pellyite.

Barium and strontium silicate minerals containing ferrous or ferric iron as their essential constituents are rather common in metamorphic rocks and uncommon in alkali plutonic rocks or their pegmatites.

II. The Mode of Occurrence

The principal occurrence of barium and strontium silicates are found in metamorphosed sedimentary rocks, alkali igneous rocks and their pegmatites. These occurrences include about 75% of the species in the presently reviewed minerals. Among metamorphosed sedimentary rocks, unique barium silicates-bearing rocks, developed at several localities in California and bedded manganese ore deposits in Japan, Sweden and Great Britain are the main source of the minerals. Especially such minerals as fresnoite, ericssonite, orthoericssonite, yoshimuraite, walstromite, verplanckite, nagashimalite, traskite, muirite, hyalotekite, krauskopfite, haradaite, suzukiite, macdonaldite, paracelsian and banalsite are exclusively known in above occurrence.

The di- and tri-valent manganese-bearing silicates and oxides found as the principal constituents in Japanese bedded manganese ore deposits are diagrammatically given in Fig. 4 in the relation of MnO (or Mn_2O_3) and SiO_2 mole ratios. Kinoshitalite occurs in high grade and low silica manganese ores represented by the assemblage of tephroite-hausmannite-jacobsite-alleganyite (or sonolite). On the contrary, yoshimuraite, orthoericssonite, haradaite, suzukiite and nagashimalite occur in rather high silica and low manganese ores represented by the assemblage of rhodonite-quartz-(Mn-amphibole)-(Mn-pyroxene)-(jacobsite)-(tephroite) (The parentheses indicate the occasional absence). Celsian appears in both assemblages with various amounts of rhodochrosite. Cymrite is found in association with rhodochrosite and braunite.

In natrolite veins cutting metamorphosed basic to ultrabasic rocks in San Benito County, California, such rare barium and strontium silicates as benitoite, jonesite and joaquinite group minerals are found. Barium and strontium tectosilicates like celsian,

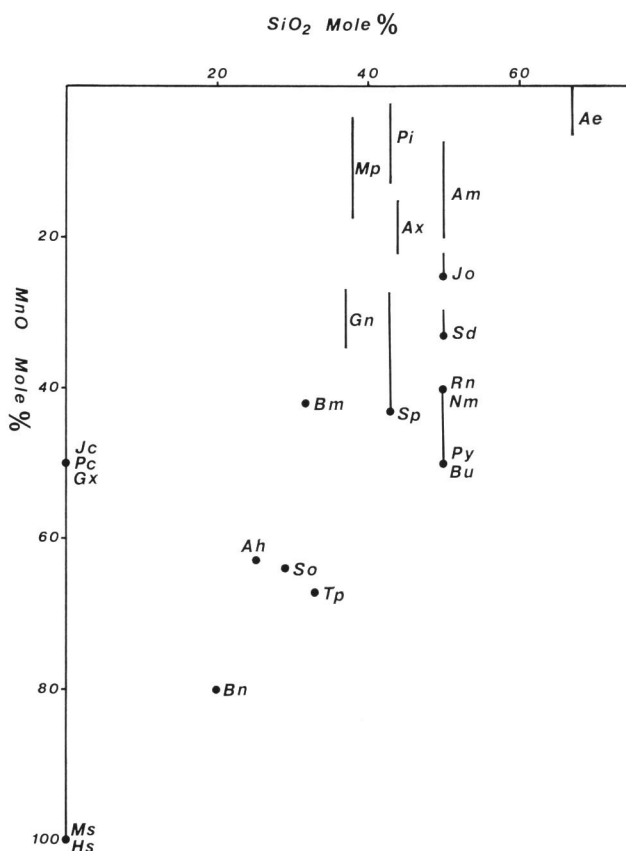


Fig. 4. A diagrammatical representation of the di- and tri-valent manganese-bearing silicates and oxides in Japanese bedded manganese ore deposits. Ae: aegirine, Ah: alleghanyite, Am: Mn-amphibole, Ax: manganaxinite & tinzenite, Bm: bementite, Bn: braunite, Bu: bustamite, Gn: ganophyllite, Gx: galaxite, Hs: hausmannite, Jc: jacobsonite, Jo: johannsenite, Mp: manganophyllite, Ms: manganosite, Nm: nambulite, Pc: pyrochroite, Pi: piemontite, Py: pyroxmangite Rn: rhodonite, Sd: serandite, So: sonolite, Sp: spessartine, Tp: tephroite.

slawsonite and stronalsite occur at veinlets cutting metamorphosed basic rocks in Shikoku, Japan.

Alkali igneous rocks, especially syenite and nepheline syenite, and their pegmatites include such barium and strontium silicates as cappelenite, lamprophyllite group minerals, bafertisite, jinshajiangite, innelite, bornemanite, strontio-chevkinite, ilimaussite, bazirite, tienshanite, magbasite, nordite and batisite. As these rocks are originally rich in barium and strontium, carbonates, sulphates and phosphates of barium and strontium are also found therein. These rocks are found in Greenland, Norway, Kola Peninsula and elsewhere in USSR, Canada, South Africa and Montana, USA, etc.

Albitite from Niigata Prefecture, Japan includes benitoite, strontio-orthojoaquinite, ohmilite and leucosphenite. This albitite is considered to have intruded a serpentinite during metamorphism.

The other occurrences are those in cavities of basalt, granite pegmatite and non-metamorphosed sedimentary rocks. The constituents of the Green River Formation are the representative sedimentary rocks involving barium minerals deposited under a hyperalkaline condition and comprise some barium silicates and carbonates.

The barium and strontium silicates are classified by their mode of occurrences as follows;

1. Metamorphic rocks

a. Metamorphic sedimentary rocks

<i>barium silicate rock</i>	<i>marble and skarn</i>	<i>gneiss and schist</i>	<i>iron ore</i>
fresnoite	pabstite	gillespite	anandite
bazirite	taramellite	baotite	
walstromite	pellyite	brewsterite	
verplanckite	wenkite	celsian	
taramellite	slawsonite	harmotome	
titantaramellite			
traskite			
muirite			
krauskopfite			
pellyite			
gillespite			
sanbornite			
macdonaldite			
cymrite			
celsian			

a'. Metamorphic bedded manganese ores and their country rocks

barylite, ericssonite, orthoericssonite, yoshimuraite, nagashimalite, krauskopfite, haradaite, suzukiite, sanbornite, kinoshitalite, cymrite, celsian, paracelsian, banalsite, harmotome, hyalotekite

b. Metamorphic igneous rocks

benitoite, joaquinite, orthojoaquinite, strontiojoaquinite, bario-orthojoaquinite, jonesite, cymrite, celsian, slawsonite, stronalsite

2. Alkali igneous rocks and their pegmatites

<i>nepheline syenite or syenite</i>	<i>albitite</i>	<i>others (alkali granite etc.)</i>
cappelenite	benitoite	bafertisite
lamprophyllite	strontio-orthojoaquinite	andremeyerite
bariolamprophyllite	ohmilite	innelite
ortholamprophyllite	leucosphenite	bornemanite
jinshajiangite		bazirite
strontio-chevkinite		baotite
ilimaussite		kinoshitalite
baotite		
tienshanite		
magbasite		
nordite		
batisite		

- leucosphenite
- edingtonite
- 3. Sedimentary rocks
 - garrelsite, leucosphenite, chernykhite, harmotome
- 4. Others (granite, basalt etc.)
 - barylite, armenite, balipholite, edingtonite brewsterite, harmotome

III. The Descriptive Mineralogy of the Selected Species

1. Orthoericssonite

The descriptive mineralogy and the crystal structure of orthoericssonite from Japan were published by MATSUBARA and NAGASHIMA (1975) and MATSUBARA (1980a), respectively. The mineral was found with rhodonite in a well-banded jacobsonite-bearing rhodonite-aegirine-tephroite ore from the Hijikuzu mine (now Shintamagawa mine), Iwate Prefecture. The bedded manganese ore deposits and the country rocks suffered strong thermal metamorphism due to Cretaceous Miyako granodiorite. Orthoericssonite crystals are flattened to (100) and reach 1×1.5 cm in maximum size. It is brown-black in colour and yellowish brown to dark brown under the microscope. The cleavage is (100), perfect. Hardness (Mohs) is $5\frac{1}{2}$ on (100). Specific gravity measured by Berman balance is 4.22. It is orthorhombic, space group $Pnmm$, with unit cell parameters: $a=20.230(5)$, $b=6.979(2)$, $c=5.392(2)\text{\AA}$, $Z=4$. The chemical analysis gave the empirical formula $(\text{Ba}_{0.658}\text{Sr}_{0.256}\text{K}_{0.024}\text{Na}_{0.013}\text{Li}_{0.003})_{\Sigma 0.984}(\text{Mn}_{1.435}^{2+}\text{Fe}_{0.546}^{2+}\text{Mg}_{0.086})_{\Sigma 2.067}(\text{Fe}_{0.921}^{3+}\text{Ti}_{0.093}\text{Al}_{0.034})_{\Sigma 1.058}\text{Si}_{7.000}\text{O}_{1.389}(\text{OH})_{0.611})_{\Sigma 2.000}$ on the basis of $\text{O}=9$, specifying the material to be a strontian and ferroan orthoericssonite.

2. Nagashimalite

This new mineral was described by MATSUBARA and KATO (1980), and its crystal structure by MATSUBARA (1980b). This is exclusively found in massive aggregates of fine-grained rhodonite ore including rhodochrosite, barite, quartz, barian roscoelite, suzukiite, alabandite, digenite, bornite and tetrahedrite as accessory constituents from the Mogurazawa mine, Kiryu City, Gumma Prefecture. The ore deposits are developed in a weakly metamorphosed Triassic chert.

The crystals of nagashimalite are tabular on (001) and elongated along the b -axis up to 1.5 cm long and form subparallel aggregates. The mineral is greenish black in colour with a submetallic to vitreous luster and the streak is green. No cleavage is discerned. Specific gravity is 4.08. Vickers microhardness is 606–681 kg/mm² (100 g load) (approx. 6 (Mohs)). The chemical analysis gave the empirical formula $\text{Ba}_{4.00}(\text{V}_{3.30}^{3+}\text{Ti}_{0.51}\text{Mn}_{0.10})_{\Sigma 3.91}\text{B}_{1.71}\text{Si}_5\text{O}_{27.64}\text{Cl}_{0.72}(\text{OH})_{1.28}$ on the basis of $\text{Si}=8$ after addition of H_2O 0.77 wt.% to give $\text{Cl}+(\text{OH})=2$. The ideal formula is $\text{Ba}_4(\text{V}^{3+}, \text{Ti})_4\text{B}_2\text{Si}_5\text{O}_{23}(\text{Cl}, \text{OH}, \text{O})_2$. It is orthorhombic, space group $Pnmm$, unit cell parameters: $a=13.937(3)$, $b=12.122(3)$, $c=7.116(2)\text{\AA}$, $Z=2$. Nagashimalite is the vanadium analogue of taramellite after the chemical and structural analyses.

3. Suzukiite

The original description has been published (MATSUBARA *et al.*, 1982). The mineral is found in a massive rhodonite-rhodochrosite ore from the weakly metamorphosed bedded manganese ore deposits of the Mogurazawa mine. The flaky crystals form aggregates which are generally concentrated around the patches of quartz or barite in the ore. It is also found in association with alabandite or nagashimalite, which rarely grows on the flake of suzukiite. The euhedral to subhedral tablets are flattened to (010) and sometimes elongated along [001] up to 5 mm long. The mineral is bright green in colour with a vitreous luster and the streak is pale green. Cleavages are perfect along (010) and distinct on (100) and (001). Specific gravity is 4.0. Hardness (Mohs) is 4 to $4\frac{1}{2}$ on (010). It is orthorhombic, space group *Amam* or *Ama2*, unit cell parameters: $a=7.089(2)$, $b=15.261(2)$, $c=5.364(1)\text{\AA}$, $Z=2$. The electron microprobe analysis gave the empirical formula $(\text{Ba}_{1.78}\text{Sr}_{0.22})_{\Sigma 2.00}(\text{V}_{2.02}^{4+}\text{Ti}_{0.02})_{\Sigma 2.04}\text{Si}_{3.97}\text{O}_{14}$ on the basis of $\text{O}=14$. The ideal formula is $\text{Ba}_2\text{V}_2^{4+}[\text{O}_2|\text{Si}_4\text{O}_{12}]$ from the analogy with haradaite, $\text{Sr}_2\text{V}_2^{4+}[\text{O}_2|\text{Si}_4\text{O}_{12}]$.

4. Barian roscoelite

The barium analogue of roscoelite is described under the name chernykhite by ANKINOVICH *et al.* (1972). However, this mineral has a marked deficiency of interlayer cations. BaO contents of two chernykhites are 9.35 and 9.60 wt.%. During the mineralogical studies on the two new minerals, nagashimalite and suzukiite, by the author from the Mogurazawa mine, a dark green mica was found in association with them. A detailed investigation of this mica indicated that it is a roscoelite containing

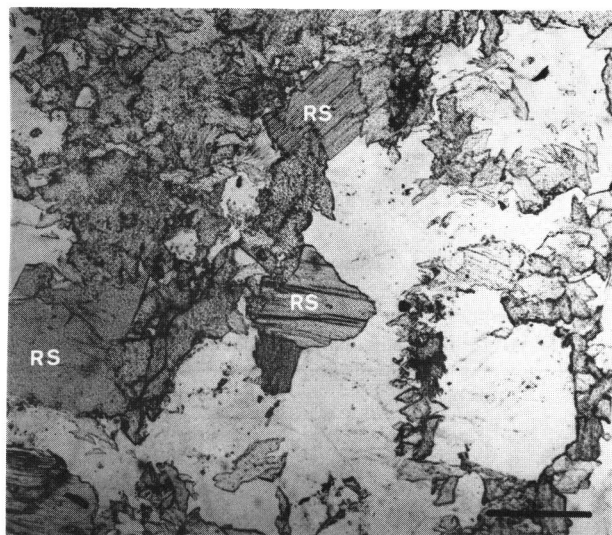


Fig. 5. Photomicrograph of barian roscoelite (RS), rhodochrosite, rhodonite and quartz. Bar=0.1 mm. One polar.

more BaO than chernykhite. However, on account of the molecular dominance of K over Ba, this is identified as a barian roscoelite.

Occurrence: The mineral is found in massive rhodonite-rhodochrosite and rhodochrosite ores from the Mogurazawa mine. The aggregates of very brittle flaky crystals are often concentrated in rhodochrosite-quartz ore including black carbonaceous material. It is also found in association with nagashimalite, suzukiite and barite in rhodonite-rhodochrosite ore. Under the microscope, almost all the barian roscoelite scales form a mosaic-like texture and subparallel aggregates interstitially developed in euhedral rhodochrosite, rhodonite and quartz grains (Fig. 5).

Optical and physical properties: Barian roscoelite is dark green in colour with a vitreous or pearly luster. Streak is greyish green. Cleavage is perfect on (001). The calculated density is 3.5 g/cm³. Vickers microhardness is 60–82 kg/mm² (25 g load) (approx. 2–2½ (Mohs)) on (001) and 103–136 kg/mm² (25 g load) (approx. 3–3½ (Mohs)) in the perpendicular direction to (001). It is optically biaxial, negative, 2V=30–35°, dispersion weak. Refractive index measured by the immersion method is: $\beta=1.690(2)$.

Table 2. The X-ray powder data for barian roscoelite.

d _{obs.}	d _{calc.}	I	hkl
10.0	10.0	55	001
4.98	4.99	15	002
3.92	3.91	1	111
3.62	3.63	1	11 $\bar{2}$
3.324	3.324	100	003
2.886	2.888	1	11 $\bar{3}$
2.493	2.492	20	004
2.428	2.425	1	201
1.994	1.994	30	005
1.735	{ 1.739	1	134
	{ 1.733		115
1.661	1.662	10	006
1.622	1.622	1	22 $\bar{5}$
1.530	1.529	2	060
1.425	1.424	5	007

Table 3. Relative intensities of basal reflections on the basis of I(005)=10 for roscoelite, barian roscoelite and chernykhite.

hkl	roscoelite	barian roscoelite	chernykhite
001	20	18	3
002	6	5	1
003	16	33	17
004	0	7	3
005	10	10	10
006	0	3	10

Pleochroism is strong with axial colours X=brownish green, Y, Z=pale green, being apparently similar to nagashimalite, but lighter in all directions.

X-ray study: The X-ray powder diffraction pattern obtained by the powder diffractometer method using Cu/Ni radiation is give in Table 2. The X-ray reflection intensity ratio of the first and the second order basal reflections to the third one decreases markedly with increase of Ba/(K+Na+Ba) in the series composed of roscoelite (JCPDS 10-496), the present barian roscoelite and chernykhite (ANKINOVICH *et al.*, 1972) (Table 3). It is very difficult to decide the exact polytype characteristics because of its mosaic and subparallel aggregated state. But the powder diffraction pattern of the present mineral is similar to those of 1M roscoelite rather than 2M₁ chernykhite, the indexing being made in terms of 1M. The calculated unit cell parameters are: $a=5.296(3)$, $b=9.175(4)$, $c=10.12(1)\text{\AA}$, $\beta=99.83(5)^\circ$.

Chemical compositions of a barian roscoelite and the associated minerals: The electron microprobe analysis of the barian roscoelite gave the results shown in Table 4 in which those of chernykhites from Kazakhstan are given for comparison. Though chernykhites contain both of tri- and tetravalent vanadium, total vanadium in the present mineral is regarded as trivalent. The empirical formula of the anhydrous part calculated on the basis of O=11 is: $(K_{0.58}Ba_{0.38}Sr_{0.01})_{\Sigma 0.97}(V_{1.65}^{3+}Al_{0.22}Mn_{0.03}Ti_{0.02}Mg_{0.01})_{\Sigma 1.93}(Si_{2.55}Al_{1.15})_{\Sigma 4.00}O_{11}$.

The electron microprobe analyses of the associated rhodochrosite, barite and rhodonite gave the results as shown in Table 5. The recast of analysis of rhodochrosite into end member molecules gives MnCO₃ 90.2, CaCO₃ 8.6, MgCO₃ 0.4%. The extreme scanty of FeO is very characteristic. The Sr/(Ba+Sr) ratio in barite is about 0.01, which is lower than those in barian roscoelite (0.03) and suzukiite (0.11), but higher than that in nagashimalite (0).

Table 4. Chemical analyses of barian roscoelite and chernykhites.

	Mogurazawa	Kazakhstan	Kazakhstan
SiO ₂	35.04	29.90	30.06
Al ₂ O ₃	14.27	25.90	27.24
TiO ₂	0.37	—	—
VO ₂	—	5.40	5.30
V ₂ O ₃	25.56	18.30	18.90
Fe ₂ O ₃	—	0.40	0.36
FeO	0.05	—	—
MnO	0.39	—	—
MgO	0.10	1.60	tr.
BaO	12.03	9.35	9.60
SrO	0.15	—	—
K ₂ O	5.59	0.70	0.90
Na ₂ O	—	1.32	—
H ₂ O ⁺	n.d.	6.00	6.10
H ₂ O ⁻	n.d.	1.10	1.00
Total	93.55	99.97	99.46

Table 5. Chemical analyses of rhodochrosite, barite and rhodonite.

	rhodochrosite	barite	rhodonite
SiO ₂	—	—	45.57
MnO	55.65	—	51.57
MgO	0.17	—	0.10
CaO	4.82	—	4.66
BaO	—	64.53	—
SrO	—	0.28	—
SO ₃	—	34.49	—
CO ₂	38.49	—	—
Total	99.14	99.30	102.21

5. Kinoshitalite

The second kinoshitalite described by MATSUBARA *et al.* (1976) is close to barium-magnesium end member with $F > OH$ in mole ratio. The mineral occurs in close association with a magnesian tephroite in the contact metamorphosed bedded manganese ore deposit at Hokkejino, Kyoto Prefecture. The ore body was located in hornfels of chert origin, which is a dominant member in the roof pendant on a fine-grained biotite-granodiorite body.

Kinoshitalite from Hokkejino is light greyish yellow scale reaching a few millimeter long or hexagonal tablets of several millimeters across. Specific gravity is 3.23. It is monoclinic, possible space group is *Cm* or *C2/m* and 1M polytype. The unit cell parameters are: $a=5.344(2)$, $b=9.200(2)$, $c=10.15(1)\text{\AA}$, $\beta=100.20(5)^\circ$. The chemical analysis yields the empirical formula $(Ba_{0.746}K_{0.254}Ca_{0.075}Na_{0.008}Sr_{0.001})_{\Sigma 1.084}(Mg_{2.635}Mn_{0.339}^{2+}Ti_{0.034}Fe_{0.031}^{3+}Al_{0.044})_{\Sigma 3.083}(Si_{2.276}Al_{1.724})_{\Sigma 4.000}O_{10.000}(O_{0.489}F_{0.760}(OH)_{0.751})_{\Sigma 2.000}$ on the basis of $(O+F+OH)=12$. The relationship between basal intensity and Ba content on the basis of fifth order one of the present kinoshitalite is satisfactory plotted on the diagram of YOSHII *et al.* (1973) except of fourth order one. Kinoshitalites from metamorphosed manganese ore deposits exhibit a wide composition range with respect to SiO₂, K₂O and $(FeO+Fe_2O_3)$ decreasing and, Al₂O₃ and $(MgO+MnO+Mn_2O_3)$ increasing with BaO content. While SiO₂, K₂O and MgO decrease and Al₂O₃ and FeO increase with the increase of BaO in the Ti-rich kinoshitalite from nephelinites from Oahu, Hawaii (MANSKER *et al.*, 1979).

6. Cymrite

In Japan cymrite occurs in weakly metamorphosed bedded manganese ore deposits in association with celsian, banalsite, rhodochrosite, albite, chlorite and sericite, and in xenolith in ultrabasic rock in association with slawsonite, prehnite and xonotlite. As the localities to the former mode of occurrence are known the Shiromaru mine, Tokyo Prefecture, the Ohmiya mine, Saitama Prefecture, the Mogurazawa mine, Gumma Prefecture, and the Yumiyama mine, Kyoto Prefecture.

Cymrite-bearing rock from the Shiromaru mine is pale brownish yellow mass

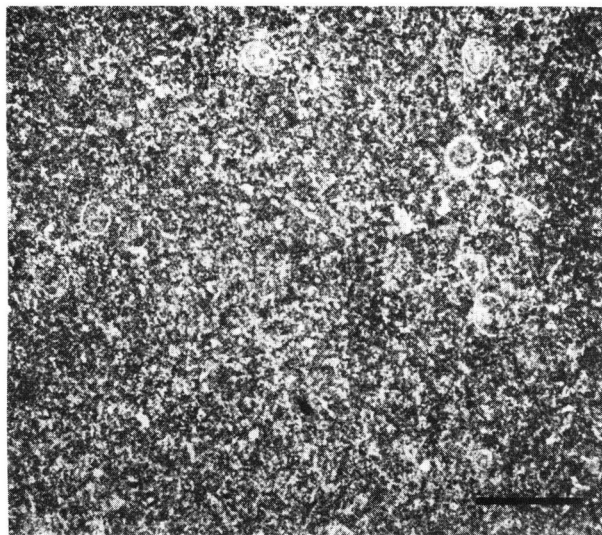


Fig. 6. Photomicrograph of radiolaria-bearing cymrite, banalsite, celsian, sericite and hydrogrossular rock. Bar=0.1 mm. One polar.

with a dull luster banded with braunite. The rock consists of extremely fine grains of cymrite, banalsite, celsian, sericite and hydrogrossular impeding the preparation of pure material and chemical analysis even by the electron microprobe. Under the microscope some fragments of radiolarian fossil were observed in the rock (Fig. 6). The results of X-ray powder diffraction study for four points in the specimen show that cymrite and banalsite are concentrated in a most distant part from braunite band which is in direct contact with a part rich in celsian and devoid of cymrite and banalsite. The X-ray powder pattern of cymrite is given in Table 6. The finally refined unit cell parameters are: $a=5.344(2)$, $b=36.77(1)$, $c=7.676(2)\text{\AA}$, $\beta=90^\circ$, in terms of the setting of DRITS *et al.* (1975). The origin of cymrite-bearing rock is considered to be argillaceous deep sea sediments including very fine detrital fragments of basic volcanic rock.

Cymrite from the Ohmiya mine occurs also as very fine grains in association with chlorite, sericite, albite and rhodochrosite. The cymrite-bearing rock is pale chocolate brown in colour and looks like a siltstone. In Table 6 the X-ray powder data are compared with those for the Shiromaru material. Though there are slight discrepancies in intensity, both of them have cell parameters very close to each other.

Cymrite from Sarusaka occurs as euhedral prismatic crystals reaching 0.5 mm long and 0.2 mm wide forming subparallel aggregates in association with slawsonite, prehnite and xonotlite (Fig. 7). It is colourless and the cleavage is perfect perpendicular to the direction of elongation. The X-ray powder pattern is nearly identical with those of the Shiromaru material, but it is difficult to calculate the unit cell parameters on account of the presence of some superimposed diffractions of admixed

Table 6. The X-ray powder data for cymrites.

Shiromaru mine			Ohmiya mine		
d _{obs.}	d _{calc.}	I	d	I	hkl
7.71	7.67	30	7.70	70	001
4.62	4.62	10	4.62	10	140
3.97	3.96	90	3.96	75	141
2.955	2.953	100	2.955	100	142
2.674	2.672	75	2.671	30	200
2.562	2.559	20	2.557	30	003
2.522	2.523	8	2.522	40	201
2.310	2.310	10	2.309	15	280
2.240	2.239	25	2.239	30	143
2.213	2.212	25	2.213	20	281
2.192	2.193	18	2.190	16	202
1.979	1.979	8	1.979	8	282
1.919	1.919	10	1.919	10	004
1.848	1.848	20	1.848	16	203
1.773	1.772	5	1.776	5	144
1.704	1.705	16	1.703	5	341
1.591	1.591	20	1.590	15	342
1.558	1.559	12	1.559	8	204
1.541	1.540	10	1.540	5	3120
1.535	1.535	5	1.536	8	005
1.458	1.457	10	1.458	12	145
1.445	1.444	5			343
1.334	1.336	8b			400
1.320	1.319	5			3123
1.293	1.293	5			344
1.280	1.279	10b			006, 285

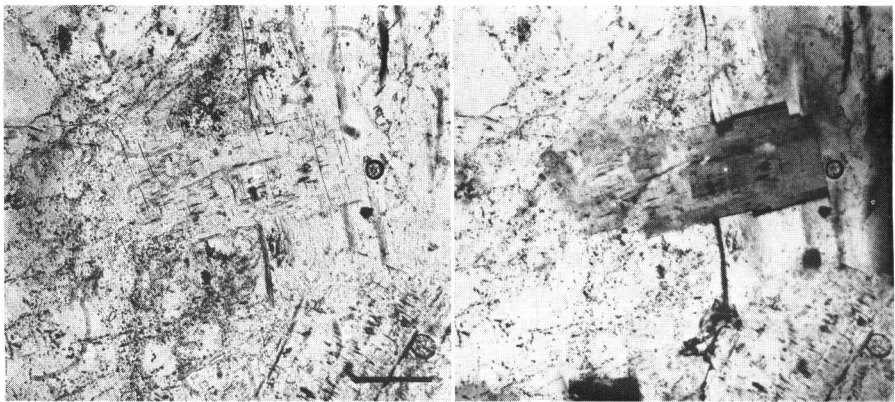


Fig. 7. Photomicrographs of cymrite crystal (C) in slawsonite. Bar=0.1 mm. Left: One polar, right: Crossed polars.

Table 7. Chemical analyses of cymrites.

	Sarusaka	Sarusaka	Benallt mine	Alaska	California
SiO ₂	28.88	29.03	45.8	32.69	30.3
TiO ₂	—	—	—	0.06	—
Al ₂ O ₃	24.86	25.39	13.0	27.53	25.9
FeO	0.05	—	—	—	—
BaO	38.07	36.64	39.0	31.98	38.7
SrO	0.34	0.43	—	—	—
CaO	0.04	0.01	—	0.35	—
Na ₂ O	0.07	0.18	—	—	—
K ₂ O	0.05	0.05	—	0.22	0.03
H ₂ O ⁺	n.d.	n.d.	2.3	7.17	4.56
Total	92.36	91.73	100.0	100.00	99.5

slawsonite. Its electron microprobe analyses gave the result as shown in Table 7 in which chemical analyses of cymrites from the Benallt mine (SMITH *et al.*, 1949), Alaska (RUNNELS, 1964) and California (ESSENE, 1967) are shown for comparison. The empirical formula calculated on the basis of O=8 in the anhydrous part is $(\text{Ba}_{1.02}\text{Sr}_{0.01}\text{Na}_{0.01})_{\Sigma 1.04}\text{Al}_{2.00}\text{Si}_{1.97}\text{O}_8 \cdot 1.74\text{H}_2\text{O}$ and $(\text{Ba}_{0.95}\text{Sr}_{0.02}\text{Na}_{0.02})_{\Sigma 1.02}\text{Al}_{2.03}\text{Si}_{1.97}\text{O}_8 \cdot 1.88\text{H}_2\text{O}$. The Sarusaka materials include considerable amounts of SrO and higher content of H₂O than other cymrites, provided that the H₂O contents are due to difference.

7. Celsian

In Japanese metamorphosed bedded manganese ore deposits the occurrences of celsian and hyalophane are not so uncommon. They are found in the Nodatamagawa mine, Iwate Prefecture, the Kaso mine (YOSHIMURA, 1936) and the Kaminagano mine, Tochigi Prefecture, the Shiromaru mine, Tokyo Prefecture, the Hamayokogawa mine, Nagano Prefecture (HIROWATARI & YOSHIE, 1978), the Taguchi mine, Aichi Prefecture (GAY & ROY, 1968; NAKANO, 1977) and Hokkejino, Kyoto Prefecture (MATSUBARA *et al.*, 1976).

In the specimen from the Shiromaru mine, celsian occurs as very fine grains in association with cymrite, banalsite, albite, braunite, sericite and hydrogrossular. The celsian-rich part has pale brownish yellow colour with slightly vitreous luster. The unit cell parameters: $a=8.632(2)$, $b=13.044(2)$, $c=14.428(2)\text{\AA}$, $\beta=115.53(5)^\circ$, are calculated from the X-ray powder pattern given in Table 8.

Celsian from the Nodatamagawa mine occurs as minute grains reaching 0.1 mm in dimension in rhodonite-bearing hornfels collected from the east side of S6 point in the 6th level of the Misago ore body. The grains of the mineral are exclusively found in mosaic aggregates of tephroite grains enclosed within rhodonite mass (Fig. 8).

Celsian from Sarusaka occurs as fine euhedral to subhedral crystals enclosed in slawsonite (Fig. 9). Also the larger mass composed of anhedral grains is found in association with diopside, grossular and chlorite. The X-ray powder pattern is given

Table 8. The X-ray powder data for celsians

Shiromaru mine			Sarusaka			hkl
d _{obs.}	d _{calc.}	I	d _{obs.}	d _{calc.}	I	
6.53	{6.52 6.51}	35	6.53	{6.52 6.51}	45	020 002
5.88	5.87	5	5.88	5.86	10	$\bar{1}$ 12
4.62	4.61	20	4.62	4.61	25	022
			4.00	4.00	5	112
3.90	3.90	15	3.90	3.90	20	200
3.795	3.796	55	3.798	3.798	30	130
3.627	3.627	20	3.627	3.623	15	$\bar{1}$ 32
3.556	3.558	25	3.553	3.549	20	$\bar{2}$ 22
3.477	3.475	70	3.474	3.473	50	$\bar{1}$ 14
3.343	3.345	85	3.348	3.348	100	220
3.290	3.292	60	3.280	3.281	30b	204
3.252	{3.255 3.262}	100	3.259	{3.263 3.258}	50	004 040
3.015	3.015	70	3.019	3.021	65	132
2.915	{2.912 2.916}	45	2.917	{2.917 2.915}	30	024 042
2.776	2.776	35	2.774	2.774	25	$\bar{1}$ 34
2.608	{2.611 2.608}	25	2.605	2.604	20	$\bar{3}$ 14 222
2.586	{2.586 2.586}	55b	2.584	{2.586 2.582}	55	114 $\bar{2}$ 42
2.549	2.546	15	2.552	2.552	15	310
2.502	2.501	3				240
2.475	2.474	5	2.473	2.472	2b	150
2.424	2.425	10	2.426	2.423	18	152
2.398	2.398	8	2.400	2.397	3b	$\bar{3}$ 32
2.333	2.333	12	2.332	2.334	18	$\bar{1}$ 16
2.272	{2.272 2.248}	10				334
			2.253	2.255	8b	134
2.236	{2.237 2.229}	5b	2.231	{2.233 2.233}	12b	$\bar{2}$ 26 330
2.217	2.214	10	2.218	2.215	10	152
2.173	{2.174 2.170}	25b	2.172	{2.172 2.175}	20	060 006
2.144	2.144	5b		2.149		242
2.130	{2.135 2.122}	5b	2.139	{2.135 2.122}	10b	$\bar{4}$ 02 $\bar{4}$ 04
			2.122	{2.122 2.122}	10	$\bar{1}$ 54
2.093	{2.093 2.090}	3b	2.101	{2.103 2.099}	10	204 312
2.083	2.082	3	2.080	2.082	2	$\bar{1}$ 36
2.062	{2.059 2.062}	5b	2.062	{2.063 2.061}	8	026 062
2.015	2.018	10	2.015	2.013	15	$\bar{4}$ 24

Table 8. (Continued)

Shiromaru mine			Sarusaka			hkl
d _{obs.}	d _{calc.}	I	d _{obs.}	d _{calc.}	I	
			2.000	2.001	6	224
1.954	{1.959 1.947	8b	1.954	{1.954 1.952	12b	336 400
1.934	{1.935 1.932	8	1.931	{1.932 1.931	15	262 352
1.910	{1.917 1.904	5b	1.910	{1.911 1.910	8	406 332
			1.877	1.878	8	116
1.863	1.864	8	1.857	{1.861 1.854	10b	354 154
1.843	1.840	5b	1.843	1.842	10	350
1.808	{1.807 1.808	10b	1.808	{1.809 1.808	15	046 064
1.802	1.804	25	1.801	1.802	15	208
1.787	1.787	5	1.787	1.786	5	442
1.736	{1.738 1.733	3b	1.735	1.737	3b	228 136
1.689	1.689	3				314
1.678	{1.679 1.675	5b	1.675	{1.676 1.676	8	356 512
1.634	1.633	8		{1.630		338
1.631	1.631	8	1.629	{1.629	20b	080
1.591	{1.596 1.586	5b				428 334
			1.583	{1.581 1.583	20b	082 028
1.577	{1.579 1.574	8b				226
1.536	1.536	5b	1.536	1.537	10	066

in Table 8 in which that of the Shiromaru material is shown for comparison. The calculated unit cell parameters are: $a=8.624(2)$, $b=13.032(2)$, $c=14.416(2)\text{\AA}$, $\beta=115.11(5)^\circ$. Electron microprobe analysis gave the empirical formula $(\text{Ba}_{0.70}\text{Ca}_{0.32}\text{Sr}_{0.01}\text{Na}_{0.01}\text{K}_{0.01})_{\Sigma 1.11}\text{Al}_{1.90}\text{Si}_{2.03}\text{O}_5$ on the basis of $\text{O}=8$, specifying the mineral to be a calcian variety which is previously reported only in gneiss from Broken Hill, New South Wales, Australia by SEGNI $\bar{T}$ (1946). The present celsian contains very small amount of strontium in spite of its close association with slawsonite. Also no paracelsian is found in this locality, despite the isomorphic relation to slawsonite. Therefore, barium and strontium are liable to be concentrated in celsian and paracelsian type structures, respectively, under such a metamorphic condition.

8. Slawsonite

Slawsonite is a new mineral mentioned by ERD *et al.* (priv. comm.) from Triassic

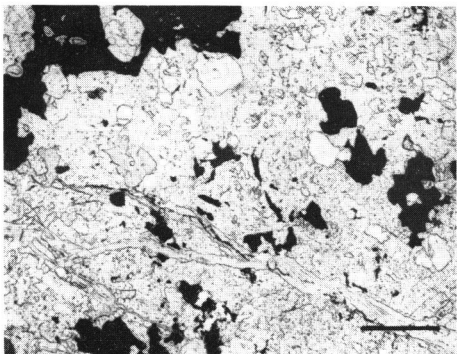


Fig. 8.

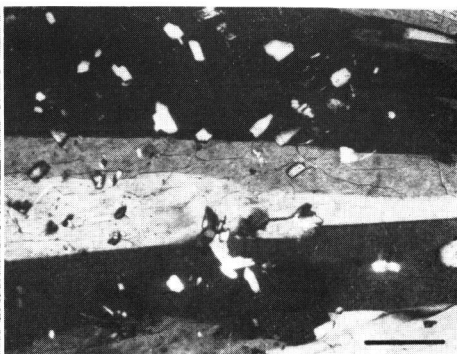


Fig. 9.

Fig. 8. Photomicrograph of celsian-bearing manganese ore. Celsian (white) grains are enclosed in tephroite (gray). Opaque minerals are chalcopyrite and pyrrhotite. Bar=0.1 mm. One polar.

Fig. 9. Photomicrograph of celsian crystals enclosed in slawsonite. Bar=0.1 mm. Crossed polars.

Martin Bridge Formation exposed in Wallowa County, Oregon, USA. The ideal formula is $\text{SrAl}_2\text{Si}_2\text{O}_8$, monoclinic, space group $P2_1/a$, corresponding to the strontium analogue of paracelsian. $\text{SrAl}_2\text{Si}_2\text{O}_8$ has another modifications, such as anorthite-type phase synthesized at about 1400°C to which slawsonite is the lower temperature phase, and hexagonal metastable phase synthesized at 1160°C .

In 1980, white radial crystals in xenolith in ultrabasic rock from Sarusaka, Kochi Prefecture, Japan were found by KATO and MATSUBARA (1980b). The X-ray powder study and electron microprobe analysis showed it to be slawsonite.

Occurrence: Around the locality situated near Sarusaka, Kagami Village, Tosa-gun, Kochi Prefecture, ultrabasic rock is exposed in weakly metamorphosed rocks

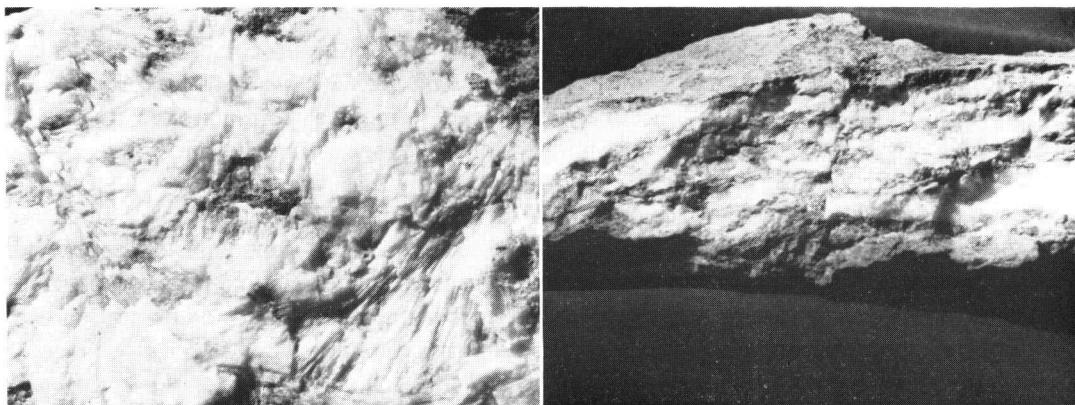


Fig. 10. Slawsonite crystals. Left: Parallel to veinlet. Specimen, approx. 14×5 cm. Right: perpendicular to veinlet. Specimen, approx. 14×9 cm.

belonging to the Ino Formation of later Devonian (MARUYAMA, 1981). In the ultra-basic rock is a xenolith elongated about 200 m in E-W direction.

Slawsonite was found in a part of xenolith as white veinlets and the crystals reach 7 cm in length along vein wall and form radial aggregates composed of long tabular crystals elongated to $[110]$ (Fig. 10). The associated minerals recognized in the vein-

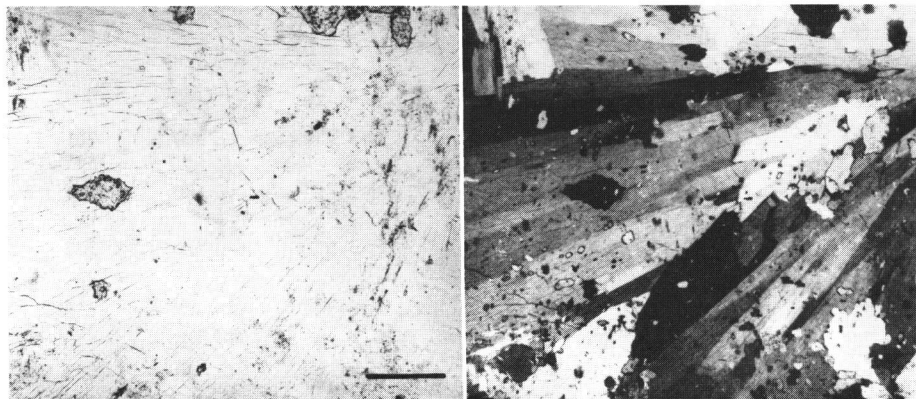


Fig. 11. Photomicrographs of slawsonite and grossular (high relief). Bar=0.1 mm. Left: One polar, right: Crossed polars.

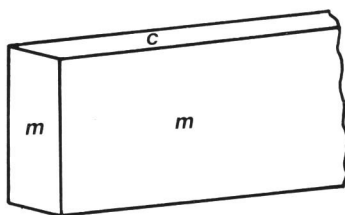


Fig. 12. An ideal drawing of the crystal forms of slawsonite. $m \{110\}$, $c \{001\}$

Table 9. Physical and optical properties for slawsonites.

	Sarusaka	Oregon
colour	colourless	medium light grey
cleavage	(100) good	(001) good, (100) fair
specific gravity	3.10 (calc.)	3.12 (calc.)
hardness (Mohs)	6–6½	5½
fluorescence	moderate (pink purple red under short wave UV light)	no
α	1.570 (2)	1.573
β	1.582 (2)	1.581
γ	1.586 (2)	1.585
2V	(–) approx. 55°	(–) 82°
dispersion	$r > v$ very weak	$r < v$ medium
$c \wedge Y$	$\leq 5^\circ$	11°

Table 10. The X-ray powder data for slawsonite and synthetic $\text{SrAl}_2\text{Si}_2\text{O}_8$.

Sarusaka				JCPDS 17-140		
$d_{\text{obs.}}$	$d_{\text{calc.}}$	I	hkl	d	I	hkl
6.47	6.46	25	110	6.46	30	110
6.25	6.24	15	011	6.22	40	011
5.12	{ 5.12 5.10	5	$\bar{1}11$ 111	5.12	10	111
4.69	4.69	5	020			
4.176	4.174	20	002	4.17	40	002
3.938	{ 3.937 3.923	80	$\bar{2}01$ 201	3.93	100	201
3.720	{ 3.721 3.715	55	$\bar{1}21$ 121	3.71	80	121
3.630	{ 3.631 3.620	15b	$\bar{2}11$ 211	3.62	20	211
3.512	{ 3.511 3.501	30	$\bar{1}12$ 112	3.50	80	112
3.231	3.231	100	220	3.22	60	220
3.120	3.119	10	022	3.11	30	022, 030
3.046	{ 3.052 3.039	5b	$\bar{2}02$ 202	3.05	20	202
	{ 2.953 2.947		130 $\bar{1}22$			
2.949	{ 2.947 2.941	35	122 122	2.940	40	122, 130
2.930	2.931	50	031	2.920	60	031
2.904	2.903	20	$\bar{2}12$			
2.893	2.892	20	212	2.895	40	212
2.834	2.832	10	310	2.830	20	310
2.685	2.685	30	$\bar{3}11$			
2.679	2.678	35	311	2.681	40	311
2.665	2.668	10b	013	2.666	10	013
	{ 2.561 2.558		230 $\bar{1}13$			
2.559	{ 2.558 2.553	30b	113 113	2.553	80	230
2.510	2.510	30	320	2.506	40	320
2.346	{ 2.348 2.347	30	$\bar{3}12$ 040	2.349	10	312
2.340	2.340	20	312	2.338	40	040
2.312	{ 2.314 2.309	20	$\bar{1}23$ 123	2.308	60	123
				2.291	10	213
2.228	2.228	5	400	2.227	10	400
2.183	{ 2.183 2.180	20b	$\bar{2}32$ 232	2.180	60	141
2.152	{ 2.154 2.150	25	401 401	2.151	60	401
2.113	2.112	10	$\bar{2}23$	2.109	30	223
2.105	2.105	12	223			

Table 10. (Continued)

Sarusaka				JCPDS 17-140		
d _{obs.}	d _{calc.}	I	hkl	d	I	hkl
2.100	{ 2.100 2.096	12b	$\bar{4}11$ 411	2.101	30	411
2.087	2.087	40	004	2.088	40	004
				2.022	10	303
2.015	{ 2.016 2.014	10	$\bar{2}41$ 241	2.007	20	241
1.990	{ 1.995 1.993 1.988 1.984	5b	$\bar{1}42$ 142 $\bar{1}14$ 114	1.986	30	114, 142
1.928	1.927	5	$\bar{4}12$			
1.920	1.920	5	412			
1.907	1.907	5	024	1.903	20	024
1.867	{ 1.867 1.866	10	$\bar{3}23$ $\bar{1}24$	1.862	40	323, 124
1.859	{ 1.863 1.861 1.860 1.858	15	124 $\bar{2}42$ 323 242			
1.841	1.842	15	340	1.833	40	150, 340
1.836	1.837	30	150			
1.832	1.832	15	051			
1.814	{ 1.815 1.815	15	430 $\bar{4}22$	1.812	30	422, 430
1.810	1.810	12	422			
1.798	{ 1.799 1.797	8	$\bar{3}41$ 341	1.794	20	341
1.775	1.775	5	$\bar{4}31$	1.771	10	431
1.772	1.772	8	431			
1.759	{ 1.760 1.758	10	$\bar{1}43$ 143			
1.755	1.755	10	$\bar{2}24$			
1.751	{ 1.751 1.751	15	224 510	1.752	40	224
1.729	1.730	5b	250			
1.714	{ 1.715 1.713 1.713 1.713	8	$\bar{5}11$ 511 $\bar{4}13$ 413			
1.707	{ 1.706 1.706	8	413 $\bar{3}33$			
1.701	1.701	5	333			
1.681	{ 1.683 1.682 1.681	6	$\bar{3}14$ $\bar{1}52$ 152			

Table 10. (Continued)

Sarusaka				JCPDS17-140		
d _{obs.}	d _{calc.}	I	hkl	d	I	hkl
1.678	1.677	5	314			
1.645	1.644	4	015			
1.634	1.635	10	$\bar{5}21$			
	1.634		$\bar{4}23$			
	1.633		521			
1.627	1.628	6	423			
1.615	1.617	5b	$\bar{5}12$			
	1.612		512			
1.598	1.599	4	$\bar{2}52$			
	1.597		252			
1.586	1.587	5b	$\bar{4}41$			
	1.585		441			
1.566	1.565	8	060			
	1.565		$\bar{2}05$			
1.559	1.561	20	205			
	1.560		$\bar{3}51$			
	1.559		351			
1.537	1.538	4	061			
1.534	1.534	4	$\bar{1}53$			
	1.533		153			
1.523	1.524	10	$\bar{5}31$			
	1.522		531			
	1.522		$\bar{4}33$			
1.517	1.518	8	433			
1.485	1.485	8	600			
	1.485		$\bar{3}52$			
1.481	1.482	6	352			

lets include celsian, cymrite, xonotlite, grossular, hydrogrossular, vesuvianite, prehnite, tobermorite (11Å), native copper and occasionally later calcite, and two undetermined secondary minerals are observed as veinlets cutting slawsonite and nearby wall rock. The country rock of veinlets consists mainly of diopside, chlorite and altered sphene, but they are devoid of igneous texture and not considered as a primary magmatic product. Under the microscope, slawsonite is colourless, and includes numerous very small crystals of celsian and cymrite, and sometimes xonotlite, prehnite, grossular and diopside closer to the country rock (Fig. 11). A subparallel multiple growth of tablets is commonly observed but no twinning is discerned.

After the present discovery, another slawsonites have been found by the author and coworkers near Miyanotani, Hidaka Village, and Rendai, Kochi City, Kochi Prefecture, where slawsonites occur as veinlets cutting pectolite veinlets, which are developed in metamorphosed xenoliths belonging to the Ino Formation.

Physical and optical properties: The present slawsonites are markedly different

Table 11. The unit cell parameters of slawsonites and paracelsian.

	Slawsonite			Paracelsian
	Sarusaka	Rendai	Oregon	Benallt mine
a (Å)	8.910 (2)	8.900 (2)	8.888 (2)	9.065 (3)
b (Å)	9.389 (2)	9.366 (2)	9.344 (2)	9.568 (1)
c (Å)	8.347 (4)	8.340 (4)	8.326 (3)	8.574 (5)
β (°)	90.24 (2)	90.22 (2)	90.33 (2)	90.00 (1)
	This study		GRIFFEN <i>et al.</i> (1977)	CRAIG <i>et al.</i> (1973)

Table 12. Chemical compositions of slawsonites.

	Sarusaka	Rendai	Oregon*	(theory)
SiO ₂	36.63	37.78	38.68	36.89
TiO ₂	—	—	0.36	—
Al ₂ O ₃	31.30	30.26	29.32	31.30
Fe ₂ O ₃	—	—	1.14	—
MgO	—	—	0.25	—
FeO	—	—	0.02	—
CaO	—	0.33	2.26	—
BaO	1.53	—	—	—
SrO	29.99	31.22	26.60	31.81
Na ₂ O	—	—	0.13	—
K ₂ O	0.06	—	0.07	—
H ₂ O ⁺	—	—	0.17	—
H ₂ O ⁻	—	—	0.09	—
total	99.51	99.59	99.09	100.00

* ERD *et al.* (priv. comm.)

from the original one in crystal habit and fluorescence. The crystals are elongated [110] (Fig. 12), and it gives off purple red fluorescence of moderate intensity under the short wave ultraviolet light. Except these, however, physical and optical properties are similar to the original material. In Table 9, some physical and optical properties of Sarusaka and original slawsonites are compared.

X-ray powder study: The X-ray powder diffraction patterns of Sarusaka and Rendai materials are very close to that of synthetic one (JCPDS 17-140) where the symmetry is assigned as orthorhombic (Table 10). The unit cell parameters are: Sarusaka, $a=8.910(2)$, $b=9.389(2)$, $c=8.347(4)$ Å, $\beta=90.24(2)^\circ$, Rendai, $a=8.900(2)$, $b=9.366(2)$, $c=8.340(4)$ Å, $\beta=90.22(2)^\circ$, in terms of the setting after GRIFFEN *et al.* (1977), who determined the crystal structure of the original slawsonite. These values are somewhat larger than those of the original material, which has $a=8.888(2)$, $b=9.344(2)$, $c=8.326(3)$ Å, $\beta=90.33(2)^\circ$, because the original material includes calcium in place of strontium up to the ratio Sr: Ca=87: 13. In Table 11, the unit cell parameters of three slawsonites and paracelsian are given.

Chemical composition: The electron microprobe analyses gave the results in Table 12, and the empirical formulae calculated on the basis of O=8 are $(\text{Sr}_{0.95}\text{Ba}_{0.03})_{\Sigma 0.98}\text{Al}_{2.01}\text{Si}_{2.00}\text{O}_8$ (Sarusaka) and $(\text{Sr}_{0.95}\text{Ca}_{0.02})_{\Sigma 1.00}\text{Al}_{1.98}\text{Si}_{2.04}\text{O}_8$ (Rendai), which are very close to the ideal formula. Sodium was under the limit of detection. The original material includes small amounts of calcium, ferric iron and minor titanium, magnesium and sodium, and is in association with calcite, phlogopite, albite and pyrite. Celsian associated with the Sarusaka slawsonite and other celsians from various localities contain no or a very small amount of strontium (DEER *et al.*, 1963). Therefore, the occurrence of celsian type $\text{SrAl}_2\text{Si}_2\text{O}_8$ is expected with difficulty under the ordinary natural conditions.

9. Banalsite

The occurrences of banalsite were reported from the metamorphosed manganese ore deposits of the Benallt mine, Wales (SMITH *et al.*, 1944) and Långban, Sweden (WELIN, 1968). During the mineralogical investigation on cymrite and celsian from the Shiromaru mine, Tokyo, the third occurrence of banalsite was recognized (KATO *et al.*, 1983).

Occurrence: There are two modes of occurrence of banalsite in this locality. One is the main component of veinlets cutting hematite-bearing celsian-cymrite rock. The other is very fine grains as a component of celsian-cymrite-analcime rock. Since the latter material is unable to be separated into monomineralic state, the mineralogical study on banalsite is made for the former one. The veinlets reach 5 mm in width. Under the microscope, banalsite is colourless and rectangular partings are observed

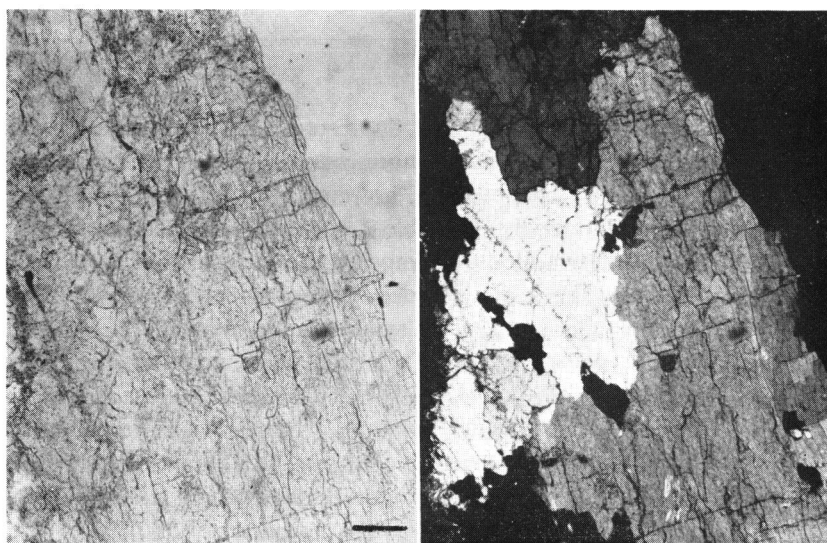


Fig. 13. Photomicrographs of banalsite. Bar=0.2 mm. Left: One polar right: Crossed polars.

Table 13. Physical properties of banalsites from the Benallt mine and the Shiromaru mine.

	Benallt	Shiromaru
Colour	white	white
Luster	vitreous	vitreous
H. (Mohs)	6	6
Density	3.065 (meas.)	3.08 (calc.)
Cleavage	(110), distinct (001), distinct	none
(+) 2V	41°	40°
α	1.5695	1.570 (2)
β	1.571	1.571 (2)
γ	1.5775	1.578 (2)
Fluorescence	red, strong SMITH <i>et al.</i> (1944)	red, strong This study

Table 14. The X-ray powder diffraction pattern of banalsites.

hkl	Långban		Shiromaru			hkl	Långban		Shiromaru		
	I	d	I	d (obs.)	d (calc.)		I	d	I	d (obs.)	d (calc.)
002	80	8.50	24	8.40	8.40	314	10	2.28	6	2.286	2.284
110	50	6.50	58	6.48	6.47	330	20	2.16	40	2.157	2.157
112	90	5.20	44	5.13	5.12	240			2	2.152	2.152
020			16	5.00	4.99	044			4	2.144	2.144
022			1	4.30	4.29	400			2	2.126	2.124
200			6	4.26	4.25	226			7	2.115	2.114
004	60	4.20	31b	4.181	4.189	332	80	2.09	55	2.088	2.089
121					4.167	242			55	2.085	2.085
202	70	3.77	39	3.795	3.790	217	10	2.06	6	2.042	2.042
114	100	3.53	81	3.517	3.516	118	20	1.994	17	1.993	1.992
123			3	3.413	3.408	420	30	1.957	19	1.956	1.955
220	80	3.21	100	3.236	3.236	316			15	1.952	1.950
024			30	3.206	3.209	028			1	1.932	1.931
130	50	3.10	43	3.098	3.098	334	10b	1.910	5	1.915	1.917
222			50	3.020	3.019	422			2	1.901	1.904
204	50	3.00	28	2.986	2.983	208	10b	1.874	5	1.879	1.878
132	80	2.90	75	2.906	2.906	046			3	1.861	1.861
006			2	2.794	2.793	343			2	1.776	1.775
310	10	2.74	12	2.728	2.725	154	20	1.765	7	1.763	1.763
125	30	2.65	20	2.644	2.644	138			1	1.735	1.735
312	10	2.60	10	2.594	2.592	253			1	1.719	1.719
231			10	2.587	2.588	336	20	1.710	14	1.708	1.707
116	40	2.56	30b	2.562	2.564	147	10	1.692	5	1.692	1.693
224					2.561	219			1	1.682	1.681
040	10	2.50	4	2.493	2.496	0010			1	1.677	1.676
134					2.491	060	10	1.666	4	1.663	1.664
321	20	2.44	17b	2.437	2.440	512			2b	1.645	1.643
026					2.438	345	10	1.636	7	1.635	1.635
042	10	2.39	8	2.391	2.393	350			2	1.632	1.632
233			6	2.370	2.372	440	10	1.621	7	1.618	1.618
206			3	2.335	2.334	426			2	1.602	1.601

Table 15. Unit cell parameters of banalsites.

	Benallt	Benallt	Långban	Shiromaru
space group	<i>Iba2, Ibam</i>	<i>Ibam</i>	<i>Iba2, Ibam</i>	<i>(Ibam)</i>
<i>a</i> (Å)	8.52	8.496 (6)	8.502	8.497 (2)
<i>b</i> (Å)	9.99	9.983 (3)	9.974	9.983 (2)
<i>c</i> (Å)	16.76	16.755 (3)	16.81	16.756 (4)
	SMITH <i>et al.</i> (1944)	HAGA (1973)	WELIN (1968)	This study

Table 16. Chemical analyses of banalsites from the Benallt mine (SMITH *et al.*, 1944) and the Shiromaru mine.

	Benallt	Shiromaru
SiO ₂	34.74	37.04
Al ₂ O ₃	31.20	31.27
MnO	0.03	0
MgO	1.00	0
CaO	0.81	0
BaO	21.99	19.19
SrO	n.d.	4.03
Na ₂ O	8.43	9.46
K ₂ O	0.66	0
H ₂ O	1.08	n.d.
Total	99.94	100.99

around the margin of crystals. The associated minerals are celsian and a calcian serandite (Fig. 13).

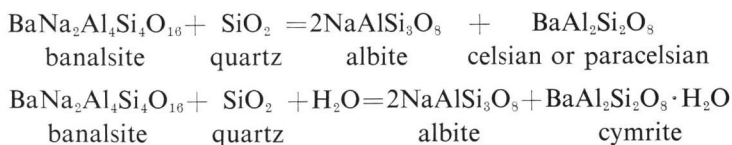
Physical and optical properties: The banalsite in veinlets is white in colour and has vitreous luster. The appearance resembles feldspar but no cleavages are observed. It gives off red fluorescence of strong intensity under the short wave ultraviolet light. In Table 13, physical and optical properties of Benallt and Shiromaru materials are compared.

X-ray powder study: The X-ray powder pattern of the present material is close to that of the Långban material (JCPDS 23-651) (Table 14). However, the diffraction lines are far richer than those of the Långban material and the overlapped peaks with different (hkl) in the Långban material are well separated in the present one. The unit cell parameters are calculated as: $a=8.497(2)$, $b=9.983(2)$, $c=16.756(4)$ Å. These values are very close to those of the Benallt material measured by HAGA (1973) (Table 15). The obtained indices are perfectly satisfied with the extinction rule of the space group *Ibam*.

Chemical composition: The EDX analysis gave the result in Table 16, and the empirical formula calculated on the basis of O=16 is $(\text{Ba}_{0.81}\text{Sr}_{0.25})_{\Sigma 1.06}\text{Na}_{1.95}\text{Al}_{3.67}\text{Si}_{3.69}\text{O}_{16}$, specifying the material to be a strontian banalsite.

Genesis: Banalsite can be dealt with as a feldspathoid and the formation is fa-

voured by a SiO_2 -deficient condition, since the composition of banalsite corresponds to the addition of K-free nepheline to celsian (or paracelsian).



If Na_2O and SiO_2 are saturated in barium-rich argillaceous sediment, the condition does not favour the formation of banalsite but that of assemblage including albite and celsian (and/or cymrite). The above assemblage are recognized at the Shiromaru mine and the Ohmiya mine.

10. Stronalsite

Stronalsite is the strontium analogue of banalsite reported by HORI *et al.* (1983) from Rendai, Kochi City, Japan.

Occurrence: The mineral is found at a serpentinite quarry at Rendai, where serpentinite occurs as huge blocks, a member of constituent of the Kurosegawa tectonic melange (MARUYAMA, 1981). The serpentinite includes large number of xenoliths of meta-basic tuff, rodingite, metagabbro and schist, etc. Stronalsite occurs as aggregates of anhedral crystals reaching 1 mm across in association with slawsonite and pectolite in veinlets cutting rodingite. The other vein minerals include prehnite, xonotlite, grossular, hydrogrossular and natrolite.

Physical and optical properties: The stronalsite is white in colour with a vitreous luster. It has no cleavage and gives no fluorescence under ultraviolet light. Hardness is $6\frac{1}{2}$ in Mohs' scale. Measured density is 2.95 g/cm^3 . Under the microscope, it is colourless and optically biaxial positive with $2V=32^\circ$. The refractive indices are: $\alpha=1.563(2)$, $\beta=1.564(\text{calc.})$, $\gamma=1.574(2)$ measured in white light. The optical orientation is $X=c$, $Y=a$, and $Z=b$.

X-ray studies: The single crystal data obtained by precession and automatic four-circle diffractometer demonstrate space group *Ibam* or *Iba2*, $a=8.407(2)$, $b=9.886(2)$, $c=16.691(5)\text{\AA}$. The X-ray powder diffraction pattern is very similar to that of banalsite. The strongest diffraction lines are: $3.504(80)$ (114), $3.206(100)$ (024, 220), $3.184(72)$ (213), $3.070(47)$ (130), $2.882(68)$ (132) and $2.066(48)$ (332, 242).

Chemical composition: The electron microprobe analysis (Table 17) yields the empirical formula $(\text{Sr}_{0.92}\text{Ba}_{0.10})_{1.02}\text{Na}_{2.35}\text{Al}_{3.97}\text{Si}_{3.92}\text{O}_{16}$ (basis $\text{O}=16$), which is idealized as $(\text{Sr}, \text{Ba})\text{Na}_2\text{Al}_4\text{Si}_4\text{O}_{16}$ with $\text{Sr} > \text{Ba}$, corresponding to the strontium analogue of banalsite.

Consideration on genesis: The vein-forming minerals from Sarusaka and Rendai are compositionally placed within the $(\text{CaO}+\text{SrO}+\text{BaO})-\text{Al}_2\text{O}_3-\text{Na}_2\text{O}$ diagram (Fig. 14), if SiO_2 content is variably chosen. Xonotlite, prehnite, slawsonite and celsian are the principal vein mineral at Sarusaka. On the contrary, at Rendai, pectolite is the most dominant vein-forming mineral. This leads to the interpretation that the original

Table 17. Chemical analysis of stronalsite.

	SiO ₂	Al ₂ O ₃	BaO	SrO	CaO	Na ₂ O	K ₂ O	Total
1.	37.95	32.63	2.44	15.35	0.04	11.89	0.01	100.31
2.	39.09	33.17	2.49	15.16		10.08		99.99

1. Stronalsite from Rendai.

2. Theory for (Sr_{0.9}Ba_{0.1}) Na₂Al₄Si₄O₁₆.

rock of the host for veinlets contained plagioclase or an alkalic pyroxene, which is actually lacking in that for slawsonite veinlets at Sarusaka. Under a sodium-rich condition in these environments, pectolite, natrolite and slawsonite are stable phases, if SiO₂ is moderately present. But if the environment is undersaturated by SiO₂, stronalsite appears vicariously to the assemblage of natrolite-slawsonite, though such a condition is infrequently occasioned.

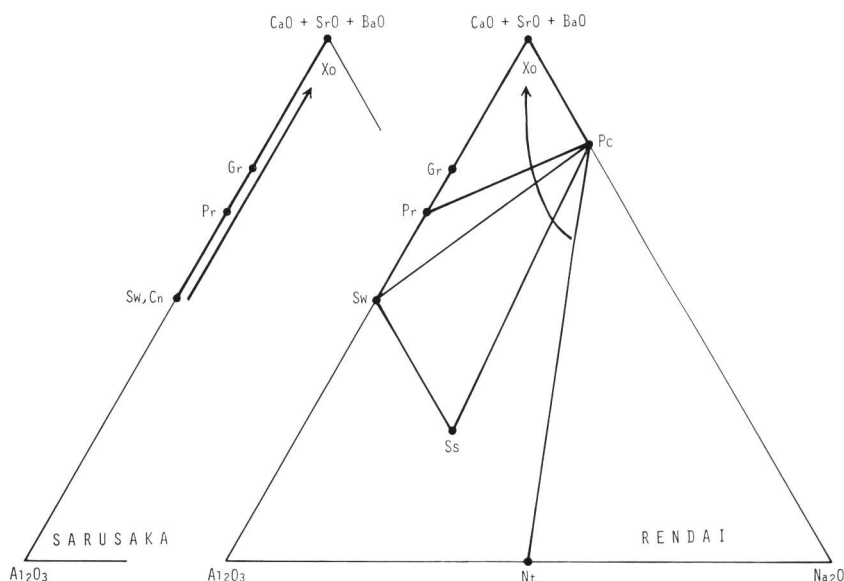


Fig. 14. Veinlet mineral assemblages at Rendai and Sarusaka. Arrows indicate the sequence of formation of veinlet minerals. Xo: xonotlite, Gr: grossular, Pr: prehnite, Sw: slawsonite, Cn: celsian, Pc: pectolite, Ss: stronalsite, Nt: natrolite.

IV. Genesis and Geological Implications of the Barium and Strontium Silicates

There are no rock-forming silicates with considerable amounts of Ba and Sr. This is partly due to their lower geochemical abundance in earth crust but mainly to being dissolved in Na, K and Ca silicates as seen in feldspars and feldspathoids (cam-

ouflaging effect). On the other hand, Ba and Sr atoms are not so similar in the crystallochemical characteristics as to make complete solid solution between Na, K and Ca analogues. Therefore, if the concentration of Ba and Sr increases in magmas, they are liable to be released from the camouflaging effect of Na, K and Ca throughout the formation of feldspars and feldspathoids, and that they may be gradually concentrated in association with other minor elements such as Ti, B and REE at a later stage of magmatic differentiation. This consideration comes from the fact that Ti, B and REE-bearing Ba and Sr silicates are often found in pegmatites of alkali plutonic rocks. In mafic minerals, less prominent camouflaging is seen except for micas, especially in some K-bearing ones. Throughout the ordinary magmatic processes the camouflaging ability of Na, K and Ca is so remarkable that no significant differentiation of these elements takes place except for such special cases in nephelinites from Oahu, Hawaii, where barian-titanian biotite (actually titanian kinoshitalite) with the relation $Ba > K$ is reported (MANSKER *et al.*, 1979). These authors ascribe the nephelinite magma to a deep-seated source, where the surrounding conditions favoured the concentration of Ba. In relation to this evidence, it is worth mentioning that FITTON and HUGHES (1981) report 15.96 wt% of SrO (max.) in melilite in nephelinite from Etinde, Cameroon, an uncommon hyperalkaline rock possibly of very deep-seated origin.

The appearance of Ba and Sr silicates is more common in the products of metamorphic processes than of igneous ones. As seen in case of slawsonite from Sarusaka, Kochi Prefecture, the appearance of this mineral was favoured by at least two independent factors. One is the higher SrO content of wallrock of slawsonite veinlets before the metamorphism, and the other is formation of such calcsilicates as clinopyroxene and garnet, severely excluding Sr and Ba. The presence of appropriate component capable of forming any anionic radical like silicates is necessary besides above-mentioned factors.

Any original rock with high concentration of Ba yields a resultant product enriched in Ba minerals, such as a high grade metamorphic rock comprising Ba feldspar from Broken Hill, New South Wales (SEGNET, 1946), where the mineralization of Pb, Zn and Mn is prevailing. Although the dimensional scale is far discrepant, there are many examples of concentration of Ba in or aside bedded manganese or manganese-iron ore deposits. Ba is generally found as barite with or without minor Sr with the exception of the case at Shiromaru, Tokyo, where celsian and cymrite are quantitatively superior to barite with certainty. In those of highly metamorphosed deposits are some examples of Ba silicates containing essential Mn like yoshimuraite and ortho-ericssonite.

The original sediments of these metamorphosed bedded manganese or manganese-iron ore deposits were formed in the sea floor. The result of seawater-oceanic basalt interaction experiments indicates that such heavy metals as Mn, Fe, Cu, Zn and Ba are leached from the rock to seawater (SEYFRIED & BISCHOFF, 1977). Therefore, the $Ba/(Na+K+Ca)$ ratio is higher in seawater than in igneous rock, and Ba is probably fixed in precipitates containing mainly Mn and Fe in the environment of volcanic activity in

Table 18. The ratios of Ba and Sr to Na, K and Ca calculated from the average abundance in manganese nodules and in the earth crust.

	manganese nodule		the earth crust	
	wt. ratio	mole ratio	wt. ratio	mole ratio
Ba/Na	0.104	0.017	0.015	0.003
Sr/Na	0.043	0.011	0.013	0.003
Ba/K	0.313	0.089	0.016	0.005
Sr/K	0.128	0.057	0.014	0.006
Ba/Ca	0.079	0.023	0.012	0.004
Sr/Ca	0.033	0.015	0.010	0.005
Ref.	CRONAN (1976)		MATSUI & BANNO (1979)	

the sea floor. Sr is expected to behave like Ba judging from the several chemical compositions of manganese nodule (e.g. CRONAN, 1976). The recognition of close association of Ba and also Sr with Mn has been already given in Challenger Report (MURRAY & RENARD, 1891) in which BaO and SrO contents in manganese nodules are given as 0.67 and 0.11 wt. %, respectively. The concentration of Ba and also Sr in manganese nodules have been recognized by many subsequent workers. The ratios of Ba and Sr to Na, K and Ca, respectively calculated from the average abundance in manganese nodules from all oceans and in earth, listed in Table 18, show notable concentration of Ba and Sr in manganese nodules. What phases contain Ba as major or minor component? It is obvious that a small amount of Ba is included in low crystalline Mn^{4+} -bearing manganese oxides forming precipitates or nodules, represented by todorokite and psilomelane. However, Ba precipitates readily as $BaSO_4$ under the presence of SO_4^{2-} in solution. CHOW and GOLDBERG (1960) pointed out that almost all the Ba in marine sediments is fixed as barite. Actually, some manganese nodules include barite crystals (e.g. BURNS & BURNS, 1978), and in bedded manganese ore deposits in Japan extensive occurrences of barite have been observed, which are more voluminous than those of Ba silicates. On the other hand, since various sulphides are often closely associated with Ba silicates, the decomposition of barite can be considered under a strong reducing condition. Recently, the occurrence of Ba-bearing carbonates was recognized in Mn-rich ores in a few metamorphosed bedded manganese ore deposits in Japan (HIROWATARI & FUKUOKA, 1983). These occurrences indicate that Ba in Ba silicates is mainly derived from manganese dioxide minerals, and partly from barite and Ba-bearing carbonates.

Another potential Ba silicate mineral in marine sediments is harmotome or Ba-bearing phillipsite (e.g. ARRHENIUS, 1963). This mineral is probably changed to Ba feldspar through diagenesis or metamorphism.

The B content in hydrothermal solution is often higher than in seawater (MIZUTANI, 1962). Therefore, the concentration of B takes place near the sea floor where volcanic activities are prominent sometimes. This environment is of such a nature

that heavy metals, as Mn, Fe and Ba, are enriched. Manganese nodules are relatively rich in B, compared with other marine sediments except glauconite rock (HARDER, 1973). If manganese nodules-bearing sediments are metamorphosed under burial condition, the formation of borosilicates (rarely Ba-bearing ones) and Mn-borates is strongly expected in case of saturated and undersaturated SiO_2 , respectively. This relation-ship corresponds to the mode of occurrence of B-bearing minerals in bedded manganese ore deposits in Japan (KATO & MATSUBARA, 1980a).

Another important source of various Ba silicates is the sanbornite deposit in metamorphic rocks in California. This deposit occurs as sanbornite-quartz rock in contact metamorphic quartzose rocks around granodiorite intrusives, and the associated minerals in the deposit include wollastonite. It is important evidence that the principal mineral assemblage of ores is very simple and that it is expressed as the assemblage in the ternary system $\text{BaO-SiO}_2\text{-H}_2\text{O}$, although some accessory Ba silicates are present after the participation of some other components, such as Al_2O_3 forming celsian, CaO forming walstromite, TiO_2 forming fresnoite and FeO forming gillespite, etc. Provided that sanbornite is a metamorphic mineral corresponding to the metamorphic grade estimated from the occurrence of wollastonite, the original state of Ba must have been combined with certain anions capable of being released during the metamorphism, such as CO_2 forming witherite. However, seeing from the dimension of the sanbornite deposit, the development of such an extensively distributed witherite rock cannot be expected. Among known Ba-containing geologic units accompanied by siliceous rocks, the most extensive and voluminous one is occurring in barite beds with novaculite and other sedimentary rocks in Arkansas, U.S.A. (SCULL, 1958). Suppose that such barite beds are regionally or contact metamorphosed up to the grade allowing the formation of wollastonite. Under reducing and higher temperature condition, decomposition of barite takes place, leaving a reactive compound, BaS , which could be a source of Ba silicates together with the siliceous rocks associated therewith. The released sulphur could be the source of pyrite and pyrrhotite, extensively distributed through the sanbornite deposit.

In the Ba silicates found in the sanbornite deposit, there are some evidences with crystallochemical implications. One is the coexistence of walstromite and wollastonite. The chemical composition of the former is derived from that of the latter by substituting Ba for Ca to obtain the ratio $\text{Ca:Ba}=2:1$. While the crystal structure of walstromite corresponds to that of high pressure form of wollastonite, we see that the presence of Ba plays a role of stabilization of the high-pressure $\text{Ca}_3\text{Si}_3\text{O}_9$ structure.

Another crystallochemical characteristics of Ba silicates in the sanbornite deposit is the appearance of Ba silicates with silicate frameworks of diverse forms. Among seven new Ba silicates therefrom (ALFORS *et al.*, 1965), anhydrous Ba silicates occur as primary metamorphic minerals. Together with the associated Ba silicates, the following examples of silicate frameworks are found as primary minerals: Sanbornite and gillespite with a sheet structure, celsian with a four-membered ring forming framework structure, fresnoite with a sorosilicate radical, and bazirite and walstromite with

a ring structure. In the cases of younger hydrous Ba silicates, the following examples are known: muirite, verplanckite and taramellite with a ring structure, krauskopfite with a chain structure, and macdonaldite with a sheets structure. That is, Ba silicates can involve various kinds of silicate frameworks even under the same or similar geological conditions. Therefore, the form of silicate framework in Ba silicates reflects the chemical environment rather than the physical one. Contrasting with Ba, there is no example of Sr silicates corresponding to the Californian sanbornite deposit.

In conclusion, it can be said that there are two major geneses of barium and strontium silicate minerals, i.e., 1) later stage products of deep-seated alkali magma or their metamorphic equivalents, and 2) constituents of metamorphosed bedded manganese and barite ores deposited in the sea floor.

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Appendix: Barium and Strontium Silicates

A. Nesosilicates

1. Cappelenite $\text{Ba}(\text{Y}, \text{RE})_6[\text{Si}_3\text{B}_6\text{O}_{24}]\text{F}_2$ Hexagonal, $P3$

Although STRUNZ (1970) gave the formula $(\text{Ba}, \text{Ca}, \text{Ce}, \text{Na})(\text{Y}, \text{Ce}, \text{La})_2[\text{B}_2\text{O}_5|\text{SiO}_4]$ a new chemical analysis for the material from Kazakhstan (SHIPOVALOV & STEPANOV, 1971) showed that the BaO content is significantly lower than previously expected and the ideal formula $(\text{Ba}, \text{Ca})(\text{Y}, \text{Ce}, \text{La})_8\text{B}_6\text{Si}_3\text{O}_{25}$ is derived. Recently SHEN and MOORE (1984) proposed the above formula from the result of their crystal structure analysis. The structure contains silicoborate $[\text{Si}_3\text{B}_6\text{O}_{24}]$ sheet composed of $[\text{B}_6\text{O}_{18}]$ rings and $[\text{SiO}_4]$ tetrahedra.

2. Garrelsite $\text{NaBa}_3[\text{B}_7\text{O}_{13}(\text{OH})_4](\text{SiO}_4)_2$ Monoclinic, $C2/c$

Garrelsite was first described by MILTON *et al.* (1955), who designated the ideal formula $(\text{Ba}, \text{Ca}, \text{Mg})_4\text{H}_6\text{Si}_2\text{B}_8\text{O}_{20}$. However, a new wet chemical and microprobe analyses validated above formula (ULBRICH & GHOSE, 1973), which was later corroborated by the crystal structure determination (GHOSE *et al.*, 1976). Garrelsite involves the pentaborate $[\text{B}_5\text{O}_{12}]^{5-}$ polyanions which are joined together by silicon to form a borosilicate chains. Two independent Ba polyhedra, square pyramids and pentagonal pyramids, are present.

B. Sorosilicates

3. Fresnoite $\text{Ba}_2\text{Ti}[\text{O}|\text{Si}_2\text{O}_7]$ Tetragonal, $P4bm$

This is one of the seven new minerals from barium silicate-bearing metamorphic rocks in California described by ALFORS *et al.* (1965). The crystal structure is analogous with those of the melilite group minerals except for pentagonal coordination of oxygen about Ti atom (MASSE *et al.*, 1967). The Ba atoms are ten-coordinated by six oxygens of the first neighbour and four of the second one.

4. Barylite $\text{BaBe}_2[\text{Si}_2\text{O}_7]$ Orthorhombic, $Pn2_1a$

The crystal structure was determined by ABRASHEV *et al.* (1964) and CANNILLO *et al.* (1969). ROBINSON and FANG (1977) refined the structure in the non-centrosymmetric space group $Pn2_1a$ according to their SHG test and confirmed that a pseudo space group $Pnma$ is resulted from the centrosymmetrically arranged Ba atom in the structure.

5. Andremerite $\text{BaFe}_2^{2+}[\text{Si}_2\text{O}_7]$ Monoclinic, $P2_1/c$

The mineral is uniquely known in a single specimen in the vesicle of melilite-leucite-nepheline block, Nyiragongo volcano in Zaire (SAHAMA *et al.*, 1973). The crystal is prismatic with a tetragonal shape developed after a multiple twin on (100). The crystallographic data were obtained from precession photographs but the crystal structure has not been determined yet.

6. Lamprophyllite $\text{Sr}_2(\text{Na}, \text{Ti})_4\text{Ti}_2[(\text{O}, \text{OH}, \text{F})_4](\text{Si}_2\text{O}_7)_2$ Monoclinic, $C2/m$

The mineral was firstly described by RAMSEY and HACKMAN (1894). The crystallography was discussed by PENG and CHANG (1965) and by MOORE (1971), who pointed out its geometrical relationship to "ortholamprophyllite".

7. Barytolamprophyllite $(\text{Ba}, \text{Ca}, \text{Sr})_2(\text{Na}, \text{Ti})_4\text{Ti}_2[(\text{O}, \text{OH}, \text{F})_4](\text{Si}_2\text{O}_7)_2$ Orthorhombic, $Pnmm$

PENG and CHANG (1965) reported the Ba analogue of lamprophyllite and coined this name. The basic structural model of this mineral was presented by WOODROW (1964), though he used the name lamprophyllite for the material with this compositional formula.

8. Ortholamprophyllite $\text{Sr}_2(\text{Na}, \text{Ti})_4\text{Ti}_2[(\text{O}, \text{OH}, \text{F})_4(\text{Si}_2\text{O}_7)_2]$ Orthorhombic, $Pnmm$

GOSSNER and DREZLER (1935) thought that lamprophyllite is orthorhombic in symmetry. But PENG and CHENG (1965) and WOODROW (1971) have independently confirmed the presence of both of monoclinic and orthorhombic lamprophyllites. They are probably isotypic with ericssonite and orthoericssonite, respectively (MOORE, 1971; MATSUBARA, 1980a). Therefore, the author here proposes a new name ortholamprophyllite in analogy with orthoericssonite. The definitive structure of the orthorhombic phase has not been determined yet.

9. Ericssonite $\text{Ba}_2\text{Mn}_4\text{Fe}_2^{3+}[\text{O}_2](\text{OH})_2(\text{Si}_2\text{O}_7)_2]$ Monoclinic, $C2/m$

This mineral is uniquely known in scheffelite-rhodonite-tephroite skarn from Långban, Sweden (MOORE, 1967). It was found with its orthorhombic dimorph called orthoericssonite (MOORE, 1971). Although its definitive crystal structure has not been described yet, the structural scheme has been proposed by MATSUBARA (1980a) from the result of his structure determination of orthoericssonite.

10. Orthoericssonite* $(\text{Ba}, \text{Sr})_2(\text{Mn}, \text{Fe}^{2+})_4(\text{Fe}^{3+}, \text{Ti})_2[(\text{O}, \text{OH})_4(\text{Si}_2\text{O}_7)_2]$ Orthorhombic, $Pnmm$

The original description of this mineral was due to MOORE (1971) from Långban, Sweden. But its intimate intergrowth with ericssonite in the specimen impeded the determination of crystal structure, or even of real space group. In 1975 MATSUBARA and NAGASHIMA reported the second occurrence of orthoericssonite in a jacobsite-bearing rhodonite-aegirine-tephroite ore from the Hijikuzu mine (now called Shintamagawa mine), Iwate Prefecture. Later, MATSUBARA (1980a) published the definitive crystal structure and discussed its structural relationship to ericssonite. The structure contains FeO_5 square pyramids as the first example of fivefold coordination polyhedra formed by oxygen atoms about Fe^{3+} .

11. Bafertisitite $\text{Ba}_2\text{Fe}_4^{2+}\text{Ti}_2[\text{O}_2](\text{OH})_4(\text{Si}_2\text{O}_7)_2]$ Monoclinic, $C2/m$

PENG (1959) and SEMENOV and CHANG (1959) described a new Ba-Fe-Ti silicate mineral with orthorhombic symmetry and chemical formula $\text{BaFe}_2\text{TiSi}_2\text{O}_8$. But the structural studies by PENG and SHENG (1963) and by KUAN *et al.* (1963) revealed the mineral to be really monoclinic and to have the above ideal formula as well as its structural proximity to lamprophyllite and ericssonite. MAUGER (1983) has reported the occurrence of bafertisitite from North Carolina, USA and proposed the ideal formula, $\text{Ba}(\text{Fe}, \text{Mn})_2\text{Ti}(\text{Si}_2\text{O}_7)\text{O}(\text{OH}, \text{F})_2$ or $\text{Ba}(\text{Fe}, \text{Mn})_2\text{Ti}(\text{Si}_2\text{O}_7)\text{O}_{1.5}\text{F}$.

GANZEEV *et al.* (1971) reported the occurrence of a manganiferous bafertisitite from northern Baikal, USSR. It is compositionally characterized by high MnO and low Fe_2O_3 contents, both replacing Fe^{2+} .

12. Jinshajiangite $(\text{Na}, \text{K})_5(\text{Ba}, \text{Ca})_4(\text{Fe}^{2+}, \text{Mn})_{15}(\text{Ti}, \text{Fe}^{3+}, \text{Nb})_8(\text{SiO}_4)_{15}(\text{F}, \text{O}, \text{OH})_{10}$ Monoclinic, $C2/m$, Cm , or $C2$

The mineral was found in an arfvedsonite-albite dyke in alkali syenite near the Jinshajiang River, western Sichuan Province, China (HONG & FU, 1982). Though they proposed the above chemical formula, $[\text{Si}_2\text{O}_7]$ radical is expected because of structural proximity to lamprophyllite group minerals.

13. Yoshimuraite* $(\text{Ba}, \text{Sr})_4[(\text{P}, \text{S})\text{O}_4]_2(\text{Mn}, \text{Fe}^{2+}, \text{Mg})_4(\text{Ti}, \text{Fe}^{3+})_2[\text{O}_2](\text{OH})_2(\text{Si}_2\text{O}_7)_2]$ Triclinic, $P\bar{1}$

The mineral was originally described in a coarse-grained pegmatitic vein composed of barian potash feldspar, quartz, a manganoan alkali amphibole, a manganoan aegirine and rhodonite in the manganese ore deposits of the Nodatamagawa mine, Iwate Prefecture by WATANABE (1959) and WATANABE *et al.* (1961). The crystal structure determined by TAKÉUCHI and HAGA (1971, 1978) may be regarded as a regular intergrowth of two kinds of slabs, one having a barite-like structure and the other consisting of two quasi-silicate sheets (TAKÉUCHI & JOSWIG, 1967) and one octahedral sheet.

The structure of the barite-like slab is very close to that of barite, though sulphur atoms are partly replaced by phosphorus atoms.

In 1963 the second occurrence of yoshimuraite was reported from the Taguchi mine, Aichi Prefecture by HIROWATARI and ISONO. Later, the author has recognized two other localities, the Hijikazu mine and the Tanohata mine, Iwate Prefecture. The mineral is known exclusively from the Japanese metamorphosed bedded manganese ore deposits of the above four localities.

14. Innelite $\text{Ba}_4[(\text{S}, \text{Si})\text{O}_4]_2(\text{Na}, \text{K}, \text{Mn}, \text{Ti})_4\text{Ti}_2[(\text{O}, \text{OH}, \text{F})_4(\text{Si}_2\text{O}_7)_2]$ Triclinic, $P1$

The mineral was found in alkali plutonic rocks of Inagli and Yakokutsk massif, southern Yakutia (KRAVCHENKO *et al.*, 1961). STRUNZ (1970) has modified the chemical formula and emphasized the isotypism with yoshimuraite. The preliminary crystal structure proposed by CHERNOV *et al.* (1971) supports this interpretation.

15. Bornemanite $\text{BaNa}_4\text{Ti}_2\text{NbSi}_4\text{O}_{17}(\text{F}, \text{OH}) \cdot \text{Na}_3\text{PO}_4$ Orthorhombic, $Ibmm$ or $Ibm2$

MENSHIKOV *et al.* (1975) described a new silicophosphate mineral compositionally close to beta-lomonosovite, above tentative formula being slightly different from it.

16. Strontio-chevkinite $(\text{Sr}, \text{REE}, \text{Ca})_4\text{Fe}^{2+}(\text{Ti}, \text{Zr})_2\text{Ti}_2\text{Si}_4\text{O}_{22}$ Monoclinic, $P2_1/a$

The mineral was found in strontian-loparite and lamprophyllite-bearing aegirine-nepheline-sanidine fenite from the Parana Basin carbonatites, Paraguay (HAGGERTY & MARIANO, 1983).

C. Cyclosilicates

17. Ilimaussite $\text{Ba}_2\text{Na}_4\text{CeFeNb}_2\text{Si}_5\text{O}_{25} \cdot 5\text{H}_2\text{O}$ Hexagonal, $P6_3/mcm$, $P6_3cm$ or $P6c2$

The mineral was found in a hydrothermal vein cutting sodalite syenite in South Greenland (SEMENOV *et al.*, 1968), and its relationship to cerite in cell dimension was suggested. STRUNZ (1970), however, placed the mineral within sorosilicate with $[\text{Si}_4\text{O}_{14}]$. FLEISCHER (1969) proposed an alternative formula $(\text{Ba}, \text{Na}, \text{K}, \text{Ce})_5(\text{Nb}, \text{Ti}, \text{Fe})_3\text{Si}_5\text{O}_{25} \cdot 5\text{H}_2\text{O}$ with a slightly different stoichiometry.

18. Benitoite* $\text{BaTi}[\text{Si}_3\text{O}_9]$ Hexagonal, $P6c2$

The mineral is found as superb crystals in natrolite veins cutting serpentinite in San Benito County, California (LOUDERBACK, 1909). In the world there are six localities including Ohmi, Niigata Prefecture (KOMATSU *et al.*, 1973), where it is found in albitite dike cutting serpentinite. The structure contains Si_3O_9 rings joined by Ti octahedra and Ba trigonal prism (ZACHARIASEN, 1930; FISCHER, 1969).

19. Pabstite $\text{Ba}(\text{Sn}, \text{Ti})[\text{Si}_3\text{O}_9]$ Hexagonal, $P6c2$

The mineral is the tin analogue of benitoite (GROSS, 1965). It is uniquely known from a recrystallized siliceous limestone in the Franciscan metamorphic zone in California.

20. Bazirite $\text{BaZr}[\text{Si}_3\text{O}_9]$ Hexagonal, $P6c2$

The mineral is the zirconium analogue of benitoite (YOUNG *et al.*, 1978). It is found in an aegirine-riebeckite granite in Scotland and barium-silicates-bearing metamorphic rocks in California.

21. Walstromite $\text{BaCa}_2[\text{Si}_3\text{O}_9]$ Triclinic, $P\bar{1}$

It is one of the seven new minerals from barium silicates-bearing metamorphic rocks in California (ALFORS *et al.*, 1965). The preliminary crystal structure determination demonstrated the presence of Si_3O_9 rings and highly distorted BaO_8 polyhedra forming a planar unit in the structure (DENT GLASSER & GLASSER, 1968).

22. Baotite $\text{Ba}_4\text{Ti}_6(\text{Nb}, \text{Fe})_2[\text{Cl}|\text{O}_{10}|\text{Si}_4\text{O}_{12}]$ Tetragonal, $P4_1/a$

The first appearance of this mineral in mineralogical literature was due to PENG (1959) under the name pao-t'ou-k'uang after the original locality name Baotou (not a compositional name!). Later SIMONOV (1960) transliterated the Chinese name into baotite. His preliminary crystal structure determination indicated the presence of Si_4O_{12} ring, which was a new example in cyclosilicate at that time.

The formula is suggested as $\text{Ba}_4(\text{Ti}, \text{Nb})_5\text{ClO}_{16}(\text{Si}_4\text{O}_{12})$. PENG and CHANG (1963) refined the structure and revised the formula as titled. The Ba atom is in a dodecahedral coordination.

23. Verplanckite $\text{Ba}_{12}(\text{Mn}, \text{Ti}, \text{Fe})_6[\text{Cl}_6](\text{OH}, \text{H}_2\text{O})_7(\text{OH}, \text{O})_2(\text{Si}_4\text{O}_{12})_3$ Hexagonal, $P6/mmm$

This is also one of the seven new barium silicates from California (ALFORS *et al.*, 1965). The original formula was revised as $\text{Ba}_2(\text{Mn}, \text{Fe}, \text{Ti})\text{Si}_2\text{O}_6(\text{O}, \text{OH}, \text{Cl}, \text{F})_2 \cdot 3\text{H}_2\text{O}$ by ALFORS and PUTMAN (1965). An electron microprobe and structural analyses by KAMPF *et al.* (1973) provided the formula $[(\text{Mn}, \text{Ti}, \text{Fe})_6(\text{OH}, \text{O})_2\text{Si}_{12}\text{O}_{36}]\text{Ba}_{12}\text{Cl}_6(\text{OH}, \text{H}_2\text{O})_7$. The structure has three dimensional framework composed of four-membered rings of silicate tetrahedra (KAMPF *et al.*, 1973).

24. Joaquinite $\text{Ba}_4\text{Na}_2\text{Fe}_2^{2+}\text{REE}_4(\text{Ti}, \text{Nb})_4[(\text{O}, \text{OH})_4](\text{Si}_4\text{O}_{12})_4 \cdot 2\text{H}_2\text{O}$ Monoclinic, $C2$

WISE (1982) confirmed that type joaquinite is monoclinic, $C2$, and identical with that studied by LAID and ALBEE (1972), though the original joaquinite was described as orthorhombic by PALACHE and FOSHAG (1932). According to the nomenclature scheme of joaquinite group minerals by WISE (1982), the name joaquinite should be used for the monoclinic member with dominant rare earths in X-site in the general formula of joaquinite advocated by CANNILLO *et al.* (1972).

The crystal structure of joaquinite was described by CANNILLO *et al.* (1972) and by DOWTY (1975) on the material from Greenland and from California, respectively. The structure involves four Si_4O_{12} rings joined by one TiO_6 octahedron forming a sheet-like unit. The coordination polyhedra around Ba atom is highly distorted and includes 11 oxygen atoms. The Ba atom is located on a pseudomirror plane between the sheets (DOWTY, 1975).

25. Orthojoaquinite $\text{Ba}_4\text{Na}_2\text{Fe}_2^{2+}\text{REE}_4(\text{Ti}, \text{Nb})_4[(\text{O}, \text{OH})_4](\text{Si}_4\text{O}_{12})_4$ Orthorhombic, $Cc2m$

WISE proposed a new name orthojoaquinite for the material with orthorhombic symmetry, which is dimorphous with the monoclinic phase as realized by LAIRD and ALBEE (1972).

DOWTY (1975) pointed out that the orthorhombic joaquinite can be structurally derived from a cell-order twinning of the monoclinic phase. If this is really the case, the real space group of orthorhombic phase can be unambiguously derived as $Cc2m$.

26. Strontiojoaquinite $\text{Ba}_4\text{Na}_{2.3}\text{Fe}_{1.4}\text{Sr}_4\text{Ti}_4[(\text{OH}, \text{O})_4](\text{Si}_4\text{O}_{12})_4 \cdot 1.7\text{H}_2\text{O}$ Monoclinic, $P2/m$

The mineral corresponds to the strontium analogue of joaquinite if minor compositional differences are disregarded (WISE, 1982). He suggested the space group as $P2/m$ from the indices given to the X-ray powder diffraction lines. The mineral has a submicroscopic twinning overgrowth on a joaquinite core.

27. Strontio-orthojoaquinite* $\text{Ba}_4\text{Na}_{2+x}\text{Fe}_{1.5}(\text{Sr}, \text{Ba}, \text{REE})_{4-x}\text{Ti}_4[(\text{O}, \text{OH})_4](\text{Si}_4\text{O}_{12})_4 \cdot 2\text{H}_2\text{O}$

Orthorhombic, $Pcam$ or $Pca2_1$

CHIHARA *et al.* (1974) described a joaquinite-like mineral from albitite dike cutting a serpentinite at Ohmi, Niigata Prefecture. They considered the mineral to be new species from the chemical composition and crystallography which are slightly but significantly different from orthojoaquinite. According to the nomenclature scheme of Wise, a new name strontio-orthojoaquinite should be used for this mineral.

28. Bario-orthojoaquinite $\text{Ba}_4(\text{Fe}, \text{Mn})_{4-x}(\text{Ba}, \text{Sr})_x\text{Ti}_4[(\text{O}, \text{OH})_4](\text{Si}_4\text{O}_{12})_4 \cdot 2\text{H}_2\text{O}$ Orthorhombic, $Ccmm$ or $Cc2m$

The mineral is the barium analogue of orthojoaquinite and found as euhedral crystals up to 8 mm in length from California (WISE, 1982). As compared with other minerals of the joaquinite group, the virtual absence of sodium is characteristic to this mineral. The detailed studies on mineralogy and crystallography have not been reported yet.

29. Taramellite $\text{Ba}_4(\text{Fe}^{3+}, \text{Ti}, \text{Fe}^{2+})_4[(\text{O}, \text{OH})_2\text{Cl}|\text{Si}_3\text{B}_2\text{O}_{27}]$ Orthorhombic, $Pmmm$

The mineral was described from Candoglia, Italy by TACCONI (1908). Its original chemical formula, $\text{Ba}_4\text{Fe}^{2+}\text{Fe}_3^{3+}\text{Si}_{10}\text{O}_{31}$ given by him was revised as $\text{Ba}_4\text{Fe}_3^{3+}\text{Fe}^{2+}\text{Ti}(\text{Si}_4\text{O}_{12})_2(\text{OH})_4$ from a new chemical analysis (MAZZI, 1957). The crystal structure of "taramellite" was reported by MAZZI and

Rossi (1965) on the material from California, using the formula $\text{Ba}_2(\text{Fe}, \text{Ti}, \text{Mg})_2\text{H}_2[\text{O}_2(\text{Si}_4\text{O}_{12})]$. However the recent study on Californian material indicated that boron and chlorine are essential to taramellite group minerals (MAZZI and Rossi, 1980). The crystal structure of taramellite by them has the same structure framework including $[\text{Si}_5\text{B}_2\text{O}_{27}]$ as that of nagashimalite, though no new chemical analysis is given in their paper.

30. Titantaramellite $\text{Ba}_4(\text{Ti}, \text{Fe}^{2+}, \text{Mg}, \text{Fe}^{3+}, \text{Mn})_4[(\text{O}, \text{Cl}, \text{OH})_3|\text{Si}_5\text{B}_2\text{O}_{27}]$ Orthorhombic, *Pmmn*

The mineral is the titanium analogue of taramellite and found in barium silicates-bearing metamorphic rocks in California described under the name taramellite by PABST (1978). According to the definition of titantaramellite (ALFORS & PABST, 1984), the material used by the Italian crystallographers is not real taramellite but titantaramellite, though they used the name titanium-rich taramellite.

31. Nagashimalite* $\text{Ba}_4(\text{V}^{3+}, \text{Ti})_4[(\text{O}, \text{OH})_2|\text{Cl}|\text{Si}_5\text{B}_2\text{O}_{27}]$ Orthorhombic, *Pmmn*

The mineral is the vanadium analogue of taramellite (MATSUBARA & KATO, 1980). It occurs in massive rhodonite ore from the bedded manganese ore deposit of the Mogurazawa mine, Gumma Prefecture. The crystal structure consists of a novel borosilicate group $[\text{Si}_5\text{B}_2\text{O}_{27}]$, which is built up of a pair of Si_4O_{12} groups linked together, sharing corners by a B_2O_7 group. The three non-equivalent Ba atoms are thirteen- and eleven-coordinated (MATSUBARA, 1980b).

32. Traskite $\text{Ba}_{24}(\text{Fe}, \text{Ti})_2(\text{Fe}, \text{Mn})_2(\text{Ca}, \text{Sr})(\text{Ti}, \text{Fe}, \text{Mg}, \text{Al})_{12}[(\text{O}, \text{OH})_{30}|\text{Cl}_8|\text{Si}_{12}\text{O}_{36}](\text{Si}_2\text{O}_7)_8 \cdot 14\text{H}_2\text{O}$
Hexagonal, *P6m2*

This is one of the seven new minerals from barium silicates-bearing metamorphic rocks in California (ALFORS *et al.*, 1965). The original chemical formula was subsequently revised as $\text{Ba}_8\text{Fe}_2\text{Ti}_2\text{Si}_{12}\text{O}_{30}(\text{OH}, \text{Cl}, \text{F})_{18}$ or $\text{Ba}_8\text{Fe}_2\text{Ti}_2\text{Si}_{12}\text{O}_{30}(\text{OH}, \text{Cl}, \text{F})_6 \cdot 6\text{H}_2\text{O}$ (ALFORS & PUTMAN, 1965). The titled chemical formula is proposed from the result of the crystal structure determination by MALINOVSKII *et al.* (1967). The structure contains 12-membered silicate rings. The Ca and Sr atoms are situated in trigonal prisms.

33. Jonesite $(\text{K}, \text{Na}, \text{Ba})_{1-2}\text{Ba}_4\text{Ti}_4[\text{Al}_2\text{Si}_{10}\text{O}_{36}] \cdot 6\text{H}_2\text{O}$ Orthorhombic, *B2212*

The mineral is found in natrolite veins in San Benito County, California, associated with neptunite and joaquinite (WISE & PABST, 1977). The crystal structure determination has not been published yet. As suggested from the formula, the presence of 12-membered aluminosilicate ring is expected.

34. Tianshanite $\text{KNa}_6\text{Ca}_2\text{Ba}_6(\text{Mn}, \text{Fe})_6(\text{Ti}, \text{Nb}, \text{Ta})_6[\text{Si}_{36}\text{B}_{12}\text{O}_{114}]\text{O}_8(\text{OH})_2$ Hexagonal, *P6/m*

The mineral occurs in a quartz-aegirine-microcline pegmatite cutting alkali syenite, southern Tianshan, U.S.S.R. (DUSMATOV, 1967). The structure contains Si_6O_{18} rings to which Si_2O_7 and BO_4 groups are linked. The original chemical formula $\text{Na}_2\text{BaMnTiB}_2\text{Si}_6\text{O}_{20}$ is revised as above after the result of structure determination by MALINOVSKII *et al.* (1978).

35. Muirite $\text{Ba}_{10}\text{Ca}_2\text{MnTiSi}_{10}\text{O}_{30}(\text{OH}, \text{Cl}, \text{F})_{10}(?)$ Tetragonal, *P4/mmm*

It is one of the seven new minerals from barium silicates-bearing metamorphic rocks in California (ALFORS *et al.*, 1965). The original formula was later revised as titled (ALFORS & PUTMAN, 1965). In 1971 KHAN and BAUR have determined the crystal structure using the another chemical formula, $\text{Ba}_{10}(\text{Ca}, \text{Mn}, \text{Ti})_5\text{Si}_5\text{O}_{24}(\text{Cl}, \text{OH}, \text{O})_{12} \cdot 4\text{H}_2\text{O}$ without any new chemical analysis. This is the first report dealing with eight-membered silicate tetrahedral ring. MALINOVSKII *et al.* (1975) refined the structure which is basically same as that of the previous determination by KHAN and BAUR (1971). However, MALINOVSKII *et al.* (1975) proposed a different chemical formula as $\text{Ba}_9(\text{Ba}, \text{Ca})(\text{Ca}, \text{Ti})_4[(\text{OH})_3(\text{Cl}, \text{OH})_3|\text{Si}_5\text{O}_{24}]$. Both of authors have referred to the original chemical analysis for the structure analysis without any comments about the rejection of the revised formula.

36. Armenite $\text{BaCa}_2\text{Al}_6\text{Si}_6\text{O}_{30} \cdot 2\text{H}_2\text{O}$ Orthorhombic (pseudo-hexagonal)(?)

A chemical formula $\text{BaCa}_2\text{Al}_6\text{Si}_6\text{O}_{28} \cdot 2\text{H}_2\text{O}$ was given in the original work on this mineral from silver-bearing calcite veins of the Armen mine, Norway by NEUMANN (1939). However, he revised

the formula as $\text{BaCa}_2\text{Al}_6\text{Si}_6\text{O}_{30} \cdot 2\text{H}_2\text{O}$ from the new chemical analysis and compared the formula with that of milarite. TENNYSON (1960) obtained the unit cell parameters of this mineral as $a=10.69$ and $c=13.90 \text{ \AA}$ from her X-ray data and considered the mineral to be a member of milarite group, too. Also, the X-ray powder data for armenite in JCPDS (No. 20-112) can be indexed on the hexagonal cell with dimensions stated above, which are reasonable as a member of milarite group. Recently POULIOT *et al.* (1984) described the second occurrence of this mineral from Rémigny Quebec, Canada. They proposed a similar hexagonal cell and the chemical formula, $(\text{Ba}, \text{Na}, \text{K})(\text{Ca}, \text{Sr}, \text{Na})_2\text{Al}_3(\text{Al}_3\text{Si}_6\text{O}_{30}) \cdot 2[(\text{H}_2\text{O}), \text{CO}_2]$ where $\text{Ba} > \text{Na}, \text{K}$ and $\text{Ca} > \text{Sr}, \text{Na}$. However, the physical and optical properties in the original and subsequent works are quite different from those of minerals belonging to the milarite group, namely, armenite has perfect and less perfect cleavages and biaxial nature with $(-)\text{2V}=60^\circ$, whereas minerals of milarite group have actually no cleavage and uniaxial nature. POULIOT *et al.* (1984) report uniaxial armenite in their materials in association with biaxial one. It is uncertain whether the uniaxial nature leads to the discouragement to the present statement or not.

As far as known from the literatures dealing with similar minerals, tuhualite, $(\text{Na}, \text{K})_2\text{Fe}_2^{2+}\text{Fe}_3^{3+}\text{Si}_{12}\text{O}_{30} \cdot \text{H}_2\text{O}$ and zektzerite, $\text{Li}_2\text{Na}_2(\text{Zr}, \text{Ti}, \text{Hf})_2\text{Si}_{12}\text{O}_{30}$ (DUNN *et al.*, 1977) have properties similar to those of armenite. That is, they are orthorhombic (pseudo-hexagonal) with the relationship of $a \times \sqrt{3} \approx b$. The X-ray powder pattern of them are very close to those of minerals of milarite group. Therefore, armenite is considered to be a member of tuhualite-zektzerite group rather than of milarite group as far as compared with known silicate minerals. If so, armenite belongs to inosilicate involving a doublesilicate chains with six-tetrahedral repeat as zektzerite (GHOSE & WAN, 1978).

37. Hyalotekite $\text{Pb}_2\text{Ba}_2\text{Ca}_2[\text{B}_2(\text{Si}_{1.5}\text{Be}_{0.5})\text{Si}_5\text{O}_{25}]\text{F}$ Triclinic, $I\bar{1}$

The original description of NORDENSKIÖLD (1877) and following chemical study by LINDSTRÖM (1887) on this mineral could not provide any reliable chemical formula on account of compositional complexity. But, very recently MOORE *et al.* (1982) solved the crystal structure after the ideal formula as titled. The structure is basically composed of polymerized Si_4O_{12} tetrahedra involving Si, Be and B as inferrable from its pseudotetragonal symmetry about c-axis.

Therefore, seeing from the nature of framework of this mineral, it may be a member of tectosilicate. However, one of the tetrahedra involving $\text{Si}_{1.75}\text{Be}_{0.25}$ as the core cation is linked with one of Si_4O_{12} by edge. The current location is therefore, tentative. Two Ba atoms in the structure are coordinated by eight oxygen and one fluorine atoms, respectively.

D. Inosilicates

38. Balipholite $\text{BaMg}_2\text{LiAl}_3[(\text{OH}, \text{F})_8(\text{Si}_2\text{O}_6)_2]$ Orthorhombic, $Ccca$

The mineral is found in zinnwaldite-quartz vein in Hunan Province, China (X-ray Laboratory of Wuhan Geological College *et al.*, 1975). The crystal structure is similar to that of carpholite group minerals including single chains of pyroxene type $[\text{Si}_2\text{O}_6]$ (X-ray Laboratory of Wuhan Geological College *et al.*, 1977). The Ba atom is in a space formed by zig-zag chains of Al and Mg octahedra, and the double zig-zag chains of (Li, Al) octahedron. The zig-zag chains of Al octahedron and the Ba atoms form a "sheet-like structural unit" parallel to (010).

39. Magbasite $\text{KBa}(\text{Al}, \text{Sc})(\text{Mg}, \text{Fe}^{2+})_8\text{Si}_6\text{O}_{20}\text{F}_2$ Monoclinic(?)

The mineral occurs as finely fibrous deposits of hydrothermal formation in USSR (SEMENOV *et al.* 1965). Although STRUNZ (1970) classified the mineral to inosilicate group because of resembling tremolite in appearance, the crystal structure has not been determined yet.

40. Nordite $(\text{La}, \text{Ce})(\text{Sr}, \text{Ca})\text{Na}_2(\text{Na}, \text{Mn})(\text{Zn}, \text{Mg})[\text{Si}_6\text{O}_{17}]$ Orthorhombic, $Pcca$

GERASIMOVSKII (1941) described the mineral from sodalite-syenite and related pegmatite in the Lovozero massif. The crystal structure contains flat nets of tetrahedra composed of $[\text{Si}_6\text{O}_{17}]$ ribbons and (Zn, Mg) tetrahedra connecting them (BAKAKIN *et al.* 1970). The coordination polyhedra about

(Sr, Ca) has the shape of a square antiprism. They concluded the structure of nordite to be an unusual combination of those of melilite and datolite-gadolinite groups.

41. Batisite $\text{Na}_2\text{BaTi}_2\text{O}_7[\text{Si}_4\text{O}_{12}]$ Orthorhombic, *Ima2*

The mineral was firstly described from a nepheline syenite pegmatite of Central Aldan, USSR by KRAVCHENKO and VLASOVA (1959). Its complete description has been published subsequently (KRAVCHENKO *et al.*, 1960). The structure contains $[\text{Si}_4\text{O}_{12}]$ branched chain consisting of four tetrahedra in two pairs and $[\text{TiO}_5]$ chain (NIKITIN & BELOV, 1962). YAKOVLEVSKAYA and EFIMOV (1963) confirmed its isostructural relation with shcherbakovite which is derived by replacing almost all Ba and approximately half of Na of batisite by K.

42. Krauskopfite* $\text{Ba}_2[\text{Si}_4\text{O}_5(\text{OH})_4] \cdot 4\text{H}_2\text{O}$ Monoclinic, $P2_1/c$

It is one of the seven new minerals from barium silicates-bearing metamorphic rocks in California (ALFORS *et al.*, 1965). Its original chemical formula ($\text{BaSi}_2\text{O}_5 \cdot 4\text{H}_2\text{O}$) has been revised after the result of the structural analysis by CODA *et al.* (1967). According to them, it contains silicate chains consisting of four tetrahedra with hydroxyl anions at the half of apices.

Recently the second occurrence has been reported from the metamorphosed manganese ore deposit of the Furumiya mine, Ehime Prefecture (HIROWATARI & FUKUOKA, 1981).

43. Ohmilite* $\text{Sr}_3(\text{Ti}, \text{Fe}^{3+})[(\text{O}, \text{OH})(\text{Si}_2\text{O}_6)_2] \cdot 2\text{-}3\text{H}_2\text{O}$ Monoclinic, $P2_1/m$

The mineral occurs in albitite cutting serpentinite at Ohmi, Niigata Prefecture (KOMATSU *et al.*, 1973). They considered the Ti to be trivalent in their original description. Later, they have revised the chemical formula as above where Ti is tetravalent (MIZOTA *et al.*, 1983). The structure consists of pair of Si_2O_6 chains connected by TiO_6 octahedra. Among three independent Sr ions, two are nine-coordinated and one is eight-coordinated (MIZOTA *et al.*, 1973, 1983).

44. Haradaite* $\text{Sr}_2\text{V}_3^{4+}[\text{O}_2[\text{Si}_4\text{O}_{12}]]$ Orthorhombic, *Amam*

The occurrence of the mineral is known exclusively in metamorphosed bedded manganese ore deposits of the Nodatamagawa mine, Iwate Prefecture, the Yamato mine Kagoshima Prefecture and the Matsuo mine, Kochi Prefecture (WATANABE *et al.* 1982; HIROWATARI *et al.*, 1972). The structure contains quasi-silicate sheets built up of Si_4O_{12} chain and VO_6 octahedra, and the Sr atoms are sandwiched by the pairs of the quasi-silicate sheets (TAKÉUCHI & JOSWIG, 1967).

45. Suzukiite* $\text{Ba}_2\text{V}_2^{4+}[\text{O}_2[\text{Si}_4\text{O}_{12}]]$ Orthorhombic, *Amam*

The mineral is the barium analogue of haradaite. The occurrence of this mineral is also known exclusively in metamorphosed bedded manganese ore deposits of the Tanohata mine, Iwate Prefecture (WATANABE *et al.*, 1973), the Mogurazawa mine, Gumma Prefecture (MATSUBARA *et al.*, 1982) and the Hamayokokawa mine, Nagano Prefecture (HIROWATARI & YOSHIE, 1978).

46. Pellyite $\text{Ba}_2\text{Ca}(\text{Fe}, \text{Mg})_2[\text{Si}_6\text{O}_{17}]$ Orthorhombic, *Cmcm*

The mineral occurs in a contact metasomatic skarn deposit in Yukon Territory, Canada and in barium silicates-bearing metamorphic rocks in California (MONTGOMERY *et al.*, 1972). The structure contains the chains consisting of alternately linked five- and six-membered rings of two independent Si and one Fe tetrahedra (MEAGHER, 1976). The ten-coordinated Ba ions are located within larger voids in the tetrahedral framework.

E. Phyllosilicates

47. Leucosphenite* $\text{Na}_3\text{Ba}_2\text{Ti}_4[\text{O}_4\text{B}_4\text{Si}_{20}\text{O}_{56}]$ Monoclinic, *Cm*

The mineral was described in pegmatite of an alkali rock in the Narsarsuk region in Greenland by FLINK (1901). The localities of subsequent finds are as follows: Sedimentary rocks of Green River Formation in Utah (MILTON *et al.*, 1953) and Wyoming (MILTON, 1957), pegmatite of ultrabasic-alkaline massif in Yakutia (EFIMOV & KATAYEVA, 1959) and Turkestan (DUSMATOV *et al.*, 1967),

U.S.S.R. and nepheline syenite of Mt. St. Hilaire, Quebec, Canada (CHAO *et al.*, 1967). In Japan, CHIHARA *et al.* (1974) reported the occurrence in albitite at Ohmi, Niigata Prefecture in their paper on a joaquinite-like mineral (currently termed strontio-orthojoaquinite). The original chemical formula $\text{BaNa}_4(\text{TiO})_2(\text{Si}_2\text{O}_5)_3$ has been revised from the results of new chemical analysis and the crystal structure determination (SHUMYATSKAYA *et al.*, 1968). The structure contains double sheets of $[\text{B}_4\text{Si}_{20}\text{O}_{56}]$ consisting of $[\text{Si}_{20}\text{O}_{56}]$ and two B_2O_7 double tetrahedra.

48. Gillespite $\text{Ba}_2\text{Fe}_2[\text{Si}_8\text{O}_{20}]$ Tetragonal, $P4/ncc$

The mineral was firstly described from a rock (possibly a recrystallized feldspathic rock) in Alaska by SCHALLER (1922). Later the mineral was discovered in a barium silicates-bearing metamorphic rock in California (ALFORS, 1965). The structure contains corrugated $[\text{Si}_8\text{O}_{20}]$ sheets consisting of tetragonal rings of tetrahedra (PABST, 1943). The Ba atoms are located between the sheets.

49. Sanbornite* $\text{Ba}_2[\text{Si}_4\text{O}_{10}]$ Orthorhombic, $Pcmm$

The mineral occurs in association with gillespite, witherite, quartz and other minerals from Mariposa County, California (ROGERS, 1932). The mineral is also found from several localities in barium silicates-bearing metamorphic rocks in California (ALFORS *et al.*, 1965). Although the mineral was firstly described as triclinic, the crystal structure determination by DOUGLASS (1958) confirmed the symmetry to be orthorhombic. The structure contains $[\text{Si}_4\text{O}_{10}]$ sheet consisting of distorted six-membered rings of Si tetrahedra. The nine-coordinated Ba atoms lie between each successive pair of sheets. HESSE and LIEBAU (1980) refined the structure and choose a different axial setting by exchanging a and b from the previous one. Consequently, the space group is changed into $Pmcn$.

Recently, HIROWATARI and FUKUOKA (1981) reported the occurrence of this mineral from the metamorphosed bedded manganese ore deposit of the Furumiya mine, Ehime Prefecture.

50. Chernykhite $(\text{Ba}, \text{Na})_{1-x}(\text{V}^{3+}, \text{Al})_2[(\text{OH})_2](\text{Si}, \text{Al})_4\text{O}_{10}]$ Monoclinic, $C2/c$

The mineral was described from carbonate rocks interbedded with vanadiferous shale in southern Kazakhstan, U.S.S.R. by ANKINOVICH *et al.* (1972). It is the Ba analogue of dioctahedral mica, roscoelite, with a marked deficiency of interlayer cations. The crystal structure was determined by ROZHDESTVENSKAYA and FRANK-KAMENETSKII (1974). The tetrahedral rotation angle is similar to that in trioctahedral micas rather than muscovite and margarite. The average interatomic distances from the interlayer cations to the inner and outer six oxygens are close to those in anandite (GIUSEPETTI & TADINI, 1972) and synthetic 1M Ba-Li-mica (MCCAULEY & NEWHAM, 1969).

51. Anandite $(\text{Ba}, \text{K}, \text{Na})(\text{Fe}, \text{Mg}, \text{Mn})_3(\text{Si}, \text{Al}, \text{Fe})_4\text{O}_{10}(\text{OH}, \text{S}, \text{Cl})_2$ Orthorhombic, $Pnmm$

The mineral was found in magnetite ore capped by banded magnetite-barite rock in Ceylon (PATTIARATCHI *et al.*, 1967), as the first Ba-bearing brittle mica. The original authors have considered that sulphur in two chemical analyses is due to the admixed pyrite and have led the ideal chemical formula $(\text{Ba}, \text{K})(\text{Fe}, \text{Mg})_3(\text{Si}, \text{Al}, \text{Fe})_4\text{O}_{10}(\text{O}, \text{OH})_2$. However, GIUSEPETTI and TADINI (1972) proposed a revised formula $\text{Ba}(\text{Fe}^{3+}, \text{Fe}^{2+})_3[\text{Si}_2(\text{Fe}^{3+}, \text{Fe}^{2+}, \text{Si})_2\text{O}_{10-x}(\text{OH})_x](\text{S}, \text{Cl})(\text{OH})$ from the results of their structure determination for 2 O-polytype and electron microprobe analysis by LOVERING and WIDOWSON (1968). They confirmed that sulphur is the essential constituent of the mineral, i.e., sulphur completes the octahedral coordination and also bridges the interlayer cation through a hole of the tetrahedral layer. Anandite has an extraordinarily large unit cell as compared with the other brittle micas, especially in a and b dimensions.

52. Kinoshitalite* $(\text{Ba}, \text{K})(\text{Mg}, \text{Mn}, \text{Al})_3[(\text{OH}, \text{F})_2]\text{Si}_2\text{Al}_2\text{O}_{10}]$ Monoclinic, $C2/m$

The mineral is the barium analogue of manganoan phlogopite. It is found in metamorphosed bedded manganese ore deposits of the Nodatamagawa mine, Iwate Prefecture (YOSHII *et al.*, 1973), Hokkejino, Kyoto Prefecture (MATSUBARA *et al.*, 1976), the Taguchi mine, Aichi Prefecture (ISHIDA & HIROWATARI, 1979) and the Ioi mine, Shiga Prefecture. The chemical composition of kinoshitalite in Hokkejino has the relation $\text{F} > \text{OH}$ in mole ratio, which is unique to all the known brittle micas.

High iron kinoshitalites have been described from nephelinites in Hawaii by MANSKER *et al.* (1979).

The crystal structure of 1M-polytype has been described by KATO *et al.* (1979). The atomic coordinates are similar to those of 1M-biotite rather than those of the calcium brittle micas.

53. Macdonaldite $\text{BaCa}_4\text{H}_2[\text{Si}_{16}\text{O}_{38}] \cdot 10\text{H}_2\text{O}$ Orthorhombic, *Cmcm*

The mineral is one of the seven new minerals in barium silicates-bearing metamorphic rocks in California (ALFORS *et al.*, 1965). In the structure two single layers containing four-membered rings are joined by every fourth tetrahedron with sharing one oxygen atom (CANNILLO *et al.*, 1968).

54. Cymrite* $\text{Ba}[\text{Al}_2\text{Si}_2\text{O}_8] \cdot \text{H}_2\text{O}$ Monoclinic, *P2₁*

The mineral was firstly described as hexagonal $\text{BaAlSi}_3\text{O}_8(\text{OH})$ from the Benallt mine, Wales, U. K. (SMITH *et al.*, 1949). Later, RUNNELLS (1964) reported the occurrence from Alaska, and the chemical composition was $2\text{BaO} \cdot 2.5\text{Al}_2\text{O}_3 \cdot 5\text{SiO}_2 \cdot 3.65\text{H}_2\text{O}$, being more aluminous and hydrous than the original one. In 1966 KASHAEV has determined the crystal structure of the Baikalian cymrite with the formula $(\text{Ba}, \text{H}_3\text{O})\text{Al}_2\text{Si}_2(\text{O}, \text{OH})_3 \cdot \text{H}_2\text{O}$ and the space group *P2₂2* for the Alaskan material described by RUNNELLS (1964). However, they determined the x-y atomic coordinates only. DRITS *et al.* (1975) have established the space group to be *P2₁* on the material from California with the chemical formula $\text{BaAl}_2\text{Si}_2\text{O}_8 \cdot \text{H}_2\text{O}$ described by ESSENE (1967). The structure involves double pseudo-hexagonal sheets parallel to (001). The nine-coordinated Ba atoms are between these sheets. The structure of cymrite is basically similar to that of α -hexagonal $\text{BaAl}_2\text{Si}_2\text{O}_8$ (TAKÉUCHI, 1958).

In Japan the present author and coworkers have confirmed the occurrence of cymrite from weakly metamorphosed bedded manganese ore deposits of the Shiromaru mine, Tokyo Prefecture, the Ohmiya mine, Saitama Prefecture, the Mogurazawa mine, Gumma Prefecture and the Yumiyama mine, Kyoto Prefecture, and from a xenolith in ultrabasic rock at Sarusaka, Kochi Prefecture.

F. Tectosilicates

55. Celsian* $\text{Ba}[\text{Al}_2\text{Si}_2\text{O}_8]$ Monoclinic, *I2/c*

It occurs mainly in manganese ore deposits and barium silicates-bearing metamorphic rocks. In Japan the mineral is found from the metamorphosed manganese ore deposits of the Kaso mine, Tochigi Prefecture (YOSHIMURA, 1936), the Shiromaru mine, Tokyo Prefecture, the Hamayokokawa mine, Nagano Prefecture (HIROWATARI & YOSHIE 1978), the Nodatamagawa mine, Iwate Prefecture and Hokkejino, Kyoto Prefecture (MATSUBARA *et al.*, 1976). The occurrence is also known from a xenolith in ultrabasic rock at Sarusaka, Kochi Prefecture (KATO & MATSUBARA, 1980b). Hyalophane is found in some hydrothermal veins and metamorphosed manganese ore deposits. The occurrence is more common than celsian.

The crystal structure was determined by NEWNHAM and MEAGAW (1960). Another monoclinic polymorph, paracelsian, and hexagonal and orthorhombic modifications of synthetic $\text{BaAl}_2\text{Si}_2\text{O}_8$ do not belong to the feldspar group because of their different framework structures.

56. Paracelsian $\text{Ba}[\text{Al}_2\text{Si}_2\text{O}_8]$ Monoclinic, *P2_{1/a}*

The mineral name was first used to indicate a poor-cleavable "celsian" from Candoglia, Italy by TACCONI (1905). The optical properties, however, are rather close to those of the ordinary celsian, and was later identified as celsian. But the material described by SPENCER (1942) from the Benallt mine, Wales under the name of paracelsian was considered to be an orthorhombic polymorph of celsian. Later the crystal structural studies by SMITH (1953) confirmed it to be monoclinic (pseudo-orthorhombic). CRAIG (1973) refined the structure which has completely ordered Al/Si distribution in its framework being thus geometrically similar to that of danburite, though different in the $\text{T}^{3+}/\text{T}^{4+}$ ordering scheme (PHILLIPS *et al.*, 1974).

57. Slawsonite* $\text{Sr}[\text{Al}_2\text{Si}_2\text{O}_8]$ Monoclinic, *P2_{1/a}*

The mineral is the strontium analogue of paracelsian (GRIFFEN *et al.*, 1977). It occurs in meta-

morphosed limestone of the Triassic Martin Bridge Formation, Oregon. KATO and MATSUBARA (1980b) have reported the second occurrence from a xenolith in ultrabasic rock at Sarusaka, Kochi Prefecture. Subsequently they discovered the mineral from Miyatotani and Rendai, Kochi Prefecture.

58. Banalsite* $\text{BaNa}_2[\text{Al}_4\text{Si}_4\text{O}_{16}]$ Orthorhombic, *Ibam*

The mineral is known from the Benallt mine, Wales (SMITH *et al.*, 1944) and Långban, Sweden (WELIN, 1968). It is chemically related to celsian or paracelsian due to the substitution of Na_2 for Ba. The crystal structure has been established by HAGA (1973) who discussed the relationship to feldspar structures.

The present author and coworkers recognize the occurrence of banalsite in association with cymrite and celsian from the Shiromaru mine, Tokyo Prefecture as the third occurrence of the mineral (KATO *et al.*, 1983).

59. Stronalsite* $\text{SrNa}_2[\text{Al}_4\text{Si}_4\text{O}_{16}]$ Orthorhombic *Ibam* or *Iba2*

The mineral is the strontium analogue of banalsite (HORI *et al.*, 1983). It occurs in rodingite at Rendai, Kochi Prefecture in association with slawsonite and pectolite. Though the crystal structure has not been established, the X-ray powder diffraction pattern and other physical properties indicate that stronalsite is isostructural with banalsite.

60. Wenkite $\text{Ba}_4(\text{Ca}, \square)_6[\text{OH}](\text{SO}_4)_3[\text{Si}_{12}\text{Al}_3\text{O}_{30}(\text{OH})] \cdot n\text{H}_2\text{O}$ Hexagonal, $P\bar{6}2m$

The mineral occurs in marble between barite layers and calcsilicate rock at Candoglia, Italy (PAPAGEORGAKIS, 1962). He gave the chemical formula as $(\text{Ba}, \text{Ca})_7\text{Al}_6\text{Si}_{12}(\text{SO}_4)_2\text{O}_{42}(\text{OH})_5$ and mentioned the relation to cancrinite. But WENK (1973) proposed the chemical formula as above from the result of his structural determination and electron microprobe analysis. The structure involves an Al/Si framework similar to that in cancrinite and gmelinite. The BaSO_4 chains extend through cavities of eight-membered rings of tetrahedra.

61. Edingtonite $\text{Ba}[\text{Al}_2\text{Si}_3\text{O}_{10}] \cdot 4\text{H}_2\text{O}$ Orthorhombic, $P2_12_12$

The mineral is one of the barium zeolites and occurs as pseudo-tetragonal prismatic crystals in cavities of basalt and nepheline syenite. The crystal structure was at first determined after the tetragonal space group $P\bar{4}_21m$ by TAYLOR and JACKSON (1933) who pointed out the true space group to be $P2_12_12$. In 1976 GALLI has refined the structure in the orthorhombic space group $P2_12_12$. The structure is based on cross-linked chains composed of linked units of five tetrahedra.

62. Brewsterite $(\text{Sr}, \text{Ba}, \text{Ca})[\text{Al}_2\text{Si}_3\text{O}_{10}] \cdot 5\text{H}_2\text{O}$ Monoclinic, $P2_1/m$

The mineral is known as the unique strontium zeolite in cavities of basalt and schist. It is classified in heulandite-stilbite group including $\text{T}_{10}\text{O}_{20}$ units of tetrahedra in the framework (PEROTTA & SMITH, 1964).

63. Harmotome* $\text{Ba}[\text{Al}_2\text{Si}_3\text{O}_{10}] \cdot 6\text{H}_2\text{O}$ Monoclinic $P2_1/m$

The mineral is one of the barium zeolites and has the same framework of linked four- and eight-membered rings as phillipsite (SADANAGA *et al.*, 1961; RINALDI *et al.*, 1974). The structure is closely related to that of feldspars.

It occurs in cavities of volcanic rocks and tuffs, sedimentary rocks and gneiss. In Japan two confirmed occurrences are known from Udo, Shimane Prefecture (KINOSHITA, 1922) and the Shiromaru mine. Barian phillipsite is common rather than harmotome.

* occurs in Japan

