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SUBSOLIDUS SKARN EQUILIBRIA IN THE SYSTEM $CaSiO_3$–$CaMgSi_2O_6$–$CaFeSi_2O_6$–$CaMnSi_2O_6$

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ABSTRACT

Based on chemical compositions of minerals of the bustamite–ferrobustamite series from three new localities in Japan, a complete solid solution is suggested from bustamite, ideally of composition $CaMnSi_2O_6$, through $CaSiO_3$-rich bustamite, to ferrobustamite of composition $Ca_5FeSi_6O_{18}$, at relatively low temperatures. Bustamite–ferrobustamite solid solutions and wollastonite from skarns or similar environments are essentially free of $MgSiO_3$ and belong to the system $CaSiO_3$–$CaFeSi_2O_6$–$CaMnSi_2O_6$, whereas clinopyroxenes associated with these pyroxenoids belong strictly to the system $CaMgSi_2O_6$–$CaFeSi_2O_6$–$CaMnSi_2O_6$. The field of such clinopyroxenes can be divided into three distinct compositional regions depending on the associated pyroxenoids.

SOMMAIRE

Nous proposons une série complète de solutions solides, à température relativement basse, allant de la bustamite ($CaMnSi_2O_6$) à la ferrobustamite ($Ca_5FeSi_6O_{18}$), en passant par les bustamites riches en $CaSiO_3$. Les solutions solides bustamite–ferrobustamite et la wollastonite des skarns ou de milieux analogues contiennent très peu de $MgSiO_3$; ces pyroxénoïdes font partie du système $CaSiO_3$–$CaFeSi_2O_6$–$CaMnSi_2O_6$, tandis que les clinopyroxènes qui leur sont associés figurent dans le système $CaMgSi_2O_6$–$CaFeSi_2O_6$–$CaMnSi_2O_6$. Le domaine de composition de tels clinopyroxènes peut se subdiviser en trois régions distinctes selon les pyroxénoïdes associés.

(Traduit par la Rédaction)

INTRODUCTION

Tilley (1937, 1947, 1948) first described natural "iron-wollastonite" from basic igneous rocks and a contact skarn; the mineral has not been reported again until recently, except for one occurrence in andesite lava (Isshiki 1954). Our understanding of this mineral has recently made rapid progress: Rutstein (1971) redetermined the position of the solvus along the join $CaSiO_3$–$CaFeSi_2O_6$ first described in the classic work of Bowen *et al.* (1933); Rutstein suggested that relatively iron-rich "iron-wollastonite" would have a bustamite-type rather than a wollastonite-type structure. In 1973, several important papers were published. Rapoport & Burnham (1973) found that "iron-wollastonite" from a contact skarn in Skye (Tilley 1948), as well as $CaFeSi_2O_6$ synthesized at 1108°C and 2 kbar, has the bustamite-type structure. Matsueda (1973a) described the occurrence of "iron-wollastonite" from the Sampo mine, Japan, and drew attention to the distinct physical properties of the mineral in comparison to those of wollastonite. Shimazaki & Yamanaka (1973) also reported new occurrences of a mineral with the bustamite-type structure from three localities in Japan, the Kagata, Ofuku and Ohta mines, and demonstrated that the mineral is a discrete phase, ideally $Ca_5FeSi_6O_{18}$, in the system $CaSiO_3$–$CaFeSi_2O_6$. Indeed, close associations of wollastonite and "iron-wollastonite" in natural specimens were interpreted by Matsueda (1974a,b) as clear evidence of a miscibility gap between these minerals.

The fact that the composition of all analyzed "iron-wollastonites" from various skarn deposits is very close to $Ca_5FeSi_6O_{18}$ led Shimazaki & Yamanaka (1973) to postulate that iron is restricted to one site among the six cation sites in the bustamite structure. This site preference of iron, due to its small ionic radius, was recently confirmed by Yamanaka *et al.* (1977). At present, "iron-wollastonite" has been recognized from more than ten localities in Japan. Based on the works cited above, tentative phase relations along the join $CaSiO_3$–$CaFeSi_2O_6$ are given in Figure 1.

Knowledge of low-temperature phase relations involving bustamite has also been accumulating (*e.g.*, Mason 1973, 1975; Hodgson 1975, Nambu *et al.* 1977). In the present paper, new data are presented on the composition and phase relations of minerals in the quaternary system $CaSiO_3$–$CaMgSi_2O_6$–$CaFeSi_2O_6$–$CaMnSi_2O_6$ from three localities in Japan, with a summary of low-temperature phase relations in this system. In accordance with Rapoport's & Burnham's (1973) nomenclature and Mason's (1975) definition, *ferrobustamite* refers here to a phase with the bustamite-type structure and with a ratio $Fe/(Fe+Mn) > 0.5$; this name has not yet been approved by the Commission on New Minerals and Mineral Names, I.M.A.

In the present discussion, only the phases occurring in skarns or similar environments will be considered. Little has been reported as to temperature conditions for these skarn deposits. From the intimate association with granitic intrusions, however, the deposits are thought to be genetically related and to have formed at temperatures below 600°C. Although no information is available on the crystal structure of "iron-wollastonite" from igneous environments (Tilley 1937, 1947; Isshiki 1954), these occurrences could be *true* iron-bearing wollastonites because they were probably formed at temperatures above 800°C. At these temperatures, wollastonite can contain considerable iron, as experimentally determined by Rutstein (1971).

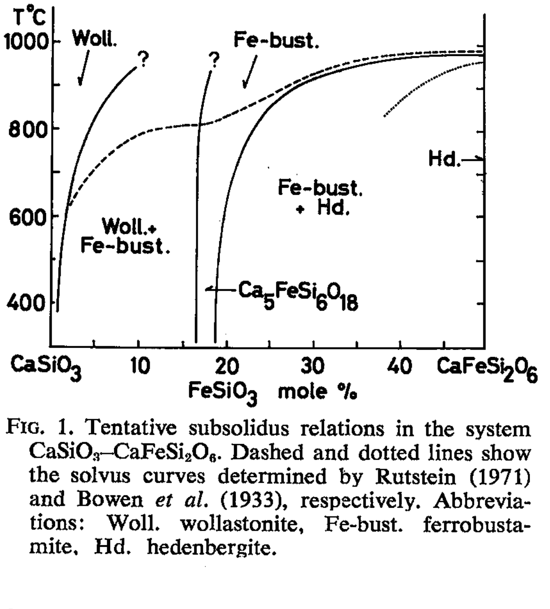

FIG. 1. Tentative subsolidus relations in the system $CaSiO_3$–$CaFeSi_2O_6$. Dashed and dotted lines show the solvus curves determined by Rutstein (1971) and Bowen *et al.* (1933), respectively. Abbreviations: Woll. wollastonite, Fe-bust. ferrobustamite, Hd. hedenbergite.

DESCRIPTION OF SPECIMENS

In the present study, specimens from three localities were investigated.

Specimens were taken from the Kasugayama deposit, located about 10 km southwest of Iida City, Nagano Prefecture. A small skarn mass replacing a limestone lens is observed in biotite schist of the Ryoke metamorphic belt. The Ryoke metamorphic rocks, including biotite schist and thin beds of chert and limestone, are intruded by granitic rocks of late Cretaceous age. The outcrop of the skarn mass was once prospected for tungsten. Three specimens collected from the outcrop were studied with an electron microprobe analyzer.

Main constituents of the skarn are grossular, having important spessartine and almandine components, ferrosalite to hedenbergite, vesuvianite, wollastonite, ferrobustamite, actinolite, epidote with 14–17 mol. % pistacite component, titanite with Al_2O_3 up to about 9 wt. %, scheelite, pyrrhotite, quartz and calcite. As clearly indicated by these minerals, the skarn is generally poor in ferric iron. This characteristic of some scheelite skarns in Japan (Shimazaki 1974, 1977) is thought to be genetically related to the relatively reduced nature of associated granitic rocks (Shimazaki 1976).

A specimen from Tsuchiarashi (*UMMI* 20337) was labeled *wollastonite* in the collection of the University Museum, University of Tokyo. The deposit is located about 15 km south-southeast of Iida City, Nagano Prefecture, and was prospected for zinc and lead several decades ago. The area consists of Ryoke metamorphic rocks, including biotite schist with small limestone lenses, and Ryoke gneissose granitic rocks. The specimen is a skarn consisting of fibrous ferrobustamite partly replaced by calcite and quartz, grossular with minor andradite, spessartine and almandine components (up to 10 mol. % each), and hedenbergite with a considerable johannsenite component.

A specimen from Kurodaké (*UMMI* 20632) was also labeled *wollastonite* in the University Museum collection, University of Tokyo. Kurodaké, a peak of about 3000 m in height, is located about 35 km southeast of Toyama City, Toyama Prefecture. The mineral paragenesis of these skarns was described by Fukuchi (1907); an old chemical analysis of garnet from this locality indicates grossular with about 9 wt. % MnO (Wada 1904). Ohmori (1941) reported that garnet from this locality is andradite. According to Fukuchi (1907), the skarns contain garnet, clinopyroxene, epidote, magnetite and quartz, and formed in limestone beds as a result of the intrusion of diorite; we have not yet had a chance to study the detailed geology of the area. Our specimen consists of fibrous bustamite, euhedral andradite showing distinct zoning with anomalous anisotropism under the microscope, clinopyroxene, quartz and calcite. As will be shown below, the compositions of bustamite and clinopyroxene are very variable in this specimen.

Analytical Procedure and Results

Three ferrobustamite-bearing specimens from Kasugayama, and two each from Tsuchiarashi and Kurodaké, were studied in detail with an electron microprobe analyzer. Count ratios of sample to standard were measured for Si, Al, Fe, Mn, Mg and Ca. The ratios were converted into oxide weight percentages using the method of Bence & Albee (1968). Detailed descriptions of the analytical procedure and the correction factors used in this study have been given by Nakamura & Kushiro (1970). In the present study, the totals of the corrected weight percentages of SiO_2, Al_2O_3, FeO, MnO, MgO and CaO generally fall in the range of 98.5 to 101.5%.

Selected analyses are given in Table 1. Compositions of coexisting phases are connected by a line in the table. A part of a specimen from Kasugayama (No. *HS*76041815) includes a mixture of subhedral crystals of three phases, ferrobustamite, clinopyroxene and wollastonite (Nos. 1–3 in Table 1). In this specimen, two two-phase assemblages, such as ferrobustamite + clinopyroxene and clinopyroxene + wollastonite, are also observed (Nos. 4–5 and 6–7 in Table 1). Clinopyroxene in contact with ferrobustamite is notably richer in hedenbergite than clinopyroxene near wollastonite. Ferrobustamites from Kasugayama and Tsuchiarashi have rather constant compositions in each specimen. On the other hand, bustamites and clinopyroxenes from Kurodaké show remarkable and irregular compositional variations. In bustamites, manganese and calcium seem to substitute for each other, with iron relatively constant. Typical analyses of bustamites and associated clinopyroxenes are given in Table 1 as Nos. 12–16 in order to show the range of variation.

Bustamite–Ferrobustamite Solid Solution

As stated above, occurrences of ferrobustamite have been recognized at more than ten localities in Japan, in addition to Skye, Scotland (Tilley 1948). These ferrobustamites are variable in composition, and ferrobustamites from Tsuchiarashi (*e.g.*, 10 in Table 1) are the richest in manganese. All analyses of ferrobustamites obtained in this study and reported in the literature are plotted (Fig. 2), as well as some analyses of CaO-rich bustamites from Broken Hill (Mason 1973), Hijikuzu (Nambu *et al.* 1977), and Kurodaké (this study).

These pyroxenoids usually contain less than 1.0 mol. % $MgSiO_3$. The maximum value among analyses plotted in Figure 2 is about 2.5 mol. % $MgSiO_3$ (data from wet chemical analyses of two bustamites from metamorphosed bedded manganese ore-deposits of the Hijikuzu mine: Nambu *et al.* 1977). This fact would justify plotting the analyses on a $CaSiO_3$–$CaFeSi_2O_6$–$CaMnSi_2O_6$ (or $CaSiO_3$–$FeSiO_3$–$MnSiO_3$) diagram.

Based on the distribution of chemical compositions, Nambu *et al.* (1977) suggested that

TABLE 1. ELECTRON PROBE ANALYSES OF BUSTAMITE SOLID SOLUTIONS, CLINOPYROXENES & WOLLASTONITES

No.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
Mineral & assemblage	FBS	CPX	WO	FBS	CPX	CPX	WO	FBS	CPX	FBS	CPX	BS	BS	BS	CPX	CPX
SiO_2	50.2	48.9	51.0	49.6	48.5	49.1	51.1	50.9	49.2	50.1	47.8	47.8	49.0	49.7	47.7	49.5
Al_2O_3	0.2	0.5	0.2	0.2	0.4	0.4	0.2	0.2	0.3	0.0	0.3	0.0	0.0	0.0	0.1	0.0
FeO*	7.0	19.9	0.8	6.9	22.9	19.9	0.7	7.3	23.1	6.3	20.1	3.8	4.0	4.2	13.1	11.2
MnO	4.5	3.5	1.5	5.2	2.6	3.1	1.2	4.7	3.5	5.6	7.2	18.3	15.3	8.6	14.2	11.6
MgO	0.2	3.6	0.1	0.1	1.8	4.1	0.1	0.1	1.7	0.1	0.8	0.0	0.0	0.1	1.3	3.9
CaO	37.9	22.9	46.3	37.6	22.9	23.3	46.6	38.3	22.7	37.7	22.4	28.3	31.0	36.5	22.5	23.2
Total	100.0	99.3	99.9	99.6	99.1	99.9	99.9	101.5	100.5	99.8	98.6	98.2	99.3	99.1	98.9	99.4
Numbers of cations on the basis of 18 oxygens																
Si	5.97	5.94	5.96	5.95	5.97	5.93	5.97	5.98	5.98	5.98	5.97	5.94	5.98	5.99	5.94	5.99
Al	0.02	0.07	0.03	0.03	0.06	0.06	0.03	0.02	0.04	0.00	0.04	0.00	0.00	0.00	0.01	0.00
Fe	0.70	2.02	0.08	0.69	2.35	2.01	0.07	0.71	2.35	0.62	2.10	0.40	0.41	0.42	1.36	1.13
Mn	0.45	0.36	0.15	0.53	0.27	0.32	0.12	0.46	0.36	0.56	0.76	1.93	1.58	0.87	1.49	1.19
Mg	0.04	0.65	0.02	0.02	0.33	0.74	0.02	0.02	0.31	0.02	0.15	0.00	0.00	0.02	0.24	0.70
Ca	4.82	2.98	5.79	4.82	3.02	3.01	5.82	4.82	2.95	4.82	2.99	3.78	4.05	4.71	3.00	3.00
Mole % of end members																
$CaSiO_3$	80.2	49.6	95.9	79.5	50.6	49.5	96.5	80.2	49.4	80.1	49.8	61.9	67.1	78.2	49.3	49.8
$MnSiO_3$	7.5	6.0	2.5	8.7	4.5	5.2	2.0	7.7	6.0	9.3	12.7	31.6	26.2	14.5	24.5	19.8
$FeSiO_3$	11.6	33.6	1.3	11.4	39.4	33.1	1.2	11.8	39.4	10.3	35.0	6.5	6.8	7.0	22.3	18.8
$MgSiO_3$	0.7	10.8	0.3	0.3	5.5	12.2	0.3	0.3	5.2	0.1	2.5	0.0	0.0	0.3	3.9	11.6

* Total Fe as FeO. Nos. 1-7: HS76041815 Kasugayama. Nos. 8-9: HS76041516 Kasugayama. Nos. 10-11: No. 20337 Tsuchiarashi. Nos. 12-16: No. 20632 Kurodaké. BS: bustamite, CPX: clinopyroxene, FBS: ferrobustamite, WO: wollastonite.

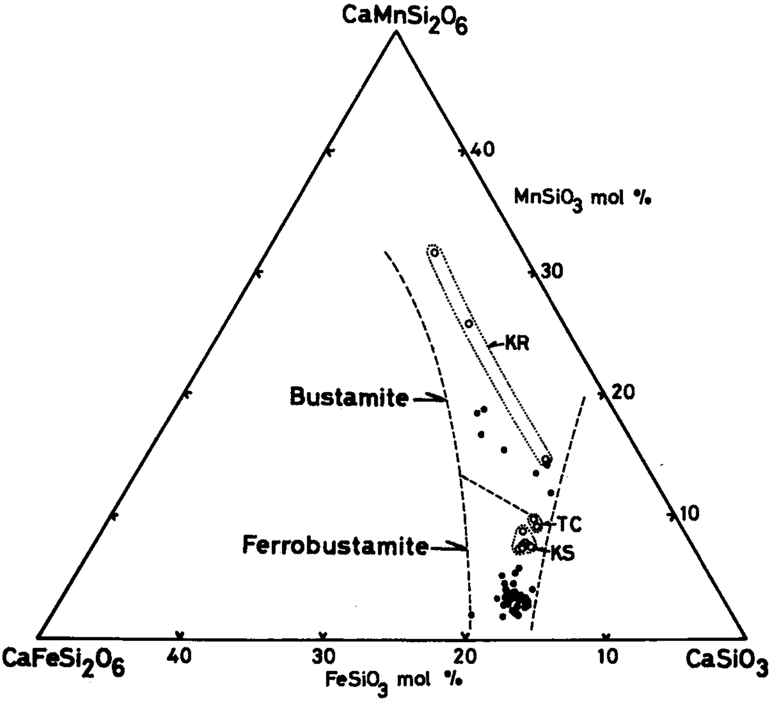

FIG. 2. Compositional distribution of bustamite–ferrobustamite solid solutions. Solid circles: analyses from the literature, including Tilley (1948, Skye), Rapoport & Burnham (1973, Skye), Matsueda (1973a,b, 1974a,b; Sampo, Kasuga, Tojo, Ohminé), Mason (1973, Broken Hill), Shimazaki & Yamanaka (1973, Kagata, Ofuku, Ohta), Matsuoka (1976, Tsumo) and Nambu *et al.* (1977, Hijikuzu). Open circles: this study (KR from Kurodaké, TC Tsuchiarashi and KS Kasugayama).

CaO–rich bustamite solid solutions could be divided into three groups: bustamite near $CaMnSi_2O_6$, CaO–rich bustamites such as those from Broken Hill and Hijikuzu, and ferrobustamites (conventional "iron-wollastonite"). As clearly shown in Figure 2, however, ferrobustamites from Tsuchiarashi and Kasugayama have compositions between CaO–rich bustamites and ferrobustamites close to $Ca_5FeSi_6O_{18}$ in composition. The composition of bustamites from Kurodaké extends over regions of CaO–rich bustamites and bustamites near $CaMnSi_2O_6$. These relations could be taken as evidence of complete solid solution from ferrobustamite of $Ca_5FeSi_6O_{18}$ composition to bustamite *s.s.* ($CaMnSi_2O_6$) at relatively low temperatures. Further mineralogical and mineral synthesis studies will be necessary to confirm the complete solid solution from bustamite to ferrobustamite.

Assuming implicitly the presence of a continuum between bustamite and ferrobustamite, Mason (1975) gave the compositional range of these minerals. Taking the results of this study and those of the study on Broken Hill minerals by Hodgson (1975) into account, the tentative compositional limit of the bustamite–ferrobustamite solid solution at relatively low temperatures is also given in Figure 2.

Matsueda (1974a) described a $CaSiO_3$–rich phase with about 9 mol. % $FeSiO_3$ and 6 % $MnSiO_3$ from the Sampo mine. Although its crystal structure is uncertain, the mineral could be a member of bustamite–ferrobustamite solid solution. Mel'nitskaya (1967) described an occurrence of "manganoferrous wollastonite" with 9–10 mol. % of both $FeSiO_3$ and $MnSiO_3$, from a Russian skarn deposit. The crystal structure of the mineral is again uncertain, but it is probably a member of bustamite–ferrobustamite solid solution, having a composition similar to those reported here from Tsuchiarashi.

SUBSOLIDUS PHASE RELATIONS IN THE SYSTEM $CaSiO_3$–$CaMgSi_2O_6$–$CaFeSi_2O_6$–$CaMnSi_2O_6$

Assemblages of bustamite–ferrobustamite plus wollastonite or clinopyroxene (or both) could be described as representative of subsolidus phase relations in the system $CaSiO_3$–$CaMgSi_2O_6$–

$CaFeSi_2O_6$–$CaMnSi_2O_6$. The phase relations in this system were previously inferred from 'ternary" systems such as $CaSiO_3$–$Ca(Mg,Fe)Si_2O_6$–$CaMnSi_2O_6$ or $CaSiO_3$–$CaMgSi_2O_6$–$Ca(Fe,Mn)Si_2O_6$ (*e.g.*, Mason 1973, Matsueda 1973b, Shimazaki & Yamanaka 1973, Hodgson 1975). As shown in the previous section, bustamite–ferrobustamite solid solutions, as well as wollastonite, essentially belong to the ternary system $CaSiO_3$–$CaFeSi_2O_6$–$CaMnSi_2O_6$. It is evident, however, that clinopyroxenes associated with these pyroxenoids cannot be represented in that system; compositions of these minerals must be discussed in the quaternary system $CaSiO_3$–$CaMgSi_2O_6$–$CaFeSi_2O_6$–$CaMnSi_2O_6$.

An examination of the chemical compositions of clinopyroxenes associated with bustamite–ferrobustamite solid solutions or wollastonite (or both) reveals that their $CaSiO_3$ contents are mostly in the range of 50 ± 1 mol. %, although there are a few exceptions: *e.g.*, about 54 mol. % $CaSiO_3$ in two clinopyroxenes from the Sampo mine, determined by wet chemical analysis (Matsueda 1973b). This fact indicates that the clinopyroxenes associated with the pyroxenoids can be represented on the ternary system $CaMgSi_2O_6$–$CaFeSi_2O_6$–$CaMnSi_2O_6$. In contrast, clinopyroxenes associated with relatively CaO-poor bustamites are subcalcic in composition, and their $CaSiO_3$ contents are less than 50 mol. %. These relations are clearly recognized in the assemblages from Broken Hill, which are given in $CaSiO_3$–$MnSiO_3$–$(Fe,Mg,Zn)SiO_3$ diagrams by Mason (1973) and Hodgson (1975), although neither reports specific chemical analyses of coexisting minerals.

In summary, the pyroxenoids of bustamite–ferrobustamite solid solution and wollastonite appear not to contain appreciable $MgSiO_3$, and clinopyroxenes associated with these pyroxenoids are saturated with $CaSiO_3$ at about 50 mol. %. Accordingly, two triangular diagrams, $CaSiO_3$–$CaFeSi_2O_6$–$CaMnSi_2O_6$ and $CaMgSi_2O_6$–$CaFeSi_2O_6$–$CaMnSi_2O_6$ suffice to describe the compositions of coexisting phases belonging to this quaternary system. Figure 3 illustrates these two planes of the tetrahedron.

In order to investigate the phase relations between pyroxenoid and clinopyroxene in the system, results of reliable chemical analyses of natural two- and three-phase assemblages are plotted (Fig. 3), together with our results from

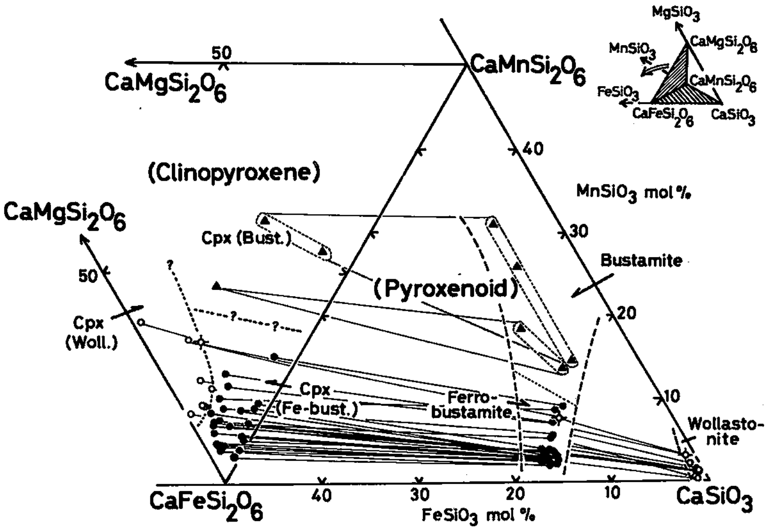

FIG. 3 Subsolidus phase relations in the $CaSiO_3$-rich portion of the system $MgSiO_3$–$FeSiO_3$–$MnSiO_3$–$CaSiO_3$. Open circles show the compositions of coexisting clinopyroxene and wollastonite, solid circles clinopyroxene and ferrobustamite, and solid triangles clinopyroxene and bustamite. Open circles with a cross represent the compositions of coexisting clinopyroxene, wollastonite and ferrobustamite from Kasugayama (Table 1, Nos. 1–3). The abbreviations cpx(bust.), cpx(Fe-bust.) and cpx(woll.) indicate fields of clinopyroxenes able to coexist with bustamite, ferrobustamite and wollastonite, respectively.

Table 1. Unfortunately no analyses of three-phase assemblages are found in the literature, except for one wollastonite–ferrobustamite–clinopyroxene assemblage obtained in the present study (analyses Nos. 1–3 in Table 1). These analyses are plotted in Figure 3 as open circles with a cross.

In Figure 3, solid triangles indicate the compositions of bustamites and associated clinopyroxenes. They include analyses of minerals from Kurodaké (Table 1, Nos. 12–16) and Hijikuzu (Nambu *et al.* 1970, 1977). They show wide variations, as stated previously in the case of Kurodaké, even in one thin section, and the number of analyses in the bustamite field of Figure 3 is not equal to the number of analyses in the field labeled clinopyroxene (bust.). With this exception, each open or solid circle in the pyroxenoid fields is connected by a tie-line with a corresponding circle in the clinopyroxene fields. Although some tie-lines cross, most of them seem to be mutually consistent, considering the limit of analytical error and possible temperature variations at the time of formation.

The composition of clinopyroxene described as being associated with "iron-wollastonite" from Skye was determined by wet analysis of a bulk composition with impurities (Tilley 1948). The result is exceptionally rich in the diopside component as compared with other clinopyroxenes associated with ferrobustamite, and is not plotted in the figure. With respect to the assemblage wollastonite–ferrobustamite, Matsueda (1974a,b) and Matsuoka (1976) have already given compositions of coexisting pairs from several Japanese skarn deposits, and these data are not repeated in the figure in the interest of clarity.

As shown in Figure 3, the field of clinopyroxene could be divided into three compositional regions, depending on the associated pyroxenoids. In the diopside–hedenbergite series, a composition of about 85–90 mol. % hedenbergite seems to divide the clinopyroxenes into those that can coexist with wollastonite and those that can coexist with ferrobustamite. The introduction of a johannsenite component expands the field of clinopyroxenes that can coexist with ferrobustamite. Finally, clinopyroxenes that are richer still in johannsenite are associated with bustamites.

Near the $CaMnSi_2O_6$ corner in Figure 3, johannsenite is unstable with respect to bustamite under the conditions being considered, especially at temperatures above 400°C (Lamb *et al.* 1972). But at temperatures below 400°C, johannsenite could be the stable phase instead of bustamite, and the field of bustamite may possibly disappear near the $CaMnSi_2O_6$ corner. The phase relations of minerals close to $CaMnSi_2O_6$ in composition remain a problem. If data were available on the compositions of clinopyroxenes that are relatively rich in diopside and johannsenite and associated with wollastonite or bustamite or both, it would be possible to extend the boundary between clinopyroxenes coexisting with wollastonite and those coexisting with bustamite in Figure 3. Unfortunately we could not find reliable compositional data on such clinopyroxenes in the literature.

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