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Compositional Limits of Wollastonite and Bustamite

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Abstract

The compositions of naturally occurring wollastonite and bustamite show that a narrow composition gap separates these two minerals. Iron-free wollastonite from Franklin, New Jersey, with up to 8.1 percent MnO coexists with bustamite with 12.3 percent MnO and 0.7 percent FeO. The maximum iron content found in wollastonite is 2.23 percent FeO in a specimen from Scawt Hill, Ireland. The limiting composition recorded for ferrobustamite is 9.29 percent FeO, 1.22 percent MnO, and 38.86 percent CaO in a specimen from Skye, Scotland.

Introduction

The late Dr. W. T. Schaller did considerable unpublished research on the compositional limits of wollastonite and bustamite. After his death in 1967 his material and notes were transferred to the Department of Mineral Sciences in the Smithsonian Institution for curating and preservation. His collection of nine analyses of bustamite, all from Broken Hill, Australia, has recently been published (Mason, 1973). His notes also include the following partial analyses of wollastonite:

	FeO	MnO	MgO
Potash Sulphur Springs, Arkansas	0.50	0.68	none
Gjellebekk, Oslo region, Norway	0.67	6.29	0.24
Orange Hill, Nabesna R., Alaska	0.31	1.76	--

For the Norwegian specimen he gave the refractive indices and density: $\alpha = 1.631$, $\beta = 1.644$, $\gamma = 1.646$; $D = 3.00$.

Experimental Results

These notes stimulated my interest, and to study the problem further I have analyzed with the microprobe 16 specimens of wollastonite, selected from as wide a range of parageneses as possible. The nine elements Si, Al, Fe, Mg, Ca, Na, K, Ti, and Mn were looked for; of these only Si, Fe, Ca, and Mn were present in measurable amounts, the remaining elements being at or below background (≤ 0.1 percent). Evidently the wollastonite structure is relatively intolerant of substitution by related elements. Of particular interest is the practical absence of Mg, even in rocks containing appreciable amounts of this element; in such rocks the wollastonite is associated with diopsidic pyroxene.

Many of the analyzed wollastonites are from metamorphosed limestones associated with quartz and/or calcite, diopsidic pyroxene, and garnet (grossular-andradite). These wollastonites are generally close to pure $CaSiO_3$ in composition, evidently reflecting the relative absence of the substituting elements Fe and Mn in the original rock and the lack of metasomatic additions of these elements. Table 1 gives a selection of the analytical data. The highest iron content is 2.2 percent FeO in wollastonite from the limestone-dolerite contact at Scawt Hill, Ireland (Tilley, 1929) and may be the result of metasomatic addition. The Oka, Quebec, wollastonite—described by Gold (1966)—occurs in a coarse-grained ijolite, associated with nepheline, sodian augite, and melanite; in spite of its relatively high-temperature igneous origin, it is not notably high in Fe or Mn. The high-Mn wollastonites are from Franklin, New Jersey, in calcsilicate bodies associated with the manganese ores (Frondel and Baum, 1974), and from Gjellebekk, Norway, at the contact of Silurian limestone with granite (Goldschmidt, 1911). The Gjellebekk specimen analyzed is not Schaller's specimen, which has not been found, but is probably comparable to it.

The Franklin specimen, which contains both wollastonite and bustamite, provides the critical information for establishing the compositional limits for these minerals. It was found in the mine in mid-1944 and its occurrence has been described by Baum (1972). It consists of a granular aggregate of calcite

TABLE 1. MnO and FeO Contents (Wt Percent) of Wollastonites and Bustamites*

USNM#	Locality	MnO Range	MnO Mean	FeO Range	FeO Mean
		Wollastonite			
128301	Canaan, New Zealand		<0.1	0.24-0.30	0.27
128300	Holyoake, New Zealand		<0.1	0.20-0.27	0.24
106525	Willsboro, New York		0.18	0.24-0.41	0.36
128299	Rameka, New Zealand		0.21	0.46-1.06	0.78
106183	Scawt Hill, Ireland		0.40		2.23
128341	Oka, Quebec	0.47-1.05	0.95	0.62-0.70	0.67
C6152-1	Franklin, New Jersey		2.71		<0.1
128339	Gjellebekk, Norway	2.37-8.38	5.13	0.18-1.03	0.53
128340	Franklin, New Jersey	2.31-8.09	4.62		<0.1
		Bustamite			
128340	Franklin, New Jersey		12.3	0.59-0.88	0.68
	Skye, Scotland (Tilley, 1948)		1.22		9.29
	Skye, Scotland (Rapoport & Burnham, 1973)		1.58		10.44

* *When no range is given, composition of mineral appears uniform.*

(white), wollastonite (cream), bustamite (pale gray), and andradite (yellow brown), with microscopic blebs of willemite confined to the bustamite. The willemite is probably an exsolution product from the bustamite, which contains 0.26 percent ZnO, whereas the wollastonite is essentially zinc-free (<0.1 percent ZnO). Under a shortwave ultraviolet lamp, the specimen is spectacular, the calcite fluorescing pink, the wollastonite orange, the willemite green, and the bustamite and andradite being nonfluorescent. The wollastonite and the bustamite have similar refractive indices and birefringence, but in thin section they are clearly distinguished because the bustamite grains are clear whereas the wollastonite grains are very turbid (Fig. 1). Microprobe examination revealed this turbidity to be due to exsolved bustamite. Exsolved bustamite has the same composition as the primary bustamite, whereas the wollastonite varies considerably in manganese content, with the highest value in a homogeneous area of 8.09 percent MnO. This suggests the phase relations illustrated in Figure 2, with the solubility of $MnSiO_3$ in wollastonite rapidly declining with decreasing temperature, whereas the limiting composition of bustamite remains almost constant. The tentative temperatures indicated on Figure 2 are derived from the crystallization temperatures of the Franklin ore-body deduced by Frondel and Baum (1974).

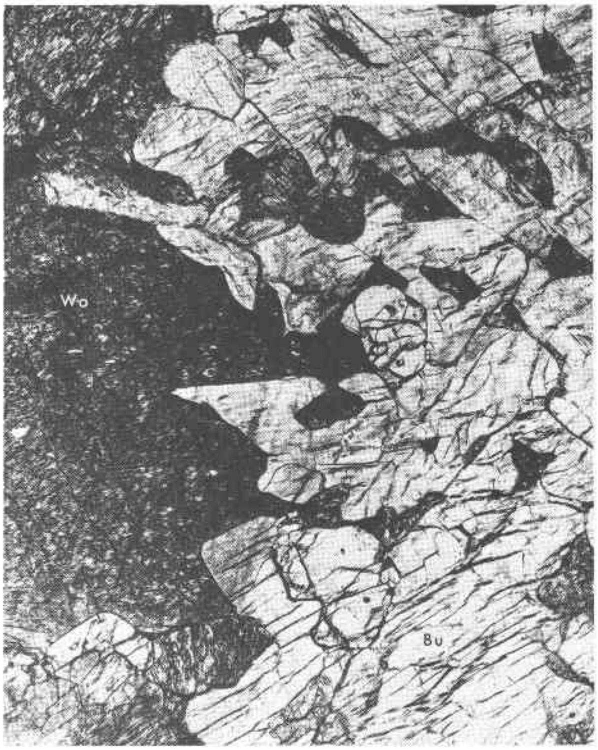

FIG. 1. Photomicrograph of coexisting wollastonite (turbid) and bustamite (clear) in a specimen from Franklin, New Jersey (width of field is 8 mm).

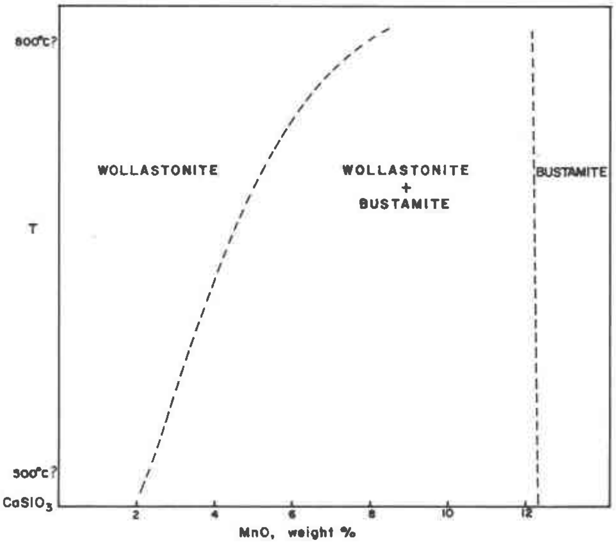

FIG. 2. Tentative subsolidus relations in the $CaSiO_3$–$MnSiO_3$ system, as indicated by wollastonite-bustamite compositions in a specimen from Franklin, New Jersey.

The Gjellebekk specimen shows compositions similar to those of the Franklin wollastonite, with an essentially identical maximum MnO content. Exsolution of bustamite was not detected, either optically or with the microprobe. Compositions appear to vary randomly from grain to grain over the range indicated in Table 1. The texture suggests a metasomatic replacement of limestone, indicating a non-equilibrium situation with the metasomatizing solutions ranging considerably in composition.

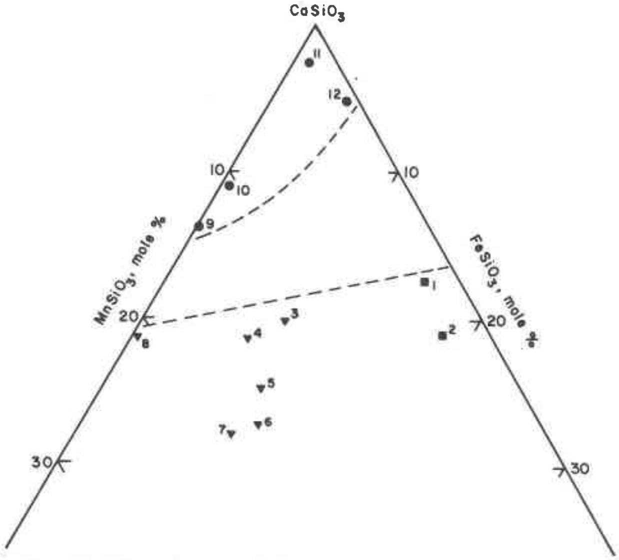

FIG. 3. Mineral compositions in the Ca-rich portion of the $CaSiO_3$–$MnSiO_3$–$FeSiO_3$ system; individual compositions are as follows: 1, "iron-wollastonite" Skye, Scotland (Tilley, 1948); 2, ferrobustamite, Skye, Scotland (Rapoport and Burnham, 1973); 3–7, bustamites, Broken Hill, Australia (Mason, 1973); 8, bustamite, Franklin, N.J.; 9, wollastonite, Franklin, N.J.; 10, wollastonite, Gjellebekk, Norway (Schaller, unpublished); 11, wollastonite, Oka, Quebec; 12, wollastonite, Scawt Hill, Ireland.

Discussion

The data from the natural minerals pertinent to establishing the composition limits are illustrated in Figure 3. Peacor and Buerger (1962) showed that there are four crystallographically distinct metal sites in bustamite: $M(1)$ and $M(2)$ in general positions, and $M(3)$ and $M(4)$ on inversion centers with half the multiplicity. Rapoport and Burnham (1973) determined that $M(3)$ apparently cannot accommodate Ca and, on that basis, suggested a limiting composition of $Wo_{5/6}Fs_{1/6}$ for ferrobustamite. This composition limit is confirmed by the compositional data presented here.

The compositional limits for wollastonite are not apparent from present knowledge of its crystal structure. Figure 3 suggests that wollastonite can accommodate considerably more Mn than Fe in its structure, which is consistent with the fact that the ionic radius of Mn^{2+} (0.83 Å) is closer to Ca^{2+} (1.00 Å) than is Fe^{2+} (0.78 Å). However, the limits for Fe substitution in wollastonite are less well defined than for the Mn substitution. Matsueda (1973) has described iron-wollastonite (ferrobustamite) occurring together with wollastonite in a skarn from the Sampo mine, Japan; the wollastonite has a maximum of 0.97 percent ($FeO + Fe_2O_3$), the ferrobustamite a minimum of 8.37 percent FeO. Shimazaki and Yamanaka (1973) have described wollastonite, ferrobustamite, and hedenbergite in skarns from the Kagata mine, Japan; the maximum FeO content in the wollastonite is 0.7 percent. These skarn wollastonites thus have a much lower iron content than the maximum of 2.2 percent FeO found in the contact-zone wollastonite from Scawt Hill. In this connection, Rutstein and White (1971) report on their synthetic studies as follows: "As iron is added to $CaSiO_3$ at 850°C, the characteristic wollastonite pattern (of vibrational spectra) persists to $Ca_{0.88}Fe_{0.12}SiO_3$." This composition is considerably more iron-rich than any of the natural wollastonites analyzed. It is not clear, however, whether the synthetic material prepared by Rutstein and White was an equilibrium product.

Rapoport and Burnham (1973) introduced the name ferrobustamite for the mineral they examined, as more appropriate than the term "iron-wollastonite" used for it by Tilley (1948), since the structure is that of bustamite, not wollastonite. I suggest that ferrobustamite be defined to include all

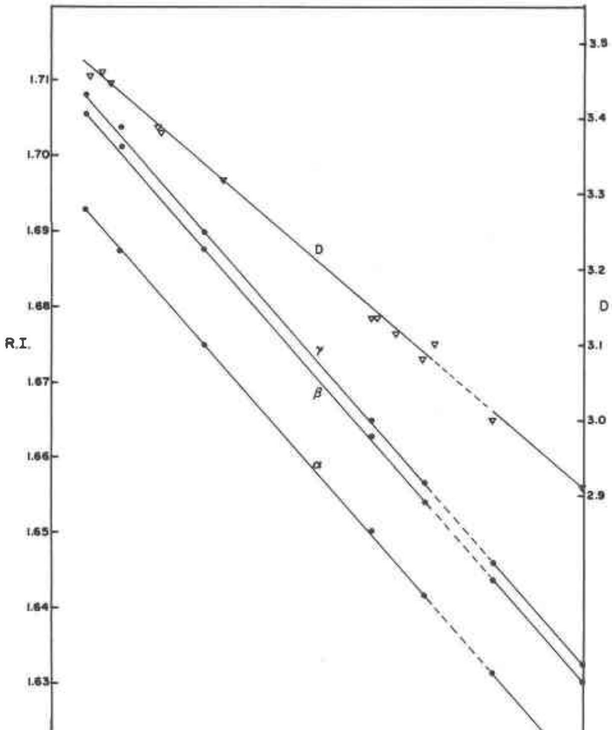

FIG. 4. Variation of refractive indices and density with composition in wollastonite and bustamite.

minerals with the bustamite structure in which the Fe/(Fe+Mn) atomic ratio exceeds 0.5. Ferrobustamite seems to be much rarer than bustamite; in parageneses which might give rise to ferrobustamite, hedenbergite is likely to crystallize, whereas the corresponding manganese pyroxene, johannsenite, is a high-pressure low-temperature polymorph of bustamite with a maximum stability temperature around 500°C in natural occurrences (Lamb, Lindsley, and Grover, 1972).

Sundius (1931), in a classic paper on the manganiferous pyroxenoids, commented on the continuity of optical properties between bustamite and wollastonite. However, this involved an extrapolation between 60 percent $CaSiO_3$ and 100 percent $CaSiO_3$, for which he had no mineral specimens. Additional data confirm the conclusions of Sundius, and a new diagram based on these data is given as Figure 4.

The lower limit of $CaSiO_3$ in bustamite—observed in a specimen from Långban, Sweden (Sundius, 1931)—is 33.1 mole percent. Bustamites of similar composition, with associated rhodonite, are known from Broken Hill, Australia (Mason, 1973). This suggests that, assuming ordering, one of the two general positions in the bustamite structure—either $M(1)$ or $M(2)$—cannot contain Mn (or Fe) and still maintain the stability of the structure.

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