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Garnet–fassaite calc-silicate nodule from La Soufrière, St. Vincent

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Abstract

The mineralogy of an unusual calc-silicate nodule brought to the surface by the 1902 eruption of La Soufrière volcano on St. Vincent (Lesser Antilles arc) is described. It consists of the crystalloblastic mineral assemblage fassaite pyroxene + grandite garnet + wollastonite ± anorthite ± calcite. The pyroxene is more aluminous ($Al_2O_3 = 19.66$ weight percent) than any previously described from terrestrial rocks, with about 45 mole percent Ca–Al Tschermak's molecule, 37 mole percent diopside, and 15 mole percent Ca–Fe^{3+} Tschermak's molecule in solid solution. Unit-cell data have been calculated on the basis of X-ray powder diffractometry data for the fassaite ($a = 9.704$, $b = 8.828$, $c = 5.204$A, $\beta = 106.95°$; $V = 426.49A^3$) and the grandite (grossular$_{78}$–andradite$_{22}$; $a = 11.905$A; $V = 1687A^3$). We infer a paragenesis related to skarn-type metamorphism of calcareous sediment.

Introduction

The 1902 eruption of La Soufrière volcano on St. Vincent in the Lesser Antilles arc brought a variety of nodules to the surface, including calc-silicate metamorphic xenoliths (Lacroix, 1949; Sandrea, 1949) and cumulus nodules (Lewis, 1964, 1973a,b). We describe here a fist-sized calc-silicate nodule (#V37472), found in the pyroclastic flow deposits of the 1902 eruption, which consists of the mineral assemblage fassaite pyroxene + grandite garnet + wollastonite ± anorthite ± calcite. It is the only known occurrence of a garnet-bearing calc-silicate xenolith associated with this volcano. The nodule also bears a fassaite pyroxene with about 45 mole percent of Ca–Al Tschermak's molecule in solid solution.

Mineralogy

The texture of the nodule is mainly crystalloblastic but in places becomes subpoikiloblastic with garnet or pyroxene enclosing smaller anhedral grains of the other silicate minerals. Because the silicates in the nodule generally appear to be interlocking, sequences of crystallization cannot be reliably inferred on the basis of texture. Calcite occurs as thin (~10 micron) layers separating silicate grains and is never observed to be completely enclosed by any silicate mineral. Borders between silicate minerals are generally sharp, often planar, and show no sign of reaction between grains. Where thin layers of calcite occur between wollastonite and other silicates, however, the border between calcite and wollastonite is more serrate, giving the appearance that calcite has replaced the wollastonite. Small irregular patches of calcite locally extend from intergranular layers into wollastonite grains. Other silicate minerals have sharp borders where they are in contact with calcite layers.

Apart from small silicate mineral inclusions and calcite, grain sizes are in the range 0.2–0.8 mm. Table 1 shows the mode of one thin section of the nodule which is believed to be representative of its assemblage.

The fassaite pyroxene in the nodule is richer in alumina than any specimen observed so far in terrestrial rocks. Table 1 shows the mean composition of 19 electron microprobe analyses of the pyroxene. The mean Al_2O_3 content is 19.66 weight percent (range 17.16 to 20.94 weight percent). Knopf and Lee (1956) described a similar skarn-type pyroxene containing 15.75 weight percent Al_2O_3 (the most aluminous pyroxene reported previously from terrestrial rocks).

The pyroxene grains are dark green in hand specimen and light golden brown in thin section. Anomalous (Berlin blue) interference colors appear near extinction under crossed nicols. The axial angle (+) is about 60–70°. Typical pyroxene cleavage is moderately well developed. Neither twins nor exsolution lamellae were observed.

The pyroxene shows a nearly stoichiometric CaO

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content, implying that all M2 sites are filled by Ca. We have used the method of Papike *et al.* (1974) to calculate relative proportions of Fe^{2+} and Fe^{3+} from our microprobe data. The results show that over 25 percent of tetrahedral sites are filled by Al and that over half of the M1 sites are occupied by trivalent species (Al and Fe^{3+}).

Norms calculated according to the conventions of Yoder and Tilley (1962, p. 366–367) show that less than half of the pyroxene's normative components lie within the pyroxene quadrilateral. Tschermak's molecule accounts for the bulk of the norm with about 45 mole percent Ca–Al Tschermak's component (CAT) and 15 mole percent Ca–Fe^{3+} Tschermak's component (FTS). The diopside component is about 37 mole percent of the norm.

As a first approximation this pyroxene may be viewed as a solution between diopside and CAT. de Neufville and Schairer (1962) report that the experimental limit of CAT solution in diopside is about 20 weight percent at 1 atm pressure. The solubility limit of CAT in diopside may be increased in two ways. Firstly, Hijikata (1973) has demonstrated experimentally that complete solid solution along the join can be attained at a pressure of 11 kbar (1020°C). Secondly, Wood (1975) has shown that addition of Fe^{2+} to a pyroxene solid solution increases CAT solubility. We suggest that addition of Fe^{3+} as FTS in the Soufrière pyroxene has also promoted increased CAT solubility. Increased CAT solubility in the Soufrière pyroxene due to high pressure is considered unlikely because the required pressure is geologically unreasonable for the inferred source region.

Unit-cell parameters of the pyroxene were calculated using X-ray powder diffractometer data ($a = 9.705$, $b = 8.828$, $c = 5.204$A, $\beta = 106.95°$; unit-cell volume = 426.49A^3). The data of two runs were averaged for the calculation. A Si calibration standard was used; no unit-cell refinement program was applied. The unit-cell dimensions differ from those expected for ideal solid solution between CAT and diopside: the *c* axis is compressed and the β angle enlarged. The unit-cell volume is also smaller than that expected from ideal solid solution (by about one percent), implying a small negative volume of mixing.

The grandite garnets in the nodule are golden brown in hand specimen and light honey brown in thin section. They are isotropic but show anomalous interference along fractures which cross-cut the grains. The composition (Table 1) shows that nearly all X positions are filled by Ca; this also implies that nearly all iron is Fe^{3+} and confined to Y positions. Hence, we infer that the garnet's composition may be expressed as grossular$_{78}$–andradite$_{22}$ (mole). There is very little pyrope component, most of the Mg in the nodule having partitioned into coexisting fassaite ($D_{Mg}^{Gar/Cpx} = 0.07$). X-ray powder diffractometer data were used to calculate the unit-cell dimension of the grandite ($a = 11.905$A; unit-cell volume = 1687A^3).

Table 1. Composition of minerals in the V37472 nodule

	Fassaite	Grandite	Wollastonite	Anorthite	Calcite
SiO_2	38.09(86)[1]	38.51(26)	49.68(65)	43.62(17)	0.36
TiO_2	0.72(10)	0.78(7)	0.01(1)	0.0	0.02
Al_2O_3	19.66(85)	16.84(51)	1.45(96)	36.31(20)	0.65
FeO*[2]	8.82(57)	7.46(73)	0.0	0.0	0.0
MnO	0.14(4)	0.28(2)	0.17(2)	0.04(0)	0.49
MgO	7.26(43)	0.52(3)	0.21(5)	0.0	0.35
CaO	24.88(31)	35.44(60)	46.47(62)	19.71(59)	52.92
Na_2O	0.03(1)	0.04(1)	0.02(1)	0.05(2)	0.0
K_2O	0.01(1)	0.0	0.0	0.0	0.0
Total	99.60(95)	99.87	98.01	99.73	54.79
#anals.	19	3	4	3	1
Modal %	73.6	23.7	2.2	0.5	0.1

Microprobe analyses were accomplished using mineral and glass standards; data reduction was accomplished using Bence and Albee (1968) alpha corrections applied automatically by a slaved PDP-11 minicomputer (Finger and Hadidiacos, 1972).

[1] Parenthesized figures represent the estimated standard deviation (e s d) in terms of least units cited for the value to their immediate left, thus 38.09(86) indicates an e s d of 0.86 wt. %.

[2] FeO* = all iron calculated as FeO.

Nearly pure wollastonite (Table 1) occurs as clear vitreous elongated grains showing good cleavage and as anhedral mineral inclusions in garnet or pyroxene. Wollastonite is the only mineral to show complex intergrowths with intergranular calcite. It is uncertain whether calcite is actually replacing wollastonite or if the opposite is true, but optically invisible intergrowths of extremely small calcite grains and wollastonite could conceivably account for the low totals in microprobe analyses of wollastonite.

The anorthite (>An$_{99}$) in the nodule is colorless in thin section; K is present in only trace amounts (Table 1). Anorthite is only a minor constituent and is most frequently observed enclosed by garnet. Albite twins and one other unidentified twin set are present. The low alkali content of the anorthite (and of the nodule in general) is a curious feature of this xenolith.

Calcite appears as thin intergranular layers in the nodule and as a possible alteration product of wollastonite, but is only a minor constituent of the nodule. It is low in Mg (Table 1).

Paragenesis

By analogy with other well-documented skarn-type occurrences of coexisting grandite garnet and

Table 2. V37472 nodule bulk composition

	V37472 nodule: bulk comp. of section plane	Nodule bulk comp. (all CaO recalculated as $CaCO_3$)	"Average Sediment" (Poldervaart, 1955)
SiO_2	38.89	31.67	44.5
TiO_2	0.69	0.56	0.6
Al_2O_3	18.45	15.03	10.9
FeO*[1]	7.85	6.39	----
FeO	----	----	0.9
Fe_2O_3	----	----	4.0
MnO	0.21	0.17	0.3
MgO	4.76	3.88	2.6
CaO	29.06	23.67	19.7
Na_2O	0.04	0.03	1.1
K_2O	0.0	0.0	1.9
CO_2	----	(18.59)	13.4
Total	99.95	99.99	99.90

[1] FeO* = all iron calculated as FeO.

fassaite pyroxene (Tilley, 1938; Shoji, 1975; Huckenholz *et al.*, 1974), we conclude that the nodule under consideration is a thermal contact-type skarn assemblage, even though the original field relations are not in evidence. Specifically, no limestones or other calcareous sediments are exposed on St. Vincent in the vicinity of La Soufrière. We propose that the nodule is derived from calcareous sediments deposited on the submerged arc crest in the St. Vincent region prior to the build-up of La Soufrière volcano from the sea-floor. Such sedimentation is likely to have occurred during the Miocene hiatus (Martin-Kaye, 1969) after cessation of activity in the Limestone Caribbees (eastern arc) and prior to the main phase of Plio–Pleistocene volcanism in the present arc. The most recent eruption of La Soufrière (April, 1979) brought marble xenoliths to the surface, which supports the idea of calcareous sediments existing at depth in the vicinity of the vent.

The calculated bulk composition of the nodule (on the basis of modal analysis) is shown in Table 2. Also shown is the bulk composition with all CaO recalculated as $CaCO_3$; this composition is similar to the "average sediment" of Poldervaart (1955, p. 132) and presumably is close to the composition of the calcareous sediment which was decarbonated by thermal metamorphism. Metasomatic processes may have played a role in determining the final bulk composition observed, but the relative compositional homogeneity of the minerals and the crystalloblastic texture of the nodule strongly suggest that the final silicate mineral assemblage observed is an equilibrium assemblage.

Calcite is considered to be a secondary alteration product for the following reasons. Firstly, thermodynamic analysis of the metamorphic reactions possible in the simple system CaO–Al_2O_3–SiO_2–CO_2 (data of Robie *et al.*, 1978) reveals that prograde reactions between calcite and silicates (*e.g.*, grossular garnet) occur at relatively modest temperatures relative to those which must have prevailed in the pyroclastic flow which carried the nodule down the flanks of the volcano. If the extremely thin layers of calcite were present in the nodule at the time of its entrainment, we feel that they would have reacted, with grandite for example, to produce a higher-grade metamorphic assemblage. There is no evidence that this occurred. Secondly, it seems unlikely that silicate minerals growing at the expense of calcite in prograde metamorphic reactions would leave behind only thin intergranular layers of remnant calcite and yet never entirely enclose any remnant carbonate grains. It seems more likely, therefore, that the calcite now in the nodule was precipitated from bicarbonate-laden meteoric water in the time intervening between the 1902 eruption and the date of sample collection.

The paragenesis of the nodule can be interpreted in light of phase relations in the simple system CaO–Al_2O_3–Fe_2O_3–SiO_2 which has been investigated experimentally by Huckenholz *et al.* (1974). An isobaric (1 atm) T,X section of the grossular–andradite join ($Ca_3Al_2Si_3O_{12}$–$Ca_3Fe_2^{3+}Si_3O_{12}$) shows that complete garnet solid solution exists at temperatures below 798°C. At higher temperatures, however, garnet solid solution breaks down to other more stable phase assemblages. One of these phase volumes contains the mineral assemblage garnet + fassaite + wollastonite (that which is observed in the nodule); it is stable over the temperature range 935 to 1140°C. We suggest, therefore, that the Soufrière nodule represents calcareous sediment which was first metamorphosed to a grandite-bearing assemblage ($T <$ 798°C); the assemblage was then heated to higher temperatures, perhaps during entrainment, and the grandite originally in the assemblage was metamorphosed into the new assemblage grandite + fassaite + wollastonite ($T >$ 935°C). Anorthite is interpreted as a remnant of some prograde assemblage and calcite as a secondary alteration product.

The effect on the host magma of the possible assimilation of calcareous sediments and incorporation of CO_2 into the melt remains an open question. But escape of assimilated CO_2 from magmas which have stoped through calcareous sediments could obviously contribute to the explosiveness of eruptions. Volcanoes intruding calcareous country rocks (*e.g.*, Vesuvius) might be profitably considered in this light.

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