

## Calc-aluminous insets in olivine of the Sharps chondrite

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**SUMMARY.** A 250  $\mu\text{m}$  olivine crystal in Sharps contains 1 to 5  $\mu\text{m}$  insets identified by microprobe analysis as ferroan monticellite, spinel, and fassaite with average compositions: olivine (host),  $(\text{Fe}_{0.44}\text{Mg}_{1.51}\text{Ca}_{0.07})(\text{Si}_{0.99}\text{Al}_{0.01})\text{O}_4$ ; ferroan monticellite,  $(\text{Ca}_{0.89}\text{Fe}_{0.41}\text{Mg}_{0.66})(\text{Si}_{1.00}\text{Al}_{0.02})\text{O}_4$ ; spinel,  $(\text{Fe}_{0.41}\text{Mg}_{0.59})(\text{Fe}_{0.06}^{3+}\text{Cr}_{0.23}\text{Al}_{1.69}\text{Si}_{0.01}\text{Ti}_{0.01})\text{O}_4$ ; and fassaite,  $\text{Ca}_{0.96}(\text{Fe}_{0.01}\text{Mg}_{0.59})(\text{Al}_{0.18}\text{Ti}_{0.07}\text{Fe}_{0.16}^{3+})\text{Si}_{1.53}\text{Al}_{0.47}\text{O}_6$ . Textural and experimental data suggest early crystallization of spinel from a calcic olivine melt, exsolution of ferroan monticellite from the host olivine, and reaction of spinel and ferroan monticellite to form fassaite. The severe depletion of alkalis and silica in this crystal suggests it is a residue from vapour fractionation.

DURING a microprobe study of chondrules in the Sharps (type H-3) meteorite, the writer encountered a single 250  $\mu\text{m}$  olivine crystal crowded with 1 to 5  $\mu\text{m}$  insets of several types. Microprobe scans for Fe, Ca, and Mg indicated that the host olivine is unusually calcic and suggested that some of the insets are ferroan monticellite and others are spinel and aluminous pyroxene.

Quantitative analysis of these phases was undertaken for three reasons: First, ferroan monticellite would, if established, be new to meteorites. Second, the olivine host is much more calcic than olivine elsewhere in Sharps and suggests an unusual thermal history. Finally, and most important, the strong enrichment of Ca, Al, and Mg relative to Si implied by the mineral assemblage resembles that to be expected of a residue from severe vapour fractionation (Walter, 1969). Such material, though apparently common in type 3 carbonaceous chondrites (see, e.g. Keil, Huss, and Wiik, 1969; Marvin, Wood, and Dickey, 1970), has not been reported previously from ordinary chondrites, and its presence or absence has important implications for the pre-accumulation history of chondritic material.

The Sharps chondrite fell in Richmond County, Virginia, in 1921. It was described first by Watson (1925) and later by Dodd (1968) and Fredriksson (1969). Its chemical classification is in dispute, the writer favouring the H-group (1968) and Fredriksson (1969) preferring the L-group, but its petrologic classification is type 3 on the basis of very limited recrystallization and the presence of olivines and pyroxenes of widely variable composition (Dodd, van Schmus, and Koffman, 1967). On the latter basis, it appears to be one of the least-metamorphosed chondrites (Dodd, 1969) and is thus particularly well suited for studies of chondrule genesis.

The crystal considered here, no. 53 in section B from the University of Virginia, is 250  $\mu\text{m}$  long (fig. 1*a*). One end is smoothly rounded, the other irregular. Several fractures traverse the crystal without evident displacement.

At high magnification, the crystal can be seen to be crowded with 1 to 5  $\mu\text{m}$  insets of several types (fig. 1*b*). Some of these are cubic or octahedral and have high relief; others differ so little from the host that they are difficult to see. Optical study of these insets is impossible for, in polarized light, they take on the interference colours of their

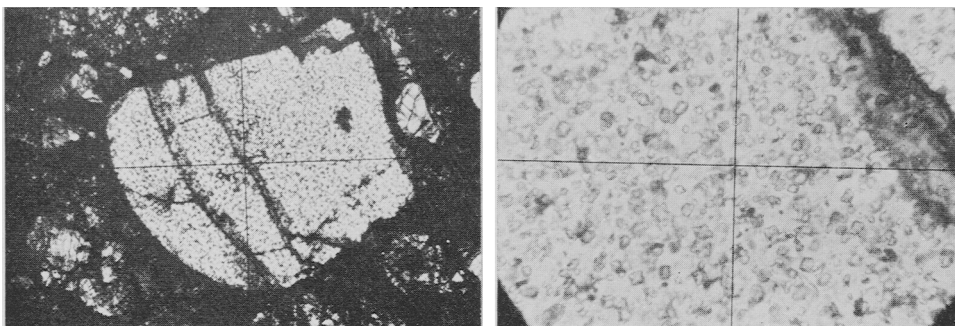


FIG. 1. Chondrule No. 53, Section B, Sharps chondrite: *a* (left). Field 400  $\mu\text{m}$  wide. *b* (right). Field 150  $\mu\text{m}$  wide.

host. X-ray analysis was considered but rejected for several reasons. First, as the crystal is apparently unique, we were reluctant to risk losing or destroying it. Second, because the crystal is small and mineralogically complex, the likelihood of securing meaningful crystallographic data is very small (C. T. Prewitt, pers. comm.). Finally, removal of the crystal would have damaged adjacent chondrules that are still under study. In the absence of crystallographic data, the identifications of the inset phases (particularly the pyroxene) must be regarded as tentative.

All phases were analysed with an ARL EMX-SM microprobe in this Department. Operating conditions included an accelerating potential of 15 KV; a specimen current of 0.015  $\mu\text{A}$  (on brass); and a spot size of 0.9  $\mu\text{m}$ . Beam current integration was used for maximum stability, and drift was less than 1% for all runs.

Intensities for the unknowns were referred to those for oxide and silicate standards, which include Elba hematite and synthetic fayalite for Fe; synthetic MgO and enstatite glass for Mg; quartz and kyanite for Si; pseudowollastonite and wollastonite glass for Ca; synthetic tephroite for Mn; synthetic rutile for Ti; Amelia albite for Na; synthetic  $\text{Al}_2\text{O}_3$  and kyanite for Al; Asbestos microcline for K; and an analysed chromite for Cr.

Because the insets rarely exceed 5  $\mu\text{m}$  in the largest dimension and are more usually 1 to 2  $\mu\text{m}$ , analysis proved both difficult and tedious. The profusion of insets made even accurate analysis of the host olivine difficult. The following procedures were adopted for each phase:

Beam-scans for Ca and Al were used to locate inclusion-free areas within the olivine. These areas were then analysed for Ca, Al, and a third element.

Ca was used to locate and centre on insets of ferroan monticellite. Preference was given to areas in which the beam could be moved a small distance at constant calcium intensity.

Ca and Al were used to locate pyroxene insets once the general levels of these elements were established. Here again, grains were sought on which more than one point could be measured.

Spinel is the only inset phase that is sufficiently distinct from the host to be identified microscopically. Individual grains of this mineral were analysed for all elements. As the smaller grains invariably

yielded substantially higher counts for Ca and Si than larger ones, and typically showed other peculiarities of composition, such small grains were omitted from the final (average) analysis.

Si, Ti, Al, Cr, Fe, Mg, Mn, Ca, K, and Na were sought in all phases. For the major elements 30 to 50 points were analysed for each phase; for the minor elements, 10 to 20 were measured. With the exception of sodium, all elements sought were detected, though K was found only in monticellite and pyroxene and there at the 0.00x wt. % level.

The analytical data for each phase were screened for consistency and extreme values were rejected. In all such cases, an unexpected value for one element was accompanied by other peculiarities, and in most cases overlap with another phase was clearly indicated. The remaining data were then averaged and the intensity ratios were reduced to oxide percentages using a computer program based on the work of Bence and Albee (1968).

On the basis of these analyses and step scans across the larger insets, it appears that each phase shows little intergrain variation: Less than 2 % relative for major elements, less than 10 % for minor elements (variations in the host olivine are described below). More precise statements about grain to grain variations are precluded by the method used to secure the data.

*Olivine.* Step scans across the olivine crystal (fig. 2) show little systematic chemical variation except within a few microns of the edge, where iron rises sharply and calcium decreases. Scans in several directions indicate that this iron-rich rim surrounds the entire crystal.

The mean composition of olivine, exclusive of the rim material, is given in table I, col. 1. The analytical sum is slightly high but acceptable, and the analysis is notable for unusually high values of CaO and Al<sub>2</sub>O<sub>3</sub> relative to most terrestrial olivines (Smith, 1966; Simkin and Smith, 1970) and olivines elsewhere in Sharps (Dodd, 1968).

*Ferroan monticellite* forms the smallest of the three types of insets and is most difficult to analyse accurately. The analysis (table I, col. 2) has a slightly high but acceptable sum, and the balance of cations and silicon is good. Calcium is somewhat less abundant relative to Fe and Mg than in an ideal member of the monticellite-kirchsteinite series, a situation also common in terrestrial monticellites (Sahama and Hytönen, 1957).

*Pyroxene* in B-53 appears to be a fassaite with the mean composition given in table I, col. 3. The analytical sum is slightly low, and there is an apparent deficiency of tetrahedral cations when the analysis is recast following Hess (1949). These problems may reflect either underestimation of silica or the presence of appreciable trivalent iron. In the fourth column of table I, sufficient FeO has been converted to Fe<sub>2</sub>O<sub>3</sub> to raise Z to 2.000 and the sum to 100.1 %. There is no clear basis for choice between the

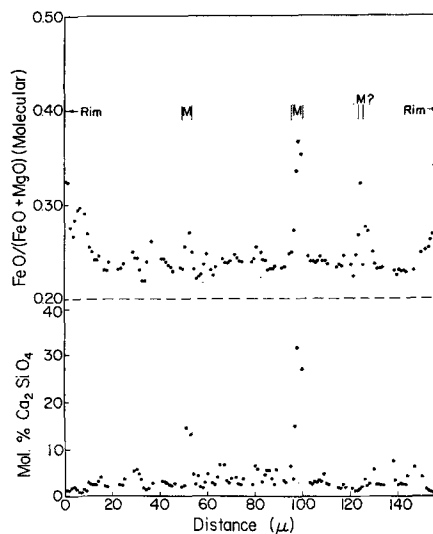


FIG. 2. Step scan, at 1  $\mu\text{m}$  interval, across Sharps chondrule B-53. 'M' denotes insets of ferroan monticellite.

TABLE I. *Phase and bulk analyses of Sharps B-53*

	1	2	3	4	5	6	7	8
SiO <sub>2</sub>	38.4	36.0	41.2	41.2	0.4 <sup>6</sup>	0.4 <sup>6</sup>	35.7	38.8
TiO <sub>2</sub>	0.0 <sup>4</sup>	0.1 <sup>1</sup>	2.4	2.4	0.4 <sup>5</sup>	0.4 <sup>5</sup>	0.1	0.1
Al <sub>2</sub> O <sub>3</sub>	0.2 <sup>5</sup>	0.6 <sup>1</sup>	15.1	15.1	53.0	53.0	4.5	0.4
Cr <sub>2</sub> O <sub>3</sub>	0.0 <sup>5</sup>	0.0 <sup>6</sup>	0.1 <sup>4</sup>	0.1 <sup>4</sup>	10.9	10.9	0.9	0.0
Fe <sub>2</sub> O <sub>3</sub>	—	—	—	5.9	—	2.8	0.3	0.1
FeO	20.4*	17.6*	5.7*	0.4	20.6*	18.1	19.4	19.6
MgO	39.6	15.9	10.8	10.8	14.6	14.6	35.2	36.8
MnO	0.2 <sup>4</sup>	0.2 <sup>3</sup>	0.0 <sup>5</sup>	0.0 <sup>5</sup>	0.1 <sup>3</sup>	0.1 <sup>3</sup>	0.2	0.2
CaO	1.70	29.8	24.2	24.2	0.1 <sup>2</sup>	0.1 <sup>2</sup>	3.7	4.0
Sum	100.7	100.3	99.6	100.2	100.3	100.6	100.0	100.0

	1	2	3	4	5	6
	Cations to 4 O		Cations to 6 O		Cations to 32 O	
Si	0.986	1.004	1.548	1.525	0.10	0.10
Al	—	—	0.405	0.475	—	—
Σ	0.986	1.004	1.953	2.000	↓	↓
Al	0.008	0.020	0.263	0.184	13.56	13.56
Cr	0.001	0.001	0.004	0.004	1.86	1.86
Fe <sup>3+</sup>	—	—	—	0.164	—	0.46
Ti	0.001	0.002	0.069	0.068	0.07	0.07
Σ	↓	↓	↓	↓	15.59	16.05
Mg	1.515	0.664	0.604	0.595	4.73	4.72
Fe <sup>2+</sup>	0.438	0.412	0.178	0.012	3.74	3.29
Mn	0.005	0.005	0.000	0.000	0.02	0.02
Σ	↓	↓	1.118	1.027	↓	↓
Ca	0.047	0.892	0.976	0.962	0.03	0.03
Σ	2.015	1.996	2.094	1.989	8.52	8.06

\* Total iron as FeO.

1. Mean composition of olivine, excluding rim. K and Na were sought but not detected.
2. Mean composition of ferroan monticellite. 0.00x % K<sub>2</sub>O is also present. Na<sub>2</sub>O was not detected.
3. Mean composition of fassaite. 0.00x % K<sub>2</sub>O is also present. Na<sub>2</sub>O was not detected.
4. Recalculated mean composition of fassaite. Sufficient FeO has been recast to Fe<sub>2</sub>O<sub>3</sub> to raise Z to 2.000.
5. Mean composition of spinel. K and Na were not detected.
6. Recalculated mean composition of spinel. Sufficient FeO has been converted to Fe<sub>2</sub>O<sub>3</sub> to balance sites.
7. Calculated bulk composition of B-53, based on columns 1, 2, 4, 6, and a modal composition of 84 % olivine, 7 % ferroan monticellite, 8 % spinel, and 1 % fassaite.
8. Calculated bulk composition, omitting spinel.

analyses in columns 3 and 4, but evidence for the presence of trivalent iron in associated spinel (see below) and the fact that terrestrial fassaite contains trivalent iron (Deer, Howie, and Zussman, 1962a) lead the writer to prefer the latter. The pyroxene in B-53 resembles terrestrial fassaite in most other respects (Deer, Howie, and Zussman, 1962a) but is slightly richer in titanium.

*Spinel.* The average composition of seven crystals of spinel is reported in table I. Intergrain variations of roughly 2 % for major oxides are probably chiefly analytical, and step scans across the larger crystals indicate no systematic compositional variation.

The spinel analysis (table I, col. 5) gives a good sum, but the atomic proportions suggest a marked deficiency of trivalent and tetravalent cations. This can be made up by assuming that part of the iron present is trivalent. If this is done (table I, col. 6) the analytical sum is increased somewhat but remains acceptable.

On the basis of its high aluminum content, the spinel in B-53 belongs to the spinel-hercynite series. It is unusual only in a rather high tenor of chromium relative to terrestrial spinels (Deer, Howie, and Zussman, 1962b).

*Phase relationships.* Electron-beam scanning photographs of B-53, using Ca, Al, and Si radiation, were used to determine the distribution and interrelationships of phases. Spinel, ferroan monticellite, and fassaite commonly occur together, often with fassaite between the other two phases. A typical situation is shown in fig. 3, which presents a composite tracing of a 24  $\mu\text{m}$  area. Small individual grains of each inset species are also present in the section, but this may be due to vagaries of sectioning. Most of the large insets are polymineralic.

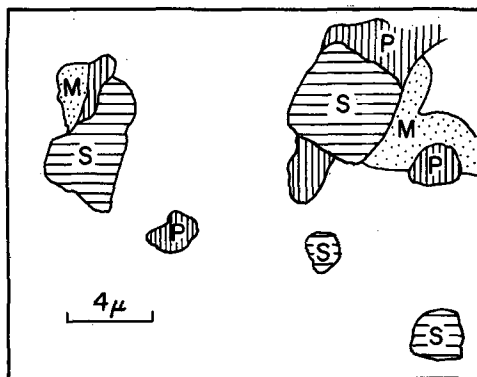


FIG. 3. Composite tracing, based on electron-beam scanning photographs for Ca, Al, and Si, of insets in Sharps chondrule B-53. M = ferroan monticellite, S = spinel, and P = pyroxene (fassaite). The host phase is olivine.

*Bulk composition.* Conventional modal analysis of B-53 is clearly impossible.

An approximate mode was determined from electron-beam scanning photographs, using a tracing similar to that in fig. 3, but at a much larger scale. The mode (84 % olivine, 8 % spinel, 7 % ferroan monticellite, 1 % fassaite) was then used, with the mineral analyses, to estimate the bulk composition of B-53 (table I, cols. 7 and 8).

If the section is assumed to be representative of the entire crystal, then the principal sources of error in the mode are beam resolution and beam penetration. The beam diameter is small (somewhat less than 1  $\mu\text{m}$ ), but large enough to slightly exaggerate the sizes and hence abundances of the insets. Penetration of the beam results in the detection of some insets that are slightly below the surface. Both effects increase the apparent abundance of insets, and their result is a slight exaggeration of the bulk

abundances of Ca, Al, and Cr. The error thus introduced is not serious, however, and should not affect conclusions based on the calculated bulk composition.

*Paragenesis.* Although associations of calcic olivine and monticellite occur in terrestrial volcanic rocks (Sahama and Hytönen, 1957) and spinel-fassaite assemblages appear in some metamorphosed limestones (Tilley, 1938), the four-phase assemblage olivine-monticellite-spinel-fassaite appears to be unique.

It is clear that B-53 crystallized at a very high temperature. To a first approximation, it consists of one part hercynitic spinel to ten parts olivine. Experimental data on the joins spinel-forsterite and hercynite-fayalite (El Shahat and White, 1966) indicate that this mixture would not be completely molten at temperatures below 1600 to 1700 °C.

The high CaO and Al<sub>2</sub>O<sub>3</sub> contents of the host olivine suggest that crystallization was very rapid. Microprobe data for terrestrial and meteoritic olivines (Smith, 1966; Simkin and Smith, 1970) indicate that most contain less than 0.5 wt % CaO and less than 0.02 % Al<sub>2</sub>O<sub>3</sub>. The higher CaO contents are found in volcanic and hypabyssal olivines and the lower values in plutonic and metamorphic olivines. Olivines as calcic as that reported here are uncommon but have been reported, with ferroan monticellite, in melilite nephelinite lavas (Sahama and Hytönen, 1957).

Olivine elsewhere in Sharps has widely variable calcium contents (0.04 to 0.61 % CaO), and the higher values are commonly associated with strong Fe-Mg zoning (Dodd, 1968 and in preparation). The absence of such zoning from B-53 (the ferrous rim, which is thought to be secondary, is discussed below) is further evidence of extremely rapid crystallization.

The crystallization sequence recorded in B-53 is somewhat obscure. It may have crystallized as a single, homogeneous olivine from which all inlets exsolved below the solidus. This seems unlikely, however, for the Al<sub>2</sub>O<sub>3</sub> and Cr<sub>2</sub>O<sub>3</sub> contents of the entire crystal (4.6 % and 0.9 % respectively) far exceed those in any known natural olivine. It is more likely that spinel precipitated first and the remainder of the melt crystallized to homogeneous olivine. The bulk composition, less spinel (table I, col. 8), has appropriately low values for Al<sub>2</sub>O<sub>3</sub> and Cr<sub>2</sub>O<sub>3</sub>, and its CaO content is below the solubility limit determined by Ricker and Osborn (1954).

Ferroan monticellite may represent exsolution during slow cooling or mild reheating of the chondrule. The latter possibility is suggested by the ferrous rim, which is thought to be secondary, because it is Ca-poor and because it follows the irregular outline of the chondrule. That the ferroan monticellite developed below the solidus is consistent with the presence of Ca-poor zones around some crystals of this mineral.

The significance of fassaite is not clear. Its tendency to occur with, and commonly between, spinel and ferroan monticellite suggests that it formed by reaction of these phases. The problem with this interpretation is accounting for the additional silica needed for the fassaite. Although the pyroxene contains much tetrahedrally coordinated aluminium, its silica content is still too high to be derived solely from olivine. This problem is unresolved, and there are no pertinent experimental data with which to determine whether the inferred reaction is feasible and, if so, under what conditions.

*Origin and implications.* The evidence discussed above suggests that B-53 crystallized rapidly from molten material and either cooled slowly or was reheated below the solidus. The source of the material and its relation to other constituents of Sharps remain to be considered. In principle, B-53 may be either a xenolith wholly unrelated to the chondrules in Sharps, or a chondrule, or chondrule fragment, albeit of a most unusual type.

If it is a xenolith, then its source is completely unknown for it is chemically distinct from all known meteorites. Though it bears a very slight resemblance to the calc-aluminous inclusions in carbonaceous chondrites (Keil, Huss, and Wiik, 1969; Marvin, Wood, and Dickey, 1970), these too are of uncertain origin.

If B-53 is cogenetic with the chondrules in Sharps, then its composition suggests extreme and unusual chemical fractionation. Although bulk analyses of Sharps chondrules are not available, Walter's data for chondrules in the Bjurböle meteorite (1969 and personal communication) suggest that they typically contain more than 40 %  $\text{SiO}_2$ , 0.1 %  $\text{K}_2\text{O}$ , and 1 %  $\text{Na}_2\text{O}$ , and less than 3 %  $\text{Al}_2\text{O}_3$ . By comparison, B-53 is deficient in silica and the alkalis (36 %  $\text{SiO}_2$ ; less than 0.01 %  $\text{K}_2\text{O}$  and  $\text{Na}_2\text{O}$ ) and enriched in alumina (4.5 %).

Simultaneous depletion of silica and alkalis from a chondritic melt is not consistent with crystal fractionation but might result from vapour fractionation at extremely high temperatures. Walter (1967) notes that silica is the most volatile of the common oxides at 2300 to 2700 °C and under various redox conditions. The alkalis are less volatile than silica, though more so than  $\text{CaO}$ ,  $\text{MgO}$ , and  $\text{Al}_2\text{O}_3$ . Vapour fractionation is thus an attractive explanation for the composition of B-53, which may be: an early condensate from the solar nebula (Suess, 1949; Wood, 1963; Marvin, Wood, and Dickey, 1970); a refractory residue from shock-vaporization (Ringwood, 1961 and 1966; Wlotzka, 1969; Dodd, in preparation); or one product of fusion of nebular dust by lightning (Whipple, 1966).

If chondrules formed in any of these ways, then the apparent rarity of material like B-53 is surprising. It may be due in part to inadequate sampling—the number of chondrules that have been carefully and completely analysed is quite small. However, the assemblage reported here is sufficiently distinct from most chondrules to be readily noted in thin section. It is more likely that vapour fractionation, if it was involved in the formation of chondrules, was typically less intense than it appears to be in the present case. B-53 may thus represent either unusually high temperatures or prolonged heating.

Proof that B-53 is related to the other constituents of Sharps must await the discovery of material intermediate in composition and mineralogy between it and orthodox chondrules. At present, it is not clear whether B-53 represents a byway in chondrite evolution or is an important clue to the main sequence.

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