American Mineralogist, Volume 62, pages 1049–1051, 1977

The origin of sulfide inclusions in pyroxene megacrysts

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Abstract

Clinopyroxene megacrysts in alkaline volcanic rocks commonly contain spherical sulfide inclusions of uncertain origin. In an augite megacryst from Nunivak Island, Alaska, numerous spherical sulfide inclusions define several sets of distinct planes corresponding to the common growth faces ($\bar{2}21$) and ($\bar{1}11$) of clinopyroxene. The sulfide spheres consist of pyrrhotite with chalcopyrite rims, and are interpreted as immiscible droplets which coated the rapidly growing faces of the pyroxene crystal. During crystal growth, local sulfide immiscibility may have been caused by the concentration of sulfur in the boundary layer between the crystal and the melt, due to crystal growth rates which exceeded melt diffusion rates.

Introduction

The clinopyroxene megacryst described in this note was collected from an alkali basalt spatter cone on Nunivak Island, Alaska, and was selected for further study because it contained numerous spherical sulfide inclusions distributed along several sets of regular planes. A similar phenomenon has been reported by Irving (1974) in clinopyroxene megacrysts from basaltic rocks of southeastern Australia.

Description

The pyroxene crystal is a glassy, black megacryst, 5 cm in maximum dimension. Basaltic scoria partially encloses the crystal and in places appears to embay it. The pyroxene composition, determined by microprobe analysis (Table 1), plots within the upper part of the augite field of the pyroxene quadrilateral as defined by Poldervaart and Hess (1951). Cell parameters calculated by a least-squares refinement of powder data obtained with a 114.6 mm diameter camera using Cu$K\alpha$(Ni) radiation are: a = 9.73(3), b = 8.88(3), c = 5.23(2)A, and β = 106.0°(3).

The clinopyroxene crystal is remarkable in that it contains ~1.2 vol. percent, spherical to slightly elongate sulfide inclusions ranging up to 0.12 mm in diameter, which define planar features within the megacryst. Sections cut from the crystal can be divided into four distinct regions (Fig. 1a). In two of these regions the sulfides clearly define planar elements of differing orientation (Fig. 1b). In the third region a poorly defined plane of sulfide droplets is observed. The fourth region of the pyroxene is devoid of sulfide inclusions. The boundaries between the four regions are curved and clearly defined by minute grains of sulfide droplets. Despite the obvious presence of these different regions in the crystal, Laue photographs taken of all major areas of the thin section indicate that the megacryst is indeed a single, untwinned, optically-continuous crystal. Detailed microprobe traverses, perpendicular to the sulfide planes, were made in the two regions with the best-defined planes in order to detect compositional zoning in the host pyroxene. No zoning was observed.

The sulfide droplets consist largely of Ni-bearing pyrrhotite (Table 1), often with narrow rims of chalcopyrite. They can be subdivided according to whether their margins exhibit a smooth or stellate (decorated) surface (Fig. 1c). The planes defined by the latter are typically coated with a vermicular growth of sulfide. In addition, such droplets are frequently connected by irregular fractures at high angles to the sulfide-defined planes. These features are absent in regions where the sulfide inclusions have smooth surfaces

A single-crystal precession study was made of a chip removed from the above section. The two best-defined planes of sulfide inclusions were found to

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Table 1. Clinopyroxene, pyrrhotite (Po) and chalcopyrite (Cpy) analyses of megacryst 13001, Nunivak Island, Alaska

	CLINOPYROXENE	
Cation	Oxide wt%	Atomic prop.
Si	49.25	1.800
Ti	01.11	0.030
Al	09.12	0.393
Fe	06.82	0.208
Mg	14.71	0.801
Cr	0.03	0.000
Mn	0.11	0.003
K	0.01	0.000
Ca	17.31	0.678
Na	1.56	0.110
Total	100.02	4.023

	CPY		PO	
Atom	wt%	Atomic prop.	wt%	Atomic prop.
Fe	31.03	1.02	58.25	0.867
Ni	0.25	0.007	3.33	0.047
Co	n.d.	n.d.	0.53	0.008
Cu	32.56	0.94	0.17	0.002
S	34.94	2.00	38.72	1.000
Total	98.78		101.00	

correspond to the $(\bar{1}11)$ and $(\bar{2}21)$ planes of the host clinopyroxene. The poorly defined set of planes in the third area is tentatively identified as (100). These planes belong to commonly-developed crystal forms of clinopyroxene.

Discussion

Although there is evidence of subsolidus reequilibration of the sulfides in the pyroxene crystal (such as vermicular fracture fillings, stellate margins, and unmixing of chalcopyrite and pyrrhotite), the fact that $(\bar{1}11)$ and $(\bar{2}21)$ are not planes of cleavage or parting in clinopyroxene, but growth planes, suggests that the planar development of sulfide inclusions is primary and occurred while the crystal was growing in a liquid. According to this interpretation, the boundaries between the regions of differing orientation of sulfide planes trace the intersections of the growth faces as the crystal grew. Their curved nature suggests that the relative growth rates of the planes involved did not remain constant. The regions in the crystal which do not show planar arrays of sulfide inclusions correspond to other growth surfaces, perhaps prism faces, which did not incorporate the sulfide spheres during growth. A search of the McGill University reference mineral collection revealed that the faces of the $\{\bar{1}11\}$ and $\{\bar{2}21\}$ forms of clinopyroxene are often dull in comparison to the {110} and {100} forms. In several instances the former terminating forms are preferentially coated with an unidentified oxide phase.

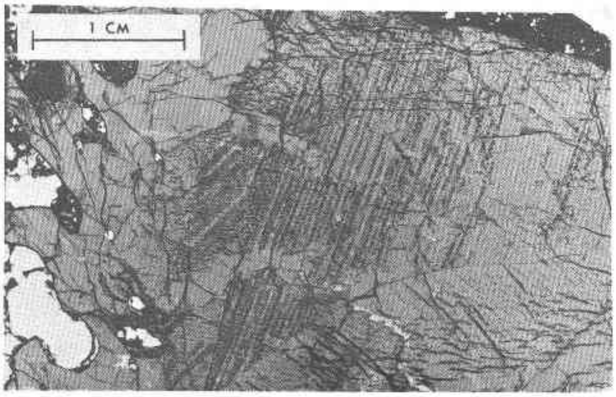

Fig. 1a. Photograph of a thin section of the clinopyroxene megacryst showing the four different regions within the crystal. Three of these regions each contain a distinct set of planes defined by sulfide inclusions. The fourth region at the far left contains no sulfides. Width of field 35 mm.

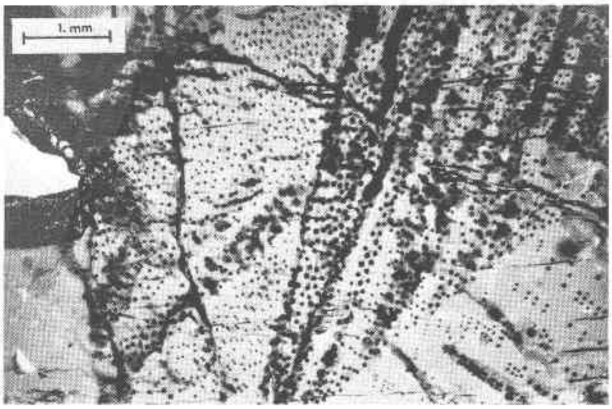

Fig. 1b. An enlargement showing the boundaries between three of the regions within the crystal. Width of field 7 mm.

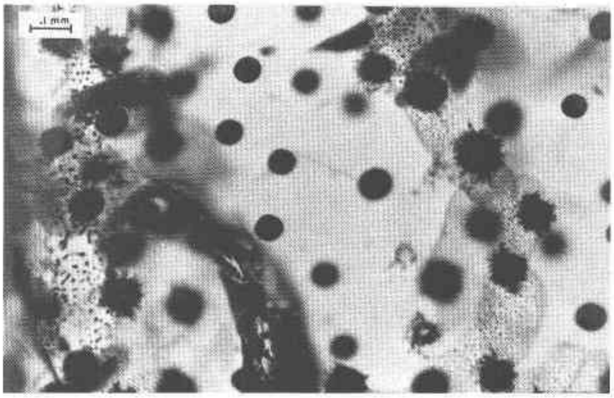

Fig. 1c. A further enlargement showing the distinction between sulfide spheres with smooth and decorated surfaces. Width of field 1.5 mm.

The regular spacing of the sulfide-defined planes within any one region suggests that the factors governing deposition of the sulfide varied periodically. Since the composition of the pyroxene does not vary, these factors must have governed sulfide miscibility in the growth liquid without significantly affecting the pyroxene composition. In the liquid boundary layer adjacent to the *fastest* growth directions, where growth is most likely to be controlled by diffusion processes (Jackson *et al.*, 1967), the concentration of certain components will differ from that of the melt as a whole. If the growth rate is higher than the diffusion of sulfur away from the growth surface, there will be a net increase in sulfur in this area until an immiscible sulfide liquid forms. The resultant coating of sulfide droplets on the adjacent crystal face would inhibit pyroxene growth and allow the boundary layer to equilibrate with the melt. Growth would then continue and the cycle repeated. The weight percent sulfur included as sulfide in the pyroxene should be equivalent to that in the liquid. This value of 0.86 weight percent is significantly higher than the usual estimates of ~0.1 weight percent sulfur solubility in basalts at near-surface pressures (personal communication, W. H. MacLean).

Conclusion

The planar arrays of sulfide inclusions in this clinopyroxene megacryst represent relict growth faces. The sulfide droplets formed by local liquid immiscibility in the boundary layer adjacent to these growth surfaces as the pyroxene crystallized from a silicate melt.

References

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Manuscript received, January 11, 1977; accepted for publication, May 13, 1977.