Electron petrography of high-temperature oxidation in olivine from the Rhum Layered Intrusion

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SUMMARY. Electron-microscope observations of the oxidation products of olivine suggest that oxidation results in the formation of platelets of an 'oxidized olivine' phase, which has a superstructure of the olivine structure. Subsequently this intermediate phase breaks down by a cellular decomposition process to a eutectoidal intergrowth of magnetite and pyroxene. This intergrowth is responsible for the dendritic magnetite inclusions commonly observed in some olivines from Rhum.

IRON-BEARING olivine is thermodynamically stable only within a limited range of oxygen fugacity. Under oxidizing conditions a change in stoichiometry will occur with the formation of Fe^{3+} centres and metal vacancies (Nitsan, 1974). Such a metastable non-stoichiometric olivine will tend to either transform to some intermediate defect-olivine type structure or break down to an Fe^{3+}-rich oxide and a more silica-rich phase. It is to be expected that the mechanism operating and the phases produced during such processes will depend on the temperature, the oxygen fugacity, the iron content of the olivine, and the relative kinetics of the processes involved. Previous work on the oxidation of olivine confirms that a number of processes may operate. Champness and Gay (1968) and Champness (1968), in experimentally oxidized olivine, have identified intermediate 'oxy-olivine' phases, which are superstructures of the olivine cell. A comparison of the work of Haggerty and Baker (1967), Champness (1970), and Kohlstedt and Vander Sande (1975), on the breakdown of olivine to iron-oxide phases reveals a complex situation with the formation of multiphase precipitates containing magnetite and/or hematite with enstatite and/or various forms of silica. Nitsan (1974) has calculated the stability fields of olivines of various fayalite contents with respect to oxidation to olivine-silica magnetite and olivine-pyroxene-magnetite assemblages.

The aim of this paper is to describe the mechanism by which the microstructure was developed during the oxidation of some cumulate olivines from the ultrabasic layered intrusion of Rhum, Inner Hebrides (Brown, 1956). In an optical microscope the olivine can be seen to contain two sets of micron-sized oriented platelets of a dark-brown opaque phase, apparently an iron oxide. At higher magnification, these display a dendritic structure as shown in fig. 1. This texture is well known in olivines from this and other intrusions. In the Rhum olivines it was first described by Judd (1885) and later by Harker (1908). Brown (1956) has referred to the texture and attempted an analysis of the intergrowth. The texture has also been
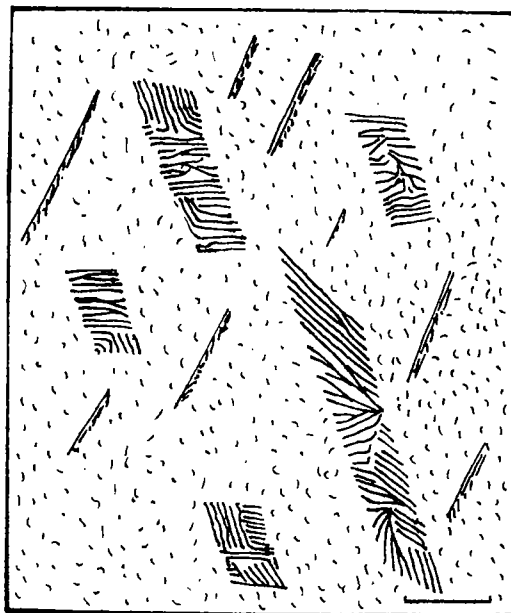

FIG. 1. Illustration of the dendritic intergrowths in the olivines from Rhum as seen in transmitted light. The dendrites lie within two sets of platelets on {101} planes of the olivine. The scale bar represents 5.0 μm.

illustrated in a number of standard text books (Harker, 1954, fig. 29a; Hatch et al., 1972, fig. 132).

To account for the dendritic nature of the iron-ore phase within the well-oriented platelets, Judd (1885) considered that 'these stellate bodies within the substance of the olivine crystals are really inclusions formed within cavities having a recti-linear outline' with the implication that the cavities were originally filled with some fluid phase. While clearly the rectilinear outline must represent some phase boundary before the dendritic crystallization, the nature of this boundary or of the enclosed phase is unknown.

Similar inclusions have been described in olivines from lunar samples (Roedder and Weiblen, 1971; Gay et al., 1972; Bell et al., 1975) although their origin may well differ from the mechanism described here for some Rhum olivines.

Specimen description and preparation. Intergrowths of the type described here can be seen in many of the peridotites of the Eastern Layered Series, Rhum. The present specimen, sample no. R 117, collected by P. Henderson (British Museum, Natural History) is from the peridotite adjacent to a chrome spinel seam at the junction of Units 13-14 (as defined by Brown, 1956) on Hallival.

Electron-microprobe analysis of the olivine matrix gave a formula $Mg_{1.73}Fe_{0.27}SiO_4$. With the electron beam over the platelets, the analyses were not significantly different, although Ca was consistently detected in amounts around 0.3 wt. % CaO. Although this gives no indication of the actual calcium content of the thin platelets, it does suggest a calcium content significantly higher than that in the olivine matrix. The Mg:Fe ratio, however, appears to be unaltered.

Suitable thin specimens were prepared for transmission electron microscopy by ion bombardment (cf. Tighe, 1976). Observations were made with an EM6G electron microscope equipped with a high-tilt specimen stage and operated at 100kV.

Results. Fig. 2 shows an electron micrograph of a section through one of the platelets. The platelets consist of an intergrowth of two phases. Electron diffraction patterns from the olivine and from the two phases within the platelet enable structural data and orientational relationships to be determined. Over ten such platelets were examined in this way and the following information was obtained:

The platelets themselves form two sets and lie on $\{101\}$ planes in the olivine structure.

The bulk of the platelet consists of clinopyroxene. The diffraction patterns are consistent with the $P2_1/c$ clinoenstatite cell. The likelihood that this phase may contain some Fe, as well as the indication from the probe analysis that Ca is present, indicate a composition and structure nearer that of a clinohypersthene.

The rounded inclusions within the clinopyroxene are sections through the rod-shaped branches of the dendritic iron-ore phase. They occur at approximately regular intervals along the length of the platelet, and produce a diffraction pattern consistent with that of magnetite, space group $Fd3m$. Although there is the possibility that some Mg may be present in solid solution, differences in lattice parameters are not sensitive enough to determine compositions along the Fe_3O_4-$MgFe_2O_4$ join from electron diffraction patterns. The magnetite itself is not completely homogeneous, and has a microstructure that produces a 'mottliness' in the diffraction contrast. This is typical of magnetites (G. D. Price, pers. comm.) and chrome spinels (Putnis, unpubl.) and may be associated with an incipient $Fd3m \rightarrow F\bar{4}3m$ ordering transformation suggested by Grimes (1973).

The orientation of the pyroxene relative to the olivine matrix appears to be completely arbitrary from one platelet to another, and diffraction patterns across an olivine-pyroxene boundary show no correspondence in lattice spacings between the two phases. Within any one platelet the pyroxene orientation is constant even when the platelet is apparently segmented by magnetite regions.

The magnetite within the platelet also bears no consistent orientational relationship to the olivine. The individual magnetite regions within a platelet are, however, in the same orientation.

There is a consistent orientation between the pyroxene and the magnetite such that there is a close correspondence between certain similar lattice spacings between the two phases. In the platelet shown in fig. 2, $[211]_{mag.}$ is parallel to $[112]_{cpx.}$ and $(111)_{mag.}$ is parallel to $(131)_{cpx.}$. The 222 reflection of magnetite is coincident with the $\bar{1}31$ reflection of the clinopyroxene. In any single platelet there is a consistent orientational relationship between the magnetite and clinopyroxene. This relationship may differ from one platelet to another, although some measure of lattice correspondence is maintained.

The orientational relationship between magnetite and the pyroxene regions indicates a cooperative nucleation and growth mechanism for the two phases. The randomness of the pyroxene-olivine and magnetite-olivine orientations, while the platelets themselves are well oriented within the olivine, suggests that the platelets were originally of a single phase which had close similarities to the olivine structure. The over-all morphology of the
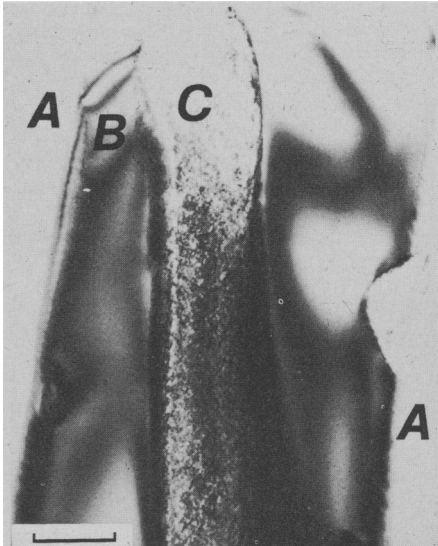
FIG. 2. A transmission electron micrograph of a cross-section through one of the dendritic platelets. The platelet is composed of a eutectoidal intergrowth of two phases: Clinopyroxene (B) and magnetite (C). The host olivine is labelled A. The scale bar represents 0.2 μm.

pyroxene–magnetite intergrowth also suggests simultaneous nucleation of the two phases from a single precursor phase, with nucleation generally occurring at the interface with the olivine matrix.

Evidence for the nature of this precursor phase comes from the existence of a second type of platelet within the olivine. These platelets, very few in number in the specimens examined, also lie on (101) planes of the olivine, and are only a single phase. Moreover, they have a structure similar to that of olivine. Fig. 3 shows an electron micrograph of this single-phase platelet, with diffraction patterns taken from (a) a region with both olivine and platelet, and (b) from the olivine only. The phase within the platelet shares the (010) lattice spacing of olivine and approximately triples the (101) spacing. Unfortunately, an insufficient number of orientations of the platelet could be obtained, even on tilting, to unambiguously define the unit cell of this phase. The conclusion that can be drawn from the diffraction patterns is that the phase is a slightly distorted, (probably) monoclinic superstructure of the olivine structure. Splitting of the superstructure reflections evident in some sections indicates that the platelets are not perfect single crystals and may have a domain structure.

The fact that these platelets lie on (101) planes of the olivine, and that they have a structure that is a modification of the olivine structure strongly suggests that they represent the precursor phase to

the magnetite–pyroxene intergrowth described above. The breakdown of olivine to magnetite and a more silica-rich phase occurs by oxidation, and the evidence suggests that the single-phase platelets are formed in the early stages of oxidation, possibly by segregation of Fe^{3+} centres and metal vacancies within the olivine. The formation of the superstructure may then be due to vacancy ordering prior to the breakdown to the magnetite-pyroxene intergrowth.

Discussion. The morphology and orientational relations between the magnetite and pyroxene have many of the characteristics of a eutectoidal decomposition of the precursor phase by a cellular (pearlitic) precipitation mechanism (Turnbull and Tu, 1968; Yund and McCallister, 1970). The duplex cell consisting of magnetite and pyroxene nucleates at the platelet boundary or at some other defect, and the two phases grow co-operatively into the precursor structure with diffusion taking place across the advancing interface. This mode of nucleation has been extensively studied in the formation of pearlite in the Fe–C system. It has also been proposed as a mechanism in the breakdown of intermediate plagioclase (Voll, 1972).
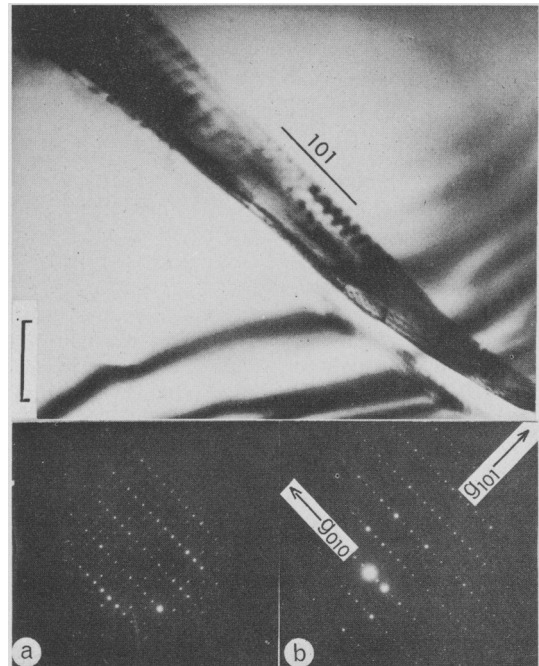

FIG. 3. A transmission electron micrograph showing a lamella of the intermediate phase. The scale bar represents 0.2 μm. The diffraction pattern (a) is taken with the selected area aperture over the lamella, while (b) is taken within the olivine host.

The formation of metastable intermediate phases is a common characteristic of precipitation reactions in metals (Aaronson et al., 1971) and in some minerals (Putnis, 1978). They form at temperatures where the direct formation of the equilibrium phase is kinetically impeded by the large activation energy required for its nucleation. The closer structural similarity between the intermediate phase and the host reduces this activation energy and kinetically favours its formation, particularly at temperatures lower than that for the formation of the equilibrium phases. The retention of the metastable phase in olivine suggests that at lower temperatures its breakdown to magnetite and pyroxene is extremely slow.

Champness (1968) has described two intermediate structures that appear in the early stages of experimental oxidation of olivine. Although both are olivine superstructures and hence presumed to be 'oxidized olivines', neither has a unit cell consistent with the diffraction patterns of the intermediate phase described here. Such a situation is, to some extent, not surprising in view of the fact that under non-equilibrium conditions the nature of the metastable phases formed is likely to be particularly sensitive to the physical and chemical environment, as the free-energy differences between such phases is likely to be small.

The nucleation of the intermediate phase has been *apparently* homogeneous, with no evidence for nucleation on dislocations as observed by Zeuch and Green (1977). The olivine is remarkably free of any dislocation structures, a fact that may well influence the initial oxidation mechanism.

Under equilibrium conditions, heterogeneous oxidation processes will result in the *direct* formation of magetite and pyroxene, forming a 'symplectite' intergrowth initiated at cracks and boundaries within the crystal. Such magnetite-enstatite intergrowths have been described by Muir and Tilley (1957) and Haggerty and Baker (1967). In some of the Rhum olivines, similar intergrowths occur around cracks, in which case an intermediate precursor phase may not have formed.

The fact that the pyroxene is monoclinic in this case may be partly explained by the stabilizing effect of calcium. The enrichment of Ca within the intergrowth relative to the surrounding olivine suggests that Ca has migrated from the olivine to the pyroxene. In a number of platelets (100) stacking faults are present in the clinopyroxene phase, a feature that has been interpreted as the initiation of the transformation to orthopyroxene (Copley and Champness, 1976).

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