Ilmenite exsolution in olivine

DAVID MOSELEY[1]

Department of Geology
University of Manchester
Manchester M13 9PL, England

Abstract

Small lamellae of ilmenite, with a maximum size of 3 μm by 0.1 μm have been observed in olivines from the Upper Zone of the Skaergaard intrusion and the Eucrite series of the Cullin Complex, Isle of Skye. They are exsolved on $(100)_{ol}$ with the approximately hexagonal close-packed oxygen planes in the two structures being parallel. The Ti probably originally substituted for Si in the host olivine.

Introduction

Numerous small lamellae were observed during an electron microscopic examination of olivines containing 35 and 72 mole percent forsterite, respectively, from specimens 4310 of the Upper Zone of the Skaergaard intrusion and SK28 collected (at National Grid Reference NG 497206) from the Eucrite series of the Cullin Complex, Isle of Skye. The largest of these lamellae had a cross section that was 3 × 0.1 μm, though more usually they are about 2 × 0.05 μm. In general the lamellae in the Skye specimen were slightly larger than those from the Skaergaard olivine. They apparently occur in clusters with the lamellar interfaces parallel to each other. However, because of their size, none of these lamellae could be found in a subsequent light microscopy study of thin sections cut from these specimens, so it has not been possible to verify this. For the same reason the overall shape of these lamellae is unknown.

The lamellar interfaces are parallel to (100) olivine, and are semicoherent (Fig. 1). At high magnifications these interfaces can be seen to be shallowly stepped in a fairly regular manner. The steps on the upper surface of the lamella in Figure 1a, which are seen edge on, are about 200Å long and 10Å high. The height is, in fact, twice the width of the lattice fringes (faintly visible on the original negative) within and parallel to the lamella. The strong fringes perpendicular to the lamella are 10.3Å wide, which

correspond to the *b* cell dimension of olivine. The steps on the lower interface in Figure 1a (inset) are inclined in this view, which accounts for the olivine lattice fringes overlapping this edge of the lamella. This same feature is also apparent in the large step in the top right hand corner of the micrograph.

Analytical interpretation

Analyses in an electron microscope microprobe analyzer showed that the lamellae contain Ti. Six analyses of four lamellae in 4310 indicated a TiO_2 content ranging from 10.3 to 23.6 weight percent. However, because the smallest spot that can be analyzed by the electron microscope used in this study (an AEI EMMA-4) is 0.1 μm in diameter, the analyses necessarily contained a substantial contribution from the olivine host and differences in the amount of Ti present are attributed to variations in the quantity of olivine incorporated in the analyses. In an attempt to obtain the probable composition of the lamellae it was assumed that they were Si-free. Si was therefore removed from the lamellar analyses along with Mg, Fe and Mn in the proportions in which they are present relative to Si in olivine (Table 1). The recalculated analyses thus obtained were ilmenite with Fe/(Fe+Ti) ranging from 46 to 59 atomic percent. However, the lowest value can be disregarded because the recalculated analysis gave about −4 weight percent of both MgO and MnO indicating that either this analysis is inaccurate or some Si is present in the ilmenite and that therefore too much Mg and Mn have been subtracted from the analysis. It is possible that some Si is present in all the lamellae, but there is no

[1] Present address: Department of Chemistry, University of Aberdeen, Meston Walk, Old Aberdeen, Aberdeen AB9 2UE, Scotland.
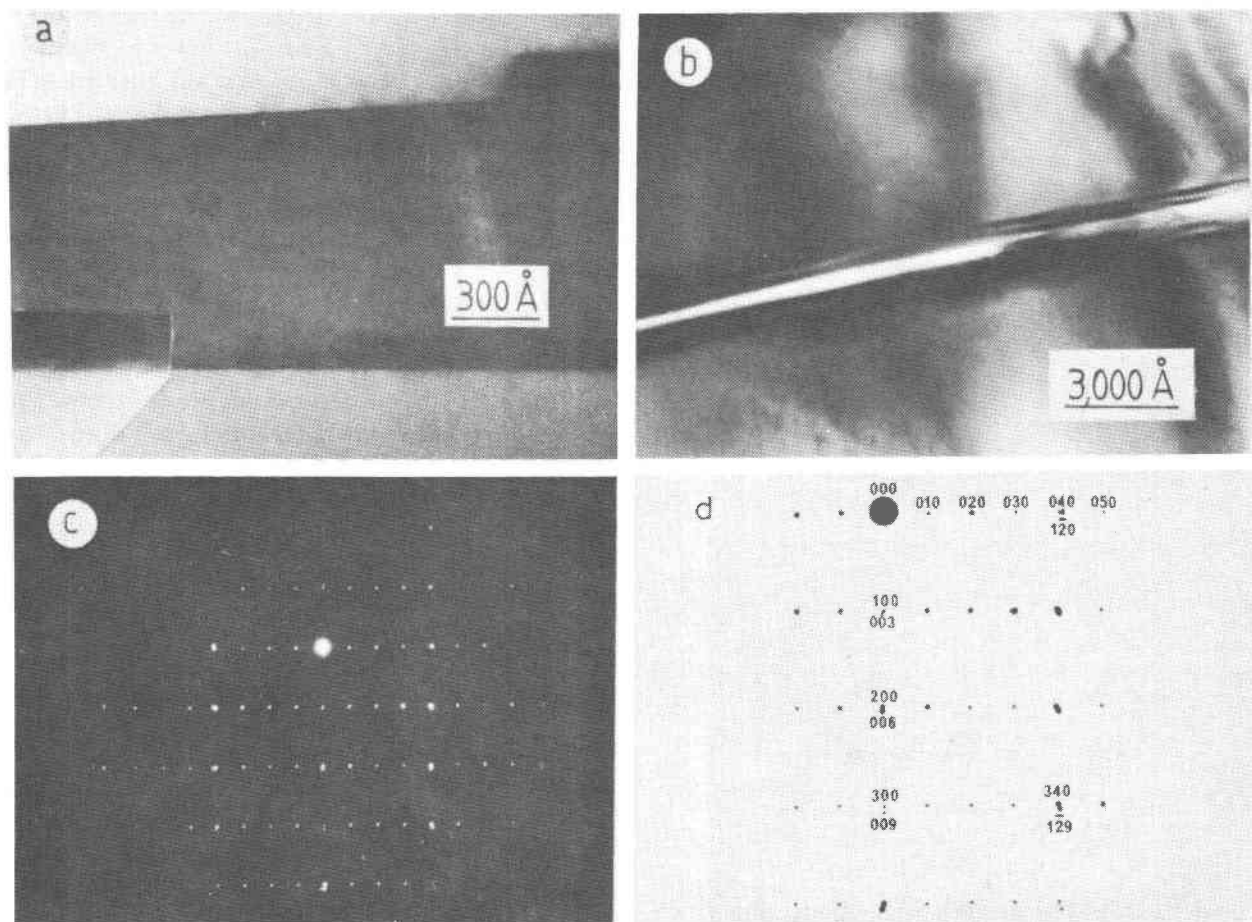
Fig. 1. (a) Edge on view of an ilmenite lamella in specimen SK 28 showing stepped interfaces with olivine. The lower interface is inclined in this view (see inset detail). The vertical lattice fringes are $(010)_{ol}$ and have a spacing of 10.3Å. Zone axis is [001]. (b) A second lamella, from specimen 4310, inclined to show the semicoherent interface with the olivine matrix. Zone axis is [111]. (c) A diffraction pattern of the lamella and host. The pattern is correctly orientated with respect to micrograph (a). (d) Part of the diffraction pattern in (c) enlarged and indexed. The indices above the spots refer to olivine, those below to ilmenite. In this interpretation $[001]_{ol}$ is parallel to $[210]_{il}$.

method of correcting for it other than by assuming that it is present in the same proportion (0.32 wt.%) as in the discrete ilmenite grains coexisting with the olivines in the rock. However, Table 1 shows that there are some significant chemical differences between the exsolved and primary ilmenites.

The adjusted analysis with the highest Fe/Ti ratio is that with the lowest measured TiO_2 content in the original analysis which presumably, therefore, contained the greatest amount of matrix. The remaining four recalculated analyses are very similar with the ratio of Fe/(Fe+Ti) varying only between 52 and 55.5 atomic percent. The lamellar analysis given in Table 1 is from this group. Four analyses of three lamellae in SK28 recalculated in the same manner as those in 4310 gave similar results. The ratio of Fe/(Fe+Ti), for example, varied from 50 to 58 atomic

percent. The main differences were that the Mg and Al contents were higher (MgO was ~4 and Al_2O_3 ~ 1 wt.%).

Diffraction analyses

All the diffraction patterns obtained from the lamellae in both specimens could be indexed as being from ilmenite. Attempts made to interpret these patterns as ulvöspinel, pseudobrookite and the various polymorphs of TiO_2 were unsuccessful. Using the hexagonal cell for ilmenite the orientation of the two lattices are $[100]_{ol}||[001]_{il}$, $[010]_{ol}||[010]_{il}$ and $[001]_{ol}||[210]_{il}$, where the subscripts ol and il refer to olivine and ilmenite respectively. The same orientation has also been found for hematite (which has a structure similar to that of ilmenite) in oxidized olivine (Champness, 1970; Kohlstedt and Vander

Table 1. Representative analyses of olivine and ilmenite in 4310

| | MICROPROBE | | E.M.M.A. - 4** | | |
| | Individual Grains | | Olivine | Exsolved Phase | |
	Olivine	Ilmenite	Host	Uncorrec.	Corrected[+]
SiO_2	32.72	0.32	32.80	16.27	0.00
TiO_2	0.00	53.49	0.00	23.57	46.77
Al_2O_3	0.00	0.00	0.00	0.17	0.34
MgO	15.44	0.71	13.99	7.16	0.43
FeO*	50.80	45.45	52.36	51.96	51.57
MnO	0.67	0.40	0.85	0.87	0.89
CaO	0.15	0.00	0.00	0.00	0.00
Total	99.77	100.45			
Cations	O = 4	O = 3	O = 4		O = 3
Si	0.995	0.008	1.002		-
Ti	-	1.001	-		0.914
Al	-	-	-		0.010
Mg	0.700	0.027	0.637		0.017
Fe	1.291	0.948	1.337		1.120
Mn	0.018	0.009	0.002		0.020
Ca	0.005	-	-		-
Mg/(Mg + Fe)	0.352		0.323		

* All iron as FeO.

** EMMA-4 analyses have been calculated assuming total oxides = 100 wt. % and without any corrections for possible absorption or fluorescence effects, which are assumed to be negligible in the ultrathin specimens used.

[+] Analysis obtained by assuming all Si in uncorrected analysis was from olivine host contamination and removing Mg, Fe and Mn in the appropriate proportions.

Sande, 1975). This relationship requires the $(100)_{ol}$ and $(001)_{il}$ layers of almost close-packed oxygen anions to be parallel and to have the same orientation, thus minimizing the interfacial energy between the two phases.

A diffraction pattern and its interpretation is given in Figure 1. This interpretation is also consistent with the spacing of the lattice fringes in Figure 1a. The strong olivine set normal to the lamella, 10.3Å wide, are $(010)_{ol}$ while the faint set, about 4.8Å in width, inside the lamella and parallel to its length correspond to $(003)_{il}$.

Discussion

A semiquantitative study of electrostatic forces between cations in olivine structures suggest that Ti^{4+} in one of the octahedral sites is unstable if another quadrivalent cation occupies the tetrahedral sites, which is obviously the case for olivines, *sensu stricto*. The situation with respect to Ti^{4+} in the four-fold coordinated sites is less clear. The calculations indicate that Ti is unstable in these sites at low temperatures, though it could be stable at high temperatures when the larger cell parameters allow greater separation between Ti^{4+} and the divalent cations, thus giv-

ing a reduction in the electrostatic repulsive forces between the 4+ and 2+ ions. The lower tolerance to charge repulsions between the M and T sites when Ti rather than Si occupies the tetrahedral sites can be simplistically interpreted as due to less effective negative screening by the oxygen anions of the more open TiO_4 tetrahedra.

The presence of primary grains of both ilmenite (Table 1) and Ti-magnetite in these samples indicate the availability of Ti^{4+} in the original magma. If the above supposition is correct, then it can be anticipated that Ti will substitute for some Si during the crystallization of the olivine. In slowly-cooled igneous bodies like the Skaergaard or Skye intrusions, the Ti would subsequently be exsolved to form a more stable phase. From stoichiometry predictions, ulvöspinel (Fe_2TiO_4) would be the more likely exsolution product, as ilmenite precipitation from olivine would require the development of a second oxide phase, *e.g.*,

$$M_2TiO_4 \rightarrow MTiO_3 + MO \qquad (1)$$
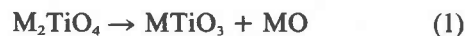
A second oxide phase could be present in these lamellae, but it has not been possible to verify this because their small size makes detailed investigations difficult. The small quantity of Mg present in the lamellae would seem to preclude the possibility of periclase being present as a second phase in them.

The necessity for a second oxide phase is partially alleviated by the exsolution of non-stoichiometric ilmenite ($Fe_{1+x}Ti_{1-x}O_3$), which implies that some ferric iron was also originally present in the olivine. The presence of Fe^{3+} in both these olivines had already been deduced from the exsolved symplectitic intergrowths of magnetite and pyroxene (Moseley, in preparation). Since long-range diffusion is necessary for the formation of these symplectites, any surplus oxide produced when ilmenite is formed might be incorporated into these intergrowths. The higher Mg content of the ilmenite in the Skye specimen may be a reflection of the more forsteritic content of its host olivine.

That Ti is exsolved from olivine as ilmenite rather than ulvöspinel is possibly due to the difference in the energies required for the nucleation and subsequent growth of the two structures from olivine. Ilmenite and olivine are both hexagonal close-packed structures whereas ulvöspinel is cubic close-packed. Consequently the growth of ulvöspinel from olivine would require two thirds of the oxygen stacking sequence to be rearranged. Ilmenite in contrast, needs only cation diffusion for its formation. This is a less energetic process though, of course, further energy

will be expended in forming a second oxide phase (eqn. 1).

The height of the steps in Figure 1a, which are $2a_{ol}$ or $2c_{il}/3$, indicate that the transformation of olivine to ilmenite involves four of the hexagonal close-packed oxygen layers. These steps are obviously aligned along more than one direction and since $[010]_{ol}$ is one of the favored growth directions of the steps, it is possible (though not verified) that the other directions are the pseudo-symmetrically related $\langle 013 \rangle_{ol}$. If this is so, then the olivine–ilmenite transformation takes place by the propagation of steps along any one of the six equivalent $\langle 2\bar{1}\bar{1}0 \rangle$ in ilmenite.

Ilmenite lamellae may be a common feature in olivines with a slow cooling history. Their very small size, however, makes them difficult to detect.

References

Champness, P.E. (1970) Nucleation and growth of iron oxides in olivines, $(Mg,Fe)_2SiO_4$. Mineralogical Magazine, 37, 790–800.

Kohlstedt, D. L. and Vander Sande, J. B. (1975) An electron microscopy study of naturally occurring oxidation precipitates in iron-bearing-olivines. Contributions to Mineralogy and Petrology, 53, 13–24.