Chemistry of ilmenites crystallized within the anhydrous melting range of a tholeiitic andesite at pressures between 5 and 26 kb

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SUMMARY. Microprobe analyses of eight ilmenites, a titaniferous magnetite, and a rutile are presented. They were synthesized at pressures from 5 to 26 kb and temperatures between 1075 and 1225 °C in the anhydrous melting interval of a tholeiitic andesite from the Snake River Plain, Idaho, U.S.A. Both the Fe/Ti distribution between coexisting ilmenite and titanomagnetite at 11 kb/1075 °C and the low calculated Fe^{3+} contents of the other ilmenites confirm previous suggestions that the f_{O_2} in these experiments was buffered by graphite capsules to values near those generated by the wüstite–magnetite assemblage. Mn in the ilmenites (0·30–0·51 % MnO) shows moderate negative correlations with both the pressures and temperatures of their formation, whilst Al (0·41–1·06 % Al_2O_3) shows poor positive correlations with these parameters. In contrast, the only significant trend shown by Mg in the ilmenites (2·09–5·26 % MgO) is with the position of each experimental run in the melting interval of the lava. $Mg/(Mg + Fe^{2+})$ of the ilmenite decreases during equilibrium crystallization at a given pressure and appears to be controlled solely by Mg/Fe^{2+} distribution amongst the coexisting ferromagnesian minerals and interstitial liquid (glass).

IT has become apparent in recent years that variations in the chemistry of ilmenite may allow this widespread mineral to be a useful indicator of petrogenetic conditions. Buddington and Lindsley (1964) and many subsequent workers have shown that the Fe and Ti contents of ilmenite coexisting in equilibrium with titaniferous magnetite are controlled by the redox conditions when these phases crystallize.

Mg is usually the third most abundant metallic element in the ilmenites of mafic igneous rocks, the group considered in this paper. The MgO content of ilmenites in both terrestrial and lunar volcanic rocks is generally less than 4 %, but values up to 8 % have been recorded from both environments. Highly magnesian ilmenites (MgO up to 19 %) are characteristic megacrysts of kimberlites. As it is generally agreed that this rock type was generated at great depths in the mantle and ascended rapidly, the possibility arises that the high Mg content of its ilmenites is at least partly a result of the high pressure under which they crystallized. Most chemical studies of ilmenite have not favoured this hypothesis. Thus, Lovering and Widdowson (1968) demonstrated a crude positive correlation between the Mg contents of ilmenites and the Mg/Fe^{2+} ratios of the rocks containing them, regardless of the depths from which these were apparently derived. Mitchell (1973) has suggested that variation in Mg/Fe^{2+} during the crystallization of kimberlite magmas caused the wide range (6–19 %) of MgO he found in their ilmenites. Most studies of lunar ilmenites (e.g. Steele, 1974;

Nehru *et al.*, 1974) have also emphasized systematic relationships between Mg/Fe^{2+} in this phase, coexisting minerals, and the rock containing them. Nevertheless, Haggerty (1973) has taken the alternative point of view, that the magnesian Luna 20 ilmenites were formed at high pressures.

The remaining elements detected in small amounts in most analyses of ilmenites from mafic rocks are Si, Al, Cr, and Mn. Only Cr has been reported to show any systematic variation. Nehru *et al.* (1974) demonstrated a positive correlation between Cr and Mg in the less-magnesian Apollo 15 ilmenites. Haggerty (1975) found a contrasting negative Cr–Mg covariance in less-magnesian kimberlite ilmenites, reversing to a positive correlation in analyses with more than 8 % MgO.

Ilmenites synthesized within the melting ranges of mafic rocks

Although a number of individual microprobe analyses of experimentally crystallized ilmenites have been published, there has been little systematic study of this phase within the melting ranges of igneous rocks. Green and Sobolev (1975) synthesized ilmenites at temperatures from 900 to 1100 °C and pressures from 21 to 40 kb from olivine basanite and pyrolite-less-40 %-olivine with various water contents. They showed that the two different bulk compositions precipitated ilmenites with distinctive ranges of Mg and Cr contents. The Mg/Fe ratios of the ilmenites varied systematically as a function of run temperatures and showed a constant relationship to Mg/Fe of coexisting garnet.

The ilmenites described in this report were synthesized during experimental study of a tholeiitic andesite (OB32) from the Snake River Plain, Idaho, U.S.A. A chemical analysis of this lava has been published previously (Thompson, 1974*a*). The experiments were conducted using anhydrous rock powder in graphite capsules within piston-cylinder apparatus. Details of the techniques used are given elsewhere (Thompson, 1974*b*). The use of graphite capsules buffers the charges at oxygen fugacities close to those of the wüstite–magnetite assemblage (Thompson and Kushiro, 1972). The *P–T* diagram for the tholeiitic andesite (Thompson, 1975*a*, fig. 3) shows an extensive field of ilmenite crystallization within its melting range. Under the redox conditions of these experiments, ilmenite precipitates within 20 °C of the lava's liquidus at 8 kb. Its stability field is restricted progressively closer to the solidus at higher pressures, until at 26 kb it crystallizes at about 90 °C below the liquidus and only 40 °C above the solidus. With rising pressure between 5 and 26 kb, the ilmenite is accompanied by the following silicate assemblages: olivine+plagioclase+clinopyroxene; plagioclase+clinopyroxene; clinopyroxene+garnet. Ilmenite coexists with titanomagnetite in the products of a near-solidus run at 11 kb and with rutile in a 26 kb run. Rutile replaces ilmenite as the near-solidus oxide phase precipitating from this lava at pressures above 26 kb.

The quantities of ilmenite in the run products range from 5 % to less than 1 %. In reflected light its crystal shapes vary from euhedral to rounded and equant to moderately elongate. Crystals up to 40 μm in length were observed but few exceeded 20 μm. Analyses were made using a computer-automated MAC model 400 electron microprobe. The standards and settings are recorded elsewhere (Thompson, 1974*a*, *b*).

TABLE I. *Microprobe analyses of ilmenites and coexisting oxides*

Pressure	5 kb	8.5	10	11	14	20	26	26	26	11
Temperature	1100°C	1125	1100	1075	1135	1175	1225	1200	1225	1075
°C below rock liq.	33	23	63	98	69	91	103	128	-	-
Mineral analysed*	Ilm	Ilm	Ilm	Ilm	Ilm	Ilm	Ilm	Ilm	Rut	Mt
Coexisting solid phases*	Ol Pl Cpx	Ol Pl Cpx	Ol Pl Cpx	Ol Pl Cpx Mt	Pl Cpx	Pl Cpx Gt	Pl Cpx Gt Rut	Pl Cpx Gt	Pl Cpx Gt Ilm	Ol Pl Cpx Ilm
SiO_2	0.22	0.23	0.21	0.19	0.21	0.21	0.19	0.23	0.26	0.33
Al_2O_3	0.41	0.57	0.50	0.50	0.71	1.06	1.01	0.98	0.36	3.41
Cr_2O_3	0.04	0.04	0.03	0.03	0.02	0.02	0.04	0.02	0.01	0.04
Fe_2O_3	-	0.65	1.40	5.95	2.59	3.40	3.26	2.65	-	14.3
FeO	39.6	38.1	41.4	40.1	41.1	41.0	40.6	41.9	1.17	52.4
MnO	0.51	0.44	0.49	0.51	0.39	0.37	0.31	0.30	0.01	0.45
MgO	4.82	5.26	2.99	2.55	3.00	2.73	2.27	2.09	0.00	1.91
TiO_2	54.4	53.2	52.4	50.1	51.9	51.2	49.9	50.8	98.2	26.0
Total	100.0	98.5	99.4	99.9	99.9	100.0	97.6	99.0	100.0	98.8
Cations to a basis of O =	6	6	6	6	6	6	6	6	2	32
Si	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.00	0.10
Al	0.02	0.03	0.03	0.03	0.04	0.06	0.06	0.06	0.01	1.18
Cr	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01
Fe^{3+}	-	0.02	0.05	0.22	0.10	0.13	0.12	0.10	-	3.17
Fe^{2+}	1.61	1.57	1.72	1.66	1.69	1.69	1.72	1.75	0.01	12.87
Mn	0.02	0.02	0.02	0.02	0.02	0.01	0.01	0.01	0.00	0.11
Mg	0.35	0.39	0.22	0.19	0.22	0.20	0.17	0.15	0.00	0.84
Ti	1.99	1.96	1.95	1.87	1.92	1.90	1.90	1.91	0.99	5.73
Total cations	4.00	4.00	4.00	4.00	4.00	4.00	3.99	3.99	1.01	24.01
Components (Mol.%)										
Al_2O_3	0.6	0.8	0.8	0.8	1.0	1.6	1.5	1.5	Sp[†]	7.4
Cr_2O_3	tr	tr	tr	tr	tr	tr	tr	tr	$MgCr_2O_4$	tr
Fe_2O_3	-	0.6	1.3	5.6	2.4	3.2	3.1	2.5	Mg_2SiO_4	1.2
$FeSiO_3$	0.5	0.5	0.5	0.4	0.5	0.5	0.5	0.5	Mg_2TiO_4	1.4
$MnTiO_3$	1.0	0.9	1.0	1.0	0.8	0.7	0.7	0.6	Mn_2TiO_4	0.7
$MgTiO_3$	17.5	19.3	11.0	9.4	11.0	10.0	8.6	7.7	Fe_2TiO_4	69.5
$FeTiO_3$	80.5	78.0	85.5	82.9	84.3	84.1	85.7	87.3	Fe_3O_4	19.7
Hem	0	0.8	1.5	6.3	2.8	3.7	3.5	2.8	Mt	22.1
Ilm	100	99.2	98.5	93.7	97.2	96.3	96.5	97.2	Usp	77.9
$Mg/(Mg+Fe^{2+})$	0.18	0.20	0.11	0.10	0.12	0.11	0.09	0.08		0.06

* Ilm = ilmenite; Mt = magnetite; Rut = rutile; Ol = olivine; Pl = plagioclase; Cpx = Ca-rich clinopyroxene; Gt = garnet; Hem = hematite; Usp = ulvöspinel.   [†] Spinel $Mg_{0.7}Fe_{0.3}Al_2O_4$.

All the ilmenites (Table I) have low and approximately constant Si contents. This feature was used to monitor silicate contamination. Wherever possible, data from at least five points showing minimum Si values were averaged to give each analysis in Table I.

Chemical variation amongst the synthetic ilmenites. The Cr contents of the ilmenites are too near the detection limit of the microprobe (for the techniques used) to show significant variation. Fe^{3+} was calculated by assuming stoichiometry, a procedure subject to considerable error (Finger, 1972). Nevertheless, the estimates are adequate

to show that Fe^{3+} in the ilmenites corresponds quite well with the anticipated oxygen fugacities of the experiments. On the basis of Thompson and Kushiro's preliminary work (1972), it may be surmised that all these runs were at values of f_{O_2} close to those generated by the wüstite–magnetite buffer, with runs below 12 kb (except the one at 1075 °C) probably in the wüstite stability field and those above 18 kb probably in the magnetite stability field. The 11 kb/1075 °C run produced coexisting ilmenite and titanomagnetite (Table I). The analyses of these phases have been calculated into binary ilmenite and magnetite components using the scheme proposed by Anderson (1968). Application of the method of Buddington and Lindsley (1964) gives $T =$ 1140 °C and $\log f_{O_2} = -9\cdot3$ for this run. The f_{O_2} falls between values appropriate to the wüstite–magnetite and fayalite–magnetite–quartz buffers at 1140 °C. The 65 °C gap between the temperature of the run and that calculated from its coexisting Fe–Ti oxides is much less significant than it seems, because the estimated temperature falls outside the range studied by Buddington and Lindsley (1964) and may only be reached by extrapolation of their data. In this region of Buddington and Lindsley's diagram (1964, fig. 5) the ilmenite and magnetite composition isopachytes intersect at very low angles, so that any small imprecisions in their original determination and extrapolation or in the experimental and analytical conditions of the present study would cause substantial errors to occur in the calculated temperature.

The Al, Mn, and Mg contents of the ilmenites vary considerably (Table I). It is not easy to show unambiguously what factors control these variations because there is quite a strong correlation between run pressures and temperatures in the experiments, with only one example each of polythermal isobaric (26 kb) and polybaric isothermal (1100 °C) pairs of runs (Table I). Al shows a moderate positive correlation with pressure up to 20 kb and then no significant variation up to 26 kb (fig. 1). The reason for this may be that the ilmenite stability field in this lava meets the garnet stability field at about 20 kb. There is a poor positive correlation between Al and run temperature in these experiments (fig. 2), consistent with the findings of Green and Sobolev (1975). Finally, Al definitely does not correlate with the position of each run within the melting range of the lava (fig. 3). This is not immediately apparent on fig. 3 because of the 'swamping' effect of the positive correlation between Al and pressure. However, the ilmenite from the run at 11 kb and 1075 °C provides the necessary confirmation.

There is a small but fairly uniform decrease with both rising pressure (fig. 1) and temperature (fig. 2) in the Mn contents of these ilmenites; this relationship is confirmed by the isothermal and isobaric pairs in Table I. Like Al, Mn shows no systematic trend on fig. 3.

The Mg contents of the ilmenites form a very scattered distribution on fig. 1, which, if anything, shows a slight negative correlation with pressure. There is therefore no support from this study for any hypothesis that high pressure at the time of formation of kimberlite ilmenites contributed to their high Mg contents. The Mg values are also largely unrelated to the temperatures at which the ilmenites were synthesized (fig. 2) but, in contrast, show a good correlation with the position of each run within the melting range of the tholeiitic andesite (fig. 3). This relationship applies also to the $Mg/(Mg+Fe^{2+})$ ratios of the ilmenites (fig. 3) and is the same as that reported else-
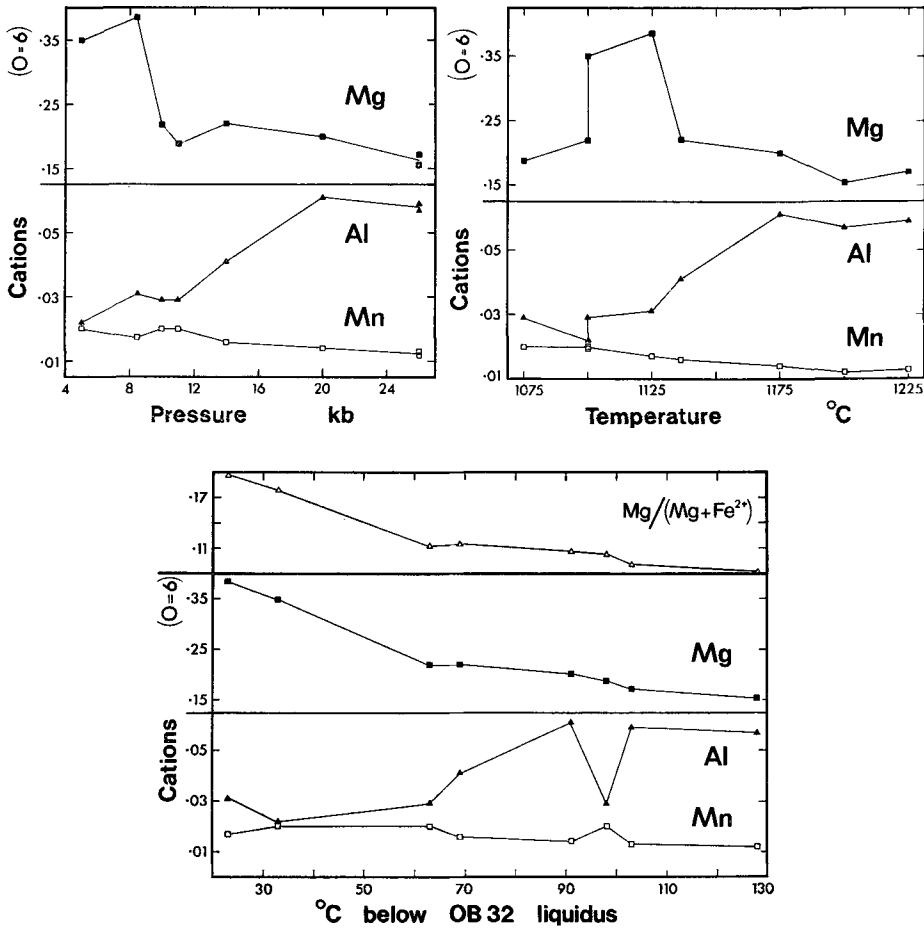
FIGS. 1 to 3: FIG. 1 (top left). Mg, Al, and Mn versus pressure for ilmenites crystallized within the anhydrous melting interval of tholeiitic andesite OB32. FIG. 2 (top right). Mg, Al, and Mn versus temperature for ilmenites crystallized within the anhydrous melting interval of tholeiitic andesite OB32. FIG. 3 (bottom). Mg, Al, Mn, and $Mg/(Mg+Fe^{2+})$ in ilmenites crystallized experimentally within the anhydrous melting interval of tholeiitic andesite OB32, plotted as a function of the difference (°C) between the temperature of each run and the liquidus of the lava at that pressure.

where by the author for olivines, clinopyroxenes, garnets, and interstitial glasses crystallized during high-pressure study of a Snake River Plain olivine tholeiite basalt (59–P–13), carried out using the same techniques as in the experiments reported here (Thompson, 1974a, 1975a, b). In basalt 59–P–13 the $Mg/(Mg+Fe^{2+})$ ratios of all ferromagnesian minerals and the liquid (quenched to glass) with which they were in equilibrium diminish with falling temperature at a given pressure. The rate at which this happens varies according to the solid assemblage present and the temperature range of the melting interval of the lava. As the latter varies from 90 °C to 140 °C for

tholeiitic andesite OB32 between 5 and 26 kb pressure, the smoothness of the over-all Mg curve on fig. 3 is remarkable.

Insufficient analyses are available of ferromagnesian minerals or interstitial glass synthesized within the polybaric melting interval of the tholeiitic andesite to prove uniform Fe-enrichment with falling temperature. However, all the data (Thompson, 1975a, table 4) are consistent with the view that this lava behaves experimentally in exactly the same way as basalt 59-P-13. It is therefore postulated that the only significant factor controlling the Mg contents of the ilmenites in Table I is the Mg/Fe^{2+} distribution amongst the solid and liquid phases at various stages of the equilibrium crystallization of the tholeiitic andesite.

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