PHASE RELATIONSHIPS IN THE SYSTEM PICROILMENTITE - CLINOPYROXENE - Cr_2O_3

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Preliminary experiments have been carried out between 15 - 35 kb and 1000-1550°C on the natural system picroilmenite - clinopyroxene - Cr_2O_3 using graphite capsules, in an attempt to determine phase relationships relevant to the petrogenesis of titanium and chromium bearing opaque oxides which occur in upper mantle xenoliths, and as megacrysts in kimberlite. A chromium-rich system, picroilmenite (21 wt%) - clinopyroxene (69.5 wt%) - Cr_2O_3 (9.6 wt%) and a relatively chromium-poor system, picroilmenite (66.5 wt%) - clinopyroxene (28.5 wt%) and Cr_2O_3 (5.0 wt%) have been examined.

In the chromium-rich system, two subsolidus runs at 15 and 35kb and 1100° and 1286°C respectively, both produced titanian chromite, chrome diopside and chromian rutile. The 15kb run also probably contained small laths of armalcolite. In the chromium-poor system, however, chromian ulvöspinel, chromian ilmenite and chrome diopside appeared in the runs at 20, 27.5 and 35kb within the temperature range studied (Figure 1). Chromian ulvöspinel is the liquidus phase, followed by chromian picroilmenite with the proportion of ilmenite relative to spinel increasing with decreasing temperature. Spinel is absent on the solidus at 35 kb but is retained as a solidus phase at 20 and 27.5 kb. Very small spinels were encountered in the subsolidus runs at 35 kb, but it is uncertain whether they are metastable phases or the products of subsolidus reaction and further experimentation is required. Clinopyroxene was encountered for the first time at 20-30°C above the solidus. In general, both the Cr_2O_3 and MgO contents of the ilmenite and the spinel decrease with decreasing temperature at each pressure studied. Some representative results are given in Table 1. Tie lines between ilmenite - spinel pairs are given in Figure 2.

The more important phase relationships which emerge from this initial experimental study are (i) the coexistence of titanian chromite and chromian rutile in the Cr_2O_3 - rich system, (ii) the coexistence of chromian ilmenite and chromian ulvöspinel in the Cr_2O_3 - poor system, and (iii) the absence of armalcolite above 20 kb. (The projected curves for the breakdown of armalcolite (Kesson and Lindsley, 1975; Friel et al, 1977) intersect the solidus between 8 and 18 kb depending on the composition of the armalcolite). In addition, it appears as if chromian ulvöspinel has a reaction relationship to ilmenite of the type,

$Fe_2TiO_4 + TiO_2$ (from liquid) $\longrightarrow 2\,FeTiO_3$.

A new suite of chromian ilmenite megacrysts containing lamellae of chromian spinel similar to those previously described by Danchin and d'Orey (1972) and Haggerty (1975) have also been analysed (Table 1). Some of these lamellae are also associated with chromian rutile. The high MgO content (>13 wt%) of these megacrysts when compared to the MgO content of the experimentally produced ilmenites (<10 wt%) possibly indicates that the former crystallized in equilibrium with an MgO-rich phase such as olivine or orthopyroxene, whereas the latter have crystallized from a clinopyroxene-rich system. Using these data and previously recorded associations of ilmenite, spinel and rutile from kimberlite and upper mantle xenoliths (Dawson and Smith, 1976; Smith and Dawson, 1975; Haggerty, 1975; Boyd and Nixon, 1975) as well as the present experimental data, it has been possible to compile a phase compatibility diagram for the system TiO_2 - (MnO + FeO + MgO) - (Fe_2O_3 + Al_2O_3 + Cr_2O_3) relevant to upper mantle conditions (Figure 3). It is to be noted that the 3 phase assemblage, spinel$_{ss}$ - ilmenite$_{ss}$ - rutile$_{ss}$ replaces the low pressure assemblage, spinel$_{ss}$ - ilmenite$_{ss}$ - ferropseudobrookite$_{ss}$ determined at atmospheric pressure within the synthetic system TiO_2 - MgO - FeO - Al_2O_3 - Cr_2O_3 (Maun et al 1971; Schreifels and Maun, 1975). The solubility of Cr_2O_3 and Al_2O_3(?) in picroilmenite is temperature dependant and probably reach maxima of approximately 13 and 1.2 (?) wt% respectively. Under subsolidus conditions the breakdown of chromian picroilmenite would be towards chromian ulvöspinel, rutile and Cr_2O_3 - depleted picroilmenite, with decreasing temperature. At low temperatures (less than approximately 1000°C) the spinel compositions may be complicated by miscibility gaps in system Mg Al_2O_4 - Mg_2TiO_4 and $FeAl_2O_4$ and Fe_2TiO_4 (Maun et al, 1972).

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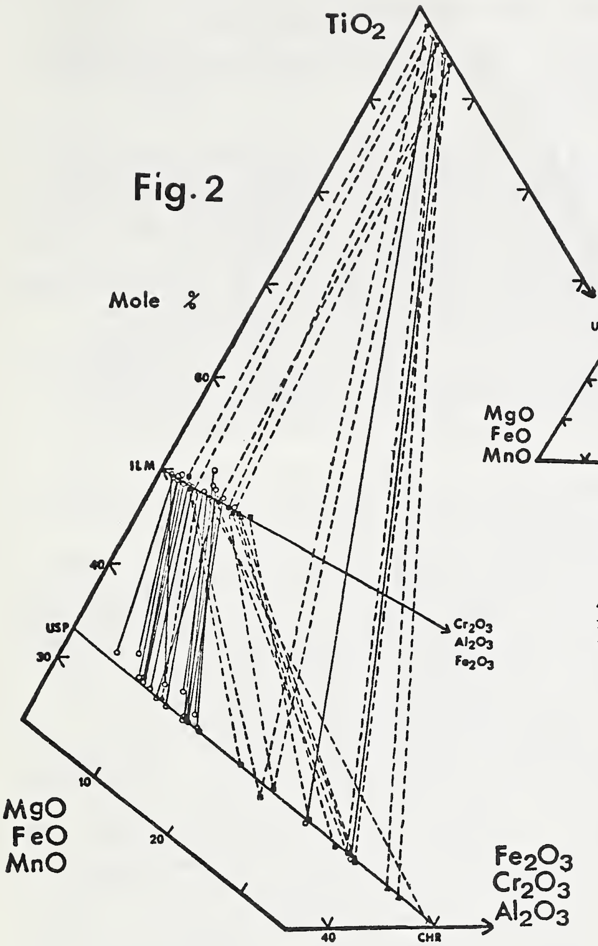
TABLE 1. Representative analyses of coexisting minerals from three experimental runs and a natural chromian picroilmenite containing lamellae of spinel and rutile.

P (kb)	EXPERIMENTAL RUNS						SPINEL AND RUTILE LAMELLAE IN ILMENITE		
T (°C)	27,5 1402		27,5 1500		35 1286				
PHASE	I	S	I	S	R	S	I	S	R
SiO_2	0.02	0.63	0.00	0.13	0.10	0.49	0.0.	0.16	0.05
TiO_2	50.39	24.66	51.21	24.18	89.94	6.34	48.46	8.11	87.86
Al_2O_3	0.41	1.81	0.70	2.62	0.30	3.24	1.02	11.40	0.21
Cr_2O_3	7.14	20.19	11.25	26.73	7.72	57.16	11.18	41.56	4.18
Fe_2O_3*	2.60	1.71			0.42	1.90	7.35	4.93	1.78
FeO	29.90	40.06	26.70	34.28		17.66	18.48	19.25	
MnO	0.11	0.21	0.13	0.19		0.28	0.18	0.26	0.03
MgO	8.31	9.19	9.70	12.08	0.11	13.63	13.96	14.22	0.48
CaO	0.40	0.62	0.26	0.30	0.46	0.39	0.03		0.11
TOTAL	99.28	99.07	99.95	100.51	99.05	101.09	100.68	99.89	94.70

* Fe_2O_3 calculated from mineral formula. I=ilmenite, S=spinel, R=rutile



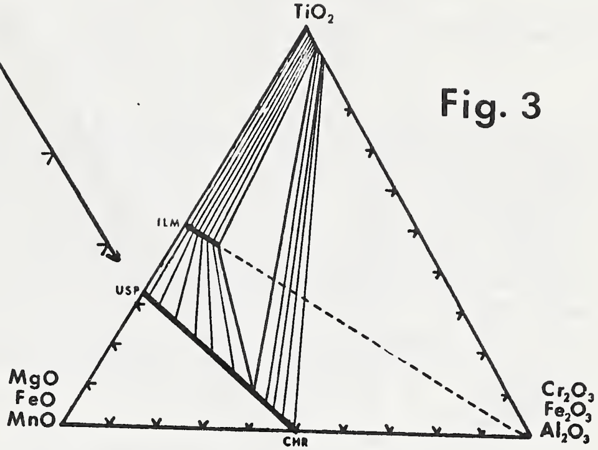


Fig. 3

Phase compatibility diagram (mole %) constructed from Fig.2 and relevant to upper mantle condiditons (>20 kb). Apices in the 3 phase triangle, usp_{ss} - $rutile_{ss}$ - ilm_{ss} will vary with temperature. Abrev. as for Fig.2.

Fig. 2

Tie lines for coexisting ilmenite, spinel and rutile. Solid lines-experimental runs, dashed lines-data for natural assemblages from this study and the literature.
NB. For experimental runs, Fe_2O_3 is absent or present in very low concentrations.
ILM=ilmenite, CHR=chromite, USP=ulvöspinel.

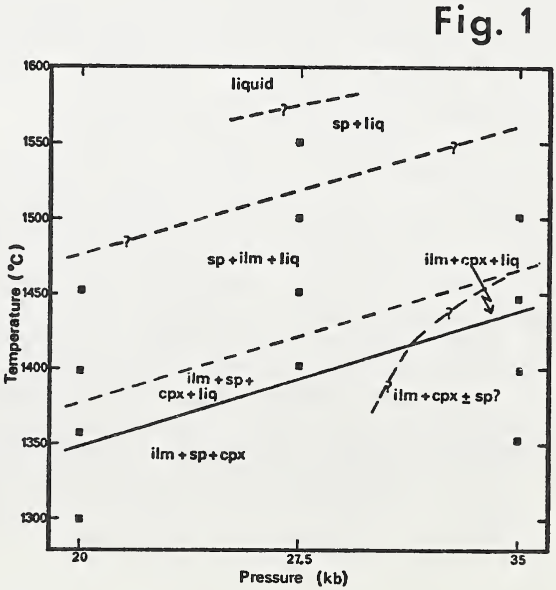


Fig. 1

Isopleth for the composition, picroilmenite (66.5 wt%) - clinopyroxene (28.5 wt%) - Cr_2O_3 (5.0 wt%). Solid squares indicate data points. ilm=chromian picroilmenite, sp=chromian ulvöspinel, cpx=clinopyroxene, liq=liquid.