

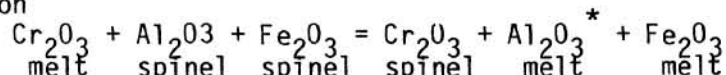
SOLUBILITY OF CHROMIUM IN A SYNTHETIC BUSHVELD / STILLWATER PARENT LIQUID AT 1 ATM. AS A FUNCTION OF TEMPERATURE AND OXYGEN FUGACITY. Stephen J. Barnes, SN4, NASA-JSC, Houston, Tx. 77058.

A series of experiments has been carried out to determine the distribution of Cr between chromite spinel and a high silica, high magnesium basaltic liquid. The starting material was a synthetic glass, having a composition (table 1) representative of the "U-type" liquids thought to be parental to the chromite - bearing cumulates of the Stillwater and Bushveld Complexes [1,2]. These experiments are therefore directly applicable to studies of chromite seams in layered intrusions.

Experiments were carried out in Deltec vertical gas mixing furnaces, using CO/CO<sub>2</sub> gas mixtures to control oxygen fugacities. The starting glass was doped with 20-30% Stillwater bronzite, and either 1% Cr<sub>2</sub>O<sub>3</sub> or 5% Stillwater chromite, to ensure the presence of both orthopyroxene and chromite as run products. Some experiments were taken up to the liquidus of the bulk composition (1360°C) and cooled to the final temperature, while others were taken directly to temperature; charges were held at the final temperature for three to eleven days.

Figure 1 shows the chrome content (expressed as wt. % Cr<sub>2</sub>O<sub>3</sub>) of the quenched glass for spinel saturated runs, as a function of temperature for runs carried out along and between the NNO, QFM, WM and IW oxygen buffer curves. The best fit curves represent the Cr content of the melt at which chromite begins to crystallize. Cr solubility increases with temperature along each buffer, and increases with decreasing oxygen fugacity at constant temperature. The latter effect is attributable to an increasing ratio of divalent to trivalent chrome in the melt, as found by [3]; Cr(II) is apparently much more soluble.

The change in Cr(III)/Cr(II) ratio may be quantified by considering the exchange reaction

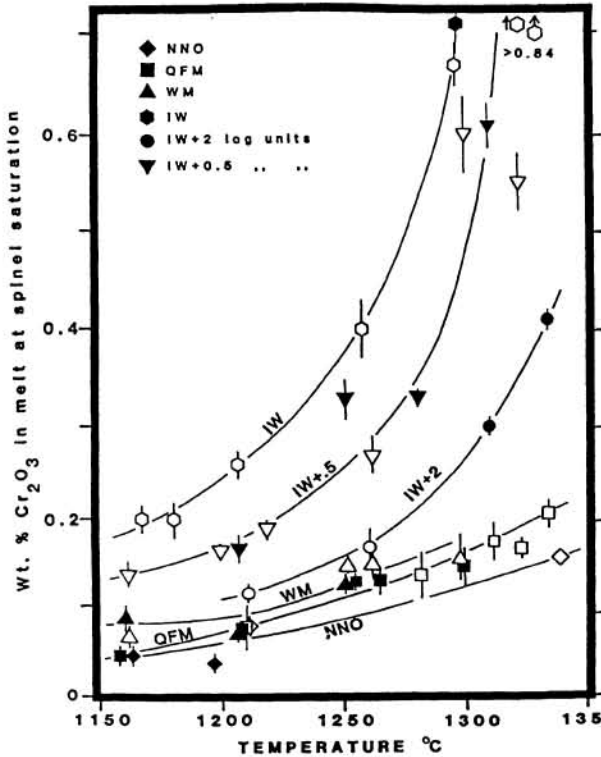


where Al<sub>2</sub>O<sub>3</sub><sup>\*</sup> indicates "free" network-modifying Al in the melt after allowing for complexing of Al to form NaAlO<sub>2</sub> and KAlO<sub>2</sub> (following the two-lattice model for silicate melt structure [4]). This approach is designed to reduce the effect of changing melt composition. The experimentally determined distribution coefficient K'<sub>D</sub> for this reaction is plotted against reciprocal temperature in figure 2, in which all Cr is expressed as Cr(III). K'<sub>D</sub> is therefore an apparent value; the ratio of this value to the true K<sub>D</sub> for the trivalent Cr only is then equal to the ratio of Cr(III) to total Cr in the melt (assuming that all the Cr in the spinel is Cr(III)). The coherence of all the experimental points at and above the WM buffer suggests that essentially all of the Cr in the melt for these runs is as Cr(III). The regression line in figure 2 therefore gives the true K<sub>D</sub>, enabling the mole fraction of Cr(III) to total Cr to be calculated for all the reduced runs. The results of this calculation are plotted in figure 3. The proportion of Cr(III) decreases systematically with lower oxygen fugacity, and is dependent only (within experimental uncertainty) on oxygen fugacity relative to that of QFM at any temperature.

Crystallization of thick, massive chromite seams requires a mechanism for pushing a magma suddenly into a field of supersaturation with respect to Cr. Either rapid cooling or rapid oxidation of a chromite - saturated liquid could achieve this result. Mixing of two magmas of contrasting redox state

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may be a potential mechanism. Mixing of two cogenetic chromite - saturated liquids at different temperatures along the IW buffer could produce supersaturation, owing to the sense of curvature of the chromite saturation surface, but this mechanism would not operate at QFM, where the saturation surface is linear with temperature.



References: [1] Cawthorne and Davis (1983) *Contribs. Min. Pet.* 83, 128-135. [2] Sharpe and Irvine (1983) *Carnegie Inst. Yb.* 82, 295-300. [3] Schreiber and Haskin (1976) *Proc. L.P.S.C.* 7, 1221-1259. [4] Bottinga et al (1982), *G.C.A.* 46, 909-919.

TABLE 1: Composition of synthetic starting glass:

SiO <sub>2</sub>	TiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	MgO	CaO	Na <sub>2</sub> O	K <sub>2</sub> O
55.2	0.4	12.6	9.6	12.3	6.9	2.0	1.0

FIGURE 1. Cr solubility (total Cr expressed as Cr203) versus temperature for oxygen fugacities along the nickel - nickel oxide (NNO), quartz - fayalite - magnetite (QFM), wustite - magnetite (WM) and iron - wustite (IW) buffer curves and intermediate conditions. Open symbols: isothermal experiments, closed: cooling runs. Error bars represent 2 x standard error of mean probe determination.

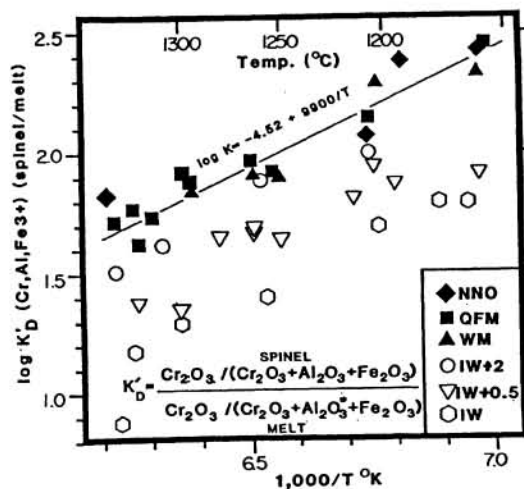


FIGURE 2. Apparent distribution coefficient  $K'_D$  for Cr - Al - Fe<sup>3+</sup> exchange between spinel and melt. Regression line is for WM and above (closed symbols) only.

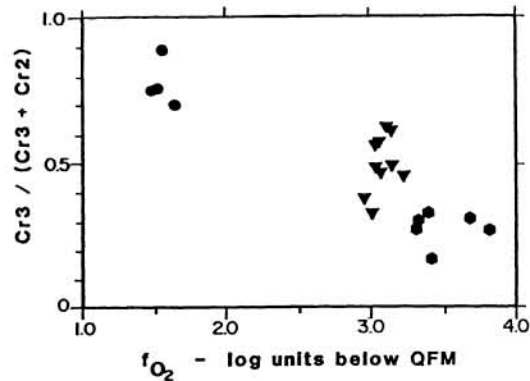


FIGURE 3. Calculated ratio of Cr(III) to total Cr as function of oxygen fugacity (relative to that of QFM buffer at temperature of each experiment).