

W.R.TAYLOR &amp; D.H.GREEN

Geology Dept, University of Tasmania, Hobart 7001

Until very recently, many petrogenetic models were based on the assumption that  $f_{O_2}$ -conditions in magma source-regions of the upper mantle were relatively oxidized, lying near the  $f_{O_2}$  defined by the synthetic assemblage fayalite-magnetite-quartz (FMQ). This was consistent with the petrogenetic role inferred for oxidized  $CO_2$ - $H_2O$  volatiles and carbonated peridotite. However, if magma generation involving volatile components takes place in a reduced environment, for example at  $f_{O_2}$ 's near the iron-wustite (IW) oxygen buffer - as suggested by intrinsic  $f_{O_2}$  measurements on mantle-derived minerals - then in the model system "peridotite"-C-O-H, volatiles will be dominantly  $CH_4 > H_2O > H_2 > C_2H_6$  mixtures and crystalline carbonates will not be stable relative to diamond or graphite (Taylor, 1986). The nature of mantle melting under reduced conditions is expected to be very different from that occurring in an oxidized environment. This problem may be investigated from both a theoretical and experimental basis.

Using a thermodynamic model for C-O-H fluids at elevated P,T, phase relations in the presence of elemental carbon may be represented on a  $\log f_{O_2}$ - $X_C$  diagram of the type devised by Frost (1979) (where  $X_C$  = mole fraction of carbon relative to  $H_2$  in the bulk fluid). This diagram may be contoured in terms of species mole fraction or fugacity as illustrated in Fig.1 at 30 kbar, 1600 K for  $H_2O$ . The curved line is an isobaric, isothermal slice of the graphite saturation surface that delineates the stability field of graphite and coexisting fluid. Oxidized and reduced fluid-only regions lie, respectively, above and to the left of the saturation curve. These regions are effectively separated by a large graphite + fluid field that extends to very water-rich fluid compositions at GW on the "nose" of the saturation curve (Fig.1). Fluids lying on the upper horizontal portion of the saturation curve are dominantly  $H_2O$ - $CO_2$  mixtures. With increasing  $X_C$  the curve intersects the  $\log f_{O_2}$  axis at a point on the graphite- $CO_2$ -CO (GCO)  $f_{O_2}$  buffer. With decreasing  $f_{O_2}$  fluids progress from  $H_2O > CH_4 > H_2$  mixtures to  $CH_4 > H_2 > C_2H_6$  mixtures at  $f_{O_2}$ 's below IW. Below and to the right of the saturation curve a metastable region exists. Fluids are carbon supersaturated and may only lie in this region if elemental carbon crystallization is suppressed e.g. fails to nucleate. The GCO buffer and the locus of points in P-T- $f_{O_2}$  space defining the maximum water mole fraction (GW) are given by the following equations (applicable over the range 5-50 kbar, 800-1700 K for P[bar] & T[K]):

$$\log(f_{O_2}/\text{bar}) = a + b \ln T + c/T + d(P/T) + e(P/T)^2$$

GCO	2.0815	2.5754E-1	-21060	0.17112	-7.4268E-4
GW	5.0186	-6.5844E-2	-22674	0.12858	-6.6384E-4

Recognizing that melting in the system peridotite-C-O-H will be largely a function of  $f_{H_2O}$ , the isobaric, isothermal solidus of graphite peridotite can be

approximated by the intersection of an  $fH_2O$  contour with the graphite saturation curve (see Fig. 2). Vapour excess melting will then be initiated at minimum  $fH_2O$ 's corresponding to either a reduced condition (point A) or an oxidized condition (point B). In Fig. 2 the stability fields of graphite-bearing and graphite-free peridotite are delineated in qualitative fashion; the lines AY and BX correspond to the solidus of graphite-free peridotite. Provided  $fO_2$  remains above GW, vapour-excess melting of graphite peridotite in the presence of  $H_2O$ - $CO_2$  fluids will not differ greatly from the graphite-free case because  $fH_2O$  and  $fCO_2$  contours extend in more or less parallel fashion from oxidized conditions towards the graphite saturation surface. The same however cannot be said for conditions more reduced than GW. While the reduced portion of the of the diagram mirrors the oxidized part in terms of phase fields, with carbide rather than carbonate as the C-bearing phase, the nature of melts formed at "A", involving  $H_2O$ - $CH_4$  fluids, are likely to be very different from melts formed at "B" where  $H_2O$ - $CO_2$  fluids predominate.

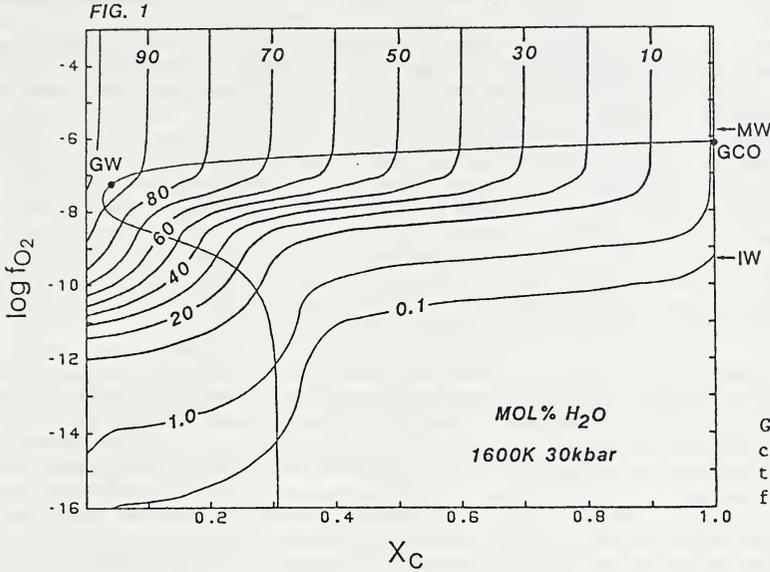
As a first step in evaluating the nature of reduced volatile interactions with silicate melts, experimental liquidus studies were undertaken in the system nepheline-forsterite-silica under conditions of  $H_2O$ ,  $CO_2$  and  $CH_4$  volatile saturation at 28 kbar to contrast the behaviour of reduced versus oxidized volatiles. Compared to the volatile-absent system, the effect of methane is to expand the Fo phase field relative to  $En_{ss}$  (melt depolymerization) and to increase significantly the activity of non-network aluminium (which leads to early appearance of garnet on the liquidus of other compositions). This contrasts with the effect of  $CO_2$  which gives rise to expansion of the  $En_{ss}$  phase field and the effect of  $H_2O$ -saturation which results in a greater expansion of the Fo field than  $CH_4$ . IR spectroscopic investigations establish the presence of both dissolved oxidized (OH groups) and reduced ("silicon monoxide" units) melt components in the  $CH_4$ -saturated glasses; reduced carbon solubility is <2000 ppm (Taylor & Green, 1986). Melt saturation with C-H fluids dominated by methane results in liquidus depressions comparable to pure  $CO_2$  (i.e.  $\sim 100^\circ C$  at  $\sim 30$  kbar), however, since methane forms no known solid compounds by interaction with silicate minerals over a large  $fO_2$ -range, reduced ( $CH_4 + H_2$ ) fluids may be important carriers of C and H from relatively undegassed regions of the mantle into regions depleted of their volatile constituents.

Volatile influx is expected to play a major role in modifying mantle  $fO_2$  environments by direct redox interaction with solid phases in an upper mantle we believe to be largely  $fO_2$  unbuffered or of limited buffer capacity. Redox interactions between reduced fluids ( $fO_2 < IW$ ) and oxidized regions of the upper mantle ( $fO_2 \sim MW$ - $FMQ$ ) will result in a progressive increase in fluid-phase  $fH_2O$  which will eventually give rise to partial melting (intersection with the reduced solidus in Fig.2) accompanied by diamond or graphite precipitation (intersection with the carbon saturation surface). Operation of such "redox melting" processes offers a ready explanation for the origin of strongly depleted harzburgites that are prominent constituents in the roots of cratons and important hosts for diamond (Boyd & Gurney,

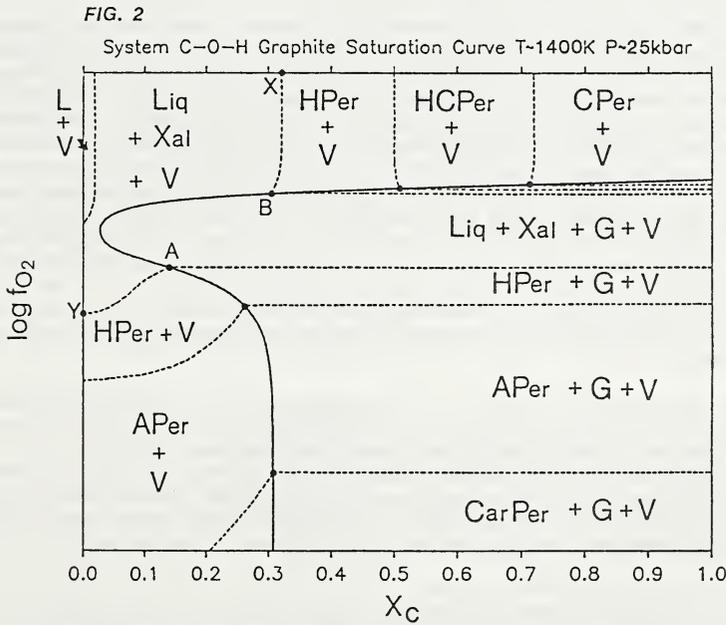
1982). Extensive "flushing" of the pre-cratonic mantle by deep mantle-derived  $\text{CH}_4 + \text{H}_2$  fluids may have led to large scale "redox melting" and associated diamond precipitation, thus effectively stripping the pre-cratonic mantle of its basaltic components.

References

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Graphite saturation curve contoured in terms of water mole fraction.



Vapour-excess phase relations of graphite-free and graphite-bearing peridotite. CPer = carbonated peridotite; HPer = hydrated peridotite; HCPeR = carbonated & hydrated peridotite; APer = anhydrous peridotite; CarPeR = carbide peridotite; G = graphite; V = vapour; Xal = anhydrous crystals; Liq = melt. Oxidized solidus = BX; Reduced solidus = AY.