SULFIDES, DIAMONDS, MANTLE fO$_2$, AND RECYCLING.

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Oxidation state (fO$_2$) of the mantle bears upon fluid speciation, partial melting, electrical conductivity, ductile flow, early Earth history, and recycling. Opinion of the early 1980's that much of the mantle is 'reduced', based on intrinsic fO$_2$ measurements of single-phase xenolithic olivines and spinels (e.g. Arculus and Delano 1981), is now in question because intrinsic measurements can perturb samples by carbon-induced reduction-exsolution or auto-oxidation (Virgo *et al.* 1988). Thermodynamic calculations on multi-phase ilmenite-bearing (Eggler 1983) or spinel-bearing (Mattioli and Wood 1986) peridotite xenoliths reestablished an older 'oxidized' view. Here we establish a new oxybarometer based on sulfides and apply it to peridotite xenoliths in alkali basalts (modern mantle) and peridotitic diamond inclusions (Archean mantle).

THERMODYNAMICS OF MSS. Monosulfide solid solution (MSS) is (Fe,Ni)$_{1-x}$S or, following Toulmin and Barton (1964), (Fe,Ni)S-S$_2$. A high P-T standard state for S$_{2,xt}$ is achieved by reintegrating T&B eqn (8) with new boundary conditions, arriving at:

$$\log a_{S2,xt} = -85.83 \ (1000/T-1) \ N_{MS} + 39.30 \ u - 39.30$$

where u = $(1 - 0.9981 N_{MS})^{0.5}$ and N_{MS} = N_{FeS} + N_{NiS} + N_{CuS} + N_{CoS} (1)

$$\log f_{S2,g} = 70030/T - 42.64 + \log a_{S2,xt} + 0.0522/T \int_1^P V_{S2,xt} \, dP \quad (2)$$

Gibbs-Duhem integration in the ternary FeS-NiS-S$_2$ gives a_{FeS}. Scott *et al.* (1974) indicate that that Fe$_{1-x}$S and Ni$_{1-x}$S mix ideally at a given mol% S, equivalent to saying that $a_{S2,xt}$ depends only on the number of cation holes in the (Fe,Ni)$_{1-x}$S structure, not on the cation species. Then

$$\log a_{FeS} = \log N_{FeS} + 85.83 \ (1000/T - 1) \ (\ln N_{MS} - N_{MS}) +$$
$$19.61 \ \ln \ ((1-u)/(1+u)) + 39.30 \ u - 0.434 \ \ln N_{MS} - 0.002 \quad (3)$$

OXYBAROMETRY. 2 Fe$_2$SiO$_4$ + S$_{2,xt}$ = 2 FeS + Fe$_2$Si$_2$O$_6$ + O$_2$ (4) Equilibrium (4) represents the assemblage olivine - orthopyroxene - MSS. For the pure phases S, ΔH$_f$, V, α, and β were taken largely from Robie *et al.* (1978) and Wood (1987). Olivine and orthopyroxene activity-composition relations are from Wood (1987). Uncertainties entirely reflect errors in analysis of phase compositions. For each trial of the Monte Carlo method a random number technique returned metal or oxide values whose overall distribution functions have standard deviations equal to 1% of the amount present in each phase. For sulfide compositions computed by a combination of phase and modal analysis, the 1% error was doubled.

ALKALI BASALT XENOLITHS. Sulfides in spinel peridotite xenoliths (e.g. Lorand and Conquere 1983; Lorand 1987; Dromgoole and Pasteris 1987) undergo: (1) Formation as cogenetic immiscible melt blebs

enclosed within silicates or interstitial to silicates; (1a)contamination with nongenetic sulfide liquid or with sulfur-bearing metasomatic fluids;

(2) Crystallization/ reequilibration to MSS-olivine-pyroxene-spinel assemblages, losing the Fe_3O_4 component of sulfide melt; (3) during ascent of host basalt, separation of Ni-Cu-rich sulfide partial melt; (4) reequilibration at ~600°C to two or more monosulfide solid solutions; (5) reequilibration/
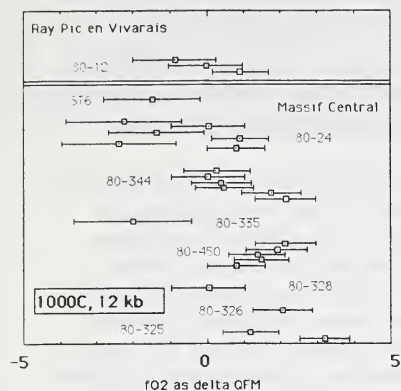

Fig. 1. Sulfide oxybarometry of spinel peridotite xenoliths in Massif Central alkali basalts, in log units relative to QFM. Groups of points indicate multiple sulfide inclusions within a single sample. Within-sample variability shows that sulfide oxybarometry is not as precise as spinel oxybarometry, but if samples are averaged it appears that fO_2's are within one log unit of QFM. Similar results have been obtained on similar modern subcontinental mantle lithosphere, using spinel oxybarometry, by Mattioli and Wood (1986) and Wood and Virgo (1989).

exsolution to PO/MSS ± PN ± CPY or PO/MSS ± PN ± CB at T <300°C; (5a) Interstitial sulfides may undergo reduction/ desulfidation attendant to serpentinization. Stage (2) represents typical mantle equilibration conditions (1000°C, 12 kb), for which sulfides included in silicates and free of magnetite are the best candidates. Their high-temperature compositions (Fig. 1) are reconstructed from modes and analyses of the low-temperature assemblages.

DIAMOND INCLUSIONS. Sulfides in the peridotitic diamond suite omit steps (1), (1a), (3), and (5a) above (Meyer 1987). Equilibrium (4) was applied to a suite of peridotitic sulfide inclusions analyzed by Yefimova *et al.* (1983) (Fig. 2). Although only one diamond contained both olivine and opx, all were assumed to have been in equilibrium with both, and the olivine was assumed to be Fo93, the mean of diamond olivines (Meyer 1987). The P&T

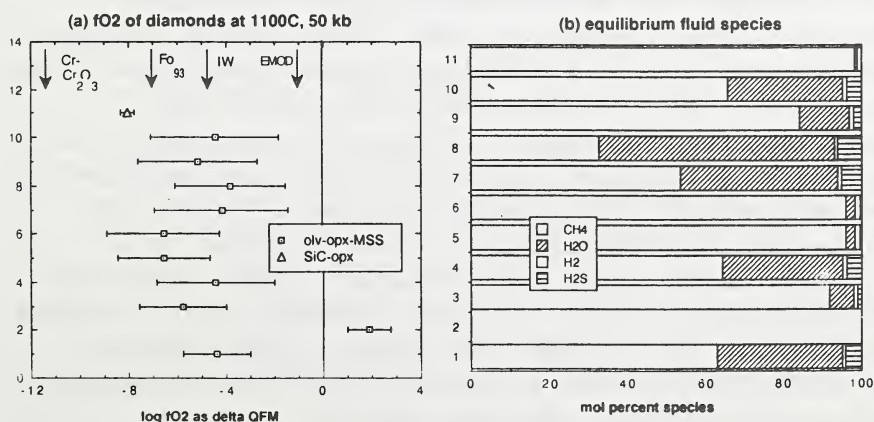Fig. 2. (a) Sulfide oxybarometry of peridotitic sulfide inclusions in Siberian diamonds, in log units relative to QFM. Also shown is one moissanite (SiC)-bearing diamond from Colorado. Reference buffers are at P&T. Diamond itself is stable to fO_2 just above EMOD. (b) Species of high P&T fluids calculated from the fO_2 and fS_2 of (a) and an MRK EOS; ordinate numbers correspond to ordinate numbers of (a).

are typical of peridotitic diamonds (Meyer 1987). Despite wide error brackets, reflecting uncertainty in a_{S2} at low contents of N_{S2}, the means of nine diamonds are surprisingly well-grouped near the IW buffer. Clearly, sulfides in diamonds formed under more reduced conditions than the sulfides calculated by the same method in Fig.1.

STABILITY OF SiC AND (Fe,Mg)O. Thermodynamic functions for moissanite, SiC (JANAF 1985) and an activity model for magnesiowustite (ferropericlase) (Hahn and Muan 1962) were added (Fig. 3) to show stability of these peridotite suite (Moore et al. 1986; Otter and Gurney 1989) minerals. If the assemblage of moissanite-Cr-diopside reported by Otter and Gurney

Fig. 3. Stability relations in the system MgO-Si-Fe-C-O at 1100°C, 50 kb. Ferromagnesian phases of univariant assemblages (numbered lines) have the Fe/(Mg+Fe) shown. Where olivine and opx coexist, the olivine composition is shown. Boxes show the various divariant assemblages. Calculations for pure iron metal; if metal is nickel-bearing, relevant curves will rise somewhat in f_{O2}. Ferropericlase must form above curve 1 and so does not indicate particularly reduced conditions. It may coexist with olivine but should not coexist with opx. Moissanite may exist 3.5 log f_{O2} units below IW; it may coexist with opx but not with olivine.

(1989) at Sloan kimberlite, Colorado also included opx, then f_{O2} is bracketed between curves 4 and 7 (Fig. 3 and Fig. 2).

IMPLICATIONS. Modern subcontinental mantle lithosphere has f_{O2} near QFM in the spinel peridotite facies (e.g. Wood and Virgo 1989). Deeper lithosphere may be more reduced (Luth *et al.*, 1990; Jaques *et al.*, 1990) in part, but the ilmenite-bearing peridotites (Eggler 1983) and carbonated mantle (EMOD) that melts to produce kimberlites certainly is not. Suboceanic asthenosphere f_{O2}'s range from QFM to about 3 log units below QFM (Bryndzia and Wood, 1990; Christie *et al.* 1986). Some, if not all, peridotitic diamonds formed beneath both the Kaapvaal and Siberian cratons about 3.3 Ga ago (Richardson *et al.*, 1984; Richardson 1986) at f_{O2} near IW (Fig. 2). A simple interpretation is that most mantle 3.3 Ga ago was more reduced than average mantle today. Mantle gases (Fig. 2) and volcanic gases and therefore the atmosphere were reduced (CH_4-H_2O-H_2S rather than CO_2-H_2O-SO_2). Hydrogen loss to space and rapid recycling of crustal O_2 created, by the Proterozoic, a more oxidized mantle- crust- atmosphere system. Some deep subcontinental mantle may be a relict of Archean conditions, as may be regions of today's asthenosphere. By this model, few regions of today's mantle are f_{O2}-buffered. Sliding equilibria such as diamond-COHS fluids, olivine-opx-spinel, and eqn (4) all reflect f_{O2} rather than control it.

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