peridotites and the stable occurrence of diamond indicate that oxygen fugacities must be sufficiently low in the Earth's mantle to reduce the CO_2 activity to a level below the stability of carbonates.(Rosenhauer et al., 1977) Intrinsic oxygen fugacity measurements of mantle derived samples indicate that fO_2 may be as low as the wüstite-iron level.(Ulmer,1980; Arculus & Delano,1980).

Thermodynamic calculations indicate that CH_4 is a stable species in a C-H-O fluid phase under 90 kb and the corresponding temperature of the mantle and fO_2 of the WI-buffer. It follows that:

1. It is possible that a fluid phase with high CH_4 concentrations is stable in the Earth's mantle, and

2. The ultimate limit for the existence of a fluid phase in a peridotitic mantle will be extended to greater depths by the formation of methane.

E4

OXYGEN FUGACITES FROM THE ASSEMBLAGE OLIVINE-ORTHOPYROXENE-SPINEL

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Spinel co-existing with olivine and orthopyroxene (ol-opx-sp) constitutes a widespread assemblage in ultramafic rocks from many environments, including upper mantle nodules in kimberlites and alkali basalts. Through the equilibrium

$$6Fe_2SiO_4 + O_2 = 3Fe_2Si_2O_6 + 2Fe_3O_4 \qquad (1)$$

the assemblage may be used as a measure of oxygen fugacity of these rocks. In practice all three of the solid components in (1) are considerably diluted in their respective phases, so that a reasonable estimate of oxygen fugacity can only be made if activity-composition relations of the phases are accurately known. To this end a model for spinel activity-composition relations has been developed, which has been calibrated against experimental determinations of the activity of magnetite in the systems Fe_3O_4-$FeAl_2O_4$, Fe_3O_4-$FeCr_2O_4$ and Fe_3O_4-$FeAl_2O_4$-$FeCr_2O_4$. To confirm the applicability of the model at high pressures and to systems which include MgO, a series of experiments in a piston-cylinder apparatus have been performed at 1100°C and 30kb in the system MgO-Cr_2O_3-SiO_2-Fe-H_2-O_2. An inner gold capsule containing ol+opx+sp+H_2O is run within a larger thicker walled Au capsule containing an oxygen buffer assemblage. The composition of the phases were determined by electron microprobe analysis. That equilibrium between the three phases is achieved in both these experiments and in rocks may be checked by comparing olivine-spinel and olivine-orthopyroxene Fe^{2+}/Mg distribution coefficients.

The results show that nodules from kimberlites equilibrated at oxygen fugacites between the iron-wüstite and wüstite-magnetite buffers. Nodules from alkali basalts show a rather wider range, from below iron-wüstite (Calton Hill, Derbyshire, England) to near nickel-nickel oxide (San Carlos, Arizona, U.S.A.). These results broadly agree with the intrinsic oxygen fugacity measurements.

E5

THE INSTRINSIC OXYGEN FUGACITES (fO_2's) of MEGACRYST ILMENITES FROM SOUTHERN AFRICA KIMBERLITES, TYPE A AND B SPINEL PERIDOTITES FROM SAN CARLOS, ARIZONA

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The oxidation state of the upper mantle and magmas generated therein is crucial to our understanding of the origin and evolution of the core-mantle-crust system. In a series of measurements with O_2-specific electrolytes, we have shown that a number of type A (or "chrome diopside" type) spinel peridotites and spinel megacrysts are close to iron wüstite (IW) in oxidation state. In contrast, thermodynamic calculations suggest that the intrinsic fO_2's of kimberlitic and alkalic magmas are close to the SiO_2-Fe_2SiO_4-Fe_3O_4 (QFM) buffer.

Homogeneous, cleansed megacryst ilmenites from the Frank Smith, Excelsior and Sekameng kimberlite pipes display 1 bar intrinsic fO_2's ranging from ≈0.5 $\log_{10}$ unit more oxidized than the Ni-NiO (NNO) buffer to a close coincidence with QFM over a temperature range of 950 - 1160°C. Despite run durations >50 hours at 1150°C, no autoreduction of these or peridotite samples took place. Fe_2O_3/FeO ranges from ≈0.32 to 0.71 and MgO from ≈4 to 13 wt%. Assuming a cognate relationship, these data suggest the kimberlite host magmas are oxidized at depth, and contrast strongly with our measurements on submarine tholeiitic basalts from the Galapagos rift and those of Sato (1972) on Hawaiian samples that are close to IW.

Further evidence for strong contrast in intrinsic fO_2's in upper mantle peridotite samples is provided by studies of samples from San Carlos. Type A peridotites are close to IW whereas Type B's ("aluminous augite") are close to NNO in the T range 950-1150°C. It is possible that alkaline basalt types and metasomatized peridotites may have a close genetic relationship.

E6

AN EXPERIMENTAL STUDY OF THE ROLE OF CO_2 IN PHYSICAL PROCESSES IN THE MANTLE

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Kimberlite magma generation in the mantle is linked to physical processes involving a fluid phase which is likely to be CO_2-rich. In peridotite xenoliths bubbles frequently occur within olivine grains in association with spinel crystals suggesting exsolution of a dissolved fluid phase during ascent of the xenolith. Experiments designed to clarify the role of CO_2 in bubble development have been conducted in a Griggs apparatus modified for high pressure. Hot-pressed olivine samples were sealed in Pt capsules with small amounts of silver oxalate, a material which breaks down to CO_2 and silver at relatively low temperature. The samples were held at p,T conditions appropriate to the lower lithosphere for periods of about a day. As expected from petrologic studies, a uniformly distributed carbonate phase occurs along grain boundaries and as inclu-