

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 f_{O_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 f_{O_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.

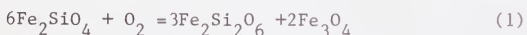
E4

OXYGEN FUGACITIES 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



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 30 kb 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 fugacities 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 INTRINSIC OXYGEN FUGACITIES (f_{O_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 f_{O_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 f_{O_2} 's ranging from $\approx 0.5 \log_{10}$ 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 auto-reduction of these or peridotite samples took place. $\text{Fe}_2\text{O}_3/\text{FeO}$ 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 f_{O_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-

sions within olivine. This is presumably magnesite generated during: Forsterite + CO₂ Magnesite + Enstatite. By varying the p,T path followed during quenching one can study either the degree of incorporation of CO₂ into olivine under conditions stabilizing the carbonate or the development of features related to the generation of free CO₂. Analysis of these samples is in progress. In addition, several samples have been deformed and have developed shear zones containing mylonitic material. Thus application of pressures up to 3.0 GPa has not precluded shear zone formation.

E7 FLUID ACTIVITY IN THE MANTLE - EVIDENCE FROM LARGE LHERZOLITE XENOLITHS

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Lherzolite xenoliths in a breccia pipe from northeastern N.S.W., Australia attain diameters of up to 60 cm. They record, approximately concentric with xenolith margins, zones of alteration by hydrous and carbonic fluids which may represent metasomatism by primary mantle volatiles. Successive zones (each about five cm. wide) decrease in alteration intensity from the outside inward. The simplified sequence of mineral assemblages is: (1) quartz / talc/Mg-Fe-Ca carbonates, (2) talc/Mg-Fe-Ca carbonates, (3) fresh spinel lherzolites. Crosscutting this concentric alteration pattern are discrete carbonate veins, rarely radial with the xenolith shape, but commonly *en echelon*.

The zonal nature of the alteration suggests that fluid invasion occurred either (a) after entrainment in the host basaltic liquid or (2) within the mantle prior to entrainment and possibly resulting from fluid activity genetically linked with the production of the host magma. If the major alteration event took place in the mantle, this implies that brecciation associated with volatile movement can occur within the mantle. This may provide a mechanism for xenolith entrainment which commonly takes place within a vertically limited horizon.

Abundant carbonate of light isotopic character is present in the host basalt and may be of primary mantle origin. This evidence of a high CO₂ content may be significant in carrying such large xenoliths to the surface.

E8 MAGNESITE AND OTHER MINERALS IN FLUID INCLUSIONS IN A LHERZOLITE XENOLITH FROM AN ALKALI BASALT

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Magnesite has been observed in CO₂-rich fluid inclusions in a typical Cr-diopside and spinel-bearing lherzolite recovered from the 1824 eruption of Lanzarote volcano, Canary Islands. The carbonate, which exists as 2-4 µm diameter crystals on inclusion walls, was identified by its rhombohedral form and electron beam-generated EDS

and WDS characteristic x-ray spectra in which C and Mg are major elements. The carbonate occurs as the sole phase in individual inclusions and has only been found in those inclusions enclosed in olivine. Phases present in other inclusions in olivine include Fe-oxide (probably pure magnetite), Fe- and Cu-Fe-sulfides, and silica. Although sulfides and magnetite may exist together in the same inclusion, most magnetite-bearing inclusions contain no other phases.

Regardless of the phases in them, mineral-bearing inclusions tend to possess irregular shapes, are relatively large (10-30 µm) and exist together in arrays which define non-crystallographic surfaces. These features distinguish them as a group from all other inclusion populations in which daughter minerals are absent.

The production of carbonate by reaction of olivine and CO₂-rich fluid requires only that CO₂ fugacities be sufficiently high for any set of assumed conditions, i.e., the mere presence of magnesite yields no information on the T and P at which it formed. However, the apparent lack of phases more siliceous than olivine, e.g., enstatite or glass, in association with magnesite (or magnetite) means that either olivine in the immediate vicinity of the inclusion is non-stoichiometric, or the carbonate crystallized in a microfracture before annealing of olivine and formation of the inclusion, presumably at mantle P-T conditions.

E9 THE MINERALOGY, STRUCTURE AND MODE OF FORMATION OF KELYPHITE AND ASSOCIATED SUB-KELYPHITIC SURFACES ON PYROPE FROM KIMBERLITE.

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The mineralogy, structure and mode of formation of kelyphite shells surrounding garnet is discussed in relation to kimberlite emplacement. Pyrope encrusted by kelyphite is commonly found in most garnet peridotites, some eclogite xenoliths from kimberlites, as well as a few garnet-bearing serpentinites. Observations made with the aid of a scanning electron microscope on 858 kelyphite-encrusted garnet grains from 30 kimberlite occurrences and petrological examinations of kelyphite rims enclosing garnet in ultrabasic nodules from kimberlite are discussed.

Although the relative abundance of kelyphite-encrusted garnet varies from one kimberlite to another, kelyphite shells are most commonly developed on mauve garnets which are most probably derived from peridotite and are least commonly found on orange varieties from eclogites. The underlying sub-kelyphitic surfaces formed on pyrope as a result of kelyphitization are described. There is a direct relationship between the different types of surface features found on the sub-kelyphitic surfaces and the structure and mineralogy of the kelyphite shells surrounding garnet and filling cracks within garnet.

During the ascent of kimberlite magma garnet lherzolite nodules are moved upwards from depths of approximately 150 km within the upper mantle resulting in the kelyphitization of pyrope within the peridotite nodules, forming shells consisting of a spinel-two pyroxene assemblage. The proposed zone of kelyphitization of pyrope lies within the spinel lherzolite stability field and is most likely to occur at temperatures of 900°C