E

Fluids in the mantle and metasomatism

E1

AN EXPERIMENTAL AND THEORETICAL ANALYSIS OF PARTIAL MELTING IN THE SYSTEM KAISi0₄-CaO-MgO-SiO₂-CO₂: A MODEL FOR ALKALIC MAG-MA, CARBONATITE AND KIMBERLITE GENESIS.

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The introduction of dolomite as a solidus phase in carbonated peridotite compositions at 25-30 kb coincides with a rapid increase in CO, solubility over a small pressure interval (several kb) and a profound depression of the solidus temperature (200°C). Partial melt compositions through this interval change rapidly from a silicate melt (alkalic near the solidus) at low P to a carbonatitic melt where dolomite is introduced as a solidus phase and back to a silicate melt (haplokimberlitic) at still higher P. The details of these transitions are important to the genesis of alkalic magmas, carbonatites and kimberlites, but are obscured by the small P interval over which large changes in melt composition occur, by several solidus reactions and melt composition occur, by several solidus reactions and melt compositions), and by the inability to rapidly quench and/or analyze partial melts generated by small degrees of partial melting. To understand better how the compositions of partial melting. To understand better how the with increasing P, a combined experimental and theoretical analysis of melting relations involving ForDi+En+Carbonate+ Potassic of phase (+CO) in the system KAISi0_4-CaO-MgO-Si0_2-CO_2 has been undertaken to about 50 kb.

Partial melts in equilibrium with Fo+Di+En+Potassic phase+CO, show increasing CaO and MgO, at constant CaO/MgO=0.7 (wt), and decreasing K_O, Al_O, and SiO, with increasing P to about 25 kb; kalsilite=component is stabilized while the diopside stability volume is depressed. Immediately above 25 kb, the CaO/MgO of partial melts increases to a value greater than I when dolomite is introduced as a solidus phase and the enstatite stability volume expands. Partial melts are never more MgO-rich than the kalsilite-dolomite-enstatite-CO, join at pressures below about 30 kb. At P>30 kb, K_O contents are low (-4 wt%); in the absence of H_O kalsilite fs the stable and refractory potassic phase. An analysis of all possible reaction topologies generated by the intersection of melting reactions (both CO₂-saturated and CO₂-undersaturated) with the subsolidus reactions En-Mag=Fo+Y and 'Di-Mag=En-Dol yield consistent conclusions: MgO and SiO, contents of partial melts increase and CaO, CO₂ and CaO/MgO decrease with increasing P.

Polybaric melt composition trends at P<25 kb mimic tabulated composition trends of strongly potassic, silica-undersaturated occurrences: Results of experiments in CaO-absent systems cannot duplicate the latter trends. The polybaric melt composition trend at P>30 kb ranges between calcite-rich and forsterite-rich extremes and is similar in this respect to differentiation trends for kimberlites. Melting reactions at the highest pressures considered in this study, involving dolomite and/or magnesite and peridotite minerals, can produce melt chemistries analogous to kimberlite compositions as cited in the literature.

E2

FUSION CURVES AND THE THERMODYNAMICS OF LIQUIDS TO HIGH PRESSURES

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Our determinations of anhydrous fusion curves of silicate and aluminosilicate minerals to high pressures reveal that marked structural and thermodynamic changes occur in the aluminosolicate liquids as functions of changing pressure and temperature. These changes prevent calculation of fusion curves from calorimetrically determined thermodynamic data; alternatively, thermodynamic data can be obtained from the fusion curves. Comparison of the solidi of albite with those of albite + quartz, sanidine, sanidine + quartz, anorthite, and diopside suggest that phase transformations in the crystalline phases have analogues in the liquids. This provides some basis for predicting the high-pressure structures of near-solidus liquids.

We have reinvestigated the systems quartz- H_2O-CO_2 , albite- H_2O-CO_2 , albite- H_2O-CO_2 , albite- H_2O , and albite- CO_2 to high pressures. These results permit calculation of activity coefficients for H_2O in the H_2O-CO_2 fluids. The albite- CO_2 solidus is the first determination of the effect of CO_2 on melting in an anhydrous, hydrogen-free environment, permitting us to determine the relationship between solubility and structure of the liquid.

Knowlegde of the nature of deep-seated liquids will enable us to better understand phenomena such as magma genesis and the distribution of elements.

E3

OXYGEN FUGACITY AND THE FLUID C-H-0 PHASE IN THE EARTH'S MANTLE.

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From experimental work it is deduced that CO_2 reacts with mantle silicates above 26 kb to form carbonates. With pressures increasing still further dolomite or magnesite are buffering mixed fluid phases to continuously lower CO_2 -activities.(Wyllie, 1978; Eggler,1978). In a similar way H₂O reacts to form hydrous phases - e.g. brucite- above about 90 kb, buffering the fluid phase to lower H₂O activities with increasing pressure. As a consequence a binary CO_2 -H₂O phase will disappear as soon as a hydrous and a carbonate phase coexist with mantle silicates. (Ellis & Wyllie, 1979,1980)

The absence of carbonates from typical mantle

peridotites and the stable occurrence of diamond indicate that oxygen fugacities must be sufficiently low in the Earth's mantle to reduce the CO₂ activity to a level below the stability of carbonates.(Rosenhauer et al., 1977) Intrinsic oxygen fugacity measurements of mantle derived samples indicate that fO₂ 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 $\rm CH_4$ 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

$$6Fe_2SiO_4 + O_2 = 3Fe_2Si_2O_6 + 2Fe_3O_4$$
(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 $_0^{-4}$ -FeAl $_0^{-4}$, Fe $_0^{-4}$ -FeCr $_0^{-4}$. 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 $_0^{-2}$.

-SiO₂-Fe-H₂-O₂. An inner gold capsule containing ol+opx+sp+H₂O 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 olivineorthopyroxene Fe²⁴/Mg distribution coefficients.

The results show that nodules from kimberlites equilibrated at oxygen fugacites between the ironwüstite 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 (fO₂'s) of MEGACRYST ILMENITES FROM SOUTHERN AFRI-CA KIMBERLITES, TYPE A AND B SPINEL PERIDO-TITES 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 coremantle-crust system. In a series of measurements with 0_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 $f0_2$'s of kimberlitic and alkalic magmas are close to the Si 0_2 -Fe $_3$ Si 0_4 -Fe $_3$ O₄ (QFM) buffer.

Homogeneous, cleansed megacryst ilmenites from the Frank Smith, Excelsior and Sekameng kimberlite pipes display 1 bar intrinsic f0_'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 autoreduction of these or peridotite samples took place. Fe₂O₃/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 tholeitic 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 fO₂'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 CO2-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 CO2 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 CO2 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-