at pipe emplacement (ii) progressively leached phlogo-
pite fractions from the same separate show a dramatic
increase in $^{87}Sr/^{86}Sr$ and $^{87}Rb/^{86}Sr$, consistent with
removal of calcite lamelli, but still define an age of
87 m.y., (iii) whole rock initial ratios are generally
lower than for diopside or K-richterite, (iv) differ-
ent portions of the same rock are not in isotopic equ-
ilibrium (see three circled points joined by a solid
line in Fig. 3) and (v) leaching of one whole rock
yielded a leached residue with a higher initial $^{87}Sr/$
^{86}Sr ratio (.70546), and a leach solution with a lower
initial ratio (.70503) than the original rock (.70525).

Summary of the above suggests that while the major
Rb and Sr hosts, phlogopite, diopside and K-richterite
are in approximate isotopic equilibrium, the rocks an-
alysed also contain (exotic?) components with un-equi-
librated strontium. These could be fluids of kimberl-
ite origin (cf. "secondary" phlogopite selvedges arou-
nd garnets in GPP rocks) since mixing plots ($^{87}Sr/^{86}Sr$
vs 1/Sr) show that this is not due to the simple add-
ition of the kimberlite itself. Rocks with lowest Rb
and Sr would be most affected; least metasomatised GP
rock AJE25 [2] has an inital ratio of .70473 while its
diopside has an initial ratio of .70512, in support of
the above contention. Thus, while some samples shown
in Fig. 3 may have had their $^{87}Sr/^{86}Sr$ ratios decreased
slightly during kimberlite emplacement, the overall
scatter is considered to be a consequence of mantle
metasomatism which has affected all the peridotites
analysed. This is emphasized by diopside analyses,
which show high and variable $^{87}Sr/^{86}Sr$ ratios (Fig.4)
and Sr contents, 200-1000 ppm Sr [2]. The metasomatic
fluids appear to have had variable $^{87}Sr/^{86}Sr$ ratios and
Sr contents and while it is possible to infer a chemi-
cal distinction in terms of Rb/Sr between the garnet-
bearing and garnet-free peridotites, no clear distinc-
tion can be made regarding the timing of metasomatic
event(s). The significance of the 150 m.y. reference
line in Fig.3, considered [2] to be related to the cess-
ation of Karoo igneous activity, remains an open ques-
tion, and must be viewed in context with the Nd-isotope
data presented in Fig. 4.

The $^{143}Nd/^{144}Nd$ data confirm the enriched nature of
the peridotites, consistent with previous data for
peridotite diopsides [3], compared with present day
Bulk Earth (intersecting lines in Fig.4), kimberlites
[4, this study] and diopside megacrysts [4]. The lower
$^{143}Nd/^{144}Nd$ ratios of peridotite diopsides, reported
as being separates from the GPP group, with respect
to the PKP rock data for a given $^{87}Sr/^{86}Sr$ value (Fig.
4), might suggest that the former indicate an earlier
metasomatic event than inferred for the PKP data, bas-
ed on consideration of Nd model (CHUR) ages. However,
the most "enriched" diopside has now been found to be

Fig. 4
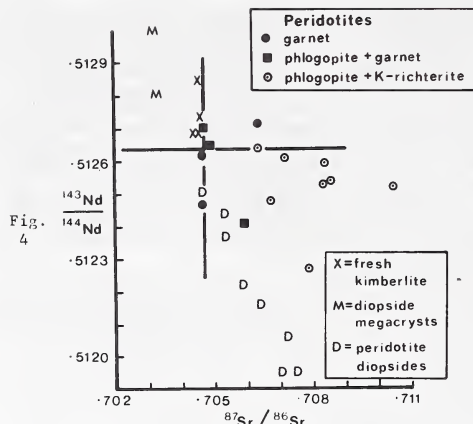
from a PKP, and not a GPP, rock. $^{143}Nd/^{144}Nd$ data for
this rock, two other GPP rocks and associated diopside
and mica analyses [3] are as follows :

Sample	Type	Rock	Diopside	Phlogopite
CK26	GPP	.51265+2	.51223+2	.51185+7
CK27	GPP	.51270+2	.51250+3	.51224+10
CK32	PKP	.51227+1	.51195+4	-

The implied disequilibrium, together with the proxim-
ity of CK26 and CK27 to the kimberlite data (Fig.4)
suggest that, as with Sr, the whole rocks contain un-
equilibrated Nd of kimberlite origin. Nevertheless, the
relatively low $^{143}Nd/^{144}Nd$ ratios in rock CK32, coupled
with the even lower ratios in its diopside (and the
phlogopites), suggest an earlier age of metasomatism
than indicated by the Sr-isotope data, and it is poss-
ible that rock CK32 may contain two mantle metasomatic
age components. More detailed isotopic work is clearly
required before the timing of mantle metasomatism and
the mantle differentiation events (melting, plume act-
ivity, subduction) possibly involved in the production
of the metasomatic fluids, can be defined.

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H13

VOLUME INSTABILITIES IN THE MANTLE AS A POSSIBLE CAUSE FOR KIMBERLITE FORM

Friedemann FREUND
Mineralogisches Institut, Unovrsität zu Köln Fed. Rep. Germany

The occurence of kimberlites and their mode
of formation are evidence for punctual instabi-
lities in the mantle which lead to the build-
up of extremely high fluid pressures in an al-
kali-rich, mostly potassic environment. The
geological setting points at the mantle under-
neath stable shields. The driving force is
provided mainly by CO_2 with additional H_2O,
but the gases contained in fluid inclusions,
for instance in diamonds, are varied. They
comprise hydrocarbons, alcohols, oxygen, nitro-
gen, and others.

In order to understand kimberlites and kim-
berlite formation it is essential to gain an
insight into the dynamic processes which occur
under the confining pressure of the mantle. Ob-
viously these processes are related to the pre-
sence and to the local accumulation of dissolved
fluid phases. Hence, it is important to under-
stand their dissolution mechanism, to know what
solute species might form and what their role
could be in the temporal evolution of a poten-
tial kimberlite source region.

The usual approach followed by petrologists
is to analyze the phases present in a given

rock and to relate these findings to experimen-
tal data from high pressure laboratory studies.
It is well known that carbonates and hydroxyl-
bearing phases precipitate from CO_2- and H_2O-
rich magmatic systems. It has therefore been
concluded that carbonate ions, CO_3^{2-}, and hydro-
xyl ions, OH^-, are the prevalent solute species.
This view has recently been challenged (FREUND
1981a and references cited therein) by the dis-
covery of solute carbon in synthetic MgO and in
natural, mantle-derived olivine which is not car-
bonate but a novel carbon species characterized
by a valence state near zero and by a special
nature of the chemical bond with the surrounding
oxygens. The name "atomic carbon" has been coined
for such dissolved carbon species which formally
derive from the CO_2 dissolution mechanism.

The "atomic carbon" dissolved in oxides and
silicates has unusual properties, both chemical
and physical unlike any carbonate carbon. The
"atomic carbon" is capable of reacting with the
lattice oxygen to give CO_2 or CO depending on
experimental parameters. With the hydrogen de-
rived from lattice-bound OH^-, i. e. from the
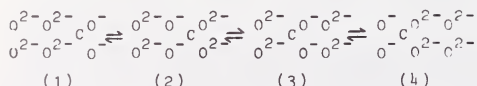dissolution mechanism of H_2O, this carbon re-

acts to give a wide variety of hydrocarbons, saturated and non-saturated, including aromatic compounds. With molecular H_2O it reacts to give alcohols; with co-dissolved nitrogen to give HCN, amines, and other complex C-N compounds. With the silicon of the silicates it may form Si-C bonds. With the cations, for instance with Mg^{2+} and Fe^{2+} in olivines, it reacts to give volatile metal-bearing organic compounds (FREUND et al. 1982).

The physical properties of the "atomic carbon" are equally outstanding and in sharp contrast to what one would expect for carbon from carbonate ions.

The diffusion of the "atomic carbon" is extremely fast even in such densely packed structures like MgO and olivine. The diffusion coefficient data which are now available cover the temperature range from $-100^{\circ}C$ to $700^{\circ}C$ WENGELER et al. 1982; KATHREIN 1982; KATHREIN et al. 1982; OBERHEUSER 1982). They indicate that the "atomic carbon" may be the fastest diffusing species in mantle rocks. Its motion is endowed with a negative activation volume of diffusion. This is nothing else but the mathematical expression for the fact that the CO_2 dissolution increases with hydrostatic pressure (BROWN and ASHBY 1980). Indeed, the CO_2 solubility rocks, both solid and liquid, increase quite dramatically above 10-20 kbars, corresponding to a depth range of 30-60 km, i. e. to the lower crust and/or upper mantle. At the same time, however, "atomic carbon" diffuses in response to stress, both microscopic and macroscopic, from regions of high stress to regions of low stress. Grain boundaries represent no diffusion barriers for the "atomic carbon", because it can convert reversibly to CO_2 and back to dissolved carbon at the grain-to-grain interface.

By combining the available physico-chemical data with the general concept of plate tectonics we are led to consider long-range carbon diffusion as a very realistic geological possibility. This carbon diffusion is expected to occur at or below the crust/mantle boundary from regions of high compressive stress to regions of tensile stress or stress shadow zones. It may transport a large flux of "atomic carbon" over distances of hundreds or thousands of kilometers within, geologically speaking, short to moderately long times.

The nature of the "atomic carbon" cannot be fully apprehended, unless one understands the process of charge transfer (CT) by which carbon becomes reduced to the essentially zerovalent state and oxygen becomes oxidized from the O^{2-} state to the O^- state (FREUND 1981b). Any O^- represents a defect electron in a given oxide or silicate structure. This O^- state is the companion of the "atomic carbon" and remains associated with it during diffusion. The $C-O^-$ bond is quite energetic, strongly covalent but at the same time spatially delocalized. This is because every neighboring O^{2-} can become an O^- by a mere electron exchange. Thus, when the "atomic carbon" diffuses, defect electrons travel along, probably two per C atom. In a very schematic way we may represent this as follows:

$$O^{2-} O^{2-} C^0 \rightleftharpoons O^{2-} O^- C^{0} \rightleftharpoons O^{2-} C^0 O^{2-} \rightleftharpoons O^- C^0 O^{2-}$$
$$O^{2-} O^{2-} C^- \rightleftharpoons O^{2-} O^- C^{2-} \rightleftharpoons O^{2-} O^0 O^{2-} \rightleftharpoons O^- O^{2-} C^{2-}$$
$$(1) \qquad (2) \qquad (3) \qquad (4)$$

During steps 1/2 and 3/4 two electrons move from left to right while the C atom executes one diffusional jump from right to left between step 2/3.

Thus, during the postulated long-range diffusion of "atomic carbon" an electron flux of equal magnitude is anticipated to occur in the opposite direction. If the "atomic carbon" accumulates in a given stress shadow zone somewhere in the mantle, this also means an accumulation of O^-, i. e. of defect electrons.

The O^-, if taken separately, are capable of forming dimers, trimers and possibly tetramers which are resonance-stabilized to various degrees through their interaction with the surrounding O^{2-} and with the atomic C. When the P, T-conditions change in a certain way such as expected for a diapiric uplift environment, both experimental data (KATHREIN 1982) and theoretical considerations indicate that the O^- stabilization breaks down. Such a breakdown is accompanied by an efflux of defect electrons, because the O^- tend to reconvert to O^{2-}. One of several possible consequences of this process is an influx of electrons from the surrounding mantle to account for the $O^- \rightleftharpoons O^{2-}$ conversion.

In such a case the mantle volume under consideration will (a) increase in volume, because the partial molar volume of O^{2-} is considerably larger than that of the O^-, and (b) acquire a differential negative charge due to the electron influx. As a result of the latter positive charges, viz. cations, will be drawn in concomitantly in order to maintain electroneutrality.

This process is essentially electrochemical. We propose to call it "electrochemically driven metasomatism". Depending upon the nature and the availability of the positive charges in the surrounding mantle and/or in the overlying crust the cation influx can be either predominantly H^+, Na^+, K^+. In any case the melting temperature will decrease, probably to a dramatic extent. The volume will increase. The pressure, both internal and that exerted on the surrounding rock, will rise. The ultimate consequence of this process is an instability in the mantle which is self-catalyzing and self-amplifying (FREUND 1981c).

If an electrochemically driven metasomatosis as outlined here develops deep in the mantle where K^+ dominates, a kimberlitic magma can be generated. It is expected to propagate towards the surface of the Earth. During the depressurisation the charge transfer (CT) processes which provide the basis for O^- formation and their reconversion to O^{2-} will become accelerated. As soon as CO_2 gas forms, two electrons per CO_2 molecule are released. The final stage is an explosive discharge of the highly potassic, CO_2-driven magma. This magma is expected to be in an unusual physical state best described as plasma-like, adiabatically cooled, but characterized by electronic CT processes which are still in progress in the fluidized solid and which will eventually be quenched by an influx of H^+ from meteoritic water leading to a late-stage serpentinisation.

In summarizing we can say that the mechanism of kimberlite formation and eruption outlined here derives from a mechanism - novel for geology - of interatomic electronic charge transfer (CT) occuring in solids as a function of P and T between oxygen as electron donor and electropositive electron as acceptors. Its background is well-founded theoretically since a long time and it has been studied in detail experimentally for the CO_2 and H_2O solubility in MgO and in mantle-derived silicate minerals such as olivine. The attractive feature of the CT mechanism and of its sequential evolution through various stages is that it leads to an entirely novel concept of magma genesis without violating, at any step, known physico-chemical principles. The kimberlite magma genesis represents an extreme case.

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H14   METASOMATISM IN THE MANTLE BENEATH PIPE 200, NORTHERN LESOTHO

E.S. SCHANDL,
Dept. of Geological Sciences, McGill University, Montreal, P.Q., Canada
D.B. CLARKE,
Dept. of Geology, Dalhousie University, Halifax, N.S., Canada

Introduction

Peridotite nodules in kimberlite contain information about the equilibria or disequilibria that prevailed in the mantle just prior to eruptio If a nodule shows signs of physical (textural) or chemical disequilibrium, then information may potentially be obtained on two or more processes which had affected the mantle in the vicinity of its origin, including the timing of those events. This is the case with a small number of nodules from Pipe 200, including some described by Carswel et al. (1979) and Mitchell et al. (1980).

The Pipe 200 (PTH) nodules consist of garnet lherzolite, garnet-chromite lherzolite, chromite lherzolite and spinel harzburgite. The rocks generally have low modal percentages of clinopyroxene and garnet, low Al$_2$O$_3$, CaO and Na$_2$O, high 100 Mg/(Mg + Fe) values of 91.0-95.4 and high 100 Cr/(Cr + Al) values of 11.6-48.9. These features are consistent with depletion caused by removal of a basaltic partial melt from more normal garnet lherzolite.

Mineralogy and Chemistry of the Altered Samples

Six different peridotite nodules (PTH 108, 202, 204 and 404 of Carswell et al· (1979), plus PTH 58 and 516 courtesy of B. Harte and M.J. O'Hara) were the subject of further study because of their unusual mineralogy and the textural associations involving those minerals. Normal PTH nodules contain some chrome pyrope garnet, usually with a rim of fine-grained kelyphite attributable to rapid alteration in the ascending kimberlite (Fig. 1A). In sample PTH 58 chrome diopside occurs as rare discrete grains in the rock, but more significantly as a collar of grains, with clear cores and cloudy, pitted margins, around the garnets. This collar also contains small amounts of phlogopite and tiny euhedral spinels. The garnet may be partially kelyphitized (PTH 58, Fig. 1B) or wholly kelyphitized (PTH 404, Fig. 1C). In sample PTH 204 (Fig. 1D), the collars around a kelyphitized garnet core are considerably wider, coarser grained, and both phlogopite and spinel are more abundant. The clinopyroxene and phlogopite show a mosaic
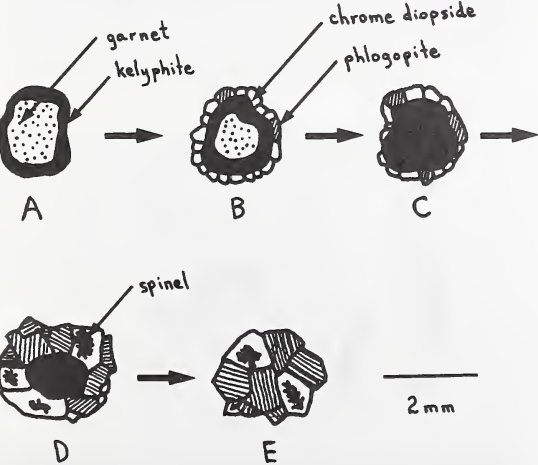

Figure 1

	PTH 58 (COLLAR)			PTH 204 (INTERMEDIATE)		
	CPX	PHL	SP	CPX	PHL	SP
SiO$_2$	55.22	41.16	–	54.51	40.26	–
TiO$_2$	–	0.29	0.96	–	0.22	–
Al$_2$O$_3$	2.52	13.18	9.45	4.45	14.92	14.8
Cr$_2$O$_3$	2.95	1.03	54.08	3.10	1.11	53.7
FeO	2.04	2.60	18.94	1.99	2.31	18.0
MnO	–	–	0.16	–	–	–
MgO	15.95	25.00	13.20	13.60	24.22	13.6
CaO	19.06	–	0.10	19.95	–	–
Na$_2$O	2.61	1.16	–	3.29	0.80	–
K$_2$O	–	9.80	–	–	9.83	–
TOTAL	100.35	94.22	96.89	100.89	93.67	100.10

	PTH 108 (POOL)		
	CPX	PHL	SP
SiO$_2$	54.31	42.48	–
TiO$_2$	–	0.23	0.73
Al$_2$O$_3$	1.28	12.38	5.35
Cr$_2$O$_3$	3.11	0.88	59.90
FeO	2.37	2.71	22.61
MnO	0.11	–	0.55
MgO	16.46	26.49	11.10
CaO	20.53	–	–
Na$_2$O	2.14	–	–
K$_2$O	–	10.03	–
TOTAL	100.31	95.20	100.24

Table 1.