tionated the bubble gas sample through preferential consumption of ^{12}C-CH$_4$. Such fractionation may occur to dissolve methane transported more slowly through the 7- to 25-cm-thick sediment cover overlying the methane production zone via molecular diffusion or to methane bubbles that become lodged in overyling sulfate-reducing sediments between low-tide bubbling episodes. Gas bubble methane transport in our site accounts for approximately 84% of the total annual methane flux of 5.7 ± 2.6 mol m^{-2} (*13*). The potential importance of carbon isotopic fractionation of methane during its transport up through an oxidizing sediment column has been discussed by Stevens and Rust (*8*).

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Eclogites, Pyroxene Geotherm, and Layered Mantle Convection

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Temperatures of equilibration for the majority (81 percent) of the eclogite xenoliths of the Roberts Victor kimberlite pipe in South Africa range between 1000° and 1250°C, falling essentially on the gap of the lower limb of the subcontinental inflected geotherm derived from garnet peridotite xenoliths. In view of the Archean age ($>2.6 \times 10^9$ years) of these eclogites and their stratigraphic position on the geotherm, it is proposed that the inflected part of the geotherm represents the convective boundary layer beneath the conductive lid of the lithospheric plate. The gradient of 8 Celsius degrees per kilometer for the inflection is characteristic of a double thermal boundary layer and suggests layered convection rather than whole mantle convection for the earth.

IN A STUDY OF UPPER MANTLE PETROLOGY, Boyd (*1*) estimated the equilibration conditions of ultramafic xenoliths containing the assemblage garnet, orthopyroxene, clinopyroxene, and olivine from kimberlites in northern Lesotho. Temperature and pressure estimates of the Lesotho xenoliths defined a curvilinear trend ranging in temperature from 900° to 1400°C corresponding to depths of 100 to 200 km. Boyd interpreted this trend as the segment of a fossil geotherm at the time of kimberlite eruption. The lower temperature-pressure end of this xenolith trend coincided essentially with the continental shield geotherm of Clark and Ringwood (*2*), although the trend showed an inflection, beginning at 1100°C, and extending to 1400°C and a depth of 200 km (Fig. 1).

Another characteristic of this geotherm is that the xenoliths plotting on the shallow limb of the geotherm displayed a coarsely granular texture whereas those that defined the inflected limb were intensely sheared. Boyd also interpreted the point of inflection on this geotherm as marking the top of the low-velocity zone beneath Lesotho at the time of kimberlite eruption around 90 million years ago. In addition to this Lesotho geotherm, inflected geotherms based on the pyroxene geothermometry-barometry approach (*1*) have also been established from other regions in southern Africa (*3–5*). The overall patterns of these geotherms are broadly similar—that is, the temperature-depth profiles of the xenoliths show agreements with the theoretical (4.2×10^{-2} W m^{-2} heat flow) continental geotherm up to 1100°C, with a perturbation at higher temperatures. This deviation has been interpreted (*6*) as a perturbed geotherm associated with the convective movements, possibly diapiric (*7*), during the eruption of the kimberlites.

Although the above thermal, chemical, and stress distribution (rheology) structure is constructed mostly on the basis of garnet lherzolite xenoliths, many other varieties of mantle-derived xenoliths, including eclogites, harzburgites, dunites, and megacrysts of pyroxene, ilmenite, garnet, phlogopite, and diamond and graphite, are also present in the xenolith population of kimberlites. Because of the lack of reliable geothermometers and geobarometers, assignment of relative depths of origin for these xenoliths are more ambiguous, but it is clear that they must lie somewhere along the ambient mantle geotherm.

We focused on the eclogite xenoliths in kimberlites, particularly those from the Roberts Victor Mine in the Orange Free State of South Africa, to evaluate the temperatures of equilibration and the depths of origin of the eclogites and the implications of these data on the thermal evolution of the subcontinental mantle. This study was also prompted by several developments: (i) oxygen isotope systematics have been used to indicate that an ancient oceanic crust altered by seawater was the original source rock for the Roberts Victor eclogites (*8, 9*); (ii) samarium-neodymium study of the eclogites indicates an Archean age (*10*); (iii) an improved experimentally determined geothermometer (*11*), based on Mg-Fe exchange between garnet and clinopyroxene, allows reasonable estimates of the temperature of equilibration; (iv) computation (*12*) of seismic velocities as a function of temperature and pressure in the upper mantle is most consistent with an olivine and orthopyroxene-rich lithosphere extending to 150 km beneath the shield areas, followed by a high-temperature gradient or change in mineralogy, or both, that serves to decrease the velocities beneath the lithosphere; and (v) proof of mantle heterogeneity by various radiogenic isotopes and geochemical data has been combined with laboratory and numerical experiments on mantle convection to suggest that convection is restricted to discrete layers (*13*).

The partition of Fe^{2+} and Mg^{2+} between coexisting garnet (gt) and clinopyroxene (cpx), expressed as $K_d = (\mathrm{Fe}^{2+}/\mathrm{Mg}^{2+})_{\mathrm{gt}}/(\mathrm{Fe}^{2+}/\mathrm{Mg}^{2+})_{\mathrm{cpx}}$, is strongly temperature-dependent, and coupled with the mole fraction of calcium in garnet assemblages (*11*) provides a sensitive thermometer for eclogitic rocks. With this thermometer, temperatures of equilibration have been calculated for 62 eclogite xenoliths from the Roberts Victor kimberlite pipe. The eclogites include examples of both types previously defined on the basis of textural, isotopic, and chemical criteria (*8, 14, 15*) and we assume no Fe^{3+} in either the garnet or the clinopyroxene. These estimated temperatures are shown in Fig. 1 and compared with the Lesotho geotherm based entirely on the garnet lherzolite xenoliths. In Fig. 1 the geotherm of Boyd (*1*) has been corrected for the presence of FeO and CaO in enstatites and garnets by the method of Wood and Banno (*16*). The histogram indicates that 81% of the analyzed Roberts Victor eclo-

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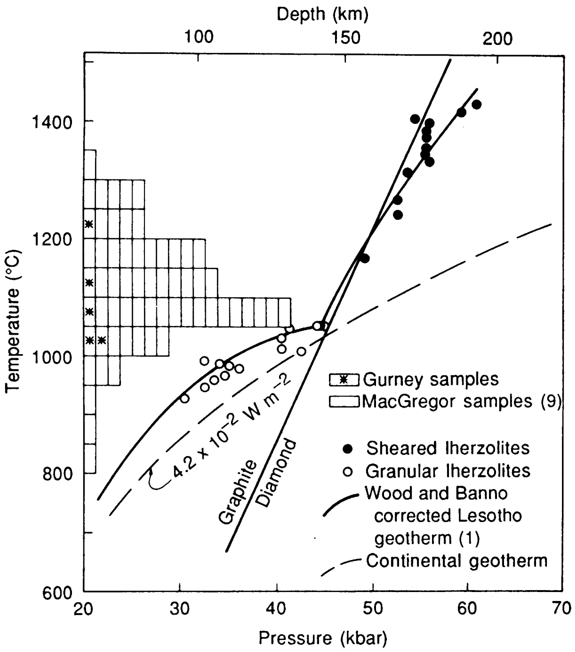

Fig. 1. Temperatures of equilibration (*11*) of 62 Roberts Victor eclogites. Temperature and depth estimates of garnet peridotite xenoliths in Lesotho kimberlites are also shown. The eclogites fill the void in the shallower part of the inflected limb of the geotherm.

gites show equilibration temperature of 1000° to 1250°C. Previous investigators also reported (*14, 17*) a similar range in temperatures of equilibration for these eclogites.

Evaluation (*18, 19*) of thermometers and barometers of garnet peridotites has shown that the inflection observed in the Lesotho and other similarly derived geotherms cannot be an artifact of the method of temperature estimation. In addition, Finnerty and Boyd (*19*) pointed out that the ultramafic xenoliths of most localities have a bimodal depth distribution. The high temperature population generally falls along the steeper inflected limb, whereas the lower temperature group plots along the normal geotherm. The minimum in the ultramafic distribution seems to fall in the lower portion of the inflected limb and is essentially coincidental with the maximum range for the Roberts Victor eclogites (Fig. 1). Although there is no geobarometer available for eclogitic xenoliths, pressures of equilibration for these eclogites can be estimated by assuming that the samples lie on the pyroxene geotherm and seeking a simultaneous solution with Ellis and Green's geothermometer (*11*). A combined estimate of temperature and pressure (Fig. 1) shows that many of the eclogites have come from the lower part of the inflected geotherm. If this observation is correct and if the inflection in the geotherm marks the top of the low-velocity zone, the Roberts Victor eclogites are derived from the lowest part of the lithosphere and the uppermost portion of the asthenosphere beneath southern Africa. The fact that the lower part of the inflected geotherm is sparsely populated by garnet peridotite xenoliths was also noted by Finnerty and Boyd (*19*), who suggested low-calcium garnet harzburgite or molten magma or both as the likely candidates for this gap. We suggest the eclogites to be a viable candidate, at least partially populating the gap in the geotherm.

Some Roberts Victor eclogites are diamond-bearing and in a few samples both diamond and graphite coexist (*14, 17*). Thus some eclogites must come from depths greater than or close to the diamond-graphite boundary (Fig. 1) that is essentially parallel (*20*) to the lower limb of the inflected geotherm. Most of the diamond-bearing kimberlites in South Africa are restricted to the thickest part of the Archean shield beneath the Kaapvaal craton (*21*), and it is thought that the depth of the transition from the low to high-temperature xenoliths varies from 125 to 170 km in southern Africa (*4, 21*). Accordingly, the depth to which either graphite or diamond is stable varies. We have arbitrarily used the intermediate Lesotho geotherm, which is most complete in its lherzolite xenolith distribution, to show that the diamond-bearing eclogites could be an important rock type at the bottom of the continental lithosphere. The increasing role of eclogite within the diamond stability field and in the lower part of the Siberian continental lithosphere has also been emphasized by Sobolev (*22*).

In reinterpreting the available geochemical, trace element, radiogenic, and stable isotope data of Roberts Victor eclogites, MacGregor (*8, 9*) proposed that these eclogites represent subducted ancient oceanic crust. This conclusion has been primarily derived from two sets of data (*9*). The oxygen isotopic compositions of the clinopyroxenes and garnets of these eclogites can only be interpreted, by analogy with ophiolites, in terms of a hydrothermally altered basaltic oceanic crust by exchange with seawater. Uranium-lead, rubidium-strontium, and samarium-neodymium systematics of the Roberts Victor eclogites (*10, 22*) indicate an age of approximately 2.7 × 10^9 years. In addition, some recent model age determinations of peridotitic inclusions in diamonds of South African kimberlites by various parent-daughter radiogenic systems (*23–26*) confirm the existence of Archean (>2.6 × 10^9 years) subcontinental lithosphere beneath southern Africa. In a sense, the correlation of Archean ages for the Roberts Victor eclogites and diamond inclusions is consistent with the oceanic crust hypothesis and poses the question of whether the diamonds are not also derived from the same ultimate source.

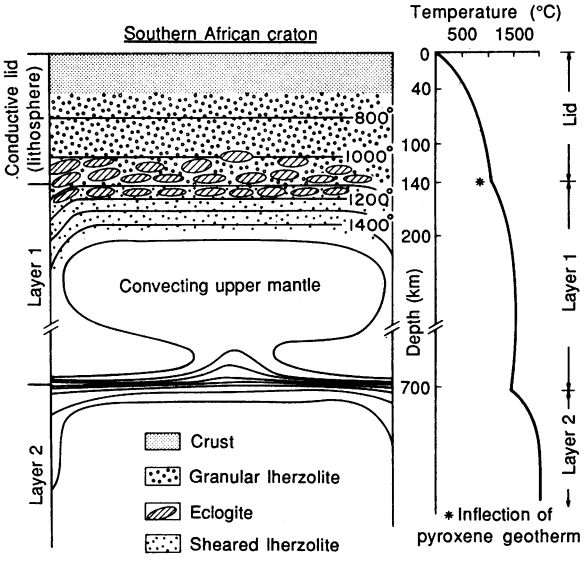

Fig. 2. Schematic cross section of the thermal and petrologic structure of the subcontinental mantle beneath the southern African craton. This diagram incorporates some eclogites in the lower part of the lithosphere; most lie in the upper part of the asthenosphere, which has the temperature distribution of the inflected geotherm. The lithospheric lid is underlain by the convective layer 1, with a steeper gradient (8°C/km) at the top of this layer that is similar to the inflection in the pyroxene geotherm. The shape of the isotherms beneath 200 km are schematic with another thermal boundary layer at 700 km depth (*13*).

Questions have arisen (*7, 27*) about whether the inflected shape of the pyroxene geotherm that marks the interpreted lithosphere-asthenosphere boundary can be maintained in a steady state. Proposals that link the kink in the geotherm to diapiric upwelling before kimberlite emplacement have also been criticized (*23*) on grounds that a great number of diapirs would have to be assumed to explain all the kimberlite occurrences in southern Africa during the Late Cretaceous. In the light of new laboratory and numerical experiments on convection confined to superimposed layers (*13*), we propose that the inflected part of the geotherm (*1*) represents convection under a conductive lid of the lithospheric plate. One of the principal conclusions of the layered convection study of Richter and McKenzie (*13*) is that the interface between the convecting layers will be characterized by a double boundary layer, which for a heat flux of 1 heat flow unit (microcalories per square centimeter per second) for the system, will result in a jump in temperature of about 5°C/km. It is interesting that the inflection of the Lesotho geotherm (Fig. 1) represents a similar (8°C/km) increase in temperature beneath the lithospheric lid. This configuration is considered to represent a special case of convection in a layered system that consists of a rigid conductive lid and an underlying convecting layer. Our analysis implies that the lithosphere does not actively participate in the convective process, and such a model should be appropriate for the ancient cratonic region of southern Africa (Fig. 2).

The shape of the convective cell in Fig. 2 is arbitrarily chosen, following some of the experimental models of Richter and McKenzie (*13*). However, the temperature depth relations in the upper part of this convection system are essentially correct and are based on the geotherm of Fig. 1. The boundary between layer 1 and 2 (Fig. 2) at 700 km roughly approximates that shown by Richter and McKenzie (*13*) in a line of reasoning that combines the effect of major element chemistry with the presumed phase transformation responsible for the 670-km seismic discontinuity. The thermal structure beneath southern Africa as suggested by Fig. 2 has many attractive elements. It implies that the thick cratonic root beneath the continent has remained unmixed and has been sustained by convection for periods as long as 2.7×10^9 years, which would also explain the reported ancient ages of eclogites and of the silicate inclusions in diamonds. Analyses of ultramafic xenoliths from the Premier pipe, an 1100-million-year-old kimberlite intrusion in South Africa (*28*), provided essentially the identical, inflected Lesotho geotherm, which implies that the thermal structure beneath South Africa that is 1100 million years old was essentially the same (Fig. 2) as in the Late Cretaceous time. The permanency of the thermal structure beneath the South African shield agrees with the thermal and petrological model of Fig. 2, which indicates that the double thermal boundary layer between isolated geochemical layers will persist as long as there is little vertical mass transfer across the interface. We are not implying that the thermal configuration in Fig. 2 has always remained the same. Rather, we propose a quasi–steady state situation for the model in Fig. 2 in which flow in layer 1 is time-dependent in a layered mantle system (*29*). Occasional perturbations within the center of the cell in layer 1 will perhaps generate kimberlitic and basaltic magmas (like the Karroo basalts) for eruption as other mechanisms for finite mass transfer.

Studies on the densities of silicate liquids (*30, 31*) in planetary interiors lend further credibility to the concept of a chemically stratified upper mantle with possible chemical boundaries at 400-km and 700-km discontinuities. Although we have constructed one single layer of convection up to the 700 km depth, the fact that the silicate liquid (*28*) may become more dense than its surrounding mantle between depths of 180 to 300 km may have some important implication for the thermal evolution of layers. One obvious implication of our model is the relative long-term stability of the lithosphere and of the upper part of the underlying convecting mantle beneath the ancient cratonic regions. Our present knowledge of geochemical mantle heterogeneities, the temperature-depth estimates of kimberlitic xenoliths, and the isotopic ages of the diamonds and eclogites can all be fit into a coherent model of layered mantle convection beneath a lithospheric conductive lid.

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$$T = \frac{X_{\mathrm{Ca}}^{\mathrm{gt}}\,(3104 + 3030 + 10.86)\,P}{\ln K_{\mathrm{d}} + 1.9034}$$

where $K_{\mathrm{d}} = (X_{\mathrm{Fe}^{2+}}/X_{\mathrm{Mg}})^{\mathrm{gt}}\,(X_{\mathrm{Mg}}/X_{\mathrm{Fe}^{2+}})^{\mathrm{cpx}}$, P is pressure (in kilobars), and X_{Mg}, $X_{\mathrm{Fe}^{2+}}$, and X_{Ca} are the mole fractions, respectively, of Mg, Fe^{2+}, and Ca, in garnet and clinopyroxene. There are some arguments in favor of the assumption that these eclogitic pyroxenes and garnets have little ferric iron. We have checked the reproducibility of the electron microprobe analyses of garnets and clinopyroxenes by reanalyzing 12 of the eclogite samples in this study. We used the JEOL superprobe 733 at Cornell University and found good correspondence between our analyses and those analyzed earlier by MacGregor (*9*) and reported by Gurney *et al.* (*14*). Some of the Roberts Victor eclogites are known to be inhomogeneous, which interferes with the determinations of temperatures and pressures of equilibration. A recent study by J. S. Ongley (thesis, University of Rochester, Rochester, 1986) of the Roberts Victor eclogites with the microprobe and SEM revealed the nature of chemical inhomogeneity to be maximum around the rims of clinopyroxenes and garnets, the primary minerals of eclogites. However, the inner cores of these minerals were shown to have relatively invariable compositions. In our analysis, we have made the assumption that these cores reflect equilibrium compositions.
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