Diamonds, Eclogites, and the Oxidation State of the Earth's Mantle

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The reaction dolomite + 2 coesite ⇄ diopside + 2 diamond + $2O_2$ defines the coexistence of diamond and carbonate in mantle eclogites. The oxygen fugacity of this reaction is ~1 log unit higher at a given temperature and pressure than the oxygen fugacities of the analogous reactions that govern the stability of diamond in peridotite. This difference allows diamond-bearing eclogite to coexist with peridotite containing carbonate or carbonate + diamond. This potential coexistence of diamond-bearing eclogite and carbonate-bearing peridotite can explain the presence of carbon-free peridotite interlayered with garnet pyroxenites that contain graphitized diamond in the Moroccan Beni Bousera massif at the Earth's surface and the preferential preservation of diamond-bearing eclogitic relative to peridotitic xenoliths in the Roberts Victor kimberlite.

Carbon may exist in the Earth's mantle as a fluid, as a carbonate mineral, or in elemental form. Studies in the 1970s established that CO_2-rich fluids are unstable in peridotitic (olivine + pyroxene) assemblages above ~1.5 GPa (~50 km depth) [reviewed in (*1*, *2*)]. The stability of graphite, or diamond at higher pressure, relative to CO_2 or carbonate depends on the oxidation state of the assemblage, which is monitored by the oxygen fugacity (f_{O_2}). In contrast with the amount of work on the reactions governing carbonate, carbon, and fluid stability in peridotitic assemblages with olivine, little attention has been paid to the analogous reactions in assemblages without any olivine, such as eclogite (clinopyroxene + garnet), despite their abundance in some mantle-derived xenolith suites. Carbonate itself is scarce in xenolithic eclogites and eclogites in high-grade metamorphic terranes (*3*).

In lherzolitic (olivine + orthopyroxene + clinopyroxene) assemblages, CO_2 reacts with olivine and clinopyroxene to form dolomite by ~1.5 GPa (*1*, *2*, *4*).

$$\underset{\text{dol}}{CaMg(CO_3)_2} + \underset{\text{opx}}{2Mg_2Si_2O_6} \rightleftarrows \underset{\text{cpx}}{CaMgSi_2O_6} + \underset{\text{ol}}{2Mg_2SiO_4} + \underset{\text{V}}{2CO_2} \qquad (1)$$

At higher pressures, the exchange reaction

$$\underset{\text{cpx}}{CaMgSi_2O_6} + \underset{\text{mag}}{2MgCO_3} \rightleftarrows \underset{\text{dol}}{CaMg(CO_3)_2} + \underset{\text{opx}}{Mg_2Si_2O_6} \qquad (2)$$

stabilizes magnesite lherzolite at the expense of dolomite lherzolite (*5*).

For harzburgitic (olivine + orthopyroxene) assemblages, reactions 1 and 2 are replaced by

$$\underset{\text{opx}}{Mg_2Si_2O_6} + \underset{\text{mag}}{MgCO_3} \rightleftarrows \underset{\text{ol}}{2Mg_2SiO_4} + \underset{\text{V}}{2CO_2} \qquad (3)$$

Calcium-depleted harzburgite assemblages, especially those containing garnet, are important because of the abundant low-Ca garnets that occur as megacrysts in kimberlites and as inclusions in diamonds (*6*, *7*). These garnets are inferred to form in clinopyroxene-free harzburgite assemblages, and a genetic link between the formation of these harzburgites and the formation of diamonds has been proposed (*7*).

To examine the stability of carbon-bearing phases in eclogite, I conducted experiments on a model carbonated eclogitic composition at 8 GPa at 1200° and 1400°C (*8*). The coexistence of dolomite, coesite, and majoritic garnet in the products is consistent with the carbonation reaction

$$\underset{\text{dol}}{CaMg(CO_3)_2} + \underset{\text{coes}}{2SiO_2} \rightleftarrows \underset{\text{cpx}}{CaMgSi_2O_6} + \underset{\text{V}}{2CO_2} \qquad (4)$$

(DCDV). The lower pressure, quartz-bearing version of this reaction has been studied previously (*1*, *9*). Coesite is generated by the carbonation of clinopyroxene in reaction 4. The fate of this reaction at lower oxygen fugacities determines the stability of elemental carbon. This extrapolation is similar to that done previously for ultramafic compositions (*2*, *10*) and may be illustrated with an isobaric section (at 5 GPa) in log f_{O_2}-T space (Fig. 1), where T is temperature and oxygen fugacity is plotted as Δlog f_{O_2}, defined as log f_{O_2}(sample) − log f_{O_2}(FsMC). This latter quantity is the log f_{O_2} of the end-member reaction

$$\underset{\text{ferrosilite}}{3Fe_2Si_2O_6} + O_2 \rightleftarrows \underset{\text{magnetite}}{2\ Fe_3O_4} + \underset{\text{coesite}}{6\ Si_2O_2} \qquad (5)$$

This reaction is the high-pressure version of the FMQ (fayalite-magnetite-quartz) oxygen buffer reaction that is stable in the diamond stability field at pressures above the fayalite + quartz ⇄ ferrosilite reaction and the quartz ⇄ coesite reaction. The reaction boundaries are calculated with an internally consistent set of thermodynamic data (*11*). Because of the considerable extrapolation to these pressures, the results should be considered as illustrative rather than quantitative.

The CCO reaction

$$C + O_2 \rightleftarrows CO_2 \qquad (6)$$

defines the maximum stability of diamond with respect to oxidation in the carbon-oxygen system and hence the maximum potential stability limit of diamond in silicate-containing systems.

The vertical line at $T \approx 1300°C$ (Fig. 1) is reaction 4 (the DCDV reaction). Upon intersection with the CCO reaction, this reaction becomes

$$\underset{\text{dol}}{CaMg(CO_3)_2} + \underset{\text{coes}}{2SiO_2} \rightleftarrows \underset{\text{cpx}}{CaMgSi_2O_6} + \underset{\text{dia}}{2C} + 2O_2 \qquad (7)$$

(DCDD). This reaction defines the most oxidizing conditions under which diamond can exist in eclogite. At higher f_{O_2} values, carbon exists as carbonate at tem-

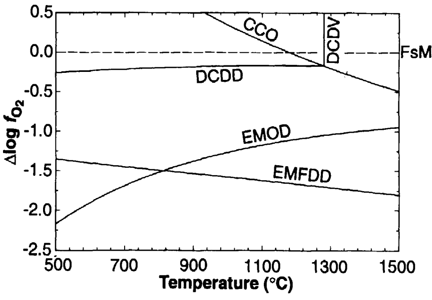

Fig. 1. Isobaric temperature-Δlog f_{O_2}(FsMC) section at 5 GPa. Between DCDD and CCO, both peridotite and eclogite contain carbonate but not diamond. Along the DCDD curve, eclogite contains both carbonate and diamond, but below the curve, it contains only diamond. Harzburgites and lherzolites contain carbonate only above reactions EMOD and EMFDD, respectively. Along EMOD, harzburgite contains both diamond and carbonate, as does lherzolite along EMFDD. Below EMOD or EMFDD, harburgite or lherzolite, respectively, contain only diamond. Reaction abbreviations: FsMC, reaction 5; CCO, reaction 6; *DCDD*, reaction 7; DCDV, reaction 4; EMOD, reaction 8; and EMFDD, reaction 9. The EMFDD values were calculated with a(Di) = 0.80, a(Cc) = 0.10, and a(Fo) = a(En) = 0.90. All other reactions were calculated for end-member compositions.

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peratures less than the DCDV reaction and as CO_2 at higher temperatures. Carbon could be present in a fluid at temperatures below the DCDV reaction if it is a CO_2-H_2O fluid.

The stability of diamond in harzburgites is given by the EMOD reaction

$$\underset{\text{opx}}{Mg_2Si_2O_6} + \underset{\text{mag}}{2MgCO_3} \rightleftarrows \underset{\text{ol}}{2Mg_2SiO_4} + \underset{\text{dia}}{2C} + 2O_2 \qquad (8)$$

(*2, 10*). This reaction intersects the CCO reaction at >1500°C, where it becomes reaction 3 with a vertical slope, paralleling DCDV (Fig. 1).

The stability of diamond in Ca-bearing lherzolite assemblages is controlled by the EMFDD reaction

$$\underset{\text{opx}}{3Mg_2Si_2O_6} + \underset{\text{mag}}{2CaCo_3} \rightleftarrows \underset{\text{ol}}{2Mg_2SiO_4} + \underset{\text{cpx}}{2CaMgSi_2O_6} + \underset{\text{dia}}{2C} + 2O_2 \qquad (9)$$

To be applied to mantle lherzolites, the effect of the reduced activities (a) of all components on this reaction must be considered. The EMFDD curve in Fig. 1 was calculated for a(Fo) = a(En) = 0.90, a(Di) = 0.80, and a(Cc) = 0.10 (*12*). This activity of the $CaCO_3$ component in the carbonate is consistent with compositions observed in experiments on model peridotites (*13*). More magnesian carbonates (mol % $CaCO_3 \approx 0.05$) have been observed on the high-pressure side of reaction 2 (*5*). Decreasing a(Cc) further will shift EMFDD to lower values of $\Delta\log f_{O_2}$ (Fig. 2). The lesser effects of varying the other activities on the calculated position of EMFDD are also shown (Fig. 2).

The location of the other reactions in Fig. 1 are less sensitive to the compositions of the phases involved (Fig. 2) because the components involved are abundant rather than dilute components in the minerals in lherzolites and harzburgites. In particular, the DCDD reaction does not shift sufficiently to cross the position of the EMOD or EMFDD reactions. The relative positions of the reactions are also insensitive to pressure variations from 4 to >8 GPa.

The difference between the position of the DCDD reaction and those of the EMOD and EMFDD reactions defines a window in f_{O_2}-T space in which diamond is stable in eclogites but carbonate is stable in harzburgites or peridotites. The significance of this window depends on what controls the oxidation state in these rocks. These controls of oxidation state in the mantle are uncertain; possible factors that may control the f_{O_2} of the mantle include diamond-fluid or silicate-carbonate-diamond reactions, the presence of S and H, and the effects of Fe^{2+} and Fe^{3+} reactions in the silicates (*14*).

It is possible that the oxidation state is imposed on the mantle by infiltrating fluids or melts (either silicate or carbonate). Alternatively, the oxidation state may be locally controlled, such that the f_{O_2} of an eclogite is defined by the DCDD reaction and that of a coexisting peridotite is defined by the EMOD or EMFDD reactions. In this case, two samples that had coexisted at the same pressure and temperature could have different f_{O_2} values. Yet another possibility would be for the f_{O_2} to be imposed on a mixed peridotite and eclogite system by the EMOD or EMFDD reactions in situations in which the peridotite is dominant volumetrically. In this case, the peridotite would contain coexisting diamond and carbonate, but the subordinate eclogite would contain only diamond.

These possibilities may be examined with the above framework in the light of some geologic observations. The Beni Bousera peridotite massif in Morocco contains garnet pyroxenite (eclogite) layers that host graphitized diamonds (*15*), but the surrounding peridotites lack graphite or diamond pseudomorphs. The pyroxenites are interpreted as crystallized melts of subducted oceanic lithosphere, not as being derived from the surrounding peridotite (*16*). Several possible scenarios may be envisioned for control of the oxidation state of this system. If local equilibrium had prevailed, with the oxidation state in the pyroxenite defined by the DCDD reaction and that in the peridotite by the EMOD or EMFDD reactions, both rock types should have contained both carbonate and diamond, which does not explain the observed preferred preservation of diamond in the pyroxenite.

Another possibility is that the oxidation state is externally imposed, such that the f_{O_2} is between those of the DCDD and either the EMOD or EMFDD reactions. In this case, diamond-bearing eclogite would coexist with carbonate-bearing peridotite in the mantle. During ascent of the massif, the peridotite would decarbonate as the pressure dropped below that in reactions 1 or 3, accounting for the observed absence of carbon in the peridotite. The question of how the intermediate f_{O_2} was imposed remains. An alternative scenario would have the peridotite impose an EMOD- or EMFDD-like f_{O_2} on the eclogite, resulting in diamond-bearing eclogite coexisting with diamond- and carbonate-bearing peridotite. During ascent, the decarbonation of the peridotite would occur as above. Further, the removal of CO_2 would drive either the EMOD or EMFDD reaction to the left, depleting the peridotite of carbon. This would require an additional source of oxygen, which could be the fluid (through the reduction of CO_2 to CO or reduction of H_2O) or the silicates bearing ferric iron. The lack of carbonate in the pyroxenite would prevent this process from happening in these rocks, and so the diamond would only graphitize.

The converse scenario, in which coexisting diamond and carbonate in the pyroxenite imposes a DCDD-like f_{O_2} on the peridotite, would not explain why diamond would be preserved in the pyroxenite rather than being consumed during ascent. This may indicate that infiltrating melts, represented by these pyroxenites (*16*), are ineffective at imposing an oxidation state on the surrounding mantle.

The Roberts Victor kimberlite pipe in South Africa contains many eclogite xenoliths but few peridotite xenoliths, in contrast to most of the pipes on this craton. The eclogite xenoliths make up 98% of the xenolith population (*17*), but disaggregated xenocrysts are dominantly peridotitic minerals. On this basis, it is estimated that the mantle sampled by the Roberts Victor kimberlite consisted of 85% peridotite and 15% eclogite (*18*). This estimate is consistent with the observation that less than 15% of the minerals included in diamonds from Roberts Victor are of eclogitic affinity (*19*).

Decarbonation reactions during ascent of xenoliths would provide sufficient CO_2 to disaggregate the xenoliths (*1, 20*). That such a process is plausible on the time scale of kimberlite ascent (hours to days) has been confirmed experimentally (*21*). The

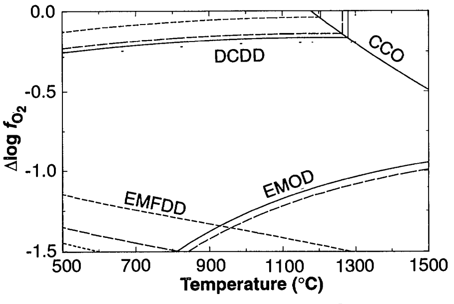

Fig. 2. Evaluation of the effect of changing activities of components for the reactions illustrated in Fig. 1 in an isobaric temperature-Δlog f_{O_2}(FsMC) section at 5 GPa. Abbreviations as in Fig. 1. DCDD: solid line, end-member reaction; long dashed line, a(Di) = 0.80 and a(dol) = 0.90; medium dashed line, a(Di) = 0.50 and a(dol) = 0.90; dotted line, a(Di) = 0.80 and a(dol) = 0.70. EMOD: solid line, end-member reaction; long dashed line, a(Fo) = a(En) = 0.90 and a(Mag) = 0.90; dotted line, a(Fo) = a(En) = 0.90 and a(Mag) = 0.70. EMFDD: in all cases, a(Fo) = a(En) = 0.90; long dashed line, a(Di) = 0.80 and a(Cc) = 0.10; medium dashed line, a(Di) = 0.50 and a(Cc) = 0.10; short dashed line, a(Di) = 0.80 and a(Cc) = 0.05.

preferential survival of the diamond-bearing eclogite would be expected if the oxidation state of the mantle beneath Roberts Victor was defined by the EMOD or EMFDD reactions in the dominant peridotite. Carbonate- and diamond-bearing peridotite would coexist with diamond-bearing eclogite. Upon incorporation into the ascending kimberlite magma, the peridotite would undergo decarbonation reactions such as reactions 1 or 3. These reactions would liberate CO_2 and disaggregate the xenolith. In contrast, the carbon-bearing eclogitic rocks would contain diamond rather than carbonate and therefore would not experience decarbonation; hence, they would be more likely to survive the trip to the surface intact. In this scenario, differential carbon contents in peridotite versus eclogite need not be invoked to explain the observations, merely that the diamond-carbonate equilibria be dictated by reactions involving olivine and orthopyroxene in the lherzolite or harzburgite and by reactions involving clinopyroxene and coesite in the eclogite.

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4. This reaction and the subsequent ones are written with the high-temperature side on the right, as is conventional. Abbreviations under the formulas refer to the phase containing the component referenced: coes, coesite; cpx, clinopyroxene; dia, diamond; dol, dolomite; mag, magnesite; ol, olivine; opx, orthopyroxene; V, vapor. Components are abbreviated: Fo, forsterite, Mg_2SiO_4; Cc, calcite, $CaCO_3$; En, enstatite, $MgSiO_3$; and Di, diopside, $CaMgSi_2O_6$.
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12. The equations for the reactions in Fig. 1 are [component abbreviations in (*4*)]

$$\begin{aligned}\Delta\log f_{O_2}(\mathrm{DCDD}) &= -0.71734 + 0.13175\,P \\ &\quad + (143.2743 - 59.1790\,P)/T \\ &\quad - 0.5\log a(\mathrm{Di}) + 0.5\log a(\mathrm{Dol}) \\ \Delta\log f_{O_2}(\mathrm{EMOD}) &= -0.68258 + 0.13320\,P \\ &\quad - (329.5898 + 258.0536\,P)/T \\ &\quad - \log a(\mathrm{Fo}) + 0.5\log a(\mathrm{En}) + \log a(\mathrm{Mag}) \\ \Delta\log f_{O_2}(\mathrm{EMFDD}) &= -0.51839 + 0.08335\,P \\ &\quad + T(-4.7750\times 10^{-4} + 7.64169\times 10^{-6}\,P) \\ &\quad - \log a(\mathrm{Fo}) - \log a(\mathrm{Di}) \\ &\quad + 1.5\log a(\mathrm{En}) + \log a(\mathrm{Cc})\end{aligned}$$

(pressure P in gigapascals and T in kelvins). The standard state for all solids is the pure solid at pressure and temperature. Both coesite and diamond are presumed to be pure phases; hence, a(Coes) and a(Dia) do not appear in these equations. These equations reproduce the values calculated with the rigorous equations and the data (*11*) to less than ±0.1 unit of $\Delta\log f_{O_2}$ in the range 4 to 7 GPa and 600° to 1300°C.
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Paleozoic Atmospheric CO_2: Importance of Solar Radiation and Plant Evolution

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Changes in solar radiation, as it affects the rate of weathering of silicates on the continents, and other changes involving weathering and the degassing of carbon dioxide (CO_2) have been included in a long-term carbon-cycle model. These additions to the model show that the major controls on CO_2 concentrations during the Paleozoic era were solar and biological, and not tectonic, in origin. The model predictions agree with independent estimates of a large mid-Paleozoic (400 to 320 million years ago) drop in CO_2 concentrations, which led to large-scale glaciation. This agreement indicates that variations in the atmospheric greenhouse effect were important in global climate change during the distant geologic past.

The weathering of Ca-Mg silicate rocks on the continents, followed by the precipitation of the Ca and Mg as carbonate minerals in the oceans, constitutes a major process whereby atmospheric CO_2 is regulated on a multimillion-year time scale. This process can be generalized in terms of the overall reactions (*1*)

$$CO_2 + CaSiO_3 \rightarrow CaCO_3 + SiO_2$$

$$CO_2 + MgSiO_3 \rightarrow MgCO_3 + SiO_2$$

Several major factors affect CO_2 uptake by Ca-Mg silicate weathering. The changes in intensity of solar radiation with time affect the surface temperature of the Earth and, thereby, the rate of rock weathering. The CO_2 greenhouse effect acts as a negative feedback mechanism to stabilize the Earth's surface temperature. The rise and evolution of vascular land plants have resulted in accelerated chemical weathering by their secretion of acids, providing ground litter for the microbial production of CO_2 and holding and recycling moisture in the soil. Finally, mountain uplift brings about the exposure of weatherable rock by erosion.

In this report, I show how solar radiation and the rise and spread of land plants were major factors affecting continental weathering, and consequently the concentrations of atmospheric CO_2, during the Paleozoic era [approximately 570 to 250 million years ago (Ma)]. Estimated CO_2 concentrations are high for this time (*2*, *3*), during which a transition from the extremely high CO_2

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