

THE STABILITY OF GRAPHITE AND DIAMOND AS A FUNCTION OF THE OXYGEN  
FUGACITY IN THE MANTLE.

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Since graphite as well as diamond are found in kimberlitic material, equation (4) of the preceding abstract :

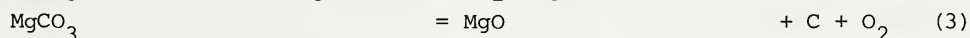
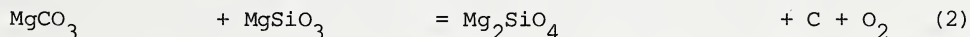
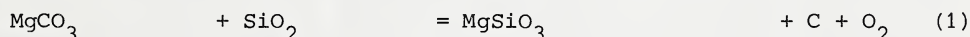
$$\log f_{O_2} = 2.74 - \frac{19559}{T} + \frac{0.13 (P-1)}{T} \quad \text{for bar and K}$$

is directly applicable for the evaluation of limiting oxygen fugacities as a function of temperature and pressure in the earth's mantle. Strictly speaking this equation is valid only as long as graphite coexists with a pure fluid carbon oxide phase.

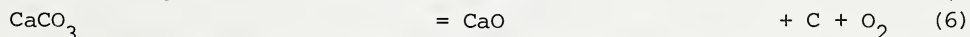
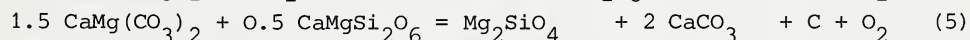
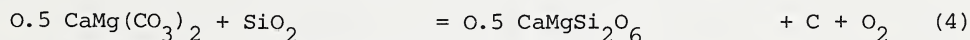
Extensive work has been performed on the model mantle system CaO-MgO-SiO<sub>2</sub>-CO<sub>2</sub> by P.J. Wyllie and coworkers and by D.H. Eggler and coworkers. In this system CO<sub>2</sub> occurs either uncombined as a fluid carbon oxide phase, or in the combined form as a carbonate phase. The addition of carbon as a further component adds another degree of freedom to this system, requiring the definition of equilibrium oxygen fugacities.

Reduction leads to several characteristic reactions in this system :

- 1.) Carbonates are reduced in several separate steps according to :



and



- 2.) Each of the above reactions constitutes in itself an oxygen buffer.
- 3.) From figure 1 it is evident that the highest oxygen fugacity for stable existence of elementary carbon is given by the CCO buffer surface.
- 4.) Below the CCO surface graphite or diamond coexist with carbonate phases.
- 5.) The lower limit of stability of carbonates is given by the CaCO<sub>3</sub>-CaO-C and MgCO<sub>3</sub>-MgO-C divariant surfaces.
- 6.) Subsolvus equilibria among silicates and carbonates are shifted to lower temperatures upon reduction.
- 7.) At the same time, since CO<sub>2</sub> is ultimately replaced by the inert graphite or diamond, the solidus temperatures will be raised to the solidus of the "volatile absent" system CaO-MgO-SiO<sub>2</sub>. (According to Wyllie (1976) this effect will be much less pronounced in natural systems containing small amounts of water).

For the genesis of diamond the P-T- $fO_2$  relations in the mantle are relevant :

Estimates of prevailing pressures and temperatures are taken from Boyd's (1975) Lesotho Geotherm.

The oxygen fugacity in a model mantle material will be controlled by a sliding buffer assemblage olivine + orthopyroxene + clinopyroxene + spinel or, at greater depths, olivine + orthopyroxene + clinopyroxene + garnet, which will be quantitatively dominant with respect to a possible carbon-carbonate oxygen buffer as defined above in a kimberlitic material. Thus an oxygen fugacity slightly below QFM may be assumed for mantle conditions, which is in agreement with observations and deductions made by other investigators, applying widely different methods. (Mitchell(1973), Ulmer et al.(1976), Ryabchikov et al.(in prep.), Brey (personal communication)

The oxygen fugacity of the CCO equilibrium has been calculated from the above equation for temperatures and pressures of the Lesotho Geotherm and plotted in figure 2. It is compared with the oxygen fugacities of the QFM and WM buffers respectively. It is evident that the QFM surface intersects the CCO surface on the geotherm at about  $T = 950^{\circ}\text{C}$ ,  $P = 39$  kbar and  $\log fO_2 = -9.1$ . At temperatures above  $950^{\circ}\text{C}$  and correspondingly greater depths elementary carbon will thus be unstable with respect to a carbon oxide phase or carbonates in a QFM buffered environment.

The hatched area in figure 2 outlines a range of oxygen fugacities slightly below QFM, according to the deductions of natural oxygen fugacities. Here the stability of carbon is extended to higher temperatures and pressures. But still a lower limit for diamond in the earth's mantle is demonstrated. On the other hand an upper limit is defined by the graphite-diamond equilibrium. Thus it may be concluded that the stability range of diamond ("diamond facies") is a restricted zone in the mantle.

From figure 2 it can be concluded that any transgression of carbon bearing and oxygen buffered mantle material across the CCO surface will lead to a redox reaction of the carbon bearing phase : Transgression towards higher temperatures and pressures results in exothermic oxidation of diamond ( $\sim 400 \text{ KJ.mol}^{-1}$ ), while transgression towards lower P-T-ranges leads to endothermic reduction of carbonates or a carbon oxide fluid phase to diamond.

Pressure oscillations across the CCO boundary will thus lead to repeated production of heat on the high pressure side, while a corresponding enthalpy is consumed on the low pressure side. This process will eventually lead to a distortion of the temperature profile of the geotherm.

This deduction may help to provide a new hypothesis for the origin of the Boyd Inflection in the Lesotho Geotherm. It requires : Diamonds may be present in lherzolite nodules from the shallower part of the mantle, as reported from various localities, while diamonds must be absent from sheared lherzolites (Boyd(1976)) from locations on the geotherm beyond the Boyd Inflection.

#### References :

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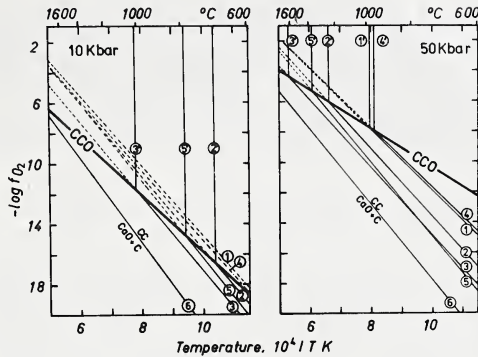


Figure 1.

Isobaric sections in the  $P$ - $T$ - $fO_2$  space of the CCO buffer and of various carbon-carbonate buffers, calculated from thermodynamic data (Kubaschewski et al. (1967), Eggler et al. (1976)). Numbers refer to reactions (1)-(6) in the text. Stippled lines in the range above the CCO curve represent meta-stable extensions of the above reactions. (1')-(6') are decarbonation reactions resulting from Schreinemakers analysis.

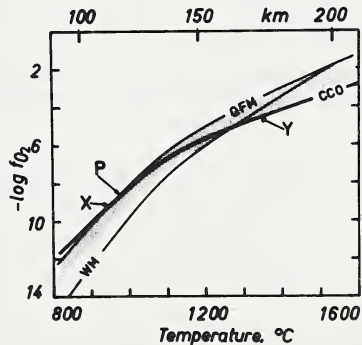


Figure 2.

Oxygen fugacities of the CCO, QFM and WM buffers at temperatures and corresponding pressures along the Lesotho Geotherm (Boyd and Finger, (1975)).  $P$  = equilibrium point graphite + diamond +  $CO_2$  on the geotherm. In a QFM buffered environment graphite will be oxidized to  $CO_2$  at  $T = 950^\circ C$ ,  $P = 39$  kbar and  $\log fO_2 = -9.1$ ; (point "X"). At an oxygen fugacity one log unit below QFM diamond will be oxidized to  $CO_2$  at  $T = 1350^\circ C$ ,  $P = 59.5$  kbar and  $\log fO_2 = -4.5$ ; (point "Y"). The distance  $P - Y$  corresponds to the width of the "diamond facies" = 55 km.