Diamond thermoelastic properties and implications for determining the pressure of formation of diamond–inclusion systems

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Abstract

The formation conditions of diamond can be determined from the residual pressure of inclusions trapped within the diamond, as measured at ambient conditions, and the equations of state (EoS) of the mineral inclusion and the host diamond. The EoS parameters of the diamond and the inclusion phase are therefore critical for determining the precision and accuracy of the calculation of formation conditions of diamonds. The questions we address are (i) How precise are these calculations? and, in particular, (ii) Do we know the EoS parameters of diamond to a precision and accuracy which do not contribute significantly to uncertainties in the geological conclusions drawn from these calculations? We present a review of the most recent compressional data, simulations, and direct elastic measurements of diamond and show them to be consistent with a room-temperature bulk modulus of $K_{0T} = 444(2)$ GPa and a pressure derivative $K' = 4.0$. In combination with a thermal-pressure model with parameters $\alpha_{V300,0} = 2.672(3) \times 10^{-6}$ K^{-1} and a single Einstein temperature $\theta_E = 1500$ K, the volume variation of diamond from room conditions to pressures and temperatures exceeding those in the Earth's transition zone is described to within the levels of uncertainty inherent in both experimental and computational determinations. For the example of olivine inclusions in diamond, these uncertainties in the diamond EoS parameters lead to uncertainties in the entrapment pressures of no more than 0.001 GPa at low temperatures and 0.008 GPa at higher temperatures.

Introduction

Determining the depths of formation of diamonds is important, but remains a major scientific challenge. They are the only direct samples we have of the deep Earth, but their depths of formation are only poorly constrained. This is partly because diamond itself is nearly chemically pure, so the traditional types of barometers used for silicate minerals, which usually rely on either cation partitioning within a single phase or between phases (see Nimis and Grütter, 2010 for a review), often cannot be employed. Studies of the inclusion minerals trapped within the diamond at the time of diamond growth therefore provide the most important constraints on the mechanisms and depths of growth of diamonds. Inclusions provide two types of information. Their compositions and, if multimineralic, their phase assemblages can in some cases provide constraints on the formation conditions of the mineral

inclusions through conventional geothermobarometric methods. If the inclusions were formed prior to diamond growth (i.e., are *protogenetic*), as recently suggested for olivine inclusions from the Udachnaya kimberlite (Nestola et al., 2014) and for sulfide inclusions from the Jwaneng (Thomassot et al., 2009) and Mir kimberlites (Spetsius et al., 2002), then the chemical information from the inclusions may not be relevant to the formation conditions of the diamond, unless the geobarometers were reset at that time. In any case, for many single-phase inclusion minerals, including olivine, conditions of formation cannot be inferred from either cation distributions or the bulk composition.

Whether the inclusions are protogenetic or grew syngenetically with the diamond as coproducts of the diamond-forming reaction, the entrapment conditions can be determined simply from measurements of the residual pressure of the inclusion within the diamond studied at ambient conditions (Barron et al., 2005; Izraeli et al., 1999; Sobolev et al., 2000; Zhang, 1998). This residual pressure arises from the contrast in the volume thermal expansion and compressibility of the diamond host and mineral inclusion. In short, at the time of entrapment,

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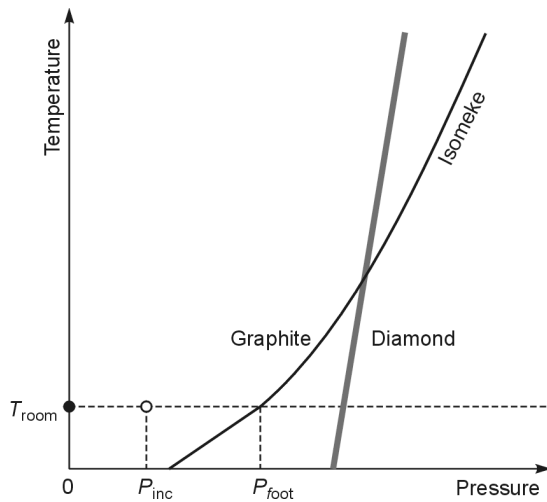*E-mail address:* rossjohnangel@gmail.com (R.J. Angel)

Fig. 1. The concept of an isomeke. At ambient conditions the inclusion is under a pressure P_{inc}, even though the host is subject to ambient pressure (essentially $P = 0$). Isothermal compression of the host-inclusion pair leads to them having the same volumes at P_{foot}, which lies on the isomeke. The isomeke is calculated from the EoS parameters of the two phases, and represents the possible entrapment pressure at each temperature. At higher temperatures the isomeke passes in to the diamond stability field and represents possible P-T conditions for entrapment of the inclusion by the diamond host.

the inclusion phase and the hole it occupies in the diamond would have had the same P, T, and volume (e.g., Howell et al., 2010, 2012b). Subsequently, the volume of the hole in the diamond expands less on decompression to room conditions than would a free crystal of the inclusion mineral. As a consequence the inclusion is compressed by the surrounding diamond and exhibits a pressure significantly greater than the external ambient pressure at room conditions. The calculation of possible formation conditions can proceed in a number of ways (e.g., Howell et al., 2010), but the following (Fig. 1) is conceptually the simplest.

When the diamond-inclusion pair is studied in the laboratory, both are at ambient temperature (T_{room}), the diamond is at ambient pressure (essentially zero pressure), and the inclusion is under a uniform small pressure P_{inc} (Fig. 1), which is typically ~ 0.2–0.4 GPa for olivines. Consider recompression of the diamond-inclusion pair at room temperature. The diamond is stiffer, so the volume of the 'hole' in the diamond that is now occupied by the inclusion will decrease in size less rapidly than the softer inclusion itself. At some pressure, the volumes of the diamond hole and the inclusion phase become equal. This point at ambient temperature is one point on the isomeke, a line in $P–T$ space that represents conditions under which the diamond and inclusion phase would have the same volumes. The isomeke is therefore the line of possible entrapment conditions for this inclusion in its diamond host. At ambient temperature (T_{room}) we call the pressure of the isomeke line P_{foot} (Fig. 1). This pressure is determined solely by the final inclusion pressure at ambient conditions (P_{inc}) and the *isothermal* EoS of the diamond and the inclusion.

Of course, while the conditions of P_{foot} and T_{room} lie on the isomeke and therefore represent possible entrapment conditions that meet the thermodynamic requirements of the problem, they are clearly not realistic, for two reasons. First, obviously, diamonds do not grow at 300 K in nature. Secondly, P_{foot} will lie, for most inclusions, outside the diamond stability field. We therefore need to calculate the path of the isomeke away from the point at P_{foot}. Because the isomeke is defined as the line along which the volumes of the two phases remain the same, its instantaneous slope is given by $(\partial P / \partial T)_{isomeke} = \Delta\alpha / \Delta\beta$, where $\Delta\alpha$ is the difference between the volume thermal expansion coefficients of the diamond and the inclusion and $\Delta\beta$ is the difference in their volume compressibilities (Rosenfeld and Chase, 1961). The path of the isomeke in $P–T$ space can therefore be calculated away from the point at P_{foot}, T_{room}, by using the EoS parameters of the two phases. If there has been no plastic relaxation that has decreased the pressure of the inclusion, and if the EoS parameters are accurate, the calculated isomeke line will pass in to the stability field of diamond, where it will then represent the possible *P-T* conditions for the growth of the diamond (Fig. 1).

The EoS parameters of the diamond and the inclusion phase therefore play the key role in determining the accuracy of the calculation of formation conditions, and hence depths, of diamonds. The questions we address here are (i) how precise are these calculations and, in particular, (ii) do we know the EoS parameters of diamond well enough so that their uncertainties do not contribute significantly to uncertainties in calculated isomeke pressures?

We choose olivine inclusions as our test case. Olivine is one of the most abundant types of inclusion found in diamond and, at the same time, represents the most abundant mineral in the upper mantle, and thus provides the unique opportunity to constrain the formation conditions of the greatest possible number of diamond deposits. The uncertainties in the calculations will then represent the smallest differences in formation conditions between different diamonds that can be resolved by this technique.

The role of EoS uncertainties in isomeke calculations

In order to demonstrate the effect of the uncertainties in EoS parameters of diamond on the calculation of isomeke pressures we take the example of the common host-inclusion system of olivine in diamond. We use the measured final pressure of 0.40 ± 0.01 GPa of a Fo92 olivine (Nestola et al., 2011a) as P_{inc}, and the EoS parameters for olivine used by those authors; $K_{0T} = 123.4$ GPa, $K' = 5.5$ (Nestola et al., 2011b) and $\partial K/\partial T = -0.02267$ GPa/K (Isaak et al., 1989) in a 3rd-order BM-EoS, and $\alpha_0 = 2.77 \times 10^{-5}$ K^{-1}, $\alpha_1 = 9.7 \times 10^{-9}$ K^{-2} and $\alpha_2 = -0.32$ K (Gillet et al., 1991) in a Fei-type model for thermal expansion (Angel et al., 2014a). At the start of the calculation, the inclusion pressure should be corrected for the mutual relaxation of the host-inclusion system that arises from the inclusion being at a higher pressure than the