A LINEAR MODEL AND TOPOLOGY FOR THE HOST–INCLUSION MINERAL SYSTEM INVOLVING DIAMOND

Lawrence M. BARRON§

Geological Survey of New South Wales, PO Box 536, St Leonards, New South Wales 1590, Australia

Abstract

A linear model of internal pressure for the host–inclusion system has been developed for diamond and a test selection of thirty minerals (excluding sulfides). Central to this model, for each diamond–inclusion pair, is the isovolume locus in P–T space, along which the relative volumes of the two phases change identically. The key ratio Θ, equal to slope of the isovolume locus divided by the slope of the graphite–diamond transition, permits unconditional assignment of a mineral to one of four universal topological groups of inclusions, namely 1) a heritage-T group, 2) a heritage-P group, 3) a group with mixed response (complete decompression inside high temperature diamond), and 4) a group that decompresses completely. About half of the test minerals may be used to determine the P–T conditions of formation through measurements of internal pressures on inclusions in natural diamond. All minerals that are typically used to age-date diamond belong to the mixed group: high-temperature inclusions in diamond will tend to reset to the emplacement age. Diamond from Argyle, Australia, only fits this model if diamond forms and adjusts through prolonged secular cooling (500°C over 500 M.y.). Most inclusions in superdeep diamond should fracture the host diamond, with published examples indicating some resealing near the conditions of formation of cratonic diamond (? temporary storage). The model topology for the converse setting (diamond as the inclusion) is critically different. The converse setting is mostly hostile to survival of diamond during delivery to the Earth's surface. Only seven of the tested host minerals (including spinel) are predicted to protect included diamond against conversion to graphite, but most minerals actually reported to carry microcrystals of diamond are excluded. However, the model predicts that the copresence of supercritical fluids (H_2O–CO_2) in the inclusion chamber would protect diamond included in almost any host mineral (glass also protects, but at a critically lower level). Minerals in graphite-bearing and coesite-bearing eclogites should be examined as potential hosts for microcrystals of diamond protected by this mechanism.

Keywords: diamond, graphite, host-inclusion relation, volcanic pipe, obduction, supercritical fluid, glass, Argyle, Australia, superdeep, polymorph, pressure indicator, topology.

Sommaire

Un modèle linéaire de la pression interne pour un système impliquant un minéral-hôte et un minéral inclus a été développé pour le diamant et une sélection de trente minéraux (les sulfures sont exclus). C'est un point central dans ce modèle que pour chaque paire diamant–inclusion, le lieu géométrique isovolumique en termes des coordonnées P–T, le long duquel les volumes relatifs des deux phases changent de façon identique. Le rapport clé Θ, égal à la pente du locus isovolumique divisé par la pente de la transition graphite–diamant, permet une attribution immédiate d'un minéral à un de quatre groupes topologiques universels d'inclusions: 1) minéral conservant l'héritage thermique, 2) minéral conservant l'héritage barique, 3) un groupe de minéraux à réponse mixte (décompression complète à l'intérieur d'un diamant de haute température, et 4) un groupe sujet à une décompression complète. Environ la moitié des minéraux pris en considération pourrait être utilisés pour déterminer les conditions P–T de formation par mesures des pressions internes sur les inclusions dans le diamant naturel. Tous les minéraux qui sont utilisés typiquement pour déterminer l'âge du diamant font partie du groupe mixte; les inclusions de haute température dans le diamant auront tendance à se ré-équilibrer à l'âge de mise en place. Le diamant à Argyle, en Australie, ne concorde avec ce modèle que si le diamant se forme et se réajuste au cours d'un refroidissement séculaire prolongé (500°C sur 500 million d'années). La plupart des inclusions dans les cristaux de diamant venant de grandes profondeurs devraient causer des fractures dans le diamant hôte, les inclusions dans la littérature indiquant un certain degré de cicatrisation près des conditions de formation du diamant cratonique (? entreposage temporaire). La topologie prédite pour la situation réciproque (diamant comme minéral inclus) diffère de façon marquée. Cette situation s'avère hostile en général à la survie du diamant pendant son transfert à la surface. Seulement sept des minéraux considérés (y inclus le spinelle) seraient aptes à protéger le diamant inclus d'une conversion au graphite, mais la plupart des minéraux cités en exemple comme porteurs de microcristaux de diamant sont exclus. Toutefois, d'après le modèle, la coprésence d'une phase fluide supercritique à H_2O + CO_2 dans la chambre de l'inclusion protégerait le diamant dans presque

§ *E-mail address*: barronjandl@optusnet.com.au

tout minéral hôte (le verre pourrait aussi protéger, mais à un niveau beaucoup plus faible). Les minéraux des éclogites à graphite et à coesite devraient être étudiés comme porteurs potentiels de microcristaux de diamant par ce mécanisme.

<div align="right">(Traduit par la Rédaction)</div>

Mots-clés: diamant, graphite, relation hôte–inclusion, conduit volcanique, obduction, fluide supercritique, verre, Argyle, Australie, grande profondeur, polymorphe, indicateur de pression, topologie.

INTRODUCTION

The confining pressure on an inclusion within a mineral varies as the conditions change from those of formation. Smith (1953), Harris *et al.* (1970), Cohen & Rosenfeld (1979) and Graham & Cybriwsky (1981) did pioneering work and investigated particular aspects of this mineral host – inclusion system in detail. More recently, the formative work of Liu *et al.* (1990) and Izraeli *et al.* (1996) led Barron (2003) to investigate this relationship for a spectrum of included minerals in diamond using a simple linear model (the Pressure Preservation Index or PPI model). In the latter work, Barron (2003) unknowingly rediscovered a useful construct (the isovolume array) first developed by Cohen & Rosenfeld (1979). Barron (2003) developed a simple topological classification for inclusions, assigning each mineral to a heritage group, a mixed group, or a third group. This approach is based on critical aspects of remnant pressure (defined as the confining pressure on an inclusion when diamond is at the Earth's surface; see Table 1 for definitions). Although the PPI model is linear and approximate, Barron (2003) demonstrated that non-linear complexities have no influence on which mineral belongs to which group of inclusions, whereas the PPI model predictions compare well with published examples of remnant pressures and stability *versus* inversion of high-pressure polymorphs. The model, as developed, is quantitative for simple monomineralic inclusions, but is useful in a qualitative way in dealing with polymineralic inclusions.

Most of the thirty minerals in Barron (2003) were selected because they have been reported as inclusions in diamond, but some were added on a more speculative basis. For instance, lawsonite was considered because it is indicative of cold subduction that may reach the stability field of diamond. Usui *et al.* (2003) provided a discussion of lawsonite coesite eclogite xenoliths in diamondiferous diatremes of the Colorado Plateau.

The PPI model is further developed herein. For a particular included mineral at the temperature of diamond formation T_f, the action pressure (P_a) is defined as the difference between the pressure of formation and the isovolume locus. As will be shown below, P_a is the most tangible parameter determining the confining pressure on the inclusion (P_c) when the host diamond is at any P–T, and uniquely determines the remnant pressure (P_r) on the inclusion once the diamond is at the Earth's surface. The host – inclusion system is formulated algebraically as part of the PPI model. This approach leads to exact linear equations that replace the approximate geometrical constructions used by Barron (2003), and permits variation of critical parameters to be examined across the spectrum of 30 minerals and across the range of conditions for diamond formation and delivery to the Earth's surface. Simple topology permits a universal four-way classification of inclusion groups to be set up. The revised PPI model is tested using published examples of studies on natural occurrences of diamond.

BASIS FOR THE HOST–INCLUSION MODEL

The PPI model is developed generally, but examined first for the case where diamond is the host mineral, then for the converse setting where diamond is the inclusion in a host mineral. The model is based on the concept of the isovolume locus, a concept first derived by Smith (1953), and called the isomeke by Adams *et al.* (1975), the isovolume locus by Liu *et al.* (1990), and the zero-volume-difference curve by Izraeli *et al.* (1999). This is the P–T locus along which the relative volumes of host and included mineral change identically.

TABLE 1. DEFINITION OF SYMBOLS AND TERMS USED

P, T	pressure (bars), temperature (°C)
P_f, T_f	P and T of formation of diamond
P_s, T_s	P and T of resealing of a ruptured inclusion chamber
P_a	Action pressure, namely the difference in pressure between P_f and isovolume locus at T_f
P_c	Confining pressure on an inclusion when rock is at general P-T
P_r	P_c when rock is at the conditions of the Earth's surface (0 bars, 0°C).
PPF	Pressure preservation factor (P_r/P_f) for inclusion
A	Coefficient of isobaric thermal expansion
A_h, A_i, A_d	A for host mineral, inclusion mineral, diamond
B	Coefficient of isothermal compressibility
MN	Mineral identification number (1-30) based on order of slope values of isovolume locus; see Table 2
Θ_i	Ratio of (slope of isovolume locus)/(slope of graphite-diamond transition) for mineral "i"; see Table 3
OP	The overpressure in forming diamond above the graphite to diamond transition at T_f
Cratonic diamond	Diamond formed beneath Archean cratons, *e.g.*, in Africa, Russia and Canada. Conditions of formation are about 1000–1500°C and 40–55 kbar. Most of the diamond presently mined is cratonic
High-temperature diamond	Diamond formed above 950°C, typically cratonic diamond. Diamond formed below this temperature is called low-temperature diamond, typically formed during collisional tectonics
Converse setting	Diamond as an inclusion in another host mineral

In the simplest first-order approximation (Barron 2003), the relative volume of a mineral at a general P–T is given by $V_i/V_i^o = 1 + T*A_i - P*B_i$, where A_i is the isobaric coefficient of thermal expansion, and B_i is the isothermal coefficient of compressibility. The reference state for V_i^o is chosen as the origin of the P–T graph (0°C, 0 bars), which for the sake of simplicity is taken as the condition of the Earth's surface. The constraint for the isovolume locus leads directly to the linear equation

$$P/T = (A_d - A_i)/(B_d - B_i) = (A_h - A_i)/(B_h - B_i) \quad [1].$$

For the thirty test minerals, equation [1] defines an array of lines radiating from the origin (0 bar, 0°C) of the P–T graph (Barron 2003). Anchoring the array of lines at the origin of the P–T graph enabled the PPI model to develop in a simple heuristic manner for the following reasons:

1) the isovolume array has a topological sense to it; the array has only positive slopes ($A_d < A_i$, $B_d < B_i$), whereas the relative volume of diamond changes more rapidly than the mineral at pressures above the relevant isovolume locus;

2) the measurements are based at the fixed conditions of the graph origin (0 bar, 0°C) rather than at some unknown point within the range of conditions of diamond formation;

3) the number of minerals in the array is large, so the minerals are sorted in order of the isovolume slope value (the MN order) to facilitate plotting and line identification. This immediately results in smoother, more coherent plots;

4) each measurement reflects some sort of difference (action pressure) between the conditions of diamond formation and the isovolume locus (the only absolute reference line for a mineral that needs no second- or third-order corrections);

5) this difference, when placed in the MN order, changes in a simple fashion relative to the isovolume locus, indicating a topological control;

6) this topological control points to the classification scheme for inclusions, and

7) these aspects mean that all crystals of diamond with simple inclusions can be considered on the one diagram.

Table 2 shows the published data used to calibrate the PPI model for 30 minerals (after Barron 2003), with the slopes values portrayed in Figure 1.

Note that Cohen & Rosenfeld developed a preliminary but analogous array of radiating lines, but their approach required this array to be anchored at the P–T conditions of capture of the inclusions within the host mineral.

The host – inclusion relation is based on the principle that the host mineral controls the volume available for the inclusion, hence it also controls *changes* in volume due to changes in P–T from the conditions of

formation. This latter control translates into the equation $(T - T_f)*A_h - (P - P_f)*B_h = (T - T_f)*A_i - (P_c - P_f)*B_i$; here P_c is the confining pressure forced on the inclusion by the host mineral at a general P–T. This expression can be rearranged to the general host – inclusion relation

TABLE 2. TEST MINERALS, CALIBRATION DATA AND SOME CALCULATED VALUES FOR THE PPI MODEL ACCORDING TO INCLUSION GROUP

Mineral (symbol)	MN	A_i /°C × 10^6	B_i /bar × 10^6	Source number A_i, B_i	Isovolume at 1000°C P kbar	$-\Delta P$ /P_f for $P_c = 0$	Super-deep P_c/P_f
Diamond		0.708	0.238	3, 3		[16]¶	[4]§
Heritage-T							
CO₂	1	520	120	25, 25	4.34	0.00	0.97
H₂O	2	860	188	25, 25	4.58	0.00	0.96
Sanidine (Sa)	3	19	1.75	14, 4	12.1	0.14	0.79
Coesite (Coe)	4	11.8	1.002	24, 17	14.5	0.24	0.68
SiC	5	4	0.4425	1, 2	16.1	0.54	0.41
Phlogopite (Phl)	6	32	1.7	23, 10	21.4	0.14	0.72
Heritage-P							
Quartz (Qtz)	7	59	2.2	12, 12	29.7	0.11	0.69
Glaucophane (Glt)	8	27	1.1	13, 13	30.5	0.22	0.60
Tremolite (Tr)	9	31.3	1.176	26, 6	32.6	0.20	0.60
Mixed							
Dolomite (Dol)	10	37.4	1.22	22, 19	37.4	0.20	0.58
Sillimanite (Sil)	11	14.4	0.585	29, 30	39.7	0.41	0.42
Enstatite (En)	12	32.2	0.9615	15, 9	43.5	0.25	0.51
Lawsonite (Lws)	13	34.7	0.98	14, 14	45.8	0.24	0.50
Titanite (Ttn)	14	25	0.76	14, 14	46.5	0.31	0.45
Jadeite (Jd)	15	24.7	0.75	5, 4	46.9	0.32	0.44
Clinozoisite (Czo)	16	27.8	0.78	14, 14	50.0	0.31	0.43
Grossular (Grs)	17	25	0.72	24, 10	50.4	0.33	0.42
Diopside (Di)	18	33.4	0.886	28, 28	50.5	0.27	0.46
Forsterite (Fo)	19	26.4	0.73	8, 21	52.2	0.33	0.41
Zircon (Zrn)	20	12.3	0.447	20, 11	55.5	0.53	0.27
Completely decompressed							
Periclase (Per)	21	31.6	0.6238	8, 8	80.1	0.38	0.25
Ferroan periclase (Fe-Per)	22	33.2	0.641	31, 16	80.6	0.37	0.25
Ilmenite (Ilm)	23	30.2	0.59	28, 28	83.8	0.40	0.22
Kyanite (Ky)	24	30	0.58	7, 7	85.6	0.41	0.21
Rutile (Rt)	25	26.5	0.47	24, 4	111	0.51	0.08
Spinel (Spl)	26	25.2	0.41	24, 24	142	0.58	-0.03
Corundum (Crn)	27	23	0.38	8, 4	157	0.63	-0.07
MgSiO₃ (perovskite Prv)	28	27.1	0.3831	8, 8	182	0.62	-0.14
Stishovite (Sti)	29	16.4	0.3185	8, 18	195	0.75	-0.12
Fe₃C	30	43.4	0.3158	27, 27	549	0.75	-0.76

Data-source numbers: 1 Accuratus Web Site (2002), 2 Ames Laboratory web site (2002), 3 Berman (1994), 4 Birch (1966), 5 Cameron et al. (1973), 6 Comodi et al. (1991), 7 Comodi et al. (1997), 8 Fei (1995), 9 Flesch et al. (1998), 10 Hazen & Finger (1976a, b), 11 calculated from data in Hazen & Finger (1979), 12 Helgeson et al. (1978), 13 Holland (1988), 14 Holland & Powell (1985), 15 Hugh-Jones (1997), 16 Jacobsen et al. (1999), 17 Levien & Prewitt (1981), 18 Luo et al. (2002), 19 Martens et al. (1982), 20 Wang (2002), 21 Olinger (1977), 22 Reeder & Markgraf (1986), 23 Robie et al. (1979), 24 Skinner (1966), 25 Smith (1963), 26 Sueno et al. (1973), 27 Vovadlo et al. (2002), 28 Wechsler & Prewitt (1984), 29 Winter & Ghose (1979), 30 Yang et al. (1997), 31 Zhang & Kostak (2002).
* Superdeep diamond presumed to form at 1660°C and 230 kbar.
Note that the inclusion-group assignment is for diamond as the host mineral. Symbols of minerals are after Kretz (1983) and Spear (1993).
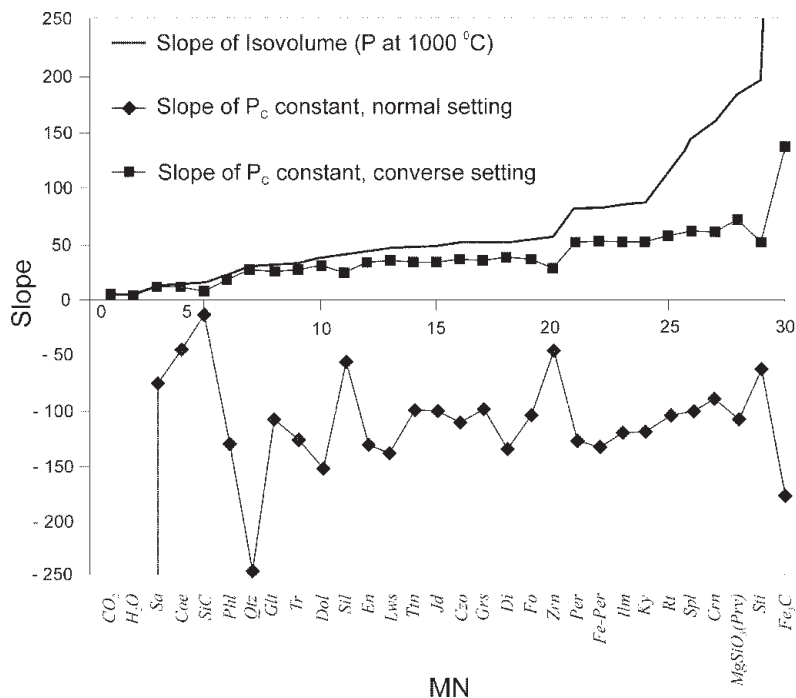¶ Converse setting, § normal setting.

FIG. 1.   Values of the slope (bar/°C), for different minerals, of isovolume loci and loci of constant confining pressure (P_c) on an inclusion in diamond. The minerals have been sorted and numbered (mineral number: MN) in order of increasing slope of the isovolume (Table 2). In the normal setting, the diamond is the host mineral, whereas in the converse setting, diamond is included in another host mineral.

$$(T - T_f)*(A_h - A_i) - P*B_h + P_c*B_i$$
$$+ P_f*(B_h - B_i) = 0 \qquad\qquad [2].$$

Remnant pressure (P_r) is the value of confining pressure P_c at (P, T) = (0 bar, 0°C); at these conditions, equation [2] reduces to

$$P_r = [T_f*(A_h - A_i) - P_f*(B_h - B_i)]/B_i$$
$$= -P_a*(B_h - B_i)/B_i \qquad\qquad [3].$$

Back-substituting equation [1] and the action pressure (P_a) into equation [3] simplifies the form of this expression and demonstrates the simple relation of P_r to the working difference (P_a) between the conditions of diamond formation and the isovolume locus. Note that the isovolume locus for a particular mineral (and lines parallel to it) represent loci of constant remnant pressure on that mineral as an inclusion in diamond. When diamond is the host mineral, P_r must have the same sign as P_a since typically $B_d \ll B_i$, hence also $P_r \approx P_a$ (representing the approximate geometrical construction used in Barron 2003). A useful measure based on P_r is the pressure preservation factor (PPF) relative to the pressure of formation and calculated as

$$PPF = P_r/P_f \qquad\qquad [4].$$

Values of this model factor can be used to convert experimentally measured values of P_r to P_f. This factor also identifies to which inclusion group the mineral belongs. Factors greater than 0.5 indicate that the mineral belongs to the heritage group (the temperature of formation can be estimated), factors significantly less than zero mean that the mineral belongs to the group of inclusions that completely decompress. Low negative and positive factors reflect minerals that belong to the mixed group; these inclusions will completely decompress under some conditions of formation, and not under others.

The slope of lines in P–T space of constant internal confining pressure P_c on an inclusion can be determined by taking the differential of equation [2] with P_c held constant, resulting in $(A_h - A_i) - B_h*dP/dT_{Pc} = 0$, or

$$dP/dT_{Pc} = (A_h - A_i)/B_h \qquad\qquad [5].$$

For a particular host – inclusion pair, equation [5] means that all lines at constant P_c have the same slope across P–T space. If diamond is the host mineral, there is an additional topological control, namely that this slope be

negative since typically $A_d < A_i$. Figure 1 shows the slope values of lines of constant P_c. Despite being placed in the MN order (monotonic in isovolume slope), the slope values for lines of constant P_c are not monotonic. However, twenty of the minerals have slopes at constant P_c of about -120 bars per°C. The intercept on the pressure axis of such a line of constant P_c (say $P_c = 0$), is found by substituting $T = 0$ into equation [2], returning

$$P (T = 0, P_c = 0) = P_a*(B_h - B_i)/B_h \qquad [6].$$

Equation [6] dictates that this intercept has the opposite sign to the action pressure P_a ($B_d < B_i$). Barron (2003) showed that some included minerals completely decompress when the diamond is inside a triangular P–T region called a "cavity triangle". The hypotenuse of this can be constructed from the above intercept [6] and slope [5], with the P–T axes completing the two sides of the right-angle portion. Any locus of constant P_c is determined by rearranging [2] for the intercept on the pressure axis, namely
$$P*B_h = P_c*B_i + P_f*(B_h - B_i) - T_f*(A_h - A_i)$$ resulting in

$$\begin{aligned} &P \text{ (intercept at } T = 0 \text{ for } P_c) \\ &= (P_c*B_i + P_f*(B_h - B_i) - T_f*(A_h - A_i) /B_h \qquad [7]. \end{aligned}$$

The decompression history of an inclusion during delivery of the host mineral to the Earth's surface is given by P_c values resulting from substituting P–T points on the delivery path into equation [2]. For example, the first stage of a delivery-path by volcanism brings the host diamond to the Earth's surface approximately at the temperature of formation T_f, so the confining pressure on the inclusion is given by

$$P_c (0 \text{ kbar}, T_f) = P_f*(B_i - B_h)/B_i \qquad [8].$$

Since compressibility of diamond is less than all other minerals ($B_d < B_i$), there is a topological constraint that no mineral can completely decompress inside host diamond during the first stage of delivery by volcanism. However, some minerals have P_a and remnant pressure P_r less than zero, so their subsequent complete decompression must take place after volcanism, during cooling at the Earth's surface.

The linear equation

$$P_f = 13301 + 29.6*T_f \qquad [9]$$

(P_f bars, T_f°C), has been calibrated for the graphite-to-diamond transition from formation values tabulated in Berman (1994). Assuming that diamond forms at the graphite–diamond transition, the influence of temperature of formation T_f on the value of remnant pressure P_r can be determined by substituting [9] into the general equation [2] and differentiating it with respect to T_f at ($P = 0$, $T = 0$), resulting in

$$dP_r/dT_f = [(A_h - A_i) - 29.6*(B_h - B_i)]/B_i \qquad [10].$$

Values of equation [10] are plotted in Figure 2. For most minerals, remnant pressure P_r reduces at 10–20 times the increase in the temperature of formation T_f. Only for minerals 1–6 (the heritage group, CO_2, H_2O, Sa, Coe, SiC, Phl) does P_r increase with T_f.

In some cases, diamond may form at pressures in excess of the graphite–diamond transition, and if this excess pressure is called OP for overpressure, the slope of remnant pressure P_r relative to OP can be determined by differentiation of [2], leading to the function

$$(dP_r/dOP)_{Tf} = (B_i - B_h)/B_i \qquad [11].$$

Values of this slope are plotted on Figure 3; P_r *increases* with OP, at the modest rate of about 0.5–0.8 times overpressure. Values of model remnant pressure P_r calculated from the host–inclusion equation [2] are presented on Figure 4a. The loci on Figure 4b are calculated for a known value of OP by re-arrangement of the combination of equations [2] and [9], namely

$$\begin{aligned} T_f = &[B_i * P_r + (OP + 13301) \\ &*(B_h - B_i)]/[(A_d - A_i) - 29.6*(B_d - B_i)] \qquad [12]. \end{aligned}$$

Influence of polymorphic transformation in an inclusion

Some inclusions may be in a high-pressure form when captured by diamond growth, then invert to a low-pressure form during delivery. How does this inversion influence P_r? This situation can be modeled for synthetic titanite, because Kunz *et al.* (2000) have determined the relevant data in experiments. The volumes and expansion coefficients for both high and low forms of synthetic titanite are as follows: with 1 representing the low form, and 2, the high form, ($V_{o1} = 369.04$, $A_1 = 20.7$, $B_1 = 0.88$), ($V_{o2} = 367.1$, $A_2 = 28$, $B_2 = 0.74$) in units of ($Å^3$, $/10^6$°C, $/10^6$ bar). Data in Kunz *et al.* (2000) indicate that high titanite would have to be under a confining pressure greater than 35 kbar at room temperature to remain stable. Since titanite is one of the mixed group (generating only low positive and negative values of P_r), an inclusion of high titanite$_2$ in diamond must invert to low titanite$_1$ by the time the diamond has reached conditions at the Earth's surface. The constraint that the host diamond determines the volume available for the inclusion results in $V_1 = V_2$, so that $V_{o1}*(1 - P_{r1}*B_1) = V_{o2}*(1 - P_{r2}*B_2)$, where P_{r2} is the remnant pressure calculated from equation [3]. Rearranging the constraint equation yields

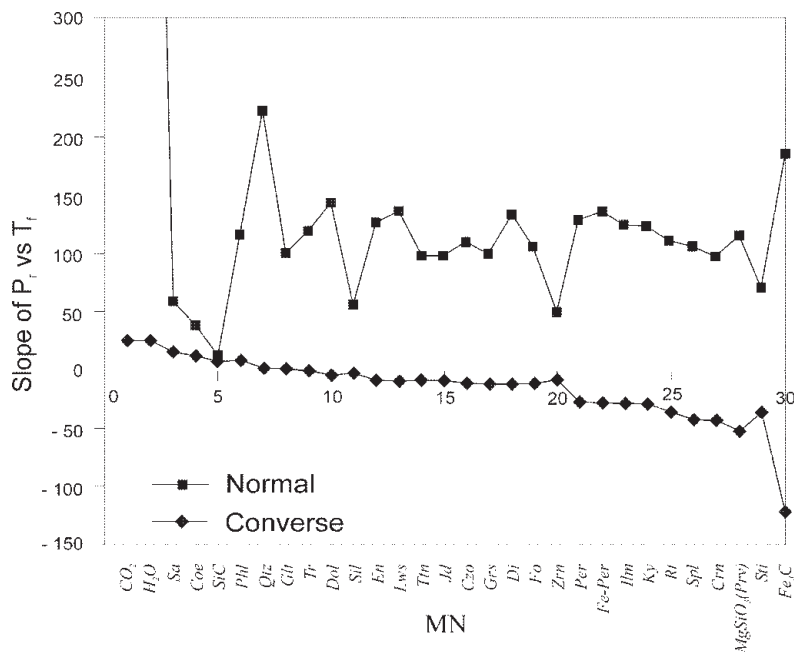$$P_{r1} = (V_{o1} - V_{o2})/V_{o1}/B_1 + V_{o2}*P_{r2}*B_2 /V_{o1}/B_1 \qquad [13].$$

FIG. 2. Values of the slope (bar/°C), for different minerals, of remnant pressure as a function of the temperature of diamond formation T_f, for diamond as the host, and for the converse setting, where diamond is the included mineral.
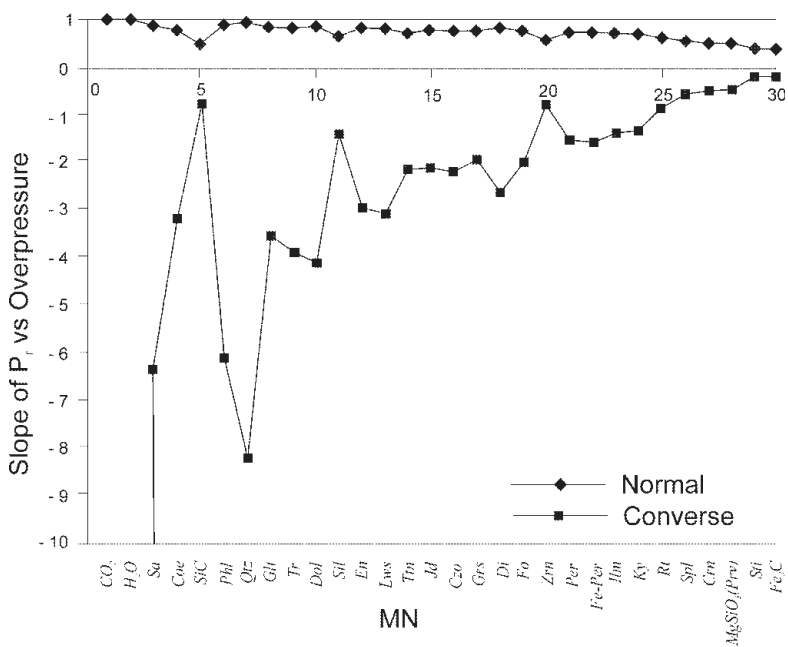

FIG. 3. Values of the slope (bar/°C), for different minerals, of remnant pressure as a function of overpressure, for diamond as the host, and for the converse setting, where diamond is the included mineral.
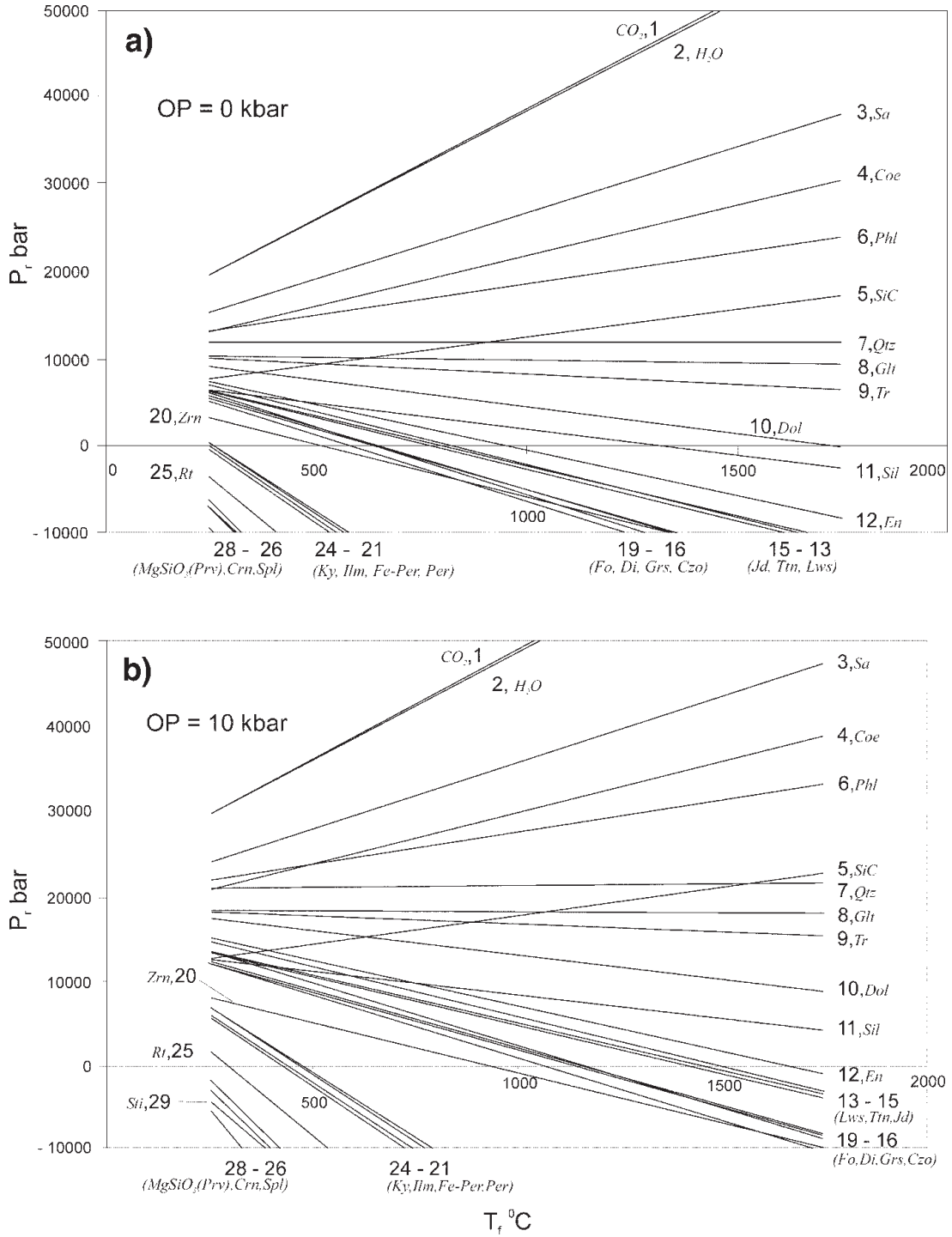
FIG. 4. Value of remnant pressure as a function of temperature of formation of host diamond. Lines are labeled with mineral sequence numbers (MN). a) T_f at the diamond–graphite transition. b) T_f at an overpressure (OP) of 10 kbar above the diamond–graphite transition.

Differentiation of [13] with regard to temperature of formation results in

$$dP_{r1}/dT_f = V_{o2}*B_2/(V_{o1}*B_1)*dP_{r2}/dT_f \qquad [14].$$

High titanite has a crossover temperature near 800°C on Figure 4a, where P_r changes from negative at low T_f to positive at high T_f. Calculations with the above data show that the sequence high titanite → inverted titanite in the inclusion chamber causes: 1) a decrease in crossover temperature of 5°C using equation [13], and 2) a reduction in the slope on Figure 4 by a factor of 0.84 using equation [14], representing a small rotation of 10° counterclockwise (Fig. 4).

The decrease in crossover temperature is small because it is roughly proportional to the percentage change in the reference volumes between the two polymorphs. The large (15%) contrast in compressibility causes most of the small rotation of the slope. A topological control exists because the **sign** of the slope (equation [14]) for the inverted mineral must remain the same as that for the original high-pressure polymorph (V_o and B are all positive). As the assignment of a mineral to a particular group of inclusions effectively is based on the topology of the slope characteristics on Figure 4, a polymorphic change during delivery to the Earth's surface will not change the membership of that mineral group in a specific group of inclusions. Preliminary calculations indicate that variations in mineral chemistry also do not change the membership.

DELIVERY PATHS: OBDUCTION *VERSUS* VOLCANISM

Delivery paths by obduction are different in time frame from delivery *via* volcanism, as the former involve a comparatively slow (but tectonically rapid) upward movement at a fairly constant temperature to some intermediate depth, followed by an even slower tectonic movement with jointly decreasing temperature and pressure. However, a topological control exists where diamond is the host mineral, because lines of constant confining pressure P_c on all included minerals have a negative slope (see [5] and Fig. 1). Thus all delivery paths steadily reduce P_c and so would appear similar in P_c–T space. Of course, the difference in time scale is critical in another way, because macrocrystals of diamond are typically converted to graphite in obducted terranes, whereas most mined diamond comes from volcanic pipes.

DISCRIMINATING CONDITIONS OF DIAMOND FORMATION, AND THE UNIVERSAL SCHEME OF CLASSIFICATION OF INCLUSIONS

Cohen & Rosenfeld (1979) presented the case for interpreting conditions of diamond formation by experimental measurement of remnant pressure on minerals included in diamond. More recently, Izraeli *et al*. (1999)

and Sobolev *et al.* (2000) have determined the remnant pressure on minerals included in diamond: olivine (1–5 kbar) for the former and coesite (36.2 kbar) in a Venezuelan diamond for the latter. Such high values of remnant pressure P_r on coesite are representative for cratonic diamond since P_r = 37 kbar was also determined on a coesite inclusion in a diamond of probable African origin (Milledge & Mendelssohn 1988, quoted in Meyer *et al.* 1997). The inclusion chamber thus sealed at conditions of formation in both cases, and remained sealed. Barron (2003) concluded that where diamond is the host mineral, the top six heritage minerals (CO_2, H_2O, Sa, Coe, SiC, Phl) in Table 2 are best for estimating the conditions of diamond formation from measurements of P_r in natural crystals of diamond, especially fluid inclusions.

Three minerals (7–9: Qtz, Glt, Tr) have the unusual aspect on Figure 4a that their slope is nearly zero. Basically they return a value of P_r that is independent of the temperature of formation of diamond. However, a comparison of Figure 4a with Figure 4b shows that P_r is sensitive to the overpressure of formation of diamond. The reason for the zero slope geometry is that these particular minerals have isovolume slopes that are nearly the same as the slope of the graphite-to-diamond transition. The value of the overpressure in forming the diamond can be determined uniquely from equation [2] by combination with equation [9] and the constraint that the value of [1] is 29.6 bar/°C. Rearrangement leads to

$$OP = B_i*P_r/(B_i - B_h) - 13301 \qquad [15].$$

Correspondingly, the predicted value of P_r for the formation of diamond on the graphite–diamond transition is P_r = 13301*$(B_i - B_h)/B_i$.

This geometrical parallelism (for minerals 7–9: Qtz, Glt, Tr) leads directly to a universal topological classification for any mineral included in diamond. This classification is based on the value of Θ defined as the following ratio

$$\Theta = \text{(slope of the isovolume locus) /}$$
$$\text{(slope of the graphite–diamond transition)} \qquad [16].$$

There are four categories in this topological classification; see Table 4 for the details and implications. Preliminary testing shows that the assignment of a particular mineral to one of these universal classes is insensitive to changes in chemical composition, as has been confirmed for several compositions of carbonate, pyroxene, olivine, and garnet. Furthermore, it is also relatively insensitive to polymorphic changes during delivery to the Earth's surface (see above). Therefore, the universal scheme of classification for inclusions is uncompromised by natural variations in minerals, such that an assignment is likely to be unconditional.

This topological classification of inclusion groups suggests a minimum-error strategy to estimate the conditions of formation:

1) Determine P_r on an inclusion of a heritage-P group mineral, and estimate OP for this special class of inclusion according to equation [15],

2) Calculate T_f using equation [13] from a measurement of P_r on a heritage-T mineral.

Alternately, determinations of remnant pressure on two or more monomineralic inclusions in the same crystal of diamond would yield two equations of the form of [3], and these can be solved simultaneously to estimate the conditions of diamond formation. The PPI model indicates which mineral combinations are likely to work. For instance, mixed-group minerals would have to be avoided if they produce $P_r < 0$. Aside from that constraint, this "simultaneous" technique is reminiscent of the pioneering work of Rosenfeld & Chase (1971), who used pairs of minerals from the mixed group. The range of minerals suitable for discrimination could be extended quite simply if a heating stage were used to change negative remnant P_r values into positive confining P_c values, somewhat analogous to the technique developed by Rosenfeld & Chase (1971).

The common inclusions found in diamond do not belong to either of the heritage groups (note that sulfides are not investigated in this treatment), indicating that a shift in the focus to other inclusions would be required for this remnant pressure technique to become influential.

Suppose that a sealed-chamber condition for an inclusion in natural diamond can be established visually for one of the minerals within the mixed group. These minerals have the PPI property that there is a sign contrast between positive remnant pressure P_r for lower-temperature diamond, and negative P_r for higher-temperature diamond. Note that negative P_r on solid inclusions would be detected as $P_r = 0$ within error-detection limits. Inside a host crystal of lower-temperature diamond, only minerals 12–15 (En, Lws, Ttn, Jd) would have P_r high enough to be above the detection limit (1–5 kbar). If the diamond forms considerably deeper than the graphite–diamond transition, the model indicates that P_r values increase by about half of the overpressure, so that potentially all of the test minerals in the mixed group would fall in the resolvable range. Thus, potentially about half of the minerals studied could be used to estimate the conditions of diamond formation (excluding minerals generating negative P_r due to the conditions of diamond formation). Because values of remnant pressure P_r are small for minerals in the mixed group, the potential percentage errors will be large (larger than for the heritage-T group of minerals). However, there will be a positive side because as remnant pressures are low for these minerals, the risk of chamber rupture is reduced.

SEALED OR RUPTURED CHAMBER OF AN INCLUSION

The heritage-T minerals 1–6 (CO_2, H_2O, Sa, Coe, SiC, Phl) are the best inclusions with which to confirm the sealed nature of an inclusion chamber. If the inclusion chamber has ruptured or adjusted after crystallization of diamond, the measured value of remnant pressure should differ considerably from the model value. According to Figure 4, one predicts that if measured values of P_r on a *fluid* inclusion are less than 15 kbar,

TABLE 3. CRITICAL ASPECTS OF GROUPS OF HOST DIAMOND – INCLUSION MINERAL PAIRS, BASED ON THE VALUE OF THE RATIO Θ

Value of ratio Θ	Universal inclusion group	Behavior of P_r and P_a	Expected values of P_r (Fig. 4)	Implication or application	PPI Minerals
0–0.9	Heritage-T	Always positive, value increases with T_f	15–45 kbar	Estimate T_f from P_r (needs correction for overpressure OP)	1–6 CO_2, H_2O, Sa, Coe, SiC, Phl
0.9–1.1	Heritage-P	Always positive, independent of T_f	10–20 kbar	Calculate OP from P_r	7–9 Qtz, Glt, Tr
1.1–2	Mixed	Sign varies, value decreases with T_f	–10 to +10 kbar	$P_r > 0$ for low-T_f diamond, $P_r < 0$ for high-T_f diamond	10–20 Dol, Sil, En, Lws, Ttn, Jd, Czo, Grs, Di, Fo, Zrn
>2	Completely decompressed	Always negative, value decreases with T_f	–10 to –30 kbar	Use uncertain	21–30 Per, Fe-Per, Ilm, Ky, Rt, Spl, Crn, $MgSiO_3$ (Prv), Sti, Fe_3C

Θ = slope of isovolume locus / slope of graphite–diamond transition. Diamond is assumed to form within 20 kbar of the graphite–diamond transition (overpressure OP is up to 20 kbar).

rupture of the inclusion chamber must have occurred. Navon (1991) reported P_r values between 15.5 and 21 kbar on fluid inclusions in natural crystals of diamond, concluded that the inclusion chambers remained sealed since formation, and estimated pressures of formation of 40–70 kbar. Although the PPI model also predicts that these inclusions remained sealed, the actual measured P_r is about one-third of that predicted, so the PPI model is not very accurate in dealing quantitatively with fluid inclusions with a high P_r. However, Navon's (1991) work showed that supercritical fluids can retain high internal pressures in diamond (and also in other host minerals), a conclusion also reached with the PPI model. Intriguingly, Navon's (1991) measured values of P_r are much closer to the values predicted for heritage-P inclusion group of minerals, whereby the range in measured values of P_r indicates the range in overpressure in forming the diamond.

Chamber rupture can also be tested in the case of solid inclusions. For instance, in a Brazilian alluvial stone that Gillet et al. (2002) identified as being a superdeep diamond, an inclusion of garnet was reported to have P_r in the range 5–8 kbar. The conditions of formation at 600–650 km depth are likely to be about 1660°C and 230 kbar, representing more than 180 kbar of overpressure above the graphite–diamond transition, whereas model values of the pressure-preservation factor P_r/P_f are listed in Table 2. It is a major extrapolation to apply the PPI model to these extreme conditions, so the following development is probably indicative rather than accurate. Although superdeep garnet (typically with elevated proportion of the majorite component) is distinct chemically from eclogitic garnet, the reasoning within the above section on polymorphic transformation indicates this is not likely to change the critical aspects of inclusion behavior for "garnet". Therefore, according to equation [4] and the PPF value in Table 2, the superdeep garnet should retain about 0.42 of P_f, so remnant pressure should be about $P_r = 97$ kbar. The extreme difference between the modeled (97 kbar) and measured (5–8 kbar) value of P_r indicates that the inclusion chamber ruptured, and resealed at a lower pressure. Images presented by Gillet et al. (2002, Fig. 1) confirm this rupture. Similar disparate values of expected versus measured P_r were reported for a crystal of garnet in another Brazilian superdeep diamond by Kunz et al. (2002), who proposed that omphacite mantling the garnet absorbed the "lost" pressure. However, the PPI model shows that pyroxene and garnet behave in roughly the same way through delivery of superdeep diamond to the Earth's surface (on Table 2, PPF values for these two minerals differ by only 10%). For pyroxene to share an inclusion chamber with garnet should not significantly reduce P_r. The disparate values probably indicate another example of a superdeep diamond that ruptured and resealed.

An apparently different but possibly related example of this recognition of superdeep diamond concerns im-

ages in Sobolev (1977, photos 10b, 11, 12). These images demonstrated pronounced internal fractures in examples of Yakutian diamond (AV7, AV10 and AV93), curving away from inclusions of chromian diopside and chromian pyrope. The PPI model predicts that crystals of cratonic diamond would have only a low positive or negative value of P_r, certainly much less than that required to cause internal fractures in diamond. Perhaps these particular Yakutian stones consist of superdeep diamond, formed under such extreme overpressure that P_r is large enough to cause internal damage to the diamond. This suggestion is compatible with recent work by Sobolev et al. (2003), who demonstrated the presence of superdeep diamond in some Yakutian diatremes. The fact that both pyroxene and garnet show these adjacent fractures is indirect but independent confirmation that the two phases respond similarly to delivery of superdeep diamond to the Earth's surface, exactly as predicted by the PPI model.

The PPI model can be used to make a crude estimate of which minerals are likely to generate internal fractures inside superdeep diamond. Sobolev et al. (2000) showed that diamond can withstand more than 36 kbar internal pressure without internal fractures, whereas Gillet et al. (2002) showed that an internal pressure of more than 90 kbar would rupture a host diamond. If 50 kbar is taken as the boundary between these two patterns of behavior, the PPI model predicts that only minerals 25–30 (Rt, Spl, Crn, $MgSiO_3$ (perovskite), Sti, Fe_3C) would be unlikely to cause internal fractures in host superdeep diamond during delivery to the Earth's surface. This prediction may broaden the recognition of superdeep diamond and minerals. For instance, neither chromian diopside nor chromian pyrope have been previously suggested to be superdeep minerals. If they can be confirmed as such, it might imply that these crystasls of unexpected superdeep diamond formed by continuing the subduction of ultrahigh pressure (UHP 40–60 kbar) diamond down to the transition zone, where they adjusted mechanically, before much later delivery back to the Earth's surface.

INFLUENCE OF THE PPI MODEL ON INTERPRETATIONS OF RADIOMETRIC AGES

The PPI model was developed originally to assess the influence of different conditions of diamond formation on the interpretation of radiometric age dates. Of principal interest are the most commonly used silicate minerals for dating, namely titanite, zircon, garnet, and clinopyroxene. The critical issue is whether the daughter products of the radioactive decay are able to diffuse out of the crystal structure of the inclusion. If they can diffuse out, then the age date would represent the last time above the closure temperature, generating the age of emplacement at the Earth's surface. Consider the situation where the material dated is an inclusion of clinopyroxene in a host diamond, dated by argon de-

rived by radioactive decay of potassium. If the inclusion is completely decompressed during delivery to the Earth's surface, the inclusion would be sitting in a shell cavity, the equivalent of a high-vacuum chamber (since diamond, with such a high density, is essentially impermeable). Most likely all of the argon within the pyroxene crystal structure would be extracted until the temperature dropped below the closure temperature. Such diamond should consistently produce the age of emplacement. This appears to be the general case in dates of clinopyroxene inclusions in cratonic diamond (Burgess *et al.* 1992). Although the reasoning is somewhat circular, this common resetting to the age of emplacement provides independent evidence that clinopyroxene inclusions in most cratonic diamond completely decompress upon delivery to the Earth's surface by volcanism. However, what happens if the inclusion did not completely decompress inside the diamond, in fact if it remained under several kbar of confining pressure? There would be no high vacuum to extract the argon from the inclusion, and no cavity for the argon to diffuse into, so conceptually it should stay within the crystal structure of the inclusion. This type of diamond should yield the age of crystallization as the standard interpretation, even if the included crystal is removed to perform the age determination.

The PPI model predicts that all of the typically preferred silicate minerals for age dating diamond belong to the mixed group (11 < MN < 21: En, Lws, Ttn, Jd, Czo, Grs, Di, Fo, Zrn). These preferred minerals have negative slopes on Figure 4, meaning that an inclusion trapped during formation of a higher-temperature diamond will completely decompress and tend to generate an age of emplacement. The same mineral, trapped during formation of a lower-temperature diamond, will remain under a positive remnant pressure, and will tend to generate the age of crystallization. A comparison of Figure 4a and 4b indicates that 10 kbar of overpressure can cause a significant increase in the crossover temperature for a particular mineral, and this fact may explain why some high-temperature cratonic diamond records an age significantly greater than the age of emplacement.

Burgess *et al.* (1998) reported on some argon dates of clinopyroxene inclusions within diamond from Copeton, New South Wales, Australia, yielding a weighted mean age of 340 Å 28 Ma. They applied the standard interpretation, namely that this is an age of emplacement, and suggested the diamond crystals may have been transported from Antarctica by subsequent Permian glaciation. The Copeton region is within a Phanerozoic Terrane, more than 1500 km from the nearest craton (Broken Hill). Although about two million diamond crystals were mined across New South Wales from alluvial deposits capped by Tertiary basalts, over 98% of these came from within two areas 20 km in diameter near Copeton. If these crystals are unique examples of low-temperature diamond formed during

Phanerozoic subduction, as proposed by Barron *et al.* (1996), and with the subduction-induced growth "confirmed" by Davies *et al.* (2003), on the basis of a study of growth textures in diamond and trapped inclusions), then the PPI model shows that the standard interpretation of dating should be as an age of crystallization. The measured age dates actually match subduction events in this part of New South Wales, so that the geology, distribution, uniqueness and age of the Copeton diamond are compatible with a local hard-rock source.

THE PPI MODEL AND AGE DATES OF ARGYLE DIAMOND

The conditions of formation and age dates for Argyle diamond are well established (1100–1500°C: Jaques & Smith 2002; 1560 –1150 Ma: Burgess *et al.* 1992). These data can be examined using the PPI model. Burgess *et al.* (1992) showed that 1) Argyle diamond retains ages of crystallization in argon dating of clinopyroxene inclusions in diamond, and 2) the age of diamond formation varies according to the K/Ca value (0.06–0.141) in the clinopyroxene inclusion. The K content of clinopyroxene is a crude barometer (Harlow 1999), so this strong variation in K/Ca of the clinopyroxene inclusions is most likely related to the pressure of diamond formation. Independent support for this inference arises from the work of Jaques & Smith (2002), who reported on different crystals of diamond forming at quite different temperatures, with a range of more than 400°C. Apparently, new generations of crystals of diamond continued to form up to the time of the emplacement of the diatreme, but all diamond formed more than 345 My after the closing of the Halls Creek Mobile Zone (1805 Ma: Myers *et al.* 1996). Prolonged substantial cooling of a hot mass of graphite-bearing eclogite at depth could produce this linked three-way variation (age–P–T). New generations of diamond crystals would form at the graphite–diamond interface as it rose up through the cooling mass of eclogite. This time-dependent cooling model makes the deeper crystals of diamond older and hotter, and the shallower crystals younger and cooler, over a period of 400 My. Presumably, the eclogitic mass at depth was too hot originally to form diamond. The retention of ages of crystallization indicates that argon was retained within the structure of the included clinopyroxene crystal, requiring the inclusion to remain under significant confining and remnant pressure at all times to the present day, irrespective of the age and temperature of formation of the diamond.

The PPI model predicts that age dates on clinopyroxene included in high-temperature diamond should be reset to the age of emplacement (Fig. 4), so the Argyle age dates should be reset, but the work of Burgess *et al.* (1992) indicates that they have not. The unusual conditions of growth of Argyle diamond represent the most likely reason for this conflicting behavior. Suppose that the older generation of diamond relaxed

mechanically during the long post-formation cooling. In effect (in terms of remnant pressures), the older crystals of diamond would appear mechanically to form at a much lower temperature at the original pressure of formation. The inclusions (being isolated within diamond) could not be reset chemically, hence they would retain the original high-temperature compositions, which is analogous to the justification used by Nimis (2002). Figure 5 shows this proposed growth-model, with the older, deeper diamond forming first, then mechanically relaxing to a lower temperature at constant pressure so that it ends up above the isovolume locus of clinopyroxene. This cooling-relaxation hypothesis of growth explains the retention of ages of crystallization, the variation of pressure with age, and the large variation in temperature of formation for different generations of diamond. It also provides a mechanism for apparently forming diamond at overpressures consistently beyond the graphite–diamond transition. In terms of the PPI model, an effective overpressure of 10 kbar (for clinopyroxene 18 on Fig. 4b) increases the cross-over temperature on Figure 4 by about 500°C, allowing $P_r >$ 0 bar for T_f up to 1100°C. This 500°C change is about the same as the proposed cooling interval for the generations of growth of Argyle diamond, implying that some diamond–inclusion pairs should show a volume relationship equivalent to an overpressure of at least 10 kbar. This difference should be detectable. Furthermore, the proposed bulk secular cooling may be responsible for some of the unusual properties of Argyle diamond (brittleness, color).

Nimis (2002) has estimated temperatures of encapsulation of inclusions in diamond and of equilibration of xenoliths that have been recovered from various mined diamondiferous diatremes around the world. Most African pipes showed a temperature difference of about 200–300°C between the highest and the lowest temperature of encapsulation, whereas the selection of Siberian pipes showed a larger difference, 600°C. The temperature difference at Argyle is between that of the African pipes and that of the Siberian pipes, yet a special interpretation is required for age dates on Argyle diamond. Therefore, perhaps it is not that diamond is made over a large range of depths that is unusual about Argyle, but rather that at each depth, each diamond crystal must adjust to a large drop in temperature (up to 500°C) after formation. Presumably, the great stability of an Archean cratonic keel prevents this large and bulk secular change in temperature from happening in the African and Siberian settings. This is supported by Nimis's (2002) observation that secular cooling was a possible but insignificant source of scatter in his measurements on cratonic diamond.

Continental collision may be another scenario where mechanical adjustment can result in significant overpressure on inclusions in diamond. For instance, Chopin (2003) concluded that obduction has raised continental material from deep subduction (40–60 kbar and 900–

1000°C), representing potentially more than 20 kbar of overpressure.

DIAMOND IN THE CONVERSE SETTING

Diamond has been found as an inclusion in a variety of host minerals, and in order to emphasize this relationship as the converse of diamond-as-host, this is called the converse setting. In recent examples, microcrystals of diamond were reported in

1) host kyanite, garnet and zircon grains in an obducted gneiss in Erzgebirge, Germany (Massonne 1999, Stockhert *et al.* 2001, Dobrzhisetaskaya *et al.* 2001, 2003), 2) in host spinel in obducted peridotite in Fjortoft, Norway (van Roermund *et al.* 2002), 3) in host garnet and diopside porphyroblasts within obducted marbles from the Kokchetav Massif, in Kazakhstan (Sobolev & Shatsky 1990, Ogasawara *et al.* 2000, Ohta *et al.* 2003), 4) in host clinopyroxene and orthopyroxene crystals in a garnet pyroxenite xenolith from lava in Hawaii (Wirth & Rocholl 2002, Rocholl & Wirth 2003), and 5) Xu *et al.* (1992) reported more than twenty 150– 700 μm crystals of diamond recovered from coesite eclogite at Dabie Shan, in China. Although the actual host site for diamond has yet to be confirmed, Han *et al.* (1997) reported the presence of rare inclusions of melt plus supercritical fluid in minerals within such eclogites.

In the Norwegian example, interstitial diamond in the rock has inverted to graphite, so van Roermund *et al.* (2002) suggested that the properties of the host grain (spinel) prevented the diamond in the converse setting from inverting.

The model equations are general, so they automatically cover the converse setting, but the values derived
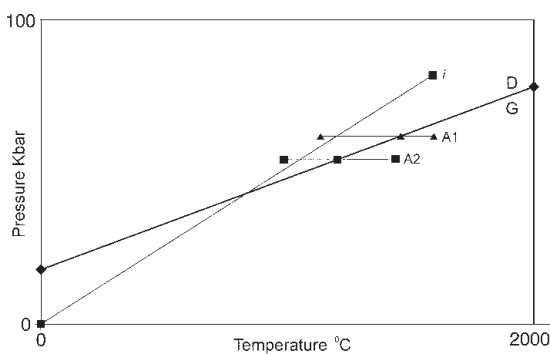

FIG. 5.   Model to form Argyle diamond able to retain the age of crystallization (argon retained within clinopyroxene inclusion). Diamond A1 forms first under deeper and hotter conditions, whereas diamond A2 forms later, under shallower and cooler conditions. Both crystals of diamond respond to the continued cooling at constant pressure by mechanical relaxation, moving above the isovolume locus for clinopyroxene.

from equations [3]–[11] change significantly in moving from the normal to the converse setting (Figs. 1–4, 6–7). Furthermore, the sign of the values may also change because A_d is less than A_i, and B_d is less than B_i. For instance, topology requires that all host minerals (diamond in the converse setting) have a positive slope value for remnant pressure P_r on Figure 2. In addition, P_r has changed sign in equation [3], so that those minerals generating a negative P_r in the normal setting generate a positive P_r in the converse setting (Fig. 6). Also, in the converse setting, note that P_r increases by typically more than 100 times the increase in temperature of formation T_f (compared with less than ±50 times, Fig. 2). Figure 3 shows the influence of overpressure on P_r, with P_r decreasing by 2–8 times the overpressure at constant T_f (compared with a 0.5–0.8 times increase for the normal setting, Fig. 3).

Surprisingly, for the converse setting, the equations show that many minerals are capable of producing remnant pressures greater than the pressure of formation ($P_r > P_f$, Fig. 6), represented by portions of the P_r lines at pressures higher than the graphite–diamond transition. However, the actual distribution of the mineral lines on Figure 6 mean that $P_r > P_f$ is most likely to occur in lower-temperature diamond (typically formed by collisional tectonics) and most likely to be found for host minerals 23–27 (Ilm, Ky, Rt, Spl, Crn).

Figure 6a shows that for diamond in the converse setting, minerals 22–30 (Fe–Per, Ilm, Ky, Rt, Spl, Crn, MgSi-perovskite, Sti, Fe$_3$C) have $P_r > 0$, virtually regardless of the temperature of formation T_f. If $T_f < 950°C$ for host minerals 1–12 (CO$_2$, H$_2$O, Sa, Coe, SiC, Phl, Qtz, Glt, Tr, Dol, Sil, En), diamond in the converse setting would have P_r less than 0. Figure 6b has been calculated by forming diamond at an overpressure of 10 kbar above the graphite–diamond transition. It shows the same pattern as Figure 6a, but the temperature patterns are raised by about 250–300°C owing to this overpressure. Because of the inherent link between remnant pressure and confining pressure P_c, overpressure also exerts a strong influence on internal pressure P_c in response to delivery to the Earth's surface if diamond is in the converse setting.

Despite the switch in sign for the above variables caused by the topology of the converse setting, neither the sign nor the value of the isovolume slope (equation [1]) changes if the host and inclusion roles are reversed and diamond is involved. This unvarying topology is lost if diamond is not involved, because the sign of [1] could change.

DISCRIMINATING THE CONDITIONS OF DIAMOND FORMATION

Measurement of P_r in natural samples will provide information about conditions of formation for diamond in the converse setting. For instance, with regard to minerals 12–30 (En, Lws, Ttn, Jd, Czo, Grs, Di, Fo, Zrn,

Per, Fe–Per, Ilm, Ky, Rt, Spl, Crn, MgSi-perovskite, Sti, Fe$_3$C), there is reasonable separation in the model values of remnant pressure (Fig. 6), potentially permitting discrimination of high-temperature from low-temperature formation of diamond. For this discrimination, overall the converse setting appears considerably more broadly reliable mathematically than the normal setting (larger values of P_r). However, some of the occurrences of $P_r > P_f$ may be so extreme that the host mineral ruptures. Furthermore, if the diamond in the converse setting has formed above the graphite–diamond transition, the overpressure drops the values of remnant pressure P_r so rapidly that it may be difficult to separate overpressure aspects from temperature of formation aspects.

As another distinct aspect of the converse setting, none of the tested minerals has a zero slope value on Figure 2 or Figure 6. It is improbable that there could be an analogous universal topological classification of host minerals for included diamonds. However, the calibration values of the volume coefficients tend to separate the array of lines on Figure 6 into three groups, corresponding to: 1) minerals 1–10 (CO$_2$, H$_2$O, Sa, Coe, SiC, Phl, Qtz, Glt, Tr, Dol), which completely decompress, so are unable to plot within the range visible on Figure 6, 2) minerals 11–20 (Sil, En, Lws, Ttn, Jd, Czo, Grs, Di, Fo, Zrn) for higher-temperature diamond, and 3) minerals 21–30 (Per, Fe–Per, Ilm, Ky, Rt, Spl, Crn, MgSi-perovskite, Sti, Fe$_3$C) for lower-temperature diamond.

Both of the latter two groups have mixed behavior, with positive remnant pressures at the higher-temperature end of the lines, and negative remnant pressures at the lower-temperature end. As with the topological classification of inclusions where diamond is the host mineral, the converse classification follows the order of increasing slope of the isovolume locus. This control is the primary one, regardless of the setting.

Delivery via volcanism

Equation [8] predicts that all diamond in the converse setting must completely decompress during the first stage of delivery by volcanism. Since the remnant pressure (diamond at the Earth's surface) is greater than zero for many of these minerals, the second stage of cooling must re-compress the inclusion. During this second stage, minerals 21–30 (Per, Fe–Per, Ilm, Ky, Rt, Spl, Crn, MgSi-perovskite, Sti, Fe$_3$C) are capable of generating remnant pressures greater than the pressures of formation. Every aspect of this confining pressure P_c history is in complete contrast to that of the normal setting. Furthermore, since the confining pressure P_c on the diamond drops about twice as rapidly as the external pressure (see next section) during the first stage of delivery (period of highest temperatures), the PPI model implies that diamond in the converse setting is likely to convert to graphite, despite the many natural examples (above) to the contrary.
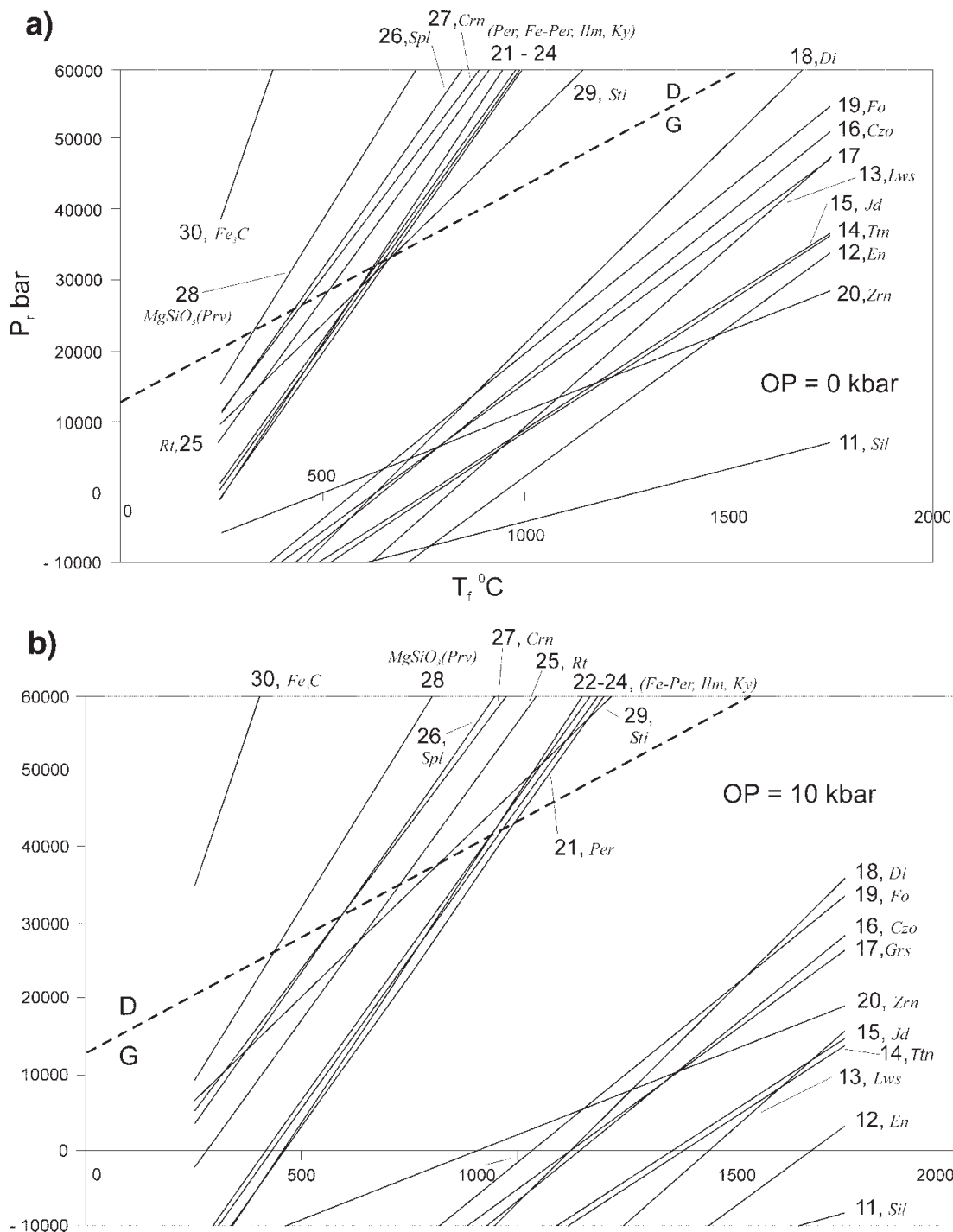
FIG. 6.   Value of remnant pressure as a function of temperature of formation of diamond, for the converse setting of microcrystals of diamond as the inclusion in the host mineral. Note that the entire P_r loci are for diamond forming at or above the graphite to diamond transition (shown as a dashed line for reference only). a) T_f at graphite–diamond transition. b) T_f for diamond forming at an overpressure (OP) of 10 kbar above the graphite–diamond transition.

Delivery via obduction

Consider the first stage of an obduction path, where the pressure is tectonically decreased, typically at a nearly constant temperature. The simplest stage-one path of obduction would be one that involved a large drop in the pressure on the host mineral at approximately the temperature of diamond formation. The impact of this situation can be modeled by determining the drop in external pressure that is required to make the confining pressure on the inclusion equal to zero ($P_c = 0$ at $T = T_f$), which can be calculated from equation [2] as

$$-\Delta P/P_f = B_i/B_h \qquad\qquad [17].$$

Values for [17] are presented in Table 2, where it can be seen that for most potential host minerals, a drop in the external pressure ($-\Delta P$) can be 30% or higher of the pressure of formation P_f before the confining pressure on the inclusion drops to zero. Thus P_c drops about twice as fast as the external pressure. However, such a large drop (>20 kbar) in external pressure is unlikely to occur during a stage-one path of obduction, so diamond in the converse setting should not completely decompress. Thus in all aspects for a diamond that has positive remnant pressure in the converse setting, topologically the

confining pressure history (at the end of stage-one delivery) is critically different for obduction (potentially no $P_c < 0$) *versus* volcanic (all $P_c < 0$) modes of delivery. This is in complete contrast to the qualitative similarity between obduction and volcanic processes for delivery of diamond where diamond is the host mineral (see text after equation [11]).

Figure 6 shows that minerals 21–30 (Per, Fe–Per, Ilm, Ky, Rt, Spl, Crn, MgSi-perovskite, Sti, Fe₃C) have rather high positive remnant pressures for conditions of formation of diamond in the converse setting. The second stage of the obduction path thus must cause the confining pressure P_c to increase for these particular minerals. Hence, a diamond in the converse setting inside these minerals can never completely decompress during obduction. For minerals 11–20 (Sil, En, Lws, Ttn, Jd, Czo, Grs, Di, Fo, Zrn), Figures 6a and 6b show that a high temperature of formation implies remnant pressures greater than zero, hence it also implies a positive confining pressure P_c. For the same minerals, diamond that formed at a lower T_f in a converse setting would completely decompress during the second stage of obduction.

According to Roselle & Engi (2002), an actual path of obduction most likely involves an initial drop in pressure of about 10 kbar, and then, during stage two, the
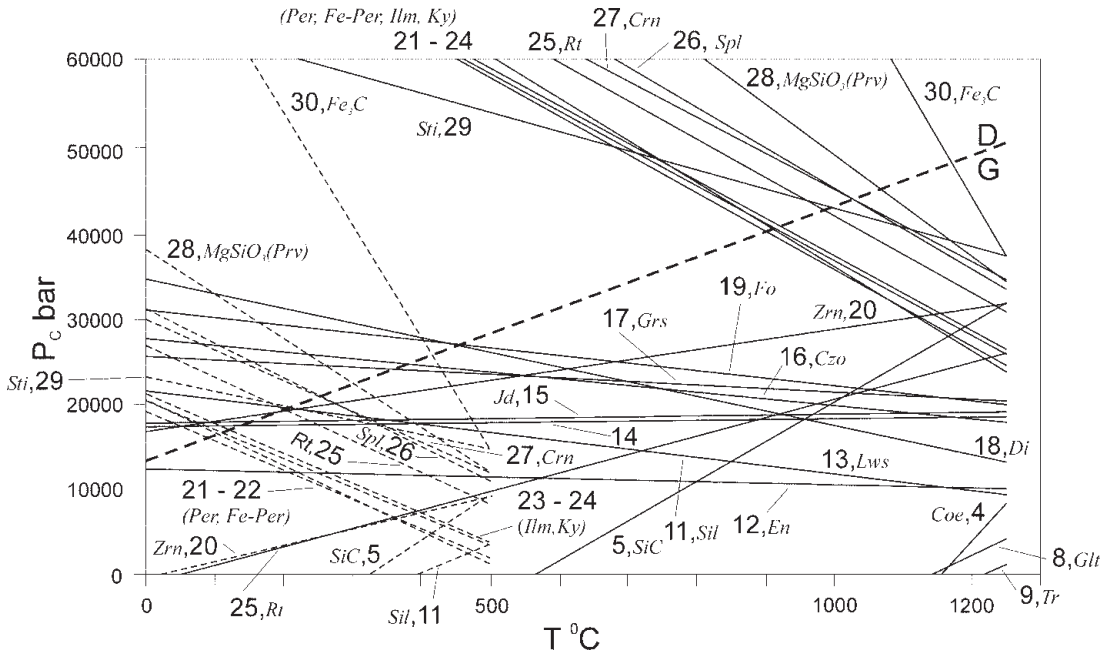

FIG. 7.   Calculated confining pressure on microcrystals of diamond inclusions (converse setting), during stage-two obduction from (T_f, P = P_f – 10 kbar) to (0°C, 0 bar). Note that the entire P_c loci are for diamond forming at the graphite-to-diamond transition (shown as a dashed line for reference only). The two arrays of lines correspond to formation of low-temperature diamond (dotted lines, 500°C) and high-temperature diamond (solid lines, 1250°C).

temperature and pressure jointly decrease more slowly and radially toward the origin (0°C, 0 bars). This stage-two part is modeled in Figure 7, with diamond forming in a converse setting at two different temperatures (500%, 1250°C). Note that the stage-two part of the obduction begins with all diamond well below the diamond–graphite inversion. Consider minerals 20 (Zrn) and 30 (Fe_3C) for high-temperature diamond in the converse setting (right-hand side of Fig. 7). The completed stage-two path of obduction for this diamond will involve a total cooling of 1250°C. However, host mineral 30 (Fe_3C) moves the inclusion into the stability field of diamond after the first 100°C of cooling (representing about 100/1250 = 8% of the duration of stage-two obduction). Contrast this with mineral 20 (Zrn), which moves the inclusion into the stability field of diamond after more than 1000°C of cooling (representing about 1000/1250 = 80% duration). These durations (8%, 80%) represent windows for potential conversion to graphite, while invariably they are at the higher-temperature end of slow obduction. For diamond formed at a low temperature T_f, this window is relatively small for minerals 26–30 (Spl, Crn, MgSi-perovskite, Sti, Fe_3C), relatively large for minerals 1–20 (CO_2, H_2O, Sa, Coe, SiC, Phl, Qtz, Glt, Tr, Dol, Sil, En, Lws, Ttn, Jd, Czo, Grs, Di, Fo, Zrn), and intermediate for minerals 21–25 (Per, Fe–Per, Ilm, Ky, Rt). For diamond formed at a high temperature T_f, the window is small for minerals 21–30 (Per, Fe–Per, Ilm, Ky, Rt, Spl, Crn, MgSi-perovskite, Sti, Fe_3C), but large for minerals 1–20 (CO_2, H_2O, Sa, Coe, SiC, Phl, Qtz, Glt, Tr, Dol, Sil, En, Lws, Ttn, Jd, Czo, Grs, Di, Fo, Zrn). Of the minerals reported to occur naturally as protective hosts of obducted low-temperature diamond in the converse setting (spinel, kyanite, garnet, zircon, clinopyroxene, orthopyroxene, see references above), only spinel is predicted to be favorable by the PPI model and it is the least protective of the model minerals 26–30 (Spl, Crn, MgSi-perovskite, Sti, Fe_3C).

The converse setting is predicted generally to be hostile to the survival of obducted diamond in the converse setting, despite many natural examples to the contrary. Either the paths of obduction are very different from those modeled herein, or some other feature has maintained an unexpected high confining pressure on the diamond inside the host mineral. Van Roermund *et al.* (2002) suggested that completely embedding the host crystal in a larger crystal might have stabilized the diamond. Certainly, embedding the host mineral in another may help it avoid rupture if actual values of remnant pressure P_r on diamond are high. However, the MN order has been assigned on the basis of values of relative slope for isovolume loci. Consequently, topology indicates that the mantling mineral has to have a considerably larger MN value than the host mineral to raise significantly the remnant pressure P_r on diamond in the converse setting. This is not the case for any of the reported examples. The same reasoning prevents most

chamber-sharing phases from contributing significantly to equilibrium stability of diamond in the converse setting.

Natural examples of diamond in converse setting: compound inclusions

Published examples of obducted terranes with host minerals carrying diamond in the converse setting do not involve simple inclusions. In most cases, the diamond shares the inclusion chamber either with other crystalline minerals plus a supercritical fluid, or with glass plus other crystalline minerals plus a supercritical fluid; see above examples. Barron (2003) suggested, on the basis of pressure-preservation factors (P_r / P_f), that sharing with a supercritical fluid would be a significant contributor to the stability of obducted diamond in the converse setting. The more exact modeling above indicates that such an additional protective mechanism is required. The presence of such a fluid is confirmed for the above natural examples of diamond in the converse setting.

Schiano (2003) has claimed that inclusions of glass in host phenocrysts of olivine remain under significant remnant pressure at the Earth's surface. For the conditions of sealing (P_s = 10 kbar, T_s = 1200°C), Schiano considered two stages, namely a first stage of volcanic delivery to (P = 0 bars, T = T_s), followed by a second stage (0 bars, cooling to 0°C). During the first stage, Schiano predicted an internal pressure P_c of 70–80% of sealing pressure, which reduced to P_r at 50–70% of sealing pressure after the second stage. If diamond shares an inclusion chamber with glass inside a host olivine crystal, Sciano's (2003) predictions imply that glass may be able to reduce the chances of diamond converting to graphite. However, although the PPI model data reproduces Schiano's predictions during the first stage, for the second stage (cooling), the PPI model predicts a completely different behavior. This difference must arise from the coefficient of thermal expansion used for the glass. Using equation [3] and olivine (mineral 19) as a host mineral (calibration data in Table 2), starting at Sciano's sealing conditions (P_s T_s) = (10 kbar, 1200°C), a value for A_{glass} can be no larger than 40 × 10^{-6}/°C before a glass inclusion would completely decompress at (0 bar, 0°C). Values for A_{glass} inherent in Fei (1995, Table 4) and Gottsmann & Dingwell (2002) are invariably greater at 50–130 × 10^{-6}/°C for a wide selection of basic and felsic glasses. Thus the PPI model predicts the complete decompression of glass inclusions in host olivine. Furthermore, these A_{glass} values result in the same behavior for potential host-minerals 12–20 (En, Lws, Ttn, Jd, Czo, Grs, Di, Fo, Zrn). Glass has a completely decompressed behavior for all host minerals reported to carry diamond + glass in the same inclusion chamber. Despite this, sharing the inclusion chamber with glass would preferentially slow the conversion of diamond (converse setting) to graphite with

respect to interstitial diamond, most specifically at the end of the first stage of volcanic delivery (high temperature but at the Earth's surface). Although many of the above examples have glass sharing the inclusion chamber, the occurrence described by van Roermund *et al.* (2002) does not, indicating that supercritical fluids are sufficient in providing this protection (Barron 2003). The PPI model indicates that glass ($P_r < 0$) would be much less effective in this protection than supercritical fluids ($P_r > 15$ kbar: Navon 1991, Barron 2003).

These preventive aids appear necessary for the reported examples of survival of diamond in the converse setting, regardless of the delivery mechanism, since the confining pressure on a diamond-only inclusion (converse setting) drops about twice as quickly as the external pressure (see above). In view of this, graphite-bearing eclogites should be examined for microcrystals of diamond in the converse setting. This is especially recommended if some aspects of mineral chemistry indicate attainment of the diamond-eclogite grade [high levels of K in clinopyroxene: Harlow (1999), high levels of Na in garnet: McCandless & Gurney (1989)]. The stability field of coesite is fairly close to that of diamond, such that the same recommendation applies to coesite-bearing rocks.

SUPERDEEP DIAMOND

Examples of superdeep diamond from the transition zone are being recorded at more places every year (Kaminsky *et al.* 2001). They have been found in diatremes with cratonic diamond (Davies *et al.* 1999, Sobolev *et al.* 2003), indicating that the last part of the delivery mechanism is a rapid rise from the depths of cratonic diamond formation within kimberlite. Periclase and ferroan periclase have pressure-preservation factors (PPF) of 0.25 (derived from [11], see last column in Table 2). This fact leads to a predicted remnant pressure of $P_r = 60$ kbar, which much less than the 200 kbar (Joswig *et al.* 1999) needed to keep such inclusions from inverting from the high-pressure form. Minerals 26–30 (Spl, Crn, MgSi-perovskite, Sti, Fe_3C) have isovolume lines that lie near or occur at higher pressures than the conditions of formation, leading tp PPF < 0 and $P_r < 0$. Hence, all of the reported superdeep minerals are predicted to completely decompress and invert inside diamond, in agreement with natural examples reported by Davies *et al.* (1999), Joswig *et al.* (1999), Kaminsky *et al.* 2001).

It is not known whether all superdeep diamond is delivered to the Earth's surface in a single stage (picking up cratonic diamond on the way) or is carried up to some intermediate depth and temporarily stored there. Calculations using equation [2] indicate that stishovite would be under a P_c of 90 kbar for an "intermediate storage at 50 kbar" scenario, and based on the stability field of stishovite shown in Zhang *et al.* (1996), this internal pressure would be sufficient to hold stishovite in the original high-pressure form. However, if the intermediate storage lasted very long, the superdeep diamond would slowly relax at the high temperature, and the stishovite inclusion would invert. This "stored" inversion should produce a different coarser texture than if the superdeep diamond is delivered from the transition zone rapidly in one stage to the Earth's surface. Thus it may be possible to evaluate texturally whether a crystal of superdeep diamond is stored at some intermediate depth. Joswig *et al.* (1999) reported a coarse equilibrium-induced inversion texture for Ca-silicate included in alluvial crystals of diamond from Guinea (identified as superdeep), suggestive of such an intermediate storage. This interpretation is not straightforward because the composition of the inclusion is different from the nearest test mineral used herein ($MgSiO_3$, perovskite structure). Furthermore, equation [2] indicates a P_c of 75 kbar for this sort of intermediate storage of $MgSiO_3$ (perovskite structure), much less than the 275 kbar required to keep the original high-pressure form, according to values quoted in Karki *et al.* (2000). Despite these differences, the extra internal pressure, and the extra time available would permit a coarser inversion-induced texture to form during an intermediate period of storage.

In the earlier section on rupture of inclusion chambers, the case was made that a superdeep crystal of diamond will generate positive P_r for most included minerals, despite the high temperature of formation. If the inclusion chamber does not rupture, relevant inclusions in superdeep diamond should yield the age of crystallization.

SEALING PRESSURE FROM THE MEASURED VALUE OF REMNANT PRESSURE

It has been shown above how a comparison of a measured remnant pressure P_r value and that predicted by the PPI model can identify an inclusion chamber that has ruptured. Where this has happened, the measured P_r actually represents the conditions of resealing. Equation [3] can be used to evaluate this situation if the resealing variables (T_s, P_s) are used in place of the formation variables (T_f, P_f). If an approximate temperature of sealing is assumed, equation [3] can be solved for the sealing pressure (P_s) as a function of the remnant pressure P_r. This is done at $T_s = 1250°C$ on Figure 8 for a range of P_r values, resulting in the traces shown. Consider the example above, of a superdeep Brazilian diamond with P_r in the range 5–8 kbar measured on a garnet inclusion (Gillet *et al.* 2002). These values of remnant pressure are high enough so that an elevated temperature of sealing T_s is appropriate; Figure 8 suggests the last rupture occurred at about 65–70 kbar, similar to the fully corrected sealing pressure of 70 kbar calculated by Gillet *et al.* (2002). Data in Kunz *et al.* (2002), if interpreted through the PPI model (see above under rupture), indicate similar values of resealing of another Brazilian

example of superdeep diamond. Resealing would thus seem to have occurred while the superdeep crystals of diamond were just below the base of the conditions of formation of cratonic diamond, possibly during some form of intermediate storage.

Graphite specks are common in diamonds. The sealing form of equation [3] can be used also to estimate the conditions under which these specks form. Values for graphite of $A_g = 8.4 \times 10^{-6}/°C$ (ESPI web site, 2004) and $B_g = 0.28 \times 10^{-6}/kbar$ (Tang *et al.* 2000) generate a slope for the isovolume locus of 3 kbar per 1000°C. This is the lowest value of the slope for all of the minerals considered herein. On the basis of this finding, graphite might behave like those minerals in the first group, as a heritage-T mineral. However, at this stage, it is not known when the specks of graphite formed, rendering the classification of graphite uncertain. These coefficients for graphite, when combined with the sealing form of [3], show that $P_s = P_r / 0.92$, relatively insensitive to temperature (a T_s of 1500°C causes P_s to be about 5 kbar higher than at $T_s = 0°C$). However, if the graphite is not well crystallized, the influence of temperature and pressure of sealing may be significantly different. Basically, as a first approximation, the remnant pressure on a graphite inclusion represents the pressure at which it formed. There do not appear to be any measurements of P_r reported for graphite specks in diamond. If the specks formed near the Earth's surface, the PPI model predicts that they will be under a P_r less than 5 kbar. However if the specks formed earlier, during growth of the diamond for example, values could be higher than 20 kbar. Gogotsi *et al.* (1999) reported graphite forming in response to deformation of diamond, so mechanical adjustment of diamond during storage at depth may cause the specks to appear after diamond formation but before delivery to the surface of the Earth.

CONCLUSIONS

A linear model of the host–inclusion mineral system is developed as a series of algebraic equations, and calibrated for thirty minerals plus diamond using published data on thermal expansion and compressibility. Every mineral can be unconditionally assigned to one of four universal groups of inclusions on the basis of a simple topological relationship. Supercritical fluid inclusions have unique properties that require further investigation. The model is topologically different if diamond is included in another host mineral, with regard to remnant
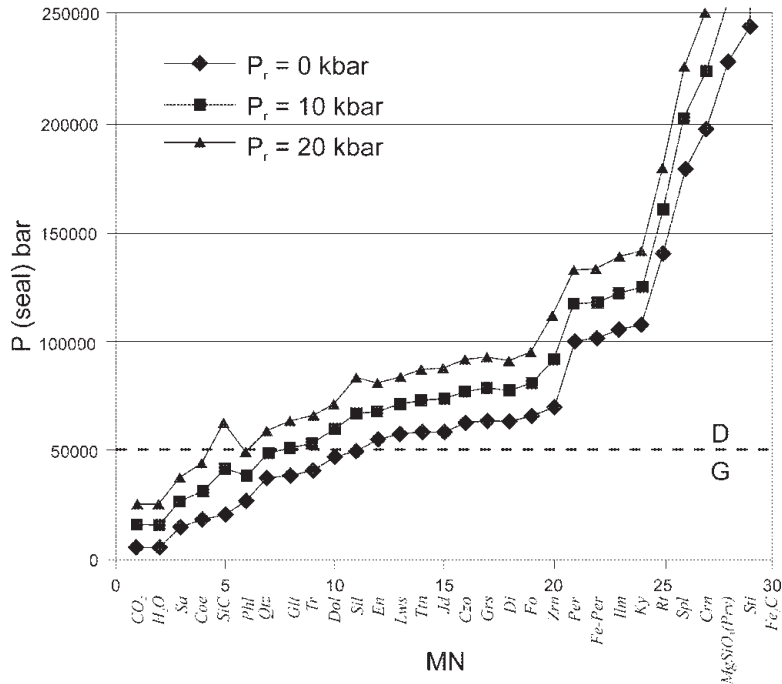

FIG. 8.   Graph for determining the chamber-sealing pressure (bars) for different minerals included in host diamond, based on measured values of remnant pressure (0, 10 , and 20 kbar). The temperature of sealing is assumed to be 1250°C.

pressure and decompression history during delivery to the Earth's surface. The model permits scientific interpretation of a wide range of textures and measurements on diamond and associated minerals.

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