APPENDIX

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REVIEW OF THERMODYNAMIC DATA FOR DIAMOND AND GRAPHITE

This appendix provides additional detail to support the choice of thermodynamic and thermophysical data summarized in Table 2. Several tables are included that illustrate the trail of citations leading to primary data. In a few cases, a cited reference could not be located despite the best efforts of professional reference librarians.

Entropy

Graphite. $S^o(298.15) = 5.74 \pm 0.21$ **J/mol•K.** DeSorbo and Tyler (1953) reported $S^o(298.16) = 5.74 \pm 0.02$ J/mol•K, based on heat capacities measured in the range 13-300 K. Modern compilations of the third law entropy of graphite depend heavily on these measurements, and report selected values that are indistinguishable from their value, within uncertainty (Table A1; Cox et al., 1971, 1989; Hultgren et al., 1973; Robie et al., 1978; Chase et al., 1982; Robie and Hemingway, 1995; Chase, 1998). Hultgren et al. (1973) selected a slightly lower value of 5.73 ± 0.04 J/mol•K based on their independent analysis of a larger body heat capacity determinations (Jacobs and Parks,1934; DeSorbo and Tyler,1953; Keesom and Pearlman,1955; DeSorbo and Nichols, 1958; van der Hoevan and Keesom, 1963). Holland and Powell (1998) accepted a value of 5.85 J/mol•K that had been adjusted, presumably on the basis of their analysis of several mineral equilibria.

Estimates of the uncertainty in the entropy of graphite differ by an order of magnitude. Based on their own measurements, DeSorbo and Tyler (1953) reported $\pm$ 0.02 J/mol•K. Hultgren et al. (1973) reported $\pm$ 0.04 J/mol•K, based on their smoothing of data from several sources. Cox et al. (1971, 1989) estimated about $\pm$ 0.1 J/mol•K, presumably because of the observed variations among samples (DeSorbo, 1955a,b). Chase et al. (1998) reported $S^o(298.15) = 5.74$ J/mol•K, based on the CODATA value (Cox et al., 1971), but suggested that the uncertainty should be expanded to $\pm$ 0.21 J/mol•K because of the variation in specific heat determinations among various samples of graphite. This uncertainty is an order of magnitude larger than originally reported by DeSorbo and Tyler (1953), and twice the uncertainty reported in other compilations, which already account for some variation among specimens. Nevertheless, the most conservative choice is to assign $S^o(298.15) = 5.74 \pm 0.21$ J/mol•K.

Diamond. $S^o(298.15) = 2.38 \pm 0.04$ **J/mol•K.** DeSorbo (1953b) reported $S^o(298.16) = 2.38 \pm 0.02$ J/mol•K and all subsequent compilations appear to accept a similar value (Table A2). Robie et al. (1978) cite Hultgren et al. (1973) who report that the selected low temperature Cp values agree with the measurements of Desnoyers and Morrison (1958) and DeSorbo (1953), but are about 2%-3% lower than the values of earlier workers.

The estimates of uncertainty in the selected values differ by an order of magnitude. DeSorbo (1953) reported ± 0.02 J/mol•K, based on his own measurements. Hultgren et al. (1973) reported a larger uncertainty (± 0.04 J/mol•K), presumably because they smoothed a larger body of data. The origins of the larger uncertainties reported by Robie et al. (1978) and Robie and Hemingway (1995) are unclear because the references they cite report different values.

Choosing S^o (298.15) = 2.38 ± 0.04 J/mol•K appears to encompass reasonable variations in the existing data for diamond. The entropy change of the diamond to graphite transition, therefore is estimated as ΔS^o (298.15) = 3.36 ± 0.21 J/mol•K

Enthalpy of formation from the elements

Graphite. $\Delta H_f^o(298,1) = \mathbf{0}$. Graphite is the reference state for carbon at 298.15 K.

Diamond. $\Delta H_f^o(298,1) = \mathbf{1872 \pm 74}$ **J/ mol.** Currently accepted values for the enthalpy of formation depend heavily on the analysis the heats of combustion of graphite and diamond determined in the 1940's (TableA2). Prosen et al. (1944) believed that the best value for the graphite-diamond transition should be based on the experiments of Jessup (1938), in which the same calorimeter was used to measure the heats of combustion of both phases, $\Delta H_f^o(298.16,1) = 1896 \pm 85$ J/mol. These early values may require minor adjustments for the standard state temperature, atomic weight of carbon, and the value of the international joule. Hawtin et al. (1966) re-determined the heats of combustion, leading to a similar value for the heat of formation of diamond, $\Delta H_f^o(298,1) = 1872 \pm 74$ J/mol. Most compilations appear to have made minor corrections of the Prosen et al. (1944) value and to have accepted it without comment.

The heat of transition is the difference between two large heats of combustion (~400 kJ) and the large uncertainties reflect this fact. The uncertainty accepted here is that reported by Hawtin et al. (1966). It is unclear why most previous compilers do not prefer the results of Hawtin et al. (1966). Although the results of the two studies cannot be distinguished within uncertainty, the results of Hawtin et al. (1966) are accepted here because the uncertainties are somewhat smaller.

High temperature heat capacity

Graphite. The high temperature heat capacity of graphite has been difficult to determine, and controversy exists whether differences among samples or experimental methods are more important sources of uncertainty (Table A1). The compilations of Chase (1998) and Chase et al. (1982) used here are virtually identical and depend on values reported by MacDonald (1965; 341-1723 K) and West and Isihara (1965; 1200 - 2600 K), which were determined by adiabatic and drop calorimetry, and by Cezairliyan (1973) and Cezairliyan and Righini (1975; 1500-3000 K), who used rapid, pulse heating techniques. Up to 1300 K, the selected values agree equally well with MacDonald (1965) and West and Ishihara (1965) (Fig. A1). In the range 1300-1900 K, the selected values agree best with West and Ishihara (1965) and at higher temperatures, with the data of Cezairliyan and Righini (1975) for so-called POCO graphite. Pyrolitic graphite determined by the same method yielded lower heat capacities (Cezairliyan and Righini,1975) (Fig. A1). Chase (1998) updated the compilation in 1983, and cited Cezairliyan, personal communication, as one source of data. Consequently, it is unclear

whether the preliminary results of Cezairliyan and Miiller (1985, 1500-3000 K) were incorporated in the evaluation.

The heat capacity function reported by Gustafson (1986) (Table A3) matches the selected values to within ± 0.06 J/K up to at least 3000 K (Fig. A2, A3). Other functions are less useful. The polynomial used by Robie and Hemingway (1995) reproduces the values selected by Chase (1998) to within ± 0.07 J/K up to 2500 K, but cannot be extrapolated to higher temperatures. The function reported by Holland and Powell (1998) is unsuitable because it cannot be extrapolated reliably above about 1200 K. At 1300 K and above, the function yields heat capacities that are systematically lower than the selected values (Fig. A3), reaching maximum values near 2000 K, above which the calculated values decline markedly (Fig. A2). The source of this discrepancy is unclear as the trail of references cited leads back to the heat capacities of Cox et al. (1989) and Chase et al. (1982), which are virtually identical to those of Chase (1998) (Table A1). Hultgren et al. (1973) based their compilation on an older compilation by Evans (1960) that contains no references to primary data. The Hultgren compilation gives heat capacities above 1300 K that are systematically lower than the more recent experimental determinations by 2-5% (Fig. A2)

The uncertainties reported by McDonald (1965) and West and Ishihara (1965) suggest that the smoothed heat capacities fit the raw data within a few tenths of one per cent. Cezairliyan and Righini (1975) and Cezairliyan and Miiller(1985) suggest that the errors in the data acquired by pulse heating are about 3%. The Gustafson function (1986) reproduces the selected values of Chase et al. (1998) with an average deviation of 0.12% and a maximum deviation of 0.06 J/mol•K, over the temperature range from 298 – 3000 K.

Diamond. Compilations of the high temperature heat capacities of diamond depend heavily on the measurements reported by Victor (1962; 273 - 1073 K) (Table A2). The smoothing function he used to describe his data is not suitable for extrapolation to higher temperatures (Table A3; Fig. A4). Robie et al. (1978) and Robie and Hemingway (1995) reported essentially identical heat capacity functions that depend ultimately on measurements reported by Victor (1962). Although they describe Victor's smoothed heat capacity values well (Fig. A5), they should not be extrapolated above the temperature range of the data (Fig. A4). The four-term polynomial used by Holland and Powell (1998) shows the least satisfactory fit to the smoothed data (Victor, 1962) (Fig. A5) and appears to extrapolate indefinitely to higher heat capacities with increasing temperature (Fig. A4).

Several estimates of the high temperature heat capacity based on Victor's (1962) measurements extrapolate appropriately to higher temperatures (Fig. A4). Gustafson (1986) used a five-term polynomial that yields values systematically lower than the data above 600 K (Table A5; Fig. A5), but extrapolates smoothly to higher temperatures (Fig. A4). Reeber and Wang (1996) reported recommended values of the isochoric specific heat from 50 - 3000K. The heat capacity values were calculated by fitting a three-frequency Einstein model to the existing data (Rossini and Jessup, 1938; Pitzer, 1938; DeSorbo, 1953; Desnoyers and Morrison, 1958; Victor, 1962). Isobaric heat capacity was calculated in this study using the relation $C_p - C_v = \alpha^2 \cdot B \cdot V \cdot T$, the recommended values of molar volume and thermal expansion (Reeber and Wang, 1996), and two constant limiting values of bulk modulus of 5560 kbar or 4400 kbar. The derived heat

capacities fit the smoothed data (Victor, 1962) very well up to 1000 K and extrapolate to higher temperatures in much the same way as Gustafson's treatment (Fig. A4).

The independent review of Reeber and Wang (1996) corroborates the extrapolation proposed by Gustafson (1986) and his function was used for all calculations. It is unfortunate that Reeber and Wang did not report their fitting function for the heat capacity because their calculations fit Victor's (1966) data quite well. The function proposed by Glushko et al. (1979) further supports the extrapolation by Gustafson (1986), although their function becomes inappropriate at the highest temperatures (Fig. A4).

The average standard deviation of the heat capacity determinations over the temperature range of Victor's (1962) experiments is 0.4%, including the fit to his smoothing function. The 2σ uncertainty envelope is ±0.04 J/K at 298 K and ±0.18 J/K at 1000 K.

The choice of Gustafson's (1986) heat capacity functions for diamond and graphite is supported further by the fact that ΔC_p for the reaction asymptotically approaches zero at high temperatures, as expected (e.g. Berman and Simon, 1955). On the other hand, ΔC_p based on Holland and Powell's (1998) functions decreases indefinitely at high temperatures.

Molar Volume

Graphite. **V(298.15) = 5.300 ± 0.001 cm³/mol.** All sources consulted lead back to the cell dimensions determined by Nelson and Riley (1945) at 15°C, sometimes modified by the observations of Bacon (1950) (Table A4). Robie et al. (1967) calculated the molar volume using older values for Avogadro's number and the conversion from kX units to Angström units. Adjusting to modern values (Cohen and Taylor; 1987; Mohr et al., 2008) and allowing for thermal expansion yields 5.300 ± 0.001 cm³/mol at 298.15 K.

Diamond. **V(298.15) = 3.4166 ± 0.0003 cm³/mol.** Most workers have chosen a value of the molar volume in the range 3.417± 0.001 cm³ (Table A5). The value accepted here was calculated using the preferred unit cell dimension (a = 3.56705 ± 0.00005 Å (1 σ)) reported in the critical survey of Reeber and Wang (1996, Table 1) and the value of Avogadro's number used by Robie and Hemingway (1995; 6.022137 E+23, Cohen and Taylor, 1987). The preferred unit cell dimension appears to be the mean value of five studies of very high or gem quality diamond (Tu, 1932; Straumanis and Aka, 1951; Thewlis and Davey, 1956; Skinner, 1957; Hom et al., 1975). Lower quality and synthetic diamonds have a slightly larger mean unit cell dimension and molar volume (3.4168 cm³/mol) that are within uncertainty of the preferred value.

The accepted molar volume agrees well with previous reports (Berman and Simon, 1955; Berman, 1965,1979; Robie et al., 1967). However, variations in the values of Avogadro's number used by various authors may create differences in the fourth significant digit. For example, the slightly larger molar volume preferred by Reeber and Wang (1996, Table 4, 3.41706 cm³/mol) implies a value of Avogadro's number (6.023050E+23) from an unknown source. It seems unlikely that the uncertainty is in the third significant digit, as implied by Holland and Powell (1998).

Bulk Modulus

Graphite. **B_0 = 338 kbar; n = 8.9.** Hanfland et al. (1989) derived values of B_o and n $(=\partial B/\partial P)_T$) in the Murnaghan (1944) equation of state that are provisionally accepted here (Table A4). The compression data from which the values were derived were

measured in a diamond-anvil cell at pressures ranging from 20 – 140 kbar, using the ruby fluorescence pressure scale of Mao et al. (1978).

Three older bodies of experimental data have also been used to determine values of B_o and n. Lynch and Drickamer (1966) reported the compression of graphite from 8-168 kbar from which Drickamer et al. (1966) derived values of B_o and n (337 kbar, 12.2) (Fig. A6). They noted that the lower pressure region is better fit by a value of n about 9.0, similar to the value determined by Hanfland et al. (1989). Birch (1966) relied on early experiments by Richardson (1915) to choose a comparable value of B_o (333 kbar). Berman (1965) derived a somewhat higher value of B_o (379 kbar) from the data of Bridgeman (1945,1948), which nevertheless appear to be compatible with the Lynch and Drickamer data.

Both Drickamer et al. (1966) and Gustafson (1986) derived parameters that pass curves comfortably through the scatter of the experimental data (Bridgeman, 1945, 1948; Lynch and Drickamer, 1966). However, the Gustafson parameters (B_0 = 333 kbar; n = 12) fit the data slightly better (sum of squared deviations is 9% lower) than those reported by Drickamer et al. (1966). The values proposed by Holland and Powell (1998), based on Birch (1966) yield compressions that deviate significantly from these experimental data at high pressures. The data of Hanfland et al. (1996) pass just outside a reasonable error envelope around the scatter of Lynch and Drickamer's (1966) data (Fig. A6).

The values reported by Hanfland et al. (1989) yield pressures that are about twenty kbar lower than the Lynchand Drickamer data for a compression of 0.88. Hanfland et al. (1986) suggested that part of this difference results from using different pressures scales. However, it appears that only about eight kbar of the discrepancy can be attributed to the differences in pressure scales at 100 kbar. Lynch and Drickamer (1966) appear to have used a scale primarily based on a previously determined compression of MgO (Perez-Albuerne and Drickamer, 1965), which yields pressures about seven kbar higher than the most recent determinations (Zha et al., 2000). Hanfland et al. (1986) used the ruby fluorescence scale of Mao et al. (1978), which yields pressures about 1 kbar lower than the new calibration (Zha et al., 2000). Thus, only eight kbar of the observed difference between the two data sets can be attributed to differences in the pressure scale.

Differences in the degree of non-hydrostatic pressures during the experiments might also contribute to systematic differences between the two bodies of data. Zha et al. (2000) demonstrated that significantly higher pressures may be required to produce a given compression in a non-hydrostatic medium. This observation may help explain the higher pressures observed in the Lynch and Drickamer (1966) experiments (Fig. A6). Although it is known that graphite begins to transform to another phase at pressures higher than 140 kbar (Hanfland et al., 1989, and references therein), there is no evidence for a change in slope of the compression data that might support such a change in the Lynch and Drickamer (1966) data.

An uncertainty of ± 30 kbar in the initial bulk modulus encompasses the range of values used by various authors and an uncertainty of ± 2 in the value of n would permit a scatter of data similar to that in the Lynch and Drickamer (1966) data and much larger than that illustrated by Hanfland et al. (1989).

Diamond. B_0 = 4460 (10) kbar; n = 3.2. Values of the initial bulk modulus adopted for diamond range from about 4400 kbar to 6250 kbar (Table A5). However, because the

bulk modulus of diamond is so high, this range of values produces differences in ∫VdP of only about 100 J at 100 kbar.

Adams (1921) and Adams and Williamson(1923) did pioneering work on the compression of diamond up to 12 kbar, and Lynch and Drickamer (1966) reported a comprehensive set of experimental data (68 – 260 kbar). They showed that the compression of the unit cell dimension (a/ao) is linear with pressure over the range of their experiments and suggested that the initial bulk modulus is 6250 kbar . Several authors used Murnaghan (1944) equations of state that produce values of V/Vo that fit comfortably within the scatter of Lynch and Drickamer's data (Drickamer et al., 1966; Gustafson, 1986; Holland and Powell, 1998). However, the values of B_0 and n (5560 kbar; 4) from Drickamer et al. (1966) yield a better fit (sum of squared deviations) to Lynch and Drickamer's data.

Generally lower values of the initial bulk modulus are found from measurements of the elastic constants by Brillouin scattering and ultrasonic methods (4423-5867 kbar; Grimsditch, 2000; see also Aleksandrov et al., 1987)). Occelli et al. (2003) used direct compression in a diamond anvil cell under hydrostatic pressures up to 1400 kbar, a synchrotron source, and energy dispersive x-ray diffraction to determine B_0 = 4460(10) kbar and n= 3.0(1) using the Vinet equation of state. Using the Murnaghan equation of state, their compression data were best fit by about n=3.2 (Occelli et al., 2003). The direct determinations of Occelli et al. (2003) agree broadly with and confirm the lower values of bulk modulus determined by Brillouin scattering and ultrasonic methods. Their values of B_0 and n yield compressions that pass just outside the scatter of Lynch and Drickamer's (1966) data. As discussed for graphite, generally less than half of the pressure differences between the two kinds of data can be explained by differences in the pressure scales used by the authors.

An uncertainty of +1000/-500 kbar in the initial bulk modulus encompasses the range of values used by various authors. The calculated values of compression are relatively insensitive to the value of n; an assumed uncertainty of 100% would permit a scatter of data similar to that in the Lynch and Drickamer (1966) data and much larger than that illustrated by Occelli et al. (2003). Consequently, an uncertainty of ± 1 was assumed (Table 2).

Temperature Dependence of Bulk Modulus

The temperature dependences of the bulk moduli of graphite and diamond are poorly known and a simple empirical approach was adopted. Based on their studies of silicate minerals, Holland et al. (1996) proposed estimating the bulk modulus at high temperatures according to $\partial B/\partial T)_P = -3a_0 B_{0,298}$, where a_0 is a parameter used to estimate the coefficient of thermal expansion. The method is based on the approximations that B_T is linear in temperature and $\partial B/\partial T)_P$ is proportional to $-\alpha B_0$, so that $\partial B/\partial T)_P$ is a constant. Although it is known that $\partial B/\partial T)_P$ is a function of temperature (e.g. Zouboulis et al., 1998; Mounet and Mazario, 2005), the linear approximation introduces errors much smaller than the large uncertainties in B_0.

Graphite. $\partial \mathbf{B}/\partial \mathbf{T})_\mathbf{P}$ = - 0.07 ± 0.02 (kbar/K). There appear to be no direct measurements of the temperature dependence of bulk modulus for graphite. Mounet and Mazario (2005) used *ab initio* calculations to calculate the elastic constants as a function of pressure. Their calculated temperature dependence of B (Mounet and Mazario, 2005, Fig 21) can be approximated reasonably well as $\partial B/\partial T)_P$ = - 0.094 (kbar/K). Using the

method proposed by Holland et al. (1996), the value of a_0 reported by Holland and Powell (1998), and B_0 from Table 2, $\partial B/\partial T)_P = -0.048$. As neither method is constrained by actual measurements, the mean of the two estimates was chosen. The assigned uncertainty encompasses the range of the two estimates.

Diamond. $\boldsymbol{\partial B/\partial T)_P = -0.3 \pm 0.1}$ **(kbar/K)**. Zouboulis et al. (1998) used Brillouin scattering to measured the elastic constants of diamond from 300 -1600 K. Over that temperature range, the average slope is approximated by $\partial B/\partial T)_P = -0.228$ (kbar/K). Mounet and Mazari (2005) calculated a temperature dependence that can be approximated as $\partial B/\partial T)_P = -0.276$ (kbar/K). Using the method proposed by Holland et al. (1996), the value of a_0 reported by Holland and Powell (1998), and B_0 from Table 2, $\partial B/\partial T)_P - 0.275$(kbar/K). Because the calculated temperature dependence becomes increasingly negative with increasing temperature (Mounet and Mazari, 2005, Fig. 20), it seems likely that the average slope over the interval 300 – 3000K should be more negative than that measured by Zouboulis et al. (1998). In fact, if their smoothing function is extrapolated to 3000 K, the average slope becomes - 0.396 (kbar/K). A slope of $\partial B/\partial T)_P = -0.3 \pm 0.1$ (kbar/K) includes all these possibilities.

Thermal Expansion

Graphite. The expression for thermal expansion of graphite given by Holland and Powell (1998) was used in this study. Nelson and Riley (1945) measured the thermal expansion of natural Ceylon graphite up to 1073 K and Holland and Powell (1998) fitted those measurements to a simple function in the square root of temperature (Fig. A8). Touloukian et. al (1977, p. 79-80) summarized numerous measurements of the linear expansion of synthetic "pyrolitic graphite" in the range 300 – 3400 K as third-order polynomials in temperature. Gustafson (1986) refit the smoothed data of Touloukian et al. with a function that reproduces the smoothed data within about 0.1 % or less (Fig. A8). Although the Gustafson function is based on measurements over a wide temperature range, the form of the function requires that the volume coefficient of thermal expansion is a linear function of temperature (Fig A9), and it is unclear whether this synthetic graphite is an appropriate analogue for natural graphite. The function of Holland and Powell (1998) has a more appropriate form, at high temperatures, and fits the data for natural graphite better than either of the functions based on pyrolitic graphite (sum of squared deviations). Consequently, the Holland and Powell function was accepted.

Diamond. Among several available descriptions, the treatment of the thermal expansion of diamond by Reeber and Wang (1996) is the most appropriate for our purposes. They conducted a careful review of the molar volume and thermal expansion of diamond and fitted selected data to a quasi-harmonic model with six adjustable parameters:

$$\ln \frac{V_T}{V_0} = 3 \sum_{i=1}^{3} \left[\frac{X_i \Theta_i}{\exp\left(\dfrac{\Theta_i}{T}\right) - 1} \right],$$

where V_T is the volume at the temperature of interest, V_0 is volume at zero Kelvin, and X_i and θ_i are adjustable parameters. They fitted only data from gem quality and synthetic

diamond (Straumanis and Aka, 1951; Thewlis and Davey, 1956; Skinner, 1957; Haruna et al., 1992; Pickrell et al., 1994).

The molar volume of diamond is constrained by measurements only at temperatures below 2000 $^\circ$C. Above that temperature, the functions used by various authors extrapolate differently (Fig. A10; Touloukian et al., 1977; Gustafson, 1986; Reeber and Wang, 1996; Holland and Powell, 1998). The function used by Touloukian et al. (1977) requires a thermal maximum in the thermal expansion coefficient at about 2000 K and is not suitable to be extrapolated to high temperature (Fig. A11). The Gustafson (1986) function also is not suitable for extrapolation as it assumes linear variation of the thermal expansion coefficient with temperature. The function used by Holland and Powell (1998) yields a distinctly lower slope of V/V_0 vs. T (Fig. A10) and is not appropriate for extrapolation of the coefficient of thermal expansion to low temperatures. The function proposed by Reeber and Wang (1996) is preferred because it fits the data well at both high and low temperatures (Reeber and Wang, 1996, Fig. 2), it extrapolates smoothly to intermediate values of molar volume at high temperature (Fig. A10) and has the appropriate thermodynamic form at both high and low temperature (Fig. A11).