“Thermoba-Raman-try”: Calibration of spectroscopic barometers and thermometers for mineral inclusions

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Mineral inclusions may develop residual pressures (P_{incl}) during cooling and exhumation because of differential expansion and compression relative to the host entrapping mineral. Shifts to Raman spectra, as determined using laser Raman microspectroscopy, permit inference of P_{incl}. Knowing the pressure-temperature (P-T) dependence of molar volumes from thermodynamic databases and the shear modulus of the host phase, entrapment P at assumed T or entrapment T at assumed P can be calculated for a measured P_{incl}. This concept is developed theoretically to fit simplified empirical expressions of entrapment P(T, P_{incl}) or T(P, P_{incl}) for a wide range of common mineral host-inclusion pairs. Typical residuals are <200 bar for barometers and <5°C for thermometers. Barometric slopes are flat (0–15 bar/°C), and even large measurement errors of ±0.5 cm\(^{-1}\) propagate to barometric precisions that are small (c. ±300 bar) for quartz inclusions in numerous silicates, apatite, oxides and pyrite, and acceptable for graphite in garnet (±2 kbar) and for garnet, olivine, and coesite in diamond (±3 kbar). Thermometric slopes are steep (40–400 bar/°C), but highly resolved measurements (at least ±0.1 cm\(^{-1}\)) are needed for thermometric precisions better than ±30°C for zircon and rutile inclusions in numerous silicates and for spinel in olivine. Applications to published data recover peak entrapment P's in some instances, but imply higher or lower P's than originally assumed in others. Disparities may arise from sample preparation, differences in conditions of mineral entrapment vs. final equilibration, or reequilibration of the host mineral via chemical diffusion, viscous flow or fracturing. Polymorphic transitions (e.g. coesite=quartz, diamond=graphite) can preclude recovery of entrapment P's except for very high P's or rapid exhumation.

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1. Introduction

Determination of pressure-temperature (P-T) conditions of mineral formation underpins many crustal and mantle petrogeologic endeavors. Trace element thermometry has greatly improved T constraints, but does require buffering assemblages or estimates of component activities (e.g. the activity of rutile), while P remains elusive and is still mainly founded on solid state net-transfer reactions restricted to particular assemblages and whole-rock compositions. Typical examples of barometric equilibria include garnet-plagioclase-kyanite-quartz (Koziol and Newton, 1988) and garnet-omphacite-phengite (Waters and Martin, 1993), which obviously require equilibration of multiple coexisting phases, and may be compromised by compositional or textural reequilibration on cooling (e.g., Spear, 1995; Kohn and Spear, 2000; Pattison et al., 2003). In principle, Raman microspectroscopic thermobarometry of mineral inclusions (Izraeli et al., 1999; Parkinson and Katayama, 1999; Sobolev et al., 2000; Barron, 2005; Enami et al., 2007) could vastly expand the range of barometers and thermometers available to petrologists.

The conceptual basis may be illustrated as follows. Consider a host mineral like garnet that entraps inclusions like quartz, titanite or rutile at elevated P or T (Fig. 1). Although highly precise thermometric lines can now be determined from Zr-in-rutile, Zr-in-titanite, or Ti-in-quartz thermometry (Fig. 1; Watson et al., 2006; Wark and Watson, 2006; Tomkins et al., 2007; Hayden et al., 2008; Thomas et al., 2010), how do we validate T if the buffering assemblage is absent, and how do we determine P from such sparse assemblages? At the P-T conditions of entrapment, no pressure mismatch occurs between inclusion and host (ΔP = P_{incl} − P_{ext} = 0, where P_{incl} is the pressure on the inclusion and P_{ext} is the external pressure). Because mineral host and inclusion have different thermal expansivities and compressibilities, however, a residual pressure develops (ΔP ≠ 0) during exhumation and cooling whose magnitude depends on entrapment P-T, the exact P-T dependence of each mineral’s molar volume, and the shear modulus (elastic response) of the host phase (see Zhang, 1998; Izraeli et al., 1999; Sobolev et al., 2000; Guiraud and Powell, 2006). For example, at high-P low-T conditions, quartz’ high compressibility
means that it attempts to expand during decompression more than the void space available to it in the host garnet. An overpressure or positive $\Delta P$ ensues, whose magnitude depends on the volume mismatch (degree to which quartz differentially expands relative to the garnet) and elastic response of the host garnet to quartz inclusion expansion (degree to which the garnet elastically deforms because of the expanding quartz). Once the rock reaches the surface, where $P_{ext}$ is essentially 0, $\Delta P = P_{incl}$. Conversely, at high-$T$ low-$P$ conditions, quartz' high thermal expansivity and occurrence of silica polymorphs with larger molar volumes (especially $\beta$-quartz) mean that it may attempt to shrink more than the space available to it. Upon exhumation and cooling, two possible responses may occur. If grain boundaries are semi-coherent, then the inclusion surface can remain “stuck” to the host phase, and the inclusion and host will stretch to fill the excess space. This stretching can be viewed theoretically as a tensile response to underpressure or negative $\Delta P$. Alternatively, if grain boundaries are weak, the inclusion might simply separate from the host phase, creating a void space and resulting in $P_{incl} = 1$ bar. The boundary between the $\Delta P > 0$ and $\Delta P < 0$ fields defines the conditions where host–inclusion expansivities and compressibilities are exactly balanced so that no residual pressure occurs on the inclusion in the cooled and exhumed rock.

Raman band positions of many minerals are $P$-dependent, and in fact may be used as pressure calibrants in diamond-anvil experiments (e.g., Schmidt and Ziemann, 2000; Schmidt et al., 2013). That is, $P_{incl}$ can be empirically determined from the measured shift to a Raman peak position, and it was expressly refined to improve volume chemical data, and it was expressly refined to improve volume

2. Methods

2.1. Calculations

Several studies have explored mineral inclusion $\Delta P$'s both theoretically and empirically (e.g., Rosenfeld, 1969; Van der Molen, 1981; Van der Molen and Van Roermund, 1986; Zhang, 1998; Izraeli et al., 1999; Parkinson and Katayama, 1999; Sobolev et al., 2000; Barron, 2005; Guiraud and Powell, 2006; Enami et al., 2007). Some of these approaches assumed constant thermal expansivities and compressibilities (or bulk moduli) rather than the more complex expressions for the $P$–$T$–dependence of molar volume that are commonly used in thermodynamic calculations (e.g., Berman, 1988; Holland and Powell, 2011). The equations of Van der Molen (1981) (also used by Enami et al., 2007) are inconsistent with other derivations and should be avoided. Guiraud and Powell (2006) provide the conceptually simplest solution for the pressure on the inclusion ($P_{incl}$) as a function of entrapment $P$–$T$ conditions:

$$P_{incl} = 1 - \frac{4\mu}{3} \left( \frac{V_{298.1 \text{ bar}}^{host}}{V_{298.1 \text{ bar}}^{host} - P_{incl}} - \frac{V_{298.1 \text{ bar}}^{host}}{V_{298.1 \text{ bar}}^{host} - P_{incl}} \right)$$

where $\mu$ is the shear modulus of the host (enclosing) phase, $V_{298.1 \text{ bar}}^{host}$ and $V_{298.1 \text{ bar}}^{incl}$ are the molar volumes of the host and inclusion minerals at the $P$–$T$ conditions of entrapment, and $V_{298.1 \text{ bar}}^{host}$ and $V_{298.1 \text{ bar}}^{incl}$ are the present molar volumes of host and inclusion. The present molar volume of the host is simply the standard state volume, but that of the inclusion is different because it is subjected to a different pressure, $P_{incl}$. Eq. (1) assumes that inclusions are so small that the host behaves as an infinite medium, which is generally met when the radius of the inclusion is less than ~3 times the distance in the host to a free surface (Tait, 1992; Zhang, 1998). That is, whereas host mineral $P$ equals $P_{incl}$ at the interface with the inclusion (barring other complicating factors – see De Wolf, 2003; Nasdala et al., 2003), it changes rapidly with distance to 1 bar. Eq. (1) does not explicitly use bulk modulus because it is embodied in the $P$-dependence of the molar volumes. Substitution of constant values for expansivity and compressibility into Eq. (1) reproduces alternative simplified treatments.

Conceptually, one might solve Eq. (1) for a current $P_{incl}$ by assuming a $P$–$T$ condition of entrapment for a host–mineral pair (defining $V_{host}^{T,P}$ and $V_{incl}^{T,P}$ and iteratively adjusting $P_{incl}$ (and hence $V_{298.1 \text{ bar}}^{incl}$) using a root-solving algorithm until Eq. (1) holds. Alternatively, one might solve for entrapment $P$ by defining $P_{incl}$ (and hence $V_{298.1 \text{ bar}}^{incl}$) and $T$, and iteratively adjusting $P$ (and hence $V_{host}^{T,P}$ and $V_{incl}^{T,P}$) until Eq. (1) holds. In this study, the former approach was taken, specifically a grid of $P$–$T$ conditions was assumed (400–900 °C, 0–25 kbar for the crust; 400–1000 °C, 25–50 kbar for coesite-in-zircon; 800–1400 °C, 35–100 kbar for diamond-bearing mantle; 800–1400 °C, 0–25 kbar for spinel-in-olivine), incrementing $T$ and $P$ by 25°C and 1 kbar. At each $P$–$T$ condition, Newton's method was applied to Eq. (1) to solve for $P_{incl}$, which was tabulated to produce a grid of $P$–$T$–$P_{incl}$ conditions. Sensitivity of calculations to shear modulus was determined by varying $\mu$ and recalculating $P$–$T$–$P_{incl}$. Mineral hosts considered were apatite, clinoxyroene (diopside and jadeite), diamond, epidote, garnet (pyrope, almandine, spessartine and grossular end-members), hornblende, ilmenite, kyanite, lawsonite, olivine, rutile, (Fe-)staurolite, titanite, tourmaline, and zircon. Inclusion minerals considered were apatite, coesite, garnet endmembers, graphite, ilmenite, quartz, rutile, spinel, titanite, tourmaline, and zircon. For two reasons, the latest Thermocalc database (Holland and Powell, 2011) was preferred for determining nearly all mineral volumes: it is the most recent and comprehensive compilation of thermochemical data, and it was expressly refined to improve volume
extrapolations to high P. Thermal expansivities and compressibilities forapatite and for A2Ba-structured titanite (the most common structure for natural titanite; Lussier et al., 2009) were derived from Angel et al. (1999), Brunet et al. (1999), Kunz et al. (2000), and Rath (2002). Shear moduli were taken from diverse sources listed in Table 1.

Ultimately, P_incl can be measured using Raman spectroscopy, so applications to rocks are facilitated by either a barometric expression for entrainment P as a function of P_incl and T, i.e. $P = f(P_{incl}, T)$ or a thermometric expression for entrainment T as a function of P_incl and P, i.e. $T = f(P_{incl}, P)$. Consequently, simple empirical functions were fit to $P - T$-$P_{incl}$ calculations. Many host–inclusion pairs are not suitable for thermoba-raman-try because P or T is inordinately sensitive to P_incl, and uncertainties in P_incl propagate to prohibitively large uncertainties in entrainment P or T. Discussion is limited to host–inclusion pairs with good thermobarometric potential and whose Raman spectra have residuals that are typically smaller than uncertainties arising from other sources, so they adequately fit synthetic data:

$$P = A_{ij} + B_{ij}P_{incl} + C_{ij} \cdot T + D_{ij} \exp \left( \frac{P_{incl}}{T \cdot E_{ij}} \right),$$

$$T = A_{ij} + B_{ij}P_{incl} + C_{ij} \cdot P$$

where the subscript ij refers to the host mineral i with inclusion j. Terms $A_{ij}$-$D_{ij}$ were obtained using simple linear regression, iteratively adjusting $E_{ij}$ (for Eq. (2a)) to maximize the $R^2$ and F statistics. If P is in bars and T in kelvins, $E_{ij}$ is typically between 10 and 30. Izraeli et al. (1999) recommend an empirical barometric equation analogous to (2a) regressed for terms A, B, and C, but replacing the exponential term with the product of $P_{incl}$ and T. Such expressions produced poorer regression diagnostics. Although equations are accurate to within a few hundred bars or a few °C within the grid of $P - T$-$P_{incl}$ conditions, they cannot be extrapolated far outside the grid. For example they do not reproduce P = 1 bar or $T = 298$ K at standard T and P. Separate regressions for quartz were performed for $P_{incl} > 0$ (Table 1) and $P_{incl} < 0$ (Table $S1$).

Most experimentally-determined shifts to Raman spectra are not specifically parameterized to recover P, but many minerals exhibit essentially linear P-dependencies, commonly about 0.3–0.4 cm$^{-1}$/kbars. Raman band positions in quartz exhibit non-linear P-dependencies, so experimental data (Schmidt and Ziemann, 2000) were fit to third-order polynomials forced through
zero for the 206 and 464 cm$^{-1}$ bands ($\Delta \nu_{206}$, $\Delta \nu_{464}$, Eqs. (3) and (4)) and the separation between the 206 and 464 cm$^{-1}$ bands ($\Delta \omega_{464-206}$, Eq. (3)) at room temperature:

$$P \text{ (bar)} = 372.9 \pm 2.8 \Delta \nu_{206} + 0.079 \pm 0.002(\Delta \nu_{206})^3,$$  \hspace{1cm} (3)

$$P \text{ (bar)} = 1118.0 \pm 7.0 \Delta \nu_{464} + 0.168 \pm 0.029(\Delta \nu_{464})^3,$$  \hspace{1cm} (4)

$$P \text{ (bar)} = 510.3 \pm 8.6 \Delta \omega_{464-206} + 0.686 \pm 0.020(\Delta \omega_{464-206})^3.$$  \hspace{1cm} (5)

Some host mineral and inclusion spectra interfere, notably spectral bands in garnet can overlap the 206 cm$^{-1}$ band in quartz (Enami, 2012). Thus, in practice the choice of equation and band for quartz depends on the host mineral spectrum. Eqs. (3)–(5) could be substituted directly into Eq. (2) for $P_{\text{incl}}$, or used to solve for $P_{\text{incl}}$ from measured laser Raman spectra on quartz inclusions. The $P_{\text{incl}}$ value would then be used with Eq. (2) to solve for $P$ at a specified $T$ or $T$ at a specified $P$.

In further calculations, pressure dependencies of Raman band positions were based on Eqs. (3)–(5) for quartz and the calibrations of Hanfland et al. (1989) for the 1580 cm$^{-1}$ band in graphite. For olivine (Fo$_{93}$), coesite, and mantle garnet (for illustration assumed to be pure pyrope), constant pressure dependencies of 0.309, 0.29, and 0.39 cm$^{-1}$/kbar were assumed for the 856 cm$^{-1}$ (olivine), 521 cm$^{-1}$ (coesite), and 927 cm$^{-1}$ (pyrope) bands respectively (Hemley, 1987; Mernagh and Liu, 1990; Wang et al., 1993). Alternatively, pressure dependencies for host mineral Raman spectra might be used, corresponding to measurements directly adjacent to a mineral inclusion, although local edge effects and pressure inhomogeneities in the host may preclude this approach (De Wolf, 2003; Nasdala et al., 2003). Solid solution behavior must be considered because it affects Raman band positions. Nearly pure minerals with experimental calibrations of Raman $P$-dependencies include SiO$_2$ polymorphs (Hemley, 1987; Schmidt and Ziemann, 2000), Al$_2$SiO$_5$ polymorphs (Mernagh and Liu, 1991), zircon (Knittle and Williams, 1993; Schmidt et al., 2013), lawsonite (Daniel et al., 2000), apatite (Comodi et al., 2001), graphite (Hanfland et al., 1989), rutile (Liu and Mernagh, 1992), corundum (Xu et al., 1995), magnetite (Shebanova and Lazor, 2003), hematite (Shim and Duffy, 2002), and diamond (Tardieu et al., 1990).

3. Results

Calibrations (Tables 1, 2, S1) are illustrated for representative host–inclusion pairs (Figs. 2–4), which show the distributions of $P_{\text{incl}}$ and Raman band shifts over $P$–$T$ space. Isopleths of $P_{\text{incl}}$ and Raman band shift for barometers generally show very flat slopes, e.g. $\sim$15 bar/$^\circ$C for quartz in most silicates (Fig. 2A–C), but as high as 40–50 bar/$^\circ$C for olivine- and pyrope-in-diamond (Fig. 3B–C; also regressed as a thermometer), and as low as 0 bar/$^\circ$C for graphite-in-garnet (Fig. 3A) and coesite-in-diamond (Fig. 3D). A strong pressure dependence of the 206 cm$^{-1}$ band in quartz confers the best theoretical resolution: a peak position uncertainty of $\pm$0.5 cm$^{-1}$ propagates to errors of only a few hundred bars (Fig. 2B). The same peak position uncertainty propagates to $\sim\pm$1 kbar for the 464 cm$^{-1}$ band in quartz (Fig. 2C) and approximately $\pm$2–3 kbar for other equilibria (Fig. 3). More
precise measurement of peak positions confers commensurately smaller $P$ uncertainties. For example commonly reported errors for the 464 cm$^{-1}$ band in quartz of $\pm 0.1$ cm$^{-1}$ result in uncertainties of only a few hundred bars. Similar volumetric properties for aluminum garnet endmembers indicate a small impact on calculated entrapment pressure from the Raman shift in quartz (Fig. 2D). In fact, most combinations of quartz inclusions in silicates or oxides produce similar $P$-dependencies (Fig. 2D), likely because the expansivity and compressibility of quartz generally differ from other minerals. However, all calculations involving $\beta$-quartz resulted in negative $P_{\text{incl}}$ because of the large negative $\Delta V$ of the $\beta$-quartz=$\alpha$-quartz transition (Fig. 2; Table S1).

Thermometric slopes range from moderate for spinel-in-olivine (c. 40–50 bar/$^\circ$C; arguably a barometer) to nearly vertical for zircon-in-rutile ($>400$ bar/$^\circ$C; Fig. 4). Uncertainties of $\pm 0.5$ cm$^{-1}$ propagate to impractically large errors of $\pm 100–200$ $^\circ$C, so application of thermometric equilibria will require measurement precisions better than $\pm 0.1$ cm$^{-1}$. The large number of potential thermometers involving zircon (because of its low thermal expansivity) and its ubiquity as micro-inclusions in silicates especially recommends further investigation.

Two alternative models for olivine-in-diamond barometry have been published (Israel et al., 1999; Barron, 2005) and can be compared to the present study’s synthetic data (Fig. 5). These models generally underpredict (Israel et al., 1999) and overpredict (Barron, 2005) entrapment pressures by $\sim 10$ kbar compared to the present calibration. Systematic differences in high- vs. low-$T$ predictions imply that these discrepancies arise from different assumptions regarding both compressibility and thermal expansivity, e.g. use of constant compressibility and expansivity terms by Barron (2005). Barron’s equations also do not account for the elastic response of the host mineral to the expansion of the inclusion, but this should generally result in underestimated, not overestimated, entrapment pressures.

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**Table 2**

<table>
<thead>
<tr>
<th>Host–inclusion</th>
<th>$\mu$ (kbar)</th>
<th>A (K)</th>
<th>B (K/kbar)</th>
<th>C (K/kbar)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Olivine–spinel</td>
<td>780</td>
<td>370.9</td>
<td>0.12485</td>
<td>0.02541</td>
</tr>
<tr>
<td>Diamond–olivine</td>
<td>5380</td>
<td>264.2</td>
<td>$-0.04264$</td>
<td>0.02415</td>
</tr>
<tr>
<td>Diopside–zircon</td>
<td>725</td>
<td>333.1</td>
<td>0.07476</td>
<td>0.02237</td>
</tr>
<tr>
<td>Epidote–zircon</td>
<td>612</td>
<td>329.2</td>
<td>0.11902</td>
<td>0.02339</td>
</tr>
<tr>
<td>Garnet–zircon</td>
<td>925</td>
<td>323.7</td>
<td>0.11315</td>
<td>0.01045</td>
</tr>
<tr>
<td>Kyanite–zircon</td>
<td>1020</td>
<td>363.8</td>
<td>0.10343</td>
<td>0.01782</td>
</tr>
<tr>
<td>Lawsonite–zircon</td>
<td>657</td>
<td>347.7</td>
<td>0.08046</td>
<td>0.01144</td>
</tr>
<tr>
<td>Rutile–zircon</td>
<td>1130</td>
<td>327.0</td>
<td>0.09293</td>
<td>0.00235</td>
</tr>
<tr>
<td>Titanite–zircon</td>
<td>480</td>
<td>264.7</td>
<td>$-0.11990$</td>
<td>0.02149</td>
</tr>
<tr>
<td>Zircon–ilmenite</td>
<td>1100</td>
<td>315.5</td>
<td>$-0.09632$</td>
<td>0.01455</td>
</tr>
<tr>
<td>Zircon–magnetite</td>
<td>1100</td>
<td>326.8</td>
<td>$-0.04215$</td>
<td>0.00465</td>
</tr>
</tbody>
</table>

Note: Full expression is $T = A + BP + CP_{\text{incl}}$, with $P$ in bars and $T$ in kelvins. Garnet is $\text{Mg}_{\text{Fe}}\text{Mg}_{\text{Ca}}\text{Mg}_{\text{Na}}\text{Mg}_{\text{Fe}}\text{Mg}_{\text{Ca}}$; olivine is $\text{Fo}_{\text{90}}$. Sources of shear moduli: diamond – McSkimin and Andreatta (1972); diopside – Sang et al. (2011); epidote – Bass (1980); garnet components – Wang and Ji (2001); lawsonite – Chantel et al. (2012); olivine – Abramson et al. (1997); rutile – Isaak et al. (1998); titanite – Salje et al. (2011); garnet – Ewing (1974) and Dutta and Mandal (2012).
4. Discussion

Observations for quartz inclusions (Enami et al., 2007), olivine-in-diamond (Izraeli et al., 1999), and coesite-in-diamond and -zircon (Parkinson and Katayama, 1999; Sobolev et al., 2000; Ye et al., 2001) are readily compared to the new calibrations and illustrate practical features of thermob-Raman-try.

4.1. Quartz inclusions

Quartz thermob-Raman-try returns various $P$’s ranging from well below peak $P$’s in eclogites (samples 1–4, Fig. 6) to well above peak $P$’s in amphibolite-facies rocks (samples 5–9, Fig. 6). Only one calculated $P$ (sample 10, Fig. 6) corresponds precisely with assumed peak $P$–$T$ conditions. Several possibilities can explain the disparities. Possibly, the thickness of garnet around some inclusions was too small. If the inclusion radius exceeds 1/3 of the thickness of the surrounding host, the host cannot be considered an infinite medium (Tait, 1992; Zhang, 1998). Expansion of such inclusions during sample preparation would lower $P$ and $T$ conditions. Inclusions entrapped at high $T$ might also
re-equilibrate through host-phase chemical diffusion (different end-members have different molar volumes; see Baumgartner et al., 2010) or viscous flow. Complete evaluation of such re-equilibration potential is beyond the scope of this discussion, but minerals more resistant to diffusion, flow, or both (possibly garnet and kyanite) might preserve higher entrapment P’s than less resistant minerals (possibly clinopyroxene and epidote). Calculated entrapment P’s could also correspond to conditions along the prograde P–T path that differ from peak conditions. For example, data from amphibolite-facies rocks (samples 5–9, Fig. 6) may well reflect clockwise P–T paths featuring early higher P’s during inclusion entrapment succeeded by exhumation with heating. Regardless, for data samples 5–9 indicate higher entrapment P’s than reported peak P’s.

4.2. Olivine-in-diamond

Olivine-in-diamond from Udachnaya, Siberia kimberlites returns entrapment P’s at 1200 °C of 52–62 kbar, somewhat higher than estimated by Izraeli et al. (1999) (44–52 kbar). Izraeli et al. (1999) note the sensitivity of their calculations to thermal expansivities: extreme values for expansivity expressions at that time implied possible entrapment P’s up to 65 kbar. Thus, the present study and Izraeli et al. (1999) are mutually consistent within the context of improved compressibility and expansivity expressions over the last ~15 years. All calculated P’s are consistent with diamond stability and with thermobarometric analysis of xenoliths from the Udachnaya pipe (Ashchepkov et al., 2010; light blue field, Fig. 3B).

4.3. Coesite inclusions

Coesite spectral data illustrate how polymorphic transitions can affect P_{incl} and preclude recovery of entrapment P. Guiraud and Powell (2006) discussed this issue extensively, and the following section briefly summarizes and builds on that work (see also Van der Molen and Van Roermund, 1986). Most importantly, coesite and diamond inclusions in most orogenic UHP rocks are expected to re-equilibrate via polymorphic transition during exhumation and cooling. For example, if no re-equilibration occurred upon cooling and exhumation to the surface, a coesite inclusion entrapped in zircon at 900 °C, 40 kbar (star, Fig. 7) would show P_{incl} ~ 13 kbar and exhibit a Raman shift of ~3.8 cm^{-1} (isopleths, Fig. 7). But quartz, not coesite, is stable at 13 kbar, so thermodynamics should drive the coesite to transform to quartz, increasing volume and the pressure of the composite inclusion until P_{incl} is buffered at the coesite–quartz boundary (i.e. at P > 20 kbar, with a corresponding band shift of ~6 cm^{-1}). Obviously, sluggish kinetics would prevent this reaction at 25 °C, but in general the P–T trajectory of coesite inclusions (blue dashed line, Fig. 7) can readily cross the coesite–quartz reaction at sufficiently high T for the reaction to proceed. Note that the inclusion crosses the reaction after the host-rock because the inclusion develops a residual pressure during exhumation and cooling, and P_{incl} always exceeds the host-rock P (Guiraud and Powell, 2006). However, most rocks will cross the reaction at some elevated T. At the crossover, a small fraction of coesite transforms to quartz and buffers P_{incl} at the coesite–quartz reaction (Van der Molen and Van Roermund, 1986). This reaction will continue until slowing kinetics impedes further transformation, possibly at T < 375–400 °C (Mosenfelder and Bohlen, 1997). The inclusion then adjusts to changing external P–T conditions elastically, but as a composite, not monomineralic inclusion (see Korsakov et al., 2010). For coesite–quartz inclusions, this leads to a slight increase in P_{incl} (Fig. 7; Guiraud and Powell, 2006). A similar argument regarding diamond=graphite applies to diamond inclusions (Guiraud and Powell, 2006) and graphite-in-diamond (Zhang, 1998).

Fig. 7. Pressure vs. temperature diagram for coesite-in-zircon contoured for shift of the 521 cm^{-1} band. Solid line shows assumed host-rock P–T path from peak P–T condition of 40 kbar, 900 °C. Blue dashed line shows inclusion P–T path. At the crossover, coesite continuously transforms to quartz, and P_{incl} tracks the coesite–quartz boundary. Gray dashed line shows calculated inclusion P–T path if coesite never transformed to quartz. If reaction ceases at T < 400 °C, expansion of inclusion increases P_{incl} slightly. Red dashed line shows inclusion P–T path from entrapment conditions of 70 kbar, 900 °C, which does not intersect the coesite=quartz reaction. See Guiraud and Powell (2006) for further discussion. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Two circumstances may allow recovery of primary entrapment pressures from coesite or diamond inclusions: either rocks are quenched (e.g. during eruption of kimberlites) so insufficient time prevents the polymorphic transition from proceeding, or entrapment P’s are so high that P_{incl} always exceeds the reaction P during exhumation. For example, Raman shifts > ~6.5 cm^{-1} to the 521 cm^{-1} band of coesite would ensure that P_{incl} always exceeded the pressure of the coesite=quartz reaction (red dashed line, Fig. 7). Such large shifts are, in fact, observed for coesite inclusions in diamond (Sobolev et al., 2000): with ΔV = 8.0 to 10.5 cm^{-1}, P_{incl} even now exceeds P of the coesite=quartz reaction by 5–15 kbar. In contrast coesite inclusions in zircon from UHP orogenic terranes commonly show Raman shifts of only 4–5 cm^{-1} (Parkinson and Katayama, 1999) and may be as low as 1–2 cm^{-1} (Ye et al., 2001). Many of these supposed “monomineralic” inclusions have associated quartz (Ye et al., 2001; see also Korsakov et al., 2010), and have partially equilibrated along the coesite=quartz reaction, exactly as predicted by Guiraud and Powell (2006). Calculated P_{incl} values below the coesite=quartz reaction probably reflect plastic flow or even rupturing of the host phase.

For zircon, radiation-driven metamictization reduces its shear modulus, possibly allowing an overpressured inclusion to expand and decrease P_{incl}. Complete metamictization reduces zircon μ below ~500 kbar (e.g., Özkan, 1976; Salje, 2006), which reduces P_{incl} by ~1/3. Thus, the Raman shift in coesite for a coesite–quartz composite inclusion might gradually diminish from ~6 to ~4 cm^{-1} as radiation damage accumulates at low T and the zircon elastically relaxes around the inclusion. This process may help explain the large number of coesite inclusions in zircon that exhibit Raman shifts of ~4 cm^{-1} (Parkinson and Katayama, 1999).

4.4. Sensitivities and potential problems

Because Raman band positions of many minerals depend on composition (e.g. olivine: Kuebler et al., 2006; garnet: Mernagh and Liu, 1990), a single measurement cannot normally recover both P_{incl} and composition. Thus, either composition or pressure must be determined independently, e.g. by liberating an inclusion after
initial in situ measurement (Izraeli et al., 1999) or by also measuring exposed inclusions or matrix grains. Alternatively, analysis could be restricted to essentially pure mineral inclusions (quartz, coesite, graphite, etc.). In the case of graphite, at temperatures below 450–500°C the “1580 cm$^{-1}$” G-band position depends not only on pressure (Hanfland et al., 1989) but also on crystallinity (Beyssac et al., 2002). For example, at rock formation conditions of $T \sim 330$ °C, $P \sim 13$ kbar, the G-band position in graphite is as high as 1595 cm$^{-1}$ (Beyssac et al., 2002). Such a shift, if caused by pressure alone, would imply $P_{\text{incl}} > 30$ kbar (Hanfland et al., 1989), which far exceeds any likely pressure. Thus, graphite geobaraman-try-try is generally sensitive (e.g., Carson and Powell, 1997) and show variations in calculated uncertainties are also $\ll$ (e.g., Ashchepkov et al., 2010). In comparison, thermoba-Raman-try is currently not feasible.

Crystal shape and crystallographically-dependent differences in expansivity and compressibility in a single mineral present as yet unknown complications. Other than minerals in the cubic crystal system, different crystallographic axes show different coefficients for expansivity and compressibility (e.g., Birch, 1966; Skinner, 1966). Few minerals also conform to the spherical geometry on which elastic theory is based. Therefore, radially asymmetric pressure distributions should occur both in the inclusion and host phase. Although such gradients are observed in some host minerals (e.g., Nasdala et al., 2003), how these quantitatively affect maximum pressures within or adjacent to the inclusion is as yet unknown. Further exploration of pressure gradients and their thermobarometric impact is required.

Inclusion size matters. Large inclusions, whose radii exceed 1/3 the distance to an interface, and breached inclusions will reequilibrate towards 1 atm, precluding accurate estimation of entrapment $P$. Differently sized inclusions may confer analytical advantages, e.g. small, wholly enclosed grains of spinel or olivine could be analyzed for $P_{\text{incl}}$, whereas larger exposed grains could be used to correct for compositional dependencies to Raman band position. Extremely small inclusions may prove problematic because edge effects are documented for thin films over distances of 1–2 μm (De Wolf, 2003; see also Enami et al., 2007), causing excess positive and negative pressures in the inclusion near the host and in the host near the inclusion respectively. Either spectroscopic depth profiling (Enami et al., 2007) or analytical emphasis on larger inclusions (at least 5 μm) in thicker sections (50–100 μm) is recommended.

Uncertainties in calibrations (Tables S2–S3; Figs. 2–4) are generally acceptable in comparison with other methods. Analytical precisions for conventional thermobarometric equilibria in crustal rocks (e.g. garnet–plagioclase–kyanite–quartz) may be as low as ±100 bar and ±5°C, but compositional heterogeneities and activity model variability each commonly contribute c. ±500 bar and ±25°C additional uncertainty (Ferry, 1980; Kohn and Spear, 1991). Comparably comprehensive error propagation has not been published for mantle equilbria, but calibrations are more compositionally sensitive (e.g., Carson and Powell, 1997) and show variations in calculated $P–T$ conditions on the order of several kilobars (e.g., Ashchepkov et al., 2010). In comparison, thermoba-Raman-try uncertainties are also $\ll$ 1 kbar for crustal rocks, a few kbar for mantle rocks, and as low as a few tens of °C. Uncertainties in $\mu$ of ±50 kbar for very stiff minerals like diamond and zircon and ±10 kbar for weak minerals like hornblende propagate to errors less than ±100 bar and ±1°C in calculated entrapment $P$'s and $T$'s (Tables S2–S3), so are smaller than other sources of error. Overall, thermoba-Raman-try's main advantage is not necessarily through higher precision estimates of $P$ or $T$, but rather by expanding the range of rock types amenable to thermobarometric calculations. For example, the number of garnet-bearing samples in which garnet crystals contain quartz or graphite inclusions in the author’s research collections far exceeds the number containing a buffering barometric mineral assemblage. Point-by-point calculation of $P–T$ conditions for inclusion-rich minerals like garnet can also allow recovery of $P–T$ paths independent of phase equilibrium calculations.

4.5. Summary and future directions

In general, large differences in thermal expansivity between any host and inclusion will confer temperature sensitivity, whereas differences in compressibility will confer pressure sensitivity. Differences can be readily assessed from published compilations (e.g., Holland and Powell, 2011). For example, quartz’ high compressibility relative to numerous minerals results in a veritable plethora of barometric equilibria (Figs. 2, S1A–U). Zircon and rutile’s low expansivities and compressibilities provide additional thermobarometric potential. Over a large array of entrapment conditions, many host minerals will contract around a zircon inclusion during exhumation, creating $P–T$-sensitive overpressures (Figs. 4A–C, S1V–Y, S2A–D), whereas an inclusion in zircon will shrink, creating $P–T$-sensitive underpressures (Fig. S2E–F). Future work should address the magnitude of overpressures that can be retained without plastic flow or fracture of the host grain (e.g., Van der Molen and Van Roermund, 1986; Zhang, 1998) and the magnitude of underpressure a host–inclusion pair can maintain before grain boundaries separate. Feldspars were not explicitly modeled in this study, but their high compressibilities and low thermal expansivities may permit numerous other thermobarometers, albeit complicated by structural state transitions. Finally, the practical usefulness of thermoba-Raman-try depends crucially on accurate volume and elasticity expressions and should be tested on thermobarometrically well-characterized rocks.

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Appendix A. Supplementary material

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References


cphane, seismic velocities and anisotropy of the subducted oceanic crust. 

Tectonophysics 494, 201–210.


Brunet, F., Allan, D.R., Redfern, S.A.T., Angel, R.J., Liletich, R., Reichmann, H.J., Ser-
gent, J., Hanfland, M., 1999. Compressibility and thermal expansivity of synthetic 


Carson, C.J., Powell, R., 1997. Garnet–orthopyroxene geothermometry and geo-

barometry: error propagation and equilibrium effects. J. Metamorph. Geol. 15, 

679–686.

Chantel, J., Mookherjee, M., Frost, D.J., 2012. The elasticity of lawsonite at high pres-
sure and the origin of low velocity layers in subduction zones. Earth Sci. Plan-


orapatite with pressure. Part II: in situ micro-Raman spectroscopic investigation. 


Koziol, A.M., Newton, R.C., 1988. Redetermination of the anorthite breakdown reac-


Luisier, A.J., Cooper, M.A., Hawthorne, F.C., Kristiansen, R., 2009. Trilomic titan-

ite from the Hefftergran granitic pegmatite, Tardal, southern Norway. Mineral. 

Mag. 73, 709–722.

McKinnon, H.J., Andreath, P., 1972. Elastic moduli of diamond as a function of pres-
sure and temperature. J. Appl. Phys. 43, 2944–2948.

Menagh, T.P., Liu, L.G., 1990. Pressure dependence of Raman spectra from the gar-

net end-members pyrope, grossularite and almandite. J. Raman Spectrosc. 21, 

305–309.


Pasteris, J.D., 1989. In situ analysis in geological thin-sections by laser Raman micro-


Pattison, D.R.M., Chacko, T., Farquhar, J., McFarlane, C.R.M., 2003. Comparative Pressure-Dependent Studies of Titania (CaTiO3SiO4) and Malayaite (CaO2SiO4) ETH, Zurich, p. 106.


ing of metamict titanite CaTiSiO3: Radiation damage and annealing. Am. 

Mineral. 96, 1254–1261.


Schmidt, C., Ziemann, M.A., 2000. In situ Raman spectroscopy of quartz: A pressure sensor for hydrothermal diamond-anvil cell experiments at elevated tempera-

Schmidt, C., Steele-Macilansis, M., Waterphall, A., Wilke, M., 2013. Calibration of zir-

con as a Raman spectroscopic pressure sensor to high temperatures and applica-


Mineral. 87, 318–326.


Mineral. 77, 146–155.


Tomkins, H.S., Powell, R., Ellis, D.J., 2007. The pressure dependence of the zirconium-

in-rutile equilibration thermometer. J. Metamorph. Geol. 25, 703–713.

Van der Molen, J., 1981. The shift of the α–β transition temperature of quartz 

associated with the thermal expansion of granite at high pressure. Tectono-

physics 73, 323–342.

