



QuIB Calc: A MATLAB[®] script for geobarometry based on Raman spectroscopy and elastic modeling of quartz inclusions in garnet

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ABSTRACT

Quartz inclusion thermobarometry utilizes the pressure- and temperature-sensitive Raman peak shifts of quartz inclusions in garnet to determine formation pressure and temperature (*PT*) conditions. The measured Raman shift indicates the pressure currently retained in the inclusions at ambient external conditions, such that entrapment *PT* conditions (i.e., *P* and *T* of garnet growth) can be determined by elastic modeling. Most generally, trapping *P* is obtained with this method, based on an independent estimate of *T*. Here we describe *QuIB Calc*, a MATLAB[®] program that iteratively solves for garnet growth conditions using the pressure retained in quartz inclusions (as revealed by Raman peak shifts). The program explicitly accounts for the anomalous effects of the quartz lambda transition on the thermal expansivity, and utilizes a mixing subroutine to account for the physical properties of garnet solid solutions. *QuIB Calc* thus facilitates sophisticated *PT* calculations using quartz inclusions, and is particularly effective for geobarometry in high pressure terranes.

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1. Introduction

Determining pressure–temperature (*P*–*T*) paths in metamorphic terranes is a key focus in metamorphic, tectonic, and structural geology. Accurate estimates of *P* and *T* are fundamental to understanding the development of subduction zones and orogenic belts, including metamorphic reactions, hydrous fluid and silicate melt production, and evolution of stress distribution in rocks (e.g. [Bebout, 2007](#); [Hacker et al., 2003](#); [Tichelaar and Ruff, 1993](#)). Estimating metamorphic pressure is commonly less straightforward than determining temperature, and pressure estimates are particularly challenging for deep-crustal or subducted rocks in which plagioclase feldspar is absent (such that the pressure-dependent garnet–plagioclase equilibrium cannot be used as a barometer).

In an effort to overcome the challenges of high-pressure geobarometry, recent studies have emphasized the potential application of quartz inclusions in garnet (e.g. [Enami et al., 2007](#)), based on the pioneering work of [Rosenfeld \(1969\)](#). Continued analytical and modeling developments have thus yielded improved resolution of pressure estimates for deeply subducted rocks by utilizing Raman spectroscopic analysis ([Ashley et al., 2014](#); [Kouketsu et al., 2014](#); [Mouri and Enami, 2008](#)). Specifically, the pressure-sensitive shifts of the ν_{464} , ν_{205} and ν_{128} peak positions for quartz ([Schmidt and Ziemann, 2000](#)) reveal the

pressure retained in inclusions in garnet. An elastic model then solves for the trapping pressure during garnet growth, based on the physical properties of inclusion and host. The approach developed by [Ashley et al. \(2014\)](#) iteratively adjusts both quartz and garnet thermal expansivities

and molar volumes as pressure is sequentially increased, solving for entrapment pressure (at known or assumed temperature). This approach uses an elastic model either from [Guiraud and Powell \(2006\)](#), [Zhang \(1998\)](#), or [Van der Molen and Van Roermund \(1986\)](#), and is based on the currently preserved pressure revealed by the measured shift of the ν_{464} Raman peak. Use of other quartz peaks for determining P_{inc} were not included in the code because the 464 cm^{-1} peak has the highest intensity and is the narrowest band, making peak fitting and determining absolute position the most accurate. In addition, there is spectral overlap between Raman peaks with garnet for the 206 cm^{-1} peak of quartz, which may incorporate additional uncertainty ([Enami, 2012](#)). Volume calculations include the elastic properties of quartz and five garnet compositional end-members in the [Holland and Powell \(2011\)](#) thermodynamic database. Molar volumes calculated at elevated *P* and *T* with these data generally yield < 0.1% difference from available experimental results (e.g. [Dorogokupets, 1995](#); [Jorgensen, 1978](#); [Raz et al., 2002](#); [Thiéblot et al., 1998](#)).

The need for an iterative solution sufficiently complicates use of this simple barometer that it requires either interfacing with existing programs to separately calculate the properties of quartz and garnet as functions of *P* and *T* (e.g. *Perple_X*'s *Frendly*

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program; Connolly, 2009), or programming the appropriate data and equations of state for these calculations. To facilitate application of quartz inclusion barometry, *QuiB Calc* was developed to robustly handle the elastic modeling within a user-friendly, graphical user interface (GUI) on the MATLAB® platform.

2. Database construction

Lookup tables for the properties of quartz, almandine, pyrope, spessartine, grossular and andradite were constructed using the Holland and Powell (2011) dataset in the program *Frendly* (Connolly, 2009) in the range 1–30,000 bar and 300–800 °C (at 10 bar and 10 °C intervals). This approach was preferred over using data from various different databases to remain internally consistency. An additional profile was calculated for quartz at room temperature, because the volume of quartz at inclusion pressure is required for the elastic model. The data tables are included in the program download as tab-delimited text files that are read by *QuiB Calc*.

3. Computational approach

Running *QuiB Calc* within MATLAB opens a pop-up window (Fig. 1) from which the user can input the following data for a given quartz inclusion: (i) measured wavenumber of the Raman ν_{464} quartz peak; (ii) assumed metamorphic temperature corresponding with quartz inclusion entrapment; and (iii) approximate garnet composition near the inclusion position (in terms of the proportions of end-members). The measured wavenumber of the quartz peak is initially used in a polynomial regression equation (Ashley et al., 2014) to calculate the current inclusion pressure and uncertainty (at room temperature, with an adjustable spectral resolution).

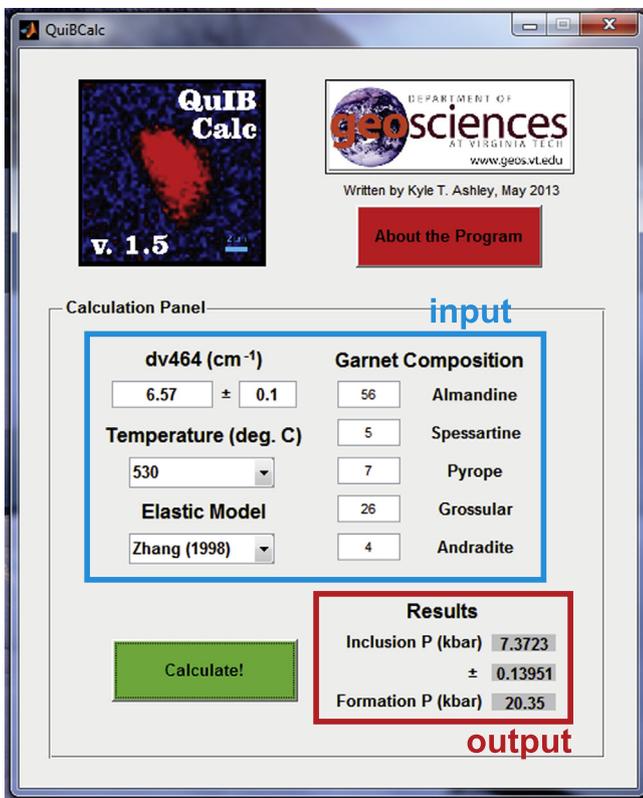


Fig. 1. Screen capture of the *QuiB Calc* program window. Input and output clusters are highlighted, with an example calculation shown.

The elastic modeling approaches used in this program may be selected via a drop-down menu. The Guiraud and Powell (2006) model requires knowledge of the volumes of quartz and garnet at room temperature and at formation conditions, and is rearranged into the following form:

$$\frac{V_{incl}(P_{incl}, 298)}{V_{incl}(P_0, T_0)} - \frac{V_h(1, 298)}{V_h(P_0, T_0)} = \frac{3}{4\mu_{grt}}(P_{incl} - 1) \quad (1)$$

where V_{incl} is the molar volume of the quartz inclusion ($\text{cm}^3 \text{mol}^{-1}$), V_h is the molar volume of the host garnet, P_0 and T_0 are pressure (bar) and temperature (K) of entrapment, respectively, P_{incl} is the current inclusion pressure (calculated by *QuiB Calc* from the wavenumber), and μ_{grt} is the shear modulus of garnet (bar). *QuiB Calc* iteratively solves the left side of Eq. (1) by adjusting P_0 at an assumed value of T_0 , until the difference between the left and right sides is minimized.

The Zhang (1998) model requires computation with the adiabatic bulk (κ) and shear (μ) moduli of quartz and garnet. Temperature dependence of the thermal expansivity (α_T) of both phases is considered by

$$\gamma = \int_{T_0}^{298 \text{ K}} \alpha_T dT \quad (2)$$

where T_0 is the temperature of inclusion formation and α_T derivations were taken from Skinner (1966, for garnet) and Dorogokupets (1995, for quartz). The elastic expression used is

$$P_{incl} = \frac{P_{ext}[(1/\kappa_{grt}) + (3/4\mu_{grt})] + P_0[(1/\kappa_{qtz}) - (1/\kappa_{grt})] + \gamma_{qtz} - \gamma_{grt}}{(1/\kappa_{qtz}) + (3/4\mu_{grt})} \quad (3)$$

where P_{incl} is the inclusion pressure (bar), P_{ext} is 1 bar, and P_0 is the formation pressure. Much like the approach taken for the Guiraud and Powell (2006) model, an iterative solution is employed, where the calculated pressure is evaluated against the input pressure until the difference between the two is minimized. The computational approach taken with the Van der Molen and Van Roermund (1986) model is identical to this, with the expression:

$$P_{incl} = \left[\frac{\kappa_{qtz}}{\kappa_{grt}(3\kappa_{qtz} + 4\mu_{grt})} \right] \left[P_{ext}(3\kappa_{grt} + 4\mu_{grt}) + P_0 4\mu_{grt} \left(\frac{\kappa_{grt}}{\kappa_{qtz}} - 1 \right) - 4\mu_{grt} \kappa_{grt} \Delta T \Delta \alpha \right] \quad (4)$$

where ΔT is room minus formation temperature (in K) and $\Delta \alpha$ is α_{grt} minus α_{qtz} at temperature and pressure (to account for the lambda transition in quartz).

Natural garnets rarely have 'end-member' compositions. Therefore a mixing subroutine is included to approximate the elastic properties of natural garnet compositions. *QuiB Calc* employs a simple ideal mixing rule, such that end-member elastic properties are combined proportionally to their relative molar abundances. Compositional differences on the order of 5–10 mol% have little effect on pressure calculations, but assuming a pure end-member host (e.g. pure grossular) can lead to significant deviations in calculated pressures (> 1 kbar) in some instances. Natural garnets do not exhibit ideal mixing between end-members (e.g. Bosenick et al., 2001), but linear scaling of thermodynamic properties in garnet solid solution is a better approximation than assuming pure end-member values. The maximum difference from linearity between the pyrope–grossular solid solution is < 0.2 cm^3/mol (Bosenick et al., 2001) – much smaller than the deviation from assuming a pure endmember (ca. 1.2 cm^3/mol).

For example, a $\Delta\nu_{464}$ of 6.57 cm^{-1} and a T estimate of 530 °C, in a garnet host of 56% almandine + 7% pyrope + 26% grossular + 5% spessartine + 4% andradite yields an estimated trapping pressure of 20.35 kbar (Zhang, 1998 model; Fig. 1) or 19.06 kbar (Guiraud and Powell, 2006 model).

A subroutine is included in the program to verify if the apparent pressure at assumed temperature is within the stability field of α -quartz. The volumetric consequences of cooling an inclusion through the β - α transition are complex and depend on the pressure at which the transition occurs, so a dialog box warns the user if the calculated formation conditions are outside of the α -quartz stability field (beyond the applicability of this program). In addition, the quartz inclusion barometry technique appears to be best suited for high- P , low- T systems (little, if any, retained inclusion pressure is expected in high- T systems). Therefore extrapolation to the β -field is not warranted.

4. Conclusions

The MATLAB[®] program *QuIB Calc* calculates pressures of quartz inclusion entrapment in a garnet host, through iterative solution of elastic properties, based on the measured position of the ν_{464} Raman peak of quartz. It provides an easy-to-use interface that requires little prior knowledge of the MATLAB[®] language, facilitating straightforward and robust pressure calculations and obviating the need to separately compute elastic parameters or volumes using other programs. The program is available for download at <http://www.metamorphism.geos.vt.edu/Resources.html>.

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Appendix. Supplementary material

Supplementary data associated with this article can be found in the online version at <http://dx.doi.org/10.1016/j.cageo.2014.01.005>.

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