COMPRESSIBILITY AND THERMAL EXPANSION OF GARNETS WITH COMPOSITIONS TYPICAL OF INCLUSIONS IN DIAMONDS

Ph.D. candidate: Sula MILANI, III course
Tutor: Prof. Fabrizio NESTOLA
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Abstract
Garnet is the most abundant inclusion found in diamonds and is one of the most important minerals of the Earth’s upper mantle. In order to obtain the depth of formation of diamond-inclusion pairs, precise and accurate thermoelastic parameters are necessary. For this reason, the bulk modulus and thermal expansion of a series of garnets with compositions similar to those found in diamonds were determined by in-situ high-pressure X-ray diffraction with a diamond anvil cell device and in-situ high-temperature X-ray diffraction by means of a microfurnace. We have determined the isothermal equation of state and thermal equation of state of a synthetic single-crystal of pyrope, as well as the isothermal equations of state of synthetic single crystals of almandine, pyrope-almandine solid solution, grossular, and uvarovite. The obtained thermoelastic parameters were used to calculate the entrapment pressures (P_e) for garnet inclusions in diamonds at mantle temperatures.

Introduction
Most of the diamonds formed in the sub-cratonic lithospheric mantle, in the so called ‘diamond window’ (Fig. 1; Stachel and Harris, 2008) but only 1% of these diamonds have mineral phases entrapped as inclusions (Stachel and Harris, 2008). Although inclusion-bearing diamonds are so rare, they are geologically important, because they are the only direct and unaltered samples that we have from the Earth’s mantle. For this reason the determination of their pressure of formation (i.e. depth of provenance) is important to better constrain the chemico-physical environment in which they formed. The pressure of formation can be estimated by two different methods. The traditional method is based on the cation partitioning between mantle minerals (i.e. geothermobarometry). However, this method can only be applied to rare cases: only when the appropriate set of mineral assemblages is present in the same inclusion within a diamond. An alternative method has been developed (e.g. Angel et al., 2014a, 2014b), which is based on the residual pressure (P_inc) of the inclusion still trapped in the diamond at room temperature and pressure. This residual pressure arises from the different elastic properties (expansivity and compressibility) of the diamond host and the inclusion, regardless the P-T-t path taken during the exhumation. This method can potentially be applied to any single mineral inclusion, but requires accurate knowledge of the thermoelastic parameters of the diamond host and inclusion and a precise determination of P_inc.

Fig 1. - Schematic vertical section of the Earth’s crust and part of the upper mantle (after Stachel and Harris, 2008).
The thermoelastic parameters of the diamond are determined to a precision that yields insignificant uncertainties in calculated entrapment pressures ($P_e$) (Angel et al., 2014a). Garnets, together with olivines, are the most abundant minerals found as inclusions in diamonds. More than 60% of garnet inclusions are peridotitic, composed by more than 90% of pyrope-almandine components, with minor grossular, uvarovite, and andradite (Stachel and Harris, 2008). However, the published data for the $P$-$V$ and $T$-$V$ Equations of State (EoS) of garnets are widely scattered. The uncertainties that arise from using the published data yield considerable uncertainties in the calculated entrapment pressures. Therefore, in order to avoid inconsistency issues arising from the use of different datasets we have measured the $P$-$V$ EoS for three compositions along the pyrope-almandine solid solution ($\text{Py}_{100}$, $\text{Py}_{60}\text{Al}_{40}$, and $\text{Al}_{100}$) and $T$-$V$ EoS for a synthetic pure pyrope by in-situ high-pressure and high-temperature single-crystal X-ray diffraction. The set of elastic coefficients obtained are therefore intrinsically internally consistent one to another and can provide a fundamental reference to estimate the compositional effect on the elastic properties and, in turn, on the entrapment pressures for pyrope-almandine-rich garnet inclusions still trapped in diamonds.

**Experimental methods**

*a) In-situ high-pressure experiments*

During three years of PhD project the Equations of State (Eos) of a synthetic single crystal of pure almandine, a $\text{Py}_{60}\text{-Al}_{40}$ solid solution, pyrope, grossular, and uvarovite were determined. High-pressure single-crystal X-ray diffraction experiment for the grossular garnet was carried out with a Huber four-circle diffractometer at the Bayerisches Geoinstitut, while the high-pressure single-crystal X-ray diffraction experiments for the other samples were carried out with a STOE STADI-IV four-circle diffractometer at the Department of Geosciences, University of Padova. Both the diffractometers were working with MoKα operating at 50 kV and 40 mA equipped with a point detector and controlled by the software SINGLE (Angel and Finger, 2011). During the centering procedure, the effect of crystal offsets and diffractometer aberration were eliminated from refined peak positions by eight-position centering method (Angel et al., 2000; King and Finger, 1979). All the crystals were loaded in an ETH-type Diamond Anvil Cell (DAC; Miletich et al., 2000), using a steel gasket, preindentented to a thickness of 100 μm and with a 300 μm – diameter hole. As an internal pressure standard a crystal of quartz was used (Angel et al., 1997) and as pressure transmitting medium a mixture 4:1 methanol-ethanol was used (such mixture transmits hydrostatically the pressure to maximum 10 GPa, Angel et al., 2007). Unit-cell parameters were determined at different pressure steps up to a maximum pressure of ca. 8.5 GPa. As can be observed in Fig. 2a, 2b it was not necessary to measure other intermediate almandine-pyrope solid solution, because both the bulk modulus and the unit-cell volume are linearly correlated.

![Fig. 2](image-url) – Diagrams showing the linear correlation between (a) composition (mol% of pyrope) and bulk-modulus and (b) composition and unit-cell volume. The error bars in (b) are smaller than the symbol size.

*b) In-situ high-temperature experiment*
The high-temperature single-crystal X-ray diffraction experiment was performed with a Philips PW1100 operating with a MoKα radiation at 50 kV and 30 mA controlled by the FEBO software (control software developed locally) equipped with a micro-furnace, which is controlled by an Eurotherm unit. The crystal was mounted inside a quartz vial (0.3 mm inner diameter and 26 mm long) and was held in place by means of quartz wool. The micro-furnace was placed on top of the goniometer head. The micro-furnace device and the calibration procedure are described in Pandolfo et al. (2014). Diffraction data have been collected up to $\theta_{\text{max}} = 34^\circ$ and $T_{\text{max}} = 1073 K$.

The unit-cell parameters were determined upon heating from 291 K to 1073 K with steps of 25 K and during cooling with steps of 50 K, in order to ensure the reproducibility of the data. At each temperature step the unit-cell parameters were calculated by least-square fitting on a group of 60 selected reflections following the LAT procedure (see Pandolfo et al., 2014 for further details). Diffraction peak profiles have been collected for each temperature step on the same set of reflections to constantly monitor the quality of the crystal.

c) Syntheses

During the second year several syntheses were carried out at the Bayerisches Geoinstitut (BGI), University of Bayreuth, Bayreuth, Germany, worldwide famous laboratory for High-Pressure experiments. In this laboratory I tried to synthesize uvarovite and grossular garnets and some solid solutions (Gr$_{50}$-Uv$_{50}$, Gr$_{75}$-Uv$_{25}$). Synthesizing single crystals of garnets is very challenging, for this reason more than one experiment have been done in order to find the optimal conditions (e.g. starting compositions, pressure, temperature, temperature path) for the syntheses.

All the experiments were done using a Multi-Anvil apparatus reaching the pressure of 6 GPa and temperatures in the range 1200–1300°C. The syntheses were done using an 18/11 assembly (Keppler and Frost, 2005), with two platinum capsules and a graphite heater. The temperature was measured during the experiments by a type D thermocouple.

The starting materials used were different stoichiometric composition of SiO$_2$, CaO, Cr$_2$O$_3$ and Al(OH)$_3$ oxides intimately grinded in an agate mortar for ca 1 hour under ethanol. In order to decrease the melting point of the oxides mixture and enhance the crystal growth water was used as a flux. For what concern the grossular garnets and the solid solutions the water used was given by the Al(OH)$_3$ component, while for the uvarovite garnets 2–3 μl of molecular water was added before closing the sample capsules.

Results and discussion

a) High-pressure experiments

The estimation for the best equation of state for the measured P-V data of the samples was made on the basis of the F$_{E}$-f$_{E}$ plot. These F$_{E}$-f$_{E}$ plot show that the data fit on a positively inclined straight line, indicating that the Birch-Murnaghan EoS, truncated at the third-order (Birch, 1947), gives the best fit of the data (Fig. 3a, b). The determination of all the EoS parameters was made using the software EoSFit7c (Angel et al., 2014c) that permit to refine simultaneously all the parameters of the equations. Comparing the data obtained for the pyrope with the data obtained for the almandine and the Al$_{40}$Py$_{60}$ solid solution (Fig. 4) we observe that the values for the volume and the isothermal bulk moduli decrease with increasing the pyrope content, thus the Mg$^{2+}$ content in the garnet. This means that the pyrope is more compressible than the almandine; the reason for this behavior is not yet well understood but a possible explanation could be the size of the cation Mg$^{2+}$, that it is too small for the big garnet dodecahedral site, allowing a larger compression.

b) High-temperature experiment

The Py$_{100}$ temperature-volume data have been fitted using EoSFit7c (Angel et al, 2014c) to a Fei-type EoS (Fei, 1995). The thermal expansion coefficients obtained are: $a_0 = 3.01(19) \times 10^{-5}$ K$^{-1}$, $a_1 = 5(20) \times 10^{-10}$ K$^{-2}$, $a_2 = -0.5(2)$ K, and $V_0 = 1504.63(8)$ from which $a_{300K, 1bar}$ is $2.5(2) \times 10^{-5}$ K$^{-1}$ (Fig. 4). The comparison between the unit-cell volume calculated from the fitting coefficient and the actual experimentally measured unit-cell volume in the high temperature regime $\delta V$, and statistical parameters from the

3
fitting, see Pandolfo et al., 2014] clearly confirmed that the used fitting equation is reliable within the whole temperature range.

![Graph A](image1.png) ![Graph B](image2.png)

**Fig. 3** – Third order Birch-Murnaghan EoS of a) almandine, pyrope, and of Al$_4$Py$_{60}$ and b) grossular and uvarovite.

Conclusions

Generally, garnets included in peridotitic diamonds have an average pyrope component of ca. 84% if the diamond is of harzburgitic origin (with ca. 11% of almandine) and ca. 73% if the diamond is of lherzolitic origin (with ca. 13% of almandine) (see Stachel and Harris, 2008 for a general review). Therefore, it is reasonable to expect that the high pyrope contents in peridotitic garnets will strongly control the calculated entrapment pressures ($P_e$).

The analysis of the shifts in the entrapment pressures caused by both the uncertainties in the EoS parameters and the data scatter clearly demonstrate that our methodology would be precise enough to guarantee reliable estimates of the $P_e$ with uncertainties smaller than 0.2 GPa. However with the current data scatter present in literature it is not possible to obtain results with an

![Graph C](image3.png)

**Fig. 4** - Temperature-volume data for pure pyrope compared with literature data from Skinner (1956) and Thieblot et al. (1998). The solid, dashed, and dotted lines are the Fei-type EoS fit to the data. The error bars are smaller than symbol size.

![Graph D](image4.png)

**Fig. 5** - $P_e$ calculated for any given Al-Py garnet inclusion in diamond assuming $P_{inc} = 0.5$ GPa and 1500 K, where the latter is the average temperature reported for lithospheric diamonds (Stachel and Harris, 2008).
accuracy better than 0.6 GPa. Since the shifts on the $P_e$ produced by the lack of accuracy are far smaller than those caused by changes in composition (i.e. Py-Al contents), with our method we can determine at least the entrapment pressures along the Py-Al join with uncertainties smaller than 3% (Fig. 5).

References

ANGEL, R.J. et al. (2014b). American Mineralogist, in press.
ANGEL, R.J. et al. (2014c). Z. Krist., 229, 405-419

SUMMARY OF ACTIVITIES

I have spent 3 months at the Institut fur Mineralogie (April 2012 – June 2012) at the Westfaelische Wilhelms-Universitaet, Muenster, Germany and 7 months (1st August 2013 – 31st January 2014) at the Bayerisches Geoinstitut (Bayreuth, Germany).

Courses:

Teaching activities:

Communications:

MILANI S., ALVARO M., NESTOLA F. 2014. Diamond-garnet geobarometry using isomekes: the role of garnet compressibility and thermal expansion. 90th SIMP meeting, September 10-12, Milano, Italy.

Publications: