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A REE-in-garnet–clinopyroxene thermobarometer for eclogites, granulites and garnet peridotites

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ABSTRACT

A REE-in-garnet–clinopyroxene thermobarometer for eclogites, granulites, and garnet peridotites has been developed on the basis of the temperature, pressure and mineral composition dependent partitioning of rare earth elements (REEs) between garnet and clinopyroxene. This new thermobarometer is derived from the garnet–clinopyroxene REE partitioning model of Sun and Liang (2014) that was calibrated against experimentally determined garnet-melt and clinopyroxene–melt partitioning data. It makes use of a group of trace elements that have similar geochemical behaviors at magmatic and subsolidus conditions, and allows one to invert temperature and pressure simultaneously using a least squares method. Application of the REE-in-garnet–clinopyroxene thermobarometer to REE partitioning data from laboratory experiments and field samples (quartz-bearing, graphite-bearing, and diamond-bearing granulites and eclogites; and well-equilibrated mantle eclogite xenoliths) published in the literature validates its reliability at both magmatic and subsolidus conditions. Application of the new thermobarometer to eclogites, garnet granulites and peridotites from various tectonic settings reveals an intriguing observation: temperatures derived from the REE-based thermobarometer are consistently higher than those derived from the widely used Fe–Mg thermometer of Krogh (1988) for samples that experienced cooling, but systematically lower than temperatures derived from the Fe–Mg thermometer for samples from thermally perturbed tectonic settings. The temperature discrepancies are likely due to the relative differences in diffusion rates between trivalent REEs and divalent Fe–Mg in garnet and clinopyroxene. Temperatures derived from the REE-based thermometer are closely related to closure temperatures for samples that experienced cooling, but are likely equilibrium or apparent re-equilibration temperatures at an early stage of heating for samples from thermally perturbed tectonic environments. The REE-in-garnet–clinopyroxene thermobarometer can shed new light on thermal histories of mafic and ultramafic rocks.

1. Introduction

The exchange of Fe–Mg between garnet and clinopyroxene has been successfully calibrated as thermometers that can be used to determine equilibrium temperatures of eclogites, garnet peridotites, and garnet pyroxenites (e.g., Råheim and Green, 1974; Ellis and Green, 1979; Ganguly, 1979; Saxena, 1979; Powell, 1985; Krogh, 1988; Ai, 1994; Ravna, 2000; Nakamura, 2009). However, all these thermometers require independent estimates of pressures, which usually need additional phases to constrain (e.g., the garnet–orthopyroxene barometer; Brey et al., 2008). Since a significant fraction of mantle eclogites is bi-mineralic, a reliable garnet–clinopyroxene barometer is a prerequisite for a better constraint of their equilibrium pressures and temperatures. Attempts have been made to calibrate garnet–clinopyroxene barometers through thermodynamic analysis of experimental data (e.g., Brey et al., 1986; Mukhopadhyay, 1991; Simakov and Taylor, 2000; Simakov, 2008), yet these barometers are still not as reliable as the garnet–orthopyroxene barometers (see Fig. 2 in Nimis and Grütter, 2010). Hence, the equilibrium temperatures of bi-mineralic eclogites are often calculated using the garnet–clinopyroxene thermometers at an assumed pressure. Because the garnet–clinopyroxene thermometers are all pressure dependent, temperature estimations can differ by up to 150 °C if the assumed pressure is off by 2 GPa. This is illustrated in Fig. 1. Assuming that the eclogites approach chemical equilibrium at a temperature and pressure along the local geotherm, one can estimate the equilibrium pressure and temperature by coupling the local geotherm with the garnet–clinopyroxene thermometers (e.g., Griffin and O'Reilly, 2007). However, the pressure along the local geotherm derived from garnet peridotite xenoliths can vary by ±1 GPa at a given temperature (Griffin et al., 2003). Thus, uncertainties in the temperature estimations are still significant.

Another important source of uncertainties in the garnet–clinopyroxene thermometers is the presence of Fe^{3+} in garnet and clinopyroxene. Given the reducing conditions imposed by graphite capsules in phase equilibrium experiments, Fe^{3+} abundances in the minerals are likely very small and thus total Fe is used to represent Fe^{2+} in the

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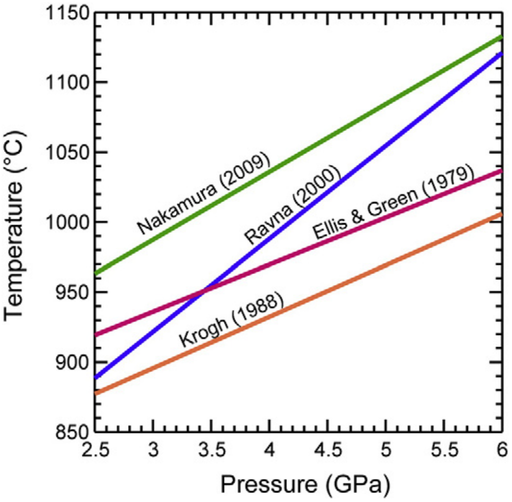

Fig. 1. Temperature variations as function of pressure derived from different garnet–clinopyroxene Fe–Mg thermometers. Major element compositions of garnet and clinopyroxene are from Huang et al. (2012; sample RV07-12).

calibration of the garnet–clinopyroxene thermometers. However, a significant amount of Fe^{3+} may be present in natural minerals. This may result in large errors (>200 °C) in temperature estimations using the garnet–clinopyroxene Fe–Mg thermometers (e.g., Ravna and Paquin, 2003). Recently, Matjuschkin et al. (2014) experimentally examined the Fe^{3+} effect on the Fe–Mg exchange thermometers at 1100–1400 °C and 5 GPa. Although they observed substantial amounts of Fe^{3+} in their experiments ($Fe^{3+}/\sum Fe = 0.116$–0.206 in garnet), the temperatures calculated using the garnet–clinopyroxene thermometer of Krogh (1988) are within 25 °C of the experimental temperatures, except that for one experiment conducted at 1400 °C ($Fe^{3+}/\sum Fe = 0.199$ in garnet). Consequently, these authors suggested that the garnet–clinopyroxene Fe–Mg thermometers are insensitive to the presence of Fe^{3+}, which contradicts the study of Ravna and Paquin (2003) on natural eclogite samples. Clearly, detailed experimental and field studies are needed to further address the Fe^{3+} problem.

In this study, we present a new garnet–clinopyroxene thermobarometer that is based on the exchange of rare earth elements (REEs) between garnet and clinopyroxene. The distribution of trace elements between minerals depends on temperature, pressure, and mineral major element compositions and can be calibrated as thermometers (e.g., Stosch, 1982; Seitz et al., 1999; Witt-Eickschen and O'Neill, 2005; Lee et al., 2007; Liang et al., 2013; Sun and Liang, 2014). Based on the temperature-dependent REE partitioning between orthopyroxene and clinopyroxene, Liang et al. (2013) developed a REE-in-two-pyroxene thermometer by combining the clinopyroxene–melt and orthopyroxene–melt REE partitioning models (Sun and Liang, 2012; Yao et al., 2012). This thermometer treats REEs as a group in temperature calculation, which helps to reduce analytical uncertainties. Through numerical simulations, Yao and Liang (in revision) showed that the temperatures calculated by the REE-in-two-pyroxene thermometer are the closure temperature of REEs in cooling two-pyroxene systems. Because diffusion coefficients of REEs in pyroxenes are about two to three orders of magnitude smaller than those of divalent cations (e.g., Ca^{2+}, Mg^{2+}, Fe^{2+}) in pyroxenes (Cherniak and Dimanov, 2010 and references therein), the REE-based thermometers can record higher closure temperatures of mafic and ultramafic rocks that experienced cooling.

We have recently developed a parameterized lattice strain model for REE partitioning between garnet and clinopyroxene (Sun and Liang, 2014). The lattice strain parameters in the models were calibrated by experimentally determined mineral–melt partitioning data. We showed that REE partitioning between garnet and clinopyroxene is very sensitive to temperature and pressure as well as mineral major element composition. Specifically, garnet–clinopyroxene REE partition coefficients decrease by up to two orders of magnitude as temperature decreases from 1300 °C to 700 °C, whereas they increase by about one order of magnitude as pressure decreases from 14 GPa to 2 GPa [see Figs. 4c–d in Sun and Liang (2014)]. Here we expand the idea of the REE-in-two-pyroxene thermometer to garnet–clinopyroxene systems and develop a REE-in-garnet–clinopyroxene thermobarometer using the garnet–clinopyroxene REE partitioning model in Sun and Liang (2014). This new thermobarometer enables us to obtain the equilibrium or closure temperature and pressure simultaneously by analyzing REEs and major elements in coexisting garnet and clinopyroxene, and shed new light on thermal histories of mafic and ultramafic rocks.

2. Developing a REE-in-garnet–clinopyroxene thermobarometer

2.1. Theoretical basis

In general, thermometers or barometers are based on the temperature- or pressure-sensitive exchange of elements (or components) of interest between two coexisting minerals. The exchange coefficient (or partition coefficient), D, can be described by the thermodynamic expression

$$\ln D = \frac{\Delta S}{R} - \frac{\Delta H + P\Delta V}{RT} - \ln\gamma_R, \tag{1}$$

where ΔS, ΔH and ΔV are the changes of entropy, enthalpy and volume of the exchange reaction, respectively; R is the gas constant; T is the temperature; P is the pressure; and γ_R represents the ratio of the activity coefficients of the element (or component) in the two minerals. Eq. (1) can also be written in a general form as

$$\ln D = A + \frac{B - f(P)}{T}, \tag{2}$$

where A and B are coefficients that depend on mineral major element compositions; $f(P)$ is a function of pressure. When the volume change of the exchange reaction is independent of pressure, $f(P)$ takes on the simple expression $C \times P$ in which C is a coefficient independent of pressure. From Eq. (2), we can obtain generalized equations for thermometers and/or barometers:

$$T = \frac{B - C \times P}{\ln D - A}, \tag{3}$$

$$P = -\frac{1}{C}[T(\ln D - A) - B]. \tag{4}$$

The temperature-, pressure-, and composition-dependent partitioning of trace elements between a pair of minerals also takes the simple form of Eq. (2) (e.g., Stosch, 1982; Seitz et al., 1999; Witt-Eickschen and O'Neill, 2005; Lee et al., 2007; Liang et al., 2013). Similar to Eq. (3a) in Liang et al. (2013), we rearrange Eq. (2) in a linear form for a group of geochemically similar elements, such as REEs,

$$B_i = T(\ln D_i - A_i) + f(P), \tag{5}$$

where i is an element in the group. If the partitioning of a group of trace elements is sensitive to both temperature and pressure, we can use Eq. (5) to determine the temperature and pressure simultaneously. In a plot of ($\ln D_i$–A_i) vs. B_i for REEs, Eq. (5) defines a line passing through all REEs in a well-equilibrated sample. The slope of this line is the equilibrium or closure temperature, and the intercept can be used to calculate the pressure.