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Garnet compositions as recorders of P-T-t history of metamorphic rocks

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ABSTRACT

On the basis of tests made in recent studies, we conclude that the simultaneous solutions of the equilibrium conditions of garnet-biotite Fe–Mg exchange and Grs = Plag + Aluminosilicate + Qtz (GASP) reactions, as formulated on the basis selected experimental data and well constrained thermodynamic mixing properties of garnet and plagioclase, offer robust estimates of *P*–*T* conditions of metapelitic assemblages that consist of the above minerals. Additional calculations are presented to show the compatibility of the retrieved *P*–*T* conditions of natural assemblages with the aluminosilicate phase diagram. We also calculate the minimum grain sizes of garnets that should be used for the calculation of the peak metamorphic *P*–*T* (*P*_p, *T*_p) conditions, using reasonable initial guessed values of minimum cooling rate and maximum *T*_p. To retrieve the thermal history of metapelites, we have developed a finite difference scheme for modeling multicomponent diffusion profiles in garnet, incorporating provisions for continuous nucleation and growth. This has been interlinked with a genetic algorithm that permits retrieval of the temperature vs. time path of metapelites through modeling of the zoning profiles in garnets, keeping several model parameters as floating variables. The numerical code has been applied to retrieve the *T*–*t* history of the low pressure–high temperature Royke metamorphic belt, Japan, by modeling the concentration profiles of Fe, Mn, Mg and Ca of garnets of different sizes that have been inferred to have developed by a process of continuous nucleation and growth.

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1. Introduction

Retrieval of pressure-temperature-time (P-T-t) history of metamorphic rocks and the constraints that it imposes in the reconstruction of the tectono-metamorphic evolution of rocks in different tectonic regimes have been among the central themes of metamorphic petrology for a long time. Major efforts have thus been made, through systematic integration of experimental studies with thermodynamic and diffusion kinetic theories, towards the retrieval of the P-T-t records that are preserved in the compositional properties of minerals. Garnet has proved to be the single most important mineral from this perspective as it is stable over a wide range of metamorphic P-T conditions and shows compositional response to the change of such condition, but without achieving complete equilibrium. Garnets in metamorphic rocks commonly show compositional zoning that preserve temporal records of the *P*–*T* history of the host rocks, which could be retrieved if the diffusion kinetic data of the major divalent cations are available. Thus, there has been major effort over nearly the past 25 years to determine the diffusion kinetic parameters of the divalent cations in garnet (Loomis et al., 1985; Elphick et al., 1985; Chakraborty and Ganguly, 1991, 1992; Ganguly et al., 1998; Freer and Edwards, 1999; Carlson, 2006; Vielzeuf et al., 2007; Perchuk et al., 2009). On the other hand, because garnet is stable over a wide range of metamorphic conditions, there are more thermobarometric formulations that are based on the equilibrium compositions of garnet and coexisting minerals than involving any other mineral group (e.g. Ganguly and Saxena, 1987).

The purpose of this paper is to (a) discuss thermobarometric methods for metapelitic assemblages involving garnet, and (b) present a new modeling protocol linked to a genetic algorithm that permits simulation of compositional zoning of major divalent cations in metapelitic garnets of different sizes to retrieve both pro- and retro-grade temperature– time paths.

2. Thermobarmetry using garnet compositions

2.1. Formulations

Thermobarometric formulations require well constrained experimental phase equilibrium data on simplified model systems or thermodynamic properties of end-member phases together with activity composition (a–X) relations of the phases involved. Conventional thermobarometry involves use of selected cation exchange and breakdown equilibria in anhydrous (or volatile free) systems, and retrieval of the peak metamorphic P–T condition of the host rock from the point or domain of intersection(s) of these equilibria in the P–Tspace. An alternative method is to use a number of equilibria or all possible equilibria within a given mineral assemblage and find the statistically optimal P–T condition that best satisfies the equilibria. The

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latter method, commonly referred to as the "average P-T method", is due to Powell and Holland (1994), and has been used extensively in metamorphic petrology literature. Gaides et al. (2008a) have developed a software package, THERIA_G, which permits one to numerically compute garnet compositional profiles along a proposed P-T-t path and thus, in principle, could be used to infer thermobarometric and temporal conditions of evolution of metapelites by comparison with the observed compositional profiles of garnet.

The "average *P*–*T* method" and the THERIA_G software package represent important advancements towards constraining P-T evolution of metamorphic rocks, but these also require much more data, especially reliable *a*–*X* relations of minerals that are often complex solid solutions, than the conventional thermobarometric methods that use a limited number of equilibria. The main distinction between the "average P-Tmethod" and conventional thermo-barometry lies in the scope of the number of equilibria that are utilized for P-T calculations. However, as remarked by Dasgupta et al. (2004), there is considerable gap in our knowledge of thermodynamic mixing properties of minerals to make the "average *P*–*T* method" a robust approach at the current state for the determination of the *P*-*T* condition of many metamorphic assemblages. Additionally, as pointed out by them, if devolatilization equilibria are used in the calculation of P-T conditions, then it is necessary to have a priori knowledge of the fluid composition, a requirement that is very difficult to satisfy.

Dasgupta et al. (2004, 2009) have tested the results from the "average P-T method" against independent phase equilibrium and observational constraints for the metamorphic rocks in the Sikkim Himalayas, and found that it gives erroneous results for some bulk compositions and mineral assemblages. Gaides et al. (2008b) also carried out comparisons of the predicted mineral assemblages, which form along P-T paths that are required for the successful forward modeling of garnet compositional profiles, with the observed mineralogy. They noted several mismatches between the predicted and observed mineralogies and remarked on the problem with the thermodynamic database as a possible explanation for the discrepancies.

It was found that in contrast to the results from the "average P-Tmethod", a software package of conventional thermobarometric formulations developed by J. Ganguly and W. Cheng (ftp://ftp.geo. arizona.edu/pub/ganguly/P-T_Calc/), which, for metapelites, rely on the simultaneous solution of garnet-biotite Fe-Mg exchange equilibrium and $Grs = Al_2SiO_5 + Plag + Qtz$ equilibrium (acronym GASP), yield *P*-*T* estimates for the Himalayan rocks in Sikkim that are in very good agreement with the independent constraints (Dasgupta et al., 2004, 2009). The data utilized in this package are the well reversed experimental data of Ferry and Spear (1978) for Fe-Mg exchange between garnet and biotite and Koziol and Newton (1989) for GASP, along with the garnet solution property of Ganguly et al. (1996), the mutually compatible biotite solution property therein, and plagioclase solution property by Elkins and Grove (1990). Holdaway (2004) has also presented formulations for the garnet-biotite and GASP equilibria, but we are unable to comment at this stage if these formulations work as well as or better than the Ganguly–Cheng formulation.

In this study, we have carried out additional tests to check the validity of the Ganguly–Cheng formulations of Grt–Bt and GASP equilibria by calculating the *P*–*T* conditions of a large number of mineral assemblages containing garnet, aluminosilicate, plagioclase, biotite and quartz. The results are illustrated in Fig. 1 and compared with the stability fields of the aluminosilicate polymorphs, as determined by Holdaway and Mukhopadhyay (1993). These assemblages were used earlier by Ganguly and Saxena (1984) to test the validity of their garnet solution model and Grt–Bt plus GASP thermobarometric formulations. The compositional data of all but the Mt. Moosilauke assemblage (Hodges and Spear, 1982a,b) have been summarized by Newton and Haselton (1981). On the basis of the distribution of the aluminosilicate polymorphs, Hodges and Spear (1982a,b) concluded that the *P*–*T*

Fig. 1. Simultaneous solutions of pressure and temperature from the equilibrium conditions of garnet–biotite Fe–Mg exchange and garnet = plagioclase + aluminosilicate + quartz (GASP) reaction in metapelitic assemblages from different localities, as indicated in the figure. The filled and open symbols indicate presence of only kyanite and only sillimanite, respectively, whereas the stars indicate assemblages that have been independently inferred by Hodges and Spear (1982a,b) to have formed near the aluminosilicate triple point. The aluminosilcate phase diagram is from Holdaway and Mukhopadhyay (1993). All data except those indicated by stars are from Newton and Haselton (1981).

condition of the Mt. Moosilauke assemblages should be near the aluminosilcate triple point. The calculated *P*–*T* conditions (star symbols) satisfy this requirement. Furthermore, except for one, the *P*–*T* conditions calculated for all samples satisfy the constraints imposed by the nature of the aluminosilicate polymorphs in these assemblages.

2.2. Selection of composition in zoned garnets and resetting of garnet composition during cooling

Metapelitic garnets are almost invariably zoned. The selection of composition within a zoned garnet crystal that effectively represents the peak metamorphic composition, and the compositions of biotite and plagioclase grains that could be used in conjunction with the selected garnet composition to retrieve the peak metamorphic *P*–*T* condition is a tricky issue. The problem has been discussed in detail by Ganguly et al. (2000) and Dasgupta et al. (2004, 2009). Regardless of what formulation or approach is issued to retrieve peak *P*–*T* condition, it is imperative that one follows a well justifiable scheme, within the framework of diffusion kinetic analysis, for choosing equilibrium compositions of garnet and coexisting mineral phases that reflect peak *P*–*T* condition.

If compositional zoning of garnet was only due to its growth up to the peak temperature and had not been significantly modified by diffusion, then the rim composition of garnet reflects its peak metamorphic composition. This is usually the case for rocks in the garnet grade and lower amphibolite facies conditions. For garnets subjected to granulite facies metamorphism, the compositional profiles often show flat core compositions along with zoning near the rim. This is due to the homogenization of growth zoning at the relatively higher temperature of granulite facies metamorphism and development of retro-grade zoning near the rim as a result of partial re-equilibration with the coexisting phases in response to changing P-T condition. In these cases, use of rim compositions of garnet for thermobarometric purpose would yield P-T conditions at which diffusion effectively ceased in the garnet grains. These diffusion closure temperatures tend to be ~500 °C or even lower.

For garnet grains in granulite facies assemblages with the above characteristics, one needs to choose core compositions of large enough grains that could be expected to have preserved the peak metamorphic compositions, considering diffusive readjustments during cooling. If the



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