Strontium isotope zoning in garnets: Implications for metamorphic matrix equilibration, geochronology, and phase equilibrium modelling

J. SOUSA, M. J. KOHN, M. D. SCHMITZ, C.J. NORTHRUP AND F. S. SPEAR

APPENDIX S1: Sample descriptions

K93-1s
Sample K93-1s (Fig. S1) was originally collected from a similar horizon as garnet analyzed by Christensen *et al*. (1989) within the Ottauquechee Formation at the Townshend Dam spillway, on the western flank of the Athens Dome in SE Vermont. Peak metamorphic conditions were 550-600°C and 8-9 kbar (Kohn & Spear, 1990; Kohn & Valley, 1994). This sample was previously characterized petrologically and for oxygen isotope zoning (Kohn & Valley, 1994). Garnet from this rock grew during an increase in temperature of 60°C. Changes in pressure were calculated from rocks within a different horizon in the same outcrop and showed an increase of 1-1.7 kbar during garnet growth. Peak metamorphism occurred at approximately 380 Ma (see summary of Kohn & Valley, 1994). Oxygen isotope zoning is consistent with closed system behaviour, i.e. there is no evidence for fluid infiltration or exchange with isotopically disparate neighbouring rocks. The garnet in this rock is ~25 x 50 mm, and was sampled across its inclusion poor, smaller dimension. The matrix assemblage in this rock includes fine-grained muscovite + paragonite + chlorite + plagioclase + quartz.

D84-1a
Sample D84-1a (Fig. S1) was collected from the Littleton Formation within the Big Staurolite Nappe of the Bronson Hill Anticlinorium in west central New Hampshire. Sample D84-1a is from the same outcrop and otherwise lithologically identical to sample D84-1c, whose petrology and *P-T* evolution were characterized by Kohn *et al*. (1992). The calculated *P-T* path for D84-1c shows initial heating of about 5°C and decrease in pressure of 0.2 kbar, followed by nearly isothermal loading of 1.3 kbar. Based on textural and regional structural correlations, garnet from the Big Staurolite Nappe was originally thought to have grown between 380±5 and 407±5 Ma (see summary of Kohn *et al*., 1992), but monazite grains in garnet rims from nearby rocks at the same structural level are c. 320 Ma (Spear *et al*., 2008).

The garnet chosen for analysis had a diameter of about ~ 9 mm. This sample was sheared and rotated with quartz trails throughout the garnet. These inclusions were not removed assuming quartz would not affect the measured isotopic composition of the garnet. The major silicate assemblage of the matrix is biotite + muscovite + chlorite + plagioclase + quartz. Unpublished oxygen isotope data are consistent with closed system behaviour.

K92-9i
Sample K92-9i (Fig. S1) was collected from the Waits River Formation in the Strafford Dome in east central Vermont. Menard & Spear (1993, 1994) determined *P-T* paths for several samples throughout the Strafford Dome. Sample K92-9i was not among those analyzed, but the *P-T* paths derived for their sample TM534 at the same

metamorphic grade shows nearly isobaric heating of 50°C. The timing of peak metamorphism for rocks of the Strafford Dome is believed to be similar to that of sample K93-1s (*c*. 380 Ma) because they are both located in analogous structures in eastern Vermont, although Wing *et al.* (2003) reported younger, *c*. 350 Ma monazite ages from this area. The garnet in this highly graphitic rock is ~15 mm in diameter. The major mineral assemblage of the matrix is biotite + chlorite + hornblende + plagioclase + epidote +quartz.

SP-9G
Sample SP-9G (Fig. S1) was collected from basement rock of the Cordillera Darwin metamorphic complex, Tierra del Fuego, Chile. *P-T* paths determined from major element zoning in garnet from this rock indicate heating of 80-100°C and loading of ~1 kbar with peak conditions at ~575 °C and 7 kbar (Kohn *et al.*, 1993), with most *P-T* changes occurring in the outer 0.5 mm of the garnet rim. Garnet from the same area shows oxygen isotope zoning patterns that are consistent with an absence of fluid infiltration or isotopic exchange with compositionally disparate rocks during metamorphism (Kohn *et al.*, 1993).

Peak metamorphism in this area has not been directly dated. Undeformed plutonic rocks that crosscut the metamorphic fabrics south of Cordillera Darwin have been dated using K-Ar and Rb-Sr on biotite and hornblende at 90-80 Ma (see summary of Kohn *et al.*, 1995). Hornblende $^{40}Ar/^{39}Ar$ cooling ages in the area where SP-9G was collected are 75 ± 2.0 Ma (Kohn *et al.*, 1995). Thus a minimum age for the peak of metamorphism of 75 Ma is assumed, with a likely peak age > 90 Ma (see discussion of Kohn *et al.*, 1995). The garnet analyzed from this rock is ~ 11 mm in diameter. The major silicate assemblage of the matrix is staurolite + biotite + chlorite + muscovite + plagioclase + quartz.

Whiteschist (WS)
The sample of whiteschist (WS; Fig. S1) was collected from the well-documented Case Ramello/Parigi locality within the Brossasco-Isasca Unit (BIU), Dora Maira Massif, western Alps. This unit consists of augen gneiss grading to medium to fine grained orthogneiss and includes discontinuous layers of whiteschist, which contains large pyrope crystals within a matrix of quartz + phengite + kyanite + rutile. Chopin (1984) first discovered the presence of metamorphic coesite as inclusions within the garnet. The maximum *P-T* conditions are 750 ± 30°C (Chopin, 1984) and ~4.0 GPa (Castelli *et al.*, 2007). The age of peak metamorphism is determined from U-Pb on metamorphic zircon at 35.4±1.0 Ma (Gebauer *et al.*, 1997). The garnet chosen from this rock, although large (~ 30 mm), was fragmentary and its original size is unknown.

Figure S1. Images of garnet analyzed in this study, showing strips removed and locations of subsamples. Image for D84-1a is a back-scattered electron image; others are photographs.
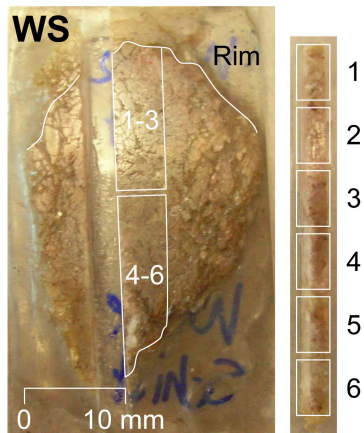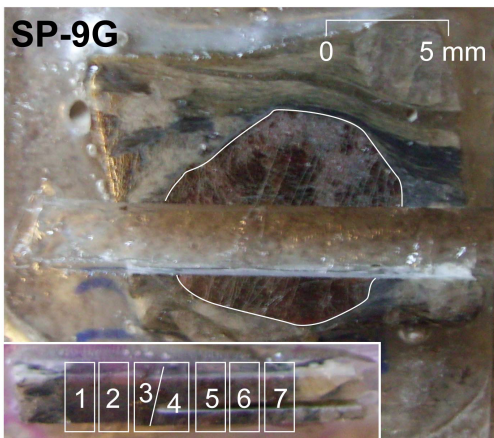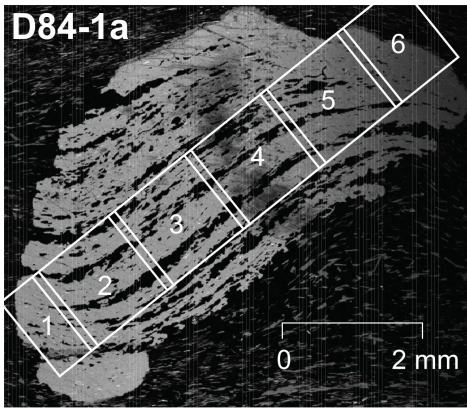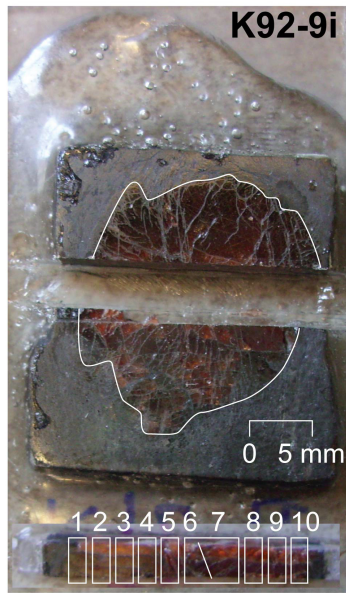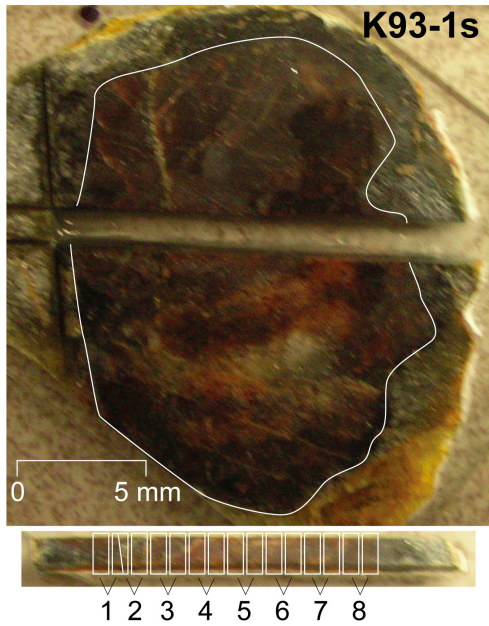
APPENDIX S2: Methods

Sampling: Garnet
A ~ 1 mm wide strip was first cut through the centre of the 1 – 2 mm garnet thick sections using a slow speed microsaw. This strip was then removed and mounted on a second glass slide using acetone-soluble glass glue and incrementally cut every 1.5 mm (Fig. S1). The blade thickness was ~0.25 mm so each resulting cube of garnet was approximately 2-4 mm^3. Sample K93-1s was initially cut at these dimensions, resulting in 16 subsamples. These were later combined into eight subsamples to represent larger intervals (~2.5 mm). The volume of garnet in each subsample of D84-1a was much smaller than the other garnet due to the presence of quartz throughout the garnet. After finding low Sr concentrations in garnet WS, it was resampled in a parallel traverse containing two large (~ 6 mm^3) subsamples.

Sampling: Matrix
Garnet-free matrix was also sampled near each garnet, assuming it represented the isotopic reservoir from which the garnet grew. This was not difficult because all of the garnet used for this study was much larger than the typical grain size of the surrounding matrix. A larger volume of matrix was obtained for each sample to ensure homogeneity (100s mg to grams). The samples were then powdered and a split of the powder was analyzed. Weights for garnet subsamples and matrix splits are given in Table 1.

Sulphuric Acid Leach
The garnet samples were crushed to a fine powder using a mortar and pestle and leached with sulphuric acid (H_2SO_4) for several days (Anczkiewicz & Thirlwall, 2003). Leaching eliminates any possible phosphate micro inclusions in the garnet that could affect the measured $^{87}Rb/^{86}Sr$ and $^{87}Sr/^{86}Sr$, especially apatite. Only half of K93-1s samples (1a-4a) were leached while the second half (5a-8a) was not to test how the leaching process affected the garnet or the chemistry process in any way. This comparison showed no obvious advantage of leaching for reducing Sr concentrations or Rb/Sr ratios. Matrix samples were not leached.

Spiking/Dissolution/Chromatography
All sample powders were spiked, dissolved, and separated by primary cation chromatography at the Boise State University radiogenic isotope geology laboratory (BSU IGL) facilities using standard methods (Pin & Bassin, 1992; Pin et al., 1994).
        To facilitate isotope dilution analysis of small amounts of Rb and Sr in garnet mineral separates, an enriched ^{87}Rb-^{84}Sr tracer solution was mixed and calibrated for use in the Boise State University Isotope Geology Laboratory. Starting materials were highly enriched ^{87}Rb (99.11%) and ^{84}Sr (SRM-988; 99.89%) obtained from Oak Ridge National Laboratory. The starting materials were diluted with 3.5M HNO_3 to make working solutions, and then mixed and diluted to make final mixed tracer solutions appropriate to spiking moderate to low-Rb/Sr samples ("WR") or high-Rb/Sr samples ("MICA"). Mixed Rb-Sr gravimetric standards were independently prepared from two starting materials: NIST SRM-3145a Rb and SRM-3153a Sr standard solutions ("BSU" standard prepared at Boise State), or stoichiometric chloride and carbonate salts ("DTM" standard prepared at Department of Terrestrial Magnetism, M. Horan pers. comm.). To calibrate the mixed tracer solutions, dilute working solutions of these two mixed gravimetric standards were equilibrated with

aliquots of the mixed tracers via repeated drying and redissolution in 6M HCl. Seven mixtures with the "WR" tracer were separated and analyzed via mass spectrometric methods described below. Three mixtures with the "BSU" standard and four mixtures with the "DTM" standard yielded a weighted mean $^{87}Rb/^{84}Sr = 2.709 \pm 0.15\%$ (1σ), which provides a basic constraint on the accuracy of sample Rb/Sr ratios, and for propagation into absolute initial Sr isotope ratio estimates.

All sample dissolution and ion chromatographic separation took place in Class 10 laminar flow hoods, using ultra-pure reagents and Teflon labware in the clean laboratory of the Boise State University Isotope Geology Laboratory. Prepared rock powders or mineral separates were spiked with a mixed ^{87}Rb-^{84}Sr tracer, dissolved with 3 mL 29M HF + 1 mL 15M HNO$_3$ in Savillex PFA beakers at 150°C for 60 hours, dried and redissolved in 5 mL 6M HCl at 150°C for 16 hours. The resulting clear solutions were dried and redissolved in 5 mL 1M HCl + 0.1M HF at 150°C overnight.

Due to the small sample sizes, the garnet was more sensitive to contamination, so extracleaning steps were taken as a precaution before column chemistry was performed. The columns were placed in a bath of 4M HCL with enough acid to cover the bottom of the columns. They were then sonicated for approximately one hour. This step was taken to ensure the frit and cap at the bottom of the column were clean. The columns were then backwashed with MQH$_2$O (using fresh MQH$_2$O for each column) and then cleaned with ~110 mL of 6M HCL. The columns were backwashed a second time (also using fresh MQH$_2$O for each column). From here the BSU IGL primary cation chromatography procedure was followed.

Rb and Sr were first separated by cation exchange chromatography, via elution in 2.5M HCl on 6 mm i.d. x 20 cm columns of AG-50W-X8 resin (H+ form, 200-400 mesh). The Rb fraction was further purified by ion exchange in 0.6M HCl on 6 mm i.d. x 10 cm columns of AG-50W-X8 resin (H+ form, 200-400 mesh). The Sr fraction was purified by ion exchange in 3.5M HNO$_3$ on Eichrom Sr-spec (50 **μ**l c.v., 50-100 **μ**m) resin. All Rb and Sr fractions were finally dried with 5 **μ**l 0.1N H$_3$PO$_4$, 30 **μ**l 16M HNO$_3$, and 30 **μ**l 30% H$_2$O$_2$.

ID-TIMS

Rb and Sr were loaded in 0.1N H$_3$PO$_4$ along with a colloidal tantalum oxide emitter solution (R. Creaser, pers. comm.) on single degassed Re filaments, and their isotope ratios measured on the Isoprobe-T in the Boise State University Isotope Geology Laboratory. The $^{87}Rb/^{85}Rb$ ratio was measured in static Faraday mode; a mass bias correction of 1.0096 ± 0.06% (1σ) was estimated by external analysis of natural Rb standards. Sr isotope ratios were analyzed in dynamic mode, fractionation corrected with an exponential law relative to $^{86}Sr/^{88}Sr = 0.1194$, and are reported as spike-stripped and bias corrected relative to the accepted value of the NBS-987 standard (0.710248). The quoted uncertainty for each analysis is the internal standard error; the external reproducibility of the NBS-987 standard over the course of the study was 0.710251 ± 3 (1σ); uncertainty in [Rb], [Sr] and $^{87}Rb/^{86}Sr$ are estimated at ≤ 0.2% (1σ) based upon fractionation and tracer calibration uncertainties. Initial $^{87}Sr/^{86}Sr$ is calculated assuming an ^{87}Rb decay constant of 1.42 x 10^{-11}y-1.

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