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Timescales between mantle metasomatism and kimberlite ascent indicated by diffusion profiles in garnet crystals from peridotite xenoliths

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ABSTRACT

Rare garnet crystals from a peridotite xenolith from the Wesselton kimberlite, South Africa, have distinct zones related to two separate episodes of mantle metasomatism. The garnet cores were firstly depleted through melt extraction, then equilibrated during metasomatism by a potentially diamond-forming carbonate-bearing or proto-kimberlitic fluid at 1100-1300 °C and 4.5-5.5 GPa. The garnet rim chemistry, in contrast, is consistent with later overgrowth in equilibrium with a kimberlite at around 1025 ± 25 °C and 4.2 ± 0.5 GPa. This suggests that the rock was physically moved upwards by up to tens of kilometres between the two metasomatic episodes. Preserved high Ca, Al and Cr contents in orthopyroxenes suggest this uplift was tectonic, rather than magmatic. Diffusion profiles were measured over the transitions between garnet cores and rims using electron microprobe (Mg, Ca, Fe for modelling, plus Cr, Mn, Ti, Na, Al) and nano Secondary Ion Mass Spectrometry (NanoSIMS; ⁸⁹Y, along with ²³Na, Ca, Cr, Fe, Mn and Ti) analyses. The short profile lengths (generally $<10 \ \mu m$) and low Y concentrations (0.2–60 ppm) make the NanoSIMS approach preferable. Diffusion profiles at the interface between the zones yield constraints on the timescale between the second metasomatic event and eruption of the kimberlite magma that brought the xenolith to the surface. The time taken to form the diffusion profiles is on the order of 25 days to 400 yr, primarily based on modelling of Y (tracer diffusion) along with Ca, Fe and Mg (multicomponent diffusion) profiles. These timescales are too long to be produced by the interaction of the mantle xenolith with the host kimberlite magma during a single-stage ascent to the crust (hours to days). The samples offer a rare opportunity to study metasomatic processes associated with failed eruption attempts in the cratonic lithosphere.

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1. Introduction

Kimberlites are deep-seated volatile-rich magmas that are responsible for transporting the majority of diamonds that reach the Earth's surface. Given that diamonds are unstable at low pressure (Kennedy and Kennedy, 1976) they must be carried to the surface and quenched extremely rapidly to survive without dissolution or conversion to graphite, and, indeed, the extremely high velocity

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https://doi.org/10.1016/j.epsl.2017.10.021 0012-821X/© 2017 Elsevier B.V. All rights reserved. of erupting kimberlites (>m/s) has been shown by several studies (compilation in Peslier et al. (2008)). However, the degree to which kimberlites are stalled or trapped below the surface is unclear as we generally are only able to sample those kimberlites that have successfully made it to the surface, or near surface.

Chemical overprinting associated with fluid-rock and/or meltrock interaction is almost ubiquitous in xenoliths from kimberlites and associated magma types (Pearson and Wittig, 2014). Such local changes in chemistry may be recorded by formation of compositional zoning in minerals, which leads to intra-grain chemical potential gradients. In response, this zoning may then be erased, or relaxed, by diffusion (review by Ganguly, 2010). The length and shape of concentration-distance profiles across compositional heterogeneities within crystals, if preserved, and shown to be diffusion profiles, may then be used in combination with experimentally determined diffusion coefficients (e.g. in garnets, Ganguly et al., 1998; Tirone et al., 2005) to determine the timeintegrated thermal history following overgrowth and, from that, estimate thermal time scales. This approach is independent of the absolute age of the rock.

Because of the long residence time (mantle timescales) at high temperature, and relatively short timescale of transport (kimberlite eruption timescales), chemical zonation in mantle-derived garnet xenocrysts is relatively rare – chemical gradients are either diffusively relaxed during the long residence times, or have insufficient time to form during transport. Such chemical zoning has, however, been identified in a small number of garnet peridotites from southern Africa, including Lesotho (Smith and Boyd, 1987), the Frank Smith mine (Griffin et al., 1989) and the Wesselton mine, South Africa (Griffin et al., 1999), as well as the Colorado Plateau, United States (Smith and Ehrenberg, 1984).

In this contribution, diffusion profiles across rare zoned garnet crystals (Hanger et al., 2015) in a garnet peridotite xenolith from the Wesselton kimberlite erupted at 86 ± 3 Ma (Allsopp and Barrett, 1975) are used to quantify the time gap between the first interaction of a percolating metasomatic agent (likely a failed kimberlite) and the peridotite body, and the final kimberlite eruption (and transport of the sample to the surface). This garnet peridotite xenolith provides a rare opportunity to interrogate very rapid geological processes occurring deep in the cratonic mantle lithosphere.

2. Methods

2.1. Samples

The garnet crystals investigated in this study are from a garnet peridotite xenolith (KBD12) from the Wesselton diamond-bearing kimberlite, and were previously described by Hanger et al. (2015). For analyses, we chose two garnet grains (ga4 and ga6) with strong, nearly step-like compositional zoning features (Fig. 1).

2.2. Methods related to geothermobarometry

The analytical methods associated with geothermobarometric calculations are presented in Hanger et al. (2015). Standard major and minor elements were determined by electron probe microanalysis (EPMA) for olivine, orthopyroxene, garnet and clinopyroxene using a Cameca SX100 electron microprobe. A suite of trace elements (including alkalis, transition metals, rare earth elements (REE), high field strength elements) was analysed by laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) using an Agilent 7500 quadrupole ICP-MS coupled to a LambdaPhysik excimer LA system, with a Helex dual volume cell. Further information, including analysed isotopes and analytical conditions, is provided in the Electronic Appendix A. EPMA and LA-ICP-MS analyses were conducted at the Australian National University.

2.3. Methods related to characterising diffusion profiles

2.3.1. Electron probe microanalysis

Quantitative analyses of the garnet compositions were performed using a Cameca SX100 as above. Linear transects across the compositional interfaces were obtained using a step size of either 1 or 2 μ m, a focused, 1 μ m diameter beam, an accelerating voltage of 15 kV and a beam current of 20 nA. Under these conditions, the electron beam excites a hemi-spherical Gaussian distributed interaction volume of around 2 μ m diameter (CASINO modelling, Hovington et al., 1997), i.e. giving overlap between neighbouring



Fig. 1. Backscattered electron images of garnets analysed in this study, plus approximate NanoSIMS analytical locations (white, black-rimmed bars). Scale bars (lower right) are 500 μ m. (a): gt4, with clear growth zoning. (b): gt6, zoning less clear but still present. Black circles are laser ablation spots.

analysis spots. The size of the beam is only $\sim 5-10 \times$ smaller than the profile length, so analytical artefacts mean that the observed profile will be longer than the true profile. However, this effect is only expected to overestimate timescales determined by diffusion modelling by around 10–15% (calculated using the formulation of Ganguly et al., 1988).

2.3.2. NanoSIMS analysis

NanoSIMS has recently become a useful tool for characterising diffusion or zoning profiles which are either too short, or have concentrations that are too low, for effective analysis by EPMA. Our scans were performed with the CAMECA NanoSIMS 50 at the Centre for Microscopy, Characterisation and Analysis, University of Western Australia, using an O⁻ primary ion beam. The magnetic field of the mass spectrometer was tuned to deflect mass 89 (Y) into the fixed detector, with the electron multipliers on four movable trolleys positioned to detect lighter elements. The second detector was always used to detect the reference isotope, ²⁹Si⁺, with three different configurations being used during analysis, as the physical size of the detectors prevents simultaneous analysis of elements with similar masses, such as ${}^{23}Na^+$ and ${}^{24}Mg^+$ or ${}^{52}Cr^+$. ⁵⁵Mn⁺ and ⁵⁶Fe⁺. The first, third and fourth detectors were positioned so that the following three suites could be detected respectively: [²³Na, ²⁹Si, ⁴⁰Ca, ⁵²Cr, ⁸⁹Y], [²⁴Mg, ²⁹Si, ⁴⁰Ca, ⁵⁵Mn, ⁸⁹Y] and [²⁷Al, ²⁹Si, ⁴⁸Ti, ⁵⁶Fe, ⁸⁹Y]. All secondary ions were detected simultaneously. The mass spectrometer was tuned to high resolution mode using an entrance slit of 30 µm, an aperture slit of 200 µm, and a 10% reduction in the signal at the energy slit. Two different spot configurations were used, one with a primary current of ~ 17 pA (large spot) and the other ~ 1.6 pA (small spot). Both used a 200 µm source aperture and a 300 µm primary aperture. Peak positions were calibrated using the NIST SRM 610 reference

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