Chemical Geology 476 (2018) 208–222

Contents lists available at ScienceDirect

Chemical Geology

journal homepage: www.elsevier.com/locate/chemgeo

Coupled Lu–Hf and Sm–Nd geochronology on a single eclogitic garnet from the Huwan shear zone, China

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ARTICLE INFO

Keywords:
Garnet
Lu–Hf
Microsampling
Sm–Nd

ABSTRACT

We present coupled Lu–Hf and Sm–Nd dates from multiple growth zones within a single large garnet porphyroblast in an eclogite from the Huwan shear zone in the Hong'an orogen, central China. The eclogite sample contains large garnet porphyroblasts up to several centimetres in diameter and a second major population of smaller, millimetre-sized garnet grains. Elemental compositions and mineral inclusions in garnet suggest that the large garnet crystal formed during an early episode of metamorphism, with the abundant small-sized garnets in the matrix growing during a late metamorphic period contemporaneous with the overgrowth of the rim of the large garnet crystal. Ten coupled Lu–Hf and Sm–Nd dates determined from five micro-sawed garnet sections of a ~2 cm garnet coherently decrease from core to rim. Lu–Hf dates from each section are consistently older than the corresponding Sm–Nd dates. Petrographic and chemical observations of the eclogite show that three generations of garnet growth occurred, with the latter two generations coincident with growth of the rim of the large garnet, and that of the smaller matrix garnets. Five micro-sawed growth zones were analysed for Lu–Hf and Sm–Nd isotopes. The calculated Lu–Hf dates from the mega garnet record garnet growth initiation at about 397 Ma, during prograde to peak metamorphic conditions of the first orogenic episode, lasting about 11 Ma. Sm–Nd garnet dates are systematically younger than corresponding Lu–Hf dates, with the Sm–Nd garnet rim date > 25 Ma younger than the Lu–Hf date. We suggest that the Sm–Nd dates represent a combination of 1) growth and simultaneous diffusion at elevated temperatures during the first metamorphic episode, 2) diffusive age resetting as a result of continued elevated temperatures during residence at mid-crustal depths and/or slow cooling between the two orogenic episodes, and 3) mixing of growth generations. U–Pb dates on three zircon inclusions from the garnet separates range from 386 to 351 Ma, possibly suggesting zircon crystallization during exhumation and cooling. This study highlights that coupled microsampling Lu–Hf and Sm–Nd chronology on a single garnet (down to ~cm in diameter) can help decipher the timescales of burial and heating (for Lu–Hf) and cooling from elevated temperatures (for Sm–Nd) from a single orogenic cycle, and that zoned Lu–Hf and Sm–Nd garnet can be utilized as a geo (thermo) -chronometer. Lastly, these Lu–Hf garnet, Sm–Nd garnet and U–Pb zircon dates confirm an early high-pressure metamorphic episode during the Devonian before the final convergence of the South China and North China Blocks in the Triassic.

1. Introduction

Garnet is an important mineral for decoding metamorphic processes, in part because its compositional zoning can be used to elucidate quantitative *P–T* paths, but also because the timescales of garnet growth can be determined from the same growth zoning by both the Lu–Hf and Sm–Nd isotope systems. In recent years, the development of high-spatial-resolution chronometers has become an increasingly important pursuit in geochronology. One of the well-developed, long-lived radiometric dating methods is zircon chronology. With the contemporaneous developments in secondary ion mass spectrometry (SIMS) and laser-ablation induced coupled plasma mass spectrometry (LA-ICP-MS), we are now able to accurately and precisely measure trace element and isotopic signatures of distinct growth zones (typically 5–30 μm pits) within a single zircon grain *in-situ*. Inevitably, zircon geochronology has become an increasingly important tool for understanding metamorphic processes. However, zircon may be absent in particular rocks and linking zircon dates with specific metamorphic

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https://doi.org/10.1016/j.chemgeo.2017.11.018
Received 29 June 2017; Received in revised form 13 November 2017; Accepted 15 November 2017
Available online 20 November 2017

events can prove challenging (e.g., Rubatto, 2017). The method of zoned-garnet geochronology (e.g., Christensen et al., 1989; Vance and O'Nions, 1990), has received less attention, mainly due to the challenges of the physical preparation and analysis of zoned minerals (Baxter et al., 2017). Obtaining an age profile from a single garnet allows not only for the determination of the pace of crystal growth but is also ideal for unravelling the timeline of tectonometamorphic processes registered in the concentric growth rings. Due to recent advances in techniques for measuring small aliquots of Nd with thermal ionization mass spectrometry (TIMS; e.g., Harvey and Baxter, 2009) and development of effective microsampling methods, we are now able to acquire high-resolution Sm–Nd geochronologic records in concentric growth shells within a single garnet of cm-size (e.g., Pollington and Baxter, 2010), possibly yielding constraints on the pace of garnet growth. Conversely, garnets have low concentrations of Hf and dissolving a normal mm-sized single garnet often yields insufficient Hf for its precise isotope analysis by multi-collector- (MC–) ICP-MS. Recently, microsampling Lu–Hf studies have been conducted on large garnet crystals (Anczkiewicz et al., 2014; Schmidt et al., 2015; Cheng et al., 2016a), building on earlier work involving core–rim Lu–Hf studies of garnet (Herwartz et al., 2011; Nesheim et al., 2012).

Spatially-resolved, coupled Lu–Hf and Sm–Nd dating may help provide new insights into why both systems typically do not provide the same result for single analytical aliquots. Garnet strongly fractionates Lu over Hf—even more than it fractionates Sm over Nd—leading to high Lu/Hf ratios in garnet cores. As a result, bulk Lu–Hf garnet growth dates can be older than bulk Sm–Nd dates from the same sample owing to resultant differences between Lu and Sm zonation across garnet crystals (Lapen et al., 2003; Skora et al., 2006). Coupled microsampling of growth zones for Lu–Hf and Sm–Nd dating would thus provide better constraints for growth (and/or cooling) history of garnet (and associated tectono-metamorphism) than a single chronometric system would, and may also resolve any volumetric mixing issues stemming from the use of bulk garnet Lu–Hf and Sm–Nd dates (Skora et al., 2006; Kylander-Clark et al., 2007; Cheng et al., 2008). This is the first study utilizing coupled microsampling and Lu–Hf and Sm–Nd dating of multiple growth zones in a single garnet crystal. Here, we report ten coupled two-point Lu–Hf and Sm–Nd dates from five micro-sawed sections within a single large garnet crystal of an eclogite collected from the Huwan shear zone in the Hong'an orogen, central China. These dates place important time constraints on garnet growth and on the duration of collisional metamorphism, as well as provide new constraints on the early convergence history between the South China Block (SCB) and the North China Block (NCB).

2. Geological outline and sample description

The eclogite sample analysed in this study was collected from the Huwan shear zone in the Hong'an orogen (Fig. 1), which lies in the central part of the Qinling–Tongbai–Hong'an–Dabie–Sulu orogenic belt. The Qinling–Tongbai–Hong'an–Dabie–Sulu orogenic belt extends > 2000 km, and underwent prolonged oceanic subduction and accretion before the final continent-continent collision between the North China and South China Blocks (e.g., Ratschbacher et al., 2003; Cheng et al., 2008; Wu et al., 2009). It records the tectonic transition from oceanic subduction to continental collision during the closure of the Paleotethyan Ocean in eastern Asia. The Huwan shear zone occurs in an east–west trend with a width of 5–10 km, marking the tectonic contact between the more inboard Qinling–Tongbai orogenic belt to the northwest and the outboard Dabie–Sulu orogenic belt in the southeast, and was involved in a complex process of collision and exhumation during convergence between the NCB and the SCB. The shear zone consists of tectonic slices of gabbros, ultramafic rocks, diabase dikes, and basalts, which collectively appear to represent a dismembered ophiolite (Liu et al., 2004; Wu et al., 2009). The zone contains metamorphic rocks, including blocks of eclogite, metagabbro, (epidote-) amphibolite, marble and quartzite; gneiss, quartzofeldspathic schist and graphitic schist form an argillic matrix to these blocks (Fig. 1b; Liu et al., 2004; Ratschbacher et al., 2006). The eclogites are found throughout this zone, occurring as massive outcrops with no obvious lithologic contacts, or occasionally as layers and lenses surrounded by metasedimentary rocks (Liu et al., 2004; Cheng et al., 2016a). The high-pressure metamorphic conditions in the northern part of the Hong'an orogen (i.e., the Huwan shear zone) are estimated to be 490–570 °C and 1.8–2.4 GPa, whereas those in the southern part are estimated to be 450–500 °C and 1.0–1.2 GPa (Liu et al., 2004; Ratschbacher et al., 2006; Cheng et al., 2009). Previous geochronological data suggest that the Huwan eclogite experienced either continual metamorphism or two separated high-pressure metamorphic events in the Devonian and Triassic, respectively (Jian et al., 1997; Sun et al., 2002; Cheng et al., 2009, 2016a; Wu et al., 2009; Brouwer et al., 2011; Zhou et al., 2014; Cheng and Cao, 2015). The timing of cooling and deformation of the Hong'an high-pressure rocks has been constrained by ^{40}Ar–^{39}Ar analyses of synkinematic minerals from the Huwan shear zone to *c.* 206 Ma (Webb et al., 1999) and *c.* 235–195 Ma (Ratschbacher et al., 2006).

The sample analysed in this study comes from an eclogite block (~5 m × 2 m, 31° 4508.37″ N, 114° 28,029.64″ E; Fig. 2a) near Qianjin Country. The high-pressure assemblage in the collected sample consists of omphacite + garnet + epidote + quartz + minor phengite (Fig. 3a). Rutile and zircon are present as accessory minerals. We identified a large garnet porphyroblast up to ~2 cm in diameter and a second major population of smaller (typically < 1 mm) garnet crystals in the matrix (Fig. 3). We herein refer to the large garnet porphyroblast as 'mega garnet' and the small garnet grains as 'matrix garnet.'

3. Methods

3.1. Chemical analyses

Microprobe mineral analyses and X-ray maps of garnets were carried out on polished thin sections using a JEOL JXA-8230 electron microprobe at Tongji University, fitted with five wavelength dispersive spectrometers (WDS). The operating conditions for analyses were an accelerating voltage 15 kV and beam current 20 nA with a beam size of 5 μm (Cheng et al., 2016b). Intensities of characteristic X-rays of Mn (Kα), Mg (Kα), Fe (Kα) and Ca (Kα) were collected at the same conditions but with a 100 nA beam current. Calibration was performed with a range of natural and synthetic standards, and a ZAF correction procedure was used. Mineral abbreviations in the text, figures and figure captions are those of Whitney and Evans (2010).

We used a conventional micro-saw sampling technique (after Cheng et al., 2016a) on the large garnet porphyroblast (Fig. 2). A cubic-shaped block containing the whole garnet grain was prepared using an industrial saw in the field. This block was cut into four chunks through the approximate geometric centre by a cut perpendicular to the surface and a second parallel cut. The chips without the mega garnet were crushed to produce a whole rock powder. The four quarters were then cut into four rectangular sections approximately along half of the garnet grain (dashed lines in Fig. 2b) using a micro-saw. The four quarters were further cut into ten garnet chips using a slow speed micro-saw, resulting in five subsamples of the mega garnet. The subsamples were carefully crushed in a steel mortar, washed, with garnet fragments, and subsequently handpicked under a binocular microscope.

Five garnet separates and two whole rock powders – one digested in a bomb and one digested only with the tabletop procedure of Cheng et al. (2009) – were analysed for Lu–Hf and Sm–Nd geochronology. The Lu–Hf and Sm–Nd isotope analyses were carried out on a Thermo Scientific™ Neptune MC–ICP-MS in the Radiogenic Isotope and Geochronology Laboratory at Washington State University. The detailed procedures for sample digestions and spiking followed the guidelines described by Cheng et al. (2008). Protocols for isotope analyses and data reduction are described in Vervoort et al. (2004). Hafnium and Nd isotopic compositions were