Decoupling of U–Pb ages and compositional zoning of garnet in a high-pressure marble from the eastern Iratsu body, Sanbagawa metamorphic terrane, Japan

Sota NIKI*, Kenta YOSHIDA**, Hikaru SAWADA***, Ryosuke OYANAGI** and Takafumi HIRATA*

*Geochemical Research Center, The University of Tokyo, Tokyo 113-0033, Japan
**Research Institute for Marine Geodynamics, Japan Agency for Marine-earth Science and Technology (JAMSTEC), Yokosuka 237-0061, Japan
***Institute for Extra-cutting-edge Science and Technology Avant-garde Research (X-star), JAMSTEC, Yokosuka 237-0061, Japan

Here we first report the in situ U–Pb dating of metamorphic grossular garnet (Grs) with distinction between internal zonation textures. The studied Grs occurs in an eclogite–facies marble collected from the eastern Iratsu body of the Sanbagawa metamorphic terrane, Japan. The Grs has a patchy texture, predominantly with pure Grs cores and andradite (Adr)–rich rims formed during eclogite–facies and exhumation stages, respectively. The U–Pb ages for the Grs core and Adr–rich rim were 97 ± 10 and 106 ± 16 Ma (95% confidence level), respectively. Despite the compositional zoning formed under different P–T conditions, the U–Pb ages of the core and rim were in similar values within analytical uncertainties. This decoupling of chemical zonation and U–Pb ages implies that the U–Pb chronological signatures of rims were inherited from cores owing to the redistribution of radiogenic Pb in cores during the rim formation through fluid-mediated dissolution and reprecipitation. The Grs U–Pb age (97 ± 10 Ma) thus directly corresponds to previously reported P–T conditions of the core formation during the eclogite–facies metamorphism. This advantage of Grt petrochronology as the combination of radiometric ages obtained by in situ analysis and P–T conditions deduced from paragenesis can contribute to reconstruct reliable metamorphic histories.

Keywords: Garnet, Grossular, U–Pb geochronology, Sanbagawa metamorphic terrane, LA-ICP-MS

INTRODUCTION

Garnet (Grt) is commonly found in metamorphic rocks and records pressure–temperature–time (P–T–t) conditions. Formation ages of the Grt can be defined by radiometric dating methods (e.g., the Sm–Nd, Lu–Hf, and U–Pb systems) and P–T conditions can be deduced from inclusion minerals in Grt crystals, based on chemical thermodynamics (e.g., Wallis et al., 2009). For the deduction of reliable P–T–t conditions, age determination should be carried out from the surrounding area of the considered inclusion minerals in equilibrium with the host Grt. Despite the advantages of Grt petrochronology, previous geochronological studies have been based mainly on Sm–Nd and Lu–Hf dating methods (e.g., Scherer et al., 2000). With such methods based on chemical decomposition/dissolution techniques, obtained age data can be erroneous due to the mixing of several zones associated with multiple crystal growth stages or inclusion minerals inside the measured samples. For the accurate interpretation of age data, chemical textures of the target mineral should be carefully observed and impeditive inclusion minerals, which are compatible with the elements employed for radiometric dating, should be completely removed from sample aliquots with mechanical and chemical separation methods (Scherer et al., 2000). Although these potential dangers with solution analysis are easily avoidable by utilizing in situ analytical methods, the practical in situ dating have been retarded mainly due to low concentrations of parent isotopes and high contents of initially incorporated daughter isotopes. One potential approach to solving this problem is the U–Pb dating of grossular (Grs)–anda-
dite (Adr). The Grs-Adr, occurring mainly in skarn deposits, may have U contents of up to a few ppm (Haack and Gramse, 1972) with negligible incorporated Pb. However, previous studies based on U-Pb dating of Grs-Adr have been limited to skarn deposits (Deng et al., 2017; Seman et al., 2017).

Here we report the first example of in situ U-Pb dating of metamorphic Grs with respect to its distinct internal textures, thus contributing to the elucidation of the geotectonic history of the Sanbagawa metamorphic terrane. This terrane contains an eclogite unit, with the duration of the eclogite–facies stage having been estimated on the basis of zircon (Zr) U-Pb ages (110–90 Ma; Okamoto et al., 2004; Aoki et al., 2020), but the analyzed Zr grains lack high-pressure metamorphic mineral inclusions. Owing to the drawback, the previously reported ages do not necessarily correspond to the eclogite–facies stage, especially for the coarse-grained bodies. On the other hand, in situ dating of Grt is a promising method for measuring each portion corresponding to its growth stage and determining the timing of specific metamorphic stages (Simpson et al., 2021). In the present study, the effectiveness of in situ dating of Grt was well demonstrated by the improved spatial resolution of Grt U-Pb dating for clarification of P-T-t histories.

GEOLoGICAL OUTLINE AND SAMPLE DETAILS

The Sanbagawa terrane is an intermediate high-P/T metamorphic type terrane, extending >800 km East–West, mainly in southwest Japan. The Sanbagawa terrane represents the deepest parts of the Cretaceous to earliest Palaeogene accretionary complex that developed in response to subduction of the Izanagi oceanic plate beneath Eurasia (Endo et al., 2012, and references therein). The major thermal structure is defined by mineral paragenesis of metapelites of low–high grade in chlorite, Grt, albite–biotite, and oligoclase–biotite zones (Fig. 1a). High-grade albite–biotite and oligoclase–biotite zones occur in central Shikoku with peak P-T conditions of 0.8–1.1 GPa and 490–635 °C (Enami et al., 1994). The high-grade zones include eclogite–facies rocks that formed under high-pressure conditions (Aoya and Endo, 2017). The discrete coarse-grained mafic bodies underwent eclogite–facies metamorphism at about 2 GPa and 600 °C, with recent studies suggesting that these mafic bodies, together with the surrounding sedimentary complex, comprised a single metamorphic eclogite unit (e.g., Kouketsu et al., 2014). Some coarse-grained eclogitic bodies record earlier metamorphic events under amphibolite– and granulite–facies conditions (Endo et al., 2009; Yoshida et al., 2021b).

The Zrn U-Pb ages of the eclogite–facies rocks are in the range of 110–90 Ma (Okamoto et al., 2004; Aoki et al., 2020). More reliable P-T-t conditions in the relevant region were determined by the combination of Grt Lu-Hf ages and P-T conditions deduced from paragenesis. For the coarse-grained bodies, Endo et al. (2009) reported a Grt-Cpx Lu-Hf age of 116 Ma for the early-stage metamorphism of an eclogite sample collected from the western Iratsu body. The presence of clear zonation of Lu at the core of the Grt implied that the measured ages reflect the amphibolite–facies stage preceding the eclogite–facies stage (early Sanbagawa metamorphism; Aoya and Endo, 2017). For the fine-grained eclogite bodies, the Lu-Hf age of 89 Ma was obtained for Grt collected from the Seba body and was related to single-stage growth of Grt under eclogite–facies conditions (Wallis et al., 2009).

The ages of non–eclogite units were constrained from white–mica K–Ar ages of 85 (oligoclase–biotite zone) to 62 Ma (chlorite zone) and the younger K–Ar age of 62 Ma corresponds to lower-grade rocks (Aoya et al., 2013; Nagata et al., 2019, and references therein).

The U-Pb dating analysis was conducted on a marble sample collected from the eastern margin of the eastern Iratsu body, which is a coarse–grained metagabbro body in the Besshi district of central Shikoku (Takasu and Kohsaka, 1987). Fundamental petrography was provided by Yoshida et al. (2021a). This coarse–grained and weakly–foliated marble (sample EI1901) comprises mainly Grs, diopside (Di), quartz (Qz), and calcite (Cal) with minor titanite (Ttn), pyrite (Py), and apatite (Ap). The Ttn in the marble matrix has a U-Pb age of 200–180 Ma, reflecting the timing of high–temperature eclogite–facies metamorphism (Yoshida et al., 2021b). The Ttn rim U-Pb age also recorded the timing of the early Sanbagawa metamorphism (~ 126 Ma; Yoshida et al., 2021b). The subsequent eclogite–facies stage was recognized in Grt in the matrix with the occurrence of omphacite and aragonite. In contrast to the matrix mineral paragenesis, the Qz–rich domain (Qz-pod), which extended concordantly along the main foliation and comprises Grs, Di, Cal, and minor Py, recorded a unique P-T-fluid history during exhumation of the eclogite–facies rock (Yoshida et al., 2021a). The Grs in the Qz-pod has a patchy texture, with an almost pure Grs core (Grs98Adr2) containing Arg and minor K-feldspar (Kfs) inclusions, and an Adr–rich rim (Grs91Adr8Alm<2) containing Cal, Qz, and datolite inclusions (Figs 2a and 2b). Based on the mineral assemblage and Qz Raman barometry, the P-T conditions at formation of the Adr–rich rim were estimated to be 1.0–1.3 GPa and 550–650 °C (Yoshida et al., 2021a), corresponding to the P-T conditions of the juxtaposition of eclogite and non–eclogite units (Fig. 1b). Although the Grs core does
not contain typical eclogite–facies index minerals such as omphacite, the Arg inclusion in the core and the Cal inclusion in the rim indicate a higher pressure for the core formation and subsequent decompression. The core can thus be attributed to the eclogite–facies stage of the coarse-grained bodies or the early stage of exhumation.

**ANALYTICAL PROCEDURE**

For precise analysis of Grs with sub–ppm U and ppb Pb contents, an in situ U–Pb dating method using multiple-spot femtosecond laser ablation–multiple collector–inductively coupled plasma–mass spectrometry (msfLA–MC–ICP–MS; Hattori et al., 2017; Obayashi et al., 2017; Makino et al., 2019) was developed at the Geochemical Research Center, the University of Tokyo, Japan. Analytical conditions for Grs U–Pb dating and the correction method of U–Pb isotopic ratios are described in the Appendices (Table A1, Table A2, and Figure A1).

Prior to msfLA–MC–ICP–MS analysis, the internal texture of the Grt was studied by electron microprobe analysis (EMPA; JXA–8500F, JEOL, Japan) at Japan Agency for Marine–Earth Science and Technology (JAMSTEC). Ablation spots on thin sections of Grt samples were positioned using backscattered–electron (BSE) images, with 13 spots each on core and rim (Fig. 2a).

**RESULTS**

The resulting U–Pb isotopic data were plotted on a Tera–Wasserburg concordia diagram (Table 1, Figs. 2c and 2d) and ages calculated from intercept points of the concordia curve and regression lines of the plotted data points for both the Grs core and Adr-rich rim. The 13 core spots yielded a lower intercept age of $97 \pm 10$ (95% confidence level) Ma with a mean–square–weighted deviation (MSWD) of 2.5; the 13 rim spots yielded an intercept age of $106 \pm 16$ (95% confidence level) Ma (MSWD = 4.1). The intercept ages of the core and rim are consistent within their errors, but the relatively large MSWD values imply that the data may relate to a mixture of multiple U–Pb isotopic sources.
DISCUSSION

Decoupling of isotopic signatures and compositional zoning in garnet

Despite the distinct zonation textures formed under different pressure conditions, the ages yielded for the core and rim did not vary significantly. This decoupling of chemical zonation and the U-Pb isotopic system may have four possible causes: (1) core and rim formation occurred beyond the closure temperature of the U-Pb system in Grt, with the two ages being cooling ages; (2) the textural relationship between the core and rim is sterically complex and a separate analysis of the two zones was not obtained; (3) the U-Pb isotopic system of the Grs core was inherited during rim formation; or (4) the difference of the formation ages between the core and the rim was hidden owing to the large analytical errors. The first possibility is precluded because the U-Pb system of Grt was not reset by thermal diffusion during metamorphism in the Sanbagawa terrane. The closure temperature of the Grt U-Pb system is estimated to be >800 °C (Mezger et al., 1991), which exhibited higher temperature conditions of the peak eclogite-facies stage and the entire exhumation.

Regarding spatial resolution (2), data acquisition involved a homogenous region with a spatial resolution of about 60 µm and with laser ablation penetrating about 30 µm, and therefore, the three-dimensional heterogeneous texture of the ablated volume was not excluded from the BSE image. As the studied Grt has a patchy texture, the possibility cannot be ruled out that the analyzed volume of the core contained small volumes of infiltrated rim and vice versa. However, it should be noted that the ranges of U contents for the core and rim exhibited a similar range. Assuming that 10% of the sampling volume was contaminated by each other and the difference of the formation ages to be 30 Myr between the core and rim, the expected deviation of U-Pb ages would be approximately 3 Myr due to the similar U content. In other words, small volume of the contamination of core-to-rim (or vice versa)

Figure 2. (a) and (b) BSE image of the studied Grs. The brighter area represents the Adr-rich rim, solid and dashed circles are analyzed spots on the core and rim, respectively. (c) and (d) U-Pb analysis results [core (c); rim (d)] for sample EH1901 plotted in Tera-Wasserburg concordia diagrams [using an in-house program modified after Noda (2017)]. Each ellipse indicates a 95% confidence level. The intercept ages were calculated for the core (c) and the rim (d) from the regression lines of data points (black lines).
which was also attributable for the multiple sources of U-Pb ages of the core. The large dispersion of the data points around the age of the rim and was closer to the formation age of the core. The possibility (3) of the inherited U-Pb content. Therefore, we conclude that the rim data were not largely affected by a small contribution of the fragmented core in terms of the present analytical precision. The possibility (3) of the inherited U-Pb signature can explain our results. Fluid activity during rim formation was inferred from the inclusion of datolite (a hydrous borosilicate: Yoshida et al., 2021a), shown with a patchy texture in Grs in Figures 2a and 2b. This texture is attributable to dissolution and reprecipitation mediated by the fluid activity. If the U and radiogenic Pb were released from the Grs core during the dissolution, and the released U and Pb were completely incorporated into the rim during reprecipitation, the U-Pb ages of the newly-grown rim would inherit the U-Pb ages of the core. In this case, the U-Pb age of the core was the formation age of the core, and the U-Pb age of the rim was deviated from the formation age of the rim and was closer to the formation age of the core. The large dispersion of the data points around the regression line was seen in the rim data (MSWD = 4.1), which was also attributable for the multiple sources of U-Pb isotopic ratios, especially inherited from the core. Such redistribution of radiogenic Pb was previously reported in metamorphic monazite that had undergone coupled dissolution-reprecipitation processes (Weinberg et al., 2020). This is another example which supports for the consistency of the U-Pb age to the formation age of the Grs core. However, the possibility (4) of the hidden time difference between the core and rim formation cannot be ruled out, as the intercept age (106 ± 16 Ma) for the rim can include the actual rim formation age within the large error in terms of the previous chronological constraints from the surrounding non-eclogite bodies (e.g., 85 Ma; Aoya et al., 2013). Future challenges include improving precision for each spot analysis to distinguish the difference of the actual formation ages between the core and rim.

### Direct dating of the eclogite-facies metamorphism by garnet

Considering the decoupling of compositional zoning and U-Pb ages, the U-Pb age of the Grs core indicate the formation of the Grs core, which contains an aragonite inclusion, occurred in the eclogite-facies stage for the coarse-grained body. The core formation age of 97 ± 10 Ma can thus be directly connected to the eclogite-facies stage for the coarse-grained body. The improved spatial resolution of Grs U-Pb dating clarified the meaning of the radiometric ages for the Grs core and rim as the core formation age and the inherited one, respectively.

In summary, we developed a high-sensitivity U-Pb dating method for low-U Grs based on msfsLA-MC-ICP-MS (Hattori et al., 2017; Obayashi et al., 2017; Makino et al., 2019), obtaining 60-µm spatial resolution, higher than those of previous Grs U-Pb dating methods (~100 µm; Seman et al., 2017) and solution methods used for Grt Lu-Hf dating. Based on the U-Pb isotopic analysis from the 60 µm areas, the Grs U-Pb age and formation conditions inferred from mineral inclusions near the analyzed spots reasonably reconstruct the \( P-T-t \) conditions during the eclogite-facies stage, indicating the effectiveness of in situ Grt petrochronology for reliable \( P-T-t \) path assessments for metamorphic terranes.

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**Table 1. Results of U-Pb analysis for sample EI1901**

| Spot domain | \(^{238}\text{U}/^{206}\text{Pb} \) | 1σ | \(^{207}\text{Pb}/^{206}\text{Pb} \) | 1σ |
|-------------|-------------------------------|----|--------------------------------|----|
| Core        | 28.0  1.1  0.559  0.033        |    |                                |    |
|             | 45.1  2.5  0.324  0.035        |    |                                |    |
|             | 33.5  1.0  0.379  0.020        |    |                                |    |
|             | 38.7  1.8  0.405  0.032        |    |                                |    |
|             | 13.36  0.44  0.678  0.032      |    |                                |    |
|             | 2.571  0.030  0.759  0.011     |    |                                |    |
|             | 51.1  3.3  0.273  0.035        |    |                                |    |
|             | 29.99  0.93  0.495  0.024      |    |                                |    |
|             | 8.96  0.31  0.630  0.030       |    |                                |    |
|             | 8.08  0.17  0.713  0.020       |    |                                |    |
|             | 9.66  0.21  0.707  0.022       |    |                                |    |
|             | 45.0  2.2  0.198  0.023        |    |                                |    |
|             | 57.2  3.6  0.136  0.027        |    |                                |    |
| Rim         | 11.59  0.35  0.671  0.029      |    |                                |    |
|             | 33.9  1.3  0.342  0.025        |    |                                |    |
|             | 22.41  0.54  0.466  0.018      |    |                                |    |
|             | 26.69  0.67  0.522  0.020      |    |                                |    |
|             | 17.5  0.93  0.653  0.048       |    |                                |    |
|             | 32.6  1.1  0.511  0.026        |    |                                |    |
|             | 10.26  0.21  0.715  0.020      |    |                                |    |
|             | 5.403  0.089  0.786  0.017     |    |                                |    |
|             | 13.25  0.57  0.593  0.037      |    |                                |    |
|             | 17.18  0.51  0.615  0.027      |    |                                |    |
|             | 54.6  2.3  0.170  0.019        |    |                                |    |
|             | 27.29  0.74  0.450  0.020      |    |                                |    |
|             | 23.23  0.70  0.579  0.026      |    |                                |    |
SUPPLEMENTARY MATERIALS

The Appendixes (Table A1, Table A2, and Figure A1) are available online from https://doi.org/10.2465/jmps.210814.

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