Determination of reaction kinetics using grain size: An application for metamorphic zircon growth

Kazuhiro Miyazaki1 | Yasushi Mori2 | Tadao Nishiyama3 | Kenshi Suga4 | Miki Shigeno2

1Geological Survey of Japan, AIST, Tsukuba, Ibaraki, Japan
2Kitakyushu Museum of Natural History and Human History, Kitakyushu, Japan
3Department of Earth and Environmental Science, Faculty of Advanced Science and Technology, Kumamoto University, Kumamoto, Japan
4Department of Earth Sciences, National Taiwan Normal University, Taipei, Taiwan

Correspondence
Kazuhiro Miyazaki, Geological Survey of Japan, AIST, Tsukuba, Ibaraki, Japan. Email: kazu-miyazaki@aist.go.jp

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Abstract
The reaction kinetics of metamorphic minerals can be subdivided into interface- and diffusion-controlled kinetics. The discrimination of reaction kinetics is crucial for estimating reaction rates. Here, we propose a new and simple method for discriminating reaction kinetics. This method requires measuring only the initial and final grain sizes during growth. The reaction kinetics is inferred from different plotted arrays of initial vs. final grain sizes after the mineral growth. Using metamorphic zircon, we take detrital core sizes as the initial sizes and post-metamorphic grain sizes as the final sizes. The application of the method to the subduction-related high-pressure Nagasaki metamorphic complex in Japan shows that this metamorphic zircon grew under interface-controlled kinetics even at the relatively low temperature of 440°C. This method is potentially applicable to other minerals that have time-markers, such as chemical zoning or internal structures that are captured at a given point in time during growth.

1 INTRODUCTION

The kinetics of metamorphic reactions are subdivided into two regimes: interface- and diffusion-controlled. Interface-controlled kinetics imply that the rates of reaction at a mineral interface determine the net reaction rate, whereas the diffusion-controlled kinetics imply that the diffusion rate of the slowest chemical component controls the net reaction rate. Most metamorphic reactions involve dehydration or hydration. Therefore, the metamorphic reaction rates constrain the fluid flux. In addition, the growth rate of metamorphic minerals from progressive metamorphic reactions governs metamorphic rock texture.

Despite the efforts of previous studies of reaction kinetics, discriminating the type of kinetics is difficult, apart from a small number of cases. For example, Miyazaki (2015) determined the diffusion-controlled reaction kinetics of the garnet-forming reaction. In this case, garnet was produced with a clear diffusion halo, which is diagnostic of diffusion-controlled kinetics. However, garnets with clear diffusional haloes are rare. As such, reaction kinetics are usually assumed a priori when determining the reaction rates and fluid fluxes as well as the evolutions of metamorphic textures. For example, interface-controlled kinetics have been assumed for field measurements of high-temperature bulk reaction rates (Baxter & DePaolo, 2002a, 2002b) and for the assessment of nonlinear reaction kinetics in the parameterization of metamorphic fluid flow (Zhao & Skelton, 2014). Diffusion-controlled metamorphic reactions have been assumed to be responsible for the textural evolutions of metamorphic rocks due to Ostwald ripening (Miyazaki, 1991, Miyazaki, 1996), diffusion-limited aggregation (DLA) (Miyazaki, 2001) and nucleation and growth (e.g. Carlson, 1989; Kelly, Carlson, & Ketchman, 2013). Evaluations of overstepping (i.e. the degree of super-saturation) also assume interface-controlled garnet growth (Gaidies, Pattison, & de Capitani, 2011). Metamorphic reaction rates and fluid fluxes derived from
metamorphic rocks as well as predicted rock textures (the metamorphic grain size and the spatial distribution of minerals), depend strongly on reaction kinetics. Here, we present a new and simple method for the discrimination of reaction kinetics. We apply the method to the subduction-related high-pressure Nagasaki metamorphic complex of Japan.

2 | METHODS

We propose a new method for discriminating reaction kinetics. The reaction kinetics of metamorphic minerals can be subdivided into interface- and diffusion-controlled types. The growth rate \( \frac{da}{dt} \) takes different forms depending on the reaction kinetics, which are written as follows (e.g. Kretz, 1994):

\[
\frac{da}{dt} = k_1 \left( \frac{a}{C_0} \right); \text{ diffusion-controlled kinetics} \quad \text{(1)}
\]

\[
\frac{da}{dt} = k_2; \text{ interface-controlled kinetics} \quad \text{(2)}
\]

where \( a \) is the grain size, and \( k_1 \) and \( k_2 \) are the kinetic coefficients for diffusion- and interface-controlled kinetics, respectively. The integrals of Equations 1 and 2 are, respectively,

\[
\sigma^2 - a_0^2 = \int_0^t k_1 dt, \text{ (diffusion-controlled kinetics)} \quad \text{(3)}
\]

\[
a - a_0 = \int_0^t k_2 dt, \text{ (interface-controlled kinetics)} \quad \text{(4)}
\]

where \( a_0 \) is the initial grain size. Individual grains have the same kinetic coefficients at a given point in time, so the integration of the right-hand term of Equation 3 is independent with respect to grain size. This remains true, even if the kinetic coefficient has a pressure-temperature dependency. The differences of the squares of the grain sizes between the initial and final sizes in the left terms of Equation 3 are constant for all grains. In the same manner, the differences of the grain sizes between the initial and final sizes in the left terms of Equation 4 are also constant for all grains.

Although the kinetic coefficients and durations of growth in Equations 3 and 4 are unconstrained, the individual grains should obey Equation 3 or 4. This leads to different relationships between \( a \) and \( a_0 \) for different growth kinetics. Assuming the initial size distribution is Gaussian, the interface-controlled kinetics results in a linear line with a slope of one on an \( a \) vs. \( a_0 \) plot (Figure 1a), whereas the diffusion-controlled kinetics result in progressive departures from this line with decreasing \( a_0 \) (Figure 1b). This departure results from the dependency of the growth rate of \( a \) in Equation 1, whereby the growth rate of a smaller initial grain is greater than that of a larger initial grain.

3 | SAMPLES

Zircons from the pelitic schists of the Nishisonogi unit (Nishiyama, Mori, & Shigeno, 2017) of the Nagasaki Metamorphic Complex on the Nishisonogi Peninsula, Kyushu, southwest Japan, were used for our experiments (Figure 2). The Nagasaki Metamorphic Complex represents the western extension of the Sanbagawa Metamorphic Complex that extends along the Japanese islands for approximately 1,000 km (Miyazaki, Ozaki, Saito, & Toshimitsu, 2016) and is a typical high-pressure and low-temperature, intermediate-type metamorphic complex. The Nishisonogi unit comprises pelitic schists with minor mafic schist, serpentinite, quartz schist and psammitic schist (Nishiyama, 1989; Nishiyama et al., 2017). The protolith of the pelitic schist is a mudstone containing carbonaceous material (CM). The pelitic schist also contains detrital zircon grains. The detrital zircon U-Pb ages from psammitic schist (Kouchi et al., 2011) and the igneous zircon U-Pb ages of a jadeite protolith (Mori, Orihashi, Miyamoto, Shigeno, & Nishiyama, 2011) indicate that the depositional age is <86 Ma. The metamorphic phengite K-Ar ages for the pelitic schists (Hattori & Shibata, 1982) and the \(^{40}\text{Ar}/^{39}\text{Ar} \) ages of the phengite and biotite from jadeite (Mori et al., 2011) show that metamorphism occurred between 85 and 60 Ma. The peak metamorphic conditions for the schists were correlated with those of the Sanbagawa metamorphic
complex, which reached the garnet zone (Nishiyama, 1990). These conditions are 7.0–8.5 kbar and 440/°C in the garnet zone (Enami, Wallis, & Banno, 1994). The pelitic schist consists of quartz, albite, phengite, chlorite and garnet, with minor CM, zircon, apatite and titanite.

To observe the internal structure of the zircons and to measure their grain sizes, we obtained images from an optical microscope as well as cathodoluminescence (CL) and backscattered electron (BSE) images. CM was found in the zircon rims and in the matrix of the pelitic schists. We measured the degree of graphitization using Raman spectrometry. The procedures for the observation of the internal structure of the zircons, the measurements of grain sizes and the Raman spectrometry are given in Appendix A.

4 | RESULTS

4.1 | Zircon core–rim structures

The zircons show clear core and rim structures (Figure 3). Optical microscope images show that small inclusions of CM occurring in the zircon rims (Figure 3a,e), whereas the zircon cores are free of CM. The BSE images show small dark domains of CM in the zircon rims (Figure 3b). Some of the CM identified by optical microscopy is not evident in the BSE images. The focal points of the CM under the optical microscope show that these are not exposed on the polished surfaces of the zircons. The CL images also show distinct zircon core–rim structures with oscillatory zoned cores and blocky rims (Figure 2c,f). The core–rim boundaries in the CL images are identical to the boundaries between the CM-present and CM-free areas in the optical microscope images. The grain sizes and morphologies of the CM in the zircon rims are identical to those in the matrix of the pelitic schists (Figure 2d).

4.2 | Raman spectra and carbonaceous material thermometer

Metamorphic temperatures were estimated by RSCM (Figure 4) using the calibration of Aoya et al. (2010). The estimated temperature is approximately 440°C, which is consistent with the previously proposed metamorphic conditions (Nishiyama, 1990). The estimated temperature for the CM inclusions in the zircon rims is identical to those for the CM in the pelitic schist matrix (Figure 4). No differences were detected in the estimated temperatures among the samples analysed.

4.3 | Zircon grain size

We measured the grain sizes of the zircon cores and the zircon cores plus rims (Figure 5). The average grain sizes of the zircon cores range from 45 to 62 μm. The development of the rims can be recognized in the vertical deviation from a line through the origin with a slope of one on a plot of zircon core size vs. the core plus rim size (Figure 5). The developments of rims vary from sample to sample. However, the plotted data form a linear array parallel to a line with a slope of one. This implies that the dispersion of the increment length of rim at an arbitrary core size is due to the dispersion around the intrinsic average of the increment length of the rim.
5.1 Metamorphic zircon rim growth

The very fine-grained CM inclusions in the zircon rims and the matrix of the pelitic schist suggest that the zircon grains occluded the CM during rim growth. In addition, the CM inclusions in the zircon rims and the matrix of the pelitic schist experienced the same thermal histories. These observations strongly suggest that the zircon rims have a metamorphic origin and that the zircon cores are detrital. As described earlier, the protolith age is <86 Ma and metamorphism occurred between 85 and 60 Ma, thereby constraining the growth of metamorphic zircons to the period between 85 and 60 Ma.

5.2 Discrimination of the growth kinetics of metamorphic zircon

We applied the discrimination method to the metamorphic zircon from the Nishisonogi unit of the Nagasaki metamorphic complex, Japan. We can take the measured $a_0$ from the detrital zircon size as the initial size. This is a unique feature of the discrimination of the growth kinetics using metamorphic zircon. The measured zircon sizes are scattered around the intrinsic average of the growth increments of each sample. We also evaluated the sectioning errors associated with measuring the grain sizes (see Appendix B). However, the scattering cannot be attributed to sectioning errors. Therefore, to compare an array of grain sizes with a calculated array, we introduce a stochastic dispersion of the kinetic coefficients $k_1$ and $k_2$. The stochastic dispersion was introduced as a stochastic dispersion of the right-hand terms in Equations 3 and 4. The initial size distribution was assumed to be Gaussian, for which the mean and variance were assumed to be similar to those of the measured zircon core sizes. The kinetic coefficients were generated randomly between the maximum and minimum values and were adjusted to replicate the values of the means and the dispersions of the measured zircon sizes. When the maximum value is three times greater than the minimum value, the stochastic dispersion replicates similar values.

Although the stochastic dispersion results in scattered arrays, the differences in the arrays between diffusion and interface-controlled kinetics are still clear (Figure 6a,b). Because individual grains in the same sample should have different interface conditions for interface-controlled kinetics or different effective diffusivities around growing
**FIGURE 5** Grain size of detrital zircon cores ($a_0$) vs. the grain size of zircon after the growth of metamorphic zircon rims ($a$). The dashed line passes through the origin with a slope of one. (a) NM10, (b) NM11, (c) NM12, (d) NM15, (e) NM16

**FIGURE 6** Initial grain size ($a_0$) vs. grain size after growth ($a$) for (a) interfacial- and (b) diffusion-controlled kinetics with dispersions of the kinetic coefficient. The initial size distribution was assumed to be Gaussian with a mean of 45 $\mu$m and standard deviation of 15 $\mu$m. The kinetic coefficients vary as a random stochastic value, where the maximum value is three times larger than the minimum value. The dashed line has a slope of one.
grains, the stochastic dispersion of the kinetic constant is reasonable for natural samples. Indeed, a growth rate dispersion depending on the surface condition of growing grains in the solution has been proposed as a real phenomenon (Srisanga et al., 2015).

The plotted arrays of $a$ vs. $a_0$ for the Nagasaki metamorphic complex (Figure 5a–f) are parallel to the line through the origin with a slope of one and are similar to the scattered array for the interface-controlled kinetics with the dispersion of the kinetic coefficient (Figure 6a). These results suggest that the metamorphic zircons in the Nagasaki metamorphic complex grew under interface-controlled kinetics. The interface-controlled kinetics implies that the rate of transport of the slowest component was sufficiently higher than the rate of the reaction at the zircon. Such a situation may be possible even at the relatively low temperature of $T = 440^\circ$C when sufficient fluid is available during metamorphism.

Metamorphic zircon growth requires a source of Zr. The source of Zr is somewhat problematic. However, it is possible that zircon grains smaller than the measured size (e.g. < 5–10 μm) dissolved through Ostwald ripening and supplied Zr for metamorphic zircon growth (e.g. Kawakami et al., 2013; Nemchin, Giannini, Bodorkos, & Oliver, 2001; Vavra, Schmid, & Gebauer, 1999). In addition, interface-controlled Ostwald ripening of zircon in a quartz + water system has been experimentally observed (Ayers, DeLaCruz, Miller, & Switzer, 2003). LSW theory (Lifshitz & Slyozov, 1961; Warner, 1961) predicts that the mean diameter $<D>$ increases with $t^{1/2}$, although individual grain size $D$, which is much larger than the critical radius, increases with $t$ for the interface-controlled kinetics at constant temperature and pressure conditions. Equation 4 shows that the individual grain size $D$ increases with $t$ at constant temperature and pressure conditions. Therefore, our results are consistent with the experimental results of Ayers et al. (2003).

5.3 | Implications

The reaction kinetics of metamorphic minerals cannot usually be directly determined from observations of natural samples (e.g. Miyazaki, 2015) due to the following factors: (1) the rarity of direct evidence of diffusion-controlled growth, such as diffusional haloes, and (2) the lack of a relationship between the interface-controlled growth and any specific spatial structure. Even if diffusion-controlled growth occurs, a diffusion halo will not form at very low degrees of super-saturation. However, the method presented in this paper could be used even in such situations, given that individual grains record reaction kinetics. The durations and kinetic coefficients do not affect the shapes of the arrays in our discrimination diagram (Figures 1a,b and 6a,b), which is solely dependent on the reaction kinetics.

The method presented in this paper is potentially applicable to other minerals that have time-markers at a given point in time, such as chemical zoning in garnet or the internal structure of amphibole with both igneous and metamorphic origins. The determination of growth kinetics should establish a clear relation between mineral size and the durations of mineral growth using Equation 3 or 4. Such a relation is crucial to understanding the progress of mineral reactions.

6 | CONCLUSIONS

We proposed a new method for the discrimination of reaction kinetics using grain size that requires measuring only the initial and final grain sizes during growth. We applied this method to metamorphic zircon growth in the Nagasaki metamorphic complex of Japan. Detrital zircon can be used to constrain the initial sizes prior to metamorphic zircon growth, which is a unique feature for discriminating reaction kinetics using metamorphic zircon. The results suggest that the metamorphic zircon grew under conditions of sufficient fluid during high-pressure and low-temperature subduction zone metamorphism. The method presented in this paper is potentially applicable to other minerals that have time-markers at a given point in time, such as the chemical zoning in garnet or the internal structure of amphibole with both igneous and metamorphic origins.

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ORCID

Kazuhiro Miyazaki http://orcid.org/0000-0002-7159-2010

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