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Metamorphic Zirconology of Crustal Rocks during Continental Collision

CHEN Renxu*, CHEN Yixiang, LI Wancai, SHENG Yingming, XIA Qiongxia and ZHENG Yongfei

CAS Key Laboratory of Crust-Mantle Materials and Environments, School of Earth and Space Sciences, University of Science and Technology of China, Hefei 230026, China

In order to decipher the origin of zircon and its bearing on U-Pb dating and petrological tracing, an integrated study of zircon mineragraphy (internal structure and external morphology), U-Pb geochronology, mineral inclusions, trace elements, and Lu-Hf and O isotopes was carried out for ultrahigh-pressure (UHP) metamorphic rocks in the Dabie-Sulu orogenic belt. The results enable to distinguish metamorphic zircon from metamorphosed zircon, providing constraints on the nature of fluid/melt action during continental subduction-zone metamorphism. On the basis of differences in the medium of zircon growth, we define metamorphic zircon as new growth from the aqueous fluid of metamorphic origin and anatectic zircon as new growth from the hydrous melt of ultrametamorphic origin. In terms of differences in the mechanism of metamorphic recrystallization of protolith zircon, we categorize the metamorphosed zircon into solid-state transformation, replacement alteration and dissolution reprecipitation, respectively. The different types of zircons occur in the UHP rocks, depending on the accessibility and physicochemical property of fluid/melt during the metamorphism. They show different characteristics in mineragraphy, trace element, U-Pb ages, and Lu-Hf and O isotopes.

The metamorphic zircon in UHP metamorphic rocks commonly occurs either as small anhedral grains or as overgrowths around relict cores of protolith zircon. It is unzoned in CL images and exhibits concordant U-Pb metamorphic ages, low Th/U (<0.1) and $^{176}Lu/^{177}Hf$ ratios, elevated $^{176}Hf/^{177}Hf$ and Hf/Y ratios, and low REE, Th and HFSE contents but high Hf contents (Xia et al., 2009; Chen et al., 2010, 2011). Its HREE patterns are flat because of garnet stability at eclogite-facies conditions. The trace element and radiogenic isotope composition of metamorphic zircon are dictated by the composition of metamorphic fluid (Zheng, 2009). Despite the presence of fluid activity during peak UHP metamorphism, zircon growth is usually episodic in UHP metasedimentary and metavolcanic rocks, primarily corresponding two episodes of fluid activity at prograde HP-UHP eclogite-facies transformation during subduction and at retrograde UHP-HP eclogite-facies transformation during exhumation, respectively (Gao et al., 2011; Zheng et al., 2011a). In contrast, only one episode of zircon growth occurs in UHP metaintrusive rocks, suggesting one episode of fluid activity during exhumation (Xia et al., 2013). Such a difference indicates that the nature of premetamorphic protolith dictates the release of metamorphic fluid and thus the zircon growth during continental collision (Zheng, 2012; Xia et al., 2013).

Metamorphic zircon also occurs as large euhedral crystals in felsic veins within UHP eclogites (Zheng et al., 2007; Wu et al., 2009; Chen et al., 2012; Sheng et al., 2012, 2013), indicating the chemical transport of element Zr by metamorphic fluid. Such fluid-grown zircon exhibits similar element and isotope characteristics to the fluid-grown zircon in the UHP metamorphic rocks, indicating origin of the aqueous fluid from metamorphic dehydration of the UHP rocks themselves. Relict cores of the protolith zircon are common in the veins (Chen et al., 2012; Sheng et al., 2012, 2013), suggesting physical transport of the protolith zircon by the metamorphic fluid. This explains the occurrence of both old relict and newly grown zircons in metamorphic vein and orogenic peridotite. The pegmatite vein and its host gneiss contain both melt- and fluid-grown zircons, which are recorded by variations in trace element contents and REE patterns (Li et al., 2013).

Partial melting has been identified in UHP metamorphic rocks in the Dabie-Sulu orogenic belt (Zheng et al., 2011b; Gao et al., 2012; Liu et al., 2012; Chen et al., 2013a, 2013b). It occurs at varying scales from thin sections to outcrops, forming different types of migmatites. This demonstrates that anatectic melts are generated by ultrametamorphism at elevated P-T conditions, postdating the peak UHP eclogite-facies metamorphism. Alkalic to granitic dykes and intrusions of synexhumation age are

* Corresponding author. E-mail: chenrx@ustc.edu.cn

highly evolved products of the anatectic melts (Liu et al., 2009b; Zhao et al., 2012). Anatectic zircon primarily occurs in migmatitic rocks and pegmatites (Wallis et al., 2005; Liu et al., 2009a, 2010, 2012; Zong et al., 2010; Zeng et al., 2011; Chen et al., 2013a, 2013b; Xu et al., 2013), whereas magmatic zircon typically occurs in synexhumation magmatic intrusions (Zhao et al., 2012). The magmatic zircon generally exhibits oscillatory zoning, high REE contents and steep REE patterns, high Th/U (>0.1) and Lu/Hf ratios, positive Ce and negative Eu anomalies. In contrast, the anatectic zircon usually exhibits weak zonation (no zoning to cloudy zoning, occasionally oscillatory zoning) and low Th/U ratios (generally <0.1), containing multiphase solid inclusions of Qtz±Ab±Kfs±Ap. Compared to the protolith zircon of magmatic origin, the anatectic zircon exhibits similar REE contents but steeper HREE patterns, lower Th contents, similar U contents, higher Hf contents, similar or higher Nb and Ta contents, similar Ce and Eu anomalies, similar Nb/Ta ratios, similar or lower Lu/Hf ratios but higher ^{176}Hf/^{177}Hf ratios. The U-Pb dating indicates that anatexis of the UHP metamorphic rocks primarily takes place at high-T/HP granulite-facies during the early exhumation. However, coesite inclusions also occur in some domains of anatectic zircon (Chen et al., 2013a, 2013b), demonstrating that the anatexis would have started still at the UHP eclogite-facies during the initial exhumation.

Most anatectic and magmatic zircons of synexhumation growth exhibit higher ^{176}Hf/^{177}Hf ratios than the relict cores of protolith zircon (Liu et al., 2009a, 2009b, 2010; Zhao et al., 2012; Chen et al., 2013b), suggesting that the anatexis is associated with the decomposition or recrystallization of high Lu/Hf minerals in the UHP metamorphic rocks. Sometimes different episodes of anatectic and magmatic zircon growths occur in the same samples (Liu et al., 2009a, 2009b, 2010, 2012; Chen et al., 2013b). They exhibit different Hf and O isotope compositions in some samples (Liu et al., 2009b; Chen et al., 2013b), implying different origins of these anatectic and magmatic melts. Although the magmatic and anatectic zircons from the migmatites and pegmatites show significant differences in element contents and ratios, their similar Hf isotopic compositions suggest the similar origins. Therefore, they record the partial melting of UHP metamorphic rock with petrological evolution from the anatectic melt to the magmatic melt during the exhumation of deeply subducted continental crust. The anatectic melt is produced by partial melting of UHP metamorphic rocks at low degrees, resulting in migmatites. The anatectic melt is not left from its parental rocks and thus not saturated yet with water and incompatible elements. In contrast, the magmatic melt has been separated from its parental rocks and transported upwards to achieve the saturation of water and incompatible elements with the equilibrium crystallization of magmatic minerals. The anatectic melt becomes magmatic melt after the petrological evolution to high extents through significant ascent and accumulation.

Metamorphic recrystallization of protolith zircon proceeds via the mechanisms of structural modification and chemical alteration (Xia et al., 2009, 2010, 2013; Chen et al., 2010, 2011). The presence or absence of fluid/ melt and the extents and behaviors of fluid action cause the three different types of recrystallization, resulting in reworking of the internal structure at different extents and the partial decouple of trace elements as well as O, U-Th-Pb and Lu-Hf isotopes during the metamorphism. The differential behaviors of different element and isotope systems during the metamorphism are dictated by the difference in their diffusion behaviors in zircon. The solid-state recrystallization of protolith zircon occurs during fluid-absent metamorphism. Its internal structure and U-Th-Pb isotopes were partially reset, with clear to blurred oscillatory zoning and apparent ^{206}Pb/^{238}U ages close to the protolith age or slightly decreasing towards the metamorphic age. Th/U ratios were decreased but still larger than 0.1. In contrast, its trace elements, Lu-Hf and O isotopes have almost completely inherited those of protolith zircon. The diffusion is a principal mechanism for, the element and isotope loss in this process. The metamorphic fluid may be present in the matrix, but it is not accessible to the solid-state recrystallization.

The replacement recrystallization of protolith zircon exhibits enhanced reworking by fluid/melt, resulting in fir-tree zoning, weak zoning or unzoning in CL images. Porphyritic texture may develop when dissolution reprecipitation happens along grain fractures and boundaries. As a whole, it exhibits lowered Th/U ratios, with apparent ^{206}Pb/^{238}U ages clearly moving towards the metamorphic age. The ^{176}Lu/^{177}Hf ratios slightly decrease and the ^{176}Hf/^{177}Hf ratios remain constant or slightly increase. The O isotope composition shows a large variation with δ^{18}O values between metamorphic and protolith zircons (Chen et al., 2011; Sheng et al., 2012). Its trace element composition is different from the protolith zircon, depending on the nature and composition of metamorphic fluid. Metasomatism is a principal mechanism for the geochemical and isotope changes in this process.

The dissolution recrystallization of protolith zircon causes the largest extent of reworking by metamorphic fluid/melt (Xia et al., 2009, 2010; Chen et al., 2010, 2011). It exhibits spongy or porous structure in CL images and young ^{206}Pb/^{238}U ages close to the metamorphic age. Concordant U-Pb ages may be obtained if the dissolution-recrystallization proceeds completely. Its Hf isotope composition depends on the openness or closure of the system. In a relatively close system, the Hf isotope composition was primarily controlled by the protolith zircon, so that the $^{176}Lu/^{177}Hf$ and $^{176}Hf/^{177}Hf$ ratios are similar to those of the protolith zircon. In an open system, the $^{176}Lu/^{177}Hf$ ratios would decrease and the $^{176}Hf/^{177}Hf$ ratios would slightly increase. Its O isotope composition was completely reset, and exhibits relatively homogeneous $\delta^{18}O$ values similar to that of metamorphically grown zircon (Chen et al., 2011; Sheng et al., 2012). Its trace element composition is different from the protolith zircon, depending on the physicochemical property and geochemical composition of metamorphic fluid. The supercritical fluid may be involved in the dissolution recrystallization of protolith (Xia et al., 2010), resulting in dissolution and reprecipitation of high-field-strength incompatible trace elements.

In summary, Zr is a HFSE element, so that Zr in the minerals is not susceptible to dissolve and transfer by the aqueous fluid. However, it can be efficiently dissolved and transported by the alkaline and supercritical fluid. As an incompatible element, Zr tends to concentrate in the hydrous melt during partial melting. New zircon growth starts as soon as the Zr saturation achieves in the metamorphic fluid and anatectic melt. The protolith zircon of magmatic and detrital origins can be modified by metamorphic recrystallization, approaching different extents of thermodynamic reequilibration. This depends on its physiochemical property (crystallinity of mineral, the presence or absence of crack in the crystal) and the accessibility to metamorphic fluid or anatectic melt. Thus, the property of zircon in premetamorphic protolith and the behaviors of Zr-bearing minerals dictate the growth and recrystallization of zircon during continental subduction-zone metamorphism.

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