



## Zircon geochemistry records the action of metamorphic fluid on the formation of ultrahigh-pressure jadeite quartzite in the Dabie orogen



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### ABSTRACT

A combined study of mineral inclusions, U–Pb ages, trace elements and Hf–O isotopes was carried out for zircons from a coesite-bearing jadeite quartzite in the Dabie orogen. The results provide insights into the action of ultrahigh-pressure (UHP) metamorphic fluids during continental deep subduction to a mantle depth and thus constraints on the origin of the jadeite quartzite in the continental subduction zone. The zircons mostly show core-rim structures in cathodoluminescence images. The overgrown rims contain rare mineral inclusions, and exhibit concordant U–Pb ages of 225 to 246 Ma and flat HREE patterns with negligible Eu anomalies. In contrast, the relict cores contain UHP metamorphic mineral inclusions such as coesite, jadeite and rutile, and show discordant U–Pb ages ranging from 983 to 2045 Ma and steep REE patterns with significant negative Eu anomalies. The U–Pb isotope data for the all cores and rims define an apparent discordia line with upper and lower intercept ages of  $2000 \pm 43$  Ma and  $234 \pm 18$  Ma, respectively. We interpret the rims with Triassic ages as the new growth of metamorphic origin and the cores with Precambrian ages as the protolith relics of magmatic origin. The relict magmatic zircons underwent two subtypes of metamorphic recrystallization, i.e., solid-state transformation and metasomatic alteration. The solid-state recrystallized zircons exhibit slightly discordant U–Pb ages close to the protolith age, steep MREE–HREE patterns, and almost unchanged Hf isotope ratios. These observations point to the lowest degree of resetting to the geochemical composition of protolith zircons. In contrast, the metasomatically recrystallized zircons exhibit partial resetting in protolith zircon REE composition and U–Pb and Lu–Hf isotopic systems. All of the zircon domains, regardless of the rims and cores, show relatively consistent  $\delta^{18}\text{O}$  values of  $4.0 \pm 0.2\%$ . Such a consistency indicates not only that the metamorphic fluids are of internal origin from the deeply subducted continental crust but also that the oxygen isotope composition of protolith zircons was reequilibrated with the UHP metamorphic fluids of Triassic age. The metasomatic recrystallization of protolith zircons is indicated by the occurrence of UHP inclusion minerals such as coesite, rutile and jadeite in sealed microcracks. In this regard, the fluid metasomatism firstly took place along fractures of the relict zircons during prograde subduction of the continental crust and then experienced the metamorphic recrystallization to result in sealing of the fractures under the UHP conditions. As such, the metasomatic recrystallization has heterogeneously reset the U–Pb and Lu–Hf isotope systems of protolith zircons. The composition of inclusion minerals within the relict zircon cores suggests that the metamorphic fluids were rich in Si, Ti, Na and Al. These elements would be acquired by the metamorphic fluids through metasomatic reaction of metagreywackes overlying the granitic orthogneiss. Therefore, the jadeite quartzite would be precipitated from the UHP metamorphic fluids that were derived from dehydration of the underlying basement orthogneiss but reacted with the metagreywackes during the continental subduction-zone metamorphism.

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### 1. Introduction

Jadeitites and jadeite-rich lithologies are relatively rare rocks on Earth. They are composed predominantly of jadeite and typically associated with tectonic blocks of high-pressure (HP) to ultrahigh-pressure (UHP) metabasites (e.g., eclogites, blueschists) in oceanic and continental subduction zones (Schertl et al., 2012; Tsujimori and Harlow, 2012;

Harlow et al., 2015). In general, most jadeitites and jadeite-bearing rocks are interpreted as precipitating directly from metamorphic fluids, or metasomatic replacement of a protolith via metamorphic fluids (Shi et al., 2005; Harlow et al., 2007, 2015; Yui et al., 2010; Tsujimori and Harlow, 2012; Schertl et al., 2012; Yui and Fukuyama, 2015). In either case, the metamorphic fluids are required to dissolve Na, Al and Si from host rocks through extensive infiltration and fluid-mineral reaction for the eventual formation of jadeite and jadeite-rich rocks. Jadeite may form through the decomposition of albite during prograde metamorphism (e.g., Holland, 1980; Zhai et al., 1992; Liou et al., 1997; Su

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et al., 1996, 2004; Zhang et al., 2014). It may also decompose to albite and nepheline when the temperature decreases at a certain pressure (Gasparik, 1990; Prewitt and Burnham, 1996).

Jadeite quartzite is basically a two-phase rock that is mainly composed of jadeite and quartz. It is also a rare rock type in continental subduction zones where it commonly occurs as intercalations in pyrope quartzites (e.g., Chopin, 1984; Schertl and Schreyer, 2008), mafic eclogites (e.g., Dobretsov, 1963; Sobolev et al., 1986; Bröcker and Keasling, 2006; Schertl et al., 2012) and felsic gneisses (e.g., Zhai et al., 1992; Okay, 1993; Zhang et al., 1995; Liou et al., 1997). Although many studies of petrology, geochemistry, geochronology and microfabrics have been devoted to jadeite quartzite, it still remains to answer the following questions. What is the protolith of jadeite quartzite? How did jadeite quartzite form during subduction-zone metamorphism? Why did jadeite quartzite form in different subduction zones? If jadeite quartzite would also form through a metasomatic process like jadeitite and jadeite-rich rocks, a resolution to its origin will provide insights into the nature of metamorphic fluids attending the fluid–rock interaction in continental subduction zones.

Accessory minerals such as zircon, rutile and titanite widely occur in UHP metamorphic rocks, especially in jadeite quartzite (e.g., Wang et al., 1995, 2010; Cong et al., 1995; Liou et al., 1997). These accessory minerals usually exhibit complex responses to fluid action during subduction-zone metamorphism (Rubatto and Hermann, 2003; Su et al., 2004; Zheng et al., 2007; Gregory et al., 2009; Gao et al., 2011; W.-C. Li et al., 2013). Among them zircon has been a very important one because it can serve as a sensitive monitor of fluid–rock interaction during subduction-zone processes (e.g., Zheng, 2009; Fu et al., 2010; Hermann et al., 2013). As a refractory mineral, protolith zircon is resistant to metamorphic reaction and thus essentially inert in the absence of metamorphic fluids. As soon as the metamorphic fluids are accessible, however, the protolith zircon may experience variable degrees of recrystallization via the mechanisms of solid-state transformation, dissolution reprecipitation, and metasomatic alteration along fractures and crystal boundaries (Hoskin and Black, 2000; Hoskin and Schaltegger, 2003; Xia et al., 2009, 2010, 2013; Chen et al., 2010, 2011; Liu et al., 2012). On the other hand, zircon may newly grow by metamorphic reactions of protolith minerals under subsolidus conditions (e.g., Fraser et al., 1997; Rubatto, 2002), or precipitated from aqueous fluids (e.g., Rubatto and Hermann, 2003; Zheng et al., 2007; Chen et al., 2010) or hydrous melts (e.g., Xia et al., 2009; Chen et al., 2013a, 2013b; W.-C. Li et al., 2013). In either case, the property of metamorphic fluids is a key not only to the recrystallization of protolith zircons under subduction-zone conditions (e.g., Rubatto and Hermann, 2007; Xia et al., 2009, 2010, 2013; Chen et al., 2010, 2011; Liu et al., 2012; Li et al., 2014) but also the growth of metamorphic and anatectic zircons (Zheng et al., 2007; Zheng, 2009; Chen et al., 2012; W.-C. Li et al., 2013; Li et al., 2014).

Both metamorphosed and metamorphic zircons occur in many UHP metamorphic rocks (e.g., Zheng, 2009; Liu and Liou, 2011; Hermann et al., 2013). The protolith zircon may suffer variable extents of modification via the different mechanisms of recrystallization during subduction-zone metamorphism, mainly depending on zircon crystallinity and fluid accessibility (Xia et al., 2009, 2010; Chen et al., 2010, 2011). Generally, the modification is not significant at low metamorphic grades where non-metamictic protolith zircons tend to survive, although they can be mechanically fractured (Wayne and Sinha, 1992; Hoskin and Schaltegger, 2003). At higher metamorphic grades, the protolith zircon may be significantly altered by metamorphic fluids to result in partial to complete re-setting of geochemical compositions (e.g., Martin et al., 2008; Xia et al., 2009, 2010; Chen et al., 2010, 2011, 2012, 2013a, 2013b). The redistribution of geochemical compositions may be recorded by compositional variations of metamorphosed zircons during HP to UHP metamorphism (Möller et al., 2003; Xia et al., 2009, 2013; Chen et al., 2010, 2011). The great advantage of zircon as a fluid monitor is that it can be accurately dated by the U–Pb method, providing an absolute age for fluid action (Zheng, 2009; Chen et al., 2012; Hermann et al., 2013). Either

metamorphic or metamorphosed zircons can be used to trace the fluid–rock interaction during subduction-zone processes (Chen et al., 2010; Zheng, 2012; Xia et al., 2013). Therefore, the fluid action during subduction-zone metamorphism can be deduced from various records of zircons in HP to UHP metamorphic rocks (Zheng, 2009; Hermann et al., 2013).

The role of metamorphic fluids during the recrystallization of protolith zircon by dissolution–reprecipitation and subsequent compositional changes has been evaluated by several studies (e.g., Geisler et al., 2001; Hoskin and Schaltegger, 2003; Xia et al., 2010). Upon the fluid action, the protolith zircon is susceptible to reworking along grain surface and internal fractures due to fluid infiltration and exchange (e.g., Valley et al., 1994; Xia et al., 2013). The precipitation of jadeite from metamorphic fluids indicates their alkalic property, which has a capacity to dissolve some fluid-immobile incompatible trace elements such as Zr (e.g., Zheng et al., 2007). The occurrence of zircons in jadeite quartzites provides us with an excellent opportunity to decipher the action of metamorphic fluids on the modification of protolith zircons. The U–Pb dating and geochemical analysis of metamorphic and metamorphosed zircons from UHP metamorphic rocks can provide insights into the action of deep fluids during subduction-zone processes (e.g., Rubatto and Hermann, 2007; Xia et al., 2009, 2010; Chen et al., 2010, 2012; Hermann et al., 2013). Thus, an integrated study of mineral inclusions, U–Pb ages and geochemical compositions in zircon from jadeite quartzites can provide constraints not only on the property and time of fluid action, but also on the mobility of elements and isotopes in subduction zones.

In order to decipher the action of metamorphic fluids in the petrogenesis of jadeite quartzites, we have carried out a combined study of zircon U–Pb ages, trace elements, and Lu–Hf and O isotopes, together with microscopic observation, cathodoluminescence (CL) imaging and laser Raman analysis, for UHP jadeite quartzite from the Dabie orogen in China. The results provide new insights not only into the origin of different zircon domains but also into the time and conditions of fluid action during continental subduction-zone metamorphism. A further constraint on the protolith nature of jadeite quartzite is also provided by the present study.

## 2. Geological setting and sample

The Dabie orogen is located between the South China Block and North China Block in east-central China (insert in Fig. 1a). It belongs to the western segment of the Dabie–Sulu orogenic belt, which was separated by the Tanlu Fault into western and eastern segments, named as the Dabie and Sulu orogens, respectively. The Dabie–Sulu orogenic belt was built by the Triassic subduction of the South China Block beneath the North China Block (e.g., Wang et al., 1995; Li et al., 1999; Zheng et al., 2009). The findings of coesite (Okay et al., 1989; Wang et al., 1989) and microdiamond (Xu et al., 1992) inclusions in metamorphic minerals from the Dabie–Sulu orogenic belt have provided petrological evidence for the deep subduction of continental crust to mantle depths of >100 km. The Dabie orogen is composed of several fault-bounded metamorphic units. Based on the lithotectonic characteristics (Zheng et al., 2005; Zheng, 2008), it is subdivided into five major zones from north to south (Fig. 1a): (1) the Beihuaiyang low-T/low-P greenschist-facies zone; (2) the North Dabie high-T/UHP granulite-facies zone with migmatization; (3) the Central Dabie mid-T/UHP eclogite-facies zone; (4) the South Dabie low-T/UHP eclogite-facies zone; (5) the Susong low-T/HP blueschist-facies zone. The metamorphic grade increases from south to north, except the Beihuaiyang zone that is the accretionary wedge formed at the early stage of continental subduction (Zheng et al., 2005). Jurassic–Cretaceous sedimentary rocks occur in the southern margin of the North China Block.

Mafic eclogites mainly occur in the mid-T/UHP eclogite-facies zone in the Dabie orogenic belt, with granitic gneisses as the major host for them. Three major metamorphic stages can be retrieved for the mid-

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