Trace element features of hydrothermal and inherited igneous zircon grains in mantle wedge environment: a case study from the Myanmar jadeitite

Weiyan Lei^{a,b}, Guanghai Shi^{a*}, M. Santosh^{a,c}, Yinok Ng^a, Yingxin Liu^a, Jing Wang^a,
Gen Xie^a, Yan Ju^d

ABSTRACT

Jadeitites are considered to crystallise in ultramafic rocks in the subduction

20 channel presumably from the overlying mantle wedge, and therefore zircons from
21 these rocks provide important insights into mantle wedge processes. Here we
22 investigate hydrothermal zircon (Group II) formed within a subduction zone and
23 compare these with the igneous zircon cores (Group I) from the Myanmar jadeitite.
24 Previous U-Pb studies reported ages of Group I and II zircons as ~163 Ma, and ~147
25 Ma respectively, and both show isotope signature of the depleted mantle. Group I
26 zircons have much higher total concentrations of rare earth elements (REEs) (500 -
27 1945 ppm) than those of Group II zircon (112 - 307 ppm), and contains relatively
28 higher abundance of Y, Nb, Ta, Ti, Th and U with higher (Sm/La)_N ratios (25.3 - 501)
29 and Ce-anomalies (8.04 - 140) but lower (Yb/Gd)_N ratios (9.76 - 57.0) than those of
30 the Group II ((Sm/La)_N ratios = 2.12 - 32.2, Ce-anomalies = 1.63 - 19.6, (Yb/Gd)_N
31 ratios = 44.8 - 142). Hf concentrations are broadly similar in both Groups. The Group
32 I zircons are considered to be magmatic and crystallised from H₂O-rich basaltic melt
33 at relatively high pressure in the mantle wedge, whereas the Group II zircon
34 overgrowth took place through recrystallisation and precipitation with distinct
35 dissolution of the Group I zircons. Variation in the concentration of trace elements in
36 zircons from Group I to II in the mantle wedge is related to an intra-oceanic
37 subduction system in the presence of Na-rich hydrothermal fluids under high-pressure
38 and low-temperature. The Ti-in-zircon thermometer yield a mean crystallisation

39 temperature of $742 \pm 141^{\circ}\text{C}$ for Group I zircons, whereas the Group II zircons yields
40 $339 \pm 33^{\circ}\text{C}$. The two groups of zircons also provide insights into the probable
41 protolith involved in formation of the Myanmar jadeitite.

42

43 *Keywords:*

44 Zircon chemistry

45 Myanmar jadeitite

46 Subduction zone

47 Mantle wedge

48 H_2O -rich basaltic melt

49

1. Introduction

Zircon is a common accessory mineral in a variety of rocks formed in various tectonic settings, and is stable over a broad range of temperatures and pressures (Bingen et al., 2001; Hoskin and Schaltegger, 2003). Its high durability and resistance to various geological processes such as erosion and transportation, sluggish intracrystalline diffusion (Watson and Cherniak, 2003), as well as the capacity to host trace elements and isotopes especially U, Th, Pb, Hf, Ti, Li, rare earth element (REE) and O (e.g. Hoskin and Schaltegger, 2003; Cherniak and Watson, 2007; Page et al., 2007; Ushikubo et al., 2008) make it an important recorder for various geochemical, isotopic and geochronological investigations. Furthermore, growth zones within single grains of zircon often record distinct geological events (e.g. Belousova et al., 2006; Shi et al., 2008; Chen et al., 2010; Flores et al., 2014). Studies of inclusions, growth patterns, isotopes and trace elements in different zircon domains are useful tools to decipher the history of the host rocks and thermal events. Thus, zircon has been widely used for evaluating petrogenesis, geochronology and tectonics (e.g. Sánchez-Rodríguez and Gebauer, 2000; Liu et al., 2010, 2015, 2016; Jiang et al., 2012; Yang et al., 2016).

Jadeitite, a rare rock composed mainly of jadeite, is typically found in serpentinite in close spatial association with high-pressure/low-temperature (HP-LT)

69 metamorphic rocks such as blueschist and eclogite. Several occurrences of jadeitite
70 have been reported from Phanerozoic orogenic belts such as Alps-Himalayan,
71 circum-Pacific, Caribbean and Caledonian regions (e.g. [Shi et al., 2001, 2008;](#)
72 [Tsujimori et al., 2005;](#) [Usui et al., 2006;](#) [Harlow et al., 2007, 2011, 2012, 2015, 2016;](#)
73 [Compagnoni et al., 2007;](#) [Morishita et al., 2007;](#) [Garcia-Casco et al., 2009;](#) [Schertl et](#)
74 [al., 2012;](#) [Shigeno et al., 2012](#)), along with jadeitite xenoliths in serpentinitised
75 ultramafic microbreccias ([Tsujimori and Harlow 2012](#)). Jadeitite has been interpreted
76 by [Tsujimori and Harlow \(2012\)](#) as P-type, which precipitated directly from
77 subduction-zone hydrous fluids ([Harlow and Sorensen, 2005;](#) [Sorensen et al., 2006;](#)
78 [Shi et al., 2005b;](#) [Morishita et al., 2007](#)) or as R-type, which formed through
79 metasomatic replacement of a protolith by subduction-zone fluid-rock interaction
80 ([Shigeno et al., 2005;](#) [Yi et al., 2006;](#) [Compagnoni et al., 2007;](#) [Mori et al., 2011;](#)
81 [Wang et al., 2012;](#) [Ng et al., 2016](#)) in ultramafic rocks of the mantle wedge overlying
82 subduction systems. In both types, zircon occurs as an accessory mineral within
83 jadeitite or jadeitised omphacitite and rodingite (e.g., [Yi et al., 2006;](#) [Wang et al., 2012;](#)
84 [Ng et al., 2016](#)).

85 Zircon in the jadeitite from several localities worldwide can be grouped into two
86 types based on their growth textures under cathodoluminescence imaging and mineral
87 inclusions as: igneous/core (Group I) and hydrothermal /rim (Group II or/and III) (e.g.

Shi et al., 2008; Mori et al., 2011; Yui et al. 2013). In the investigation of Myanmar jadeitite by Shi et al. (2008), two main groups of zircons (Group I and II) were distinguished based on their mineral inclusions, growth texture, and SHRIMP U-Pb age, with minor Group III zircon considered to mark a later stage hydrothermal event. Recently, Yui et al. (2013) reported three Groups of zircons in one sample (BUR Z1), and recognised one group (their Type II) showing lower U-Pb age limit of ~ 77 Ma. Another sample (BUR Z2) does not have the Type II zircons, but zircon data are very similar to ours (Shi et al., 2008), and close to those reported by Qiu et al. (2009).

In this study, we use the zircon grains from a sample of the Myanmar jadeitite previously dated by Shi et al. (2008, 2009a) to investigate the chemical features using Laser Ablation Inductively-Coupled Mass Spectrometry (LA-ICP-MS) through *in situ* analyses of twenty-one trace elements in the two genetic types.

2. Geological setting and sample descriptions

The jadeitite investigated in this study is located in the northern part of the Sagaing fault belt at the Jade Mine Tract (also called the jadeite uplift), Hpakan area, Kachin state (Fig.1a). The jadeite uplift forms an important link between the Indo-Burma Range and the Myitkyina Belt. The Indo-Burma Range, to the west of the Tract, covers the areas between the Myanmar Central Basin and the western border.

Rocks in this range are progressively younger from east to west. The eastern boundary of the Range is generally defined by a discontinuous line of serpentinite mélange and/or mélange -derived blocks (Bender, 1983; Morley, 2004). The Myitkyina Belt, also called the Tagaung-Myitkyina Belt (Acharyya, 2007; Mitchell et al., 2007; Searle et al., 2007) or the Bhamo-Myitkyina Belt (Cruickshank and Ko, 2003) is composed of a serpentinite mélange zone, known as the Myitkyina-Mandalay serpentinite mélange in the Myitkyina valley, north of Mandalay. It has been suggested that the Tagaung-Myitkyina Belt and the Indo-Burma Range was a single belt, which was separated by the Sagaing Fault, leaving the jadeite uplift straddling along the fault between the Belt and the Range (Shi et al., 2014). The Sagaing fault is a major right-lateral strike-slip continental one which extends over 1200 km and reaches the Andaman spreading center at the southern end.

Primary jadeitite deposits occur as blocks or veins (known as P-Type) in the Hpakan-Tawmaw serpentinite mélange, along with boulders in drainages (Fig. 1b). Country rocks adjacent to the mélange include high-pressure rocks such as phengite-bearing glaucophane schist and stilpnomelane-bearing quartzite, and amphibolite facies rocks such as garnet-bearing amphibolite and diopside-bearing marble (Shi et al., 2001). Jadeitite vein commonly has a boundary zone of amphiboles consisting of eckermannite, magnesiokatophorite, glaucophane, richterite, winchite

and nyböite (Shi et al., 2003; Nyunt, 2009). Located within or inside the amphibole boundary, kosmochlor, Cr-bearing jadeite and Cr-bearing omphacite occur as coronal aggregates with or without a chromite core or as small blocks (Shi et al., 2005a). Small blocks of jadeitised omphacite and rodingite are also found as R-type formed through replacement by Na-rich fluids (Yi et al., 2006; Wang et al., 2012; Ng et al., 2016). Late-stage albitite veins locally crosscutting jadeite are commonly less than 5 mm wide (Wang et al., 2013).

Jadeite samples are white to pale grey, and are composed dominantly of jadeite with minor omphacite, amphibole and accessory minerals: zircon, galena and pyrite, titanite and ilmenite (Shi et al., 2008, 2012; Ng et al., 2016). Albite and analcime occur as rare secondary alteration products. Most jadeites are very pure, with jadeite (X_{Jd}) contents of more than 98 mol% (Shi et al., 2003, 2005b), whereas jadeite from grey- jadeite contains minor diopside component (normally $X_{Di} < 10$ mol%) (Shi et al., 2005b; Yi et al., 2006). It is texturally heterogeneous. Some domains are slightly deformed or undeformed, consisting of coarse-grained jadeite prisms, some even up to >20 mm long. Rhythmic zoning patterns in these large crystals are revealed in CL images, similar to the observations by Harlow (1994) and Sorensen et al. (2006). In contrast, other parts of the sample show ductile deformation domains characterised by fine-grained aggregates of oriented jadeite crystals, with some broken zircons grains

distributed along the foliation of the jadeite and occasionally omphacite (Shi et al., 2008, 2009b).

3. Summary and new classification of the studied zircons

The pale grey jadeitite sample (5.8 kg, rough) comes from the Myanmar tract (sample location is shown in Fig. 1b). About 200 zircon grains or fragments were extracted using conventional separation procedure (crushing, sieving, gravity separation, electromagnetic separation and microscopic selection) at the Langfang Laboratory, Hebei Geology and Resource Bureau. Data on mineral inclusions, SHRIMP U-Pb ages and Hf isotopic compositions of the zircons in the present study have been previously reported (Shi et al., 2008, 2009a). The selected zircons, together with standard zircons, were mounted in epoxy resin, abraded, polished and imaged by cathodoluminescence (CL) (Fig.2).

These zircons were grouped into Group I, Group II and Group III by Shi et al. (2008). Group I zircons, occurring as cores with a mean U-Pb age of ~163 Ma, are characterised by oscillatory zoning in CL images with Na-free Mg-rich silicate mineral inclusions, and were inferred to be inherited from igneous rocks formed before the jadeitite. Group II zircons, occurring as rims with a mean U-Pb age of ~147 Ma, are bright and mostly unzoned in CL images with jadeite and jadeite-rich

pyroxene inclusions, and were suggested to be hydrothermal origin, formed coevally with jadeitite. Group III zircon is represented by a single zircon domain (see Fig.3 zircon No. 1.2 (III)), with U-Pb age of ~122 Ma and occurs within small late-stage veins crosscutting Group I and Group II zircons, obviously formed during a later event after jadeitite formation. This zircon domain is too small and shows indistinguishable trace element concentrations with those of Group I zircons in this investigation, and is thus excluded from the following discussions. All groups of zircon show similar positive $\epsilon\text{Hf}(t)$ values ranging from 15.5 to 20.0, indicating their derivation from rapid reworking of juvenile oceanic crust and the presence of Mesozoic intra-ocean subduction between the Eastern Indian Plate and the Burmese Platelet (see details in Shi et al., 2008, 2009a).

The zircons from jadeitites in this region were classified by Yui et al. (2013) into Type I, Type II zircons and Type III zircons. Type I zircons show almost the same features as the Group I ones by Shi et al. (2008), whereas their Type II were interpreted to be of metasomatic/hydrothermal origin, yielding a (minimum) jadeitite formation age of 77 ± 3 Ma. The Type III zircons were regarded as incompletely recrystallised grains, with non-coherent and geologically meaningless ages from 153 to 105 Ma. They interpreted that the Myanmar jadeitites might have formed during the Late Cretaceous (77 ± 3 Ma) subduction event. However, out of their Type II and

III zircons, only three analyses from one sample are ~77 Ma. In contrast, at least 6 analyses from another sample are ~147 Ma. Unfortunately, these authors seem to have selectively chosen the minor age of ~77 Ma, disregarding the major age of ~147 Ma. The ~147 Ma age reported previously by Shi et al. (2008) is considered as the main jadeitite formation age, and their interpretations are in conflict with the $^{40}\text{Ar}/^{39}\text{Ar}$ dating results (Qi et al., 2013; Shi et al., 2014). Although their zircon data of Yui et al. (2013) may indicate new event at ~77 Ma, their age interpretations have resulted in controversy and confusion in understanding the formation age of the Myanmar jadeitite.

In this investigation, we focus on the trace element features of hydrothermal and inherited igneous zircons with a view to devising a new classification incorporating the previous data. The zircons can be classified into two groups: igneous (Group I) and hydrothermal (Group-II). The Group I ages reported by Shi et al. (2008), Yui et al. (2013) and Qi et al. (2014) show a narrow range of ages from 155 Ma to 172 Ma, with a weighted mean age of 158 ± 4 Ma, 160 ± 1 Ma to 163 ± 3.3 Ma. The Group II hydrothermal zircons display more complicated U-Pb ages than those from Group I, and can be classified into two subgroups, one with narrow age cluster and the other showing scattered ages. Subgroup I shows a weighted mean age of ~147 Ma as suggested by Shi et al. (2008), and Subgroup II has a weighted a mean age of ~77 Ma

as revealed by the data of Yui et al. (2013). In this new classification, Group II of Shi et al. (2008) and most of Type III of Yui et al. (2013) fall into the Subgroup I. Type II zircons (three points) of Yui et al. (2013) and five zircons with younger age of Qi et al. (2014) are regrouped into the Subgroup II. U-Pb ages of the other Subgroup might represent minor local events, or fall in between the ages of the other groups.

Group I zircon grains/domains in this investigation are mostly are broken fragments showing irregular outline but with well-formed straight growth zones. Some zircons have narrow fractured bands filled with lighter domains (Group II zircons) under CL, reflecting an overgrowth of Group II zircons. Group II zircons occur as overgrown rims, wrapping distinctly around the Group I zircons (Fig. 2, 3), and ranging from several μm to 50 μm wide. No discrete grains of Group II grains were found. Jadeite inclusion in Group II zircon from jadeitite suggests that they were precipitated from fluids (e.g., Schaltegger, 2007; Shi et al., 2008; Mori et al., 2011; Yui et al., 2010, 2012; Flores et al., 2014; Harlow et al., 2015) coeval with or later than the formation of the jadeitite.

4. Analytical methods

Trace element compositions were analysed on polished zircon mount by in-situ LA-ICP-MS at the Geological Lab Center, China University of Geosciences, Beijing.

The laser ablation system is a New Wave UP193SS, which is equipped with a 193 nm ArF excimer laser. An Agilent 7500A ICP-MS instrument was used to acquire ion-signal intensities. Laser ablation spots were set to be 35 μm in diameter, with the laser energy of 60 mJ, a frequency of 5 Hz and a beam energy of 12 J/cm². The procedure of laser sampling is 5-s pre-ablation, 20-s sample-chamber flushing and 40-s sampling ablation.

Standard materials for off-line selection and integration of background signals, and time-drift correction and quantitative calibration were performed using workstation data-processing program included with the 7500A operating system. The NIST SRM 610 was used as a reference material for calibration, and NIST SRM 612 as a quality control material (QCM). The concentrations of various elements (V, Cr, Mn, Co, Ni, Rb, Sr, Y, Zr, Nb, Cs, Ba, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Hf, Ta, Th, U) were acquired using Ca as internal standard. Analytical uncertainties for most elements are less than 10%, except for Cr, Ta and Cd which are less than 15%. To ensure highest reliability of data, the time-resolved spectrum of every element for each sample was carefully examined. Data for which fluctuations in the spectrum were observed were discarded (e.g., [Ng et al., 2016](#)). The analyses are listed in [Table. 1](#).

5. Results

Trace element compositions of the analysed zircon grains/domains show significant differences between different Groups (Table. 1). Total concentrations of REEs in Group I zircon (ranging from 500 to 1945 ppm) are much higher than those of Group II zircon (112 to 307 ppm). The chondrite-normalised REE patterns for both groups show similar rising slopes from Sm to Lu along with variable positive Ce-anomalies (Fig. 4). Group I zircon patterns are mainly characterised by higher $(\text{Sm/La})_N$ ratios of 25.3 - 501, higher Ce-anomalies of 8.04 - 140 and lower $(\text{Yb/Gd})_N$ ratios of 9.76 - 57.0, whereas Group II zircon patterns have lower $(\text{Sm/La})_N$ ratios of 2.12 - 32.2, lower Ce-anomalies of 1.63 - 19.6 and elevated $(\text{Yb/Gd})_N$ ratios of 44.8 - 142. Group I zones in zircon lack or exhibit a negligible Eu-anomalies, whereas, Group II zircons exhibit variable Eu-anomalies, Among five analyses of Group II zircon, two show slightly positive Eu-anomaly ($\text{Eu/Eu}^* = 1.78$ and 1.41), one slightly negative Eu-anomaly (0.79) and two do not have any obvious Eu-anomaly (0.99 and 0.98). Group I zircon contains relatively higher Y, Nb, Ta, Ti, Th and U than Group II zircon. The Hf concentrations (9528 – 14718 ppm) of Group I and -II zircons (9223 - 11870 ppm) are almost the same.

6. Discussion

259
260 *6.1. Origin of Group I zircon and formation environment of the Myanmar jadeitite*

261 Trace element features of Group I zircons confirm their igneous origin. Previous
262 results (broad-band zoning and presence of Mg-Fe-rich silicate mineral inclusions)
263 suggested that the Group I zircon formed prior to the jadeitite formation, either from
264 magmatism or from serpentinisation / rodingitisation (Shi et al., 2008). As
265 serpentinisation or rodingitisation are processes driven by hydrous fluids, origin of the
266 Group I zircon was not precisely constrained then due to inadequate and
267 well-constrained data.

268 In this investigation, the obvious positive Ce-anomalies and (Sm/La)_N ratios of
269 25.3 to 501, steep MREE-HREE patterns with high (Yb/Gd)_N ratios of 9.76 to 57.0
270 (Table 1 and Fig. 4), and total REE concentrations of Group I zircon (500-1945 ppm)
271 suggest that these zircons crystallised from mafic melts, implying igneous origin (e.g.,
272 Belousova et al., 2002; Hoskin and Schaltegger, 2003; Hoskin, 2005). There is a
273 general trend of increasing REE concentrations in igneous zircons from ultramafic
274 through mafic to granitic rocks (Belousova et al., 2002). The REE content of Group I
275 zircons is comparable to that of magmatic zircons from mafic rocks. As the
276 zircon-bearing jadeitite occurs in serpentinised peridotite in the subduction zone,
277 possible sources of the Group I zircon could be either from mantle wedge or from

subducted oceanic slab.

Of the two possibilities, Group I igneous zircons are more likely to have formed in the mantle wedge. Abundant data reveal that zircon grains formed in oceanic crustal rocks (such as plagiogranite, gabbro, and metamorphosed ultramafic rocks) commonly show significantly negative Eu-anomaly (e.g., average $\text{Eu}/\text{Eu}^* = 0.25$, [Grimes et al., 2009](#)), which is due to the fact that plagioclase fractionation consumes Eu from the magma prior to or during zircon crystallisation ([Ballard et al., 2002](#); [Hoskin and Schaltegger, 2003](#); [Grimes et al., 2007, 2009](#)). Igneous zircon from subducted oceanic slab would show significant negative Eu-anomaly. Thus, absence of an obvious negative Eu-anomaly (average $\text{Eu}/\text{Eu}^* = 0.97$, [Table 1 and Fig.4](#)) for the Group I zircons exclude the possible source of subducted oceanic slab. Zircon xenocrysts from basalts or kimberlites show lack of negative Eu anomalies ([Hoskin and Schaltegger, 2003](#); [Qiu et al., 2007](#); [Siebel et al., 2009](#); [Schärer et al., 2011](#)). Therefore, a reasonable source for Group I zircons without Eu-anomaly is mantle wedge rather than subducted oceanic slab.

Zircon is absent in primitive peridotites due to unsaturation of both Zr and Si. , However, abundant zircon grains have been reported from peridotites (e.g., [Griffin et al., 2000](#); [Grieco et al., 2001](#); [Zheng et al., 2003](#); [Song et al., 2005, 2009](#); [Zhang et al., 2005](#); [Meng and Zhang, 2009](#); [Liu et al., 2010](#)). High modal content of magmatic

zircons have been observed in garnet peridotite in Alaskan-type ultramafic cumulate intrusions ([Song et al., 2005, 2009](#)). Zircon has also been found in melt/fluid-metasomatised mantle peridotites (e.g., [Grieco et al., 2001](#); [Meng and Zhang, 2009](#); [Liu et al., 2010](#)). [Shervais \(2008\)](#) reported that the Elder Creek ophiolite contains almost all of the components of a classic ophiolite (mantle tectonites, cumulate ultramafics and gabbro, dyke complex, volcanics), and has substantial volumes (25%-30% of the complex) of felsic plutonic rocks intimately associated with the other lithologies; the latter rocks crystallised abundant zircons.

Plagioclase crystallisation-suppressed melt in mantle wedge is one of the viable options for the Group I zircons without Eu-anomaly. Zircon formed through melt-peridotite interaction normally shows a negative Eu-anomaly. [Liu et al. \(2010\)](#) reported igneous zircons in pyroxenite veins within melt-metasomatised mantle peridotites with negative Eu-anomaly (average $\text{Eu}/\text{Eu}^* = 0.42$) which is different from Group I zircons without Eu-anomaly (average $\text{Eu}/\text{Eu}^* = 0.97$). If aqueous fluids from the dehydration of the subducted slab are added into the mantle wedge, basaltic melts can be generated by partial melting of mantle wedge through fluid-peridotite interaction (e.g. [Elliott et al., 1997](#); [Woodhead et al., 1998](#)). Again, if water content is high enough ($\text{H}_2\text{O} > 3\%$) in the basaltic partial melt, plagioclase crystallisation will be suppressed at high pressures ($> 1.2 \text{ GPa}$) ([Müntener et al., 2001](#)), hence zircon

crystallising from this melt would not show a negative Eu-anomaly (Guo et al., 2007).

In other words, Group I zircons possibly crystallised from H₂O-rich melt generated by partial melting of mantle wedge during fluid-peridotite interaction within mantle wedge.

The high positive $\epsilon_{\text{Hf}}(t)$ values (15.5 – 20.0) of the Group I zircon (Shi et al., 2009a) indicates that the Group I zircons inherited the mantle Hf composition. As Hf is relatively immobile in fluid, a reasonable interpretation is that magma responsible for the igneous Group I zircons was generated by partial melting of mantle wedge through addition of slab-derived fluids, as slab-derived partial melts would have lowered $\epsilon_{\text{Hf}}(t)$ values of zircon, whereas the fluids would not (e.g., Hanyu et al., 2006).

Back-calculated REE pattern also supports the suggestion that the Group I zircon crystallised in mantle-derived basaltic magma generated by partial melting. Based on zircon/melt partition coefficients of REEs and average REE composition of the Group I zircons, we back-calculated the REE pattern of the melt, or the presumed protolith prior to the Myanmar jadeitite (Fig.5). Zircon/melt partition coefficients from Sano et al. (2002) provide an approximation to the predicted REE behavior based on lattice strain theory (Hanchar and van Westrenen, 2007; Grimes et al., 2009). The results (Fig.5) display a slightly LREE-enriched pattern $((\text{Pr}/\text{Tm})_{\text{N}} = 2.71)$, similar to the

REE pattern ($(\text{Pr}/\text{Tm})_{\text{N}} = 4.48$) of the Surigao peninsula low-silica adakite (56.7 wt.% SiO_2) generated by fractional crystallisation of H_2O -rich basaltic magma derived from mantle in subduction zone (Macpherson et al., 2006). Different magnitudes of Eu-anomaly between Myanmar jadeitite protolith ($\text{Eu}/\text{Eu}^* = 2.01$) and the Surigao peninsula adakites ($\text{Eu}/\text{Eu}^* = 0.96$) probably reflect varying level of fractional crystallisation. Using the same way, Yui et al. (2012) proposed that the probable protolith of the Tone jadeitite was adakitic granites related to melt-peridotite interaction due to their similar REE patterns ($(\text{Pr}/\text{Tm})_{\text{N}} = 26.0$, $\text{Eu}/\text{Eu}^* = 1.72$ for the Tone jadeitite vs. 13.9 and 1.77 for adakitic granites). Other probable protoliths for the Group I zircons might include tonalite-trondhjemite-diorite suite, which are commonly associated with ophiolites (e.g., Shervais, 2008)

6.2. Characteristics of hydrothermal zircon in jadeitite

Group II hydrothermal zircons show features of formation from or altered by hydrothermal fluids (Hoskin et al., 1998; Whitehouse and Kamber, 2002; Hoskin, 2005; Grimes et al., 2009). They are significantly different from the Group I zircons in trace element composition. Except for Hf, Group II zircons are depleted in almost all analysed trace elements relative to the Group I, including Ti, Th, U, Nb, Ta, Y, and

the Σ REE (Fig.6). They also show lower (Sm/La)_N ratios and Ce/Ce* but elevated (Yb/Gd)_N (Table 1 and Fig.6).

Available data show that hydrothermal zircons in jadeitites have some similarity in trace element composition relative to Group I zircon. However, they exhibit slight differences among the different localities worldwide. The Th and U concentrations in hydrothermal zircon vary apparently among the individual localities. Hydrothermal zircons from Guatemala and Tone jadeitites (Fig.7) have low Th/U ratios (< 0.005, or < 0.1 and < 0.06, respectively; Yui et al., 2010; Mori et al., 2011; Flores et al. 2013), whereas those from Myanmar and Osayama have higher Th/U ratios (0.10 – 0.20 (Fig. 3), 0.21 – 0.34, respectively; Fu et al., 2010). The enrichment of Hf and U in hydrothermal zircon from Tone jadeitite, Japan (Mori et al., 2011) is not observed in the hydrothermal zircon from Myanmar jadeitite. All hydrothermal zircons exhibit low Ce/Ce* but variable Eu/Eu* (Fig.7), reflecting complex variations of fluid chemistry during jadeitite formation, as suggested by Yui et al. (2010). Because the magnitude of Ce-anomaly is in part a function of the redox conditions of the melt/fluid from which zircon crystallised (Ballard et al., 2002; Hoskin and Schaltegger, 2003; Grimes et al., 2009), decreasing Ce-anomalies and transition from negative Eu-anomalies to positive ones of Guatemala Group II zircons suggest that jadeite-forming fluid there became more reducing with the time (Yui et al., 2010).

374 6.3. Overgrowth of hydrothermal zircon and corresponding changes in trace

375 elements

377 Group II zircons with lower $^{176}\text{Lu}/^{177}\text{Hf}$ but almost unchanged $^{176}\text{Hf}/^{177}\text{Hf}$ and Hf
378 concentration relative to Group I, reflect aqueous fluids with variable composition,
379 from which hydrothermal zircon could form either through the dissolution
380 recrystallisation of Group I zircons or by overgrowth from the metasomatic fluid with
381 same Hf isotope composition of the metasomatic fluid (Yui et al., 2010; Mori et al.,
382 2011). Some of the features such as the lower $(\text{Sm}/\text{La})_{\text{N}}$, low Ce/Ce^* , low $(\text{Y}+\Sigma\text{REE})$
383 and Ti contents of the zircons could be regarded as influence from the
384 subduction-related jadeite-forming fluids (Fig. 6,7).

385 The hydrothermal zircon overgrowth took place by precipitation with some
386 recrystallisation, but without distinct dissolution of Group I zircons, as revealed by the
387 CL imaging. Irregular shapes of Group I zircons, some even with sharp edge (zircon
388 No. 9.2(I) and 17.3(I) in Fig. 3) allow us to exclude the possibility of distinct
389 dissolution of the Group I zircon, which deviate from the essential overgrowth
390 mechanism by dissolution recrystallisation for most hydrothermal zircons (e.g., Zheng
391 et al., 2005, 2006; Flowerdew et al., 2006; Shi et al., 2009a; Chen et al., 2010). We

consider the following mechanism for its formation. From Group I zircons to the hydrothermal zircons coeval with the formation of the Myanmar jadeitite, three progressive events might have occurred: weak ductile deformation of the Group I, overgrowth of the Group II and weak ductile deformation overlapped on some zircons of both groups. Some zircons might have experienced one event (zircon No. 3.1(I) in [Fig 3](#)), and others witnessed more than three events (zircon No. 1 in [Fig. 3](#)).

This process shows slight differences from the proposed mechanism of Group II zircon from other localities. Based on the back-calculated REE pattern of the presumed protolith and Hf isotopic compositions of Group I zircon, [Yui et al. \(2012\)](#) proposed the most possible protolith of the Tone jadeitite to be subduction- zone- related adakitic granite formed through partial melting of subducted oceanic crust, while in Guatemala, the samples contain only Group II zircon and may have formed through a mechanism of vein precipitation ([Yui et al., 2010](#); [Flores et al., 2013](#)).

Growth of hydrothermal zircon requires high fluid/rock ratios and dissolution of Zr from other sources ([Rubatto and Hermann, 2007](#)). [Bingen et al. \(2001\)](#) proposed that ilmenite could provide Zr for zircon growth during metamorphism. That numerous zircons were found inside titanite and relict ilmenite in Myanmar jadeitite and related rocks ([Shi et al., 2012](#); [Ng et al., 2016](#)), more or less, explain the supply of Zr for zircon in Myanmar jadeitite. Titanite was found in omphacitite and is

411 essentially absent in Myanmar jadeitite, confirming low Ti content. Our observations
412 show that zircon occurs rarely occur in pure jadeitite from Myanmar. As Na-rich
413 hydrothermal fluids prevailed during the formation of the jadeitite (e.g., [Shi et al.,](#)
414 [2012; Harlow et al., 2015](#)), growth of the hydrothermal zircon consequently points to
415 high-pressure and low-temperature conditions.

416 An important question is how aqueous fluid penetrating the mantle wedge can
417 interact with adakite or other probable rocks that should have ascended up-T and
418 down-P through a mantle wedge. According to the life cycle of suprasubduction zone
419 (SSZ) ophiolites as summarised by [Shervais \(2001\)](#), plutonic rocks including layered
420 gabbro, troctolite, dunite, hornblende diorites, quartz diorites, tonalites, and
421 trondhjemites form during the first three stages. Stage 3 plutonic rocks typically
422 intrude at higher levels within the plutonic complex, forming tabular, sill-like bodies
423 between the layered gabbros and the sheeted dyke complex. They also form dykes and
424 sills at both deeper and shallower levels of the complex. Since aqueous jadeitic fluid
425 is chemically active, jadeitite crystallisation clearly requires an ultramafic rock at
426 subsolidus conditions (see [Harlow et al., 2015](#)). As revealed previously (see [Shi et al.,](#)
427 [2012 and references therein](#)), replaced sodic-calcic amphiboles, replaced kosmochlor,
428 and jadeitised rodingite are common in Myanmar. Thus, zircons belonging to Groups
429 I and record further information on the probable protolith involved in formation of the

Myanmar jadeitite.

6.4. Ti-in-zircon thermometer

The Ti content of zircon coexisting with rutile or other Ti-rich phases has a systematic variation attributed to difference in crystallisation temperature (Watson and Harrison, 2005; Watson et al., 2006). The initial formulation of Ti-in-zircon thermometer (Watson et al., 2006) did not account for corrections for reduced oxide activities (TiO₂ and SiO₂).

$$T (^{\circ}\text{C}) = \frac{5080 \pm 30}{(6.01 \pm 0.03) - \log (\text{Ti}_{\text{-in-zircon in ppm}})} - 273$$

Crystallisation temperature of Group I zircons is estimated as $742 \pm 141^{\circ}\text{C}$ (2 SD, $n = 21$), which is comparable to Ti-in-zircon temperatures for zircons from mafic rocks and kimberlitic mantle megacryst (average: $758 \pm 111^{\circ}\text{C}$, $n = 261$ and $758 \pm 98^{\circ}\text{C}$, $n = 84$, respectively) and significantly higher than that for zircons from felsic and intermediate rocks ($653 \pm 124^{\circ}\text{C}$, $n = 60$; Fu et al., 2008). This result is consistent with our conclusion that Group I zircons crystallised from basaltic melt.

Group II zircons exhibit lower Ti-in-zircon temperature ($634 \pm 68^{\circ}\text{C}$, $n = 5$) than that of the Group I. However, the temperature is much higher than formation temperature of the host jadeitite ($250 \sim 370^{\circ}\text{C}$) by Shi et al. (2003). As Fu et al. (2010)

obtained lower temperatures ($< 580\text{ }^{\circ}\text{C}$) using speculatively low a_{SiO_2} , further calibration would be needed to apply the thermometer to hydrothermal zircons.

A revised Ti-in-zircon thermometer (Ferry and Watson, 2007) considered the activities of $\text{SiO}_2(a_{\text{SiO}_2})$ and $\text{TiO}_2(a_{\text{TiO}_2})$ related to the Ti content of zircon as well as temperature T:

$$\log(\text{ppm}_{\text{Ti-in-zircon}}) = (5.711 \pm 0.072) - (4800 \pm 80)/T(\text{K}) - \log a_{\text{SiO}_2} + \log a_{\text{TiO}_2}$$

Where both quartz and rutile coexist with zircon, the a_{SiO_2} and a_{TiO_2} are 1, with the two equations above yielding identical temperatures. Absence of coexisting quartz and rutile with zircon will reduce the activities of SiO_2 and TiO_2 . As the Group I zircons are inherited and mostly rimmed by the Group II zircons, it is difficult to estimate the activities of SiO_2 and TiO_2 . Thus the following discussion focuses mainly on the Group II zircon.

Because jadeitites commonly occur in direct contact with serpentinites, the a_{SiO_2} appears to be extreme low ($a_{\text{SiO}_2} = 0.002$) during jadeitite formation (Fu et al., 2010). Fu et al. (2010) obtained lower temperatures ($< 580\text{ }^{\circ}\text{C}$) for hydrothermal zircon in jadeitites from other localities using revised equation of Ferry and Watson (2007). In this study, titanite and ilmenite are present in Myanmar jadeitite (Ng et al., 2016), but no rutile has been found. Thus a_{TiO_2} is assumed to be 0.7 (Gao and Zheng, 2011) and the zirconium-in-rutile thermometer (e.g., Tomkins et al., 2007) could not be adopted.

Using the same low a_{SiO_2} ($= 0.002$), the average temperature for Group-II zircon is 339 ± 33 °C (2 SD, $n=5$). This estimate is comparable to the formation temperature of the host jadeitite (250 - 370°C) reported by Shi et al. (2003), signifying the importance of considering a_{SiO_2} and a_{TiO_2} .

7. Conclusions

Trace element data on previously dated zircon grains from the Myanmar jadeitite reveal two groups of zircon (Group I and Group II). Group I zircon is igneous, with low total REE concentrations similar to zircon crystallising from mafic melts, with a possible mantle wedge source rather than subducted oceanic slab. Their Hf isotope data, lack of Eu-anomaly and back calculation for protolith of zircon suggest growth from a melt generated by partial melting of mantle wedge during fluid-peridotite interaction within mantle wedge.

Group II zircon shows trace element features related to hydrothermal origin. The low Ti, Y and the ΣREE , and lower $(\text{Sm/La})_{\text{N}}$ and Ce/Ce^* values together with elevated $(\text{Yb/Gd})_{\text{N}}$ are typical of hydrothermal zircons worldwide. The slight differences in trace element compositions of hydrothermal zircon grains reflect of the compositional diversity of related fluids and subduction zone processes. The Group II

zircon overgrowth on Group I grains occurred through precipitation and
recrystallisation, but without distinct dissolution of the Group I zircons.

Based on Ti-in-zircon thermometer, the Group I zircons yield a mean
crystallisation temperature of $742 \pm 141^{\circ}\text{C}$ without making corrections for reduced
oxide activities (a_{TiO_2} and a_{SiO_2}) whereas the Group II zircons yields 339°C after
adopting new thermodynamic models and revised calibrations for the Ti-in-zircon
thermometer.

Acknowledgements

We are indebted to R.X. Zhu, M.C. Du and L.C. Chen, for their kind supports during
the field trip and subsequent research, as well as Su L. for her help with LA-ICP-MS
analyses. Constructive and thoughtful reviews by G.E. Harlow and anonymous
referee, as well as comments and editorial handling of Dr Andrew Kerr (Editor)
helped to improve the quality of the manuscript greatly. This study was supported by
the National Basic Research Program of China (2015CB452606), the National
Science Foundation of China (No. 41373055) and the Doctoral Program of Higher
Education of China (20120022110004)

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Figure captions

Fig. 1. (a) Geological framework of Myanmar, showing the jade Mine Tract. (b) Geological sketch map of the Myanmar Jade Mine Tract (modified after [Bender, 1983 and Morley, 2004](#)).

Fig.2. Representative cathodoluminescence images of zircons from the Myanmar jadeitite sample. The labeled LA-ICP-MS spot numbers correspond to those in Table 1. Note the presence of a jadeite inclusion in G978-39.

Fig.3. Cathodoluminescence images of zircons grains from the Myanmar jadeitite with the marked SHRIMP spot numbers, Group type, U/Th ratios and ^{207}Pb -corrected $^{206}\text{Pb}/^{238}\text{U}$ ages (Modified after Figure 7 in [Shi et al. \(2008\)](#)).

Fig.4. Chondrite-normalised REE patterns of zircon from Myanmar jadeitite.

Chondrite data refer to [McDonough and Sun \(1995\)](#)

Fig.5. Calculated REE pattern of the presumed protoliths of Myanmar jadeitite in this study and Tone jadeitite from Japan reported by [Mori et al. \(2011\)](#) and [Yui et al. \(2012\)](#). Also shown are REE compositions of adakite ([Macpherson et al., 2006](#)), as

well as average REE compositions of subduction-zone adakitic granite within the NE Jiangxi ophiolite (Li and Li, 2003). La and Ce were excluded due to large uncertainties related with low concentrations of La and the anomalous model Ce values resulting from zircon Ce-anomalies.

Fig.6. Plot showing variation of trace element compositions of hydrothermal zircon in jadeitites. Zircon compositions other than the Myanmar jadeitite are from Fu et al. (2010), Yui et al. (2010) and Mori et al. (2011).

Fig.7. Plot showing trace element characteristics of hydrothermal zircon rims (Group II zircon) relative to igneous cores (Group I zircon). Zircon compositions other than the Myanmar jadeitite are from Fu et al. (2010), Yui et al. (2010) and Mori et al. (2011).

861 Table captions

862 Table 1. Trace element compositions of zircons from the Myanmar jadeitite

863

Figure1a

Figure1b

Figure 2

Figure 3

Figure-4

Figure 5

Figure-6

□ Myanmar(Group II) △ Tone(type II)
 ○ Osayama(type II) ◇ Gutemala(type II)

Figure-7

Table 1

Table 1. Trace element compositions of zircons from Myanmar jadeitite																											
	Hf	Ti	Y	Nb	Ta	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	Th	U	(Sm/La) _N	(Yb/Gd) _N	Ce/Ce*	Eu/Eu*	Temp	U-Pb age
	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm					°C	Ma
Group-I zircon cores																											
G978-02	9534	6.45	2049	0.25	0.05	0.01	3.35	0.01	0.53	2.97	2.91	28.2	12.1	162	68.4	328	84.5	1006	245	52.0	333	501	44.2	68.6	0.97	704	163.6±4.4
G978-03	10309	5.09	1324	0.18	0.04	0.08	1.74	0.04	0.21	1.23	1.52	15.4	6.84	98.0	42.3	211	58.2	702	178	17.6	160	25.3	56.3	8.04	1.07	685	172.9±4.7
G978-04	9930	3.45	1410	0.18	0.03	0.03	2.41	0.03	0.34	1.86	1.98	19.1	8.06	109	46.5	231	60.8	742	183	30.4	226	112	48.0	19.4	1.01	655	159.7±6.6
G978-06	9859	6.96	1855	0.31	0.04	0.01	3.50	0.02	0.51	3.03	2.86	27.6	11.5	149	60.9	293	75.6	897	220	58.0	315	437	40.1	51.2	0.95	710	—
G978-14	10476	26.2	1401	1.51	0.18	0.07	15.9	0.09	2.54	8.26	6.46	44.8	14.1	145	46.0	176	39.6	416	89.2	650	1617	203	11.5	49.6	1.02	833	163.1±4.5
G978-16	13951	8.46	1604	0.99	0.15	0.13	8.02	0.07	0.90	2.53	2.20	24.4	10.1	129	48.6	219	50.5	517	149	102	666	31.7	26.2	21.0	0.85	726	—
G978-17	11499	9.81	865	0.84	0.14	0.02	7.05	0.04	0.94	3.05	2.66	20.7	7.00	82.2	29.2	124	30.5	350	78.4	330	917	241	20.9	63.4	1.02	739	—
G978-18	12121	79.7	2470	2.38	0.25	0.02	18.6	0.05	1.47	5.75	5.63	57.2	21.0	232	75.4	301	68.4	738	151	231	1200	463	16.0	140	0.95	964	—
G978-19	11383	15.5	1692	0.98	0.11	0.04	8.43	0.07	0.81	3.69	3.63	33.8	11.7	146	50.1	209	49.8	467	120	238	815	162	17.1	41.6	0.99	781	173.4±4.6
G978-20	11348	15.2	2227	0.70	0.08	0.05	6.08	0.05	1.00	3.18	3.36	36.9	15.2	192	71.9	313	74.6	812	194	72.5	346	111	27.2	32.3	0.95	779	—
G978-21	12414	6.11	965	0.77	0.13	0.02	4.91	0.02	0.49	1.86	1.69	16.1	6.63	83.3	30.2	136	34.2	401	91.9	45.9	514	150	30.8	64.6	0.94	699	—
G978-23	14718	10.6	848	1.09	0.22	0.20	13.2	0.13	2.24	6.20	3.63	27.0	8.18	82.8	26.0	105	22.2	213	56.0	822	1074	49.4	9.76	20.0	0.86	746	—
G978-26	11567	8.94	635	0.46	0.08	0.07	4.43	0.04	0.76	1.88	1.38	11.8	4.47	54.1	19.3	86	20.8	241	54.9	70.4	454	40.7	25.3	20.7	0.89	731	162.3±4.4
G978-30	10267	4.16	915	0.13	0.07	0.02	1.41	0.03	0.36	1.18	1.16	10.8	4.74	67.9	29.2	147	40.2	498	130	20.0	159	108	57.0	15.7	1.00	669	—
G978-33	11381	9.23	1027	0.66	0.07	0.06	5.01	0.03	0.65	1.94	1.93	15.6	6.55	85.1	31.5	139	34.2	396	92.6	100	425	54.5	31.4	28.7	1.07	734	—
G978-36	11484	8.85	824	0.59	0.12	0.01	4.80	0.03	0.51	1.86	1.62	13.5	5.38	69.4	26.6	125	32.0	377	90.3	151	644	292	34.5	71.2	0.98	730	157.9±4.3
G978-40	9528	30.6	1608	1.01	0.10	0.06	10.5	0.07	1.47	7.07	6.66	43.4	14.7	158	49.1	184	40.4	412	86.2	397	798	206	11.7	41.3	1.16	850	—
G978-43	12491	5.97	1266	0.25	0.06	0.04	2.75	0.03	0.62	1.98	1.85	17.0	7.44	97.4	39.1	188	48.4	568	141	36.2	326	81.3	41.3	20.7	0.97	698	—
G978-44	14391	7.39	1565	0.34	0.10	0.06	3.54	0.06	0.73	2.29	2.05	21.0	8.83	114	46.0	218	50.9	537	166	49.7	279	61.3	31.6	14.5	0.90	715	—
G978-45	9805	10.0	1747	0.30	0.02	0.01	4.03	0.02	0.38	2.26	2.40	26.4	10.7	141	56.1	265	61.9	633	198	34.9	204	285	29.6	61.6	0.95	741	—
G978-48	10152	5.05	1629	0.17	0.02	0.04	2.15	0.03	0.49	1.76	1.86	19.3	8.44	119	52.4	265	69.2	791	225	24.8	194	64.2	50.8	15.1	0.97	684	—
Group II zircon rims																											
G978-31	11870	4.07	159	0.13	0.04	0.08	0.62	0.03	0.35	0.36	0.27	1.97	0.66	9.86	4.62	27.7	8.65	125	48.9	9.92	79.8	7.56	78.2	3.01	0.99	668	155.7±9.5
G978-34	11107	1.89	135	0.20	0.05	0.10	0.93	0.09	0.54	0.62	0.29	2.01	0.73	8.71	3.92	19.8	5.56	72.9	20.7	11.8	116	9.83	44.8	2.34	0.79	613	149.0±7.2
G978-39	9223	3.10	123	0.13	0.07	0.09	0.29	0.02	0.30	0.11	0.09	0.64	0.35	5.14	2.87	17.7	5.84	73.7	32.6	9.69	90.5	2.12	142	1.63	0.98	648	140.2±6.4
G978-42	10180	1.24	111	0.09	0.06	0.05	0.44	0.02	0.23	0.15	0.22	0.93	0.37	5.73	2.83	17.1	4.69	56.6	23.0	15.1	74.3	5.27	75.2	3.24	1.78	586	—
G978-50	10979	3.59	229	0.29	0.13	0.03	1.71	0.02	0.36	0.58	0.67	3.55	1.35	17.4	7.24	39.9	12.2	172	50.8	59.6	302	32.2	59.7	19.6	1.41	658	—

Notes:

- 1 .Subscript N indicates values normalized to chondrite abundances after [McDonough & Sun \(1995\)](#).
2. Anomalies were calculated as $Ce/Ce^* = Ce_N/(La_N \times Pr_N)^{1/2}$, $Eu/Eu^* = Eu_N/(Sm_N \times Gd_N)^{1/2}$.
3. Age data are from [Shi et al. \(2008\)](#).