



Hydrothermal zircon: Characteristics, genesis and metallogenic implications

Wei Zhai^{a,b,c,*}, En Zhang^{d,*}, Si-qi Zheng^{a,1}, M. Santosh^{e,f}, Xiao-ming Sun^{a,b,d}, He-cai Niu^g, Bin Fu^h, Yu Fu^a, Deng-feng Li^a, Yu-hang Jiang^g, Fei Liangⁱ, Wei-peng Lin^j, Yan Zhao^g, Song-yan Han^a

^a School of Marine Sciences, Sun Yat-sen University, Zhuhai 519082, China

^b Guangdong Provincial Key Laboratory of Marine Resources and Coastal Engineering, Zhuhai 519082, China

^c Southern Marine Science and Engineering Guangdong Laboratory, Zhuhai 519082, China

^d School of Earth Sciences and Engineering, Sun Yat-sen University, Zhuhai 519082, China

^e State Key Laboratory of Geological Processes and Mineral Resources, China University of Geosciences, Beijing 100083, China

^f Department of Earth Sciences, University of Adelaide, Adelaide SA 5005, Australia

^g Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, Guangzhou 510640, China

^h Research School of Earth Sciences, the Australian National University, Canberra ACT 2601, Australia

ⁱ Ruima Mining Investment Co. Ltd, Foshan 528000, China

^j 940 Geological Brigade, Nonferrous Metals Geological Bureau of Guangdong Province, Qingyuan 511520, China

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ABSTRACT

Zircon is a principal source of zirconium and hafnium, as well as a key mineral both for petrogenetic modeling and age dating. Although zircon occurrences have been reported from hydrothermal mineral systems, detailed studies on zircon that crystallized entirely from saturated hydrothermal fluid are rare. Here we report on hydrothermal zircon crystals dated at about 1911 Ma that crystallized from boiling high-salinity H₂O-CO₂ hydrothermal fluid with fluid inclusion homogenization temperatures of 295 to 325 °C and the corresponding pressure of 71 bar. These zircon crystals were then overprinted by two stages of hydrothermal zircon veins at 1864 Ma and 528 Ma. The zircon veins crystallized from boiling hydrothermal fluids of moderate to low salinities with fluid inclusion homogenization temperatures and the corresponding pressures of 302 to 329 °C and 75 bar and 290 to 320 °C and 70 bar, respectively. The zircon crystals in our study show sharp and regular cathodoluminescent oscillatory zonation and low and consistent trace element concentrations and Th/U ratios that decrease with fluid salinity. The Th/U ratios of these zircons lie between the magmatic zircon values (>0.5) and metamorphic zircon values (≤0.1). The rare earth element concentrations and trace element spidergram patterns of the zircon samples do not record their hydrothermal origin. Importantly, the low concentrations of HfO₂ (<1%), Y (<400 ppm) and Ti (<4 ppm) can discriminate hydrothermal zircon from igneous and metamorphic zircons. Hydrothermal zircon is considered as an effective tool for the dating of mineral deposits and also represents one of the main sources of critical elements such as zirconium and hafnium.

1. Introduction

Zircon is a robust accessory mineral widely used in igneous and metamorphic geochronology, and detrital zircon grains are used to derive information on provenance and timing of sedimentation (Sircombe, 1999; Hoskin and Schaltegger, 2003). As most mineral deposits are the products of multiple hydrothermal pulses and because of the low

blocking temperatures of hydrothermal minerals for dating, the selection of a robust mineral to precisely date the different mineralizing events is challenging. Hydrothermal zircon and other accessory minerals such as monazite, titanite, rutile, xenotime and apatite, are typically used to constrain the timing of hydrothermal ore deposits (Claoue-Long et al., 1990; Schandl et al., 1990; Schandl and Gorton, 2004; Sarma et al., 2011; Chen et al., 2019). In the past three decades, several cases

* Corresponding authors.

E-mail addresses: eeszw@mail.sysu.edu.cn (W. Zhai), eeszen@mail.sysu.edu.cn (E. Zhang).

¹ Present address: Guangzhou Institute of Marine Geological Survey, Guangzhou 510080, China.

have been reported where zircon phases are associated with hydrothermal mineralization and related alteration assemblages and they are interpreted to be of hydrothermal origin. For example, hydrothermal zircon is documented in orogenic gold deposits, e.g., within auriferous quartz veins and alteration zones in the Abitibi greenstone belt (Claoue-Long et al., 1990; Kerrich and King, 1993; Kerrich and Kyser, 1994), the giant Golden Mile deposit (McNaughton et al., 2005), the Tamlalt-Menhouhou (Pelleter et al., 2007), and in the Gidginbung epithermal high sulfidation Au-Ag deposit (Lawrie et al., 2007). Hydrothermal zircon also occurs in tungsten- and/or tin-bearing quartz veins and alteration rocks in the Mole Granite (Pettke et al., 2005), the Boggy Plain zoned pluton (Hoskin, 2005), the Nanling tungsten deposits (Wang et al., 2016), the chloritized stockwork zone in the Iberian Pyrite Belt (Nesbitt et al., 1999; Toscano et al., 2014), the skarn orebodies at Sierra Blanca Peaks (Rubin et al., 1989), the Fe-oxide-(Cu-Au or apatite) mineralization zone in the Adirondack Mountains (Valley et al., 2009) and Dahongshan (Zhao et al., 2017), in copper-bearing quartz vein in the Dexing porphyry copper deposit (Zhou et al., 2012), and Zr-rare earth element (REE)–Nb mineralization associated with the Baerzhe alkaline granite (Yang et al., 2013, 2014). Although hydrothermal zircon is considered as a robust mineral for the age dating of mineral deposits, the identification of its hydrothermal origin remains poorly constrained due to the lack of systematic documentation of its key characteristics. No consistent definition of morphology, internal texture and chemical composition has been published yet in order to distinguish hydrothermal zircon from magmatic and metamorphic zircon grains. Anhedral and faceted morphologies, zoned and unzoned crystals, and both low Pb and high Pb zircons have been described as hydrothermal (Hoskin and Schaltegger, 2003). The trace element characteristics of hydrothermal zircon from different locations or even the same hydrothermal ore vein show large variations. For example, both the Boggy Plain zoned pluton and the Mole Granite (Hoskin, 2005; Pettke et al., 2005), have W or Sn-W mineralization associated with fluid derived from magmatic differentiation, and they have similar geological contexts. However, the zircon compositional characteristics are contradictory, with zircon in the Boggy Plain zoned pluton being enriched in REEs by approximately two orders of magnitude and zircon in the Mole Granite being depleted by 1 to 3 orders of magnitude in REEs relative to igneous zircon (Hoskin, 2005; Pettke et al., 2005). Consequently, suggestions of a hydrothermal origin for zircon have been met with skepticism (Hoskin and Schaltegger, 2003; Schaltegger, 2007). The validity of the first age results for hydrothermal zircon from gold-bearing orogenic quartz veins in the Abitibi greenstone belt (Claoue-Long et al., 1990) was challenged, and the suggestion was made that these zircon grains were instead inherited from the wall rocks (Corfu and Davis, 1991). The mis-interpreted hydrothermal zircon at the Gidginbung epithermal deposit has subsequently been confirmed to have a magmatic origin on the basis of trace elements and oxygen and hafnium isotopic compositions (Fu et al., 2009). Currently, the most common arguments for the hydrothermal origin of a zircon grain are its occurrence in hydrothermal quartz or carbonate together with other hydrothermal minerals, its spongy texture from the presence of fluid and/or hydrothermal mineral inclusions, and higher concentrations of trace elements such as REEs than zircon from igneous rocks related to hydrothermal fluids (Hoskin and Schaltegger, 2003; Schaltegger, 2007; Toscano et al., 2014; Westhues et al., 2017). In fact, the occurrence of zircon in hydrothermal veins, or even as inclusions in hydrothermal minerals, is not a robust evidence to infer that the zircon likewise crystallized from the hydrothermal fluid. For example, zircon xenocrysts from the wall rock were identified along with the so-called hydrothermal zircon in quartz veins in the Dexing porphyry copper deposit (Zhou et al., 2012) and the Dongping gold deposit (Bao et al., 2014). Zircon from an assimilated host rock may be the only mineral phase that did not completely dissolve into a quartz-depositing hydrothermal fluid, as evidenced by its persistence in heavy mineral deposits, as grains in high-grade metamorphic rocks and as inherited grains in magmatic rocks

(Kennedy, 1999; Corfu et al., 2003; Hoskin and Schaltegger, 2003). In addition, experimental studies on zircon and zircon from metamorphic rocks, in the presence of a fluid phase, have proven to be re-equilibrated or domains formed by metasomatic recrystallization or diffusion reactions, and coupled dissolution-reprecipitation. For example, porosity in metamorphic zircon occurs in the form of fluid and mineral inclusions composed of “nonformula” elements in zircon and solvent cations, and the U–Pb ages of pristine zircon are fully or partially reset by Pb loss (Putnis, 2002; Geisler et al., 2003, 2007; Tomaschek et al., 2003; Kusiak et al., 2009; Vonlanthen et al., 2012). Accordingly, ore and gangue minerals can occur in altered zircon during hydrothermal mineralization, and many reported hydrothermal zircons from ore deposits with hydrothermal mineral inclusions are most likely formed by hydrothermal alteration. Nevertheless, these hydrothermal zircon ages have still been used to infer the ages and mineralization and more precise genetic models were proposed based on ^{39}Ar – ^{40}Ar , Re–Os and other isotope dating methods (Claoue-Long et al., 1990; Pelleter et al., 2007; Valley et al., 2009; Zhou et al., 2012; Wang et al., 2016). In this paper, we propose a consistent definition of hydrothermal zircon crystallized from boiling hydrothermal fluids on the basis of habitus, mineralogy, cathodoluminescence (CL) images, fluid inclusion assemblages, U–Pb isotope ages and trace elements, respectively.

2. Materials and methods

2.1. Samples and preparation

Zircon samples were collected 24 km southwest of Iklamavony, Fianarantsoa Province in central Madagascar (Fig. 1a). The central to southern Madagascar is underlain by the Neoproterozoic to Proterozoic Antananarivo Domain and Itremo and Iklamavony Groups, the Proterozoic Anosy, Androyan and Vohibory Domains, and undifferentiated Phanerozoic volcanic and sedimentary rocks (Tucker et al., 2011, 2014; Archibald et al., 2015). The basement experienced amphibolite to granulite facies metamorphism at the end of Neoproterozoic (Paquette et al., 2004; Tucker et al., 2014). Accretionary events between the South Madagascar-India-Wanni-Highland (SIWH) terrane and the Great Dharwar Craton at 2.0 to 1.8 Ga, the Ediacaran orogeny, including the East African Orogeny at 0.63 to 0.61 Ma, and the Kuunga Orogeny at 580 to 510 Ma, involving widespread metamorphism and magmatism have also been recorded in Madagascar (Tucker et al., 2011, 2014). Granulite-facies metamorphism during the Late Neoproterozoic-Cambrian period associated with Gondwana assembly involved ultrahigh-temperature conditions of up to 1000 °C and pressures in the range of 5 to 9 kbar in the central to southern Madagascar region (Markl et al., 2000; Tucker et al., 2014).

The zircon crystals in this study occur in the form of veins or saccular bodies in faults or cracks within the Iklamavony Group rocks, which comprise migmatite gneiss, paragneiss, quartzite and marble (Fig. 1b, c). The surface outcrops of the vein or saccular body are very poor due to strong weathering, and the veins have a discontinuous outcrop length of 10 to 20 m, and width of 0.3 to 1.0 m, with striking NNE to NE and dipping NW or SE at nearly 90 °C. These veins are oriented roughly parallel to or obliquely cross the foliation. The bleaching induced by the alteration of dark minerals in the adjacent wall rocks is obvious around the veins (Fig. 1b). The zircon crystals also occur in residual sediments as the result of strong weathering in the region. These veins and saccular bodies are mainly composed of zircon, with a minor titanite, diopside, tourmaline, baddeleyite, quartz and vesuvianite. Three zircon samples (numbers 10ZR-1, 10ZR-2 and 10ZR-3, Fig. 2) were selected in this study and were processed into doubly polished thin sections with a thickness of approximately 0.2 mm for analyses; 10ZR-1 and 10ZR-3 were cut parallel to and 10ZR-2 perpendicular to the c-axis.

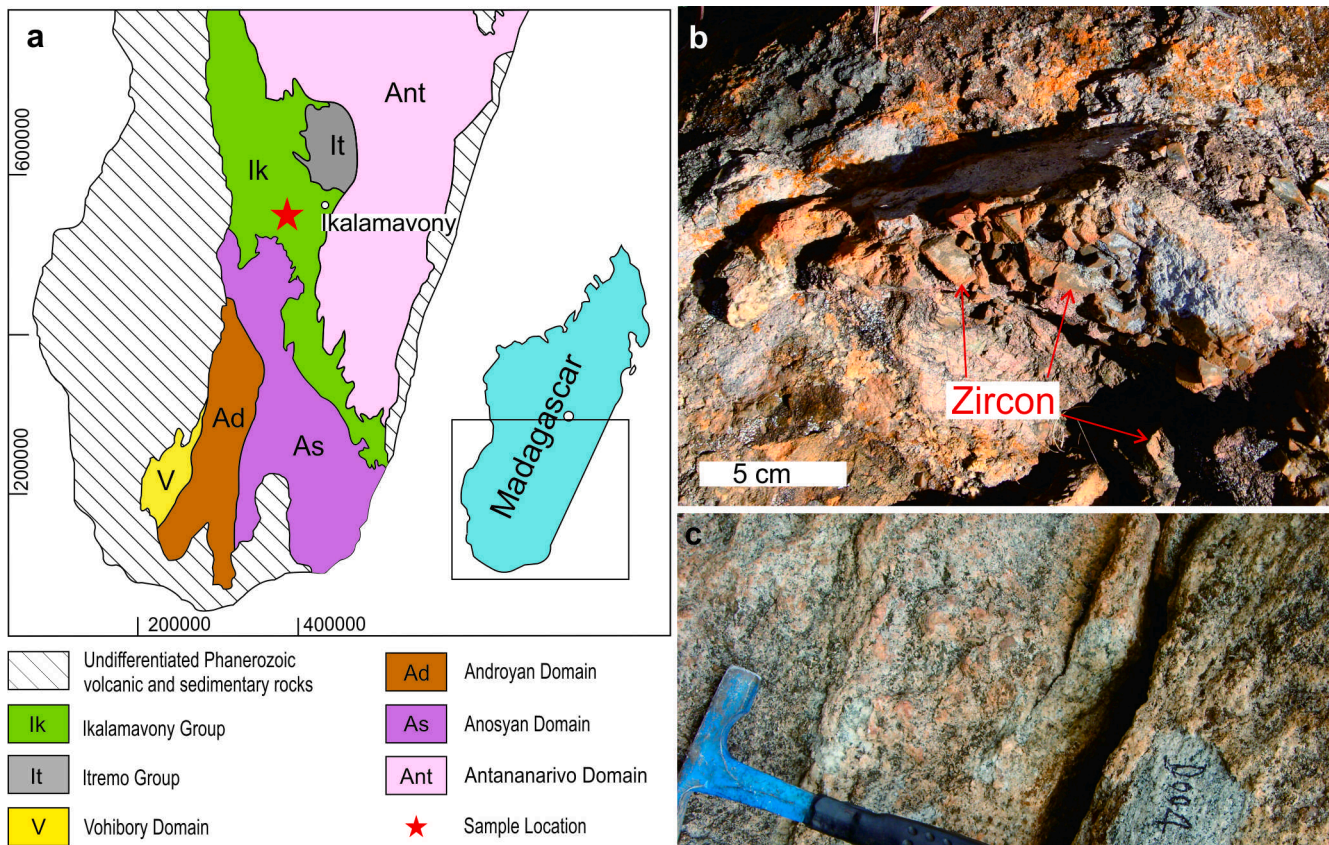


Fig. 1. (a) Simplified geology of central-south Madagascar (after Tucker et al., 2014) and sample location. (b) Hydrothermal zircon vein intersecting gneiss. (c) Gneiss wall rock of zircon vein.

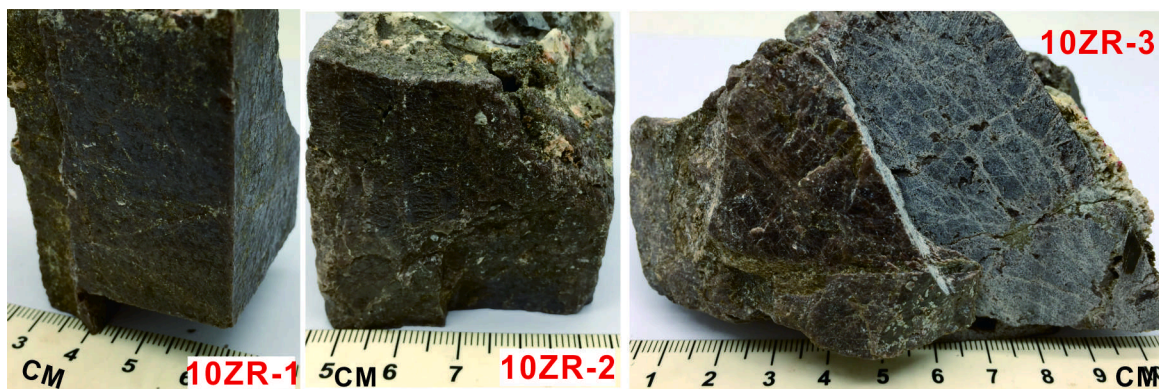


Fig. 2. Photographs of three zircon crystal samples.

2.2. CL imaging

The CL imaging of zircon sections was carried out at the Nanjing Hongchuang Geological Exploration Technology Service Co., Ltd., employing a TESCAN MIRA 3LIMH scanning electron microscope fitted with CL detectors. The operating conditions were a voltage of 7.0 kV, a current of 1.2 nA, a working distance of 19–20.5 mm and a focal depth of 4.0–4.4 mm.

2.3. Fluid inclusion analyses

Petrographic observations and microthermometric measurements of fluid inclusions in zircon were performed using an Olympus BS51 microscope equipped with a Linkam FTIR600 heating-freezing stage with a

temperature range of -196 to 600 °C and a Qimage MP5.0 color camera allowing observation on a PC monitor in the School of Marine Science, Sun Yat-Sen University, China. Calibration was performed using synthetic $\text{H}_2\text{O}-\text{CO}_2$ fluid inclusions and critical density pure-water inclusions at -56.6 °C, 0.0 °C, and 374.1 °C. The salinities, densities and pressures at the homogenization temperatures of the fluid inclusions were determined using a numerical tool to calculate the PVYTX properties and trapping conditions of $\text{H}_2\text{O}-\text{NaCl}$ (Steele-MacInnis et al., 2012).

2.4. Raman spectroscopy

Laser Raman spectra were collected with a Horiba Xplora laser Raman microspectroscopy instrument at the Key Laboratory of

Mineralogy and Metallogeny, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences. The operating conditions included a 532 nm line of a 44 mW Ar⁺ laser, a spectral scanning range of 100 to 4000 cm⁻¹, an accumulation time of 10 s for each scan, and a spectral resolution of 0.65 cm⁻¹.

2.5. LA-ICP-MS analyses

Laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) analyses of the U–Pb age and trace elements of zircon were performed simultaneously using an Agilent 7500a ICP-MS equipped with a pulsed 193 nm ArF excimer laser (MicroLas Pro) at the National Key Laboratory of Continental Dynamics, Department of Geology, Northwest University, China. A 32 µm spot diameter was used with a laser repetition rate of 6 Hz and an output energy of 100 mJ. Zircon 91,500 was used as an external reference standard to correct both instrumental mass bias and depth-dependent elemental and isotopic fractionation. NIST610 was also used as an external reference standard, and Si with a concentration of 15.3 % was used as an internal standard for calibrating trace element contents. Zircon GJ1 with a TIMS age of 608 ± 0.4 Ma (Jackson et al., 2004) was used as a quality control standard. A typical analytical run commenced with one NIST610, one 91,500 and one GJ1 analysis, followed by four unknowns, one 91,500 analysis, then four unknowns, and then one NIST610, one 91500, and one GJ1 analysis, with this sequence repeated. The analyses that yielded a mixed age for zircon and/or the involvement of mineral inclusions in the ablation when drilling down into the crystal were excluded. The raw data were processed using GLITTER 4.0 (Van Achterbergh et al., 2001) to calculate the ratios of ²⁰⁷Pb/²⁰⁶Pb, ²⁰⁶Pb/²³⁸U, ²⁰⁷Pb/²³⁵U and ²⁰⁸Pb/²³²Th. The ages were calculated using the ISOPLOT program (Ludwig, 2003). No analyses were corrected for common Pb since most analytical values of ²⁰⁴Pb were below the detection limit, and ²⁰⁴Hg interfering with ²⁰⁴Pb was also ignored. The internal errors propagated to the final ages are at 2σ. The weighted mean ages were quoted at the 95 % confidence level. The analytical details are described in Yuan et al. (2004) and Liu et al. (2007). The concordia age of zircon 91,500 is 1060 ± 6.3 Ma (n = 15, MSWD = 0.0089), which is consistent with the TIMS age of 1065 Ma within uncertainty (Wiedenbeck et al., 1995). The determined weighted mean and concordia ages for zircon GJ1 were 604 ± 4.0 Ma (n = 11, MSWD = 0.83) and 603 ± 4.4 Ma (n = 11, MSWD = 0.2) (Supplementary material, Fig. A.1a, A.1b), which is in agreement with the TIMS age within uncertainty (Jackson et al., 2004). The chondrite-normalized REE patterns of GJ1 are shown in Supplementary material, Fig. A.1c, which show that the analytical quality is stable and reliable.

In this study, several daughter mineral-bearing two-phase aqueous liquid–vapor inclusions in zircon were analyzed for the cations Si, Zr, Na, K, Ca, Mg, Fe, Mn, P, Pb and Sr with an Agilent 7700x ICP-MS equipped with a pulsed 193 nm ArF excimer laser (GeoLas Pro) at the School of Marine Science, Sun Yat-Sen University. The measurements involved a spot diameter of 32 µm, a laser repetition rate of 6 Hz and an output energy of 100 mJ. The analyses were calibrated against standard NIST610, and the acquired data were processed using the software package “Sills” developed by Guillon et al., (2008).

3. Results

3.1. Mineralogy and cathodoluminescence

The zircon crystals utilized in this study are brown, opaque, subhedral and faceted as prisms along {011}; and they lack {100} and pyramid forms with two groups of incomplete joints parallel to {011}. The crystals vary in width from 3.5 to 6 cm, and their lengths range from 5 to 10 cm (Fig. 2). CL images reveal that the host zircon crystals underwent two stages of zircon vein overprinting, during which zircon vein one (V1) and vein two (V2) were formed in cracks in the host grains,

with crosscutting relationships. Compared to the host zircon, the V1 zircon has lighter luminescence, and the V2 zircon has even light luminescence in CL images (Fig. 3). From core to rim, the host zircons have clear and regular oscillatory zoning in CL, and there are at least two discontinuities in zircon crystals 10ZR-1 and 10ZR-3 and three discontinuities in zircon 10ZR-2 (Fig. 3a, d, e). These features are particularly obvious at the corner of oscillatory zonation in crystals shown in sections cut perpendicular to the c-axis (Fig. 3a, b). The host zircons have no obvious spongy texture caused by mineral inclusions, which has been considered diagnostic of hydrothermal zircon. The nonluminescent mineral vesuvianite (Groat, et al., 1992), the presence of which was confirmed by single crystal X-ray diffraction analysis, and quartz are associated with or occur as mineral inclusions in the V2 zircon (Fig. 3).

3.2. Fluid inclusions and microthermometry

The host zircon crystals contain abundant primary fluid inclusions displaying temporal relationships with respect to crystal growth zonation, and most fluid inclusions are columnar and/or prismatic or in the form of negative zircon crystals. The petrographic features allow the “fluid inclusion assemblages (FIAs)” (Goldstein, 2003) to be classified (Fig. 4, Supplementary material, Fig. A.2a–d). These fluid inclusions can be divided into three types. Type 1 consists of daughter mineral-bearing fluid inclusions with the solid phase occurring different volumes among fluid inclusions within a given assemblage, including daughter mineral-bearing aqueous liquid–vapor inclusions (type 1a) or aqueous–CO₂ inclusions (type 1b) (Table 1; Fig. 4h–j). They homogenize to liquid, and the dissolution temperatures of the daughter minerals are lower than the total homogenization temperatures. Type 2 includes two-phase aqueous inclusions with ≥15 vol% vapor to nearly entirely vapor, and no gases other than H₂O were detected by Raman spectroscopy and microthermometry; type 2 includes liquid-dominated (type 2a) and vapor-dominated (type 2b) inclusions, which homogenize to liquid and vapor during heating measurements, respectively (Fig. 4a–f, j, k). Type 3 consists of carbonic inclusions, including aqueous–CO₂ (type 3a) and two-phase liquid–vapor hydrocarbon inclusions (type 3b) (Table 1; Supplementary material, Fig. A.2a–d). Among the three types of fluid inclusions, type 2 inclusions are dominant, type 1a inclusions and type 3a inclusions are less common, and type 1b inclusions and type 3b inclusions are rare.

The coexistence of different types of fluid inclusions in a given FIA (Fig. 4c, j, k) implies heterogeneous fluid entrapment during precipitation of the host zircon crystals (Bodnar, 2003; Diamond, 2003; Goldstein, 2003). These features indicate a multiple component boiling hydrothermal system consisting of aqueous solution, carbonic phase and hydrocarbon, which can be simplified as a two end-member system composed of high-density (corresponding to type 1 fluid inclusions) and low-density fluids formed by boiling (Diamond, 2003). Simultaneously, the low-density fluid unmixed into a liquid-dominated aqueous fluid (corresponding to type 2a fluid inclusions) and vapor-dominated fluid (corresponding to type 2b fluid inclusions), including the CO₂-dominated and hydrocarbon-dominated type 3 fluid inclusions (Supplementary material, Fig. A.2c, d), which homogenized to carbonic and hydrocarbon phases, respectively. The homogenization temperatures of fluid inclusions with two dominant end-member components, corresponding to the type 1 fluid inclusions with maximum daughter mineral enrichment (or the most liquid-enriched type 2a fluid inclusions) and type 2b fluid inclusions with maximum vapor enrichment (including the most carbonic- or hydrocarbon-enriched type 3 fluid inclusions) in the FIAs can represent the formation temperature of the host zircon, and the corresponding homogenization pressure of the fluid inclusions at the lowest homogenization temperature represents the formation pressure, while the homogenization temperatures of other fluid inclusions with compositions intermediate between the two end-members are meaningless (Diamond, 2003, Figs. 5–26a). As the vapor-dominated type 2b fluid inclusions and the carbonic-dominated and hydrocarbon-

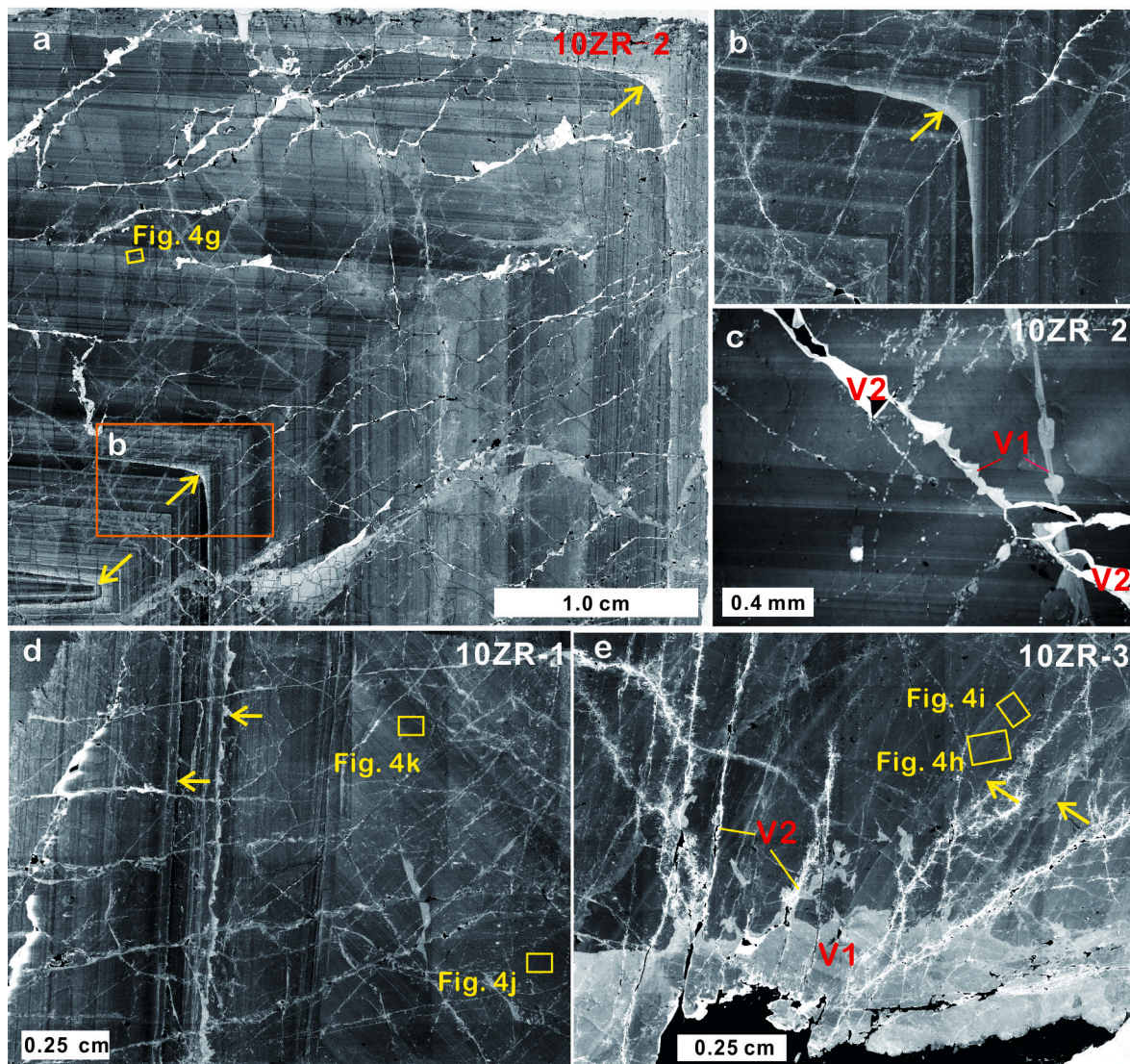


Fig. 3. CL images of the host zircon as well as V1 and V2 zircons from three zircon samples. (a), (b) A quarter of the host zircon 10ZR-2CL image in the plane perpendicular to the c-axis showing clear and regular oscillatory zonation and two-stage zircon veins. (c) Zircon V1 and V2 crosscutting the host zircon 10ZR-2 in turn. (d) Zircon 10ZR-1CL image of the plane parallel to the c-axis showing clear and regular oscillatory zonation and two-stage zircon veins. (e) CL image showing V1 and V2 zircons crosscutting the host zircon 10ZR-3 in turn. The nonluminescent minerals associated with or occurring in the V2 zircon are quartz and vesuvianite. Arrows point to disconformities in the growth zonations caused by dissolution and recrystallization of hydrothermal zircon due to multiple pulses of hydrothermal fluids. Yellow rectangles show the positions of photomicrographs in Fig. 4. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

dominated type 3 fluid inclusions homogenize to vapor, CO₂ and hydrocarbon phases, their homogenization temperatures cannot be accurately measured (Diamond, 2003) and the type 1b inclusions and type 3 inclusions are rare, and therefore the microthermometric measurements were done on type 1a and type 2b fluid inclusions. The results reveal that the eutectic temperatures for type 1a and type 2 inclusions are in the range of −22.0 to −26.1 °C, suggesting that the inclusion fluids contain dominantly salts of NaCl and KCl, with a small number of other cations (Bodnar, 2003). LA-ICP-MS analyses of four type 1a fluid inclusions also confirm that the main cations are K and Na with Na/K ratios of 2.5, 2.7, 3.1, and 3.3 and that the concentrations of Pb and Sr are higher than those of the host zircon (Supplementary material, Fig. A.3). For the most daughter mineral-enriched type 1a inclusions, the dissolution temperatures of daughter mineral correspond to salinities in the range of 26.7 to 31.4 wt% NaCl equivalent and their homogenization temperatures range from 304 to 325 °C, with the pressure at the lowest homogenization temperature estimated as 71 bar. For the most liquid-enriched

type 2a inclusions, the ice melting temperatures indicate that the salinities range from 13.1 to 20.3 wt% NaCl equivalent, their homogenization temperatures range from 295 to 324 °C, and the pressure at the lowest homogenization temperature is also 71 bar (Table 2; see Supplementary material, Table A.1 for details).

For type 3a inclusions, no systematic microthermometric measurements were conducted; however, several inclusions were measured for the CO₂ phase, which yielded melting temperatures of −56.5 to 56.7 °C, clathrate melting temperatures of 7.5 to 7.6 °C and partial homogenization temperatures of 16.3 to 26.5 °C, indicating nearly pure CO₂, in keeping with the typical Raman spectrum (Supplementary material, Fig. A.2g). For type 3b inclusions, laser Raman spectroscopy analyses indicate that the liquid- and vapor-phase hydrocarbons have consistent chemical compositions, comprising alkanes and polycyclic aromatic hydrocarbons (Zhai et al., 2014) (Supplementary material, Fig. A.2h).

In the V1 and V2 zircons and associated quartz, only type 2a and 2b fluid inclusions are identified (Table 1; Supplementary material,

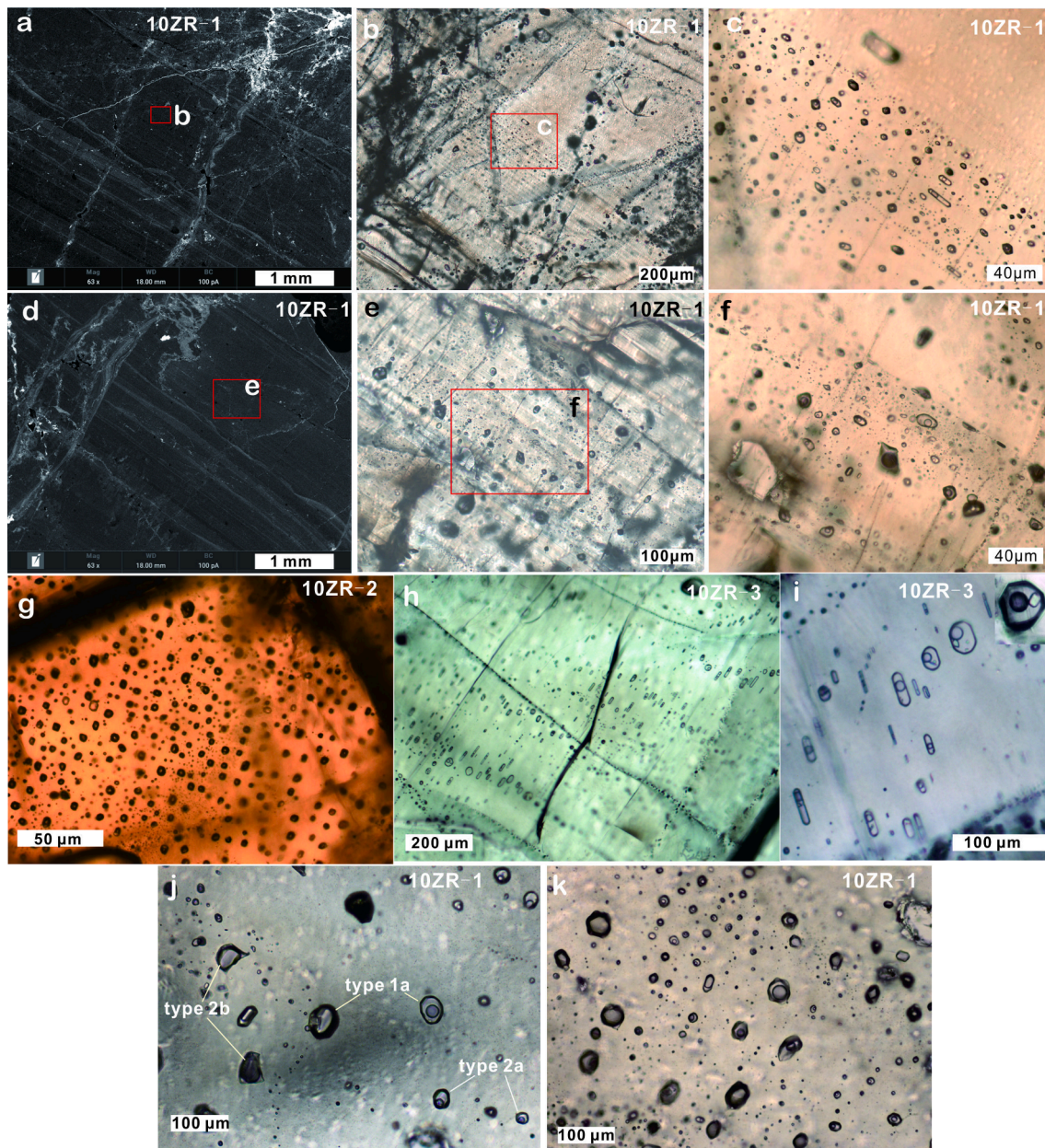


Fig. 4. CL images and photomicrographs of fluid inclusions in the host zircon. (a), (b), (c), (d), (e) and (f) CL images, type 2a and type 2b fluid inclusions in the form of prismatic or negative crystals distributed along the growth zonation in a thin section parallel to the c-axis. (g) Spongy fluid inclusions in a thin section perpendicular to the c-axis. (h), (i) Primary prismatic or negative crystal type 1a and type 2a fluid inclusions distributed along the growth zonations in thin sections cut parallel to the c-axis, and secondary fluid inclusions formed in the V1 or V2 zircon distributed along cracks. (j) Immiscible FIA in a thin section parallel to the c-axis. (f) Immiscible FIA composed of type 2a and type 2b fluid inclusions in a thin section parallel to the c-axis. The positions of (g), (h), (i), (j) and (k) on CL images are shown in Fig. 3.

Fig. A.2b, A.2e and A.2f), implying that the two-stage veins also crystallized under heterogeneous boiling fluid conditions. In the V1 zircon, for the most liquid-enriched type 2a inclusions, the ice melting temperatures reveal salinities of 14.9 to 21.5 wt% NaCl equivalent. This indicates that the bulk salinity of the V1 zircon-forming fluid is lower than that of the hydrothermal fluid from which the host zircon crystallized. The homogenization temperatures range from 302 to 329 °C, and the pressure at the lowest homogenization temperature is 75 bar. In the V2 zircon and associated quartz, the most liquid-enriched type 2a inclusions have salinities of 7.2 to 11.9 wt% NaCl equivalent, which are lower than those of the host and V1 zircon-forming fluids. The homogenization temperatures range from 290 to 320 °C, and the pressure at the lowest homogenization temperature is 70 bar (Table 2; see

Supplementary material, Table A.1 for details). The host zircon, V1 zircon, and V2 zircon exhibit similar formation temperatures and pressures; however, the relative bulk salinity of the zircon-forming hydrothermal fluids decreases gradually from the host zircon to the V1 zircon to the V2 zircon (Table 2, Fig. 5).

3.3. U–Pb ages and trace elements

The fourteen points of LA–ICP–MS age analyses on the three host zircon crystals (Supplementary material, Table A.2) are plotted on the Tera–Wasserburg concordia diagram where six points fall below the concordia line, and one point plots above the concordia line (Fig. 6a). Thus obviously, there is a disturbance in the U–Th–Pb system, which

Table 1

Distribution of different types of fluid inclusions in zircon samples.

Sample No.	Type 1	Type 2	Type 3
Host zircon	10ZR-1 Type 1a	Type 2a, type 2b	Type 3a
	10ZR-2 Type 1a	Type 2a, type 2b	Type 3a
	10ZR-3 Type 1a, type 1b	Type 2a, type 2b	Type 3a, type 3b
V1 zircon	10ZR-1	Type 2a, type 2b	
	10ZR-2	Type 2a, type 2b	
	10ZR-3	Type 2a, type 2b	
V2 zircon	10ZR-2	Type 2a, type 2b	
	10ZR-3	Type 2a, type 2b	
V2 quartz	10ZR-3	Type 2a, type 2b	

Note: Type 1a = Daughter mineral-bearing aqueous liquid–vapor inclusions. Type 1b = Daughter mineral-bearing aqueous–CO₂ inclusions. Type 2a = Liquid-dominated two-phase aqueous inclusions. Type 2b = Vapor-dominated two-phase aqueous inclusions. Type 3a = Aqueous–CO₂ inclusions. Type 3b = Two-phase liquid–vapor hydrocarbon inclusions.

might have been caused by the two stages of hydrothermal V1 and V2 zircon overprinting. However, the eight points plotting on the concordia line yield a weighted mean ²⁰⁷Pb/²⁰⁶Pb age of 1911 ± 24 Ma (2σ, MSWD = 0.16), representing the age of the host zircon (Supplementary material, Table A.2; Fig. 6a, b). Zircon 10ZR-2 was systematically analyzed from core to mantle to rim, and the resulting ²⁰⁷Pb/²⁰⁶Pb ages are consistent (Supplementary material, Table A.2). For the V1 zircon, 10 analyses were obtained (Supplementary material, Table A.2). On the Tera-Wasserburg concordia diagram, 3 data points plot above the concordia line, indicating Pb loss, which could be attributed to hydrothermal V2 zircon overprinting. The other 7 points plot on or near the concordia line and yield a weighted mean ²⁰⁷Pb/²⁰⁶Pb U–Pb age of 1864 ± 27 Ma (2σ, MSWD = 1.10) (Fig. 6c, d), representing the age of the V1 zircon. For the V2 zircon, 15 analyses were obtained (Supplementary material, Table A.2). They show younger (Phanerozoic) ages and have relatively low levels of ²⁰⁷Pb. Hence, the ²⁰⁷Pb/²⁰⁶Pb ages are unsuitable for precise dating, and the ²⁰⁶Pb/²³⁸U ages are used. On the Tera-Wasserburg concordia diagram, 5 data points plot above the concordia line, and 10 points plot on the concordia line, yielding a weighted mean ²⁰⁶Pb/²³⁸U ages of 528 ± 15 Ma (2σ, MSWD = 6.0), representing the

age of the V2 zircon (Fig. 6e, f).

The zircon grains show narrow ranges of Th and U concentrations and Th/U ratios, and these values decrease gradually from the host to V1 to V2 zircons (Fig. 7; Supplementary material, Table A.3). The concentrations of Th and U in the host zircon crystals range from 135 to 366 ppm and 354 to 672 ppm, respectively; those in the V1 zircon range from 41 to 149 ppm and 190 to 419 ppm, respectively; and those in the V2 zircon range from 0.3 to 2.4 ppm and 13.2 to 45.7 ppm, respectively. The Th/U ratios in the host zircon are 0.38 to 0.55, those in the V1 zircon are 0.19 to 0.36 and those in the V2 zircon are 0.01 to 0.09.

The host zircons have total REE concentrations (ΣREEs) ranging from 53 to 285 ppm with an average of 130 ppm; the ΣREEs for the V1 and V2 zircons range from 24 to 85 ppm with an average of 43 ppm and from 6 to 83 ppm with an average of 28 ppm, respectively (Supplementary material, Table A.3). For the V2 zircon, the contents of most light REEs (LREEs) and middle REEs (MREEs) are lower than the detection limit. All zircons have heavy REE (HREE)-enriched chondrite-normalized REE patterns (Fig. 8). The host zircons have La_N values approximately 0.04 to 0.5 times that of chondrites, Sm_N values 4 to 40 times that of chondrites and Lu_N values 100 to 700 times that of chondrites, and they have consistent REE concentrations and patterns (Fig. 8a). The V1 zircon has La_N values approximately 0.1 to 4 times that of chondrites, Sm_N values 1 to 7 times that of chondrites and Lu_N values 60 to 200 times that of chondrites (Fig. 8b). The V2 zircon has La_N values approximately 0.01 to 1 times that of chondrites, Sm_N values 0.1 to 0.6 times that of chondrites and Lu_N values 30 to 500 times that of chondrites (Fig. 8c). The host and V1 zircons have strong positive Ce anomalies, with Ce_N/*Ce_N ratios ranging from 6.8 to 49.9 and 3.0 to 20.1, respectively. They also exhibit moderate negative Eu anomalies, with Eu_N/*Eu_N ratios ranging from 0.19 to 0.3 and 0.11 to 0.32, respectively. Additionally, they have nearly equal Yb_N and Lu_N values, with Lu_N/Yb_N ratios ranging from 1.02 to 1.13 and 1.05 to 1.19, respectively. In contrast, the V2 zircon has weak positive Ce anomalies, with Ce_N/*Ce_N ratios ranging from 1.0 to 1.6, steep HREE patterns, Lu_N/Gd_N ratios between 118 and 261 and higher Lu_N/Yb_N ratios ranging from 1.44 to 1.76 (Supplementary material, Table A.3; Fig. 8c). The host zircon has Y concentrations ranging from 72 to 396 ppm, with an average of 179 ppm; the V1 zircon has Y concentrations ranging from 32 to 107 ppm, with an average of 55 ppm; and the V2 zircon has Y concentrations ranging from 5.1 to 69.9 ppm, with an average of 22.4 ppm.

The host, V1 and V2 zircons also have low and relatively homogeneous concentrations of HfO₂, Ti, Nb and Ta, respectively. Ti decreases from the host to V1 to V2 zircons: the values range from 2.2 to 3.9 ppm in the host zircons, 1.6 to 2.7 ppm in V1 and 0.22 to 0.47 ppm or lower in V2. The host and V1 zircons have similar HfO₂, Nb and Ta

Table 2

Microthermometric data of the most daughter mineral-bearing type 1a inclusions and the liquid-rich type 2a inclusions.

Sample No	Amount of FIA	Fluid inclusion type	T _m (ice) (°C)	T _m (daughter mineral) (°C)	T _h (°C)	Salinity (wt% NaCl equiva.)	Pressure at T _h (bar)
<i>Host zircon</i>							
10ZR-1	2	Type 1a		87 to 103	317 to 322	27.6 to 28.3	85 to 91
	7	Type 2a	−12.8 to −9.2		304 to 324	13.1 to 16.7	81 to 107
10ZR-3	6	Type 1a		45 to 177	304 to 325	26.7 to 31.4	71 to 95
	9	Type 2a	−17.1 to −8.8		295 to 322	12.6 to 20.3	71 to 101
<i>Vein one zircon</i>							
10ZR-3	9	Type 2a	−18.7 to −10.9		302 to 329	14.9 to 21.5	75 to 112
<i>Vein two zircon</i>							
10ZR-3	4	Type 2a	−8.2 to −4.5		298 to 320	7.2 to 11.9	80 to 104
<i>Vein two quartz</i>							
10ZR-3	1		−5.4 to −5.3		290 to 293	8.3 to 8.4	70 to 74

Notes: FIA = Fluid inclusion assemblage. T_m(ice) = Ice melting temperature. T_m(daughter mineral) = Daughter mineral melting temperature. T_h = Homogenization temperature.

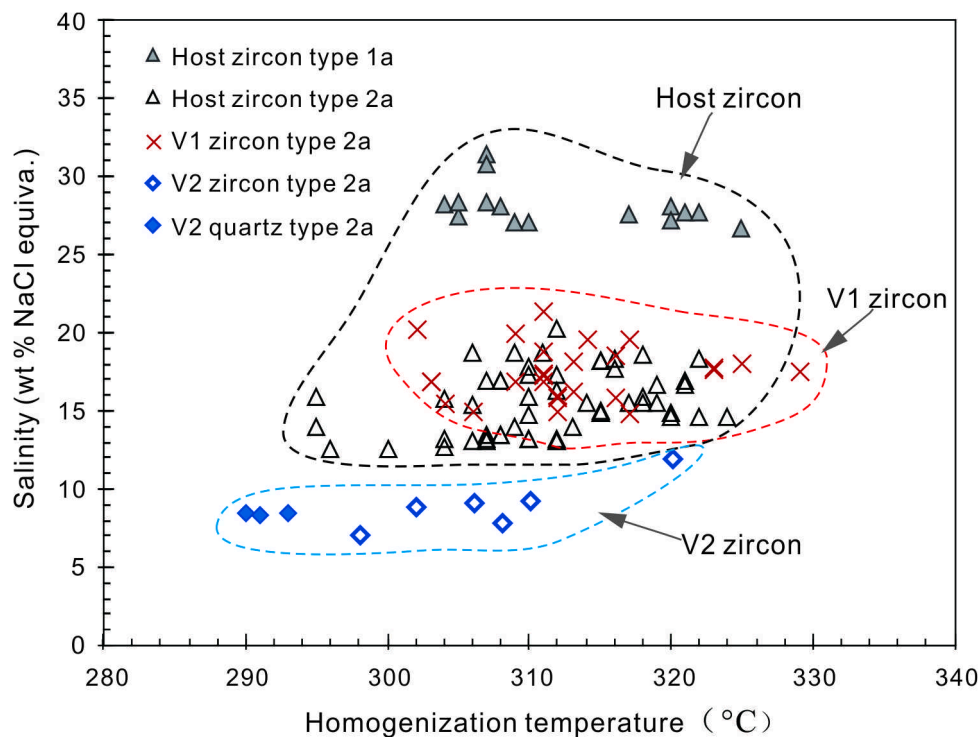


Fig. 5. Homogenization temperature and salinity plot of fluid inclusions in the host zircon as well as in V1 and V2 zircons.

concentrations: the HfO_2 concentration in the host zircon ranges from 0.75 to 0.86 % (average 0.82 %) and that in the V1 zircon ranges from 0.79 to 0.89 % (average 0.84 %). The Nb concentration in the host zircons ranges from 0.17 to 0.35 ppm (average 0.29 ppm) and that in the V1 zircon ranges from 0.2 to 0.4 ppm (average 0.26 ppm). The Ta concentration in the host zircons ranges from 0.04 to 0.112 ppm (average 0.07), and that in the V1 zircon ranges from 0.03 to 0.103 ppm (average 0.06). Compared to the host and V1 zircons, the V2 zircons have higher HfO_2 , Nb and Ta concentrations, ranging from 0.82 to 1.0 % (average 0.89 %), 0.14 to 1.0 ppm (average 0.37 ppm) and 0.02 to 0.99 ppm (average 0.42 ppm), respectively.

4. Discussion

4.1. Formation temperature, pressure and precipitation mechanism

In the host zircon crystals, the coexistence of primary FIAs composed of type 1 daughter mineral-bearing fluid inclusions, type 2 two-phase aqueous inclusions and type 3 carbonic-bearing inclusions, with prismatic or negative zircon crystals (Fig. 4, Supplementary material, Fig. A.2c, A.2d), provide robust evidence for a hydrothermal origin. These FIAs are different from secondary fluid inclusions, which may be entrapped by pores produced by mineral replacement reactions, such as diffusion–reaction processes in radiation-damaged zircon and zircon crystallization by coupled dissolution–reprecipitation processes (Tomaschek et al., 2003; Geisler et al., 2007). The coexistence of different types of fluid inclusions with large variation in volume fractions of phases in a given FIA indicate heterogeneous boiling fluid entrapment (Bodnar, 2003; Diamond, 2003; Goldstein, 2003) during precipitation of the host zircon. Most daughter mineral-enriched type 1a inclusions and most liquid-enriched type 2a inclusions have consistent homogenization temperatures, these temperatures and the lowest homogenization temperature corresponding pressure represent trapping temperature and pressure values. This interpretation means that the host zircon crystallized from a saturated heterogeneous high-salinity $\text{H}_2\text{O}-\text{CO}_2$ hydrothermal fluid with trace amounts of hydrocarbons at temperatures of

295 to 325 °C and a pressure of 71 bar theoretically (Table 2).

In addition, trace element data provide further information. From core to rim, the host zircon crystals have consistent CL patterns, and there are at least two discontinuities in 10ZR-1 and 10ZR-3 and three discontinuities in 10ZR-2. These discontinuities may have been produced by hydrothermal fluid pulses during crystallization, which caused the dissolution and recrystallization of previously crystallized zircon (Fig. 3a, b, d, e). The growth zonations caused by hydrothermal pulses have the same ages and trace element concentrations (Supplementary material, Tabs. A.2, A.3; Fig. 6a, 8a and 9). Thus, they differ from those and the xenocrystic cores of igneous and metamorphic zircons, which exhibit different CL patterns, ages, and trace element contents (Belousova et al., 2002; Corfu et al., 2003; Hoskin and Schaltegger, 2003; Rubatto, 2017), indicating that the host zircon crystallized in the same hydrothermal period with at least three pulses of hydrothermal fluid.

The V1 and V2 zircons in healed cracks within the host zircon were formed during two stages of hydrothermal fluid infiltration. The FIAs indicate that they also crystallized from heterogeneous boiling hydrothermal fluids with relatively moderate and low bulk salinities at theoretical temperatures and pressures of 302 to 325 °C and 75 bar for V1 zircon and 290 to 320 °C and 70 bar for V2 zircon, respectively (Table 2). Given that the average geothermal gradient of Proterozoic crust was 32 °C/km (Nicoli et al., 2016) and the geothermal gradient for metamorphism of Ikalamavony Group during the Kuunga Orogeny derived from peak P - T conditions was also 32 °C/km (Markl et al., 2000), the depths corresponding to the formation pressures for the host, V1 and V2 zircons were 9 to 10 km (lithostatic), which are far higher than actual trapping pressures of 70 to 75 bar. The low trapping pressures can be attributed to the boiling and accompanying drops in fluid pressure during decompression, when high temperature hydrothermal fluids sourced from the wall rocks migrated into closed faults or fractures at depth. This process is explained to a large degree by the fault-valve model (Sibson et al., 1988) and piston model analysis (Weathery and Henley, 2013), and was also the possible mechanism leading to the saturation of hydrothermal fluid and crystallization of the zircons through fluid boiling. However, the post entrapment re-equilibration of

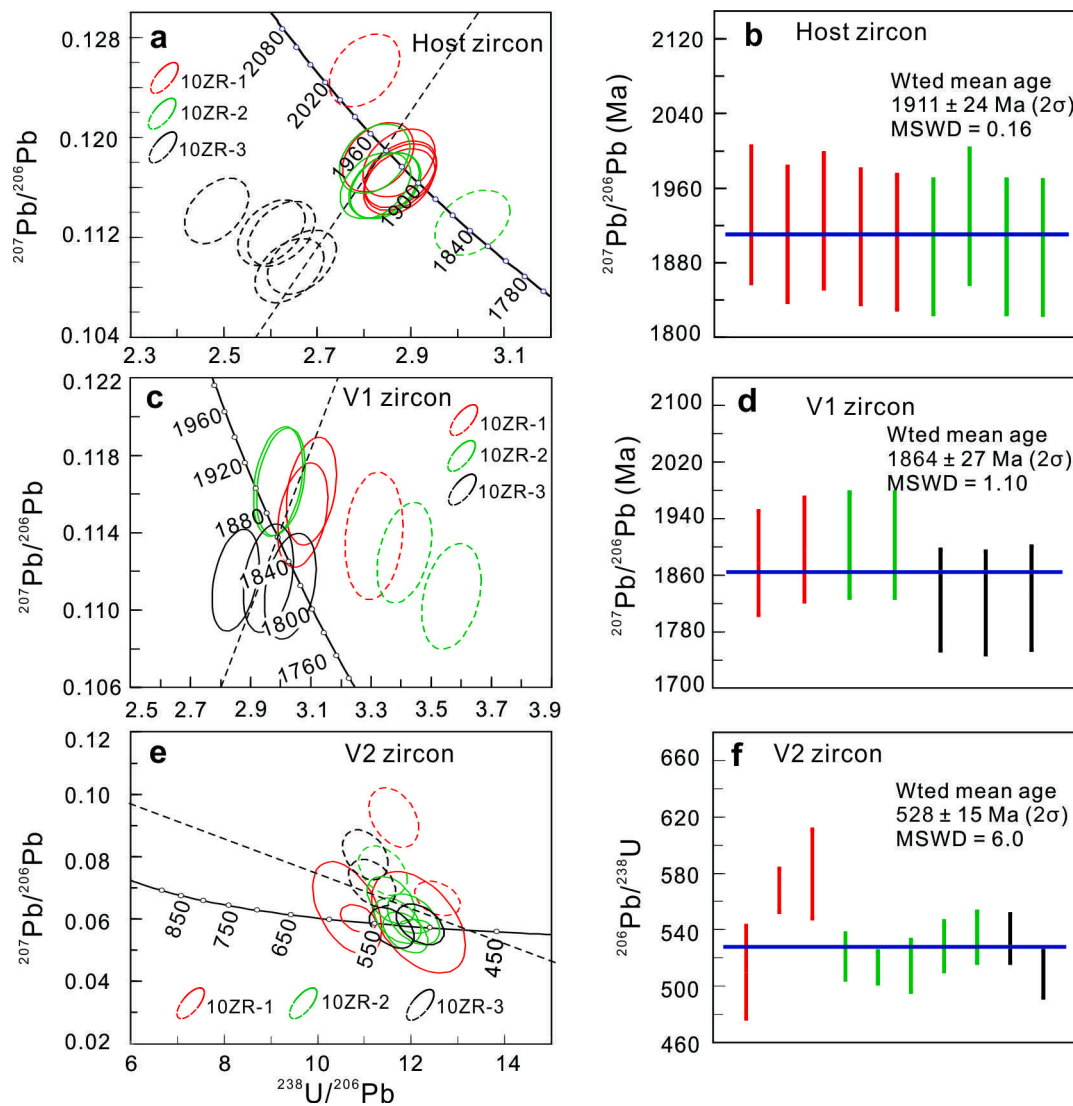


Fig. 6. Plots of the zircon U-Pb age on Tera-Waserburg concordia diagrams and weighted mean ages. (a), (b) Host zircon. (c), (d) V1 zircon. (e), (f) V2 zircon. Weighted mean ages based on real line data points with error ellipses that overlapped on the concordia line. The errors are 2σ . MSWD – mean square of weighted deviates.

fluid inclusions may be an important factor leading to the reductions of trapping pressure. In central to south Madagascar, metamorphic monazite, zircon growth rims, and magmatic zircon with ages of 580 Ma to 520 Ma have been identified in the Ikalamavony Group and Anoyan Domain (Berger et al., 2006; Giese et al., 2011; Tucker et al., 2014). The V2 zircon has an age consistent with the age of granulite-facies metamorphism and magmatism during the Kuunga Orogeny, which indicates that this zircon may have crystallized from metamorphic or magmatic fluids related to this orogenic event. During subsequent uplift of the orogenic belt, the fluid inclusions in these zircons will re-equilibrate in response to a decreasing confining pressure from the wall rocks, leading to a decrease in the original entrapping pressures. Such processes have been confirmed by the experimental results of synthetic fluid inclusions in quartz (Sterner and Bodnar, 1989; Vityk and Bodnar, 1995), and the research data of CO_2 fluid inclusions in quartz from granulite facies rocks in southern Norway (van den Kerkhof et al., 1994). The host, V1 and V2 zircons have different CL texture, trace element concentrations, fluid inclusion salinities and U-Pb ages although they have a similar fluid inclusion trapping temperatures and pressures of 290 to 325 °C and 70 to 75 bar. The most obvious explanation is that after the formation, these zircons underwent density reversal during uplift of the orogenic belt. As the zircon crystals were not

recrystallized and their inclusion fluids were not homogenized, their original inclusion compositions did not change during the re-equilibration, which is in agreement with the experimental results of fluid inclusion quartz (Sterner and Bodnar, 1989; Vityk and Bodnar, 1995). However, the lack of experimental data about re-equilibration of fluid inclusions and scarcity of fluid inclusion data in zircon limit the detailed evaluations on the post entrapment re-equilibration of fluid inclusions in the studied zircon crystals.

4.2. Trace elements

The Th/U ratios of the studied zircons range from 0.01 to 0.55, which broadly overlap with the compositional ranges of magmatic zircon values of >0.5 and the metamorphic zircon values of approximately ≤ 0.1 (Hoskin and Schaltegger, 2003; Rubatto, 2017; Kirkland et al., 2015; Yakymchuk et al., 2018). Their Th and U compositions are different from those of previously reported hydrothermal zircons. More specifically, highly variable Th and U contents are documented in the W and Sn mineralized Mole Granite and Boggy Plain zoned pluton, Australia (Hoskin, 2005; Pettke et al., 2005), with Th and U concentrations ranging between 95 and 6054 ppm and from 297 to 19314 ppm, respectively, and Th/U ratios between 0.06 and 0.94. A wide range of Th

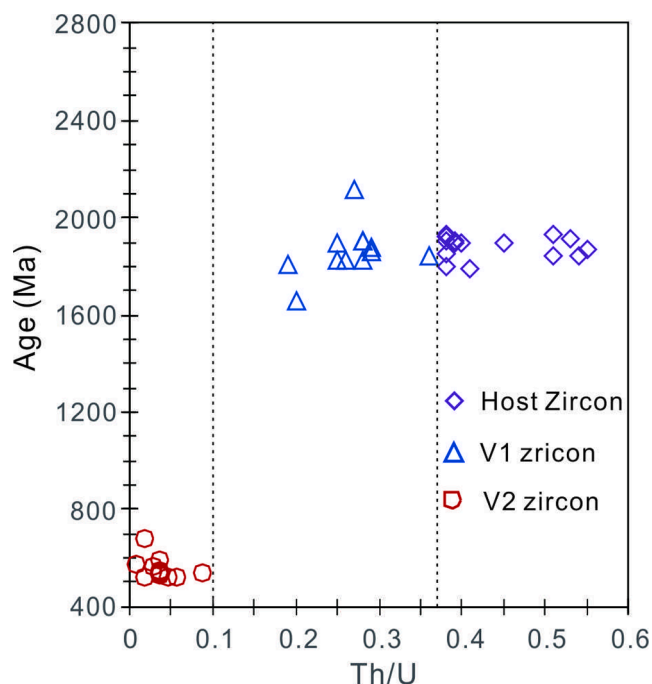


Fig. 7. Age and Th/U ratio plot of the host, V1 and V2 zircons.

and U contents (509 to 1333 ppm Th and 447 to 5446 ppm U and Th/U ratios between 0.24 and 1.14) are also recorded from hydrothermal zircon phases at the Dexing porphyry Cu deposit, China (Zhou et al., 2012). The investigated hydrothermal zircons also differ from typical magmatic zircons that are defined by significant compositional intra-grain and intergrain variations in their Th and U contents and Th/U ratios (Hoskin and Schaltegger, 2003). They are also different from metamorphic zircons which have relatively low to medium Th and U contents and Th/U ratios < 0.1 (Rubatto, 2017; Yakymchuk et al., 2018). Two of the forty analyses (one V1 and one V2) have ^{204}Pb values of 10.15 ppm and 3.03 ppm (Supplementary material, Table A.3), which result in discordant ages, and these Pb values were likely caused by high Pb concentrations in mineral inclusions or inclusion fluids, similar to those of the host zircon (Supplementary material, Fig. A.3). The other analyses are near or below the detection limit, indicating that these zircons have low concentrations of ^{204}Pb .

The zircons in this study have REE patterns that are similar to those of previously reported hydrothermal zircon and igneous rocks, but the concentrations are lower, with the V1 and V2 zircons having REE and Y contents similar to those of kimberlite and carbonatite zircons of mantle origin (Fig. 8) (Belousova et al., 1998; Hoskin and Ireland, 2000). By contrast, most previously documented hydrothermal zircons all have high REE and Y concentrations, e.g., Lu_N from 10^3 to 10^4 (Fig. 8d) and Y from 300 to 2×10^4 times that of chondrites (Hoskin, 2005; Pettke et al., 2005; Pelleter et al., 2007; Zhou et al., 2012; Yang et al., 2014; Toscano et al., 2014; Zhao et al., 2017; Westhues et al., 2017; Li et al., 2018). Igneous zircon populations from various rock types including gabbro, basalt, syenite, and granitoids all have high REE and Y concentrations with Lu_N values exceeding 10^3 times those of chondrites (Fig. 8f) (Hoskin and Ireland, 2000; Hoskin and Schaltegger, 2003; Kaczmarek et al., 2008; Yu et al., 2010; Wang et al., 2012; Zhang et al., 2014). The REE patterns and concentrations are similar to or lower than those of metamorphic zircon, especially zircon grains derived from amphibolite- and granulite-facies units (Schaltegger et al., 1999; Hermann et al., 2001; Rubatto, 2002). However, Eu anomalies are absent in high-pressure zircon (Rubatto, 2017), including zircon crystals sited in high-pressure veins that were previously interpreted to have precipitated from the same hydrothermal fluid as the host veins themselves

(Fig. 8e).

Zircon in granitic pegmatite crystallizes from a phase transition from pegmatitic melt to hydrothermal fluid during fractional crystallization, and these zircon grains or zircon domains are generally subjected to hydrothermal or metasomatic alteration and recrystallization (Uher and Cerny, 1998; Zhang et al., 2004; Wang et al., 2007; Thomas et al., 2009; Soman et al., 2010; Van Lichtenvelde et al., 2009; Lv et al., 2012; Tang and Zhang, 2015; Yin et al., 2013). In highly fractionated pegmatites, zircon crystals are characterized by high contents of HfO_2 (>2.4 wt% and typically exceeding the HfO_2 concentrations of zircons from their granitic host rocks; see: Wang et al., 2010). Distinctly high values of up to 58.88 wt% and 35.21 wt% are recorded in the Koktokay No. 1 and No. 3 granitic pegmatites, Altai, China (Zhang et al., 2004; Yin et al., 2013), 48.3 wt% in the Vasin-Mylk pegmatites, Kola Peninsula, Russia (Kudryashov et al., 2020), and 38.9 wt% in the Tanco pegmatite, Manitoba, Canada, respectively (Van Lichtenvelde et al., 2009). Additionally, these zircon crystals have high concentrations of REEs, Y, Nb, Ta, Th and U, which are attributed to the enrichment of these incompatible elements in the pegmatitic melts derived via fractional crystallization from granitic magma (Wang et al., 2007; Thomas et al., 2009; Lv et al., 2012; Tang and Zhang, 2015). The zircon phases in pegmatite veins in the Sulu orogen are interpreted to have crystallized from the transition of a pegmatitic melt into an aqueous fluid during partial melting of ultrahigh-pressure metamorphic country rocks. These zircons have HfO_2 concentrations ranging from 1.1 to 1.98 %, Y concentrations ranging from 183 to 4079 ppm, ΣREEs concentrations ranging from 209 to 3238 ppm, Lu_N values > 10^3 and Th/U ratios < 0.1, which are similar to those of metamorphic zircon from the country rocks of gneiss and granitic leucosomes (Liu et al., 2010; Li et al., 2013). Their mineral chemistry suggests that our studied zircons are not the product of fractional crystallization of a pegmatitic melt.

The studied zircons have low and consistent trace element concentrations, which may also indicate that they crystallized directly from hydrothermal solutions, with homogeneous and low concentrations of trace elements (Linnen et al., 2014). The REE abundances and chondrite-normalized patterns of the studied zircons do not indicate a hydrothermal origin and therefore cannot be used to discriminate hydrothermal zircon from magmatic and metamorphic zircons (Fig. 8). The positive Ce and negative Eu anomalies and HREE-enriched patterns reflect the characteristics of the zircon crystal structure and chemical composition because the ionic radii of Ce^{4+} and $(\text{HREE})^{3+}$ are generally close to that of Zr^{4+} , and these ions substitute into zircon, while Eu^{2+} substitutes into plagioclase prior to or during zircon crystallization (Hoskin and Schaltegger, 2003). From the host to V1 to V2 zircons, the decreases in REEs, Y, Ti, Th, and U concentrations and Th/U ratios reflect a decrease in the bulk salinity of the hydrothermal fluids from which the zircon crystallized, from relatively high salinity to moderate salinity to low salinity (Table 2; Fig. 5). Equilibrium experiments between topaz rhyolite melt and aqueous fluids at high temperature and pressure indicate that the lithophile trace elements Li, Rb, Sr, Y, Nb, Cs, Ba, Ce, Th and U concentrate into the fluid with increasing Cl (Webster et al., 1989; Keppler and Wyllie, 1990). Except for Th-fluoride complexes, Th^{4+} has concentrations in aqueous solutions that are much lower than those of U^{6+} or U^{4+} complexed with chloride or carbonate (Hazen et al., 2009). The decrease in the salinity of zircon-forming fluids may cause the concentration of Th to decrease more rapidly than that of U in hydrothermal solutions, and the Th/U ratios of the host, V1 and V2 zircons decrease correspondingly (Supplementary material, Table A.3, Fig. 7). In host zircon 10ZR-2, systematic trace element analyses indicate that from core to rim, the HfO_2 concentration, trace element concentrations and Th/U ratios have consistent values (Supplementary material, Table A.3, Fig. 8a, 9). This suggests that these large host zircons crystallized rapidly in a hydrothermal environment with relatively stable temperature and pressure conditions. The host and V1 zircons have consistent trace element variation trends and REE patterns, and the REE concentrations and patterns are consistent with those of some high-

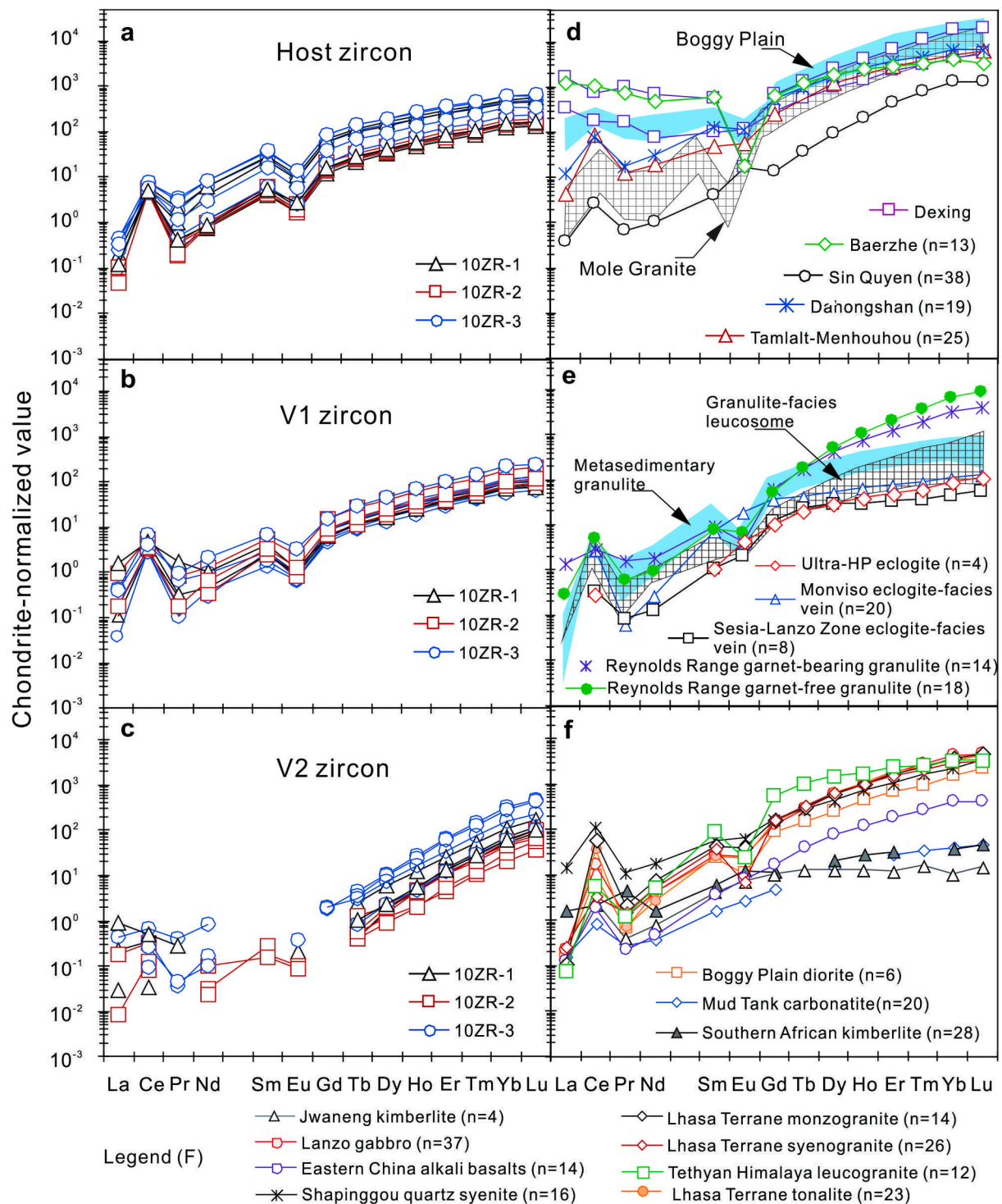


Fig. 8. Chondrite-normalized REE patterns for the host, V1, V2, previously reported hydrothermal, igneous and metamorphic zircons, respectively. (a) Host zircon. (b) V1 zircon. (c) V2 zircon. (d) The reported hydrothermal zircon from the Boggy Plain zoned pluton W and Mole Granite W-Sn mineralizations (Hoskin, 2005; Pettke et al., 2005), Tamlalt-Menhouhou Au deposit (Pelletier et al., 2007), Dexing porphyry Cu deposit (Zhou et al., 2012), Dahongshan iron dioxide Cu-Au deposit (Zhao et al., 2017), Sin Quyen Fe-Cu-REE-Au deposit (Li et al., 2018), and Baerzhe Zr-REE-Nb mineralization (Yang et al., 2014). (e) Metamorphic zircon from the Sesia-Lanzo Zone and Monviso eclogite-facies veins, Reynolds Range garnet-bearing and garnet-free granulites and ultrahigh-pressure eclogite (Rubatto, 2002; Rubatto and Hermann, 2003), metasedimentary granulite and granulite-facies leucosome zircon from Schaltegger et al., (1999). (f) Igneous zircon from the Mud Tank carbonatite (Hoskin and Ireland, 2000), Southern African and Jwaneng kimberlites (Belousova et al. 1998; Hoskin and Ireland 2000), eastern China alkali basalts (Yu et al., 2010), Lanzo Gabbro (Kaczmarek et al., 2008), Boggy Plain diorite (Hoskin and Ireland, 2000), Shapinggou quartz syenite (Zhang et al., 2014), Lhasa Terrane tonalite, monzogranite, syenogranite and Tethyan Himalayan leucogranite (Wang et al., 2012). The data in (d), (e), and (f) are averages except for the hydrothermal zircon from the Dexing porphyry Cu deposit, Boggy Plain zoned pluton W mineralization and the Mole Granite W-Sn deposit as well as zircons from metasedimentary granulite and granulite-facies leucosome. The *n* in parentheses represents the number of samples. Chondrite values are from McDonough and Sun (1995).

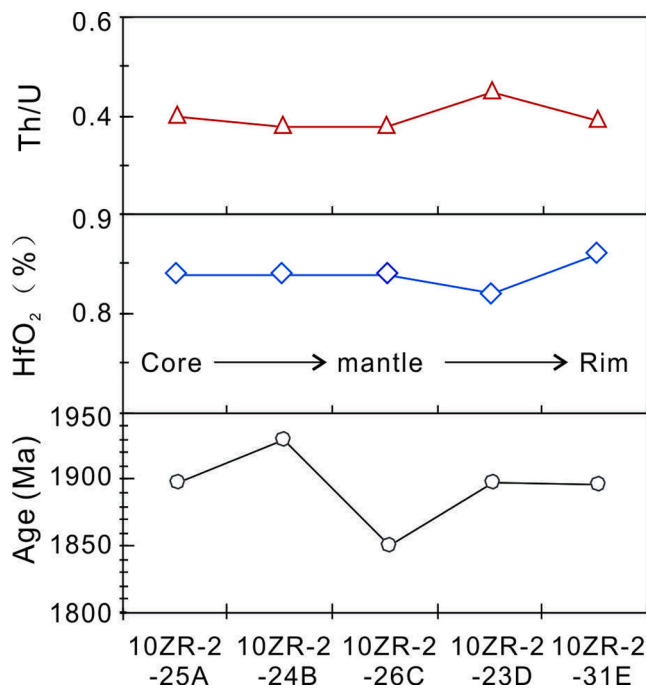


Fig. 9. Age, Th/U ratio and HfO₂ concentration characteristics of host zircon 10ZR-2.

grade metamorphic zircon (Fig. 8a, b, e) (Schaltegger et al., 1999; Hermann et al., 2001; Rubatto et al., 2011, 2017). The fluid inclusions of the host zircon contain CO₂ and trace amounts of hydrocarbons, which excludes the possibility that the host zircon-forming hydrothermal fluid originated from magmatic fluid. The host and V1 zircons have similar ages within the 2σ uncertainty. Therefore, we hypothesize that the zircon-forming hydrothermal fluids associated with the host and V1 zircons have similar origins and they have been derived from metamorphic devolatilization of zirconium-enriched sedimentary rocks. Paleoproterozoic detrital zircons (2.2 to 1.8 Ga) have been identified from meso-Neoproterozoic metasedimentary-igneous rocks in the Antananarivo, Anosy and Androyan Domains and Itremo and Ikalamavony Groups (Cox et al., 1998, 2004; Fernandez et al., 2003; Tucker et al., 2011, 2014; Archibald et al., 2015). This finding led Tucker et al. (2011, 2014) to suggest that extensive amounts of Paleo-Proterozoic crust existed in central and southern Madagascar, composing part of a large SIWH terrane that accreted with the Great Dharwar Craton at 2.0 to 1.8 Ga. The ages of the host and V1 zircons are consistent with this accretion event, suggesting that the host and V1 zircons formed during two stages of metamorphic hydrothermal fluid pulses derived from metamorphic devolatilization of the Neoproterozoic to Paleoproterozoic Ikalamavony Group during regional metamorphism related to the accretion event. In the V2 zircon, the (Lu/Yb)_N, (Lu/Gd)_N, HfO₂, Nb and Ta values are slightly higher, and the bulk salinity of the zircon-forming hydrothermal fluid is lower than that of the host and V1 zircon, which may suggest that the composition and origin of the hydrothermal fluid associated with the V2 zircon were somewhat different from those of the host and V1 zircon. The zircon-forming fluid associated with the V2 zircon may have originated from magmatic or granulite facies metamorphic fluids related to the Kuunga orogenic event.

4.3. Zirconium solubility in hydrothermal fluid

Zirconium, Ti and Hf are high field strength elements (HFSEs) with similar geochemical properties, and they strongly partition into accessory minerals such as rutile, zircon and baddeleyite in many lithologies over a wide temperature and pressure range (Brenan et al., 1994; Hoskin and Schaltegger, 2003). Hence, these minerals control the mobility of Ti,

Zr and Hf in hydrothermal systems. The solubilities of these minerals in water are very low, even at high temperature and pressure (Tropper and Manning, 2005; Audétat and Keppler, 2005; Antignano and Manning, 2008; Ayers et al., 2012; Wilke et al., 2012; Bernini et al., 2013). However, experiments have shown that an alkaline fluid will dissolve zircon and mobilize its Zr content and that the aqueous solubility of zircon increases with molality of NaOH (pH) at 0.2 GPa and 450 to 750 °C; Zr concentrations in NaOH solutions in equilibrium with baddeleyite range from 32 ppm at 300 °C and 60 MPa to 359 ppm at 600 °C and 930 MPa (Wilke et al., 2012). Furthermore, zirconium complexing with silica also increases zircon solubility, and zirconium may be mobile in silica-rich fluids (Ayers et al., 2012). Data on solubility of partially metamict natural zircon in basic solutions at 87 °C and 2 atm, indicate Zr contents between 0.027 and 12.27 ppm depending on the degree of metamictization (Ewing et al., 1982). In a solution with 15 wt% NaCl, zircon solubility at 893 °C, 14.4 kbar and $a_{\text{H}_2\text{O}} = 1$ is 4.5 ppm Zr, which represents a solubility increase by a factor of three over the solubility in pure water under the same conditions (Bernini et al., 2013). The zircon solubility in H₂O + Na₂O + SiO₂ ± Al₂O₃ fluid is strongly enhanced by addition of Na₂Si₃O₇ to H₂O. The degree of enhancement increases with Na₂Si₃O₇ concentration. At 30 wt% Na₂Si₃O₇, the Zr concentration reached 997 ppm at 600 °C and 440 MPa. The Zr concentration in fluids decreases considerably with pressure and increases slightly with temperature. Alkali zircon-silicate complexes are considered to be responsible for increasing the Zr concentrations in Na-Al-silicate-bearing solutions and very likely play an important role in the mobility of the HFSEs (Wilke et al., 2012). In the case of rutile, experimental data on the solubility in NaF, NaCl and KCl aqueous fluids from 0.5 to 2.79 GPa and 250 to 650 °C show that the fluid composition controls the rutile solubility; the solubility of rutile increases with the 2nd to 3rd power of the Cl⁻ concentration, and the 3rd to 4th power of the F⁻ concentration, additionally, increasing temperature has a positive, albeit weak effect (Tanis et al., 2016). The solubility of rutile was measured in H₂O-SiO₂-NaSi₃O₈ fluid at 700 to 1000 °C, 0.7 to 2.0 GPa (Antignano and Manning, 2008). The results indicate that the solubility of rutile increases linearly with dissolved Na-Al silicate at constant temperature and pressure, and the slope of the isothermal change in Ti concentration with dissolved silicate becomes steeper as the temperature increases from 700 to 900 °C. In a 6.3 wt% silicate solution, rutile solubility is relatively high at 1.5 GPa; however, the temperature dependence is less strong. At 800 °C, the increase in rutile solubility in 6.3 wt% silicate solution remains linear in pressure, but the temperature dependence is enhanced (Antignano and Manning, 2008). These experimental results indicate that high pressure facilitates the dissolution and mobilization of Ti in hydrothermal fluids. This is consistent with the occurrence of hydrothermal rutile or rutile-bearing veins or segregations in high-pressure and ultrahigh-pressure metamorphic mafic rocks (Philippot and Selverstone, 1991; Selverstone et al., 1992; Gao and Klemd, 2001; Gao et al., 2007; Ni et al., 2008). However, low pressure conditions facilitate the solubility of zircon in aqueous fluids (Wilke et al., 2012). Minute zircon outgrowths in metapelites (Rasmussen, 2005) and authigenic zircon in voids and cracks at the micrometer scale in shales (Bojanowski et al., 2012) have been reported, and they are attributed to the dissolution-reprecipitation process of detrital zircon from shales in fluids with high concentrations of fluorine, chlorine, phosphate and carbonate at 250 to 270 °C. The Ikalamavony Group, in which the studied zircons are hosted, is rich in quartz and alkali-silicate, and the zircon-forming fluids contain moderate- to high-salinity compositions in the H₂O-NaCl-KCl-CO₂ system with trace amounts of hydrocarbons. They facilitated the dissolution of zircon in quartz-enriched sedimentary rocks, e.g., littoral-facies quartz sandstone, to form zircon-bearing fluid related to Paleoproterozoic (2.0 to 1.8 Ga) medium pressure regional metamorphism and granulite-facies regional metamorphism during the Kuunga orogenic period (580 to 510 Ma) (Markl et al., 2000; Tucker et al., 2011, 2014; Nicoli et al., 2016), and the studied hydrothermal zircons with low concentrations of Ti crystallized from this fluid.

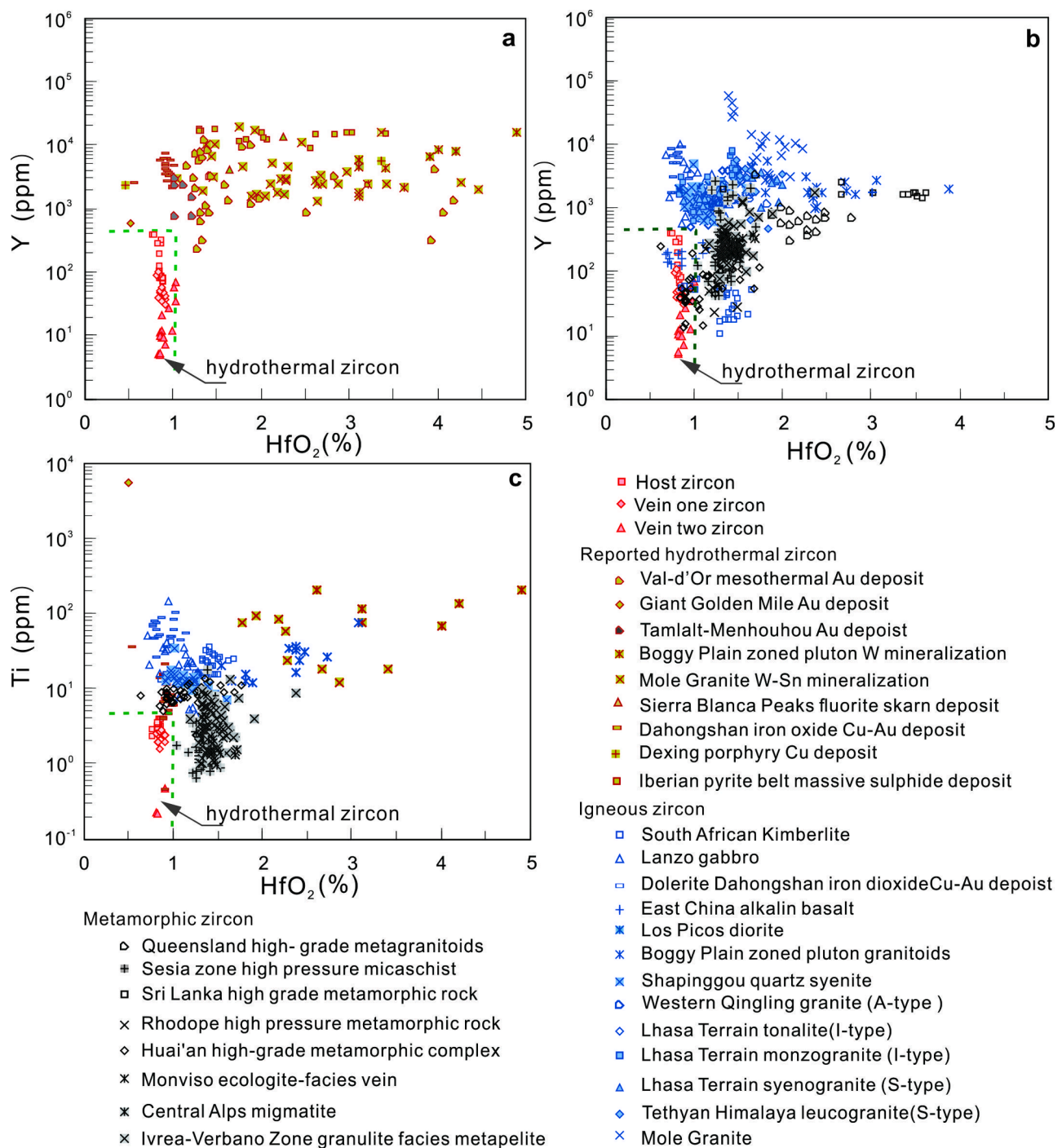


Fig. 10. HfO₂, Y and Ti compositions of the investigated zircons. (a) Y versus HfO₂ plot of the host, V1 and V2 zircons and the reported so-called hydrothermal zircon from the Val-d'Or mesothermal, giant Golden Mile and Tamlalt-Menhouhou Au deposits (Kerrich and King, 1993; McNaughton et al., 2005; Pelleter et al., 2007), the Boggy Plain zoned pluton W mineralization and Mole Granite W-Sn deposits (Hoskin et al., 1998; Hoskin, 2005; Pettke et al., 2005), the Sierra Blanca Peaks skarn deposit (Rubin et al., 1989), Dahongshan iron oxide Cu-Au deposit (Zhao et al., 2017), Dexing porphyry Cu deposit (Zhou et al., 2012) and Iberian Pyrite Belt massive sulfide deposit, respectively (Nesbitt et al., 1999). (b) Y versus HfO₂ plot of the host, V1, V2 zircons; metamorphic zircon from Queensland high-grade metagranitoids (Hoskin and Black, 2000), Sesia zone high-pressure mica schist (Rubatto et al., 2011), Sri Lanka high-grade metamorphic rock (Hoskin, 1998), Rhodope high-pressure metamorphic rock (Liati, 2005), Huai'an high-grade metamorphic complex (Wang et al., 2010), Monviso eclogite-facies vein (Rubatto and Hermann, 2003), Central Alps migmatite (Rubatto et al., 2009), Ivrea-Verbano zone granulite-facies metapelite (Ewing et al., 2013); and igneous zircons from a southern African kimberlite (Belousova et al., 1998), Lanzo gabbro (Kaczmarek et al., 2008), dolerite Dahongshan iron dioxide Cu-Au deposit (Zhao et al., 2017), eastern China alkali basalts (Yu et al., 2010), Los Picos diorite (Ballard et al., 2002), Boggy Plain zoned pluton granitoids (Hoskin and Ireland, 2000), Shapinggou quartz syenite (Zhang et al., 2014), Western Qingling granite, Tethyan Himalaya leucogranite, Lhasa Terrane tonalite, monzogranite and syenogranite (Wang et al., 2012), and Mole Granite, respectively (Pettke et al., 2005). (c) Ti versus HfO₂ plot of the host, V1, and V2 zircons and igneous zircon from a southern African kimberlite (Belousova et al., 1998), Lanzo gabbro (Kaczmarek et al., 2008), dolerite Dahongshan iron dioxide Cu-Au deposit (Zhao et al., 2017), Boggy Plain zoned pluton granitoids (Hoskin et al., 2000), Shapinggou quartz syenite (Zhang et al., 2014), metamorphic zircon from the Sesia zone high-pressure mica schist (Rubatto et al., 2011), Huai'an high-grade metamorphic complex (Wang et al., 2010), and Ivrea-Verbano zone granulite-facies metapelite, respectively (Ewing et al., 2013).

4.4. Discrimination of hydrothermal zircon

On biaxial Y-HfO₂ diagrams, the host, V1 and V2 zircons with concentrations of HfO₂ < 1.0 % and Y < 400 ppm are discriminated from the other reported so-called hydrothermal zircon (Hoskin, 2005; Pettke et al., 2005; Pelleter et al., 2007 and reference therein), igneous zircon (Belousova et al., 1998; Hoskin et al., 2000; Zhao et al., 2017 and reference therein) and metamorphic zircon (Hoskin and Black, 2000; Rubatto and Hermann, 2003; Wang et al., 2010 and reference therein) (Fig. 10a, b). Although there is some overlap with zircons derived from kimberlites and basalts as well as zircons from high-grade metamorphic units (Belousova et al., 1998; Yu et al., 2010; Wang et al., 2010) (Fig. 10b), igneous and metamorphic zircons have high Ti concentrations (Belousova et al., 1998; Hoskin et al., 2000; Kaczmarek et al., 2008; Wang et al., 2010; Rubatto et al., 2011; Ewing et al., 2013; Zhang et al., 2014; Zhao, et al., 2017). Hence, in Ti versus HfO₂ biaxial diagrams they are effectively discriminated from the hydrothermal zircons from our study which have Ti concentrations of <4.0 ppm (Fig. 10c).

5. Conclusions and implications

Our study reports on hydrothermal zircons that crystallized from saturated heterogeneous relatively high-salinity hydrothermal fluids (with the maximum fluid inclusion salinity of 31.4 wt% NaCl equivalent) caused by boiling with fluid inclusion homogenization temperatures of 295 to 325 °C and the corresponding pressure of 71 bar. These zircon crystals were subsequently overprinted by two phases of boiling hydrothermal fluids with relatively moderate and low salinities (with the maximum fluid inclusion salinities of 21.5 wt% NaCl equivalent and 11.9 wt% NaCl equivalent, respectively). The fluid inclusion homogenization temperatures and the corresponding pressures range between 302 and 329 °C and 75 bar and 290 to 320 °C and 70 bar, respectively. These zircons show CL oscillatory zoning and consistently low trace element concentrations and Th/U ratios that decrease with fluid salinity. The Th/U ratios of these zircons fall between the typical values of magmatic (>0.5) and metamorphic zircons (approximately ≤ 0.1). The low concentrations of HfO₂, Y and Ti in the studied zircons can be used to discriminate hydrothermal zircon from igneous and metamorphic zircons.

Zircon is the principal economic source of zirconium and the primary source of hafnium and it is mainly produced as a byproduct of the mining and processing of heavy mineral placer deposits (Kennedy, 1999). However, the hydrothermal zircon veins described in our study composed mainly of distinctly large zircon grains that crystallized from saturated hydrothermal solutions may also represent a potential source of zirconium and hafnium.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.oregeorev.2022.105111>.

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