Chemical lattice expansion of natural zircon during the magmatic-hydrothermal evolution of A-type granite

Ling-Jun Zeng\textsuperscript{1,2}, He-Cai Niu\textsuperscript{1,3}, Zhi-Wei Bao\textsuperscript{1}, Wu-Bin Yang\textsuperscript{1,3,*}

\textsuperscript{1}Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, 511 Kehua Street, Guangzhou 510640, China

\textsuperscript{2}University of Chinese Academy of Sciences, 19 Yuquan Road, Beijing 100049, China

\textsuperscript{3}Guangdong Provincial Key Laboratory of Mineral Physics and Materials, 511 Kehua Street, Guangzhou 510640, China

* Corresponding author: yangwubin@gig.ac.cn

ABSTRACT

Although thermal lattice expansion is a well-documented nature of crystals, including zircon and zircon-type minerals, chemical lattice expansion of natural mineral is rarely reported. Here we report a comprehensive investigation on three types of natural zircon that recorded the evolution of the granitic system in Xiangshan, North China, and show expanding crystallographic parameters induced by chemical incorporation instead of thermal expansion. Prismatic and oscillatory zoned zircon grains (Type-1A), crystallized early in the granitic magma at high temperatures in a volatile-undersaturated environment, have the smallest lattice parameters (a=6.603Å, c=5.971Å). Prismatic and altered zircon grains (Type-1B), formed under
volatile-saturated conditions and in the presence of F-rich fluid with numerous thorite
and xenotime inclusions, have intermediate lattice parameters (a=6.649Å, c=6.020Å).
Pyramidal zircon grains (Type-2), formed in a subsolvus granite system at relatively
low temperatures and coexisted with fluid inclusions, have the biggest lattice
parameters (a=6.677Å, c=6.010Å). Trace element, including Hf, Th, Ti, Y and REE,
and volatiles contents increase in the structure of zircons from the early- to
late-magmatic origin, which is consistent with the expansion of the lattice parameters.
The occurrence of the three zircon types in the Xiangshan arfvedsonite granites is
interpreted to reflect the progressive fractionation of granitic melt from hypersolvus to
subsolvs conditions. Therefore, we conclude that the lattice expansion of zircon in
this study results from chemical incorporation of trace element and volatile
components during the magmatic to hydrothermal evolution of granitic magma.
Besides, the textural and compositional evolution of zircon can be used as efficient
indices for the fractionation and evolution of A-type granitic system.

Keywords: Chemical lattice expansion, zircon, fractionation crystallization,
magmatic-hydrothermal evolution, A-type granite

INTRODUCTION
Zircon is a common accessory mineral in granitic rocks. It is chemically resistant,
relatively insoluble and refractory, and can withstand weathering and recycling, as
well as high temperature metamorphism and anataxis (El-Bialy and Ali 2013). It is
widely accepted that zircon can provide reliable and robust estimates of age,
compositions of coexisting minerals and melts, and constraints on the petrogenesis of host rocks (Valley 2003). In spite of its apparently simple chemical composition (ZrSiO$_4$), zircon is able to accept substantial amounts of other minor and trace elements into its crystal lattice (e.g., Hf, Th, U, Ti, Nb, Ta, P, Y and REE) (Breiter et al. 2014). Zircon crystals that are not affected by intense metamictization could provide information about the chemical composition of the melt from which they crystallized. In contrast, the metamict crystals may accumulate substantial amounts of non-formula elements, re-equilibrated with the hydrothermal and low-temperature fluids (Geisler et al. 2007; Yang et al. 2014).

In granitic systems, zircon is generally considered to form early in the crystallization history (Valley 2003). However, in some A-type granites it can crystallize during the whole process of magmatic crystallization, with significant distinction in both texture and composition (Belousova et al. 2006; Breiter and Škoda 2012; Pupin 1980). Although geologically complicated, the behavior of trace elements in zircon depends on physical-chemical conditions and partition coefficients between zircon and melt (Belousova et al. 2006). Presently, there are several speculations have been proposed regarding zircon texture and composition, which include that zircon can record the processes of (1) magmatic and hydrothermal crystallization (Van Lichtervelde et al. 2009; Yang et al. 2013), (2) hydrothermal alteration (Zheng et al. 2007), (3) country-rock assimilation, (4) magma mixing (Griffin et al. 2002), or even (5) tectonic setting (Grimes et al. 2007, 2009).

This study reports analyses of textures and compositions of three types of zircon
from an A-type granite in north China. The purposes of this article are (1) to
determine the variation of zircon in both structure and composition that may influence
the lattice expansion, and (2) to test the speculation that zircon could record the
processes of magmatic and hydrothermal evolution of the host granite. All samples
come from the Xiangshan arfvedsonite-bearing granite. Zircon structures were
analyzed by X-ray diffraction (XRD), cathodoluminescence (CL) and Raman
spectroscopy. Major and trace element compositions of zircon were measured by
EMPA and LA-ICPMS.

GEOLOGICAL BACKGROUND

The Xiangshan complex crops out over 217 km² in the NNE-trending Yanshan
Mountains (northeastern Hebei province), on the northern margin of the North China
Craton (NCC) (Fig. 1a). It intruded into the Lower Sinian migmatite, with limestones
of the Cambrian Fushanjun Formation and the Jurassic Mentougou Formation in the
northeast. It consists of medium-grained arfvedsonite granite in the center and
porphyritic biotite granite on the margins (Fig.1b). The arfvedsonite granites mainly
consist of quartz (25–30 vol%), perthite (45–55 vol%), K-feldspar (10–15 vol%),
plagioclase (5 vol%) and minor arfvedsonite (5 vol%). Accessory minerals mainly
consist of zircon, magnetite, sphere, fluorite and rutile. The quartz is subhedral to
euhedral and 1–3 mm in size. The perthite is commonly subhedral and 1–4 mm in size,
with perthitic texture. The K-feldspar is also commonly subhedral and 2–4 mm in size.
The arfvedsonite is blue to dark blue in color, euhedral to subhedral with distinct
pleochroism. Some arfvedsonite grains occur as inclusions within quartz or perthite,
implying they crystallized earlier than quartz and perthite. The other arfvedsonite is intergranular, indicating it crystallized simultaneously with or later than quartz and perthite. Graphic intergrowths of quartz and K-feldspar occur as vermicular to cuneiform patterns in the arfvedsonite granites in margin of the central part. In contrast, the biotite granite on the marginal of the complex is porphyritic-like, with 15–30 vol% phenocrysts and 70–80 vol% groundmass. The phenocrysts consist of euhedral quartz (0.1–0.2 mm in size), subhedral plagioclase (0.2–1.5 mm in size) and biotite. The groundmass consist of the same phases as the phenocrysts. Accessory minerals are mainly zircon and magnetite. This study mainly focuses on zircon in arfvedsonite granite from the central part of the Xiangshan complex.

The occurrence of alkali-feldspar and sodic-amphibole (arfvedsonite) in the arfvedsonite granites show the affinity of A-type granite (Yang et al., 2008), which is characterized by high alkalis and iron-rich mafic mineralogy (Frost and Frost 2010). According to the A-type granite division of Eby (1990, 1992) whole-rock compositions (Supplemental Data Table 1), the Xiangshan arfvedsonite granites samples plot in the A₁ subgroup, compatible with an intraplate setting (Figs. 2a and 2b).

ANALYTICAL METHODS

Zircon grains were separated using conventional density and magnetic separation techniques, and then handpicked under a binocular microscope. Representative zircon grains were set in epoxy mounts which were then polished to nearly half section to
expose the internal structures. The crystals were documented with transmitted and reflected light micrographs as well as by CL images to reveal their external and internal textures.

Single crystal micro-XRD analyses were conducted using a Rigaku D/max RapiIIR micro-XRD system at the Central South University, Changsha, China. All analyses were carried out with a beam diameter of ~100 μm under 40 kV and 250 mA (CuKα) with exposures of 20 minutes.

Laser Raman spectra of zircon crystals were collected using the HORIBA XploRA Plus Laser Raman micro-spectroscope at the Key Laboratory of Mineralogy and Metallogeny, Chinese Academy of Sciences (CAS), Guangzhou, China. An Ar ion laser, operating at 10mW was used to produce the excitation wavelength of 532 nm. The beam was coupled with a grating of 1200 grooves per mm. The scanning range of the spectra was set between 100 and 1500 cm⁻¹ with an accumulation time of 8 s for each scan.

Major element compositions of zircon grains and host inclusions were analyzed using a JEOL JXA 8230 electron microprobe (EMPA) at the Key Laboratory of Mineralogy and Metallogeny, Guangzhou Institute of Geochemistry, CAS, Guangzhou, China. The operating conditions were as follows: 15 kV accelerating voltage, 20 nA beam current and 1 μm beam diameter. Zr and Si were analyzed for 20s on peak and 10s on background whereas Fe, P, Ti, U, Y, Hf and Th were analyzed for 40s on peak and 20s on background. Standards used for analyses of the zircon
samples include zircon for Zr, Si, and Hf, magnetite for Fe, rutile for Ti, monazite for U, Y and Th and apatite for P. ZAF calibration procedures were used for data correction.

Trace element analyses of the zircon grains was conducted with an Agilent 7500a ICP-MS coupled with a Resonetics RESOlution M-50 193nm laser-ablation system at Key Laboratory of Mineralogy and Metallogeny, CAS. More detailed analytical procedures were described by Li et al. (2012) and Tu et al. (2011). All analyses were carried out with a beam diameter of 31 μm and a repetition rate of 10Hz with an energy of 80mJ. Helium was used as the carrier gas. NIST SRM610 and TEMORA2 (TEM) were used as external standards (Black et al. 2004; Pearce et al. 1997), and $^{29}$Si as an internal standard (Anczkiewicz et al. 2001). All analysis spots were carefully selected to avoid mineral and melt inclusions and cracks in zircons. Only smooth LA-ICPMS signals were chosen.

RESULTS

Zircon morphology and textures

Zircons in the Xiangshan arfvedsonite granites can be morphologically classified into prismatic (Type-1) and pyramidal (Type-2) types. Moreover, the prismatic zircon grains can be further subdivided into two subtypes, bright and zoned zircon (Type-1A) and murky and spongy zircon (Type-1B), according to their internal structures.

Type-1A zircons commonly intergrowth with quartz, K-feldspar and arfvedsonite, or enclosed in arfvedsonite (Fig. 3a). They are euhedral prismatic crystals 80–120 μm
in length with c/a ratios of 2:1 to 3:1. They are transparent in transmitted light, display multiple oscillatory growth zones in CL images but are homogeneous under BSE, consistent with zircon of magmatic origin (Fig. 3d). They have well-developed \{101\} pyramids and \{100\} and \{110\} prisms, similar to typical morphologies of high temperature zircon in alkaline magma (Pupin 1980). Inclusions in the zircon grains commonly consist of melt and/or crystallized minerals such as apatite (Fig. 3g).

Type-1B zircons are usually intergrowth with quartz, K-feldspar and arfvedsonite (Fig. 3b), or enclosed in quartz and K-feldspar, with apparent radiohalo. These zircon crystals are euhedral prismatic crystals 100–200 μm in length with c/a ratios of 2:1 to 3:1. They are cloudy and red-brown in transmitted light, with no oscillatory growth zones in CL images (Fig. 3e). They have well-developed \{101\} pyramids and \{100\} and/or \{110\} prisms, similar to the typical morphologies of high temperature zircons (Pupin, 1980). Inclusions in the zircons crystals commonly consist of melt and/or crystallized minerals such as apatite, thorite, Fe-oxide and xenotime (Fig. 3h). Sometimes, the murky Type-1B zircon can also be found as overgrowths of Type-1A zircon crystals (Figs. 4a and 4b).

Type-2 zircons are usually enclosed in quartz, K-feldspar or graphic textured occurrences of the two (Fig. 3c). Halite-bearing fluid inclusions can be observed in the host quartz coexist with the Type-2 zircon (Fig. 3i). The Type-2 zircon grains are dipyramidal with lengths of 100–280 μm. They are cloudy and red-brown in transmitted light, and have a transparency between Type-1A and Type-1B zircons. They display slight oscillatory growth zones in CL images (Fig. 3f) with rare
inclusions. They have well-developed \{111\} crystal faces with sporadically
less-developed \{110\} faces.

**XRD patterns**

The XRD pattern of Type-1A zircon crystals have cell parameters of $a=6.603(2)\ \text{Å}$ and $c=5.971(4)\ \text{Å}$ identical to the standard zircon (06-0266, $a=6.607\ \text{Å}$, $c=5.982\ \text{Å}$) (Table 1) (Robinson et al. 1971). The strong intensity, small cell parameters, along with the sharp two-theta of \{220\} peak of full-widths at half-maximum (FWHM) of 0.174° (Fig. 5), indicating that they are well-crystallized and of magmatic origin (Crepaldi et al. 2003). The cell parameters of the Type-1B zircon are $a=6.649(6)\ \text{Å}$ and $c=6.020(2)\ \text{Å}$ which are higher than both the Type-1A zircon and the standard zircon. The shifting of \{220\} peak position to slightly lower two-theta and a remarkable reduction in intensity and broadening of the peak (FWHM=0.635°) suggest that the Type-1B zircon grains have low crystallinity (Fig. 5). The cell parameters of the Type-2 zircon are $a=6.677(7)\ \text{Å}$ and $c=6.010(4)\ \text{Å}$. The \{220\} peak position shifts to lower two-theta than the other two types of zircon with low peak intensities between the other two types of zircon. The FWHM of the Type-2 zircon is 0.172° which is similar to that of the Type-1A zircon (Fig. 5).

**Zircon compositions**

Major and trace element compositions of the zircons are listed in Supplemental Data Table 2 and Supplemental Data Table 3, respectively. Type-1A zircons have 31.6–33.0 wt% SiO$_2$, 63.2–65.7 wt% ZrO$_2$, 1.06–1.82 wt% HfO$_2$ and 0.03–1.42 wt% Y$_2$O$_3$.
(mostly in the range of 0.03–1.00 wt%). Total REE contents vary from 855 to 2902 ppm with LREE/HREE ratios of 0.03 to 0.05. They display positive Ce anomalies and negative Eu anomalies with Ce/Ce* and Eu/Eu* ratios ranging from 9.50–53.7 and 0.008–0.05, respectively (Fig. 6a). They have La and Pr concentrations ranging from 0.08 to 3.15 ppm, 0.12 to 1.05 ppm, respectively. Type-1A zircons have relatively low contents of Y (1274–4652 ppm), Th (51.6–465 ppm) and U (96.6–693 ppm), with Th/U ratios ranging from 0.39–0.67 (Fig. 6b).

Type-1B zircons have 30.8–32.6 wt% SiO₂, 59.5–65.9 wt% ZrO₂, 1.29–4.34 wt% HfO₂ and 0.05–2.36 wt% Y₂O₃ (mostly in the range of 1.00–2.36 wt%). Total REE contents vary from 4,240 to 16,057 ppm with LREE/HREE ratios of 0.03 to 0.11. They display positive Ce anomalies and negative Eu anomalies with Ce/Ce*and Eu/Eu* ratios ranging from 1.31–43.0 and 0.009–0.07, respectively (Fig. 6a).

Compared to Type-1A zircons, Type-1B zircons have much higher contents of Y (5178–27020 ppm), Th (2308–27524 ppm) and U (3099–11450 ppm) (Figs. 4d–e), with Th/U ratios ranging from 0.59–2.42. Notably, they also have much higher La, Pr, Hf, Y, P, Nb and Ta concentrations than the Type-1A zircons (Figs. 4f–h and 6b).

Type-2 zircons have 30.2–32.3 wt% SiO₂, 53.3–61.4 wt% ZrO₂, 1.33–3.08 wt% HfO₂ and 1.07–6.29 wt% Y₂O₃. They have the highest total REE contents varying from 14952 to 24139 ppm with LREE/HREE ratios of 0.05 to 0.11. They display obviously positive Ce anomalies and negative Eu anomalies with Ce/Ce*and Eu/Eu* ratios ranging from 24.0–117 and 0.007–0.01, respectively (Fig. 6a). They have La, Pr concentrations ranging from 0.45 to 3.25 ppm, 8.01 to 17.3 ppm, respectively.
Compared to Type-1A and Type-1B zircons, Type-2 zircons have relatively high contents of Y (27347–42189 ppm), Th (3935–17265 ppm) but moderate U (616–4982 ppm) contents, with highest Th/U ratios ranging from 2.46–12.9. They also have much higher Hf, Y, P, Nb, Ta contents than Type-1A zircon grains (Fig. 6b).

DISCUSSION

Origin of the three types of zircon

The different morphology, texture and composition of the three zircon types in the Xiangshan arfvedsonite granites is interpreted to indicate that they formed under different physical and chemical conditions during the magmatic-hydrothermal evolution of the intrusion. In typical I- and S-type granites, zircon is one of the first crystallizing minerals (Belousova et al. 2006; Breiter and Škoda 2012), however, in some A-type granites it can crystallize throughout the fractionation process (Breiter and Škoda 2012), consistent with what is seen in the zircons from the Xiangshan arfvedsonite granites. The texture and composition of zircon can reflect the evolution process of magma and provide information to the role played by volatiles (Erdmann et al. 2013).

Type-1A zircons show magmatic textural and compositional features (Pupin 1980) particularly the oscillatory zoning. In addition, the well-developed {101} pyramids and {100} prisms, as well as the occurrence of melt and apatite inclusions, indicate that they crystallized from high temperature alkaline magma (Pupin 1980). Furthermore, the low Th, U and Hf concentrations and high ZrO₂/HfO₂ ratios (Figs.
7a–c) indicate they crystallized from a volatile-undersaturated magma (Erdmann et al. 2013). Therefore, the Type-1A zircons are most likely primary magmatic zircon that crystallized early in the evolution of the granitic magma.

The presence of Type-1B zircon overgrowths on some Type 1A zircons indicates they crystallized later in the evolution of the magma (Figs. 5a–b). They have higherFWHMs of Raman and XRD than Type-1A zircon crystals (Figs. 5c and 6), indicating lower crystallinities. The Type-1B zircons show altered textures and exotic composition and well-developed {101} pyramids and {100} prisms, but larger grain size, higher Th, U and HfO₂ concentrations, lower ZrO₂/HfO₂ (Figs. 7a–c), and no oscillatory growth zones compared to Type-1A. The porous and altered features are similar to those of the zircon from evolved granite plutons at Melville Peninsula in northern Canada which were interpreted to be from volatile-saturated magmas (Erdmann et al. 2013). In addition, thorite and xenotime, which commonly form at the late stage of the magmatic evolution, can be observed as inclusions in the Type-1B zircons. Combined these features suggests that the Type-1B zircons crystallized from a relatively evolved magma and were subsequently altered in a volatile-saturated magma.

The Type-2 zircons show morphology characteristic of low-temperature and fluid-rich magmas (Pupin 1980). The well-developed {111} crystal faces with sporadically less-developed {110} faces are similar to synthetic, flux-grown zircon crystals (Burakov et al. 2002). In addition, some Type-2 zircon crystals are intergrowth with quartz and K-feldspar, which would have formed under subsolvus
condition. Formation of myrmekitic texture involve a series of short pluses of infiltration of an aqueous fluid at about 500 °C during the subsolvus evolution of the granite (Abartet al. 2014). The coexistence of halite-bearing fluid inclusions with Type-2 zircon crystals is consistent with a late magmatic or hydrothermal origin (Schaltegger 2007). So we suggest that the Type-2 zircons formed under subsolvus conditions with volatile over-saturated.

Lattice expansion of zircon induced by chemical incorporation

Standard zircon has tetragonal symmetry with a=6.607 Å, c=5.982 Å, Z=4 and belongs to the space group I41/amd (Robinson et al. 1971). Such crystal structure is documented that can be expanded by thermal heating, metamictization and chemical incorporation (Robinson et al. 1971; Patwe et al. 2009). In this study, natural zircon lattice show expansion from the early- to late-stage zircon types that formed during the cooling and fractionation of the Xiangshan granitic magma, instead of thermal heating. Meanwhile, the XRD and Raman data also lend little support for remarkable influence of metamictization. The altered Type-1B zircon shows the most metamict features among the three zircon types, but the crystallographic parameters is not the biggest type (Fig. 5). Therefore, chemical incorporation in zircon lattice should be the mostly plausible cause. Since chemical compositions of zircon from igneous rocks are controlled by the behavior of trace element and partition coefficient between zircon and melt (Belousova et al. 2006), the remarkable increasing of trace element substitution and volatile contents in zircon lattice of this study depend on physical-chemical conditions of the evolving granitic system.
Substitution increases from early to late zircon lattice.

In granitic rocks, non-formula elements, such as Hf, Th, U, REE and Y can enter into the zircon lattice by simple or coupled substitution mechanisms (Hanchar et al. 2001; Hoskin and Schaltegger 2003). IV charge (+4) cations, such as Hf$^{4+}$, Th$^{4+}$, U$^{4+}$ and Ti$^{4+}$, can substitute for Zr$^{4+}$, whereas other charge cations, such as Y$^{3+}$, REE$^{3+}$, Nb$^{5+}$, Ta$^{5+}$, P$^{5+}$ and Fe$^{2+}$, can undergo coupled substitution for Zr$^{4+}$ and Si$^{4+}$. In this study, the substitution contents of such non-formula elements are much more favored in the late-stage zircon formed during the magmatic-hydrothermal evolution of alkaline granite (Table 2).

IV charge non-formula cations usually occur as major element in zircon. For example, Hf$^{4+}$ and Zr$^{4+}$ have identical charge (+4) and similar cation radius (0.83 Å for Hf$^{4+}$ and 0.84 Å for Zr$^{4+}$), so they can substitute for each other and form complete zircon-hafnon solid solution series. It was confirmed by the study of Wang et al. (1996), who found an extreme Hf enrichment (up to 34.8 wt% HfO$_2$) in zircon from an A-type granite in Suzhou, China. Besides, Th$^{4+}$ and U$^{4+}$ have the same charge (IV) but larger cation radius (1.05 Å for U$^{4+}$ and 1.00 Å for Th$^{4+}$), and can also substitute Zr$^{4+}$ in zircon (Hoskin and Hanchar 2003). For example, the Th and U contents in zircons from the A-type granite in the Pitinga tin deposit, Brazil, can reach 6000 ppm and 2900 ppm, respectively, and the ThO$_2$ and UO$_2$ contents in zircons from the Beauvoir S-type granite, France can reach 0.35 wt% and 7.6 wt%, respectively (Cheng et al. 1992). In this study, the altered magmatic zircon (Type-1B) and late zircon (Type-2) from the Xiangshan arfvedsonite granite have significantly higher...
contents of Hf, U and Th than the early zircon (Type-1A) (Figs. 7a–c), indicating that Hf, U and Th can be concentrated in both residual melt and late zircon during the fractional crystallization. It is consistent with the well-documented zircon–hafnon solid solution that natural zircon may contain high contents of Hf, and changes into hafnian zircon or even hafnon in some high fractionated granite systems (Wang et al. 1996; Yin et al. 2013). The isomorphous substitutions of Th$^{4+}$ and U$^{4+}$ for Zr$^{4+}$ lead to the expansion of unit-cell, which is reflected in the low-degree shift of XRD peaks of the Type-1B and Type-2 zircons (Fig. 5). The extensive substitutions of Th$^{4+}$ and U$^{4+}$ resulted in the metamictization of the Type-1B zircon which reacted with magmatic exsolved fluids. It seems likely that the substitution of IV charge cation in zircon lattice can become easier in the late magmatic stage.

Alternatively, the other charge cations, REE$^{3+}$ and Y$^{3+}$ in particular, usually occur as incompatible trace elements in zircon. REE-bearing zircon commonly contains P, and owing to crystal chemical resemblance between Y$^{3+}$ and heavy REE$^{3+}$, substitution of Zr$^{4+}$ by REE$^{3+}$ or Y$^{3+}$ and Si$^{4+}$ by P$^{5+}$ in zircon is commonly explained by the coupled xenotime-type substitution to maintain charge balance $[(Y, \text{REEs})^{3+} + P^{5+} \rightarrow Zr^{4+} + Si^{4+}]$. If xenotime substitution is the sole mechanism by which charge balance is maintained in zircon crystals that have undergone REE-substitution (Hoskin 2003), the atomic ratio (REE+Y)/P should approach 1. As the majority of (REE+Y)/P ratios in zircons from the Xiangshan arfvedsonite granites are higher than 1 (Fig. 7d), this suggests a more complex charge-balance mechanism (Cavosie et al. 2006; Finch and Hanchar 2003). Because the Type-1B and Type-2 zircons have
relatively high Nb and Ta contents and low total weight of EMPA data, the
substitution \((Y,\text{REEs})^{3+}(\text{Nb},\text{Ta})^{5+}\rightarrow 2\text{Zr}^{4+}\) and \((\text{ZrO})^{2+}\rightarrow (\text{YOH})^{2+}\) or \((\text{ZrO})^{2+}\rightarrow (\text{YF})^{2+}\) proposed by Es’kova (1959) may also play a role. Nevertheless, the obvious increase of REE and Y concentrations from the early to late zircon structure suggests that the coupled substitution in the zircon lattice increases from early to late magmatic stage.

**Volatile becomes saturated.**

The deficit in the total weight of EMPA is commonly ascribed to the presence of the OH⁻ and F⁻ in the zircon’s structure or molecular \(\text{H}_2\text{O}\) in the amorphous domains of the metamict zircon structure (Breiter and Škoda 2012). Previous authors predicted that hydration takes place only in tetrahedral sites \((\text{SiO}_4)\) without affecting the occupancy of the Zr position (Hoskin 2003). For example, up to 8.8 wt\%\(\text{H}_2\text{O}\) was found in Archaean zircon from Jack Hills, Australia (Nasdala et al. 2009), and as much as 0.8 apfu \((\text{OH,F})_4\) replacing the \((\text{SiO}_4)\) group was found in synthetized zircon (Caruba et al. 1985). In this study, the deficits of the \(\text{SiO}_2\) contents (32.8-\(\text{SiO}_2\) wt\%) of Type-1B (0.2–2.0 wt\%) and Type-2 (0.5–2.6 wt\%), which are much higher than that of Type-1A zircon (0–1.2 wt\%), are indicative of their increasing of volatiles substitution. Giving that the F and Cl contents nearly below detection limit (Supplemental Data Table2), the dominate volatile is probably \(\text{H}_2\text{O}\) or \(\text{OH}^-\) in the three types of zircon. Meanwhile, the significant deficits of the total weight (1-Total) of Type-1B (1.1–5.3 wt\%) and Type-2 (1.6–6.7 wt\%) are indicative of their increasing of trace elements as well as volatiles (Fig. 8).

The logarithms of REE partition coefficients between mineral and melt against
Ionic radii show a simple parabolic relationship (Onuma et al. 1968), which is consistent with the crystal structural strain modelling (Blundy and Wood 1994). Most REEs of Type-1A and Type-2 zircon grains fall on the parabola, except for Ce and Eu (Figs. 9a and 9c), which are largely affected by their valences. On the contrary, the Type-1B zircon grains have more elements (e.g., Ce, Eu, La, Pr and Nd) deviating from the predicted parabolic behavior (Fig. 9b), suggesting hydrothermal alteration plays an essential role in the enrichment of La, Pr and Nd. Such non-charge-and-radius-controlled behaviors of REE distribution has been attributed to the transition between pure silicate melts and hydrothermal fluids by Bau (1996). The trace element behaviors, therefore, also support that the Type-1B and Type-2 zircons were formed in subsolvus granitic melt with volatile-saturated at the late magmatic stage.

**IMPLICATIONS**

Accordingly, magmatic-hydrothermal evolution of granitic magma usually comes along with fractional crystallization and fluid exsolution, which could be recorded in zircon (Fig. 10). The formation of the altered zircon crystals (Type-1B) suggests that they formed during the magmatic-hydrothermal transition stage in the evolution of granitic magma. Such transitional stages are characterized by the coexistence of melt, crystal, and fluid phases (Burnham 1979). The incompatible elements (including HFSEs and volatiles) would concentrate in the alkaline and fluid-rich residual melt, from which subsolvus granite later crystallized. Exsolved magmatic fluids and other volatiles that are enriched in HFSEs and F could alter the previous minerals, including
zircon. Meanwhile, metamictization caused by self-irradiation would generate structural damage that would facilitate fluid-mineral interaction during the magmatic-hydrothermal transition. Therefore, the enhancing substitution of trace elements and volatile component in zircons could undoubtedly result in chemical lattice expansion, during the magmatic-hydrothermal evolution of granitic magma.

This study also shows that magmatic-hydrothermal evolution can be an efficient way to mobilize Zr from the magmatic to the hydrothermal system, even in ore-barren alkaline granite. Because HFSEs have high charge-to-ionic-radius ratios, they are generally incompatible during magmatic fractionation (Finlow-Bates and Stumpfl, 1981). There is increasing evidence that these elements are mobile in some cases and can be concentrated as a result of high degrees of fractional crystallization from evolved granitic and pegmatitic melts, especially in rare-metal mineralized alkaline-peralkaline system (Aja et al. 1995; Ayers et al. 2012; Bau and Dulski 1995; Rubin et al. 1993; Veksler et al. 2005). For example, the hypersolvus granite of the Strange Lake complex contains ca. 3000 ppm Zr on average, and ca. 500 ppm REE and Y, whereas the subsolvus granite has 3.25 wt% ZrO₂, 0.66 wt% Y₂O₃ and 1.30 wt% REE oxides (Salvi and Williams-Jones 2006), indicating highly remobilization of Zr, REE, and Y during magmatic-hydrothermal evolution. Similar cases are also reported in peralkaline granites from the Amis complex in Namibia (Schmitt et al. 2002) and from the Khadlzan-Buregtey in Mongolia (Kovalenko et al. 1995). In the Baerzhe pluton, the contents of ZrO₂ increases from < 0.5 wt% in the hypersolvus granite to 3 wt% in the subsolvus granite, and Nb₂O₅ from < 0.02 to 0.28 wt% and Ce₂O₃ from <
0.1 to 0.4 wt%, indicating that Zr, REE, and Nb are mainly precipitated in the late-stage subsolvus melt that was rich in H₂O, alkalis, and F (Yang et al. 2014). Mobility of HFSEs is also documented in ore-barren alkaline granitic system. For example, hafnium was documented sharply increase within zircon from the late-facies of the Suzhou granite (Wang et al. 1996). Similarly, high concentration of Th in zircon, from peralkaline granite in Eastern China, was also mobilized as thorite inclusion by hydrothermal alteration (Xie et al. 2005). In this study of the Xiangshan alkaline granite, the textures and compositions of the altered and late magmatic zircon types indicate that the mobility of Zr, Hf, U, Th, Y and REE, as well as volatiles, and can also be efficient during the magmatic-hydrothermal evolution of ore-barren alkaline A-type granites.

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Figure captions

FIGURE 1. (a) Simplified geological map of eastern China, showing major tectonic units (modified after Wu et al. 2005). (b) Simplified geological map of the Cretaceous Xiangshan complex, where the arfvedsonite granites are surrounded by biotite granites.

FIGURE 2. (a) \((Zr+Nb+Ce+Y)\) vs \((Na_2O+K_2O)/CaO\) diagram, showing the Xiangshan arfvedsonite granites are of A-type affinity. (b) \(Y/Nb\) vs \(Yb/Ta\) diagram for the Xiangshan arfvedsonite granites (according to Eby, 1992). Composition data are listed in Supplemental Data Table 1. OIB=oceanic island basalt; IAB=island arc basalt. Fields with dashed lines represent A1- and A2-type granites of Eby (1990).

FIGURE 3. Plan-polarized microphotographs, CL and BSE images of zircons from the Xiangshan arfvedsonite granites. (a) Microphotograph of interstitial Type-1A zircon between quartz and arfvedsonite. (b) Microphotograph of interstitial Type-1B zircon between quartz and K-feldspar. (c) Microphotograph of Type-2 zircon enclosed in graphic texture. (d) CL image of Type-1A zircon with oscillatory zoning. (e) CL image of Type-1B zircon with pores and inclusions, and with no oscillatory growth zones. (f) CL image of Type-2 zircon with slight oscillatory growth zones. (g) BSE image of Type-1A zircon with melt inclusions. (h) BSE image of Type-1B zircon with thorite and Fe-oxide. (i) Microphotograph of Type-2 zircon coexisted with fluid inclusions.
FIGURE 4. Type-1B zircon occurs as overgrowth on Type-1A zircon. (a) CL image. (b) BSE image. (c) Full-widths at half-maximum (FWHM) mapping by Raman spectrum. (d–i) Element mapping by EMPA show the distribution of Th, U, Hf, Y, P and Fe, respectively.

FIGURE 5. XRD patterns adopted in situ on single zircon crystals from the Xiangshan arfvedsonite granites, compared with the standard zircon (06-0266).

FIGURE 6. (a) Chondrite-normalized REE diagram for zircons from the Xiangshan arfvedsonite granites. (b) Primitive Mantle normalized trace elements diagram for zircons from the Xiangshan arfvedsonite granites. Chondrite and PM data are from Sun and McDonough (1989).

FIGURE 7. Variation diagrams of trace element contents for zircon from the Xiangshan pluton. (a) Zr+Hf (apfu) vs. Si (apfu) diagram, the dashed line show ideal occupation (Zr+Hf)/Si=1 (b) Hf (apfu) vs. Zr (apfu) diagram, apfu means atoms per formula units. (c) Th (ppm) vs. U (ppm) diagram. (d) REE+Y (mole) vs. P (mole) diagram, cation contents were calculated on the basis of one mole zircon.

FIGURE 8. Variation diagrams of SiO$_2$ vs. 1-Total contents, showing the increasing trace elements and volatiles contents of zircons from early- to late-granitic system.
The relative deviations of SiO$_2$ contents from 32.8 wt% are indicative of volatile contents.

**FIGURE 9.** Zircon-melt trace element partition coefficients as a function of ionic radius, showing the increasing of trace elements partitioning from early- to late-stage zircon. Data is taken from the average values of Type-1A zircon (a), Type-1B zircon (b), and Type-2 zircon (c) to whole-rock compositions (Table 2). The REE curves is showing least-squares fits of the Blundy and Wood (1994) theoretical structural strain model to the data.

**FIGURE 10.** A schematic drawing illustrates the formation of the three zircon types during the magmatic-hydrothermal evolution of the Xiangshan arfvedsonite granites. The temperature of solvus was assumed at ca. 725 °C at 100 Mpa. The critical point of the evolution curve of granitic melt with H$_2$O contents is referred from Thomas et al. (2006). The inset show morphological types of zircon observed in the Xiangshan arfvedsonite granites, according to Pupin (1980).
Table 1 Cell parameters of three types of zircon determined by XRD, compared with standard zircon (06-0266).

<table>
<thead>
<tr>
<th>Zircon types</th>
<th>a</th>
<th>c</th>
<th>V</th>
<th>c/a</th>
<th>Two theta (at ca. 27°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Type-1A</td>
<td>6.603(2)</td>
<td>5.971(4)</td>
<td>260.3</td>
<td>0.904</td>
<td>26.94</td>
</tr>
<tr>
<td>Type-1B</td>
<td>6.649(6)</td>
<td>6.020(2)</td>
<td>266.1</td>
<td>0.905</td>
<td>26.82</td>
</tr>
<tr>
<td>Type-2</td>
<td>6.677(7)</td>
<td>6.010(4)</td>
<td>267.9</td>
<td>0.900</td>
<td>26.65</td>
</tr>
<tr>
<td>Zircon (06-0266)</td>
<td>6.607</td>
<td>5.982</td>
<td>261.1</td>
<td>0.905</td>
<td>26.98</td>
</tr>
</tbody>
</table>

Notes: unit-cell parameters (a,c) in Å; unit-cell volume in Å³.

Table 2 Trace element partition coefficients of the three types of zircon to host melt (whole-rock composition) and the ionic radii.

<table>
<thead>
<tr>
<th>Elements</th>
<th>Type-1A/Melt</th>
<th>Type-1B/Melt</th>
<th>Type-2/Melt</th>
<th>Ionic radii (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P⁵⁺</td>
<td>2.65</td>
<td>21.6</td>
<td>51.4</td>
<td>0.520</td>
</tr>
<tr>
<td>Ti⁴⁺</td>
<td>0.005</td>
<td>0.046</td>
<td>1.50</td>
<td>0.745</td>
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<tr>
<td>Y³⁺</td>
<td>56.7</td>
<td>317</td>
<td>777</td>
<td>1.040</td>
</tr>
<tr>
<td>Nb⁵⁺</td>
<td>0.48</td>
<td>19.2</td>
<td>15.7</td>
<td>0.780</td>
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<tr>
<td>La³⁺</td>
<td>0.02</td>
<td>0.54</td>
<td>0.02</td>
<td>1.172</td>
</tr>
<tr>
<td>Ce³⁺</td>
<td>0.34</td>
<td>2.36</td>
<td>5.24</td>
<td>1.150</td>
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<tr>
<td>Pr³⁺</td>
<td>0.03</td>
<td>0.82</td>
<td>0.79</td>
<td>1.130</td>
</tr>
<tr>
<td>Nd³⁺</td>
<td>0.11</td>
<td>1.25</td>
<td>3.90</td>
<td>1.123</td>
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<tr>
<td>Sm³⁺</td>
<td>1.06</td>
<td>5.16</td>
<td>50.3</td>
<td>1.098</td>
</tr>
<tr>
<td>Eu³⁺</td>
<td>0.55</td>
<td>3.43</td>
<td>9.16</td>
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<tr>
<td>Gd³⁺</td>
<td>7.62</td>
<td>26.1</td>
<td>252</td>
<td>1.078</td>
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<tr>
<td>Tb³⁺</td>
<td>14.9</td>
<td>60.4</td>
<td>417</td>
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<tr>
<td>Dy³⁺</td>
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<td>129</td>
<td>602</td>
<td>1.052</td>
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<td>Ho³⁺</td>
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<td>253</td>
<td>771</td>
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<td>Er³⁺</td>
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<td>423</td>
<td>852</td>
<td>1.030</td>
</tr>
<tr>
<td>Tm³⁺</td>
<td>101</td>
<td>622</td>
<td>894</td>
<td>1.020</td>
</tr>
<tr>
<td>Yb³⁺</td>
<td>133</td>
<td>895</td>
<td>913</td>
<td>1.008</td>
</tr>
<tr>
<td>Lu³⁺</td>
<td>150</td>
<td>968</td>
<td>748</td>
<td>1.001</td>
</tr>
<tr>
<td>Hf⁴⁺</td>
<td>874</td>
<td>1534</td>
<td>1578</td>
<td>0.850</td>
</tr>
<tr>
<td>Ta⁵⁺</td>
<td>3.12</td>
<td>95.7</td>
<td>78.8</td>
<td>0.780</td>
</tr>
<tr>
<td>Th⁴⁺</td>
<td>12.5</td>
<td>664</td>
<td>551</td>
<td>1.080</td>
</tr>
<tr>
<td>U⁴⁺</td>
<td>109</td>
<td>2321</td>
<td>472</td>
<td>1.030</td>
</tr>
</tbody>
</table>
Figure 1

Cretaceous arfvedsonite granite
Cretaceous prophyric biotite granite
Ordovician limestone
Jurassic sandstone
Archean metamorphic diorite
Cambrian limestone
Quaternary

Fig. 1b

Sampling location
Figure 2

(a) Diagram showing the distribution of A-type granitoids based on the (Na$_2$O+K$_2$O)/CaO vs. Zr+Nb+Ce+Y (ppm) plot. The plot is divided into regions labeled FG, OTG, and A-type granitoids.

(b) Diagram showing the distribution of Yb/Ta vs. Y/Nb for different tectonic settings: IAB, A2, A1, and OIB.
Figure 3

- **Figure 3a**: Type-1A
- **Figure 3b**: Type-1B
- **Figure 3c**: Type-2
- **Figure 3d**: Qz
- **Figure 3e**: Fe-oxide
- **Figure 3f**: Thorite
- **Figure 3g**: Melt inclusion
- **Figure 3h**: Fluid inclusion
- **Figure 3i**: Type-2
Figure 4
Figure 5

[Graph showing X-ray diffraction patterns for types of zircon: Type-2, Type-1B, Type-1A, and Zircon(06-0266).]

- Two theta (deg) on the x-axis.
- Intensity on the y-axis.
- Peaks labeled for Type-2, Type-1B, Type-1A, and Zircon(06-0266).

Legend:
- Type-2 zircon
- Type-1B zircon
- Type-1A zircon
- Zircon(06-0266)
Figure 6

(a) Zircon/Primitive Mantle

(b) Zircon/Chondrite

Type-1A zircon
Type-1B zircon
Type-2 zircon
Figure 7

(a) 

(b) 

(c) 

(d) 

(Zr+Hf)/Si = 1

Hf/Zr = 0.01

Hf/Zr = 0.04

(REE+Y)/P = 1
Figure 8

The figure shows a scatter plot with data points representing the relationship between SiO$_2$ (wt.%) and 1-Total (wt.%). The plot includes a dashed line at 32.8% and a vertical arrow indicating an increasing trend of volatiles.
Figure 9

(a) Ionic radii (Å)

(b) Ionic radii (Å)

(c) Ionic radii (Å)
Figure 10

Evolution curve of alkaline granite melt

Type 1A

Type 1B

Type 2

Hypersolvus

Subsolvus

Critical

Evolution curve of alkaline granite melt

Temperature (°C)

H₂O (wt. %)

Al/(Na+K) (IndexA)