1 REVISION 1

2 **Chemical lattice expansion of natural zircon during the**

3 **magmatic-hydrothermal evolution of A-type granite**

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13 **ABSTRACT**

14 Although thermal lattice expansion is a well-documented nature of crystals,

15 including zircon and zircon-type minerals, chemical lattice expansion of natural

16 mineral is rarely reported. Here we report a comprehensive investigation on three

17 types of natural zircon that recorded the evolution of the granitic system in Xiangshan,

18 North China, and show expanding crystallographic parameters induced by chemical

19 incorporation instead of thermal expansion. Prismatic and oscillatory zoned zircon

20 grains (Type-1A), crystallized early in the granitic magma at high temperatures in a

21 volatile-undersaturated environment, have the smallest lattice parameters (a=6.603Å,

22 c=5.971Å). Prismatic and altered zircon grains (Type-1B), formed under

23   volatile-saturated conditions and in the presence of F-rich fluid with numerous thorite

24   and xenotime inclusions, have intermediate lattice parameters (a=6.649Å, c=6.020Å).

25   Pyramidal zircon grains (Type-2), formed in a subsolvus granite system at relatively

26   low temperatures and coexisted with fluid inclusions, have the biggest lattice

27   parameters (a=6.677Å, c=6.010Å). Trace element, including Hf, Th, Ti, Y and REE,

28   and volatiles contents increase in the structure of zircons from the early- to

29   late-magmatic origin, which is consistent with the expansion of the lattice parameters.

30   The occurrence of the three zircon types in the Xiangshan arfvedsonite granites is

31   interpreted to reflect the progressive fractionation of granitic melt from hypersolvus to

32   subsolvus conditions. Therefore, we conclude that the lattice expansion of zircon in

33   this study results from chemical incorporation of trace element and volatile

34   components during the magmatic to hydrothermal evolution of granitic magma.

35   Besides, the textural and compositional evolution of zircon can be used as efficient

36   indices for the fractionation and evolution of A-type granitic system.

37   **Keywords:** Chemical lattice expansion, zircon, fractionation crystallization,

38   magmatic-hydrothermal evolution, A-type granite

39

40   **INTRODUCTION**

41   Zircon is a common accessory mineral in granitic rocks. It is chemically resistant,

42   relatively insoluble and refractory, and can withstand weathering and recycling, as

43   well as high temperature metamorphism and anataxis (El-Bialy and Ali 2013). It is

44   widely accepted that zircon can provide reliable and robust estimates of age,

45 compositions of coexisting minerals and melts, and constraints on the petrogenesis of

46 host rocks (Valley 2003). In spite of its apparently simple chemical composition

47 ($ZrSiO_4$), zircon is able to accept substantial amounts of other minor and trace

48 elements into its crystal lattice (e.g., Hf, Th, U, Ti, Nb, Ta, P, Y and REE) (Breiter et

49 al. 2014). Zircon crystals that are not affected by intense metamictization could

50 provide information about the chemical composition of the melt from which they

51 crystallized. In contrast, the metamict crystals may accumulate substantial amounts of

52 non-formula elements, re-equilibrated with the hydrothermal and low-temperature

53 fluids (Geisler et al. 2007; Yang et al. 2014).

54   In granitic systems, zircon is generally considered to form early in the

55 crystallization history (Valley 2003). However, in some A-type granites it can

56 crystallize during the whole process of magmatic crystallization, with significant

57 distinction in both texture and composition (Belousova et al. 2006; Breiter and Škoda

58 2012; Pupin 1980). Although geologically complicated, the behavior of trace elements

59 in zircon depends on physical-chemical conditions and partition coefficients between

60 zircon and melt (Belousova et al. 2006). Presently, there are several speculations have

61 been proposed regarding zircon texture and composition, which include that zircon

62 can record the processes of (1) magmatic and hydrothermal crystallization (Van

63 Lichtervelde et al. 2009; Yang et al. 2013), (2) hydrothermal alteration (Zheng et al.

64 2007), (3) country-rock assimilation, (4) magma mixing (Griffin et al. 2002), or even

65 (5) tectonic setting (Grimes et al. 2007, 2009).

66   This study reports analyses of textures and compositions of three types of zircon

67 from an A-type granite in north China. The purposes of this article are (1) to

68 determine the variation of zircon in both structure and composition that may influence

69 the lattice expansion, and (2) to test the speculation that zircon could record the

70 processes of magmatic and hydrothermal evolution of the host granite. All samples

71 come from the Xiangshan arfvedsonite-bearing granite. Zircon structures were

72 analyzed by X-ray diffraction (XRD), cathodoluminescence (CL) and Raman

73 spectroscopy. Major and trace element compositions of zircon were measured by

74 EMPA and LA-ICPMS.

GEOLOGICAL BACKGROUND

76 The Xiangshan complex crops out over 217 km^2 in the NNE-trending Yanshan

77 Mountains (northeastern Hebei province), on the northern margin of the North China

78 Craton (NCC) (Fig. 1a). It intruded into the Lower Sinian migmatite, with limestones

79 of the Cambrian Fushanjun Formation and the Jurassic Mentougou Formation in the

80 northeast. It consists of medium-grained arfvedsonite granite in the center and

81 porphyritic biotite granite on the margins (Fig.1b). The arfvedsonite granites mainly

82 consist of quartz (25–30 vol%), perthite (45–55 vol%), K-feldspar (10–15 vol%),

83 plagioclase (5 vol%) and minor arfvedsonite (5 vol%). Accessory minerals mainly

84 consist of zircon, magnetite, sphere, fluorite and rutile. The quartz is subhedral to

85 euhedral and 1–3 mm in size. The perthite is commonly subhedral and 1–4 mm in size,

86 with perthitic texture. The K-feldspar is also commonly subhedral and 2–4 mm in size.

87 The arfvedsonite is blue to dark blue in color, euhedral to subhedral with distinct

88 pleochroism. Some arfvedsonite grains occur as inclusions within quartz or perthite,

4

89   implying they crystallized earlier than quartz and perthite. The other arfvedsonite is

90   intergranular, indicating it crystalized simultaneously with or later than quartz and

91   perthite. Graphic intergrowths of quartz and K-feldspar occur as vermicular to

92   cuneiform patterns in the arfvedsonite granites in margin of the central part. In

93   contrast, the biotite granite on the marginal of the complex is porphyritic-like, with

94   15–30 vol% phenocrysts and 70–80 vol% groundmass. The phenocrysts consist of

95   euhedral quartz (0.1–0.2 mm in size), subhedral plagioclase (0.2–1.5 mm in size) and

96   biotite. The groundmass consist of the same phases as the phenocrysts. Accessory

97   minerals are mainly zircon and magnetite. This study mainly focuses on zircon in

98   arfvedsonite granite from the central part of the Xiangshan complex.

99   The occurrence of alkali-feldspar and sodic-amphibole (arfvedsonite) in the

100   arfvedsonite granites show the affinity of A-type granite (Yang et al., 2008), which is

101   characterized by high alkalis and iron-rich mafic mineralogy (Frost and Frost 2010).

102   According to the A-type granite division of Eby (1990, 1992) whole-rock

103   compositions (Supplemental Data Table 1), the Xiangshan arfvedsonite granites

104   samples plot in the A_1 subgroup, compatible with an intraplate setting (Figs. 2a and

105   2b).

ANALYTICAL METHODS

107   Zircon grains were separated using conventional density and magnetic separation

108   techniques, and then handpicked under a binocular microscope. Representative zircon

109   grains were set in epoxy mounts which were then polished to nearly half section to

110   expose the internal structures. The crystals were documented with transmitted and

111   reflected light micrographs as well as by CL images to reveal their external and

112   internal textures.

113   Single crystal micro-XRD analyses were conducted using a Rigaku D/max Rapis

114   IIR micro-XRD system at the Central South University, Changsha, China. All

115   analyses were carried out with a beam diameter of ~100 μm under 40 kV and 250 mA

116   (Cu$K\alpha$) with exposures of 20 minutes.

117   Laser Raman spectra of zircon crystals were collected using the HORIBA XploRA

118   Plus Laser Raman micro-spectroscope at the Key Laboratory of Mineralogy and

119   Metallogeny, Chinese Academy of Sciences (CAS), Guangzhou, China. An Ar ion

120   laser, operating at 10mW was used to produce the excitation wavelength of 532 nm.

121   The beam was coupled with a grating of 1200 grooves per mm. The scanning range of

122   the spectra was set between 100 and 1500 cm^{-1} with an accumulation time of 8 s for

123   each scan.

124   Major element compositions of zircon grains and host inclusions were analyzed

125   using a JEOL JXA 8230 electron microprobe (EMPA) at the Key Laboratory of

126   Mineralogy and Metallogeny, Guangzhou Institute of Geochemistry, CAS,

127   Guangzhou, China. The operating conditions were as follows: 15 kV accelerating

128   voltage, 20 nA beam current and 1 μm beam diameter. Zr and Si were analyzed for

129   20s on peak and 10s on background whereas Fe, P, Ti, U, Y, Hf and Th were analyzed

130   for 40s on peak and 20s on background. Standards used for analyses of the zircon

131   samples include zircon for Zr, Si, and Hf, magnetite for Fe, rutile for Ti, monazite for

132   U, Y and Th and apatite for P. ZAF calibration procedures were used for data

133   correction.

134   Trace element analyses of the zircon grains was conducted with an Agilent 7500a

135   ICP-MS coupled with a Resonetics RESOlution M-50 193nm laser-ablation system at

136   Key Laboratory of Mineralogy and Metallogeny, CAS. More detailed analytical

137   procedures were described by Li et al. (2012) and Tu et al. (2011). All analyses were

138   carried out with a beam diameter of 31 μm and a repetition rate of 10Hz with an

139   energy of 80mJ. Helium was used as the carrier gas. NIST SRM610 and TEMORA2

140   (TEM) were used as external standards (Black et al. 2004; Pearce et al. 1997), and

141   ^{29}Si as an internal standard (Anczkiewicz et al. 2001). All analysis spots were

142   carefully selected to avoid mineral and melt inclusions and cracks in zircons. Only

143   smooth LA-ICPMS signals were chosen.

RESULTS

Zircon morphology and textures

146   Zircons in the Xiangshan arfvedsonite granites can be morphologically classified

147   into prismatic (Type-1) and pyramidal (Type-2) types. Moreover, the prismatic zircon

148   grains can be further subdivided into two subtypes, bright and zoned zircon (Type-1A)

149   and murky and spongy zircon (Type-1B), according to their internal structures.

150   Type-1A zircons commonly intergrowth with quartz, K-feldspar and arfvedsonite,

151   or enclosed in arfvedsonite (Fig. 3a). They are euhedral prismatic crystals 80–120 μm

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152   in length with c/a ratios of 2:1 to 3:1. They are transparent in transmitted light, display

153   multiple oscillatory growth zones in CL images but are homogeneous under BSE,

154   consistent with zircon of magmatic origin (Fig. 3d). They have well-developed {101}

155   pyramids and {100} and {110} prisms, similar to typical morphologies of high

156   temperature zircon in alkaline magma (Pupin 1980). Inclusions in the zircon grains

157   commonly consist of melt and/or crystallized minerals such as apatite (Fig. 3g).

158   Type-1B zircons are usually intergrowth with quartz, K-feldspar and arfvedsonite

159   (Fig. 3b), or enclosed in quartz and K-feldspar, with apparent radiohalo. These zircon

160   crystals are euhedral prismatic crystals 100–200 μm in length with c/a ratios of 2:1 to

161   3:1. They are cloudy and redbrown in transmitted light, with no oscillatory growth

162   zones in CL images (Fig. 3e). They have well-developed {101} pyramids and {100}

163   and/or {110} prisms, similar to the typical morphologies of high temperature zircons

164   (Pupin, 1980). Inclusions in the zircons crystals commonly consist of melt and/or

165   crystallized minerals such as apatite, thorite, Fe-oxide and xenotime (Fig. 3h).

166   Sometimes, the murky Type-1B zircon can also be found as overgrowths of Type-1A

167   zircon crystals (Figs. 4a and 4b).

168   Type-2 zircons are usually enclosed in quartz, K-feldspar or graphic textured

169   occurrences of the two (Fig. 3c). Halite-bearing fluid inclusions can be observed in

170   the host quartz coexist with the Type-2 zircon (Fig. 3i). The Type-2 zircon grains are

171   dipyramidal with lengths of 100–280 μm. They are cloudy and red-brown in

172   transmitted light, and have a transparency between Type-1A and Type-1B zircons.

173   They display slight oscillatory growth zones in CL images (Fig. 3f) with rare

174   inclusions. They have well-developed {111} crystal faces with sporadically

175   less-developed {110} faces.

176   **XRD patterns**

177   The XRD pattern of Type-1A zircon crystals have cell parameters of a=6.603(2)

178   Å and c=5.971(4) Å identical to the standard zircon (06-0266, a=6.607 Å, c=5.982 Å)

179   (Table 1) (Robinson et al. 1971). The strong intensity, small cell parameters, along

180   with the sharp two-theta of {220} peak of full-widths at half-maximum (FWHM) of

181   0.174° (Fig. 5), indicating that they are well-crystallized and of magmatic origin

182   (Crepaldi et al. 2003).The cell parameters of the Type-1B zircon are a=6.649(6) Å and

183   c=6.020(2) Å which are higher than both the Type-1A zircon and the standard zircon.

184   The shifting of {220} peak position to slightly lower two-theta and a remarkable

185   reduction in intensity and broadening of the peak (FWHM=0.635°) suggest that the

186   Type-1B zircon grains have low crystallinity (Fig. 5). The cell parameters of the

187   Type-2 zircon are a=6.677(7) Å and c=6.010(4) Å. The {220} peak position shifts to

188   lower two-theta than the other two types of zircon with low peak intensities between

189   the other two types of zircon. The FWHM of the Type-2 zircon is 0.172° which is

190   similar to that of the Type-1A zircon (Fig. 5).

191   **Zircon compositions**

192   Major and trace element compositions of the zircons are listed in Supplemental

193   Data Table 2and Supplemental Data Table 3, respectively. Type-1A zircons have 31.6–

194   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_2O_3

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195   (mostly in the range of 0.03–1.00 wt%). Total REE contents vary from 855 to 2902

196   ppm with LREE/HREE ratios of 0.03 to 0.05. They display positive Ce anomalies and

197   negative Eu anomalies with Ce/Ce* and Eu/Eu* ratios ranging from 9.50–53.7 and

198   0.008–0.05, respectively (Fig. 6a). They have La and Pr concentrations ranging from

199   0.08 to 3.15 ppm, 0.12 to 1.05 ppm, respectively. Type-1A zircons have relatively low

200   contents of Y (1274–4652 ppm), Th (51.6–465 ppm) and U (96.6–693 ppm), with

201   Th/U ratios ranging from 0.39–0.67 (Fig. 6b).

202   Type-1B zircons have 30.8–32.6 wt% SiO_2, 59.5–65.9 wt% ZrO_2, 1.29–4.34 wt%

203   HfO_2 and 0.05–2.36 wt% Y_2O_3 (mostly in the range of 1.00–2.36 wt%). Total REE

204   contents vary from 4,240 to 16,057 ppm with LREE/HREE ratios of 0.03 to 0.11.

205   They display positive Ce anomalies and negative Eu anomalies with Ce/Ce*and

206   Eu/Eu* ratios ranging from 1.31–43.0 and 0.009–0.07, respectively (Fig. 6a).

207   Compared to Type-1A zircons, Type-1B zircons have much higher contents of Y

208   (5178–27020 ppm), Th (2308–27524 ppm) and U (3099–11450 ppm) (Figs. 4d–e),

209   with Th/U ratios ranging from 0.59–2.42. Notably, they also have much higher La, Pr,

210   Hf, Y, P, Nb and Ta concentrations than the Type-1A zircons (Figs. 4f–h and 6b).

211   Type-2 zircons have 30.2–32.3 wt% SiO_2, 53.3–61.4 wt% ZrO_2, 1.33–3.08 wt%

212   HfO_2 and 1.07–6.29 wt% Y_2O_3. They have the highest total REE contents varying

213   from 14952 to 24139 ppm with LREE/HREE ratios of 0.05 to 0.11. They display

214   obviously positive Ce anomalies and negative Eu anomalies with Ce/Ce*and Eu/Eu*

215   ratios ranging from 24.0–117 and 0.007–0.01, respectively (Fig. 6a). They have La, Pr

216   concentrations ranging from 0.45 to 3.25 ppm, 8.01 to 17.3 ppm, respectively.

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217   Compared to Type-1A and Type-1B zircons, Type-2 zircons have relatively high

218   contents of Y (27347–42189 ppm), Th (3935–17265 ppm) but moderate U (616–4982

219   ppm) contents, with highest Th/U ratios ranging from 2.46–12.9. They also have

220   much higher Hf, Y, P, Nb, Ta contents than Type-1A zircon grains (Fig. 6b).

221   <div align="center">**DISCUSSION**</div>

222   **Origin of the three types of zircon**

223   The different morphology, texture and composition of the three zircon types in the

224   Xiangshan arfvedsonite granites is interpreted to indicate that they formed under

225   different physical and chemical conditions during the magmatic-hydrothermal

226   evolution of the intrusion. In typical I- and S-type granites, zircon is one of the first

227   crystallizing minerals (Belousova et al. 2006; Breiter and Škoda 2012), however, in

228   some A-type granites it can crystallize throughout the fractionation process (Breiter

229   and Škoda 2012), consistent with what is seen in the zircons from the Xiangshan

230   arfvedsonite granites. The texture and composition of zircon can reflect the evolution

231   process of magma and provide information to the role played by volatiles (Erdmann et

232   al. 2013).

233   Type-1A zircons show magmatic textural and compositional features (Pupin 1980)

234   particularly the oscillatory zoning. In addition, the well-developed {101} pyramids

235   and {100} prisms, as well as the occurrence of melt and apatite inclusions, indicate

236   that they crystallized from high temperature alkaline magma (Pupin 1980).

237   Furthermore, the low Th, U and Hf concentrations and high ZrO_2/HfO_2 ratios (Figs.

<div align="center">11</div>

238   7a–c) indicate they crystallized from a volatile-undersaturated magma (Erdmann et al.

239   2013). Therefore, the Type-1A zircons are most likely primary magmatic zircon that

240   crystallized early in the evolution of the granitic magma.

241   The presence of Type-1B zircon overgrowths on some Type 1A zircons indicates

242   they crystallized later in the evolution of the magma (Figs. 5a–b). They have higher

243   FWHMs of Raman and XRD than Type-1A zircon crystals (Figs. 5c and 6), indicating

244   lower crystallinities. The Type-1B zircons show altered textures and exotic

245   composition and well-developed {101} pyramids and {100} prisms, but larger grain

246   size, higher Th, U and HfO_2 concentrations, lower ZrO_2/HfO_2 (Figs. 7a–c), and no

247   oscillatory growth zones compared to Type-1A. The porous and altered features are

248   similar to those of the zircon from evolved granite plutons at Melville Peninsula in

249   northern Canada which were interpreted to be from volatile-saturated magmas

250   (Erdmann et al. 2013). In addition, thorite and xenotime, which commonly form at the

251   late stage of the magmatic evolution, can be observed as inclusions in the Type-1B

252   zircons. Combined these features suggests that the Type-1B zircons crystallized from

253   a relatively evolved magma and were subsequently altered in a volatile-saturated

254   magma.

255   The Type-2 zircons show morphology characteristic of low-temperature and

256   fluid-rich magmas (Pupin 1980). The well-developed {111} crystal faces with

257   sporadically less-developed {110} faces are similar to synthetic, flux-grown zircon

258   crystals (Burakov et al. 2002). In addition, some Type-2 zircon crystals are

259   intergrowth with quartz and K-feldspar, which would have formed under subsolvus

260   condition. Formation of myrmekitic texture involve a series of short pluses of

261   infiltration of an aqueous fluid at about 500 °C during the subsolvus evolution of the

262   granite (Abartet al. 2014). The coexistence of halite-bearing fluid inclusions with

263   Type-2 zircon crystals is consistent with a late magmatic or hydrothermal origin

264   (Schaltegger 2007). So we suggest that the Type-2 zircons formed under subsolvus

265   conditions with volatile over-saturated.

266   **Lattice expansion of zircon induced by chemical incorporation**

267   Standard zircon has tetragonal symmetry with a=6.607 Å, c=5.982 Å, Z=4 and

268   belongs to the space group *I4$_1$/amd* (Robinson et al. 1971). Such crystal structure is

269   documented that can be expanded by thermal heating, metamictization and chemical

270   incorporation (Robinson et al. 1971; Patwe et al. 2009). In this study, natural zircon

271   lattice show expansion from the early- to late-stage zircon types that formed during

272   the cooling and fractionation of the Xiangshan granitic magma, instead of thermal

273   heating. Meanwhile, the XRD and Raman data also lend little support for remarkable

274   influence of metamictization. The altered Type-1B zircon shows the most metamict

275   features among the three zircon types, but the crystallographic parameters is not the

276   biggest type (Fig. 5). Therefore, chemical incorporation in zircon lattice should be the

277   mostly plausible cause. Since chemical compositions of zircon from igneous rocks are

278   controlled by the behavior of trace element and partition coefficient between zircon

279   and melt (Belousova et al. 2006), the remarkable increasing of trace element

280   substitution and volatile contents in zircon lattice of this study depend on

281   physical-chemical conditions of the evolving granitic system.

13

282   **Substitution increases from early to late zircon lattice.**

283   In granitic rocks, non-formula elements, such as Hf, Th, U, REE and Y can enter

284   into the zircon lattice by simple or coupled substitution mechanisms (Hanchar et al.

285   2001; Hoskin and Schaltegger 2003). IV charge (+4) cations, such as Hf^{4+}, Th^{4+}, U^{4+}

286   and Ti^{4+}, can substitute for Zr^{4+}, whereas other charge cations, such as Y^{3+}, REE^{3+},

287   Nb^{5+}, Ta^{5+}, P^{5+} and Fe^{2+}, can undergo coupled substitution for Zr^{4+} and Si^{4+}. In this

288   study, the substitution contents of such non-formula elements are much more favored

289   in the late-stage zircon formed during the magmatic-hydrothermal evolution of

290   alkaline granite (Table 2).

291   IV charge non-formula cations usually occur as major element in zircon. For

292   example, Hf^{4+} and Zr^{4+} have identical charge (+4) and similar cation radius (0.83 Å

293   for Hf^{4+} and 0.84 Å for Zr^{4+}), so they can substitute for each other and form complete

294   zircon-hafnon solid solution series. It was confirmed by the study of Wang et al.

295   (1996), who found an extreme Hf enrichment (up to 34.8 wt% HfO_2) in zircon from

296   an A-type granite in Suzhou, China. Besides, Th^{4+} and U^{4+} have the same charge (IV)

297   but larger cation radius (1.05 Å for U^{4+} and 1.00 Å for Th^{4+}), and can also substitute

298   Zr^{4+} in zircon (Hoskin and Hanchar 2003). For example, the Th and U contents in

299   zircons from the A-type granite in the Pitinga tin deposit, Brazil, can reach 6000 ppm

300   and 2900 ppm, respectively, and the ThO_2 and UO_2 contents in zircons from the

301   Beauvoir S-type granite, France can reach 0.35 wt% and 7.6 wt%, respectively

302   (Cheng et al. 1992). In this study, the altered magmatic zircon (Type-1B) and late

303   zircon (Type-2) from the Xiangshan arfvedsonite granite have significantly higher

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304   contents of Hf, U and Th than the early zircon (Type-1A) (Figs. 7a–c), indicating that

305   Hf, U and Th can be concentrated in both residual melt and late zircon during the

306   fractional crystallization. It is consistent with the well-documented zircon–hafnon

307   solid solution that natural zircon may contain high contents of Hf, and changes into

308   hafnian zircon or even hafnon in some high fractionated granite systems (Wang et al.

309   1996; Yin et al. 2013). The isomorphous substitutions of Th^{4+} and U^{4+} for Zr^{4+} lead to

310   the expansion of unti-cell, which is reflected in the low-degree shift of XRD peaks of

311   the Type-1B and Type-2 zircons (Fig. 5). The extensive substitutions of Th^{4+} and U^{4+}

312   resulted in the metamictization of the Type-1B zircon which reacted with magmatic

313   exsolved fluids. It seems likely that the substitution of IV charge cation in zircon

314   lattice can become easier in the late magmatic stage.

315   Alternatively, the other charge cations, REE^{3+} and Y^{3+} in particular, usually occur

316   as incompatible trace elements in zircon. REE-bearing zircon commonly contains P,

317   and owing to crystal chemical resemblance between Y^{3+} and heavy REE^{3+},

318   substitution of Zr^{4+} by REE^{3+} or Y^{3+} and Si^{4+} by P^{5+} in zircon is commonly explained

319   by the coupled xenotime-type substitution to maintain charge balance

320    $[(Y,REEs)^{3+}+P^{5+}\rightarrow Zr^{4+}+Si^{4+}]$. If xenotime substitution is the sole mechanism by which

321   charge balance is maintained in zircon crystals that have undergone REE-substitution

322   (Hoskin 2003), the atomic ratio (REE+Y)/P should approach 1. As the majority of

323   (REE+Y)/P ratios in zircons from the Xiangshan arfvedsonite granites are higher than

324   1 (Fig. 7d), this suggests a more complex charge-balance mechanism (Cavosie et al.

325   2006; Finch and Hanchar 2003). Because the Type-1B and Type-2 zircons have

326   relatively high Nb and Ta contents and low total weight of EMPA data, the

327   substitution $(Y,REEs)^{3+}+(Nb,Ta)^{5+}\rightarrow2Zr^{4+}$ and $(ZrO)^{2+}\rightarrow(YOH)^{2+}$ or $(ZrO)^{2+}\rightarrow(YF)^{2+}$

328   proposed by Es'kova (1959) may also play a role. Nevertheless, the obvious increase

329   of REE and Y concentrations from the early to late zircon structure suggests that the

330   coupled substitution in the zircon lattice increases from early to late magmatic stage.

331   **Volatile becomes saturated.**

332   The deficit in the total weight of EMPA is commonly ascribed to the presence of

333   the OH^- and F^- in the zircon's structure or molecular H_2O in the amorphous domains

334   of the metamict zircon structure (Breiter and Škoda 2012). Previous authors predicted

335   that hydration takes place only in tetrahedral sites (SiO_4) without affecting the

336   occupancy of the Zr position (Hoskin 2003). For example, up to 8.8 wt%H_2O was

337   found in Archaean zircon from Jack Hills, Australia (Nasdala et al. 2009), and as

338   much as 0.8 apfu $(OH,F)_4$ replacing the (SiO_4) group was found in synthetized zircon

339   (Caruba et al. 1985). In this study, the deficits of the SiO_2 contents (32.8-SiO_2 wt%)

340   of Type-1B (0.2–2.0 wt%) and Type-2 (0.5–2.6 wt%), which are much higher than

341   that of Type-1A zircon (0–1.2 wt%), are indicative of their increasing of volatiles

342   substitution. Giving that the F and Cl contents nearly below detection limit

343   (Supplemental Data Tble2), the dominate volatile is probably H_2O or OH^- in the three

344   types of zircon. Meanwhile, the significant deficits of the total weight (1-Total) of

345   Type-1B (1.1–5.3 wt%) and Type-2 (1.6–6.7 wt%) are indicative of their increasing

346   of trace elements as well as volatiles (Fig. 8).

347   The logarithms of REE partition coefficients between mineral and melt against

348   ionic radii show a simple parabolic relationship (Onuma et al. 1968), which is

349   consistent with the crystal structural strain modelling (Blundy and Wood 1994). Most

350   REEs of Type-1A and Type-2 zircon grains fall on the parabola, except for Ce and Eu

351   (Figs. 9a and 9c), which are largely affected by their valences. On the contrary, the

352   Type-1B zircon grains have more elements (e.g., Ce, Eu, La, Pr and Nd) deviating

353   from the predicted parabolic behavior (Fig. 9b), suggesting hydrothermal alteration

354   plays an essential role in the enrichment of La, Pr and Nd. Such

355   non-charge-and-radius-controlled behaviors of REE distribution has been attributed to

356   the transition between pure silicate melts and hydrothermal fluids by Bau (1996). The

357   trace element behaviors, therefore, also support that the Type-1B and Type-2 zircons

358   were formed in subsolvus granitic melt with volatile-saturated at the late magmatic

359   stage.

360   **IMPLICATIONS**

361   Accordingly, magmatic-hydrothermal evolution of granitic magma usually comes

362   along with fractional crystallization and fluid exsolution, which could be recorded in

363   zircon (Fig. 10). The formation of the altered zircon crystals (Type-1B) suggests that

364   they formed during the magmatic-hydrothermal transition stage in the evolution of

365   granitic magma. Such transitional stages are characterized by the coexistence of melt,

366   crystal, and fluid phases (Burnham 1979). The incompatible elements (including

367   HFSEs and volatiles) would concentrate in the alkaline and fluid-rich residual melt,

368   from which subsolvus granite later crystallized. Exsolved magmatic fluids and other

369   volatiles that are enriched in HFSEs and F could alter the previous minerals, including

17

370   zircon. Meanwhile, metamictization caused by self-irradiation would generate

371   structural damage that would facilitate fluid-mineral interaction during the

372   magmatic-hydrothermal transition. Therefore, the enhancing substitution of trace

373   elements and volatile component in zircons could undoubtedly result in chemical

374   lattice expansion, during the magmatic-hydrothermal evolution of granitic magma.

375   This study also shows that magmatic-hydrothermal evolution can be an efficient

376   way to mobilize Zr from the magmatic to the hydrothermal system, even in ore-barren

377   alkaline granite. Because HFSEs have high charge-to-ionic-radius ratios, they are

378   generally incompatible during magmatic fractionation (Finlow-Bates and Stumpfl,

379   1981). There is increasing evidence that these elements are mobile in some cases and

380   can be concentrated as a result of high degrees of fractional crystallization from

381   evolved granitic and pegmatitic melts, especially in rare-metal mineralized

382   alkaline-peralkaline system (Aja et al. 1995; Ayers et al. 2012; Bau and Dulski 1995;

383   Rubin et al. 1993; Veksler et al. 2005). For example, the hypersolvus granite of the

384   Strange Lake complex contains ca. 3000 ppm Zr on average, and ca. 500 ppm REE

385   and Y, whereas the subsolvus granite has 3.25 wt% ZrO_2, 0.66 wt% Y_2O_3 and 1.30 wt%

386   REE oxides (Salvi and Williams-Jones 2006), indicating highly remobilization of Zr,

387   REE, and Y during magmatic-hydrothermal evolution. Similar cases are also reported

388   in peralkaline granites from the Amis complex in Namibia (Schmitt et al. 2002) and

389   from the Khadlzan-Buregtey in Mongolia (Kovalenko et al. 1995). In the Baerzhe

390   pluton, the contents of ZrO_2 increases from < 0.5 wt% in the hypersolvus granite to 3

391   wt% in the subsolvus granite, and Nb_2O_5 from < 0.02 to 0.28 wt% and Ce_2O_3 from <

392 0.1 to 0.4 wt%, indicating that Zr, REE, and Nb are mainly precipitated in the

393 late-stage subsolvus melt that was rich in H_2O, alkalis, and F (Yang et al. 2014).

394 Mobility of HFSEs is also documented in ore-barren alkaline granitic system. For

395 example, hafnium was documented sharply increase within zircon from the late-facies

396 of the Suzhou granite (Wang et al. 1996). Similarly, high concentration of Th in zircon,

397 from peralkaline granite in Eastern China, was also mobilized as thorite inclusion by

398 hydrothermal alteration (Xie et al. 2005). In this study of the Xiangshan alkaline

399 granite, the textures and compositions of the altered and late magmatic zircon types

400 indicate that the mobility of Zr, Hf, U, Th, Y and REE, as well as volatiles, and can

401 also be efficient during the magmatic-hydrothermal evolution of ore-barren alkaline

402 A-type granites.

403

411

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591

592

593   **Figure captions**

594   **FIGURE 1.** (a) Simplified geological map of eastern China, showing major tectonic

595   units (modified after Wu et al. 2005). (b) Simplified geological map of the Cretaceous

596   Xiangshan complex, where the arfvedsonite granites are surrounded by biotite

597   granites.

598

599   **FIGURE 2.** (a) $(Zr+Nb+Ce+Y)$ vs $(Na_2O+K_2O)/CaO$ diagram, showing the

600   Xiangshan arfvedsonite granites are of A-type affinity. (b) Y/Nb vs Yb/Ta diagram for

601   the Xiangshan arfvedsonite granites (according to Eby, 1992). Composition data are

602   listed in Supplemental Data Table 1. OIB=oceanic island basalt; IAB=island arc basalt.

603   Fields with dashed lines represent A_1- and A_2-type granites of Eby (1990).

604

605   **FIGURE 3.** Plan-polarized microphotographs, CL and BSE images of zircons from

606   the Xiangshan arfvedsonite granites. (a) Microphotograph of interstitial Type-1A

607   zircon between quartz and arfvedsonite. (b) Microphotograph of interstitial Type-1B

608   zircon between quartz and K-feldspar. (c) Microphotograph of Type-2 zircon enclosed

609   in graphic texture. (d) CL image of Type-1A zircon with oscillatory zoning. (e) CL

610   image of Type-1B zircon with pores and inclusions, and with no oscillatory growth

611   zones. (f) CL image of Type-2 zircon with slight oscillatory growth zones. (g) BSE

612   image of Type-1A zircon with melt inclusions. (h) BSE image of Type-1B zircon with

613   thorite and Fe-oxide. (i) Microphotograph of Type-2 zircon coexisted with fluid

614   inclusions.

29

615

616   **FIGURE 4.** Type-1B zircon occurs as overgrowth on Type-1A zircon. (a) CL image.

617   (b) BSE image. (c) Full-widths at half-maximum (FWHM) mapping by Raman

618   spectrum. (d–i) Element mapping by EMPA show the distribution of Th, U, Hf, Y, P

619   and Fe, respectively.

620

621   **FIGURE 5.** XRD patterns adopted in situ on single zircon crystals from the

622   Xiangshan arfvedsonite granites, compared with the standard zircon (06-0266).

623

624   **FIGURE 6.** (a) Chondrite-normalized REE diagram for zircons from the Xiangshan

625   arfvedsonite granites. (b) Primitive Mantle normalized trace elements diagram for

626   zircons from the Xiangshan arfvedsonite granites. Chondrite and PM data are from

627   Sun and McDonough (1989).

628

629   **FIGURE 7.** Variation diagrams of trace element contents for zircon from the

630   Xiangshan pluton. (a) Zr+Hf (apfu) vs. Si (apfu) diagram, the dashed line show ideal

631   occupation (Zr+Hf)/Si=1 (b) Hf (apfu) vs. Zr (apfu) diagram, apfu means atoms per

632   formula units. (c) Th (ppm) vs. U (ppm) diagram. (d) REE+Y (mole) vs. P (mole)

633   diagram, cation contents were calculated on the basis of one mole zircon.

634

635   **FIGURE 8.** Variation diagrams of SiO_2 vs. 1-Total contents, showing the increasing

636   trace elements and volatiles contents of zircons from early- to late-granitic system.

637   The relative deviations of SiO_2 contents from 32.8 wt% are indicative of volatile

638   contents.

639

640   **FIGURE 9.** Zircon-melt trace element partition coefficients as a function of ionic

641   radius, showing the increasing of trace elements partitioning from early- to late-stage

642   zircon. Data is taken from the average values of Type-1A zircon (a), Type-1B zircon

643   (b), and Type-2 zircon (c) to whole-rock compositions (Table 2). The REE curves is

644   showing least-squares fits of the Blundy and Wood (1994) theoretical structural strain

645   model to the data.

646

647   **FIGURE 10.** A schematic drawing illustrates the formation of the three zircon types

648   during the magmatic-hydrothermal evolution of the Xiangshan arfvedsonite granites.

649   The temperature of solvus was assumed at ca. 725 °C at 100 Mpa. The critical point

650   of the evolution curve of granitic melt with H_2O contents is referred from Thomas et

651   al. (2006). The inset show morphological types of zircon observed in the Xiangshan

652   arfvedsonite granites, according to Pupin (1980).

653

654   Table 1 Cell parameters of three types of zircon determined by XRD, compared with

655   standard zircon (06-0266).

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

656   Notes: unit-cell parameters (a,c) in Å; unit-cell volume in Å^3.

657

658

659   Table 2 Trace element partition coefficients of the three types of zircon to host melt

660   (whole-rock composition) and the ionic radii.

Elements	Type-1A/Melt	Type-1B/Melt	Type-2/Melt	Ionic radii (Å)
P^{5+}	2.65	21.6	51.4	0.520
Ti^{4+}	0.005	0.046	1.50	0.745
Y^{3+}	56.7	317	777	1.040
Nb^{5+}	0.48	19.2	15.7	0.780
La^{3+}	0.02	0.54	0.02	1.172
Ce^{3+}	0.34	2.36	5.24	1.150
Pr^{3+}	0.03	0.82	0.79	1.130
Nd^{3+}	0.11	1.25	3.90	1.123
Sm^{3+}	1.06	5.16	50.3	1.098
Eu^{3+}	0.55	3.43	9.16	1.087
Gd^{3+}	7.62	26.1	252	1.078
Tb^{3+}	14.9	60.4	417	1.063
Dy^{3+}	29.0	129	602	1.052
Ho^{3+}	52.6	253	771	1.041
Er^{3+}	77.8	423	852	1.030
Tm^{3+}	101	622	894	1.020
Yb^{3+}	133	895	913	1.008
Lu^{3+}	150	968	748	1.001
Hf^{4+}	874	1534	1578	0.850
Ta^{5+}	3.12	95.7	78.8	0.780
Th^{4+}	12.5	664	551	1.080
U^{4+}	109	2321	472	1.030

661

Figure 1

Figure 2

(a)

A-type granitoids

FG

OTG

(Na$_2$O+K$_2$O)/CaO
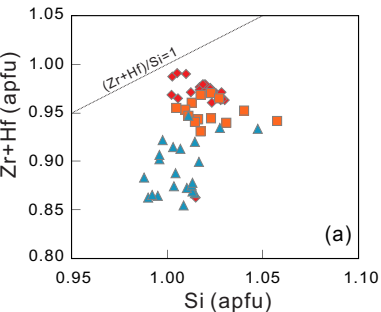
Zr+Nb+Ce +Y(ppm)

(b)

IAB

A2

A1

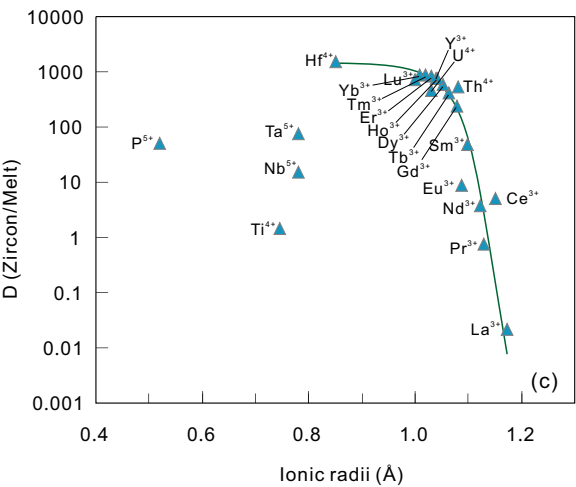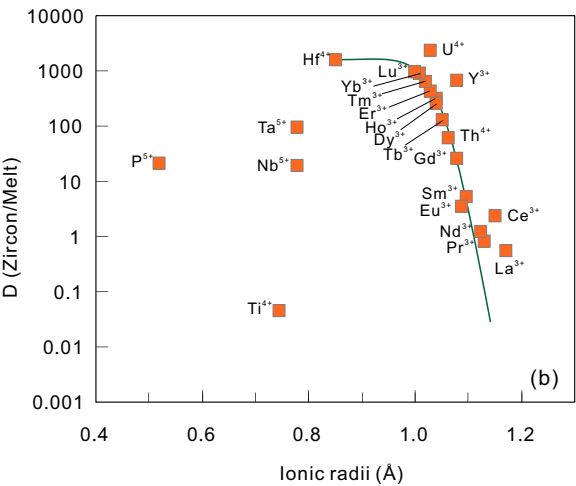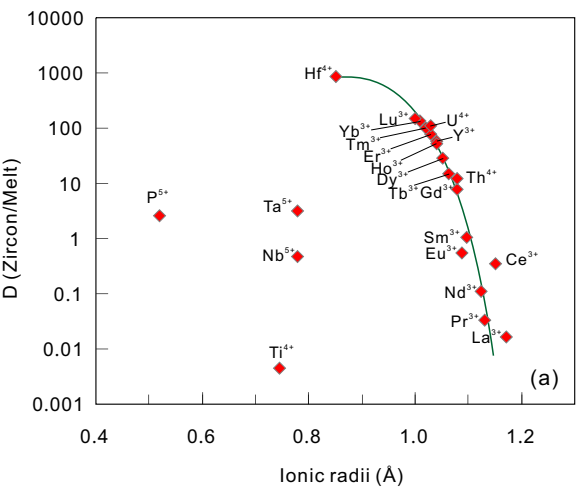OIB

Yb/Ta

Y/Nb
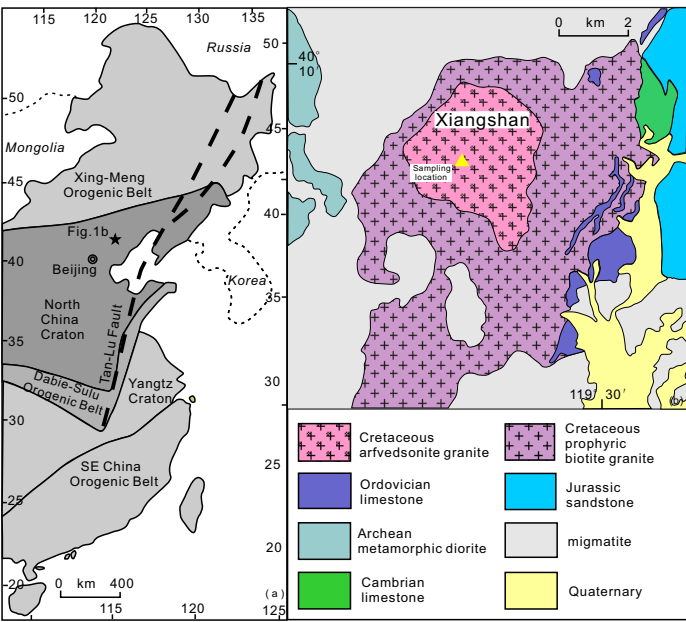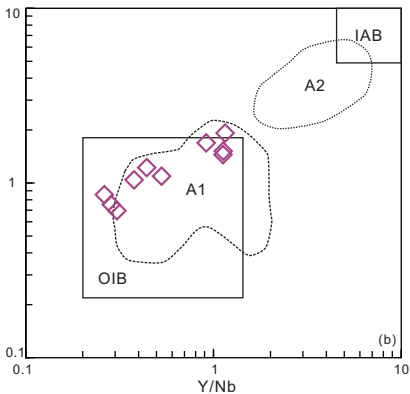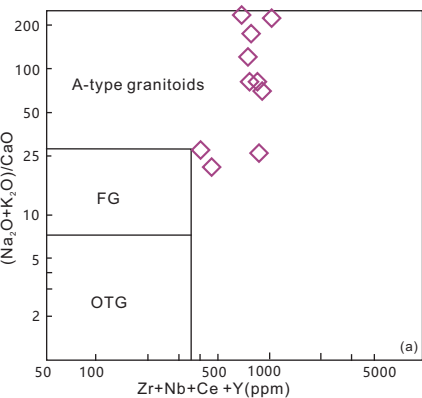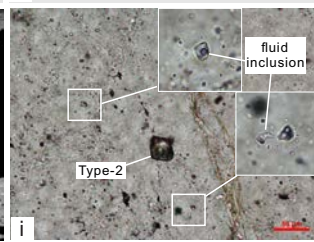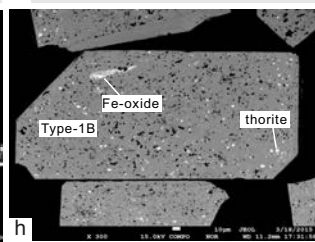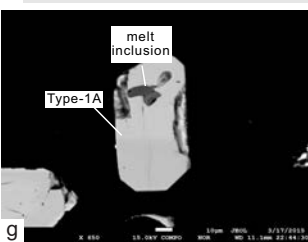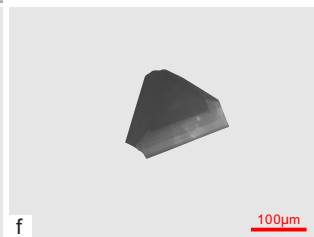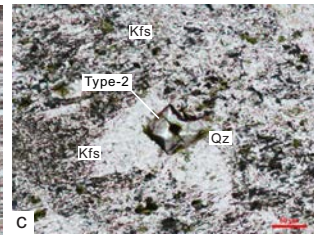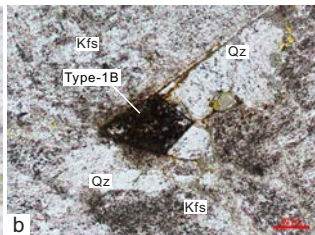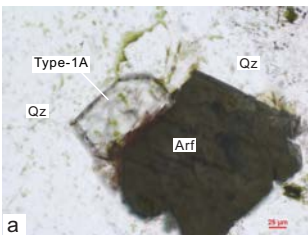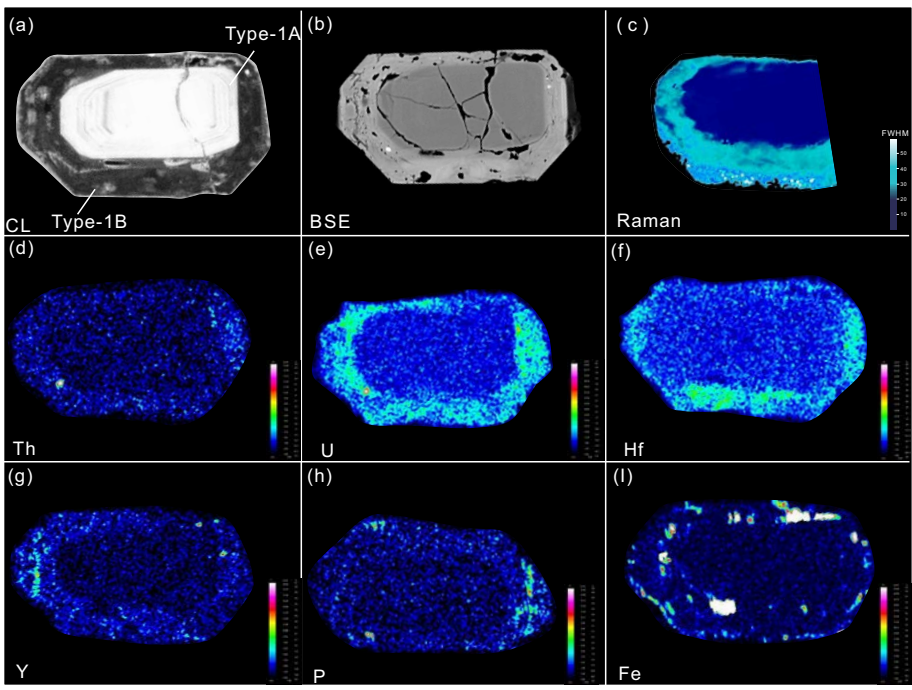
Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

Figure 8

Figure 9

Figure 10