

DISTRIBUTION AND EVOLUTION OF ZIRCONIUM MINERALIZATION IN PERALKALINE GRANITES AND ASSOCIATED PEGMATITES OF THE KHAN BOGD COMPLEX, SOUTHERN MONGOLIA

JINDŘICH KYNICKÝ[§]

Department of Geology and Pedology, Mendel University, Zemedelska 3, CZ-613 00 Brno, Czech Republic

ANTON R. CHAKHMOURADIAN

Department of Geological Sciences, University of Manitoba, Winnipeg, Manitoba R3T 2N2, Canada

CHENG XU

*Laboratory of Materials of the Earth's Interior and Geofluid Processes, Institute of Geochemistry,
Chinese Academy of Sciences, Guiyang 550002, People's Republic of China*

LUKAS KRMICEK

Institute of Geological Sciences, Masaryk University, Kotlarska 2, CZ-611 37 Brno, Czech Republic

MICHAELA GALIOVA

Department of Chemistry, Faculty of Science, Masaryk University, Kotlarska 2, CZ-611 37 Brno, Czech Republic

ABSTRACT

The western part of the Khan Bogd complex, in the south Gobi desert, southern Mongolia, comprises (in order of emplacement): microcline-phyric granite, peralkaline aegirine–arfvedsonite granite (main intrusive phase) and aplite–pegmatite veins confined predominantly to the apical parts of the intrusion. These rocks are interpreted to represent products of extreme fractional crystallization involving alkali feldspar, quartz and, to a lesser extent, ferromagnesian silicates and, in the final stages of magma evolution, release of a silica-saturated orthomagmatic fluid. Geochemically, this evolutionary path involved an increase in peralkalinity index (from 1.0 in the porphyritic granite to 1.3 in the main phase to 2.5 in the pegmatite) and whole-rock Zr content (864 to 1130 to 16900 ppm, respectively). In the porphyritic granite, zircon with a low Hf content (Zr/Hf in the range 55–75) is the principal Zr phase, whereas alkali–Ca zirconosilicate minerals are characteristically absent. Zirconium mineral parageneses in the peralkaline granites and associated aplite–pegmatite bodies are texturally and compositionally complex products of Zr enrichment during the differentiation of magma, followed by reaction of the granitic rocks with a calcic CO₂–F-rich fluid. In the peralkaline unit and pegmatites, Ca-poor elpidite is an early magmatic host of Zr, along with appreciable levels of the rare-earth elements ($n \times 10^3$ ppm REE + Y). The hydrothermal stage involved replacement of the primary elpidite by late-stage Ca-rich elpidite or armstrongite, and then precipitation of minor gittinsite and abundant zircon. With the exception of zircon [(La/Yb)_{CN} ≈ 0.1], all secondary zirconosilicates exhibit relative enrichment in light REE [(La/Yb)_{CN} in the range 0.3–5.0]. Enrichment of the light REE in the fluid due to the sequestration of heavy REE in zircon led to the deposition of light-REE fluorocarbonates associated with calcite and minor fluorite. The fluid probably separated at the final stages of the evolution of the peralkaline granitic magma, but a crustal input, indicated by Ca enrichment of the fluid, cannot be ruled out. The observed variations in the modal composition of the secondary paragenesis can be explained by changes in fluid regime, and the activity of silica and other dissolved species during the hydrothermal stage.

Keywords: peralkaline granite, granitic pegmatite, Zr mineralization, elpidite, armstrongite, gittinsite, zircon, Khan Bogd, Gobi desert, Mongolia.

[§] E-mail address: jindrak@email.cz

SOMMAIRE

Dans sa partie occidentale, le complexe de Khan Bogd, dans le sud du désert de Gobi, du sud de la Mongolie, contient, dans l'ordre de mise en place, un granite porphyritique à microcline, un granite hyperalcalin à aegyrine–arfvedsonite (la phase intrusive principale) et des veines d'aplite et de pegmatite, limitées aux parties apicales de l'intrusion. Ces roches représenteraient des produits de cristallisation fractionnée extrême impliquant feldspath alcalin, quartz et, à un degré moindre, les silicates ferromagnésiens; au stade final de l'évolution du magma, une phase fluide orthomagmatique saturée en silice s'est échappée. Du point de vue géochimique, ce tracé évolutif a mené à une augmentation de l'indice d'hyperalcalinité (de 1.0 dans le granite porphyritique à 1.3 dans la phase principale et jusqu'à 2.5 dans les pegmatites) et à une augmentation en Zr dans ces roches (de 864 à 1130 à 16900 ppm, respectivement). Dans le granite porphyritique, le zircon, minéral principal de Zr, possède une teneur relativement faible en Hf (Zr/Hf dans l'intervalle 55–75), tandis que les zirconsilicates à alcalins et Ca sont absents. Les paragenèses de minéraux de zirconium des granites hyperalcalins et des venues d'aplite et de pegmatite associées, témoignant d'un enrichissement en Zr au cours de la différenciation du magma, sont complexes dans leurs textures et leurs compositions, et elles montrent les effets d'une réaction avec une phase fluide calcique contenant CO₂ et F. Dans les roches hyperalcalines et les pegmatites, l'elpidite à faible teneur en Ca est un hôte précoce du Zr, et de quantités non négligeables des terres rares ($n \times 10^3$ ppm REE + Y). Le stade hydrothermal a impliqué un remplacement de l'elpidite primaire par une elpidite tardive enrichie en Ca ou par l'armstrongite, suivi d'une précipitation de gittinsite mineure et de zircon abondant. À l'exception du zircon [(La/Yb)_{CN} ≈ 0.1], tous les zirconsilicates secondaires démontrent un enrichissement relatif en terres rares légères [(La/Yb)_{CN} dans l'intervalle 0.3–5.0]. L'enrichissement en terres rares légères dans la phase fluide, due à la séquestration de terres rares lourdes dans le zircon, a mené à la formation de fluorocarbonates de terres rares associés à la calcite et à un peu de fluorite. La phase se serait probablement séparée au stade final de l'évolution du magma granitique hyperalcalin, mais nous ne pouvons écarter la possibilité d'une contribution de Ca venant des roches encaissantes. On peut expliquer les variations observées dans la composition modale des assemblages secondaires en invoquant des changements des attributs de la phase fluide et de l'activité de la silice et autres espèces dissoutes au cours des ajustements hydrothermaux.

(Traduit par la Rédaction)

Mots-clés: granite hyperalcalin, pegmatite granitique, minéralisation en Zr, elpidite, armstrongite, gittinsite, zircon, Khan Bogd, désert de Gobi, Mongolie.

INTRODUCTION

Intrusions of A-type and peralkaline granitic rocks commonly host rare-metal mineralization represented by a plethora of exotic Nb, Zr and rare-earth minerals (typically, niobosilicates, zirconsilicates and fluorocarbonates). This type of mineralization is found in the Khan Bogd (or Khan Bogdo or Khan-Bogdinskii) igneous complex, in Mongolia, one of the largest known intrusions of peralkaline granite (*ca.* 1500 km² at the current level of erosion).

The enrichment of peralkaline granites in high-field-strength elements (HFSE), notably Zr, Nb and the rare-earth elements, is typically interpreted to arise from enrichment at their source or from extreme differentiation involving fractional crystallization and liquid immiscibility (Kovalenko *et al.* 1995, Schmitt *et al.* 2002, Kogarko 2005, Xie *et al.* 2006, Peretyazhko *et al.* 2007). However, most peralkaline granitoids also display convincing textural and geochemical evidence of hydrothermal reworking involving remobilization of HFSE and other rare elements (*e.g.*, Boily & Williams-Jones 1994, Mungall & Martin 1996, Marks *et al.* 2003). Such hydrothermal reworking is most conspicuous in parageneses containing high levels of HFSE commonly bound in various zirconsilicate minerals. For example, zones of Zr–Nb–Y–rare-earth mineralization in the Thor Lake and Strange Lake complexes, in Canada (Trueman *et al.* 1988, Salvi & Williams-Jones 1990, 1996, 2006,

Taylor & Pollard 1996, Roelofsen & Veblen 1999) are well documented. Compelling evidence for precipitation of HFSE minerals directly from aqueous fluids comes from the study of inclusions (Salvi & Williams-Jones 1990, 2006), miarolitic and other hydrothermal parageneses (Bonin 1988, Pettke *et al.* 2005), as well as from experimental work (Aja *et al.* 1995, Korzhinskaya 1999, Schmidt *et al.* 2006). Hence, there seems little doubt that HFSE enrichment of peralkaline granitic intrusions is the combined outcome of magmatic and hydrothermal processes.

Although alkali–Ca zirconsilicate minerals are relatively common accessory constituents in peralkaline granites and silica-undersaturated igneous and metasomatic rocks (Semenov 1969, Birkett *et al.* 1992, Kovalenko *et al.* 1995, Chakhmouradian & Mitchell 2002, Pekov 2002, Yakovenchuk *et al.* 2005, among many others), there are virtually no published data on the trace-element composition of any these phases with the exception of eudialyte (*e.g.*, Harris & Rickard 1987, Olivo & Williams-Jones 1999, Schilling *et al.* 2009). Hence, the role of these minerals in the sequestration or dispersal of Y, the REE and other elements that are substituting for Na, K, Ca and Zr in their structure remains poorly understood. The recent revival of interest in complex Zr–Y–REE deposits (*e.g.*, Knox *et al.* 2009, Nebocat 2009, Paul & Stubens 2009) necessitates further studies of this type of mineralization and

the placement of small-scale mineralogical observations in a broader petrological context.

The present paper is the first in a planned series of contributions on the petrology and mineralogy of the Khan Bogd peralkaline complex. In this study, we focus on the major mineralogical and geochemical aspects of the Zr mineralogy in these rocks, in particular on the trace-element composition of the widespread parental elpidite I and its alteration products, and in general on the behavior of the HFSE during the evolution of the complex.

GEOLOGICAL SETTING

The Khan Bogd complex is located in Ömnögovi aimag (South Gobi district) in southern Mongolia, approximately 520 km south of Ulaanbaatar and only several kilometers east of the very large Hugo Dummett deposit in the Oyu Tolgoi Cu–Mo–Au porphyry district. The complex was discovered in the 1960s and subsequently investigated by joint Soviet–Mongolian expeditions (Kovalenko *et al.* 1973, 2006, Vladykin *et al.* 1981). Early work showed that the Khan Bogd pluton consists of alkali granites emplaced in the Gobi–Tien Shan belt as part of the Late Paleozoic rift-related province of peralkaline rocks. The pluton can be subdivided into western and eastern bodies, both surrounded by Paleozoic continental sedimentary and volcanic rocks of the Tsokiot Formation. The circular structure of the western body is underscored by thousands of well-exposed ring dikes (Fig. 1). The ages of most intrusive and extrusive phases within the complex, determined by a variety of techniques, fall within the range 292–283 Ma (Early Permian), and only a porphyritic biotite granite gave a significantly younger age, 272 Ma (Kovalenko *et al.* 2006, Vaglio 2007). The youngest and most evolved intrusive units are represented by ekerites, aplites and pegmatites. Field observations indicate that their emplacement occurred during repeated transitions from the ductile to brittle tectonic regime (Kynický *et al.* 2003, 2009, Vaglio 2007).

The geochemistry of the Khan Bogd rocks (Vladykin *et al.* 1981, Vaglio 2007, this work) indicates that they originated from granitic magma(s) of type A2 (*sensu* Eby 1992), *i.e.*, magmas believed to originate by melting of continental crust or crustal underplate formed through a cycle of continent–continent collision with a possible contribution from island-arc magmatism. The melting could have been triggered by a mantle plume or upwelling of hot asthenospheric mantle following post-collisional delamination (Kovalenko *et al.* 2006, Vaglio 2007). Broadly coeval granitic magmatism occurred elsewhere in the Gobi–Tien Shan belt and other Late Paleozoic belts in the Central Asian Orogen following the early stages of collision between the North China and Siberian cratons (Yarmolyuk & Kovalenko 2002, Jahn *et al.* 2009, Blight *et al.* 2010).

PETROGRAPHY

The Khan Bogd pluton is composed predominantly of peralkaline granites. The main intrusive phase, which constitutes the bulk of the western body, is a medium- to coarse-grained rock consisting of quartz (48–53 modal %), potassium feldspar (up to 35 modal %), aegirine (up to 11 modal %) and arfvedsonite (up to 12 modal %). Accessory minerals are represented predominantly by zirconosilicates; titanite, rutile and, less commonly, apatite are subordinate accessory phases. Metasomatically altered samples (Fig. 2) contain Fe–Mn oxides, calcite and rare-earth fluorocarbonates (typically, bastnäsite and synchysite). The potassium feldspar is represented by microcline with characteristic “tartan” twinning, exsolution lamellae of albite and inclusions of quartz, aegirine and arfvedsonite. Arfvedsonite and aegirine, which is commonly observed to replace the arfvedsonite, show oscillatory-type growth zonation. Quartz occurs interstitially with respect to microcline and mafic silicates, as well as forming granophyric textures. The accessory minerals are confined to interstices among the early-crystallizing minerals.

Locally, the main intrusive phase is preceded by porphyritic alkali granite containing microcline phenocrysts up to 2 cm across. The porphyritic unit is much more strongly altered to white mica and is partially digested by, the younger granite. In other respects, the two units are texturally and modally similar (Kovalenko *et al.* 1973, Kynický *et al.* 2003, Kynický & Trundova 2004).

The Khan Bogd complex is well known among mineralogists for its “cupola pegmatites” typically associated with layered sequences of aplite and ekerite. A typical pegmatite vein exhibits three major zones (Kovalenko *et al.* 1973, 2005, Vladykin *et al.* 1981) differing in the size of crystals and distribution of major minerals: 1) A border zone is relatively thin, generally ~ 0.5 m in width, and contains clusters and discrete crystals of euhedral F-rich arfvedsonite (1.8–2.5 wt.% F) embedded in albitized microcline. Zirconosilicates are relatively rare. 2) A blocky zone is significantly thicker than, but modally similar to, the border zone (on average, 1.5 m, rarely up to 4 m in width). Characteristic for this zone are the replacement of arfvedsonite by aegirine and the presence of large (up to 0.5 cm) crystals of elpidite. The size of the microcline crystals in the blocky zone is not much larger than that in the border zone, whereas arfvedsonite crystals in this zone can reach 1 m in length, extending into the adjacent zones. 3) A quartz core is an essentially monomineralic brecciated zone reaching 20 m in diameter. Opal (or chalcedony) and calcite are minor accessory minerals confined to fractures.

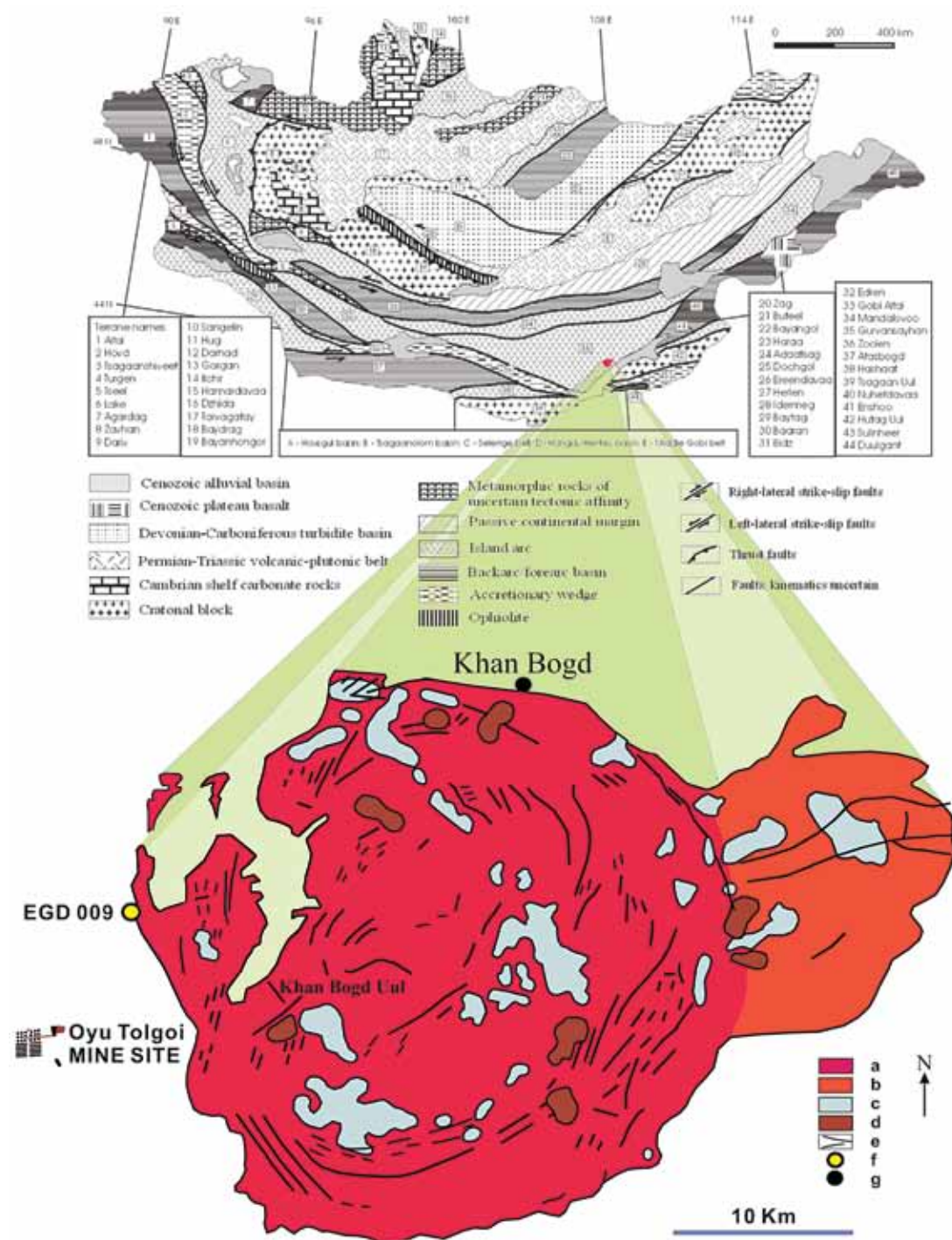


FIG. 1. Schematic geological map of the complex, modified after Kovalenko *et al.* (2006), and the position of Khan Bogd in the terrane map of Mongolia after Badarch *et al.* (2002). Legend: (a) peralkaline granite of the main intrusive phase, (b) fine-grained aegirine granite, (c) bimodal volcanic rock association of the Tsokiot Formation, (d) older granitic rocks (remnants of the Devonian Tsagaan Suburgaa pluton?), (e) major dikes, (f) position of drill hole EGD 009, (g) settlements.

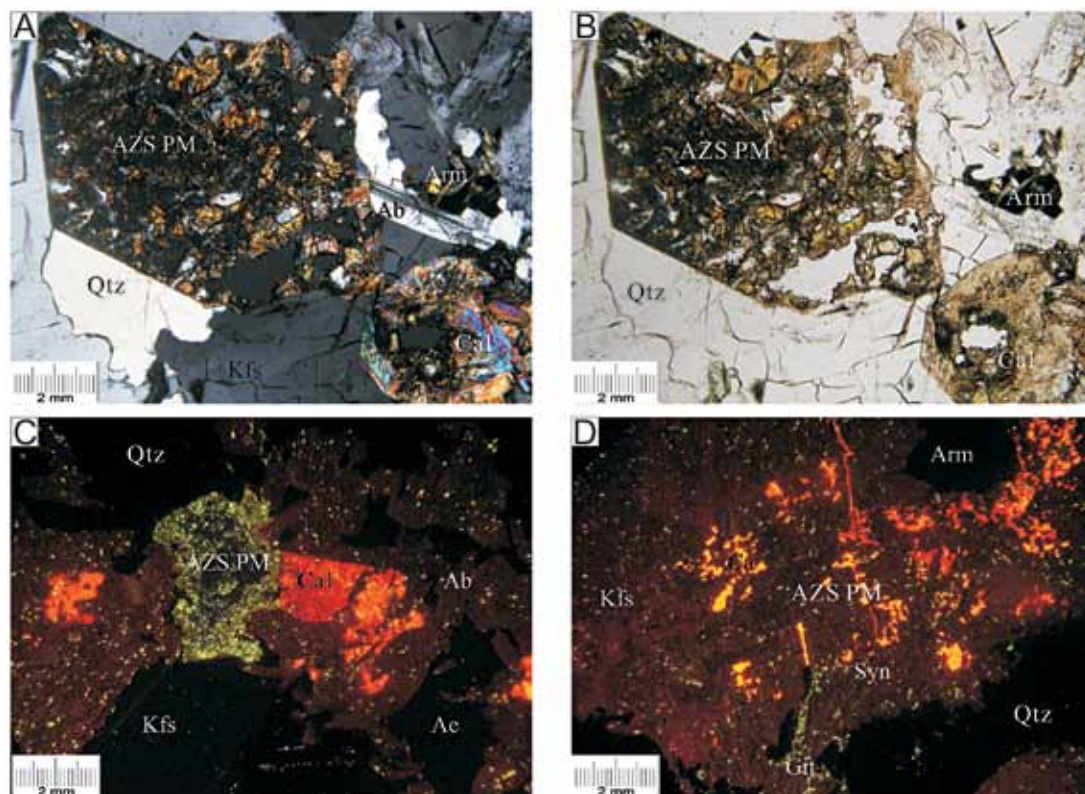


FIG. 2. Polarized-light (PL) and cathodoluminescence images of late-stage HFSE and REE mineral parageneses in strongly altered elpidite samples. (A) Complex pseudomorph of disintegrated elpidite I replaced by armstrongite, gittinsite and quartz, PL, crossed nicols. (B) Complex pseudomorph after elpidite I from A, PL. (C) Zirconosilicate mineralization (predominantly zircon and gittinsite) after primary elpidite I in pegmatite. (D) Alkali zirconosilicate and fluorocarbonate mineralization associated with calcite after elpidite I in the main-phase peralkaline granite. Symbols: AZS PM: alkali-Ca-zirconosilicate pseudomorph, Ab: albite, Ae: aegirine, Arm: armstrongite, Cal: calcite, Git: gittinsite, Kfs: potassium feldspar, Qtz: quartz, Syn: synchysite.

METHODOLOGY

Sampling

More than 700 samples of peralkaline granites, aplites, pegmatites, volcanic and subvolcanic trachytic rocks, as well as xenolithic material, were collected during fieldwork at Khan Bogd in 2003–2009. In addition, we examined in detail and sampled material from drill-hole EGD 009 drilled by Ivanhoe Mines Ltd. approximately 200 m west of the western intrusive contact (Fig. 1). The 50 samples selected from this drill core represent the two main intrusive phases of granite and several pegmatite and aplite veins intersected to a depth of *ca.* 800 m. All of the examined rock units contain Zr minerals (zircon, elpidite, armstrongite and gittinsite: Figs. 2, 3).

Analytical methods

The major-element compositions of selected minerals were measured by wavelength-dispersive X-ray spectrometry (WDS) using a CAMECA SX100 electron microprobe at the Laboratory of Electron Microscopy and Microanalysis, a joint facility of Masaryk University and the Czech Geological Survey in Brno. The microprobe was operated at a beam current of 10 nA and an accelerating voltage of 15 kV. The beam was defocused to a spot size of 5–10 μm to minimize beam damage and the thermal decomposition of the sample. The following standards and X-ray emission lines were used in the analysis of Zr-bearing minerals: albite (Na, $K\alpha$), sanidine (K, $K\alpha$), augite (Si, $K\alpha$), zircon (Zr, $L\alpha$), almandine (Al, $K\alpha$), synthetic HfO_2 (Hf, $M\alpha$), apatite (Ca, $K\alpha$), ThO_2 (Th, $M\alpha$), metallic U ($M\beta$), Y–Al garnet (Y, $L\alpha$), YbPO_4 (Yb, $L\alpha$), rhodo-

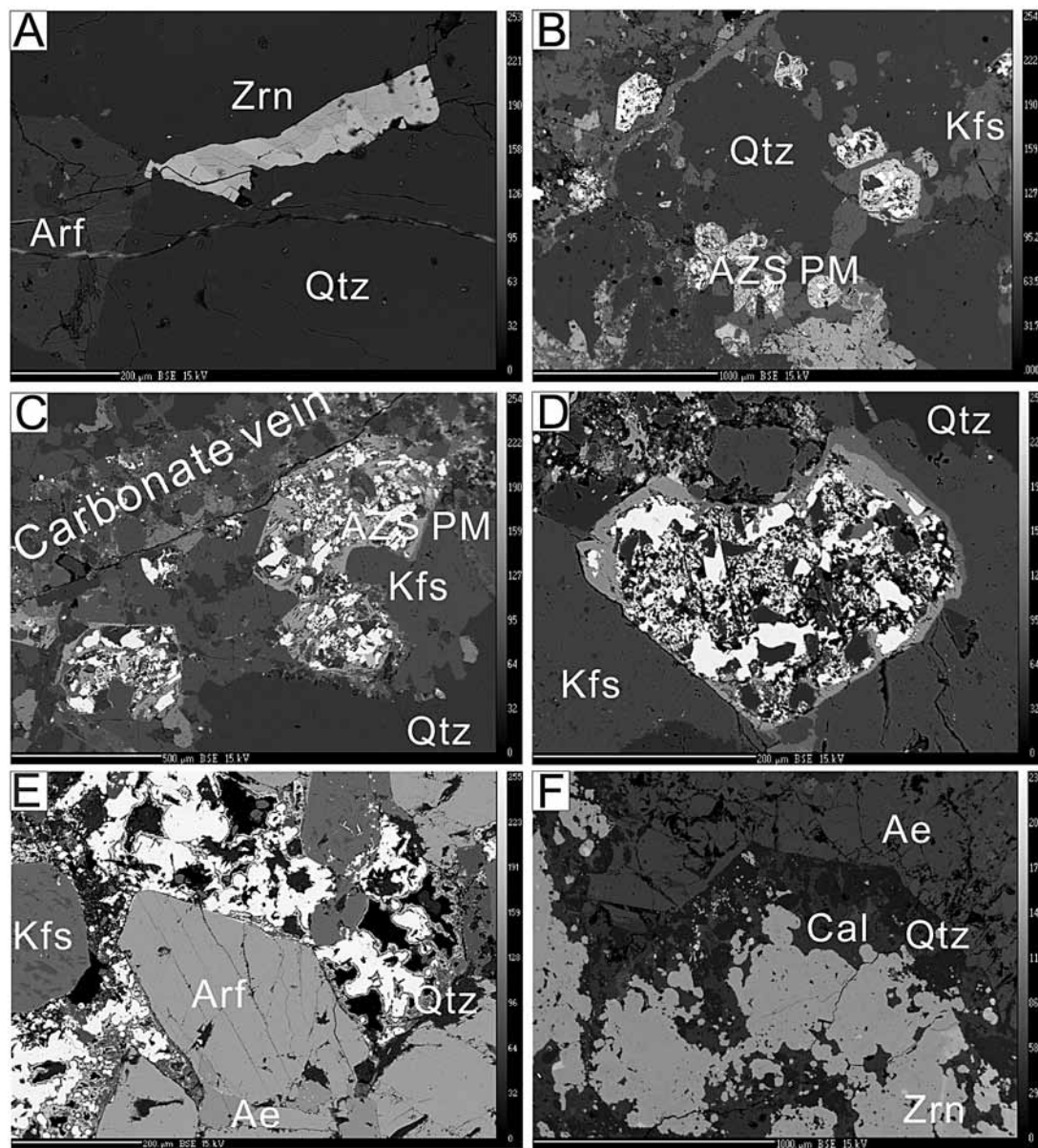
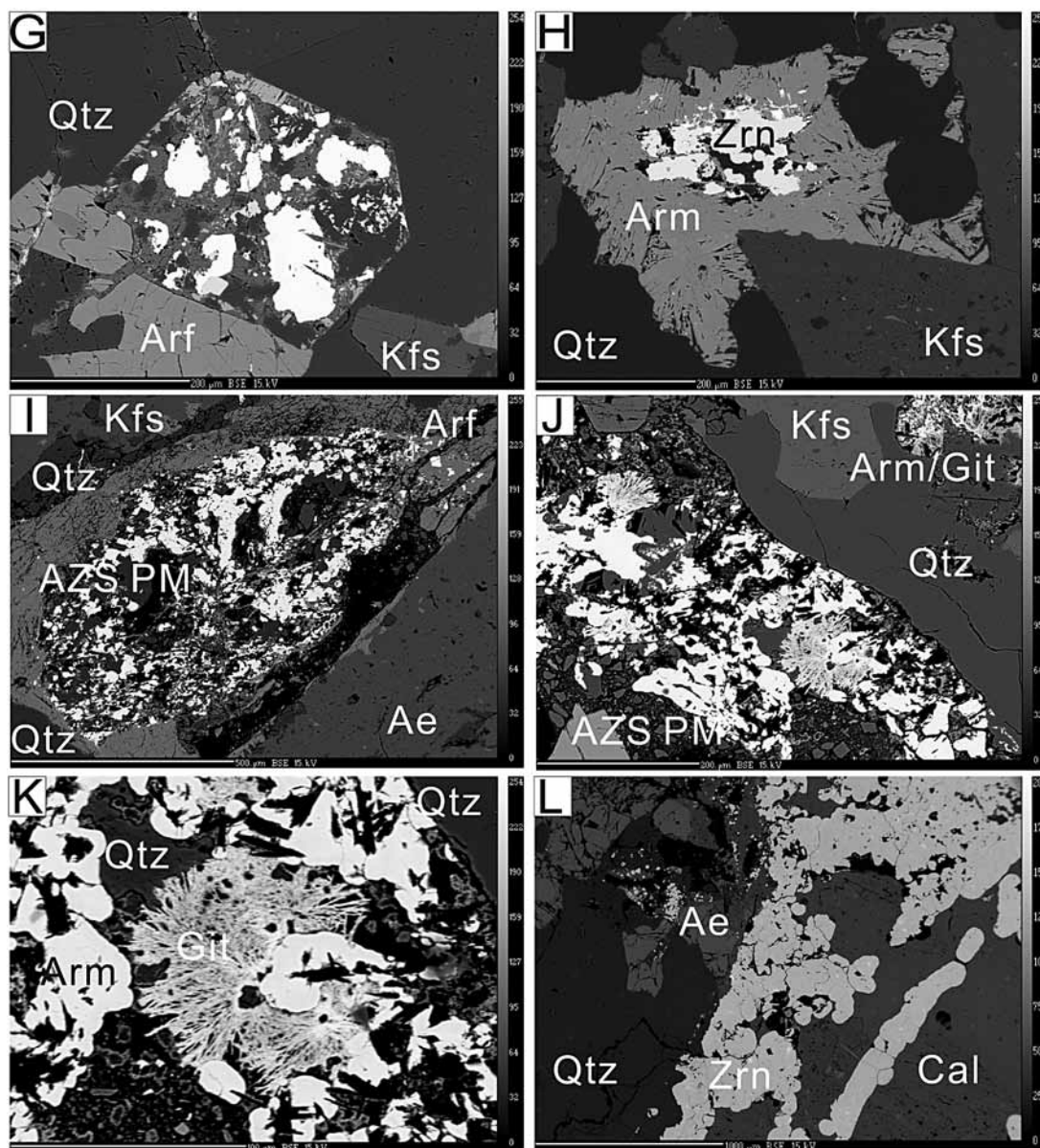


FIG. 3. Back-scattered-electron (BSE) images illustrating the most characteristic microtextures involving zirconosilicate minerals. (A) Zoned zircon (Zrn) in alkali porphyry granite consisting of euhedral crystals overgrown by younger anhedral zircon. (B) Alkali-Ca-zirconosilicate pseudomorphs (AZS PM) consisting mainly of armstrongite and zircon developed after primary elpidite in the main-phase peralkaline granite. (C) Alkali-Ca-zirconosilicate pseudomorphs (AZS PM) after primary elpidite in the main-phase peralkaline granite, spatially close to carbonate veins and microbreccias. (D) Complex zonal pseudomorph after elpidite I consisting of elpidite II rim, armstrongite in second (lighter) zone, and zircon, gittinsite and quartz aggregate in the largest central zone of pseudomorph, in the main-phase peralkaline granite. (E) Late-stage zirconosilicate mineralization (predominantly zircon and gittinsite) after primary elpidite in the main-phase peralkaline



granite. (F) Pseudomorphs after elpidite I composed of anhedral zircon (Zrn), calcite (Cal) and quartz (Qtz), associated with aegirine (Ae) replacing arfvedsonite in the main-phase peralkaline granite. (G) Complex aggregate of armstrongite, gittinsite and quartz replacing elpidite I in the border zone of a pegmatite vein. (H) Zonal aggregate of armstrongite and zircon replacing elpidite I in the border zone of a pegmatite vein. (I) Irregular zirconosilicate pseudomorph composed of armstrongite, zircon and gittinsite developed after elpidite I in the blocky zone of pegmatite. (J) Zirconosilicate pseudomorph composed of armstrongite (Arm) and radiating gittinsite (Git) developed after elpidite I in the blocky zone of pegmatite. (K) Detail of gittinsite (Git) from I. (L) Late-stage zircon and calcite after elpidite I in the blocky zone of pegmatite. Other symbols: Arf: arfvedsonite, Kfs: potassium feldspar.

nite (Mn, $K\alpha$), andradite (Fe, $K\alpha$), topaz (F, $K\alpha$), and synthetic TiO_2 (Ti, $K\alpha$). The data were reduced and corrected using the PAP routine (Pouchou & Pichoir 1984). The Al and F contents of Zr-bearing minerals were found to be consistently below their lower limit of detection by WDS.

Trace-element analysis of selected zirconosilicate minerals by laser-ablation – inductively coupled plasma – mass-spectrometry (LA-ICP-MS) was performed at the Laboratory of Atomic Spectrochemistry, Masaryk University, using an Agilent 7500ce spectrometer and a UP-213 pulsed Nd:YAG laser system operated at a wavelength of 213 nm and pulse duration of 4.2 ns. This ablation system is equipped with a 33-cm³ SuperCell sample chamber (New Wave Research) designed for rapid evacuation of the laser-generated aerosol. Helium was used as a carrier gas with a flow rate of 1 L/min. The samples were analyzed using a spot diameter of 55 μ m, dwell time of 60 s, repetition rate of 10 Hz, and fluence of 5 J/cm². The calcium content determined by WDS was used as an internal standard, and external calibration was performed using glass standard NIST 612.

The abundances of major elements in selected whole-rock samples from surface outcrops in the western part of the Khan Bogd complex and drill core were determined by X-ray fluorescence at the Institute of Geochemistry, Chinese Academy of Sciences. Trace-element abundances were measured at the same facility using ICP-MS. Fifty mg of whole-rock powder was dissolved in a Teflon bomb using 1 mL of HF (38%) and 0.5 mL of HNO_3 (68%). The bomb was then sealed, heated in an electric oven to 190°C for 24 h and cooled to room temperature. The cooled solution was spiked with 1 mL of 1 ppm Rh solution and evaporated on a hot plate. One mL of HNO_3 was added, evaporated to dryness and followed by a second cycle of acid dilution and evaporation. The final residue was redissolved in 8 mL of HNO_3 , placed in a Teflon bomb and heated in an electric oven to 110°C for 3 h. The final solution was diluted to 100 mL by addition of de-ionized distilled water for ICP-MS analysis. The analytical precision of the ICP-MS measurements for most of the elements is better than 10%.

DISTRIBUTION AND PARAGENESIS OF ZIRCONIUM MINERALS

At Khan Bogd, Zr minerals are represented by Na–Ca zirconosilicates; these minerals are common in both the main intrusive phase and cross-cutting younger rocks (especially pegmatites). The most important Zr phase is primary elpidite (elpidite I), whose modal content ranges from << 1% to 30% in some pegmatite samples. The greatest abundances of zirconosilicates are observed in large bodies of zoned pegmatite. With the exception of microgranite dikes (Fig. 3A), the rocks examined in the present work lack primary zircon.

Accessory late-stage zircon occurs in all other granitic rocks as a product of replacement of elpidite I in association with either calcite or late-stage Ca-enriched elpidite (elpidite II), armstrongite, gittinsite and quartz (Figs. 3B–L).

The main intrusive phase

Elpidite is the most common zirconosilicate phase in our samples, ranging from *ca.* 0.1 to 5 vol.% in abundance. This mineral occurs as euhedral crystals up to 5 mm across developed interstitially with respect to phenocrysts and commonly replaced by texturally complex aggregates of Ca zirconosilicates (*e.g.*, Figs. 3B, C and D). Armstrongite is less abundant than elpidite, but is the most common late-stage zirconosilicate developed in alteration zones along fractures or in intimate association with Ca-bearing elpidite II in exsolution textures, confined to the contact between elpidite I and zircon ($\pm$ gittinsite and quartz). Armstrongite does not form discrete crystals and occurs exclusively in the rim and along fractures in pseudomorphs after elpidite I in an assemblage with calcite and Fe oxyhydroxides, clearly indicating subsolidus replacement. Gittinsite typically occurs only in strongly altered samples as radiating aggregates. Zircon replaces all other zirconosilicate minerals mentioned above as the latest alteration phase to form. This mineral is particularly common in samples containing large replaced crystals of elpidite I. Late-stage zircon is most typically associated with gittinsite and armstrongite (Figs. 3B–E and, less commonly, calcite (Fig. 3F)). On the basis of textures observed in drill core, the replacement of elpidite I is more intense in fractured samples taken near the surface than in samples from greater depths. At a depth of 150–180 m along the drill core, elpidite I, elpidite II and armstrongite are extensively replaced by gittinsite and zircon near the contact of granites and pegmatites with the host-rock lithologies. Gittinsite forms feathery radiating crystals up to 0.1 mm in length. The morphology of the aggregates of late-stage zirconosilicate minerals and the presence of relict grains suggest that these aggregates are pseudomorphs exclusively after elpidite I; neither fresh nor relict eudialyte has been observed in any of the samples.

The pegmatite–aplite series

Elpidite is the principal zirconosilicate mineral in the pegmatite–aplite series. It forms euhedral crystals up to 1 mm in length in the aplites and up to 0.5 m in length in the blocky zone of some large pegmatite bodies. The abundance of elpidite ranges from 1 to 2 vol.% in the aplites, from 1 to 5 vol.% in the border zone, and from 2 to 30 vol.% in the blocky zone. Crystals of primary elpidite are typically replaced to a variable degree by complex aggregates of late-stage zirconosilicate phases. Textural relations among these zirconosilicate minerals

are very similar to those described above for the main-phase peralkaline granite; typical examples are shown in Figures 3G–L. In both granites and pegmatites, pseudomorphs of gittinsite and quartz after elpidite I invariably contain a large proportion (up to 50%) of pore space (e.g., Figs. 3D, E, I, J, K).

Porphyritic alkali granite

Porphyritic granite from drill core EGD 009 and petrographically similar varieties of granite from surface outcrops are devoid of alkali-Ca zirconosilicate minerals. The major host of Zr in these rocks is primary zircon present as small crystals and clusters of multiple crystals <1 mm in size showing simple zonation (Fig. 3A).

THE CHEMICAL COMPOSITION OF ZIRCONIUM MINERALS

Representative and average chemical compositions of Zr minerals from different rock types are summarized in Tables 1 and 2. In addition to the WDS analyses, selected samples were studied by cathodolumines-

cence and back-scattered-electron imaging techniques to constrain compositional variation in individual zirconosilicates, establish their order of crystallization, and identify grains most suitable for trace-element analysis by laser-ablation ICP–MS. More than 70% of the grains selected initially were too small or too intimately intergrown with other minerals for reliable trace-element analysis and were eventually discarded. Although extreme care was taken in choosing areas for laser-ablation analysis, the presence of submicroscopic compositional heterogeneities could not be accounted for. Thus, the REE contents listed in Table 1 represent average values.

Elpidite

Elpidite is the major zirconosilicate phase in all of the granitic rocks with the exception of porphyritic alkali granite. In plane-polarized light, elpidite crystals appear turbid owing to the pervasive presence of armstrongite inclusions (lamellae, drop-shaped inclusions and intergrowths) conspicuous in BSE images.

Elpidite I is characterized by a uniform composition with but small variations in Ca content in each of

TABLE 1. AVERAGE CHEMICAL COMPOSITION OF ZIRCONOSILICATE MINERALS

	Main-phase granite				Pegmatites					Aplitic rocks		
	Elp I	Elp II	Arm	Zrn	Elp I	Elp II	Arm	Git	Zrn	Elp I	Arm	Zrn
CaO wt. %	1.31	3.45	8.29	1.71	0.25	2.21	8.13	16.76	0.08	1.48	8.43	1.38
Na ₂ O	7.43	4.81	0.18	b.d.	6.19	5.41	0.05	0.15	b.d.	6.63	0.14	b.d.
K ₂ O	0.11	0.08	b.d.	b.d.	0.11	0.05	0.06	0.06	b.d.	0.22	0.09	b.d.
SiO ₂	60.82	62.14	58.11	31.42	62.40	60.52	59.48	40.07	31.78	60.56	60.73	28.71
ZrO ₂	20.54	18.45	20.32	63.75	21.57	18.83	19.24	39.58	63.66	20.61	19.58	59.66
HfO ₂	0.32	0.56	0.74	1.04	0.44	0.41	0.64	0.82	0.97	0.35	0.41	0.94
MnO	0.07	b.d.	0.17	0.11	b.d.	0.02	0.04	0.05	0.02	b.d.	0.04	0.10
FeO	0.14	0.11	1.18	0.37	0.22	0.07	0.34	0.45	0.39	0.14	0.34	1.07
TiO ₂	b.d.	0.04	0.15	0.26	0.13	0.02	0.03	0.11	0.06	b.d.	b.d.	0.44
Y ₂ O ₃	0.18	0.54	0.72	0.92	0.22	0.79	0.37	0.49	n.a.	0.45	0.62	0.83
Total	90.92	90.18	89.86	99.54	91.53	88.33	88.38	98.54	96.96	90.44	90.40	93.13
La ppm	356.9	1875.1	1761.1	116.9	378.7	615.2	1992.0	518.7	105.5	240.4	1204.8	86.1
Ce	689.3	3574.9	3146.0	419.1	757.4	1099.3	3778.3	962.8	278.5	536.4	2493.4	221.7
Pr	83.9	437.6	385.4	59.1	93.2	118.6	365.3	104.4	38.9	75.8	324.9	31.2
Nd	356.3	2373.6	2137.8	288.8	386.8	397.2	1503.0	320.8	179.1	355.4	1579.0	134.6
Sm	126.4	659.6	516.4	105.3	113.6	107.2	386.2	95.5	71.4	120.3	472.8	54.9
Eu	8.9	14.9	11.1	7.1	8.1	10.1	9.9	8.3	6.8	9.3	13.3	7.1
Gd	282.0	734.9	490.6	176.0	174.5	168.8	354.6	100.7	122.9	417.7	578.3	147.5
Tb	35.6	97.3	71.0	35.6	23.8	27.0	36.2	16.6	23.2	66.4	95.7	24.5
Dy	241.6	1035.1	676.5	386.5	266.8	275.1	445.0	180.5	232.0	602.0	815.9	252.4
Ho	61.7	277.1	175.0	132.4	88.0	86.8	116.7	59.9	69.9	141.1	187.6	73.2
Er	246.9	927.4	799.2	565.9	308.8	313.1	394.2	245.5	251.6	472.2	685.4	277.6
Tm	37.0	155.4	98.4	152.9	49.4	50.7	62.8	47.0	56.8	74.2	91.0	60.7
Yb	195.0	754.3	519.5	1933.6	281.8	253.3	484.6	300.2	569.6	413.5	577.2	594.5
Lu	19.8	83.8	47.8	312.2	34.1	31.3	63.0	30.8	107.0	38.1	60.5	122.0

Notes: Elp I: elpidite I, Elp II: elpidite II, Arm: armstrongite, Git: gittinsite, Zrn: zircon, b.d.: below detection. The compositions listed are average results of seven analyses. The concentrations of the major elements were established by wavelength-dispersion spectrometry; concentrations of the rare-earth elements were established by laser-ablation ICP–MS.

the samples studied. Overall, the lowest Ca content in elpidite I was observed in samples from pegmatites; the Zr/Hf value is somewhat higher (~ 75) in elpidite I from the main-phase granite than in that from aplites or pegmatites (<70). Elpidite I from all rock types contains on the order of $n \times 10^3$ ppm REE+Y (Table 1), but samples from pegmatites and, especially, aplites, are significantly enriched in heavy lanthanides (HREE) relative to those from the main-phase granites (Fig. 4A). The chondrite-normalized La/Yb value $[(La/Yb)_{CN}]$ decreases from *ca.* 1.2 in samples from the main-phase granite to <1 in elpidite I from the pegmatites and <0.4 in the aplite paragenesis. The $(La/Nd)_{CN}$ value ranges from 1.7 to 2.8 in elpidite I from the main-phase granite, 1.5 to 2.9 in pegmatites, and 0.7 to 1.8 in aplites. A

negative Eu anomaly is well pronounced in all of the samples.

Only superposed metasomatic zoning is observed in the elpidite crystals, which involves partial substitution of Na by Ca and is accompanied by replacement of primary elpidite by elpidite II or armstrongite. Elpidite II typically contains several times more Ca (up to *ca.* 5.7 wt.% CaO or 0.6 atoms of Ca per formula unit) in comparison with its precursor (<1.5 wt.% CaO). In the main-phase peralkaline granites, elpidite II is systematically enriched in Hf (near-chondritic Zr/Hf), Y and REE relative to the primary elpidite, in contrast to their counterparts from pegmatites, which show essentially identical Zr/Hf values and REE patterns (Figs. 4B, C). Chondrite-normalized REE profiles of elpidite II are

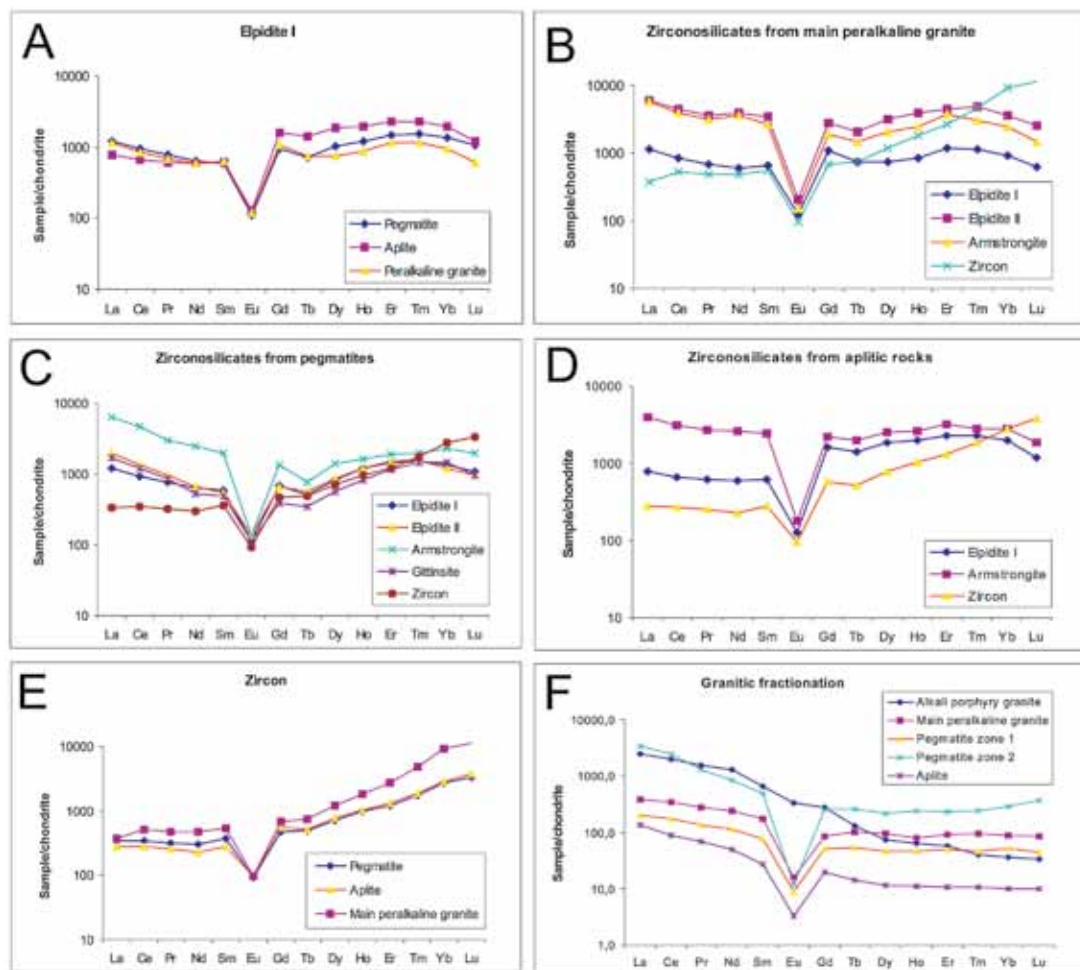


FIG. 4. Chondrite-normalized average REE abundances in elpidite (A) and other zirconosilicate minerals from the main-phase peralkaline granites (B), pegmatites (C) and aplites (D). (E) Compositional variation of late-stage zircon in granites, pegmatites and aplites. (F) Chondrite-normalized REE patterns of representative whole-rock samples.

essentially flat with a prominent negative Eu anomaly (Figs. 4B, C). The $(\text{La/Yb})_{\text{CN}}$ value is consistent and close to 1.6, whereas the $(\text{La/Nd})_{\text{CN}}$ value is 1.2–1.8 in elpidite II from the main-phase granite and noticeably higher (2.5–3.7) in pegmatites.

Armstrongite

Armstrongite is characterized by a uniform composition and significant REE enrichment in comparison with its precursor elpidite I in all analyzed samples. The range of Zr/Hf values (32–53) is comparable to that in elpidite II, but armstrongite is enriched in light rare-earth elements (LREE) relative to HREE [$1 < (\text{La/Yb})_{\text{CN}} < 3$]. Samples from the main-phase granite and aplite–pegmatite series exhibit similar ranges of $(\text{La/Nd})_{\text{CN}}$ values (on average, ~2.6 and 1.5, respectively).

Gittinsite

Gittinsite is devoid of detectable zonation and exhibits very little compositional variation across the entire set of samples. Only a few grains depleted in Zr relative to Si and Y were observed in association with stoichiometric gittinsite in the pegmatite–aplite series. In terms of its trace-element composition (Zr/Hf ratio and REE distribution), gittinsite from pegmatites is comparable to late-stage elpidite II (Table 1, Fig. 4C).

Zircon

In porphyritic alkali granite, zircon is the earliest Zr phase to crystallize. This primary zircon is not associated with any other Zr minerals. Unzoned crystals are nearly stoichiometric in composition; Ca, Mn, Fe, Ti, Th and U contents are near or below their limits of detection by WDS (Table 2). The zircon is characterized

by low levels of Y (*ca.* 1000 ppm) and superchondritic Zr/Hf values (*ca.* 55). Crystals of zircon projecting into interstitial spaces exhibit simple zonation consisting of a core compositionally identical to the unzoned crystals and an overgrowth enriched in Ca, Fe, Y, Yb, U and Th, but depleted in Hf (average Zr/Hf = 75) relative to the core (Fig. 3A, Table 2).

In all other rock types examined in the present work, zircon is one of the latest products of elpidite replacement. This late-stage zircon is compositionally similar to overgrowths on primary zircon in porphyritic granite in that it is enriched in Ca, Fe and Y, but depleted in Hf (Zr/Hf in the range 72–77). The chondrite-normalized REE patterns of late-stage crystals from different rock-types are similar and show enrichment in HREE [$(\text{La/Yb})_{\text{CN}} \approx 0.1$] and a negative Eu anomaly (Fig. 4E). Samples from the main-phase granite contain significantly higher levels of REE relative to those from pegmatites and aplites (Table 1) and show higher $(\text{La/Nd})_{\text{CN}}$ values ranging from 0.6 to 0.9 in the main-phase granite and from 0.9 to 1.4 in pegmatites and aplites.

WHOLE-ROCK GEOCHEMISTRY

A representative set of average whole-rock analyses is presented in Table 3. Relative to the earlier-emplaced porphyritic unit, the main-phase granite contains higher levels of SiO_2 , Zr, Nb, HREE and Y, but significantly lower Al_2O_3 , Mg, Ca, Sr, Ba, Ti, P and LREE contents. The decrease in Al content translates into an increase in the peralkalinity index [$(\text{K}_2\text{O} + \text{Na}_2\text{O})/\text{Al}_2\text{O}_3$, molar ratio] from 1.0 to 1.3. The K:Na ratio increases concomitantly with the level of differentiation. The Zr/Hf, Th/U, Nb/Ta, Y/Ho and Yb/Y values approach chondritic values in both rock types, whereas on average, $(\text{La/Yb})_{\text{CN}}$ decreases dramatically from 69 in the porphyritic unit to 4.5 in the main-phase granite. The REE pattern of the porphyritic granite is characterized by a steep positive slope and lacks a Eu anomaly, which is in sharp contrast with the pattern of the main-phase granite (Fig. 4F). Aplites are similar to the main-phase peralkaline granites in terms of their major-element geochemistry, but feature significantly lower levels of all trace elements documented (Table 3). Importantly, however, the Zr/Hf, Th/U, Nb/Ta, Y/Ho and $(\text{La/Yb})_{\text{CN}}$ values in the aplite samples are very close to those in the main-phase granite (46, 3.6, 20, 22 and 3.0, respectively). In the aplite–pegmatite series, the index of peralkalinity increases from 1.4 in the aplite to 2.5 in the blocky zone (zone 2) of pegmatites, which reflects a drop in Al_2O_3 content toward the interior of pegmatite veins. This is accompanied by a drastic increase in Mn, Sr, Ba, Y, REE, Zr, Nb, Ta, Th and U contents and a decrease in Na content, whereas the abundances of other elements do not follow a consistent pattern of variation. In the blocky zone, all key trace-element ratios greatly deviate from chondritic values [Zr/Hf = 1083, Th/U = 1.7, Nb/Ta = 70, Y/Ho = 93, Yb/Y = 0.04 and $(\text{La/Yb})_{\text{CN}}$

TABLE 2. REPRESENTATIVE AVERAGE CHEMICAL COMPOSITION OF PRIMARY ZIRCON FROM PORPHYRITIC ALKALI GRANITE

	1	2a	2b
CaO	b.d.	0.12	1.69
ThO ₂	0.09	0.11	0.15
UO ₂	b.d.	b.d.	0.21
SiO ₂	32.47	32.56	31.78
ZrO ₂	65.48	65.63	63.66
HfO ₂	1.42	1.47	0.97
MnO	b.d.	0.06	b.d.
FeO	0.05	0.08	0.16
TiO ₂	0.06	0.05	0.05
Y ₂ O ₃	0.13	0.11	1.87
Yb ₂ O ₃	b.d.	0.10	0.26
Total	99.70	100.29	100.80

Notes: (1) unzoned crystal, (2a) core of a zoned zircon crystal shown in Figure 3A, (2b) overgrowth on (2a); b.d.: below detection. The compositions were acquired by wavelength-dispersion spectrometry (*n* = 10).

CN = 11]. The border zone is geochemically transitional between the blocky zone and aplite.

DISCUSSION

Magmatic evolution

The observed trend of decreasing Ca, Sr and Ba contents, increasing peralkalinity and depletion in Eu relative to other REE (see above) suggests that the main-phase granites evolved from the same magma as the porphyritic unit by fractionation of potassium feldspar and Ca-rich albite. The drastic decrease in the content of LREE coupled with an enrichment in HREE and Zr in the main-phase unit is more difficult to explain. Fractionation of zircon, which is the main accessory constituent of the porphyritic granite (see above), would have produced an evolutionary trend of LREE

enrichment and Zr depletion, as seen, for example, in alkali granites of the Wiborg pluton in Finland (*e.g.*, Lukkari 2002). Trends remarkably similar to those observed in the Khan Bogd granites have been reported for A-type granites from Suzhou in China (Charoy & Raimbault 1994) and El-Sibai in Egypt (Abdel-Rahman & El-Kibbi 2001). The Suzhou and El-Sibai trends involve a decrease in Sr and Ba contents, an increase in Zr and Nb contents, “flattening” of the chondrite-normalized REE profile, and a depletion in Eu toward more evolved members of the magmatic series. In addition to fractionation of feldspars, which accounts for the depletion of large-ion lithophile elements, Charoy & Raimbault (1994) invoked segregation of an accessory phase enriched in LREE (such as allanite or monazite) and complexing of the HFSE with F to explain the observed enrichment in Zr, Nb and HREE. Abdel-Rahman & El-Kibbi (2001) proposed a similar petrogenetic scenario, but argued that the enrichment in HREE at El-Sibai is also due to the complexing of these elements with Na and F in the melt, which presumably culminates with the crystallization of arfvedsonite. The lack of accessory LREE hosts in the porphyritic granite from Khan Bogd suggests that the observed variations in the REE budget (Fig. 4F) were also driven by preferential partitioning of the HREE into evolved peralkaline melts, rather than early removal of LREE in allanite or monazite. The importance of fluorine in the fractionation of the HFSE in felsic melts has been further demonstrated in experimental and melt-inclusion studies (*e.g.*, Schaller *et al.* 1992, Keppler 1993, Schmitt *et al.* 2002). Although the existence of Zr–F complexes has been questioned on the basis of spectroscopic evidence derived from synthetic systems, the depolymerizing effect of F on the melt structure will increase the proportion of non-bridging oxygen atoms, which is conducive to enhanced Zr solubility (*e.g.*, Farges 1996).

Another key parameter that has a significant effect on Zr solubility in granitic melts is the level of their enrichment in alkalis. It has been well established experimentally (Watson 1979, Watson & Harrison 1983, Ellison & Hess 1994, Scaillet & Macdonald 2003) that the solubility of Zr is greatly enhanced by the formation of alkali zirconosilicate complexes in peralkaline systems. According to the experimental data of Marr *et al.* (1998) and Currie & Zaleski (1985), elpidite is a saturating phase only at low temperatures ($T \approx 600^\circ\text{C}$ at $P \approx 1$ kbar) and is replaced by vlasovite ($\text{Na}_2\text{ZrSi}_4\text{O}_{11}$) and zircon (Å quartz) with increasing T . Unaltered peralkaline granites at Khan Bogd and Strange Lake contain abundant elpidite, but lack primary zircon (Salvi & Williams-Jones 1995, Roelofsen & Veblen 1999, this work); development of elpidite after vlasovite in less-evolved members of the igneous sequence has been observed at Strange Lake (Birkett *et al.* 1992). The latter rocks were interpreted to have formed between 500 and 600°C and $P = 0.7$ kbar (Salvi & Williams-Jones 1992, 2006, Marr *et al.* 1998). The stability field

TABLE 3. REPRESENTATIVE AVERAGE CHEMICAL COMPOSITIONS OF SELECTED WHOLE-ROCK SAMPLES

	Porphyritic alkali granite EGD 009 264–350 m n = 3	Main- phase granite EGD 009 164–194 m n = 5	Pegmatite zone 1 KB-SO, EGD 009 n = 5	Pegmatite zone 2 KB-SO, EGD 009 n = 7	Aplitic rocks KB-SO, EGD 009 n = 3
No. of anal.					
SiO ₂ wt. %	72.08	74.21	71.16	76.82	73.56
TiO ₂	0.46	0.28	0.36	0.23	0.22
Al ₂ O ₃	12.93	10.36	7.38	4.41	10.08
Fe ₂ O ₃	3.31	4.59	9.81	8.66	5.15
MnO	0.18	0.22	0.22	0.37	0.16
MgO	0.29	0.10	0.09	0.16	0.11
CaO	0.74	0.48	0.37	0.29	0.26
Na ₂ O	4.63	4.82	6.13	4.18	6.23
K ₂ O	5.19	4.97	4.09	3.86	3.73
P ₂ O ₅	0.16	0.05	0.19	0.17	0.08
L.O.I.	0.36	0.41	0.48	0.69	0.35
Total	100.33	100.49	100.28	99.84	99.93
Ba ppm	378	94	14	161	19
Sr	92.0	28.1	12.0	53.0	6.7
Zr	864.4	1129.5	738.4	16897.0	586.0
Hf	18.4	31	3.7	15.6	12.8
Nb	23.9	60.4	21.5	431.8	5.93
Ta	1.35	3.5	1.08	6.18	0.3
Th	15.2	17.3	4.4	184.1	2.5
U	3.3	5.7	1.9	107.6	0.7
Y	113.5	158.3	49.8	1964.1	15.2
La	759.8	120.9	63.1	1059.6	41.9
Ce	1633.1	275.5	140.0	1969.5	71.6
Pr	192.5	33.4	16.8	157.2	8.5
Nd	784.9	144.0	68.5	513.3	30.1
Sm	125.8	34.3	14.9	95.7	5.3
Eu	24.6	1.2	0.7	0.9	0.2
Gd	71.3	22.1	13.6	66.2	5.0
Tb	6.1	4.9	2.5	12.4	0.7
Dy	23.6	30.4	15.1	69.1	3.6
Ho	4.6	5.7	3.4	17.1	0.8
Er	12.2	18.9	10.3	49.5	2.2
Tm	1.3	3.1	1.5	7.9	0.3
Yb	7.6	18.7	10.7	60.5	2.5
Lu	1.1	2.7	1.5	11.8	0.4

Note: this table was compiled on the basis of analyses of fresh samples from drill core (EGD 009) and surface outcrops (KB-SO).

of elpidite expands with P (Currie & Zaleski 1985), but, taking into account the history of tectonic uplift and the very slow rates of erosional unroofing in the South Gobi during the Mesozoic and Cenozoic (Kovalenko *et al.* 2006, Vassallo *et al.* 2007), it is unlikely that the currently exposed parts of the Khan Bogd complex were emplaced much below a depth of 1 km.

The pegmatite bodies and associated aplitic zones are undoubtedly related genetically and probably represent the most evolved magma-types at Khan Bogd. We used the whole-rock compositions in Table 3 and the mass-balance algorithm of Stormer & Nicholls (1978) to estimate the degree of crystal fractionation required to produce a typical pegmatite from a peralkaline granitic melt such as that which produced the main-phase granite. The best model, yielding a residual sum of squares of 0.1, requires fractionation of *ca.* 70 wt.% of alkali feldspar plus quartz with subordinate contributions from alkali amphibole and aegirine. Geochemical variations within the aplite–pegmatite series cannot be accounted for exclusively by crystal fractionation. The two most notable characteristics of the pegmatites are that their enrichment in LREE [$(La/Yb)_{CN} = 11$] is coupled with enrichment in Y to a greater extent than the similar-sized HREE ($Y/Ho = 93$, $Yb/Y = 0.04$), and that their key HFSE ratios deviate greatly from those in the host granites. This unusual trace-element budget, coupled with the absence in the early paragenesis of any primary phases that could selectively scavenge Hf and Ta from the melt, imply that some of the HFSE and REE were retained in the liquid, producing concomitant enrichment of that fluid in Zr, Nb, Y and U. A similar process of fractionation probably took place on a very small and limited scale in the porphyritic granite, where the late-stage zircon overgrowths projecting into

interstices are enriched in Zr relative to Hf, U relative to Th, and Y relative to Yb in comparison with the earlier-crystallized cores (Table 2). The significance and composition of this hypothetical fluid are discussed below.

Postmagmatic evolution and HFSE remobilization

Although the enrichment of granitic rocks at Khan Bogd in Zr and other HFSE can be attributed first and foremost to magmatic differentiation, there is no doubt that these elements were remobilized during the postmagmatic evolution of the complex (*cf.* Boily & Williams-Jones 1994, Mungall & Martin 1996, Schmitt *et al.* 2002). Field and textural evidence indicates that postmagmatic alteration affected both main-phase and aplite–pegmatite units, but is most extensive in apical parts of the intrusion. The extent of alteration, probably reflecting variations in fluid–rock ratio (see below), ranges from isolated thin veinlets of secondary zirconosilicates cross-cutting the precursor elpidite, to pseudomorphs lacking any relict material. The alteration appears to have been a two-step process, involving (1) replacement of the primary elpidite by Ca-rich elpidite II or armstrongite, and (2) development of zircon at the expense of the elpidite and armstrongite. The late-stage zircon is associated with either calcite or gittinsite plus quartz. The REE fluorocarbonate minerals are also an important component of these late-stage parageneses (Fig. 5). The occurrence of zircon and carbonate minerals appears to be restricted to the areas where the granite and associated pegmatites were affected by intense faulting and fracturing, recognizable on the scale of an outcrop. Importantly, there is little evidence for large-scale dispersal of Zr by the fluid; the late-stage

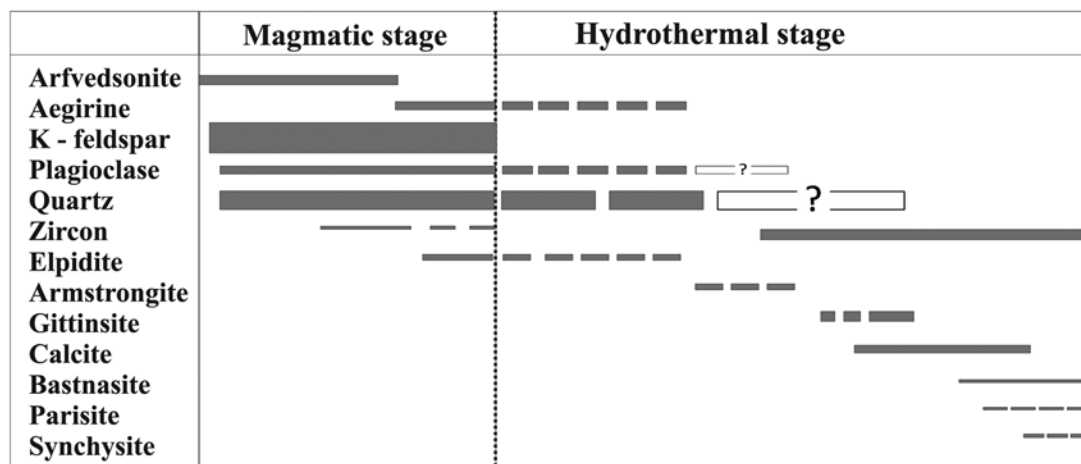
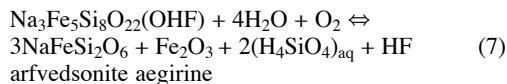
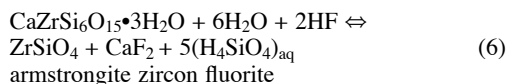
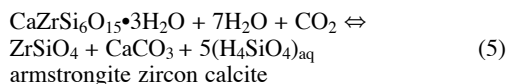
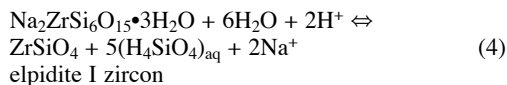
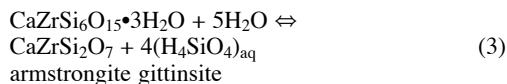
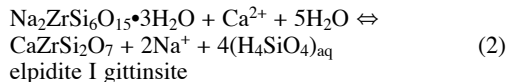
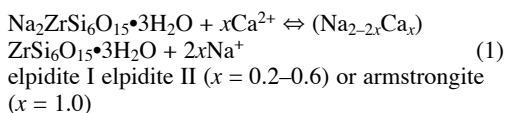


FIG. 5. Generalized paragenetic sequence for the system granite – pegmatite – aplite.

carbonate-bearing parageneses outside the zirconosilicate pseudomorphs contain only scarce grains of an unidentified Y–Zr phase too small for accurate analysis.

That most secondary zirconosilicates replacing primary elpidite I contain significant Ca and are associated with calcite, fluorocarbonates and fluorite indicates that the fluid responsible for remobilization of Zr and other HFSE at Khan Bogd was enriched in Ca, CO₂ and F. Preferential partitioning of the LREE+Y and Zr into the fluid relative to HREE and Hf would explain the observed trend of increasing whole-rock (La/Yb)_{CN}, Y/Ho and Zr/Hf values from granites to pegmatites, as well as comparatively lower (La/Yb)_{CN}, Y/Ho and Zr/Hf values in primary elpidite from pegmatites (see above), assuming that the pegmatite-forming melt reached elpidite saturation after the separation of the fluid. This interpretation is consistent with the published trace-element compositions for hydrothermal zircon and fluorite, which indicate that CO₂-bearing fluids facilitate Y–Ho and Zr–Hf decoupling in granites (Rubin *et al.* 1989, Bau & Dulski 1995, Schmitt *et al.* 2002). Unfortunately, the paucity of experimental data on HFSE and REE partitioning between conjugate felsic melts and fluids does not allow for a meaningful comparison with the geochemical trends observed at Khan Bogd.

Calcic metasomatism involving a CO₂–F-rich fluid has been also proposed as the driving force behind the replacement of primary elpidite and remobilization of HFSE at Strange Lake (Salvi & Williams-Jones 1995, 2006, Roelofsen & Veblen 1999). Manifestations of this metasomatism are remarkably similar in the two complexes, *i.e.*, the composition of pseudomorphs after elpidite, the order of crystallization and morphology of secondary zirconosilicates, and their association with vein-hosted REE mineralization and zones of conversion of primary arfvedsonite to aegirine (Salvi & Williams-Jones 2006). The most notable difference between the two localities is the much greater abundance of armstrongite and late-stage zircon among the replacement products at Khan Bogd. In our samples, armstrongite is about ten times more abundant than gittinsite, whereas zircon–armstrongite pseudomorphs are even more abundant than those composed entirely of armstrongite. In addition, the association of late-stage zircon with calcite is very common in our samples (*e.g.*, Figs. 3F, L), but has not been reported by either Salvi & Williams-Jones (1995) or Roelofsen & Veblen (1999). Fluorite occurs at both localities, but is much more common at Strange Lake. The above observations can be summarized in the form of the following reactions:



The physical parameters governing the subsolidus crystallization of secondary zirconosilicates and aegirine have been discussed in detail by Boily & Williams-Jones (1994), Marks *et al.* (2003), and Salvi & Williams-Jones (2006). According to their estimates, the Ca metasomatism involved a low-temperature oxidizing and weakly acidic fluid ($\leq 300^\circ\text{C}$, HM buffer, pH > 4.7) derived from, or equilibrated with, the metamorphic wallrocks. Although an extrinsic source of metasomatic fluid cannot be ruled out completely in our case, the available geochemical evidence indicates that it could be derived from evolved pegmatite-forming melts (see above).

The reasons for the initial replacement of elpidite by armstrongite (reaction 1) at Khan Bogd, as opposed to gittinsite (reaction 2; Salvi & Williams-Jones 1995) are not clear. We hypothesize that initially, the activity of silica in the system was maintained at a relatively high level by dissolution of feldspar and quartz at a low fluid:rock ratio. A subsequent drop in $a(\text{H}_4\text{SiO}_4)_{\text{aq}}$ owing to cooling and an increase in $P(\text{CO}_2)$ (Shmulovich *et al.* 2001, Wang *et al.* 2004, Newton & Manning 2009), caused probably by “opening” of the system, initiated progressive replacement of the armstrongite and relict elpidite by gittinsite and zircon (equilibria 2–7). The overwhelming majority of pseudomorphs after elpidite I are porous (*e.g.*, Figs. 3D–K) and the proportion of pore space ranges significantly in general agreement with the changes in molar volume calculated by Salvi & Williams-Jones (1995). We agree with these authors that the ubiquitous presence of quartz in the secondary parageneses containing gittinsite and zircon does not mean that the fluid was inherently saturated

with respect to quartz. It appears more likely that a drop in silica solubility (*e.g.*, due to cooling) triggered precipitation of quartz in the final stages of metasomatic reworking of the granites and pegmatites.

Secondary zircon replacing the earlier-formed zirconosilicates contains lower levels of REE and, especially, the light lanthanides [(La/Yb)_{CN} in the range 0.1–0.3 *versus* ≥ 1.0 in the earlier-formed phases], which indicates that a significant proportion of these elements was released in reactions (4) and (5). These elements were then sequestered as the late-stage REE fluorocarbonate mineralization confined to veinlets and pseudomorphs after elpidite I. A simple mass-balance calculation, based on the average compositions of armstrongite [$\Sigma\text{REE} = 10750$ ppm, (La/Yb)_{CN} = 2.6] and zircon [$\Sigma\text{REE} = 4050$ ppm, (La/Yb)_{CN} = 0.3], shows that during the mole-for-mole replacement of armstrongite by zircon (reaction 5), up to 90% of the total REE was released into the fluid, and the lanthanide budget of that fluid was dominated by LREE [(La/Yb)_{CN} = 4.7]. This result is in agreement with the composition of fluorocarbonate minerals associated with the late-stage zircon and calcite (authors' unpubl. data). A more precise assessment of changes in HFSE and REE budget accompanying reactions (1–6) is difficult because of the textural complexity of the secondary parageneses. The source of F required for the precipitation of REE fluorocarbonates and minor fluorite (reaction 6) is somewhat problematic because, according to experimental data, this element partitions strongly into the melt in alkali-rich systems (Xiong *et al.* 1998, Chevychelov *et al.* 2005). We infer that the principal source of F enrichment in the metasomatic fluid was the conversion of primary arfvedsonite containing *ca.* 2 wt.% F (reaction 7) to aegirine.

Subsolidus processes in alkaline silicate rocks: comparisons with published data

Late-stage mineral parageneses produced by reaction of CO₂–F-rich fluids with primary HFSE-bearing phases appear to be a common, if not ubiquitous, characteristic of evolved alkali granites and pegmatites (Montero *et al.* 1998, Wang *et al.* 2000, Schmitt *et al.* 2002, Salvi & Williams-Jones 2006, Berger *et al.* 2008, Breiter *et al.* 2009, Thomas *et al.* 2009). Similar processes have also been documented in peraluminous granites and silica-undersaturated syenitic rocks (*e.g.*, Maruéjol *et al.* 1990, Chakhmouradian & Mitchell 2002, Andersson & $\Leftrightarrow$ 2003). However, few of these authors attempted to constrain the physical parameters of fluid–rock interaction, or the source of fluid(s). Most workers are in agreement that the hydrothermal overprint occurred at shallow crustal levels (<2.5 km), but the published temperature estimates range from as high as 600°C (Salvi & Williams-Jones 2006) to <50°C for those parageneses that contain zeolites (*e.g.*, Thomas *et al.* 2009). Overall, we agree with the latter authors that the

transition from magma to fluid is “somewhat obscure” and that the hydrothermal stage probably spans a range of temperatures. Although the fluid is typically interpreted to be of orthomagmatic origin, in many cases, there is convincing trace-element or isotopic evidence for contributions from crustal reservoirs of fluid (*e.g.*, Maruéjol *et al.* 1990, Boily & Williams-Jones 1994, Breiter *et al.* 2009). Because the published experimental data on Ca partitioning between conjugate felsic melts and fluids lack consistency, it is impossible to establish if the low-Ca peralkaline granitic melts at Khan Bogd (*ca.* 0.5 wt.% CaO) were capable of producing a calcic metasomatizing fluid. We consider it likely that at least some of the Ca in the fluid was derived from the country rocks, all of which contain much higher levels of Ca than the granite, reaching 11 wt.% CaO in Carboniferous volcanoclastic units (Wainwright 2008).

A survey of the literature shows that the most distinctive characteristic of late-stage hydrothermal parageneses in evolved granites is the presence of members of the bastnäsite–synchysite series [Ca_xREE(CO₃)_{1+x}(F,OH)] that act as the principal host for the lanthanides and show a wide range of REE patterns from extremely LREE-enriched [(La/Y)_{CN} > 5000; Schmitt *et al.* 2002] to nearly flat (Breiter *et al.* 2009) to HREE-enriched [(La/Y)_{CN} < 2; Maruéjol *et al.* 1990]. Interestingly, there appears to be no correlation between the relative degree of enrichment of these minerals in specific lanthanides and the presence or absence of HREE-rich phosphate (rarely, arsenate) phases in the same assemblage. For example, late-stage Y phases have been reported in association with both (Ce,La)- and Y-dominant fluorocarbonates (Maruéjol *et al.* 1990, Breiter *et al.* 2009). The contents of Ca, Th and other substituent elements also vary significantly among these different localities, resulting in a plethora of fluorocarbonate minerals including such exotic compositions as bastnäsite-(La) and “parisite-(Y)”. At Khan Bogd, the crystallization of abundant late-stage zircon after earlier formed elpidite II and armstrongite enriched in HREE [(La/Yb)_{CN} $\leq$ 0.3] led to progressive enrichment of the fluid in light lanthanides, which were deposited as Ce-dominant fluorocarbonates late in the hydrothermal stage (Fig. 5).

The behavior of Zr and Hf during the subsolidus alteration involving a CO₂–F-rich fluid is less well constrained. In the majority of secondary parageneses described in the literature, zircon appears to be the major Zr–Hf host in a wide range of physical conditions. It may represent a primary phase unaffected by alteration (Berger *et al.* 2008), a primary mineral re-equilibrated with the fluid (Breiter *et al.* 2009), or a newly formed phase precipitated from the fluid (Andersson & Förster 2003). From the published data and our own observations, it appears that zircon is a stable hydrothermal phase over a wide range of temperatures and fluid regimes, especially in terms of $a(\text{H}^+)$, $a(\text{F}^-)$, and $P(\text{CO}_2)$ values, and the limits of

its stability are essentially defined by the activities of silica, Na^+ and Ca^{2+} in the aqueous fluid (see reactions 4–6 above). These limitations explain why gaidonayite, catapleiite (both $\text{Na}_2\text{ZrSi}_3\text{O}_9 \cdot 2\text{H}_2\text{O}$) and calcio-catapleiite ($\text{CaZrSi}_3\text{O}_9 \cdot 2\text{H}_2\text{O}$) are stable hydrothermal zirconosilicate phases in undersaturated syenites and carbonatites [low $a(\text{H}_4\text{SiO}_4)$, high $a(\text{Na}^+)$ or $a(\text{Ca}^{2+})$], whereas armstrongite and elpidite occur in silica-saturated parageneses characterized by higher levels of $a(\text{H}_4\text{SiO}_4)$ in the fluid (Salvi & Williams-Jones 1995, Chakhmouradian & Mitchell 2002, Chakhmouradian & Zaitsev 2002, Yakovenchuk *et al.* 2005, this work). Thermodynamic calculations (Marr & Wood 1992) indicate that with increasing temperature, catapleiite-type phases and elpidite are replaced by an assemblage of quartz plus parakeldyshite ($\text{Na}_2\text{ZrSi}_2\text{O}_7$) or vlasovite ($\text{Na}_2\text{ZrSi}_4\text{O}_{11}$), respectively, but the temperature at which these desilication reactions occur has not been constrained experimentally.

CONCLUSIONS

The evolution of an alkali-rich granitic magma at Khan Bogd produced primitive microcline–phyric granites and, through subsequent fractionation of feldspar, more evolved HFSE–HREE-enriched and Sr–Ba-depleted peralkaline granites and, ultimately, aplite–pegmatite bodies in the apical parts of the intrusion. In contrast to the porphyritic unit, where HFSE are concentrated primarily in zircon, peralkaline granites and their associated pegmatites host polyphase Zr mineralization composed of primary Ca-poor elpidite and secondary zirconosilicates produced by reaction of the primary elpidite with a Ca – CO_2 – F -rich fluid. Hydrothermal alteration involved successive replacement of primary elpidite by late-stage Ca-rich elpidite and armstrongite, followed by crystallization of gittinsite and, finally, zircon developed at the expense of the Ca zirconosilicates. Replacement of primary elpidite is more complete in near-surface samples than in drill-core material from a depth greater than 180 m. The crystallization of late zircon was accompanied by deposition of calcite, LREE fluorocarbonates and minor fluorite in thin veinlets and stringers. The development of these secondary parageneses involved a low-temperature weakly acidic fluid of orthomagmatic lineage, possibly enriched in Ca through interaction with volcanic and sedimentary country-rocks. The mineralogical and textural complexity of zirconosilicate pseudomorphs after elpidite and their association with carbonates can be explained by variations in the activity of silica and other dissolved components accompanying cooling and changes in fluid:rock ratio at the hydrothermal stage.

ACKNOWLEDGEMENTS

We thank Stefano Salvi and Axel K. Schmitt for their constructive reviews of this manuscript, and Tyson

Birkett and Robert F. Martin for editorial comments that led to improvements. We also acknowledge the help of Uondon Majigsuren with the organization of fieldwork in Mongolia, and Ivanhoe Mines Mongolia Inc. for allowing us to examine and sample material from drill hole EGD 009. Miroslava Gregerova, Hana Cihlarova, Marketa Hola, Petr Gadas and Radek Skoda helped in the acquisition of analytical data. This work was supported by grant MSM0021622412 and an industry grant from The Anchor House Inc. (ARC), whose generosity is gratefully acknowledged.

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Received February 28, 2010, revised manuscript accepted August 27, 2011.

