Mineral compositions of syn-collisional granitoids and their implications for the formation of juvenile continental crust and adakitic magmatism

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Abstract:

Continental collision zones have been proposed as primary sites of net continental crustal growth. Therefore, studies on syn-collisional granitoids with mafic magmatic enclaves (MMEs) are essential for testing this hypothesis. The Baojishan (BJS) and Qumushan (QMS) syn-collisional plutons in the North Qilian Orogen (NQO) on the northern margin of the Tibetan Plateau have abundant MMEs in sharp contact with host granitoids, sharing similar constituent minerals but with higher modal abundances of mafic minerals in MMEs. The QMS host granitoids have high Sr/Y and La/Yb ratios showing adakitic compositions, different from the BJS granitoids. Based on bulk-rock compositions and zircon U-Pb age dating, recent studies on these two plutons proposed that MMEs represent cumulates crystallized early from the same magmatic system as their host granitoids, and their parental melts are best understood as andesitic magmas produced by partial melting of the underthrusting upper ocean crust upon collision with some terrigenous sediments under amphibolite facies.

Here, we focus on trace element geochemistry of the constituent mineral phases of both MMEs and their host granitoids of the QMS and BJS plutons. We show that different mineral phases preferentially host different trace elements, e.g., most rare earth elements (REEs and Y) reside in titanite (only found in the QMS pluton), amphibole, apatite, epidote and zircon (mostly heavy-REEs), and high field strength elements (HFSEs) reside in biotite, titanite, amphibole and zircon. Based on the mineral chemical data, we testify that for these two plutons, MMEs are of similar cumulate origin, crystallized from primitive andesitic melts in the early stage of granitoid magmatism. The primitive andesitic melts for these syn-collisional granitoids are most likely produced by partial melting of the oceanic crust, supporting the hypothesis of
continental crustal growth considering the syn-collisional granitoids represent juvenile continental crust.

As evidenced by distinct mineral compositions, the two plutons have different parental magma compositions, e.g., higher TiO$_2$ content, higher Sr/Y and La/Yb ratios in the QMS parental magmas, a signature best understood as being inherited from the source. The higher TiO$_2$ content of the parental magma for the QMS pluton leads to the common presence of titanite in the QMS pluton (absent in the BJS pluton), crystallization of which in turn controls the trace element (REE, Y, Nb, Ta and others) systematics in the residual melts towards an adakitic signature. Therefore, parental magmas with high TiO$_2$ content and high Sr/Y and La/Yb ratios, as well as their further fractionation of titanite, are important factors in the development of adakitic compositions, as represented by the QMS host granitoids. This model offers a new perspective on the petrogenesis of adakitic rocks. The present study further demonstrates that in general, mineral chemistry holds essential information for revealing the petrogenesis of granitoid rocks.

**Keywords**: adakitic rocks; mineral chemistry; mafic magmatic enclaves; North Qilian Orogen; syn-collisional granitoid petrogenesis
INTRODUCTION

The bulk continental crust is inferred to be produced by low degree partial melting of the primitive mantle in Earth’s early history because of the compositional complementarity between incompatible element enriched continental crust and incompatible element depleted oceanic crust, the depletion of which is thought to be inherited from the upper mantle, depleted as the result of continental crust extraction (e.g., O’Nions et al., 1979; Hofmann, 1988). However, how the continental crust with andesitic composition may have derived from mantle-derived basaltic magmas remains unclear. While it is widely accepted that island arcs are the main building blocks responsible for the growth of the continental crust (e.g., Taylor, 1967, 1977), considerable amounts of the continental crustal materials have also been recognized to be lost during crustal destruction by subduction removal (e.g., Stein and Scholl, 2012). Meanwhile, the growth of the continental crust is episodic (e.g., Condie, 1998). Hence, the “Island-arc” model (Taylor, 1967, 1977) may not be responsible for continental crustal growth.

On the basis of studies of the syn-collisional andesites and granitoids from southern Tibet (Niu et al., 2007; Mo et al., 2008), Niu et al. (2013) proposed that continental collision zones are primary sites for net continental crust growth. Importantly, Niu et al. (2013) demonstrates that syn-collisional andesites and granitoids show remarkable similarity to bulk continental crustal compositions in all the major and trace element abundances and ratios, suggesting that syn-collisional granitoids represent juvenile continental crust resulting from partial melting of the subducting/subducted upper oceanic crust with minor terrigenous sediments under amphibolite facies (Mo et al., 2008; Niu & O’Hara, 2009; Niu et al., 2013). Studies on the petrogenesis of syn-collisional granitoids are important for testing this hypothesis. Our studies on syn-
collisional granitoids with mafic magmatic enclaves (MMEs) from orogens on the Tibetan Plateau and adjacent regions (e.g., Qinling, Kunlun and Qilian orogens) support this hypothesis in many aspects, including significant mantle Nd-Hf isotopic contributions to the granitoids (Huang et al., 2014, 2015, 2016, 2017; Chen et al., 2015, 2016, 2018; Li et al., 2016, 2017; Duan et al., 2016; Zhang et al., 2016; Kong et al., 2017). Nevertheless, quantification is necessary in order to develop this testable hypothesis into a comprehensive theory. This requires refined experimental petrology on oceanic crust melting in the context of continental collision and detailed major and trace element systematics in the constituent minerals of syn-collisional granitoids and the hosted MMEs.

As magmatic products, the mineralogy and mineral compositions hold the key to magmatic conditions and processes (e.g., Sha & Chappell, 1999; Belousova et al., 2002a; Hoskin & Schaltegger, 2003; Piccoli et al., 2011; Bruand et al., 2019), such as oxygen fugacity (e.g., Belousova et al., 2002b), magma mixing (McLeod et al., 2011; Bruand et al., 2014; Laurent et al., 2017; Hu et al., 2017), fractional crystallization (Marks et al., 2008) and subsequent metasomatism (e.g., Smith et al., 2009). Comprehensive geochemical studies on both major and accessory minerals are thus necessary to genuinely understand the petrogenesis of igneous rocks (e.g., Bachmann et al., 2005; Gao et al., 2009). In this paper, we present mineral in situ trace element data on two well-characterized syn-collisional granitoid plutons, i.e., the Baojishan (BJS) and Qumushan (QMS) plutons in the North Qilian Orogen (NQO) on the northern margin of the Tibetan Plateau (Chen et al., 2015, 2016, 2018). Both QMS and BJS plutons have similarly abundant MMEs in sharp contact with host granitoids, while the QMS host granitoids show adakitic characteristics, which is different from the QMS MMEs or the
BJS granitoids (Chen et al., 2015, 2016). Although the adakitic QMS host granitoids have been interpreted as resulting from fractional crystallization of primitive andesitic magmas (Chen et al., 2016), it needs quantifying by considering detailed and specific controls of different crystallized minerals in the granitoid systems. Our data provide further constraints on the petrogenesis of MMEs in the context of syn-collisional granitoid magmatism, and also help explain why the QMS host granitoids have adakitic compositions, whereas the BJS granitoids do not, offering new insights into the widely discussed and debated origin of adakite and adakitic rocks.

GEOLOGICAL BACKGROUND AND PETROLOGY

The NQO at the northern margin of the Tibetan Plateau is an early Paleozoic suture zone formed through the subduction of the Qilian seafloor and subsequent collision between the Alashan Block and the Qilian-Qaidam Block (Fig. 1a,b; Song et al., 2006, 2013, 2014a,b). It comprises the southern and northern ophiolite belts, separated by an island-arc igneous complex. The ophiolite in the southern belt is thought to represent the ocean crust formed at the ocean ridge, while the ophiolite in the northern belt is of a back-arc basin origin (Fig. 1a,b; Xia et al., 2003, 2012; Xia & Song, 2010; Song et al., 2013; Xiao et al., 2013). The Qilian ocean basin is thought to be formed since c. 710 Ma with a recorded seafloor subduction history between c. 520 and c. 440 Ma, just prior to continental collision (Song et al., 2013). The BJS and QMS granitoid plutons are located in the northern ophiolite belt of the eastern NQO. Both BJS and QMS plutons show a zircon U-Pb crystallization age of c. 430 Ma (Chen et al., 2015, 2016), which is consistent with the timing of continental collision (i.e., c. 440 – 420 Ma; Song et al., 2009, 2013).
The BJS and QMS plutons contain abundant MMEs of varying shape and size (a few to tens of centimeters in diameter) in sharp contact with their host granitoids (Fig. 1c,d). The hosts of both plutons are granodioritic, mainly composed of plagioclase (c. 40 – 50 %) + quartz (c. 20 – 30 %) + biotite (c. 10 – 20 %) + amphibole (c. 5 – 10 %; Fig. 2). The MMEs are dioritic with the same mineralogy as their host, but have finer grain size and greater modal amphibole, less modal plagioclase and quartz, i.e., amphibole (c. 25 – 45 %) + biotite (c. 15 – 20 %) + plagioclase (c. 20 – 40 %) + quartz (c. 5 – 10 %; Fig. 2). Pyroxene is not found in the MMEs and their host granitoids in either pluton. Accessory minerals are mainly apatite, epidote, titanite, zircon, muscovite and K-feldspar with varying modal abundances in both MMEs and their host plutons (Fig. 2). Among others, epidote is more common in the BJS pluton (especially in host granodiorites; e.g., Fig. 2a-c), while apatite is more common in the QMS pluton. Titanite (up to c. 500 µm in length) is only found in the QMS pluton (e.g., Fig. 2e-h). Apatite crystals are always euhedral. Epidote crystals are anhedral, and some of them occur as inclusions in amphibole. Titanite is anhedral and shows varying colored patches.

ANALYTICAL METHODS

MMEs and their host granitoids of the QMS and BJS plutons were prepared as 60 µm thick sections, and major and accessory minerals were analyzed using LA-ICP-MS in the Laboratory of Ocean Lithosphere and Mantle Dynamics (LOLMD) at the Institute of Oceanology, Chinese Academy of Sciences. We used a 193 nm ultra-short pulse excimer laser ablation system (Analyte Excite produced by Photon-machines Company) coupled with an Agilent 7900 ICP-MS instrument. Operation conditions of LA-ICP-MS analysis are summarized in Table DR2 (see details in caption of Fig. DR1). Considering the relatively
homogeneous compositions of igneous minerals, a large spot size of 40 µm was used with a low energy density (4.72 J/cm²) to ensure fractionation with increasing ablation depths was minimized. During each run, fifty-three elements, including both major and trace elements, were analyzed. Acquisition times for background (gas blank) and subsequent sampling were 25 s and 50 s, respectively. The Agilent Chemstation was utilized for the acquisition of each individual analysis.

Off-line data reduction, including signal selection, drift correction and quantitative calibration was done using ICPMSDataCal (Liu et al., 2008; Lin et al., 2016). For anhydrous minerals (feldspar, titanite and zircon), all the analyzed elements in each run were normalized to 100 % and calibrated using an ablation yield correction factor (AYCF; Liu et al., 2008) based on analysis of multiple reference materials, i.e., NIST SRM 610, USGS BCR-2G, BIR-1G, BHVO-2G and a synthesized glass GSE-1G (Jochum et al., 2005). For hydrous minerals (amphibole, biotite, epidote, apatite, muscovite and carbonate), we chose 42Ca (for apatite and carbonate) and 28Si (for silicate minerals) as the internal standards for data calibration, which were previously analyzed using an electron probe micro-analyzer (EPMA; Chen et al., 2015, 2016). In some cases, we instead used mineral compositional data from the rocks with similar composition and mineralogy to our rocks from the literature (Dahlquist, 2002; Tables DR3,4,6,7,9). Each batch of sample analysis started and ended with the analysis of the multiple reference materials (i.e., NIST SRM 610, USGS BCR-2G, BIR-1G, BHVO-2G and GSE-1G). Analysis of every five samples was bracketed with analysis of GSE-1G twice, one of which was used for monitoring drift and applying drift correction (if any), the other indicating the analytical precision and accuracy, i.e., within 5 % and below 10 % respectively for most
analyzed elements (Fig. DR1; recommended values are referred to GeoReM). During the analysis, we purposely chose spots of fresh areas and avoided other mineral inclusions to ensure representativeness of the analyzed mineral compositions.

RESULTS

Mineral chemical data for both MMEs and their host granodiorites from both plutons are summarized in Tables DR3-9, and primitive mantle normalized trace element data for these minerals are presented in Fig. 3b-h, with the primitive mantle normalized trace element diagram for the average bulk rock compositions for comparison (Fig. 3a).

Amphibole

Amphibole from the QMS pluton has higher Mg# (63.2 to 70.4 vs. 53.8 to 62.5) and lower Al$_2$O$_3$ (4.63 – 8.49 wt.% vs. 7.33 – 10.56 wt.%) than that from the BJS pluton (Fig. 4; Table DR3). The QMS amphibole contains higher light rare earth elements (LREEs) and lower heavy rare earth elements (HREEs)-Y than the BJS amphibole (e.g., [La/Yb]$_N$ = 2.03 – 7.08 vs. 0.19 – 1.81; Fig. 3b), consistent with greater LREE/HREE fractionation in the QMS bulk rocks (Fig. 3a and Table DR1). The QMS amphibole has higher Nb/Ta than the BJS amphibole (Figs. 3b&4g and Table DR3). The QMS amphibole also has higher Ni and lower Sc contents than the BJS amphibole (Fig. 4h). Amphiboles in MMEs contain consistently higher Ni-Cr and lower Sc than those of their host granitoids in both plutons (e.g., Fig. 4h) but share similar contents for most other analyzed trace elements (Table DR3).

Biotite

Biotite from the QMS pluton shows higher Mg# (59.3 to 64.2 vs. 52.6 to 58.6) and lower
Al₂O₃ (13.45 to 15.22% vs. 14.82 to 16.71%) than that of the BJS pluton (Fig. 5; Table DR4).

Both QMS and BJS biotite contains high Ba-Rb-Cs-K, c. 1000 times the primitive mantle values (Fig. 3c). The QMS biotite has somewhat higher LREEs-Sr contents and much lower Ta (Fig. 3c) with higher Nb/Ta ratios (Fig. 5a-b,d) than the BJS biotite (Table DR4). Furthermore, Nb/Ta ratios of biotite slightly decrease rimwards (Fig. 5a,b). Some small muscovite crystals (Fig. 2a) were also analyzed, containing the highest Rb contents of all analyzed minerals, up to 731 ppm (Table DR4). For both plutons, biotites from MMEs show a similar composition to those of their host granitoids (Table DR4).

**Feldspar**

Plagioclase An% (Ca/[Ca+Na+K]) values gently decrease toward crystal rims (Fig. 6a-d), and the QMS plagioclase has lower An values than that in the BJS pluton (Fig. 6e-h), 22% vs. 39% on average (Table DR5). Plagioclase has high Pb, Sr, Ba, Cs and LREEs contents (Fig. 3c), which generally decrease with decreasing An (Fig. 6e-h), except gentle increase of Ba for the BJS plagioclase (Fig. 6f). Plagioclase in the QMS pluton shows obviously higher Ba-Cs-Sr and lower Y than that in the BJS pluton (e.g., Figs. 3d&6e-h), consistent with such differences in bulk rocks between the two plutons (Fig. 3a; Table DR1). For both plutons, plagioclase from MMEs show similar compositions to those of their host granitoids (Fig. 3d; Table DR5).

**Apatite**

Apatite contains consistently high Th, U and REEs contents, c. 1000 times the primitive mantle values (Fig. 3e). Apatite from the QMS pluton shows higher LREEs, lower HREEs and thus higher [La/Yb]₈ than that in the BJS pluton (Fig. 3e and Table DR6), which is consistent with what is observed in the bulk rocks (Fig. 3a; Table DR1).
Epidote

Epidote contains the highest Sr and Pb contents of all analyzed minerals (c. 100 and c. 1000 times primitive mantle values, respectively; Fig. 3f). Because of small grain sizes, epidote in MMEs of the QMS pluton was not analyzed. Epidote from the QMS host granitoids has higher Sr and LREEs and lower HREEs than that from the BJS pluton (Fig. 3f), consistent with the bulk-rock compositions (Fig. 3a).

Titanite

Titanite is only found in host and MMEs of the QMS pluton and has the highest Nb-Ta-Ti-Th-U-LREEs contents of all minerals analyzed, up to c. 10^4 times the primitive mantle values (Fig. 3g). Some titanite crystals show great variations in color and composition, with firtree-like zoning or patches and can be divided into two parts, i.e., more reddish parts and less reddish parts (Fig. 7). The more reddish parts show higher Nb-Ta-Zr-Hf-Th-U-Pb-REE-Y contents to variable extents (e.g., Figs. 7&8; Table DR8), but their LREE/HREE (e.g., La/Yb) and Th/U ratios generally overlap with those of the less reddish parts (Fig. 8d). No obvious titanite compositional differences exists between MMEs and their host rocks (Figs. 3g&8).

Others (zircon and carbonate)

Our in situ mineral analysis in thin sections (Table DR9) and previous analysis on zircon separates (Chen et al., 2015, 2016; Table DR10) show that zircon has the highest Zr-Hf-HREE contents and the lowest [LREE/HREE]_N among all the minerals analyzed (Fig. 3h; Tables DR9&10), e.g., c. 10^3 times the primitive mantle values for HREEs. Relative to the BJS zircon, the QMS zircon has generally higher Th-U-LREE contents with relatively higher [LREE/HREE]_N and Th/U ratios (0.7 vs. 0.4 on average), and lower Eu/Eu* (=...
Eu$_N$/[Sm$_N$$\times$Gd$_N$]$^{1/2}$, 0.55 vs. 0.61 on average) and Ce/Ce* values (= Ce$_N$/[La$_N$$\times$Pr$_N$]$^{1/2}$, 71 vs. 125 on average; Fig. 3h; Tables DR9&10). Some small carbonate crystals are analyzed to show high Sr (up to c. 400 ppm) and variably high LREEs and U (Table DR9).

DISCUSSION

Identifying trace element budgets

Previous studies have reported that accessory minerals (mainly focused on titanite, apatite and zircon) can be significant trace element hosts (especially for REEs and high field strength elements [HFSEs]; e.g., Sha & Chappell, 1999; Tiepolo et al., 2002; Belousova et al., 2002a,b; Hoskin and Schaltegger, 2003; Marks et al., 2008; McLeod et al., 2011; Piccoli et al., 2011; Bruand et al., 2014). To better understand how elements are controlled by different minerals, we reconstructed element budgets for average bulk-rock compositions of the MMEs and their host granitoids from the BJS and QMS plutons using average mineral compositions and modal mineralogy (Table DR11) normalized to averaged values of analyzed element contents in bulk rocks (Fig. 9). Modal proportions for amphibole-plagioclase-biotite-epidote-apatite-titanite-carbonate-zircon are estimated using average bulk-rock major element contents through Cramer’s rule (see details in Table DR11). Considering that Si is the only major component for quartz, the proportion of quartz is simply calculated by using 1 minus the sum of other mineral proportions. The estimated mineral proportions are consistent with our petrologic observations, suggesting both are reliable. Some large uncertainties for trace element budgets are caused by uncertainties associated with modal estimation and mineral compositional variations at both crystal and bulk-rock scales. The compositional reconstruction in Fig. 9 is useful for understanding trace element distribution between phases (Table DR12) in the bulk-rock make-
up, which is essential in correctly interpreting the petrogenesis.

Different trace elements have their phase preference. For example, elements K-Rb-Cs-Ba are dominantly hosted in biotite; Pb-Sr in feldspar and epidote; Th-U-REEs-Y mainly in amphibole, titanite (only found in the QMS pluton), apatite and epidote; Nb-Ta-Zr-Hf in titanite, zircon (also for some HREEs) and amphibole; transition metals (e.g., Sc-V-Cr-Ni) mainly in amphibole and biotite. Biotite is also an important host for Ti-Nb-Ta. All these indicate that accessory minerals, such as titanite, apatite, zircon and epidote, are as important as major minerals in hosting their preferred trace elements in bulk rocks. The understanding on trace element budgets forms the basis for understanding which mineral fractionation can control what geochemical variations during magma evolution. In the following, we use this knowledge to discuss the petrogenesis of MMEs and their host granitoids for the QMS and BJS plutons.

**Genetic link between the QMS and BJS plutons and the formation of MMEs**

*Petrogenesis of MMEs and syn-collisional granitoids*

Strictly speaking, granitoids like other intrusive rocks do not represent melts, but “mechanical” mixtures of solidified “interstitial” melts and crystalline phases (Niu, 2005). Hence, the bulk-rock composition of granitoids is largely determined by the type and mode of minerals present. It follows that mineral-mode controlled bulk-rock composition alone may not provide unique information on the parental magmas. Because minerals must be in equilibrium with the melt from which they crystallize, mineral compositions thus directly record the melt compositions. Therefore, both mineral chemistry and bulk-rock composition are required to constrain the petrogenesis of these granitoids and their MMEs, including the compositions of their parental magmas, magma sources, as well as the petrogenetic processes operating.
Both BJS and QMS syn-collisional granitoid plutons are situated in the eastern NQO (Fig. 1b). They were produced in the same tectonic setting through the same process and at the same time (the same zircon crystallization age of c. 430 Ma; Chen et al., 2015, 2016). Specifically, the MMEs and host granitoids of both plutons have similar mineral assemblages with more abundant mafic phases in MMEs than their host, and share similarly high large ion lithophile elements (LILEs) and low HFSEs with relatively flat HREE patterns (Fig. 3a) and positive $\varepsilon_{Hf}$ (t) values (Chen et al., 2015, 2016). Based on these geochemical features, Chen et al. (2015, 2016) concluded that primitive magmas parental to both plutons resulted from partial melting of the underthrusting upper oceanic crust upon collision, with minor terrigenous sediment contributions under amphibolite facies (Niu et al., 2013; Fig. 10).

For the formation of MMEs, different models have been proposed in the literature. The MMEs are thought to represent mantle-derived basaltic magmas mixing with granitic magmas (e.g., Vernon, 1984; Chen et al., 2009; McLeod et al., 2011; Bruand et al., 2014), refractory restite after granitic magma extraction (e.g., Chappell and White, 1991), or early crystallized mafic cumulate fragments dispersed in the co-genetic granitic magmas (e.g., Dahlquist, 2002; Niu et al., 2013). Specifically, for the BJS and QMS plutons, the compositional similarity of minerals from MMEs and their host granitoids shown in this study (Figs. 3-8) indicates that both the MMEs and their host granitoids share common parental magmas, with their mineral compositions strongly dependent on parental magma compositions. The generally overlapping mineral compositions are inconsistent with MMEs being of restite origin or external origin (e.g., Hu et al., 2017). Furthermore, the relatively uniform compositions for all the analyzed individual mineral crystals (i.e., rather weak core-to-rim variations without complex zoning;
Figs. 4-7) indicate the absence of disequilibrium, arguing against a magma-mixing origin of the MMEs (Browne et al., 2006; Chen et al., 2009; Bruand et al., 2014; McLeod et al., 2011; Laurent et al., 2017). Hence, our new mineral data support that MMEs and respective host granitoids share the same parental magmas. This is consistent with the results of previous studies (Chen et al., 2015, 2016) on bulk-rock geochemistry (e.g., uniform Sr-Nd-Hf isotopic composition) and the same zircon U-Pb age of MMEs and host granitoids for these two plutons.

Our studied MMEs show a finer grain size than their host granitoids, which is in fact consistent with an earlier cumulate origin of the same magmatic systems if we consider the process of magma emplacement, “magma chamber” development and evolution (Fig. 10). When the primitive magmas intrude into the “cold” crust to develop a magma chamber, rapid cooling can significantly enhance crystal nucleation and result in the crystallization of fine-grained cumulates dominated by mafic minerals near the walls and base of the magma chamber. These fine-grained cumulates are later dispersed as MMEs in the slowly cooling magma bodies that solidified as the coarse-grained granitoid host. Hence, fine-grained MMEs of cumulate origin can be present in the host granitoid through this process.

Despite the similarities in bulk-rock incompatible element patterns (Fig. 3a) and mineral compositions (Figs. 3-8) between MMEs and host granitoids as a result of their same parental magma, MMEs also show some compositional differences from their host granitoids in the BJS and QMS plutons, e.g., significantly higher middle (M)-HREE contents (Fig. 3a) and Sc-V-Cr-Ni (Table DR1). These differences are in fact controlled by their high modal amphibole content, as these elements are less incompatible in amphibole (e.g., Bottazzi et al., 1999; Tang et al., 2017; Zhang et al., 2019), which is consistent with amphibole to be the primary host mineral
for M-HREEs in our modelling results (Table DR11 and Fig. 9), and our petrologic observations (Fig. 2). The slight differences of LREEs between MMEs and host granitoids from the QMS (Fig. 3a) are caused by titanite, which is only present in the QMS. Hence, bulk-rock REE variations between MMEs and their host granitoids for both the QMS and BJS plutons are controlled by different modal abundances of amphibole (and titanite also for the QMS pluton), i.e., more amphibole and titanite for higher REEs in the MMEs. Similarly, the bulk-rock variations of Sc-V-Cr-Ni between MMEs and their host granitoids for the two plutons (Table DR1) result from the varying modal abundances of amphibole and biotite, which are the most important minerals for hosting these elements (Fig. 9). All of these chemical characteristics are consistent with the much stronger fractionation of these minerals (e.g., amphibole, biotite) at earlier stages of magma evolution, in support of MMEs representing the early cumulate formed from the same magmatic system, followed by the formation of their host granitoids.

*Implications on continental crustal growth*

Experimental studies have shown that Fe/Mg ratios of amphibole positively correlate with that of their equilibrium andesitic melt and that the amphibole Mg# systematically decreases with decreasing temperature during magma fractionation at both low- and high-pressure conditions (Alonso-Perez *et al.*, 2009). Thus, the amphibole Mg# can be used to evaluate the Mg# and degree of fractionation of the equilibrium melt, which reflects whether amphibole formed from primary basaltic melts or andesitic melts (Carmichael, 2002; Hidalgo & Rooney, 2010; Rooney *et al.*, 2011; Tiepolo *et al.*, 2012; Ribeiro *et al.*, 2016).

The overlapping Mg# values of our analyzed amphibole from MMEs and host granitoids also indicate the same parental magma for MMEs and host granitoids in each pluton (Fig. 4).
These analyzed Mg\# values (i.e., 63 – 70 for the QMS amphibole and 54 - 63 for the BJS amphibole) overlap with those of the liquidus amphiboles in experiments on andesitic melts (< 65; Alonso-Perez et al., 2009; Prouteau and Scaillet, 2013), indicating that MMEs and host granitoids of the two plutons are derived from andesitic melts. Although andesitic melts can also result from the evolution of basaltic melts, the observed mineral assemblage of amphibole and feldspar without pyroxene, together with the positive $\varepsilon_{\text{Hf}}$ (t) values (mantle signature) of these rocks (Chen et al., 2015, 2016) and recent modelling for the fractionation effects of NQO syn-collisional granitoids (Chen et al., 2018) suggest that parental magmas for syn-collisional granitoids from these two plutons are most likely primitive andesitic melts. Importantly, the volume of andesitic melts as the result of basaltic magma evolution is minor and the fractionation of basaltic magmas cannot produce volumetrically rather significant (on the order of $c. 10^5$ – $10^6$ km$^3$) syn-collisional granitoids along each and every orogenic belt we studied and globally (Niu, 2005; Niu et al., 2013). Hence, our new data on mineral compositions further support that these syn-collisional granitoids result from primitive andesitic magmas produced by partial melting of the underthrusting oceanic crust in response to continental collision (Fig. 10), which can contribute to the net continental crust growth if these syn-collisional granitoids are preserved in continental collision zones (Mo et al., 2008; Niu & O’Hara, 2009; Niu et al., 2013; Chen et al., 2015, 2016, 2018).

**Geochemical differences between the QMS and BJS plutons and the adakitic characteristics of the QMS host granitoids**

*Compositionally distinct parental magmas for the two plutons*

Although the QMS and BJS plutons share a common tectonic setting in space and time
as discussed above, bulk-rock compositions of the QMS granitoids and MMEs are clearly
different from those of the respective BJS granitoids and MMEs, e.g., the QMS granitoids and
MMEs have higher Mg#, TiO₂, REEs and HFSEs with higher LREE/HREE ratios and lower
CaO (Fig. 3a and Table DR1; Chen et al., 2015, 2016). The same mineral phases in the two
plutons also show systematic differences accordingly (Figs 4-6, 11). Amphibole and biotite in
the QMS pluton have higher Mg# (Figs. 4-5), while feldspar exhibits lower An % (Fig. 6). The
REE-hosting minerals (i.e., amphibole, apatite, epidote and zircon) in the QMS pluton show
generally higher LREE/HREE ratios than those in the BJS pluton (Figs. 3&11). Biotite and
amphibole, which are important hosts for Nb and Ta, in the QMS plutons have similar Nb
contents but variably lower Ta contents than those in the BJS pluton (Tables DR3 and DR4),
resulting in characteristically higher Nb/Ta ratios of these two minerals from the QMS pluton
(Figs. 3b,c&4g&5d). Hence, the bulk-rock chemical differences between MMEs and host
granitoids are controlled by varied modal mineralogy as a consequence of magma evolution
(e.g., more amphibole crystallized in MMEs responsible for higher REE contents of MMEs),
while it is the mineral compositional differences between QMS and BJS plutons that determine
the bulk-rock compositional differences between the two plutons. Because mineral
compositions record the compositions of melts in equilibrium with the minerals, these
systematic mineral compositional differences (e.g., Figs. 3-8) indicate that the two plutons
evolved from compositionally different parental magmas.

Because amphibole as the liquidus phase has “similar” chemistry to andesitic magmas, it
can be used to constrain the parental melt compositions (Hidalgo et al., 2007; Tiepolo et al.,
2012; Chambefort et al., 2013; Ribeiro et al., 2016; Tang et al., 2017). Considering the effect
of melt compositions, we used partition coefficients between amphibole and basaltic-andesitic melts (data source from https://earthref.org/GERM/ and Hidalgo et al., 2007; Table DR13) to calculate trace element compositions of the melt in equilibrium with the amphibole. The calculated compositions of melt in equilibrium with the QMS amphibole show greater REE fractionation (e.g., give the range of \([La/Yb]_N > 7.58 - 26.4 \) vs. \(0.72 - 6.75\) for the BJS equilibrium melt) and higher Sr/Y ratios than those for the BJS pluton (Figs. 12&13). Therefore, this further demonstrates that the andesitic magmas parental to the two plutons are distinctly different, reflecting compositional differences of their magma source.

*The adakitic characteristics of the QMS host granitoid*

“Adakite” is defined by its distinctive geochemical signatures, i.e., high SiO$_2$ (≥ 56 wt.%), Al$_2$O$_3$ (≥ 15 wt.%), Sr (> 400 ppm), Sr/Y (> 40) and La/Yb ratios (> 20), low Y (< 18 ppm) and HREEs (Yb < 1.9 ppm), and is originally thought to be produced by melting of young (no older than 25 Ma) and warm subducting oceanic crust under eclogite or garnet amphibolite facies conditions (Defant & Drummond, 1990). However, recent studies have found that adakitic rocks can be produced in different tectonic settings through different geological processes, e.g., mixing of basaltic and felsic magmas (Chen et al., 2013; Streck et al., 2007), melting of mafic lower crust (Gao et al., 2004; Chung et al., 2003), and fractional crystallization of parental basaltic magmas (e.g., Castillo et al., 1999, 2012; Wang et al., 2005, 2007; Macpherson et al., 2006; Rodríguez et al., 2007; Ribeiro et al., 2016).

The QMS host granitoids show adakitic characteristics, i.e., high Sr/Y and La/Yb ratios (89 and 33 on average, respectively; Fig. 13 and Table DR1), which is different from the QMS MMEs or the BJS granitoids. In this study, we discuss detailed and specific controls of all the
crystallized minerals such as amphibole, plagioclase, biotite, apatite, zircon, titanite, epidote in
the granitoid systems as illustrated in Fig. 13. The bulk-rock MMEs and host granitoids of the
QMS pluton consistently show higher Sr/Y and La/Yb ratios than those of the BJS pluton (Fig.
13; Chen et al., 2015, 2016), which is also true for their constituent minerals (e.g., amphibole,
biotite, plagioclase and apatite; Fig. 11&13d, Tables DR3-9). In Fig. 13, the high Sr/Y and
La/Yb ratios of the calculated melts in equilibrium with the MME amphiboles for the QMS
pluton resemble adakitic compositions, while those for the BJS pluton do not, reflecting that
the parental magma of the QMS pluton had high Sr/Y and La/Yb ratios. Thus, the systematic
differences of Sr/Y and La/Yb ratios in both bulk-rock and mineral compositions between the
two plutons (Figs. 11-13) must have been inherited from their different parental magmas. All
these observations demonstrate explicitly that compositions of parental magmas exert a primary
control on whether they have the potential to evolve to adakitic compositions.

Despite the relatively higher Sr/Y and La/Yb ratios of the parental magma for the QMS
pluton, it is the host granitoid, not the MMEs, of the QMS pluton that clearly shows adakitic
characteristics (Fig. 13a,b; Table DR1). The Sr/Y and La/Yb ratios of MMEs are lower than
their parental magmas (Fig. 13a,b). This is consistent with the understanding that the MMEs do
not represent melt compositions but are of cumulate origin. This, in turn, indicates that primitive
andesitic melts parental to the QMS granitoid with high La/Yb and Sr/Y can further evolve into
adakitic melts through fractional crystallization of the MME mineral assemblage. This MME
fractionation that leads to adakitic melts is modelled in Fig. 13. For this, we (1) assume the
parental andesitic melts are in equilibrium with the MME amphibole of the QMS pluton, (2)
apply Rayleigh fractional crystallization, and (3) use the modelled mineral modal abundances

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in the QMS MMEs (Table DR11) to approximate the co-precipitating phase assemblage of 25% amphibole + 45% plagioclase + 20% biotite + 1.7% apatite + 0.5% titanite + 2.4% epidote + 0.03% zircon, which is generally consistent with the petrographic observation (Fig. 2). Note that the bulk-rock compositions of the MMEs and samples of their host granitoid plot in complement with respect to the model parental melt, which is best illustrated in Fig. 13a.

Modelling shows that about 20% fractionation of the melts can produce the high Sr/Y and La/Yb ratios observed in the QMS host rocks (Fig. 13). Considering the mineral fractionation model in Fig. 13a, 0.1 – 0.2 % titanite fractionation is enough to increase Sr/Y ratios in the melts to be as high as in the QMS host rocks, which is consistent with the very low Sr/Y ratios of titanite (c. 0.02; Fig. 13d and Table DR8) and its relatively common presence in the QMS pluton (Fig. 2e-h). Amphibole (< 40%) and zircon (< 1%) fractionation can also lead to the increase of Sr/Y ratios in the melts as high as the values of the QMS host rocks (Fig. 13a). The effect of apatite fractionation is insignificant, i.e., c. 5 – 7% apatite is required to increase Sr/Y ratios in the melts to be similar to the values of the QMS host rocks (Fig. 13a), which is not supported by apatite modal abundances (no more than 2% based on the analyzed P₂O₅ contents of bulk rocks, Table DR11). In addition, considering zircon (with [La/Yb]₆ << 1.0) and titanite have the highest Yb contents (up to hundreds of ppm) among all the minerals analyzed (Fig. 3 and Tables DR8,9), 0.2% titanite or zircon can lead to the increase of La/Yb ratios to be as high as in the QMS host rocks (Fig. 13b). No more than 40% amphibole fractionation will result in the observed increase of La/Yb ratios in the melts. All of these are consistent with our modelled mineral modal abundances of the QMS MMEs (Table DR11) and much lower Sr/Y and La/Yb ratios of these minerals than in primitive melts parental to the QMS pluton (Figs. 8e,f, 11, 13d).
Furthermore, Eu/Eu* values of the melts can also increase correspondingly with the fractionation of titanite (0.2 %), according to the Eu/Eu* difference we observed between MMEs and their host granitoids of the QMS pluton (Fig. 13c).

Considering the distinction of mineral assemblages between the two plutons, i.e., the common presence of titanite in the QMS pluton and the absence of titanite in the BJS pluton (Table DR11), our data indicate that the fractionation of titanite is the most important mineral to effectively increase both Sr/Y and La/Yb ratios in the residual melts and is most likely required for the formation of the adakitic characteristics of the QMS host rocks (Figs. 10&13). Although amphibole fractionation can also result in the increase of Sr/Y and La/Yb ratios in the residual melts, the higher degree of amphibole fractionation in the BJS pluton than in the QMS pluton (e.g., 44% vs. 25% in MMEs in the modelling, Table DR11) is expected to result in even greater increases of Sr/Y and La/Yb ratios, which are inconsistent with the observed lower Sr/Y and La/Yb ratios in the BJS host granitoids (Fig. 13a,b). Thus, the effect of the amphibole fractionation to cause the adakitic signatures is not as important as that of the titanite fractionation. Although plagioclase crystallization will tend to decrease La/Yb and especially Sr/Y ratios in the residual melts, its effect on these ratios may have been suppressed by the fractionation of other minerals such as titanite and amphibole (Fig. 13).

Titanite crystallization may be controlled by magmatic conditions. However, because both BJS and QMS granitoids are produced by partial melting of the underthrusting oceanic crust in response to continental collision under the amphibolite facies at the same time, it is more likely that the QMS and BJS pluton share similar magmatic conditions. Using AlT (i.e., Al content on tetrahedral site, which is sensitive to pressure) and Na + K (a temperature-sensitive indicator)
of amphibole, Chen et al. (2018) have shown that most syn-collisional granitoids from the NQO, including both QMS and BJS granitoids, have crystallized under similar conditions at upper crustal pressures of c. 200 MPa and temperatures of 785 – 900 °C. Hence, the magmatic crystallization condition is not the cause responsible for the different mineral fractionation in the QMS and BJS plutons. It may also be considered that titanite is likely to be crystallized in relatively oxidized rocks, but this crystallization process is actually accompanied with the stabilisation of other minerals, e.g., the hydration of pyroxene to hornblende (7 Hedenbergite + 3 Ilmenite + 5 Quartz + 2 H₂O = 3 Titanite + 2 Fe-Actinolite; Frost et al., 2000). However, neither pyroxene nor significant variations of ilmenite/magnetite modal abundances is observed in the QMS granitoids. In addition, there is no clear difference in analyzed LOI contents and hydrous mineral abundances between these two plutons, indicating their similar water/volatile contents. In fact, fractionation of titanite is thus primarily controlled by the melt composition (e.g., Front et al., 2000; Seifert & Kramer, 2003), e.g., titanite can crystallize only if it is on the liquidus in melt compositions with high Ti and Ca/Al ratios, with high Ca facilitating the stabilisation of titanite (over ilmenite). Both QMS and BJS granitoids are metaluminous, supporting the formation of titanite (e.g., Frost et al., 2000; Seifert & Kramer, 2003; Prowatke and Klemme, 2003), yet titanite is only found in the QMS granitoids. Considering Ti is the requisite major component for titanite (CaTiSiO₅), the crystallization of titanite in the QMS granitoids is thus most likely caused by the higher TiO₂ content of the parental melt, which is inherited from the source. This is also consistent with the noticeably higher TiO₂ content of the QMS granitoids than the BJS granitoids (e.g., 0.97 wt.% in averaged QMS MMEs composition vs. 0.65 wt.% in averaged BJS MMEs composition). The high TiO₂ content in parental magmas
facilitated the formation of titanite, the fractionation of which then further controlled the trace element (REE, Y, Nb, Ta and others) systematics in the residual melts towards an adakitic signature.

Considering the highly variable composition of melts caused by the partial melting of the subducting/subducted ocean crust with varied compositions (e.g., Niu & Batiza, 1997), the ultimate control is the parental magma composition (major, minor and trace elements), which determines the mineralogy, phase equilibria and trace element behavior during magma evolution. Magmas parental to the QMS pluton with high TiO$_2$ content and Sr/Y and La/Yb ratios will finally evolve to melts with adakitic signatures after the titanite fractionation, whereas the non-adakitic compositions of the BJS granitoids may be attributed to lower Sr/Y and La/Yb ratios of their parental magmas and the absence of titanite as a result of low TiO$_2$ content. Therefore, parental magmas with high TiO$_2$ content, high Sr/Y and La/Yb ratios and their further fractionation of titanite due to this original composition, are important characteristics of magmas evolving towards adakitic compositions, as represented by the QMS host granitoids. The potential role of parental magma compositional variation as a result of source compositional variation and the subsequent magma evolution in generating adakitic signature proposed here offer a new insight towards better understanding the widely debated petrogenesis of adakitic rocks.

CONCLUSIONS

In this study, we report major and trace element data on minerals from two well-characterized syn-collisional granitoid plutons in the NQO on the northern margin of the Tibetan plateau to understand the petrogenesis of syn-collisional granitoids with MMEs, which
allows us to test the hypothesis that continental collision zones are primary sites for net continental crustal growth.

(1) Different trace element budgets in syn-collisional granitoids are systematically identified, and this forms the basis for understanding the effects of mineral fractionation on the compositional variation of the residual melt.

(2) Mineral chemistry further testifies that for both QMS and BJS plutons, MMEs are cumulates produced by earlier crystallization of the primitive andesitic melts, which originated from partial melting of subducting/subducted oceanic crust, whereas their host rocks represent the more evolved melt. Given that these syn-collisional granitoids represent juvenile continental crust, our studies support the hypothesis that continental collision zones are primary sites for net continental crust growth by partial melting of the subducted oceanic crust.

(3) The mineral compositional differences between QMS and BJS plutons indicate compositionally different parental magmas, corroborated by different compositions of the calculated melts in equilibrium with amphibole. We propose that parental magma composition with high TiO₂ content and high Sr/Y and La/Yb ratios exert a primary control on the formation of adakite and adakitic rocks as in the case of the QMS host granitoids. Among other factors, parental magma compositional variations due to magma source compositional variations control the mineralogy, mineral chemistry and trace element behavior during subsequent magmatic evolution.

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**SUPPLEMENTARY MATERIALS**

Supplementary data can be found in the online version of this article:

**Table DR1** Average bulk-rock compositions for MMEs and hosts from the BJS and QMS plutons in the eastern NQO (Chen et al., 2015, 2016)

**Table DR2** Operation conditions of LA-ICP-MS for analysis of mineral compositions in this study

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Table DR3 Analytical results of amphibole in the BJS and QMS plutons using LA-ICP-MS

Table DR4 Analytical results of biotite and muscovite in the BJS and QMS plutons using LA-ICP-MS

Table DR5 Analytical results of plagioclase and orthoclase in the BJS and QMS plutons using LA-ICP-MS

Table DR6 Analytical results of apatite in the BJS and QMS plutons using LA-ICP-MS

Table DR7 Analytical results of epidote in the BJS and QMS plutons using LA-ICP-MS

Table DR8 Analytical results of titanite in the BJS and QMS plutons using LA-ICP-MS

Table DR9 Analytical results of carbonate and zircon in the BJS and QMS plutons using LA-ICP-MS

Table DR10 Analytical results of zircon by Chen et al. (2015, 2016) in the BJS and QMS plutons using LA-ICP-MS

Table DR11 Modelling mineral weight proportions and chemical element budgets in MMEs and host rocks of the QMS and BJS plutons

Table DR12 Partition coefficients for several selected mineral pairs in our studied rocks

Table DR13 Calculated compositions of the melts in equilibrium with amphibole and partition coefficients between amphibole and melts used in this study.

Fig. DR1 Analytical accuracy (RE in %; a) and precision (RSD in %; b) of LA-ICP-MS analysis determined by a synthesized reference glass GSE-1G (Jochum et al., 2005) as an unknown sample.
FIGURE CAPTIONS

Figure 1 (a-b) Geological map of NQO and sample locations for this study (after Chen et al., 2015, 2016). (c-d) Field photos showing the sharp contact between host rocks and MMEs.

Figure 2 (a-h) Photomicrographs for host granitoids (in the left column, i.e., a,c,e,g) and MMEs (in the right column, i.e., b,d,f,h) in pairs from the BJS and QMS plutons in the eastern NQO. (a-d) are for granitoids from the BJS pluton with more epidote; (e-h) are for granitoids from the QMS pluton with abundant titanite. Mineral abbreviations are: AB – albite, AMP – amphibole, AP – apatite, BT – biotite, EP – epidote, MUS – muscovite, QZ – quartz, TTN – titanite, ZRN – zircon. Primitive mantle values are from Sun & McDonough (1989).

Figure 3 (a) Primitive mantle (Sun & McDonough, 1989) normalized trace element pattern for average bulk-rock compositions of MMEs and their host rocks from the BJS and QMS plutons (Chen et al., 2015, 2016). (b-h) Primitive mantle (Sun & McDonough, 1989) normalized average mineral compositions of MMEs and their host granitoids from the QMS and BJS plutons respectively.

Figure 4 (a-d) Mg# (= 100*Mg/[Mg+Fe²⁺]) and Nb/Ta ratio profiles for amphibole in MMEs and their host granitoids from the BJS (a-b) and QMS (c-d) plutons. H – Host, M – MME, AVG – average. Numbers are read as follows, e.g., ⑧ 64.5/29.3 means analytical spot 8 has Mg# = 64.5 and Nb/Ta = 29.3 given in Table DR3. (e-h) Elemental and ratio co-variation diagrams for amphibole from the two plutons.

Figure 5 (a-b) Nb/Ta ratio variation of biotite from the BJS and QMS plutons. Numbers are read as follows, e.g., 8: 15.5 means analytical spot 8 has Nb/Ta = 15.5 given in Table DR4. (c-d) Mg# variation diagrams for Al₂O₃ and Nb/Ta ratios of biotite from the two plutons.
**Figure 6 (a-d)** Anorthite and Sr content variation for plagioclase in MMEs and their host granitoids from the BJS (a-b) and QMS (c-d) plutons. Numbers are read as follows, e.g., ⑧ or 8: 44/723 means analytical spot 8 has An = 44 and Ba = 723 ppm given in Table DR5. **(e-h)** An-variation diagrams for Sr, Ba, La and Y of plagioclase from the two plutons.

**Figure 7** Titanite compositional variation for the BJS and QMS plutons. Analytical spot numbers in both left and right panels are as given in Table DR8. The position numbers highlighted in red in the right panels represent those analyzed points with more reddish colour, the element contents of which plot in grey areas as indicated in the right panels. This shows that the more reddish parts tend to have higher Nb-Ta-Zr-Hf-Th-U-Pb-La (LREE)-Lu (HREE).

**Figure 8** Elemental and ratio co-variation diagrams for titanite from the QMS pluton. In (e-f), the modelled bulk parental magma composition using the average composition of amphibole in MMEs of the QMS pluton (Sr/Y = 30, La/Yb = 23) is also plotted, for comparison. The extremely low Sr/Y and La/Yb ratios of titanite relative to those of the bulk parental magma indicate that the fractionation of titanite can effectively increase these ratios in the residual melts.

**Figure 9** Reconstructed elemental budgets in bulk-rock MMEs and their host rocks from the BJS and QMS plutons, normalized against their average bulk-rock compositions (Table DR1). “% whole rock” = 100% * \[ \frac{\sum_{i=1}^{n} \sum_{j=1}^{m} X_{ij} Y_{j}}{Z_{j}} \], where i refers to different mineral phases, j refers to different chemical elements, X refers to modelled mineral modal proportions (Table DR11), Y refers to average content of chemical element j in analyzed mineral i (Tables DR3-9), Z refers to average content of chemical element j in analyzed bulk-rock samples (Table DR1), as indicated by the red dot-dashed lines in each panel. Bars with different colours
represent different mineral hosts.

**Figure 10** Cartoon illustrating the petrogenesis of MMEs and host rocks. The development of MMEs in the context of the syn-collisional granitoid magma generation and evolution can be generalized in three stages (Niu *et al.*, 2013; Chen *et al.*, 2015, 2016, 2018): Stage I – Compositionally heterogeneous ocean crust plus some terrigenous sediments melt to produce andesitic magmas during the continental collision under amphibolite facies conditions; Stage II – Interaction of such magmas with mantle peridotite during ascent; Stage III – intrusion of the andesitic magmas into the “cold” crust to develop a magma chamber with the rapid cooling resulting in the crystallization of fine-grained cumulate dominated by mafic minerals near the walls and base of the magma chamber to be later dispersed as MMEs in the slowly cooling magma bodies that solidified as the granitoid host. Among other minerals, fractionation of titanite, zircon and amphibole will lead to significant increase in Sr/Y and La/Yb ratios as observed in host rocks, which may lead to the formation of adakitic signatures as displayed by the QMS host rocks. BCC – bulk continent crust.

**Figure 11** Co-variation diagrams for Sr/Y vs. Sr and La/Yb vs. La of various minerals in the BJS and QMS plutons. The parental magma composition calculated using the average composition of amphibole in the QMS MMEs (Sr/Y = 30, La/Yb = 23) is also indicated for comparison. Notably, fractionation of those minerals with lower Sr/Y and La/Yb ratios than the bulk parental magma will increase these two ratios in the residual melts.

**Figure 12** Primitive mantle (PM; Sun & McDonough, 1989) normalized trace element abundances for calculated compositions of melt in equilibrium with amphibole from MMEs and their host rocks of the BJS and QMS plutons, respectively. The thick black lines are the
average bulk rock compositions of MMEs and their host granitoids from the two plutons, respectively. Average mineral compositions in Tables DR3-9 are also plotted to indicate the contribution of various minerals.

**Figure 13** Co-variation diagrams of Sr/Y – Y (a), La/Yb – Yb (b) and Eu/Eu* – [La/Yb]_N (c) for melts in equilibrium with amphibole in MMEs of QMS (the red area) and BJS (the grey area) plutons. In (d), the average Sr/Y and La/Yb ratios of different minerals in the QMS MMEs are plotted for comparison, i.e., those lower than the original melt composition (Sr/Y = 30, La/Yb = 23) can effectively increase these two ratios in the residual melts. The original melt composition is calculated by using the average composition of amphibole in the QMS MMEs. (a-c) Also shown are modelling results for the evolution of the original melt initially in equilibrium with MME amphibole in the QMS pluton, assuming mineral modal abundances as in Table DR 11 (25% amphibole + 45% plagioclase + 20% biotite + 1.7% apatite + 0.5% titanite + 2.4% epidote + 0.03% zircon). The insert diagrams in (a-c) show modelling results for the related Rayleigh fractional crystallization of various minerals. The parental magmas of the QMS pluton (the red area) clearly show higher Sr/Y and La/Yb ratios than those of the BJS pluton (the grey area), and are comparable to adakites. The fractionation of amphibole, titanite, and zircon further increases these two ratios and finally form the adakitic characteristics of the QMS host granitoids. The selected partition coefficient values are from Green *et al.* (1993), Hidalgo *et al.* (2007), Matsui (1977) and Klein *et al.* (1997), and are given in Table DR13. The discrimination lines in (a-b) are from Defant & Drummond (1990) and Richards & Kerrich (2007), respectively.
Xiao et al., Fig 1, Geological map

Fig. 1 Geological map
Xiao et al., Fig. 2 Photomicrographs

Fig. 2 Photomicrographs
Xiao et al. Fig. 3 PM normalized trace element distributed patterns of averaged bulk-rock composition and different minerals.

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Fig. 3 Trace element distributed diagrams
Xiao et al., Fig. 4 Mg# and Nb/Ta profiles in amphibole

Fig. 4 Amphibole compositional profiles
Xiao et al., Fig. 5 Nb/Ta profiles of biotite

Fig. 5 Biotite Nb-Ta profile

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Fig. 6 Plagioclase compositional profile
Fig. 7 Titanite compositional profile
Xiao et al., Fig. 8 Element co-variation for titanite

![Graphs showing compositional profiles of titanite elements](http://www.petrology.oupjournals.org/)

**Fig. 8 Titanite compositional profiles**

- Graph (a): La vs. Yb
- Graph (b): Th vs. U
- Graph (c): Nb/Ta vs. Nb
- Graph (d): La/Yb vs. Th/U
- Graph (e): Sr/Y vs. Sr
- Graph (f): La/Yb vs. La

Legend:
- Light / reddish colour:
  - **MME**
  - **Host**

Sources:
- [Xiao et al.](http://www.petrology.oupjournals.org/)
Xiao et al., Fig. 9 Reconstructed element budgets normalized by analyzed element contents

Fig. 9 Trace element budgets
Xiao et al., Fig. 10 Mechanism diagram for the petrogenesis of MMEs and adakitic rocks

**Stage I:**
- **Andesitic magmas** (with mantle isotope signature and BCC composition)
- Melting under amphibolite facies
- 95% Compositional heterogeneity
- Ocean crust + 5% Continental materials

**Stage II:**
- High Mg# and Cr-Ni
- Interact with mantle peridotite
- Andesitic magmas

**Stage III:**
- Host rocks
- Residual melts with adakitic signatures
- MMEs
- Fractional crystallization
- TTN, ZRN, AMP, PL + BT + EP
- Andesitic magmas

Fig. 10 Mechanism diagram
Fig. 11 La/Yb vs. Sr/Y for minerals

Xiao et al., Fig. 11 La/Yb vs. La and Sr/Y vs. Sr for minerals

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Fig. 12 Calculated melt compositions of melt in equilibrium with amphibole for two plutons
Fig. 13 Adakitic signatures of QMS host rocks

Fig. 13 Mechanism of adakitic magma evolution