Lithos 248–251 (2016) 455–468

Contents lists available at ScienceDirect

Lithos

journal homepage: www.elsevier.com/locate/lithos

Syn-collisional adakitic granodiorites formed by fractional crystallization: Insights from their enclosed mafic magmatic enclaves (MMEs) in the Qumushan pluton, North Qilian Orogen at the northern margin of the Tibetan Plateau

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ARTICLE INFO

Article history:
Received 2 November 2015
Accepted 28 January 2016
Available online 12 February 2016

Keywords:
Adakitic rocks
Mafic magmatic enclaves
Cumulate
Syn-collisional granodiorite
North Qilian Orogen

ABSTRACT

The Qumushan (QMS) syn-collisional granodiorite, which is located in the eastern section of the North Qilian Orogen at the northern margin of the Greater Tibetan Plateau, has typical adakitic characteristics and also contains abundant mafic magmatic enclaves (MMEs). This recognition offers an unprecedented insight into the petrogenesis of both the adakitic host granodiorite and the enclosed MMEs. The MMEs and their host granodiorites share many characteristics in common, including identical crystallization age (~430 Ma), same mineralogy, similar mineral chemistry and whole-rock isotopic compositions, indicating their genetic link. The MMEs are most consistent with being of cumulate origin formed at earlier stages of the same magmatic system that produced the QMS adakitic granodiorite. Subsequent replenishment of adakitic magmas could have disturbed the cumulate piles as "MMEs" dispersed in the adakitic granodiorite host during emplacement. The geochemical data and petrogenetic modeling of trace elements suggest that the QMS adakitic host granodiorite is most consistent with fractional crystallization dominated by the mineral assemblage of the MMEs. The parental magma for the QMS granodiorite is best explained as resulting from partial melting of the ocean crust together with recycled terrigenous sediments during continental collision, which may have also experienced interaction with mantle peridotite during ascent.

1. Introduction

"Adakite" was introduced by Defant and Drummond (1990) after the name of Adak Island in the Aleutian arc. It refers to a group of intermediate-felsic igneous rocks observed in modern oceanic and continental arcs genetically associated with seafloor subduction. They are characterized by high Sr, light rare Earth elements (REEs), Sr/Y (>40) and La/Yb (>20), low Y and heavy REEs, and lack of obvious Eu anomalies. It was initially considered that adakites were derived by partial melting of young (≤25Myrs) and warm subducting/subducted ocean crust in subduction zones (Defant and Drummond, 1990). The origin of adakite has since been one of the most popular subjects of research in igneous petrology due to its use for tectonic finger-printing (see Castillo, 2006, 2012), yet recent studies have shown that adakite or rocks with adakitic compositions can be produced in various ways and in different settings (Castillo et al., 1999; Chen et al., 2013a; Chung et al., 2003, 2005; He et al., 2013; Macpherson et al., 2006; RodrIguez et al., 2007; Song et al., 2014a; Streck et al., 2007; Wang et al., 2005, 2007; Xu et al., 2002). Because adakite is defined on the basis of certain trace element characteristics as detailed above, geochemistry in combination with experimental geochemistry has been widely used to discuss the petrogenesis of adakites and adakitic rocks (e.g., Castillo, 2006, 2012; Castillo et al., 1999; Defant and Drummond, 1990; Sen and Dunn, 1994; Wang et al., 2005; Xiong et al., 2005; Xu et al., 2002). However, a petrological approach is essential for petrological problems and is expected to offer insights into the petrogenesis of adakites and adakitic rocks. Indeed, mafic magmatic enclaves (MMEs) hosted in adakitic rocks have been recently recognized, and the processes of the MME formation may offer a fresh perspective on the petrogenesis of the adakitic host (e.g., Chen et al., 2013b; RodrIguez et al., 2007).

In this paper, we report our petrological, mineralogical and geochemical analyses and trace-element modeling on an MME-bearing

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http://dx.doi.org/10.1016/j.lithos.2016.01.033
0024-4937/

adakitic pluton well exposed in the eastern section of the North Qilian orogenic belt (NQOB) (Fig. 1a). This pluton was previously studied using the "standard" geochemical method with the MMEs being overlooked (e.g., Tseng et al., 2009; Wang et al., 2006a; Yu et al., 2015). Here we present a simple but effective model of fractional crystallization to successfully address both the origin of MMEs and their host adakitic granodiorite.

2. Geological setting

The NW–SE-trending NQOB is located between the Alashan Block to the northeast and the Qilian Block to the southwest, and is offset to the northwest by the Altyn–Tagh Fault (Fig.1a). It is made up of Early Paleozoic subduction-zone complexes including ophiolitic melanges, blueschists and eclogites, Silurian flysch formations, Devonian molasse, and Carboniferous to Triassic sedimentary cover sequences (Fig. 1a) (Song et al., 2007, 2013; Zhang et al., 2007). It is composed of three subunits, i.e., (1) the southern ophiolite belt, (2) the middle arc magmatic belt and (3) the northern back-arc basin ophiolite-volcanic belt (Fig. 1a) (Chen et al., 2014; Song et al., 2007, 2013; Zhang et al., 2007). It is generally accepted that the NQOB is an Early Paleozoic suture zone, which records a long tectonic history from seafloor spreading/subduction to the ultimate continental collision and mountain-building (see Song et al., 2013). The Qumushan (QMS) pluton we studied is about 60 km^2 in outcrop located in the eastern section of the NQOB. It lies approximately 10 km southeast of the Baojishan (BJS) pluton (Fig.1b). The QMS pluton intruded the Ordovician sedimentary and metamorphic rocks of Yingou group (Fig.1b). MMEs are widespread in the host granodiorite (Fig. 2a).

3. Analytical methods

3.1. Zircon U–Pb ages

Zircons were separated by using combined methods of heavy liquid and magnetic techniques before hand-picking under a binocular microscope. The selected zircons were set in an epoxy mount that was polished to expose zircon interiors. Cathodoluminescence (CL) images were taken at China University of Geosciences in Wuhan (CUGW) to examine the internal structure of individual zircon grains. The zircon U–Pb dating was done using LA-ICP-MS at China University of Geosciences in Beijing (CUGB). The instrument consists of an Agilent 7500a quadrupole inductively coupled plasma mass spectrometry (ICP-MS) coupled with a UP-193 Solid-State laser (193 nm, New Wave Research Inc.). Laser spot size was set to be ~30 μm. Zircon 91500 (Wiedenbeck et al., 1995) and a secondary standard zircon TEMORA (417 Ma) (Black et al., 2003) was used as an external standard. The analytical procedure is given in Song et al. (2010a). Isotopic ratios and element concentrations of zircons were calculated using GLITTER (ver. 4.4, Macquarie University). Common Pb correction was applied using the method of Andersen (2002). Results are given in Appendix 1.

3.2. Mineral compositions

Mineral chemistry was determined using a JXA-8100 microprobe at Chang'an University, China. The operating conditions were a 15 kV accelerating potential with a probe current of 10 nA and the electron beam diameter of 1 μm. Results are given in Appendix 2 and Appendix 3.

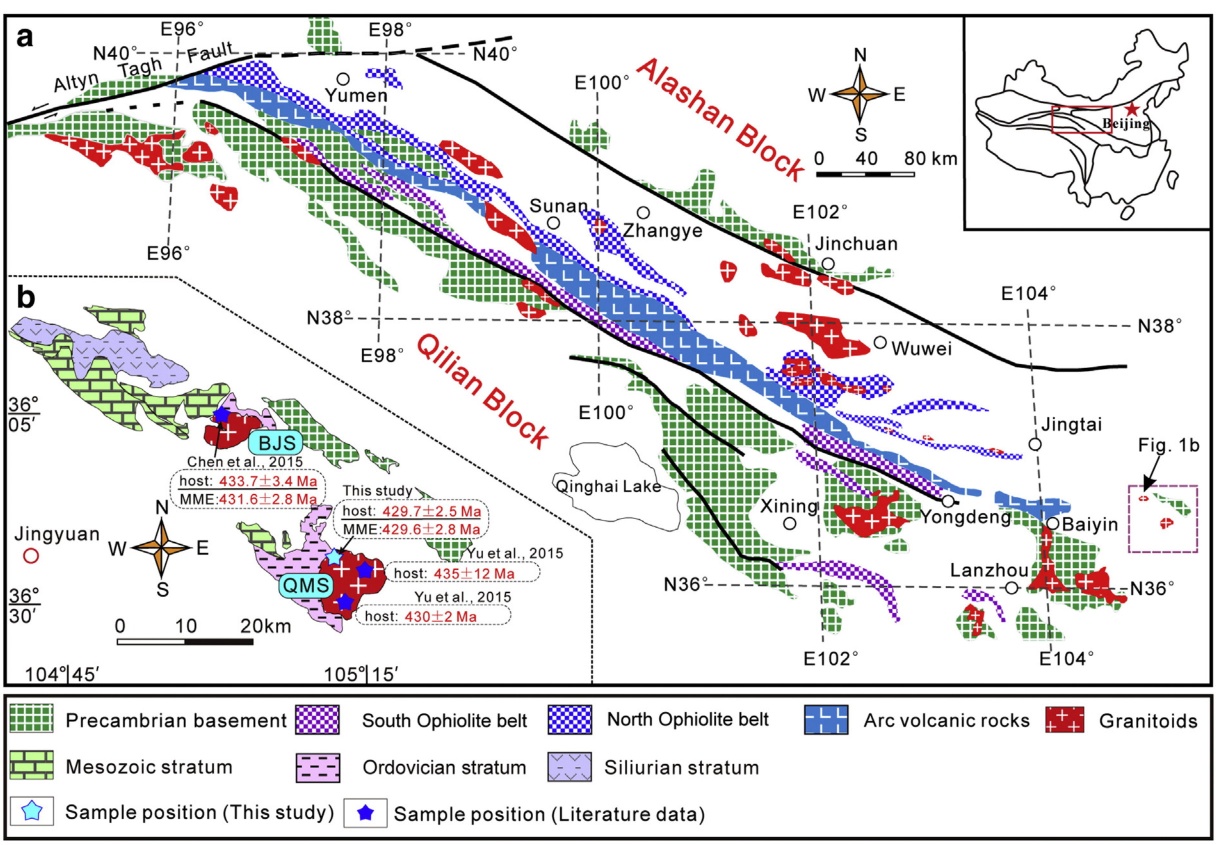

Fig. 1. (a) Simplified geological map of the North Qilian Orogen showing distributions of the main tectonic units (modified after Song et al., 2013; Chen et al., 2015). (b) Simplified map of the Qumushan (QMS) and Baojishan (BJS) area in the eastern section of the North Qilian Orogen. U–Pb ages are shown for granodiorite and MMEs in the BJS and QMS plutons from Chen et al. (2015), Yu et al. (2015) and this study as indicated.

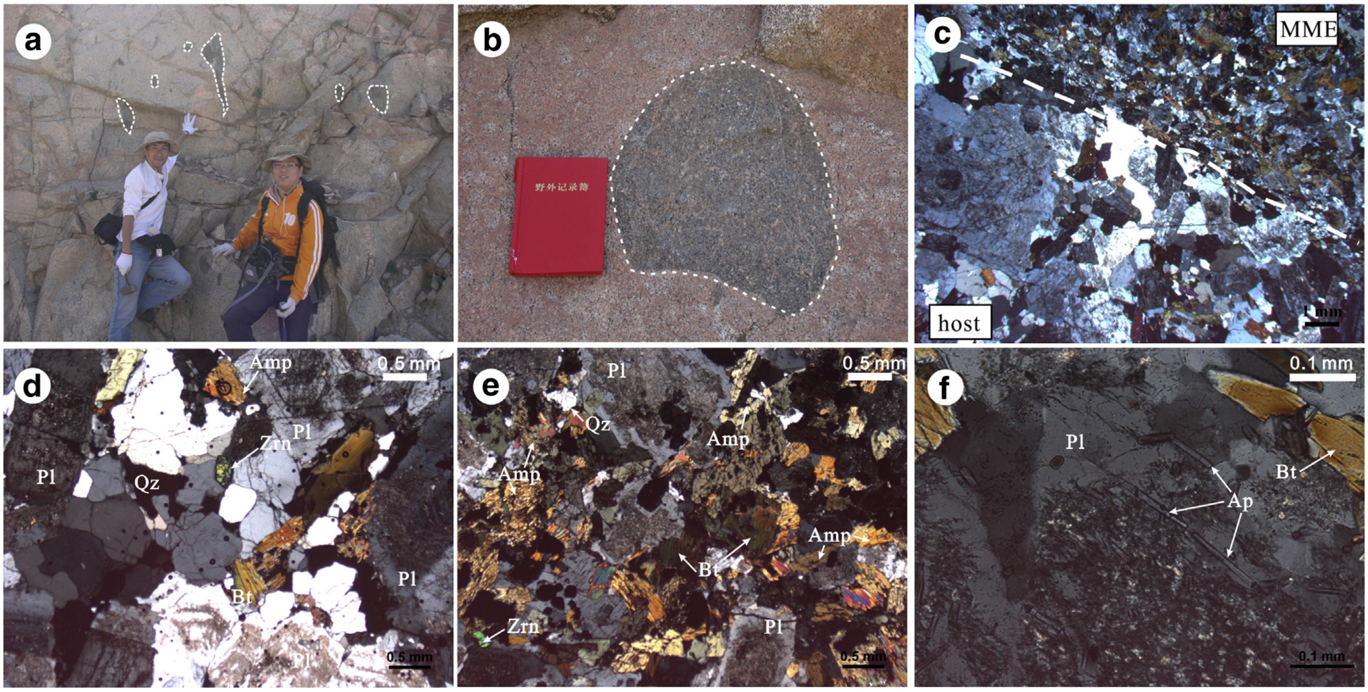

Fig. 2. Photographs of the adakitic granodiorite and the MMEs in the field and in thin-sections. (a), (b) and (c) show the sharp contact of MMEs of varying sizes with their host granodiorite with MMEs being finer-grained than the host; (d) shows the mineral assemblage of the adakitic host granodiorite (QMS12-02host) and (e) and (f) show the mineral assemblage of MMEs (QMS12-02MME, QMS12-06MME). Amp = amphibole; Bt = biotite; Pl = plagioclase; Qz = quartz; Ap = apatite; Zrn = zircon. Plates c–f are taken under cross-polarized light.

3.3. Major and trace elements

The bulk-rock major and trace elements were analyzed using Leeman Prodigy inductively coupled plasma-optical emission spectroscopy (ICP-OES) and Agilent-7500a inductively coupled plasma mass spectrometry (ICP-MS) at CUGB, respectively. The analytical uncertainties are generally less than 1% for most major elements with the exception of TiO_2 (~1.5%) and P_2O_5 (~2.0%). The loss on ignition was measured by placing 1 g of sample powder in the furnace at 1000 °C for several hours before cooling in a desiccator and reweighting. The analytical details are given in Song et al. (2010b). The data are presented in Appendix 4.

3.4. Whole-rock Sr–Nd–Hf isotopes

Whole-rock Sr–Nd–Hf isotopic analyses were done in Guangzhou Institute of Geochemistry, Chinese Academy of Sciences (GIG-CAS). The rock powders were digested and dissolved in HF–HNO_3 acid mixtures and dried on a hot-plate. Sr–Nd–Hf fractions were separated using small Sr Spec resin columns to obtain Sr and Nd–Hf bearing fractions. Sr isotopic compositions were determined using a Neptune Plus multi-collector ICP-MS (MC-ICP-MS) following Ma et al. (2013a). Nd fractions were then separated by passing through cation columns followed by HDEHP columns. Separation of Hf from the matrix and rare Earth elements was carried out using a combined method of Eichrom RE and HDEHP columns. Nd and Hf isotopic compositions were determined using a Micromass Isoprobe MC-ICP-MS following Li et al. (2009) and Ma et al. (2013b). Repeated analysis of NBS-987 run during the same period of sample analysis gave $^{87}Sr/^{86}Sr$ = 0.710283 ± 27 (2σ, n = 13). Repeated analysis of BHVO-2 and JB-3 during the same period of sample analysis yielded $^{143}Nd/^{144}Nd$ 0.512977 ± 14 (2σ, n = 8) and 0.513053 ± 18 (2σ, n = 13), respectively. During the course of this study, the mean $^{176}Hf/^{177}Hf$ ratios for BHVO-2 and JB-3 are respectively 0.283099 ± 15 (2σ, n = 13) and 0.283216 ± 15 (2σ, n = 6). All measured $^{87}Sr/^{86}Sr$, $^{143}Nd/^{144}Nd$ and $^{176}Hf/^{177}Hf$ ratios were normalized to $^{86}Sr/^{88}Sr$ = 0.1194, $^{146}Nd/^{144}Nd$ = 0.7219 and $^{179}Hf/^{177}Hf$ = 0.7325, respectively. The USGS rock standards JB-3 and BHVO-2 run with our samples give values consistent with the reported reference values (GeoREM, http://georem.mpch-mainz.gwdg.de/). Results are given in Appendix 5.

4. Petrography and mineral chemistry

4.1. Granodiorite

The QMS pluton is of granodioritic composition with a mineral assemblage of plagioclase (45 vol.%–50 vol.%), quartz (35 vol.%–42 vol.%), amphibole (3 vol.%–10 vol.%), biotite (2 vol.%–10 vol.%), minor K-feldspar, and accessory minerals such as apatite, sphene, zircon and Fe–Ti oxides (Fig. 2d). Plagioclase crystals are euhedral to subhedral, and are of oligoclase composition with $An_{12–24}$ (Fig. 3a). Zoned-plagioclase crystals display normal zoning with more anorthitic cores rimmed by less calcic compositions (Fig. 3a). Amphibole is always present as euhedral to subhedral crystals despite the variably small abundances (Fig. 2d). Amphibole grains are usually homogeneous and rarely display disequilibrium textures. Amphiboles from the host granodiorite can be classified as edenite (Appendix 3, Fig. 4) following Leake et al. (1997). They have medium SiO_2, and low TiO_2 (0.37–1.24 wt.%), Na_2O (0.87–1.48 wt.%) and K_2O (0.29–1.69 wt.%).

4.2. Mafic magmatic enclave

MMEs are abundant in the QMS pluton (Fig. 2a), showing varying shape and size from centimeters to tens of centimeters in diameter (Fig. 2a). They differ from the host by having finer grain-size (Fig. 2a–c), but have the same mineralogy albeit with greater mafic modes (e.g., 35–50 vol.% amphibole, 5–15 vol.% biotite, 40–50 vol.% plagioclase, minor quartz, K-feldspar, along with accessory minerals such as apatite, sphene, zircon and Fe–Ti oxides), thus giving a dioritic bulk composition. Plagioclase mostly occurs as subhedral grains with compositions similar to those in the host granodiorite. Zoned-plagioclase in the MMEs shows a compositional continuum with cores slightly more anorthitic than the rims (Fig. 3b). Amphibole in the MMEs is compositionally

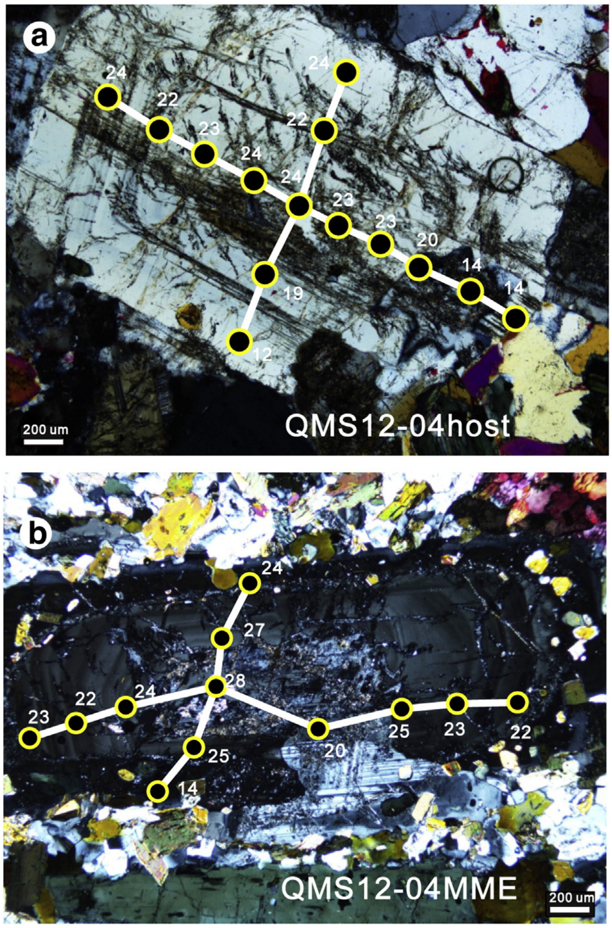

Fig. 3. Photomicrographs showing a plagioclase crystal with a high-Ca core rimmed by a euhedral overgrowth of low-Ca plagioclase in both (a) adakitic rocks (e.g., QMS12-04host) and (b) MMEs (e.g., QMS12-04MME). Numerals are the An contents. See Appendix 2 for compositional data.

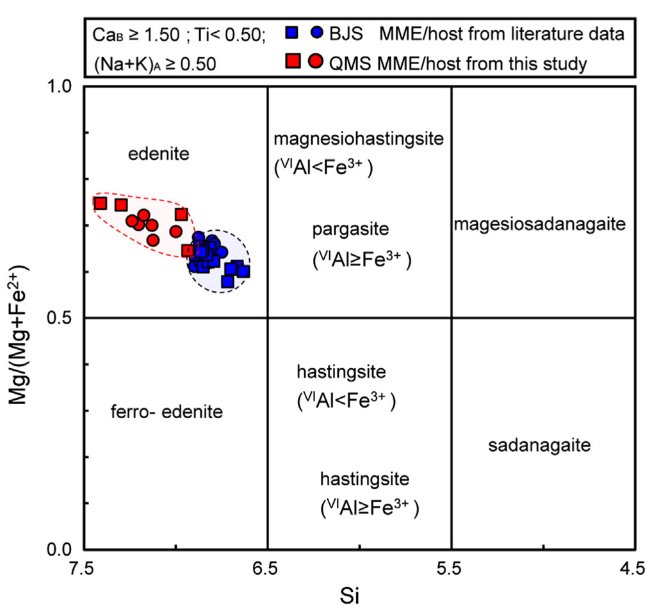

Fig. 4. Chemical compositions of amphiboles from the host granodiorite and MMEs in the amphibole classification diagram (Leake et al., 1997). Data from the host granodiorites and the MMEs of BJS pluton (Chen et al., 2015) are also shown for comparison.

identical to that in the host granodiorite (Fig. 4). Biotite is yellow brown with subhedral to euhedral forms. The MMEs show no chilled margins nor textures of crystal resorption or reactive overgrowth. These rocks mainly exhibit porphyritic-like textures.

5. Results

5.1. Zircon U–Pb ages

Four samples (2 host–MME pairs) were chosen for dating. In CL images (Fig. 5a, c), zircons from the host granodiorites (QMS12-04host and QMS12-10host) are transparent, colorless, and mostly euhedral columnar crystals of varying sizes (~150–300 μm long with length/width ratio of 1:1–3:1) with well-developed oscillatory zoning. The zircons have varying U (~28–386 ppm) and Th (~69–423 ppm) with Th/U ratio of 0.3–1.4. All these characteristics are consistent with the zircons being of magmatic origin (Hoskin and Schaltegger, 2003). After excluding discordant ages, zircons from the two host granodiorite samples yielded weighted mean $^{206}Pb/^{238}U$ ages of 429.7 ± 2.5 Ma (1σ, MSWD = 0.15, n = 23) and 431.5 ± 2.6 Ma (1σ, MSWD = 0.19, n = 20), respectively (Fig. 5a, c), representing the crystallization age (~430 Ma) of the host granodiorite. These age data are in agreement with those in the literature (Tseng et al., 2009; Yu et al., 2015).

Zircons from the MMEs (QMS12-04MME and QMS12-10MME) show similar optical properties to those in the host with oscillatory zoning (Fig. 5b, d) and varying size (~150–200 μm in length length/width ratio of ~1:1–2:1). They have varying Th (27–548 ppm), U (50–541 ppm), and Th/U (0.1–2.4). They are also of magmatic origin. Zircons in the 2 MMEs yielded the same weighted mean ages as zircons in the host within error, i.e., 429.6 ± 2.8 Ma (1σ, MSWD = 0.48, n = 18) and 431.2 ± 2.8 Ma (1σ, MSWD = 0.2, n = 19), respectively (Fig. 5b, d).

5.2. Major and trace elements

Eleven representative QMS granodiorite samples and their hosted MMEs (including 5 host–MME pairs) were analyzed for whole-rock major and trace element compositions (Appendix 4). The granodiorite samples have high SiO_2 (64.37–65.49 wt.%), Al_2O_3 (16.09–17.61 wt.%), Na_2O (4.86–5.12 wt.%) and Na_2O/K_2O (2.11–3.82) with medium total alkalis ($Na_2O + K_2O$ = 6.46–7.25 wt.%), and plot in the granodiorite field (Fig. 6a). They have low $Fe_2O_3^T$ (2.86–3.43 wt.%), MgO (2.14–2.60 wt.%) and CaO (3.60–4.10 wt.%). They are calc-alkaline (Fig. 6b) and metaluminous to weakly peraluminous (A/CNK = 0.93 to 1.03) (Fig. 6c), which is typical for I-type granitoids (Chappell and White, 1992). In contrast, the MMEs plot in the fields of diorite, monzodiorite and monzonite (Fig. 6a). They are compositionally high-K calc-alkaline to calc-alkaline (Fig. 6b), and metaluminous with A/CNK ranging from 0.74 to 0.84 (Fig. 6c). They have lower SiO_2 (52.06–58.59 wt.%), higher $Fe_2O_3^T$ (6.12–8.50 wt.%), MgO (5.09–7.22 wt.%), CaO (4.99–6.57 wt.%), P_2O_5 (0.49–1.01 wt.%), and slightly higher Mg# (0.63–0.68; Mg# = Mg / [Mg + Fe^{2+}]) than the host granodiorites.

In the chondrite-normalized REE diagram, the QMS granodiorite samples are characterized by a relatively flat heavy REE (HREE) pattern ($[Dy/Yb]_N$ = 1.32–1.54), slightly negative to positive Eu anomalies (Eu/Eu* = 0.88–1.13), and lower total REE contents (ΣREE = 76–134 ppm) than the hosted MMEs. The REE patterns of the QMS granodiorites are similar to the field defined by the BJS granodiorites (cf. Chen et al., 2015) (Fig. 7), but display greater light REE (LREE) enrichment ($[La/Sm]_N$ = 4.77–5.36). The MMEs show similar REE patterns, but have significantly higher HREEs (Fig. 7a, b), which is consistent with greater modes of REE-enriched minerals (e.g., amphibole, apatite and zircon). They have negative Eu anomalies (Eu/Eu* = 0.6–0.8).

In the multi-element spider diagram (Fig. 8), the host granodiorite and MMEs both show enrichment of large ion lithophile elements (LILE, e.g., P, K, Pb) and depletion in high field strength elements (HFSE, e.g., Nb, Ta and Ti). Sr appears to have a positive anomaly in

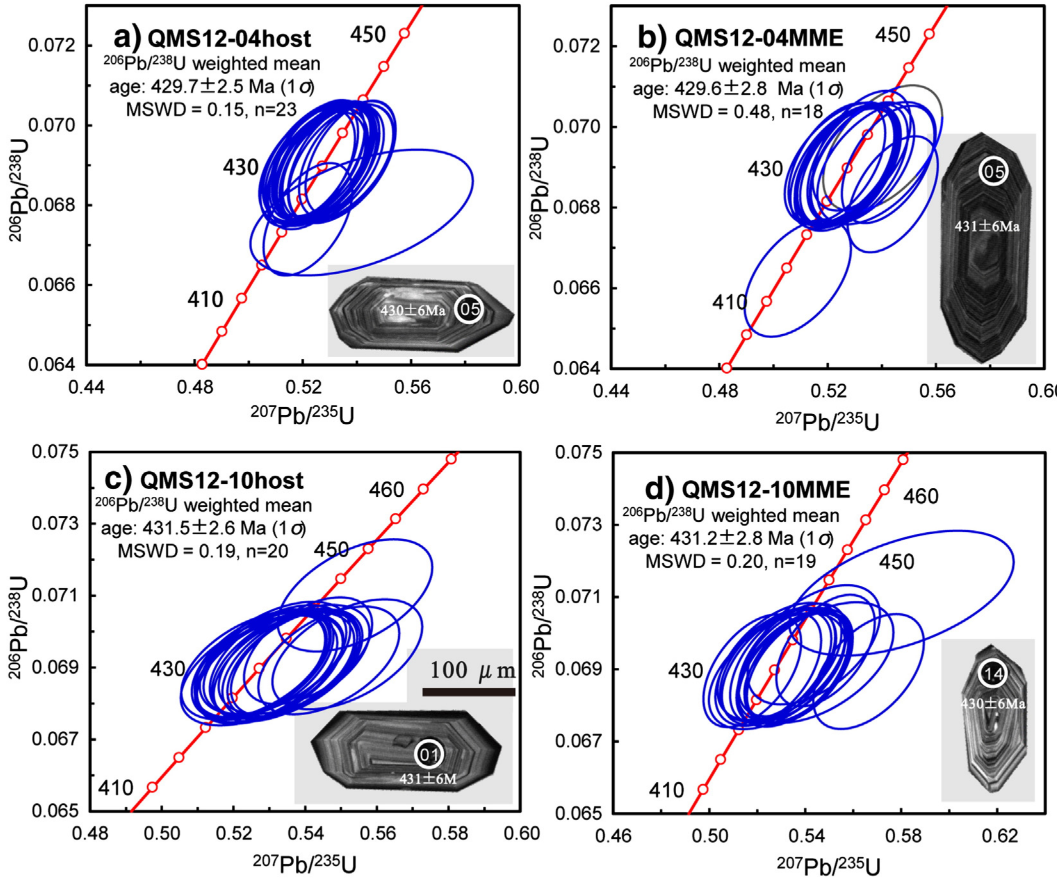

Fig. 5. Concordia diagrams of LA-ICP-MS U–Pb zircon age data and representative CL images of zircon grains showing spots for the host adakitic granodiorites (a, c) and the MMEs (b, d) in the QMS pluton.

the host (Sr/Sr* = 1.66–2.96), but varying anomalies for the MMEs (Sr/Sr* = 0.5–1.19). In particular, compared to the BJS granodiorites (Chen et al., 2015), the QMS granodiorite samples have adakitic signatures with high Sr/Y and La/Yb ratios, and lower Y and Yb abundances, thus plotting in the adakite fields in the discrimination diagrams (Fig. 9a–b), while most MMEs plot in the normal arc rock field.

5.3. Sr–Nd–Hf isotopic geochemistry

Whole-rock Sr–Nd–Hf isotopic compositions for the MMEs and their host granodiorite are given in Appendix 5. The initial $^{87}Sr/^{86}Sr_{(t)}$, $\varepsilon_{Nd}(t)$ and $\varepsilon_{Hf}(t)$ values are calculated at 430 Ma using the zircon age data (see Fig. 5 above). On the plots of $^{87}Sr/^{86}Sr_{(t)}$, $\varepsilon_{Nd}(t)$ and $\varepsilon_{Hf}(t)$ against SiO_2 (Fig. 10j–l), both host granodiorite and MME samples are indistinguishable and overlapping within a narrow range (also see Appendix 5).

On SiO_2-variation diagrams (Fig. 10), the MMEs and their host granodiorite define linear trends for most elements (e.g., TiO_2, $Fe_2O_3^T$, MnO, MgO, CaO, P_2O_5, Eu and Hf abundances) and trace element ratio (e.g., Hf/Sm) (Fig. 10a–i), but show no correlations of initial Sr, Nd, and Hf isotopic compositions with SiO_2 (Fig. 10j–l).

6. Discussion

6.1. Petrogenesis of the mafic magmatic enclaves

Several models have been proposed for the origin of MMEs in the literature, including foreign xenoliths (usually country rocks; e.g., Vernon, 1983; Xu et al., 2006), refractory and residual phase assemblages derived from granitoid sources (e.g., the restite model; Chappell et al., 1987; Chappell and White, 1991), chilled material or cumulate of early-formed co-genetic crystals (e.g., Chen et al., 2015; Dahlquist, 2002; Dodge and Kistler, 1990; Donaire et al., 2005; Huang et al., 2014; Niu et al., 2013; Rodriguez et al., 2007), and basaltic melt material incompletely digested and homogenized during a magma mixing process (e.g., Barbarin, 2005; Barbarin and Didier, 1991; Castro et al., 1990; Chappell and White, 1991; Chen et al., 2009a, 2013b; Didier, 1987; Dorais et al., 1990; Vernon, 1983; Wang et al., 2013). We critically evaluate these interpretations below.

6.1.1. Textural and chemical relationships of the MMEs and their hosts

The textural and chemical relationships of the QMS MMEs and their host granodiorite concur with the findings for the BJS pluton (Chen et al., 2015), and are summarized as follows: (1) the MMEs in the QMS granodiorites are ellipsoidal, or elongate, show no chilled margins, no textures of crystal resorption nor reactive overgrowth, but exhibit typical magmatic texture (Fig. 2a–f); (2) they have a mineral assemblage identical to, and more mafic phases than, their host granodiorite (Fig. 2c–f); (3) they have mineral compositions (e.g., amphibole and plagioclase) identical to those of their host (Figs. 3–4); (4) they have the same age (~430 Ma) as their host (Fig. 5); (5) their different major and trace element abundances from their hosts are controlled largely by mineral modal proportions, i.e., MMEs have greater modes of REE-enriched minerals (amphibole, apatite and zircon) and thus have higher MgO, Fe_2O_3, CaO and trace elements easily incorporated into these phases (e.g., TiO_2, P_2O_5, Hf and HREEs) (Fig. 10a–i); and (6) more importantly, they have overlapping and indistinguishable Sr–Nd–Hf isotopes with their host granodiorite (Fig. 10j–l).

Any successful models for the origin of MMEs must be consistent with these observations. Models for MMEs as foreign xenoliths from country rocks (e.g., Xu et al., 2006) can be readily rejected, as there is no evidence of reaction textures for the MMEs. Likewise, the identical

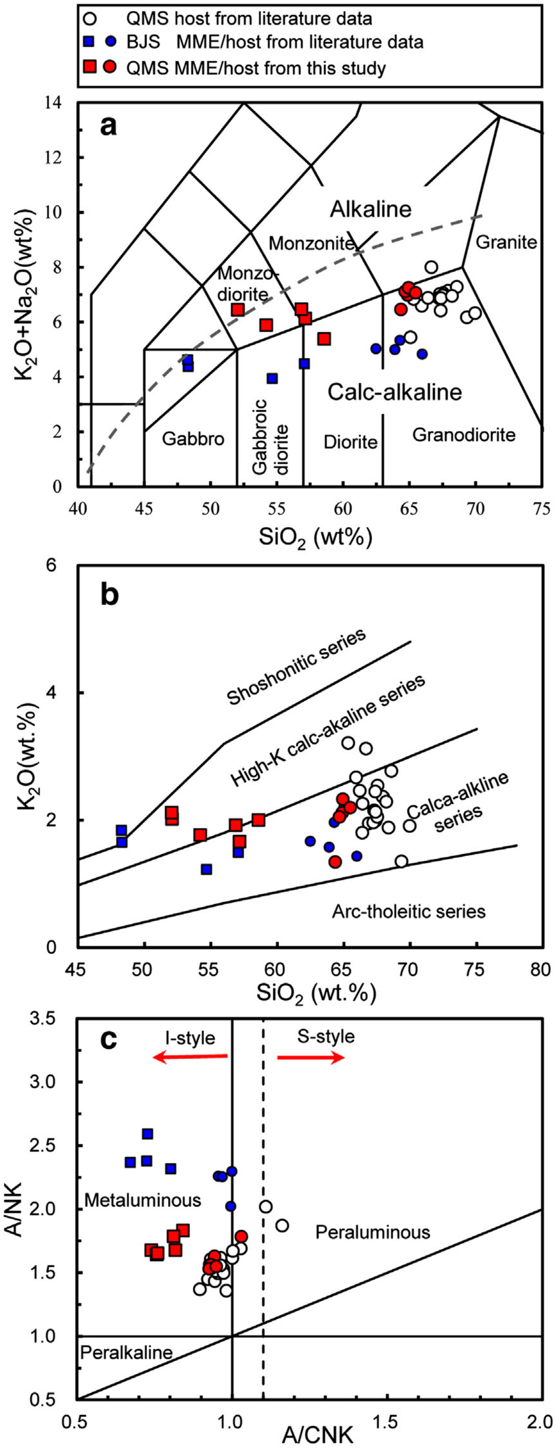

Fig. 6. Classification diagrams of the host granodiorites and the MMEs in the QMS pluton. (a) Total alkalis vs. SiO_2 (Le Maitre et al., 1989), (b) K_2O vs. SiO_2, and (c) A/NK vs. A/CNK. The blue circles and squares are data from BJS granodiorites and their MMEs (Chen et al., 2015), and the open circles are literature data on the QMS granodiorites (Tseng et al., 2009; Wang et al., 2006a; Yu et al., 2015). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

age (~430 Ma) of the MMEs and their host as well as the magmatic textures, constitute a strong argument against the restite origin (e.g., Chappell et al., 1987). In addition, the MMEs do not contain peraluminous minerals and their metaluminous composition (Fig. 6c) also excludes their derivation by melting of peraluminous restites (Barbarin, 2005). Therefore, the most straightforward interpretation is that the MMEs and their hosts formed as different products of a common magmatic system.

6.1.2. Assessing the origin of magma mixing

Similar observations mentioned above between the MMEs and their host granitoids have been identified first by Pabst (1928) and by many others since then. The MMEs were thus described as "autoliths", referring to "cogenetic" or part of the same system. Despite the "autoliths" nature of the MMEs with the host, this interpretation has been questioned: (1) Why are isotopic values of some MMEs intermediate between those of crustal and mantle materials (e.g., Barbarin, 2005; DePaolo, 1981)? (2) Why are the MMEs fine-grained (e.g., Barbarin and Didier, 1991)? Because of these questions, a model of magma mixing between mantle-derived mafic magma and crust-derived felsic magma was proposed to address the above issues: (1) the intermediate isotopic values of the MMEs were commonly interpreted as the result of magma mixing between a mantle-derived mafic magma and a crust-derived felsic magma, because a mafic magma derived from upper mantle provides not only material but also the heat necessary for melting and subsequently mixing with the crustal rocks (e.g., Barbarin, 2005); (2) the fine-grained MMEs were interpreted as due to quenching against host felsic magmas (e.g., Barbarin, 2005; Furman and Spera, 1985; Vernon, 1984), owing to their higher liquidus and solidus temperatures compared to felsic magmas. As a result, the magma mixing model has been the most popular interpretation for the petrogenesis of the MMEs (see critical review by Niu et al., 2013).

Actually, there are many compelling lines of evidence for magma mixing in many granitoids, especially (1) where a clear isotopic contrast exists between the MMEs and the hosts (e.g., Chen et al., 2009b; Holden et al., 1987; Liu et al., 2013); and (or) (2) where disequilibrium features occur in the MMEs, e.g., complex zoning of clinopyroxene crystals that have distinctly low-MgO cores surrounded by high-MgO rims (e.g., Chen et al., 2013a; Wang et al., 2013), or resorption textures or reversed zoning of plagioclase (Chen et al., 2009a,b; Pietranik et al., 2006). In the case of our study, however, none of the above has been observed. Instead, many lines of evidence argue against the magma mixing origin.

First, the MMEs and their host granodiorites in the QMS pluton have overlapping and indistinguishable Sr–Nd–Hf isotopes (vs. isotopic contrast in magma mixing model). In spite of this, some authors would still argue that the isotopic and mineral compositional similarity between the enclaves and the host could result from chemical and isotopic equilibration during magma mixing (e.g., Barbarin, 2005; Chen et al., 2009b; Dorais et al., 1990; Zhang et al., 2010), using some experimental interpretations that isotopic equilibration is generally more easily achieved than chemical equilibration (Lesher, 1990). However, we emphasize that it is physically unlikely that isotopes become homogenized whereas major and trace elements are not (Niu et al., 2013), because isotopes are "carried" by the relevant chemical elements and isotopic diffusion cannot take place without the diffusion of the "carrying" elements (Chen et al., 2015). In fact, there are two forceful arguments against thermal and chemical equilibration: (1) the MMEs exhibit no textures of crystal resorption or reactive overgrowth (Fig. 2b–c), and (2) plagioclase in the MMEs and their host granodiorite shows no compositional or textural disequilibrium (Fig. 3). In addition, although the fine-grained texture of the MMEs could be interpreted as resulting from quenching in the magma mixing model, quenching of the mafic magma would lead to a significantly high viscosity contrast between the solidified enclaves and the felsic host magma, thereby inhibiting deformation, mechanical mixing (Caricchi et al., 2012; Farner et al., 2014) and isotope homogenization between the MMEs and the host.

Second, strongly correlated variations between major and trace elements (Fig. 10a–i) are consistent with modal mineralogy control, as the result of magma evolution (i.e., the MMEs are cumulate and the host represents residual melt) rather than mixing of two magmas with entirely different origins because magma mixing is a complex,

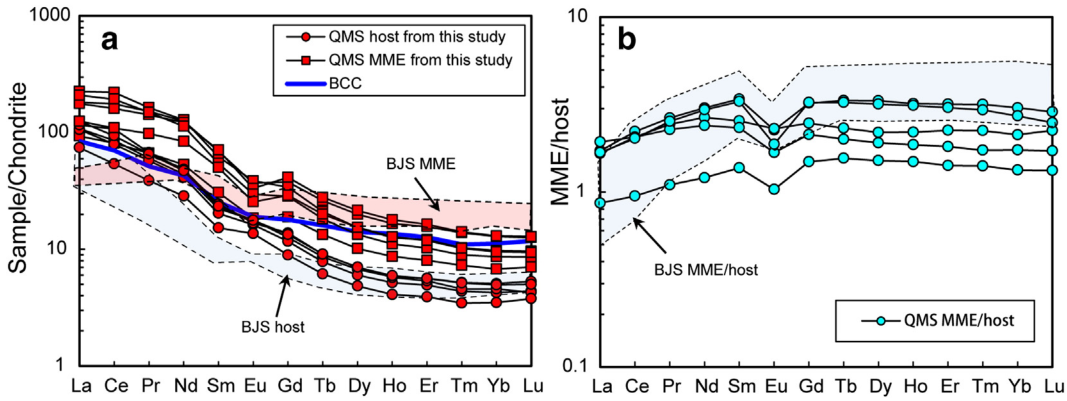

Fig. 7. (a) Chondrite normalized REE patterns for the QMS host adakitic granodiorites and the MMEs; (b) host rock-normalized REE patterns of MMEs. Chondrite REE values and bulk continental crust (BCC) are from Sun and McDonough (1989) and Rudnick and Gao (2003), respectively. Shaded fields of BJS granodiorite and the MMEs are from Chen et al. (2015).

multi-stage process in which linear trends can be disturbed (e.g., Chen et al., 2015; Clemens, 1989; Donaire et al., 2005). Moreover, the distinctive high abundances of some elements in the MMEs, such as Zr and P (Fig. 11), cannot be explained by magma mixing because these elements are controlled by the presence of accessory phases, such as zircon and apatite. As shown in Fig. 11, mantle derived basaltic magmas would have much lower Zr and P_2O_5 than in the QMS MMEs. For example, quantitative calculations by Lee and Bachmann (2014) suggested that 10–20% melting of an upper mantle with 5 ppm Zr and 0.019 wt.% P_2O_5 (equivalent to that estimated for depleted mid-ocean ridge basalt mantle), would yield primary liquids with 25–50 ppm Zr and 0.1–0.2 wt.% P_2O_5. These concentrations are much lower than in the QMS MMEs. Additionally, boninites are thought to result from partial melting of highly depleted harzburgitic mantle peridotites induced by subduction-zone slab dehydration (Niu, 2005), but they also have lower Zr and P_2O_5 contents (Fig. 11). More importantly, magma mixing between a basalt with any silicic end-member (e.g., rhyolite) would generate a mixing array (Fig. 11a–b, the dash lines) totally different from the linear trend (Fig. 11a–b, the solid lines) defined by the QMS granodiorite and their MMEs. In contrast, all of these observations are consistent with the interpretation that the MMEs represent earlier cumulate with greater amounts of zircon and apatite than their hosts (e.g., Donaire et al., 2005).

6.1.3. Formation of the mafic magmatic enclaves

The foregoing observations, illustrations and discussion leave us with the best interpretation that the MMEs represent the earlier crystallized cumulate that were later disturbed by subsequent melt replenishment and induced magma convection in the magma chamber. As illustrated in Fig. 12, when a primitive magma body is emplaced into a cold environment (e.g., developing a magma chamber) with the wall-rock having temperatures below the liquidus of the magma, magma quench and rapid crystallization are inevitable because of the thermal contrast. For an andesitic primitive magma parental to the syn-collisional granitoids (Niu et al., 2013), the first major liquidus phases would be amphibole, biotite, plagioclase and accessory minerals such as zircon and apatite, and rapid quench will facilitate abundant nucleation without between-nuclei space for rapid growth, thus resulting in the formation of fine-grained cumulate (Chen et al., 2015). This is a fundamentally important petrologic concept with which any interpretation must comply. This early formed fine-grained mafic cumulate piles (largely plastic before complete solidification) can be readily disturbed by subsequent magma replenishment and induced convection, resulting in the dispersion of the MMEs in the host granodiorite.

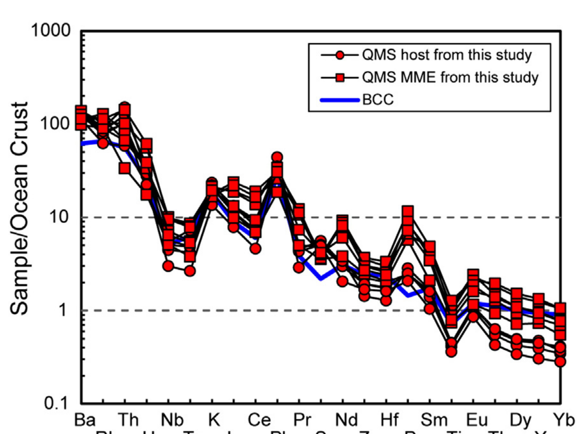

Fig. 8. Average ocean crust-normalized (OC; Niu and O'Hara, 2003) trace element patterns for the QMS host adakitic granodiorites and the MMEs.

6.2. Petrogenesis of QMS adakitic granodiorite

6.2.1. Implication from the MMEs

Recently, mixing of basaltic and felsic magmas was proposed for the genesis of some high-Mg and low SiO_2 adakitic rocks from Mount Shasta and the North China Craton using the presence of ubiquitous MMEs as evidence (Chen et al., 2013b) and also based on the disequilibrium petrographic characteristics in high-Mg andesites (Chen et al., 2013a; Streck et al., 2007). This interpretation could be reasonable, but it is not the case here because there is no petrographic and compositional evidence for magma mixing as elaborated above. That is, the MMEs in the QMS adakitic granodiorite are not evidence for magma mixing, but rather they are of cumulate origin without direct asthenospheric mantle participation (e.g., Dahlquist, 2002). More importantly, the MMEs comprise dominantly amphibole and plagioclase, which are common cumulate minerals of andesitic melts. If the parental melts were basaltic, the typical cumulate from such evolved basaltic melt would be gabbro dominated by clinopyroxene and plagioclase (Chen et al., 2015). It can be inferred from this important petrological concept that the parental magmas of the MMEs and their host granodiorite was mafic andesitic (Chen et al., 2015; Niu et al., 2013).

6.2.2. Assessing the model of melting of mafic lower continental crust

To date, some intra-continental high-MgO or -$Mg^{\#}$ (also high Cr and Ni contents) adakitic rocks have been considered to originate from melting of delaminated lower crust (e.g., Gao et al., 2004; Wang et al., 2006b; Xu et al., 2002). By accepting and applying this model, it has been previously interpreted that the QMS adakitic rocks were derived from delaminated lower crust, and they subsequently interacted with mantle peridotite during ascent (Tseng et al., 2009; Yu et al., 2015).

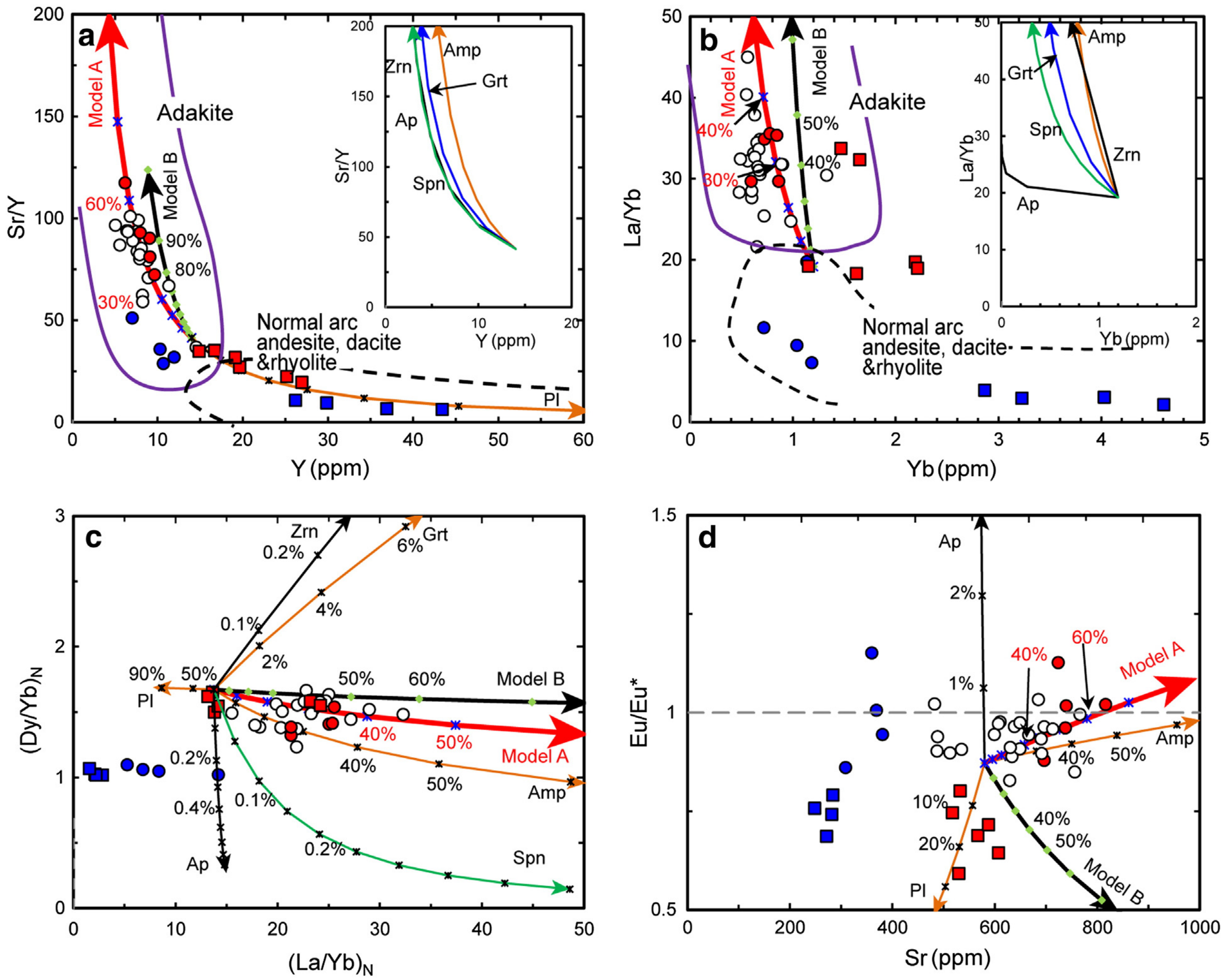

Fig. 9. Plots of (a) Sr/Y vs. Y, where fields of adakite, and normal arc andesite–dacite–rhyolite are from Defant and Drummond (1990); (b) La/Yb vs. Yb, discrimination lines are from Richards and Kerrich (2007); (c) $(Dy/Yb)_N$ vs $(La/Yb)_N$, and (d) Eu/Eu* vs. Sr. Results in a–d using Rayleigh fractional crystallization models indicate the effects of garnet, amphibole, plagioclase, zircon and apatite fractionation on Sr/Y and Y (a), on La/Yb and Yb (b), on $(Dy/Yb)_N$ and $(La/Yb)_N$ (c), and on Eu/Eu* and Sr (d). The partition coefficients used and modeling details are given in Appendix 6. Two crystallization models were designed to elucidate the effect of crystallization on bulk-rock (assumed to approximate melt) trace element systematics: (1) Model A, in reasonable agreement with observed mineral proportions of the MMEs, 50% amphibole, 40% plagioclase, 7.52% biotite, 2.2% apatite, 0.2% zircon and 0.03% sphene; (2) Model B, 50% amphibole, 40% plagioclase, 7.6% biotite, and 2.4% garnet. Data sources for the QMS and BJS plutons are the same as in Fig. 6. Amp = amphibole; Bt = biotite; Pl = plagioclase; Ap = apatite; Zrn = zircon; Grt = garnet; Spn = sphene.

Although this model seems plausible and applicable to the QMS adakitic rocks, it has more difficulties than certainties. First, the QMS adakitic granodiorites have lower $(Dy/Yb)_N$, $(La/Yb)_N$, and distinctive low K_2O/Na_2O ratios (Fig. 13b), which are significantly different from the composition of adakitic rocks inferred to be derived from partial melting of the thickened or delaminated lower continental crust. Second, the Nd and Hf isotopic data of the QMS adakitic granodiorite indicate a significant mantle input, which is also inconsistent with those of lower continental crust origin (Fig. 14a). Finally, the existence of the Paleo-Qilian ocean is manifested by the ophiolites and eclogites in the North Qilian orogenic belt; the ocean basin started its subduction at ~520 Ma, and was eventually closed at the end of the Ordovician (~445 Ma) followed by continental collision (see Song et al., 2013). Accordingly, the coeval (~430 Ma) MMEs and their adakitic host granodiorite of the QMS pluton are best interpreted as a magmatic response to the collision between the Qilian–Qaidam block and Alashan block, thereby being contrary to the environment of crustal extension required by a delaminated lower crustal origin. In fact, continuous lithosphere extension and delamination in the NQOB occurred at <400 Ma, which resulted in strong magmatic activity and formed a number of diorite–granodiorite–granite plutons with ages of ~400–360 Ma (Song et al., 2013, 2014b).

6.2.3. A fractional crystallization model for the petrogenesis of the QMS adakitic granodiorites

An origin of adakitic rocks by fractional crystallization has been proposed in the literature. However, it should be noted that all these crystallization models require basaltic parental magmas derived from the metasomatized mantle wedge in arc settings, such as in the complex Philippine arc (Castillo et al., 1999; Macpherson et al., 2006) and Ecuadorian Andes (Chiaradia et al., 2004). It is important to note that our crystallization model differs from the basaltic magma crystallization model of arc magmas in the literature.

In our model, the magmas parental to the MMEs and their host granodiorite are the same mafic andesitic magmas in a syn-collisional setting, rather than basaltic magmas in an arc setting of active seafloor subduction advocated in the literature (e.g., Macpherson et al., 2006). That is, the QMS adakitic granodiorites are products of fractional crystallization dominated by the mineral assemblage indicated by the MMEs from mafic andesitic magmas. We can further consider two fractional crystallization models to elucidate the effect of crystallization of the observed mineralogy on trace elements using closed-system Rayleigh fractionation equation: (1) Model A, in reasonable agreement with observed mineral proportions of the MMEs, 50% amphibole, 40%

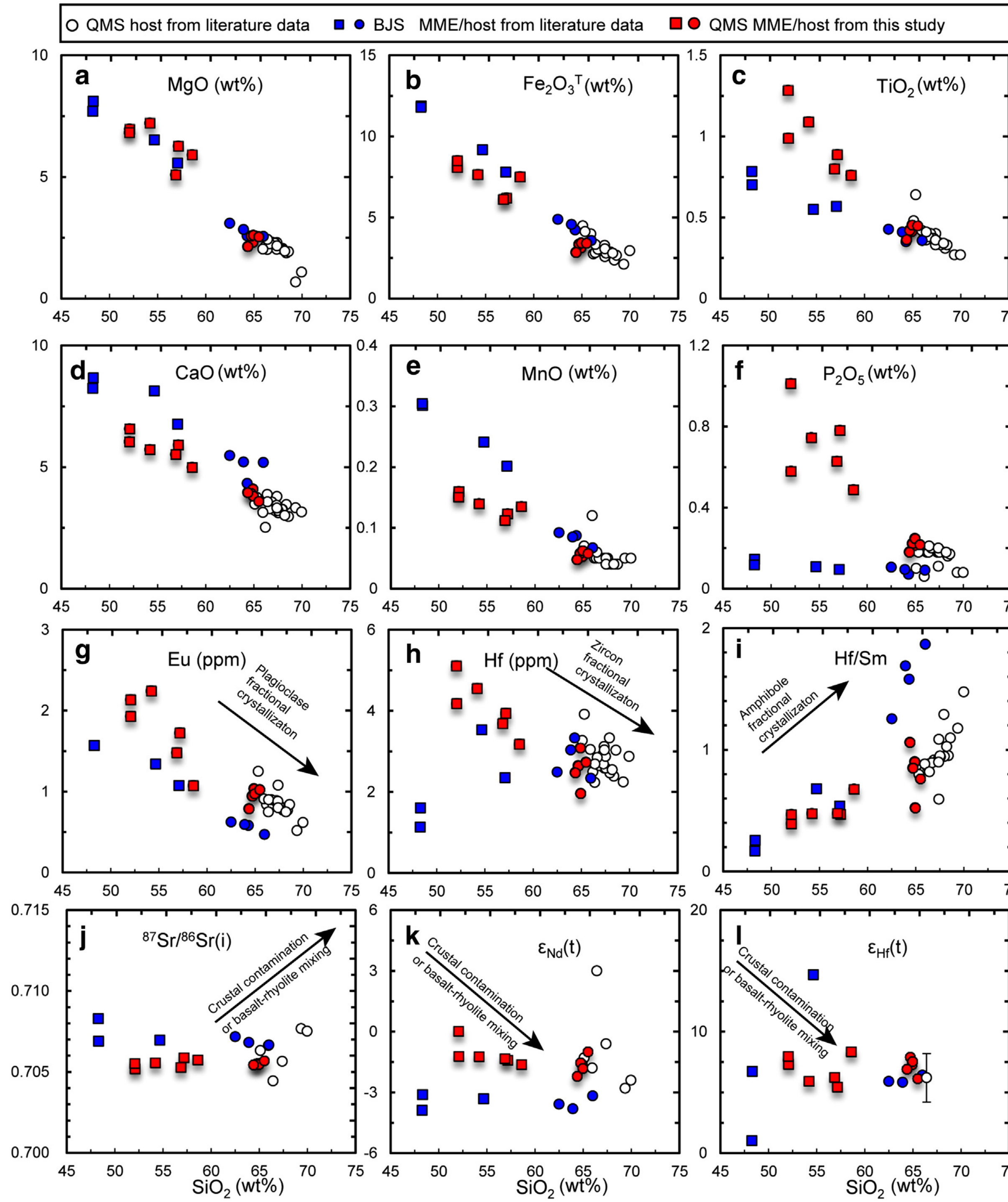

Fig. 10. SiO_2 variation diagrams of (a) MgO, (b) $Fe_2O_3^T$, (c) TiO_2, (d) CaO, (e) MnO, (f) P_2O_5, (g) Eu, (h) Hf, (i) La/Sm, (j) $^{87}Sr/^{86}Sr_{(t)}$, (k) $\varepsilon_{Nd}(t)$ and (l) $\varepsilon_{Hf}(t)$. Fractional crystallization trends in g–i: the inverse linear trend of SiO_2 versus Eu and Hf indicate the effects of plagioclase and zircon fractional crystallization, respectively. Because Sm is incorporated more easily than Hf in amphibole (Fujimaki et al., 1984; Klein et al., 1997), amphibole crystallization will cause Hf/Sm increase in residual magmas (i). Crustal contamination and (or) basalt–rhyolite mixing trend in j–l are after Wang et al. (2008). Data sources of the QMS and BJS pluton are the same as in Fig. 6. The average zircon $\varepsilon_{Hf}(t)$ isotopic data (6.2 ± 2, 2σ) calculated from Yu et al. (2015) is also presented in (l).

plagioclase, 7.52% biotite, 2.2% apatite, 0.2% zircon and 0.03% sphene; and (2) Model B, which incorporates fractionation of garnet, 50% amphibole, 40% plagioclase, 7.6% biotite, 2.4% garnet. The partition coefficients used in the calculations are for intermediate-felsic magmas (Appendix 6). For convenience (see below), the assumed parental magma (Appendix 6) is very similar to the bulk continental crust (BCC) composition (Rudnick and Gao, 2003) (Fig. 15), which is the same as the ~60 Ma Linzizong andesite in southern Tibet (Mo et al., 2008; Niu et al., 2013), in terms of major and trace element abundances.

Notably, removal of garnet would yield a smooth decrease of LREE-to-HREE pattern (Richards and Kerrich, 2007) with elevated $(Dy/Yb)_N$ and $(La/Yb)_N$ in the evolving melt (Fig. 9c). However, the $(Dy/Yb)_N$ ratio in the QMS adakitic granodiorites remain constant with increasing $(La/Yb)_N$ (Fig. 9c), which indicate that the effect of garnet fractionation

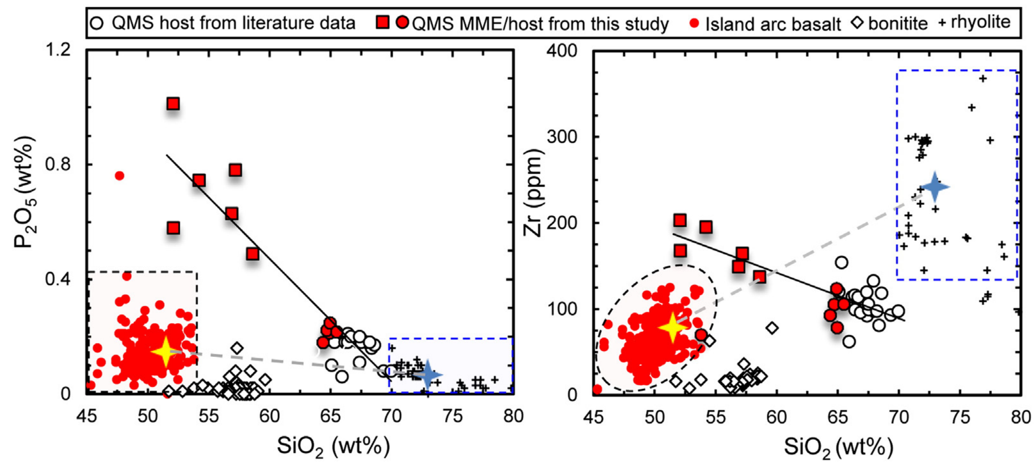

Fig. 11. (a) SiO_2 versus P_2O_5; (b) SiO_2 versus Zr. Data for Island arc basalt (n = 284 for P and 277 for Zr), boninite (n = 37 for P and 34 for Zr) and rhyolite (n = 66 for P and 45 for Zr) are from the Georoc database (http://georoc.mpch-mainz.gwdg.de/georoc/). Dashed and solid lines in a–b are hypothetical mixing lines and linear trend defined the QMS granodiorite and their MMEs, respectively. Data sources of the QMS and BJS plutons are the same as in Fig. 6.

in generating the QMS adakitic granodiorites is unimportant. Simple modal calculation of fractional crystallization using Model B indicates that the participation of garnet is no more than 3% (Fig. 9), but the low garnet proportion in combination with a large amount of amphibole–plagioclase fractionation can hardly generate the adakitic signature shown in the QMS pluton (Fig. 9a–b). Besides, mineralogically, garnet has been observed neither in the QMS MMEs and their host adakitic granodiorite, nor in the coeval igneous rocks in the eastern section of the NQOB. In addition, our preferred source for the QMS MMEs and their host adakitic granodiorite is partial melting of the ocean crust at amphibolite facies conditions (<40 km) (Mo et al., 2008; Niu and O'Hara, 2009; Niu et al., 2013) (see below), rather than the presence of garnet as a residual phase at garnet amphibolite or eclogite conditions.

It is also impossible to generate QMS adakitic granodiorites by fractionation of amphibole–plagioclase alone, because they trend to produce concave-upwards patterns between the MREE and HREE and lead to decreasing $(Dy/Yb)_N$ with increasing $(La/Yb)_N$ (Fig. 9c), owing to the affinity of calcic amphiboles for MREEs over the HREEs (Klein et al., 1997). Additionally, removal of amphibole–plagioclase would result in negative Eu anomalies in the residual melts, which is inconsistent with QMS adakitic granodiorites (Fig. 9d). In the case of our study, we emphasize that the widespread accessory minerals such as zircons and apatites in both QMS host adakitic granodiorite and particularly their cumulate MMEs played a significant role in generating QMS adakitic granodiorites. For example, zircon fractionation would increase $(Dy/Yb)_N$ (Fig. 9c) and the La/Yb and Sr/Y ratios of residue magmas (Fig. 9a–b), because $Kd^{Dy/Yb}_{zircon} = 0.140$, and $Kd^{La/Yb}_{zircon} = 0.005$ (Bea et al., 1994). Apatite fractionation can also increase the Sr/Y ratio (Fig. 9a–b), but decrease $(Dy/Yb)_N$ (Fig. 9c). Importantly, apatite fractionation would increase Eu/Eu* (Fig. 9d), because $Kd^{Sm}_{apatite} = 46$, $Kd^{Eu}_{apatite} = 25.5$, and $Kd^{Gd}_{apatite} = 43.9$ (Fujimaki et al., 1984). Note that the simple calculation of Model A (Appendix 6; Figs. 9 and 15), which involves a small proportion of zircon, apatite and sphene in combination with amphibole, biotite and plagioclase to form the fractionation assemblage can explain the characteristics of the QMS adakitic granodiorites. Although uncertainties exist for mineral partition coefficients, our model offers insights into the petrogenesis of the adakitic granodiorite as well as the enclosed MMEs in syn-collisional environments.

6.3. Constraints on the source

As discussed above, the primary magmas parental to the MMEs and their host granodiorite are most consistent with mafic andesitic magmas

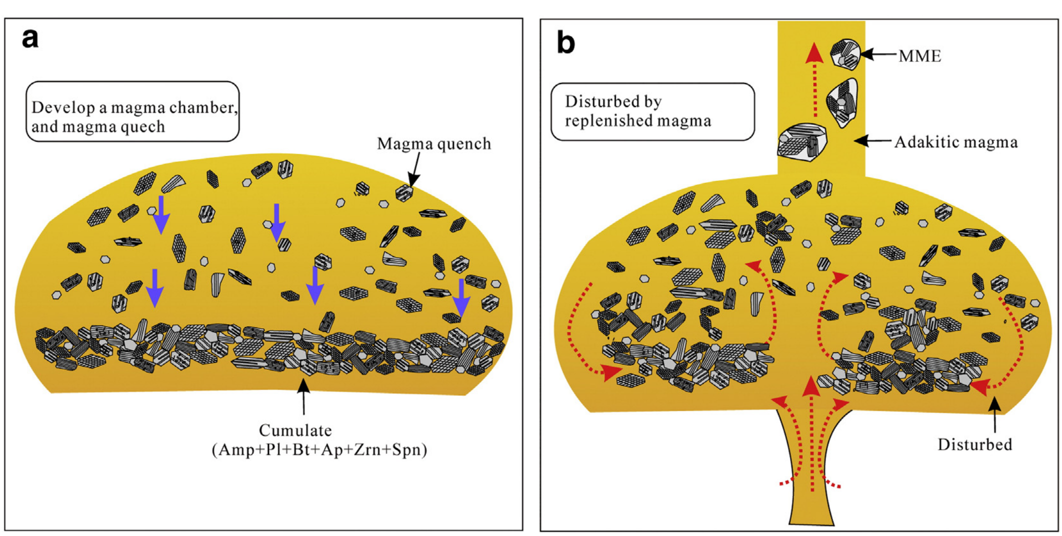

Fig. 12. Cartoon illustrating a possible scenario for MME formation. Earlier crystallized cumulate with the mineral assemblage of amphibole, biotite, plagioclase and accessory minerals such as zircon and apatite (a), which was later disturbed by subsequent magma replenishment in the magma chamber, constituting MMEs in the dominant host granodiorite.

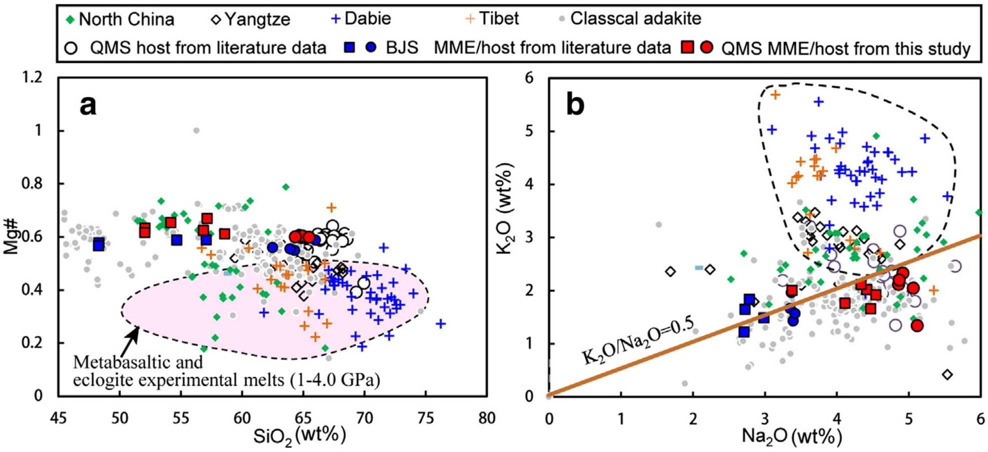

Fig. 13. Plots of (a) SiO_2 versus $Mg^{\#}$; (b) Na_2O versus K_2O. Data sources: classical adakite, resulting from partial melting of subducted ocean crust in modern arcs, are from the GeoRoc database (http://georoc.mpch-mainz.gwdg.de/georoc/); Tibet Plateau (Chung et al., 2003; Wang et al., 2005), Dabie Orogen (He et al., 2013; Wang et al., 2007), Yangtze Craton (Wang et al., 2006b; Xu et al., 2002); North China Craton (Chen et al., 2013a; Ma et al., 2015), experimental data (Sen and Dunn, 1994; Rapp and Watson, 1995). Data sources of the QMS and BJS plutons are the same as in Fig. 6.

of ocean crust origin during continental collision. In addition, our new data and the whole-rock Sr–Nd and zircon Hf isotopic data in the literature on the QMS pluton (Tseng et al., 2009; Yu et al., 2015) exhibit quite uniform Sr–Nd–Hf composition (Figs. 10j–l). Though the radiogenic Sr and slightly unradiogenic Nd isotopes indicate the input of crustal materials, the whole-rock $\varepsilon_{Hf}(t)$ values (+5.5 to +8.4) of this study and the zircon $\varepsilon_{Hf}(t)$ values (+4.2 to +7.7) in the literature (Yu et al., 2015) are indicative of significant mantle input or juvenile mafic continental crust derived from the mantle in no distant past (Zhang et al., 2016). As noted above, many adakitic rocks can be generated from the lower continental crust, but this is not applicable in our study (see above). In our case, the most likely source for the andesitic magmas with inherited mantle isotopic signatures parental to the QMS pluton is partial melting of the remaining part of the North Qilian ocean crust (Chen et al., 2015). On the other hand, contribution from continental crust is also required. This may occur in the melting region or in an evolving magma chamber rather than simple crustal level assimilation, because the Sr–Nd–Hf isotopes for the MMEs and their host granodiorites are closely similar and show a respectively narrow range of variation, and they do not show correlated variations with SiO_2 (Fig. 10j–l). Melting of recycled terrigenous sediments of upper continental crust and remaining part of the North Qilian oceanic crust in the melting region is more likely (Chen et al., 2015; Mo et al. 2008; Niu and O'Hara, 2009).

In the broad context of the continental collision, the model of partial melting of the remaining part of the ocean crust and the recycled terrigenous sediments has been proposed and tested by Niu and co-workers in southern Tibet, East Kunlun and Qilian Orogenic Belts (e.g., Chen et al., 2015; Huang et al., 2014; Mo et al., 2008; Niu and O'Hara, 2009; Niu et al., 2013; Zhang et al., 2016). In their model, during collision, the underthrusting North Qilian ocean crust would subduct/underthrust slowly, tend to attain thermal equilibrium with the superjacent warm active continental margin, and evolve along a high T/P path in P–T space as a result of retarded subduction and enhanced heating (Appendix Fig. S1). The warm hydrated ocean crust of basaltic composition and sediments of felsic composition with rather similar solidi would melt together under the amphibolite facies conditions (for details see Niu et al., 2013; also see Appendix Fig. S1).

Importantly, this model can generate andesitic magmas not only with inherited mantle isotopic signatures but also compositions similar to the bulk continental crust (BCC), except for notable depletion in highly compatible elements like Mg, Cr and Ni (Mo et al., 2008). This model together with experimental results of melting of metabasalt

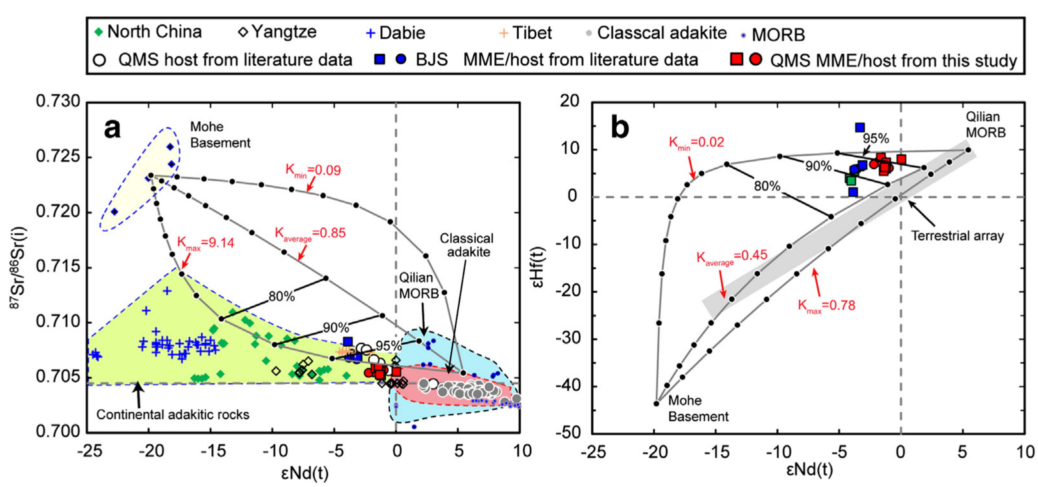

Fig. 14. (a) Nd–Sr and (b) Nd–Hf isotope diagrams for the QMS adakitic rocks and their MMEs. The MORB data are from Niu and Batiza (1997) and Niu et al. (2002), other data sources are the same as Fig. 13. Binary isotope mixing calculations between North Qilian Ocean MORB (average composition: Sr = 159.6 ppm, Nd = 10.5 ppm, Hf = 2.41, $^{87}Sr/^{76}Sr_{(t)} = 0.7054$, $\varepsilon_{Nd}(t) = 5.44$, $\varepsilon_{Hf}(t) = 9.93$) and Mohe Basement (average composition: Sr = 586 ppm, Nd = 32.97 ppm, Hf = 3.44, $^{87}Sr/^{76}Sr_{(t)} = 0.7234$, $\varepsilon_{Nd}(t) = -19.80$, $\varepsilon_{Hf}(t) = -43.65$) are after Chen et al. (2015) and references therein. $K = [(Sr/Nd)_{MORB}] / [(Sr/Nd)_{Mohe\ basement}]$, where K_{max}, K_{min}, and $K_{average}$ are the maximum, minimum and average values respectively.

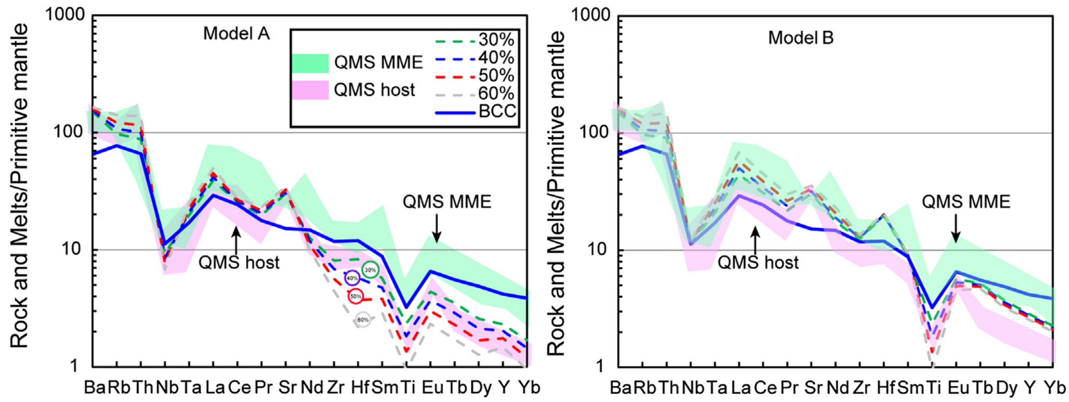

Fig. 15. Shows 30%, 40%, 50% and 60% fractional crystallization of mineral assemblages of Model A and Model B from the assumed magma along with the BCC and QMS adakitic granodiorites and their MMEs on primitive mantle normalized multi-element diagram. The light red and green shaded regions are the field of QMS adakitic granodiorite and MMEs, respectively. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

and eclogite (Fig. 13a) implies that the relatively high $Mg^{\#}$ (also high Cr and Ni) contents in QMS adakitic granodiorites may indeed reflect melt interaction with mantle peridotite during ascent. Although magmas produced through the above process lack the adakitic signature, it can be the ideal source that generates QMS adakitic granodiorites through fractional crystallization dominated by mineral assemblages represented by the MMEs. Note that this interpretation is consistent with binary isotope mixing calculations as proposed by Chen et al. (2015) (Fig. 14a–b), and with trace element model calculations (see above) (Figs. 9 and 15). As illustrated by these mass balance calculations, ~95% ocean crust and ~5% continental materials contribute to the source of the QMS pluton (Fig. 14), and 30%–50% fractional crystallization dominated by mineralogy and modes of the MMEs can lead to the highly evolved granodioritic composition of the QMS pluton with the adakitic signature (Figs. 9 and 15).

7. Conclusions

(1) The zircon U–Pb dating of the QMS pluton yields the same age (~430 Ma) for both the MMEs and their host granodiorite, which is the same as the closure time of the Qilian ocean and continental collision at ~440–420 Ma.
(2) The MMEs and their host granodiorite also share the same mineralogy with indistinguishable isotopic compositions, all of which indicate that the MMEs are cumulate formed at earlier stages of the same magmatic system rather than representing mantle melt required by the popular magma mixing model.
(3) The QMS host granodiorite has adakite-like major and trace element features, including high Sr, Sr/Y and La/Yb, but low Y and Yb. By accepting our model for the petrogenesis of the MMEs, it follows that the QMS adakitic granodiorite resulted from fractional crystallization dominated by mineral assemblages represented by the MMEs.
(4) The parental magma for the QMS pluton is best explained as resulting from partial melting of the remaining part of ocean crust together with recycled terrigenous sediments during continental collision. The resulting magma may have also experienced interaction with mantle peridotite during ascent.

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.lithos.2016.01.033.

Acknowledgments

We thank Li Su for the assistance with whole rock major, trace elements and zircon U–Pb age analysis, Minwu Liu with electron microprobe analysis, and Jinlong Ma, Xirong Liang and Zhongyuan Ren with whole rock Sr–Nd–Hf isotope analysis. Pu Sun, Huixiang Cui and Yuxing Ma are thanked for their help with sample preparation. We also thank editor Sun-Lin Chung for handling this manuscript and Prof. Michael Roden and one anonymous reviewer for constructive comments and suggestions. This work was supported by the National Natural Science Foundation of China (NSFC: 91014003, 41130314), Chinese Academy of Sciences (Innovation Grant Y42217101L) and grants from regional and local authorities (Shandong Province and City of Qingdao), two projects of Chinese Geological Survey Departments and Offices (1212011121092, 1212011220928).

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