## 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.

Highlights:

1. The QMS adakitic granodiorites and their MMEs formed at ~430 Ma.

2. The MMEs are cumulate rocks formed at earlier stages of the same magmatic systems.

3. The QMS adakitic granodiorites resulted from fractional crystallization dominated by mineral assemblages represented by the MMEs.

4. 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	Syn-collisional adakitic granodiorites formed by fractional crystallization:
2	insights from their enclosed mafic magmatic enclaves (MMEs) in the Qumushan
3	pluton, North Qilian Orogen at the northern margin of the Tibetan Plateau
4	Shuo Chen <sup>a,b*</sup> , Yaoling Niu <sup>a, c*</sup> , Jiyong Li <sup>a,b</sup> , Wenli Sun <sup>a</sup> , Yu Zhang <sup>d</sup> , Yan Hu <sup>a,b</sup> , Fengli Shao <sup>a,b</sup>
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6	<sup>a</sup> Institute of Oceanology, Chinese Academy of Sciences, Qingdao 266071, China.
7	<sup>b</sup> University of Chinese Academy of Sciences, Beijing 100049, China
8	<sup>c</sup> Department of Earth Sciences, Durham University, Durham DH1 3LE, UK
9	<sup>d</sup> School of Earth Sciences, Lanzhou University, Lanzhou 730000, China
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15	*Corresponding authors:
16	Mr. Shuo Chen (chenshuo528@foxmail.com)
17	Professor Yaoling Niu (yaoling.niu@foxmail.com)
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# 23 Abstract

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25	North Qilian Orogen at the northern margin of the Greater Tibetan Plateau, has typical adakitic
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27	an unprecedented insight into the petrogenesis of both the adakitic host granodiorite and the enclosed
28	MMEs. The MMEs and their host granodiorites share many characteristics in common, including
29	identical crystallization age (~430 Ma), same mineralogy, similar mineral chemistry and whole-rock
30	isotopic compositions, indicating their genetic link. The MMEs are most consistent with being of
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32	granodiorite. Subsequent replenishment of adakitic magmas could have disturbed the cumulate piles as
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35	consistent with fractional crystallization dominated by the mineral assemblage of the MMEs. The
36	parental magma for the QMS granodiorite is best explained as resulting from partial melting of the
37	ocean crust together with recycled terrigenous sediments during continental collision, which may have
38	also experienced interaction with mantle peridotite during ascent.
39	Keywords: Adakitic rocks; Mafic magmatic enclaves; Cumulate; Syn-collisional granodiorite; North

40 Qilian Orogen

# 41 1. Introduction

42	"Adakite" was introduced by Defant and Drummond (1990) after the name of Adak Island in the
43	Aleutian arc. It refers to a group of intermediate-felsic igneous rocks observed in modern oceanic and
44	continental arcs genetically associated with seafloor subduction. They are characterized by high Sr,
45	light rare earth elements (REEs), Sr/Y (>40) and La/Yb (>20), low Y and heavy REEs, and lack of
46	obvious Eu anomalies. It was initially considered that adakites were derived by partial melting of
47	young ( $\leq 25$ Myrs) and warm subducting/subducted ocean crust in subduction zones (Defant and
48	Drummond, 1990). The origin of adakite has since been one of the most popular subjects of research in
49	igneous petrology due to its use for tectonic finger-printing (see Castillo, 2006, 2012), yet recent
50	studies have shown that adakite or rocks with adakitic compositions can be produced in various ways
51	and in different settings (Castillo et al., 1999; Xu et al., 2002; Chung et al., 2003, 2005; Wang et al.,
52	2005, 2007; Macpherson et al., 2006; RodrIguez et al., 2007; Streck et al., 2007; He et al., 2013; Chen
53	et al., 2013a; Song et al., 2014a). Because adakite is defined on the basis of certain trace element
54	characteristics as detailed above, geochemistry in combination with experimental geochemistry has
55	been widely used to discuss the petrogenesis of adakites and adakitic rocks (e.g., Defant and
56	Drummond, 1990; Sen and Dunn, 1994; Castillo et al., 1999; Xu et al., 2002; Wang et al., 2005; Xiong
57	et al., 2005; Castillo, 2006, 2012). However, a petrological approach is essential for petrological
58	problems and is expected to offer insights into the petrogenesis of adakites and adakitic rocks. Indeed,
59	mafic magmatic enclaves (MMEs) hosted in adakitic rocks have been recently recognized, and the
60	processes of the MME formation may offer a fresh perspective on the petrogenesis of the adakitic host
61	(e.g., RodrIguez et al., 2007; Chen et al., 2013b).

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In this paper, we report our petrological, mineralogical and geochemical analyses and

trace-element modeling on an MME-bearing 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., Wang et al., 2006a; Tseng et al., 2009; 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.

## 68 2. Geological setting

69 The NW-SE-trending NQOB is located between the Alashan Block to the northeast and the Qilian 70 Block to the southwest, and is offset to the northwest by the Altyn-Tagh Fault (Fig.1a). It is made up of 71 Early Paleozoic subduction-zone complexes including ophiolitic melanges, blueschists and eclogites, 72 Silurian flysch formations, Devonian molasse, and Carboniferous to Triassic sedimentary cover 73 sequences (Fig. 1a) (Song et al., 2007, 2013; Zhang et al., 2007). It is composed of three subunits, i.e., 74 (1) the southern ophiolite belt, (2) the middle arc magmatic belt and (3) the northern back-arc basin 75 ophiolite-volcanic belt (Fig. 1a) (Song et al., 2007, 2013; Zhang et al., 2007; Chen et al., 2014). It is 76 generally accepted that the NQOB is an Early Paleozoic suture zone, which records a long tectonic 77 history from seafloor spreading/subduction to the ultimate continental collision and mountain-building 78 (see Song et al., 2013). The Qumushan (QMS) pluton we studied is about 60km<sup>2</sup> in outcrop located in 79 the eastern section of the NQOB. It lies approximately 10 km southeast of the Baojishan (BJS) pluton 80 (Fig.1b). The QMS pluton intruded the Ordovician sedimentary and metamorphic rocks of Yingou 81 group (Fig.1b). MMEs are widespread in the host granodiorite (Fig. 2a).

### 82 **3. Analytical methods**

#### 83 3.1. Zircon U–Pb ages

84 Zircons were separated by using combined methods of heavy liquid and magnetic techniques 85 before hand-picking under a binocular microscope. The selected zircons were set in an epoxy mount 86 that was polished to expose zircon interiors. Cathodoluminescence (CL) images were taken at China 87 University of Geosciences in Wuhan (CUGW) to examine the internal structure of individual zircon 88 grains. The zircon U-Pb dating was done using LA-ICP-MS at China University of Geosciences in 89 Beijing (CUGB). The instrument consists of an Agilent 7500a quadrupole inductively coupled plasma 90 mass spectrometry (ICP-MS) coupled with a UP-193 Solid-State laser (193 nm, New Wave Research 91 Inc.). Laser spot size was set to be  $\sim 30 \mu m$ . Zircon 91500 (Wiedenbeck et al., 1995) and a secondary 92 standard zircon TEMORA (417 Ma) (Black et al., 2003) was used as an external standard. The 93 analytical procedure is given in Song et al. (2010a). Isotopic ratios and element concentrations of 94 zircons were calculated using GLITTER (ver. 4.4, Macquarie University). Common Pb correction was 95 applied using the method of Andersen (2002). Results are given in Appendix 1.

#### 96 *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 1µm. Results are given in Appendix 2 and Appendix 3.

100 3.3. Major and trace elements

101 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  $TiO_2(\sim 1.5\%)$  and  $P_2O_5(\sim 2.0\%)$ . 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.

## 108 3.4. Whole-rock Sr-Nd-Hf isotopes

109 Whole-rock Sr-Nd-Hf isotopic analyses were done in Guangzhou Institute of Geochemistry, 110 Chinese Academy of Sciences (GIG-CAS). The rock powders were digested and dissolved in 111 HF-HNO<sub>3</sub> acid mixtures and dried on a hot-plate. Sr-Nd-Hf fractions were separated using small Sr 112 Spec resin columns to obtain Sr and Nd-Hf bearing fractions. Sr isotopic compositions were 113 determined using a Neptune Plus multi-collector ICP-MS (MC-ICP-MS) following Ma et al. (2013a). 114 Nd fractions were then separated by passing through cation columns followed by HDEHP columns. 115 Separation of Hf from the matrix and rare earth elements was carried out using a combined method of 116 Eichrom RE and HDEHP columns. Nd and Hf isotopic compositions were determined using a 117 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 (2 $\sigma$ , n=13). 118 119 Repeated analysis of BHVO-2 and JB-3 during the same period of sample analysis yielded <sup>143</sup>Nd/<sup>144</sup>Nd 120  $0.512977\pm14$  (2 $\sigma$ , n=8) and  $0.513053\pm18$  (2 $\sigma$ , 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 (2 $\sigma$ , n = 13) and 0.283216 121  $\pm$  15 (2 $\sigma$ , n=6). All measured <sup>87</sup>Sr/<sup>86</sup>Sr, <sup>143</sup>Nd/<sup>144</sup>Nd and <sup>176</sup>Hf/<sup>177</sup>Hf ratios were normalized to <sup>86</sup>Sr/<sup>88</sup>Sr 122

123 = 0.1194, <sup>146</sup>Nd/<sup>144</sup>Nd = 0.7219 and <sup>179</sup>Hf/<sup>177</sup>Hf = 0.7325, respectively. The USGS rock standards JB-3

124 and BHVO-2 run with our samples give values consistent with the reported reference values (GeoREM,

125 <u>http://georem.mpch-mainz.gwdg.de/</u>). Results are given in Appendix 5.

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# 6 4. Petrography and mineral chemistry

# 127 4.1. Granodiorite

128 The QMS pluton is of granodioritic composition with a mineral assemblage of plagioclase (45 129 vol. %-50 vol. %), quartz (35 vol. %-42 vol. %), amphibole (3 vol. %-10 vol. %), biotite (2 vol. %-10 130 vol. %), minor K-feldspar, and accessory minerals such as apatite, sphene, zircon and Fe-Ti oxides (Fig. 131 2d). Plagioclase crystals are euhedral to subhedral, and are of oligoclase composition with  $An_{12-24}$  (Fig. 132 3a). Zoned-plagioclase crystals display normal zoning with more anorthitic cores rimmed by less calcic 133 compositions (Fig. 3a). Amphibole is always present as euhedral to subhedral crystals despite the 134 variably small abundances (Fig. 2d). Amphibole grains are usually homogeneous and rarely display 135 disequilibrium textures. Amphiboles from the host granodiorite can be classified as edenite (Appendix 136 3, Fig. 4) following Leake et al. (1997). They have medium SiO<sub>2</sub>, and low TiO<sub>2</sub> (0.37-1.24 wt. %), 137 Na<sub>2</sub>O (0.87-1.48 wt. %) and K<sub>2</sub>O (0.29-1.69 wt. %).

## 138 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 (Figs. 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

143	minerals such as apatite, sphene, zircon and Fe-Ti oxides), thus giving a dioritic bulk composition.
144	Plagioclase mostly occurs as subhedral grains with compositions similar to those in the host
145	granodiorite. Zoned-plagioclase in the MMEs shows a compositional continuum with cores slightly
146	more anorthitic than the rims (Fig. 3b). Amphibole in the MMEs is compositionally identical to that in
147	the host granodiorite (Fig. 4). Biotite is yellow brown with subhedral to euhedral forms. The MMEs
148	show no chilled margins nor textures of crystal resorption or reactive overgrowth. These rocks mainly
149	exhibit porphyritic-like textures.

150 **5. Results** 

## 151 5.1. Zircon U–Pb ages

152 Four samples (2 host-MME pairs) were chosen for dating. In CL images (Figs. 5a, c), zircons from 153 the host granodiorites (QMS12-04host and QMS12-10host) are transparent, colorless, and mostly 154 euhedral columnar crystals of varying size (~150-300µm long with length/width ratio of 1:1-3:1) with 155 well-developed oscillatory zoning. The zircons have varying U (~ 28-386 ppm) and Th (~ 69-423 ppm) 156 with Th/U ratio of 0.3-1.4. All these characteristics are consistent with the zircons being of magmatic 157 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 (1 $\sigma$ , MSWD=0.15, n=23) 158 159 and  $431.5 \pm 2.6$  Ma (1 $\sigma$ , MSWD=0.19, n=20), respectively (Figs. 5a, c), representing the crystallization 160 age (~430 Ma) of the host granodiorite. These age data are in agreement with those in the literature 161 (Tseng et al., 2009; Yu et al., 2015). 162 Zircons from the MMEs (QMS12-04MME and QMS12-10MME) show similar optical properties

163 to those in the host with oscillatory zoning (Figs. 5b, d) and varying size (~150-200 $\mu$ m 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.  $429.6 \pm 2.8$  Ma (1 $\sigma$ , MSWD=0.48, n=18) and  $431.2 \pm 2.8$  Ma (1 $\sigma$ , MSWD=0.2, n=19), respectively (Figs. 5b, d).

168 5.2. Major and trace elements

169 Eleven representative QMS granodiorite samples and their hosted MMEs (including 5 host-MME 170 pairs) were analyzed for whole-rock major and trace element compositions (Appendix 4). The 171 granodiorite samples have high SiO<sub>2</sub> (64.37-65.49 wt.%), Al<sub>2</sub>O<sub>3</sub> (16.09-17.61 wt.%), Na<sub>2</sub>O (4.86-5.12 172 wt.%) and Na<sub>2</sub>O/K<sub>2</sub>O (2.11-3.82) with medium total alkalis (Na<sub>2</sub>O+K<sub>2</sub>O = 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 173 174 CaO (3.60-4.10 wt.%). They are calc-alkaline (Fig. 6b) and metaluminous to weakly peraluminous 175 (A/CNK= 0.93 to 1.03) (Fig. 6c), which is typical for I-type granitoids (Chappell and White, 1992). In 176 contrast, the MMEs plot in the fields of diorite, monzodiorite and monzonite (Fig. 6a). They are 177 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<sub>2</sub> (52.06-58.59 wt.%), higher Fe<sub>2</sub>O<sub>3</sub><sup>T</sup> (6.12-8.50 wt.%), 178 179 MgO (5.09-7.22 wt.%), CaO (4.99-6.57 wt.%), P2O5 (0.49-1.01 wt.%), and slightly higher Mg<sup>#</sup>  $(0.63-0.68; Mg^{\#}=Mg/[Mg+Fe^{2+}])$  than the host granodiorites. 180

181 In the chondrite-normalized REE diagram, the QMS granodiorite samples are characterized by a 182 relatively flat heavy REE (HREE) pattern ( $[Dy/Yb]_N = 1.32-1.54$ ), slightly negative to positive Eu 183 anomalies (Eu/Eu\*=0.88-1.13), and lower total REE contents ( $\Sigma REE=76-134$  ppm) than the hosted 184 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]<sub>N</sub> = 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 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

194 high Sr/Y and La/Yb ratios, and lower Y and Yb abundances, thus plotting in the adakite fields in the

195 discrimination diagrams (Figs. 9a-b), while most MMEs plot in the normal arc rock field.

# 196 5.3. Sr-Nd-Hf isotopic geochemistry

197 Whole-rock Sr-Nd-Hf isotopic compositions for the MMEs and their host granodiorite are given in 198 Appendix 5. The initial <sup>87</sup>Sr/<sup>86</sup>Sr <sub>(t)</sub>,  $\varepsilon_{Nd}(t)$  and  $\varepsilon_{Hf}(t)$  values are calculated at 430 Ma using the zircon 199 age data (see Fig. 5 above). On the plots of <sup>87</sup>Sr/<sup>86</sup>Sr <sub>(t)</sub>,  $\varepsilon_{Nd}(t)$  and  $\varepsilon_{Hf}(t)$  against SiO<sub>2</sub> (Figs. 10j-l), both 109 host granodiorite and MME samples are indistinguishable and overlapping within a narrow range (also 100 see Appendix 5).

202 On SiO<sub>2</sub>-variation diagrams (Fig. 10), the MMEs and their host granodiorite define linear trends 203 for most elements (e.g.,  $TiO_2$ ,  $Fe_2O_3^T$ , MnO, MgO, CaO, P<sub>2</sub>O<sub>5</sub>, Eu and Hf abundances) and trace 204 element ratio (e.g., Hf/Sm) (Figs. 10a-i), but show no correlations of initial Sr, Nd, and Hf isotopic 205 compositions with SiO<sub>2</sub> (Figs. 10j-1).

#### 206 6. Discussion

#### 207 6.1. Petrogenesis of the mafic magmatic enclaves

208	Several models have been proposed for the origin of MMEs in the literature, including foreign
209	xenoliths (usually country rocks; e.g., Vernon, 1983; Xu et al., 2006), refractory and residual phase
210	assemblages derived from granitoid sources (e.g., the restite model; Chappell et al., 1987; Chappell and
211	White, 1991), chilled material or cumulate of early-formed co-genetic crystals (e.g., Dodge and Kistler,
212	1990; Dahlquist, 2002; Donaire et al., 2005; RodrIguez et al., 2007; Niu et al., 2013; Huang et al., 2014;
213	Chen et al., 2015), and basaltic melt material incompletely digested and homogenized during a magma
214	mixing process (e.g., Vernon, 1983; Didier, 1987; Castro et al., 1990; Dorais et al., 1990; Barbarin and
215	Didier, 1991; Chappell and White, 1991; Barbarin, 2005; Chen et al., 2009a, 2013b; Wang et al., 2013).
216	We critically evaluate these interpretations below.
217	6.1.1. Textural and chemical relationships of the MMEs and their hosts

218 The textural and chemical relationships of the QMS MMEs and their host granodiorite concur 219 with the findings for the BJS pluton (Chen et al., 2015), and are summarized as follows: (1) the MMEs 220 in the QMS granodiorites are ellipsoidal, or elongate, show no chilled margins, no textures of crystal 221 resorption nor reactive overgrowth, but exhibit typical magmatic texture (Figs. 2a-f); (2) they have a 222 mineral assemblage identical to, and more mafic phases than, their host granodiorite (Figs. 2c-f); (3) 223 they have mineral compositions (e.g., amphibole and plagioclase) identical to those of their host (Fig. 224 3-4); (4) they have the same age (~430 Ma) as their host (Fig. 5); (5) their different major and trace 225 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<sub>2</sub>O<sub>3</sub>, CaO and trace elements easily incorporated into these phases (e.g., TiO<sub>2</sub>, P<sub>2</sub>O<sub>5</sub>, Hf and HREEs) (Figs. 10a-i); and (6) more importantly, they have overlapping and indistinguishable Sr-Nd-Hf

- isotopes with their host granodiorite (Figs. 10j-l).
- 230 Any successful models for the origin of MMEs must be consistent with these observations. 231 Models for MMEs as foreign xenoliths from country rocks (e.g., Xu et al., 2006) can be readily rejected, 232 as there is no evidence of reaction textures for the MMEs. Likewise, the identical age (~430 Ma) of the 233 MMEs and their host as well as the magmatic textures, constitute a strong argument against the restite 234 origin (e.g., Chappell et al., 1987). In addition, the MMEs do not contain peraluminous minerals and 235 their metaluminous composition (Fig. 6c) also excludes their derivation by melting of peraluminous 236 restites (Barbarin, 2005). Therefore, the most straightforward interpretation is that the MMEs and their 237 hosts formed as different products of a common magmatic system.
- 238 6.1.2. Assessing the origin of magma mixing

239 Similar observations mentioned above between the MMEs and their host granitoids have been 240 identified first by Pabst (1928) and by many others since then. The MMEs were thus described as 241 "autoliths", referring to "cogenetic" or part of the same system. Despite the "autoliths" nature of the 242 MMEs with the host, this interpretation has been questioned: (1) Why are isotopic values of some 243 MMEs intermediate between those of crustal and mantle materials (e.g., DePaolo, 1981; Barbarin, 244 2005)? (2) Why are the MMEs fine-grained (e.g., Barbarin and Didier, 1991)? Because of these 245 questions, a model of magma mixing between mantle-derived mafic magma and crust-derived felsic 246 magma was proposed to address the above issues: (1) the intermediate isotopic values of the MMEs 247 were commonly interpreted as the result of magma mixing between a mantle-derived mafic magma and 248 a crust-derived felsic magma, because a mafic magma derived from upper mantle provides not only 249 material but also the heat necessary for melting and subsequently mixing with the crustal rocks (e.g., 250 Barbarin, 2005); (2) the fine-grained MMEs were interpreted as due to quenching against host felsic 251 magmas (e.g., Vernon, 1984; Furman and Spera, 1985; Barbarin, 2005), owing to their higher liquidus 252 and solidus temperatures compared to felsic magmas. As a result, the magma mixing model has been 253 the most popular interpretation for the petrogenesis of the MMEs (see critical review by Niu et al., 254 2013).

255 Actually, there are many compelling lines of evidence for magma mixing in many granitoids, 256 especially (1) where a clear isotopic contrast exists between the MMEs and the hosts (e.g., Holden et 257 al., 1987; Chen et al., 2009b; Liu et al., 2013); and (or) (2) where disequilibrium features occur in the 258 MMEs, e.g., complex zoning of clinopyroxene crystals that have distinctly low-MgO cores surrounded 259 by high-MgO rims (e.g., Chen et al., 2013a; Wang et al., 2013), or resorption textures or reversed 260 zoning of plagioclase (Pietranik et al., 2006; Chen et al., 2009a, 2009b). In the case of our study, 261 however, none of the above has been observed. Instead, many lines of evidence argue against the 262 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., Dorais et al., 1990; Barbarin, 2005; Chen et al., 2009b; Zhang et al., 2010) using some experimental interpretations that isotopic equilibration is generally more easily achieved than chemical equilibration 269 (Lesher, 1990). However, we emphasize that it is physically unlikely that isotopes become 270 homogenized whereas major and trace elements are not (Niu et al., 2013), because isotopes are "carried" 271 by the relevant chemical elements and isotopic diffusion cannot take place without the diffusion of the 272 "carrying" elements (Chen et al., 2015). In fact, there are two forceful arguments against thermal and 273 chemical equilibration: (1) the MMEs exhibit no textures of crystal resorption or reactive overgrowth 274 (Figs. 2b-c), and (2) plagioclase in the MMEs and their host granodiorite shows no compositional or 275 textural disequilibrium (Fig. 3). In addition, although the fine-grained texture of the MMEs could be 276 interpreted as resulting from quenching in the magma mixing model, quenching of the mafic magma 277 would lead to a significantly high viscosity contrast between the solidified enclaves and the felsic host 278 magma, thereby inhibiting deformation, mechanical mixing (Caricchi et al., 2012; Farner et al., 2014) 279 and isotope homogenization between the MMEs and the host.

280 Second, strongly correlated variations between major and trace elements (Figs. 10a-i) are 281 consistent with modal mineralogy control, as the result of magma evolution (i.e., the MMEs are 282 cumulate and the host represents residual melt) rather than mixing of two magmas with entirely 283 different origins because magma mixing is a complex, multi-stage process in which linear trends can be 284 disturbed (e.g., Clemens, 1989; Donaire et al., 2005; Chen et al., 2015). Moreover, the distinctive high 285 abundances of some elements in the MMEs, such as Zr and P (Fig. 11), cannot be explained by magma 286 mixing because these elements are controlled by the presence of accessory phases, such as zircon and 287 apatite. As shown in Fig. 11, mantle derived basaltic magmas would have much lower Zr and P<sub>2</sub>O<sub>5</sub> than 288 in the QMS MMEs. For example, quantitative calculations by Lee and Bachmann (2014) suggested that 289 10-20% melting of an upper mantle with 5 ppm Zr and 0.019 wt.%  $P_2O_5$  (equivalent to that estimated 290 for depleted mid-ocean ridge basalt mantle), would yield primary liquids with 25-50 ppm Zr and 291 0.1-0.2 wt.% P<sub>2</sub>O<sub>5</sub>. These concentrations are much lower than in the QMS MMEs. Additionally, 292 boninites are thought to result from partial melting of highly depleted harzburgitic mantle peridotites 293 induced by subduction-zone slab dehydration (Niu, 2005), but they also have lower Zr and  $P_2O_5$ 294 contents (Fig. 11). More importantly, magma mixing between a basalt with any silicic end-member 295 (e.g., rhyolite) would generate a mixing array (Figs. 11a-b, the dash lines) totally different from the 296 linear trend (Figs. 11a-b, the solid lines) defined by the QMS granodiorite and their MMEs. In contrast, 297 all of these observations are consistent with the interpretation that the MMEs represent earlier cumulate 298 with greater amounts of zircon and apatite than their hosts (e.g., Donaire et al., 2005).

299 6.1.3. Formation of the mafic magmatic enclaves

300 The foregoing observations, illustrations and discussion leave us with the best interpretation that 301 the MMEs represent the earlier crystallized cumulate that were later disturbed by subsequent melt 302 replenishment and induced magma convection in the magma chamber. As illustrated in Fig. 12, when a 303 primitive magma body is emplaced into a cold environment (e.g., developing a magma chamber) with 304 the wall-rock having temperatures below the liquidus of the magma, magma quench and rapid 305 crystallization are inevitable because of the thermal contrast. For an andesitic primitive magma parental 306 to the syn-collisional granitoids (Niu et al., 2013), the first major liquidus phases would be amphibole, 307 biotite, plagioclase and accessory minerals such as zircon and apatite, and rapid quench will facilitate 308 abundant nucleation without between-nuclei space for rapid growth, thus resulting in the formation of 309 fine-grained cumulate (Chen et al., 2015). This is a fundamentally important petrologic concept with 310 which any interpretation must comply. This early formed fine-grained mafic cumulate piles (largely 311 plastic before complete solidification) can be readily disturbed by subsequent magma replenishment

#### 313 6.2 Petrogenesis of QMS adakitic granodiorite

314 6.2.1 Implication from the MMEs

315 Recently, mixing of basaltic and felsic magmas was proposed for the genesis of some high-Mg 316 and low SiO<sub>2</sub> adakitic rocks from Mount Shasta and the North China Craton using the presence of 317 ubiquitous MMEs as evidence (Chen et al., 2013b) and also based on the disequilibrium petrographic 318 characteristics in high-Mg andesites (Streck et al., 2007; Chen et al., 2013a). This interpretation could 319 be reasonable, but it is not the case here because there is no petrographic and compositional evidence 320 for magma mixing as elaborated above. That is, the MMEs in the QMS adakitic granodiorite are not 321 evidence for magma mixing, but rather they are of cumulate origin without direct asthenospheric 322 mantle participation (e.g., Dahlquist, 2002). More importantly, the MMEs comprise dominantly 323 amphibole and plagioclase, which are common cumulate minerals of andesitic melts. If the parental 324 melts were basaltic, the typical cumulate from such evolved basaltic melt would be gabbro dominated 325 by clinopyroxene and plagioclase (Chen et al., 2015). It can be inferred from this important petrological 326 concept that the parental magmas of the MMEs and their host granodiorite was mafic andesitic (Niu et 327 al., 2013; Chen et al., 2015).

# 328 6.2.2 Assessing the model of melting of mafic lower continental crust

To date, some intra-continental high-MgO or -Mg<sup>#</sup> (also high Cr and Ni contents) adakitic rocks have been considered to originate from melting of delaminated lower crust (e.g., Xu et al., 2002; Gao et al., 2004; Wang et al., 2006b). By accepting and applying this model, it has been previously interpreted

332	that the QMS adakitic rocks were derived from delaminated lower crust, and they subsequently
333	interacted with mantle peridotite during ascent (Tseng et al., 2009; Yu et al., 2015). Although this
334	model seems plausible and applicable to the QMS adakitic rocks, it has more difficulties than
335	certainties. First, the QMS adakitic granodiorites have lower (Dy/Yb) <sub>N</sub> , (La/Yb) <sub>N</sub> , and distinctive low
336	K <sub>2</sub> O/Na <sub>2</sub> O ratios (Fig. 13b), which are significantly different from the composition of adakitic rocks
337	inferred to be derived from partial melting of the thickened or delaminated lower continental crust.
338	Second, the Nd and Hf isotopic data of the QMS adakitic granodiorite indicate a significant mantle
339	input, which is also inconsistent with those of lower continental crust origin (Fig. 14a). Finally, the
340	existence of the Paleo-Qilian ocean is manifested by the ophiolites and eclogites in the North Qilian
341	orogenic belt; the ocean basin started its subduction at ~520 Ma, and was eventually closed at the end
342	of the Ordovician (~445 Ma) followed by continental collision (see Song et al., 2013). Accordingly,
343	the coeval (~430 Ma) MMEs and their adakitic host granodiorite of the QMS pluton are best
344	interpreted as a magmatic response to the collision between the Qilian-Qaidam block and Alashan
345	block, thereby being contrary to the environment of crustal extension required by a delaminated lower
346	crustal origin. In fact, continuous lithosphere extension and delamination in the NQOB occurred at
347	<400 Ma, which resulted in strong magmatic activity and formed a number of
348	diorite-granodiorite-granite plutons with ages of ~400-360 Ma (Song et al., 2013, 2014b).

349

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.

356 In our model, the magmas parental to the MMEs and their host granodiorite are the same mafic 357 andesitic magmas in a syn-collisional setting, rather than basaltic magmas in an arc setting of active 358 seafloor subduction advocated in the literature (e.g., Macpherson et al., 2006). That is, the QMS 359 adakitic granodiorites are products of fractional crystallization dominated by the mineral assemblage 360 indicated by the MMEs from mafic andesitic magmas. We can further consider two fractional 361 crystallization models to elucidate the effect of crystallization of the observed mineralogy on trace 362 elements using closed-system Rayleigh fractionation equation: (1) Model A, in reasonable agreement 363 with observed mineral proportions of the MMEs, 50% amphibole, 40% plagioclase, 7.52% biotite, 2.2% 364 apatite, 0.2% zircon and 0.03% sphene; (2) Model B, which incorporates fractionation of garnet, 50% 365 amphibole, 40% plagioclase, 7.6% biotite, 2.4% garnet. The partition coefficients used in the 366 calculations are for intermediate-felsic magmas (Appendix 6). For convenience (see below), the 367 assumed parental magma (Appendix 6) is very similar to the bulk continental crust (BCC) composition 368 (Rudnick and Gao, 2003) (Fig. 15), which is the same as the ~ 60 Ma Linzizong andesite in southern 369 Tibet (Mo et al., 2008; Niu et al., 2013), in terms of major and trace element abundances. 370 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)<sub>N</sub> ratio in the QMS adakitic granodiorites remain constant with increasing  $(La/Yb)_N$  (Fig. 9c), which indicate that the effect of garnet fractionation in generating the QMS adakitic granodiorites is

374 unimportant. Simple modal calculation of fractional crystallization using Model B indicates that the

375 participation of garnet is no more than 3% (Fig. 9), but the low garnet proportion in combination with a 376 large amount of amphibole-plagioclase fractionation can hardly generate the adakitic signature shown 377 in the QMS pluton (Figs. 9a-b). Besides, mineralogically, garnet has been observed neither in the QMS 378 MMEs and their host adakitic granodiorite, nor in the coeval igneous rocks in the eastern section of the 379 NQOB. In addition, our preferred source for the QMS MMEs and their host adakitic granodiorite is 380 partial melting of the ocean crust at amphibolite facies conditions (<40km) (Mo et al., 2008; Niu and 381 O'Hara, 2009; Niu et al., 2013) (see below), rather than the presence of garnet as a residual phase at 382 garnet amphibolite or eclogite conditions.

383 It is also impossible to generate QMS adakitic granodiorites by fractionation of 384 amphibole-plagioclase alone, because they trend to produce concave-upwards patterns between the 385 MREE and HREE and lead to decreasing (Dy/Yb)<sub>N</sub> with increasing (La/Yb)<sub>N</sub> (Fig. 9c), owing to the 386 affinity of calcic amphiboles for MREEs over the HREEs (Klein et al., 1997). Additionally, removal of 387 amphibole-plagioclase would result in negative Eu anomalies in the residual melts, which is 388 inconsistent with QMS adakitic granodiorites (Fig. 9d). In the case of our study, we emphasize that the 389 widespread accessory minerals such as zircons and apatites in both QMS host adakitic granodiorite and 390 particularly their cumulate MMEs played a significant role in generating QMS adakitic granodiorites. 391 For example, zircon fractionation would increase (Dy/Yb)<sub>N</sub> (Fig. 9c) and the La/Yb and Sr/Y ratios of residue magmas (Figs. 9a-b), because  $Kd_{zircon}^{Dy/Yb} = 0.140$ , and  $Kd_{zircon}^{La/Yb} = 0.005$  (Bea et al., 1994). 392 393 Apatite fractionation can also increase the Sr/Y ratio (Figs. 9a-b), but decrease (Dy/Yb)<sub>N</sub> (Fig. 9c). Importantly, apatite fractionation would increase Eu/Eu\* (Fig. 9d), because  $Kd_{apatite}^{Sm} = 46$ , 394  $Kd_{apatite}^{Eu} = 25.5$ ,  $Kd_{apatite}^{Gd} = 43.9$  (Fujimaki et al., 1984). Note that the simple calculation of Model A 395 396 (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.

401 6.3 Constraints on the source

402 As discussed above, the primary magmas parental to the MMEs and their host granodiorite are 403 most consistent with mafic andesitic magmas of ocean crust origin during continental collision. In 404 addition, our new data and the whole-rock Sr-Nd and zircon Hf isotopic data in the literature on the 405 QMS pluton (Tseng et al., 2009; Yu et al., 2015) exhibit quite uniform Sr-Nd-Hf composition (Figs. 406 10j-1). Though the radiogenic Sr and slightly unradiogenic Nd isotopes indicate the input of crustal 407 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 408 +7.7) in the literature (Yu et al., 2015) are indicative of significant mantle input or juvenile mafic 409 continental crust derived from the mantle in no distant past (Zhang et al., 2015). As noted above, many 410 adakitic rocks can be generated from the lower continental crust, but this is not applicable in our study 411 (see above). In our case, the most likely source for the andesitic magmas with inherited mantle isotopic 412 signatures parental to the QMS pluton is partial melting of the remaining part of the North Qilian ocean 413 crust (Chen et al., 2015). On the other hand, contribution from continental crust is also required. This 414 may occur in the melting region or in an evolving magma chamber rather than simple crustal level 415 assimilation, because the Sr-Nd-Hf isotopes for the MMEs and their host granodiorites are closely 416 similar and show a respectively narrow range of variation, and they do not show correlated variations 417 with SiO<sub>2</sub> (Figs. 10j-1). Melting of recycled terrigenous sediments of upper continental crust and 418 remaining part of the North Qilian oceanic crust in the melting region is more likely (Mo et al. 2008;

419 Niu and O'Hara 2009; Chen et al., 2015).

420 In the broad context of the continental collision, the model of partial melting of the remaining part 421 of the ocean crust and the recycled terrigenous sediments has been proposed and tested by Niu and 422 co-workers in southern Tibet, East Kunlun and Qilian Orogenic Belts (e.g., Mo et al., 2008; Niu and 423 O'Hara, 2009; Niu et al., 2013; Huang et al., 2014; Chen et al., 2015; Zhang et al., 2015). In their model, 424 during collision, the underthrusting North Qilian ocean crust would subduct/underthrust slowly, tend to 425 attain thermal equilibrium with the superjacent warm active continental margin, and evolve along a 426 high T/P path in P-T space as a result of retarded subduction and enhanced heating (Appendix Fig. S1). 427 The warm hydrated ocean crust of basaltic composition and sediments of felsic composition with rather 428 similar solidi would melt together under the amphibolite facies conditions (for details see Niu et al., 429 2013; also see Appendix Fig. S1).

430 Importantly, this model can generate andesitic magmas not only with inherited mantle 431 isotopic signatures but also compositions similar to the bulk continental crust (BCC), except for 432 notable depletion in highly compatible elements like Mg, Cr and Ni (Mo et al., 2008). This model 433 together with experimental results of melting of metabasalt and eclogite (Fig. 13a) implies that the relatively high Mg<sup>#</sup> (also high Cr and Ni ) contents in QMS adakitic granodiorites may indeed 434 435 reflect melt interaction with mantle peridotite during ascent. Although magmas produced through 436 the above process lack the adakitic signature, it can be the ideal source that generates QMS 437 adakitic granodiorites through fractional crystallization dominated by mineral assemblages 438 represented by the MMEs. Note that this interpretation is consistent with binary isotope mixing 439 calculations as proposed by Chen et al. (2015) (Figs. 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).

### 445 **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 ~440-420Ma.

(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.

453 (3) The QMS host granodiorite has adakite-like major and trace element features, including high Sr,

454 Sr/Y and La/Yb, but low Y and Yb. By accepting our model for the petrogenesis of the MMEs, it

- 455 follows that the QMS adakitic granodiorite resulted from fractional crystallization dominated by
- 456 mineral assemblages represented by the MMEs.
- 457 (4) The parental magma for the QMS pluton is best explained as resulting from partial melting of the
- 458 remaining part of ocean crust together with recycled terrigenous sediments during continental collision.
- 459 The resulting magma may have also experienced interaction with mantle peridotite during ascent.

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743

# 744 **Figure captions:**

745	Fig.1: (a) Simplified geological map of the North Qilian Orogen showing distributions of the main
746	tectonic units (modified after Song et al., 2013; Chen et al., 2015). (b) Simplified map of the Qumushan
747	(QMS) and Baojishan (BJS) area in the eastern section of the North Qilian Orogen. U-Pb ages are
748	shown for granodiorite and MMEs in the BJS and QMS plutons from Chen et al. (2015), Yu et al.
749	(2015) and this study as indicated.
750	Fig. 2: Photographs of the adakitic granodiorite and the MMEs in the field and in thin-sections. (a), (b)
751	and (c) showing the sharp contact of MMEs of varying size with their host granodiorite with MMEs
752	being finer-grained than the host; (d) showing the mineral assemblage of the adakitic host granodiorite
753	(QMS12-02host) and (e), (f) showing the mineral assemblage of MMEs (QMS12-02MME,
754	QMS12-06MME). Amp = amphibole; Bt = biotite; Pl= plagioclase; Qz = quartz; Ap = apatite; Zrn=
755	zircon. Plates c-f are taken under cross-polarized light.
756	Fig. 3: Photomicrographs showing a plagioclase crystal with a high-Ca core rimmed by a euhedral
757	overgrowth of low-Ca plagioclase in both (a) adakitic rocks (e.g., QMS12-04host) and (b) MMEs (e.g.,
758	QMS12-04MME). Numerals are the An contents. See Appendix 2 for compositional data.
759	Fig. 4: Chemical compositions of amphiboles from the host granodiorite and MMEs in the amphibole
760	classification diagram (Leake et al., 1997). Data from the host granodiorites and the MMEs of BJS
761	pluton (Chen et al., 2015) are also shown for comparison.
762	Fig. 5: Concordia diagrams of LA-ICP-MS U-Pb zircon age data and representative CL images of
763	zircon grains showing spots for the host adakitic granodiorites (a, c) and the MMEs (b, d) in the QMS

764 pluton.

765 Fig. 6: Classification diagrams of the host granodiorites and the MMEs in the QMS pluton. (a) Total 766 alkalis vs. SiO<sub>2</sub> (Le Maitre et al., 1989), (b) K<sub>2</sub>O vs. SiO<sub>2</sub>, and (c) A/NK vs. A/CNK. The blue circles 767 and squares are data from BJS granodiorites and their MMEs (Chen et al., 2015), and the open circles 768 are literature data on the QMS granodiorites (Wang et al., 2006a; Tseng et al., 2009; Yu et al., 2015). 769 Fig. 7: (a) Chondrite normalized REE patterns for the QMS host adakitic granodiorites and the MMEs; 770 (b) host rock-normalized REE patterns of MMEs. Chondrite REE values and bulk continental crust 771 (BCC) are from Sun and McDonough (1989) and Rudnick and Gao (2003), respectively. Shaded fields 772 of BJS granodiorite and the MMEs are from Chen et al. (2015). 773 Fig. 8: Average ocean crust-normalized (OC; Niu and O'Hara, 2003) trace element patterns for the

774 QMS host adakitic granodiorites and the MMEs.

775 Fig. 9: Plots of (a) Sr/Y vs. Y, where fields of adakite, and normal arc andesite-dacite-rhyolite are from 776 Defant and Drummond (1990); (b) La/Yb vs. Yb, discrimination lines are from Richards and Kerrich 777 (2007); (c)  $(Dy/Yb)_N$  vs  $(La/Yb)_N$ , and (d) Eu/Eu\* vs. Sr. Results in a-d using Rayleigh fractional 778 crystallization models indicate the effects of garnet, amphibole, plagioclase, zircon and apatite 779 fractionation on Sr/Y and Y (a), on La/Yb and Yb (b), on (Dy/Yb)<sub>N</sub> and (La/Yb)<sub>N</sub> (c), and on Eu/Eu\* 780 and Sr (d). The partition coefficients used and modeling details are given in Appendix 6. Two 781 crystallization models were designed to elucidate the effect of crystallization on bulk-rock (assumed to 782 approximate melt) trace element systematics: (1) Model A, in reasonable agreement with observed 783 mineral proportions of the MMEs, 50% amphibole, 40% plagioclase, 7.52% biotite, 2.2% apatite, 0.2% 784 zircon and 0.03% sphene; (2) Model B, 50% amphibole, 40% plagioclase, 7.6% biotite, 2.4% garnet. 785 Data sources for the QMS and BJS plutons are the same as in Fig. 6. Amp = amphibole; Bt = biotite;

786 Pl= plagioclase; Ap = apatite; Zrn=zircon; Grt = garnet; Spn=sphene.

Fig. 10: SiO<sub>2</sub> variation diagrams of (a) MgO, (b)  $Fe_2O_3^T$ , (c) TiO<sub>2</sub>, (d) CaO, (e) MnO, (f) P<sub>2</sub>O<sub>5</sub>, (g) Eu, 787 (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 788 789 inverse linear trend of SiO<sub>2</sub> versus Eu and Hf indicate the effects of plagioclase and zircon fractional 790 crystallization, respectively. Because Sm is incorporated more easily than Hf in amphibole (Fujimaki et 791 al., 1984; Klein et al., 1997), amphibole crystallization will cause Hf/Sm increase in residual magmas 792 (i). Crustal contamination and (or) basalt-rhyolite mixing trend in j-l are after Wang et al. (2008). Data 793 sources of the QMS and BJS pluton are the same as in Fig. 6. The average zircon  $\varepsilon_{Hf}(t)$  isotopic data 794  $(6.2\pm2, 2\sigma)$  calculated from Yu et al. (2015) is also presented in 1. 795 Fig. 11: (a) SiO<sub>2</sub> versus  $P_2O_5$ ; (b) SiO<sub>2</sub> versus Zr. Data for Island arc basalt (n=284 for P and 277 for 796 Zr), boninite (n=37 for P and 34 for Zr) and rhyolite (n=66 for P and 45 for Zr) are from the Georoc 797 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.

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<sub>2</sub> versus Mg<sup>#</sup>; (b) Na<sub>2</sub>O versus K<sub>2</sub>O. 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),
- 807 Dabie Orogen (He et al., 2013; Wang et al., 2007), Yangtze Craton (Xu et al., 2002; Wang et al.,
- 808 2006b); North China Craton (Chen et al., 2013a; Ma et al., 2015), experimental data (Sen and Dunn,

809 1994; Rapp and Watson, 1995. Data sources of the QMS and BJS plutons are the same as in Fig. 6.

810 Fig. 14: (a) Nd–Sr and (b) Nd-Hf isotope diagrams for the QMS adakitic rocks and their MMEs. The 811 MORB data are from Niu and Batiza (1997) and Niu et al. (2002), other data sources are the same as 812 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,  $\epsilon_{Nd}$  (t)=5.44,  $\epsilon_{Hf}$  (t)=9.93) and Mohe 813 Basement (average composition: Sr=586 ppm, Nd=32.97 ppm, Hf=3.44, <sup>87</sup>Sr/<sup>76</sup>Sr (t)=0.7234, E<sub>Nd</sub> 814 815 (t) = -19.80, $\varepsilon_{Hf}$  (t)=-43.65) are after Chen et al. (2015) and references therein. 816 K=[(Sr/Nd)<sub>MORB</sub>]/[(Sr/Nd)<sub>Mohe basement</sub>], where K<sub>max</sub>, K<sub>min</sub>, and K<sub>average</sub> are the maximum, minimum and 817 average values respectively. 818 Fig. 15: Shows 30%, 40%, 50% and 60% fractional crystallization of mineral assemblages of Model A 819 and Model B from the assumed magma along with the BCC and QMS adakitic granodiorites and their 820 MMEs on primitive mantle normalized multi-element diagram. The light red and green shaded regions 821 are the field of QMS adakitic granodiorite and MMEs, respectively. 822 Appendix Fig. S1: Simplified phase diagram showing hydrous solidi of basalts and granitic rocks 823 modified from Niu et al. (2013) (after Niu, 2005). The red line with arrow illustrates the concept of the

824 underthrusting North Qilian oceanic crust evolve along a high T/P path as a result of retarded

- subducting and enhanced heating upon continental collision at a prior active continental margin setting.
- 826

#### 827 Appendix tables captions:

Appendix 1: U-Th-Pb analyses by LA-ICP-MS for zircons from host granodiorites (QMS12-04host and
QMS12-10host) and the mafic magmatic enclaves (QMS12-04MME and QMS12-10MME).

- 830 Appendix 2: Microprobe analysis of representative plagioclase in the host granodiorites and the mafic
- 831 magmatic enclaves.
- 832 Appendix 3: Microprobe analysis of representative amphibole in the host granodiorites and the mafic
- 833 magmatic enclaves.
- 834 Appendix 4: Whole-rock major and trace elements analysis of the host adakitic granodiorites and the
- 835 mafic magmatic enclaves in the NQOB.
- 836 Appendix 5: Whole rock Sr-Nd-Hf isotopic analyses for the host adakitic granodiorites and the mafic
- 837 magmatic enclaves in the NQOB.
- 838 Appendix 6: Relevant partition coefficients, assumed melt and model compositions.

839

1	Syn-collisional adakitic granodiorites formed by fractional crystallization:
2	insights from their enclosed mafic magmatic enclaves (MMEs) in the Qumushan
3	pluton, North Qilian Orogen at the northern margin of the Tibetan Plateau
4	Shuo Chen <sup>a,b*</sup> , Yaoling Niu <sup>a, c*</sup> , Jiyong Li <sup>a,b</sup> , Wenli Sun <sup>a</sup> , Yu Zhang <sup>d</sup> , Yan Hu <sup>a,b</sup> , Fengli Shao <sup>a,b</sup>
5	
6	<sup>a</sup> Institute of Oceanology, Chinese Academy of Sciences, Qingdao 266071, China.
7	<sup>b</sup> University of Chinese Academy of Sciences, Beijing 100049, China
8	<sup>c</sup> Department of Earth Sciences, Durham University, Durham DH1 3LE, UK
9	<sup>d</sup> School of Earth Sciences, Lanzhou University, Lanzhou 730000, China
10	
11	
12	
13	
14	
15	*Corresponding authors:
16	Mr. Shuo Chen (chenshuo528@foxmail.com)
17	Professor Yaoling Niu (yaoling.niu@foxmail.com)
18	
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# 23 Abstract

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

40 Qilian Orogen

# 41 1. Introduction

42	"Adakite" was introduced by Defant and Drummond (1990) after the name of Adak Island in the
43	Aleutian arc. It refers to a group of intermediate-felsic igneous rocks observed in modern oceanic and
44	continental arcs genetically associated with seafloor subduction. They are characterized by high Sr,
45	light rare earth elements (REEs), Sr/Y (>40) and La/Yb (>20), low Y and heavy REEs, and lack of
46	obvious Eu anomalies. It was initially considered that adakites were derived by partial melting of
47	young ( $\leq 25$ Myrs) and warm subducting/subducted ocean crust in subduction zones (Defant and
48	Drummond, 1990). The origin of adakite has since been one of the most popular subjects of research in
49	igneous petrology due to its use for tectonic finger-printing (see Castillo, 2006, 2012), yet recent
50	studies have shown that adakite or rocks with adakitic compositions can be produced in various ways
51	and in different settings (Castillo et al., 1999; Xu et al., 2002; Chung et al., 2003, 2005; Wang et al.,
52	2005, 2007; Macpherson et al., 2006; RodrIguez et al., 2007; Streck et al., 2007; He et al., 2013; Chen
53	et al., 2013a; Song et al., 2014a). Because adakite is defined on the basis of certain trace element
54	characteristics as detailed above, geochemistry in combination with experimental geochemistry has
55	been widely used to discuss the petrogenesis of adakites and adakitic rocks (e.g., Defant and
56	Drummond, 1990; Sen and Dunn, 1994; Castillo et al., 1999; Xu et al., 2002; Wang et al., 2005; Xiong
57	et al., 2005; Castillo, 2006, 2012). However, a petrological approach is essential for petrological
58	problems and is expected to offer insights into the petrogenesis of adakites and adakitic rocks. Indeed,
59	mafic magmatic enclaves (MMEs) hosted in adakitic rocks have been recently recognized, and the
60	processes of the MME formation may offer a fresh perspective on the petrogenesis of the adakitic host
61	(e.g., RodrIguez et al., 2007; Chen et al., 2013b).

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In this paper, we report our petrological, mineralogical and geochemical analyses and

trace-element modeling on an MME-bearing 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., Wang et al., 2006a; Tseng et al., 2009; 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.

# 68 2. Geological setting

69 The NW-SE-trending NQOB is located between the Alashan Block to the northeast and the Qilian 70 Block to the southwest, and is offset to the northwest by the Altyn-Tagh Fault (Fig.1a). It is made up of 71 Early Paleozoic subduction-zone complexes including ophiolitic melanges, blueschists and eclogites, 72 Silurian flysch formations, Devonian molasse, and Carboniferous to Triassic sedimentary cover 73 sequences (Fig. 1a) (Song et al., 2007, 2013; Zhang et al., 2007). It is composed of three subunits, i.e., 74 (1) the southern ophiolite belt, (2) the middle arc magmatic belt and (3) the northern back-arc basin 75 ophiolite-volcanic belt (Fig. 1a) (Song et al., 2007, 2013; Zhang et al., 2007; Chen et al., 2014). It is 76 generally accepted that the NQOB is an Early Paleozoic suture zone, which records a long tectonic 77 history from seafloor spreading/subduction to the ultimate continental collision and mountain-building 78 (see Song et al., 2013). The Qumushan (QMS) pluton we studied is about 60km<sup>2</sup> in outcrop located in 79 the eastern section of the NQOB. It lies approximately 10 km southeast of the Baojishan (BJS) pluton 80 (Fig.1b). The QMS pluton intruded the Ordovician sedimentary and metamorphic rocks of Yingou 81 group (Fig.1b). MMEs are widespread in the host granodiorite (Fig. 2a).

#### 82 3. Analytical methods

#### 83 3.1. Zircon U-Pb ages

84 Zircons were separated by using combined methods of heavy liquid and magnetic techniques 85 before hand-picking under a binocular microscope. The selected zircons were set in an epoxy mount 86 that was polished to expose zircon interiors. Cathodoluminescence (CL) images were taken at China 87 University of Geosciences in Wuhan (CUGW) to examine the internal structure of individual zircon 88 grains. The zircon U-Pb dating was done using LA-ICP-MS at China University of Geosciences in 89 Beijing (CUGB). The instrument consists of an Agilent 7500a quadrupole inductively coupled plasma 90 mass spectrometry (ICP-MS) coupled with a UP-193 Solid-State laser (193 nm, New Wave Research 91 Inc.). Laser spot size was set to be ~30µm. Zircon 91500 (Wiedenbeck et al., 1995) and a secondary 92 standard zircon TEMORA (417 Ma) (Black et al., 2003) was used as an external standard. The 93 analytical procedure is given in Song et al. (2010a). Isotopic ratios and element concentrations of 94 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 AAppendix 1. 95

#### 96 3.2. Mineral compositions

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Mineral chemistry was determined using a JXA-8100 microprobe at Chang'an University, China. 98 The operating conditions were a 15 kV accelerating potential with a probe current of 10 nA and the 99 electron beam diameter of 1µm. Results are given in Appendix B Appendix 2 and Appendix C Appendix 100 <u>3</u>.

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  $TiO_2(\sim 1.5\%)$  and  $P_2O_5(\sim 2.0\%)$ . 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 <u>Table 1Appendix 4</u>.

109 3.4. Whole-rock Sr-Nd-Hf isotopes

110 Whole-rock Sr-Nd-Hf isotopic analyses were done in Guangzhou Institute of Geochemistry, 111 Chinese Academy of Sciences (GIG-CAS). The rock powders were digested and dissolved in 112 HF-HNO<sub>3</sub> acid mixtures and dried on a hot-plate. Sr-Nd-Hf fractions were separated using small Sr 113 Spec resin columns to obtain Sr and Nd-Hf bearing fractions. Sr isotopic compositions were 114 determined using a Neptune Plus multi-collector ICP-MS (MC-ICP-MS) following Ma et al. (2013a). 115 Nd fractions were then separated by passing through cation columns followed by HDEHP columns. 116 Separation of Hf from the matrix and rare earth elements was carried out using a combined method of 117 Eichrom RE and HDEHP columns. Nd and Hf isotopic compositions were determined using a 118 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 (2 $\sigma$ , n=13). 119 120 Repeated analysis of BHVO-2 and JB-3 during the same period of sample analysis yielded <sup>143</sup>Nd/<sup>144</sup>Nd 121  $0.512977\pm14$  (2 $\sigma$ , n=8) and  $0.513053\pm18$  (2 $\sigma$ , n=13), respectively. During the course of this study, the

mean <sup>176</sup>Hf/<sup>177</sup>Hf ratios for BHVO-2 and JB-3 are respectively 0.283099±15 ( $2\sigma$ , n = 13) and 0.283216 ± 15 ( $2\sigma$ , n=6). All measured <sup>87</sup>Sr/<sup>86</sup>Sr, <sup>143</sup>Nd/<sup>144</sup>Nd and <sup>176</sup>Hf/<sup>177</sup>Hf ratios were normalized to <sup>86</sup>Sr/<sup>88</sup>Sr = 0.1194, <sup>146</sup>Nd/<sup>144</sup>Nd =0.7219 and <sup>179</sup>Hf/<sup>177</sup>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, <u>http://georem.mpch-mainz.gwdg.de/</u>). Results are given in <u>Table 2Appendix 5</u>.

# 127 **4. Petrography and mineral chemistry**

#### 128 4.1. Granodiorite

129 The QMS pluton is of granodioritic composition with a mineral assemblage of plagioclase (45 130 vol. %-50 vol. %), quartz (35 vol. %-42 vol. %), amphibole (3 vol. %-10 vol. %), biotite (2 vol. %-10 131 vol. %), minor K-feldspar, and accessory minerals such as apatite, sphene, zircon and Fe-Ti oxides (Fig. 132 2d). Plagioclase crystals are euhedral to subhedral, and are of oligoclase composition with  $An_{12-24}$  (Fig. 133 3a). Zoned-plagioclase crystals display normal zoning with more anorthitic cores rimmed by less calcic 134 compositions (Fig. 3a). Amphibole is always present as euhedral to subhedral crystals despite the 135 variably small abundances (Fig. 2d). Amphibole grains are usually homogeneous and rarely display 136 disequilibrium textures. Amphiboles from the host granodiorite can be classified as edenite (Appendix 137 CAppendix 3, Fig. 4) following Leake et al. (1997). They have medium  $SiO_2$ , and low  $TiO_2$  (0.37-1.24) 138 wt. %), Na<sub>2</sub>O (0.87-1.48 wt. %) and K<sub>2</sub>O (0.29-1.69 wt. %).

## 139 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

142	grain-size (Figs. 2a-c), but have the same mineralogy albeit with greater mafic modes (e.g., 35-50 vol.%
143	amphibole, 5-15 vol.% biotite, 40-50 vol.% plagioclase, minor quartz, K-feldspar, along with accessory
144	minerals such as apatite, sphene, zircon and Fe-Ti oxides), thus giving a dioritic bulk composition.
145	Plagioclase mostly occurs as subhedral grains with compositions similar to those in the host
146	granodiorite. Zoned-plagioclase in the MMEs shows a compositional continuum with cores slightly
147	more anorthitic than the rims (Fig. 3b). Amphibole in the MMEs is compositionally identical to that in
148	the host granodiorite (Fig. 4). Biotite is yellow brown with subhedral to euhedral forms. The MMEs
149	show no chilled margins nor textures of crystal resorption or reactive overgrowth. These rocks mainly
150	exhibit porphyritic-like textures.

151 **5. Results** 

# 152 5.1. Zircon U–Pb ages

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

163Zircons from the MMEs (QMS12-04MME and QMS12-10MME) show similar optical properties164to those in the host with oscillatory zoning (Figs. 5b, d) and varying size (~150-200µm in length165length/width ratio of ~ 1:1-2:1). They have varying Th (27-548 ppm), U (50-541 ppm), and Th/U166(0.1-2.4). They are also of magmatic origin. Zircons in the 2 MMEs yielded the same weighted mean167ages 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 Ma168(1σ, MSWD=0.2, n=19), respectively (Figs. 5b, d).

#### 169 5.2. Major and trace elements

170 Eleven representative QMS granodiorite samples and their hosted MMEs (including 5 host-MME 171 pairs) were analyzed for whole-rock major and trace element compositions (Table 1 Appendix 4). The 172 granodiorite samples have high SiO<sub>2</sub> (64.37-65.49 wt.%), Al<sub>2</sub>O<sub>3</sub> (16.09-17.61 wt.%), Na<sub>2</sub>O (4.86-5.12 173 wt.%) and Na<sub>2</sub>O/K<sub>2</sub>O (2.11-3.82) with medium total alkalis (Na<sub>2</sub>O+K<sub>2</sub>O = 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 174 175 CaO (3.60-4.10 wt.%). They are calc-alkaline (Fig. 6b) and metaluminous to weakly peraluminous 176 (A/CNK= 0.93 to 1.03) (Fig. 6c), which is typical for I-type granitoids (Chappell and White, 1992). In 177 contrast, the MMEs plot in the fields of diorite, monzodiorite and monzonite (Fig. 6a). They are 178 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<sub>2</sub> (52.06-58.59 wt.%), higher Fe<sub>2</sub>O<sub>3</sub><sup>T</sup> (6.12-8.50 wt.%), 179 180 MgO (5.09-7.22 wt.%), CaO (4.99-6.57 wt.%), P<sub>2</sub>O<sub>5</sub> (0.49-1.01 wt.%), and slightly higher Mg<sup>#</sup> 181  $(0.63-0.68; Mg^{\#}=Mg/[Mg+Fe^{2+}])$  than the host granodiorites. 182 In the chondrite-normalized REE diagram, the QMS granodiorite samples are characterized by a 183 relatively flat heavy REE (HREE) pattern ([Dy/Yb]<sub>N</sub> = 1.32-1.54), slightly negative to positive Eu anomalies (Eu/Eu\*=0.88-1.13), and lower total REE contents ( $\Sigma REE=76-134$  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]<sub>N</sub> = 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 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 (Figs. 9a-b), while most MMEs plot in the normal arc rock field.

197 5.3. Sr-Nd-Hf isotopic geochemistry

Whole-rock Sr-Nd-Hf isotopic compositions for the MMEs and their host granodiorite are given in Table 2<u>Appendix 5</u>. The initial <sup>87</sup>Sr/<sup>86</sup>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 <sup>87</sup>Sr/<sup>86</sup>Sr (t),  $\varepsilon_{Nd}(t)$  and  $\varepsilon_{Hf}(t)$  against SiO<sub>2</sub> (Figs. 10j-1), both host granodiorite and MME samples are indistinguishable and overlapping within a narrow range (also see Table 2<u>Appendix 5</u>).

203 On SiO<sub>2</sub>-variation diagrams (Fig. 10), the MMEs and their host granodiorite define linear trends 204 for most elements (e.g., TiO<sub>2</sub>,  $Fe_2O_3^{T}$ , MnO, MgO, CaO, P<sub>2</sub>O<sub>5</sub>, Eu and Hf abundances) and trace element ratio (e.g., Hf/Sm) (Figs. 10a-i), but show no correlations of initial Sr, Nd, and Hf isotopic
compositions with SiO<sub>2</sub> (Figs. 10j-l).

207 6. Discussion

### 208 6.1. Petrogenesis of the mafic magmatic enclaves

- 209 Several models have been proposed for the origin of MMEs in the literature, including foreign 210 xenoliths (usually country rocks; e.g., Vernon, 1983; Xu et al., 2006), refractory and residual phase 211 assemblages derived from granitoid sources (e.g., the restite model; Chappell et al., 1987; Chappell and 212 White, 1991), chilled material or cumulate of early-formed co-genetic crystals (e.g., Dodge and Kistler, 213 1990; Dahlquist, 2002; Donaire et al., 2005; RodrIguez et al., 2007; Niu et al., 2013; Huang et al., 2014; 214 Chen et al., 2015), and basaltic melt material incompletely digested and homogenized during a magma 215 mixing process (e.g., Vernon, 1983; Didier, 1987; Castro et al., 1990; Dorais et al., 1990; Barbarin and 216 Didier, 1991; Chappell and White, 1991; Barbarin, 2005; Chen et al., 2009a, 2013b; Wang et al., 2013). 217 We critically evaluate these interpretations below.
- 218 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 (Figs. 2a-f); (2) they have a mineral assemblage identical to, and more mafic phases than, their host granodiorite (Figs. 2c-f); (3) they have mineral compositions (e.g., amphibole and plagioclase) identical to those of their host (Fig. 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<sub>2</sub>O<sub>3</sub>, CaO and trace elements easily incorporated into these phases (e.g., TiO<sub>2</sub>, P<sub>2</sub>O<sub>5</sub>, Hf and HREEs) (Figs. 10a-i); and (6) more importantly, they have overlapping and indistinguishable Sr-Nd-Hf isotopes with their host granodiorite (Figs. 10j-1).

231 Any successful models for the origin of MMEs must be consistent with these observations. 232 Models for MMEs as foreign xenoliths from country rocks (e.g., Xu et al., 2006) can be readily rejected, 233 as there is no evidence of reaction textures for the MMEs. Likewise, the identical age (~430 Ma) of the 234 MMEs and their host as well as the magmatic textures, constitute a strong argument against the restite 235 origin (e.g., Chappell et al., 1987). In addition, the MMEs do not contain peraluminous minerals and 236 their metaluminous composition (Fig. 6c) also excludes their derivation by melting of peraluminous 237 restites (Barbarin, 2005). Therefore, the most straightforward interpretation is that the MMEs and their 238 hosts formed as different products of a common magmatic system.

# 239 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., DePaolo, 1981; Barbarin, 2005)? (2) Why are the MMEs fine-grained (e.g., Barbarin and Didier, 1991)? Because of these 246 questions, a model of magma mixing between mantle-derived mafic magma and crust-derived felsic 247 magma was proposed to address the above issues: (1) the intermediate isotopic values of the MMEs 248 were commonly interpreted as the result of magma mixing between a mantle-derived mafic magma and 249 a crust-derived felsic magma, because a mafic magma derived from upper mantle provides not only 250 material but also the heat necessary for melting and subsequently mixing with the crustal rocks (e.g., 251 Barbarin, 2005); (2) the fine-grained MMEs were interpreted as due to quenching against host felsic 252 magmas (e.g., Vernon, 1984; Furman and Spera, 1985; Barbarin, 2005), owing to their higher liquidus 253 and solidus temperatures compared to felsic magmas. As a result, the magma mixing model has been 254 the most popular interpretation for the petrogenesis of the MMEs (see critical review by Niu et al., 2013). 255

256 Actually, there are many compelling lines of evidence for magma mixing in many granitoids, 257 especially (1) where a clear isotopic contrast exists between the MMEs and the hosts (e.g., Holden et 258 al., 1987; Chen et al., 2009b; Liu et al., 2013); and (or) (2) where disequilibrium features occur in the 259 MMEs, e.g., complex zoning of clinopyroxene crystals that have distinctly low-MgO cores surrounded 260 by high-MgO rims (e.g., Chen et al., 2013a; Wang et al., 2013), or resorption textures or reversed 261 zoning of plagioclase (Pietranik et al., 2006; Chen et al., 2009a, 2009b). In the case of our study, 262 however, none of the above has been observed. Instead, many lines of evidence argue against the 263 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.,

Dorais et al., 1990; Barbarin, 2005; Chen et al., 2009b; Zhang et al., 2010) using some experimental 268 269 interpretations that isotopic equilibration is generally more easily achieved than chemical equilibration 270 (Lesher, 1990). However, we emphasize that it is physically unlikely that isotopes become 271 homogenized whereas major and trace elements are not (Niu et al., 2013), because isotopes are "carried" 272 by the relevant chemical elements and isotopic diffusion cannot take place without the diffusion of the 273 "carrying" elements (Chen et al., 2015). In fact, there are two forceful arguments against thermal and 274 chemical equilibration: (1) the MMEs exhibit no textures of crystal resorption or reactive overgrowth 275 (Figs. 2b-c), and (2) plagioclase in the MMEs and their host granodiorite shows no compositional or 276 textural disequilibrium (Fig. 3). In addition, although the fine-grained texture of the MMEs could be 277 interpreted as resulting from quenching in the magma mixing model, quenching of the mafic magma 278 would lead to a significantly high viscosity contrast between the solidified enclaves and the felsic host 279 magma, thereby inhibiting deformation, mechanical mixing (Caricchi et al., 2012; Farner et al., 2014) 280 and isotope homogenization between the MMEs and the host. 281 Second, strongly correlated variations between major and trace elements (Figs. 10a-i) are 282 consistent with modal mineralogy control, as the result of magma evolution (i.e., the MMEs are 283 cumulate and the host represents residual melt) rather than mixing of two magmas with entirely

different origins because magma mixing is a complex, multi-stage process in which linear trends can be disturbed (e.g., Clemens, 1989; Donaire et al., 2005; Chen et al., 2015). 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 290 10-20% melting of an upper mantle with 5 ppm Zr and 0.019 wt.%  $P_2O_5$  (equivalent to that estimated 291 for depleted mid-ocean ridge basalt mantle), would yield primary liquids with 25-50 ppm Zr and 292 0.1-0.2 wt.% P<sub>2</sub>O<sub>5</sub>. These concentrations are much lower than in the QMS MMEs. Additionally, 293 boninites are thought to result from partial melting of highly depleted harzburgitic mantle peridotites 294 induced by subduction-zone slab dehydration (Niu, 2005), but they also have lower Zr and  $P_2O_5$ 295 contents (Fig. 11). More importantly, magma mixing between a basalt with any silicic end-member 296 (e.g., rhyolite) would generate a mixing array (Figs. 11a-b, the dash lines) totally different from the 297 linear trend (Figs. 11a-b, the solid lines) defined by the QMS granodiorite and their MMEs. In contrast, 298 all of these observations are consistent with the interpretation that the MMEs represent earlier cumulate 299 with greater amounts of zircon and apatite than their hosts (e.g., Donaire et al., 2005).

### 300 6.1.3. Formation of the mafic magmatic enclaves

301 The foregoing observations, illustrations and discussion leave us with the best interpretation that 302 the MMEs represent the earlier crystallized cumulate that were later disturbed by subsequent melt 303 replenishment and induced magma convection in the magma chamber. As illustrated in Fig. 12, when a 304 primitive magma body is emplaced into a cold environment (e.g., developing a magma chamber) with 305 the wall-rock having temperatures below the liquidus of the magma, magma quench and rapid 306 crystallization are inevitable because of the thermal contrast. For an andesitic primitive magma parental 307 to the syn-collisional granitoids (Niu et al., 2013), the first major liquidus phases would be amphibole, 308 biotite, plagioclase and accessory minerals such as zircon and apatite, and rapid quench will facilitate 309 abundant nucleation without between-nuclei space for rapid growth, thus resulting in the formation of 310 fine-grained cumulate (Chen et al., 2015). This is a fundamentally important petrologic concept with 311 which any interpretation must comply. This early formed fine-grained mafic cumulate piles (largely 312 plastic before complete solidification) can be readily disturbed by subsequent magma replenishment 313 and induced convection, resulting in the dispersion of the MMEs in the host granodiorite.

314 6.2 Petrogenesis of QMS adakitic granodiorite

# 315 6.2.1 Implication from the MMEs

316 Recently, mixing of basaltic and felsic magmas was proposed for the genesis of some high-Mg 317 and low SiO<sub>2</sub> adakitic rocks from Mount Shasta and the North China Craton using the presence of 318 ubiquitous MMEs as evidence (Chen et al., 2013b) and also based on the disequilibrium petrographic 319 characteristics in high-Mg andesites (Streck et al., 2007; Chen et al., 2013a). This interpretation could 320 be reasonable, but it is not the case here because there is no petrographic and compositional evidence 321 for magma mixing as elaborated above. That is, the MMEs in the QMS adakitic granodiorite are not 322 evidence for magma mixing, but rather they are of cumulate origin without direct asthenospheric 323 mantle participation (e.g., Dahlquist, 2002). More importantly, the MMEs comprise dominantly 324 amphibole and plagioclase, which are common cumulate minerals of andesitic melts. If the parental 325 melts were basaltic, the typical cumulate from such evolved basaltic melt would be gabbro dominated 326 by clinopyroxene and plagioclase (Chen et al., 2015). It can be inferred from this important petrological 327 concept that the parental magmas of the MMEs and their host granodiorite was mafic andesitic (Niu et 328 al., 2013; Chen et al., 2015).

329 6.2.2 Assessing the model of melting of mafic lower continental crust

330 To date, some intra-continental high-MgO or -Mg<sup>#</sup> (also high Cr and Ni contents) adakitic rocks

331	have been considered to originate from melting of delaminated lower crust (e.g., Xu et al., 2002; Gao et
332	al., 2004; Wang et al., 2006b). By accepting and applying this model, it has been previously interpreted
333	that the QMS adakitic rocks were derived from delaminated lower crust, and they subsequently
334	interacted with mantle peridotite during ascent (Tseng et al., 2009; Yu et al., 2015). Although this
335	model seems plausible and applicable to the QMS adakitic rocks, it has more difficulties than
336	certainties. First, the QMS adakitic granodiorites have lower $(Dy/Yb)_N$ , $(La/Yb)_N$ , and distinctive low
337	K <sub>2</sub> O/Na <sub>2</sub> O ratios (Fig. 13b), which are significantly different from the composition of adakitic rocks
338	inferred to be derived from partial melting of the thickened or delaminated lower continental crust.
339	Second, the Nd and Hf isotopic data of the QMS adakitic granodiorite indicate a significant mantle
340	input, which is also inconsistent with those of lower continental crust origin (Fig. 14a). Finally, the
341	existence of the Paleo-Qilian ocean is manifested by the ophiolites and eclogites in the North Qilian
342	orogenic belt; the ocean basin started its subduction at ~520 Ma, and was eventually closed at the end
343	of the Ordovician (~445 Ma) followed by continental collision (see Song et al., 2013). Accordingly,
344	the coeval (~430 Ma) MMEs and their adakitic host granodiorite of the QMS pluton are best
345	interpreted as a magmatic response to the collision between the Qilian-Qaidam block and Alashan
346	block, thereby being contrary to the environment of crustal extension required by a delaminated lower
347	crustal origin. In fact, continuous lithosphere extension and delamination in the NQOB occurred at
348	<400 Ma, which resulted in strong magmatic activity and formed a number of
349	diorite-granodiorite-granite plutons with ages of ~400–360 Ma (Song et al., 2013, 2014b).

# 350 6.2.3 A fractional crystallization model for the petrogenesis of the QMS adakitic granodiorites

351 An origin of adaktic 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.

357 In our model, the magmas parental to the MMEs and their host granodiorite are the same mafic 358 andesitic magmas in a syn-collisional setting, rather than basaltic magmas in an arc setting of active 359 seafloor subduction advocated in the literature (e.g., Macpherson et al., 2006). That is, the QMS 360 adakitic granodiorites are products of fractional crystallization dominated by the mineral assemblage 361 indicated by the MMEs from mafic andesitic magmas. We can further consider two fractional 362 crystallization models to elucidate the effect of crystallization of the observed mineralogy on trace 363 elements using closed-system Rayleigh fractionation equation: (1) Model A, in reasonable agreement 364 with observed mineral proportions of the MMEs, 50% amphibole, 40% plagioclase, 7.52% biotite, 2.2% 365 apatite, 0.2% zircon and 0.03% sphene; (2) Model B, which incorporates fractionation of garnet, 50% 366 amphibole, 40% plagioclase, 7.6% biotite, 2.4% garnet. The partition coefficients used in the 367 calculations are for intermediate-felsic magmas (Table 3Appendix 6). For convenience (see below), the 368 assumed parental magma (Table 3Appendix 6) is very similar to the bulk continental crust (BCC) 369 composition (Rudnick and Gao, 2003) (Fig. 15), which is the same as the ~ 60 Ma Linzizong andesite 370 in southern Tibet (Mo et al., 2008; Niu et al., 2013), in terms of major and trace element abundances. 371 Notably, removal of garnet would yield a smooth decrease of LREE-to-HREE pattern (Richards 372 and Kerrich, 2007) with elevated (Dy/Yb)<sub>N</sub> and (La/Yb)<sub>N</sub> 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),

374 which indicate that the effect of garnet fractionation in generating the QMS adakitic granodiorites is 375 unimportant. Simple modal calculation of fractional crystallization using Model B indicates that the 376 participation of garnet is no more than 3% (Fig. 9), but the low garnet proportion in combination with a 377 large amount of amphibole-plagioclase fractionation can hardly generate the adakitic signature shown 378 in the QMS pluton (Figs. 9a-b). Besides, mineralogically, garnet has been observed neither in the QMS 379 MMEs and their host adakitic granodiorite, nor in the coeval igneous rocks in the eastern section of the 380 NQOB. In addition, our preferred source for the QMS MMEs and their host adakitic granodiorite is 381 partial melting of the ocean crust at amphibolite facies conditions (<40km) (Mo et al., 2008; Niu and 382 O'Hara, 2009; Niu et al., 2013) (see below), rather than the presence of garnet as a residual phase at 383 garnet amphibolite or eclogite conditions.

384 It is also impossible to generate QMS adakitic granodiorites by fractionation of 385 amphibole-plagioclase alone, because they trend to produce concave-upwards patterns between the 386 MREE and HREE and lead to decreasing  $(Dy/Yb)_N$  with increasing  $(La/Yb)_N$  (Fig. 9c), owing to the 387 affinity of calcic amphiboles for MREEs over the HREEs (Klein et al., 1997). Additionally, removal of 388 amphibole-plagioclase would result in negative Eu anomalies in the residual melts, which is 389 inconsistent with QMS adakitic granodiorites (Fig. 9d). In the case of our study, we emphasize that the 390 widespread accessory minerals such as zircons and apatites in both QMS host adakitic granodiorite and 391 particularly their cumulate MMEs played a significant role in generating QMS adakitic granodiorites. 392 For example, zircon fractionation would increase (Dy/Yb)<sub>N</sub> (Fig. 9c) and the La/Yb and Sr/Y ratios of residue magmas (Figs. 9a-b), because  $Kd_{zircon}^{Dy/Yb} = 0.140$ , and  $Kd_{zircon}^{La/Yb} = 0.005$  (Bea et al., 1994). 393 394 Apatite fractionation can also increase the Sr/Y ratio (Figs. 9a-b), but decrease (Dy/Yb)<sub>N</sub> (Fig. 9c). Importantly, apatite fractionation would increase Eu/Eu\* (Fig. 9d), because  $Kd_{apatite}^{Sm} = 46$ , 395

396	$Kd_{apatite}^{Eu} = 25.5$ , $Kd_{apatite}^{Gd} = 43.9$ (Fujimaki et al., 1984). Note that the simple calculation of Model A
397	(Table 3 <u>Appendix 6</u> ; Figs. 9 and 15), which involves a small proportion of zircon, apatite and sphene in
398	combination with amphibole, biotite and plagioclase to form the fractionation assemblage can explain
399	the characteristics of the QMS adakitic granodiorites. Although uncertainties exist for mineral partition
400	coefficients, our model offers insights into the petrogenesis of the adakitic granodiorite as well as the
401	enclosed MMEs in syn-collisional environments.

#### 402 6.3 Constraints on the source

403 As discussed above, the primary magmas parental to the MMEs and their host granodiorite are 404 most consistent with mafic andesitic magmas of ocean crust origin during continental collision. In 405 addition, our new data and the whole-rock Sr-Nd and zircon Hf isotopic data in the literature on the 406 QMS pluton (Tseng et al., 2009; Yu et al., 2015) exhibit quite uniform Sr-Nd-Hf composition (Figs. 407 10j-1). Though the radiogenic Sr and slightly unradiogenic Nd isotopes indicate the input of crustal 408 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 409 +7.7) in the literature (Yu et al., 2015) are indicative of significant mantle input or juvenile mafic 410 continental crust derived from the mantle in no distant past (Zhang et al., 2015). As noted above, many 411 adakitic rocks can be generated from the lower continental crust, but this is not applicable in our study 412 (see above). In our case, the most likely source for the andesitic magmas with inherited mantle isotopic 413 signatures parental to the QMS pluton is partial melting of the remaining part of the North Qilian ocean 414 crust (Chen et al., 2015). On the other hand, contribution from continental crust is also required. This 415 may occur in the melting region or in an evolving magma chamber rather than simple crustal level 416 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<sub>2</sub> (Figs. 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 (Mo et al. 2008;
Niu and O'Hara 2009; Chen et al., 2015).

421 In the broad context of the continental collision, the model of partial melting of the remaining part 422 of the ocean crust and the recycled terrigenous sediments has been proposed and tested by Niu and 423 co-workers in southern Tibet, East Kunlun and Qilian Orogenic Belts (e.g., Mo et al., 2008; Niu and 424 O'Hara, 2009; Niu et al., 2013; Huang et al., 2014; Chen et al., 2015; Zhang et al., 2015). In their model, 425 during collision, the underthrusting North Qilian ocean crust would subduct/underthrust slowly, tend to 426 attain thermal equilibrium with the superjacent warm active continental margin, and evolve along a 427 high T/P path in P-T space as a result of retarded subduction and enhanced heating (Appendix Fig. S1). 428 The warm hydrated ocean crust of basaltic composition and sediments of felsic composition with rather 429 similar solidi would melt together under the amphibolite facies conditions (for details see Niu et al., 430 2013; also see Appendix Fig. S1).

431 Importantly, this model can generate andesitic magmas not only with inherited mantle 432 isotopic signatures but also compositions similar to the bulk continental crust (BCC), except for 433 notable depletion in highly compatible elements like Mg, Cr and Ni (Mo et al., 2008). This model 434 together with experimental results of melting of metabasalt and eclogite (Fig. 13a) implies that the relatively high Mg<sup>#</sup> (also high Cr and Ni ) contents in QMS adakitic granodiorites may indeed 435 436 reflect melt interaction with mantle peridotite during ascent. Although magmas produced through 437 the above process lack the adakitic signature, it can be the ideal source that generates QMS 438 adakitic granodiorites through fractional crystallization dominated by mineral assemblages

439	represented by the MMEs. Note that this interpretation is consistent with binary isotope mixing
440	calculations as proposed by Chen et al. (2015) (Figs. 14a-b), and with trace element model
441	calculations (see above) (Figs. 9 and 15). As illustrated by these mass balance calculations, ~95%
442	ocean crust and ~5% continental materials contribute to the source of the QMS pluton (Fig. 14),
443	and 30%-50% fractional crystallization dominated by mineralogy and modes of the MMEs can
444	lead to the highly evolved granodioritic composition of the QMS pluton with the adakitic
445	signature (Figs. 9 and 15).

#### 446 **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 ~440-420Ma.

(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.

454 (3) The QMS host granodiorite has adakite-like major and trace element features, including high Sr,

455 Sr/Y and La/Yb, but low Y and Yb. By accepting our model for the petrogenesis of the MMEs, it

456 follows that the QMS adakitic granodiorite resulted from fractional crystallization dominated by457 mineral assemblages represented by the MMEs.

458 (4) The parental magma for the QMS pluton is best explained as resulting from partial melting of the

459 remaining part of ocean crust together with recycled terrigenous sediments during continental collision.

460 The resulting magma may have also experienced interaction with mantle peridotite during ascent.

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- 743 (in press).

745 Figure captions:

746 Fig.1: (a) Simplified geological map of the North Qilian Orogen showing distributions of the main 747 tectonic units (modified after Song et al., 2013; Chen et al., 2015). (b) Simplified map of the Qumushan 748 (QMS) and Baojishan (BJS) area in the eastern section of the North Qilian Orogen. U-Pb ages are 749 shown for granodiorite and MMEs in the BJS and QMS plutons from Chen et al. (2015), Yu et al. 750 (2015) and this study as indicated. 751 Fig. 2: Photographs of the adakitic granodiorite and the MMEs in the field and in thin-sections. (a), (b) 752 and (c) showing the sharp contact of MMEs of varying size with their host granodiorite with MMEs 753 being finer-grained than the host; (d) showing the mineral assemblage of the adaktic host granodiorite 754 (QMS12-02host) and (e), (f) showing the mineral assemblage of MMEs (QMS12-02MME, 755 QMS12-06MME). Amp = amphibole; Bt = biotite; Pl= plagioclase; Qz = quartz; Ap = apatite; Zrn= 756 zircon. Plates c-f are taken under cross-polarized light. 757 Fig. 3: Photomicrographs showing a plagioclase crystal with a high-Ca core rimmed by a euhedral 758 overgrowth of low-Ca plagioclase in both (a) adakitic rocks (e.g., QMS12-04host) and (b) MMEs (e.g., 759 QMS12-04MME). Numerals are the An contents. See Appendix B Appendix 2 for compositional data. 760 Fig. 4: Chemical compositions of amphiboles from the host granodiorite and MMEs in the amphibole 761 classification diagram (Leake et al., 1997). Data from the host granodiorites and the MMEs of BJS 762 pluton (Chen et al., 2015) are also shown for comparison. 763 Fig. 5: Concordia diagrams of LA-ICP-MS U-Pb zircon age data and representative CL images of

764 zircon grains showing spots for the host adakitic granodiorites (a, c) and the MMEs (b, d) in the QMS

765 pluton.

766 Fig. 6: Classification diagrams of the host granodiorites and the MMEs in the QMS pluton. (a) Total 767 alkalis vs. SiO<sub>2</sub> (Le Maitre et al., 1989), (b) K<sub>2</sub>O vs. SiO<sub>2</sub>, and (c) A/NK vs. A/CNK. The blue circles 768 and squares are data from BJS granodiorites and their MMEs (Chen et al., 2015), and the open circles 769 are literature data on the QMS granodiorites (Wang et al., 2006a; Tseng et al., 2009; Yu et al., 2015). 770 Fig. 7: (a) Chondrite normalized REE patterns for the QMS host adakitic granodiorites and the MMEs; 771 (b) host rock-normalized REE patterns of MMEs. Chondrite REE values and bulk continental crust 772 (BCC) are from Sun and McDonough (1989) and Rudnick and Gao (2003), respectively. Shaded fields 773 of BJS granodiorite and the MMEs are from Chen et al. (2015). 774 Fig. 8: Average ocean crust-normalized (OC; Niu and O'Hara, 2003) trace element patterns for the 775 QMS host adakitic granodiorites and the MMEs. 776 Fig. 9: Plots of (a) Sr/Y vs. Y, where fields of adakite, and normal arc andesite-dacite-rhyolite are from 777 Defant and Drummond (1990); (b) La/Yb vs. Yb, discrimination lines are from Richards and Kerrich 778 (2007); (c)  $(Dy/Yb)_N$  vs  $(La/Yb)_N$ , and (d) Eu/Eu\* vs. Sr. Results in a-d using Rayleigh fractional 779 crystallization models indicate the effects of garnet, amphibole, plagioclase, zircon and apatite 780 fractionation on Sr/Y and Y (a), on La/Yb and Yb (b), on (Dy/Yb)<sub>N</sub> and (La/Yb)<sub>N</sub> (c), and on Eu/Eu\* 781 and Sr (d). The partition coefficients used and modeling details are given in Table 3Appendix 6. Two 782 crystallization models were designed to elucidate the effect of crystallization on bulk-rock (assumed to 783 approximate melt) trace element systematics: (1) Model A, in reasonable agreement with observed 784 mineral proportions of the MMEs, 50% amphibole, 40% plagioclase, 7.52% biotite, 2.2% apatite, 0.2% 785 zircon and 0.03% sphene; (2) Model B, 50% amphibole, 40% plagioclase, 7.6% biotite, 2.4% garnet. 786 Data sources for the QMS and BJS plutons are the same as in Fig. 6. Amp = amphibole; Bt = biotite;

787 Pl= plagioclase; Ap = apatite; Zrn=zircon; Grt = garnet; Spn=sphene.

Fig. 10: SiO<sub>2</sub> variation diagrams of (a) MgO, (b) Fe<sub>2</sub>O<sub>3</sub><sup>T</sup>, (c) TiO<sub>2</sub>, (d) CaO, (e) MnO, (f) P<sub>2</sub>O<sub>5</sub>, (g) Eu, 788 (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 789 790 inverse linear trend of SiO<sub>2</sub> versus Eu and Hf indicate the effects of plagioclase and zircon fractional 791 crystallization, respectively. Because Sm is incorporated more easily than Hf in amphibole (Fujimaki et 792 al., 1984; Klein et al., 1997), amphibole crystallization will cause Hf/Sm increase in residual magmas 793 (i). Crustal contamination and (or) basalt-rhyolite mixing trend in j-l are after Wang et al. (2008). Data 794 sources of the QMS and BJS pluton are the same as in Fig. 6. The average zircon  $\varepsilon_{Hf}(t)$  isotopic data 795  $(6.2\pm2, 2\sigma)$  calculated from Yu et al. (2015) is also presented in 1. 796 Fig. 11: (a) SiO<sub>2</sub> versus  $P_2O_5$ ; (b) SiO<sub>2</sub> versus Zr. Data for Island arc basalt (n=284 for P and 277 for 797 Zr), boninite (n=37 for P and 34 for Zr) and rhyolite (n=66 for P and 45 for Zr) are from the Georoc 798 database (http://georoc.mpch-mainz.gwdg.de/georoc/). Dashed and solid lines in a-b are hypothetical 799 mixing lines and linear trend defined the QMS granodiorite and their MMEs, respectively. Data sources 800 of the QMS and BJS plutons are the same as in Fig. 6. Fig. 12: Cartoon illustrating a possible scenario for MME formation. Earlier crystallized cumulate with 801

the mineral assemblage of amphibole, biotite, plagioclase and accessory minerals such as zircon and

- 803 apatite (a), which was later disturbed by subsequent magma replenishment in the magma chamber,
- 804 constituting MMEs in the dominant host granodiorite.

**Fig. 13:** Plots of (a) SiO<sub>2</sub> versus Mg<sup>#</sup>; (b) Na<sub>2</sub>O versus K<sub>2</sub>O. Data sources: classical adakite, resulting

- 806 from partial melting of subducted ocean crust in modern arcs, are from the GeoRoc database
- 807 (http://georoc.mpch-mainz.gwdg.de/georoc/); Tibet Plateau (Chung et al., 2003; Wang et al., 2005),
- 808 Dabie Orogen (He et al., 2013; Wang et al., 2007), Yangtze Craton (Xu et al., 2002; Wang et al.,

809 2006b); North China Craton (Chen et al., 2013a; Ma et al., 2015), experimental data (Sen and Dunn,

Fig. 14: (a) Nd–Sr and (b) Nd-Hf isotope diagrams for the QMS adakitic rocks and their MMEs. The

- 810 1994; Rapp and Watson, 1995. Data sources of the QMS and BJS plutons are the same as in Fig. 6.
- 812 MORB data are from Niu and Batiza (1997) and Niu et al. (2002), other data sources are the same as 813 Fig. 13. Binary isotope mixing calculations between North Qilian Ocean MORB (average composition: 814 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 815 Basement (average composition: Sr=586 ppm, Nd=32.97 ppm, Hf=3.44,  ${}^{87}$ Sr/ ${}^{76}$ Sr (t)=0.7234,  $\varepsilon_{Nd}$ 816 (t)=-19.80,  $\varepsilon_{Hf}$  (t)=-43.65) are after Chen et al. (2015) and references therein. 817 K=[(Sr/Nd)<sub>MORB</sub>]/[(Sr/Nd)<sub>Mohe basement</sub>], where K<sub>max</sub>, K<sub>min</sub>, and K<sub>average</sub> are the maximum, minimum and 818 average values respectively.
- **Fig. 15:** Shows 30%, 40%, 50% and 60% fractional crystallization of mineral assemblages of Model A
- 820 and Model B from the assumed magma along with the BCC and QMS adakitic granodiorites and their
- 821 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.
- Appendix Fig. S1: Simplified phase diagram showing hydrous solidi of basalts and granitic rocks modified from Niu et al. (2013) (after Niu, 2005). The red line with arrow illustrates the concept of the underthrusting North Qilian oceanic crust evolve along a high T/P path as a result of retarded subducting and enhanced heating upon continental collision at a prior active continental margin setting.
- 827

811

## 828 Table captions:

Table 1: Whole rock major and trace elements analysis of the host adakitic granodiorites and the mafic

- 830 magmatic enclaves in the NQOB.
- 831 Table 2: Whole rock Sr Nd Hf isotopic analyses for the host adakitic granodiorites and the mafic
   832 magmatic enclaves in the NQOB.
- 833 Table 3: Relevant partition coefficients, assumed melt and model compositions.
- 834 Appendix AAppendix 1: U-Th-Pb analyses by LA-ICP-MS for zircons from host granodiorites
- 835 (QMS12-04host and QMS12-10host) and the mafic magmatic enclaves (QMS12-04MME and
- 836 QMS12-10MME).
- 837 Appendix <u>BAppendix 2</u>: Microprobe analysis of representative plagioclase in the host granodiorites
- and the mafic magmatic enclaves.
- 839 Appendix CAppendix 3: Microprobe analysis of representative amphibole in the host granodiorites and
- 840 the mafic magmatic enclaves.
- 841 Appendix 4: Whole-rock major and trace elements analysis of the host adaktic granodiorites and the
- 842 <u>mafic magmatic enclaves in the NQOB.</u>
- 843 Appendix 5: Whole rock Sr-Nd-Hf isotopic analyses for the host adakitic granodiorites and the mafic
- 844 <u>magmatic enclaves in the NQOB.</u>
- 845 Appendix 6: Relevant partition coefficients, assumed melt and model compositions.

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Figure 5 Click here to download high resolution image



## Figure 6 Click here to download high resolution image























Appendix tables Click here to download Supplementary Interactive Plot Data (CSV): Appendix tables.xlsx