

Electronic Appendix for

**Revisiting the genesis of the adakite-like granitoids in collisional zones: water-fluxed melting of intermediate to felsic rocks with dilution by low Sr/Y phases**

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## GEOLOGICAL SETTING

The Qinling orogenic belt (QOB) in the central part of China welds the North China Block (NCB) and the Yangtze Block (YB) (Fig. 1a). The Huicheng Basin or the Foping Dome divide the QOB into the East (EQOB) and the West Qinling orogenic belt (WQOB) (Hu et al., 2019; Li et al., 2013; Zhu et al., 2011). The latter is bounded to the north by the Qilian Terrane along the Qinghai Lake–Nanshan–Linxia–Wushan–Tianshui Fault (the western extension of the Shangdan Suture), to the west by the East Kunlun and Qaidam Terranes along the Wenquan–Wahongshang Fault, and to the south by the Songpan–Garzê Terrane along the A'nimaque–Mianlue Suture (Fig. 1b; Zhang et al., 2018).

The oldest exposed crystalline basement in the WQOB is the Mesoproterozoic Qinling Group that primarily consists of gneisses, amphibolites, and marble (Dong and Santosh, 2016). Widely exposed Phanerozoic strata in the WQOB are mainly Devonian–Triassic sedimentary successions (Luo et al., 2012; Wu et al., 2014; Yan et al., 2006). During the Late Permian to Triassic, the northward subduction of the Paleo-Tethys Ocean (i.e., A'nimaque–Mianlue Ocean) and the ensuing oblique collision between the NCB and the YB produced extensive granitoid intrusions throughout the WQOB (Li et al., 2014; Meng and Zhang, 2000). These Indosinian granitoids (271–201 Ma) extend roughly parallel to the A'nimaque–Mianlue suture zone (Fig. 1b; Meng and Zhang, 2000; Zeng et al., 2018). The granitoids in the eastern segment of the WQOB predominately have ages of

230–200 Ma (Fig. 1b; Feng et al., 2002), and this magmatic phase coincided with the oblique collision between the NCB and the YB (Xing et al., 2020).

## ANALYTICAL METHODS

### **In-situ major element analysis**

Major element compositions of minerals were analyzed at the Shandong Key Laboratory of Mineralization Geological Processes and Resource Utilization in Metallic Minerals at the Shandong Geological Science Institute by a JEOL JXA-8230 electron microprobe. The operating conditions were 15 kV with an emission current of 10 nA. The beam sizes were 10  $\mu\text{m}$  for plagioclase and 1–5  $\mu\text{m}$  for biotite, amphibole, and pyroxene. The standard materials were pure oxides and silicates of the Astimex series [orthoclase (K), albite (Na), diopside (Mg, Ca and Si), rutile (Ti), synthetic MnO (Mn), hematite (Fe), jadeite (Al) and NiO (Ni)], and results were corrected using the ZAF-method (Z, atomic number; A, absorption; F, fluorescence). The In-situ major element analysis results of standard materials were shown in the Table OM3, and the analytical precision was better than  $\pm 2\%$  (2s). The analytical procedures were described in detail by Hu et al. (2019) and Xing et al. (2020).

### **LA-ICP-MS in-situ trace element analyses and mapping**

In-situ trace-element analysis of pyroxene, amphibole, and plagioclase, as well as element mapping of clinopyroxene, orthopyroxene, amphibole, and biotite, were

conducted at the Ore Deposit and Exploration Centre (ODEC), School of Resources and Environmental Engineering, Hefei University of Technology. Analyses were conducted by laser ablation using a PhotonMachines Analyte HE with 193-nm ArF Excimer laser coupled to a quadrupole-based inductively coupled plasma-mass spectrometer (ICP-MS, Agilent 7900). Helium was the carrier gas and was mixed with Ar via a T-connector before entering the ICP-MS. In-situ trace-element analysis was performed at a laser repetition rate of 8 Hz, an energy density of 2 J/cm<sup>2</sup>, with laser spot sizes of 10–30 μm. For each analysis, 20 s gas blank signal was monitored before ablating the mineral. Standard reference materials GSE-1G, BCR-2G, NIST 610, and NIST 612 were used as external standards for data calibration. Reference materials BCR-2G, NIST 610, and NIST 612 were analyzed after every 10 unknowns spot analysis, while GSE-1g was analyzed at the start and the end of each mapping for data calibration. Off-line data processing was performed using the software ICPMSDataCal (Liu et al., 2008). The data of standard materials were shown in the Table OM4, and the analytical precision was better than ±5% (2s).

Mapping was performed at a laser repetition rate of 10 Hz, a laser spot size of 20 μm, and a translation speed of 20 μm/s. The trace element maps were calibrated against multiple-references materials (SRM 610, SRM 612, and BCR-2G) without applying internal standardization. The longitudinal resolution (along the Y-axis of the thin section) of the maps is 20μm (i.e. the diameter of the laser beam), and the transverse resolution (along the X-axis) is approximately equal to 6μm (the translation speed of the laser multiplied by the total integral time of all the elements

analyzed; Wang et al., 2017). The uncertainties of all elements are better than 10%, and the accuracy was better than 30%. LaIcpMsSoftware, a mapping reduction software based on Matlab, was used to compile and process the mineral element mapping images. During the whole analysis process, the LaIcpMsSoftware can automatically deduct the background value of each element signal, and correct each element signal according to the signal drift of the standard sample (Wang et al., 2017a). In order to determine the accuracy of the LA-ICP-MS mapping, we compared the results of in-situ analysis qualitatively with those of LA-ICP-MS. The compositional variations of the element contents in the minerals obtained from the LA-ICP-MS mapping are in good agreement with the results of single spot analysis (Table OM4).

### **Crystal size distribution (CSD)**

Crystal size distributions (CSD) were determined for amphibole from the Zhuyuan granodiorites on two polished thin sections measuring 2.5 cm × 4.9 cm. Photomicrographs of each thin section were captured under plane-polarized light using a computer-assisted high-resolution petrographic microscope, and the crystal margins in the selected regions were delineated with the software CorelOMAW. The outline images of the amphiboles were analyzed in Image-J to determine the long and short axes and area of the best-fitting ellipse of each crystal (Herwegh, 2000). Finally, the best-fitting three-dimensional habits were calculated with the

CSDslice template (Morgan and Jerram, 2006), and the CSD of amphibole crystals were calculated with the program CSDCorrections 1.6 (Higgins, 2000).

## RESULTS

### Whole-rock major and trace element geochemistry

Whole-rock major and trace element contents of the Zhuyuan granodiorites were collected from Xie et al. (in preparation) and summarized in Table OM2. All the Zhuyuan samples are subalkaline, metaluminous to peraluminous granodiorites and display a relatively narrow compositional range (e.g., SiO<sub>2</sub>: 62.5–67.2 wt.%, Al<sub>2</sub>O<sub>3</sub>: 15.64–17.32 wt.%). Mg#s range from 49.7–60.9 and A/CNK values (= molar Al<sub>2</sub>O<sub>3</sub>/[CaO + Na<sub>2</sub>O + K<sub>2</sub>O]) range from 0.87 to 1.13 (Manier and Piccoli, 1989). Chondrite-normalized rare-earth element patterns display significant enrichments in light rare-earth elements (LREEs) with high (La/Yb)<sub>N</sub> of 15–21 (N denotes normalization to the chondrite values of Sun and McDonough, 1989) and weakly negative Eu anomalies (Eu/Eu\* = 0.78–0.89). The Zhuyuan granodiorites contain high Sr (471–697 ppm) but rather low Y (12.2–15.4 ppm) and Yb (1.03–1.24 ppm), resulting in Sr/Y values of 33–46. These geochemical features resemble those of typical adakitic rocks (Sr > 400 ppm, Y < 18 ppm, and Yb < 1.9 ppm; Defant and Drummond, 1990) or high-Si adakites (> 60 SiO<sub>2</sub> wt.%) according to the criteria proposed by Martin et al. (2005).

## DISCUSSION

## The critical role of magma mixing and antecryst recycling

We combine whole-rock geochemical characteristics with in-situ mineral compositions to highlight the potential role of magma mixing in the formation of the Zhuyuan granodiorites. The Zhuyuan granodiorites are characterized by a broad range in Cr (28.6–135 ppm) and Ni (9.69–56.8 ppm) abundances and high Mg# (49.7–60.9), testifying to the input of mafic, and likely mantle-derived components (Xie et al., 2023; Rapp and Watson, 1995). In addition, the Zhuyuan granodiorites have a relatively wide range of zircon  $\epsilon_{\text{Hf}}(t)$  values (-5.0 to +2.2, our unpublished data), which may be explained by crustal contamination or hybridization of distinct magma batches (Hu et al., 2016). According to Wang et al. (2010), if the Zhuyuan granodiorites were significantly modified by crustal materials, they would show a positive correlation between La/Sm and La/Nb. However, such a crustal contamination trend is at odds with our observation (Fig. OM2b). Therefore, the wide zircon  $\epsilon_{\text{Hf}}(t)$  ranges are more likely the result of magma mixing.

The presence of several pyroxene populations implies an open magmatic plumbing system where magma recharging or mixing was significant. An Fe–Mg exchange coefficient of  $0.27 \pm 0.03$  between Cpx and the equilibrium melt was utilized to trace the nature of their parental magmas (Pichavant and Macdonald, 2007; Putirka, 2008; Sisson and Grove, 1993) and calculated melts in equilibrium with Type-1 and Type-2 Cpx have Mg# of 39.5–55.5, 41.3–54.2, respectively. While the large range in Mg# of the calculated melts in equilibrium with the two types of Cpx points to fractionation, the Type-3 Cpx show pronounced high-Cr and -Ni rim, clearly implying the injection

of a mafic magma pulse (Fig. 7). We therefore suggest that both magma mixing (recharging) and differentiation were the prevailing mechanisms in the trans-crustal magmatic system that generated the Zhuyuan pluton (e.g., Tecchiato et al., 2018).

The mafic magma end-members from which Cpx and Opx crystallized are more difficult to define due to the effects of both magma recharging and crystal fractionation, and we are unable to determine whether pyroxene populations have a genetic relationship with each other. The Ce/Pb value is relatively stable during variable degrees of partial melting or subsequent fractional crystallization, i.e. the magma Ce/Pb value can be used as a tracer for the source regions (Hofmann, 1988; Owen, 2008; Su et al., 2017). High Ce/Pb values generally characterize mantle sources such as mid-ocean ridge basalt ( $\sim 25 \pm 5$ ), ocean island basalt ( $\sim 25 \pm 5$ ), and primitive-mantle ( $\sim 9$ ), whereas low Ce/Pb values coincide with crustal sources ( $\sim 4$ ; Hofmann et al., 1986; Sims and DePaolo, 1997). However, high Mg# and high Ce/Pb values (5.07–156) of the melts in equilibrium with both Cpx and Opx indicate a mantle origin. Therefore, both Cpx and Opx are suggested to be antecrysts.

Higgins (1996) suggested the mixing of diverse magmas with contrasting CSDs yields a CSD with a steep slope at small sizes and a gentle slope at larger sizes. The kinked Amp CSDs (Fig. 10) are in good agreement with the magma mixing scenario where coarse grains and fine grains assembled in the magma reservoir at shallow crustal levels.

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