

Article

Titanite Textures, U–Pb Dating, Chemistry, and In Situ Nd Isotopes of the Lalingzaohuo Mafic Magmatic Enclaves and Host Granodiorites in the East Kunlun Orogen Belt: Insights into Magma Mixing Processes

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Abstract

Widespread Triassic granitic magmatism is archived in the East Kunlun Orogen Belt (EKOB) of Northern Qinghai–Tibet Plateau. Mafic magmatic enclaves (MMEs), commonly hosted in these plutons, are generally interpreted as products of magma mixing; however, the specific magmatic processes remain poorly understood. In this study, we present new data on the complex zoning patterns, in situ U–Pb ages, trace element compositions, and Nd isotopic characteristics of titanite grains from the MMEs and host granodiorite of Laningzaohuo Zhongyou pluton. Whole-rock geochemical data indicate that the pluton is composed of volcanic arc-related, calc-alkaline, metaluminous I-type granodiorite. Titanite in the MMEs and the granodiorite yield similar U–Pb ages of ~244 Ma but display distinct textural and compositional features. Titanite from the granodiorite is typically euhedral, characterized by magmatic core and mantle with deuteritic rim, and exhibits sector and fir-tree zoning in the core. In contrast, titanite from the MMEs is generally anhedral, also showing magmatic core and mantle as well as deuteritic rims, but exhibits oscillatory zoning and incomplete sector and fir-tree zoning in the core. Titanite cores in the MMEs have $\epsilon_{\text{Nd}}(t)$ ranging from -2.5 to -3.4 , comparable to those of the coeval gabbro and MMEs elsewhere in the EKOB. These cores also show higher LREE/HREE ratios compared to titanite cores in the granodiorite, suggesting crystallization from mixed magmas with greater contributions from enriched lithospheric mantle sources. Titanite mantles in the MMEs yield $\epsilon_{\text{Nd}}(t)$ of -4.0 to -4.8 , slightly lower than the cores in the MMEs but higher than those of titanite cores and mantles in the granodiorite (-4.6 to -5.5). The mantle can be interpreted as crystallized from mixed magmas with less mafic components. Titanite rims in the MMEs have $\epsilon_{\text{Nd}}(t)$ of -5.0 to -5.7 , identical to those in the granodiorite, and have REE concentrations and Th/U and Nb/Ta ratios consistent with the titanite rims in the granodiorite, clearly indicative of crystallization from evolved, hydrated, granodioritic magmas. Plagioclase in the MMEs exhibits disequilibrium textures such as sieve texture and reverse zoning, with An_{36-66} , contrasting with the more uniform An contents (An_{35-37}) in the granodiorite. This suggests that plagioclase in the MMEs crystallized in an environment influenced by both mafic and felsic magmas. Amphibole thermobarometry indicates that amphibole in the MMEs crystallized at ~788 °C and ~295 MPa, slightly higher than the crystallization conditions in the granodiorite (~778 °C and ~259 MPa). We thus propose that the chemical and textural differences between titanite in the MMEs and granodiorite suggest that the MMEs formed



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within a mushy hybrid layer generated by injection of upwelling basaltic magma into a pre-existing granitic magma chamber. Titanite cores and mantles in the MMEs likely crystallized from variably mixed magmas. They subsequently underwent resorption and disequilibrium growth within the hybrid layer, and were eventually overgrown by rims formed from evolved interstitial granitic melts within the mushy enclaves. These findings demonstrate that the complex zoning and geochemical titanite in the MMEs provide valuable insights into magma mixing processes.

Keywords: titanite; magma mixing; in situ Sm–Nd isotope; mafic magmatic enclaves; East Kunlun Orogenic Belt

1. Introduction

Mafic magmatic enclaves (MMEs) are commonly found within granitic plutons and silicic volcanic rocks [1–4]. However, the origin of MMEs remains a subject of considerable debate. The MMEs have been attributed to mixing of mafic and felsic magma [5–9], restites of refractory material remaining after partial melting of source rocks, xenolithic fragments derived from country rocks [1], or autoliths composed of early-formed cumulate mafic minerals [10]. The MMEs formed by magma mixing are typically characterized by fine-grained igneous texture and various disequilibrium microstructures, including resorbed plagioclase, acicular apatite and amphibole, and quartz ocelli [11]. These features provide evidence for the involvement of mafic magmas in the initiation and evolution of granitic systems [12]. Whole-rock chemical compositions of MMEs and their host granitic rocks may obscure the identities of the original end-member magmas and thus fail to clearly record the mixing processes [13,14]. In contrast, minerals such as zircon, feldspar, apatite, and titanite preserved within MMEs can be used to reconstruct magma mixing histories [15–17].

Titanite (CaTiSiO_5) is a common accessory mineral found in igneous [18–20], metamorphic [21–23], and hydrothermally altered rocks [24–27]. Extensive elemental substitutions occur in titanite: Ca can be replaced by REE, Y, Na, Mn, Sr, Ba, U, Th, and Pb; Ti by Mg, Al, Fe^{2+} , Fe^{3+} , Cr, V, Mo, Nb, Ta, Zr, and Sn; O can be substituted by OH, F, and Cl; and Si by Al [25,27–35]. Rare earth elements (REEs) and high field strength elements (HFSEs) diffuse slowly in titanite, preserving primary zoning patterns [18,36]. Titanite is also an important reservoir for Nb, Ta, and REEs, playing a significant role in controlling the fractionation behavior of these elements during partial melting, magmatic differentiation, and mixing in granitic systems [23,35,37,38]. Therefore, titanite zoning serves as a powerful tool for reconstructing magmatic processes. Titanite typically contains high concentrations of U and has a high closure temperature (up to 700 °C), making it ideal for U–Pb geochronology [33]. It also has relatively high Nd concentrations and low Sm/Nd ratios, enabling in situ Nd isotope analysis. Thus, the Sm–Nd isotopic system in titanite can be used to trace magma sources [39]. Additionally, Zr can substitute for Ti via isomorphic replacement, and due to the extremely slow diffusion rate of Zr, titanite can serve as a reliable geothermometer [40]. Moreover, the concentrations of metallic elements in titanite can provide insights into the ore-forming potential of magmas [25,27,41,42].

Voluminous Early Paleozoic and Triassic arc-related granodiorites in the East Kunlun Orogen Belt (EKOB) were generated by the subduction of the Paleo-Tethys lithosphere and the subsequent continent–continent collision [43]. The Lalingzaohuo Zhongyou pluton is one such pluton and comprises granodiorite with abundant MMEs. In this study, we present new U–Pb ages, elemental compositions, and Nd isotopic data of titanite, as well as whole-rock geochemical data and amphibole-based crystallization pressures and temperatures

from the MMEs and host granodiorite in the Zhongyou pluton. These integrated datasets allow us to investigate the magmatic processes recorded by titanite in the MMEs. Our results provide new insights into magma mixing processes associated with slab breakoff and asthenospheric upwelling in the EKOB.

2. Geological Background

The EKOB, located in the northern Tibetan Plateau, is a key tectonic unit bounded by the Qaidam Basin to the north, the Qinling Orogenic Belt to the east, the Bayan Har–Songpan–Ganzi Terrane to the south, and the West Kunlun Belt across the Altyn Tagh Fault to the west (Figure 1a). The EKOB can be subdivided into the Northern Qimantagh, Central Kunlun, and Southern Kunlun belts, as well as the Bayanhar Terrane, separated by three major boundary faults: the Northern, Central, and Southern Kunlun faults, respectively. These faults are widely recognized as ophiolitic mélanges and are discontinuously distributed within the Qimantagh–Xiangride ophiolitic mélange (QXM) zone, the Aqikekulehu–Kunzhong ophiolitic mélange (AKM) zone, and the Muztagh–Buqingshan–Animaqen ophiolitic mélange (MBAM) zone (Figure 1b; [44,45]). The EKOB is generally considered to have been situated in an intraplate tectonic setting during the Late Triassic [44,46]. Slab breakoff at ~240 Ma is thought to have triggered lithospheric thinning and asthenospheric upwelling, processes that ultimately promoted the emplacement of Late Triassic granitic intrusions [47]. Precambrian basement rocks are exposed throughout all three terranes and are overlain by early Paleozoic sedimentary sequences [48]. The oldest basement unit is the Paleoproterozoic Mohe gneiss of the Jinshuikou Group, exposed southeast of Xiangride Town, with a crystallization age of ~2390 Ma [49]. The “Kunlun Batholith”—one of the two largest granitic batholiths on the Tibetan Plateau, consists mainly of monzonite and granodiorite emplaced predominantly during the Triassic, although magmatic activity spans from the Proterozoic to the Late Mesozoic [44,48]. This batholith is characterized by abundant MMEs and synplutonic mafic dike swarms, which are considered petrological indicators of periodic basaltic magma underplating and crust–mantle interactions [43,50].

The Laningzaohuo district, located in the central EKOB to the west of Golmud City, hosts the giant Xiarihamu magmatic Ni–Cu sulfide deposit and the Zhongyou skarn Mo–Cu deposit (Figure 1b,c). The exposed intrusions are mainly Middle to Late Triassic granitoids, with minor Permian and Devonian granitic bodies (Figure 1c). The Middle to Late Triassic granitoids in this area exhibit typical I-type geochemical signatures and belong to the high-K calc-alkaline series [47]. The surrounding strata are dominated by the Paleoproterozoic Jinshuikou Group, with small outcrops of the Late Devonian Maoniushan Group (Figure 1c). The Zhongyou pluton consists of medium- to coarse-grained granodiorite with abundant MMEs (Figure 2). The MMEs in this pluton are typically circular to oval in shape, ranging from 10 to 20 cm in diameter (Figure 2a,b). They are sharply bounded by the host granodiorite and locally exhibit chilled margins. Plagioclase phenocrysts are commonly observed within the MMEs (Figure 2a,d).

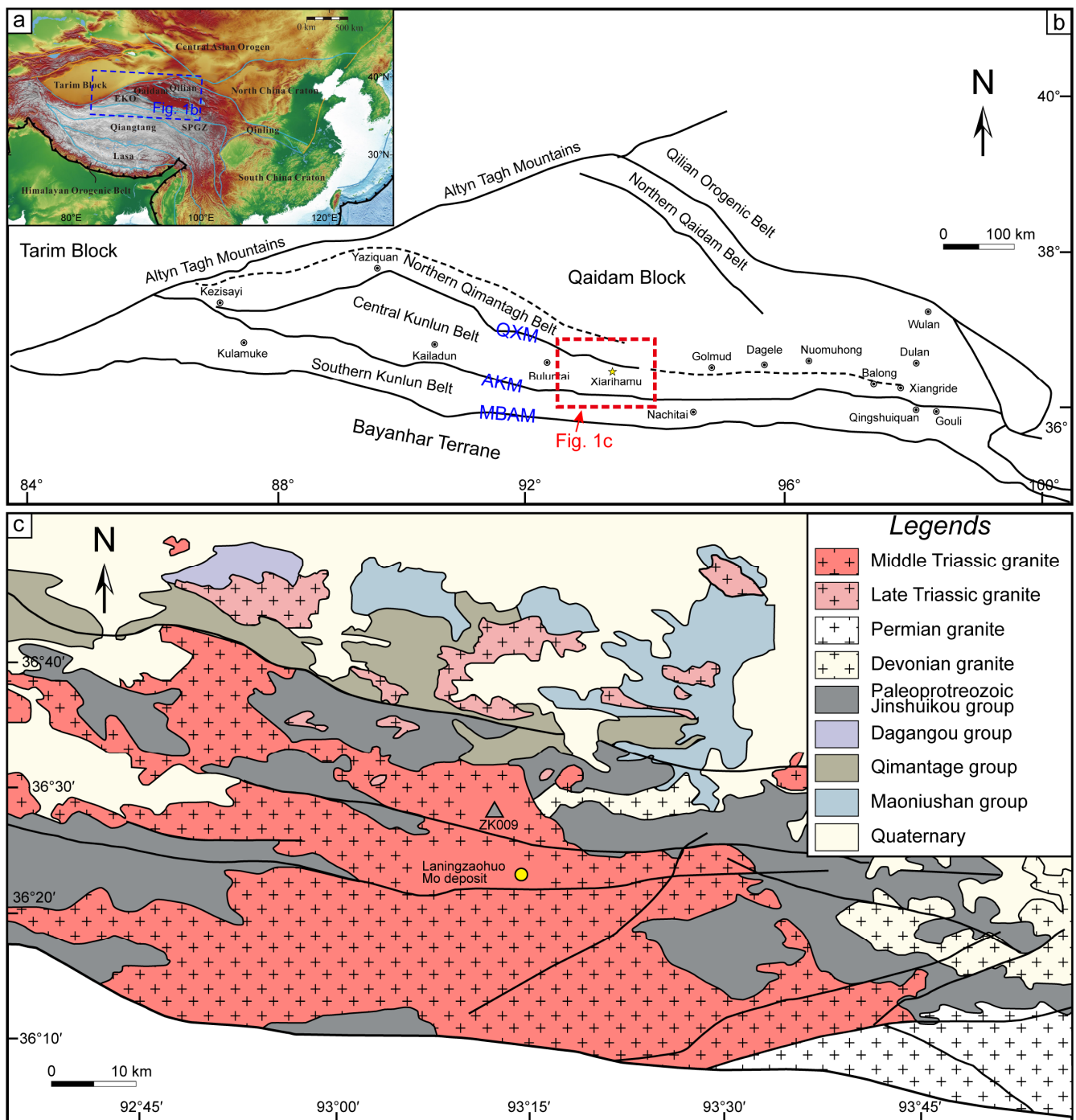


Figure 1. (a) Tectonic map showing the location of the East Kunlun Orogen Belt (EKOB), and its tectonic relationship with adjacent blocks [51]. (b) Simplified tectonic map of the EKOB showing its major tectonic divisions [45]. (c) Geological map of the Lalingzaohuo district showing the sampling locations [47]. QXM, Qimantagh–Xiangride melange zone; AKM, Aqikekulehu–Kunzhong ophiolitic melange zone; MBAM, Muztagh–Buqingshan–Animaqen ophiolitic melange zone.

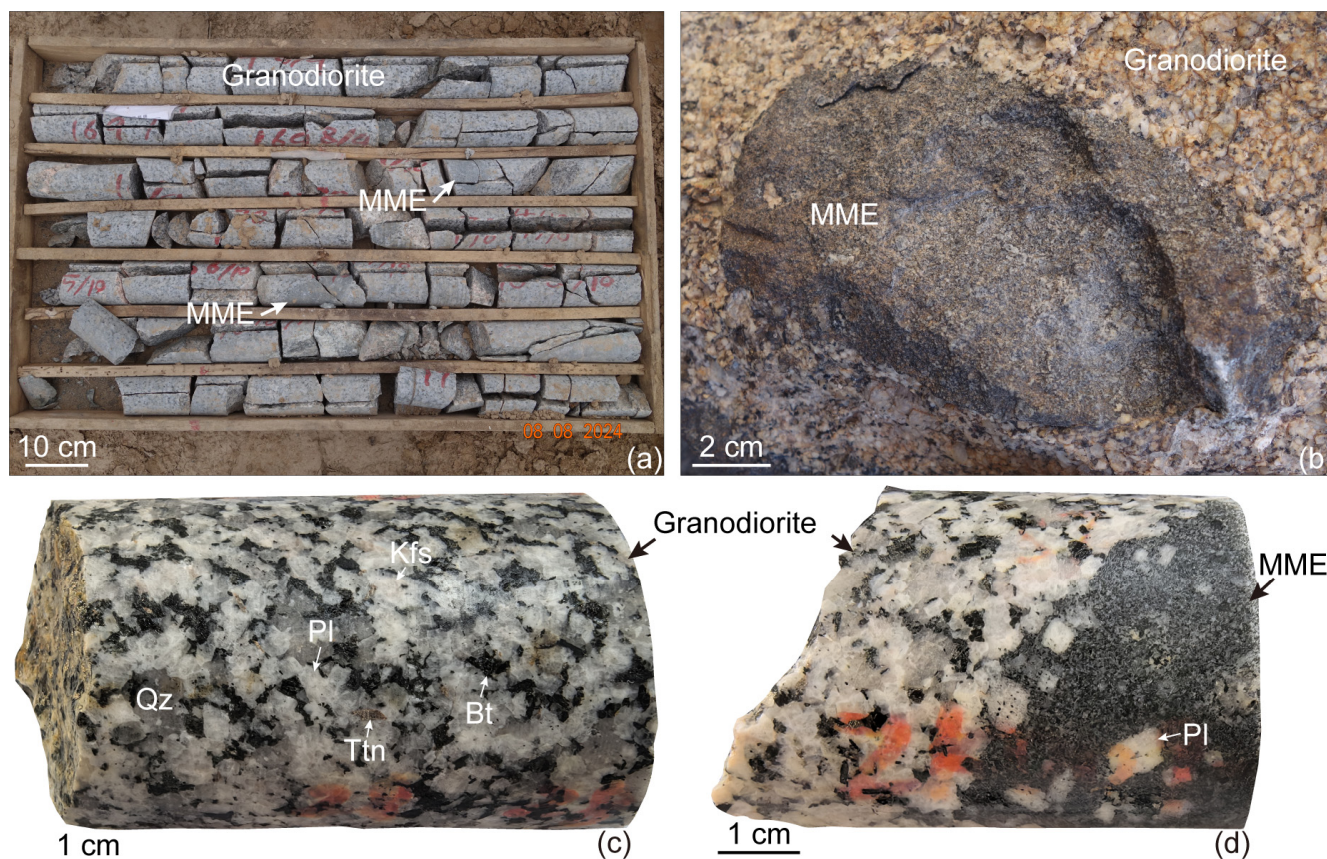


Figure 2. (a) Drill core ZK009 showing the vertical distribution of host granodiorite and mafic magmatic enclaves (MMEs). (b) Outcrop photograph showing circular MMEs. (c) Granodiorite composed of (Pl), K-feldspar (Kfs), biotite (Bt), quartz (Qz) and titanite (Ttn). (d) Sharp contact between MME and granodiorite, with the MME composed of plagioclase phenocrysts and a fine-grained matrix.

3. Petrography

The granodiorite consists of 35–40 vol.% plagioclase, 25–30 vol.% K-feldspar, 25–30 vol.% quartz and ~5 vol.% biotite, with minor amounts of amphibole, titanite, zircon and apatite. The rock shows medium- to coarse-grained texture. Plagioclase and K-feldspar laths are subhedral to euhedral, ranging from 1 to 5 mm in length, with some reaching up to 8 mm. The remaining consists of medium-grained quartz, accompanied by minor amounts of biotite and amphibole (Figure 3a,b).

The MMEs hosted in the granodiorite comprise 30–40 vol.% phenocrysts and 60–70 vol.% fine-grained matrix. Phenocrysts are primarily composed of plagioclase (20–25 vol.%) and K-feldspar (10–15 vol.%). The matrix consists of plagioclase (25–30 vol.%), K-feldspar (5–10 vol.%), amphibole (5–10 vol.%), biotite (5–10 vol.%), and quartz (~5 vol.%), with minor magnetite, titanite, apatite, and zircon (Figure 3c,d). Plagioclase phenocrysts, ranging from 2 to 8 mm in length, commonly show sieve texture in their mantles (Figure 3c) and some form of glomerocrysts. Plagioclase grains in the matrix are 0.5 to 2 mm in length and frequently display dissolved cores (Figure 3d). Amphibole grains are subhedral to anhedral, ranging from 0.5 to 2 mm in size (Figure 3c,d). Acicular apatite is commonly enclosed within plagioclase (Figure 3d). Biotite microcrystals are enclosed within amphibole (Figure 3d).

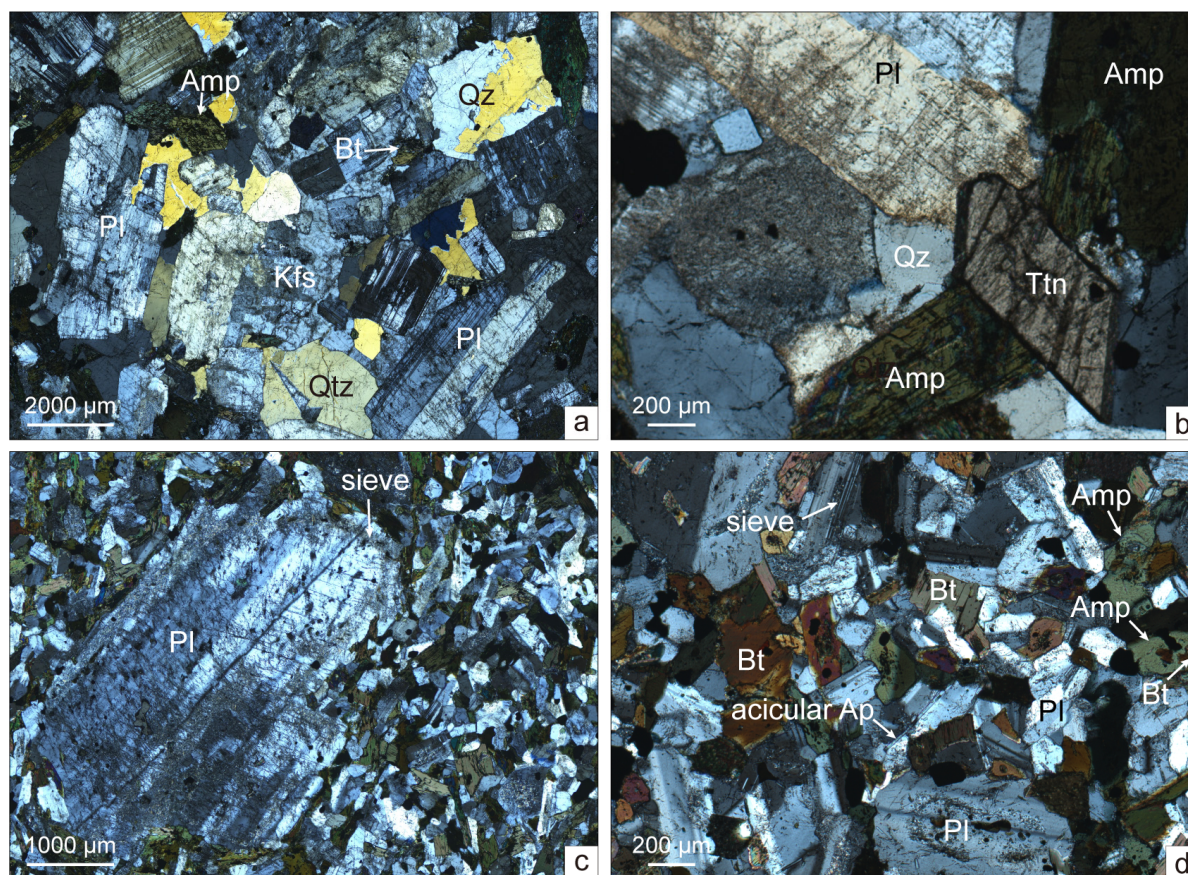


Figure 3. Photomicrographs of the granodiorite and MMEs from the Zhongyou pluton. (a) Coarse-grained granodiorite consisting of plagioclase (Pl), K-feldspar (Kfs), biotite (Bt), amphibole (Amp), and quartz (Qz). (b) Titanite (Ttn) in the host granodiorite is interstitial to plagioclase and amphibole (Qtz). (c) Plagioclase phenocryst in the MMEs showing sieve texture in the mantle. (d) Fine-grained matrix in the MMEs containing sieve-textured plagioclase, amphibole, biotite, and acicular apatite. All images taken under cross-polarized light.

4. Analytical Methods

4.1. Whole-Rock Major and Trace Element Analyses

Six rock samples were analyzed for whole-rock major and trace elemental compositions at the Guangzhou Tuoyan Analytical Technology Co., Ltd. (Guangzhou, China). Major oxides were measured using a PANalytical PW2424 scanning wavelength dispersive X-ray fluorescence (XRF) spectrometer (PANalytical, Malvern, UK). The analyses were calibrated against rock standards (GSR-8, GSR-9, JB-1b, and JA-2; [52]), with relative uncertainties of less than 5% for major elements.

Trace element concentrations were analyzed using an Agilent 7900 inductively coupled plasma mass spectrometry (ICP-MS) (Agilent, Santa Clara, CA, USA). Approximately 50 mg of powder sample was digested in steel-jacketed Teflon bombs with a mixture of 1.5 mL HF, 1.5 mL HNO₃, and 0.01 mL HClO₄. The mixture was dried and then treated with 1 mL HF and 0.5 mL HNO₃ at 190 °C for 12 h in a Teflon bomb. After cooling, 1 mL of Rh solution was added as an internal standard, followed by drying at 150 °C. The residue was then dissolved in 1 mL of HNO₃, dried again, and this process was repeated twice. The final residue was dissolved in 8 mL HNO₃ and heated at 110 °C for 3 h in sealed Teflon bombs on a hot plate. The final solution was diluted to 100 mL with distilled deionized water. Calibration was performed using rock standards (GSR-1, GSR-2, GSR-3, and GSR-7; [53]),

ensuring a relative accuracy better than 5% for most trace elements. The whole-rock major and trace element data are presented in Supplementary Table S1.

4.2. Major Oxide Compositions Analyses and Elemental Intensity X-Ray Mapping

The major oxide compositions of titanite, amphibole, and plagioclase were analyzed using a JEOL JXA-8230 electron probe microanalyzer (EPMA) (JEOL, Akishima, Japan) at the State Key Laboratory of Deep Earth Processes and Resources (DEEPER), Guangzhou Institute of Geochemistry, Chinese Academy of Sciences (GIGCAS). Analytical conditions included an accelerating voltage of 15 kV, a beam current of 20 nA, and a beam diameter of 2 μm . The peak, upper and lower background counting times were set to 40, 20, and 20 s for Ti, Mn, and Mg; 20, 10, and 10 s for Si, Fe, Ca, and Al; and 10, 5, and 5 s for F, Cl, K, and Na. Calibration was performed using American SPI standards: olivine for Si and Mg, plagioclase for Ca and Si, rutile for Ti, almandine for Al, magnetite for Fe, rhodonite for Mn, Cr-diopside for Ca and Si, albite for Na, orthoclase for K, BaF₂ for F, and tugtupite for Cl. All data were processed using ZAF correction and the element detection limit was 0.01%. The analytical accuracy and 1 σ precision were better than 4% for major elements. The major oxide compositions of titanite, amphibole, and plagioclase are provided in Supplementary Table S2.

The X-ray 2-D elemental intensity maps for titanite were acquired using the same EPMA with a dwell-time of 90 ms for each point. These maps are semi-quantitative in nature. Mapping operation conditions were at 20 kV, 500 nA and 2.5 μm beam. Nb L α was analyzed using a PETH crystal, and Nd L α was analyzed using a LIFH crystal.

4.3. U–Pb Dating and Trace Element Analyses for Titanite

The U–Pb dating and trace element analysis of titanite were conducted in situ using an Agilent 7500x ICP-MS coupled with a Resolution S155 excimer laser ablation (LA) system (Agilent, Santa Clara, CA, USA) at DEEPER, GIGCAS. A laser beam spot size of 43 μm and an ablation repetition rate of 6 Hz were employed. Raw data were processed using the Iolite 4 software [54]. The U–Pb isotopic data (1 sigma, 95% CL) were plotted on Tera–Wasserburg diagrams [55], with the intercept on the y -axis corresponding to the common $^{207}\text{Pb}/^{206}\text{Pb}$ composition. Lower intercepts were used to approximate the crystallization ages of the samples. Common Pb correction was performed using the measured ^{207}Pb composition. The Tera–Wasserburg diagrams were plotted using Isoplot (v4.15) [56]. MKED1 (1521 ± 3 Ma, [57]) and OLT (1011 ± 6 Ma, [58]) was used as the external and monitor standard for U–Pb dating.

Trace element concentrations of titanite were calibrated using ^{29}Si as the internal standard and NIST SRM 610 as the external standard. The SiO₂ content used for internal standardization was derived from average EPMA measurements. The recommended trace element concentrations of NIST SRM 610 are consistent with those obtained in this study. The U–Pb data and trace element compositions of titanite are provided in Supplementary Table S3.

4.4. In Situ Sm–Nd Isotopic Analysis for Titanite

The Sm–Nd isotopic composition of titanite was measured in situ on grains with established U–Pb ages using a Thermo Fisher Neptune Plus multi-collector (MC)-ICPMS (Thermo Fisher Scientific, Waltham, MA, USA) coupled with a Resolution M-50 193 nm LA system at DEEPER, GIGCAS. Analyses were conducted in single-point mode with a laser beam spot diameter of 60 μm , an ablation frequency of 10 Hz, and a laser fluence of ~ 6 J/cm². Reference materials T3 and OLT1 were used as the standards during analyses. The $^{147}\text{Sm}/^{144}\text{Nd}$ and $^{143}\text{Nd}/^{144}\text{Nd}$ ratios were calibrated using exponential law after correcting for the isobaric interference of ^{144}Sm on ^{144}Nd . In this study, T3 and OLT1

yielded $^{143}\text{Nd}/^{144}\text{Nd}$ of 0.512632 ± 26 and 0.512229 ± 44 , respectively, consistent with previously referenced values within uncertainties [58]. The Sm-Nd isotopic compositions of titanite are provided in Supplementary Table S4.

5. Results

5.1. Texture of Titanite

Titanite grains in the host granodiorite are typically euhedral and exhibit a well-developed core–mantle–rim texture (Figure 4a–c). The cores display distinct sector and fir-tree zoning patterns, while the mantles form narrow layers enveloping the core (Figure 4a–c). The outer deuteritic rims are irregular in shape and appear to have crystallized from interstitial melts (Figure 4c). Titanite grains with overgrowth rims are relatively rare compared to those lacking such features. In some cases, deuteritic veinlets locally penetrate the inner domain of titanite (Figure 4a,b).

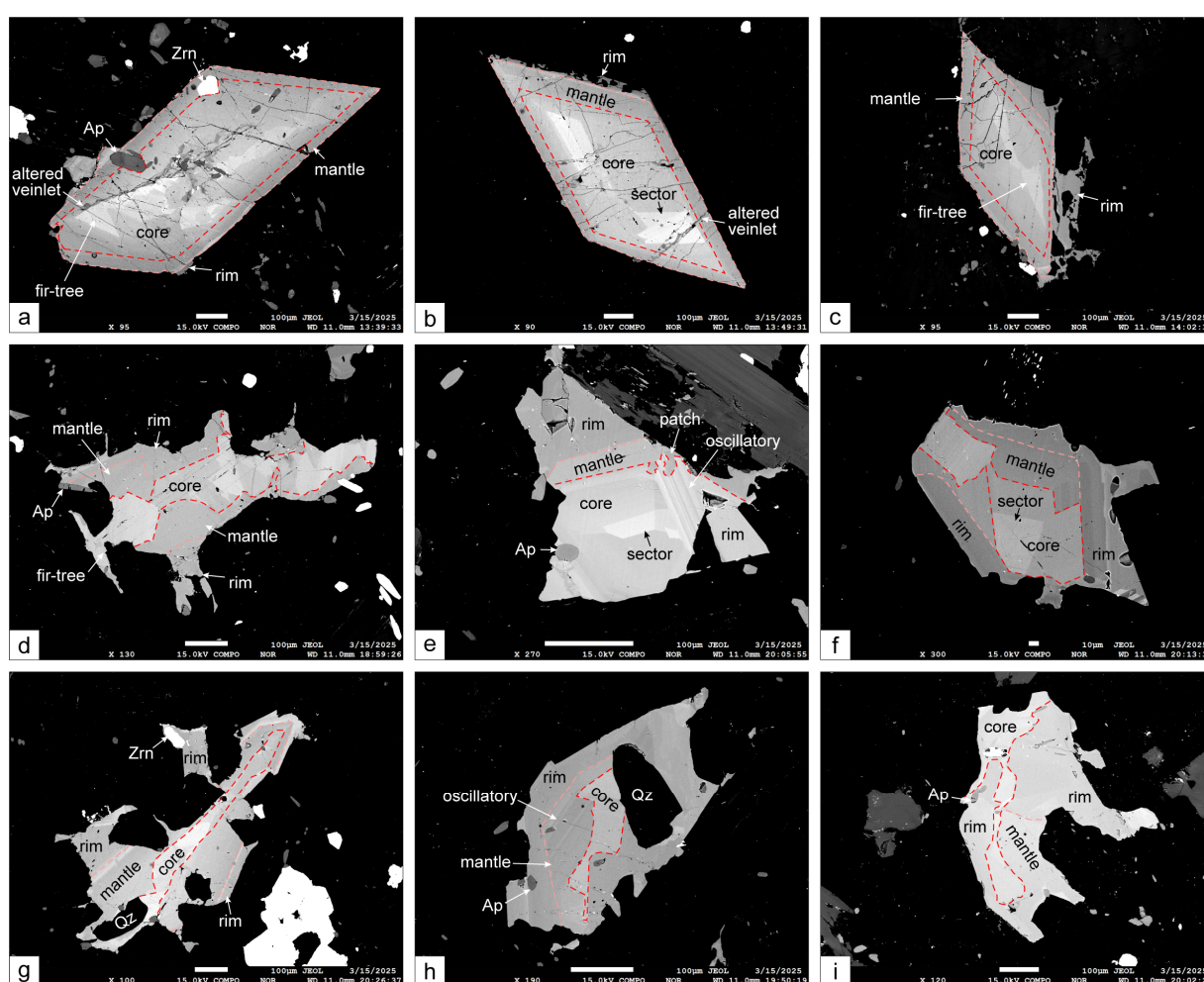


Figure 4. Backscattered electron (BSE) images of titanite from the granodiorite and MMEs of the Zhongyou pluton. (a–c) Euhedral titanite in the granodiorite showing sector and fir-tree zoning with irregular deuteritic rim; zircon (Zrn) and apatite (Ap) inclusions are present. (d–i) Anhedral titanite in the MMEs with core–mantle–rim textures, displaying incomplete sector and fir-tree zoning and oscillatory zoning in the core, with irregular deuteritic rims; quartz (Qz), zircon, and apatite inclusions are present.

In contrast, titanite grains in the MMEs are anhedral but similarly display a core–mantle–rim texture. The cores are irregularly shaped and show embayment features, characterized by oscillatory zoning as well as incomplete sector and fir-tree zoning (Figure 4d–i).

The mantles typically contain abundant inclusions of quartz and plagioclase, and the rims are frequently corroded.

5.2. Whole-Rock Major and Trace Elemental Compositions

The samples of host granodiorite from the Zhongyou pluton contain 62.1–62.3 wt.% SiO_2 with $\text{Mg\#}$ [$100 \times \text{Mg}/(\text{Mg} + \text{Fe})$] of ~46, belonging to granodiorite in composition (Figure 5a). These rocks are calc-alkaline and metaluminous, with A/CNK [molar ratios $\text{Al}_2\text{O}_3 / (\text{CaO} + \text{Na}_2\text{O} + \text{K}_2\text{O})$] ranging from 0.95 to 0.98 (Figure 5b). They have TiO_2 of 0.72 wt.%, Al_2O_3 of 16.45–16.79 wt.%, total Fe_2O_3 of 4.86–5.26 wt.%, MgO of 2.11–2.28 wt.% and CaO of 4.64–4.68 wt.% (Supplementary Table S1). The MMEs in the Zhongyou pluton are mafic in composition ($\text{SiO}_2 = 48.66\text{--}49.62$ wt.%), corresponding to monzogabbro and monzodiorite in composition (Figure 5a). They are also alkaline and metaluminous, with $\text{Mg\#}$ values of 47–51 and A/CNK ratios of 0.85–0.90 (Figure 5a). Compared to the host granodiorite, the MMEs contain higher TiO_2 (1.16–1.26 wt.%), Al_2O_3 (18.98–19.41 wt.%), total Fe_2O_3 (9.42–9.91 wt.%), MgO (4.32–5.12 wt.%), and CaO (6.86–7.52 wt.%) (Supplementary Table S1).

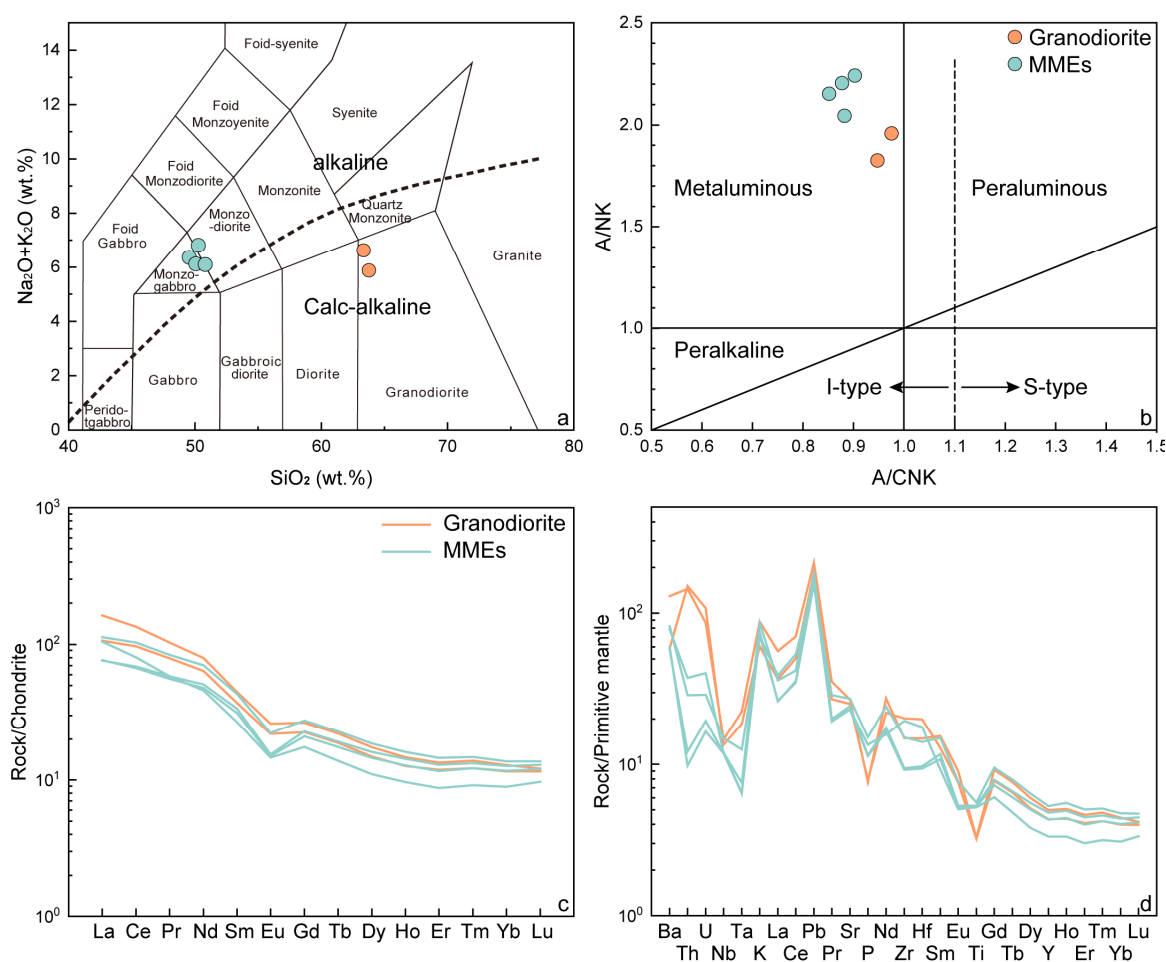


Figure 5. The plots of $\text{Na}_2\text{O} + \text{K}_2\text{O}$ vs. SiO_2 (a), A/NK [$\text{Al}_2\text{O}_3 / (\text{Na}_2\text{O} + \text{K}_2\text{O})$] vs. A/CNK [molar ratio $\text{Al}_2\text{O}_3 / (\text{CaO} + \text{Na}_2\text{O} + \text{K}_2\text{O})$] (b), chondrite-normalized rare earth element patterns (c), and primitive mantle-normalized trace element patterns (d) for the granodiorite and MMEs samples from drill core ZK009, Zhongyou pluton. Chondrite and primitive mantle normalization values are from [59].

Chondrite-normalized REE patterns are shown in Figure 5c. The granodiorites exhibit higher total REE contents than the MMEs. Both the MMEs and granodiorites are enriched

in light REEs (LREEs) and depleted in heavy REEs (HREEs). The MMEs display more pronounced negative Eu anomalies ($\text{Eu}/\text{Eu}^* = 0.54\text{--}0.66$) compared to the host granodiorites ($\text{Eu}/\text{Eu}^* = 0.73\text{--}0.74$) (Figure 5c; Supplementary Table S1). On the primitive mantle-normalized trace element patterns, both the granodiorite and MMEs show varying degrees of enrichment in light REE, U, Pb and Ta and depletion in Nb, P, Zr and Ti (Figure 5d). Thorium (Th) is enriched in host granodiorites and depleted in the MMEs. The granodiorite shares characteristics with volcanic arc granites (Figure 6).

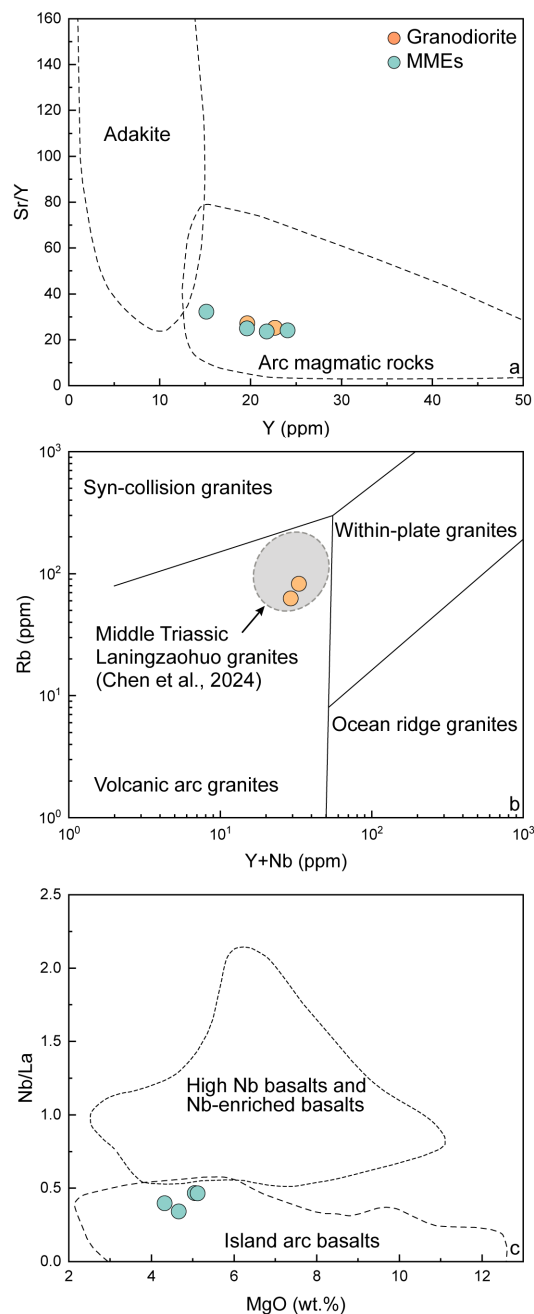


Figure 6. Plots of Sr/Y vs. Y (a), Rb vs. Y + Nb (b) and Nb/La vs. MgO (c) for the granodiorite and MMEs samples of the Zhongyou pluton [47].

5.3. Titanite U–Pb Ages

Titanite grains from both the host granodiorite and MMEs were analyzed for U–Pb ages (Supplementary Table S3). In the Tera–Wasserburg diagrams (Figure 7), titanite grains from the host granodiorite yield an upper intercept of $^{207}\text{Pb}/^{206}\text{Pb}$ of 0.88 ± 0.02 and a

lower intercept age of 244.0 ± 0.9 Ma (MSWD = 1.0, $n = 35$). Similarly, titanite grains from the MMEs produce upper intercepts of $^{207}\text{Pb}/^{206}\text{Pb}$ of 0.88 ± 0.04 and a lower intercept age of 243.8 ± 0.9 Ma (MSWD = 1.1, $n = 34$). These results indicate that the U–Pb ages of titanite in the host granodiorite and the MMEs are identical within analytical error.

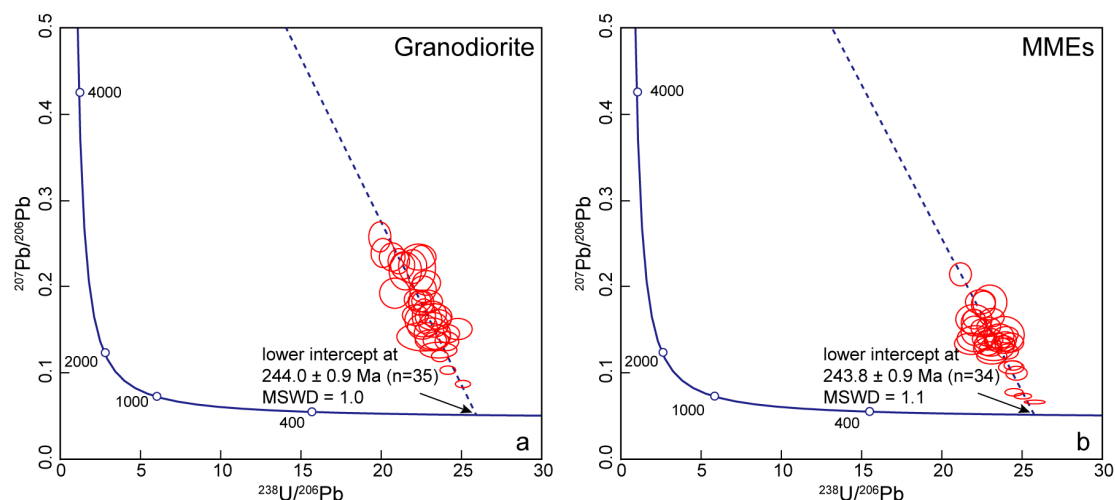


Figure 7. Tera–Wasserburg U–Pb plots of titanite in the granodiorite (a) and MMEs (b) from the Zhongyou pluton.

5.4. Major and Trace Element Compositions of Titanite

The titanite grains of the MMEs and host granodiorite exhibit an overall negative correlation between $\text{Al}_2\text{O}_3 + \text{FeO}$ and TiO_2 , and a positive correlation between Al_2O_3 and F (Figure 8; Supplementary Table S2). The core and mantle of titanite grains in the MMEs exhibit REE patterns similar to those of titanite in the granodiorite. These are characterized by enrichment in LREEs, depletion in HREEs, and obvious negative Eu anomalies. The rims of titanite grains in the MMEs and granodiorite also display similar REE patterns—enriched in LREEs and depleted in HREEs. However, in contrast to cores and mantles, the rims with lowest REE and show positive Eu anomalies (Figure 9). In both the MMEs and granodiorite, REE concentrations are highest in the cores, intermediate in the mantles, and lowest in the rims (Figure 9, Supplementary Table S3).

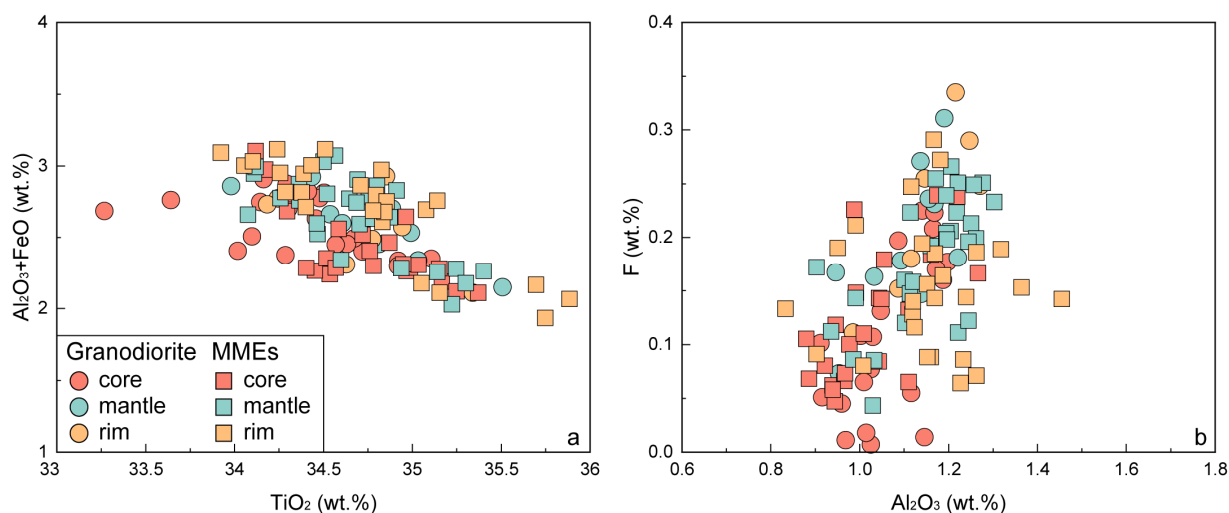


Figure 8. Plots of $\text{Al}_2\text{O}_3 + \text{FeO}$ vs. TiO_2 (a) and F vs. Al_2O_3 (b) for the titanite in the MMEs and granodiorite of the Zhongyou pluton.

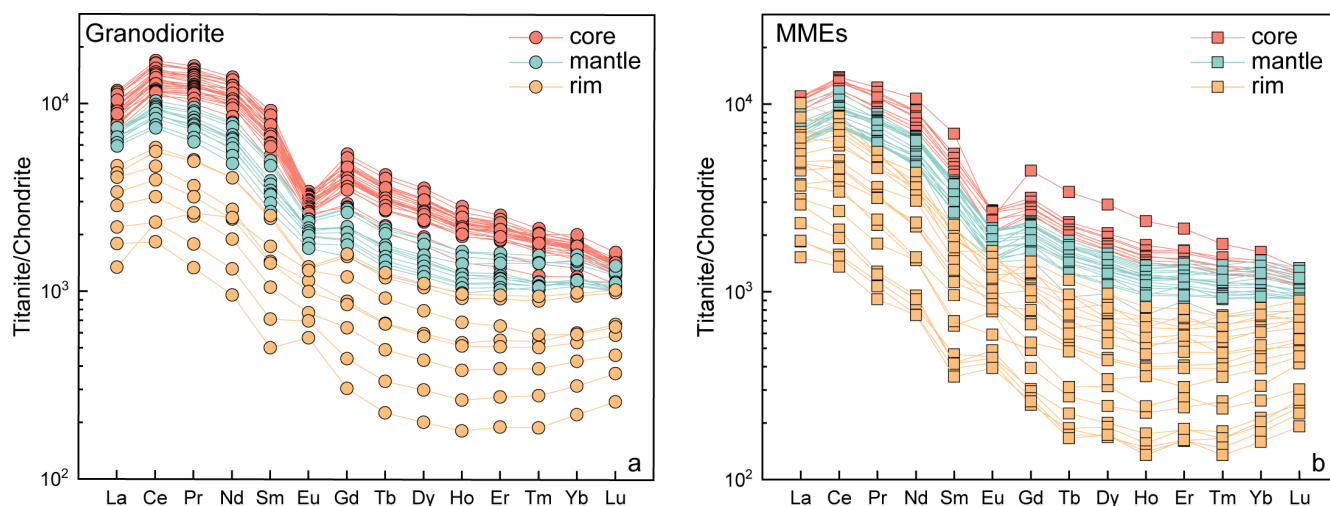


Figure 9. Chondrite-normalized rare earth element patterns for the titanite in the granodiorite (a) and MMEs (b) of the Zhongyou pluton. Chondrite normalization values are from Sun and McDonough (1989) [57].

The concentrations of Sr, Nb, Ta, Zr, and Th in titanite grains from both the MMEs and granodiorites decrease gradually from the cores to the mantles, followed by a sharp decrease from the mantles to the rims. Moreover, rim compositions display a wide range of variabilities (Figure 10; Supplementary Table S3). The Nb/Ta ratios of titanite also increase gradually from cores to the mantles and rise sharply from mantles to rims, with considerable variability in the rim values (Figure 10b). The Th/U ratios in the core and mantles of titanite are generally greater than 1 and vary widely, whereas the rims have $\text{Th/U} < 1$ with relatively limited variation (Figure 10). The Eu/Eu^* values of cores and mantles are typically less than 1, while many rims exhibit $\text{Eu/Eu}^* > 1$, which tend to increase as Eu concentrations decrease (Figures 9 and 10e). Additionally, the LREE/HREE ratios in the rims are mostly higher than those in the cores and mantles and exhibit broad variation (Figure 10f).

5.5. In Situ Nd Isotopic Compositions of Titanite

Titanite from the host granodiorite exhibits consistent $\epsilon_{\text{Nd}}(t = 244 \text{ Ma})$ values, ranging from -4.6 to -5.5 (Figure 11; Supplementary Table S4). Specifically, the cores yield $\epsilon_{\text{Nd}}(t)$ values of -4.6 to -4.9 and the mantles range from -5.0 to -5.5 . The rims were too narrow for reliable isotopic analysis. In contrast, titanite cores in the MMEs display the highest $\epsilon_{\text{Nd}}(t)$ values among all analyzed titanite grains, ranging from -2.5 to -3.4 (Figure 11; Supplementary Table S4). The mantles of MMEs titanite show slightly lower $\epsilon_{\text{Nd}}(t)$ values, ranging from -4.0 to -4.8 , which are still slightly higher than those of titanite in the granodiorite (Figure 11; Supplementary Table S4). The rims of the MMEs titanite exhibit $\epsilon_{\text{Nd}}(t)$ values of -5.0 to -5.7 , closely resembling those of titanite in the granodiorite (Figure 11; Supplementary Table S4).

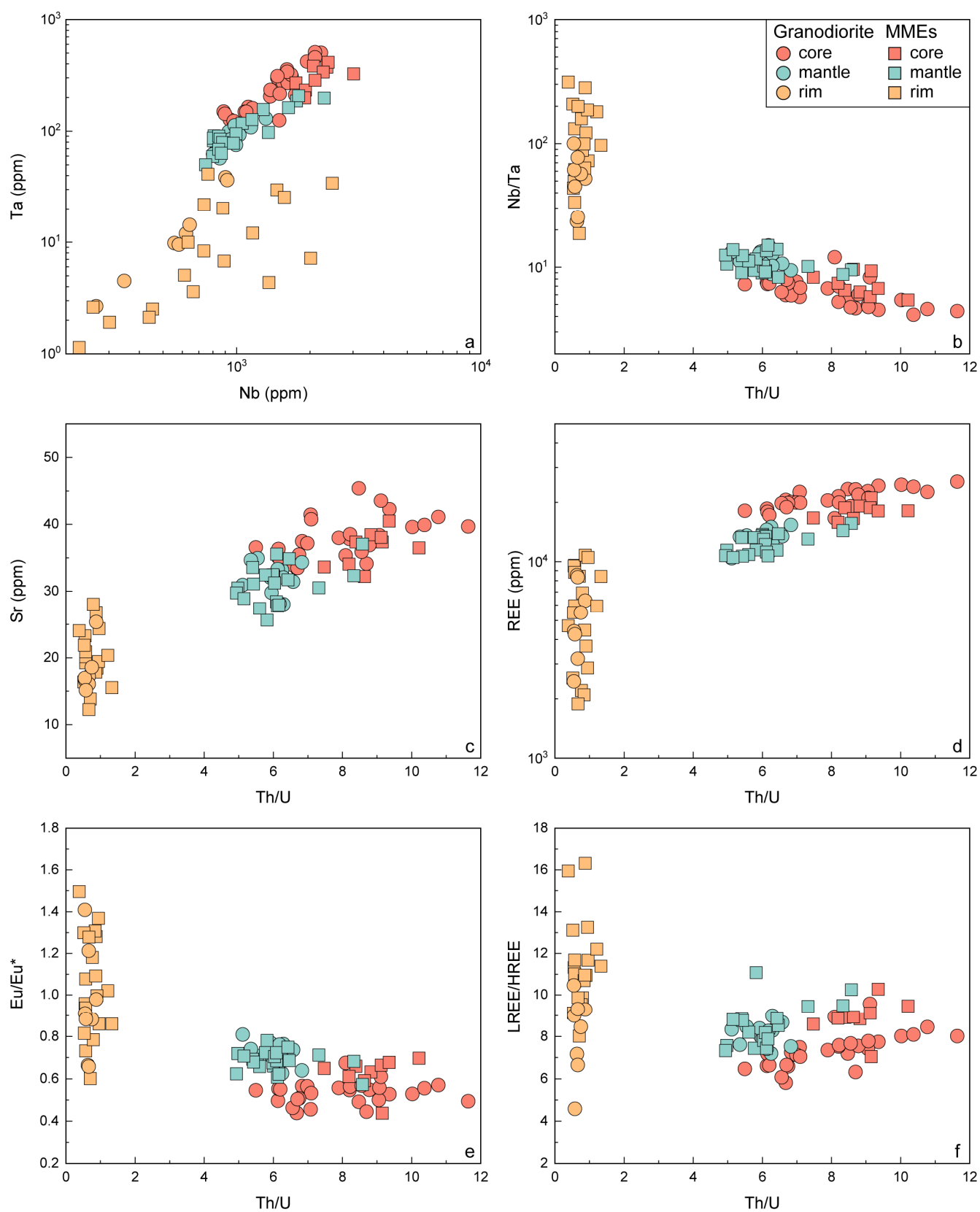


Figure 10. Plots of Ta vs. Nb (a), and Nb/Ta (b), Sr (c), REE (d), Eu/Eu* (e) and LREE/HREE (f) vs. Th/U for the titanite in the granodiorite and MMEs of the Zhongyou pluton.

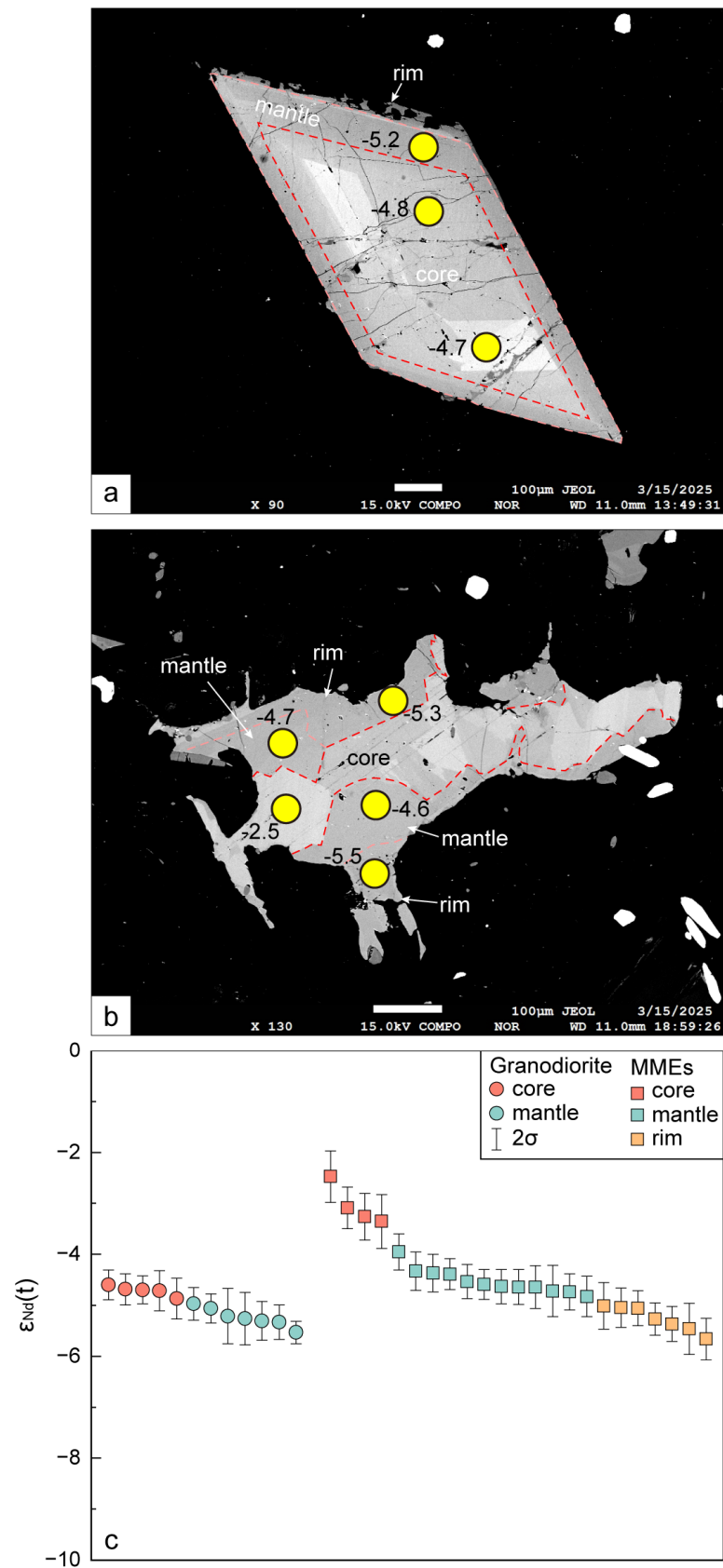


Figure 11. Variation of $\epsilon_{Nd}(t)$ within titanite in the host granodiorite (a) and in the MMEs (b), and comparison of $\epsilon_{Nd}(t)$ values for the core, mantle, and rim of titanite from the granodiorite and MMEs of the Zhongyou pluton (c).

6. Discussion

6.1. Origin of the MMEs

In the Lalingzaohuo Zhongyou pluton, titanites from the MMEs and host granodiorite yield consistent U–Pb ages (Figure 7), suggesting that the MMEs and the granodiorite were formed simultaneously in the magma chamber. The MMEs exhibit typical igneous textures (Figure 3c,d), indicating that they are neither xenoliths nor restites from partial melting. Although the MMEs and granodiorite share similar mineral assemblages, minerals in the MMEs are generally finer-grained, occur occasionally as phenocrysts, and are less euhedral compared to those in the granodiorite. The occurrence of biotite microcrysts enclosed within the amphibole in the MMEs (Figure 3d), is inconsistent with the Bowen reaction series, and further indicates that the MMEs did not form through normal fractional crystallization. Quenched textures such as acicular apatite (Figure 3d) and fine-grained groundmass (Figure 3c,d) are well developed in the MMEs, implying rapid crystallization by undercooling upon injection into the granitic magma chamber, which also explains the sharp contact observed between the MMEs and the host granodiorite (Figure 2). These disequilibrium textures in the MMEs, caused by variations in magma temperature and composition (Figure 3), provide direct evidence for magma mixing [11,60].

Whole-rock compositions indicate that the pluton comprises subduction-related, high-K calc-alkaline, metaluminous I-type granodiorite (Figure 5). In contrast, the MMEs are compositionally mafic, corresponding to alkaline monzogabbro to monzodiorite (Figure 5a). The MMEs and granodiorite exhibit typical arc magmatic geochemical signatures. However, the MMEs show geochemical affinities with island arc basalts, whereas the granodiorite shares characteristics with volcanic arc granites, similar to the Middle Triassic Lalingzaohuo granitoids (Figure 6; [47,61,62]). The $\epsilon_{\text{Nd}}(t)$ values of titanite cores in the MMEs range from -2.5 to -3.4 (Figure 11), suggesting a significant contribution from mantle-derived components. These values, consistent with those of coeval gabbros and MMEs in the EKOB, coupled with low Co (23.8–27.0 ppm), Ni (9.60–16.7 ppm), and Cu (53.0–68.4 ppm) concentrations (Supplementary Table S1), suggest derivation from an enriched lithospheric mantle source [43].

The An content ($X_{\text{An}} = \text{molar Ca}/[\text{Ca} + \text{Na} + \text{K}]$) of phenocrystic and matrix plagioclase in the MMEs varies widely (36%–64%), while plagioclase in the granodiorite consistently exhibits lower An values, comparable to those of the rims in MME plagioclase (Figure 12). The X_{An} of phenocrystic plagioclase shows an increase from core to mantle followed by a decrease toward the rim, indicating the presence of reverse zoning (Figure 12). The sieve texture in MME plagioclase phenocrysts appears as a dusty mantle zone, which is more calcic than the core and rim (Figures 3c and 12b). This texture is likely formed due to the reaction between low-An plagioclase and a hotter, more calcic melt [63,64], driven by chemical disequilibrium between the plagioclase core and surrounding granitic melt, and further enhanced by decompression during ascent [65].

The matrix plagioclase displays coarse sieve textures with opaque cores (Figure 3d), which may have developed under decompression, as suggested by experimental studies [66]. In H_2O -undersaturated, plagioclase-rich magma, an increase in H_2O pressure during ascent can lead to plagioclase destabilization and partial dissolution [66–68]. The similarity in An contents between plagioclase rims in the MMEs and the granodiorite indicates crystallization from the same granitic melt, providing further evidence for magma mixing.

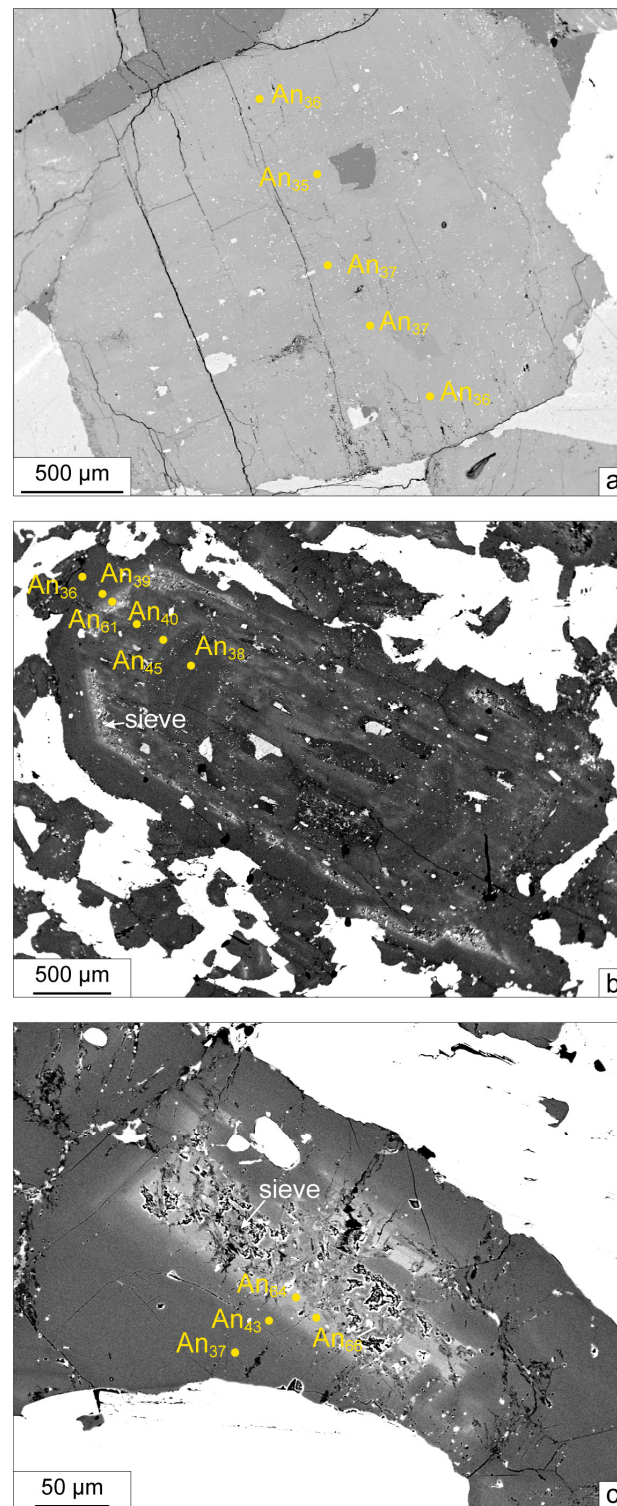


Figure 12. (a) BSE image of plagioclase in the granodiorite showing consistent X_{An} values. (b) BSE image of plagioclase phenocryst in the MME showing various X_{An} of An_{36-61} and the highest X_{An} in the sieve-texture mantle. (c) BSE image of plagioclase in the matrix in the MMEs showing various X_{An} of An_{37-66} and the highest X_{An} in the sieve-texture core.

We used amphibole thermometer [69] and barometer [70] to calculate the crystallization temperature and pressure of amphibole in the MMEs and granodiorite. The equations of the pressure-independent thermometer and geobarometer are expressed as

$$T (^{\circ}\text{C}) = 1781 - 132.74 (\text{Si}^{\text{Amp}}) + 116.6 (\text{Ti}^{\text{Amp}}) - 69.41 (\text{Fe}_t^{\text{Amp}}) + 101.62 (\text{Na}^{\text{Amp}}) \quad (1)$$

$$P \text{ (MPa)} = 100 \times [0.5 + 0.331(8) \times Al^{Amp} + 0.995(4) \times (Al^{Amp})^2] \quad (2)$$

where Si^{Amp} , Ti^{Amp} , Na^{Amp} , and Al^{Amp} are the cations in amphibole that are calculated based on 23 O atoms; Fe_t^{Amp} represents the total Fe cations.

The results show that the amphibole in the MMEs and granodiorite crystallized at comparable temperatures (777–795 °C and 772–787 °C, respectively), but the MMEs record slightly higher pressures (272–308 MPa) than the granodiorite (245–276 MPa) (Figure 13a). These pressure–temperature conditions indicate that the MMEs may have formed within a hybrid boundary layer, where ascending mafic magma was injected into the bottom of overlying granitic magma body. This process produced a thermal and compositional boundary layer in which crystal-laden mafic magma mixed with granitic melt, leading to the formation of molten MMEs that were subsequently entrapped within the granodiorite [65,71].

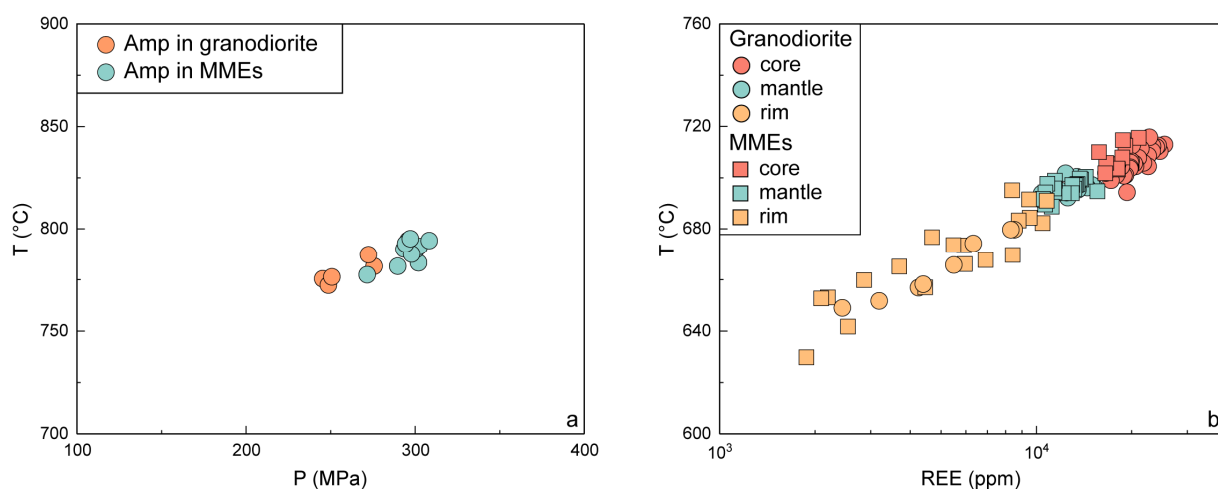


Figure 13. (a) Crystallization temperature and pressure of amphibole grains and (b) plot of REE vs. crystallization temperature of titanite from the granodiorite and MMEs in the Zhongyou pluton.

6.2. Magma Mixing Processes Recorded in Titanite

The sector, fir-tree, and oscillatory zoning patterns are commonly observed in the cores of titanite grains from the MMEs and host granodiorite (Figure 4). The crystallization temperatures for the cores and mantles of titanite in the MMEs and granodiorite, estimated using the Zr-in-titanite geothermometer [40] with $a_{TiO_2} = 0.5$ and $a_{SiO_2} = 1$, range from 689 to 716 °C, indicating magmatic origins [18,32,38,72,73]. In contrast, the rims of titanite in the MMEs and the host granodiorite show lower crystallization temperatures (630–691 °C; Figure 13b), mostly below the water-saturated granite solidus [74], suggesting subsolidus growth [73]. Compared to the relatively homogeneous and euhedral titanite in the granodiorite, the complex core–mantle–rim zoning and variable compositions in the MMEs reflect a more dynamic growth history, likely associated with magma mixing.

Due to the similar ionic radii of Fe^{3+} and Ti^{4+} [75], Fe^{3+} tends to substitute for Ti^{4+} in the octahedral sites of titanite at high temperatures, while REEs typically replace Ca^{2+} [37]. During titanite crystallization from granitic melt, a coupled substitution reaction occurs: $Ca^{2+} + Ti^{4+} = (REE, Y)^{3+} + (Fe, Al)^{3+}$, leading to a negative correlation between Ti and (Al + Fe) contents (Figure 8a). X-ray elemental maps reveal REE and HFSE enrichment in fir-tree zoning in titanite from the MMEs and granodiorite (Figure 14), attributed to the substitution of Ca^{2+} by REE^{3+} and Y^{3+} [38].

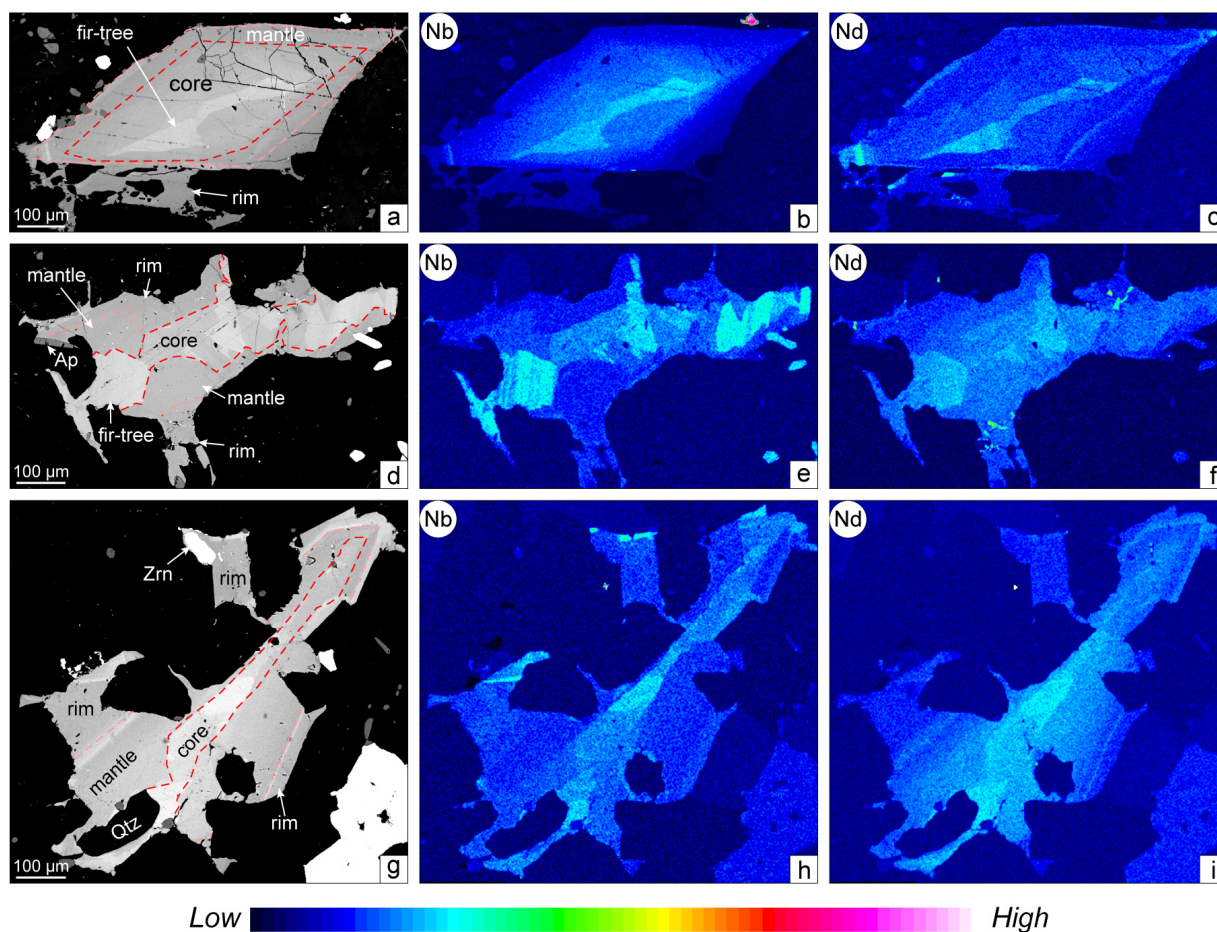


Figure 14. EPMA X-ray elemental intensity maps of Nb and Nd in representative titanite grains from the granodiorite (a–c) and MMEs (d–i) of the Zhongyou pluton.

Titanite core and mantle in the granodiorite have Nb/Ta ratios of 4.1–14.9, comparable to those in Early Cretaceous Guojialing and Fangshan granodiorites and the Sanguliu monzogranite in the North China Craton [19,73,76], but significantly lower than those in metamorphic or hydrothermal titanite [22,23,77]. Their REE patterns show pronounced negative Eu anomalies (Figures 9a and 10e), likely resulting from early plagioclase crystallization, indicating that titanite crystallized later than plagioclase in the granodiorite. Therefore, the titanite core and mantle in the granodiorite are interpreted as magmatic in origin. Similarly, titanite in the MMEs exhibits low Nb/Ta ratios (5.9–14.9), also indicating a magmatic origin. Experimental studies suggest that titanite crystallized from mafic magmas has higher LREE/HREE partition coefficient than that from felsic melts [78]. The cores of titanite in the MMEs have slightly higher LREE/HREE ratios compared to those in the granodiorite (Figure 10f), and their Nd isotopic compositions also suggest derivation from an enriched mantle source (Figure 11) [47], confirming crystallization from mafic magma.

Titanite rims in the MMEs yield $\epsilon\text{Nd}(t)$ values of -5.0 to -5.7 , similar to the core and mantle values in the granodiorite (Figure 11), suggesting crystallization from granitic melt rather than mixed magma. The rims in the MMEs display distinct compositional features compared to cores and mantles of titanite in the MMEs and granodiorite, including higher F, lower Ta, elevated Nb/Ta ratios, and relatively uniform Th/U ratios (Figures 8b and 10a–b). Generally, Nb and F are more incompatible than Ta and tend to concentrate in evolved melts or fluids [35,42,78]. The elevated Nb/Ta ratios in the rim of MMEs titanite may result from the breakdown of biotite and amphibole during late-stage magma evolution, which released more Nb than Ta into the melt [22,23]. In F-rich fluids, Nb solubility

increases [42], explaining the higher Nb content in titanite rims formed from evolved melts. The positive Eu anomaly in the rims likely reflect the release of Eu^{2+} from plagioclase during albitization under low-temperature deuteric fluid conditions [38,77]. Uranium is also a highly incompatible element that becomes enriched in residual fluid or melt phases [78]. Previous studies have shown that Th/U ratios < 1 are characteristic of hydrothermal titanite [21], interpretation that rims crystallized from hydrated, evolved, granitic melts.

The rims of titanite in the granodiorite also show enrichment in F, elevated Nb/Ta and δEu values, and Th/U ratios similar to those in the MMEs rims (Figure 10). Their lower crystallization temperatures and lower REE and HFSE contents are consistent with characteristics typical of metamorphic–hydrothermal titanite. Therefore, we suggest that the rims of titanite in the granodiorite also crystallized from a late-stage magmatic–hydrothermal fluid, which may have infiltrated fractures within titanite cores, partially altering the grains (Figure 4a–c). Similar alteration textures have been reported in titanite from the Roxby Downs granite (Olympic Dam IOCG deposit) and the Sanguliu pluton in Liaodong, China [73,77].

In summary. We propose that the euhedral titanite in the granodiorite crystallized under relatively stable magmatic conditions, whereas the anhedral titanite in the MMEs likely reflects rapid crystallization under undercooled conditions in the hybrid layer, as well as potential growth inhibition in a crystal-rich environment.

7. Conclusions

Titanite grains in the MMEs and host granodiorite of the Lalingzaohuo Zhongyou pluton yield similar U–Pb ages, probably corresponding to the timing of slab breakoff and asthenosphere upwelling in the EKOB. The titanite grains in the MMEs display core-mantle-rim texture which could have resulted from magma mixing near the base of a granitoid magma chamber (zone of magma mush). The cores and mantles crystallized from mixed magmas containing variable proportions of two end-member components within the hybrid layer. The molten, mushy globules generated from the hybrid layer may have ascended and become entrapped by granitic magmas, subsequently solidifying to form the MMEs. The titanite rims crystallized from the hydrated, evolved interstitial granitic melts within the mushy enclaves.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/min15090886/s1>, Table S1: Whole-rock compositions of the MMEs and host granodiorite in the Zhongyou pluton; Table S2: The major oxide contents (wt.%) of the kaersutite and plagioclase standard from SPI Supplies (USA); Table S3: The trace elemental (ppm) compositions of the titanite in the MMEs and host granodiorite of the Zhongyou pluton; Table S4: The Nd isotopic compositions of the titanite in the MMEs and host granodiorite of the Zhongyou pluton.

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