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Petrogenesis of the Early Cretaceous Aolunhua Adakitic Monzogranite Porphyries, Southern Great Xing'an Range, NE China: Implication for Geodynamic Setting of Mo Mineralization

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Abstract: This paper reports on whole-rock major- and trace-elemental and Sr–Nd isotopic compositions of the Aolunhua adakitic monzogranite porphyries from the Xilamulun district in the southern Great Xing'an Range, Northeast (NE) China. The high-K calc-alkaline Aolunhua monzogranite porphyries are characterized by high Sr/Y ratios (34.59–91.02), Sr (362–809 ppm), and low Y contents (7.66–10.5 ppm), respectively. These rocks also show slightly enriched Sr and Nd isotopes ($(^{87}\text{Sr}/^{86}\text{Sr})_i = 0.7051\text{--}0.7058$; $\epsilon_{\text{Nd}}(t) = -2.98\text{--}0.92$), with young two-stage model ages ($T_{2\text{DM}} = 0.84\text{--}1.16$ Ga). Such a signature indicates that these rocks were most likely formed by partial melting of juvenile mafic lower crust. Based on equilibrium melting and batch-melting equations, we performed incompatible trace elements modeling. Low $\text{FeO}^T/(\text{FeO}^T + \text{MgO})$ values indirectly reflect these adakitic rocks were derived from an oxidizing source related to magnesian granitoids. The decreasing content of TiO_2 , Fe_2O_3 , Nb/Ta ratio, and moderately negative Eu anomalies suggest that minimal fractionation of Fe–Ti oxides and plagioclase may have occurred in their evolutionary history. The result shows that the Aolunhua adakitic porphyries and coeval adakitic intrusive rocks in this area had not experienced extensive fractional crystallization and were derived from 20%–40% partial melting of lower continental crust, which was composed of ~25%–40% and 5%–20% garnet-bearing amphibolite, respectively. Integrating with rock assemblages and regional tectonic evolutionary history in this regime, high $(\text{Sm}/\text{Yb})_{\text{SN}}$ (SN—source normalized data, normalized to mafic lower continental crust with $\text{Yb} = 1.5$ ppm and $\text{Sm}/\text{Yb} = 1.87$ for continental adakite) and low Yb_{SN} ratios suggest that these rocks were generated in an extensional environment related to lithospheric delamination without crustal thickening. The collision between North China and Siberian cratons around 160 Ma blocked the westward movement of the lithosphere as a result of the subduction of Pacific plate, which then led to lithospheric delamination induced by asthenospheric upwelling and underplating. Subsequently, partial melting of mafic lower crust caused by mantle upwelling resulted in the Early Cretaceous magmatic activities of adakitic rocks and associated Mo mineralization in the southern Great Xing'an Range.

Keywords: adakites; partial melting; delamination; Mo mineralization; Early Cretaceous; Great Xing'an Range

1. Introduction

Adakites with high Sr/Y ratios (≥ 20), Sr contents (≥ 400 ppm), and low Y (≤ 18 ppm) and Yb (≤ 1.9 ppm) contents were initially proposed to be melts derived from young subducted oceanic crust (≤ 25 Ma) by Defant and Drummond [1] and are usually interpreted to be indicators of convergent margin tectonic setting with slab subduction. Subsequent studies demonstrated that a series of crustal processes related to subduction (e.g., melting of an oceanic slab and thickened lower crust of collision zones) may have occurred since the Neoproterozoic to produce adakitic magmas [2–5]. Thus, adakitic rocks were proposed to refer to as intermediates to felsic igneous rocks ($\text{SiO}_2 \geq 56$ wt. %) with geochemical characteristics similar to those of above-mentioned adakites related with young subducted oceanic crust. Recent studies have found numerous adakitic rocks that were thought to have been generated in subduction zones, rather may have formed by partial melting of basaltic rocks in thickened crust of collision zones [3,4] and even in intraplate settings without crustal thickening [2,5]. To distinguish the model for the generation of adakites, source nature and magmatic evolutionary process should be fully considered. In addition, it has been reported that a large number of Cu–Mo mineralized systems are genetically related to adakitic intrusives [6,7], and that adakites possess similar geochemical signatures to tonalite–trondhjemite–granodiorite (TTG) suites. Thus, adakites have played an important role in our understanding of the growth of continental crust and associated Cu–Mo mineralization [2,8–10].

The Aolunhua pluton with Mo mineralization is an excellent natural laboratory to help elucidate the petrogenesis and geodynamic setting of the Mo mineralization-related adakitic rocks within the Xilamulun metallogenic belt in the southern Great Xing'an Range, Northeast (NE) China. Contemporaneous adakitic plutons with Mo mineralization in this area (e.g., Banlashan, Haisugou, and Yangchang plutons which are listed in the Table 1) are well documented based on petrology, geochemistry, geochronology, and fluid inclusions [11–15]. However, the nature of the source region, magmatic evolutionary history, and geodynamic setting of these adakitic rocks are still debatable. In this contribution, whole-rock major and trace elements and Sr–Nd isotopes for the Aolunhua monzogranite porphyries were analyzed in order to decipher their source characteristics, magmatic evolution, and geodynamic setting. These results, in combination with previously published data, could help us better understand the petrogenesis and geodynamic setting of Early Cretaceous magmatism and associated Mo mineralization in the southern Great Xing'an Range.

Table 1. Summary of zircon U–Pb ages, lithology, and Sr–Nd isotopic compositions for adakitic rocks in the Xilamulun district within the southern Great Xing'an Range, Northeast (NE) China.

Intrusive Name	GPS Positions	Lithology	Age (Ma)	$(^{87}\text{Sr}/^{86}\text{Sr})_i$	$\epsilon_{\text{Nd}}(t)$	Reference
Aolunhua	44°32' N, 120°13' E	granitic porphyries	131.9 ± 0.5	0.7021–0.7074	from −2.9 to 2.5	[13] and this study
Banlashan	44°06' N, 120°02' E	granodiorite porphyry	133.5 ± 1.7	-	-	[16]
Shabutai	44°20' N, 119°01' E	monzogranite	138.4 ± 1.5	0.7051–0.7058	from −2.4 to −3.0	[17]
Haisugou	44°18' N, 119°03' E	granite	137.6 ± 0.9	0.7040–0.7074	from 0.2 to 1.6	[14]
Yangchang	43°32' N, 119°05' E	monzogranite	137.4 ± 2.1	0.7043–0.7056	from −1.5 to −2.0	[15]
Huanggang	43°35' N, 117°29' E	granite	136.7 ± 1.1	0.7021–0.7073	from −0.8 to 0.9	[18]
Xiaodonggou	43°01' N, 117°44' E	porphyric granite	142.0 ± 2.0	0.7050–0.7055	from −2.4 to −2.8	[19]

2. Regional Geological Setting

The Aolunhua intrusion is a small granitic pluton occurring in the Xilamulun metallogenic belt belonging to the southern Great Xing'an Range, which is located in NE China and surrounded by the Mongol–Okhotsk suture to the north and the Solonker–Xilamulun suture to the south (see Figure 1a). The Xilamulun metallogenic belt was formed during the collision of the Great Xing'an Range and the North China Craton during the late Permian and Early Triassic and marked the final closure of the Paleo–Asian ocean [20]. In this district, there are numerous Northeast–Southwest (NE–SW) and Northwest–Southeast (NW–SE) oriented faults including the Chifeng–Kaiyuan, Solonker–Xilamulun, Nengjiang, and Hegenshan–Heihe faults (Figure 1b). The oldest formation in this region is the

Xilinhot massif, which is a Precambrian high-grade metamorphic complex and composed mainly of plagioclase-bearing, biotite-bearing granitic gneiss and mica schist [21,22]. Additionally, Early Paleozoic volcanic and sedimentary rocks consisting variably of schist, sandy slate, marble, and andesite, and Mesozoic (Jurassic–Cretaceous) continental, intermediate-acidic volcanic and sedimentary rocks with weak metamorphism also occur in this region [18]. Voluminous Mesozoic intrusions mainly composed of granite, granodiorite, monzogranite, granite porphyry, and diorite porphyry were emplaced into the sedimentary strata as mentioned above. Previous studies indicate that Cu–Mo mineralization is closely related to the generation of these Cretaceous intrusions (ca. 132–142 Ma), such as the Aolunhua, Banlashan, Haisugou, Shabutai, Yangchang, and Huanggang plutons in the Xilamulun district (see Figure 1b) [13,15,17,23–25].

Figure 1. (a) Tectonic division of the southern Great Xing'an Range, NE China (after Zhao et al. [26]). (b) A simplified geological map of the Xilamulun district in the southern Great Xing'an Range, NE China (after Wu et al. [12]), and (c) simplified geological map of the Aolunhua region (after Ma et al. [13]).

3. Sampling and Analytical Methods

Twelve monzogranite porphyries with slight alteration and Mo mineralization were collected from different parts of the Aolunhua intrusion in the northeastern Xilamulun district (Figure 1c). Monzogranite porphyries were emplaced in the Upper Permian Linxi Formation comprised of metasedimentary rocks (Figure 2a, e.g., slate, siltstone, and sandstone with slight metamorphism) and exhibit porphyritic characteristics (Figure 2b–f). Mineralogically, they are composed of quartz (~29%), K-feldspar (24%–37%, showing slight kaolinite alteration), plagioclase (~40%, generally euhedral and subhedral crystal with polysynthetic twinning), biotite (4%–8%), minor hornblende (~4%), and other accessory minerals (e.g., apatite, titanite, zircon, and titanomagnetite). The phenocryst minerals mainly comprise of plagioclase, biotite, and K-feldspar, which are 1–3 mm in grain size, but aplitic groundmass are less than 20 μm .

Figure 2. Representative photos of field relationships, hand specimen, and photomicrographs of the Aolunhua monzogranite porphyries. (a) Field outcrop of Aolunhua monzogranite porphyries; (b,c): hand specimen with some larger plagioclase, K-feldspar, and biotite crystals and the occurrence of sulfides such as molybdenite, chalcopyrite, and pyrite, which are disseminated in rocks; (d–f) photomicrographs under cross polarized transmitted light, exhibiting obvious porphyritic texture comprising of phenocrysts and groundmass. The phenocryst minerals mainly comprise of slightly altered plagioclase, K-feldspar, and biotite, which are generally greater than 300 μm and show sericitization, kaolinization, and epidotization, respectively. Abbreviations: Kfs—K-feldspar; Qz—quartz; Pl—plagioclase; Bt—biotite; and Ms—muscovite.

3.1. Whole-Rock Major and Trace Elements

Twelve samples were chosen for analysis of major and trace elements and then pulverized to less than 200 mesh. An Axios PW4400 sequential X-ray fluorescence spectrometer (XRF) with Rh-anode tube was used to measure the major element oxides at Australian Laboratory Services (ALS) Chemex (Guangzhou) Co. Ltd., following the detailed analytical methods described in the article

by Liu et al. [27]. All major element oxide concentrations are reported on a volatile-free basis. Trace elements, including rare earth elements (REEs), were fused glassed dissolved in nitric acid, and then were analyzed following nitric acid dissolution and measured by inductively coupled plasma–mass spectrometry (ICP–MS) at the State Key Laboratory of Geological Processes and Mineral Resource (SKLGPMR), China University of Geosciences (Wuhan), Rh was added as an internal standard to 1% HNO₃ following the procedures of Liu et al. [27]. The international standard reference materials (e.g., BCR–2, AGV–1, and BHVO–1) were used to monitor the stability and accuracy of the instrument during analyses. Accuracy and precision of the data are better than 5% for trace elements.

3.2. Sr–Nd Isotopes

Eight samples from Aolunhua monzogranite porphyries were chosen for Sr and Nd isotopic analyses. Firstly, sample powders were dissolved in an acidic mixture of HNO₃ (1 mL), and HF (4 mL) in Teflon bombs on a hotplate at 150 °C for 48 h. The acid was then dried down to incipient dryness and the digestion process was repeated. Solutions were separated by cation and HDEHP–coated columns using conventional cation–exchange techniques. We followed the procedures described by Li et al. [28] to perform sample preparation and chemical separation. Sr–Nd isotopic measurements were performed on a Thermo Triton Thermal Ionization Mass Spectrometer (TIMS) at the State Key Laboratory of Ore Deposit Geochemistry (SKLOG), Institute of Geochemistry, Chinese Academy of Sciences (IGCAS). Mass fractionation corrections for Sr and Nd isotopic ratios are based on $^{86}\text{Sr}/^{88}\text{Sr} = 0.1194$ and $^{146}\text{Nd}/^{144}\text{Nd} = 0.7219$, respectively. The $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of the National Institute of standard and Technology Standard Reference Materials (NIST SRM) 987 (formerly National Bureau of Standards 987) Sr standard was 0.710258 ± 7 (2 σ), and the measured $^{143}\text{Nd}/^{144}\text{Nd}$ ratios of the La Jolla and JNDI–1 Nd standard solutions were 0.511841 ± 3 (2 σ) and 0.512104 ± 5 (2 σ), respectively [29,30].

4. Results

4.1. Major and Trace Element Geochemistry

Data for major and trace elements for 12 granitic porphyry samples are listed in Table 2. Most samples are Mo-bearing monzogranite porphyries with low loss-on-ignition (LOI) values ranging from 0.60 to 2.59 wt. %. The studied samples display high SiO₂ (66.34–72.16 wt. %), Al₂O₃ (12.79–16.13 wt. %), and Fe₂O₃^T (1.46–3.40 wt. %), and low MgO (0.62–1.04 wt. %) and Mg[#] (36.09–48.63). Samples have moderate K₂O (2.38–5.74 wt. %) concentrations and higher K₂O/Na₂O (0.52–1.83) compared with typical slab–derived adakites [31,32]. All Aolunhua monzogranite porphyries plot in the granite and granodiorite fields in (K₂O + Na₂O) vs. SiO₂ (TAS) diagram (see Figure 3a) and mostly fall in the high–K calc–alkaline field in the K₂O–SiO₂ diagram (see Figure 3b). Most samples show weakly peraluminous–metaluminous affinity with A/CNK indexes of 0.89–1.11 in the A/CNK–A/NK diagram (Figure 3c), resembling the Early Cretaceous adakitic rocks (A/CNK indexes = 0.81–1.15) in the Xilamulun district [12–16,25,33]. The Aolunhua monzogranite porphyries have similar chondrite-normalized REE patterns to those of Early Cretaceous adakitic rocks in the Xilamulun district and display slight fractionation between LREE and HREE (La_N/Yb_N = 13.45–23.23) and moderately negative to weakly positive Eu anomalies ($\delta\text{Eu} = 0.65$ –1.17, Figure 4a). They exhibit relative enrichment of large–ion incompatible elements (LILEs; Rb, Ba, and Sr) and depletion in high–field–strength elements (HFSEs; Nb, Ta, and Ti) in the primitive–mantle–normalized trace element spider diagram (e.g., Figure 4b). Notably, the Aolunhua monzogranite porphyries are enriched in Sr (362–809 ppm), are low in Y (7.7–10.5 ppm) and Yb (0.54–0.95 ppm), and have high Sr/Y ratios (34.59–91.02), which are typical characteristics of adakites defined by Defant and Drummond [1] and similar to other adakitic rocks from the Xilamulun district (Figure 5a).

Figure 3. Plots of $(K_2O + Na_2O)$ vs. SiO_2 (a), K_2O vs. SiO_2 (b), and A/CNK–A/NK (c) of adakitic granites in the Xilamulun district. Use LOI-free SiO_2 for all plots in this study. Data sources of adakitic granites are from references [13,15,17,23–25].

Figure 4. Rare earth elements (REEs) and trace element distribution diagrams for Aolunhua monzogranite porphyries and adakitic granites in the Xilamulun district. (a) Plots of chondrite-normalized REE patterns; (b) Primitive mantle-normalized spider diagram. Primitive-mantle and chondrite normalization values are from Sun and McDonough [34] and Boynton [35], respectively. Data sources of adakitic granites are the same as those in Figure 3.

Figure 5. Plots of (a) Sr/Y vs. Y, (b) Nb/Ta vs. Zr/Sm, (c) K₂O/Na₂O vs. CaO/Al₂O₃, and (d) MgO vs. SiO₂ for the Aolunhua monzogranite porphyries and adakitic granites in the Xilamulun district, southern Great Xing'an Range, NE China. (a) Fields of adakites and classical island andesite–dacite–rhyolite (ADR) rocks are modified from Defant and Drummond [1], partial-melting curves are calculated for batch melting of the mafic lower crust (Y = 16.5 ppm and Sr/Y = 21) with melt fractions (white circles) on each of the model curves; (b) Fields of island arc basalts, mid-ocean-ridge basalt (MORB), Trondhjemite–Tonalite–Granodiorite (TTG), and adakites are from Foley et al. [36]; (c) Slab-derived adakites are from Kamei et al. [37]; Kay et al. [38]; Stern and Kilian [39]; Yogodzinski et al. [40], lower crustal-derived adakites are from Guan et al. [41]; (d) Metabasaltic and eclogite melts (1–4.0 GPa) after Rapp et al. [42], subducted oceanic crust-derived adakites after Wang et al. [43], thickened and delaminated lower crust–derived adakites after references [43–45], Low-SiO₂ adakites and high-SiO₂ adakites after Martin et al. [46]. Data sources of adakitic granites are the same as those in Figure 3.

4.2. Sr–Nd Isotope Geochemistry

Data for the eight granitic porphyry samples chosen for Sr and Nd isotopic analyses are listed in Table 3. The initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratios and $\epsilon_{\text{Nd}}(t)$ values were calculated at $t = 132$ Ma, derived from the zircon U–Pb dating result in previous literature [12,13]. In addition, we used the model proposed by DePaolo [46] to calculate the depleted mantle Nd model ages (T_{DM}). The results show that Sr–Nd isotopic compositions of Aolunhua monzogranite porphyries are characterized by relatively homogenous initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of 0.705117 to 0.705793, and $\epsilon_{\text{Nd}}(t)$ values of -2.98 to 0.92 . The calculated values of the corresponding two-stage depleted-mantle Nd model ages ($T_{2\text{DM}}$) are from 0.84 to 1.16 Ga as listed in Table 3.

Table 2. Major and trace element compositions for the Aolunhua monzogranite porphyries in the southern Great Xing'an Range, NE China.

Rock Type	Granitic Porphyry											
Sample No.	ALH-03	ALH-07	ALH-12	ALH-13	ALH-15	ALH-16	ALH-17	ALH-18	ALH-21	ALH-22	ALW-07	ALW-14
Major element oxides (wt. %)												
SiO ₂	66.81	69.20	66.34	72.16	70.00	67.64	68.58	69.24	71.09	67.28	66.84	68.93
Al ₂ O ₃	15.53	13.96	16.13	12.79	14.32	15.92	15.62	15.78	12.85	14.33	15.67	15.93
Fe ₂ O ₃ ^T	2.26	1.51	2.51	1.48	1.71	2.45	2.24	2.16	2.49	1.46	3.40	1.36
CaO	1.85	1.70	2.53	1.75	2.11	2.42	2.27	2.43	2.02	2.62	2.26	2.06
MgO	0.85	0.7	0.95	0.63	0.75	0.87	0.80	0.82	0.71	0.62	1.04	0.65
Na ₂ O	4.97	3.49	4.86	3.26	3.66	4.58	4.49	4.45	4.62	3.13	3.80	4.73
K ₂ O	3.16	4.66	3.03	4.22	4.74	2.98	3.26	3.49	2.38	5.74	3.45	3.34
TiO ₂	0.44	0.34	0.52	0.32	0.40	0.48	0.43	0.44	0.49	0.48	0.55	0.38
MnO	0.05	0.05	0.02	0.04	0.03	0.03	0.03	0.03	0.10	0.03	0.04	0.01
P ₂ O ₅	0.136	0.116	0.162	0.111	0.131	0.160	0.148	0.138	0.177	0.152	0.157	0.122
LOI	2.42	2.3	1.28	1.61	0.52	1.34	0.96	0.82	2.48	2.59	1.21	0.60
Total	98.58	98.12	98.49	98.45	98.48	99.02	98.96	99.93	99.49	98.53	98.56	98.22
K ₂ O + Na ₂ O	8.45	8.51	8.12	7.72	8.57	7.74	7.91	8.01	7.22	9.25	7.45	8.27
K ₂ O/Na ₂ O	0.64	1.34	0.62	1.29	1.30	0.65	0.73	0.78	0.52	1.83	0.91	0.71
A/CNK	1.04	1.01	1.02	0.98	0.96	1.05	1.04	1.02	0.93	0.89	1.11	1.05
A/NK	1.47	1.22	1.58	1.22	1.22	1.62	1.53	1.50	1.44	1.12	1.60	1.50
CaO/Na ₂ O	0.37	0.49	0.52	0.54	0.58	0.53	0.51	0.55	0.44	0.84	0.59	0.44
Mg [#]	42.69	47.87	42.84	45.74	46.48	41.29	41.43	42.92	36.09	45.68	37.73	48.63
σ	2.70	2.48	2.61	1.89	2.58	2.28	2.32	2.39	1.72	3.15	2.16	2.48
Trace Element (ppm)												
Li	21.5	15.5	20.9	13.3	4.83	18.1	15.5	15.7	26.3	19.5	21.4	7.16
Be	3.34	3.40	4.09	3.43	4.11	2.84	3.20	3.31	3.03	4.87	3.90	3.23
Sc	4.24	2.92	4.43	2.13	2.33	3.23	3.26	3.67	4.80	3.54	3.80	2.64
V	36.7	29.4	48.0	29.4	34.3	37.2	33.8	37.1	43.7	56.0	44.6	28.5
Cr	-	-	0.56	13.4	-	-	-	-	0.65	0.73	4.35	-
Co	3.45	2.41	4.56	2.7	2.55	3.83	3.67	3.84	4.01	3.41	3.17	3.54
Ni	0.82	-	0.74	7.24	-	0.12	0.43	0.15	0.46	1.23	1.61	0.94
Cu	92.2	45.3	634	415	19.4	312	23.7	37.3	186	77.1	2.29	157
Zn	47.0	41.7	55.4	101	18.5	67.9	39.3	21.4	201	33.3	52.7	14.8
Ga	20.7	19.2	21.8	16.9	18.9	20.1	20.3	20.4	18.0	21.0	20.1	19.7
Ge	1.00	1.08	1.32	1.37	1.78	1.10	1.20	1.29	1.04	1.76	1.06	1.31

Table 2. Cont.

Rock Type		Granitic Porphyry										
Sample No.	ALH-03	ALH-07	ALH-12	ALH-13	ALH-15	ALH-16	ALH-17	ALH-18	ALH-21	ALH-22	ALW-07	ALW-14
Major element oxides (wt. %)												
As	5.97	6.61	5.75	5.43	4.85	5.09	5.14	4.91	6.71	6.23	7.25	5.16
Rb	104	131	101	111	109	67.4	84.3	105	77.0	145	103	55.6
Sr	509	429	809	436	564	677	656	642	362	519	597	620
Y	9.29	7.66	8.88	7.72	8.72	9.32	9.66	9.29	10.5	9.55	10.4	9.94
Zr	111	91.1	141	74.7	101	120	122	103	138	110	148	105
Nb	6.64	5.42	5.97	5.01	5.69	5.88	6.10	6.04	7.80	5.44	7.37	5.49
Mo	25.1	1343	12.8	3101	1434	1.75	97.1	24.8	4691	456	-	4.37
Ag	1.07	0.64	5.49	5.24	0.18	1.97	0.28	0.25	6.92	1.65	0.41	0.64
Cs	5.40	4.70	4.33	2.52	1.30	2.83	2.17	1.69	3.02	3.37	5.83	0.432
Ba	648	739	1020	609	675	784	721	685	547	589	919	670
La	21.7	15.4	18.3	14.5	17.2	21.3	19.2	17.4	15.1	17.2	24.3	15.0
Ce	39.9	31.7	35.2	29.5	35.1	42.4	37.7	34.8	31.3	37.4	48.5	31.6
Pr	4.54	3.71	3.99	3.50	4.20	4.90	4.51	4.07	3.87	4.51	5.55	3.86
Nd	16.3	13.7	15.3	12.8	15.3	18.1	16.9	15.0	14.7	17.2	20.5	15.3
Sm	2.87	2.51	2.62	2.44	2.80	3.16	2.87	2.68	2.81	2.91	3.69	2.86
Eu	0.682	0.643	0.887	0.565	0.769	0.814	0.795	0.724	0.537	0.864	0.837	0.737
Gd	2.22	2.05	2.04	1.77	2.12	2.48	2.26	2.03	2.24	2.43	2.92	2.23
Tb	0.278	0.246	0.288	0.255	0.294	0.321	0.304	0.281	0.301	0.316	0.364	0.327
Dy	1.32	1.26	1.30	1.21	1.41	1.44	1.48	1.38	1.54	1.53	1.71	1.58
Ho	0.265	0.237	0.280	0.226	0.276	0.292	0.271	0.271	0.326	0.308	0.335	0.306
Er	0.745	0.673	0.769	0.603	0.736	0.763	0.731	0.734	0.820	0.852	0.920	0.826
Tm	0.098	0.096	0.105	0.084	0.106	0.106	0.095	0.097	0.119	0.121	0.121	0.113
Yb	0.670	0.644	0.698	0.540	0.745	0.735	0.694	0.691	0.805	0.797	0.950	0.781
Lu	0.106	0.093	0.107	0.081	0.108	0.108	0.088	0.101	0.110	0.116	0.136	0.109
Hf	2.36	2.16	2.80	1.74	2.48	2.79	2.53	2.33	2.94	2.33	3.52	2.40
Ta	0.411	0.351	0.335	0.319	0.399	0.378	0.369	0.399	0.601	0.325	0.601	0.394
W	4.41	4.07	16.2	97.8	15.8	4.28	9.71	11.8	13.3	297	2.22	5.14
Tl	0.675	0.617	0.476	0.489	0.265	0.335	0.296	0.315	0.512	0.506	0.917	0.172
Pb	8.28	9.91	12.9	206	5.15	8.36	8.01	6.23	226	19.9	9.00	6.62
Th	4.59	3.85	2.99	3.90	3.94	4.24	4.19	4.81	5.78	3.22	8.10	4.23
U	1.62	2.61	1.39	1.44	1.61	1.06	1.78	1.98	1.94	1.62	2.30	1.35

Table 2. Cont.

Rock Type		Granitic Porphyry										
Sample No.	ALH-03	ALH-07	ALH-12	ALH-13	ALH-15	ALH-16	ALH-17	ALH-18	ALH-21	ALH-22	ALW-07	ALW-14
Major element oxides (wt. %)												
ΣREE	91.70	72.96	81.88	68.07	81.16	96.92	87.90	80.26	74.58	86.55	110.83	75.63
LREE	85.99	67.66	76.30	63.31	75.37	90.67	81.98	74.67	68.32	80.08	103.38	69.36
HREE	5.70	5.30	5.58	4.77	5.79	6.24	5.92	5.59	6.26	6.47	7.45	6.27
LREE/HREE	15.07	12.78	13.67	13.28	13.01	14.52	13.84	13.36	10.91	12.38	13.87	11.06
La/Yb	32.39	23.91	26.22	26.85	23.09	28.98	27.67	25.18	18.76	21.58	25.58	19.21
δEu	0.83	0.87	1.17	0.83	0.97	0.89	0.95	0.95	0.65	0.99	0.78	0.89
δCe	0.99	1.03	1.01	1.02	1.01	1.02	0.99	1.01	1.00	1.04	1.02	1.02
Sr/Y	54.73	55.93	91.02	56.40	64.61	72.57	67.84	69.04	34.59	54.28	57.62	62.31
Rb/Sr	0.204	0.306	0.125	0.255	0.193	0.100	0.129	0.164	0.213	0.280	0.173	0.090
Zr/Hf	47.03	42.18	50.36	42.93	40.73	43.01	48.22	44.21	46.94	47.21	42.05	43.75
Nb/Ta	16.14	15.44	17.82	15.71	14.26	15.57	16.54	15.14	12.99	16.73	12.27	13.95
Y/Ho	35.07	32.33	31.73	34.17	31.61	31.93	35.66	34.29	32.07	31.02	30.91	32.49
T _{Zr} (°C)	787	791	855	840	814	814	804	794	784	742	801	779

Mg[#] = 100 molar × MgO/(Mg + FeO^T), assuming Fe₂O₃^T = Fe₂O₃ + 1.111 × FeO; total iron as Fe₂O₃^T; T_{Zr} is calculated according to zircon saturation thermometry [47].

Table 3. Whole-rock Sr–Nd isotopic compositions for the Aolunhua monzogranite porphyries in the southern Great Xing'an Range, NE China.

Sample No.	Rb	Sr	⁸⁷ Rb/ ⁸⁶ Sr	⁸⁷ Sr/ ⁸⁶ Sr	2sigma	(⁸⁷ Sr/ ⁸⁶ Sr) _i	ε _{Sr} (t)	Sm	Nd	¹⁴⁷ Sm/ ¹⁴⁴ Nd	¹⁴³ Nd/ ¹⁴⁴ Nd	2sigma	(¹⁴³ Nd/ ¹⁴⁴ Nd) _i	ε _{Nd} (t)	T _{2DM} (Ma)
ALH-07	131	431	0.879370	0.707139	0.000005	0.705489	16.27	2.51	13.7	0.110758	0.512470	0.000002	0.512374	−1.88	1068
ALH-12	101	811	0.360271	0.705979	0.000004	0.705303	13.62	2.62	15.3	0.103522	0.512492	0.000002	0.512403	−1.33	1019
ALH-17	84.3	658	0.370615	0.705812	0.000004	0.705117	10.98	2.87	16.9	0.102664	0.512491	0.000003	0.512402	−1.33	1019
ALH-20	71.0	469	0.437960	0.706470	0.000004	0.705648	18.53	1.95	11.1	0.106201	0.512440	0.000002	0.512348	−2.39	1107
ALH-21	77.0	364	0.611998	0.706735	0.000005	0.705587	17.65	2.81	14.7	0.115559	0.512418	0.000005	0.512318	−2.98	1160
ALH-22	145	521	0.805196	0.706992	0.000005	0.705481	16.15	2.91	17.2	0.102278	0.512440	0.000003	0.512352	−2.32	1099
ALW-07	103	599	0.497474	0.706726	0.000004	0.705793	20.57	3.69	20.5	0.108820	0.512612	0.000002	0.512518	0.92	839
ALW-14	55.6	622	0.258592	0.706014	0.000007	0.705529	16.83	2.86	15.3	0.113004	0.512442	0.000002	0.512344	−2.46	1117

Chondrite uniform reservoir (CHUR) values used are ⁸⁷Rb/⁸⁶Sr = 0.0847, ⁸⁷Sr/⁸⁶Sr = 0.7045; ¹⁴⁷Sm/¹⁴⁴Nd = 0.1967, ¹⁴³Nd/¹⁴⁴Nd = 0.512638; λ_{Rb} = 1.42 × 10^{−11} year^{−1} [48]; λ_{Sm} = 6.54 × 10^{−11} year^{−1} [49]. (⁸⁷Sr/⁸⁶Sr)_i, (¹⁴³Nd/¹⁴⁴Nd)_i, and ε_{Nd}(t) are calculated considering age as 132 Ma; two-stage model age (T_{2DM}) calculation method is from Jahn et al. [50].

5. Discussion

5.1. Characteristics of the Source Region of Early Cretaceous Adakitic Rocks in the Xilamulun District

Experimental studies suggest that the composition of source rocks plays a crucial role for generating adakitic melts with different geochemical characteristics and that this can occur in <50 km thick crust [51,52]. The Aolunhua monzogranite porphyries show enrichment in Sr (362–809 ppm), depletion in Y (7.66–10.5 ppm) and Yb (0.54–0.95 ppm), with high Sr/Y ratios (34.59–91.02). These geochemical signatures indicate that they are typical of adakitic rocks. This is also supported by the depletion of HFSEs (negative Nb, Ta, and Ti anomalies in primitive mantle-normalized spider diagram, Figure 4b). Furthermore, as both Nb and Ta are immobile elements and are hardly affected by fractional crystallization or hydrothermal overprint in later geological events, intermediate Nb/Ta ratios (Table 2) can be used to trace magma sources [53]. As shown in Figure 4b, the negative Nb and Ti concentration anomalies rule out the origin of normal mid-ocean-ridge basalt (N-MORB) or ocean island basalt (OIB)-type sources in non-subduction zone environments, with associated melts characterized by typically positive Nb and Ti anomalies [54]. The studied samples have low $Mg^\#$ values (36.09–48.63), Ni (<20 ppm), and Cr (<10 ppm) contents, which is inconsistent with melts derived from classical primary mantle [5]. Instead, they mostly exhibit geochemical characteristics of high-K calc-alkaline affinities consistent with melts from partial melting of continental crust (Figure 3b). Normally, potassium concentration in melt is controlled by the presence of K-bearing phases in the residue and the degree of partial melting [55], thus the K_2O contents of adakitic rocks can provide additional information for deciphering their source. Typical adakites derived from oceanic slab have lower K_2O/Na_2O and higher CaO/Al_2O_3 than those of lower crustal-derived adakites because of K-bearing phases in the residue and small degrees of partial melting of eclogitic mid-ocean-ridge basalt (MORB) [39]. The Aolunhua samples exhibit high K_2O/Na_2O (0.62 to 1.83) and low CaO/Al_2O_3 (0.12–0.18) ratios that are distinct from those of melts derived from oceanic slab, but closely resemble lower crustal derived adakitic rocks (Figure 5c). In addition, relatively low MgO contents (0.62–1.04) of the Aolunhua samples are consistent with experimental melts originated from metabasalt and eclogite at 1–4.0 GPa with involvement of mafic magmas derived from lithospheric mantle or melting of thickened lower crust (see Figure 5d) [42,55]. This result is consistent with the occurrence of mafic microgranular enclaves (MMEs) in these granitic porphyries from the Aolunhua district [13], indicating that a crust-mantle interaction process is necessary for the generation of monzogranite porphyries. Moreover, compared to classical adakites derived from young subducted oceanic slab, the samples possess slightly enriched $(^{87}Sr/^{86}Sr)_i$ ratios of 0.7051 to 0.7058 and negative $\epsilon_{Nd}(t)$ values varying from −2.98 to 0.92, with young T_{2DM} values of 0.84 to 1.16 Ga, which are similar to adakitic rocks in this region [11–20,22–26]. Considering these geochemical signatures of adakitic granites in the Xilamulun district, it is suggested that they are not partial melting products of depleted mantle or oceanic slab sources because of the reasons discussed above. Instead, these granitic rocks exhibit geochemical affinity of a dominantly juvenile mafic lower crustal source. Therefore, the geochemical data combined with Sr–Nd isotopic compositions (Figure 6) suggest that Aolunhua monzogranite porphyries and adakitic granites in the Xilamulun district are the results of partial melting of juvenile lower continental crust, with continuous magmatic underplating supplying the heat for melting.

Figure 6. Plots of $\epsilon_{Nd}(t)$ vs. $^{87}Sr/^{86}Sr(t)$ for Aolunhua monzogranite porphyries and adakitic granites in the Xilamulun district, southern Great Xing'an Range, NE China. The rocks have Sr–Nd isotopic compositions distinct from MORB and Precambrian basement, but similar to basaltic andesites derived from lithospheric mantle [56] in the southern Great Xing'an Range. Data sources of adakitic granites are the same as those in Figure 3.

5.2. Evolution of Adakitic Magma

Several processes have been proposed to decipher the genesis of adakitic rocks: (a) the partial melting of the mafic lower crust [2,5], (b) crystal fractionation of basaltic magma at high-pressure [57,58], and (c) crystal fractionation of basaltic magma with mixing processes at low-pressure in both arc or non-arc tectonic environments [59]. In this study, modeling of trace element ratios were carried out to better understand the melting conditions and evolutionary processes of adakitic parental magmas. Due to the low partition coefficients ($\ll 1.0$) of La and Sm [60], the La/Sm ratio is extremely insensitive to partial melting process and then can be used to distinguish fractional crystallization and partial melting processes (Figure 7a). Geochemical results show that partial melting has played a key role in the formation of adakitic rocks in the Xilamulun district. There is no obvious evidence for fractional crystallization, which is also demonstrated by the unfractionated granite fields (OGT) plotted in the diagrams of $(K_2O + Na_2O)/CaO$ vs. $Zr + Nb + Ce + Y$ and FeO^T/MgO vs. $Zr + Nb + Ce + Y$ (Figure 8a,b) and relatively constant range of Zr/Hf ratio (Figure 9a). In addition, Zr/Hf and Nb/Ta ratios are generally constant in igneous rocks without fractional crystallization, because the element pairs are similarly incompatible and have similar partition coefficients. However, the removal of certain accessory minerals such as zircons, Fe–Ti oxides, and titanites would lead to markedly decrease the Zr/Hf and Nb/Ta ratios [61,62]. In this study, the Aolunhua monzogranite porphyries have Zr/Hf (40.73–50.36) and Nb/Ta (12.27–16.54) ratios encompassing the values of lower continental crust (Zr/Hf = 41.25, Nb/Ta = 13.45, according to Wedephol [63]) and are different from the chondritic value (Zr/Hf = 34.3, Nb/Ta = 19.9, according to Münker et al. [64]), indicating that they may be derived from lower continental crust and have not experienced obvious fractional crystallization of accessory minerals. However, the slightly decreasing trend of Nb/Ta ratios exhibited in the Nb/Ta vs. SiO_2 diagram (Figure 9b) may indicate that minor fractional crystallization of Fe–Ti oxides have happened, which is also supported by the decreasing TiO_2 and Fe_2O_3 in the Harker diagram (Figure 10). The moderately negative Eu anomalies ($\delta Eu = 0.65$ – 0.95) for most samples are indicative of plagioclase fractionation, which is also supported by a decreasing CaO in the Harker diagram (Figure 10) and a slightly decreasing trend of Ba contents (Figure 9c). Thus, we suggest that the studied Aolunhua samples and adakitic granites in the Xilamulun district may have experienced minimal fractionation of plagioclase and Fe–Ti oxides. All samples are plotted in the magnesian area in the $FeO^T/(FeO^T + MgO)$

vs. SiO_2 diagram (Figure 9d), indicating that they were probably derived from an oxidizing source, which are often related to magnesian granitoids [65]. The increasing $\text{FeO}^T/(\text{FeO}^T + \text{MgO})$ values with the increase of SiO_2 contents indirectly reflects a trend from strong to weak oxidation, which is also indicative of the fractionation of Fe–Ti oxides in late stage and supported by the occurrence of titanomagnetite in the Aolunhua monzogranite porphyries [13]. This result is consistent with some less fractionated Mo-bearing porphyries derived from adakitic oxidizing magma differentiation, which is a common and crucial process for the Mo–Cu mineralization associated with adakitic rocks [66–68].

Figure 7. Diagrams of La vs. La/Sm (a) and Sm/Yb vs. La/Yb (b) for the Aolunhua monzogranite porphyries and adakitic granites in the Xilamulun district: (a) showing a partial melting trend for adakitic rocks; (b) the modal-batch melting curves are inserted in the Figure 7b. Partition coefficients are from Mckenzie and Onions [69] and Adam and Green [60]. Lower continental crust [70] and average N–MORB [71] were used as representative for amphibolitic lower continental crust (ALCC) and eclogitic oceanic crust (EOC) end-members, respectively. Data sources of adakitic granites are the same as those in Figure 3.

Figure 8. Cont.

Figure 8. Plots of $(K_2O + Na_2O)/CaO$ vs. $Zr + Nb + Ce + Y$ (a), FeO^T/MgO vs. $Zr + Nb + Ce + Y$ (b), $(Sm/Yb)_{SN}$ vs. Yb_{SN} (c), and Ba/Th vs. Nb/La (d) for the Aolunhua monzogranite porphyries and adakitic granites in the Xilamulun district, southern Great Xing'an Range, NE China. (a,b) Samples and adakitic rocks are plotted in the OGTs area in discriminant diagrams after Whalen et al. [72], indicating that these adakitic rocks have not experienced obvious fractional crystallization. Abbreviations: A—A-type granite; I—I-type granite; S—S-type granite; FG—fractionated felsic granite; OGT—unfractionated M-, I-, and S-type granite; (c) SN—source normalized data, normalized to mafic lower continental crust with $Yb = 1.5$ ppm and $Sm/Yb = 1.87$ for continental adakite [52]; (d) Ba/Th vs. Nb/La diagram for partial melting of mafic lower crust [52] showing that most samples cluster around the lower pressure line (1) (<33 km) confirming the generation of adakites by processes associated with continental crust of near normal thickness. Data sources of adakitic granites are the same as those in Figure 3.

Figure 9. Diagrams of Zr/Hf vs. SiO_2 (a), Nb/Ta vs. SiO_2 (b), Ba vs. SiO_2 (c), and $FeO^T/(FeO^T + MgO)$ vs. SiO_2 (d) for the Aolunhua monzogranite porphyries and adakitic granites in the Xilamulun district. (a) A relatively constant range of Zr/Hf ratio for adakitic rocks, probably indicating no intensive fractional crystallization in the evolutionary process; (b) a slightly decreasing Nb/Ta trend for adakitic rocks, indicating a small fractional crystallization of Fe–Ti oxides; (c) a slightly decreasing trend of Ba contents for adakitic rocks, suggesting a small fractional crystallization of plagioclase; and (d) samples are plotted in magnesian area with minimal iron-enrichment, indicating that these adakitic rocks are probably related to relatively oxidizing magmas, Fe^* line is $FeO^T/(FeO^T + MgO) = 0.486 + 0.0046 \times SiO_2$ (wt. %) (after Frost et al. [65]). Data sources of adakitic granites are the same as those in Figure 3.

To elucidate the effect of source inheritance and melting pressure on continental adakitic rocks, a series of partial-melting models were proposed. Equilibrium melting modeling based on incompatible trace elements by using batch-melting model was an important way and employed to test the mechanism for the generation of these adakitic rocks. La/Yb and Sm/Yb ratios are indicative of the presence of garnet and amphibole in the residue and are investigated using the compositions for amphibolitic lower continental crust (ALCC) and eclogitic oceanic crustal (EOC) source compositions [69,70]. We modally calculated melting trajectories for Sm/Yb vs. La/Yb for both sources mentioned above by varying the amount of garnet present (see Figure 7b). The results indicate that Early Cretaceous adakitic rocks in the Xilamulun district are produced by partial melting of amphibolitic lower continental crust. Modal garnet for the Aolunhua was ~25%–40% at 20%–40% degrees of partial melting, whereas garnet for other adakitic rocks was 5%–20% at 20%–40% degrees of partial melting. Our modelling results are consistent with the experimental studies by Qian and Hermann [51], which show that 10%–40% partial melting of hydrous meta-basaltic lower crust at 10–12.5 kbar (33–41 km depth) and 800–950 °C can produce adakitic melts (Figure 5a). In this model, three different melting depths, e.g., ≤33 km, 33–40 km and >45 km correspond to different residual mineral assemblages defined by melting experiments. Therefore, we conclude that adakitic rocks in this area originated from 20% to 40% partial melting of amphibolitic lower continental crust at low pressure, which is also supported by Dai et al. [58] who proposed that adakites with $Sr/Y < 200$ can be generated at different depths in the continental crust in lower pressure environments.

5.3. Geodynamic Setting for Mo Mineralization During Early Cretaceous Period

Adakitic rocks associated with Mo mineralization provide a probe to constrain the geodynamic setting for Mo deposits. As presented in recent studies, adakitic rocks formed from the partial melting of continental crust are widely used as a geodynamic indicator of lithospheric delamination, orogenic collapse, or crustal thickening [10,52]. Crustal thickening is common in a continental collision orogeny caused by object extrusion pressure, where deep-seated adakitic melts (derived from >50 km depth) occur at high pressure. However, this situation is rare in intraplate settings [52]. Generally, lower crust-derived adakitic rocks in orogenic setting have high $(Sm/Yb)_{SN}$ and low Yb_{SN} because of a garnet-rich residue in the source region which decreases the Yb content in melts. In contrast, adakites derived from intraplate lower crust without thickening have lower $(Sm/Yb)_{SN}$ and higher Yb_{SN} [52]. Our samples plot in the fields of intraplate adakites in an $(Sm/Yb)_{SN}$ vs. Yb_{SN} diagram (Figure 8c), indicating that the Aolunhua monzogranite porphyries were not generated in a crustal thickening or orogenic collapse setting, but a common intraplate setting. This is also supported by the Ba/Th vs. Nb/La for modelled melts from partial melting of mafic normal lower crust (depth <33 km, see Figure 8d), not a thickened lower crust. Considering the rock assemblage and evolutionary history in this area, the extensional setting is also supported by the presence of widespread coeval A-type granites, calc-alkaline volcanic rocks formed by decompressional partial melting of lithospheric mantle, metamorphic core complexes, and numerous mafic and felsic dykes [73–75]. This result is also consistent with previous studies suggesting that NE China was in an extensional environment related to lithospheric delamination during the Early Cretaceous [11,20,73,76,77]. Thus, we favor a lithospheric mantle delamination model to interpret the occurrence of Early Cretaceous adakites in the Xilamulun district. These adakitic rocks may be generated in an extensional setting related to lithospheric delamination, as the depicted in Figure 11. The collision between North China and Siberian cratons around 160 Ma blocked the westward movement of the lithosphere which induced the subduction of the Pacific plate and led to lithospheric delamination triggered by asthenospheric upwelling and underplating. Subsequently, the heat from mantle caused partial melting of mafic lower crust, which result in Early Cretaceous magmatic activities of adakitic rocks and associated Mo mineralization in the southern Great Xing'an Range.

Figure 10. Harker diagrams for the Aolunhua monzogranite porphyries and adakitic granites in the Xilamulun district. Data sources of adakitic granites are the same as those in Figure 3.

Figure 11. Inferred geodynamic model for the Early Cretaceous adakitic magmatism and associated Mo mineralization in the southern Great Xing'an Range, NE China. The collision between North China and Siberian cratons around 160 Ma obstructed the westward movement of the lithosphere induced by the subduction of Pacific plate and led to lithospheric delamination triggered by asthenospheric upwelling and underplating. Subsequently, the heat from mantle caused partial melting of mafic lower crust, which resulted in Early Cretaceous magmatic activities of adakites and associated Mo mineralization in the southern Great Xing'an Range.

6. Conclusions

A comprehensive compilation of new and published geochemical data for adakitic rocks in the Xilamulun district reveals the following insights:

- (1) The Aolunhua monzogranite porphyries in the Xilamulun district are characterized by high Sr and Sr/Y, low Y and HREE abundances, without significantly negative Eu anomalies and the depletion of HFSEs (e.g., Nb, Ta, and Ti), typically characteristic of adakites. The characteristics of high $(^{87}\text{Sr}/^{86}\text{Sr})_i$ and negative $\varepsilon_{\text{Nd}}(t)$ with young two-stage Nd model ages ($T_{2\text{DM}} = 0.84\text{--}1.16$ Ga) suggest that they were derived from a dominantly juvenile mafic lower crustal source with minor involvement of mantle-derived mafic magma, which is also evidenced by high $\text{K}_2\text{O}/\text{Na}_2\text{O}$, low $\text{CaO}/\text{Al}_2\text{O}_3$.
- (2) Positive correlation between La and La/Sm suggest that a partial melting process play an important role in the generation of adakitic rocks in the Xilamulun district. Incompatible trace element modeling shows that adakitic rocks in this area originated from 20%–40% partial melting of amphibolitic lower continental crust at low pressure. Low $\text{FeO}^T/(\text{FeO}^T + \text{MgO})$ values indirectly reflect these adakitic rocks were derived from an oxidizing source related to magnesian granitoids. The decreasing content of TiO_2 , Fe_2O_3 , Nb/Ta ratio, and moderately negative Eu anomalies suggest that minimal fractionation of Fe–Ti oxides and plagioclase may have occurred in their evolutionary history.
- (3) Considering the rock assemblages and the evolutionary history in the Xilamulun district, these Early Cretaceous adakites are interpreted to be generated in an extensional setting related to lithospheric delamination.

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