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Neoproterozoic and Paleoproterozoic K-rich granites in the Phan Si Pan Complex, north Vietnam: Constraints on the early crustal evolution of the Yangtze Block

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Abstract

Precambrian igneous and metamorphic rocks of the Phan Si Pan Complex, North Vietnam, constitute the southern extension of the Yangtze Block, and provide a valuable record of the early evolution of the continental crust. We present results of U-Pb zircon geochronology and geochemistry for Precambrian granites in this complex to constrain their emplacement age and genesis. Granites from three plutonic bodies yielded ages of 2848 ± 15 Ma, 2768 ± 19 Ma and 1869 ± 30 Ma, which represent newly-recognized late Archean to

Paleoproterozoic potassic granite plutonism in the southern Yangtze Block. The average $\epsilon_{\text{Hf}(t)}$ values range from -6.2 to 0.1 for the 2.85 – 2.77 Ga granitic rocks and -13.1 to -9.2 for the ca. 1.86 Ga granitic rocks, with two-stage model ages of 3.64 to 3.20 Ga and 3.31 to 3.07 Ga, respectively, suggesting derivation from partial melting of Paleoproterozoic and Mesoproterozoic crust. The late Archean potassic granites exhibit high K_2O , and high Sr/Y and $(\text{La}/\text{Yb})_{\text{N}}$ ratios with negligible Eu anomalies, indicating derivation from melting of the thickened lower crust, which is inferred to have occurred in an active margin setting. The late Paleoproterozoic alkali feldspar granites are characterized by high $\text{FeO}_{\text{T}}/(\text{FeO}_{\text{T}} + \text{MgO})$ (0.96 – 0.99) and $10000 \cdot \text{Ga}/\text{Al}$ (2.75 – 2.94) ratios, showing an affinity of A-type granite. These A-type granites exhibit flat chondrite-normalized HREE patterns and strong negative Eu anomalies, and low Sr/Y and $(\text{La}/\text{Yb})_{\text{N}}$ ratios, corresponding to melting at a shallow depth, probably in a post-collisional extension setting.

Comparison of the rock units and events recorded by the Phan Si Pan complex with other Archean to Paleoproterozoic complexes (Houhe, Dongchuan, Yudongzi, Douling, Zhongxiang and Kongling complexes) in the Yangtze Block indicate spatially distinct histories of crustal growth, and thus may reflect independent terranes. The ca. 1.86 Ga post-collisional magmatism, which succeeds a 2.0 – 1.9 Ga metamorphic event, is distributed throughout the Yangtze Block, including the Phan Si Pan Complex, suggesting assembly of the disparate terranes and final cratonization of the Yangtze Block overlaps with, and may be related to, assembly of the Nuna supercontinent.

Keywords: Zircon U-Pb-Hf isotopes; Geochemistry; Yangtze Block; Neoproterozoic; Paleoproterozoic; Nuna supercontinent

1. Introduction

The Meso- to Neoproterozoic Era (3.2–2.5 Ga) is a crucial period for the formation and stabilization of the Earth's continental crust. During this period, the crust experienced a marked change in composition from sodic tonalitic–trondhjemitic–granodioritic (TTG) assemblages to medium- and high-potassium calc-alkaline granite–granodiorite suites and sanukitoids (Cawood et al., 2013a, 2018a; Chen et al., 2019; Condie and O'Neill, 2010; Farina et al., 2015; Guo et al., 2018a; Laurent et al., 2014, 2018). The specific timing of this change varies from craton to craton (Cawood et al., 2018a; Laurent et al., 2014) and is accompanied by significant changes in geodynamic settings associated with crustal thickening and reworking that contributed to the final stabilization of the cratons (Hartnady and Kirkland, 2019; Laurent et al., 2014; Moyen, 2011; Simon et al., 2018).

Archean potassic granites are characterized by high K_2O/Na_2O , high contents of large ion lithophile elements (LILE) and light rare earth elements (LREE), variable Y contents, and low CaO and Mg# (Laurent et al., 2014; Sylvester, 1994). They are interpreted to have formed by partial melting of preexisting crust, including TTG and meta-sedimentary rocks (Moyen et al., 2003; Laurent et al., 2014; Sylvester, 1994; Kampunzu et al., 2003). Neoproterozoic potassic granites occur in the Yangtze Block, but their petrogenesis and geodynamic implications are not well understood (Chen et al., 2019; Wang et al., 2018b; Wang et al., 2018c; Zhou et al., 2015). Moreover, late Paleoproterozoic granites are widely distributed in the Yangtze Block, yet their origin and tectonic implications are equivocal (Sun et al., 2008; Chen et al., 2016; Guo et al., 2018; Li et al., 2019; Han et al., 2019). In this paper, we present zircon U-Pb ages, zircon Hf isotopes and whole-rock geochemistry of Neoproterozoic and Paleoproterozoic granitic rocks from the Phan Si Pan Complex exposed in northern Vietnam, a southern extension of the Yangtze Block. These new data provide robust constraints on the age and petrogenesis of the granites. In combination with published data from other known Archean–Paleoproterozoic crustal provinces in the Yangtze Block, we

explore the evolving spatial and temporal changes in crustal composition across the block and relate this to an evolutionary history of crust formation and stabilization.

2. Geological setting

The South China Craton is one of three cratons in China (Zhao and Cawood, 2012). It comprises two continental blocks, the Yangtze Block and the Cathaysia Block, which amalgamated along the Jiangnan Belt in the Neoproterozoic (Fig. 1; Cawood et al., 2013b, 2018b; Zhao et al., 2018, 2019a; Zhang et al., 2019; Yao et al., in press). The South China Craton is separated from the North China Craton by the Qinling-Dabie-Sulu orogenic belt and from the Indochina Block by Song-Ma Suture (Fig. 1). In the Yangtze Block, Archean to Early Neoproterozoic crystalline basement is covered by Neoproterozoic-Quaternary sedimentary rocks.

The oldest magmatism preserved in the Yangtze Block is Paleoproterozoic (~3.45 Ga) (Guo et al., 2014). The Yangtze Block, in contrast to the North China Craton which contains abundant Archean to Paleoproterozoic magmatic and sedimentary rocks, is largely covered by Neoproterozoic and Phanerozoic strata with rare exposure of Archean to Paleoproterozoic basement on its northern and southern margins (Fig. 1). Although an increasing number of pre-Neoproterozoic rocks have been reported in the Yangtze Block over the past few years (Guo et al., 2015; Han et al., 2017; Wang et al., 2018a; Xiang et al., 2018; Zheng et al., 2006; Zhang et al., 2019), the nature of the Precambrian crystalline basement to the block and its evolutionary record remain unclear. For example, the isolated and spatially separated nature of the Archean rocks in the block has led to speculation as to whether they represent a single, evolving segment of crust or a series of independent fragments that were subsequently amalgamated (Ling et al., 2001; Wang et al., 2018b; Wang et al., 2018c; Zhao et al., 2019b; G. Zhou et al., 2018).

The study area is in northern Vietnam (Fig. 1 and 2) at the tectonic junction of the South China and Indochina blocks. The Precambrian basement in northern Vietnam contains rocks of similar overall age, geochemical composition, and tectonic setting to those in the northern part of the Yangtze Block (Lan et al., 2000; Nam et al., 2002; X. Zhou et al., 2018). The southern boundary of the Precambrian assemblage in northern Vietnam is marked by the Song Ma suture zone, which formed in the early Mesozoic during amalgamation of South China with Indochina (Findlay and Trinh, 1997; Zhao et al., 2017). The Phan Si Pan Complex is considered the oldest crystalline basement in northern Vietnam, and is represented by ~2.9 Ga TTGs (Lan et al., 2001; Nam et al., 2003), ~2.8–2.7 Ga potassic granites (new data from this study) and Paleoproterozoic granitic rocks (~2.3 Ga, 2.1 Ga and 1.8 Ga). In addition, zircon U-Pb chronological data indicate that the Phan Si Pan Complex was metamorphosed at ~2.36 Ga and 1.97–1.85 Ga (Wang et al., 2016). The Phan Si Pan Complex is intruded by Neoproterozoic igneous rocks (Li et al., 2018), and is unconformably overlain by Paleozoic sedimentary rocks (Fig. 2).

3. Samples and Methods

We collected 21 representative samples from three localities within the Phan Si Pan Complex (Fig. 2), including eight granites (17VNB26), eight quartz monzonites (17VNB10), and five alkali feldspar granites (17VN07) (Fig. 2). The samples are fresh and massive (Fig. 3A–B). Contact relations between these various lithologies are masked by poor exposure. Eight granites (17VNB26-1 to 17VNB26-8) were collected from an outcrop of 5 m², eight quartz monzonites (17VNB10-1 to 17VNB10-8) were collected from an outcrop of 4 m² and five alkali feldspar granites (17VN07-1 to 17VN07-5) were collected from an outcrop of 5 m² (Fig. 2). Different samples from same localities belong to same pluton. The granites (Fig. 3A and D, 17VNB26, 21°34'26"N, 104°47'50"E) are gray to dark gray, fine to medium grained, and consist of alkali feldspar, quartz, plagioclase, minor muscovite and accessory

minerals, such as zircon, apatite, and opaque oxide minerals. The quartz monzonites (Fig. 3B and E, 17VNB10; 22°09'24"N, 104°19'13"E) are yellow or pink, medium to coarse grained, and mainly consist of quartz, alkali feldspar, and plagioclase with minor biotite and amphibole, and the main accessory minerals are zircon, apatite and magnetite. The alkali feldspar granites (Fig. 3F and G, 17VN07; 21°03'44"N, 105°01'15"E) are pink in color, and are composed of quartz and alkali feldspar, with minor plagioclase, and biotite. Accessory minerals include zircon and Fe-Ti oxide.

3.1 Zircon U-Pb dating and Hf isotope analyses

Zircon crystals for U–Pb dating were prepared using standard rock crushing, magnetic separation, and heavy-hydro density techniques. The zircon grains, handpicked under a binocular microscope, were mounted into 2.54 cm epoxy disks and then polished to expose the internal sections of the crystals. Prior to isotopic analysis, the zircon crystals, coated with gold, were photographed by cathodoluminescence (CL) imaging using a Gatan MonoCL 4+ scanning electron microscope to show their internal structures and morphologies.

The zircon U–Pb isotope measurements were performed on an Agilent 7700e Laser Ablation–Inductively Coupled Plasma Mass Spectrometer (ICP-MS) instrument connected to a 193 nm COMPexPro 102 ArF excimer laser and a MicroLas optical system at the Wuhan SampleSolution Analytical Technology Co., Ltd., following the procedure described by (Zong et al., 2017). All data were acquired with a laser ablation spot size of 32 μm . The data quality and trace element calibration were monitored by analyzing external standards: zircon GJ-1, zircon 91500, and glass NIST610. Each analysis was determined in time–resolved mode with 20–30 seconds gas blank followed by 50 s of data signal measurement. The 91500 standard was analyzed twice every 6 unknown analyses. The raw U–Pb isotopic data were reduced offline using ICPMSDataCal (Liu et al., 2008) including integration of background and analytical signals, time-drift correction, and quantitative calibration. Concordia diagrams

and weighted mean calculations were constructed using Isoplot/Ex_ver3 (Ludwig, 2003). All the age data are presented in supplementary Table 1.

In situ zircon Lu–Hf isotopic analyses were conducted on dated zircon grains using a Geolas 2005 excimer ArF laser ablation system linked to Neptune Plus MC-ICP-MS at the State Key Laboratory of Geological Processes and Mineral Resources, China University of Geosciences, Wuhan. Detailed operating conditions, instrumental correction and data processing procedures are described by Hu et al. (2012). Each analysis consisted of 20–30 s of background signal followed by 50 s of ablation signal acquisition on the same domains used to date the zircons. The external standard zircon 91500 was analyzed twice every six analyses. Throughout the analyses, the $^{179}\text{Hf}/^{177}\text{Hf}$ and $^{173}\text{Yb}/^{171}\text{Yb}$ ratios were normalized to 0.7325 and 1.1248, respectively, for corrections of mass bias (Blichert-Toft et al., 1997). The ^{176}Lu decay constant of $1.865 \times 10^{-11}\text{a}^{-1}$ was used for calculation of initial epsilon Hf values and $^{176}\text{Hf}/^{177}\text{Hf}$ ratios (Scherer et al., 2001). The Hf model ages (T_{DM}) based on the depleted mantle model were calculated using $^{176}\text{Lu}/^{177}\text{Hf}$ ratio of 0.015 for mean continental crust (Griffin et al., 2006). The analytical results are presented in supplementary Table 2.

3.2 Whole-rock geochemical analysis

Whole-rock geochemical data, including major, trace-element and Nd isotopes of powdered samples were acquired at the State Key Laboratory of Geological Processes and Mineral Resources, China University of Geosciences, Wuhan. Fresh and unaltered parts of the studied samples were chosen, crushed and powdered into 200 mesh in a WC mill. The sample powders were heated to 900 °C to determine loss on ignition (LOI). Whole-rock major elements were determined using an X-ray fluorescence (XRF) facility with an Axios MAX spectrometer. Specimen preparation for major elements analysis was made by melting 0.5 g of a pulverized sample with 5 g of compound flux ($\text{Li}_2\text{B}_4\text{O}_7:\text{LiBO}_2 = 12:22$) in high-frequency melting furnace followed by casting of homogeneous glassy disc. Trace elements,

including rare earth elements (REE), in all studied samples were measured on an Agilent 7700e ICP-MS, and the sample dissolution is described in detail by Liu et al. (2008). Analytical precision for major elements is better than 5% and for trace elements is better than 10%. Whole-rock major and trace elements results are listed in supplementary Table 3.

For Nd isotopic analysis of whole-rock samples, Nd was separated/concentrated using standard chromatographic columns with AG50W-X8 and HDEHP resins. Details of the analytical procedures are given in Gao et al. (2004). The $^{143}\text{Nd}/^{144}\text{Nd}$ ratios were normalized to $^{146}\text{Nd}/^{144}\text{Nd} = 0.7219$ to correct for mass fractionation. Sr-Nd isotope results are shown in supplementary Table 4.

4. Analytical Results

4.1. Zircon U-Pb geochronology

Zircon grains from sample 17VNB26-1 (granite) display a euhedral-subhedral shape with clear oscillatory growth zones in CL images (Fig. 4). The crystal size varies between 100 and 250 μm with a length/width ratio of 1:2–1:3. The zircon grains have low to moderate Th and U contents varying from 43 ppm to 577 ppm and from 66 ppm to 688 ppm, respectively, with Th/U ratios of 0.27–1.36. Twenty-one analyses define an upper intercept age of 2853 ± 16 Ma (MSWD = 0.81), which is interpreted as the crystallization age of the granite. The 16 most concordant analyses (> 90%) yielded a weighted mean $^{207}\text{Pb}/^{206}\text{Pb}$ date of 2848 ± 15 Ma (MSWD = 0.33; Fig. 5A), consistent with the upper intercept age.

Zircons from sample 17VNB10-1 (quartz monzonite) are colorless, tabular in form, and 60–190 μm in length with length/width ratios of 3:1–1:1. In CL images, the zircon grains show well developed oscillatory-zoning and are lined with thin, luminous overgrowths, indicating a magmatic origin for the zircon, which was overprinted by later metamorphic fluid/melt (Fig. 4). Twenty spots for U–Pb dating and trace element analysis were performed on the zircons from this sample, but the rims were too narrow to be analyzed by laser ablation.

These analyses yielded highly variable concentrations of Th (68–1055 ppm) and U (222–1897 ppm), with high Th/U ratios ranging from 0.39 to 0.68, consistent with a magmatic origin. The 20 zircon analyses define a regression line with an upper intercept age of 2777 ± 15 Ma (Fig. 5B; $n = 20$; MSWD = 1.3), which is taken as the crystallization age of the quartz monzonite magma. The sixteen most concordant data yielded a weighted mean of 2768 ± 19 Ma (Fig. 5A; MSWD = 1.2), consistent with the upper intercept age.

Zircon grains in sample 17VN07-1 (alkali feldspar granite) are short, prismatic and 30–160 μm in size. Most grains are colorless and transparent under transmitted light, with no obvious zoning observed in CL images (Fig. 4). Their Th and U concentrations are 70–199 ppm and 525–2059 ppm, respectively, with Th/U ratios of 0.09–0.17 (Table S1), indicating a magmatic origin. The 13 analyses yield an upper intercept age of 1869 ± 30 Ma (Fig. 5C; $n = 13$; MSWD = 1.7), which is interpreted as the igneous crystallization age of the granite. The eight most concordant data yielded a weighted mean $^{207}\text{Pb}/^{206}\text{Pb}$ age of 1861 ± 46 Ma (Fig. 8C; MSWD = 1.7), consistent with the upper intercept age.

4.2. Zircon Lu–Hf isotopes

Zircon Lu–Hf analyses were performed on the same domains analyzed for U–Pb dating, and the results are given in Table S2 and presented in Figure 6. Twenty-one analyses from sample 17VNB26 yielded $^{176}\text{Hf}/^{177}\text{Hf}$ ratios ranging from 0.280837 to 0.280913. The calculated $\epsilon_{\text{Hf}(t)}$ values vary from -6.2 to -3.6, and their two stage model ages ($T_{\text{DM}2}$) from 3.64 Ga to 3.48 Ga. Seventeen Lu–Hf analyses were carried out on zircon from sample 17VNB10 and yielded initial $^{176}\text{Hf}/^{177}\text{Hf}$ values ranging from 0.280969 to 0.281068. When calculated at 2777 Ma, their $\epsilon_{\text{Hf}(t)}$ values range from -3.9 to 0.1 and $T_{\text{DM}2}$ from 3.45 to 3.20 Ga. Zircons from sample 17VN07 have $^{176}\text{Hf}/^{177}\text{Hf}$ ratios ranging from 0.281253–0.281386, and $\epsilon_{\text{Hf}(t)}$ values from -13.1 to -9.2. The corresponding $T_{\text{DM}2}$ are from 3.31 to 3.07 Ga.

4.3 Whole-rock major and trace elements

The major and trace element, and Nd isotope compositions of the studied samples are listed in Table S3 and S4. The primary igneous mineral phases and textures are preserved despite limited degrees of deformation of the samples. The samples have very low LOI values of 0.58–0.98 wt.%, consistent with our observations that the samples are fresh. This is also supported by the coherent patterns displayed in the trace element diagrams (Fig. 7). Zirconium is considered immobile during low-grade metamorphism, weathering and diagenesis (Polat and Hofmann, 2003). Good correlations between Zr and selected elements and their ratios, including immobile and mobile elements (Al_2O_3 , MgO, CaO, FeOT, $\text{K}_2\text{O}/\text{Na}_2\text{O}$, A/CNK, La, Sr, and Nb) (Fig. S1), indicate that the effect of alteration on the chemical composition of these samples is insignificant.

The 2.85 Ga samples contain 69.9–71.5 wt% SiO_2 , 4.2–4.5 wt% K_2O , and 2.9–3.2 wt% Na_2O with $\text{K}_2\text{O}/\text{Na}_2\text{O}$ ratios of 1.3 to 1.4 (Table S3). They have low $\text{Fe}_2\text{O}_3\text{T}$ (2.9–3.3 wt%) and MgO (0.7–0.8 wt%) with Mg# (where $\text{Mg\#} = \text{Mg} / (\text{Mg} + \text{Fe}) \times 100$) of 35–37. On the An–Ab–Or ternary classification diagram, the 2.85 Ga samples fall in the granite field (Fig. 8A). They belong to high-K calc-alkaline series in the K_2O vs SiO_2 diagram (Fig. 8B), and are strongly peraluminous ($\text{A}/\text{CNK} = 1.11\text{--}1.23$; Fig. 8C and D). They have a low Fe index ($\text{Fe\#} = 0.78\text{--}0.79$, $\text{Fe\#} = \text{FeO}_\text{T}/(\text{FeO}_\text{T} + \text{MgO})$) and belong to the magnesian series (Fig. 8C; Frost et al., 2001). The primitive mantle-normalized trace element patterns (Fig. 7A) of the 2.85 Ga granites display enrichment in LILE, and depletion in high field-strength elements (HFSE), whereas their chondrite-normalized REE patterns (Fig. 7B) show strong fractionations of REEs ($(\text{La}/\text{Yb})_\text{N} = 41 - 92$ and $(\text{Gd}/\text{Yb})_\text{N} = 1.40 - 1.55$), and moderate negative Eu anomalies ($\delta\text{Eu} = 0.68\text{--}0.71$, $\delta\text{Eu} = \text{Eu}/\sqrt{(\text{Sm}*\text{Gd})}$).

The 2.77 Ga samples have lower SiO_2 (64.6–68.8 wt.%) compared with the 2.85 Ga granites. They are characterized by high K_2O (3.5–4.5 wt.%), but low $\text{Na}_2\text{O}/\text{K}_2\text{O}$ (0.6–0.8) and Mg# (35–43). The 2.77 Ga rocks are classified as quartz monzonites (Fig. 8A), and show

high-K calc-alkaline, magnesian, and weakly peraluminous features with A/CNK values of 1.02 to 1.08 (Fig. 8B, C and D). They also have a low Fe index ($Fe\# = 0.74\text{--}0.76$) and belong to the magnesian series (Fig. 8C; Frost et al., 2001). Their primitive mantle-normalized trace element patterns display enrichment in LILE and depletion in HFSE (Fig. 7A), with lower total REE abundance ($\Sigma REE = 212\text{--}369$ ppm) relative to the 2.85 Ga granites (Fig. 7B). The chondrite-normalized REE patterns show that the rocks are moderately depleted in HREE ($(La/Yb)_N = 46\text{--}76$) with weak negative Eu anomalies ($\delta Eu = 0.70\text{--}0.91$).

The 1.86 Ga samples have high SiO_2 contents (72.8–73.6 wt%) and high $K_2O + Na_2O$ contents (7.4–7.9 wt%). On the An–Ab–Or ternary classification diagram, they lie in the granite field (Fig. 8A). They are weakly peraluminous with A/CNK ratios ranging from 1.04 to 1.05 (Fig. 8D), and have low Mg# (2.87–7.44) but high Fe index ($Fe\# = 0.96\text{--}0.99$), similar to ferroan granites (Fig. 8C; Frost et al., 2001). The PM-normalized trace element patterns of the 1.86 Ga granites show enrichment of LILEs (such as Rb, K, Th and U) and HFSEs but depletion of Ba, Nb, Ta and Ti (Fig. 7C). The 1.86 Ga granites are characterized by low total REEs (146–192 ppm), moderately fractionated REE patterns ($(La/Yb)_N = 7.87\text{--}8.92$) with flat heavy REE patterns ($(Gd/Yb)_N = 1.22\text{--}1.33$), and significant negative Eu anomalies ($\delta Eu = 0.54\text{--}0.57$).

4.4 Whole-rock Nd isotopic compositions

Whole rock Nd isotope results are presented in Table S4. The 2.85 Ga granites have $^{143}Nd/^{144}Nd$ ratios ranging from 0.510296 to 0.510300, corresponding to $\epsilon Nd_{(t)}$ values of -2.54 to -1.62 and two-stage model ages (T_{DM2}) of 3422 Ma to 3348 Ma calculated using their crystallization age. The 2.76 Ga granites have $^{143}Nd/^{144}Nd$ ratios of 0.510558 to 0.510571, with calculated $\epsilon Nd_{(t)}$ values of -1.83 to -1.67 and T_{DM2} of 3288 Ma to 3275 Ma. The measured $^{143}Nd/^{144}Nd$ ratios for the 1.86 Ga granites are also relatively consistent ranging

from 0.511165 to 0.511195, corresponding to $\epsilon\text{Nd}_{(t)}$ values from -11.34 to -10.93 at 1.86 Ga. Their T_{DM2} ages are 3294–3262 Ga.

5. Discussion

5.1 Petrogenesis of the Neoproterozoic granitic rocks

The Archean granitic rocks exhibit variable SiO_2 contents (64.6–68.8 wt.% for 2.77 Ga and 69.9–71.1 wt.% for 2.85 Ga). These samples have high K_2O contents, low MgO , $\text{Na}_2\text{O}/\text{K}_2\text{O}$ (2.77 Ga: 0.61–0.88 and 2.85 Ga: 0.68–0.74), and Mg\# (2.77 Ga: 40–43 and 2.85 Ga: 35–37). These geochemical features are significantly different from TTGs but similar to the potassic granitic rocks formed during the later stages in the evolution of Archean cratons around the world (Laurent et al., 2014) (Fig. 8A). The two Neoproterozoic granite suites analyzed in this study are both magnesian, and distinct from A-type granites (Fig. 9; Eby, 1992; Whalen et al., 1987).

Compared with TTG gneisses, which are considered to form by partial melting of mafic lithosphere at high pressures (Martin and Moyen, 2002), Archean potassic granites can form across a range of depths and from variable potential sources (Joshi et al., 2017). Archean K-rich granites can result from partial melting of pre-existing TTG or sedimentary rocks, from low-degree melting of mafic rocks, and from fractional crystallization of mafic-intermediate magmas (Laurent et al., 2014). The lack of contemporaneous mafic rocks in the study area suggests that fractional crystallization did not play an important role during the formation of these potassic rocks. Moreover, fractional crystallization of a mafic source should exhibit a continuous compositional trend from mafic through intermediate to felsic rocks (e.g. Hoffmann et al., 2016), which is not recognized in our samples.

The 2.85 Ga granites are all strongly peraluminous with negative zircon $\epsilon_{\text{Hf}(t)}$ (Fig. 8D and 6). These geochemical features suggest that they may have formed by partial melting of relatively enriched and potassic sources (Moyen et al., 2007). When plotted in the diagram

displaying the partial melting of common crustal sources obtained from experimental melts, the 2.85 Ga granites plot in the fields of greywackes and metasedimentary source (Fig. 10). Moreover, the whole-rock Nd model ages (Table S4) and zircon $Hf_{(t)}$ model ages (Table S2) suggest that the parental magma was most likely derived by partial melting of Paleoproterozoic crust. The 2.77 Ga quartz monzonites are weakly peraluminous, indicative of an affinity to I-type granite. Sisson et al. (2005) showed that low-degree melting of medium-to-high-K basaltic rocks could produce K-rich granites. The 2.77 Ga quartz monzonites plot in the fields of amphibolites and high-K mafic rocks (Fig. 10), indicative of derivation from mafic sources. Thus, late Neoproterozoic high-K granites from northern Vietnam are heterogeneous in composition and were derived from intracrustal recycling.

Fractionated REE patterns along with Sr/Y, $(La/Yb)_N$ and Gd/Yb ratios are pressure-dependent, and can be used as indices of the melting pressure and depth (Martin et al., 2005; Moyen et al., 2009). The studied Archean granites are characterized by fractionated REE patterns with high $(La/Yb)_N$ (41–92 and 46–76 for the 2.85 Ga and 2.77 Ga granites, respectively) and moderately fractionated HREE patterns (Figs. 8; $(Gd/Yb)_N$: 2.85 Ga: 2.5–3.1 and 2.77 Ga: 3.0–3.9) with weakly negative Eu anomalies and high Ba and Sr, similar to average TTGs (Fig. 11). These geochemical features have been related to partial melting of thickened continental crust or of subducted basaltic oceanic slab (Martin et al., 2005; Moyen and Martin, 2012). However, slab-derived melts coming into contact with overlying peridotite mantle will result in increasing Cr, Co and Ni concentrations of the magma, which are not observed in our samples. Thus, the high Ba and Sr concentrations and $(La/Yb)_N$ ratios, but low Y and Yb, together with weak negative Eu anomalies, suggest that genesis involved melting thickened crust and amphibole and/or garnet with minor plagioclase in the residue.

Furthermore, garnet is strongly enriched in HREEs whereas amphibole is strongly enriched in MREEs. The 2.85 Ga granites show flat pattern of HREE, suggesting the

presence both of garnet and amphibole in the residue. Considering trace element data, the 2.77 Ga quartz monzonites have weaker Eu anomalies, lower HREE and higher Sr/Y and $(La/Yb)_N$ than the 2.85 Ga granitic rocks, indicating fractionation related to garnet instead of amphibole in their magma source. Moreover, the late Archean granites in Phan Si Pan Complex have high calculated zircon saturation temperatures (2.77 Ga: 794–827°C and 2.85 Ga: 857–881°C) (Watson and Harrison, 1983). It is therefore inferred that the late Archean potassic granites in the Phan Si Pam Complex were formed by partial melting of enriched but heterogeneous sources at different temperatures in thickened continental crust, similar with other late Archean potassic granitic rocks worldwide (Laurent et al., 2014; Sylvester, 1994).

5.2 Petrogenesis of the late Paleoproterozoic granitic rocks

The 1.86 Ga granites have high SiO_2 , $(K_2O+Na_2O)/CaO$ and Ga/Al (2.75-2.94), but low CaO and MgO. They are enriched in HFSEs (e.g., Zr, Nb and Y), but depleted in Cr, Ni, Eu, Sr and Ba. The high $FeO_T/(FeO_T + MgO)$ ratios are akin to ferroan granites (Frost and Frost, 2011). These geochemical features are comparable with those of A-type granites (Fig. 9; Eby, 1992; Frost and Frost, 2011; Whalen et al., 1987).

A-type granites can form by two mechanisms: partial melting of crustal sources (e.g., tonalite to granodiorite) or fractional crystallization of alkali basaltic magma (Creaser et al., 1991; Patiño Douce, 1997; Turner et al., 1992; Whalen et al., 1987). Contemporaneous mafic rocks have only been recorded in the Kongling Complex of the northern Yangtze Block (Peng et al., 2009). However, the zircon $\epsilon_{Hf(t)}$ values of the 1.86 Ga granites are much lower than the mafic rocks of similar age in the Kongling Complex (Fig. 6). Moreover, the 1.86 Ga granites have high SiO_2 (> 73 wt.%), low Mg#, and negative zircon $\epsilon_{Hf(t)}$ and whole-rock $\epsilon_{Nd(t)}$ values (Fig. 8E), suggesting derivation from partial melting of older crust. The 1.86 Ga granites have strongly negative zircon $\epsilon_{Hf(t)}$ and whole-rock $\epsilon_{Nd(t)}$ values, corresponding to two-stage model ages of 3.31–3.07 Ga, suggesting that they were most likely formed by

partial melting of Archean continental crust. These values fall in the range defined for the evolution of the 2.77 Ga quartz monzonites (Table S4). Moreover, the geochemical characteristics of the 1.86 Ga A-type granites have high K_2O/Na_2O , low CaO and depletion in Eu and Sr, consistent with that of the experimental melts formed by high temperature partial melting of calc-alkaline felsic crustal materials (Eby, 1992; King et al., 1997; Rogers et al., 1993). The 1.86 Ga granites are characterized by slight enrichment in LREE and flat in HREE (Fig. 8D), with strong negative Eu anomalies ($Eu/Eu^* = 0.54-0.57$), as well as high Yb (2.7–2.8) and Y (27–30 ppm) but low Sr/Y and $(La/Yb)_N$ ratios. These geochemical characteristics indicate that they were produced at middle-upper crust where plagioclase is stable in the residual phase, with negligible amphibole/or garnet. The calculated zircon saturation temperature of the 1.86 Ga granites is in good agreement with a high temperature origin (average 870°C; Table S3). Thus, the 1.86 Ga granites were formed by shallow remelting (anatexis) of Archean felsic crustal materials (e.g., the 2.77 Ga quartz monzonite in the Phan Si Pan Complex) at high-temperature.

A-type granites are considered to have formed in back-arc extensional, anorogenic or within plate settings (Eby, 1992; Mesquita et al., 2017; Mukherjee et al., 2018; Nédélec et al., 2016). The 1.86 Ga granites fall in the within-plate field on figure 12. Furthermore, the 1.86 Ga granites postdate the 1.98-1.93 Ga metamorphic event recorded in the Phan Si Pan Complex (Wang et al., 2016), suggesting they were formed in a post-collisional extensional tectonic setting.

5.3 Implications for the early evolution and formation of the Yangtze Block

5.3.1 Comparison with other complexes in the Yangtze Block

The 2.85–2.77 Ga K-rich granites confirm the existence of late Archean magmatic components in the Phan Si Pan complex. On a global-scale, the Archean K-rich granitic rocks were emplaced during a short period (~0.05 Ga on average) but with emplacement ages

varying from craton to craton (Cawood et al., 2018a; Laurent et al., 2014). Such variations occur within the Yangtze Block. Figure 13 shows the time-space distribution of magmatic and metamorphic rocks in the Yangtze Block. The emergence of potassic granites after the end of TTG magmatism is not synchronous across the block, occurring at ca. 2.85 Ga in the Phan Si Pan Complex, 2.8 Ga in the Kongling Complex, 2.67 Ga in the Zhongxiang Complex, 2.65 Ga in the Yudongzi Complex, and 2.5 Ga in the Douling Complex. The diachronous generation of K-rich granites suggests that the timing of initial continental crustal stabilization is different for these Archean complexes, and thus, they might have experienced distinct crustal evolution histories. This interpretation is consistent with the distinct sources and melting conditions of Archean TTGs in the different Archean basement units (Wang et al., 2018b; Wang and Dong et al., in press), and different magmatic and metamorphic records in distinct Archean components of the Yangtze Block (Fig. 13; Zhao et al., 2019b).

The nature of the basement to the Yangtze Block and its early Precambrian evolution remains obscure, due to the limited and sporadic occurrence of the Archean rock record. Figure 14 is a compilation of zircon Hf crustal model ages for Archean to Paleoproterozoic magmatic rocks. The two-stage Hf model age of zircon is considered a good indication of the separation timing of their crustal source from the mantle, that is, the crustal formation age (Hawkesworth et al., 2010). Zircon Hf model age data have been used to reveal the crustal growth history of the Yangtze Block based on records of the individual Archean to Paleoproterozoic complexes in the Yangtze Block. The time of Phan Si Pan crustal growth is more complex, involving pulses of activity at 3.9–3.8 Ga, 3.6 Ga, 3.3 Ga, 3.0–2.9 Ga and 2.6–2.5 Ga. In the Dongchuan area, the main crustal growth episodes are at ~3.0 Ga, 2.7–2.6, ~2.5 Ga, 2.4–2.3 and 1.85–1.75 Ga. In the Houhe Complex, crustal growth occurred at 3.0–2.8 Ga. The Yudongzi Complex is characterized by 3.2–3.1 Ga and 2.9 Ga phases of crustal growth. The Douling Complex is characterized by 3.3–3.1 Ga and 2.9–2.8 Ga crustal growth

episodes. In the Zhongxiang Complex, crustal growth is thought to have occurred at 3.6–3.5 Ga and 3.3–3.1 Ga. The Kongling Complex crustal growth has a wide age range from 4.2 Ga to 2.4 Ga, with major peaks at 3.8 Ga, 3.7–3.6 Ga, 3.4 Ga, 3.3–3.2 Ga and 2.5–2.4 Ga. Thus, different and heterogeneous crustal growth histories in the distinct parts of the Yangtze Block are consistent with it consisting of discrete Archean nuclei.

5.3.2 Formation of the Yangtze Block by amalgamation of micro-blocks during Nuna assembly

The global distribution of Paleoproterozoic (2.1–1.8 Ga) tectonic, magmatic, and metamorphic events mark assembly of the supercontinent Nuna (Gibson et al., 2018; Meert and Santosh, 2017; Rogers and Santosh, 2002; Zhao et al., 2002). In the northern Yangtze Block, the subduction-collisional event is represented by the 2.15–2.08 Ga supra-subduction zone ophiolitic mélange and arc-related magmatic rocks in the Kongling and Houhe complexes (Wu et al., 2012; Han et al., 2017, 2018). In the southern Yangtze Block, metamorphism at 2.03–1.95 Ga and ~1.83 Ga corresponds to the assembly of the supercontinent Nuna, similar to processes happening in NW Laurentia and Siberia, such as the Thelon Orogen, Taltson magmatic zone, the Trans-Hudson Orogen and Akitkan Orogen (Wang et al., 2016). Therefore, the identified 2.0–1.9 Ga orogenic belt in the Yangtze Block has been used to suggest it is an important part of the Nuna supercontinent (Chen et al., 2016; Wang et al., 2016). Alternatively, on the basis of similar age spectra of detrital zircons and similar IOCG deposits, the Yangtze Block was considered to be linked with the North Australian Craton during the latest Paleoproterozoic (Zhou et al., 2014).

Our new data, for the first time, document a 1.86 Ga A-type granite in the northern Vietnam portion of the Yangtze Block and relate it to a post-collisional extensional setting. The A-type granite plutonism, along with 1.97–1.93 Ga metamorphism (Wang et al., 2016)

and 1.85 Ga S-type granite plutonism (Anh et al., 2015) in the Phan Si Pan Complex, are interpreted as recording one or more orogenic pulses in this region between 1.97–1.85 Ga. The occurrence of A-type granite in the Phan Si Pan Complex suggests a tectonic switch from syn-orogenic compression to post-orogenic extension. Moreover, ca. 1.85 Ga detrital zircons are ubiquitous in Paleoproterozoic in the Phan Si Pan Complex as well as in nearby, younger Neoproterozoic sedimentary sequences (Hieu et al., 2012; X. Zhou et al., 2018).

Zhao et al. (2019) suggests that the Phan Si Pan Complex in northern Vietnam experienced an independent early Paleoproterozoic evolutionary history different to that of the northern Yangtze basement. The Yangtze Block is characterized by widespread post-orogenic extension-related magmatism at 1.85–1.78 Ga along with the earlier 2.0–1.9 Ga metamorphic event (Fig.13; Zhou et al., 2017, and references therein).. It is likely that craton-scale orogenesis is related to micro-continent amalgamation, which took place during the late Paleoproterozoic in the Yangtze Block (Wang et al., 2018a). Moreover, the basement of the Yangtze Block is overlain by Neoproterozoic sedimentary sequences and locally intruded by Neoproterozoic igneous plutons, suggesting a unified Yangtze Block by the beginning of the Neoproterozoic. No known Mesoproterozoic to Neoproterozoic collisional orogen has been found in Yangtze Block. Therefore, we speculate that the assembly of the multiple microblocks to form a unified Yangtze Block occurred during regional metamorphism at 2.0–1.93 Ga, which marks the final cratonization of the Yangtze Block and its incorporation into the Nuna supercontinent. This is consistent with results from the Zhongxiang Complex indicating multiple pieces of crust amalgamating in the Paleoproterozoic (Wang et al., 2018a; Wang and Dong, in press). The ca. 1.85 Ga A-type granites and associated regional extension may be related to separation of the Yangtze Block from other components of the supercontinent (e.g., Wang et al., 2016).

6. Conclusion

- (1) New U–Pb–Hf isotope analyses indicate two distinct felsic magmatic events in the Phan Si Pan Complex in northern Vietnam: 2.85–2.77 Ga K-rich granites and ca. 1.86 Ga A-type granites.
- (2) The genesis of late Archean potassic granites likely involved partial melting of mafic rocks and metasedimentary rocks at high temperature in thickened continental crust, whereas the late Paleoproterozoic A-type granites were formed by remelting of the Archean felsic crustal materials at high-temperature and low pressure in a post-collisional extensional tectonic setting.
- (3) The transition from Na-rich TTG to later K-rich granites varies between areas of Archean rocks across the Yangtze Block, suggesting that the block is made up of spatially discrete Archean crustal fragments that were subsequently amalgamated.
- (4) Large scale magmatic and metamorphic activity at ca. 2.0–1.93 Ga, followed by ~ 1.85 Ga post-collisional magmatism, across the Yangtze Block suggests that these multiple Archean basements had amalgamated by this time to form a unified Precambrian basement to the Yangtze Block. The coincidence of these events with those elsewhere in Nuna suggests that the Yangtze Block formed part of this supercontinent cycle.

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Fig. 1 Simplified geological map of the South China Craton, showing the Precambrian outcrops (modified from Cawood et al., 2018b; Zhao et al., 2019). Sources of age data of the Houhe and Kongling complex from Han et al. (2017, 2018) and Wu et al. (2012).

Fig. 2 Geological map of the northern Vietnam region, showing sample locations (modified from Zhao et al., 2019). ASRR = Ailaoshan-Red River. Geochronological data cited are from 1: Wang et al. (2016); 2: Lan et al. (2001); 3: Anh et al. (2015). 4: Zhao et al. (2019).

Fig. 3. Field photographs and photomicrographs of selected granites. (A and D): 17VNB26; (B and E): 17VNB10; (C and F): 17VN07. Bi = biotite; Kfs = K-feldspar; Ms = muscovite; Pl = plagioclase; Qz = quartz.

Fig. 4 CL images of representative zircons for U-Pb ages and Hf isotope analyses. Red solid circles indicate the analysis spots for U-Pb age and yellow dash ellipses demonstrate the analysis spots for Hf isotopes.

Fig. 5 Concordia diagrams of LA-ICPMS zircon U–Pb dating for Phan Si Pan Complex granites (A) 17VNB26, (B) 17VNB10, and (C) 17VN07.

Fig. 6 Plot of zircon $\varepsilon_{\text{Hf}(t)}$ values versus zircon age of magmatic rocks from different complexes in the Yangtze Block. Data are from Zhang et al. (2006), Jiao et al. (2009), Wu et al. (2012), Guo et al. (2014, 2015, 2018), Wang et al. (2015, 2018b, c), Zhou et al. (2015), Chen and Xing (2016) and Han et al. (2018).

Fig. 7 Primitive mantle-normalized trace element patterns and chondrite-normalized REE patterns for the samples from the Phan Si Pan Complex. Normalization values are from Sun and McDonough (1989).

Fig. 8 Geochemical discriminations of the granite samples in (A) Normative An-Ab-Or triangle diagram (O'Connor, 1965); (B) K_2O versus SiO_2 diagram (Middlemost, 1994); (C) $FeO_T/(FeO + MgO)$ versus SiO_2 diagram (Frost et al., 2001); (D) A/NK versus A/CNK diagram (Frost et al. 2001). (E) Mg# versus SiO_2 . Experimental melt compositions are from Rapp et al. (1999) and Smithies (2000).

Fig. 9 Geochemical discrimination diagrams for the granitic rocks in the Phan Si Pan Complex. (A) FeO_T/MgO versus 10,000 Ga/Al; (B) Nb versus 10000 Ga/Al; (C) Y versus 10000 Ga/Al and (D) Zn versus 10000 Ga/Al (after Whalen et al., 1987).

Fig. 10 (A) $CaO + FeO_T + MgO + TiO_2$ (wt.%) versus $CaO/(FeO_T + MgO + TiO_2)$ diagram, showing the source compositions of the studied samples (modified after Patiño Douce, 1999). (B) $3*CaO-Al_2O_3/(FeO_T + MgO)-5*K_2O/Na_2O$ ternary diagrams (Laurent et al., 2014), showing the source compositions of the studied samples.

Fig. 11 $(La/Yb)_N$ versus $(Yb)_N$ discrimination diagrams for the granites from Phan Si Pan complex after Drummond and Defant (1990).

Fig.12. Nb versus Yb discrimination diagram for the granites from Phan Si Pan complex after Pearce et al. (1984). VAG + syn-COLG: volcanic arc granite and syn-collisional granite; ORG: ocean ridge granite; WPG: within-plate granite.

Fig. 13 Time-space plot for Archean to Paleoproterozoic rocks in the Yangtze Block, showing the time of major plutonic, mafic dyke emplacement and metamorphic events. Potassic granite refer to K-rich granites in the Archean, other granite include all kinds of granite after Archean. Data sources are as follows: Phan Si Pan Complex (Nam et al., 2003; Lan et al., 2001; Anh et al., 2015; Zhao et al., 2019) and this study; Dongchuan Area (Chen et al., 2013; Cui et al., 2018; Lu et al., 2019); Houhe Complex (Wu et al., 2012); Yudongzi Complex (Chen et al., 2019; Hui et al., 2017; Zhou et al., 2018); Douling Complex (Hu et al., 2013; Wu et al., 2014); Zhongxiang Complex (Wang et al., 2018b; Z. Wang et al., 2015, 2018; Zhou et al., 2017, 2015; Zhang et al., 2011); Kongling Complex (Wu et al., 2009; Guo et al., 2018, 2015; Han et al., 2018; Jiao et al., 2009; Peng et al., 2009, 2012; Xiong et al., 2009; Yin et al., 2013); and Tongbai, Huangtuling, Dongling areas (Sun et al., 2008; Wu et al., 2008; Xiang et al., 2014). (modified after Wang et al., 2018a).

Fig. 14 Histograms of zircon Hf model ages from different Archean-Paleoproterozoic complex in Yangtze Block. The data sources are same as figure 13. n = number of rock samples. The locations of the regions are same as Fig. 13.

- Late Archean and late Paleoproterozoic magmatism occurs in the Phan Si Pan Complex, North Vietnam, of the Yangtze Block.
- The 2.85-2.76 Ga potassic granites formed during collision-related crustal thickening.
- The ca. 1.86 Ga A-type granite formed within an extensional tectonic setting.
- The spatial changes in crustal compositions in the different Archean complexes of the Yangtze Block suggest they constitute separate terranes.
- Final cratonization of the Yangtze Block likely relates to the assembly of the Nuna supercontinent.