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Petrology and zircon U–Pb dating of meta-calcsilicate from the Jiaobei terrane in the Jiao-Liao-Ji Belt of the North China Craton

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Abstract

The Precambrian basement of the Jiaobei terrane consists of Archean metavolcanic and metasedimentary rocks, tonalitic – trondjemitic – granodioritic gneisses (TTGs), Paleoproterozoic metasedimentary sequences, as well as lenses of metamorphic mafic–ultramafic rocks. Petrological, geochemical and in situ zircon U-Pb studies were conducted on meta-calcsilicates, which occur as irregular blocks within TTG gneisses. Samples were collected at Nanshankou, Jiaobei terrane of Shandong Peninsula at the north-eastern part of the North China Craton (NCC).

Two groups of meta-calcsilicate rocks were distinguished, which originate from a metavolcanic-metasedimentary series. The respective bulk rock composition is a result of different proportions of source rock material involved. One group which is higher in CaO and lower in Na₂O demonstrates a higher contribution material from a sedimentary source, whereas volcanoclastic to pyroclastic precursor dominates in the second group. The meta-calcsilicates are generally composed of Ca-bearing silicates with a peak pressure assemblage of Grt-Cpx-Zo-Am-Qz-Ttn; they experienced epidote amphibolite facies metamorphism constrained by P-T conditions of 580°C / 1.08–1.13 GPa. Late prehnite-, albite-, calcite- and actinolite-bearing veins refer to the subgreenschist conditions at the late exhumation stage.

In situ zircon U-Pb dating of 173 detrital zircons from the meta-calcsilicate rocks yield Archean ages up to 3.04 Ga; a further predominant age population clusters at ca. 2.68 Ga with subordinate clusters at ca. 2.87, 2.78, which are interpreted to represent magmatic ages. A subordinate cluster at 2.51 Ga associated with zircon rim domains reflects a metamorphic event. Further frequently textureless rims of zircon of an age range between ca. 2.5 and –2.1 Ga indicate subsequent metamorphic events. The deposition of the meta-calcsilicate precursors occurred around of shortly after 2.1 Ga on an Archean basement.

Keywords: metamorphism; zircon U–Pb ages; meta-calcsilicate; Jiaobei terrane; Jiao-Liao-Ji Belt; North China craton

1. Introduction

The North China craton (NCC) represents a significant Precambrian core terrane in Asia. Basement rocks of the NCC have been divided into Eastern and Western blocks, separated by the Trans-North China Orogen on the basis of lithologic associations, structures, metamorphism and isotopic ages (Fig.

1) (e.g., Zhao et al., 1998, 2001, 2005; Wan et al., 2006; Zhao and Zhai, 2013). The Western Block is characterized by a NW-trending khondalite-dominated supracrustal belt of early Palaeoproterozoic age and late Archaean tonalitic-trondhjemitic-granodioritic (TTG) gneisses (Fig. 1) (Zhao et al., 2005; Yin et al., 2009; Santosh et al., 2010; X.-P. Li et al., 2011b). The Eastern Block is dominated by TTGs, minor amounts of supracrustal rocks of early to mid-Archaean age, and the NE-trending early Palaeoproterozoic Jiao-Liao-Ji Belt (JLJB), which is characterized by high-pressure (HP) pelitic granulite and mafic granulite (Zhao et al., 2005; Jahn et al., 2008; X.-P. Li et al., 2011a and b, Chen et al., 2018; Zhao & Zhai, 2013). The central Trans-North China orogenic zone consists of late Archaean TTGs, granitoids, metamorphosed ultramafic to felsic volcanic rocks and metasediments, and represents a collision zone that results from amalgamation of the Eastern and Western Blocks (Zhao et al., 2000a and b, 2001; S.W. Liu et al., 2002, 2012; Zhai et al., 2003; Kusky and Li, 2003, Zhao GC et al., 2005). There are different views as to the timing and assembling of the Eastern and Western Blocks which form the central orogen. Some authors concluded that the final collision of the NCC took place at ~2.5 Ga and that the respective rocks underwent a later deformation at ~1.85 Ga (Zhai et al., 2003; Kusky and Li, 2003; Kusky et al., 2007a; Zhai & Santosh, 2011). Other authors suggested that a collision of the two blocks occurred at ~1.85 Ga which resulted in high-pressure granulite facies metamorphism and the formation of the Trans-North China Orogen (Zhao, 2001; Wilde and Zhao, 2005; Kröner et al., 2006; Wan et al., 2006; S. W. Liu et al., 2006; Xia et al. 2006, 2009; Zhao et al., 2010).

The Jiaobei terrane, located in the Shandong Peninsula, is exposed in the Qixia area of the Eastern Block of the NCC as part of the Jiao-Liao-Ji Belt (JLJB) (Fig. 1 and 2a). Its Precambrian basement consists of Archean metavolcanic and metasedimentary rocks, Archean TTG gneisses with lenses of metamorphic and meta-mafic to ultramafic rock inclusions, and Paleoproterozoic metasedimentary sequences (Li et al., 1997; Zhai & Liu, 2003; Jahn et al., 2008; Tam et al., 2011; J. H. Liu et al., 2013, Zhao and Zhai, 2013; P.H. Liu et al., 2013, 2014; F. L. Liu et al., 2014; S.J. Liu et al., 2015; Jiang et al., 2016).

Great progress has been made in the last twenty years to represent the development of the JLJB. Studies involving metamorphic petrology and geochronology in the JLJB are primarily based on HP pelitic and mafic granulites (Bai, 1993; Liu et al., 1998; J.B. Zhou et al., 2008; X. Zhou et al., 2008; P.H. Liu et al., 2013, 2014; Tam et al., 2011; Tam et al., 2012a, b, c). The peak metamorphism was reported to range from 1.95 to 1.85 Ga, whereas medium-pressure – low-pressure granulite to

amphibolite facies retrogression occurred at 1.85–1.82 Ga (Tam et al., 2011; Li et al., 1997; P.H. Liu et al., 2013, 2014; S.J. Liu et al., 2015). The HP mafic granulites also record a clockwise metamorphic P-T path (metamorphic age 1.9–1.82 Ga) with the following stages: prograde - 740–770°C, 9–10 kbar; peak metamorphic conditions – 850–880°C, 14.5–16.5 kbar; retrograde – 780–830°C, 6.5–8.2 kbar and 590–650°C, 6.2–8.2 kbar (P.H. Liu et al., 2013; see also Tam et al., 2011; Li et al., 1997; P.H. Liu et al., 2014; S.J. Liu et al., 2015). Note that the TTG gneisses and HP mafic granulites experienced a polymetamorphic history. Jahn et al. (2008) and J.H. Liu et al. (2013) reported an earlier metamorphic event that took place at 2.487–2.501 Ga and 2.5–2.51 Ga, respectively (TTG gneisses) and recently J.H. Liu et al. (2015) derived a metamorphic age of 2.473 Ga from the HP mafic granulites. Two consistent metamorphic age groups (2.5 Ga and 1.9–1.8 Ga) were also reported from Wu et al. (2014) on supracrustal rocks and granitoid gneisses from the close surrounding (Jiaobei), and a metamorphic age of 2.49–2.48 Ga on an equivalent rock series from the Laodong Peninsula about 500 km to the NE (Wu et al., 2016), which belongs to the same belt. The Archean supracrustal rocks, named the Jiaodong Group, occur sparsely within TTGs (Zhai et al., 2003; Zhao et al., 2005; Jahn et al., 2008; Zhao & Zhai, 2013); they comprise 2.8–2.7 Ga old lithotectonic assemblages and are reported from the Qixia Complex in eastern Shandong within the JLJB (Jahn et al., 2008; J. H. Liu et al., 2013; Wu et al., 2014; Jiang et al., 2016). The exposure of these assemblages is much less volumetric than that of the 2.55–2.5 Ga lithotectonic assemblages, which occupy more than 80% of the Archean basement in the NCC (Zhao and Zhai, 2013). The 2.8–2.7 Ga old supracrustal rocks, however, are well exposed in the vicinity of Nanshankou Village, our research area (Fig. 2a).

In this study, we report results from the metamorphic calcsilicate series, which form rock inclusions within the TTG suite of the Precambrian basement of the Jiaobei terrane. The metamorphic evolution is discussed on the basis of the mineral assemblages and P–T conditions. There was not much attention paid yet on U–Pb isotopic studies of detrital zircon from the meta-calcsilicates in the Jiao-Liao-Ji belt, which however provide direct information on both, their provenances and maximum deposition ages. The meta-calcsilicates originate from a metavolcanic-metasedimentary series, but didn't record the peak pressure stage of metamorphism preserved by the HP mafic granulite, also forming rock intercalations in the TTG gneisses of the Jiao-Liao-Belt. Since the zircons from the meta-calcsilicates are of different origin and contain various domains formed at different stages, their geochronological evaluation is expected to deliver important data which help to understand the early

metamorphic evolution of North China craton.

2. Geology and petrography

2.1 Regional geology

The Jiaobei terrane is located in the Eastern Block of the NCC, bordered by the Bo Sea in the north and by the Tanlu Fault in the west side and the Wulian–Yantai Fault to the southeast, which is located between the Jiaobei terrane and the Sulu HP-UHP orogenic belt (Fig. 2a), extending northeast over the Bo Sea with linkage to the Liaoji terrane. The Precambrian metamorphic basement as an important core of the Jiaobei terrane, is dominated by late Archean TTG gneisses and the Paleoproterozoic Jingshan and Fenzishan Groups, the Neoproterozoic Penglai Group, some lenses and sheets of metamorphic mafic–ultramafic rocks and miscellaneous rock types (Fig. 2a, b). TTG gneisses, exposed in the central and eastern parts of the Jiaobei terrane, contain HP mafic granulite and amphibolite lenses, and are in tectonic contact with minor occurrences of supracrustal rocks.

The TTG and granitic gneisses are widespread in the Jiaobei terrane which extends from northern Qixia to the area south of Laixi–Laiyang. They are extensively deformed, migmatized and widely metamorphosed to granulite facies. The respective melts nowadays represented by the Jiaobei TTG and granitic gneisses were intruded around ~2.9 Ga, 2.75–2.7 Ga, 2.55–2.50 Ga, and record two high-grade metamorphic events at ~2.5 Ga and ~1.86 Ga, respectively (Tang et al., 2007; Jahn et al., 2008; J.B. Zhou et al., 2008; X. Zhou et al., 2008; Wan et al., 2011a, b; J.H. Liu et al., 2011, P.H. Liu et al., 2013). The Paleoproterozoic khondalite series in the Jiaobei terrane is composed of the Jingshan and Fenzishan Groups, which unconformably overlie the Archean banded orthogneiss. The lithological types of the Jinshan Group are mainly Sil–Grt–Bt schist to gneiss and quartzo–feldspathic gneiss, intercalated with amphibolite, mafic granulite and marble. Metamorphic studies have shown that these pelitic granulites in the Jinshan Group reached peak P–T conditions of 1.25–1.66 GPa and 830–890°C, and record magmatic zircon U–Pb ages from 2.9 to 2.1 Ga, and metamorphic ages of 1.95–1.80 Ma (Wan et al., 2006; X. Zhou et al., 2008; Tam et al., 2011 and 2012a, b, c; P.H. Liu et al., 2013; Zou et al., 2017). The Fenzishan Group comprises pelitic schists, marble, calcsilicate marble and minor metabasites, which record upper greenschist to lower amphibolite-facies metamorphism (X. Zhou et al., 2008; Wang et al., 2010; Tam et al., 2011). Detrital zircons of the the Fenzishan Group have similar geochronological characteristics such as those of the Jinshan Group in that they have silimilar

magmatic intrusion ages and metamorphic ages (Wan et al., 2006; Tam et al., 2011). Locally rocks of the Neoproterozoic Penglai Group, which is mainly composed of meta-limestone, slates, and quartzites, unconformably overlies the Paleoproterozoic Fenzishan and Jinshan groups. In situ U–Pb ages obtained from detrital zircons of the Penglai Group range from 1700 to 1100 Ma, probably indicating Late Mesoproterozoic deposition (X.H. Li et al., 2007; Chu et al., 2011).

Previous studies have mainly focused on outcrops of HP mafic granulites within the Jiaobei terrane, which mostly occur as rock inclusions and lenses within TTG and granite gneisses (P. H. Liu et al., 2013, 2014; Tam et al., 2012c; Li et al., 1997; X.-P. Li et al., 2013; S.J. Liu et al., 2015; Chen et al., 2018). U–Pb zircon geochronological studies indicate that the protoliths of the HP mafic granulites were formed in the Neoproterozoic (2.9–2.5 Ga) and metamorphosed in the Paleoproterozoic at ~1.95–1.90 Ga and ~1.86–1.80 Ga (Li et al., 1997; Tang et al., 2007; Jahn et al., 2008; Tam et al., 2011; P.H. Liu et al., 2013, 2014; F.L. Liu et al., 2014; This study). The meta-calcsilicates of this study were collected in the Nanshankou village close to the Maliangzhuang town, in the northern part of Laixi District, Shandong Province (Fig. 2); our key focus is on petrology and U–Pb zircon dating (Table 1). Mineral abbreviations used are after Whitney & Evans (2010).

2.2 Petrography of meta-calcsilicates

Meta-calcsilicate samples were collected both sides of the county road of the village Nanshankou (Fig. 2 b). They occur as blocks up to $0.5 \times 0.5 \times 1.5 \text{ m}^3$ which are scattered within late Archean TTG gneisses of the Jiaobei terrane (Fig. 3a–d) and have heterogeneous massive to taxitic structures. At thin section scale, all meta-calcsilicate rocks have a fine-grained crystalloblastic texture, generally composed of Ca- and water-bearing silicates such as calcareous garnet, diopside, amphibole, epidote, prehnite, and occasionally muscovite and chlorite (Fig. 4). Garnet occurs in equilibrium with clinopyroxene, amphibole, epidote and clinozoisite. The meta-calcsilicates are cross-cut by late prehnite-, clinozoisite- and calcite veins (Fig. 4a, c).

On the basis of their heterogeneous bulk composition and variable mineral assemblages, meta-calcsilicates basically can be divided into two groups: group I: Grt + Cpx + Amp + Prh + Ab + Cal + Ttn $\pm$ Chl, and group II: Grt + Cpx + Ep + Ab + Cal + Ttn (Fig. 4e–f). Grain sizes of the minerals are generally small and mostly < 0.5 mm (Fig. 4a–d).

Group I meta-calcsilicates (09LY14, 12LX15, 12LX16, 12LX18) typically contain amphibole but are scarce in epidote group minerals. They consist of 20–30 modal% garnet, 10–20% diopside, 10–20%

calcite, 5–15% prehnite, 5–15% amphibole, and less than 10% each of chlorite, albite, epidote, and quartz, respectively.

Group II meta-calcsilicates (09LY11, 09LY12, 09LY13, 09LY22, 10LX07, 12LX17) have appreciable amounts of epidote group minerals (20–30%) with 5–15 garnet, 15–30% diopside, 20–30% calcite, 5–10% prehnite; the amounts of albite and quartz are less than 10%. Grt and Ep form intergrowth textures (Fig. 4e). Occasionally diopside is surrounded by small rims of prehnite.

Discordant actinolite-, prehnite- and calcite-bearing veins cut both groups of meta-calcsilicates (Fig. 3a, Fig. 4c–d). Accessory minerals are titanite, apatite and ilmenite in the all rocks.

3. Analytical methods

Electron microprobe analyses were performed using JXA-8800R at Peking University, operated at an acceleration voltage of 15 kV with a beam current of 20 nA; and a CAMECA SX100 electron microprobe (EMP) at the Ruhr-University Bochum, Germany, operated at an accelerating voltage of 15 kV with a beam current of 20 nA and focussed beam. The natural minerals jadeite (Si), forsterite (Mg), hematite (Fe), albite (Na, Al), diopside (Ca), rutile (Ti), rhodonite (Mn) and sanidine (K) served as analytical standards.

Bulk-rock geochemical analyses were made using a Philips PW1400 X-ray fluorescence spectrometer at Ruhr-University Bochum, Germany. Total iron was determined as $\text{Fe}_2\text{O}_{3(\text{t})}$ wt%. FeO was analyzed by potentiometry (Ungethüm, 1965); Fe_2O_3 was then calculated by difference ($\text{Fe}_2\text{O}_{3(\text{t})} - \text{FeO} \times 1.1113$). Water content was determined using Coulomb Karl-Fischer titration method (Johannes and Schreyer, 1981); the analysis of CO_2 was performed by heating in an O_2 atmosphere at 1100 °C, using Coulomb determination and titration methods.

Zircon grains from the meta-calcsilicate samples were collected using magnetic separator and heavy liquid techniques; they were subsequently purified by hand-picking under a binocular microscope. Zircon grains were mounted in epoxy discs that were polished and gold coated. Cathodoluminescence (CL) images of zircon grains were obtained using a Chroma Cathodoluminescence emitter on a HITACHI S-3000N scanning electron microscope at the Beijing SHRIMP Centre, Chinese Academy of Geological Sciences, Beijing, China. Zircon U–Pb dating and in situ trace element analyses were carried out at the State Key Laboratory of Continental Dynamics, Northwest University, Xi'an, China. Zircon U–Th–Pb measurements were made on 30 μm diameter

regions of single grains using an ICP-MS (Agilent 7500a) and an excimer laser-ablation system (193 nm, Geolas 200 M, Lambda Physic); trace element and U–Th–Pb isotopic data were acquired simultaneously using the same spot. The analytical procedure is similar to that reported by Yuan et al. (2007). Isotopic ratios and trace element concentration of zircons were calculated using GLITTER 4.4.1 and calibrated using ^{29}Si as an internal normalizing isotope and NIST612 as an external standard reference material. Concordia ages and diagrams were obtained using software Isoplot 3 (Ludwig 2003). Isotopic ratios and single ages reported are with 1σ errors, whereas mean ages are at a 95% confidence level. A common lead correction was applied using LA-ICP-MS Common Lead Correction (ver. 3.15) following the method of Anderson (2002).

4. Mineral chemistry

Garnet composition is variable in the different samples, but dominated by grossular component. Because of this heterogeneity, and since garnet represents a major constituent of the rocks, the bulk composition of meta-calcsilicate should be also variable. Garnet composition varies from $\text{Grs}_{41.13}\text{Alm}_{41.48}\text{Prp}_{7.73}\text{Spe}_{8.09}\text{Adr}_{0.25}$ to $\text{Grs}_{54.36}\text{Alm}_{27.53}\text{Prp}_{6.41}\text{Spe}_{8.35}\text{Adr}_{2.09}$ for group I calcsilicates and from $\text{Grs}_{54.55}\text{Alm}_{31.29}\text{Prp}_{7.62}\text{Spe}_{4.60}\text{Adr}_{1.02}$ to $\text{Grs}_{83.83}\text{Alm}_{5.95}\text{Prp}_{0.49}\text{Spe}_{2.22}\text{Adr}_{7.18}$ for group II (Table 2(1)). Note that garnet occurs as grains of variable composition, single grains however are generally unzoned. *Clinopyroxene* is diopside-dominant and homogeneous in composition in both rock groups. Group I clinopyroxene is relatively low in SiO_2 (50.52–51.67 wt%) and high in Al_2O_3 (0.87–2.20 wt%), Na_2O (0.21–0.37 wt%), and TiO_2 (0.11–1.15 wt.%) whereas group II clinopyroxenes are slightly higher in SiO_2 (51.82–53.19 wt%) and low in Al_2O_3 (0.85–1.06 wt%), Na_2O (0.11–0.20 wt%) and TiO_2 (0–0.11 wt.%) (Table 2(2)). $\text{Mg}^\#$'s are similar and vary between 0.61 and 0.69).

Amphiboles in group I meta-calcsilicates are pargasite and actinolite, representing two metamorphic species with a range of $\text{Mg}^\#$ between 0.61 and 0.76, while those in group II meta-calcsilicates are mostly ferroactinolite with $\text{Mg}^\#$'s between 0.42 and 0.52 (Table 2(3)).

Epidote group minerals are epidote with Ps ~16.43–19.72 (group II meta-calcsilicates; Table 2(4)).

Plagioclase is end-member albite (Ab ~0.99–1.0, Table 2(4)).

Chlorite is generally fine grained, and has relatively Fe-rich compositions with $X_{\text{Mg}} = \text{Mg}/(\text{Fe}^{2+} + \text{Mg})$ between 0.39 and 0.43.

White mica is phengite with an average of about 3.15 atoms Si p.f.u.

Other minerals are prehnite, titanite, calcite and quartz; average compositions are listed in table 2(4).

5. Bulk rock compositions

Bulk rock compositions of the meta-calcsilicates are variable (Table 3), which is to be expected due to the heterogeneous massive to taxitic structures of the different samples and the different proportions of respective sedimentary and volcanic source material they are consisting of. On the basis of proportions of silicate and carbonate, the meta-calcsilicates can be divided into two major groups, group I and group II (Table 3). All rocks higher in SiO_2 have higher Na_2O than K_2O (group I), indicating that the protoliths of the meta-calcsilicates originate from an igneous source. The group I rocks, close to mafic volcanic compositions, are characterized by SiO_2 ~47.94–49.78 wt.%, relatively low amounts of CaO (14.08–18.56 wt.%) and CO_2 (0.40–0.90 wt.%), and relatively high amounts of Al_2O_3 (8.20–13.06 wt.%), TiO_2 (0.47–0.85 wt.%), Na_2O (1.32–2.97 wt.%) and K_2O (0.50–0.81 wt.%). The group II rocks are close to a calcareous-siliceous sedimentary composition with SiO_2 ~42.28–48.33 wt.%, higher CaO (20.54–25.60 wt.%) and CO_2 (1.20–4.41 wt.%), but lower Al_2O_3 (5.77–9.25 wt.%), TiO_2 (0.15–0.45 wt.%), Na_2O (0.26–0.96 wt.%) and K_2O (0.13–0.57 wt.%). Other chemical constituents similar in both groups are Fe_2O_3 (8.21–11.52 wt.%), MgO (5.17–8.88 wt.%) and P_2O_5 (0.03–0.06 wt.%).

In a plot of A-CN-K (Al_2O_3 -($\text{CaO}+\text{Na}_2\text{O}$)- K_2O) the compositions of meta-calcsilicates reach from igneous areas towards calcareous sedimentary areas (Fig. 5a). This trend is also documented using a Si *versus* [(al+fm)-(ca+alk)] diagram (Fig. 5b).

6. P–T pseudosection modeling

The mineral assemblages and bulk composition described above can be used to elucidate the P–T conditions at which the meta-calcsilicates have been stable during its metamorphic evolution. P–T pseudosection modeling is employed to construct the respective stable mineral assemblages at a certain P–T condition with a given bulk-rock composition. Here the system NCFMASHCO (Na_2O – CaO – FeO – MgO – Al_2O_3 – SiO_2 – H_2O – CO_2) is chosen for the pseudosection modeling. Three samples are used for group I (12LX16, 12LX18) and group II (09LY12) meta-calcsilicates; respective mineral assemblages and textures of three samples are displayed in Fig. 4. The pseudosection diagrams

were computed using the Domino/Theriak software of de Capitani and Brown (1987). The thermodynamic data from Berman (1988), and thermodynamics of garnet solutions follow the solution model of Berman (1990). The bulk chemical compositions from the XRF analysis are listed in Table 3. For the modeling, they have been recalculated on a basis of wt.% oxide to 100%.

The P-T pseudosections calculated for samples 12LX16, 12LX18 and 09LY12 are presented in Fig. 6 and their electron microprobe data of the rock forming minerals are given in Table 2. The mineral assemblage of the samples is Grt + Cpx + Prg + Act $\pm$ Ep + Prh $\pm$ Chl + Ab + Cal + Ttn (Table 1), and the P-T stability for each sample falls in the shaded green areas of Fig. 6a, b and c, respectively. When subjected to cathodoluminescence (CL) imaging, the carbonates show faint yellow to yellow colors (Fig. 4c) which is typical for calcite, whereas aragonite typically is greenish (Schertl et al., 2013, 2015). The reaction line of calcite = aragonite (arg in), is used to constrain the upper boundary of the stable HP mineral assemblage (Fig. 6), it should however be noted that aragonite rarely survives retrogression and typically converts to calcite during exhumation. The PT-range of Fig. 6a, b and c marked in green is constrained to the high-temperature side by calcite = aragonite and low-temperature side by the by reactions involving orthopyroxene, which are not observed in the rocks. The contours of Xgrs in garnet in the shaded area of the pseudosection also fit the relevant garnet composition between Grs_{41.13} and Grs_{47.71}, Grs_{43.48} and Grs_{54.36} and Grs_{54.55} and Grs_{75.9} in all three samples (Table 2(1) and Fig. 6). The corresponding P-T conditions constrained by these three samples is < 580°C / 1.12 GPa for 12LX16, <580°C / 1.08 GPa for 12LX18 and < 580°C / 1.13 GPa for 09LY10. Since no compositional zoning of the minerals in the rock was observed, a detailed metamorphic P-T path of meta-calcsilicates is difficult to define. Calcite and prehnite veins, however, indicate a late retrograde event (Fig. 4a, c, d and f). The retrogressive reaction rim of prehnite around clinopyroxene in sample 09LY12 is indicative for the retrograde P-T evolution (Fig. 4f). The presence of late-calcite and prehnite veins is consistent with the increase of the grossular end-member in the garnet compositions towards lower temperatures (Fig. 6a, b and c).

It is clear that the higher the CaO content of the rock (Table 2(4)), the higher the Grs endmember composition of garnet is. Investigated meta-calcsilicates of all three samples document that metamorphic PT conditions reach 580°C / 1.08–1.13 GPa (epidote amphibolite facies conditions); the retrograde P-T path is documented by the occurrence of prehnite.

7. U–Pb dating and corresponding REE characteristics of zircons

Zircon U–Pb age and isotope data from the meta-calcsilicates are listed in Table S1. A total of 173 analyses on samples 09LY12, 12LX15, 12LX16 and 12LX18 were conducted. Relative probability plots of zircon ^{207}U – ^{206}Pb ages and concordant diagrams from these four meta-calcsilicate samples show broadly similar age patterns and the zircons were all formed before the middle Mesoproterozoic (>1600 Ma).

CL images show that zircon grains are stubby, generally about 100 μm in diameter and mostly display dark oscillatory zoning; some zircons are overgrown by highly luminescent, structureless recrystallized rims (Fig. 7), indicating cores of igneous and rims of metamorphic origins. A few zircons are almost completely replaced (e.g., Fig. 7 09LY12-41, 12LX15-43) by highly luminescent, structureless recrystallized domains but contain relict oscillatory zoned cores, which are typical for magmatic zircons (e.g., Hoskin and Schaltegger, 2003; Tang et al., 2007; J.H. Liu et al., 2013; S.J. Liu et al., 2015). The metamorphic recrystallization however often did not erase their igneous age characteristics. Most of the bright rims are too small to be analyzed, and the majority of analyses were made on dark cores. The few dated overgrowth rims on magmatic cores indicate metamorphic ages (i.e., Fig. 7 12LX18-12r). The majority of the magmatic cores with $\text{Th}/\text{U} > 0.30$, indicate an igneous origin (Hoskin and Schaltegger, 2003). Typical metamorphic domains have Th/U ratios mostly between -0.1 and -0.3 (Table 5).

Since most zircon U–Pb analyses are discordant in this study, and there is no strong overprint at a younger metamorphic age for each group, the probability density plots of $^{207}\text{Pb}/^{206}\text{Pb}$ ages are discussed for each sample and later on for whole analytical data. The $^{207}\text{Pb}/^{206}\text{Pb}$ age is like plotting a Discordia from 0 Ma through the discordant analysis onto Concordia. Plotting $^{207}\text{Pb}/^{206}\text{Pb}$ ages on a probability density diagram would show where there are peaks of the same age, which is equivalent to plotting a Discordia through data, as long as there is no strong overprint at a younger metamorphic age (i.e. Mondal et al., 2002).

Forty-nine analyses from 48 detrital zircon grains of meta-calcsilicate from sample 09LY12 were performed, of which 85.7% are discordant. The ^{207}U – ^{206}Pb zircon ages range from 2970 ± 23 Ma to 2029 ± 29 Ma (Table S1, Fig. 8). A large population (79.6%) that falls between 2979 Ma and 2564 Ma defines five probability density peaks of ^{207}U – ^{206}Pb ages at 2975, 2876, 2777, 2719 and 2685 Ma. Paleoproterozoic zircons (19.4%) have ages from 2470 ± 25 Ma to 2029 ± 29 Ma defining three

population peaks at 2435, 2182 and 2051 Ma, respectively.

Fifty analyses of 47 detrital zircon grains from sample 12LX15 were analyzed, of which 79.6% are discordant. Their ^{207}U - ^{206}Pb ages range from 2867 ± 24 Ma to 2210 ± 26 Ma. The predominant Neoarchean 2867–2519 Ma zircon population (64%) has three probability density peaks at 2818, 2675 and 2551 Ma, respectively (Fig. 8). The Paleoproterozoic ages (46%) has two peaks at 2462 and 2276 Ma.

Forty-nine analyses on 48 zircon grains from sample 12LX16 were performed, of which 89.8% are discordant. The ^{207}U - ^{206}Pb zircon ages of this sample range from 2971 ± 34 Ma to 1875 ± 26 Ma (Table S1, Fig. 8). A large Neoarchean population (76%) that falls between 2971 and 2525 Ma has two probability density peaks at 2793 and 2684. Paleoproterozoic zircon domains (26%) of ages from 2414 to 1875 Ma have three minor population peaks at 2343, 2204 and 2105 Ma.

For sample 12LX18, 25 analyses in 23 zircon grains were made; 84% of the ^{207}U - ^{206}Pb zircon ages are discordant. The entire zircon population includes grains and domains of Archean (84%) and Paleoproterozoic (16%) ages (Fig. 8). Archean grains are mostly 2500–2887 Ma old defining peaks at 2877, 2690, 2632 and 2500 Ma. The 2493–2081 Ma zircon population forms one minor peak around 2081 Ma.

The U-Pb ages of the zircons from the meta-calcsilicates generally can be divided into two groups, which are of Archean and of Paleoproterozoic ages. The majority of the Archean zircons (> 2500 Ma) have chondrite-normalized rare earth element (REE) patterns interpreted as magmatic in origin. Some zircons are overprinted by a metamorphic event, but the magmatic “memory” is still not completely erased (Table S2 and Fig. 9a, see also discussion below). The majority of the zircon REE patterns show weak negative Eu anomalies and moderate positive Ce anomalies which point to a magmatic origin, except those which refer to metamorphic domains. Such examples which indicate a metamorphic overprint are analyses No. 19 and No. 45 in sample 09LY12, No. 3 and No. 39r in sample 12LX15, No. 22, No. 32 and No. 46 in sample 12LX16, and No. 12r, No. 14 and No.15 in the sample 12LY18 (Fig. 9, see also discussion below). Further numbers indicating metamorphic overgrowth are not listed for simplicity. Most of zircons of this Archean age group (> 2500 Ma) have typical steep chondrite-normalized REE patterns, indicating magmatic origin (McDonough & Sun 1995). Metamorphic zircon domains, however, show variable steep REE patterns, leading to variable slopes in the range of middle REE (MREE) to HREE, where values of $(\text{Gd}/\text{Yb})_{\text{N}}$ are between 0.02 and 0.23

(Table S2).

The zircon domains which refer to Paleoproterozoic ages (< 2500 Ma) form a smaller group in comparison to the zircons reflecting Archean ages. Majority of chondrite-normalized REE patterns of zircons in this Paleoproterozoic group are similar to those of the metamorphic zircons (Fig. 9b). REEs can be conspicuously higher in this group of zircon than those above in the Archean age group of zircons, although some REE abundance of single grains' could be also much lower (Fig. 9b). The REE patterns mostly show weak moderate positive Eu anomalies and weak positive Ce anomalies. Most zircons of this Paleoproterozoic age group have variable and less steep chondrite-normalized REE patterns (McDonough & Sun 1995), and $(\text{Gd/Yb})_N$ is variable between 0.002 and 0.34.

As generally accepted, zircon of magmatic origin has steep chondrite-normalized REE patterns (McDonough & Sun 1995), oscillatory zoning under CL, and relatively high Th/U ratios (usually > 0.1). By contrast, zircon of metamorphic origin displays a less steep chondrite-normalized REE pattern, generally relatively structureless CL textures, and low Th/U ratios (usually < 0.1) (e.g. Hoskin and Schaltegger, 2003; Tang et al., 2007; J.H. Liu et al., 2013; S.J. Liu et al., 2015).

Most analyses of U-Pb ages are consistent in CL image, REE patterns, Th/U ratio and apparent age with regard of genetic information. For instance, No. 5 (magmatic) and No. 41 (metamorphic) in sample 09LY 12 (Fig. 9a and b); No. 36 (magmatic) and No. 43 (metamorphic) in sample 12LX15 (Fig. 7 and Fig. 9a and b); No. 41 (Magmatic), No. 27 and No. 31 (metamorphic) in sample 12LX16 (Fig. 7 and Fig. 9a and b); and No. 12c (magmatic) and No. 12r (metamorphic) in sample 12LX18 (Fig. 7 and Fig. 9a), which indicate a typical igneous or metamorphic origin, respectively.

Some other analyses, for instance, No.19 in sample 09LY12 (Fig. 7 and Fig. 9a), No. 3 in sample 12 LX15 (Fig. 7 and Fig. 9a), No. 7 in sample 12LX18 (Fig. 7 and Fig. 9b), are inconsistent with respect to CL images, REE pattern and inherited magmatic /metamorphic ages (Table S2, Fig. 7 and 9) and thus could not be unambiguously classified. Such apparent ^{207}U - ^{206}Pb ages do probably not reflect real rock ages, especially if they – as in this case – are discordant.

Since all samples of this study derive from same rock type, and generally show similar age distribution, REE and CL characteristics, Fig. 10 puts together all 173 age analyses from the four rock samples for comparative reasons and to strengthen the interpretation. In essence, zircons from the meta-calcsilicate rock yield the Archean ^{207}U - ^{206}Pb ages up to 3.04 Ga, while most analyses yield ages of 2.51–2.87 Ga, with major populations of 2.87, 2.78, 2.68 and 2.51 Ma. Most of the U–Pb data are

discordant, but several analyses are concordant, also in the age interval 2.51–2.87 Ga (Fig. 10b). The Paleoproterozoic U-Pb age data rarely distribute along the concordia curve in the age interval 2.46–2.09 Ga. The pervasive metamorphic ages from zircon of the HP pelitic and mafic granulites in the NCC are reported to range between 1.97–1.91 Ga and 1.89–1.81 Ga (Tang et al., 2007; J.B. Zhou et al., 2008; X. Zhou et al., 2008; Tam et al., 2011; Tam et al., 2012a, b, c; P.H. Liu et al., 2013, 2014; S.J. Liu et al., 2015; Chen et al., 2018). Similar ages, however, were only rarely found in zircon from the meta-calcsilicates, but, if so, not all are located on the concordant curve (Fig. 8b and 10b). The upper deposition age of the meta-calcsilicates, therefore, can be constrained at ~ 2.09 Ga.

8 Discussion

The Jiao-Liao-Ji Belt is composed of sedimentary and volcanic successions, which were reported to be deformed and metamorphosed under greenschist to lower amphibolite facies conditions at around 2.55–2.1 Ga (Luo et al., 2004; Lu et al., 2006; Jahn et al., 2008; J.B. Zhou et al., 2008; J.H. Liu et al., 2013; Wu et al., 2014, 2016), and tectonically associated with granitoid and gabbroic intrusions (Lu et al., 2006; Tang et al., 2007; Lan et al., 2014, 2015; P.H. Liu et al., 2013; Li and Chen, 2014; S.J. Liu et al., 2015). Similar to HP mafic granulite blocks from the close vicinity, the meta-calcsilicates from Nanshankou are included in the Neoarchean TTG gneisses (Fig. 2b). Although the HP mafic granulite as well as pelitic granulite of the Jiao-Liao-Ji Belt have attained general attention (i.e. X.-P. Li et al., 2011a and b; Zhao & Zhai, 2013; Tam et al., 2011; Li et al., 1997; P.H. Liu et al., 2013, 2014; S.J. Liu et al., 2015), the meta-calcsilicates are poorly studied and a number of questions remain open, as: What is their geochemical character? Are there different types of rock present or do they have homogeneous compositions? Is it possible to detect the maximum PT-conditions the meta-calcsilicates and do they record an *insitu*-metamorphism compared to the TTG gneiss hosts and the nearby HP mafic granulite from Jiaobei terrane? Is it possible to discover more than one metamorphic stage and are there zircons and zircon domains present, which have recorded inherited pre-metamorphic and magmatic stages? All these questions have to be addressed and discussed in the scope of data which are available from the regional rock sequences in the Jiao-Liao Ji Belt, especially since the meta-calcsilicates contains rock material of very diverse provenance. In order to understand these data in a broader context, in the final chapter a short review of – in parts controversially discussed – ages related the entire Jiao-Liao-Ji Belt is given.

8.1 Geochemical and geobarometrical insights from the meta-calcsilicates

From the geochemical point of view, the meta-calcsilicate blocks occur as two groups. One group which is high in $\text{Na}_2\text{O} + \text{K}_2\text{O}$ demonstrates a closer relationship to an igneous source, whereas the other group (group II) reflects a more sedimentary nature. The respective bulk rock composition is demonstrated to be variable, which can be considered as a result of different proportions of source material involved, sedimentary calcsilicate *versus* volcanoclastic to pyroclastic. With respect to the pseudosection modeling in the NCFMASHCO system the meta-calcsilicates of both groups have experienced the same maximum PT-conditions i.e. epidote amphibolite facies at about 580 °C and 0.9–1.1 GPa. Late veins of albite-, prehnite- and calcite-associations document a late sub-greenschist facies overprint during exhumation. PT-data from the metasediments and metavolcanics of Jiaobei terrane are not available and thus future PT-estimates are needed in order to prove a possible coincidence of the peak metamorphic conditions and exhumation path.

8.2 Zircons of the meta-calcsilicates: indications of metamorphic and magmatic growth domains

The ages derived from the meta-calcsilicates of our studies, which are in the range of ages derived from various meta-sedimentary rocks within the Jingshan and Fenzishan groups of previous studies, represent a major period of juvenile crustal growth and Paleoproterozoic metamorphic and magmatic periods, respectively, in the NCC (i.e. Wan et al., 2006; Tang et al., 2007; X. Zhou et al., 2008; Tam et al., 2011; J.H. Liu et al., 2013).

As shown by the ^{173}Lu age analyses of this study shown in Fig. 10, zircons from the meta-calcsilicate rock yield Archean ^{207}U - ^{206}Pb ages up to a maximum of 3.04 Ga. The major populations exhibit ages of 2.87, 2.78, 2.68 and 2.51 Ga, and Paleoproterozoic ^{207}U - ^{206}Pb ages which are between 2.46 and 2.09 Ga (Fig. 8b and 10b). Th/U ratios of zircons document a general decreasing trend in Fig. 11a from Archean to Paleoproterozoic.

Generally, Eu/Eu^* is higher in zircons of Paleoproterozoic age (< 2.5 Ga) than in those of Archean age (> 2.5 Ga). Occasionally also some zircons of Archean age are present which show an extremely high Eu/Eu^* ratio, possibly resulting from a metamorphic overprint (Fig. 11b). The total REE contents, which are much lower in Paleoproterozoic zircons compared to Archean zircons, indicate distinct

genetic sources (Fig. 11c). This is shown using a U/Ce vs. Th diagram, which allows to distinguish between magmatic and metamorphic zircon domains. The Archean zircons basically contain magmatic cores; some contain rims which record metamorphic ages (Table S2, 09LY12-11r, 12LX15-35r, 12LX16-2r, 12LX18-10r and 12LX18-12r).

As to the origin of the Paleoproterozoic zircons/zircon domains, most U-Pb zircon ages are of metamorphic origin as documented by their CL image, REE pattern and U/Ce – Th diagram (Figs. 7, 9 and 11d). To figure out the depositional time and geological implication of the meta-calcsilicate rocks, a special focus is on the Paleoproterozoic zircons formed at 2.46–2.09 Ga.

Important criteria regarding U–Pb geochronology of zircon refer to the utilization of CL images to highlight internal texture variations within zircon grains and to the variations in Th/U values of zircon domains. Magmatic zircons commonly show perfectly euhedral shapes with pronounced oscillatory zoning in CL images, suggesting a crystallization from melt. On the other hand, metamorphic zircons commonly have rounded shapes and CL images exhibit complex growth patterns, suggesting that they experienced several tectono-thermal events (i.e. Hoskin & Ireland, 2000; Rubatto et al., 2001; Andersson et al., 2002; Cavosie et al., 2004; Wan et al., 2006; Lopez-Sanchez et al., 2016). Th/U values in zircon are commonly used to discriminate between magmatic ($\text{Th/U} > 0.1$) and metamorphic ($\text{Th/U} < 0.1$) origin of zircon / zircon domains (i.e. Rubatto, 2002; Hoskin & Schaltegger, 2003; Wan et al., 2006; Lopez-Sanchez et al., 2016).

If, in general, the U-Pb ages are discordant, they do not reflect their genetic characteristics (i.e. Claesson et al., 2015 and references therein). In the current study only the data between 2.46 and 2.09 Ga after Paleoproterozoic are located on the concordant curve which are thus used for further discussion. There are six typical analyses of zircon out of 173 chosen, to discuss their ages and respective normalized REE patterns and CL images (see Fig. 12).

Among these six zircon analyses, two analyses show typical metamorphic characteristics in the light of both REE pattern and CL image (Fig. 12, No. 12 in sample 12LX15, No. 31 in sample 12LX16). Two other zircons show a typical magmatic CL image, but typical metamorphic REE patterns (Fig. 12, No. 5 and No. 16 in sample 12LX15). Contrary, another two zircons show characteristics of metamorphic CL image, but more magmatic REE patterns (Fig. 12, No. 11 in sample 12LX15, No. 13 in sample 09LY12); in addition they show weak to moderate positive Eu anomalies, which are different from those observed in the magmatic REE patterns of Archean zircons (showing a negative Eu

anomaly; Fig. 12a). In short, the Paleoproterozoic zircon ages formed at 2.46–2.09 Ga are either completely recrystallized during thermal events, presenting both, typical metamorphic REE patterns and CL images, or keep somewhat inherited REE patterns or CL images, which show transitional characteristics from magmatic zircon to metamorphic zircon.

Inherited magmatic U-Pb ages of 2.87–2.68 Ga from this study, indicate a less evident crustal reworking event after directly extracted from the mantle (Wu et al., 2005; Xia et al., 2009; Jiang et al., 2010; Wang and Liu, 2012). Previous studies have demonstrated that inherited (magmatic or detrital) zircons from various meta-sedimentary rocks of the Jingshan and Fenzishan groups record ages of 2450–2100 Ma (Luo et al., 2004; Wan et al., 2006; Tang et al., 2007; J.B. Zhou et al., 2008; Jahn et al., 2008). Paleoproterozoic meta-gabbro and granitic gneiss have also been identified in the northern part of the Laiyang area; they exhibit magmatic ages of 2102–2095 Ma (Wan et al., 2006; J.H. Liu et al., 2013; Lan et al., 2014, 2015), indicating that an important Paleoproterozoic juvenile magmatic crust was formed at this time (Wan et al., 2006; Tang et al., 2007; J.B. Zhou et al., 2008; J.H. Liu et al., 2013; Tam et al., 2011). All the zircons of the current study contain the Paleoproterozoic metamorphic rims with ages ranging from ~2.51 Ga to ~2.09 Ga, mostly discordant. It can be concluded that the protolith of the meta-calcsilicates was deposited at ~2.1 Ga on an Archaean (> 2.5 Ga) basement along the Paleoproterozoic Jiao-Liao-Ji belt, and contains rock material which originates not only from different provenances, but which also contains rock material (or inherited zircons) that already experienced an earlier metamorphism prior to the 1.85-1.95 event. The zircons of the meta-calcsilicates thus provide invaluable information on the evolution of the entire Jiao-Liao-Ji orogenic belt. Thus, in chapter 8.3 the ages of the current study are reviewed in the light of age data, available from the entire Jiao-Liao-Ji orogenic belt.

8.3 Formation and evolution of the Jiao-Liao-Ji orogenic Belt

The Jiao-Liao-Ji Belt of Precambrian basement is composed of (1) a metamorphosed and deformed basement that includes Meso- and Neoarchean rocks, which are dominated by TTG gneisses and associated supracrustal rocks; (2) voluminous meta-sedimentary and volcanic successions that represent the Macheonayeong Group in North Korea, the Ji'an and Laoling Groups in the southern Jilin, the North and South Liaohé Groups in the eastern Liaoning Peninsula, the Fenzishan and Jingshang Groups in the Jiaobei massif, and the Wuhe Group in the Anhui Province. They form a transitional

unit from a basal sedimentary clast-rich sequence and a lower bimodal-volcanic sequence, through a middle carbonate-rich sequence, to an upper pelite-rich sequence; (3) associated with the sedimentary and volcanic rocks are abundant Paleoproterozoic granitoid and mafic intrusions (e.g. Zhao et al., 2005; 2012; Liu et al., 2017a, b).

Due to the development of technical innovations and therefore the availability of high resolution techniques during the last two decades, geochronological studies have achieved abundant new findings and updates. Thus more detailed and new data are now available from rocks of the entire Jiao-Liao-Ji orogenic belt. Since the meta-calcsilicates studied contain sedimentary as well as igneous (plus metamorphic) source material and since the ages derived from the meta-calcsilicates have to be seen in the context of the ages of the surrounding rocks, this chapter tries to briefly review age data from the entire Jiao-Liao-Ji orogenic Belt and to deliver a coherent view (Table S3 and Fig. 13). Much progress has been made with respect to the following points to outline the development of the JLJB:

(1) The Archean TTGs of Jiaobei terrane illustrate three magmatic emplacement ages of Mesoarchean at ~2.9 Ga and Neoarchean at ~2.75–2.7 Ga and ~2.55–2.5 Ga (J.H. Liu, 2013; Wu et al., 2014, 2016; Jiang et al., 2016). Nd and Hf isotope data of 2.9 Ga indicate that the protoliths of TTG gneisses originate from a relatively juvenile crust (Jahn et al., 2008; J. H. Liu et al., 2013). The age of 2.7 Ga represents the most significant crust-forming episode in the Jiaobei Terrane (Tang et al., 2007; Jahn et al., 2008; Tam et al., 2011; J.H. Liu et al., 2013) and represent large juvenile crustal additions, which are derived from depleted mantle. (Wu et al., 2005; Jiang et al., 2010; Wan et al., 2011, Wang and Liu, 2012). Most of the Neoarchean basement rocks in the Eastern Block were formed at ~2.6–2.5 Ga, while only a few were formed at 2.8–2.7 Ga, implicating magmatic emplacement ages. (Tang et al., 2007; Wan et al., 2011; J.H. Liu et al., 2013; Zhao et al., 2012; Zhao and Zhai, 2013; Wu et al., 2014, 2016). The discovery of 2.5 Ga sanukitoid intrusions (high Mg-granitoids) in the TTGs of the Jiaobei terrane suggests that it could have originated from a mantle wedge, metasomatized most likely by slab-derived fluids (Jiang et al., 2016). Superimposed ~2.5 Ga tectonothermal events present both magmatic and metamorphic events in the TTG gneisses of the Jiao-Liao-Ji orogenic belt, as well as in other terranes of the NCC (Zhai et al., 2003; Lu et al., 2006; Tang et al., 2007; Jahn et al., 2008; Luo et al., 2008; J.H. Liu et al., 2013; Meng et al., 2013; Wu et al., 2014; This study). After these ~2.5 Ga events have occurred, the TTG gneisses recorded Paleoproterozoic HP metamorphic ages of ~1.9–1.8 Ga in Jiao-Liao-Ji Belt (Li and Zhao, 2007; Tang et al., 2007; J.H. Liu et al., 2013; Wu et al., 2014; Liu

et al., 2017).

(2) Supracrustal rocks and metapelites from the Jingshan and Fengzishan Group rocks of the Jiaobei Terrane and Liaohe Group rocks of the Liao-Ji area were deposited in a rift basin that developed in the period ~2.3–2.0 Ga on an Achaean (~2.5 Ga) basement within the Paleoproterozoic JLJB (e.g., Wan et al., 2006; X. Zhou et al., 2008; Tam et al., 2011; P.H. Liu et al., 2013). Subsequently, these rocks experienced amphibolite to granulite facies metamorphism, following a clockwise P-T path that resulted from subduction and collision, which involved the closure of the rift basin during the period 1.92–1.76 Ga (Lu et al., 2006; S.Z. Li et al., 2006; Wan et al., 2006; Tang et al., 2007; Luo et al., 2004, 2008; X. W. Zhou et al., 2008; S.Z. Li et al., 2011; Tam et al., 2011; Zhao & Zhai 2013; Kusky et al., 2016).

(3) The JLJB was formed during a rifting event in the period ~2.3–1.9 Ga, that involved the emplacement of A-type granitoids (Liaoji granites). The granitoids lead to the opening of an incipient ocean that broke up the Eastern Block into two small blocks (i.e. the Longgang and Langrim Blocks) (Zhang and Yang, 1988; Luo et al., 2004, 2008; Wan et al., 2006; Li and Zhao, 2007; Zhao et al., 2011 and 2012; S.Z. Li et al., 2012; Zhao et al., 2015; Lan et al., 2014, 2015).

(4) Geochronological studies on the HP mafic granulites suggest that their protolith ages are mainly in the range of ~2.7–2.5 Ga. The peak metamorphic ages range from 1.95 to 1.85 Ga, whereas the medium-pressure - low-pressure (MP–LP) granulite–amphibolite facies retrogression occurred at 1.85–1.82 Ga (Tam et al., 2011; Li et al., 1997; Q.S. Liu et al., 2013; P.H. Liu et al., 2013, 2014; S.J. Liu et al., 2015). The mafic granulites also record a clockwise metamorphic P-T path (Tam et al., 2011; Li et al., 1997; P.H. Liu et al., 2013, 2014; S.J. Liu et al., 2015). In addition, they however experienced an earlier metamorphism around 2.5 Ga as shown by Jahn et al. (2008) and S.J. Liu et al. (2015).

(5) Large volumes of A-type granites intruded into the JLJB at 2.2–2.1 Ga. The deposition of the Jingshan and Fengzishan supracrustal rocks was accompanied by an emplacement of A-type granites, gabbroic and doleritic dykes within an extensional setting (Li et al., 2001a, b, 2004a; Luo et al., 2004; Li and Zhao, 2007; S.Z. Li et al., 2011; Lan et al., 2015).

The tectonic nature of the Jiao-Liao-Ji Belt is discussed controversially for more than 20 years, but basically three tectonic evolution models exist:

(1) continent–arc–continent collision model: The model postulates that the JLJB Belt constituted an island arc and a back arc basin system, which was considered to have developed on the southern

margin of the Longgang Block by the north-directed subduction of the oceanic crust, connected to a passive-type continental margin on the northern side of the Langrim Block (Bai, 1993; Bai and Dai, 1998). Alternatively, the mafic–ultramafic rocks are considered to have been associated with the North Liaohe Group as an active continental arc (magmatic belt) developing on a south-directed subduction zone. This subduction zone that was interpreted to be located between the northern Archean Anshan block (Longgang Block) and the Palaeoproterozoic southern block, and which consisted of magmatic and sedimentary rocks originating from the South Liaohe Group (Faure et al., 2004, Lu et al., 2006). Subsequently, this magmatic belt was overthrust upon the northern Archean basement during the arc–continent collision.

(2) The rifting-closure model: This model was initially proposed by Zhang and Yang (1988), and was refined by a group of further researchers, who suggest that the eastern part (Eastern Block) of the NCC underwent rifting during early Paleoproterozoic time, leading to a deposition of sedimentary-volcanic rock series and to an intrusion of granitoids and mafic rocks. This rift basin was closed (without subduction process) in the late Paleoproterozoic to form the JLJB (Li and Zhao, 2007; S.Z. Li et al., 2001a,b, 2004a, 2006, 2012; Luo et al., 2004, 2008). Indicators for such a model reported are (i) the presence of bimodal volcanic assemblages in the JLJB, represented by a large amount of meta-mafic volcanics (greenschists and amphibolites) and meta-rhyolites (Peng and Palmer, 1995; Zhang and Yang, 1988, Lu et al., 2006; Li & Chen 2014), (ii) large volumes of A-type granite of an intrusion age of ~2.1–2.2 Ga in the JLJB (Zhai et al., 1985; Peng and Palmer, 1995; Zhao & Zhai 2013 and references therein, Lan et al., 2014, 2015, Liu et al., 2017), and (iii) low-pressure, anticlockwise P–T paths of metamorphic rocks of the Ji'an, South Liaohe and Jingshan Groups in the southern zone of the JLJB (He and Ye, 1998; Lu et al., 1996, Lan et al., 2015). In addition, A-type granites are shown to be geochemically and geochronologically similar to the late Archean TTG basement gneisses and mafic dyke swarms of the metamorphic rocks of the JLJB (Zhang and Yang, 1988), or genetically are related to the TTGs (Lan et al., 2015). This model, however, cannot sufficiently explain the polyphase compressive deformation and clockwise P–T paths of the Laoling, North Liaohe and Fenzishan Groups in the northern zone of the JLJB.

(3) The rifting-subduction-collision model: The formation and evolution of the JLJB is characterized by an initial rifting to form incipient oceanic basins, followed by subduction and collision (rift basin closure) to form various high-pressure (HP) granulites in the JLJB (Kröner et al., 2006;

Wang et al., 2010; Tam et al., 2012a, b, c; Zhao et al., 2012; Zhao and Zhai, 2013; Zou et al., 2017). Supracrustal rocks and pelitic rocks from the Jingshan and Fengzishan Group rocks of the Jiaobei Terrane and Liaohe Group rocks of the Liao-Ji area were deposited in a rift basin that developed in the period 2.3–2.0 Ga, sitting on top of an Achaean (~2.5 Ga) basement within the Paleoproterozoic JLJB. Subsequently, these rocks experienced amphibolite to granulite facies metamorphism during a clockwise P-T path, that resulted from subduction and collision in response to the closure of the rift basin at 1.92–1.76 Ga (Lu et al., 2006; S.Z. Li et al., 2006; Wan et al., 2006; Tang et al., 2007; Luo et al., 2004, 2008; X. Zhou et al., 2008; S.Z. Li et al., 2011; Tam et al., 2011; Zhao & Zhai, 2013; Kusky et al., 2016).

Due to expanded studies in last twenty years, the knowledge for understanding the tectonic nature of JLJB increasingly developed, leading to the three different models mentioned above. Evidences for the “rifting-subduction-collision model” are obvious, in that it proposes sediments and mafic rocks to be subducted in order to form pelitic and mafic HP metamorphic granulites. In addition, an active continental margin and magmatic arc geochemistry were recognized in the northern segment of the Jiao-Liao-Ji Belt (e.g., Li and Chen, 2014; Meng et al., 2013, 2014; Xu et al., 2018). More data supporting this model became available during the last years which indicate that supracrustal rocks in the southern segment of the JLJB experienced clockwise P-T paths (e.g., S.Z. Li et al., 2003; Lu, 1996; Tam et al., 2011, 2012a, b, c; Wang et al., 2010).

Geochronological studies document that the rifting phase in the Jiao-Liao-Ji Belt lasted from 2.3 Ga to 2.0 Ga (Table S3, Fig. 13). The youngest group of detrital zircon ages recorded magmatic ages (2.3–2.1 Ga) are obtained from the Fengzishan and Jingshan groups (Wan et al., 2006; Tam et al., 2011; Lan et al., 2014), and metamorphic ages from this study (2.51–2.01 Ga) of the southern segment of Jiaobei terrane. Zircon studies from the North and South Liaohe groups of the northern segment basically indicate magmatic ages of 2.2–2.0 Ga (Luo et al., 2004, 2008; Wan et al., 2006). This means that the rifting of Jiao-Liao-Ji Belt started from south-west and developed towards north-east. The extensive emplacement of A-type granites, gabbroic and doleritic dykes were interpreted to be a result of an extensional characteristics of the JLJB at 2.2–2.1 Ga (S.Z. Li et al., 2001a, b, 2004a; Luo et al., 2004a, b; Li and Zhao, 2007; S.Z. Li et al., 2011; Lan et al., 2015). The emplacement of meta-basalts of the Liao-Ji area yield ages of ~2.2–2.0 Ga (Lu et al., 2006; Li & Chen 2014, Meng et al., 2014). Such a long-lasting extension within the JLJB supports the potential to form an incipient ocean. Although not

much indications of magmatic signatures are available which would be indicative of an extension-related oceanic environment, data from ultramafic rocks and HP mafic granulite provide evidence of an oceanic affinity (X.-P. Li et al., 2011a, 2013; Kong et al., 2015). Geochemical signatures of HP mafic granulite show that an emplacement of its protolith in an active continental margin environment is very likely.

Combined petrological and zircon U-Pb geochronological data support the hypothesis that the formation and evolution of the JLJB is related to the initial rifting to form an incipient oceanic basins (X.-P. Li et al., 2011a, 2013; Kong et al., 2015) followed by subduction and collision to form various high-pressure granulite rocks (P.H. Liu et al., 2013 and 2014; X.-P. Li et al., 2011a and 2013). An upgraded tectonic model even proposed a ca. 2.1 Ga oceanic plate subduction event that induced a back-arc basin opening, and closed to form the JLJB in the period of ca. 1.9 Ga (Xu et al., 2018). The enormous volumina of sedimentary rocks are mainly sourced from the Paleoproterozoic granitic rocks within the JLJB and the metamorphic basement of the surrounding ancient blocks. The sedimentary rocks were deposited between 2.15 and 1.95 Ga (Liu et al., 2017). Deposition of the source material of the meta-calcsilicates, that already contained metamorphic detritus, occurred at about 2.1 Ga.

Although the studies on the meta-calcsilicates fill an important gap of knowledge related to the ages prior to the local metamorphic event between 1.95 and 1.85 Ga, which is derived from the TTG gneisses and the HP mafic granulite (Liu et al., 2013, and references therein), some questions still remain open. Both, meta-calcsilicate and HP mafic granulite form lenses within the TTG gneisses likely experienced a coherent P-T history. Whereas, however, for the HP mafic granulite a peak metamorphic stage at 850-880°C, 14.5-16.5 kbar was derived (Liu et al., 2013), the maximum P-T conditions derived from the meta-calcsilicates are only around 580°C and 10.8–11.4 kbar (which are also a bit too high in pressure, to fit the exhumation path of Liu et al. (2013)). Either way, possibly, due to a strong reequilibration at amphibolite facies conditions, it might be difficult to discover relics or relic mineral assemblages of earlier stages. Further studies, preferentially on mineral inclusions in very rigid and robust accessories such as zircon, rutile and monazite are perhaps successful to discover such relics and allow to uncover the early prograde and peak metamorphic stages the meta-calcsilicates experienced between 1.95 and 1.85 Ga. Possibly extensive studies which focus on mineral inclusions in the metamorphic zircon rim domains that give ages between 2.51 and

2.01, contribute to a better understanding of the early metamorphic stage(s). A further important issue refers to the metamorphic ages of 1.95-1.85 which were recorded by zircons of the TTG gneisses and the HP mafic granulites, but not from the zircons of the meta-calcsilicates. This can be due to a dry local environment, or the lack of zirconium-bearing minerals to breakdown and to deliver the element zirconium, necessary for the formation of zircon. It is well known from UHP localities in the western Alps, that crustal rocks which were subducted into mantle depths, failed to have reached isotopic equilibrium (even (OH)-group minerals such as biotite did not), and that in some cases no zircon was formed to record these ages, although the respective rocks have experienced temperatures exceeding 700°C (e.g., Gebauer et al., 1997; Tilton et al., 1997). A further alternative, of course, would be, that the meta-calcsilicate did experience a different P-T history than its country rock TTG gneisses and the HP granulites therein, which however would call for a very complex geotectonic solution.

9. Conclusions

(1) The meta-calcsilicates which are in the focus of the current study belong to a volcano-sedimentary rocks sequence, which contain different proportions of source rock material, even material that experienced an early metamorphic stage. In one group of meta-calcsilicates studied, relatively high amounts of SiO₂, Na₂O and K₂O and low amounts of CaO material of volcanic source predominate, whereas the second group higher in CaO and lower in Na₂O demonstrates an essential contribution of sedimentary as well as volcanic precursors.

(2) The precursor of the meta-calcsilicates were deposited into a rift basin at about 2.1 Ga together with the protoliths of the TTG gneisses and mafic granulites, and are structurally located on top of an Achaean (~2.5 Ga) basement within the Paleoproterozoic JLJB. They are belonging to a supracrustal rock series of a volcano-sedimentary origin.

(3) Magmatic zircon domains display an oscillatory zoning under CL and steep chondrite-normalized REE patterns. Metamorphic zircon and zircon domains are structureless under CL and show variable and less steep chondrite-normalized REE patterns; the (Gd/Yb)_N ratio is variable and between 0.002 and 0.23. Some zircon domains, which are characterized by transitional characteristics of REE patterns (magmatic to metamorphic), are either discordant or concordant.

(4) The studied rocks have experienced epidote-amphibolite facies conditions at ~580°C /

1.08–1.14 GPa; late prehnite- and calcite-dominant veins document subgreenschist facies overprint. Petrological indications of an earlier P-T history could not be detected.

(5) Most detrital zircons of meta-calcsilicate from Jiaibei terrane show discordant U-Pb ages, which are interpreted to be a result of Eoarchean zircon Pb loss during late thermal events. One U-Pb zircon age group of 3.0 Ga and an additional group that includes ages of 2.87 Ga, 2.78 Ga and 2.68 Ga, are all interpreted as Archean magmatic crystallization ages. A subordinate cluster of ages at 2.51 Ga and further ages between 2.51 and 2.01 Ga, derived from zircon rims of the meta-calcsilicate, are interpreted to represent metamorphic ages.

(6) Zircon U-Pb studies on the meta-calcsilicate did not record ages in the range of 1.95–1.85 Ga which were determined on zircons from the surrounding TTG gneisses and HP mafic granulite intercalations. This can be due to a dry local environment, or the lack of zirconium-bearing minerals to breakdown at this stage and to release zirconium, necessary for the formation of zircon

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Captions

Table captions

Table 1. Mineral assemblages of meta-calcsilicate from the Nanshankou, Jiaobei terrane, eastern Shandong.

*I rock samples containing rather mafic volcanic components, II rock samples containing rather calcareous-siliceous sedimentary components.

Table 2. EPM analyses of representative major minerals from meta-calcsilicates of the Nanshankou, Jiaobei terrane.

- (1) EPM analyses of garnet from meta-calcsilicates (based on O=12).
- (2) EPM analyses of pyroxene from meta-calcsilicates (based on O=6).
- (3) EPM analyses of amphibole from meta-calcsilicates (based on O=23).
- (4) EPM analyses of other minerals from meta-calcsilicates.

Numbers of ions on the basis of following oxygen numbers: Ep =12.5, Pl=8, Prh=11, Ttn=4.5, Ms=11, Chl=28, Ps ($= 100 \times \text{Fe}^{3+}/(\text{Fe}^{3+} + \text{Al})$) for pistacite, * for number of average composition.

Table 3. Major element (%) and trace element (ppm) compositions of meta-calcsilicates rocks from the the Nanshankou, Jiaobei terrane.

Table S1. U-Pb isotopic data of detrital zircons (samples 09LX12, 12LX15, 12LX16 and 12LX18) from the meta-calcsilicates of the Nanshankou, Jiaobei terrane (*-c = zircon core, -r = zircon rim).

Table S2. Trace-element compositions (ppm) of detrital zircons (samples 09LX12, 12LX15, 12LX16 and 12LX18) from the meta-calcsilicates of the Nanshankou, Jiaobei terrane (*-c = zircon core, -r = zircon rim).

Table S3. Summary of geochronological data of major lithological types of the Jiao-Liao-Ji Orogenic Belt. The data are visualized in Fig. 13.

Figure captions

Fig. 1. Tectonic subdivision of the North China Craton (after Zhao et al., 2005).

Fig. 2. Geological schematic map of research area. (a) Structural sketch diagram of the Eastern Block of the North China Craton (modified after X.W. Zhou et al., 2008); (b) Distribution of Precambrian rocks in the Jiaobei terrane and sample localities (modified after Li et al., 2013).

Fig. 3. Field outcrops of meta-calcsilicates showing heterogeneous structures of meta-calcsilicates (a-d) from massive (a-b; a with calcite veins) to taxitic (c-d).

Fig. 4. Microphotographs of the meta-calcsilicates in the Nanshankou, Jiaobei terrane. (a–d) fine grained group I meta-calcsilicate texture and mineral assemblage of Grt + Cpx + Amp + Prh $\pm$ Chl + Ab + Cal + Ttn; (c) CL image, bright yellow colors = Cal, bluish = Prh; Grt and Amp are lacking luminescence; (d) mineral association of late veins rich in Prh and Cal; (e–f; group II) mineral assemblage of Grt + Cpx + Ep $\pm$ Chl + Ab + Cal + Ttn (e) and assemblage of Grt + Ep + Cal; (f). Photo (b) was taken under plane-polarized light, (c) represents a color CL image (f) under crossed polars; all the others are BSE images.

Fig. 5. Discrimination diagrams of meta-calcsilicates (data present in table 3), (a) A-CN-K diagram showing the rock compositions of type I and II meta-calcsilicates (modified after Xiang et al., 2015 and reference therein), compositional ranges of Grt, Cpx, Prg and epidote group mineral taken from this study (table 2-5); (b) [(al+fm)-(ca+alk)]-Si diagram of calc-silicates from the Nanshankou, Jiaobei terrane of the NNC (on the basis of the sum = $(\text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3 + \text{CaO} + \text{MnO} + \text{MgO} + \text{Na}_2\text{O} + \text{K}_2\text{O})$, al = $100 \times \text{Al}_2\text{O}_3 / \text{sum}$, fm = $100 \times (\text{Fe}_2\text{O}_3 + \text{MgO}) / \text{sum}$, ca = $100 \times \text{CaO} / \text{sum}$, alk = $100 \times (\text{Na}_2\text{O} + \text{K}_2\text{O}) / \text{sum}$ and si for $100 \times \text{SiO}_2 / \text{sum}$) (after Simonen, 1953.)

Fig. 6. Assemblage stability diagrams (P-T pseudosections) for meta-calcsilicates; shaded (green) areas represent the observed mineral assemblages of the representative samples. Dashed lines represent X_{Grs} isopleths of garnet. (a) Calculated with an effective bulk composition normalized on the basis of wt% oxide for sample 12LY16 as $\text{SiO}_2 = 49.63$, $\text{Al}_2\text{O}_3 = 8.20$, $\text{CaO} = 17.64$, $\text{MgO} = 7.00$, $\text{FeO} = 7.50$, $\text{Fe}_2\text{O}_3 = 2.21$, $\text{Na}_2\text{O} = 3.07$, $\text{H}_2\text{O} = 1.57$, $\text{CO}_2 = 0.93$; (b) sample 12LY18 normalized on the basis of wt% oxide for sample 12LY18 as $\text{SiO}_2 = 51.15$, $\text{Al}_2\text{O}_3 = 8.42$, $\text{CaO} = 18.12$, $\text{MgO} = 8.40$, $\text{FeO} = 8.38$, $\text{Fe}_2\text{O}_3 = 1.84$, $\text{Na}_2\text{O} = 1.62$, $\text{H}_2\text{O} = 1.16$, $\text{CO}_2 = 0.90$; (c) sample 09LY12 normalized on the basis of wt% oxide as $\text{SiO}_2 = 49.52$, $\text{Al}_2\text{O}_3 = 6.13$, $\text{CaO} = 23.92$, $\text{MgO} = 8.93$, $\text{FeO} = 6.95$, $\text{Fe}_2\text{O}_3 = 1.37$, $\text{Na}_2\text{O} = 0.27$, $\text{H}_2\text{O} = 1.08$, $\text{CO}_2 = 1.84$.

Fig. 7. Representative CL images of zircons from the Mesoarchean meta-calcsilicate samples 09LY12, 12LX15, 12LX16 and 12LX18, collected from the Jiaobei terrane, North China Craton. The circles mark the areas of the LA-ICP-MS measurements for $^{207}\text{Pb}/^{206}\text{Pb}$ age dating; numbers in circles refer to analysis in table S1).

Fig. 8. Zircon ages from investigated meta-calcsilicate samples of the Jiaobei terrane, North China Craton, (a) histograms with probability density plots of $^{207}\text{Pb}/^{206}\text{Pb}$ age for samples 09LY12 and 12LX15 (group I), 12LX16 and 12LX18 (group II), minor axis ticks at 50 Ma intervals; (b) U-Pb concordia diagrams of analyses for samples 09LY12 and 12LX15 (group I), 12LX16 and 12LX18 (group II); Numbers refer to the zircon analysis shown in table 5 (1).

Fig. 9. Chondrite normalized REE diagrams of detrital zircons from meta-calcsilicates of samples 009LY12 and 12LX15 (group I), 12LX16 and 12LX18 (group II) from the Nanshankou, Jiaobei terrane; (a) for $^{207}\text{Pb}/^{206}\text{Pb}$ ages older than 2500 Ma, (b) for $^{207}\text{Pb}/^{206}\text{Pb}$ ages younger than 2500 Ma (right row). Chondrite values are from McDonough and Sun (1995) (red lines are examples for typical magmatic origin, green lines are examples for typical metamorphic origin).

Fig. 10. Whole data set for 173 detrital zircon ages of four analyzed samples of the meta-calcsilicates from Jiaobei terrane, North China Craton. (a) histogram with probability density plots of $^{207}\text{Pb}/^{206}\text{Pb}$ age, minor axis ticks at 50 Ma intervals; (b) U-Pb concordia diagram.

Fig. 11. Variation diagrams of trace element data from zircon, showing the chondrite-normalized ratios of (a) Th/U vs. Age, (b) Eu/Eu* vs. Age, (c) [Sm/La]_N vs. Σ REE, and (d) U/Ce ratio vs. Th concentration diagram (after Castiñeiras et al., 2010) which separates magmatic from metamorphic zircons.

Fig. 12. REE patterns and CL images of zircon < 2.5 Ga which only plot along the concordia.

Fig. 13. Summary of age data and respective localities in the Jiao-Liao-Ji Orogenic Belt (MG represent for magmatic age, MM for metamorphic ages. For further information see Table 6.

Table 1. Mineral assemblages of meta-calcsilicate from Nanshankou, Jiaobei terrane, eastern Shandong

Sample	Major minerals (>10%)		Minor minerals (<10%)	group classification*
	amphibolite facies	subgreen schist facies		
09LY14	Grt, Cpx, Amp, Ab	Prh, Chl, Ab, Cal	Chl, Ap, Ttn	I
12LX16	Grt, Cpx, Amp, Ab	Act, Prh, Ab, Cal	Ttn, Ap	I
12LX17	Grt, Cpx, Amp, Ab	Act, Prh, Ab, Ms, Cal	Ttn, Ep	I
12LX18	Grt, Cpx, Amp	Act, Ab, Chl, Prh, Cal	Chl, Ab, Ttn	I
09LY11	Grt, Di, Ep, Cal,	Act, Prh, Cal	Ttn	II
09LY12	Grt, Di, Ep, Cal,	Act, Prh, Cal	Ttn	II
09LY13	Grt, Di, Ep, Cal,	Prh, Cal	Ttn	II
09LY22	Grt, Di, Ep, Cal,	Cal, Prh	Ttn, Prh	II
10LX07	Grt, Di, Ep, Cal, Qtz	Cal	Ttn	II
12LX15	Grt, Di, Ep, Cal,	Act, Prh, Cal	Ttn	II

*group I rock samples containing more mafic volcanic components, group II rock samples containing rather calcareous-siliceous sedimentary components.

Table 2. EPM analyses of representative major minerals from meta-calcsilicates

(1) EPM analyses of garnet from meta-calcsilicates (based on O=12).

anal.	group I calc-silicates						group II calc-silicates														
	12LX16					12LX18						09LY12					12LX17				
	No.	1.2	2.8	3.2	3.3	3.4	1.1	1.2	1.5	1.6	2.1	2.2	1.1	1.2	1.3	1.4	1.5	3.4	3.5	3.6	3.7
SiO ₂	38.1	38.1	38.16	38.3	38.55	38.5	38.3	38.3	38.3	38.2	38.4	38.9	39.0	38.6	39.1	38.9	38.9	38.9	38.7	38.8	38.7
	4	4		2		4	5	4	0		3	7	2	3	3	4	1	3	7	0	4
TiO ₂	0.15	0.15	0.13	0.11	0.17	0.13	0.08	0.07	0.11	0.08	0.09	0.08	0.47	0.31	0.08	0.17	0.37	0.12	0.09	0.09	0.10
Al ₂ O ₃	21.5	21.6	21.77	21.0	21.20	21.1	20.9	20.4	20.3	20.9	21.5	20.7	21.8	21.2	20.3	21.3	20.8	20.9	21.0	21.0	21.1
Cr ₂ O ₃	9	4		7		4	6	6	5	6	8	5	9	4	8	1	6	2	7	9	1
	0.00	0.00	0.08	0.00	0.03	0.17	0.12	0.09	0.14	0.05	0.33	0.12	0.00	0.00	0.08	0.03	0.09	0.00	0.03	0.03	0.08
	18.9	18.5	18.08	15.7	15.44	13.3	13.3	16.1	17.3	13.5	13.3	6.27	10.7	14.8	5.86	13.5	6.23	5.06	9.17	5.17	7.75
FeO	2	2		2		7	3	0	7	5	0		4	4		1					
	4.03	4.03	4.16	4.09	4.26	4.63	4.24	3.59	3.62	4.4	3.79	1.83	1.25	2.11	1.80	1.27	1.03	1.02	1.73	1.73	2.64
MnO	1.97	1.97	1.76	1.97	2.14	1.84	1.62	2.07	2.10	1.59	1.65	1.61	2.26	1.99	1.13	2.15	0.53	0.13	0.43	0.43	0.88
MgO	14.8	14.8	15.90	18.3	18.36	20.3	20.6	18.9	17.5	20.5	20.6	30.0	23.9	20.4	31.2	22.4	31.5	33.2	28.5	32.1	28.4
CaO	3	3		1		4	6	6	3	2	9	5	0	7	9	7	6	3	9	4	4
Na ₂ O	0.04	0.04	0.03	0.00	0.02	0.00	0.02	0.02	0.03	0.02	0.01	0.02	0.00	0.00	0.02	0.02	0.00	0.01	0.01	0.01	0.01
K ₂ O	0.04	0.04	0.03	0.02	0.00	0.00	0.00	0.00	0.00	0.00	0.02	0.00	0.02	0.02	0.00	0.00	0.00	0.01	0.01	0.01	0.01
NiO	0.00	0.00	0.00	0.02	0.00	0.00	0.01	0.01	0.01	0.00	0.00	0.01	0.02	0.02	0.01	0.00	0.06	0.03	0.00	0.00	0.00

Total	99.7 0	99.9 6	100.1 0	99.6 3	100.1 8	100. 16	99.6 8	99.7 2	99.5 6	99.3 7	99.8 9	99.7 1	99.5 8	99.6 2	99.7 9	99.8 7	99.6 4	99.4 6	99.9 0	99.5 1	99.7 3
Si	2.98	2.99	2.98	2.99	2.99	2.98	2.99	2.99	3.00	2.98	2.98	2.97	2.99	3.00	2.98	3.00	2.98	2.98	2.98	2.97	2.97
Al	1.95	2.00	2.00	1.94	1.94	1.93	1.93	1.88	1.88	1.93	1.97	1.86	1.98	1.94	1.83	1.93	1.88	1.89	1.91	1.90	1.91
Ti	0.01	0.01	0.01	0.01	0.01	0.01	0.00	0.00	0.01	0.00	0.01	0.00	0.03	0.02	0.00	0.01	0.02	0.01	0.01	0.01	0.01
Cr	0.00	0.00	0.00	0.00	0.00	0.01	0.01	0.01	0.01	0.00	0.02	0.01	0.00	0.00	0.01	0.00	0.01	0.00	0.00	0.00	0.00
Fe ³⁺	0.09	0.00	0.02	0.06	0.06	0.08	0.07	0.12	0.10	0.10	0.04	0.19	0.00	0.02	0.19	0.05	0.11	0.15	0.12	0.16	0.13
Mg	0.22	0.23	0.20	0.23	0.25	0.21	0.19	0.24	0.25	0.19	0.19	0.18	0.26	0.23	0.13	0.25	0.06	0.01	0.05	0.05	0.10
Fe ²⁺	0.92	1.24	1.16	0.96	0.94	0.79	0.80	0.93	1.04	0.79	0.82	0.21	0.69	0.94	0.18	0.82	0.29	0.18	0.46	0.17	0.37
Mn	0.29	0.27	0.28	0.27	0.28	0.30	0.28	0.24	0.24	0.29	0.25	0.12	0.08	0.14	0.12	0.08	0.07	0.07	0.11	0.11	0.17
Ca	1.54	1.25	1.33	1.53	1.53	1.69	1.73	1.59	1.47	1.72	1.72	2.45	1.97	1.70	2.56	1.85	2.59	2.72	2.35	2.63	2.33
Na	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
K	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Ni	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Alm	30.9 9	41.4 8	39.12 9	32.1 9	31.43	26.3 5	26.6 1	31.0 2	34.7 3	26.4 5	27.5 3	7.23	23.0 1	31.2 9	6.13 8	27.2	9.60	5.95 9	15.5 9	5.86 7	12.3
Pyr	7.37	7.73	6.87	7.65	8.26	7.12	6.31	8.03	8.18	6.21	6.41	6.15	8.64	7.62	4.31	8.22	2.00	0.49	1.67	1.67	3.39
Spe	9.86	8.98	9.25	9.03	9.35	10.1	9.36	7.94	8.01	9.76	8.35	3.98	2.72	4.60	3.89	2.75	2.23	2.22	3.77	3.77	5.78
Adr	4.31	0.25	0.89	3.10	3.02	3.82	3.68	6.09	4.85	4.73	2.09	8.99	0.00	1.02	9.38	2.54	5.47	7.18	6.11	7.60	6.37
Uvr	0.00	0.00	0.24	0.00	0.09	0.51	0.37	0.27	0.43	0.15	1.00	0.35	0.00	0.00	0.25	0.09	0.28	0.00	0.10	0.10	0.23
Sch	0.29	0.44	0.37	0.32	0.49	0.37	0.23	0.20	0.32	0.23	0.26	0.22	1.35	0.92	0.24	0.50	1.07	0.34	0.25	0.25	0.29
Grs	47.1 8	41.1 3	43.25	47.7 1	47.36	51.6 9	53.4 5	46.4 3	43.4 8	52.4 7	54.3 6	73.1 0	64.2 8	54.5 5	75.7 9	58.6 2	79.3 5	83.8 3	72.5 1	80.7 5	71.5 7

(2) EPM analyses of pyroxene from meta-calcsilicates (based on O=6).

anal.	12L X16					12L X18					09L Y12					12L X17		
No.	1.1	2.5	2.6	3.7	3.8	1.1	1.3	1.4	2.4	2.5	1.1	1.2	1.3	2.1	2.2	1.3	1.4	3.3
SiO ₂	51.6	51.4	50.6	51.1	51.1	51.6	51.3	51.6	50.7	51.2	52.0	51.9	52.9	52.7	52.7	52.3	51.9	51.6
	0	5	0	6	3	4	1	7	5	1	7	0	6	0	6	3	1	2
TiO ₂	0.17	0.59	0.56	0.98	1.15	0.10	0.14	0.11	0.16	0.11	0.08	0.11	0.05	0.06	0.04	0.00	0.04	0.06
Al ₂ O ₃	1.09	1.33	2.21	1.20	1.34	0.87	0.93	0.95	1.56	1.33	0.85	1.06	0.80	0.74	0.77	1.02	1.02	0.93
Cr ₂ O ₃	0.06	0.15	0.00	0.09	0.01	0.06	0.02	0.01	0.09	0.01	0.03	0.00	0.00	0.04	0.09	0.03	0.02	0.00
	10.8	10.7	11.5	11.6	11.4	11.5	11.6	10.4	11.3	10.9	10.2	10.3	10.1	10.6	10.7	9.44	9.65	10.6
FeO	7	6	8	0	6	8	8	8	8	6	0	8	6	8	2			4
	0.64	0.67	0.59	0.65	0.59	0.76	0.78	0.89	0.75	0.84	0.84	0.80	0.83	0.67	0.68	0.77	0.91	0.88
MnO																		
	11.1	11.1	10.5	10.4	10.3	11.0	10.7	11.3	10.7	10.8	11.1	11.1	11.0	10.8	10.9	11.6	11.6	11.1
MgO	3	8	0	4	6	6	1	7	1	7	7	6	1	0	1	4	3	1
CaO	23.9	23.3	23.2	23.2	23.3	23.3	23.5	24.0	24.1	23.9	24.2	24.2	23.7	23.8	23.9	24.4	24.5	24.4
	0	8	3	7	9	7	6	3	8	0	1	6	0	1	1	4		3
Na ₂ O	0.37	0.28	0.36	0.24	0.21	0.35	0.35	0.32	0.36	0.37	0.15	0.20	0.16	0.13	0.19	0.11	0.12	0.17
K ₂ O	0.00	0.07	0.02	0.00	0.00	0.01	0.01	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.01	0.00	0.02	0.00
NiO	0.04	0.00	0.07	0.09	0.00	0.02	0.04	0.04	0.00	0.00	0.01	0.14	0.04	0.06	0.00	0.03	0.08	0.00
Total	99.8	99.8	99.7	99.7	99.6	99.8	99.5	99.8	99.9	99.6	99.6	100.	99.7	99.6	100.	99.7	99.9	99.8
	7	8	2	3	6	2	4	7	2	0	3	01	1	9	08	9		4
Si	1.96	1.95	1.93	1.95	1.95	1.97	1.97	1.96	1.94	1.96	1.99	1.97	2.00	2.00	2.00	1.99	1.97	1.97
Al	0.05	0.06	0.10	0.05	0.06	0.04	0.04	0.04	0.07	0.06	0.04	0.05	0.04	0.03	0.03	0.05	0.05	0.04

Ti	0.00	0.02	0.02	0.03	0.03	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Cr	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Mg	0.63	0.63	0.60	0.59	0.59	0.63	0.61	0.64	0.61	0.62	0.64	0.63	0.62	0.61	0.62	0.66	0.66	0.63
Fe ²⁺	0.35	0.34	0.37	0.37	0.37	0.37	0.37	0.33	0.36	0.35	0.33	0.33	0.32	0.34	0.34	0.30	0.31	0.34
Mn	0.02	0.02	0.02	0.02	0.02	0.02	0.03	0.03	0.02	0.03	0.03	0.03	0.03	0.02	0.02	0.02	0.03	0.03
Ca	0.97	0.95	0.95	0.95	0.96	0.96	0.97	0.98	0.99	0.98	0.97	0.97	0.96	0.97	0.97	0.96	0.98	0.98
Na	0.03	0.02	0.03	0.02	0.02	0.03	0.03	0.02	0.03	0.03	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
K	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Ni	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
En	0.32	0.33	0.31	0.31	0.31	0.32	0.31	0.33	0.31	0.32	0.33	0.33	0.33	0.32	0.32	0.34	0.34	0.32
Fs	0.18	0.18	0.19	0.19	0.19	0.19	0.19	0.17	0.19	0.18	0.17	0.17	0.17	0.18	0.18	0.16	0.16	0.17
Wo	0.50	0.49	0.50	0.50	0.50	0.49	0.50	0.50	0.50	0.50	0.50	0.50	0.50	0.50	0.50	0.50	0.50	0.50
Mg#	0.65	0.65	0.62	0.62	0.62	0.63	0.62	0.66	0.63	0.64	0.66	0.66	0.66	0.64	0.64	0.69	0.68	0.65

(3) EPM analyses of amphibole from meta-calcsilicates (based on O=23).

[illegible]

Mg# 0.63 0.62 0.65 0.61 0.63 0.64 0.63 0.61 0.64 0.65 0.72 0.73 0.76 0.72 0.43 0.43 0.46 0.45 0.52 0.42 0.45 0.49

(4) EPM analyses of other minerals from meta-calcsilicates.

anal.	epidote group					plagioclase				prehnite				titanite			calcite		chlorite	muscovite
	09LY12			12LX17		12L	12LX	09LY	12LX	12LX	12LX	09LY	12LX	12LX	09LY	10LX	12LX	09LY	12LX	12LX1
No.	ep-1.1	ep-1.2	ep-2.1	ep 1	ep 2	X16	-18	-12	17	16	-18	-12	17	16	-12	07	-18	12	-16	7
	3*	2*	2*	3*	4*	3*	3*	3*	4*	2*	2*	2*	1*	2*	2*	1*	2*	2*	2*	2*
SiO ₂	38.37	38.38	38.26	39.05	39.68	68.50	68.50	68.56	68.50	43.54	43.25	43.79	43.54	30.62	29.93	30.62	-	-	27.33	47.24
TiO ₂	0.05	0.19	0.12	0.04	0.05	0.01	0.01	0.00	0.01	0.03	0.04	0.00	0.03	37.97	38.95	37.97	-	0.02	0.08	0.09
Al ₂ O ₃	26.57	26.65	26.44	24.63	24.53	19.48	19.30	19.11	19.48	23.80	23.61	24.01	23.80	2.21	2.96	2.21	0.02	0.08	17.26	34.96
Cr ₂ O ₃	0	0	0	0.03	0.04	0.02	0.02	0.03	0.02	0.02	0.02	0.01	0.02	0.10	0.09	0.10	0.01	0.02	0.23	0.00
FeO	7.7	8.3	8.8	9.4	9.0	0.03	0.12	0.02	0.03	0.24	0.56	0.19	0.24	0.19	0.29	0.19	0.43	0.42	30.10	1.07
MnO	0.2	0.7	0.1	0.2	0.2	0.01	0.01	0.00	0.01	0.04	0.02	0.02	0.04	0.01	0.02	0.01	0.08	1.12	0.57	0.04
MgO	0	0.0	0.0	0.0	0.0	0.00	0.01	0.00	0.00	0.00	0.02	0.02	0.00	0.01	0.00	0.01	0.01	0.16	11.57	0.89
CaO	23.	22.	23.	23.	23.	0.11	0.20	0.07	0.11	26.60	26.15	26.56	26.60	28.63	28.44	28.63	53.56	53.27	0.35	0.16

	52	69	31	50	63																			
Na ₂ O	0	0.0	0	0.0	0.0	11.87	12.20	11.93	11.87	0.02	0.04	0.04	0.02	0.03	0.02	0.03	0.00	0.04	0.11	0.15				
		3		5	5																			
K ₂ O	0.0	0	0.0	0.0	0.0	0.04	0.04	0.02	0.04	0.01	0.01	0.01	0.01	0.00	0.01	0.00	0.01	0.02	0.10	10.72				
	2		1	1	0																			
NiO	0.0	0	0	0.0	0.0	0.03	0.04	0.01	0.03	0.00	0.03	0.04	0.00	0.03	0.01	0.03	0.01	-	0.01	0.00				
	1			6	4																			
Total	96.	97.	97.	97.	97.	100.1	100.4	99.75	100.1	94.30	93.75	93.97	94.30	99.77	100.6	99.77	54.12	55.15	87.72	95.29				
	46	08	22	06	27	0	0		0															
Si	3.0	3.0	3.0	3.0	3.1	2.99	2.99	3.00	2.99	3.03	3.03	3.04	3.03	0.99	0.96	0.99	-	-	5.93	3.15				
	2	1	0	7	2																			
Al	2.4	2.4	2.4	2.2	2.2	1.00	0.99	0.99	1.00	1.96	1.95	1.96	1.96	0.08	0.11	0.08	-	-	4.42	2.75				
	7	6	4	8	7																			
Ti	0.0	0.0	0.0	0.0	0.0	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.92	0.94	0.92	-	-	0.01	0.00				
	0	1	1	0	0																			
Cr	0.0	0.0	0.0	0.0	0.0	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	-	-	0.04	0.00				
	0	0	0	0	0																			
Fe ³⁺	0.4	0.5	0.5	0.5	0.4					0.00	0.00	0.00	0.00				-	-		0.00				
	9	0	5	6	9																			
Mg	0.0	0.0	0.0	0.0	0.0	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	-	-	3.74	0.09				
	0	1	0	1	1																			
Fe ²⁺	0.0	0.0	0.0	0.0	0.1	0.00	0.00	0.00	0.00	0.01	0.03	0.01	0.01	0.01	0.01	0.01	-	-	5.46	0.06				
	2	5	3	6	0																			
Mn	0.0	0.0	0.0	0.0	0.0	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	-	-	0.10	0.00				
	1	5	1	1	1																			

Ca	1.9 8	1.9 1	1.9 6	1.9 8	1.9 9	0.00	0.01	0.00	0.00	1.99	1.97	1.97	1.99	0.99	0.98	0.99	-	-	0.08	0.01
Na	0.0 0	0.0 0	0.0 0	0.0 1	0.0 1	1.00	1.03	1.01	1.00	0.00	0.01	0.00	0.00	0.00	0.00	0.00	-	-	0.05	0.02
K	0.0 0	0.0 0	0.0 0	0.0 0	0.0 0	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	-	-	0.03	0.91
Ni	0.0 0	0.0 0	0.0 0	0.0 0	0.0 0	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	-	-	0.00	0.00
Ps	16. 43	16. 79	18. 43	19. 72	17. 90															
Ab						1.00	0.99	1.00	1.00											
An						0.00	0.01	0.00	0.00											

Numbers of ions on the basis of following oxygen numbers: Ep =12.5, Pl=8, Prh=11, Ttn=4.5, Ph=11, Chl=28, Ps (= $100 \times \text{Fe}^{3+}/(\text{Fe}^{3+} + \text{Al})$) for pistacite, * for number of average composition.

Table 3. Major element oxides (wt.%) and trace element (ppm) compositions of meta-calcisilicates rocks.

anal. No.	group I*				group II					
	09LY14	12LX16	12LX17	12LX18	09LY11	09LY12	09LY13	09LY-22	10LX07	12LX15
SiO ₂	49.58	47.94	48.08	49.78	48.87	48.33	47.22	42.28	42.70	46.48
TiO ₂	0.74	0.85	0.47	0.49	0.29	0.30	0.45	0.45	0.42	0.15
Al ₂ O ₃	9.92	13.06	8.22	8.20	5.77	5.98	6.93	9.25	8.91	5.81
Fe ₂ O ₃	11.29	10.18	11.47	10.85	10.55	8.87	8.21	10.06	10.21	11.52
MnO	0.46	0.52	0.51	0.46	0.59	0.63	0.58	0.61	0.61	0.64
MgO	7.79	6.76	8.64	8.18	8.88	8.72	7.12	5.17	5.54	8.84
CaO	15.72	14.08	18.56	17.64	20.54	23.35	24.13	25.6	25.40	23.59
Na ₂ O	2.34	2.97	1.32	1.58	0.96	0.26	0.94	0.53	0.50	0.26
K ₂ O	0.52	0.81	0.65	0.50	0.24	0.14	0.13	0.57	0.53	0.20
P ₂ O ₅	0.07	0.07	0.02	0.05	0.03	0.05	0.06	0.05	0.05	0.03
H ₂ O	1.11	1.52	1.21	1.13	1.15	1.05	1.19	0.69	0.70	0.80
CO ₂	0.40	0.90	0.72	0.88	1.70	1.80	2.05	4.41	4.09	1.20
Total	99.93	99.76	99.88	99.74	99.58	99.47	99.01	99.67	99.66	99.53
FeO	8.32	7.24	8.17	8.15	7.58	6.78	6.22	6.95	7.14	8.50
Fe ₂ O ₃	2.04	2.14	2.39	1.79	2.13	1.33	1.29	2.34	2.28	2.07
Cl	4	10	17	2	1	3	0	8	9	7
Ba	85	20	29	93	264	27	8	322	30	2
Cd	5	6	6	8	7	6	6	5	5	5
Ce	21	15	11	19	22	15	22	27	24	1
Co	36	29	36	12	20	15	18	8	8	13
Cr	171	176	207	103	62	99	330	71	177	128
Cu	18	12	16	6	17	6	6	17	16	7
Ga	11	8	8	6	21	8	9	24	22	6
Hf	4	5	5	4	6	5	6	4	4	5
Nb	10	12	11	11	14	12	13	3	8	10
Ni	67	58	60	53	41	56	110	34	57	49
Pb	1	1	1	0	6	1	2	13	12	0
Rb	11	5	7	8	18	3	2	62	56	3
Th	3	4	3	2	2	3	5	5	5	0
U	1	1	1	1	0	1	2	4	4	0
V	179	116	138	50	122	62	84	38	38	40
Y	17	12	13	9	14	9	11	9	10	6
Zn	41	34	38	10	44	46	80	15	15	14
Zr	46	63	57	44	42	42	71	49	48	36