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**PETROLOGICAL AND GEOCHEMICAL
INVESTIGATION OF
POLYMETAMORPHIC METABASIC ROCKS
FROM THE
SONGSHUGOU OPHIOLITE, CHINA**

Master Thesis

by

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2 Abstract

The Qinling Orogenic Belt is one of the major collisional orogens in eastern Asia and marks the natural boundary between North China Craton and South China Craton. (Zhang et al., 1989, 1995; Dong et al., 2011c). The Songshugou ophiolite is the largest ophiolite to be found in the North Qinling Belt. It is comprised of a series of ultrabasic and metabasic rocks, which were emplaced as a lense shaped body into the southern margin of the Qinling Group during the Proterozoic closure of the Songshugou Ocean (Dong et al., 2008). A detailed geochemical and petrological investigation of garnet amphibolites of the metabasic unit was conducted. Mineral chemical analyses and whole rock analyses were performed with electron microprobe analysis, inductively coupled plasma mass spectrometry, and wavelength dispersive X-ray fluorescence spectroscopy. The metabasic unit can be divided into garnet amphibolites and amphibolites. Amphibolites show trends of tholeiitic differentiation. Garnet amphibolites show different trends, probably related to amphibole fractionation. Garnet amphibolites display highly fractionated REE_N patterns ($La_N/Yb_N = 2.3 - 4.6$), similar to trends observed in EMORB and OIB, but with higher overall REE abundance ($\sum REE_N = 130 - 700$). Amphibolites are far less enriched in REEs and hardly show any REE fractionation ($\sum REE_N = 48 - 70$). Based upon trace elements, and REE patterns, amphibolites represent oceanic tholeiitic basalts with T-MORB and E-MORB character; Grt amphibolites, however, represent either unusual SiO₂ – poor FeO and TiO₂-rich E-MORB melts; or probably evolved dikes of alkaline affinity. To determine metamorphic conditions, the petrography was studied thoroughly, pseudosections were generated and conventional geothermobarometric calculations were performed. Thermodynamic modelling of garnet zoning patterns of major and trace elements along with inclusions, as well as textural analysis indicate a polymetamorphic history. Garnets clearly show characteristics of discontinuous growth; as they display a sudden increase in grossular, and decrease in almandine, components at the rims. REE distribution patterns of garnets also show clear trends, with rims enriched in Tb, Dy and Ho (compared to garnet cores), which can be attributed to the breakdown of amphibole at higher PT conditions. In various samples, symplectitic pyroxenes with inclusions of Mg-hornblende + plagioclase ± quartz were observed. The presence of symplectitic pyroxenes after omphacite, is commonly regarded as evidence of prior eclogite-facies metamorphism, generated in response to post-peak decompression (Wilkerson et al., 1988; O'Brien et al., 1990; Droop et al., 1990; Zhao et al., 2001). Recalculated preliminary pyroxene compositions indicate a high pressure metamorphic event. This theory is supported by garnet isopleth geothermobarometry, where garnet core isopleths indicate an older amphibolite to granulite facies metamorphic episode (630°C–740°C and 0.7–0.9 GPa). Garnet-rim isopleths, however, represent eclogite facies conditions (570°C–630°C and 1.7–2.1 GPa). Different stages of garnet breakdown to plagioclase + amphibole, were also observed. In stronger retrograded samples, plagioclase + amphibole ± quartz pseudomorphs entirely replace former garnet grains. Certain coronas and symplectites also contain Prehnite which was formed during late retrograde stages at low PT conditions (200°C–350°C). On grounds of our study, a polymetamorphic history of Songshugous metabasic rocks can be concluded. The age of the eclogite facies metamorphic event is probably related to the closure of the Shangdan Ocean during the early Paleozoic, while the age of garnet core growth remains enigmatic. Those characteristic retrograde textures together with the PT path point at decompression and later cooling possibly related to two stages of lifting in North Qinling at around 450Ma and 420Ma (Liu et al., 2013; Li Tang et al., 2016).

Keywords: Songshugou ophiolite; Qinling orogen; North Qinling Belt; HP eclogite facies

3 Zusammenfassung

Das O-W verlaufende Qinling Gebirge ist eines der Hauptkollisionsorogene Ostasiens und befindet sich zwischen dem North- und dem South China Kraton. Die O-W verlaufende Shangdan Suture Zone (SSZ) unterteilt das Gebirge in das North- und das South Qinling Terrane (Zhang et al., 1989, 1995; Dong et al., 2011c). Der Songshugou Ophiolith ist der größte, zahlreicher entlang der SSZ aufgeschlossenen Ophiolithe, und besteht aus einer ultrabasischen und einer metabasischen Einheit, die im Zuge der proterozoischen Schließung des Songshugou Ozeans auf den südlichen Teil der Qinling Group aufgeschoben wurden (Dong et al., 2008). Diese Arbeit befasst sich mit dem detaillierten petrologischen Studium der Metabasite. Proben wurden petrographisch und mineralchemisch untersucht (Elektronenstrahlmikrosonde, LA-ICPMS) und Gesamtgesteinschemismen mittels Röntgenfluoreszenzanalyse und ICPMS bestimmt. Die metabasische Einheit beinhaltet Amphibolite und Granat Amphibolite. Erstere folgen tholeiitischen Differentiationstrends, während geochemische Trends der Granat Amphibolite auf Amphibolfraktionierung zurückzuführen sind. Im Gegensatz zu den Amphiboliten ($\sum \text{REE}_N=48-70$, $\text{La}_N/\text{Yb}_N=0.8-2.0$), sind die Granat Amphibolite stark an REE angereichert ($\sum \text{REE}_N=130-700$) und zeigen EMORB/OIB ähnliche, ausgeprägte REE-Fraktionierung ($\text{La}_N/\text{Yb}_N=2.3-4.6$). Die Chemismen und REE Muster der Amphibolite sind charakteristisch für ozeanische tholeiitische Basalte mit T-MORB und E-MORB Charakter. Granat Amphibolite hingegen haben Chemismen, die entweder ungewöhnliche, SiO_2 untersättigte, an FeO und TiO_2 angereicherte E-MORB Schmelzen, oder weit entwickelte, mafische, alkaline Dikes darstellen. Granatzonierungsmuster lassen auf diskontinuierliches Wachstum schließen. Mit vergleichsweise hoher Grossular- und geringer Almandinkomponente, unterscheiden sich die Granatränder eindeutig von den -kernen. Auch REE Verteilungsmuster von Granatkern- und Randbereichen differieren stark. Die Granatränder sind an Tb, Dy, und Ho angereichert, was auf den Zusammenbruch von Amphibol bei höheren PT Bedingungen während des Granatwachstums hinweist. Matrix-Klinopyroxen tritt meist als Symplektit mit Verwachsungen von $\text{Mhbl}+\text{Pl}\pm\text{Qz}$ auf. Derartige Symplektite resultieren üblicherweise aus dem Zusammenbruch von Omphazit während dekompressiver Tektonik (Wilkerson et al., 1988; O'Brien et al., 1990; Droop et al., 1990; Zhao et al., 2001). Das Rückrechnen der Symplektite zu ursprünglichen Klinopyroxenchemismen ergab jadeitreiche Omphazitchemismen (symptomatisch für Paragenesen hochgradiger Metamorphose). Zur PT Bestimmung des Granatwachstums wurden Granatkern- und -ränder zusammen mit den darin vorkommenden Einschlüssen mineralchemisch quantifiziert und konventionelle Geothermobarometer als auch Granat-soplethengeothermobarometrie angewandt. Die Berechnungen ergaben: 1) amphibolithfazielle bis granulitfazielle Bedingungen für das initiale Granatwachstum ($630^\circ\text{C}-740^\circ\text{C}$ und $0.7-0.9$ GPa), 2) eklogitfazielle Bedingungen für Granatränder ($570^\circ\text{C}-630^\circ\text{C}$ und $1.7-2.1$ GPa). Die Bildung von Klinopyroxensymplektit, Koronen um Granat und Reaktionsbändern zwischen Matrix-Klinopyroxen und Granat, deuten auf einen dekompressionsgeprägten retrograden PT Pfad. Prehnit, welcher teilweise in Cpx-Symplektiten und Plagioklaskoronen auftritt, wurde während später Phasen des retrograden Pfades bei sehr geringen Temperaturen ($200^\circ\text{C}-350^\circ\text{C}$) gebildet. Vorliegende Ergebnisse lassen auf eine polymetamorphe Geschichte der Metabasite schließen. Die eklogitfazielle Metamorphose könnte im Bezug zur Schließung des Shangdan Ozeans im frühen Paläozoikum stehen. Das Auftreten retrograder Texturen und niedergradiger Minerale wie Prehnit, lässt auf einen retrograden PT Pfad mit anfänglicher Dekompression und späterem Abkühlen schließen der möglicherweise im Bezug zur 2 phasigen Hebung des North Qinlings um 450Ma und 420Ma steht (Liu et al., 2013; Li Tang et al., 2016).

Schlagwörter: Songshugou Ophiolith; Qinling Orogen; North Qinling Belt; HP eklogitfaziell

4 INDEX

| | | |
|------------|---|-----------|
| 1 | ACKNOWLEDGEMENT | 2 |
| 2 | ABSTRACT | 3 |
| 3 | ZUSAMMENFASSUNG | 4 |
| 4 | INDEX | 5 |
| 5 | INTRODUCTION | 7 |
| 5.1 | Geological Frame | 7 |
| 5.1.1 | The Qinling Orogenic Belt (QOB) | 8 |
| 5.1.2 | Tectonic belts of the QOB | 8 |
| 5.1.3 | Songshugou ophiolite | 11 |
| 5.2 | Analytical techniques | 13 |
| 5.2.1 | REM and electron microprobe analysis: | 13 |
| 5.2.2 | Trace element and REE mineral analysis: | 14 |
| 5.2.3 | Whole rock chemistry: | 14 |
| 5.3 | Sampling | 16 |
| 6 | PETROGRAPHY | 17 |
| 6.1 | Reaction-bands between garnet and Cpx-symplectite | 17 |
| 6.2 | Clinopyroxene-symplectites | 22 |
| 7 | MINERAL CHEMISTRY | 24 |
| 7.1 | Cpx-symplectites | 24 |
| 7.1.1 | Cpx-Amp-Pl symplectites | 25 |
| 7.1.2 | Cpx-Qz ± Pl symplectites | 26 |
| 7.1.3 | Cpx-Amp-Prh-Pl symplectites | 27 |
| 7.1.4 | Cpx-Qz-Pl-Pmp-Amp symplectites | 28 |
| 7.1.5 | Mhb-Act-Pl symplectites | 29 |
| 7.2 | Reaction-bands between garnet and Cpx-symplectite | 31 |
| 7.3 | Matrix minerals | 34 |
| 7.3.1 | Apatite | 34 |
| 7.3.2 | Sphene | 35 |
| 7.3.3 | Clinozoisite/epidote, Chlorite, Ilmenite | 36 |
| 7.4 | Trace elements and REE of matrix amphibole and apatite | 37 |
| 8 | GARNET CHEMISTRY AND ZONING PATTERNS | 39 |
| 8.1 | Trace and REE chemistry of garnet | 45 |
| 8.2 | Mineral Chemistry of garnet inclusions | 55 |

| | | |
|-----------|--------------------------------------|-----------|
| 9 | GEOCHEMISTRY | 62 |
| 9.1 | Major and trace element geochemistry | 62 |
| 9.2 | REE geochemistry and spider diagrams | 67 |
| 9.3 | Discrimination diagrams | 70 |
| 10 | PSEUDOSECTIONS | 76 |
| 11 | DISCUSSION AND INTERPRETATION | 84 |
| 12 | REFERENCES | 90 |

5 Introduction

5.1 Geological Frame

China is located in one of the most complicated tectonic areas in the world. Since archaic Archean China underwent 17 significant tectonic events which lead to a tectonically complex framework. It is comprised of three major Precambrian cratons and several surrounding Phanerozoic orogenic belts i.e. (North China Craton NCC, South China Craton SCC and Tarim Craton). All cratons evolved individually and amalgamated during the Paleozoic period through the Upper Triassic, forming the main part of the Eastern Asia Continent. The SCC is subdivided into the Yangtze Block (YZB) and the Cathaysia Block (CTB) which were cohered during the Neoproterozoic (Zhou et al., 2008; Shu, 2012). All major tectonic units (cratons, and fold systems) are displayed in Fig. 1.

The NCC (North China Craton) is considered to be one of the oldest cratons in the world (3.8 Ga) and mainly comprises late Paleoproterozoic to Paleozoic sedimentary covers, Precambrian metamorphic basements and Mesozoic intrusions. The craton extends over an area of about 1.700.000 km² in north-eastern China, northern Korea and the southern parts of Mongolia; and is composed of several micro-blocks that had been amalgamated about 2.5 Ga ago (Zhai 2011; Zhai and Bian, 2001).

The SCC (South China Craton) consists of the Yangtze Craton, and the Cathaysia Craton; which are separated by the Jiangnan Orogenic Belt. The Yangtze Craton contains two basements: An upper-level metamorphic fold basement in the upper part, and a middle-level metamorphic basement in the lower part (Ren et al., 1990).

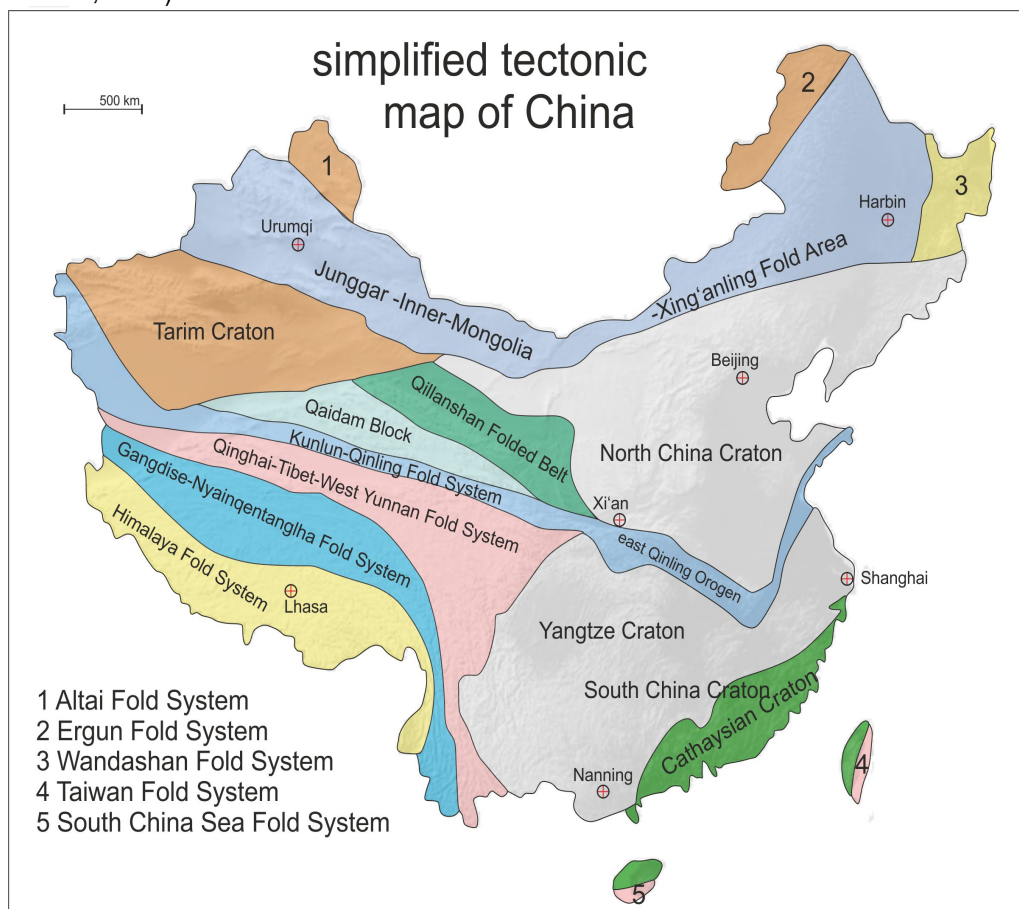


Fig. 1 Chinese map of regional geological units (modified after Ren et al. 1990)

5.1.1 The Qinling Orogenic Belt (QOB)

The Qinling Orogenic Belt (QOB) extends west-east nearly 2500 km across Central China. Conjoined with the Dabie, Qilian and Kun Lun mountains, it is one of the major collisional orogens in eastern Asia situated in between North China Craton (NCC) and South China Craton (SCC). To the west, this belt unites with the Qilian and Kun Lun belts. To the east, it is truncated by the N-S striking Tan Lu Fault. Multiple stages of convergence between the two cratonic blocks (NCC, SCC) induced a complex geologic framework (Tseng et al., 2009; Dong et al., 2011c; Wu and Zheng, 2013). The QOB was thrust onto the southern margin of the NCC along the Lingbao-Lushan-Wuyang fault (LLWF) in the north; and onto the northern margin of the SCC along the Mianlue-Bashan-Xianguang fault (MBXF) in the south. The Shangdan Suture Zone (SSZ), a massive fault system, traverses the orogenic belt from east to west dividing it into North Qinling Belt (NQB) and South Qinling Belt (SQB) (GW.Zhang et al., 1995a; S.G. Li et al., 1996; Dong et al., 1999; GW.Zhang et al., 2001; Xu et al., 2002; Dong et al., 2014). Along this zone, several early Paleozoic ophiolites and subduction-accretion related volcanic arc assemblages are exposed, hence, it has been regarded as the main collision zone between NCC and SCC.

Previously, NCC and SCC were assumed to represent former parts of a united China continent; before they were segregated by the opening of the Shangdan Ocean (Yuan, 1991; Zhang et al., 1991). Yet further study has shown that that Precambrian Basement and cover sequences of both units diverge significantly. Hence, independent tectonic histories of the NCC and SCC before Phanerozoic collision were concluded (Zhang et al., 1996; G.W. Zhang et al., 2001; Zhu, 2001; Zhai, 2013, 2014; Zhao and Zhai, 2013; Dong et al., 2014).

Among most authors, the assumption of the Shangdan suture zone (SSZ) representing the main subduction and collision zone of NCC and SCC, is widely accepted. A temporal allocation of those events, however, is controversial. According to different authors it ranges from early Paleozoic, Devonian to Triassic (e.g.; Kröner et al., 1993; Li et al., 1993a; Okay and Sengör, 1993; Yin and Nie, 1993; Li, 1994; Gao et al., 1995; Ames et al., 1996; Zhang et al., 1997a; Hacker et al., 1998; Zhai et al., 1998; Zhang et al., 2001).

5.1.2 Tectonic belts of the QOB

With the Paleozoic Shangdan Suture Zone (SSZ), the Triassic Mianlue Suture Zone (MLSZ) and several other major strike-slip faults, the QOB can be tectonically divided into 5 basic zones: **1** Southern North China Craton (S-NCC), **2** North Qinling Belt (NQB), **3** Central Qinling Belt (CQB), **4** South Qinling Belt (SQB) and **5** northern South China Craton (N-SCC).

The S-NCC is bounded by the Lingbao-Lushan-Wuyang fault (LLWF) in the north and the Luonan-Luanchuan fault (LLF) in the south. It mainly comprises deformed and metamorphosed (dominantly amphibolite facies) Upper Archean – Lower Proterozoic basement complexes such as the Taihua Group and the Tietonggou Group (Zhang et al., 2000) which are superimposed by: **1** low-grade to non-metamorphic Mid-Proterozoic rift-related volcanic rocks, **2** Mid- to Neo-Proterozoic marine facies clastic and carbonate sequence, **3** Uppermost Neoproterozoic tillite (G.W. Zhang et al., 2001) and **4** Cambrian to Ordovician passive continental margin sequences. All those overlaying rocks were thrust along the LLWF onto the NCC. During Cretaceous, manifold granitoid plutons intruded into S-NCC (e.g. Lantian, Laoniushan and Huashan granitoids) (Mao et al., 2005; Li et al., 2006a; Ye et al., 2006; Zhu et al., 2008a; Zhang et al., 2010). In the south, the S-NCC is bounded by the LLF and the Kuanping Suture (KPS) to the NQB. (Dong et al., 2011, 2016).

The CQB is situated between SSZ and the MXDZ and mainly consists of Neoproterozoic gneiss and amphibolite basement rocks represented by the Foping Group, and the Tongbaishan (Tongbai and

Hong'an Groups). Cover sequences of the eastern CQB are mainly represented by pelagic turbidite rocks, which were deposited into a forland basin during Devonian times (Dong et al., 2013). In the west, the CQB includes a northern Upper Paleozoic zone and a southern Triassic zone separated by the Minxian-Danchang and Fengxian fault.

The SQB is bounded by the Mianlue Suture Zone (MXLZ) in the north and the Yangpingguan fault (YPGF) as well as the Mianlui-Bashan-Xianguang fault (MBXF) in the south. Along the MBXF, the QOB was thrust onto the northern margin of the SCC during Late Paleozoic to Middle Triassic times (Zhang et al., 1995). The SQB largely consists of: **1** Neoproterozoic basement, **2** Neoproterozoic clastic and volcanic rocks, and **3** Upper Proterozoic to Lower Paleozoic successions, as well as minor Upper Paleozoic to Middle Triassic strata in the northern SQB (Dong and Santosh., 2016; Zhang et al., 2001).

The N-SCC, also known as the foreland fold-thrust belt, is bound to the SQB by the MBXF, and progressively grades into undeformed Mesozoic sequences within Jiangnan and Sichuan basins in the main region of the SCC. The SCC is comprised of a highly metamorphosed Neoproterozoic crystalline basement, greenschist facies Meso-Neoproterozoic transitional basement, and a cover sequence of non-metamorphosed Proterozoic-Mesozoic clastic and carbonate rocks (G.W.Zhang et al., 1995a,b, 2000; Dong et al., 2011a).

The NQB is situated between the LLF and the SSZ (Shangdan Suture Zone). It extends over 1000 km from east to west and mainly comprises: **1** Precambrian crystalline basement units, **2** Neoproterozoic-Lower Paleozoic ophiolites and **3** Mesoproterozoic-Paleozoic volcano-sedimentary assemblages which are sparsely overlain by Phanerozoic cover rocks such as Carboniferous and/or Permian clastic sediments (Dong et al., 2011a). The Precambrian basement underwent amphibolite facies metamorphism at ~ 1.0 Ga and greenschist facies metamorphism at ~ 400 Ma (Liu et al., 1993; Zhang et al., 1994b).

The main units exposed in the NQB from north to south have been designated as the Kuanping Group, Erlangping Group, Qinling Group, Songshugou ophiolite and Danfeng Group (Danfeng ophiolite included). Those units are separated by thrust faults and ductile shear zones.

The Meso-Neoproterozoic Kuanping Group consists mainly of an ophiolite unit (greenschist, amphibolite facies) and a meta-sedimentary unit (quartzite, mica schist, marble). Protoliths of the ophiolitic metabasites are tholeiitic basalts with N-MORB to T-MORB geochemistry, representing metamorphosed oceanic crust (Zhang and Zhang, 1995; Diwu et al., 2010; Dong et al., 2014). The metasedimentary unit is considered to represent overlying accretionary wedge material possibly related to the closure of the Paleozoic Erlangping back-arc basin with youngest detrital zircon ages approaching 610 to 500 Ma. (C.L.Zhang et al., 1994, 2004; Yan et al., 2008; Dong et al., 2011b). Sm-Nd whole rock isochron ages range from 0.94 to 1.2 Ga (Zhang et al., 1994; Zhang and Zhang, 1995).

The Erlangping Group is comprised of three units: **1** the Erlangping ophiolite (pillow basalts, sparse ultra-mafic rock, sheeted dike basalt, gabbro and radiolarian chert), **2** clastic sedimentary rocks, and **3** carbonate rocks. Geochemistry of basalts and radiolarites suggest a back-arc basin existing during Ordovician and Silurian (Wang et al., 1995; Sun et al., 1996).

The Danfeng Group discontinuously outcrops along the SSZ, and contains metavolcanic and meta-sedimentary rocks. Meta-mafic rocks of this unit are regarded as ophiolite formed during early Paleozoic (Dong et al., 2011b).

The Qinling Group is generally regarded as micro continental terrain (G.W.g et al., 1995). It consists of gneiss, amphibolite, and marble (clastic rocks and limestone as protolith) (You et al., 1991). Zircon ages of gneiss and amphibolite suggest an evolutionary history of late Paleoproterozoic to Mesoproterozoic

times (You et al., 1991; Shi et al., 2009; Yang et al., 2010; Wan et al., 2011; Diwu et al., 2012). A simplified tectonic map of the eastern QOB with its main geological units is displayed in Fig. 2.

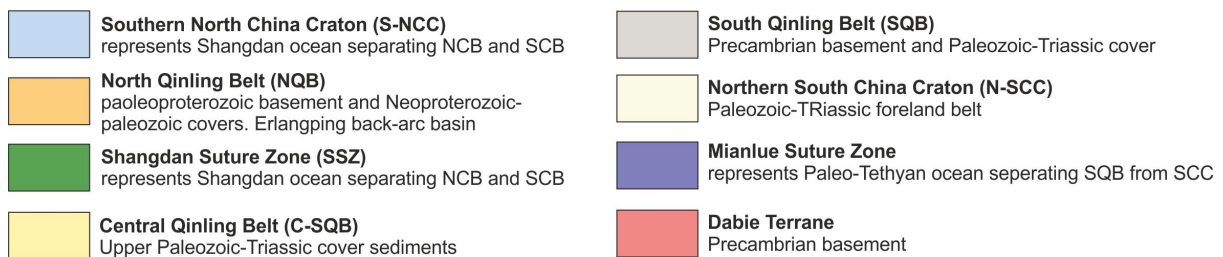
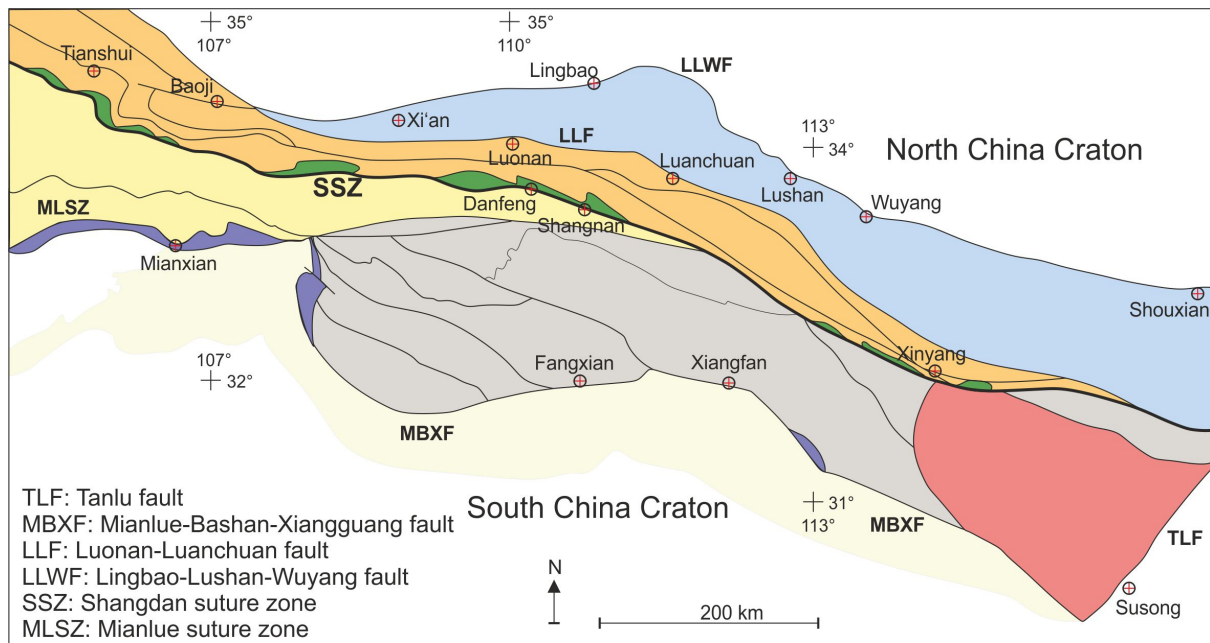


Fig. 2 Simplified tectonic map of the eastern QOB showing tectonic divisions. Modified after Dong et al. 2011a

5.1.3 Songshugou ophiolite

The Songshugou ophiolite complex is located in eastern Shaanxi Province and western Henan Province. It outcrops along the SSZ as a rootless nappe which was emplaced into the southern margin of the Qinling Group. The complex forms a SE-NW trending block about 27 km long and 3 km wide. In the north, the ophiolite has been thrust along the Jiuling ductile shear zone onto the Qinling group. In the south it is bound to the Qinling Group and the Fushui gabbroic complex by the Xigou fault (Fig. 4, & Fig. 3).

It consists mainly of a series of ultrabasic, and a variety of tholeiitic metabasic, rocks. REE patterns, Trace element geochemistry and isotope composition show that the mafic rocks are mainly E-MORB and T-MORB metabasalts (Dong et al., 2008b). Nd, Sr and Pb isotopic data (Dong et al., 2008a) are isotopically similar to those of Indian Ocean MORB (Xu et al., 2002; Xu and Castillo, 2004). Hence, the metabasalts are believed to have been derived from a mantle source with a DUPAL isotope anomaly produced by exchange between the asthenosphere and a mantle plume (e.g. Dupre and Allegre, 1983; Hamelin et al., 1986; Mertz et al., 1991). The country rocks of Qinling Group are marble, and a gneiss-migmatite complex (Zhou et al., 1995).

Within the ophiolite sequence, fresh peridotites (mostly dunites and harzburgites), can be found. Fine grained dunites and harzburgites display schistose deformation with mylonitic textures and relict olivine porphyroblasts. Medium to coarse grained dunites exhibit typical cumulate textures without any conspicuous metamorphic overprint (Dong et al., 1996). Harzburgite crops out as undeformed to slightly deformed patches, lenses and veins penetrating dunite mylonite. Dunite mylonites show typical high-temperature deformational fabrics and dislocation, probably imposed by shearing processes in a subduction environment at temperatures beyond 1000°C (Dong et al., 1996). Low CaO (<0.39 wt.%) and Al₂O₃ (<0.51 wt.%) in conjunction with high MgO (41–48 wt.%) contents classify the peridotites as depleted, non-fertile mantle rocks. Dunites and harzburgites mainly consist of heterogranular forsterite rich olivine, enstatite rich orthopyroxene, Ca-amphibole (tremolite) and Mg-Fe-Mn amphibole (cummingtonite) ± chlorite ± talc ± chromite. Chromite occurs as disseminated phase but sometimes forms massive chromite bands. Chromites show increasing Fe-Cr zoning patterns towards their rim, which could be symptomatic of serpentinization or metamorphic processes (Pohl 2005). Chromite commonly includes sulfides e.g. pentlandite, pyrrhotine and Laurite (RuS₂) rich PGMs (platinum group minerals). Podiform chromite mineral chemistry clearly confirms the ophiolitic origin of Songshugou metabasic unit. The peridotite unit is cut by granitic, pegmatitic and dioritic intrusives. An up to 10 m wide serpentinized zone separates the peridotite from the metabasic unit.

The Metabasic unit occurs structurally underneath the peridotite body. It mainly consists of **1** hornblende amphibolite, **2** augen amphibolite and **3** garnet amphibolite. Hornblende amphibolite is structurally located at the lowermost part; in other words, the outmost parts of the unit. Augen amphibolite, presumably emerged out of garnet bearing metabasites, outcrops as 10 – 200 m wide areas structurally between garnet amphibolite and hornblende amphibolite. Garnet amphibolites occur as discontinuous lenses in the innermost or uppermost part of the metabasic unit. The modal abundance of garnet increases towards the core of the lenses, probably due to different degrees of garnet retrogression. Even though previously considered to represent a contact aureole around the peridotitic unit (Huang, 1984), garnet amphibolites were ascribed as retrograde eclogites in later publications (An et al., 1985; Liu et al., 1995; Chen et al., 1993; Liu & Zhou., 1994; Zhang, 1999). Garnet amphibolites and peridotites are separated by a ~ 10 m wide zone of serpentinization. Whole rock chemistry analyses of metabasic rocks point at basaltic protoliths with N-MORB and E-MORB characteristics (Zhou et al., 1995; Liu et al., 2004; Dong et al., 2008). Other subordinate rocks occurring in the metabasic Songshugou unit are felsic granulites close to the Xigou fault as well as marble and peridotitic rocks outcropping as elongated blocks. The

genesis of garnet amphibolites is considered to be related to oceanic subduction, and the emplacement of the Songshugou ophiolite (Liu et al., 1995). Several publications suggest a peak metamorphic age of 537 – 480 Ma based on obtained zircon U-Pb age data (Su et al., 2004; Chen et al., 2004; Liu et al., 2009; Qian et al., 2013; Li et al., 2014b, Li Tang et al., 2016). Metabasic rocks yield Sm-Nd whole rock isochron ages of 1030 ± 46 Ma, with depleted mantel model ages (T_{DM}) ranging from 1271 to 1440 Ma, describing the age of basaltic protolith (Dong et al., 2008a). Garnet amphibolites are the focus of this present study.

The Fushui meta-gabbroic complex is situated to the south of the Songshugou complex. It consists mainly of metagabbro and metadiorite, and lesser amounts of tonalite and ultrabasic rocks. With an area of about 52.5 km² it outcrops as the largest meta-gabbroic complex in the NQB. Geochemistry indicates arc-magmatic signatures with calc-alkalic rocks cross-cutting tholeiitic rocks (Zhang Z-J. 1991). Whole - rock Sm-Nd model ages (1290-1570 Ma) of metagabbros, point at a Jinningian related evolution of Fushui complex.

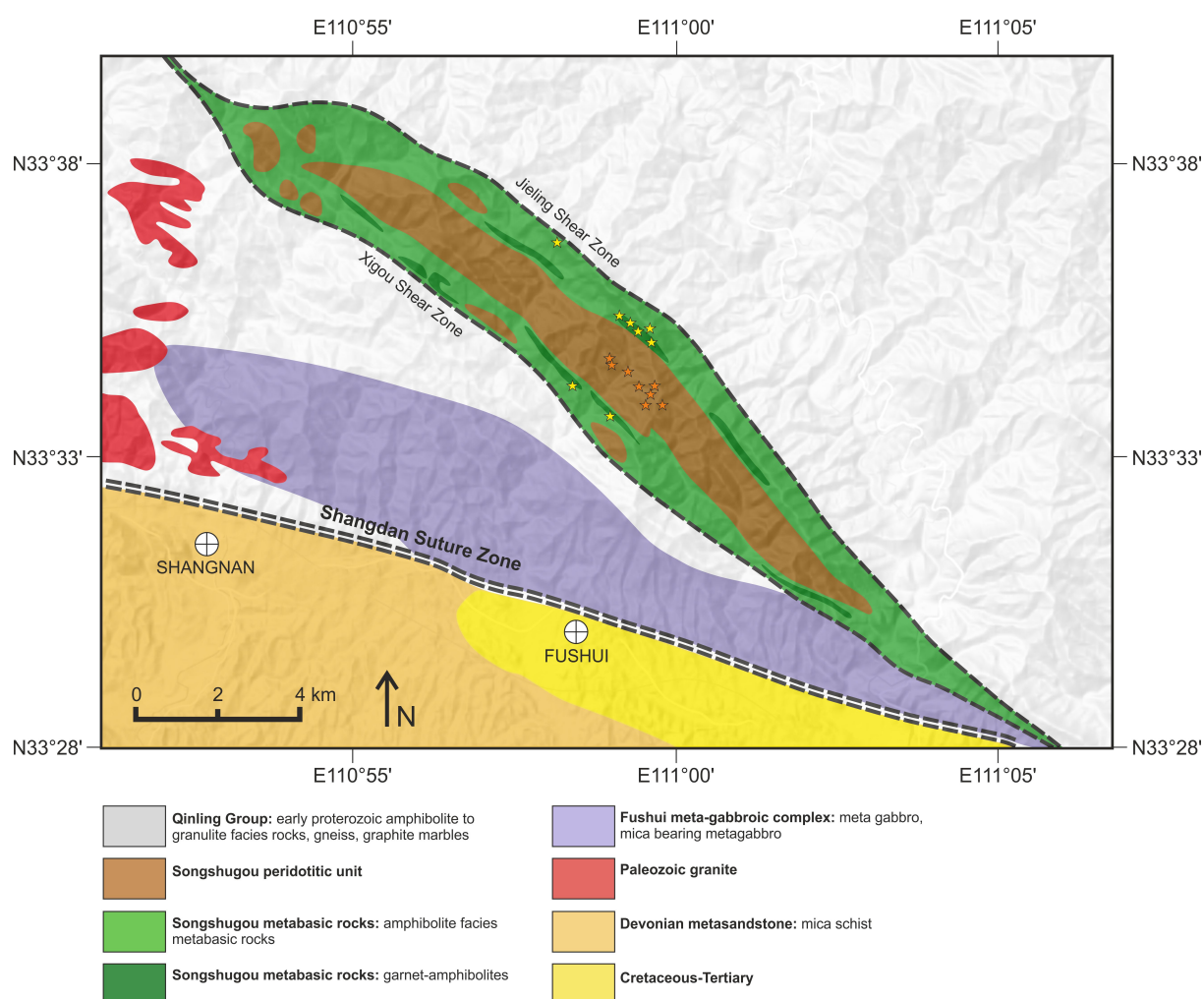


Fig. 3 Geological map of the Songshugou ophiolite, NQB (after Dong et al., 2008) yellow stars represent metabasic samples, orange ones samples of peridotite

5.2 Analytical techniques

5.2.1 REM and electron microprobe analysis:

Samples were prepared as polished thin sections (~30µm) and thick sections (~120µm); and then, thoroughly investigated by transmitted and reflected light microscopy. Quantitative mineral analyses and chemical mappings, were carried out by using a scanning electron microscope JEOL JSM 6310 with a LINK ISIS energy dispersive system (measurement time for energy dispersive elements 100 sec) equipped with a MICROSPEC wavelength dispersive system (measurement time for wavelength dispersive elements 20 sec on peak position) at the Institute of Earth Sciences, Mineralogy and Petrology, University of Graz. Then, additionally, a JEOL JXA 8200 electron microprobe (UZAG EUGEN F.STUMPFL Electron Microprobe Laboratory, at the Montanuniversity, Leoben) was utilized for detailed petrology on carbon-coated thin sections. Conditions of measurements on both devices were ~ 5 (SEM) and 12 (EPMA) nA beam current, ~1 µm beam diameter (point mode) and 15 kV acceleration voltage. Most minerals were measured in point mode except for plagioclase, which was analyzed using a rastered beam (10 x 10 µm) to minimize loss of Na and K, if grain sizes permitted. Acceleration voltage was increased to 20 kV for sulfur compound analysis. Natural and synthetic standards used for element calibration on the JEOL JSM 6310 are listed in table 1 and table 2. Element distribution mappings were executed with a JEOL JXA 8200 electron microprobe.

table 1 used standards for silicates for energy and wavelength dispersive analysis with JEOL JSM 6310

| element | dispersive system | standard |
|---------|-------------------|----------------------------------|
| F | WDX | F-phlogopite S61 HO88 |
| Na | WDX | jadeite MS 2970 A Clear Creek |
| Mg | EDX | garnet S6 #12442 Gore Mountain |
| Al | EDX | adular S1 |
| Si | EDX | adular S1 |
| P | EDX | F-apatite S3 Wilberforce |
| Cl | EDX | atacamite S9 NMW |
| K | EDX | adular S1 |
| Ca | EDX | wollastonite Auerbach |
| Ti | EDX | titaniteS4 Bündner Oberland ETHZ |
| V | EDX | chromite S7 53-IN-8 |
| Cr | EDX | chromite S7 53-IN-8 |
| Mn | EDX | rhodonite S5 660-388 |
| Fe | EDX | garnet S6 #12442 Gore Mountain |
| Ni | EDX | NiO_Ni-Tiegel |
| Cu | EDX | Cu-Metall |
| Zn | EDX | ghanite USNM 145883 |

table 2 Standards used for sulphides, for energy analysis with JEOL JSM 6310

| element | dispersive system | standard |
|---------|-------------------|---|
| S | EDX | chalcopyrite Western mines |
| Cr | EDX | chromite 53-in-8 |
| Fe | EDX | chalcopyrite Western mines |
| Ni | EDX | nickel-metal |
| Cu | EDX | chalcopyrite Western mines |
| Zn | EDX | %C21 Zn60.3Fe6.43S33.27 |
| As | EDX | Cabri-526 (PtAs ₂) |
| Ru | EDX | Ru-metal |
| Rh | EDX | Rhodium-metal |
| Pd | EDX | Cabri-461 (Pd ₃ As) |
| Sb | EDX | Cabri-141 (NiSb) |
| Te | EDX | Dutrizac (Bi ₂ Te ₃) |
| Os | EDX | Osmium-metal |
| Ir | EDX | Iridium-metal |

Mineral formulas and geothermobarometry were calculated using the program PET 7 (Dachs, 1998).

5.2.2 Trace element and REE mineral analysis:

Trace elements and REEs of mineral phases were obtained in polished thick sections through laser ablation inductively coupled plasma mass spectrometry (LA-ICP MS) (NAWI Graz Labs for Water, Mineral and Rocks, Graz University of Technology) with an ESI New Wave 193 Excimer Laser (193nm wavelength) attached to a quadrupole Agilent 7500 CX mass spectrometer. A beam size diameter of 35 µm, 60 s of ablation and a dwell time of 35 msec for each mass data acquisition was used for element analyses. NIST SRM 612 glass was used for standardization and the USGS reference glass BCR-2G was analyzed as monitor standard. The quality of spot measurements was assessed using the software GLITTER. For garnet and amphibole analysis Si was taken as internal calibration element, Ca for apatite.

5.2.3 Whole rock chemistry:

Sample preparation was carried out at the Institute of Petrology and Mineralogy, University of Graz. Fresh rock samples were crushed and powdered using a carbide mill. Whole rock major element concentrations were obtained by wavelength dispersive fluorescence spectrometry (WDXRF) on fused glass discs using a Bruker Pioneer S4 under standard conditions (Institute of Earth Sciences, Mineralogy and Petrology, University of Graz). For quality control of the method, one randomly selected sample was analyzed twice. Whole rock data processing was executed using the R language based software package GCDkit (Geochemical Data Toolkit, version 3) (Janousek et al., 2006a). Perplex_X version 6.7.3 (Connolly, 2005) was used for thermodynamic phase equilibrium calculations with the revised hp04ver.dat dataset from Holland and Powell (1998).

Inductively coupled plasma mass spectrometry (ICP MS) was used to determine whole rock trace element and rare earth element REE concentrations with abundances < 20 ppm (Institute of chemistry, University of Graz) with a quadrupole Agilent 7500 CX mass spectrometer.

Mineral abbreviations used according to Whitney and Evans (2010) are displayed in table 3.

table 3 Mineral abbreviations used according to Whitney and Evans (2010)

| Mineral abbreviations after Whitney and Evans, 2010 | | | |
|--|-----------------|-----|--------------------|
| Act | actinolite | Jd | jadeite |
| Aeg | aegirine | Kfs | K-feldspar |
| Ab | albite | Lws | lawsonite |
| Afs | alkali feldspar | Liq | liquid |
| Alm | almandine | Mhb | magnesiohornblende |
| Als | alumosilicate | Mag | magnetite |
| Amp | amphibole | Mnz | monazite |
| An | anorthite | Ol | olivine |
| Ap | apatite | Omp | omphacite |
| Aug | augite | Or | orthoclase |
| Bt | biotite | Opx | orthopyroxene |
| Ccp | chalcopyrite | Prg | pargasite |
| Chl | chlorite | Pn | pentlandite |
| Chr | chromite | Ph | phengite |
| Czo | clinozoisite | Pl | plagioclase |
| Coe | coesite | Prh | prehnite |
| Cum | cummingtonite | Pmp | pumpellyite-(Al) |
| Di | diopside | Py | pyrite |
| Ed | edenite | Prp | pyrope |
| En | enstatite | Po | pyrrhotite |
| Ep | epidote | Qz | quartz |
| Fsp | feldspar | Rt | rutile |
| Grt | garnet | Sps | spessartine |
| Ged | gedrite | Spn | sphene |
| Gln | glaucophane | Tlc | talc |
| Grs | grossular | Tr | tremolite |
| Hst | hastingsite | Ts | tschermakite |
| Hbl | hornblende | Zrn | zircon |
| Ilm | ilmenite | Zo | zoisite |

5.3 Sampling

Schistose plagioclase amphibolites (X32, X33), garnet amphibolites (X35, X36, X37) and augen amphibolites (X38, X42, QS2D) were collected from the Songshugou metabasic-ultramafic complex together with harzburgites, dunites and chromite-peridotites (QS2H1, QS2H1.2, QS2A, QS2B, QS2C, QS2E, QS2F, QS2G). Sample locations with rough descriptions are presented in table 4 and table 5. The focus of this study was on the metabasic unit, especially the garnet-amphibolites. Peridotitic rocks are only mentioned peripherally.

table 4 metabasic samples, Songshugou ophiolite

| sample nr. | rock type | locality | mineralogy |
|------------|-----------------------------------|------------------------|---|
| X32 | schistose plagioclase-amphibolite | 33-33.895N 110-58.369E | Qz, Pl, Amp |
| X33 | schistose plagioclase-amphibolite | 33-34.230N 110-58.236E | Qz, Pl, Amp |
| X35 | garnet-amphibolite | 33-34.671N 110-58.038E | Amp, Grt, Cpx, Pl, Qz, Ilm, Czo/Ep, Ap |
| X36 | garnet-amphibolite | 33-34.671N 110-58.038E | Amp, Grt, Cpx, Pl, Qz, Ilm, Czo/Ep, Ap, Spn, Bt |
| X37 | garnet-amphibolite | 33-34.671N 110-58.038E | Amp, Grt, Cpx, Pl, Qz, Ilm, Czo/Ep, Ap |
| X38 | augen-amphibolite | 33-34.671N 110-58.038E | Amp, Grt, Cpx, Pl, Qz, Ilm, Czo/Ep |
| X42 | augen-amphibolite | 33-34.671N 110-58.038E | Amp, Pl, Qz, Ilm, Czo/Ep, Bt |
| QS2D | augen-amphibolite | 33-34.671N 110-58.038E | Amp, Pl, Ilm, Czo/Ep |

table 5 peridotite samples, Songshugou ophiolite, PGM abbreviation for platinum group minerals

| sample nr. | rock type | locality | mineralogy |
|------------|----------------------|------------------------|-----------------------------|
| QS2H1 | chromite-harzburgite | 33-32.109N 110-57.881E | Ol, Amp, Chl, Chr, PGM, Opx |
| QS2H2 | chromite-harzburgite | 33-32.109N 110-57.881E | Ol, Amp, Chl, Chr, PGM, Opx |
| QS2B | harzburgite | 33-32.109N 110-57.881E | Ol, Amp, Chr, Opx |
| QS2E | chromite-dunite | 33-32.109N 110-57.881E | Ol, Amp, Chr |
| QS2F | ol-orthopyroxenite | 33-32.109N 110-57.881E | Ol, Amp, Chl, Chr, Opx |
| QS2C | chromite-harzburgite | 33-32.109N 110-57.881E | Ol, Amp, Chr, Opx |
| QS2G | harzburgite | 33-32.109N 110-57.881E | Ol, Amp, Chl, Chr, Opx, Tlc |
| QS2A | harzburgite | 33-32.109N 110-57.881E | Ol, Amp, Chr, Opx |

6 Petrography

Metabasic rocks were collected and studied in thin sections. Sample locations are displayed in Fig. 3. Seven samples were selected for detailed electron microprobe analysis. As already described by Zhang et al. (1999), the metabasic unit can be subdivided into three groups according to mineral assemblage and textures: (1) hornblende amphibolite, (2) augen amphibolite, and (3) garnet amphibolite. Hornblende amphibolite is a massive to foliate rock which mainly consists of fine to medium-grained green and brown Amp + Pl + Qz + Ilm ± Czo/Ep. (Fig. 4a, b, c). Augen amphibolite is comprised of fine to medium-grained green amphibole and fine-grained mineral aggregates (Pl + Qz ± Amp augen) which post-date garnet porphyroblasts. Aggregates after garnet are more or less elongated parallel to the foliation (Fig. 4h, i). Garnet amphibolite is a coarse to medium-grained massive inhomogeneous rock, which shows compositional layering defined by modal variation of Grt, Cpx and Amp. Garnet mode within rocks can vary dramatically at the centimeter scale from 60 vol.% to near zero. (Fig. 4d, e, f, g). Garnet amphibolite exhibits a mineral assemblage of poikiloblastic Grt, Cpx, various generations of calcic Amp, Pl, Qz, Czo/Ep, Ilm, Ap and minor amounts of Rt, Zrn ± Prh ± Pmp ± Bt ± Spn ± sulfides ± Chl. In certain samples sphene occurs in higher proportions. Garnets are usually embedded in a fine-grained symplectitic matrix of tightly intergrown Cpx, Amp and Pl. Various conspicuous reaction textures were observed such as vermicular Cpx-symplectites, coronal reaction bands developed between garnet and symplectitic Cpx and fine grained mineral aggregates after Grt or Cpx. These were clearly caused by retrogression. Garnet is generally rounded with grain sizes of 0.3 – 5 mm. In some cases the approximate location of the original grain boundary of euhedral garnets can be inferred by observation of hexagonal outlines of Pl-Amp aggregates replacing garnet. Pargasitic Amp, albitic Pl, Czo/Ep, Ilm, Ap, Zrn, Rt ± Cpx commonly occur as garnet inclusions. Compared to garnet rims, cores appear lighter in the microscope and are inclusion rich. Occasionally inclusion alignment of snowball structure is observed in garnet cores (Fig. 4g), which is indicative of syntectonic growth. Garnet porphyroblasts show chemical zoning patterns with cores low in X_{Grs} , a sudden increase in X_{Grs} marking Rim1 and a decrease marking Rim2. Zoning patterns and mineral chemistry will be discussed in subsequent chapters. High abundances of sphene are idiosyncratic for sample X36, where big idiomorphic to sub-idiomorphic grains (with lengths of up to 500 μm) occur as matrix minerals and garnet inclusions.

6.1 Reaction-bands between garnet and Cpx-symplectite

50 – 500 μm wide reaction bands separate garnet from fine-grained Cpx-symplectite. Those reaction bands can be divided into 4 zones as is illustrated in Fig. 5 and Fig. 6. Zone 1: intact Grt; Zone 2: coronal textures around Grt (Pl ± Amp); Zone 3: thin layer of zoned amphibole (\pm Ilm ± Czo/Ep ± Ap); and Zone 4: Cpx-symplectite. Mineral assemblages throughout the reaction-bands become progressively less hydrous towards Grt. Fisher specified the following criteria for recognizing textures generated by diffusion-controlled reactions: “..diffusion-controlled structures characteristically have a strong spatial organization, with well-defined mineral zones showing sharp changes in compositions at zone boundaries, all arranged in an orderly sequence of increasing or decreasing chemical potential” (Fisher., 1977). The coronas around the garnet display a variety of well-organized textures, diagnostic of diffusion-controlled reaction. The most commonly observed coronal textures from Zone 2 are: (1) Pl coronas, (2) vermicular Pl-Amp coronas, (3) vermicular Pl-Amp-Prh coronas, and (4) granular Pl-Qz-Amp coronas surrounding garnet remnants in strongly retrograded samples (X38, X42). Coronas with vermicular textures are radially arranged around garnet grains with internal structures perpendicular to the surface of the garnet. Czo/Ep with grain sizes up to 100 μm sometimes occurs in reaction zones 2 and 3, as well as small (~20 μm) grains of ilmenite. Prominent reaction bands are displayed in Fig. 5 and Fig. 6.

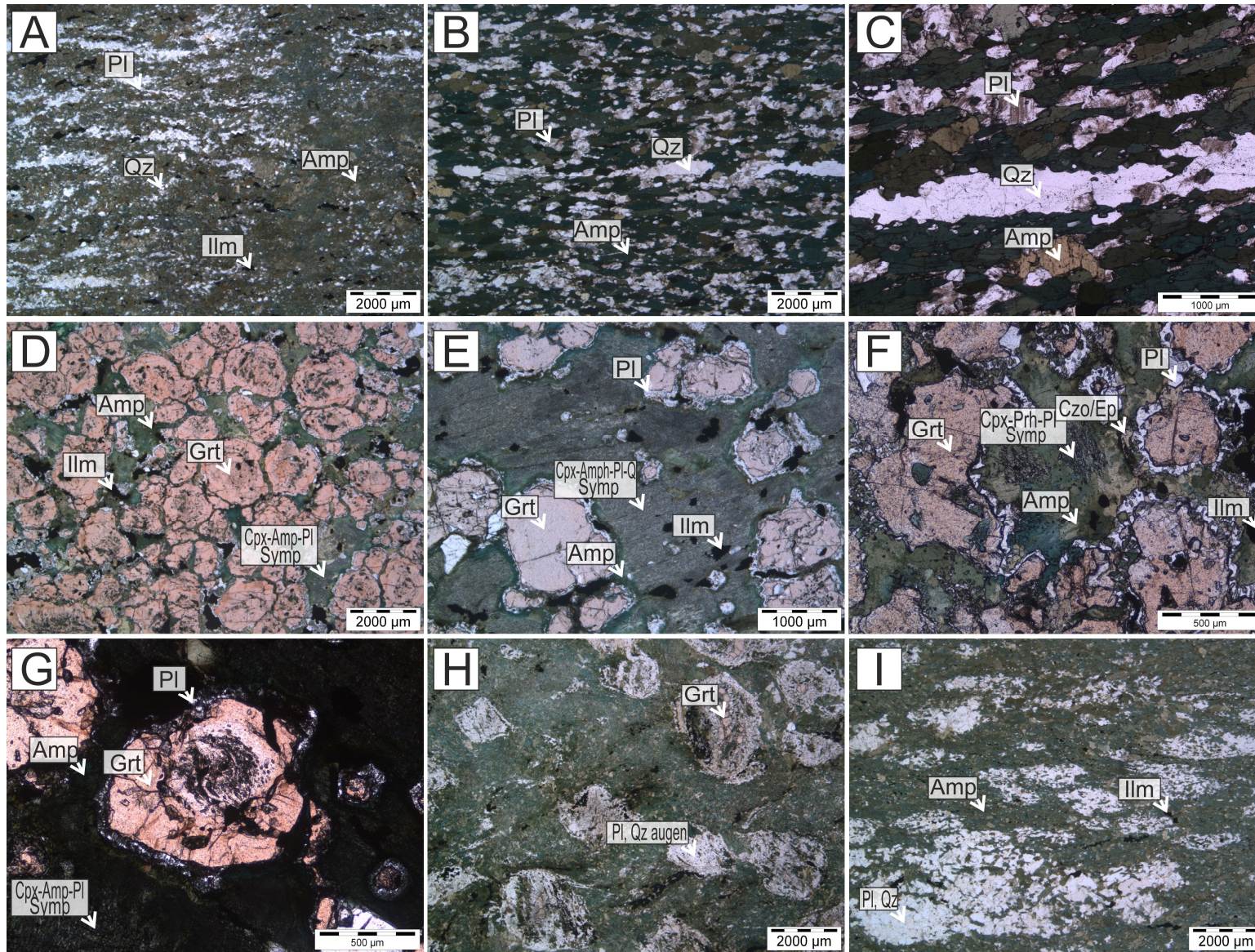


Fig. 4 Photomicrographs of metabasic rocks from the Songshugou metabasic unit. **(A)** Medium to fine grained schistose hornblende amphibolite sampled to the south of peridotitic unit. It mainly consists of green calcic Amp and PI (white). To lesser amounts mineral phases like Qz, Czo/Ep and Ilm occur. Schistosity is shown by alignment of PI-Qz layers. Q-PI aggregates show granoblastic textures. Sample X32. **(B,C)** Coarse-grained schistose hornblende amphibolite from metabasites south of peridotitic unit. Green calcic Amp, PI and Qz represent major mineral assemblage. To lesser amounts Ilm and Czo/Ep. Alignment of elongated Amp reveals strong schistosity. Qz appears frequently as ~ 300μm wide layers parallel to the alignment of nematoblastic green amphiboles. (Sample X33). **(D, E, F)** Grt-amphibolite consisting mainly of Grt (up to 60 vol.%), Amp and Cpx-symplectite. Garnet grains are subhedral and display 20μm – 200μm wide well organized coronal textures consisting of PI ± Amp ± Prh ± Ilm ± Czo/Ep. Garnet cores contain many inclusions such as Amp, Ilm, PI, Qz, Czo/Ep, Ap, Zrn, ± Spn. Rims in general contain fewer inclusions, such as Amp, Ru, Ap, Zrn. Cpx symplectites are rimmed by Amp and show a variety of exsolution textures. D and F are photomicrographs of Sample X37, E of X35. **(G)** Subhedral Grt grain with many inclusions of Amp, Qz, Czo/Ep, Ilm in the core. The rim is almost inclusion free. A PI-Amp corona of about 50-100μm surrounds the garnet. Snowball texture observed in garnet core indicates synmetamorphic growth. (Sample X35) **(H)** Medium-grained augen amphibolite containing mineral assemblage of Amp, PI, Grt, Qz to lesser amounts Czo/Ep, Ilm, and as accessory minerals monazite, zr, magnetite. Aggregates of PI and q have mostly replaced garnet grains. Those aggregates show garnet-like outlines and granoblastic texture. (Sample X39) **(I)** Medium-grained augen amphibolite mainly consisting of Amp, PI and q. To lesser amounts Ilm, Czo/Ep and sphene occur. In most cases, mineral aggregates of PI

and q have totally replaced preliminary Grt due to retrogression. Nematoblastic Amp grains are aligned along foliation. (Sample X42)

Garnets of sample X35 and X36 exhibit two different types of coronal structures around garnet: **(1)** narrow coronas (20 - 70 μm) which mostly consist of plagioclase (Fig. 5b), **(2)** wide (30 - 150 μm) vermicular PI + Amp coronas (Fig. 5c,d). Sample X37 shows narrow coronas (20 - 40 μm), which in several cases are only partly evolved, and consist mainly of PI. Certain coronas also contain prehnite, which always occurs adjacent to albitic PI and was presumably formed during late stages of retrogression at very low PT conditions (Fig. 5e). Strongly retrograded samples (X38, X42, QS2D), where garnet is heavily or sometimes even entirely consumed, show up to 600 μm wide granular coronas/mineral aggregates of mainly PI and to lesser extent Amp + Qz \pm Ilm \pm Czo/Ep (Fig. 5a). Fractures are common in garnet grains and typically filled by calcic Amp (tschermakite and/or hornblende).

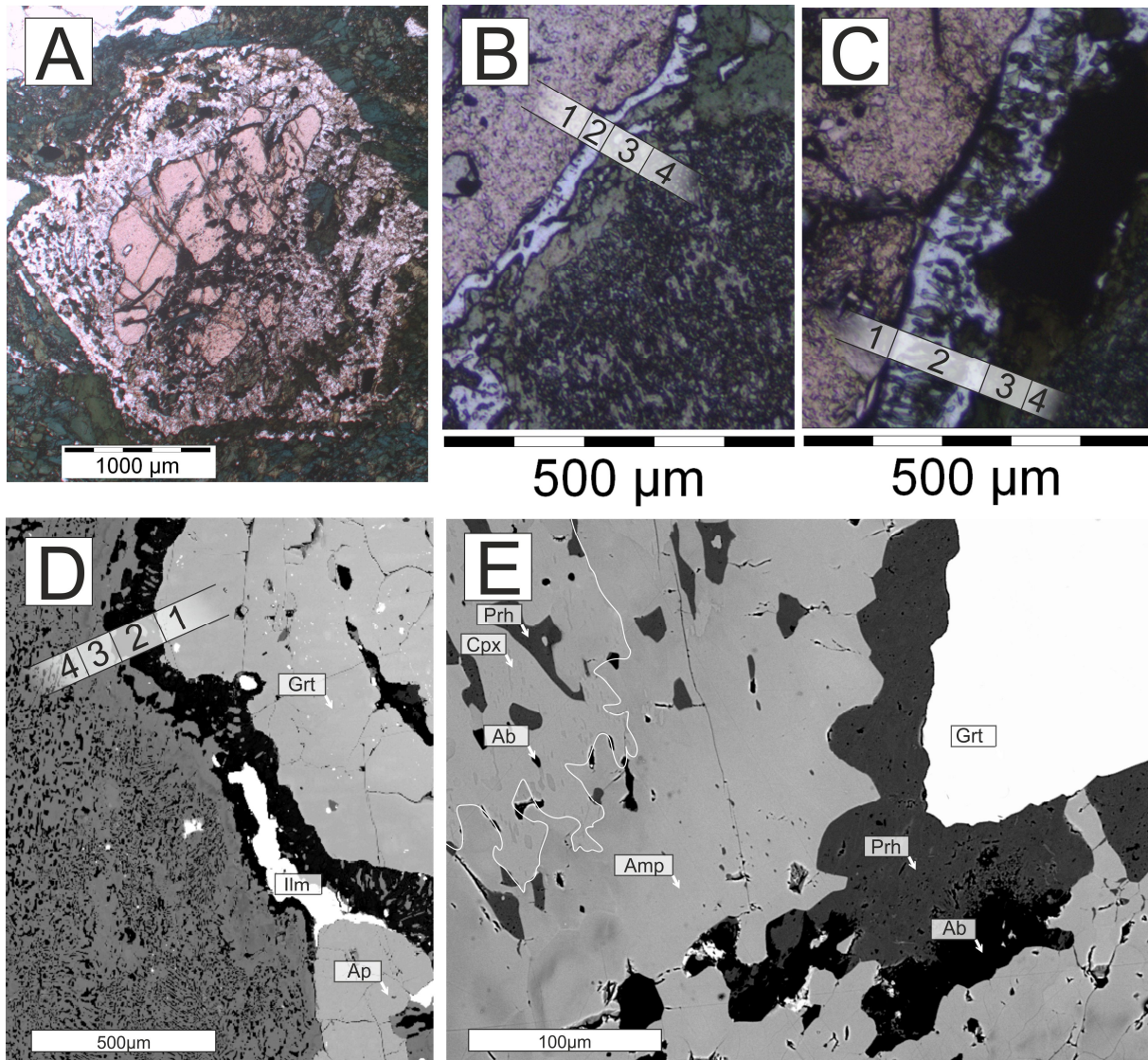


Fig. 5 Photomicrographs and BSE (Backscattered-electron) images of various garnet-omphacite reaction textures observed in Grt-amphibolites. Numerals in graphics divide reaction textures into 4 zones. (1 = Grt, 2 = coronal textures around garnet, 3 = Amp \pm Ilm \pm Ap \pm Czo/Ep, 4 = Cpx-symplectite) **(A)** Photomicrograph of strongly retrograded garnet. Corona comprises mineral aggregates of granular PI, Amp, Qz, Ilm, Czo/Ep. The approximate location of the original surface of a euhedral garnet grain is marked by hexagonal outlines of PI-Amp-aggregates. **(B)** Photomicrograph of narrow ~ 30 μm wide PI corona around garnet grain. Zone 2 consists of plagioclase and less Amp. Cpx-symplectites in zone 4 comprise very fine-grained ~ 20 μm PI and Amp intergrowths evenly distributed. **(C)** Photomicrograph of PI-Amp corona. Zone 2 is approximately 130 μm wide. Besides PI, it contains vermicular grains of Amp; aligned perpendicular to the garnets surface. Zone 3 contains up to 500 μm long grains of Ilm (black in photomicrograph). **(D)** BSE image of reaction textures with Ilm and Ap included in zone 3. **(E)** BSE image. Garnet corona consists of Prh and albitic PI. Prh is also occurs as intergrowths in nearby Cpx symplectites. Cpx grain is white rimmed for easier distinction. Prh probably evolved during very late stages of retrogression.

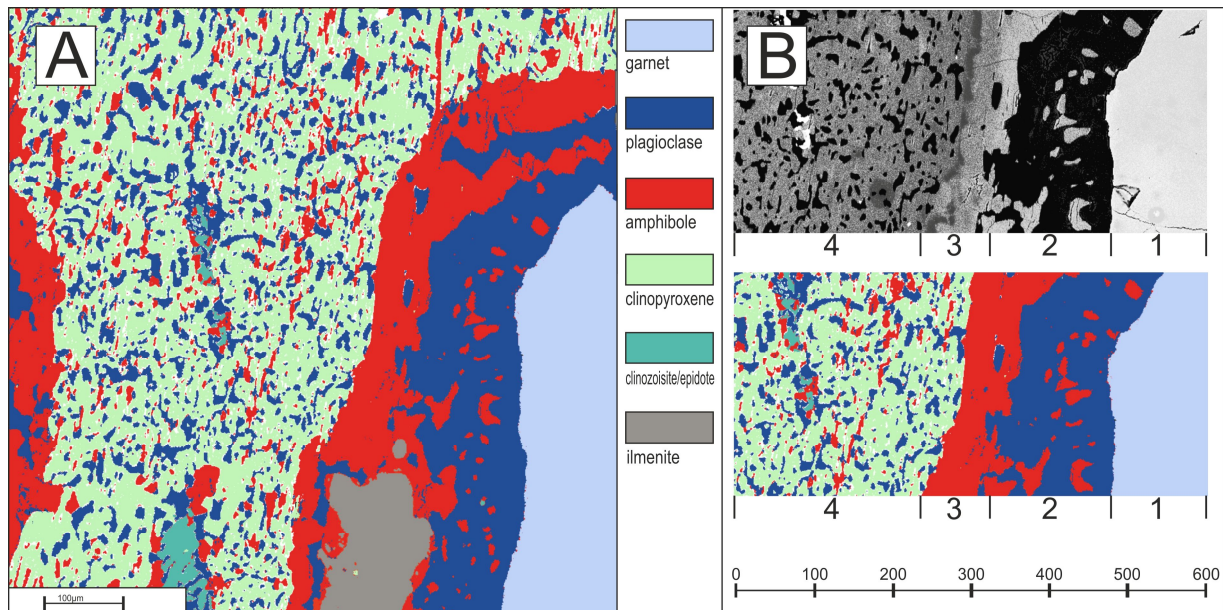


Fig. 6 Mineral map of Cpx-Grt reaction bands. (A) Element distribution images were used to generate mineral maps of Cpx-Grt reaction bands. Modes of intergrowths in Cpx-Pl-Amp symplectite have been calculated by segregating phases according to their specific element distribution signature in X-ray element distribution images; utilizing the imageJ software package (58.9 vol.% Cpx, 24.4 vol.% Pl and 10.5 vol.% Amp). (B) BSE image and mineral map divided into 4 zones. Scale bar in μm at the bottom.

Element distribution images of Cpx-Grt reaction bands reveal chemical zoning of coronal plagioclase and amphibole. The X_{An} component in Pl in zone 2 increases towards Grt ($X_{\text{An}} = 0.30\text{--}0.85$). That is clearly displayed in element distribution images by elevated Ca and Al contents, and a drop in Na and Si towards Grt. This distribution pattern coincides with a change in the compositions of the associated amphibole. Na and Al of amphibole in zones 2 and 3 decrease towards Cpx-symp (pargasitic composition close to garnet and Mg-hornblende close to Cpx-symplectite) (Fig. 7). Symplectitic Pl, intergrown Cpx is albite rich with $X_{\text{Ab}} > 0.6$. Similar Cpx-Grt reaction bands have been studied in mafic amphibolites of the Liano Uplift of central Texas (Carlson and Johnson, 1991; Wilkerson et al., 1988). Carlson and Johnson propose an open-system diffusion-controlled model for garnet-omphacite reaction bands based on material balance calculations. In quartz-rich regions, they observed an additional zone of Opx between zones 3 and 4. The stability of Opx is strongly regulated by the local activity of silica in the intergranular fluid. However, Opx was not observed in Songshugou Grt-amphibolites which indicates that silica rich fluids were probably not present or that Opx was totally replaced by Amp during retrogression. The SiO_2 depleted whole rock composition and the absence of Qz in the samples, argue for lower SiO_2 activity in the fluid phase. Prehnite replacing plagioclase in certain coronas and Cpx-symplectites, indicates retrogression at very low PT conditions which could also contribute to an Opx breakdown in presence of an aqueous fluid in favour of hornblende.

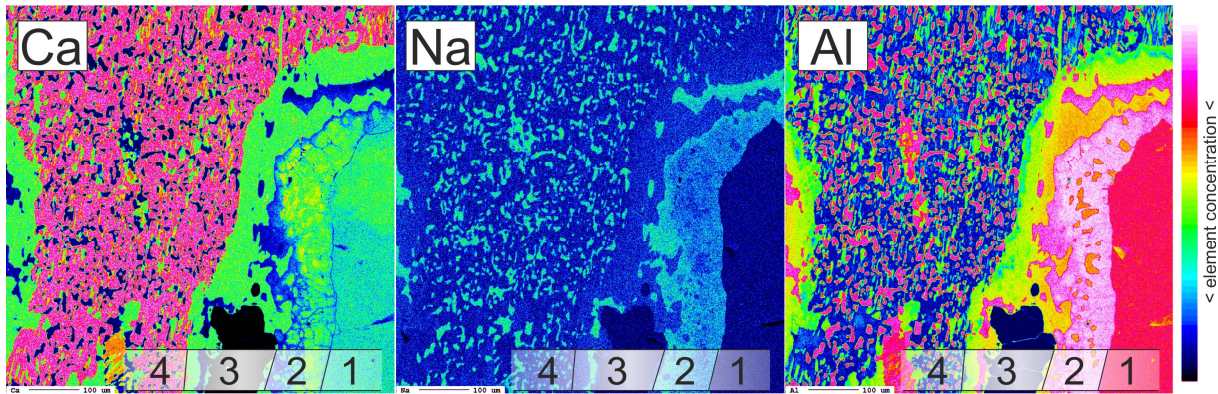


Fig. 7 Element distribution image of Cpx-Grt reaction bands. Pl in zone 2 increases in Na towards zone 3. Amp in zone 3 is richer in Al towards Grt.

Reaction bands between Grt and Cpx-symplectite have possibly arisen by reaction of garnet with omphacitic Cpx during the retrograde stage of metamorphism. This assumption is based upon the observations that in some areas of less retrograded samples (X36), where Cpx is less symplectitic and thus is richer in jadeite component, reaction bands are not always fully developed. Omphacitic Cpx still occurs as stable mineral phase adjacent to Grt.

In sample X37 amphibole is found in different microstructures with unusual Cl-rich composition. It either appears as ~ 20 μ m wide veinlets that crosscut matrix amphibole or as thin layers along the boundary of Pl-coronae and matrix-amphibole (Fig. 8). Significant Cl contents in amphiboles (2 – 3 wt.%) suggest that chlorine rich fluids attended the vein and corona formation. Hydration reactions in a closed fluid-rock system could lead to Cl richer fluids since Cl partitions strongly into an aqueous fluid relative to OH-bearing minerals. (Kullerud, 1995, 1996). Close to those Cl-amphibole veinlets, CaCO₃ occasionally appears as small inclusions in matrix hornblende (Fig. 8B).

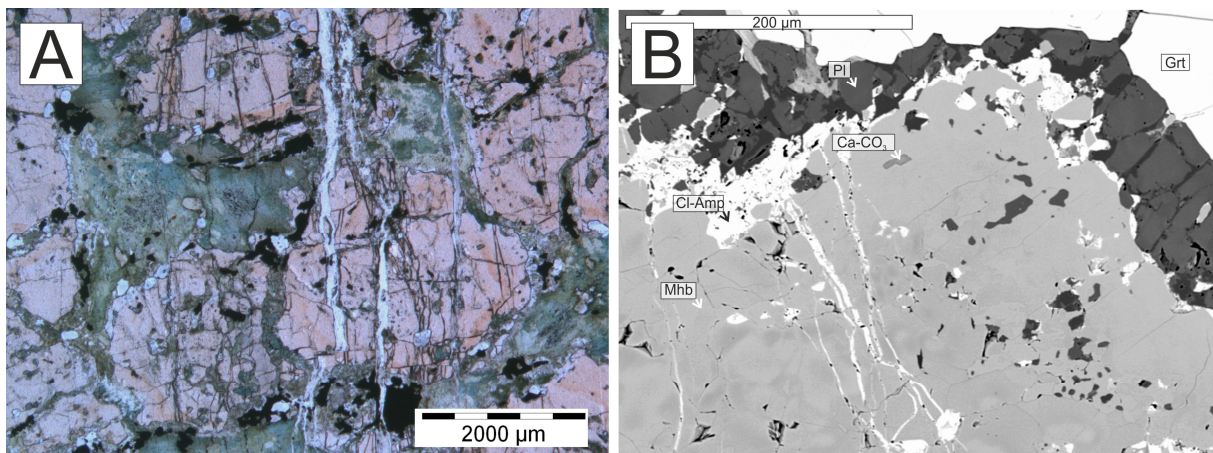


Fig. 8 (A) photomicrograph of Grt-amphibolite. Veins crosscutting garnet grains. (B) BSE image of Grt-amphibolite. Cl-amphibole appears as narrow veinlets crosscutting matrix amphibole and around coronal textures.

6.2 Clinopyroxene-symplectites

Symplectites of $\text{Cpx} + \text{Pl} \pm \text{Amp} \pm \text{Qz}$ are evidence of prior eclogite-facies or high-pressure (HP) metamorphism caused by replacement of omphacite by a mineral assemblage of lower density. They commonly occur in metabasites from HP and UHP metamorphic belts; and are usually generated in response to post-peak decompression (Eskola, 1921; Griffin and Raheim, 1973; Wilkerson et al., 1988; O'Brien et al., 1990; Droop et al., 1990; Zhao et al., 2001). All Px found in the matrix exhibit these symplectitic features. Most likely, they developed simultaneously with the Grt-Cpx reaction bands; since both represent hydration and reequilibration at lower pressures. In contrast to Grt-Cpx reaction bands, Cpx symplectites have generated textures without strong spatial organization. They usually appear as larger grains with diameters up to 30 mm and are typically surrounded by Mhb. Various exsolution textures are observed including (1) Qz rods, compound inclusions composed of (2) Amp + Pl, (3) lamellar intergrowths of Pl + Cpx + Amp + Qz, (4) Cpx + Pl + Amp + Prh compounds, (5) Cpx + Pl + Amp + Pmp + Qz compounds and (6) Qz + Pl intergrowths. Most prominent are Pl + Amp intergrowths. There is a positive correlation between the grain size of intergrowths and their abundance. All observed Cpx showed exsolution textures; hence no pristine Cpx composition is preserved. In the literature symplectite-forming reactions are often assumed to behave isochemically; therefore, original Omp compositions are estimated by reintegration of symplectite phases. This assumption is controversial. Several authors postulate that fluid transport plays a major role in facilitating cations at nettransfer reactions, implying open-system behavior at the grain scale (Heinrich, 1982; Messiga and Bettini, 1990; Yang, 2004). Cpx in most symplectites is of diopsidic and augitic composition. Omphacite ($X_{\text{Na}} = \text{Na}/(\text{Na}+\text{Ca}) = \sim 0.23$) occurs in aggregates with very few intergrowths. Pl in Cpx symplectites ($X_{\text{Na}} = \text{Na}/(\text{Na}+\text{Ca}) = < 0.10$) shows $X_{\text{Ab}} = 0.5-0.8$. Various Cpx symplectites occurring in Grt-amphibolites are displayed in Fig. 9.

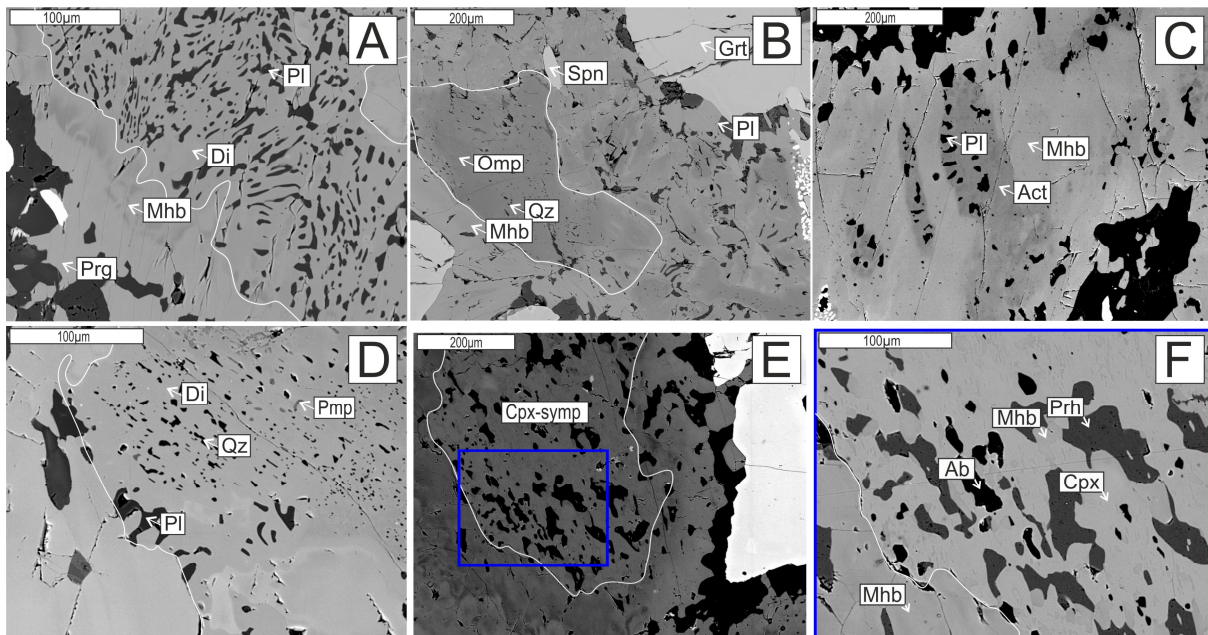


Fig. 9 various Cpx symplectites of metabasic Grt-amphibolites, BSE images. (A) Cpx-PI-Amp symplectite, the most common type of Cpx exsolution texture found in Songshugou Grt-metabasites. Cpx grain is contoured by a white line. PI intergrowths ($X_{\text{Ab}} = 0.5-0.8$) have vermicular shapes with lengths from 20 μm to 50 μm . Amp included in symplectite (difficult to distinguish from Cpx on BSE images) is Mg-Hbl. Amp in zone 3 increases in Al and Na and decreases in Si and Mg towards Grt, leading to pargasitic compositions. Cpx is mainly of diopsidic and augitic composition. **(B)** Symplectite with few Qz inclusions. Cpx, outlined by a white line, is of omphacitic composition. Coronas around garnet grains are marginally developed, which indicates less retrogression. **(C)** Amp-PI symplectite. Actinolite and PI intergrowths ($X_{\text{Ab}} = 0.8$) surrounded by Mg-Hbl. **(D)** Cpx-Qz-PI-Pmp-Amp symplectite. Amp, Qz and Pmp appear as $\sim 10\mu\text{m}$ round to elliptical intergrowths in diopsidic Cpx. PI intergrowths are bigger in size (30 μm – 100 μm) and are chiefly observed along the grain boundary to surrounding Mg-hornblende. **(E,F)** Prh-Cpx-PI-Amp symplectite. PI is almost pure albite. Prh possibly replaced PI during late stages of retrogression. Intergrowths of PI and Prh are of vermicular to round shape with grain lengths up to 90 μm .

The matrix assemblage which mainly consists of symplectitic Cpx and Amp also comprises Qz, Ilm, Czo/Ep, Zr ± Spn ± Prh ± Ap as subordinate phases. Sphene occurrence is restricted to certain samples (e.g., X36). Grain shapes are euhedral to subhedral, with grain sizes up to 500 μm. Sphene occurs as Grt inclusions, as well as in the matrix. Matrix Spn commonly shows reaction textures and is partly replaced by symplectites consisting of Ilm + Cpx (Fig. 10).

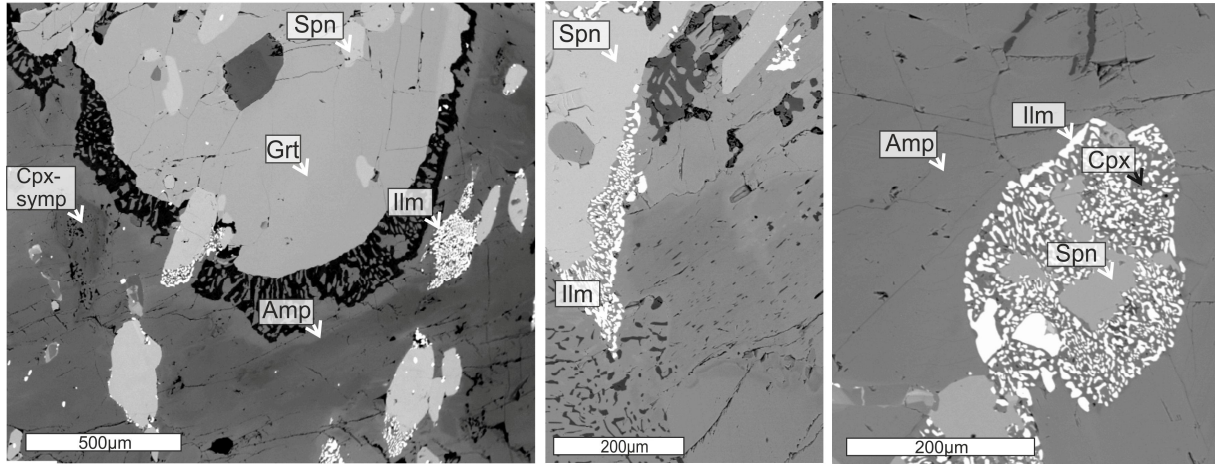


Fig. 10 Spn-Ilm-Cpx exsolution textures

Clinozoisite/epidote appears as Grt inclusions, in the matrix and sometimes included in zone 2 and 3 of Grt-Cpx reaction bands (Fig. 11a). Clinozoisite/epidote grains frequently show compositional zoning, clearly visible in BSE images where Ep rich areas containing REEs appear brighter. Ilmenite occurs included in Grt-cores, in zone 3 of reaction Grt-Cpx reaction bands and as matrix mineral (

Fig. 5d). Ilmenite included in Grt shows significantly smaller grain size (< 80 μm) compared to grains found in matrix and Grt coronae (up to 600 μm). Apatite is commonly included in Grt as well as in the matrix. Grain shapes are euhedral to subhedral with grain sizes of 30 - 70 μm for grains included in Grt and 50 - 500 μm for matrix Ap (Fig. 11b).

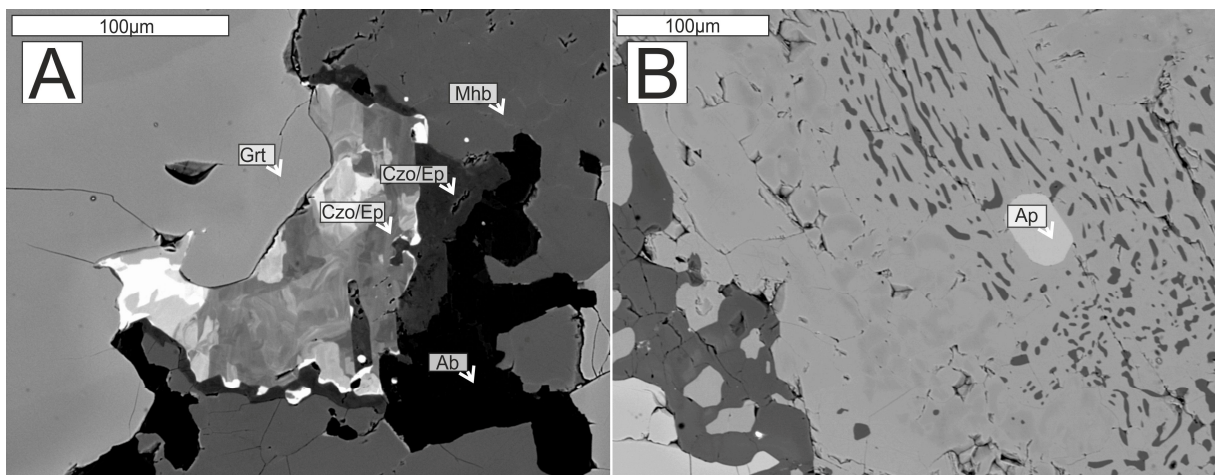


Fig. 11 BSE images (A) Czo/Ep rimming garnet (B) euhedral Ap grain in matrix

7 Mineral chemistry

7.1 *Cpx-symplectites*

Mineral data was processed using the mathematica based program PET (Dachs, 1998). Pyroxene formulae were calculated on the basis of six oxygens. Fe²⁺ and Fe³⁺ in pyroxene, garnet and Fe-Ti-oxides were calculated according to Droop 1987; and for amphibole, after Leake et al., 1997.

7.1.1 Cpx-Amp-Pl symplectites

The Cpx-Amp-Pl symplectite is the most common variety of cpx-symplectites in garnet amphibolites. Diopsidic or augitic Cpx functions as a host for round or vermicular Amp and Pl intergrowths. Plagioclase is Na rich with $X_{Ab} = 0.6-0.8$. Amphibole is Mhb with X_{Mg} ranging from 0.5 to 0.6 and TiO_2 below 0.7 wt.% (Fig. 9a, table 6). Mineral modes of Cpx-Amp-Pl symplectites have been evaluated by analyzing phases according to their specific element distribution signature in X-ray element distribution images with the imageJ software package (Amp: 10.5 vol.%, Cpx: 58.9 vol.%, Pl: 24.4 vol.%). Pristine Cpx composition has been calculated converting the phase volume to wt.% with assumed densities of 2.70 g/cm³ for Pl, 3.23 g/cm³ for Amp and 3.28 g/cm³ for Cpx. Symplectite phase reintegration is only valid if the system behaved isochemically. Representative mineral compositions and reintegrated Cpx composition of Cpx-Amp-Pl symplectites are presented in table 6.

table 6 representative mineral compositions of Cpx-Amp-Pl symplectites.

| representative mineral compositions of cpx-amph-plag symplectites | | | | | | | | | | | | | |
|---|------------------|---------------|---------------|---------------|---------------------|---------------|---------------|---------------|-------------------|---------------|---------------|---------------|-------|
| | amphibole (O=23) | | | | clinopyroxene (O=6) | | | cpx | plagioclase (O=8) | | | | |
| Sample | Gt3-50 | Gt3-54 | 3a21 | 3a26 | Gt3-52 | Gt3-55 | Gt3-56 | reintegrated | Gt3-59 | Gt3-60 | 3a25 | 3c56 | |
| Mineral (IMA) | Mg-hornblende | | | | diopside | | | omph | | | | | |
| SiO ₂ | 45.19 | 45.59 | 46.59 | 48.21 | 51.77 | 52.83 | 53.27 | 51.02 | 63.44 | 62.94 | 62.37 | 63.17 | |
| TiO ₂ | 0.64 | 0.57 | 0.47 | 0.40 | 0.17 | 0.00 | 0.00 | 0.34 | - | - | - | - | |
| Fe ₂ O ₃ | - | - | - | - | - | - | - | - | 0.34 | 0.78 | 0.38 | 0.61 | |
| Al ₂ O ₃ | 10.01 | 8.98 | 9.00 | 7.71 | 1.69 | 0.67 | 1.22 | 11.74 | 23.28 | 22.75 | 23.45 | 23.31 | |
| Cr ₂ O ₃ | <0.10 | <0.10 | <0.10 | 0.11 | <0.10 | <0.10 | <0.10 | <0.10 | - | - | - | - | |
| FeO | 19.05 | 19.03 | 18.98 | 17.92 | 11.20 | 10.83 | 11.05 | 14.22 | - | - | - | - | |
| MnO | 0.18 | 0.08 | 0.09 | 0.13 | 0.15 | 0.13 | 0.13 | 0.08 | - | - | 0.10 | - | |
| MgO | 10.02 | 10.84 | 9.55 | 10.80 | 12.24 | 12.75 | 12.03 | 9.03 | <0.10 | 0.38 | <0.10 | <0.10 | |
| CaO | 11.49 | 11.71 | 11.14 | 11.44 | 22.50 | 22.70 | 22.67 | 10.84 | 4.66 | 6.72 | 4.98 | 5.87 | |
| Na ₂ O | 2.00 | 1.71 | 2.00 | 1.43 | 0.69 | 0.38 | 0.55 | 3.06 | 8.67 | 7.19 | 9.04 | 7.60 | |
| K ₂ O | <0.10 | <0.10 | <0.10 | <0.10 | - | - | - | - | - | - | - | - | |
| F | <0.10 | 0.15 | 0.36 | 0.24 | <0.10 | <0.10 | <0.10 | 0.13 | - | - | - | - | |
| Total | 98.58 | 98.66 | 98.18 | 98.39 | 100.41 | 100.29 | 100.92 | 100.46 | 100.39 | 100.76 | 100.32 | 100.56 | |
| Si | 6.651 | 6.687 | 6.907 | 7.061 | 1.934 | 1.978 | 1.985 | 1.874 | 2.791 | 2.771 | 2.760 | 2.778 | |
| Ti | 0.071 | 0.063 | 0.052 | 0.044 | 0.005 | 0.000 | 0.000 | 0.009 | - | - | - | - | |
| Al | 0.577 | 0.748 | 0.378 | 0.413 | 0.098 | 0.043 | 0.016 | 0.508 | 0.011 | 0.026 | 0.013 | 0.020 | |
| Fe ³⁺ | 1.736 | 1.552 | 1.573 | 1.331 | 0.074 | 0.030 | 0.054 | - | 1.207 | 1.180 | 1.223 | 1.208 | |
| Cr | 0.000 | 0.000 | 0.000 | 0.013 | 0.000 | 0.000 | 0.000 | - | - | - | - | - | |
| Fe ²⁺ | 1.768 | 1.586 | 1.975 | 1.782 | 0.252 | 0.296 | 0.328 | 0.437 | - | - | - | - | |
| Mn | 0.022 | 0.010 | 0.011 | 0.016 | 0.005 | 0.004 | 0.004 | 0.003 | - | - | 0.003 | - | |
| Mg | 2.199 | 2.370 | 2.111 | 2.358 | 0.682 | 0.712 | 0.668 | 0.495 | 0.000 | 0.025 | 0.000 | 0.000 | |
| Ca | 1.812 | 1.840 | 1.770 | 1.795 | 0.901 | 0.910 | 0.905 | 0.427 | 0.220 | 0.317 | 0.236 | 0.277 | |
| Na | 0.571 | 0.486 | 0.575 | 0.406 | 0.050 | 0.028 | 0.040 | 0.218 | 0.740 | 0.614 | 0.776 | 0.648 | |
| K | - | - | - | - | - | - | - | - | - | - | - | - | |
| F | 0.000 | 0.070 | 0.169 | 0.111 | 0.000 | 0.000 | 0.000 | 0.015 | - | - | - | - | |
| SumCat | 15.407 | 15.412 | 15.333 | 15.518 | 3.997 | 3.998 | 4.000 | 3.986 | 4.969 | 4.933 | 5.010 | 4.931 | |
| X_{Mg} | 0.554 | 0.599 | 0.570 | 0.517 | 0.723 | 0.704 | 0.671 | 0.531 | X_{Ab} | 0.771 | 0.659 | 0.765 | 0.701 |

7.1.2 Cpx-Qz ± PI symplectites

Cpx-Qz symplectites usually contain less and smaller (~10 μm) intergrowths compared to all other symplectite varieties (Fig. 9b). They can also occur as small areas within Cpx-PI-Amp symplectites. Minor amounts of albitic PI do occasionally appear. However, the majority of Cpx is of omphacitic composition close to those of the reintegrated ones from Cpx-Amp-PI symplectites with $X_{Na}=0.20-0.24$ and $X_{Mg}=0.70-0.85$. Representative analyses of Cpx are presented in table 7.

table 7 representative analyses of Cpx in Cpx-Qz symplectites.

| representative analyses of Cpx-Qz symplectites ± PI | | | | | | |
|---|---------------|---------------|--------------|--------------|--------------|---------------|
| clinopyroxene (O = 6) | | | | | | |
| Sample | a_3 | a_15 | a_16 | 4_29 | 4_27 | 4_28 |
| Mineral (IMA) | omphacite | | | augite | | diopside |
| SiO ₂ | 54.74 | 54.35 | 54.38 | 53.86 | 53.80 | 54.07 |
| TiO ₂ | 0.14 | < 0.10 | < 0.10 | < 0.10 | < 0.10 | 0.10 |
| Al ₂ O ₃ | 3.77 | 3.80 | 3.61 | 3.94 | 4.10 | 4.30 |
| FeO | 7.51 | 7.76 | 7.62 | 8.31 | 9.25 | 8.78 |
| MnO | < 0.10 | 0.10 | < 0.10 | < 0.10 | < 0.10 | < 0.10 |
| MgO | 12.03 | 11.92 | 11.30 | 11.07 | 11.20 | 11.40 |
| CaO | 18.95 | 19.61 | 19.36 | 18.35 | 18.36 | 18.87 |
| Na ₂ O | 2.98 | 3.13 | 3.30 | 3.01 | 2.63 | 2.59 |
| Total | 100.12 | 100.67 | 99.68 | 98.54 | 99.62 | 100.55 |
| Si | 1.998 | 1.972 | 1.994 | 2.005 | 1.983 | 1.974 |
| Ti | 0.004 | 0.000 | 0.000 | 0.000 | 0.002 | 0.003 |
| Al | 0.162 | 0.162 | 0.156 | 0.173 | 0.178 | 0.185 |
| Fe ³⁺ | 0.045 | 0.114 | 0.080 | 0.034 | 0.083 | 0.062 |
| Fe ²⁺ | 0.184 | 0.121 | 0.153 | 0.224 | 0.203 | 0.206 |
| Mn | 0.000 | 0.003 | 0.000 | 0.000 | 0.000 | 0.000 |
| Mg | 0.655 | 0.645 | 0.618 | 0.614 | 0.616 | 0.620 |
| Ca | 0.741 | 0.762 | 0.761 | 0.732 | 0.725 | 0.738 |
| Na | 0.211 | 0.220 | 0.235 | 0.217 | 0.188 | 0.183 |
| SumCat | 4.000 | 3.999 | 3.997 | 4.000 | 4.000 | 4.000 |
| X _{Mg} | 0.781 | 0.842 | 0.802 | 0.733 | 0.752 | 0.751 |
| X _{Na} | 0.222 | 0.224 | 0.236 | 0.229 | 0.206 | 0.199 |

7.1.3 Cpx-Amp-Prh-PI symplectites

Cpx-Amp-Prh-PI symplectites contain diopsidic Cpx with compositions similar to those of Cpx-Amp-PI symplectites (Fig. 9ef). PI is rich in $X_{Ab} = 0.7-1.0$. Green Amp is classified as Mhb with $X_{Mg} \sim 0.6$ and low TiO_2 (<0.25 wt.%). The close spatial relation of PI and Prh indicates that Prh formed after PI at low PT conditions. Representative mineral compositions are presented in table 8.

table 8 representative analyses of Prh-Cpx-PI-Amp symplectites

| representative analyses of pre-cpx-amph-plag symplectites | | | | | | | | | | | | | | | |
|---|--------------------|---------------|---------------|-----------------------|--------------|---------------|-------------------|--------------|--------------|--------------|--------------|-----------------------|--------------|--------------|-------|
| | amphibole (O = 23) | | | plagioclase (O = 8) | | | prehnite (O = 11) | | | | | clinopyroxene (O = 6) | | | |
| Sample | 3_6 | 3_7 | 3_8 | 3_10 | 3_11 | 3_15 | 3_1 | 3_2 | 3_4 | 3_9 | 3_14 | X373_3 | X373_5 | X373_13 | |
| Mineral | Mg-hornblende | | | PI ($X_{Ab} > 0.7$) | | | prehnite | | | | | diopside | | | |
| SiO ₂ | 50.26 | 50.35 | 49.71 | 69.85 | 62.08 | 69.57 | 44.80 | 44.80 | 45.26 | 45.49 | 45.83 | 53.27 | 53.21 | 52.95 | |
| TiO ₂ | <0.10 | 0.16 | 0.22 | - | - | - | - | - | - | - | - | <0.10 | <0.10 | <0.10 | |
| Fe ₂ O ₃ | - | - | - | 0.35 | 0.38 | 0.24 | 0.79 | 0.46 | 0.47 | 0.71 | 0.36 | - | - | - | |
| Al ₂ O ₃ | 6.71 | 5.90 | 6.89 | 19.75 | 24.11 | 19.89 | 24.89 | 24.76 | 24.83 | 25.20 | 25.28 | 1.05 | 0.59 | 0.91 | |
| Cr ₂ O ₃ | <0.10 | <0.10 | <0.10 | - | - | - | - | - | - | - | - | <0.10 | <0.10 | <0.10 | |
| FeO | 17.21 | 16.52 | 16.97 | - | - | - | - | - | - | - | - | 10.92 | 11.14 | 10.74 | |
| MnO | <0.10 | <0.10 | 0.11 | - | - | - | - | - | - | - | - | <0.10 | 0.13 | 0.10 | |
| MgO | 11.80 | 12.60 | 11.78 | - | - | - | - | - | - | - | - | 11.82 | 12.31 | 11.26 | |
| CaO | 11.29 | 11.24 | 11.31 | 0.15 | 5.20 | 0.26 | 25.80 | 25.56 | 25.67 | 25.46 | 25.46 | 22.05 | 22.20 | 22.05 | |
| Na ₂ O | 0.79 | 0.82 | 0.88 | 10.36 | 7.77 | 10.17 | 0.04 | 0.18 | 0.07 | <0.10 | 0.16 | 0.36 | 0.31 | 0.45 | |
| K ₂ O | <0.10 | 0.01 | <0.10 | <0.10 | <0.10 | <0.10 | - | - | - | - | - | - | - | - | |
| F | 0.24 | 0.33 | 0.27 | - | - | - | - | - | - | - | - | - | - | - | |
| Cl | <0.10 | <0.10 | <0.10 | - | - | - | - | - | - | - | - | - | - | - | |
| Total | 98.3 | 98.18 | 98.48 | 100.46 | 99.54 | 100.13 | 96.32 | 95.76 | 96.3 | 96.86 | 97.09 | 99.47 | 99.89 | 98.46 | |
| Si | 7.308 | 7.323 | 7.226 | 3.015 | 2.754 | 3.012 | 3.039 | 3.052 | 3.063 | 3.058 | 3.070 | 2.006 | 2.002 | 2.016 | |
| Ti | 0.000 | 0.018 | 0.024 | - | - | - | - | - | - | - | - | 0.001 | 0.000 | 0.003 | |
| Al | 0.275 | 0.324 | 0.335 | 1.005 | 1.261 | 1.015 | 1.990 | 1.988 | 1.981 | 1.997 | 1.996 | 0.047 | 0.026 | 0.041 | |
| Fe ³⁺ | 1.150 | 1.011 | 1.180 | 0.011 | 0.013 | 0.008 | 0.040 | 0.024 | 0.024 | 0.036 | 0.018 | - | - | - | |
| Cr | 0.000 | 0.000 | 0.009 | - | - | - | - | - | - | - | - | 0.002 | 0.003 | 0.000 | |
| Fe ²⁺ | 1.818 | 1.716 | 1.759 | - | - | - | - | - | - | - | - | 0.344 | 0.351 | 0.342 | |
| Mn | 0.000 | 0.000 | 0.014 | - | - | - | - | - | - | - | - | 0.003 | 0.004 | 0.003 | |
| Mg | 2.558 | 2.732 | 2.553 | - | - | - | - | - | - | - | - | 0.664 | 0.691 | 0.639 | |
| Ca | 1.759 | 1.752 | 1.762 | 0.007 | 0.247 | 0.012 | 1.875 | 1.866 | 1.862 | 1.834 | 1.828 | 0.890 | 0.895 | 0.900 | |
| Na | 0.223 | 0.231 | 0.248 | 0.867 | 0.668 | 0.854 | 0.005 | 0.024 | 0.009 | 0.000 | 0.021 | 0.026 | 0.023 | 0.033 | |
| K | - | - | - | - | - | - | - | - | - | - | - | - | - | - | |
| F | 0.110 | 0.156 | 0.124 | - | - | - | - | - | - | - | - | - | - | - | |
| Cl | - | - | - | - | - | - | - | - | - | - | - | - | - | - | |
| SumCat | 15.201 | 15.263 | 15.234 | 4.905 | 4.943 | 4.901 | 6.949 | 6.954 | 6.939 | 6.925 | 6.933 | 3.983 | 3.995 | 3.977 | |
| X_{Mg} | 0.590 | 0.610 | 0.590 | X_{An} | 0.010 | 0.270 | 0.010 | | | | | X_{Mg} | 0.660 | 0.660 | 0.650 |
| | | | | X_{Ab} | 0.990 | 0.730 | 0.980 | | | | | X_{Na} | 0.030 | 0.030 | 0.040 |

7.1.4 Cpx-Qz-Pl-Pmp-Amp symplectites

Cpx-Qz-Pl-Pmp-Amp symplectites contain diopsidic Cpx, Mhb, Pmp and Pl ($X_{Ab} = 0.5 - 0.7$) (Fig. 9d). Pumpellyite was presumably formed during late stages of retrogression similar to Prh. Representative mineral analyses are displayed in table 9.

table 9 representative analyses of Cpx-Qz-Pl-Pmp-Amp symplectites

| representative analyses of Cpx-Qz-Pl-Pmp-Amp symplectites | | | | | | |
|---|---------------|---------------|--------------|--------------|----------------|---------------|
| Mineral | Pl (O = 8) | | Cpx (O = 6) | | Pmp (O = 24.5) | |
| | s_1 | s_5 | s_3 | s_7 | s_2 | s_6 |
| | plagioclase | | diopside | | pumpellyite | |
| SiO ₂ | 52.93 | 59.20 | 52.82 | 52.95 | 37.18 | 38.65 |
| TiO ₂ | - | - | 0.14 | 0.17 | 0.00 | 0.09 |
| Fe ₂ O ₃ | 0.48 | 0.35 | - | - | - | - |
| Al ₂ O ₃ | 28.73 | 24.84 | 2.93 | 1.87 | 24.60 | 24.32 |
| FeO | - | - | 10.30 | 10.37 | 2.92 | 3.86 |
| MnO | 0.04 | 0.00 | 0.11 | 0.06 | 0.08 | 0.00 |
| MgO | 0.07 | 0.00 | 10.66 | 11.09 | 2.17 | 2.44 |
| CaO | 11.96 | 6.93 | 21.35 | 22.03 | 22.15 | 20.11 |
| Na ₂ O | 5.89 | 9.12 | 1.29 | 0.86 | 0.13 | 0.38 |
| Total | 100.09 | 100.44 | 99.60 | 99.40 | 89.23 | 89.85 |
| Si | 2.407 | 2.645 | 1.983 | 1.996 | 6.176 | 6.345 |
| Ti | - | - | 0.004 | 0.005 | 0.000 | 0.011 |
| Al | 1.540 | 1.308 | 0.130 | 0.083 | 4.816 | 4.706 |
| Fe ³⁺ | 0.016 | 0.012 | - | - | - | - |
| Fe ²⁺ | - | - | 0.323 | 0.327 | 0.406 | 0.530 |
| Mn | 0.002 | 0.000 | 0.003 | 0.002 | 0.011 | 0.000 |
| Mg | 0.005 | 0.000 | 0.597 | 0.623 | 0.537 | 0.597 |
| Ca | 0.583 | 0.332 | 0.859 | 0.890 | 3.942 | 3.537 |
| Na | 0.519 | 0.790 | 0.094 | 0.063 | 0.042 | 0.121 |
| SumCat | 5.072 | 5.087 | 3.993 | 3.989 | 15.930 | 15.847 |
| X _{Ab} | 0.471 | 0.702 | xMg | 0.649 | 0.656 | |
| X _{an} | 0.529 | 0.295 | xNa | 0.099 | 0.066 | |

7.1.5 Mhb-Act-Pl symplectites

Within large Mhb grains, symplectites consisting of Act and albitic Pl ($X_{Ab} \sim 0.8$) can be observed (Fig. 9c). Representative data of mineral compositions are displayed in table 10. Actinolite, typically abundant at greenschist facies conditions, is generated during the retrograde exhumation path. Chemical compositions of Act and Mhb are plotted in Fig. 13 (Al IV vs. A-site occupancy and Al VI vs. Si plots).

table 10 representative analyses of Amp-Pl symplectites

| representative analyses of amph-plag symplectite | | | | | | |
|--|------------------|---------------|------------------|---------------|-------------------------|--------------|
| Sample | surrounding amph | | amph symplectite | | plagioclase intergrowth | |
| | x353s_4 | x353s_7 | x353s_1 | x353s_8 | x353s_5 | x353s_6 |
| Mineral | Mg-horn | | actinolite | | plagioclase | |
| SiO ₂ | 46.70 | 48.62 | 52.54 | 52.67 | 64.33 | 65.68 |
| TiO ₂ | 0.52 | 0.37 | 0.21 | 0.12 | - | - |
| Fe ₂ O ₃ | - | - | - | - | 0.69 | 0.52 |
| Al ₂ O ₃ | 8.35 | 6.89 | 3.94 | 3.91 | 22.57 | 21.35 |
| Cr ₂ O ₃ | <0.10 | <0.10 | <0.10 | <0.10 | - | - |
| FeO | 18.81 | 18.11 | 16.20 | 16.18 | - | - |
| MnO | 0.12 | <0.10 | <0.10 | <0.10 | - | - |
| MgO | 10.48 | 11.30 | 13.26 | 13.29 | - | - |
| CaO | 11.14 | 11.27 | 11.07 | 11.21 | 3.81 | 2.50 |
| Na ₂ O | 1.65 | 1.60 | 0.70 | 0.72 | 9.25 | 9.73 |
| F | 0.32 | <0.10 | 0.30 | <0.10 | - | - |
| Cl | <0.10 | <0.10 | <0.10 | <0.10 | - | - |
| Total | 98.09 | 98.16 | 98.22 | 98.10 | 100.65 | 99.78 |
| Si | 6.895 | 7.117 | 7.612 | 7.615 | 2.818 | 2.889 |
| Ti | 0.057 | 0.041 | 0.023 | 0.013 | - | - |
| Al | 0.543 | 0.450 | 0.153 | 0.169 | 1.165 | 1.107 |
| Fe ³⁺ | 1.453 | 1.189 | 0.673 | 0.667 | 0.023 | 0.017 |
| Cr | 0.000 | 0.000 | 0.000 | 0.000 | - | - |
| Fe ²⁺ | 1.779 | 1.766 | 1.810 | 1.788 | - | - |
| Mn | 0.015 | 0.000 | 0.000 | 0.000 | - | - |
| Mg | 2.308 | 2.465 | 2.864 | 2.865 | - | - |
| Ca | 1.762 | 1.767 | 1.718 | 1.737 | 0.179 | 0.118 |
| Na | 0.471 | 0.453 | 0.197 | 0.202 | 0.786 | 0.830 |
| F | 0.151 | 0.000 | 0.137 | 0.000 | - | - |
| Cl | 0.015 | 0.000 | 0.000 | 0.000 | - | - |
| SumCat | 15.449 | 15.246 | 15.186 | 15.056 | 4.971 | 4.961 |
| X _{Mg} | 0.565 | 0.583 | 0.613 | 0.616 | X _{Na} | 0.815 |
| Al(IV) | 1.105 | 0.889 | 0.394 | 0.392 | X _{Ca} | 0.185 |
| Al(VI) | 0.349 | 0.299 | 0.279 | 0.274 | | |

In Fig. 12 Cpx analyses of the various Cpx-symplectites are plotted into the J-Q and the ternary Q-Jd-Aeg diagram. Pyroxene occurring in highly developed symplectites e.g. (Cpx-Amp-PI, Prn-Cpx-Amp-PI, Cpx-Qz-PI-Pmp-Amp) is of diopsidic and augitic composition and plots in the Quad area (Ca-Fe-Mg pyroxenes). Pyroxene of Cpx-Qz \pm PI symplectites, which is considered to be less influenced by retrogression, plots partly as omphacite in the ternary Q-Jd-Aeg diagram along with reintegrated Cpx compositions of Cpx-PI-Amp symplectites.

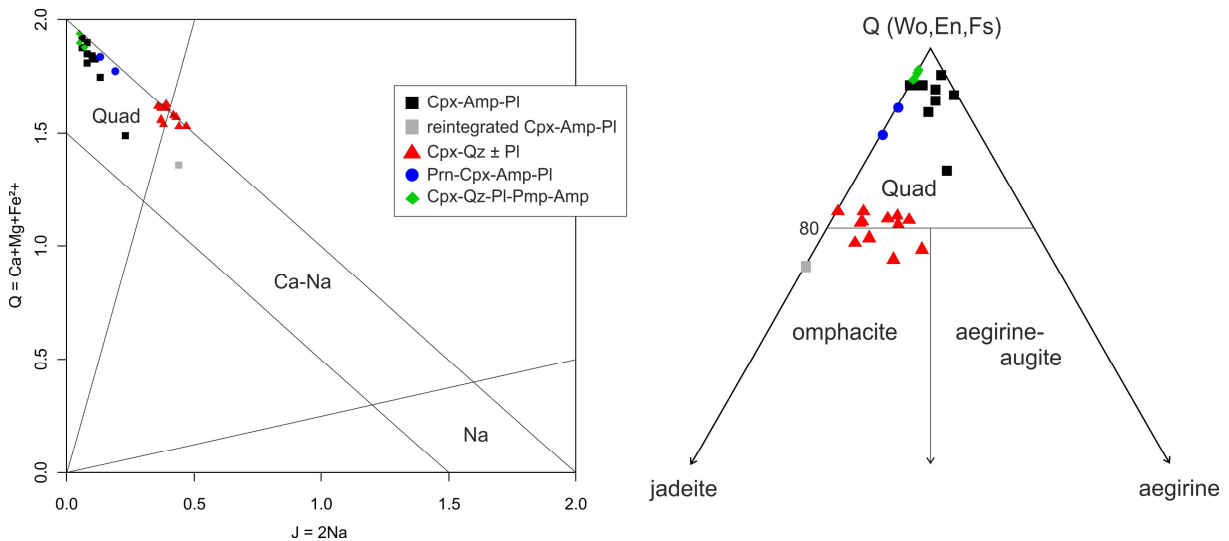


Fig. 12 Q-J diagram for pyroxenes of various symplectites on the left, Q-Jd-Ae ternary diagram on the right. Quad represents the Ca-Mg-Fe pyroxene area. (Morimoto, 1988)

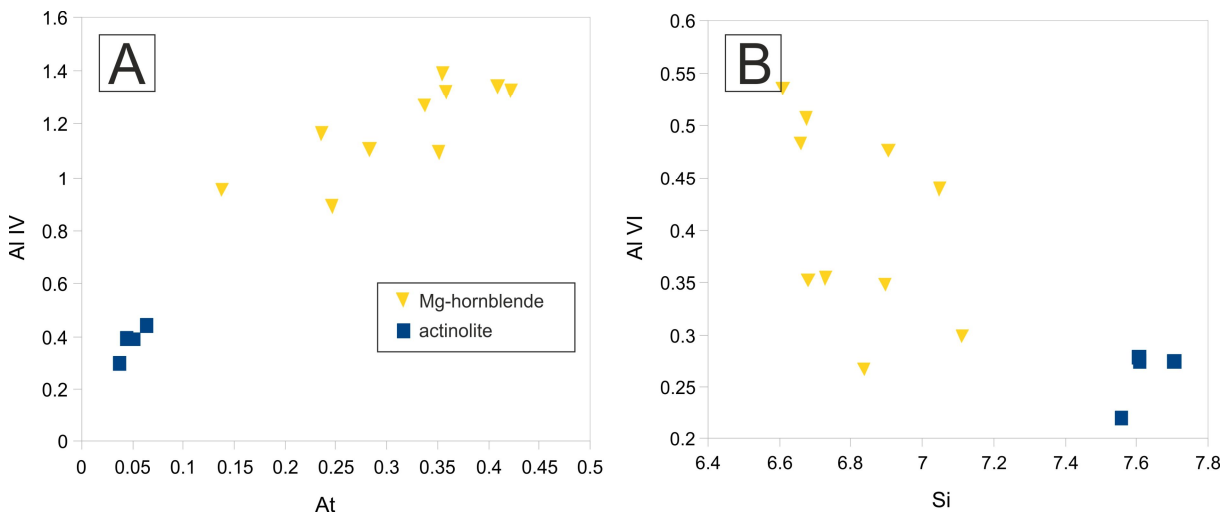


Fig. 13 Amp mineral data plots from Amp-PI symplectites (A) Al IV vs. A-site occupancy, showing compositional gaps between actinolite and hornblende (B) Al VI vs. Si showing compositional gaps between actinolite and hornblende.

7.2 Reaction-bands between garnet and Cpx-symplectite

Amphiboles occurring in zone 2 and zone 3 of the Cpx-Grt reaction zones show variation in chemical composition. Amphibole in zone 2 is of Fe-pargasitic composition. Reaction zone 3, which separates Cpx-symplectite from Grt-corona, consists mainly of Amp, which is compositionally zoned with increasing Al_2O_3 and Na_2O and decreasing SiO_2 towards Grt representing the edenite exchange vector. Thus Mhb compositions occur close to Cpx-symplectite and pargasitic to hastingsitic compositions occur towards garnet. In Fig. 14a the edenite-exchange substitution of $\text{Al}_{\text{IV}}(+)$ $\text{Na}_{\text{A}}(+)$ $\text{Si}_{\text{IV}}(-)$ is clearly defined by plotting the relevant mineral chemical parameters of different Amp compositions from the reaction rims. Richterite-type substitution effects were eliminated by subtraction of Na_{M4} (Czamanske et al., 1981). Consequent substitution of Al_{IV} in tetrahedral sites (T1, T2) is chiefly compensated by partial occupancy of the 10 to 12-fold A-sites by Na; and to lesser amounts K, along with the substitution of Al_{VI} and Ti in octahedral sites (M1, M2, M3 and M4), as displayed by the linear relationship in Fig. 15b. Samples show a slight deficiency in Al_{IV} . That indicates that the excess A-site and octahedral charge is not fully balanced by the Al_{IV} substitution, and might be balanced by the substitution of Na and K by $2+$ charged elements at the M4 site. A binary total alkalis (At) vs. Si plot for chemical classification of amphiboles is displayed in Fig. 15a (Leake 1978). Plagioclase in reaction zone 2 is compositionally zoned, with increasing $X_{\text{An}} = 0.35\text{-}0.85$, towards Grt (Fig. 14b). Single idiomorphic grains of Amp, which occasionally appear in the matrix, are Mhb. Cl rich amphibole (Fig. 8) occurs as narrow veinlets crosscutting matrix amphibole and in coronal textures, and is of hastingsitic and pargasitic composition, strongly enriched in Fe, K, Cl, Na and Al compared to surrounding Mhb. Representative mineral analyses of Amp and Pl, in respect of their spatial distribution, are displayed in table 11 and table 12.

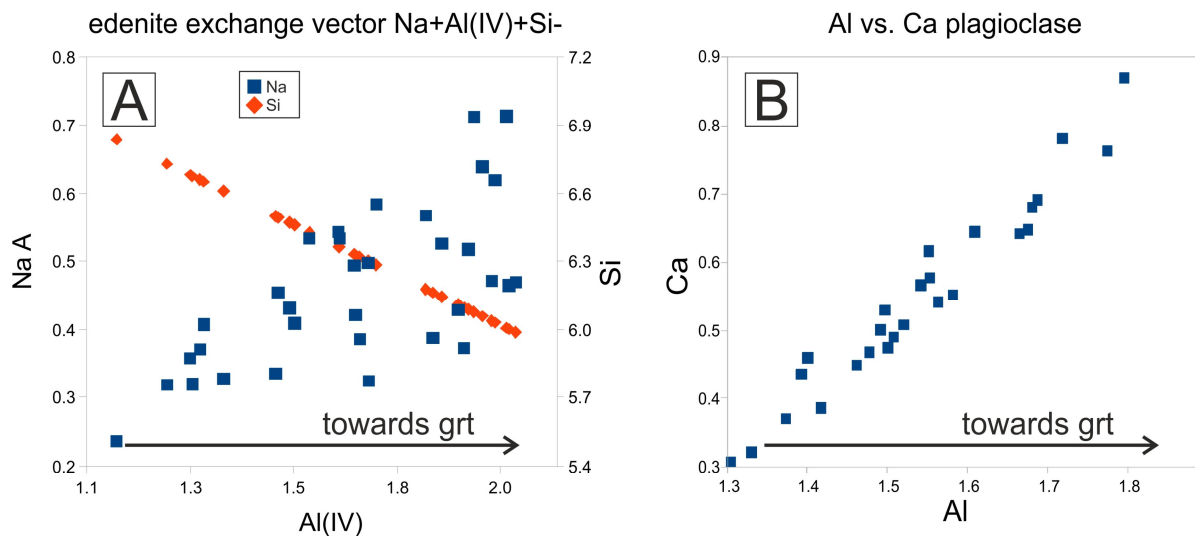


Fig. 14 (A) $\text{Al}(\text{IV})$ vs. Na_A and Si plot of amphiboles occurring in reaction zones 2 and 3. **(B)** Ca vs. Al plot of plagioclase in reaction zone 2.

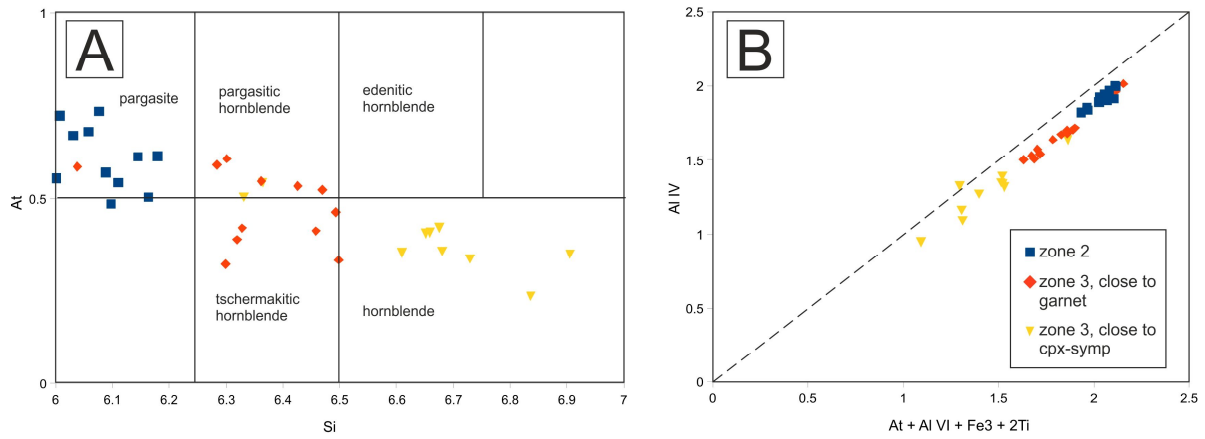


Fig. 15 (A) Binary plot A_{Na+K} vs Si. Nomenclature according to Leake (1978). Different symbols and colours indicate location of amphibole measurements in the reaction zone. **(B)** Plot of Al IV vs $At + Al VI + Fe^{3+} + 2Ti$. Trend line indicates prognosticated values for perfect substitution. Trend line after Czamanske et al. (1981).

table 11 representative analysis of plagioclase in Grt-coronae

| representative analysis of Pl (O = 8) of reaction zone 2 | | | | | | |
|--|---------------|---------------|--------------|--------------|--------------|--------------|
| Spatial distrib. | close to Grt | | | middle | | close to Cpx |
| sample | c35 | 4_40 | a_25 | Gt3-34 | Gt3-40 | 7g212 |
| SiO ₂ | 49.46 | 48.72 | 46.82 | 56.28 | 56.64 | 56.93 |
| Fe ₂ O ₃ | 0.46 | 0.58 | 0.63 | 0.42 | 0.37 | 0.61 |
| Al ₂ O ₃ | 32.12 | 33.17 | 32.98 | 25.81 | 26.24 | 26.74 |
| MnO | 0.09 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| CaO | 16.05 | 15.69 | 17.56 | 8.88 | 9.49 | 8.00 |
| Na ₂ O | 2.73 | 2.15 | 1.68 | 6.76 | 6.54 | 7.66 |
| K ₂ O | 0.00 | 0.00 | 0.00 | 0.01 | 0.00 | 0.00 |
| Total | 100.91 | 100.63 | 99.67 | 98.18 | 99.31 | 99.97 |
| Si | 2.246 | 2.212 | 2.164 | 2.576 | 2.565 | 2.561 |
| Al | 1.719 | 1.775 | 1.796 | 1.393 | 1.401 | 1.417 |
| Fe ³⁺ | 0.016 | 0.020 | 0.022 | 0.014 | 0.013 | 0.021 |
| Mn | 0.003 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 |
| Ca | 0.781 | 0.763 | 0.870 | 0.436 | 0.460 | 0.386 |
| Na | 0.240 | 0.189 | 0.151 | 0.600 | 0.574 | 0.668 |
| K | 0.000 | 0.000 | 0.000 | 0.001 | 0.000 | 0.000 |
| SumCat | 5.006 | 4.972 | 5.002 | 5.020 | 5.015 | 5.054 |
| X _{Ab} | 0.235 | 0.199 | 0.148 | 0.579 | 0.555 | 0.634 |
| X _{An} | 0.765 | 0.801 | 0.852 | 0.420 | 0.445 | 0.366 |

table 12 representative mineral analysis of amphibole in reaction bands and matrix

| representative analysis of amphibole (O = 23) | | | | | | | | | | | | | |
|---|---------------|---------------|---------------|---------------------|---------------|---------------|---------------------|---------------|---------------|---------------|---------------|---------------|---------------|
| | zone 2 | | | zone 3 close to grt | | | zone 3 close to cpx | | | Cl-amph veins | | matrix | |
| | d35 | d38 | c39 | Gt3-61 | 5_30 | 5_26 | d39 | c59 | 4_35 | 4_26 | 4_27 | 4_31 | 4_24 |
| IMA | Fe-Parg | | | Fe-Parg | | Hast | Mg-Horn | | | FeParg | Hast | Mg-Horn | |
| SiO ² | 39.79 | 40.78 | 40.00 | 42.63 | 40.13 | 39.87 | 44.46 | 45.30 | 45.27 | 36.88 | 37.03 | 49.15 | 49.52 |
| TiO ² | 0.80 | 0.70 | 0.73 | 1.05 | 0.67 | 1.18 | 0.26 | 0.29 | 0.32 | 0.63 | <0.10 | <0.10 | <0.10 |
| Al ² O ³ | 14.91 | 14.22 | 14.85 | 12.42 | 15.13 | 14.91 | 11.00 | 9.28 | 10.54 | 13.74 | 10.85 | 6.30 | 6.52 |
| Cr ² O ³ | <0.10 | <0.10 | <0.10 | <0.10 | <0.10 | <0.10 | <0.10 | <0.10 | <0.10 | <0.10 | <0.10 | <0.10 | <0.10 |
| FeO | 20.60 | 20.16 | 20.80 | 19.73 | 20.03 | 20.17 | 20.03 | 19.48 | 16.06 | 27.23 | 30.57 | 17.30 | 17.32 |
| MnO | <0.10 | <0.10 | <0.10 | 0.13 | 0.12 | <0.10 | 0.17 | <0.10 | <0.10 | <0.10 | 0.15 | 0.13 | 0.13 |
| MgO | 6.92 | 7.23 | 6.93 | 8.40 | 7.53 | 7.70 | 8.64 | 9.84 | 10.92 | 0.98 | 1.02 | 11.92 | 11.79 |
| CaO | 11.83 | 11.81 | 11.77 | 11.52 | 11.34 | 11.20 | 11.75 | 11.83 | 11.51 | 11.16 | 10.85 | 11.45 | 11.57 |
| Na ² O | 2.38 | 2.21 | 2.48 | 2.38 | 2.13 | 2.21 | 1.59 | 1.51 | 1.75 | 0.25 | 0.31 | 0.87 | 0.82 |
| K ² O | 0.27 | 0.24 | 0.21 | <0.10 | 0.60 | 0.65 | 0.14 | 0.10 | 0.55 | 3.21 | 3.39 | <0.10 | <0.10 |
| F | 0.19 | 0.12 | 0.16 | 0.16 | 0.24 | 0.16 | 0.19 | 0.18 | 0.23 | 0.36 | 0.29 | 0.24 | 0.33 |
| Cl | <0.10 | <0.10 | 0.19 | <0.10 | <0.10 | <0.10 | <0.10 | <0.10 | <0.10 | 2.63 | 2.85 | <0.10 | <0.10 |
| Total | 97.69 | 97.48 | 98.12 | 98.43 | 97.91 | 98.04 | 98.22 | 97.81 | 97.15 | 97.06 | 97.31 | 97.36 | 97.99 |
| Si | 6.041 | 6.179 | 6.058 | 6.362 | 6.038 | 5.997 | 6.612 | 6.737 | 6.717 | 6.148 | 6.239 | 7.222 | 7.240 |
| Ti | 0.091 | 0.079 | 0.084 | 0.118 | 0.075 | 0.134 | 0.029 | 0.032 | 0.036 | 0.078 | 0.000 | 0.000 | 0.000 |
| Al | 2.668 | 2.539 | 2.650 | 2.185 | 2.683 | 2.643 | 1.928 | 1.627 | 1.844 | 2.699 | 2.154 | 1.091 | 1.123 |
| Cr | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 |
| Fe ³⁺ | 0.504 | 0.443 | 0.500 | 0.456 | 0.659 | 0.639 | 0.570 | 0.610 | 0.371 | 0.165 | 0.659 | 0.480 | 0.413 |
| Fe ²⁺ | 2.112 | 2.111 | 2.133 | 2.006 | 1.861 | 1.898 | 1.921 | 1.813 | 1.622 | 3.632 | 3.649 | 1.646 | 1.705 |
| Mn | 0.000 | 0.000 | 0.000 | 0.017 | 0.015 | 0.000 | 0.022 | 0.000 | 0.000 | 0.000 | 0.022 | 0.016 | 0.016 |
| Mg | 1.565 | 1.633 | 1.563 | 1.869 | 1.688 | 1.726 | 1.915 | 2.182 | 2.415 | 0.244 | 0.256 | 2.611 | 2.569 |
| Ca | 1.925 | 1.917 | 1.910 | 1.843 | 1.828 | 1.805 | 1.872 | 1.885 | 1.831 | 1.994 | 1.958 | 1.803 | 1.812 |
| Na | 0.700 | 0.650 | 0.729 | 0.690 | 0.622 | 0.645 | 0.457 | 0.435 | 0.503 | 0.082 | 0.102 | 0.248 | 0.232 |
| K | 0.051 | 0.047 | 0.041 | 0.000 | 0.114 | 0.124 | 0.027 | 0.019 | 0.103 | 0.683 | 0.730 | 0.000 | 0.000 |
| F | 0.093 | 0.058 | 0.077 | 0.076 | 0.115 | 0.077 | 0.090 | 0.085 | 0.109 | 0.192 | 0.156 | 0.112 | 0.154 |
| Cl | 0.000 | 0.000 | 0.049 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.742 | 0.813 | 0.000 | 0.000 |
| SumCat | 15.750 | 15.656 | 15.794 | 15.622 | 15.698 | 15.688 | 15.443 | 15.425 | 15.551 | 16.659 | 16.738 | 15.229 | 15.264 |
| Al(IV) | 1.969 | 1.821 | 1.942 | 1.638 | 1.962 | 2.013 | 1.391 | 1.271 | 1.325 | 1.862 | 1.765 | 0.790 | 0.768 |
| Al(VI) | 0.695 | 0.718 | 0.708 | 0.547 | 0.721 | 0.625 | 0.535 | 0.353 | 0.507 | 0.833 | 0.388 | 0.299 | 0.353 |
| X _{Mg} | 0.426 | 0.436 | 0.423 | 0.482 | 0.476 | 0.476 | 0.499 | 0.546 | 0.598 | 0.063 | 0.066 | 0.613 | 0.601 |

7.3 Matrix minerals

7.3.1 Apatite

Apatite found in matrix is fluorapatite, with F contents > 1 wt.% and F/Cl > 1. FeO contents in apatites are below 1 wt.% with Ca/P of ~ 1.65. MnO, Na₂O contents are below detection limit of microprobe analysis. Apatite grains show no compositional zoning of major elements. Mineral analysis of matrix apatite is presented in table 13. Trace-element contents of matrix apatites and amphiboles were measured by LA-ICP-MS and are displayed in table 16.

table 13 representative analysis of matrix apatite

| representative matrix apatite analysis (O = 25) | | | | | | | | | |
|---|---------------|---------------|---------------|---------------|---------------|---------------|---------------|---------------|---------------|
| Sample | Gt3-48 | Gt3-49 | 35d_31 | 35d_32 | 35c_46 | 35c_47 | 35c_48 | 7g2_20 | 7g2_21 |
| Mineral | | | | | apatite | | | | |
| P ₂ O ₅ | 42.27 | 41.76 | 42.45 | 42.50 | 42.44 | 42.37 | 42.63 | 43.45 | 42.96 |
| Al ₂ O ₃ | 0.12 | 0.18 | 0.21 | <0.10 | 0.11 | <0.10 | <0.10 | <0.10 | <0.10 |
| Cr ₂ O ₃ | <0.10 | <0.10 | <0.10 | <0.10 | <0.10 | 0.10 | <0.10 | <0.10 | <0.10 |
| FeO | 0.21 | 0.14 | 0.38 | 0.10 | 0.15 | 0.36 | 0.31 | 0.28 | 0.05 |
| CaO | 56.12 | 56.30 | 55.41 | 55.65 | 56.11 | 55.58 | 55.69 | 54.14 | 54.18 |
| F | 1.16 | 1.35 | 1.49 | 1.57 | 1.30 | 1.45 | 1.12 | 1.81 | 1.95 |
| Cl | <0.10 | <0.10 | 0.16 | 0.16 | 0.19 | 0.19 | 0.17 | <0.10 | <0.10 |
| Total | 99.88 | 99.73 | 100.10 | 99.98 | 100.30 | 100.05 | 99.92 | 99.68 | 99.13 |
| P | 5.965 | 5.926 | 5.994 | 6.010 | 5.978 | 5.993 | 6.009 | 6.123 | 6.102 |
| Al | 0.024 | 0.036 | 0.041 | 0.000 | 0.022 | 0.000 | 0.000 | 0.000 | 0.000 |
| Cr | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.013 | 0.000 | 0.000 | 0.000 |
| Fe ²⁺ | 0.029 | 0.020 | 0.053 | 0.014 | 0.021 | 0.050 | 0.043 | 0.039 | 0.007 |
| Ca | 10.023 | 10.111 | 9.901 | 9.960 | 10.002 | 9.949 | 9.935 | 9.654 | 9.739 |
| F | 0.612 | 0.715 | 0.786 | 0.829 | 0.684 | 0.766 | 0.590 | 0.952 | 1.034 |
| Cl | 0.000 | 0.000 | 0.045 | 0.045 | 0.054 | 0.054 | 0.048 | 0.000 | 0.000 |
| SumCat | 16.653 | 16.808 | 16.820 | 16.858 | 16.761 | 16.825 | 16.625 | 16.768 | 16.882 |

7.3.2 Sphene

Sphene occurs as accessory mineral in sample X36. Sphene is compositionally homogenous, without obvious zoning. The Al and Fe contents are relatively low with ~ 0.05 apfu (atoms per formula unit), with small amounts of F. Representative mineral analyses are given in table 14.

table 14 representative analysis of matrix sphene

| representative matrix sphene analysis (O = 5) | | | | | | |
|---|--------------|--------------|--------------|--------------|--------------|--------------|
| | b_23 | b_25 | 4_24 | 36x4 | 36x5 | 36x15 |
| sphene | | | | | | |
| SiO ₂ | 30.77 | 30.62 | 30.46 | 30.89 | 31.12 | 31.12 |
| TiO ₂ | 37.97 | 37.24 | 38.11 | 37.26 | 37.11 | 37.11 |
| Fe ₂ O ₃ | 0.53 | 0.92 | 0.82 | 0.97 | 0.78 | 0.78 |
| Al ₂ O ₃ | 1.46 | 1.81 | 1.32 | 1.40 | 1.82 | 1.82 |
| Cr ₂ O ₃ | 0.11 | <0.10 | 0.12 | 0.11 | <0.10 | <0.10 |
| MgO | <0.10 | <0.10 | 0.00 | 0.12 | <0.10 | <0.10 |
| CaO | 27.71 | 27.63 | 27.58 | 27.35 | 27.13 | 27.13 |
| F | 0.60 | 0.45 | 0.38 | 0.54 | 0.70 | 0.70 |
| Total | 99.15 | 98.67 | 98.80 | 98.64 | 98.66 | 98.66 |
| Si | 1.015 | 1.013 | 1.007 | 1.023 | 1.029 | 1.029 |
| Ti | 0.941 | 0.927 | 0.948 | 0.928 | 0.923 | 0.923 |
| Al | 0.057 | 0.071 | 0.052 | 0.055 | 0.071 | 0.071 |
| Fe ³⁺ | 0.013 | 0.023 | 0.020 | 0.024 | 0.019 | 0.019 |
| Cr | 0.003 | 0.000 | 0.003 | 0.003 | 0.000 | 0.000 |
| Mg | 0.000 | 0.000 | 0.000 | 0.006 | 0.000 | 0.000 |
| Ca | 0.979 | 0.980 | 0.977 | 0.970 | 0.961 | 0.961 |
| F | 0.063 | 0.047 | 0.040 | 0.056 | 0.073 | 0.073 |
| SumCat | 3.071 | 3.061 | 3.047 | 3.065 | 3.076 | 3.076 |
| Al+Fe ³⁺ | 0.070 | 0.094 | 0.072 | 0.079 | 0.090 | 0.090 |

7.3.3 Clinozoisite/epidote, Chlorite, Ilmenite

Czo/Ep occurs in reaction zone 2, as well as in matrix; and shows compositional zoning. Brighter zones in BSE images probably contain substantial amounts of REEs (Fig. 11a). All epidote compositions belong to the clinozoisite/epidote solid solution series. The pistacite content ($Fe^{3+}/(Fe^{3+}+Al)$), varies from 15 to 30%. Small grains of chlorite (~ 20 μm) rarely occur around Grt in reaction zone 2 and are of Fe-rich chamositic composition. Ilmenite contains minor amounts of MnO and MgO. Fe^{3+} Recalculation for ilmenite was carried out according to Droop (1987). Representative mineral analyses are displayed in table 15.

table 15 representative analyses of matrix Czo/Ep, Chl and Ilm.

| representative analyses of Czo/Ep (O = 12.5), Chl (O = 14), Ilm (O = 3) | | | | | | |
|---|--------------|--------------|--------------|--------------|--------------|--------------|
| | X375_10 | 37g3_12 | Gt3-33 | x37g221 | x353c9 | x353c10 |
| mineral | clinozoisite | epidote | chlorite | | ilmenite | |
| SiO ₂ | 38.93 | 34.97 | 26.33 | 0.25 | 0.28 | 0.27 |
| TiO ₂ | 0.00 | 0.00 | 0.00 | 51.52 | 51.37 | 51.05 |
| Al ₂ O ₃ | 30.35 | 20.93 | 19.56 | - | - | - |
| Fe ₂ O ₃ | 5.36 | 12.13 | - | - | - | - |
| V ₂ O ₃ | - | - | - | <0.10 | 0.37 | 0.50 |
| FeO | - | - | 30.96 | 47.97 | 47.42 | 47.57 |
| MnO | - | - | <0.10 | 0.41 | 0.57 | 0.67 |
| MgO | <0.10 | 0.55 | 11.47 | 0.19 | 0.29 | 0.00 |
| CaO | 23.26 | 18.93 | 0.16 | 0.08 | 0.10 | 0.16 |
| F | <0.10 | 0.30 | - | 0.46 | - | - |
| Total | 97.9 | 87.8 | 88.6 | 100.4 | 100.4 | 100.2 |
| Si | 2.995 | 3.084 | 2.827 | 0.006 | 0.007 | 0.007 |
| Ti | 0.000 | 0.000 | 0.000 | 0.953 | 0.967 | 0.965 |
| Al | 2.752 | 2.175 | 2.475 | 0.000 | 0.000 | 0.000 |
| Fe ³⁺ | 0.310 | 0.805 | 0.000 | 0.153 | 0.044 | 0.047 |
| V | 0.000 | 0.000 | 0.000 | 0.000 | 0.007 | 0.010 |
| Fe ²⁺ | 0.000 | 0.000 | 2.780 | 0.834 | 0.949 | 0.953 |
| Mn | 0.000 | 0.000 | 0.000 | 0.009 | 0.012 | 0.014 |
| Mg | 0.000 | 0.072 | 1.836 | 0.007 | 0.011 | 0.000 |
| Ca | 1.917 | 1.789 | 0.018 | 0.002 | 0.003 | 0.004 |
| F | 0.000 | 0.084 | 0.000 | 0.036 | 0.000 | 0.000 |
| CatSum | 7.974 | 7.993 | 9.932 | 1.847 | 2.007 | 2.008 |

7.4 Trace elements and REE of matrix amphibole and apatite

Trace elements and REEs of matrix apatite and amphibole were measured with LA-ICP MS. REE were normalized to chondritic values after Nakamura, 1974. Apatite contains minor amounts of Mn (900 ppm), Sr (60 – 110 ppm) and Y (< 220 ppm) and displays REE abundances of $\sum\text{REE}_N$ 200 – 260 with REE patterns peaking at Tb. Concerning chondrite normalized REE patterns, no Eu or Ce anomaly can be located (Fig. 16). Amphibole contains variable amounts of REE with abundances of $\sum\text{REE}_N$ from 60 to 130. Chondrite normalized REE patterns display ascending LREEs ($\text{Eu}_N/\text{La}_N = 20 - 27$). Cr contents are fairly low with ~20 ppm. Low LREE concentrations in matrix Amp could be due to the presence of Ep, Spn and Ap which preferably partition LREEs. Representative trace element analysis of matrix Amp and Ap are shown in table 16.

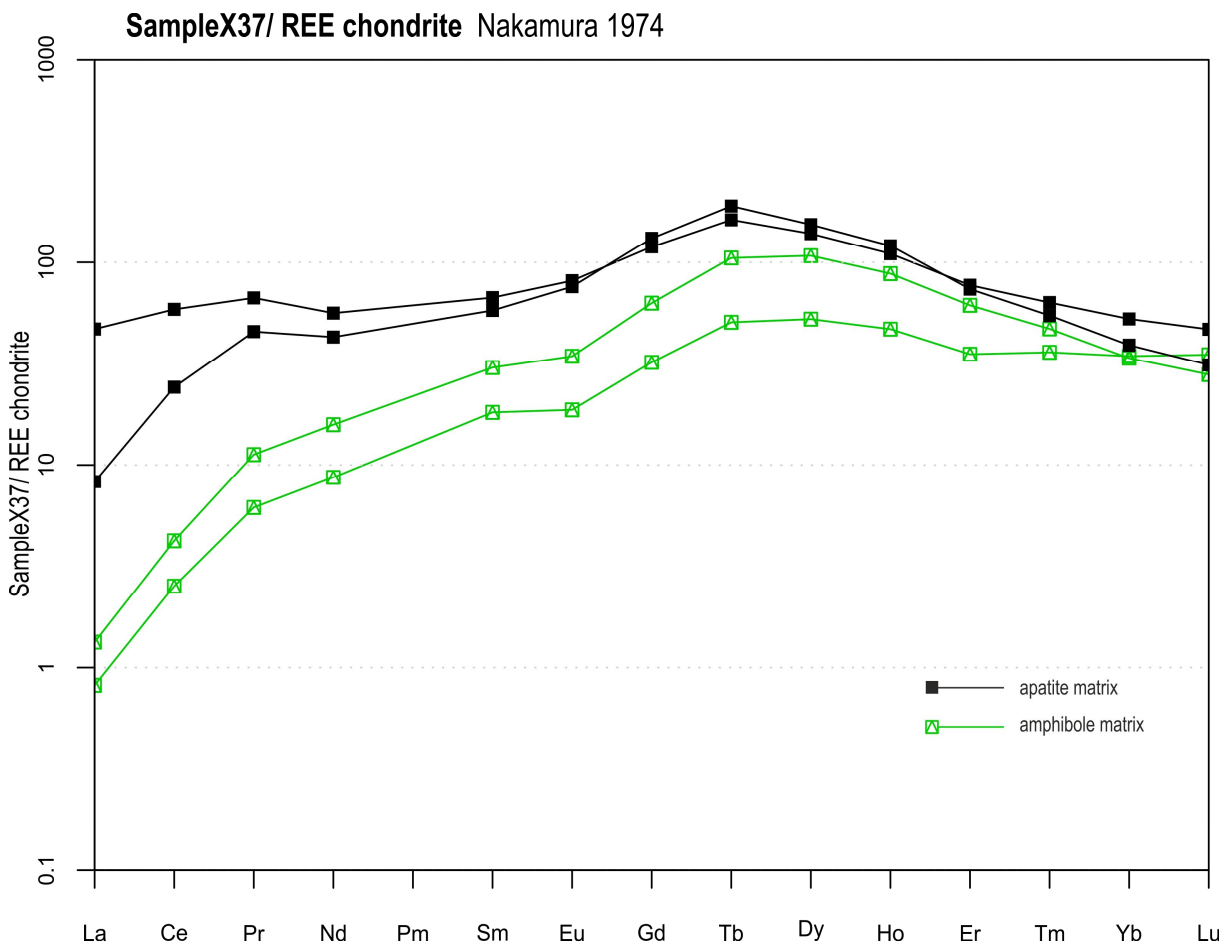


Fig. 16 chondrite normalized REE plot of matrix amphibole and apatite (Nakamura 1974)

table 16 trace element concentrations of matrix apatite and amphibole, quantified by LA-ICPMS

| Sample | apatite | | amphibole | |
|-------------------|---------|---------|-----------|---------|
| | 059XS48 | 062XS51 | 060XS49 | 061XS50 |
| ⁷ Li | 55.5 | 1.37 | 2.39 | 7.45 |
| ⁹ Be | <0.05 | 0.07 | 0.38 | 0.76 |
| ⁴⁹ Ti | 45.9 | 37.8 | 348 | 646 |
| ⁵¹ V | 5.25 | 7.44 | 240 | 180 |
| ⁵³ Cr | 0.77 | 1.89 | 18.6 | 19.4 |
| ⁵⁵ Mn | 829 | 756 | 1110 | 806 |
| ⁵⁹ Co | 17.6 | 3.60 | 56.4 | 60.7 |
| ⁶⁰ Ni | 11.9 | 6.37 | 50.2 | 40.1 |
| ⁶⁶ Zn | 38.9 | 19.0 | 178 | 180 |
| ⁷¹ Ga | 3.63 | 1.89 | 8.69 | 12.77 |
| ⁸⁵ Rb | 0.06 | 0.26 | 0.24 | 0.68 |
| ⁸⁸ Sr | 101 | 68.6 | 2.49 | 4.73 |
| ⁸⁹ Y | 201 | 199 | 80.0 | 141 |
| ⁹⁰ Zr | 37.0 | 4.29 | 51.8 | 20.3 |
| ⁹³ Nb | <0.05 | <0.05 | 1.81 | 0.71 |
| ¹³³ Cs | 0.22 | 0.06 | 0.27 | 0.45 |
| ¹³⁷ Ba | 0.69 | 1.33 | 1.91 | 9.64 |
| ¹³⁹ La | 15.5 | 2.73 | 0.27 | 0.44 |
| ¹⁴⁰ Ce | 50.7 | 20.9 | 2.18 | 3.65 |
| ¹⁴¹ Pr | 7.48 | 5.10 | 0.69 | 1.26 |
| ¹⁴⁶ Nd | 35.4 | 27.0 | 5.47 | 9.96 |
| ¹⁴⁷ Sm | 13.6 | 11.8 | 3.69 | 6.14 |
| ¹⁵³ Eu | 6.25 | 5.84 | 1.44 | 2.65 |
| ¹⁵⁷ Gd | 32.9 | 36.3 | 8.86 | 17.37 |
| ¹⁵⁹ Tb | 7.63 | 8.92 | 2.38 | 4.94 |
| ¹⁶³ Dy | 47.6 | 52.7 | 18.0 | 37.0 |
| ¹⁶⁵ Ho | 7.72 | 8.46 | 3.28 | 6.16 |
| ¹⁶⁶ Er | 17.4 | 16.6 | 7.93 | 13.8 |
| ¹⁶⁹ Tm | 1.90 | 1.64 | 1.08 | 1.41 |
| ¹⁷² Yb | 11.6 | 8.59 | 7.58 | 7.41 |
| ¹⁷⁵ Lu | 1.59 | 1.06 | 1.19 | 0.95 |
| ¹⁷⁸ Hf | 1.74 | 0.32 | 1.10 | 0.80 |
| ¹⁸¹ Ta | <0.05 | 0.05 | 0.07 | 0.05 |
| ²⁰⁸ Pb | 2.46 | 2.76 | 0.64 | 1.47 |
| ²³² Th | 0.11 | 0.12 | <0.05 | <0.05 |
| ²³⁸ U | 0.98 | 1.51 | <0.05 | <0.05 |

All values are reported in ppm

8 Garnet Chemistry and Zoning Patterns

Garnet is considered as a valuable mineral, since its composition shows a very sensitive response to pressure and temperature changes; but also, because cation diffusion functions sufficiently slow to preserve compositional differences within a grain at PT conditions below granulite facies. Growth zoning essentially depends on temperature, pressure, growth rate and the interaction with surrounding matrix minerals that are in equilibrium with the garnets surface (Spear, 1993; Menard and Spear, 1993). Therefore studying chemical zoning of garnet grains can reveal important information in order to reconstruct the rock's evolutionary history. Within the garnet amphibolite of the Songshugou metabasic unit, garnets play an important role in understanding the evolutionary history, since it is the only mineral which remained mostly unaltered during retrogression. In general, Grt of the Songshugou metabasic unit is almandine-rich ($X_{Alm} > 0.55$). Most grains show a characteristic chemical zoning pattern, particularly remarkable in X_{Grs} , which depicts a sharp boundary between Grt core and rim1 with an abrupt rise, and between rim1 and rim 2 with a sharp decline. Cation-diffusion experiments investigating cations that occupy the dodecahedral X site of garnet such as Mn, Mg, Fe and Ca have shown that volume diffusion of Ca in Grt functions remarkably slower (by an approximated factor of 5) than volume diffusion of Mg, Fe, and Mn, not least because of the larger ionic size of Ca. (Chakraborty and Ganguly 1991; Tracy 1992, Schwandt et al., 1996). Therefore distribution of Ca and other slow diffusing trace elements such as Y and P offer a convenient way to identify and determine compositional zones throughout Grt grains. Steep compositional gradients observed in the zoning pattern are diagnostic of discontinuous growth, and permit to subdivide garnets of the Songshugou metabasic unit into 3 distinctive compositional zones: Core, Rim1, and Rim2. Sluggish element supply to the garnets surface could cause growth interruption, and consequently steep compositional gradients (Spear and Daniel, 2001). Representative garnet analysis from the different growth zones of the least retrogressed samples X35, X36 and X37 are given in table 17, table 18 and table 19. X_{Sps} decreases from core to rim. In sample X35 a drop in X_{Sps} is observed at the core rim boundary. In X37 X_{Sps} contents are low with $X_{Sps} < 0.26$ and show flat distributions. Garnet cores are approximately homogeneous with $X_{Alm} \sim 0.60$ in X35 and X37 and $X_{Alm} \sim 0.53$ in X36, $X_{Prp} \sim 0.10$ in X35 and X37 and $X_{Prp} \sim 0.15$ in x36 and $X_{Grs} = 0.23-0.28$. Rim1 exhibits a remarkably high plateau in $X_{Grs} = 0.29-0.35$. Rim2 has similar composition to garnet core but significantly less X_{Sps} . In sample X35 X_{Prp} increases towards rim, in some cases stepwise in others gradually, in the contrary to X36 and X37 where X_{Prp} decreases in rim1 and increases in rim2. The most conspicuous feature is the abrupt increase of X_{Grs} between core and rim1, and the drop of X_{Grs} between rim1 and rim2; which is ubiquitously in all garnets. Ternary $Fe^{2+} - Ca - Mg$ plots in Fig. 17 illustrate chemical differences of garnet zones. In general, FeO contents of garnet from sample X36 are ~ 3 wt.% lower than in X35 and X37, reflecting its different chemical composition.

Garnet zoning profiles and 2D X-ray element distribution maps were produced to reveal characteristic zoning patterns of major elements in garnet. Trace elemental data along transects across selected garnet grains was obtained by LA-ICPMS. Garnet zoning profiles of samples X35, X36 and X37 are presented in Fig. 18. Garnet grains from sample X37 show a Mn enrichment at the outmost area of the outer rim which might indicate garnet resorption during retrogression where Mn is retained or re-enters the residual garnet.

table 17 representative garnet mineral analysis of sample X35

| sample X35, representative garnet mineral analysis (O = 13) | | | | | | |
|---|---------------|---------------|---------------|---------------|--------------|--------------|
| | core | | rim1 | | rim2 | |
| sample | 14 | 15 | 6 | 7 | xd4 | xd33 |
| SiO ₂ | 37.88 | 37.68 | 38.17 | 37.99 | 38.14 | 37.85 |
| TiO ₂ | 0.15 | 0.18 | <0.10 | 0.19 | <0.10 | <0.10 |
| Al ₂ O ₃ | 20.91 | 20.89 | 20.86 | 20.73 | 20.65 | 20.09 |
| FeO | 28.10 | 28.04 | 27.30 | 27.03 | 28.97 | 29.91 |
| MnO | 1.82 | 3.58 | 0.69 | 0.98 | 0.29 | 0.77 |
| MgO | 2.81 | 2.18 | 3.12 | 2.94 | 4.30 | 3.11 |
| CaO | 8.45 | 8.28 | 10.61 | 10.36 | 7.42 | 7.90 |
| Total | 100.12 | 100.83 | 100.84 | 100.22 | 99.78 | 99.63 |
| Si | 3.003 | 2.983 | 2.988 | 2.995 | 3.012 | 3.019 |
| Ti | 0.009 | 0.011 | 0.000 | 0.011 | 0.000 | 0.000 |
| Al | 1.954 | 1.949 | 1.925 | 1.926 | 1.922 | 1.889 |
| Fe ²⁺ | 1.840 | 1.794 | 1.688 | 1.720 | 1.858 | 1.922 |
| Fe ³⁺ | 0.023 | 0.062 | 0.099 | 0.062 | 0.055 | 0.073 |
| Mn | 0.122 | 0.240 | 0.046 | 0.065 | 0.019 | 0.052 |
| Mg | 0.332 | 0.257 | 0.364 | 0.346 | 0.506 | 0.370 |
| Ca | 0.718 | 0.702 | 0.890 | 0.875 | 0.628 | 0.675 |
| SumCat | 8.001 | 7.998 | 8.000 | 8.000 | 8.000 | 7.996 |
| X _{Alm} | 0.611 | 0.599 | 0.565 | 0.572 | 0.617 | 0.637 |
| X _{Grs} | 0.238 | 0.235 | 0.298 | 0.291 | 0.209 | 0.224 |
| X _{Prp} | 0.110 | 0.086 | 0.122 | 0.115 | 0.168 | 0.123 |
| X _{Sps} | 0.041 | 0.080 | 0.015 | 0.022 | 0.006 | 0.017 |

table 18 representative garnet mineral analysis of sample X36

| sample X36, representative garnet mineral analysis (O = 13) | | | | | | |
|---|--------------|---------------|--------------|--------------|---------------|--------------|
| | core | | rim1 | | rim2 | |
| sample | 62 | 67 | 111 | 125 | 1133 | 1120 |
| SiO ₂ | 38.16 | 38.39 | 38.57 | 38.13 | 38.53 | 38.63 |
| TiO ₂ | <0.10 | <0.10 | 0.26 | <0.10 | 0.10 | <0.10 |
| Al ₂ O ₃ | 20.74 | 21.36 | 20.39 | 20.62 | 20.74 | 21.25 |
| FeO | 24.95 | 25.05 | 23.99 | 24.54 | 25.93 | 25.15 |
| MnO | 2.87 | 2.33 | 0.98 | 0.23 | 0.70 | 0.22 |
| MgO | 3.85 | 3.97 | 3.26 | 3.83 | 3.78 | 3.79 |
| CaO | 9.13 | 9.17 | 12.25 | 11.45 | 10.53 | 10.63 |
| Total | 99.79 | 100.28 | 99.70 | 98.80 | 100.31 | 99.76 |
| Si | 3.010 | 3.004 | 3.035 | 3.000 | 3.035 | 3.016 |
| Ti | 0.000 | 0.000 | 0.015 | 0.002 | 0.015 | 0.000 |
| Al | 1.928 | 1.970 | 1.891 | 1.912 | 1.891 | 1.923 |
| Fe ²⁺ | 1.594 | 1.618 | 1.570 | 1.460 | 1.570 | 1.579 |
| Fe ³⁺ | 0.052 | 0.022 | 0.009 | 0.155 | 0.009 | 0.045 |
| Mn | 0.192 | 0.154 | 0.065 | 0.015 | 0.065 | 0.015 |
| Mg | 0.453 | 0.463 | 0.382 | 0.449 | 0.382 | 0.452 |
| Ca | 0.772 | 0.769 | 1.033 | 0.965 | 1.033 | 0.970 |
| SumCat | 8.000 | 8.000 | 8.000 | 7.958 | 8.000 | 7.989 |
| X _{Alm} | 0.529 | 0.539 | 0.515 | 0.505 | 0.515 | 0.524 |
| X _{Grs} | 0.256 | 0.256 | 0.339 | 0.334 | 0.339 | 0.322 |
| X _{Prp} | 0.150 | 0.154 | 0.125 | 0.155 | 0.125 | 0.150 |
| X _{Sps} | 0.064 | 0.051 | 0.021 | 0.005 | 0.021 | 0.005 |

table 19 representative garnet mineral analysis of sample X37

| sample X37, representative garnet mineral analysis (O = 13) | | | | | | |
|---|--------------|--------------|---------------|---------------|--------------|---------------|
| | core | | rim1 | | rim2 | |
| sample | 57 | 5_1 | 149 | 153 | 1143 | 1119 |
| SiO ₂ | 37.97 | 37.63 | 38.02 | 37.70 | 37.87 | 38.16 |
| TiO ₂ | <0.10 | <0.10 | 0.28 | 0.31 | <0.10 | <0.10 |
| Al ₂ O ₃ | 20.49 | 20.05 | 19.33 | 19.14 | 20.65 | 20.82 |
| FeO | 28.10 | 27.34 | 27.65 | 27.56 | 28.78 | 28.22 |
| MnO | 1.16 | 2.78 | 1.06 | 1.04 | 0.82 | 0.86 |
| MgO | 2.51 | 2.06 | 2.62 | 2.67 | 2.97 | 3.85 |
| CaO | 9.74 | 9.15 | 11.98 | 12.11 | 8.53 | 8.41 |
| Total | 99.99 | 99.09 | 100.94 | 100.53 | 99.68 | 100.39 |
| Si | 3.015 | 3.028 | 2.989 | 2.975 | 3.013 | 2.999 |
| Ti | 0.006 | 0.000 | 0.017 | 0.018 | 0.000 | 0.000 |
| Al | 1.913 | 1.963 | 1.791 | 1.780 | 1.937 | 1.929 |
| Fe ²⁺ | 1.651 | 1.649 | 1.619 | 1.586 | 1.879 | 1.783 |
| Fe ³⁺ | 0.046 | 0.000 | 0.199 | 0.233 | 0.037 | 0.072 |
| Mn | 0.046 | 0.015 | 0.071 | 0.070 | 0.055 | 0.057 |
| Mg | 0.441 | 0.443 | 0.307 | 0.314 | 0.352 | 0.451 |
| Ca | 0.883 | 0.893 | 1.009 | 1.024 | 0.727 | 0.708 |
| SumCat | 8.000 | 7.990 | 8.000 | 8.000 | 8.000 | 8.000 |
| X _{Alm} | 0.547 | 0.550 | 0.539 | 0.530 | 0.624 | 0.595 |
| X _{Grs} | 0.292 | 0.298 | 0.336 | 0.342 | 0.241 | 0.236 |
| X _{Prp} | 0.146 | 0.148 | 0.102 | 0.105 | 0.117 | 0.150 |
| X _{Sps} | 0.015 | 0.005 | 0.024 | 0.023 | 0.018 | 0.019 |

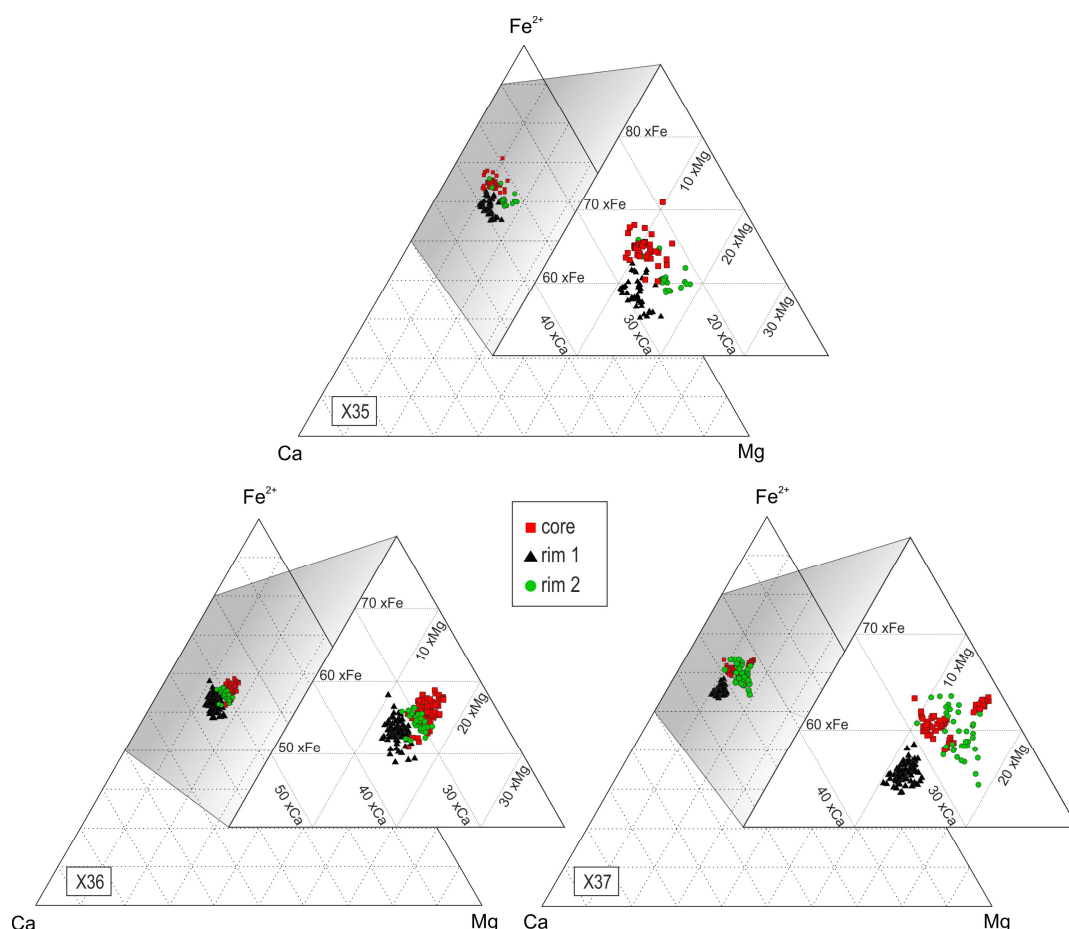


Fig. 17 ternary Fe²⁺ - Ca - Mg plot of garnets. XFe = 100* Fe²⁺/(Fe²⁺ + Ca + Mg); XCa = 100*Ca/(Fe²⁺ + Ca + Mg); XMg = 100* Mg/(Fe²⁺ + Ca + Mg). Red, black and green symbols represent garnet core, rim1 and rim2 compositions.

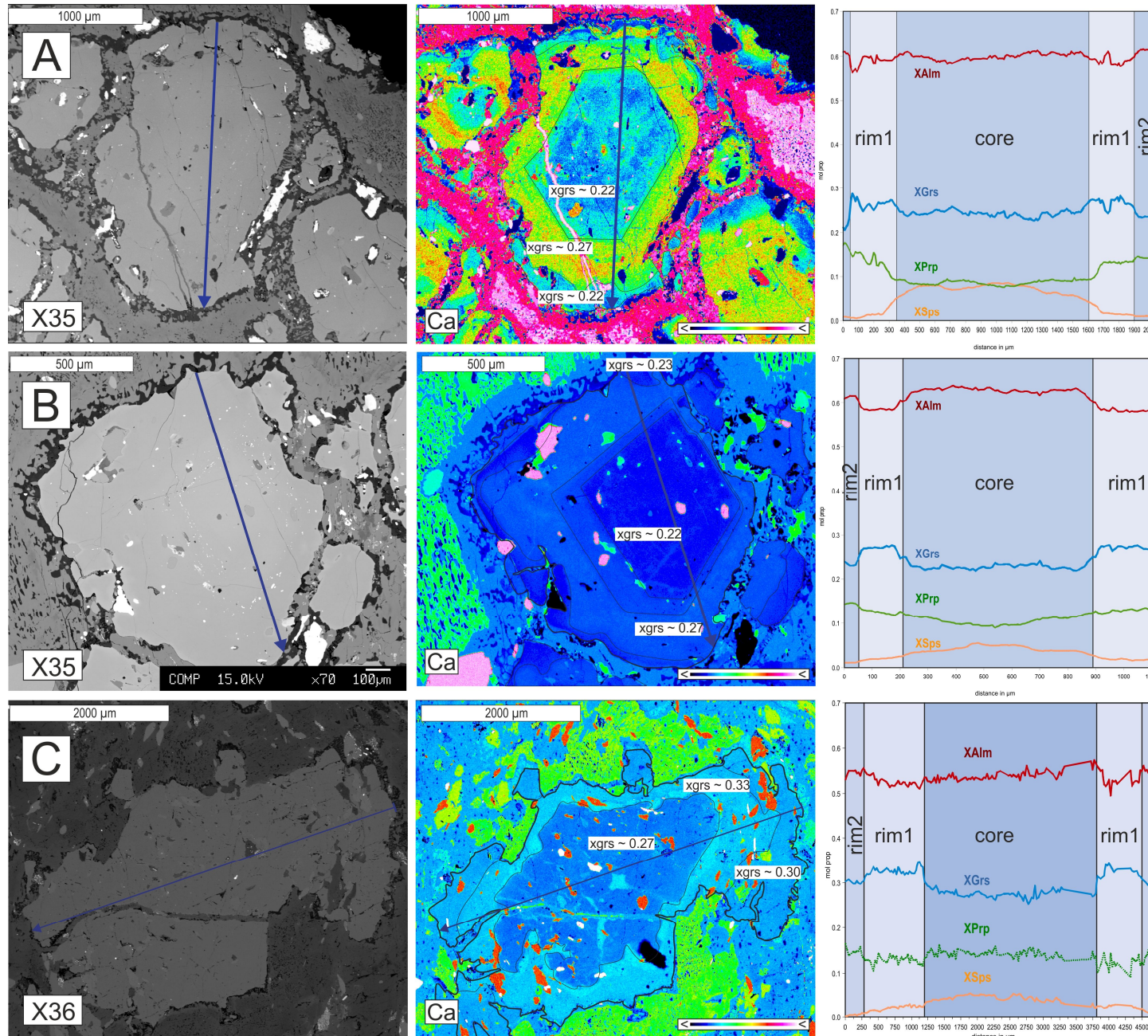
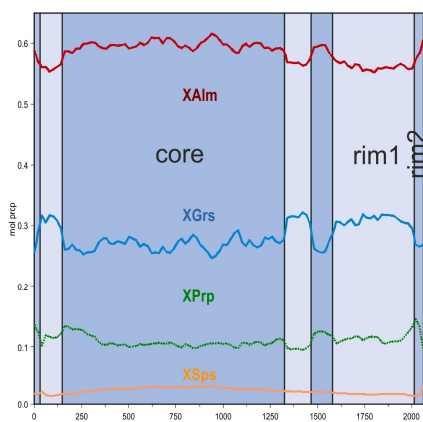
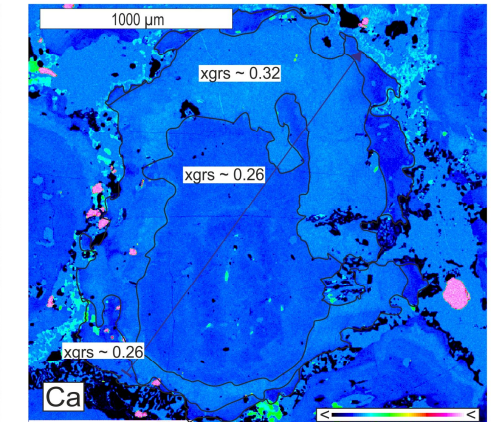
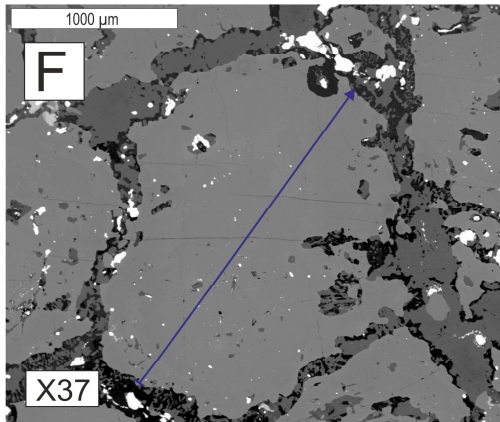
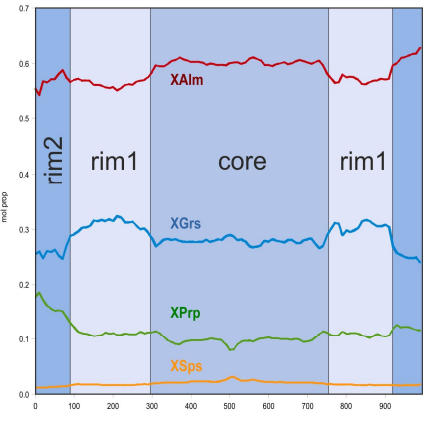
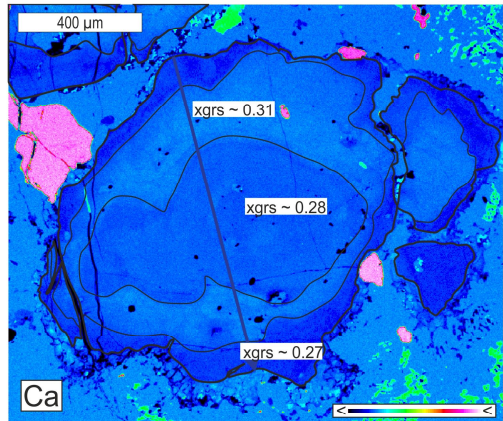
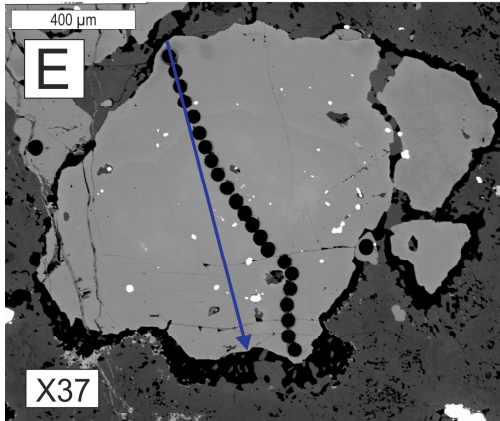
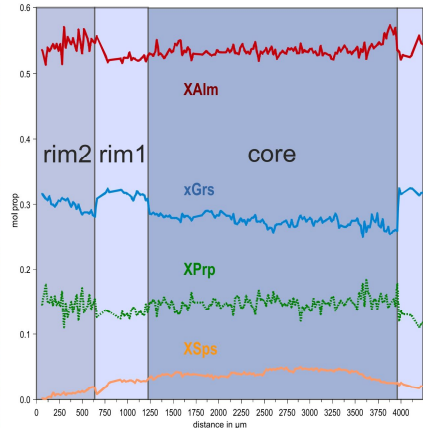
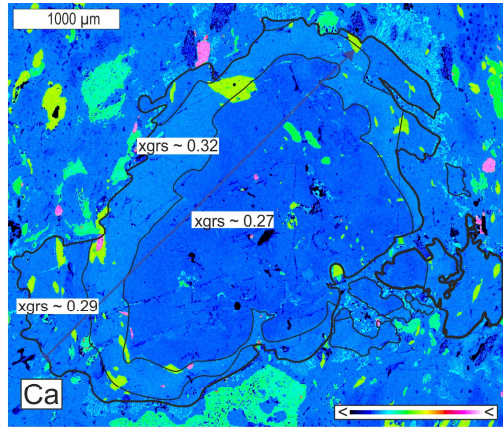
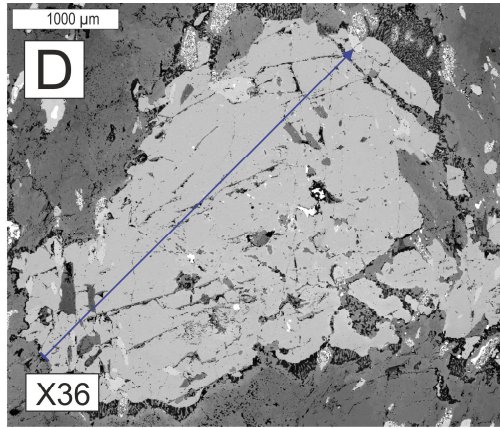


Fig. 18 Various garnet zonation profiles of garnet amphibolite samples, X35, X36 and X37. From left to right: BSE image, Ca-distribution image and profile are displayed. Profile line is drawn into BSE and Ca-distribution image. Garnet grains of Ca-distribution images were contoured for easier differentiation between garnet grain and matrix minerals. **(A)** Garnet profile of sample X35. X_{Sps} is enriched in core with values of ~0.09 and decreases with a steep compositional gradient at the core-rim1 boundary before continuously decreasing at a remarkably lower gradient. X_{Grs} shows enrichment in rim1, which is the most prominent feature in garnet zonation profiles and appears ubiquitous in all measured garnet profiles. X_{Alm} has almost constant values throughout the whole garnet profile with a slight moat in rim1. X_{Prp} increases stepwise at core – rim1 boundary and rim1 - rim2 boundary. **(B)** Sample X35. Garnet zoning pattern is very similar to profile A, with the characteristic X_{Grs} plateau in rim1. X_{Alm} shows an inverse X_{Grs} pattern with a compositional moat marking rim1. This might be caused by less overall MnO in the garnets chemistry, and therefore less X_{Sps} in the core. In contrast to profile A, where X_{Prp} increases stepwise, it increases in a continuous manner. **(C)** Garnets of rock sample X36 contain lower amounts of FeO, resulting in lower X_{Alm} contents around 0.55 instead of 0.60 which is observed in the garnet compositions of samples X35 and X37. X_{Sps} shows a roughly bell shaped distribution. X_{Grs} component is commonly elevated compared to X35 profiles, and displays the same plateau like patterns in rim1. Differently to X35 profiles, X_{Prp} decreases in rim1 before it increases again in rim2.



(D) Sample X36. Profile D shows similar characteristics like profile C. Again with X_{Grs} plateaus in rim1 and increasing X_{Prp} in rim2. (E) Garnet profile of sample X37. Black dots in BSE image were generated by laser ablation. Profiles of X37 are similar to those of X35 but slightly enriched in X_{Grs} and contain less amounts of X_{Alm} . There is a X_{Grs} plateau marking rim1. X_{Sps} decreases almost gradually towards the rim. X_{Prp} shows constant values in core and rim1 and increases in rim2. X_{Alm} shows an inverse X_{Grs} zoning, with enriched cores and usually also an increase in rim2. (F) Garnet zonation profile of sample X37 shows very similar zoning patterns compared with profile E. A X_{Grs} plateau and a X_{Prp} moat indicates rim1. X_{Alm} component shows inverse X_{Grs} zoning patterns. X_{Sps} displays a flat distribution from core to rim.

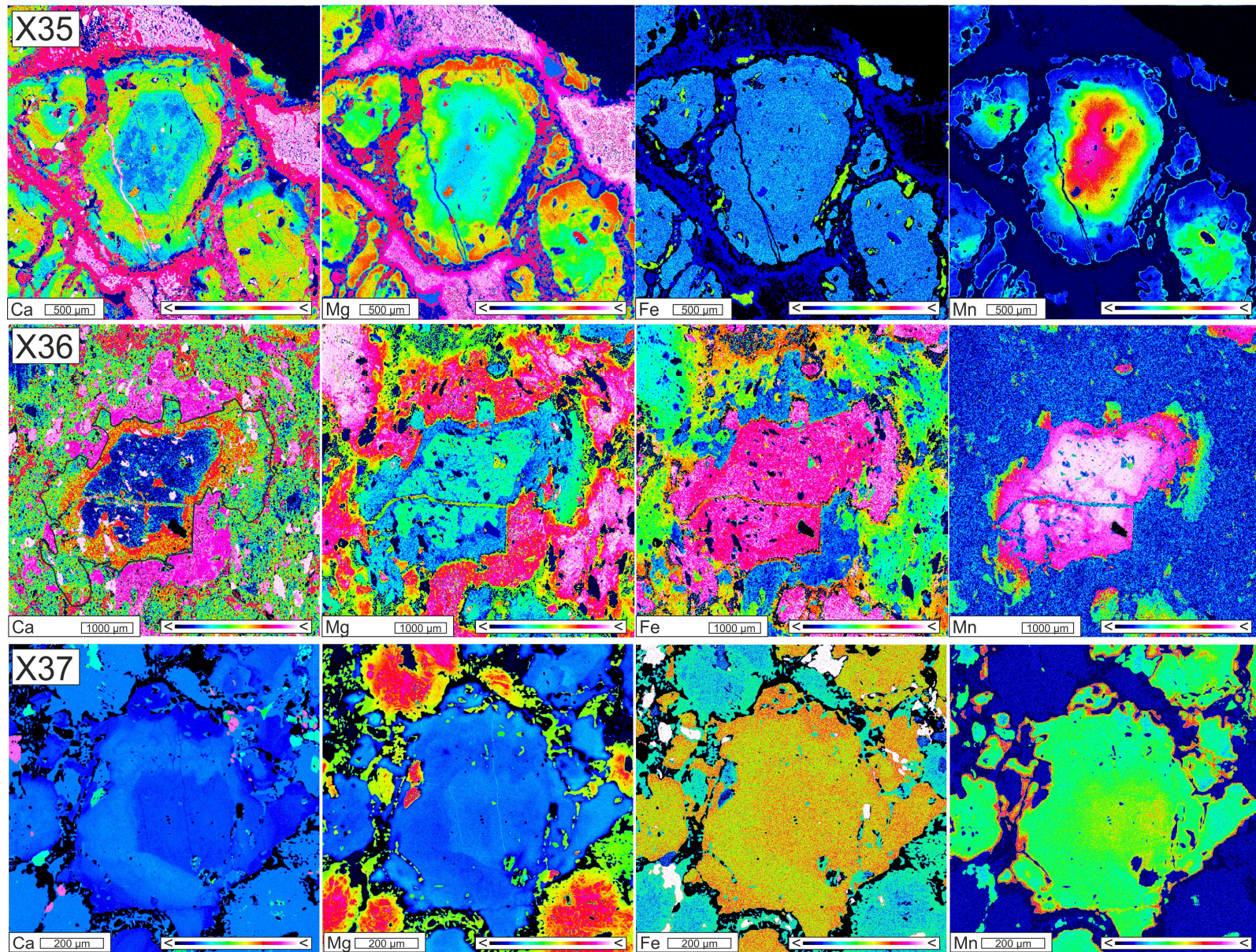


Fig. 19 element distribution images of samples X35, X36 and X37. Garnet grain displayed in Ca-distribution image of X36 is contoured for more convenient discrimination with adjacent matrix mineral phases.

8.1 Trace and REE chemistry of garnet

The distribution of trace elements and REEs in metamorphic minerals can reveal important information of the rocks metamorphic history when coupled with the fact that diffusion of trace elements and REEs functions, in general, are considerably slower than diffusion of major elements (Volkova et al., 2014). Concerning REEs, garnets show increasing partition coefficients along with higher atomic number. That usually leads to typical chondrite normalized REE patterns with highly enriched HREEs. Nevertheless, breakdown of surrounding minerals while garnet growth could introduce REEs into the system and consequently contribute to a change of chondrite normalized REE distribution patterns. In metabasic rocks, substantial amounts of REEs are incorporated into Grt, Cpx, Amp, and Czo/Ep. But also accessory minerals such as Ap and Spn partition decent quantities of LREEs and traces and therefore should not be neglected. In basic rocks, amphibole shows remarkably higher partition coefficients for light HREEs such as Sm and Nd compared to garnet. Therefore Amp breakdown could cause an enrichment of those elements in garnet REE distribution patterns which might be the case in the trends observed in garnet grains of the Songshugou garnet amphibolites. Partition coefficient data of elements for all types of rocks and minerals were taken from <http://earthref.org>. For LA ICPMS analysis, inclusion- and crack-poor garnets were chosen. BSE images with major element zoning patterns and selected trace and REE profiles of garnet grains from sample X35, X36 and X37 are displayed in Fig. 21, Fig. 22 and Fig. 23. In the following, trace and REE geochemistry of a garnet grain of sample X37 (Fig. 23) is described in detail. V, Ni and Cr show remarkable zoning patterns with very low abundances in the core and a sudden increase in rim1. Ilmenite occurs as a prominent mineral included in garnet cores, but is hardly existant, if at all, in rims. This indicates that garnet rims evolved at PT conditions beyond Ilm stability. Ilmenite usually contains significant amounts of Cr, Ni, Sc, and V. Thus the observed increase in V, Ni and Cr in garnet rim1 points to a breakdown of Ilm to Grt and Rt.

LREE (Sc, La, Ce, Pr, Nd, Pm, Sm, Eu, Gd) : The elements La to Pr are typically very low or not detectable in garnets. Neodymium, Sm, Eu and Gd show similar zoning trends with low abundances in the core and an abrupt increase at rim 1, which would be symptomatic for the breakdown of Amp, which preferentially incorporates these elements. The absence of a negative Eu anomaly in the chondrite normalized REE pattern of garnet indicates that Pl did not play a role in the distribution of Eu.

HREE (Y, Tb, Dy, Ho, Er, Tm, Yb, Lu): the elements Er, Tm, Yb and Lu show typical Rayleigh fractionation. Yttrium, Tb, Dy and Ho have similar zoning patterns like Nd, Pm, Sm, Eu, Gd. Contents are significantly increasing towards the garnet rims. Again, the breakdown of amphibole would account for the observed distribution pattern. Representative trace element and REE data of garnets from samples X35, X36 and X37 is given in Table 20, Table 21 and Table 22. Garnet of sample X35 and X37 is strongly depleted in LREE with average chondrite-normalized (Nakamura 1974) La_N of $<0.05 - 0.06$ but enriched in HREE with Yb_N up to 640 in sample X37 and Yb_N up to 352 in sample X35. Garnets of sample X36 show similar fractionation trends but with significantly lower overall REE abundances ($Yb_N < 60$).

Chondrite normalized REE patterns from the core, rim 1 and rim 2 of samples X35, X36 and X37 are shown in Fig. 24, Fig. 25 and Fig. 26. Garnet core measurements (red lines) show typical HREE enrichments of garnet. Concerning Grt of sample X37, Grt rim measurements (black lines for rim 1, green lines for outermost rim 2) are slightly enriched in the lighter HREEs (Tb, Dy, Ho) with $(Dy/Yb)_N = 1.0 - 1.5$ for rim1 and $(Dy/Yb)_N = 2.0 - 3.6$ for rim2, in contrast to garnet core with $(Dy/Yb)_N = 0.08 - 0.5$. Same trends are observed in samples X35 and X36 with $(Dy/Yb)_N = 0.20 - 0.60$ for grt core, $(Dy/Yb)_N = 0.70 - 2.50$ for rim1 and $(Dy/Yb)_N = 1.90 - 3.60$ for rim2 and $(Dy/Yb)_N = 0.30 - 1.00$ for grt core, $(Dy/Yb)_N = 0.50 - 4.00$ for rim1 and $(Dy/Yb)_N = 4.00 - 12.16$ for rim2, respectively. The elements Sm, Tb, Dy, Ho and Er are preferably incorporated in Amp and Ep. Breakdown of Amp and/or Ep during garnet rim growth could nourish the system with those elements leading to the observed distribution pattern. Epidote also incorporates Y. Therefore at phase breakdown Y would be available for garnet. Fig. 20 displays a calculated pseudosection of sample X37. Amp modes, plotted as orange lines, decrease towards higher PT conditions. Hence, increasing PT conditions lead to Amp breakdown which

could result in the observed chondrite normalized REE patterns of Grt rims with enriched Sm, Eu, Gd, Tb and Dy.

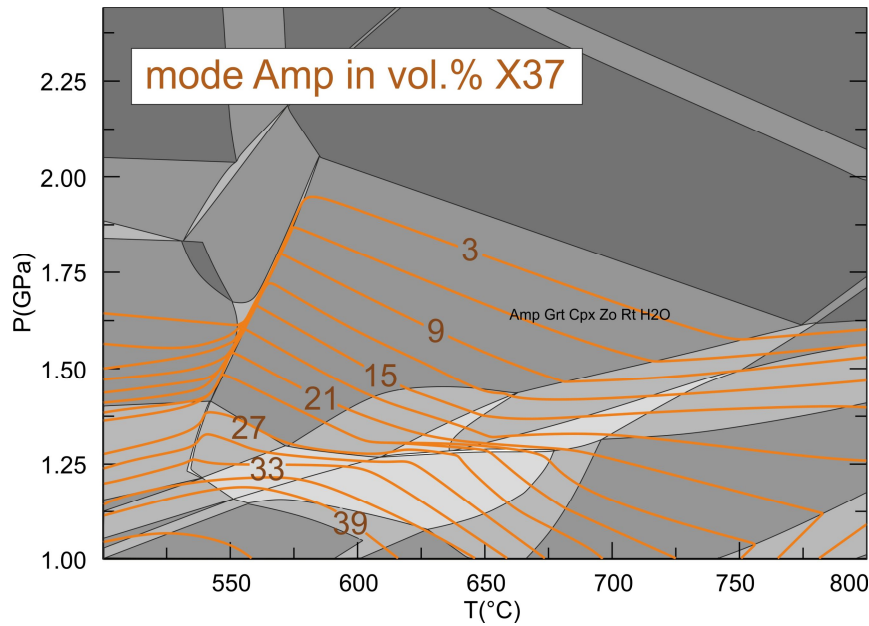


Fig. 20 Pseudosection calculated for sample X37. Orange lines represent Amp mode in vol.%.

In all rock samples, garnets show a general rimward decrease in heavy HREE, with Lu_N up to 360 in garnet core to 6 in the outmost rim for X35, with Lu_N up to 60 in garnet core to 4 in the outmost rim for X36 and Lu_N up to 760 in garnet core to 30 in the outmost rim for X37, which can be explained by HREE depletion of the matrix during garnet growth in a closed system.

Concerning REE and trace element distribution, garnet grains of sample X35 and X36 show similar zoning patterns like sample X37. LREEs such as: Nd, Sm, Eu, Gd and Tb are enriched in garnet rim compared to core. Ho, Er, Tm, Yb and Lu show typical Rayleigh distribution. In contrast to sample X36 and X37, grains of X35 do not show a clear zoning pattern in V and Cr but the garnet cores are enriched in Li.

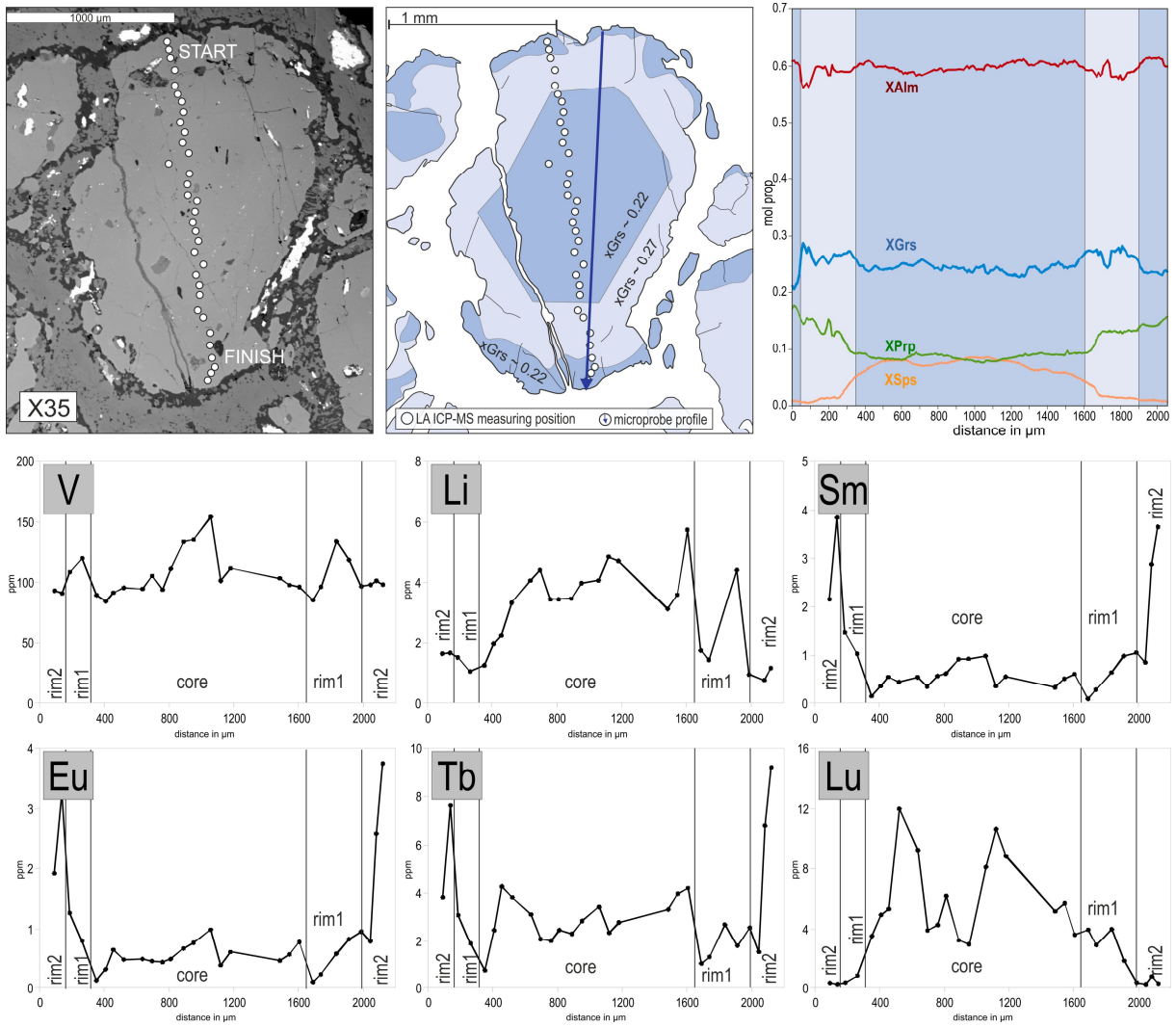


Fig. 21 Top left: BSE image of garnet grain (sample X35). Top centre: redrawn garnet grain, zones: core, rim1, and rim2 are contoured after Ca-element distribution image to clearly correlate LA ICP-MS measurements with corresponding garnet zones. Top right: major element zoning pattern, with ubiquitous X_{Grs} plateau marking rim1. Bottom: Trace element and REE zoning patterns.

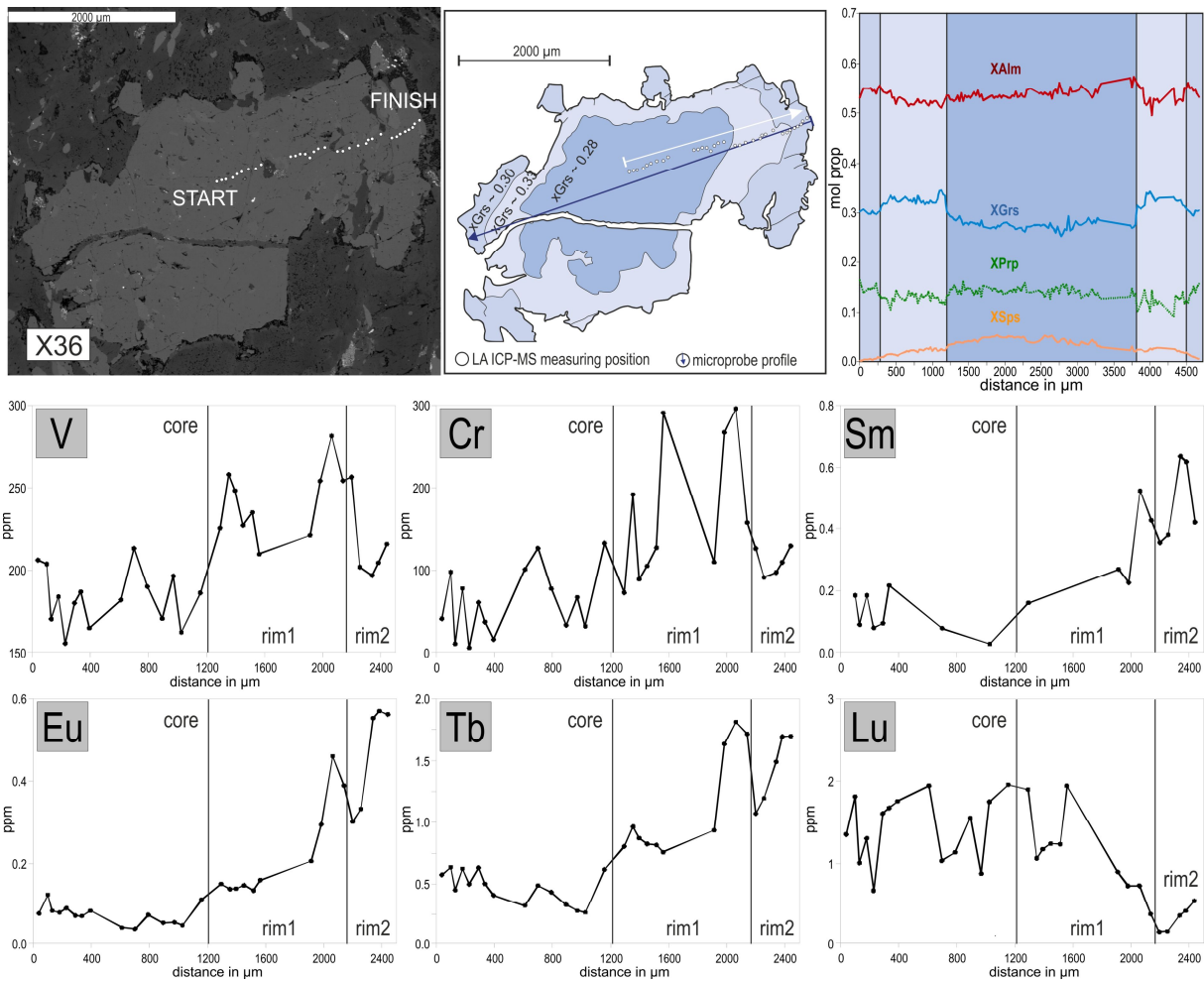


Fig. 22 Top left: BSE image of garnet grain (sample X36). Top centre: redrawn garnet grain, zones: core, rim1, and rim2 are contoured after Ca-element distribution image to clearly correlate LA ICP-MS measurements with corresponding garnet zones. Top right: major element zoning pattern, with ubiquitous X_{Grs} plateau marking rim1. Bottom: Trace element and REE zoning patterns.

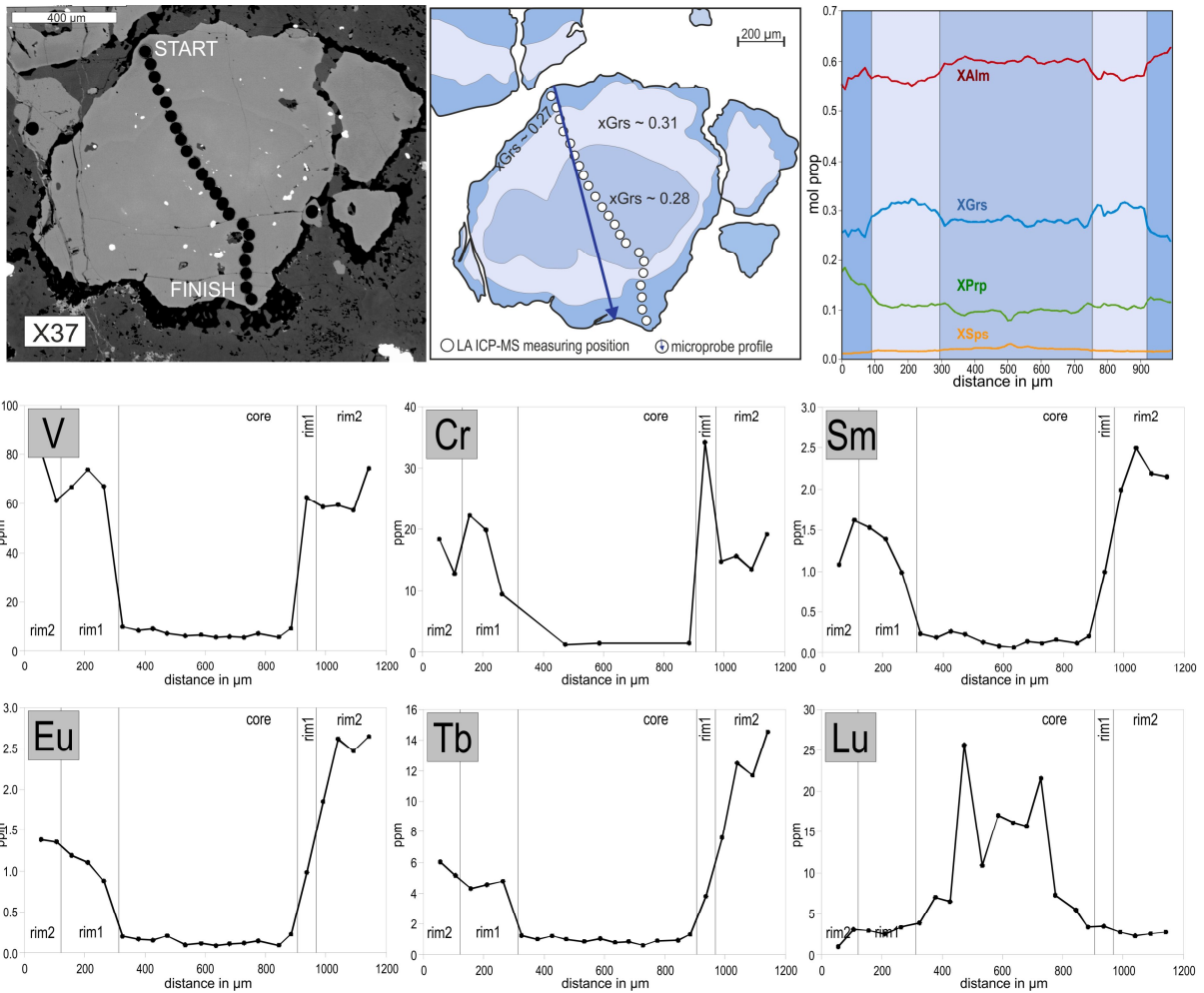


Fig. 23 Top left: BSE image of garnet grain (sample X37). Top centre: redrawn garnet grain, zones: core, rim1, and rim2 are contoured after Ca-element distribution image to clearly correlate LA ICP-MS measurements with corresponding garnet zones. Top right: major element zoning pattern, with ubiquitous X_{Grs} plateau marking rim1. Bottom: Trace element and REE zoning patterns.

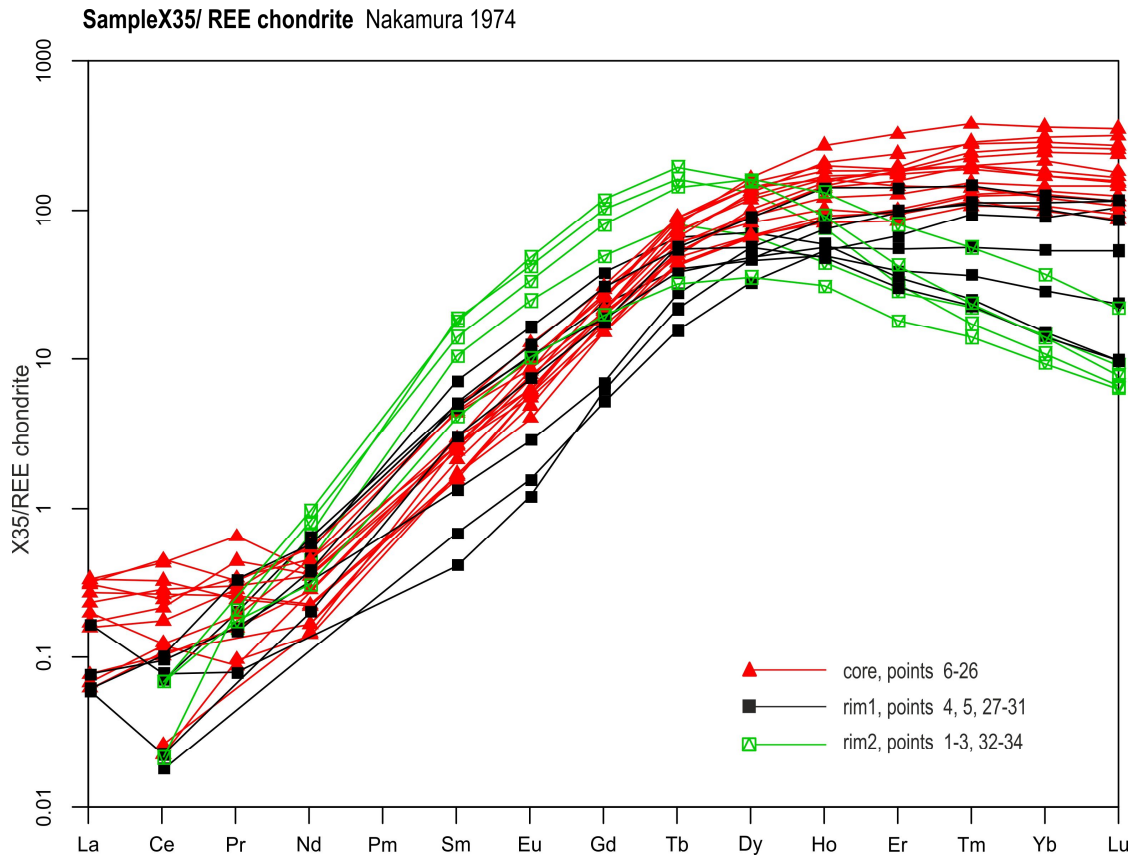


Fig. 24 chondrite normalized REE plot of garnet after Nakamura 1974 (sample X35). Garnet-core, rim1 and rim2 are plotted as red, black and green lines.

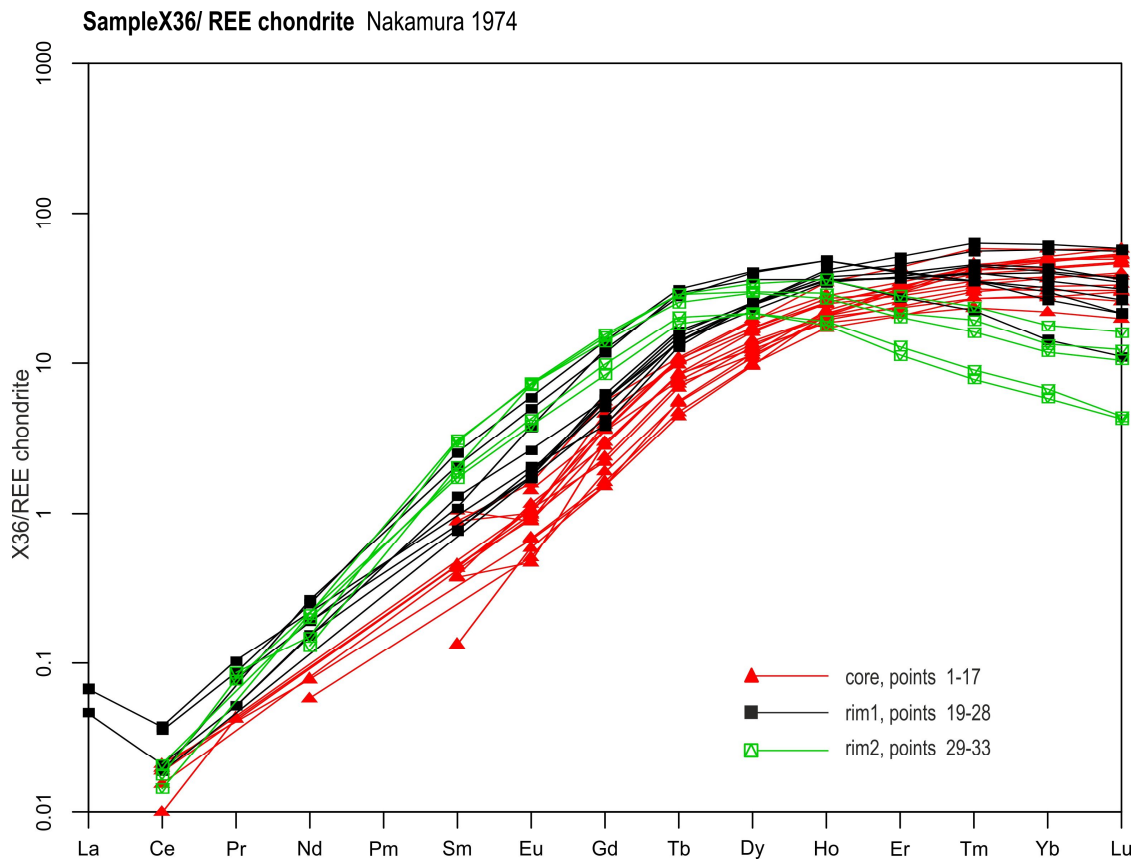


Fig. 25 chondrite normalized REE plot of garnet after Nakamura 1974 (sample X36). Garnet-core, rim1 and rim2 are plotted as red, black and green lines.

Sample X37/ REE chondrite Nakamura 1974

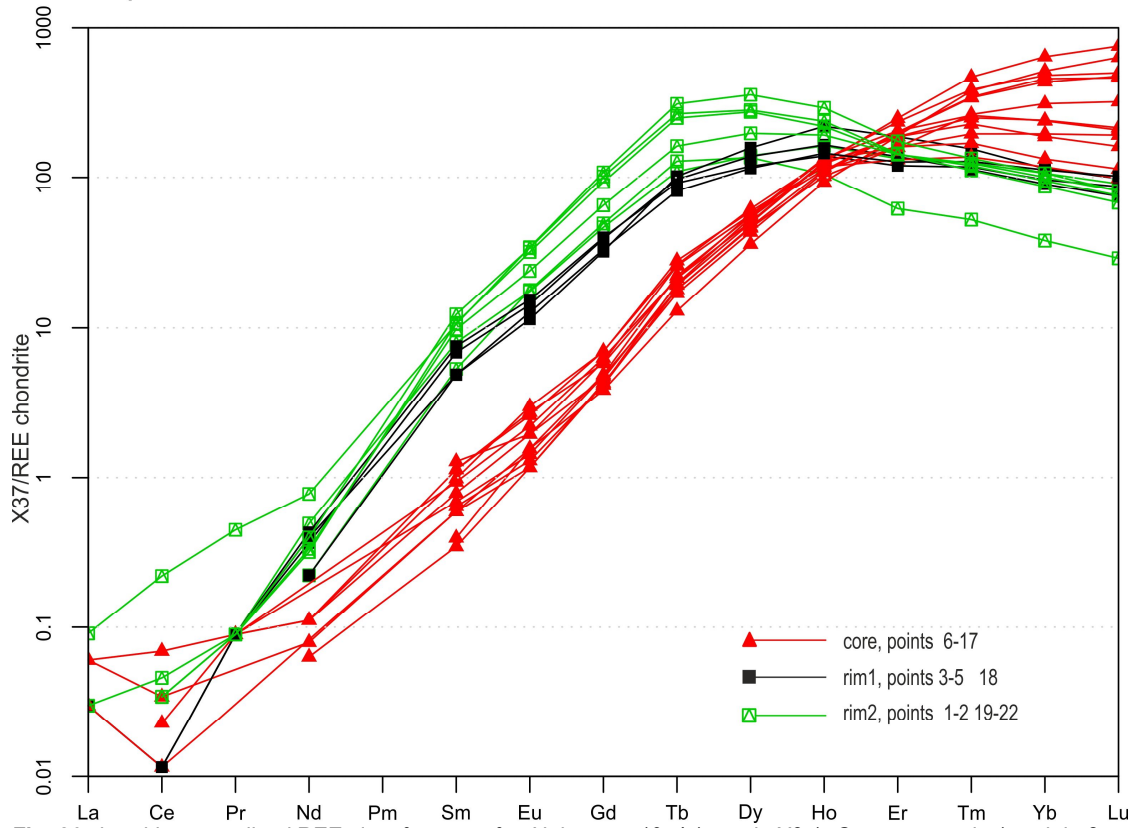


Fig. 26 chondrite normalized REE plot of garnet after Nakamura 1974 (sample X37). Garnet-core, rim1 and rim2 are plotted as red, black and green lines.

Table 20 representative garnet analyses of trace elements and REEs obtained by LA-ICP-MS. Sample X35

| representative analysis of trace elements and REEs, sample X35 | | | | | | |
|--|-------|-------|-------|-------|-------|-------|
| Point | core | | rim1 | | rim2 | |
| | 8 | 25 | 3 | 4 | 1 | 2 |
| ⁷ Li | 3.32 | 3.59 | 1.52 | 1.05 | 1.64 | 1.67 |
| ³¹ P | 41.5 | 31.3 | 43.8 | 51.7 | 54.4 | 45.3 |
| ⁴⁹ Ti | 713 | 795 | 285 | 337 | 430 | 310 |
| ⁵¹ V | 95.6 | 97.9 | 109 | 120 | 93.2 | 91.0 |
| ⁵³ Cr | <0.05 | <0.05 | 2.93 | 11.1 | 7.76 | 1.94 |
| ⁵⁹ Co | 21.7 | 22.6 | 33.2 | 31.4 | 47.4 | 43.6 |
| ⁶⁰ Ni | 1.00 | 0.91 | 1.40 | 2.01 | 0.75 | 1.00 |
| ⁶⁶ Zn | 99.2 | 97.5 | 96.9 | 94.9 | 83.9 | 101.7 |
| ⁷¹ Ga | 13.3 | 13.9 | 18.2 | 18.3 | 11.5 | 17.4 |
| ⁸⁸ Sr | 0.07 | 0.10 | 0.06 | 0.20 | <0.05 | <0.05 |
| ⁸⁹ Y | 549 | 382 | 97.1 | 89.8 | 80.4 | 140 |
| ⁹⁰ Zr | 33.8 | 11.5 | 1.01 | 1.79 | 2.47 | 1.25 |
| ¹³⁹ La | <0.05 | 0.08 | <0.05 | <0.05 | <0.05 | <0.05 |
| ¹⁴⁰ Ce | <0.05 | 0.25 | <0.05 | 0.06 | <0.05 | <0.05 |
| ¹⁴¹ Pr | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 |
| ¹⁴⁶ Nd | 0.11 | 0.23 | 0.33 | 0.41 | 0.29 | 0.43 |
| ¹⁴⁷ Sm | 0.43 | 0.50 | 1.46 | 1.02 | 2.15 | 3.84 |
| ¹⁵³ Eu | 0.48 | 0.57 | 1.27 | 0.80 | 1.92 | 3.27 |
| ¹⁵⁷ Gd | 5.97 | 7.13 | 10.6 | 6.53 | 13.6 | 28.5 |
| ¹⁵⁹ Tb | 3.82 | 3.97 | 3.08 | 1.90 | 3.82 | 7.6 |
| ¹⁶³ Dy | 57.0 | 48.8 | 24.5 | 16.0 | 23.6 | 45.8 |
| ¹⁶⁵ Ho | 19.04 | 13.08 | 4.22 | 3.45 | 3.12 | 5.34 |
| ¹⁶⁶ Er | 72.2 | 41.3 | 8.08 | 8.86 | 6.45 | 7.33 |
| ¹⁶⁹ Tm | 11.2 | 5.97 | 0.76 | 1.11 | 0.68 | 0.52 |
| ¹⁷² Yb | 79.4 | 40.1 | 3.35 | 6.33 | 3.21 | 2.42 |
| ¹⁷⁵ Lu | 11.98 | 5.72 | 0.34 | 0.81 | 0.32 | 0.23 |
| ¹⁷⁸ Hf | 0.74 | 0.35 | 0.11 | 0.07 | 0.09 | 0.21 |
| ¹⁸¹ Ta | 0.12 | 0.09 | <0.05 | <0.05 | <0.05 | <0.05 |

data in ppm, beam size diameter 35 μm , 0.6 C He, 11 Hertz, irradiance 1.71 gW/cm^2 , Fluence 9 J/cm^2

Table 21 representative garnet analyses of trace elements and REEs obtained by LA-ICP-MS. Sample X36

| representative analysis of trace elements and REEs, sample X36 | | | | | | |
|--|-------|-------|-------|-------|-------|-------|
| Point | core | | rim1 | | rim2 | |
| | 17 | 8 | 20 | 23 | 31 | 32 |
| ⁷ Li | 1.13 | 1.69 | 1.54 | 1.43 | 0.83 | 0.91 |
| ³¹ P | 39.2 | 36.2 | 36.5 | 38.9 | 32.0 | 42.3 |
| ⁴⁹ Ti | 748 | 1015 | 673 | 530 | 424 | 485 |
| ⁵¹ V | 186 | 165 | 258 | 235 | 197 | 204 |
| ⁵³ Cr | 133 | 15.8 | 192 | 127 | 97 | 109 |
| ⁵⁹ Co | 43.0 | 35.0 | 36.5 | 39.9 | 41.8 | 45.3 |
| ⁶⁰ Ni | 1.35 | 1.24 | 2.15 | 2.02 | 1.58 | 1.25 |
| ⁶⁶ Zn | 65.9 | 43.8 | 58.0 | 62.3 | 67.7 | 72.1 |
| ⁷¹ Ga | 12.4 | 12.8 | 13.7 | 13.7 | 12.8 | 14.1 |
| ⁸⁸ Sr | 0.06 | 0.14 | <0.05 | 0.07 | <0.05 | <0.05 |
| ⁸⁹ Y | 62.2 | 44.0 | 70.6 | 76.3 | 49.3 | 51.6 |
| ⁹⁰ Zr | 4.93 | 4.81 | 3.55 | 3.47 | 2.44 | 2.25 |
| ¹³⁹ La | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 |
| ¹⁴⁰ Ce | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 |
| ¹⁴¹ Pr | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 |
| ¹⁴⁶ Nd | <0.05 | <0.05 | 0.12 | <0.05 | 0.14 | 0.10 |
| ¹⁴⁷ Sm | <0.05 | <0.05 | <0.05 | <0.05 | 0.63 | 0.62 |
| ¹⁵³ Eu | 0.11 | 0.08 | 0.14 | 0.13 | 0.55 | 0.57 |
| ¹⁵⁷ Gd | 1.00 | 0.62 | 1.74 | 1.18 | 3.84 | 4.28 |
| ¹⁵⁹ Tb | 0.49 | 0.33 | 0.77 | 0.65 | 1.19 | 1.35 |
| ¹⁶³ Dy | 6.47 | 4.43 | 8.60 | 8.59 | 10.10 | 10.29 |
| ¹⁶⁵ Ho | 2.42 | 1.52 | 2.46 | 2.60 | 1.87 | 2.04 |
| ¹⁶⁶ Er | 9.74 | 6.58 | 8.31 | 9.05 | 4.51 | 4.88 |
| ¹⁶⁹ Tm | 1.71 | 1.26 | 1.19 | 1.36 | 0.48 | 0.58 |
| ¹⁷² Yb | 12.5 | 10.3 | 7.82 | 9.48 | 2.63 | 2.94 |
| ¹⁷⁵ Lu | 1.96 | 1.76 | 1.06 | 1.23 | 0.36 | 0.42 |
| ¹⁷⁸ Hf | 0.06 | <0.05 | 0.18 | 0.08 | 0.09 | 0.06 |
| ¹⁸¹ Ta | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 |

data in ppm, beam size diameter 35 μ m, 0.6 C He, 11 Hertz, irradiance 1.71 gW/cm², Fluence 9 J/cm²

Table 22 representative garnet analyses of trace elements and REEs obtained by LA-ICP-MS. Sample X37

| representative analysis of trace elements and REEs, sample X37 | | | | | | |
|--|-------|-------|-------|-------|-------|-------|
| Point | core | | rim1 | | rim2 | |
| | 11 | 12 | 4 | 5 | 2 | 20 |
| ⁷ Li | 2.17 | 0.77 | 1.10 | 1.81 | 1.05 | 2.95 |
| ³¹ P | 18.5 | 17.2 | 25.5 | 23.5 | 21.4 | 21.9 |
| ⁴⁹ Ti | 392 | 297 | 363 | 887 | 298 | 245 |
| ⁵¹ V | 6.6 | 5.6 | 73.7 | 67.0 | 61.3 | 59.4 |
| ⁵³ Cr | 1.45 | <0.05 | 19.9 | 9.45 | 12.8 | 15.7 |
| ⁵⁹ Co | 13.3 | 12.7 | 20 | 21.1 | 23.8 | 28.3 |
| ⁶⁰ Ni | 1.09 | 1.00 | 1.82 | 1.75 | 1.31 | 1.42 |
| ⁶⁶ Zn | 138 | 134 | 106 | 105 | 89.8 | 85.1 |
| ⁷¹ Ga | 12.6 | 11.1 | 10.1 | 14.0 | 12.7 | 14.9 |
| ⁸⁸ Sr | 0.06 | 0.08 | <0.05 | <0.05 | <0.05 | 0.23 |
| ⁸⁹ Y | 281 | 232 | 291 | 374 | 284 | 404 |
| ⁹⁰ Zr | 28.6 | 98.5 | 3.35 | 3.96 | 1.17 | 10.9 |
| ¹³⁹ La | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 |
| ¹⁴⁰ Ce | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 |
| ¹⁴¹ Pr | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 |
| ¹⁴⁶ Nd | <0.05 | <0.05 | 0.23 | 0.14 | 0.31 | 0.25 |
| ¹⁴⁷ Sm | 0.08 | 0.07 | 1.39 | 0.99 | 1.62 | 2.50 |
| ¹⁵³ Eu | 0.12 | 0.09 | 1.10 | 0.88 | 1.35 | 2.62 |
| ¹⁵⁷ Gd | 1.35 | 1.19 | 10.8 | 8.91 | 12.9 | 28 |
| ¹⁵⁹ Tb | 1.05 | 0.8 | 4.56 | 4.78 | 5.15 | 12.5 |
| ¹⁶³ Dy | 18.9 | 14.9 | 47.4 | 54.1 | 47.9 | 96.5 |
| ¹⁶⁵ Ho | 9.24 | 7.59 | 11.6 | 15.3 | 11.4 | 16.6 |
| ¹⁶⁶ Er | 52.7 | 44.5 | 31.0 | 42.1 | 30.1 | 32.5 |
| ¹⁶⁹ Tm | 11.6 | 10.2 | 3.39 | 4.66 | 3.76 | 3.34 |
| ¹⁷² Yb | 106 | 95.7 | 19.9 | 25.3 | 23.4 | 19.1 |
| ¹⁷⁵ Lu | 17.02 | 16.13 | 2.54 | 3.34 | 3.08 | 2.31 |
| ¹⁷⁸ Hf | 0.67 | 2.25 | 0.28 | 0.33 | 0.29 | 0.74 |
| ¹⁸¹ Ta | 0.07 | 0.05 | 0.06 | 0.09 | 0.07 | 0.09 |

data in ppm, beam size diameter 35 μ m, 0.6 C He, 11 Hertz, irradiance 1.71 gW/cm², Fluence 9 J/cm²

8.2 Mineral Chemistry of garnet inclusions

Garnet grains have grain sizes up to 5 mm, and are typically inclusion rich. Metamorphic rocks such as the metabasic unit of the Songshugou ophiolite were exposed to recrystallization processes under changing PT conditions. Therefore mineral assemblages related to an early metamorphic overprint may only be preserved in Grt as mineral inclusions (Chopin, 1984; Zhang et al., 1997; Perchuk et al., 1998). The abundance and distribution of garnet inclusions is not uniform in all Grt amphibolite rock samples of the Songshugou ophiolite. The most common inclusions include Amp, albitic Pl, Qz, Czo/Ep, Ilm, Ap, Zrn and in some samples, Spn. Other mineral phases like Cpx, Bt, Rt, and sulfides are rarely found. Few grains show snowball-like inclusion alignments in their cores, which is indicative of syntectonic growth of the garnet core (Fig. 4g). Sketch maps of garnets redrawn after BSE images of samples X35, X36 and X37 are located in Fig. 27, Fig. 28 and Fig. 29. Different shades of blue represent garnet zones, contoured according to their Ca content. As mentioned earlier, most garnets comprise 3 different zones: 1) core, 2) X_{Grs} rich rim1 and 3) slightly less X_{Grs} rich rim2. In some cases rim 2 is entirely consumed due to retrogression (Fig. 27, left garnet). Cracks are usually filled by Amp. Some minerals like Ilm, Pl, Qz, \pm Prh are restricted to garnet cores whereas Ap, Zrn, Amp \pm Cz/Ep occur in all zones.

Amphibole, both in core and rim1, is of pargasitic composition. There is significant chemical variation among samples with respect to weight percent Al_2O_3 (15 – 20), MgO (5 – 10), FeO (15 – 22), Na_2O (2 – 3.5). Amphibole inclusions in rim1 and rim2 as well as Amp inclusions in the core are not distinctively different in composition. Only a slight elevation in MgO and CaO conjoined with lower FeO is sometimes observed in rim1. However, Amp grains enclosed in Grt cores adjacent to Czo/Ep contain less Al_2O_3 . Representative mineral analyses are displayed in table 23. Plagioclase inclusions are restricted to Grt cores and almost purely of albitic composition ($X_{\text{Ab}} \sim 0.99$). In seldom cases polyphase inclusions of albitic Pl and Kfs are found. Representative microprobe data of Pl is presented in table 23. Sphene occurrence is observed in sample X36 as inclusions in rim and core. Sphene shows a positive compositional correlation between F and $\text{Al} + \text{Fe}^{3+}$ and a negative linear correlation between Ti and $\text{Al} + \text{Fe}^{3+}$, indicating the coupled substitution: $\text{Ti}^{4+} + \text{O}^{2-} = (\text{Al}, \text{Fe}^{3+}) + (\text{F}, \text{OH})^-$ (Enami et al., 1993). Thin rods of Rt sometimes occur within Grt rims. Representative microprobe data of Spn is presented in table 24. Apatite found as inclusions in Grt rim and core is Fluorapatite with $\text{F/Cl} > 1$. FeO contents are below 1 wt.%. Core Ap shows higher F contents (2 – 2.5 wt.%) than Ap included in the rim (F = 1.2 – 1.5 wt.%). Ca/P is slightly higher for Ap included in Grt rim with ~ 1.7 compared to ~ 1.6 for those found in core. Small Ca/P ratios trigger the augmentations of vacancies in the apatitic structure. Microprobe analyses are presented in table 25. Clinzoisite/epidote occurs commonly in Grt cores and sometimes rim1 and rim2. Grains display a strong zoning in Al_2O_3 and Fe_2O_3 varying from 21 to 27 wt.% and 9 to 12 wt.%, respectively. REEs were not quantitatively analyzed but were observed in EDX spectrum when total sum was low. Clinzoisite/epidote microprobe analyses are given in table 24. Zircon occurs in all Grt zones, with grain sizes usually smaller than 20 μm . Sample X37 exhibits an exceedingly amount of Zrn inclusions compared to other samples. Rutil rarely appears as thin rods in Grt rim. Quartz occurs as small rounded or rod shaped grains in Grt core or in aggregates together with Amp and Pl.

Chemical zoning patterns in garnets (REEs and majors) and different mineral assemblages associated with core and rim compositions indicate a poly-phase metamorphic history.

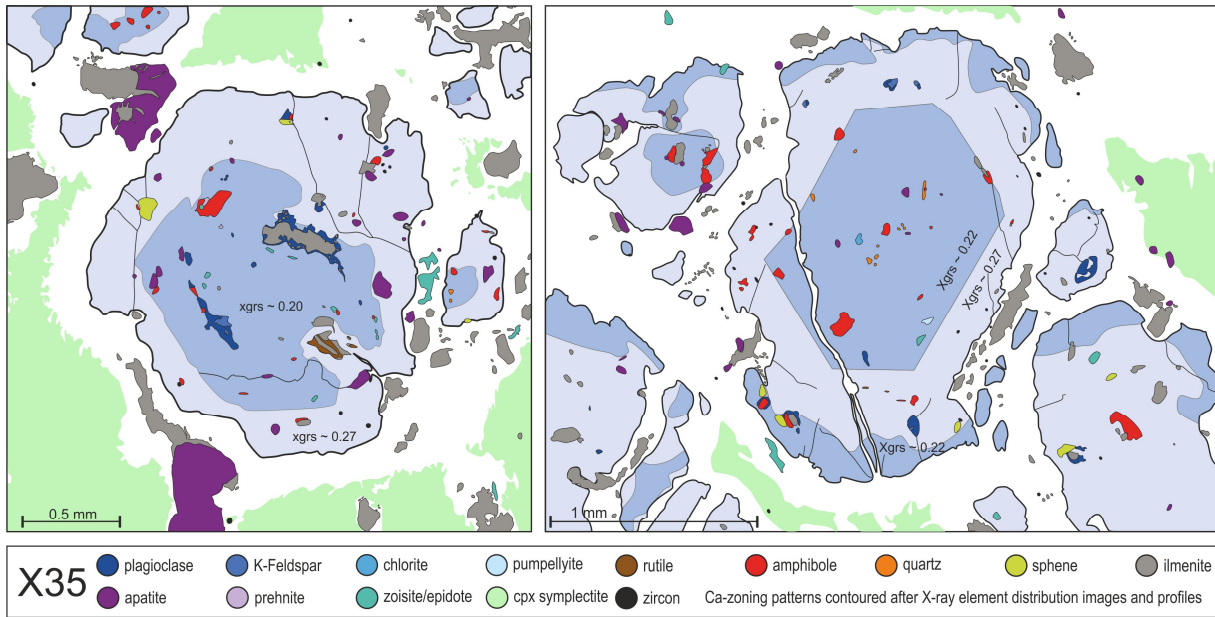


Fig. 27 Sample X35. Redrawn garnet grains. Blue areas represent garnet zones contoured after X-ray Ca-distribution images.

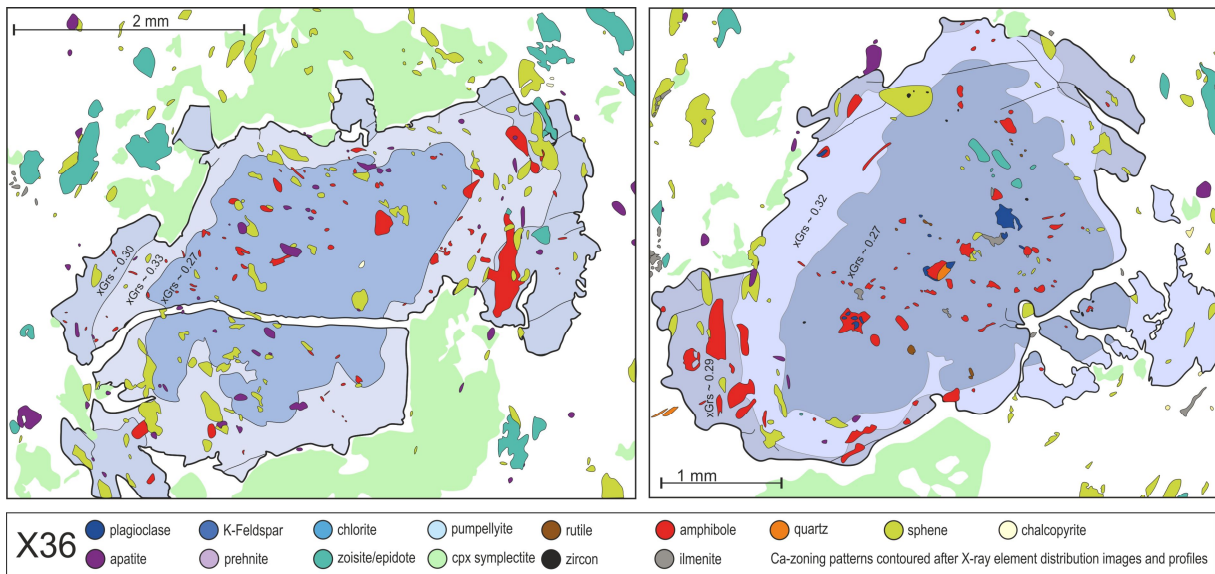


Fig. 28 Sample X36. Redrawn garnet grains. Blue areas represent garnet zones contoured after X-ray Ca-distribution images.

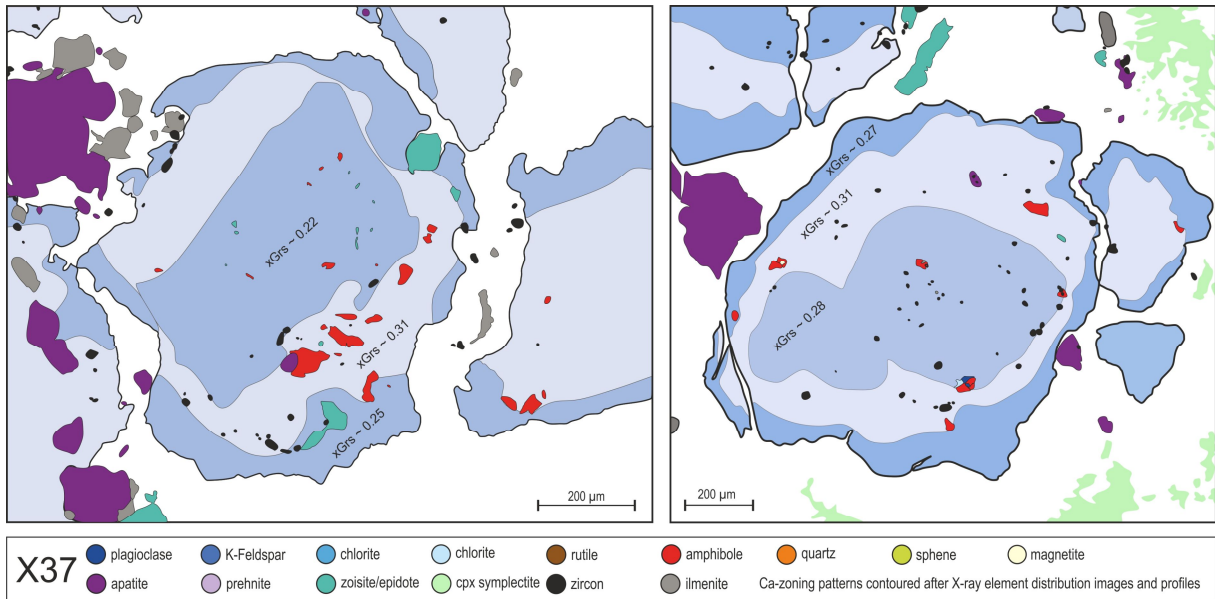


Fig. 29 Sample X37. Redrawn garnet grains. Blue areas represent garnet zones contoured after X-ray Ca-distribution images.

table 23 representative microprobe analysis of amphibole included in garnet

| representative analysis of amphibole included in garnet (O = 23) | | | | | | | | | |
|---|---------------|---------------|---------------|---------------------|---------------|---------------|---------------|---------------|---------------|
| | core | | | adjacent to epidote | | | rim1 | | |
| | x353d8 | 4_54 | x36a_31 | x33d12 | x33d13 | x33d14 | 4_55 | 37g1_3 | x353d_26 |
| IMA | | pargasite | | | pargasite | | | pargasite | |
| SiO ₂ | 38.68 | 37.90 | 38.29 | 41.55 | 40.46 | 39.12 | 39.20 | 39.66 | 38.70 |
| TiO ₂ | 0.26 | 0.17 | 0.38 | 0.76 | 0.29 | 0.36 | 1.50 | 0.32 | 0.86 |
| Al ₂ O ₃ | 18.63 | 20.63 | 19.15 | 14.63 | 15.94 | 17.36 | 18.94 | 18.70 | 18.41 |
| Cr ₂ O ₃ | <0.10 | <0.10 | <0.10 | <0.10 | <0.10 | <0.10 | <0.10 | <0.10 | <0.10 |
| FeO | 18.71 | 19.68 | 17.23 | 16.73 | 18.50 | 18.48 | 16.27 | 16.57 | 16.97 |
| MnO | 0.15 | 0.16 | 0.13 | 0.11 | 0.13 | <0.10 | <0.10 | <0.10 | <0.10 |
| MgO | 7.32 | 5.87 | 8.78 | 9.60 | 8.75 | 7.69 | 8.26 | 8.66 | 8.52 |
| CaO | 10.88 | 10.85 | 11.76 | 11.01 | 10.96 | 10.85 | 11.74 | 11.10 | 11.44 |
| Na ₂ O | 3.08 | 2.29 | 2.56 | 2.96 | 3.05 | 3.10 | 2.24 | 2.88 | 2.64 |
| K ₂ O | <0.10 | <0.10 | <0.10 | <0.10 | <0.10 | <0.10 | <0.10 | <0.10 | <0.10 |
| F | <0.10 | 0.17 | <0.10 | 0.25 | 0.38 | 0.27 | 0.20 | <0.10 | 0.17 |
| Cl | <0.10 | <0.10 | <0.10 | 0.11 | <0.10 | <0.10 | <0.10 | 0.18 | <0.10 |
| Total | 97.70 | 97.72 | 98.29 | 97.70 | 98.46 | 97.23 | 98.36 | 98.07 | 97.72 |
| Si | 5.785 | 5.688 | 5.629 | 6.174 | 5.999 | 5.887 | 5.763 | 5.849 | 5.742 |
| Ti | 0.030 | 0.019 | 0.042 | 0.084 | 0.032 | 0.040 | 0.166 | 0.035 | 0.096 |
| Al | 3.283 | 3.648 | 3.317 | 2.562 | 2.786 | 3.079 | 3.282 | 3.251 | 3.219 |
| Fe ³⁺ | 0.536 | 0.461 | 0.810 | 0.486 | 0.675 | 0.548 | 0.476 | 0.480 | 0.616 |
| Cr | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 |
| Fe ²⁺ | 1.804 | 2.009 | 1.308 | 1.593 | 1.619 | 1.778 | 1.524 | 1.563 | 1.489 |
| Mn | 0.019 | 0.021 | 0.016 | 0.014 | 0.017 | 0.000 | 0.000 | 0.000 | 0.000 |
| Mg | 1.632 | 1.313 | 1.925 | 2.126 | 1.934 | 1.725 | 1.811 | 1.904 | 1.885 |
| Ca | 1.743 | 1.745 | 1.852 | 1.752 | 1.740 | 1.750 | 1.849 | 1.754 | 1.819 |
| Na | 0.892 | 0.667 | 0.728 | 0.852 | 0.877 | 0.905 | 0.640 | 0.824 | 0.758 |
| K | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 |
| F | 0.000 | 0.082 | 0.000 | 0.118 | 0.177 | 0.126 | 0.095 | 0.000 | 0.081 |
| Cl | 0.000 | 0.000 | 0.000 | 0.028 | 0.000 | 0.000 | 0.000 | 0.045 | 0.000 |
| SumCat | 15.724 | 15.653 | 15.627 | 15.789 | 15.856 | 15.838 | 15.606 | 15.705 | 15.705 |
| X _{Mg} | 0.475 | 0.395 | 0.595 | 0.572 | 0.544 | 0.492 | 0.543 | 0.549 | 0.559 |
| Al(IV) | 2.215 | 2.312 | 2.371 | 1.826 | 2.001 | 2.113 | 2.237 | 2.151 | 2.258 |
| Al(VI) | 1.067 | 1.336 | 0.946 | 0.736 | 0.784 | 0.966 | 1.045 | 1.100 | 0.961 |

table 24 representative microprobe analysis of sphene and clinozoisite/epidote included in garnet

| representative sphene (O = 5) and Czo/Ep (O = 12.5) analysis included in garnet | | | | | | | | | |
|--|--------------|--------------|--------------|--------------|--------------|--------------|----------------------|--------------|--------------|
| sample | core | | | rim1 | | rim2 | core | | |
| | b_20 | 4_58 | 7_15 | f_9 | 4_59 | 4_60 | 7_8 | 7_9 | Gt3-24 |
| Mineral | sphene | | | sphene | | | clinozoisite/epidote | | |
| SiO ₂ | 30.21 | 30.37 | 30.56 | 30.54 | 30.75 | 30.16 | 38.18 | 37.87 | 34.55 |
| TiO ₂ | 37.43 | 37.96 | 37.37 | 37.95 | 38.08 | 38.14 | 0.12 | 0.28 | 0.18 |
| Fe ₂ O ₃ | 0.83 | 0.88 | 1.00 | 0.70 | 0.69 | 1.10 | 9.40 | 10.23 | 11.90 |
| Al ₂ O ₃ | 1.40 | 1.59 | 1.48 | 1.30 | 1.59 | 1.83 | 26.75 | 25.89 | 21.85 |
| Cr ₂ O ₃ | <0.10 | <0.10 | <0.10 | <0.10 | <0.10 | <0.10 | <0.10 | <0.10 | <0.10 |
| MnO | <0.10 | <0.10 | <0.10 | <0.10 | <0.10 | <0.10 | 0.14 | 0.14 | <0.10 |
| MgO | 0.00 | 0.00 | 0.10 | 0.11 | 0.00 | 0.00 | 0.12 | 0.00 | 0.25 |
| CaO | 27.61 | 27.43 | 27.29 | 27.48 | 27.88 | 27.42 | 22.18 | 21.97 | 18.34 |
| F | 0.41 | 0.44 | 0.47 | 0.29 | 0.42 | 0.22 | 0.13 | 0.21 | 0.00 |
| Total | 97.97 | 98.91 | 98.32 | 98.45 | 99.73 | 99.21 | 97.05 | 96.64 | 87.06 |
| Si | 1.009 | 1.005 | 1.016 | 1.012 | 1.010 | 0.995 | 3.011 | 3.013 | 3.053 |
| Ti | 0.940 | 0.945 | 0.934 | 0.946 | 0.941 | 0.946 | 0.007 | 0.017 | 0.012 |
| Al | 0.021 | 0.022 | 0.025 | 0.017 | 0.017 | 0.027 | 0.558 | 0.612 | 0.791 |
| Fe ³⁺ | 0.055 | 0.062 | 0.058 | 0.051 | 0.062 | 0.071 | 2.486 | 2.427 | 2.276 |
| Cr | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 |
| Mn | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.009 | 0.009 | 0.000 |
| Mg | 0.000 | 0.000 | 0.005 | 0.005 | 0.000 | 0.000 | 0.014 | 0.000 | 0.033 |
| Ca | 0.988 | 0.973 | 0.972 | 0.976 | 0.981 | 0.969 | 1.874 | 1.873 | 1.736 |
| F | 0.043 | 0.046 | 0.049 | 0.030 | 0.044 | 0.023 | 0.032 | 0.053 | 0.000 |
| SumCat | 3.057 | 3.048 | 3.061 | 3.039 | 3.041 | 3.027 | 7.992 | 8.006 | 7.892 |
| Al+Fe ₃ | 0.076 | 0.084 | 0.083 | 0.068 | 0.079 | 0.098 | | | |

table 25 representative microprobe analysis of apatite and ilmenite included in garnet

| representative apatite analysis (O = 25) included in garnet | | | | | | |
|--|---------------|---------------|---------------|---------------|---------------|---------------|
| sample | core | | rim | | core | |
| | 4_46 | 4_47 | Gt3-46 | Gt3-47 | x353c7 | x353c8 |
| Mineral | apatite | | apatite | | ilmenite | ilmenite |
| P ₂ O ₅ | 42.94 | 42.45 | 41.61 | 41.40 | - | 0.25 |
| TiO ₂ | - | - | - | - | 50.99 | 51.10 |
| V ₂ O ₃ | - | - | - | - | 0.50 | 0.61 |
| Al ₂ O ₃ | 0.22 | 0.00 | 0.29 | 0.18 | - | - |
| FeO | 0.30 | 0.38 | 0.35 | 0.53 | 47.85 | 47.40 |
| MnO | - | - | - | - | 0.61 | 0.74 |
| MgO | - | - | - | - | - | - |
| CaO | 53.86 | 53.80 | 55.73 | 56.01 | <0.10 | 0.30 |
| F | 2.18 | 2.47 | 1.44 | 1.26 | - | - |
| Cl | 0.14 | <0.10 | <0.10 | <0.10 | 0.16 | 0.25 |
| Total | 99.64 | 99.10 | 99.42 | 99.38 | 100.11 | 100.65 |
| P | 6.090 | 6.079 | 5.927 | 5.905 | 0.000 | 0.005 |
| Ti | 0.000 | 0.000 | 0.000 | 0.000 | 0.964 | 0.959 |
| Fe ³⁺ | 0.000 | 0.000 | 0.000 | 0.000 | 0.075 | 0.075 |
| V | 0.000 | 0.000 | 0.000 | 0.000 | 0.010 | 0.012 |
| Al | 0.043 | 0.000 | 0.058 | 0.036 | 0.000 | 0.000 |
| Fe ²⁺ | 0.042 | 0.054 | 0.049 | 0.075 | 0.931 | 0.914 |
| Mn | 0.000 | 0.000 | 0.000 | 0.000 | 0.013 | 0.016 |
| Mg | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 |
| Ca | 9.668 | 9.750 | 10.047 | 10.110 | 0.000 | 0.008 |
| F | 1.155 | 1.321 | 0.766 | 0.671 | 0.000 | 0.000 |
| Cl | 0.040 | 0.000 | 0.000 | 0.000 | 0.007 | 0.011 |
| SumCat | 17.038 | 17.204 | 16.847 | 16.797 | 2.000 | 2.000 |
| Ca/P | 1.588 | 1.604 | 1.695 | 1.712 | | |

table 26 representative microprobe analysis of plagioclase included in garnet cores.

| representative plagioclase analysis (O = 8) | | | | |
|--|---------------|--------------|--------------|--------------|
| included in garnet core | | | | |
| | Gt3-6 | Gt3-19 | Gt3-20 | Gt3-21 |
| Mineral | plagioclase | | | |
| SiO ₂ | 67.22 | 63.52 | 66.50 | 66.55 |
| Al ₂ O ₃ | 20.50 | 17.80 | 19.98 | 19.68 |
| Fe ₂ O ₃ | 0.90 | 0.41 | 0.40 | 0.81 |
| CaO | 0.44 | 0.00 | 0.82 | 0.80 |
| Na ₂ O | 11.35 | 0.12 | 11.13 | 11.23 |
| K ₂ O | 0.03 | 16.76 | 0.01 | 0.04 |
| Total | 100.48 | 98.62 | 98.88 | 99.16 |
| Si | 2.935 | 2.993 | 2.947 | 2.948 |
| Al | 1.055 | 0.989 | 1.044 | 1.027 |
| Fe ³⁺ | 0.029 | 0.015 | 0.013 | 0.027 |
| Ca | 0.021 | 0.000 | 0.039 | 0.038 |
| Na | 0.961 | 0.011 | 0.956 | 0.964 |
| K | 0.002 | 1.007 | 0.001 | 0.002 |
| SumCat | 5.0 | 5.0 | 5.0 | 5.0 |
| X _{Ab} | 0.98 | 0.01 | 0.96 | 0.96 |
| X _{An} | 0.02 | 0.00 | 0.04 | 0.04 |
| X _{Or} | 0.00 | 0.99 | 0.00 | 0.00 |

9 Geochemistry

9.1 Major and trace element geochemistry

Metamafic rocks from the Songshugou ophiolite exhibit a wide range of whole rock compositions. All analyzed samples are of basic to ultrabasic composition. Metabasic rocks were subdivided according to their whole rock chemistry and mineralogy into Grt amphibolites and amphibolites. Amphibolites, which were subdivided into schistose amphibolites and augenamphibolites by previous authors, are herein combined, by reason of their geochemic similarity. Amphibolites contain SiO_2 ranging from 45 wt.% to 49 wt.%, whereas Grt-amphibolites contain less SiO_2 varying from 38 wt.% to 42 wt.%. Loss on ignition (LOI) is fairly low with values less than 0.7 wt.% in all samples. Whole rock data from previous studies by Zhang et al. (1999), Dong et al. (2008) and Li Tang et al. (2016) is plotted along with the data from this study, for comparative reasons (Fig. 40).

Amphibolites show a wide variation in $\text{Fe}_2\text{O}_3\text{t}$ (12 - 17 wt.%) and have low P_2O_5 with ~ 0.15 wt.%. CaO varies from 8.5 wt.% to 13.5 wt.% and TiO_2 ranges from 1.4 wt.% to 1.8 wt.%. Grt-amphibolites contain elevated TiO_2 (2.3 - 3.3 wt.%), P_2O_5 (0.3 – 0.8 wt.%) and $\text{Fe}_2\text{O}_3\text{t}$ (18 - 25 wt.%) values. Concerning amphibolites, CaO plotted against MgO shows a positive correlation whereas Na_2O , SiO_2 , TiO_2 , P_2O_5 correlates negatively, which is typical for tholeiitic differentiation (Fig. 30). Trace elements like Ni and Cr decrease with increasing MgO, which is symptomatic for Ol and Cpx or spinel fractionation. LILE and HFSE are incompatible in most minerals and therefore accumulate in the residual liquid. That trend is well established with increasing Zr, Ba, Ce and Th conjoint with decreasing MgO. Sc shows a positive correlation with MgO which could be an indication of pyroxene fractionation (Fig. 31).

Garnet amphibolites show different trends with MgO correlating positively with Na_2O and K_2O whereas TiO_2 , FeO_t and P_2O_5 show a negative trend (Fig. 32). A negative correlation between Zr, Ce, Th, Y, Yb vs. MgO is observed. Ni, Cr, V, Rb, Sr, Sc and Ba show a positive correlation (Fig. 33). The fractionation of Amp could contribute to the positive trend observed for Na_2O , K_2O , Rb, and Sr. Sc shows a positive correlation with MgO which can also be contributed to Amp or probably Px fractionation.

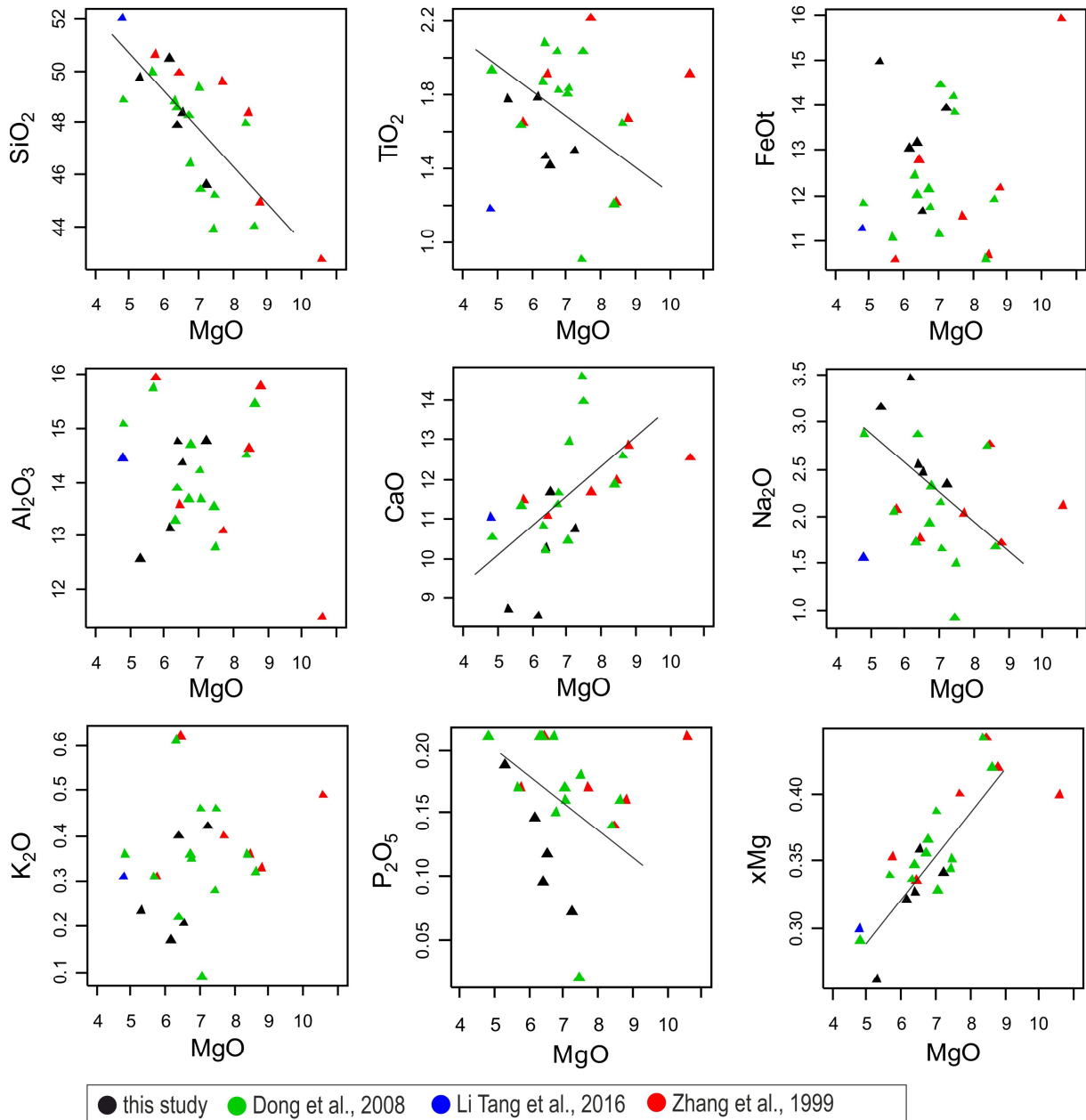


Fig. 30 amphibolites of the Songshugou ophiolite, majors vs MgO i.e. SiO₂, TiO₂, FeO_t, Al₂O₃, CaO, Na₂O, K₂O, P₂O₅, XMg.

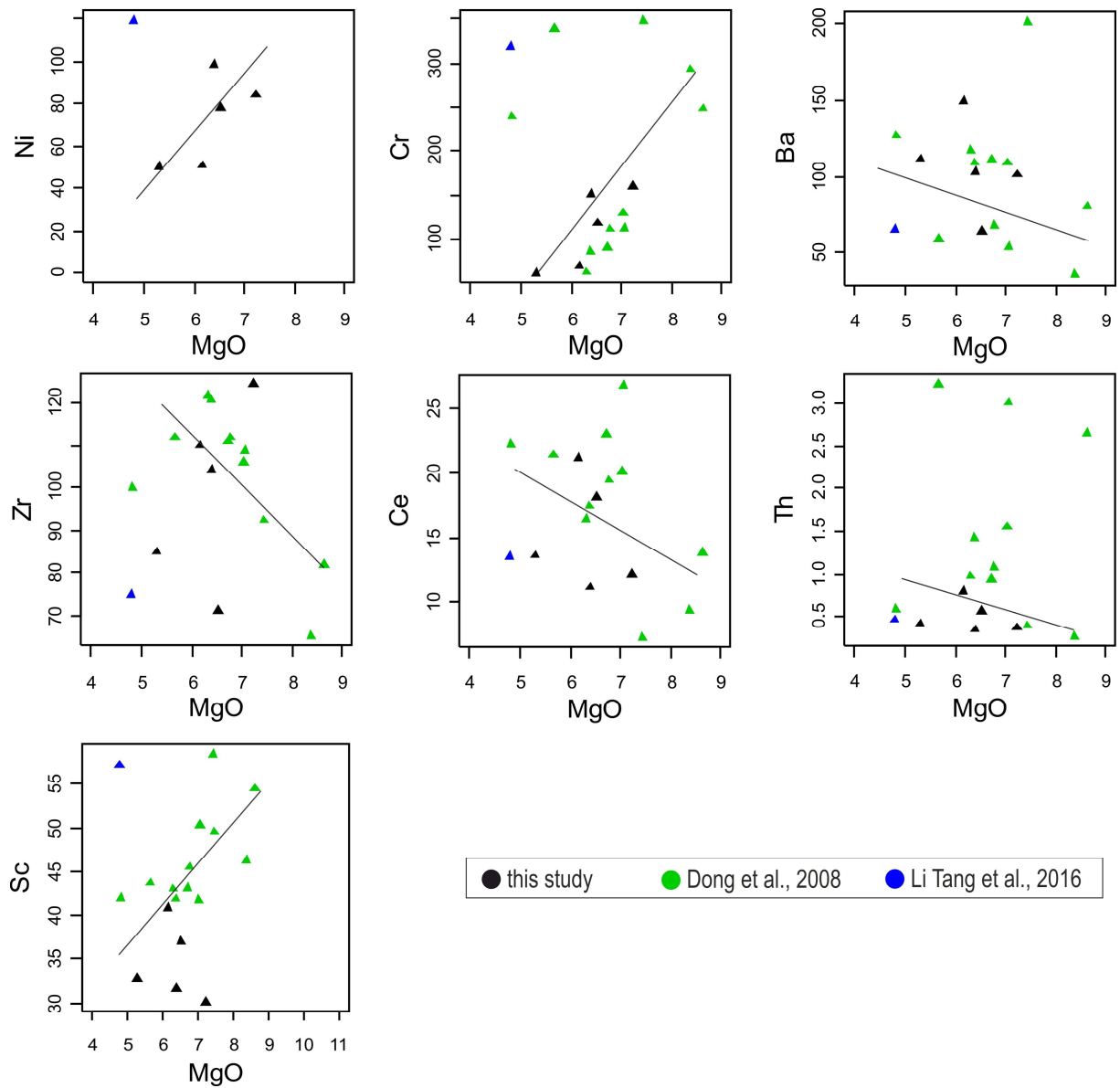


Fig. 31 amphibolites of the Songshugou ophiolite, traces vs MgO i.e. Ni, Cr, Ba, Zr, Ce, Th, Sc.

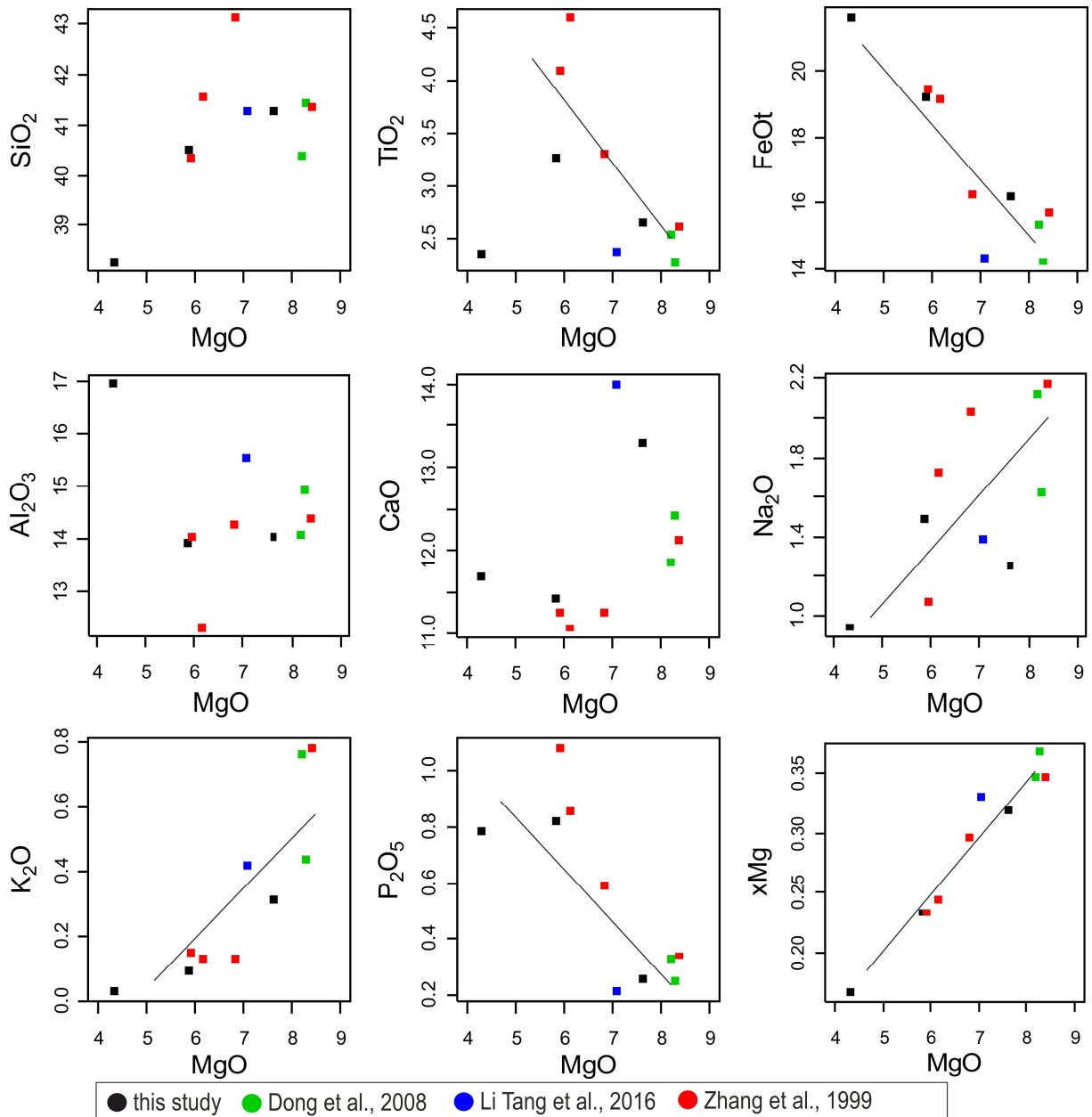


Fig. 32 Grt amphibolites of the Songshugou ophiolite, majors vs MgO i.e. SiO₂, TiO₂, FeO_t, Al₂O₃, CaO, Na₂O, K₂O, P₂O₅, XMg.

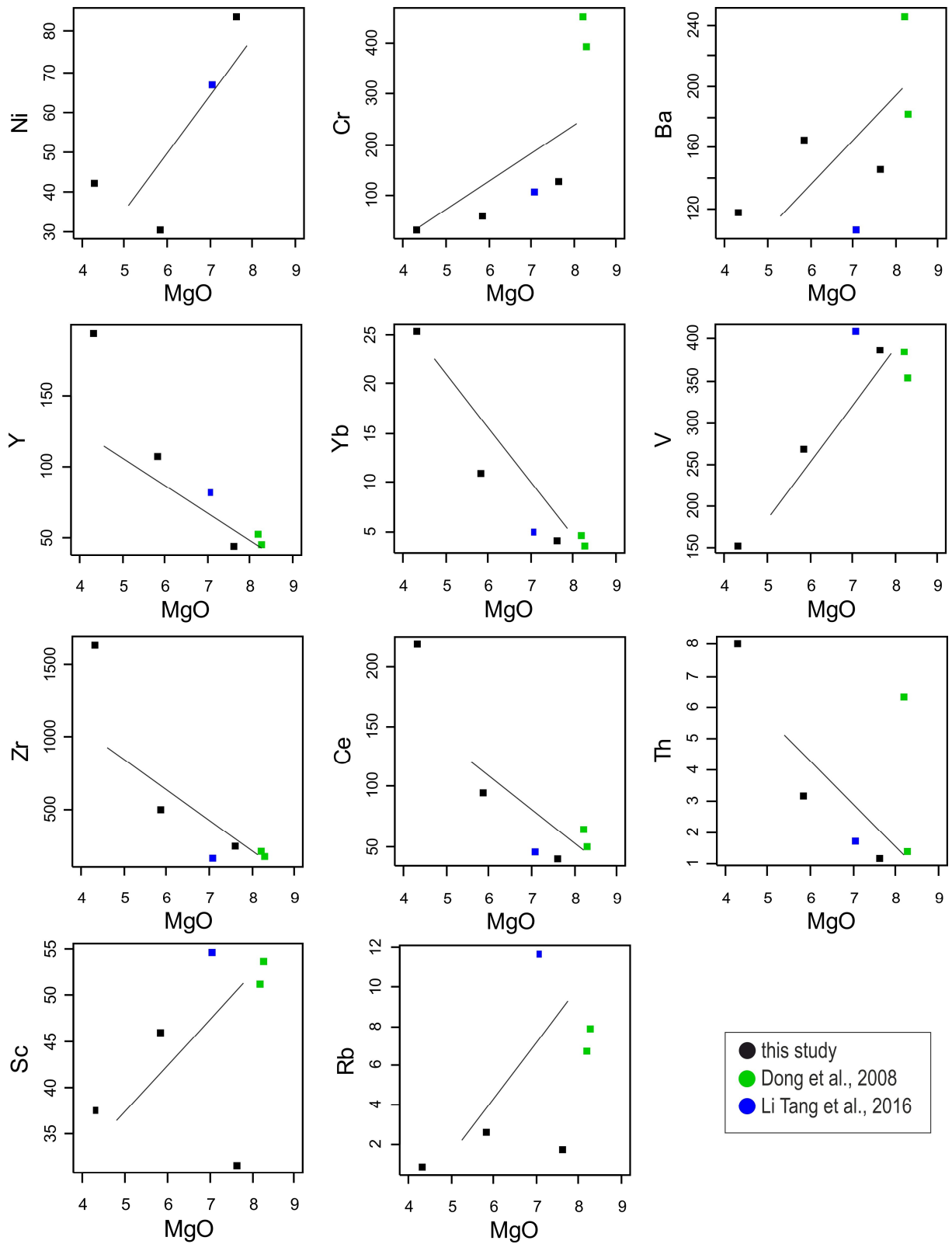


Fig. 33 Grt amphibolites of the Songshugou ophiolite, traces vs MgO i.e. Ni, Cr, Ba, Yb, Y, V, Zr, Ce, Th, Sc, Rb.

9.2 REE geochemistry and spider diagrams

The REE patterns of metamorphic rocks might be affected by metamorphism, however, HFSE including the REEs are considered as immobile elements even during metamorphic overprint. REE plotted against Zr is considered as one of the most valid tests to assess possible alteration or metamorphic effects on the REE geochemistry (Fig. 34) (Pearce and Cann, 1973; Pearce, 1975; Frey, 1983; Frey and Green, 1974; Frey et al., 1978). REE abundances increase systematically along with increasing Zr, suggesting that REE patterns haven't changed significantly by alteration and metamorphism.

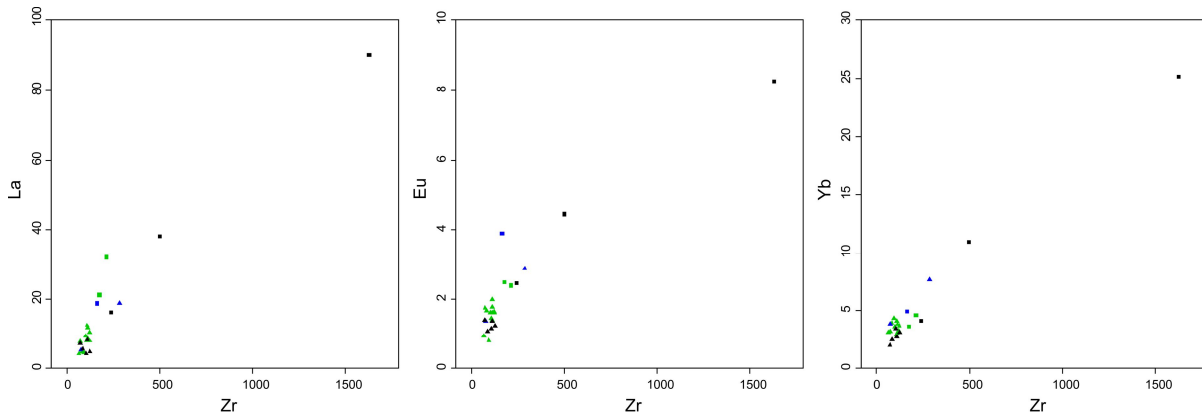


Fig. 34 Zr vs REE (in ppm) of metabasic rocks from the Songshugou ophiolite

REE were normalised to chondritic values after Nakamura 1974, who used the average value of ten common stony chondrites (3 carbonaceous (Orgueil C1, Murchison C2 and Allende C3) and 7 ordinary olivine-bronzite H chondrites). Normalisation to chondritic standards eliminates the Oddo-Harkins effect and the resulting REE diagram can directly be compared to primordial solar system composition. Grt amphibolites and amphibolites show distinctive REE_N patterns and distributions. Grt amphibolites show higher abundances of REE with $\sum \text{REE}_N$ of 130 – 700 and show higher overall REE fractionation with La_N/Yb_N of 2.3 – 4.6. Amphibolites have $\sum \text{REE}_N$ of 48 – 70 with a lower La_N/Yb_N 0.8 – 2. Those fractionation patterns are visualized in chondrite normalized REE plots (Fig. 35) where Grt-amphibolites in general show a stronger enrichment of REEs with highly enriched LREEs similar to trends observed in EMORB and OIB but with higher overall REE abundance. In most Grt amphibolites, heavy LREEs and HREEs display a plateau like pattern with $\text{Tb}_N/\text{Yb}_N = 1 - 2$. Amphibolites are far less enriched in REEs and hardly show overall REE fractionation. The REE concentrations of Grt amphibolites also increase along with increasing differentiation; which is shown in the $\sum \text{REE}_N$ vs. MgO diagram, in contrast to amphibolites that retain constant values of $\sum \text{REE}_N$ along with increasing MgO (Fig. 36). Grt-amphibolites are enriched in LREE as well as in other HFSE such as TiO_2 and P_2O_5 . These enrichment patterns of LREE could not be easily caused by partial melting, or fractional crystallization, to that extent; and therefore, a different mantle source for Grt amphibolites seems very likely. Grt amphibolites exhibit stronger LREE fractionation with La_N/Sm_N ratios of 1.4 – 2.6. This is typical of E-MORB in contrast to amphibolites with lower La_N/Sm_N ratios of 0.8-1.3, and is supported by the Zr-Nb-Y discrimination plot after Meschede, where the majority of Grt-amphibolites plot in the E-MORB field (Fig. 46c). Some of the Grt-amphibolites show an insignificant negative Eu anomaly probably attributed to minor PI fractionation. Crustal contamination causing elevated LREEs seems very unlikely since Grt-amphibolites are very low in SiO_2 , K_2O , Na_2O , K and Rb, but they exhibit higher FeO_t and account of high Ni contents in some low MgO samples. Furthermore rocks affected by crustal contamination usually show a trough in Nb and Ta in chondrite normalized spider plots, which is not observed in garnet amphibolites of the Songshugou metabasic unit. The phenomenon of Nb and Ta troughs occurs in all crustal contaminated rocks as well

as subduction related magmatic rocks, since Nb and Ta often is locked into Ti bearing phases such as Ilm and Spn which hardly play a role in crustal contamination due to their refractory nature. Suspicious troughs of Rb, K, Sr in the chondrite normalized spider plot of Grt amphibolites could be caused by Amp fractionation (Fig. 37).

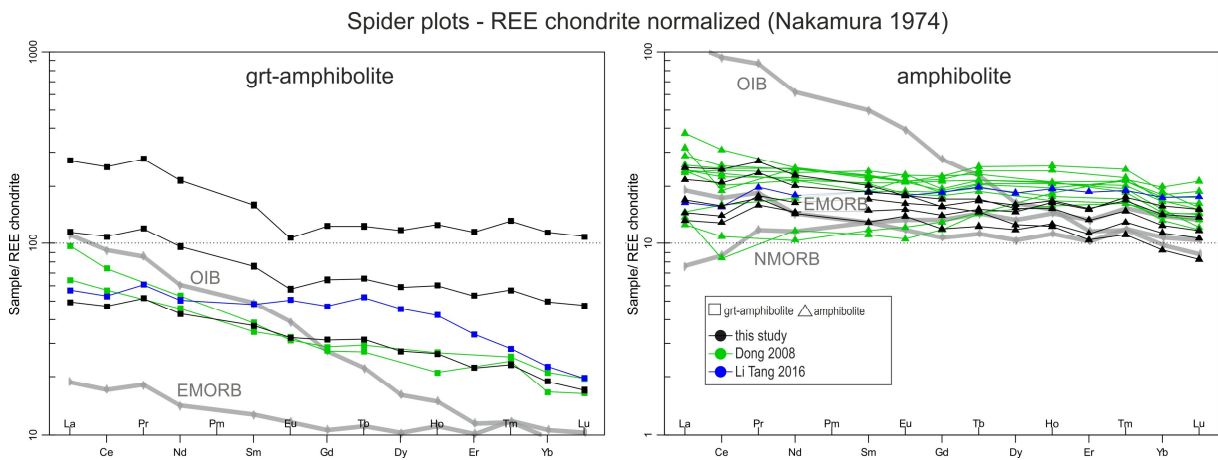


Fig. 35 REE chondrite normalized spider plots of Grt-amphibolites and amphibolites from the Songshugou metabasic unit (Nakamura 1974)

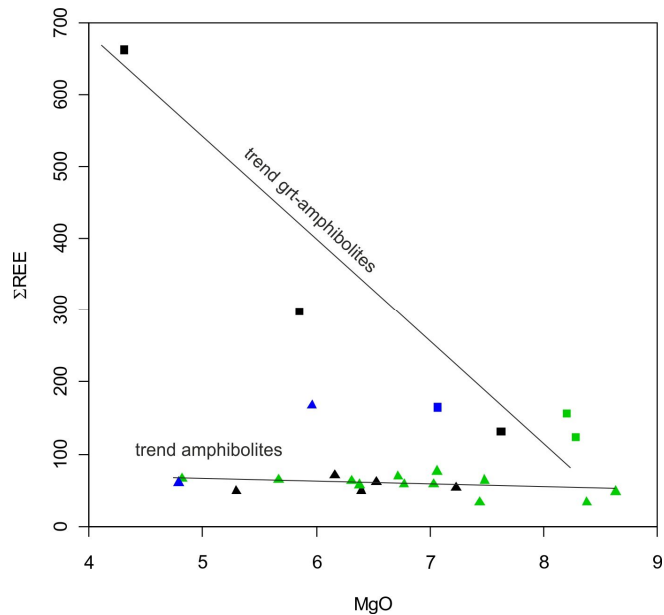


Fig. 36 MgO vs sum_REE_N (Nakamura 1976)

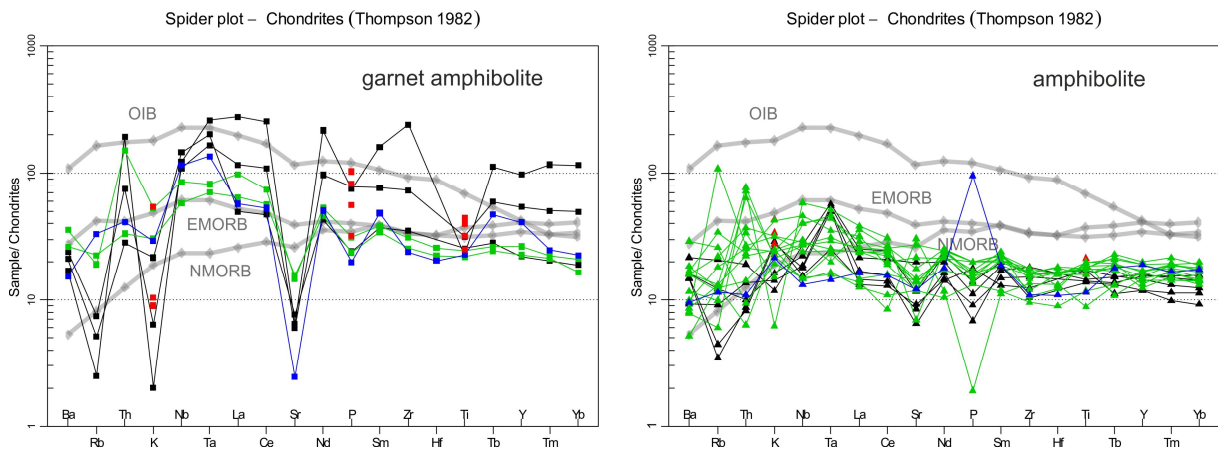


Fig. 37 chondrite normalized spider plot after Thompson 1982

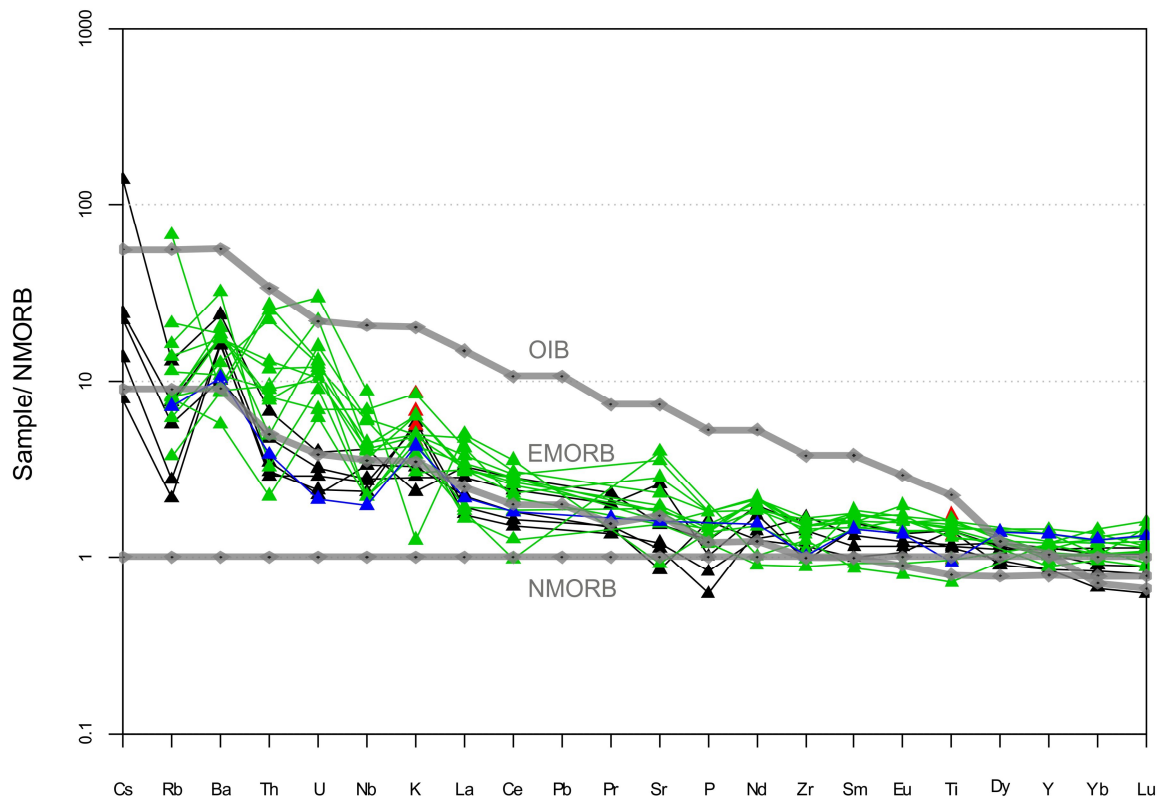


Fig. 38 Amphibolite NMORB normalized after Sun and McDonough 1989. NMORB, EMORB and OIB data after Sun and McDonough 1989

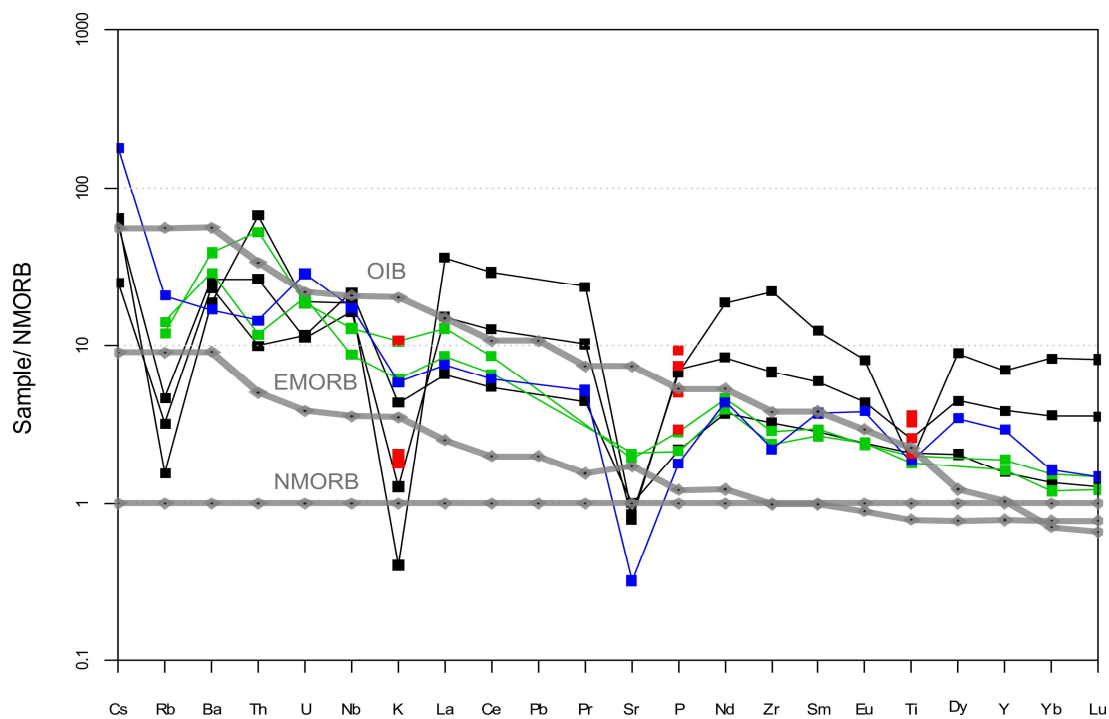


Fig. 39 Garnet amphibolite NMORB normalized after Sun and McDonough 1989. NMORB, EMORB and OIB data after Sun and McDonough 1989.

9.3 Discrimination diagrams

In the TAS diagram, amphibolites plot in the field of subalkaline basalt; the majority of Grt-amphibolites in the alkaline field (Fig. 40, Fig. 44b). In the Al_2O_3 - TiO_2 discrimination diagram after Pearce 1983, amphibolite data plot as basalt and garnet-amphibolite data mainly as Fe-Ti basalt (Fig. 41). None of the samples fall in the cumulate field. In the TiO_2 - K_2O - P_2O_5 discrimination diagram proposed by Pearce 1975 most samples plot into the field of oceanic basalts (Fig. 42). This diagram is only effective for primitive basalts; therefore all analyses were plotted in the AFM diagram (Fig. 44a) where an isoalkaline line of 20 % functions as recommended upper limit (Pearce et al., 1975). On the triangular 100 mg - c - al+alk (mg = $\text{MgO}/(\text{FeO}+\text{MnO}+2\text{Fe}_2\text{O}_3+\text{MgO})$), other Niggli values are oxides converted to their equivalent molecular numbers i.e. $\text{CaO} = \text{c}$, $\text{Al}_2\text{O}_3 = \text{al}$ and SrO , BaO , Li_2O , Rb_2O , Na_2O and $\text{K}_2\text{O} = \text{alk}$) diagram after Leake et al. 1964, all samples plot along the basic igneous trend line between middle and late stage differentiation (Fig. 43).

Post-depositional processes can also affect the mobility of certain elements. Therefore data was plotted in the $\text{CaO}/\text{Al}_2\text{O}_3$ - MgO - SiO_2 diagram proposed by Schweitzer and Kröner 1985 (Fig. 44b). All samples plot in the field of 'unaltered basalts'. The ternary AFM diagram suggests an association of a tholeiitic magmatic trend for all samples, which is typically observed at mid ocean ridge submarine volcanism (Fig. 44). That is substantiated by the ternary $\text{Zr}+\text{Y}-\text{Cr}-\text{TiO}_2$ plot after Davies et al. 1979 where most samples plot close to the tholeiitic trend line (Fig. 44c). REE, HFSE (high field strength elements) as well as some transition metals remain immobile during most hydrothermal alterations in contrary to LIL (large ion lithophile) elements like Na, K, Sr, Rb, Ba, U being mobile even under low-grade metamorphic conditions. (Pearce, 1984; Camire et al., 1995; Swinden et al., 1990; Schiano et al., 1993). Hence, Davies diagram might be of more significance than the AFM diagram, as it is based on immobile trace elements which more likely represent original igneous trends. The discrimination scheme of Jensen 1976 allows subdividing the samples furthermore. The majority of samples plot in the field of 'high Fe tholeiite basalt' (Fig. 45). Discrimination diagrams after Pearce & Cann 1973, Wood 1980 and Meschede 1986, employing immobile trace elements, classify most metabasic samples of the Songshugou ophiolite as E-MORB (Fig. 46). That is substantiated by the Ta/Yb vs. Th/Yb plot after Pearce 1983. Vectors drawn into the diagram illustrate the influence of subduction components (S), within-plate enrichment (W), crustal contamination (C) and fractional crystallization (f). Most of the samples follow the mantle array (Fig. 47).

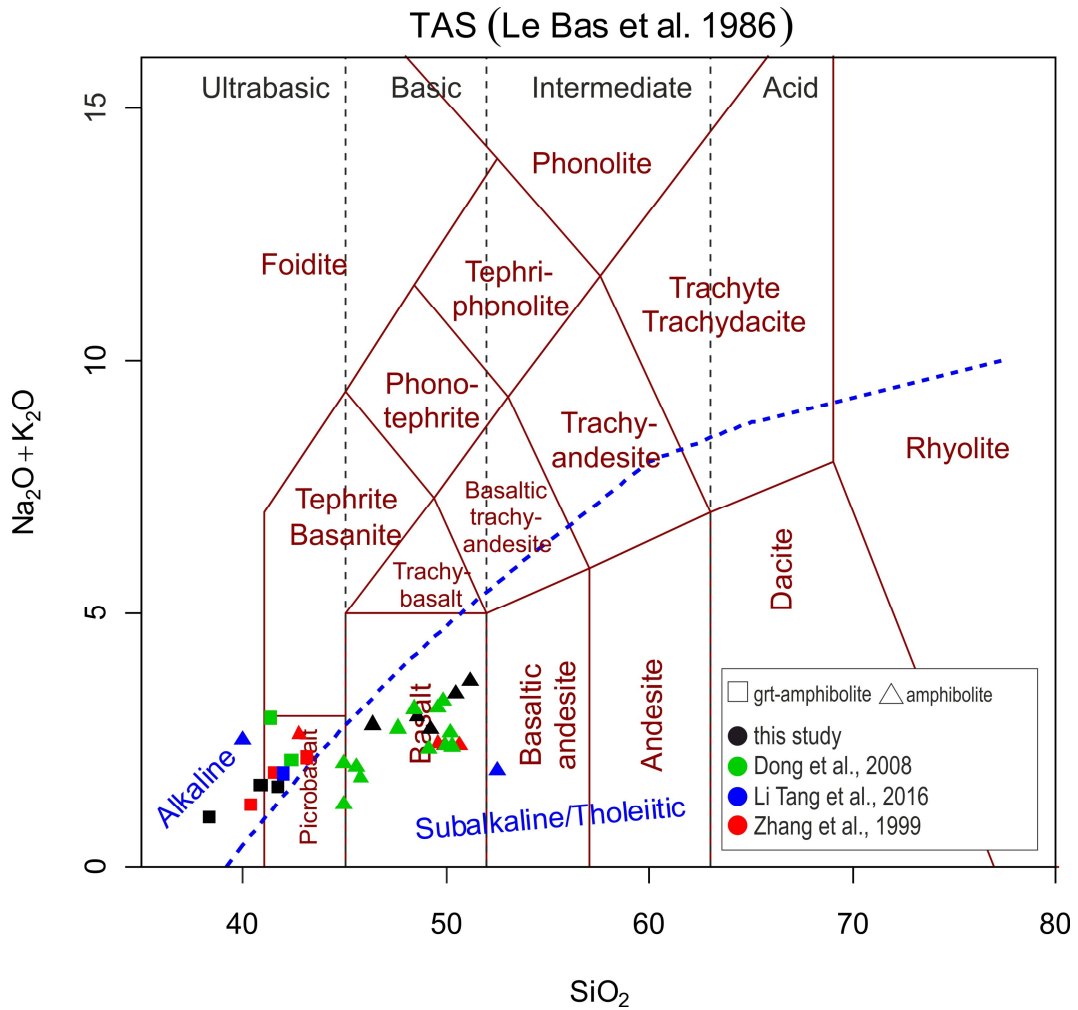


Fig. 40 TAS diagram after le Bas et al. 1986. Plots with rectangular shape represent Grt amphibolites, and triangular ones amphibolites.

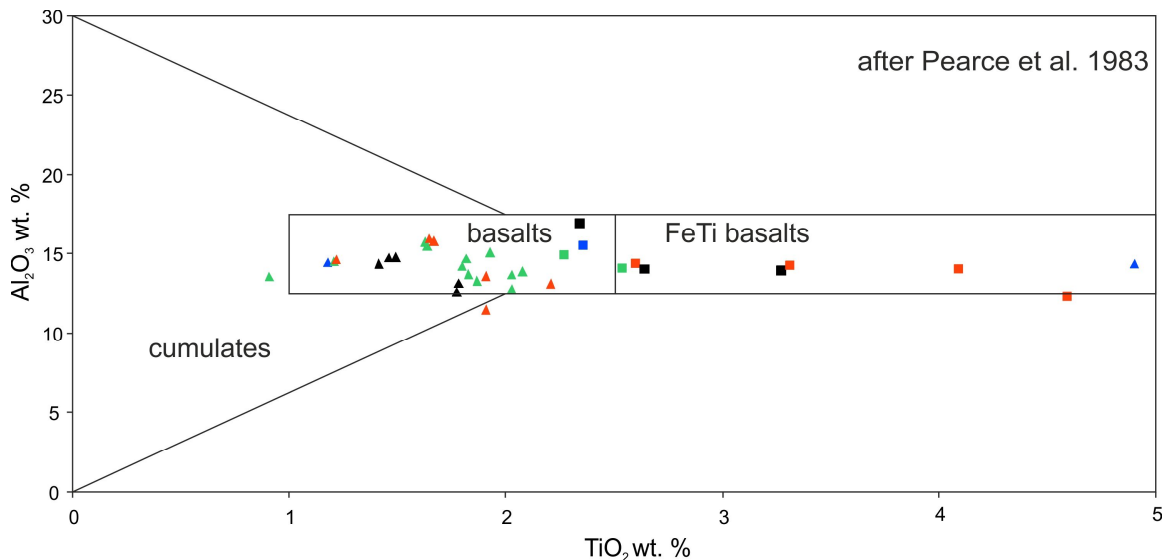


Fig. 41 binary Al_2O_3 - TiO_2 (wt. %) diagram for mafic rocks after Pearce (1983). The area of cumulates represents a mixture of Ol, Pl and basaltic melt. Whole rock analyses of the Songshugou metabasites are plotted into the diagram. Sympology of data points according to legend in Fig. 40.

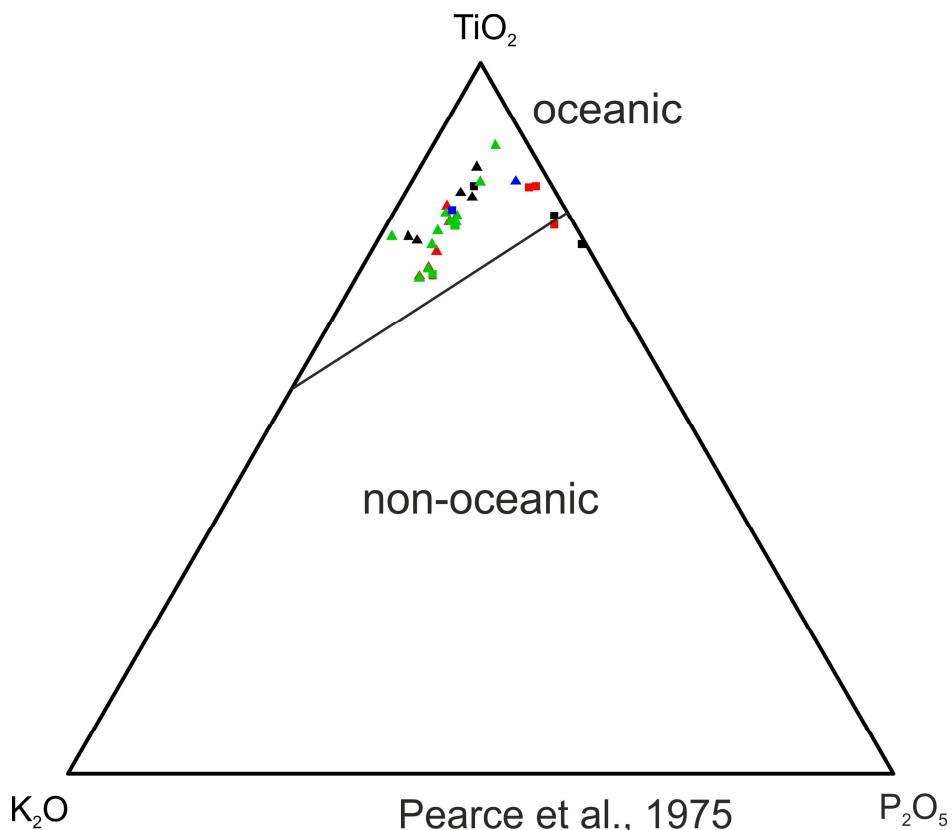


Fig. 42 Proposed ternary $\text{TiO}_2\text{-K}_2\text{O-P}_2\text{O}_5$ plot for discrimination between oceanic and continental basalt after Pearce et al., 1975. The separating line has the following coordinates: TiO_2 :54.5%, and TiO_2 79.6%, P_2O_5 20.4 %. Alteration and metamorphism of oceanic basalts generally contribute to enrichment of K_2O relative to TiO_2 and P_2O_5 .

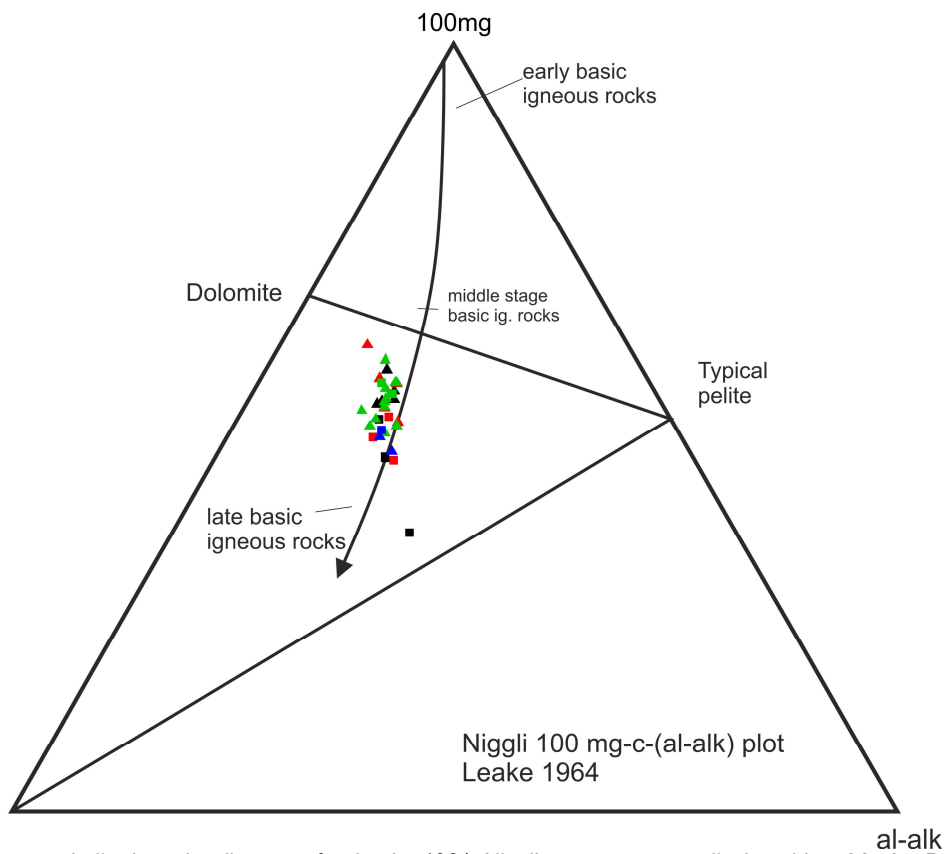


Fig. 43 100mg - c - al-alk triangular diagram after Leake 1964. Niggli parameters are displayed in **table 27**. Data is plotted along basic igneous trend line.

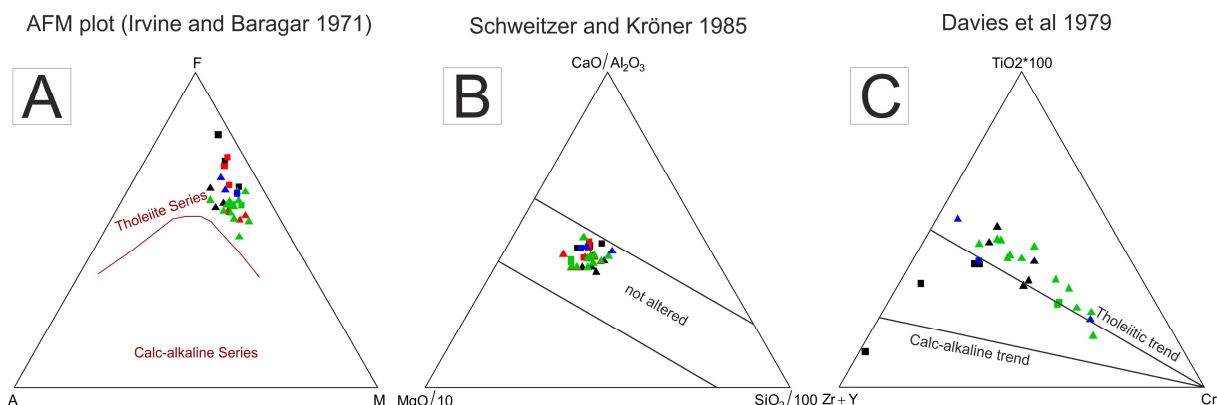


Fig. 44 Plots with rectangular shape representing Grt amphibolites, and triangular ones amphibolites. **(A)** AFM diagram after Irvine and Baragar 1971, **(B)** TiO_2 -Zr+Y-Cr diagram after Davies et al. 1979 sustaining tholeiitic affinity of Songshugou metabasites. **(C)** $\text{CaO}/\text{Al}_2\text{O}_3$ -MgO- SiO_2 diagram after Schweitzer and Kröner 1985 showing unaltered geochemistry of Songshugou metabasic rocks.

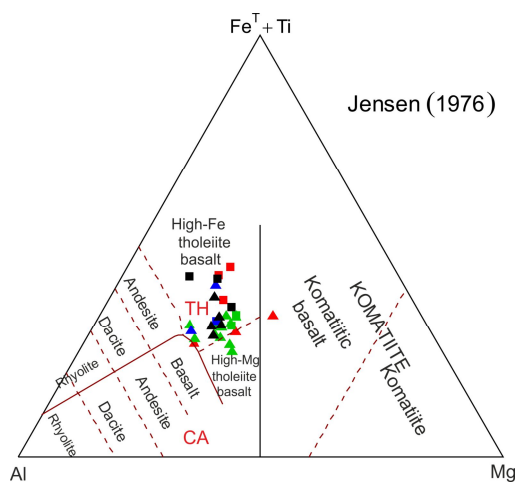


Fig. 45 Cationic discrimination scheme after Jensen 1976. Samples plot in High-Fe tholeiitic basalt field. Sympology of data points according to legend in Fig. 40.

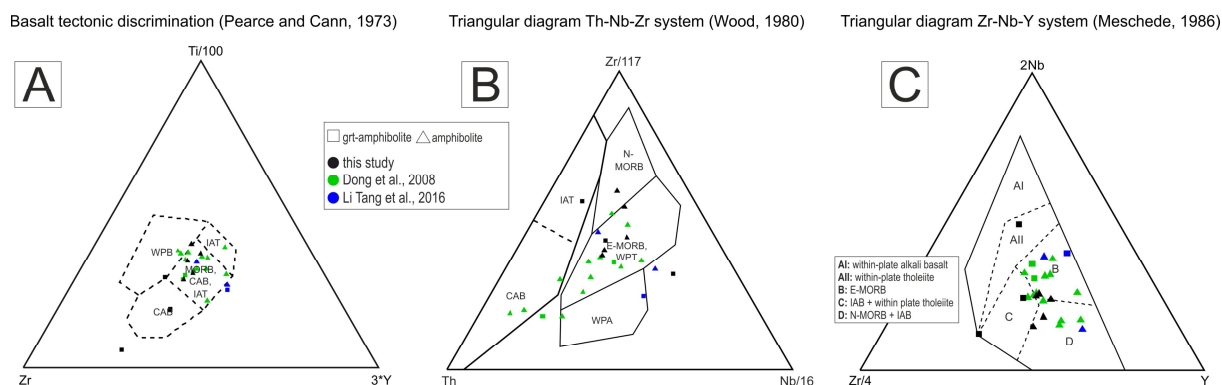


Fig. 46 discrimination diagrams for basalts. Grt amphiboles, plotted as rectangles, tend to diverge from amphibolite data **(A)** ternary Zr-Y-Ti plot after Pearce and Cann 1973. Most data plots in the field of MORB. **(B)** Discrimination diagram Th-Nb-Zr after Wood 1980. Samples mainly plot in the E-MORB field. **(C)** Zr-Nb-Y triangular diagram after Meschede 1986 with data plotting within E-MORB field and to lesser extent in the N-MORB field.

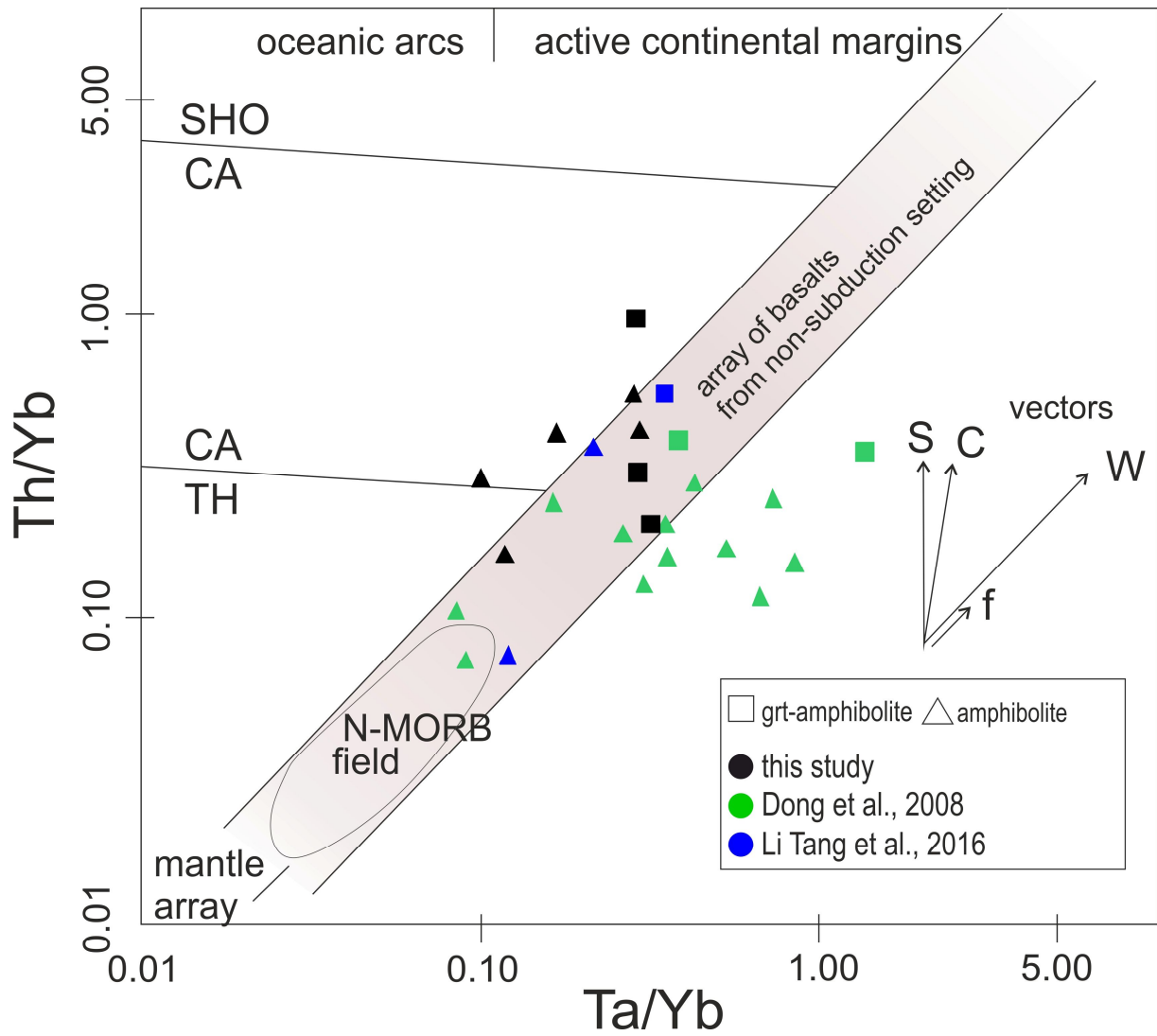


Fig. 47 Ta/Yb versus Th/Yb (Pearce, 1983), used symbology right at the bottom. Vectors show the influence of subduction components (**S**), within-plate enrichment (**W**), crustal contamination (**C**) and fractional crystallization (**f**). Tholeiitic (**TH**), calc-alkaline (**CA**) and shoshonitic (**SHO**).

table 27 Whole rock major and trace elemental compositions for various rock types from the Songshugou ophiolite. Trace elements and REEs were obtained by ICP-MS. Trace elements given in ppm.

| | garnet-amphibolite | | | amphibolite | | | | |
|-------------------------------------|--------------------|-------|-------|-------------|-------|-------|-------|-------|
| Sample | X 35 | X 36 | X 37 | X 38 | X 39 | X 382 | X 42 | QS2D |
| SiO ₂ (%) | 40.51 | 41.25 | 38.27 | 47.89 | 49.75 | 45.60 | 50.50 | 48.38 |
| TiO ₂ (%) | 3.27 | 2.64 | 2.34 | 1.46 | 1.78 | 1.49 | 1.78 | 1.42 |
| Al ₂ O ₃ (%) | 13.94 | 14.04 | 16.94 | 14.75 | 12.58 | 14.78 | 13.15 | 14.36 |
| Fe ₂ O _{3t} (%) | 21.36 | 17.98 | 24.01 | 14.64 | 16.65 | 15.50 | 14.51 | 12.94 |
| MnO (%) | 0.42 | 0.24 | 0.62 | 0.21 | 0.26 | 0.22 | 0.25 | 0.20 |
| MgO (%) | 5.85 | 7.62 | 4.31 | 6.40 | 5.30 | 7.23 | 6.16 | 6.53 |
| CaO (%) | 11.42 | 13.29 | 11.69 | 10.27 | 8.72 | 10.76 | 8.54 | 11.68 |
| Na ₂ O (%) | 1.49 | 1.25 | 0.94 | 2.55 | 3.15 | 2.34 | 3.45 | 2.47 |
| K ₂ O (%) | 0.09 | 0.31 | 0.03 | 0.40 | 0.24 | 0.42 | 0.17 | 0.21 |
| P ₂ O ₅ (%) | 0.82 | 0.26 | 0.79 | 0.10 | 0.19 | 0.07 | 0.15 | 0.12 |
| LOI (%) | 0.09 | 0.39 | 0.23 | 0.30 | 0.36 | 0.38 | 0.25 | 0.49 |
| Sum (%) | 99.17 | 98.90 | 99.94 | 98.65 | 98.62 | 98.41 | 98.66 | 98.31 |
| ⁷ Li | 8.42 | 4.29 | 9.41 | 13.3 | 4.27 | 12.9 | 30.1 | 12.4 |
| ⁹ Be | 0.98 | 1.41 | 0.36 | 0.62 | 0.49 | 0.64 | 0.49 | 0.37 |
| ⁴⁹ Ti | 46.0 | 31.6 | 37.4 | 31.6 | 32.8 | 30.1 | 40.9 | 37.1 |
| ⁵¹ V | 268 | 386 | 153 | 298 | 454 | 299 | 312 | 303 |
| ⁵³ Cr | 59.0 | 127 | 31.6 | 151 | 62.0 | 160 | 69.7 | 118 |
| ⁵⁵ Mn | 72.5 | 78.4 | 67.2 | 84.1 | 83.2 | 60.6 | 77.2 | 86.5 |
| ⁵⁹ Co | 30.6 | 83.7 | 42.1 | 98.9 | 50.2 | 84.2 | 50.7 | 78.1 |
| ⁶⁰ Ni | 105 | 25.0 | 31.5 | 31.8 | 55.9 | 33.0 | 115 | 179 |
| ⁶⁶ Zn | 139 | 177 | 82.2 | 104 | 115 | 114 | 104 | 84.8 |
| ⁷¹ Ga | 20.3 | 25.7 | 17.2 | 17.8 | 19.6 | 18.4 | 17.9 | 19.4 |
| ⁸⁵ Rb | 2.60 | 1.79 | 0.87 | 1.56 | 4.29 | 1.21 | 7.29 | 3.20 |
| ⁸⁸ Sr | 70.7 | 90.0 | 76.4 | 108 | 76.1 | 100 | 137 | 234 |
| ⁸⁹ Y | 108 | 44.1 | 194 | 30.6 | 23.7 | 31.6 | 29.2 | 23.6 |
| ⁹⁰ Zr | 499 | 240 | 1628 | 104 | 84.9 | 125 | 110 | 71.1 |
| ⁹³ Nb | 37.9 | 50.7 | 42.8 | 6.29 | 7.83 | 5.47 | 9.54 | 6.54 |
| ¹³³ Cs | 0.41 | 0.17 | 0.45 | 0.10 | 0.17 | 0.05 | 0.97 | 0.15 |
| ¹³⁷ Ba | 165 | 146 | 118 | 103 | 111 | 101 | 150 | 63.9 |
| ¹³⁹ La | 38.0 | 16.3 | 90.0 | 4.37 | 5.60 | 4.77 | 8.27 | 7.15 |
| ¹⁴⁰ Ce | 94.1 | 40.6 | 218 | 11.2 | 13.6 | 12.1 | 21.2 | 18.1 |
| ¹⁴¹ Pr | 13.4 | 5.80 | 31.1 | 1.78 | 1.94 | 1.99 | 3.03 | 2.63 |
| ¹⁴⁶ Nd | 60.8 | 26.9 | 135 | 9.20 | 9.03 | 10.3 | 14.4 | 12.6 |
| ¹⁴⁷ Sm | 15.5 | 7.52 | 32.4 | 3.03 | 2.62 | 3.46 | 4.08 | 3.76 |
| ¹⁵³ Eu | 4.44 | 2.46 | 8.25 | 1.16 | 1.07 | 1.25 | 1.37 | 1.39 |
| ¹⁵⁷ Gd | 17.8 | 8.62 | 34.1 | 3.88 | 3.30 | 4.34 | 4.71 | 4.29 |
| ¹⁵⁹ Tb | 3.07 | 1.47 | 5.79 | 0.71 | 0.58 | 0.79 | 0.80 | 0.69 |
| ¹⁶³ Dy | 20.6 | 9.31 | 40.2 | 5.04 | 4.05 | 5.50 | 5.27 | 4.30 |
| ¹⁶⁵ Ho | 4.22 | 1.84 | 8.79 | 1.15 | 0.89 | 1.18 | 1.07 | 0.87 |
| ¹⁶⁶ Er | 12.0 | 5.00 | 25.9 | 3.40 | 2.54 | 3.43 | 3.00 | 2.35 |
| ¹⁶⁹ Tm | 1.71 | 0.69 | 3.94 | 0.53 | 0.39 | 0.51 | 0.45 | 0.33 |
| ¹⁷² Yb | 10.9 | 4.16 | 25.2 | 3.46 | 2.50 | 3.13 | 2.74 | 2.03 |
| ¹⁷⁵ Lu | 1.61 | 0.58 | 3.69 | 0.52 | 0.36 | 0.47 | 0.40 | 0.28 |
| ¹⁷⁸ Hf | - | - | - | - | - | - | - | - |
| ¹⁸¹ Ta | 3.30 | 4.00 | 5.13 | 1.00 | 1.02 | 0.51 | 1.14 | 1.10 |
| ²⁰⁸ Pb | - | - | - | - | - | - | - | - |
| ²³² Th | 3.16 | 1.19 | 8.00 | 0.35 | 0.42 | 0.37 | 0.80 | 0.57 |
| ²³⁸ U | 0.52 | 0.54 | 0.88 | 0.13 | 0.11 | 0.11 | 0.19 | 0.15 |

| Niggli parameters calculated after Leake et al., 1964 | | | | | | | | |
|---|--------------------|-------|-------|-------------|--------|--------|--------|--------|
| | garnet-amphibolite | | | amphibolite | | | | |
| Sample | X 35 | X 36 | X 37 | X 38 | X 39 | X 382 | X 42 | QS2D |
| si | 86.01 | 84.14 | 78.98 | 111.01 | 122.50 | 100.44 | 124.17 | 112.12 |
| al | 17.44 | 16.88 | 20.61 | 20.15 | 18.26 | 19.18 | 19.05 | 19.61 |
| fm | 53.39 | 51.19 | 51.63 | 48.04 | 50.84 | 49.84 | 49.96 | 45.52 |
| c | 25.97 | 29.05 | 25.84 | 25.51 | 23.02 | 25.39 | 22.49 | 29.01 |
| alk | 3.19 | 2.89 | 1.93 | 6.31 | 7.89 | 5.59 | 8.50 | 5.85 |
| k | 0.04 | 0.14 | 0.02 | 0.09 | 0.05 | 0.11 | 0.03 | 0.05 |
| mg | 0.35 | 0.45 | 0.26 | 0.46 | 0.38 | 0.48 | 0.45 | 0.50 |
| c/fm | 5.22 | 4.06 | 3.64 | 2.55 | 3.29 | 2.48 | 3.30 | 2.47 |
| ti | 0.74 | 0.22 | 0.69 | 0.09 | 0.20 | 0.07 | 0.15 | 0.12 |
| p | 0.49 | 0.57 | 0.50 | 0.53 | 0.45 | 0.51 | 0.45 | 0.64 |

| chondrite normalized REEs after Nakamura 1974 | | | | | | | | |
|---|--------------------|--------|--------|-------------|-------|-------|-------|-------|
| | garnet-amphibolite | | | amphibolite | | | | |
| Sample | X35 | X36 | X37 | X38 | X39 | X382 | X42 | QS2D |
| La _N | 115.27 | 49.28 | 272.84 | 13.24 | 16.98 | 14.46 | 25.06 | 21.66 |
| Ce _N | 108.79 | 46.89 | 251.92 | 12.90 | 15.70 | 14.01 | 24.49 | 20.89 |
| Pr _N | 120.02 | 51.77 | 277.92 | 15.91 | 17.31 | 17.77 | 27.03 | 23.45 |
| Nd _N | 96.44 | 42.74 | 214.93 | 14.61 | 14.33 | 16.42 | 22.83 | 20.06 |
| Pm _N | NA | NA | NA | NA | NA | NA | NA | NA |
| Sm _N | 76.10 | 37.03 | 159.56 | 14.91 | 12.92 | 17.06 | 20.12 | 18.53 |
| Eu _N | 57.68 | 31.95 | 107.16 | 15.10 | 13.95 | 16.19 | 17.86 | 18.09 |
| Gd _N | 64.62 | 31.22 | 123.55 | 14.08 | 11.95 | 15.71 | 17.05 | 15.55 |
| Tb _N | 65.43 | 31.30 | 123.28 | 15.17 | 12.34 | 16.81 | 17.13 | 14.70 |
| Dy _N | 59.05 | 27.15 | 117.26 | 14.69 | 11.80 | 16.02 | 15.36 | 12.55 |
| Ho _N | 60.27 | 26.34 | 125.61 | 16.40 | 12.66 | 16.79 | 15.29 | 12.36 |
| Er _N | 53.24 | 22.23 | 115.08 | 15.10 | 11.29 | 15.25 | 13.32 | 10.45 |
| Tm _N | 56.97 | 23.13 | 131.47 | 17.57 | 12.93 | 16.87 | 14.83 | 11.13 |
| Yb _N | 49.63 | 18.90 | 114.54 | 15.71 | 11.38 | 14.25 | 12.45 | 9.20 |
| Lu _N | 47.35 | 17.00 | 108.62 | 15.18 | 10.65 | 13.79 | 11.71 | 8.26 |
| Eu/Eu* | 0.82 | 0.94 | 0.76 | 1.04 | 1.12 | 0.99 | 0.96 | 1.07 |
| La _N /Yb _N | 2.32 | 2.61 | 2.38 | 0.84 | 1.49 | 1.02 | 2.01 | 2.35 |
| Tb _N /Yb _N | 1.32 | 1.66 | 1.08 | 0.97 | 1.08 | 1.18 | 1.38 | 1.60 |
| La _N /Sm _N | 1.51 | 1.33 | 1.71 | 0.89 | 1.31 | 0.85 | 1.25 | 1.17 |
| Ce _N /Yb _N | 2.19 | 2.48 | 2.20 | 0.82 | 1.38 | 0.98 | 1.97 | 2.27 |
| Ce _N /Sm _N | 1.43 | 1.27 | 1.58 | 0.87 | 1.21 | 0.82 | 1.22 | 1.13 |
| Eu _N /Yb _N | 1.16 | 1.69 | 0.94 | 0.96 | 1.23 | 1.14 | 1.43 | 1.97 |
| Sum_REE | 297.84 | 131.20 | 662.76 | 49.38 | 48.45 | 53.27 | 70.75 | 60.78 |

10 Pseudosections

The evaluation of the P-T evolution of mafic HP rocks was complicated due to the high number of variances, and the refractory nature of the mineralogy. Growth zoning conserved in garnets is widely regarded as evidence for a change in effective bulk composition during metamorphism similar to fractional crystallisation (Marmo et al., 2002). Hence, the effective bulk composition which applies to matrix phases depends on the amounts of elements already fractionated into garnets, and the transport rate of these elements (Carlson, 1989; Chernoff and Carlson 1997).

In order to model metamorphic evolution of the investigated area, pseudosections were calculated for selected samples. The Gibbs free energy minimization software package *Perple_X* version 6.7.3 (Connolly, 2005, updated in 2016) and the internally consistent thermodynamic data set *hp04ver.dat* (Holland and Powell, 1998, revised in 2004) was used. Plots of mineral modes and isopleths of mineral compositions were obtained by the program *PyWerami* version 2.0.1 (Lexa, 2011). The chemical system $\text{MnO-Na}_2\text{O-CaO-FeO-MgO-Al}_2\text{O}_3\text{-SiO}_2\text{-H}_2\text{O-TiO}_2$ (MnNCFMASHT) was applied with the following solution models: orthopyroxene (Holland and Powell, 1999), chlorite (Holland et al., 1998), amphibole (Holland and Powell, 1998), feldspar (Benisek et al., 2010), spinel (Holland and Powell, 1998), garnet (Ganguly, Cheng & Tirrone, 1996), clinopyroxene (Holland and Powell, 1996) and omphacite for high-pressure calculations (Diener and Powell, 2011). A water content of 1.00 wt.% was applied based on mineralogy, and an empirical correction for ferric iron (15 wt.% of total iron) content was undertaken.

Based on petrographic observations described in the previous chapters, a three stage garnet growth was concluded. The first stage of garnet growth was modelled by applying the measured bulk-rock composition. Pseudosections were calculated for the samples X35, X36 and X37 (Fig. 48, Fig. 49 and Fig. 50). Since matrix minerals are not in equilibrium with garnet core compositions, calculated isopleths for all Grt endmembers and X_{Mg} of pargasitic amphibole inclusions in garnet cores were used to obtain a PT field of initial garnet growth. In addition, the garnet-hornblende FeMg-1 exchange geothermometry, calibrated by Dale et al., (2000), further constrained PT conditions of 630°C – 740°C and 0.7 – 0.9 GPa. For the geothermometer smaller Amp grains were chosen adjoined to Grt core and no other mineral phases. The theoretical full mineral assemblage at these conditions include Amp-Pl-Grt-Cpx-Ilm-H₂O. All phases with the exception of Cpx could also be found within the garnet cores. Calculated pseudosections of X35, X36 and X37 do not differentiate significantly with isopleths intercepting at similar PT conditions.

In order to calculate the metamorphic PT evolution recorded by Rim1 and Rim2 of the garnet porphyroblasts, the effective bulk composition used in pseudosection calculation has to be adapted, since it has changed from the previously used whole rock composition by the formation and chemical fractionation of the garnet cores. At temperatures below 600–700°C all major chemical components in garnet have very low intragranular diffusivity (Chakraborty & Ganguly, 1992; Spear, 1988; Thompson & England, 1984; Tracy, 1982). Therefore pseudosections calculated for garnet rim growth were chemically adjusted in consideration of elements being locked in cores. Similar corrections have been utilized by several authors (Spear et al., 1998; Evans, 2004; Gaidies et al., 2011). Authors like Evans (2004) estimated garnet fractionation by using Mn partitioning between whole rock and garnet as proxy. Therefore, a consistent Mn distribution in garnet grains, usually described by Rayleigh fractionation, is necessary. However, Songshugou samples do not exhibit any consistent pronounced zoning in Mn due to diffusional modifications. Therefore, the chemical correction for this effect was accomplished by estimating the volume of garnet cores in thin-sections using the software package *ImageJ* (<http://imagej.net>). The chemical composition, and the variations within the garnet core, were determined by applying element profiles across the garnet core; and analyzing element distribution images. The obtained garnet core vol.% was

then converted into wt.% with an estimated garnet density of 4.1 g/cm³. Chemically adjusted pseudosections of samples X35, X36 and X37 are illustrated in Fig. 51, Fig. 52 and Fig. 53, respectively. For PT estimations, calculated isopleths of Grt endmembers and isopleths of Omp (X_{Mg} , X_{Na}) were plotted into the pseudosections. For Omp isopleths, matrix Cpx analyses with highest X_{Na} values found in Cpx-Qz symplectites were taken since they are considered to be least influenced by retrogression. In the pseudosection of sample X37, no Cpx isopleths were plotted solely because all Cpx found in matrix occurs as strongly developed symplectites and supposedly yields extremely altered compositions. In the pseudosections of all three samples, isopleths intersect at 1.7 – 2.1 GPa and 570 – 640 °C, representing minimum PT conditions of a HP eclogite facies metamorphic event. This is substantiated by Cpx-Grt FeMg-1 geothermobarometric calculations (Krogh, 2000), where microprobe analyses of Grt rim and omphacitic Cpx found in Cpx-Qz symplectites in matrix resulted in a temperature window of 500 to 650°C. Within the obtained PT window the mineral assemblage Grt-Omp-Amp-Rt-H₂O±Zo, which is also observed in the samples, remained stable.

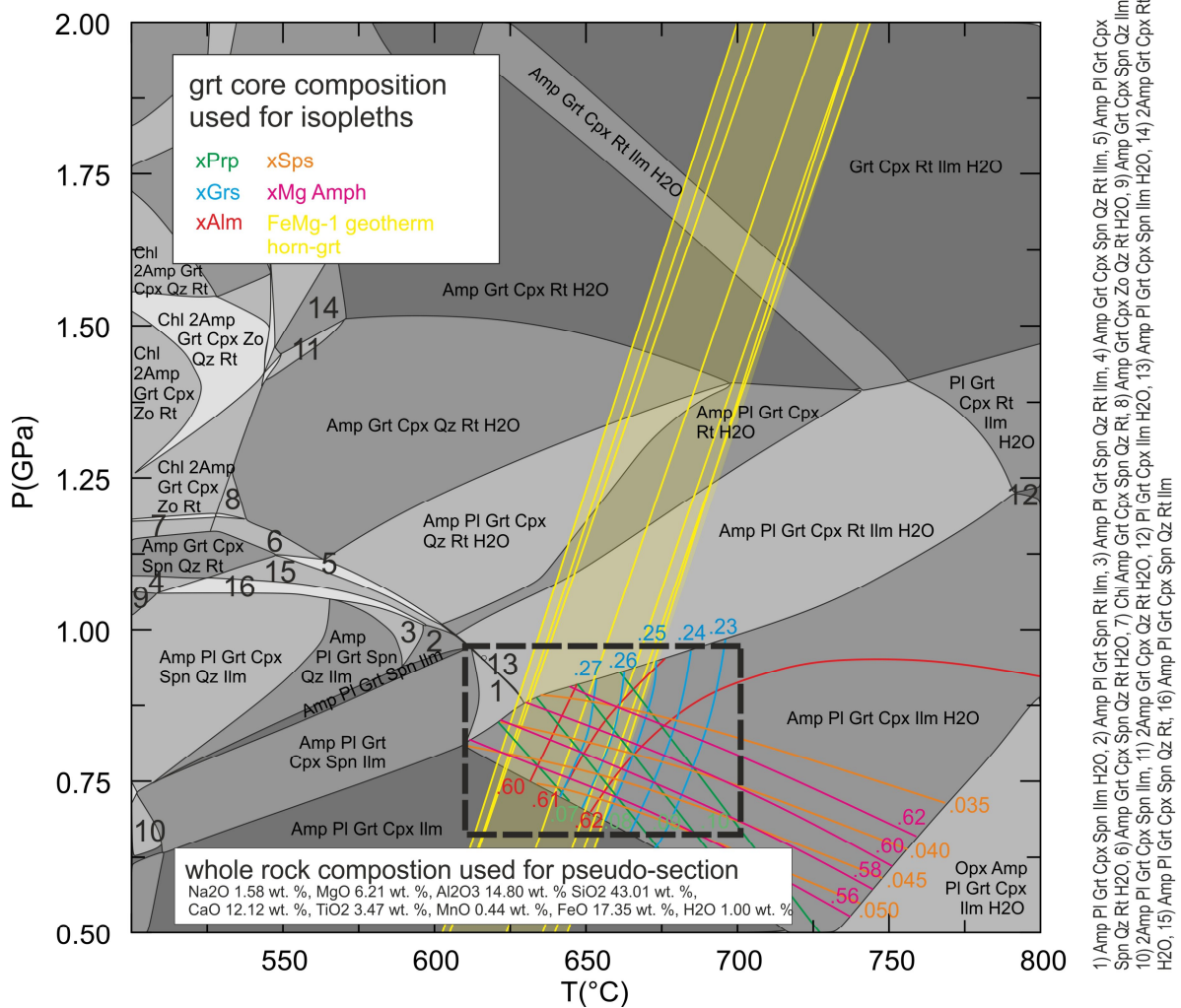


Fig. 48 Calculated pseudosection of bulk-rock composition representing initial garnet growth of sample X35. Isopleths intercept inside the dashed rectangle in the field of Amp, Pl, gt, Cpx, Ilm and H₂O. Used bulk rock composition is found at the bottom of the diagram.

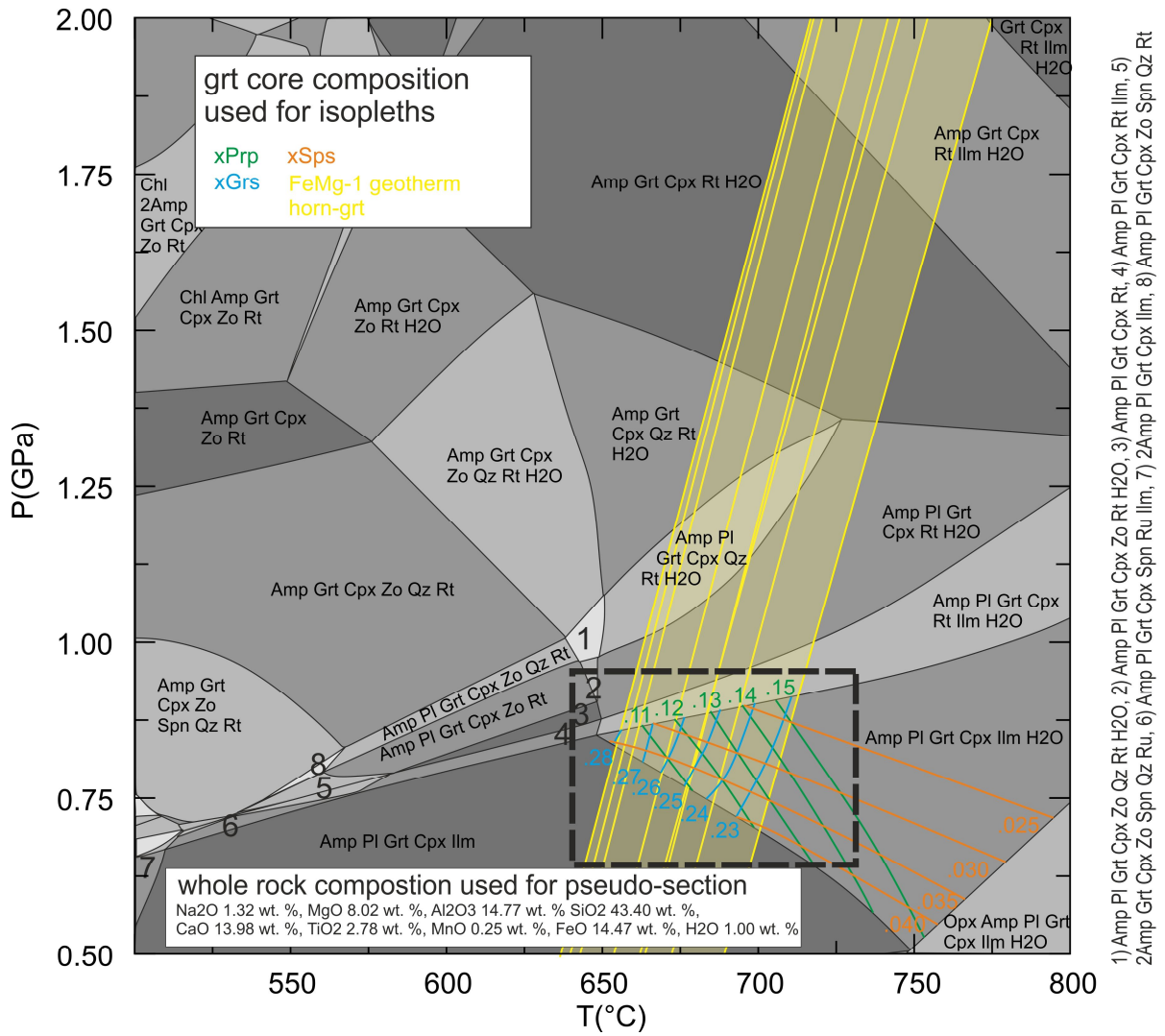


Fig. 49 Calculated pseudosection of bulk-rock composition representing initial garnet growth of sample X36. Isopleths intercept inside the dashed rectangle in the field of Amp, Pl, gt, Cpx, Ilm and H₂O. Used bulk rock composition is found at the bottom of the diagram.

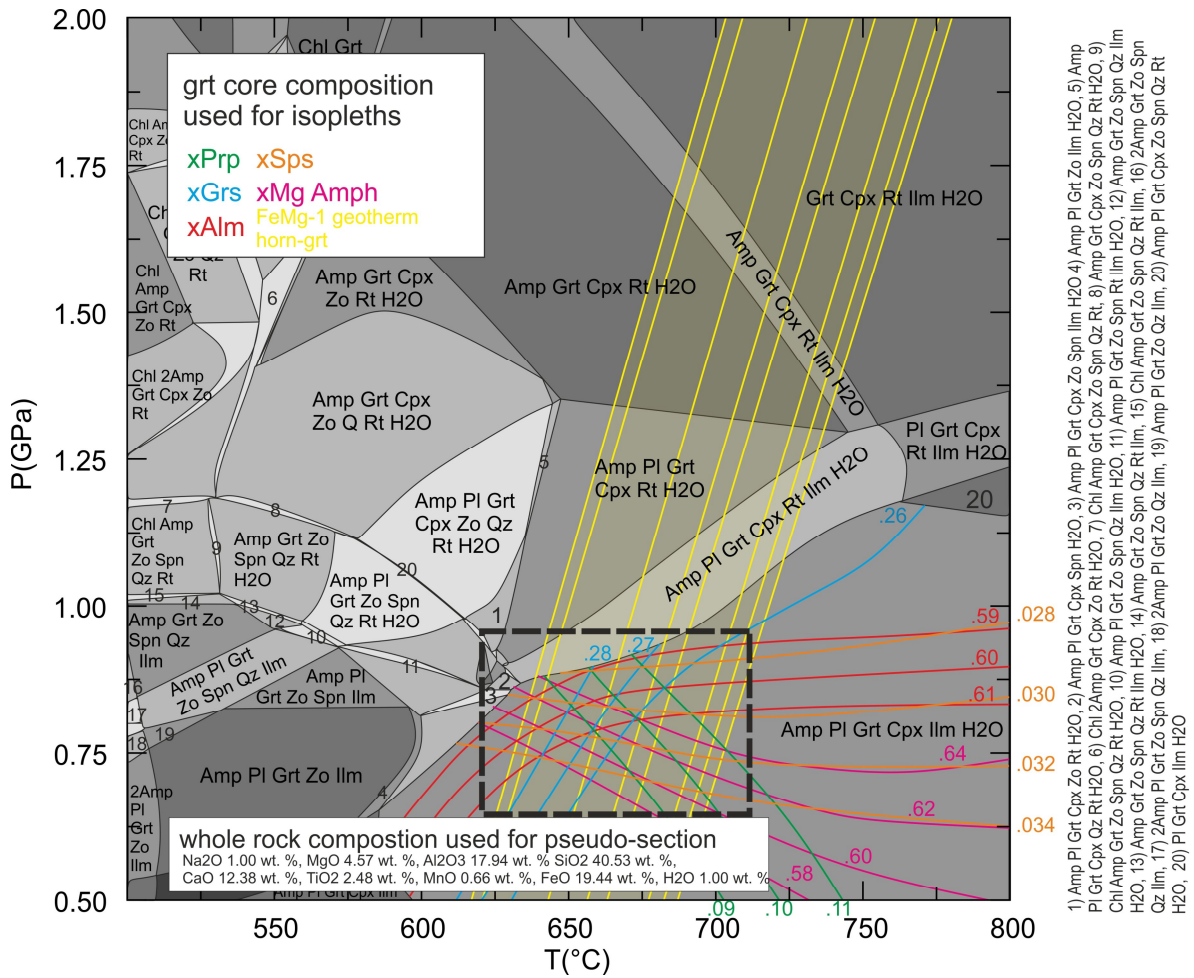


Fig. 50 Calculated pseudosection of bulk-rock composition representing initial garnet growth of sample X37. Isopleths intercept inside the dashed rectangle in the field of Amp, Pl, Grt, Cpx, Ilm and H₂O. Used bulk rock composition is found at the bottom of the diagram.

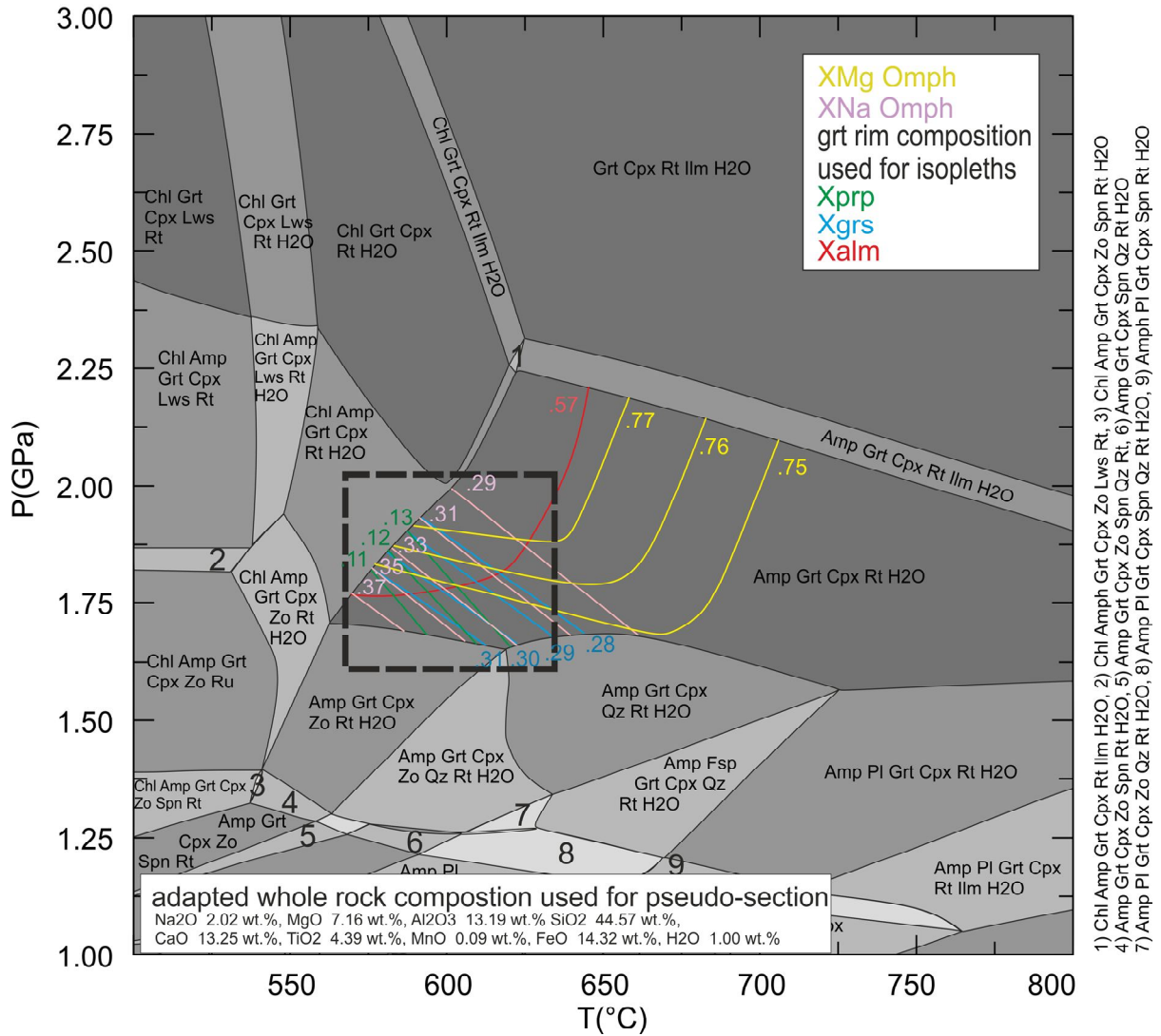


Fig. 51 Calculated pseudosection of recalculated bulk-rock composition representing garnet rim growth of sample X35. Iso-pleths intercept inside the dashed rectangle in the field of Amp, Grt, Cpx, Rt and H₂O. Used bulk rock composition is found at the bottom of the diagram.

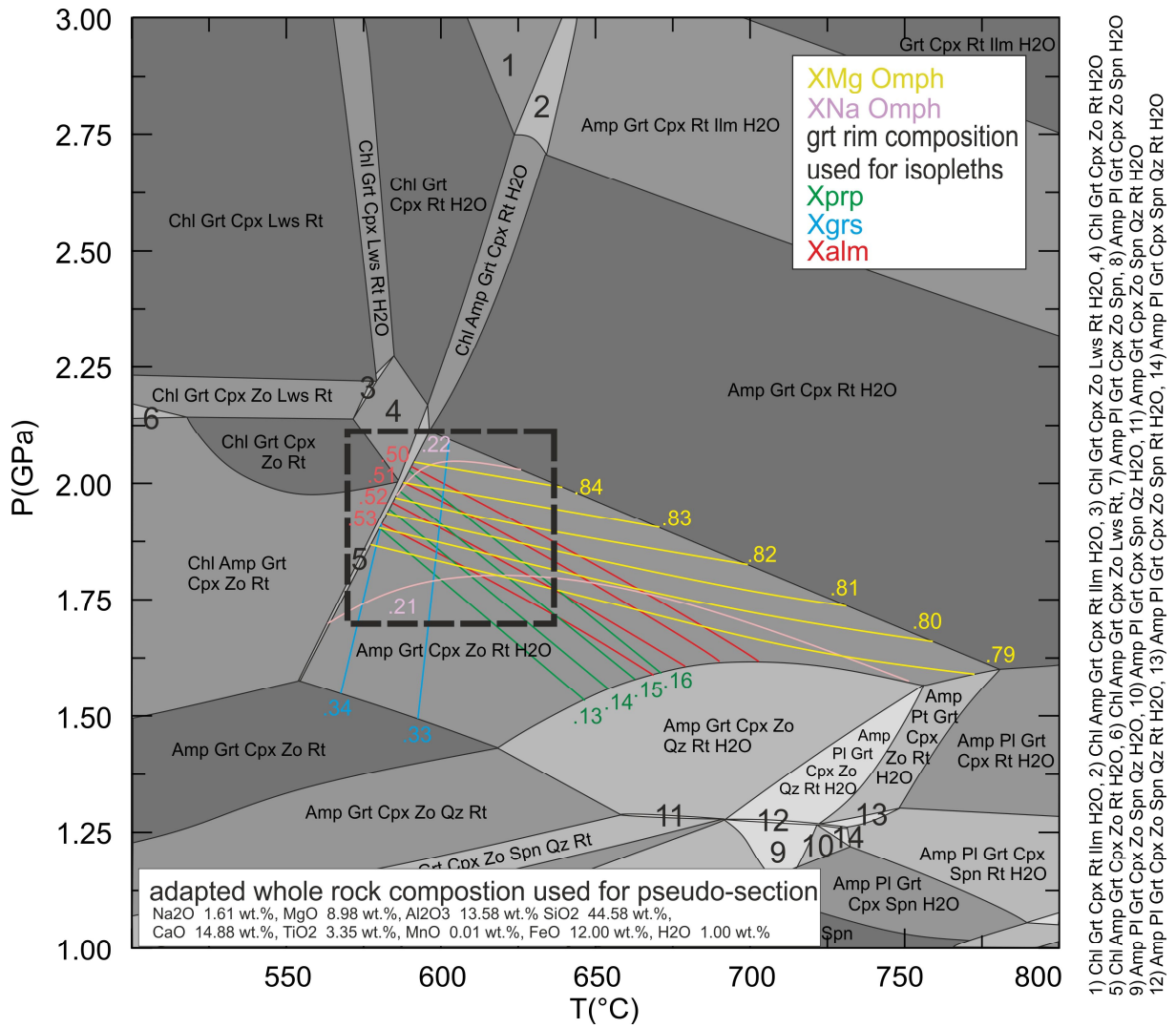


Fig. 52 Calculated pseudosection of recalculated bulk-rock composition representing garnet rim growth of sample X36. Iso-pleths intercept inside the dashed rectangle in the field of Amp, Grt, Cpx, Zo, Rt and H₂O. Used bulk rock composition is found at the bottom of the diagram.

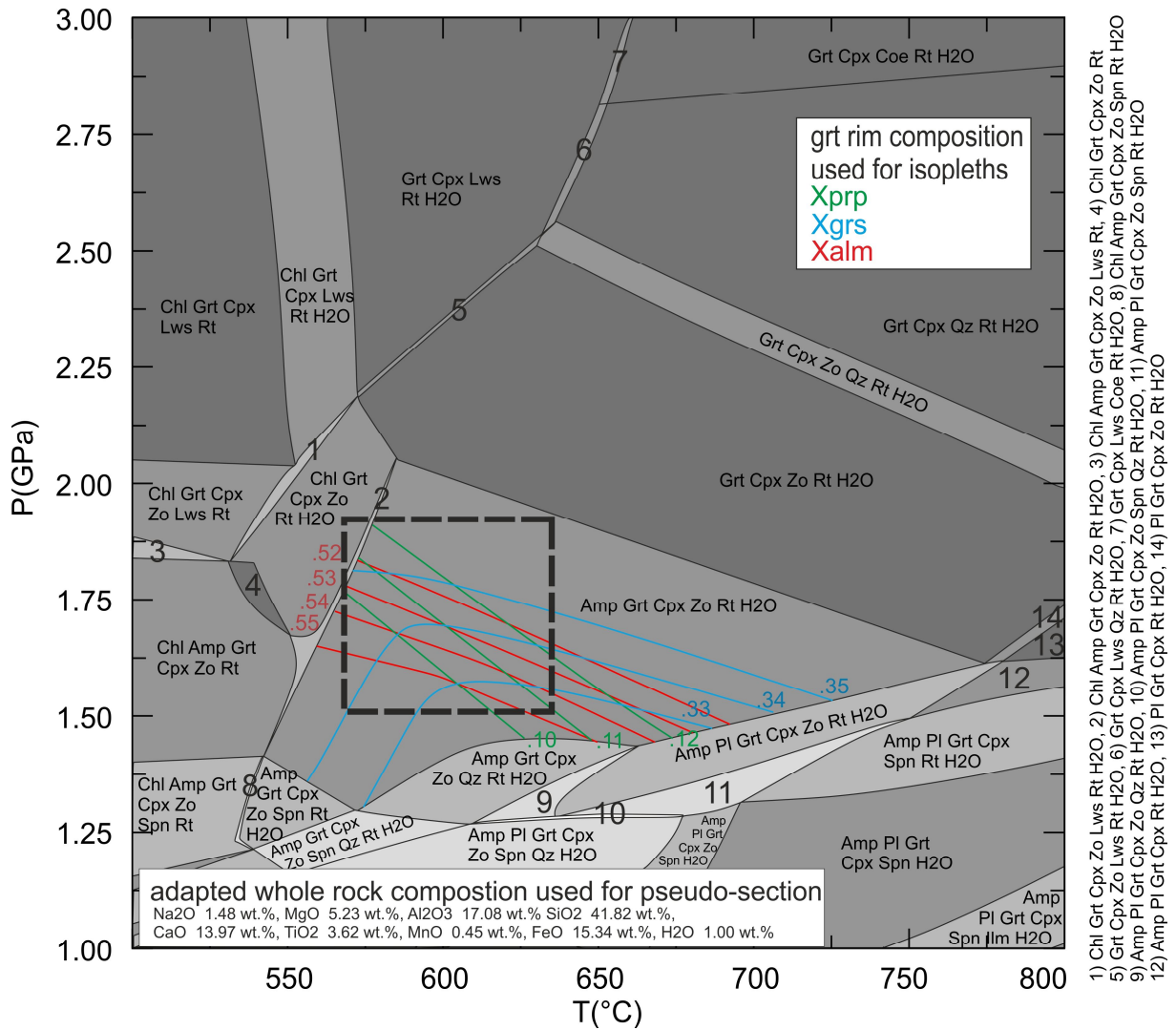


Fig. 53 Calculated pseudosection of recalculated bulk-rock composition representing garnet rim growth of sample X37. Isoleths intercept inside the dashed rectangle in the field of Amp, Grt, Cpx, Zo, Rt and H₂O. Used bulk rock composition is found at the bottom of the diagram.

11 Discussion and Interpretation

The metabasic unit of the Songshugou ophiolite can be divided into garnet amphibolites and amphibolites. Based upon their trace elements, and REE patterns, amphibolites are interpreted as oceanic tholeiitic basalts with T-MORB and E-MORB character. Amphibolites contain SiO₂ ranging from 45 wt.% to 49 wt.%, whereas Grt-amphibolites contain less SiO₂ varying from 38 wt.% to 42 wt.%. Amphibolites show typical trends of tholeiitic differentiation. Garnet amphibolites show different trends, probably related to amphibole fractionation (positive correlation between MgO and Na₂O, K₂O, Rb, and Sr; Rb, K, Sr troughs in chondrite normalized spider plots). Garnet amphibolites are highly enriched in LREEs similar to trends observed in EMORB and OIB but with higher overall REE abundance; and are enriched in HFSE e.g. (TiO₂, P₂O₅). Amphibolites are far less enriched in REEs and hardly show overall REE fractionation. The REE enrichment patterns of garnet amphibolites point at a different mantle source compared to amphibolites; crustal contamination seems unlikely since no Nb and Ta troughs were observed. Grt amphibolites represent either unusual SiO₂ – poor FeO and TiO₂-rich E-MORB melts, or probably evolved dikes of alkaline affinity. Grt amphibolite showed textural evidence of decompression and retrogression; in terms of various symplectites formed after omphacite, and reaction bands between Grt and Cpx. The reaction bands can be divided into 4 zones: 1=Grt, 2=Pl-Amp corona, 3=Amp, 4=Cpx symplectite. In analyzed samples, strong spatial organization and chemical zoning of minerals was observed, occurring in the reaction zones; with continuous edenite exchange of Amp towards Grt in zones 2 and 3, and continuous increase in X_{An} component of Pl towards Grt in zone2. This is typical for diffusion-controlled reactions. The phenomenon of Cl-rich amphibole rarely forming thin layers along the boundary of Pl-coronae (zone2) and matrix-amphibole (zone3), or crosscutting matrix assemblage as narrow veinlets, suggests that Cl rich fluids were at least partly involved in reaction-band formation. Reintegration of Cpx-Amp-Pl symplectites resulted in former omphacitic compositions similar to those acquired in Cpx grains that are almost free of intergrowths.

Garnet zoning

Garnet grains show a pronounced chemical zoning pattern with three distinctive compositional zones (core, rim1, & rim2). In some cases, rim2 was entirely consumed due to retrogression. Since the chemical composition of Grt is very susceptible to PT changes, the observed chemically homogenous Grt cores indicate that Grt core growth occurred within a small PT window or was homogenized through diffusion at high temperatures. The most conspicuous feature is the abrupt increase of X_{Grs} between core and rim1, and the drop of X_{Grs} between rim1 and rim2 ; and is ubiquitous in all garnets. X_{Alm} usually shows inverse zoning. Garnet poikiloblasts are typically inclusion rich. Inclusions of Amp + albitic Pl + Ilm + Ap + Zrn ± Czo/Ep ± Qtz are commonly enclosed in garnet cores and Amp + Rt + Ap ± Zrn ± Czo/Ep in garnet rim1. Trace element patterns show an abrupt increase in V, Ni and Cr at the core - rim1 boundary. Ilmenite usually contains significant amounts of Cr, Ni, Sc, and V. Thus, the observed increase in V, Ni and Cr in garnet rim1 indicates a breakdown of ilmenite to garnet and rutile. Chondrite normalized REE patterns of Grt core and rim (1+2) clearly diverge. Garnet cores show strong HREE enrichment. Grt rim(1+2) measurements are slightly enriched in the lighter HREEs. A general rimward decrease in heavy HREE is observed, which is symptomatic for HREE depletion in the matrix during garnet growth in a closed system. Neodymium, Sm, Tb, Dy and Ho show similar zoning trends with low abundances in the core and an abrupt increase at rim1, which can be attributed to the breakdown of Amp which has high partition coefficients for these elements. Breakdown of Amp could also contribute to the observed enrichment in Cr and V at garnet rim1. Fig. 54 displays a calculated pseudosection of sample X37 with Amp modes plotted as orange lines. Modal Amp content decreases towards higher PT conditions. Therefore, we conclude that an Amp breakdown during Grt rim growth at high PT conditions contributed to the observed chondrite normalized REE patterns of the Grt rims.

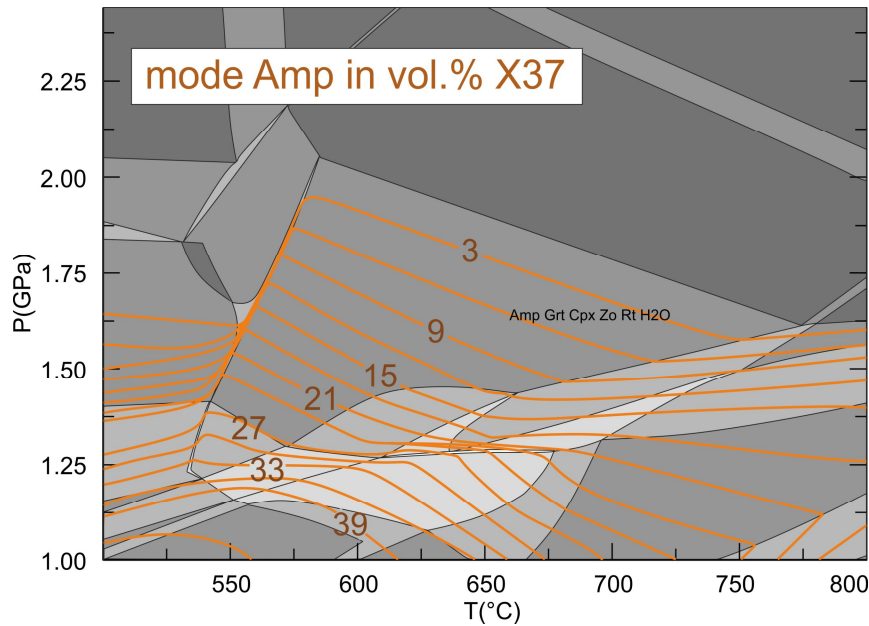


Fig. 54 Pseudosection calculated for sample X37. Orange lines represent Amp mode in vol.%.

Chemical zoning patterns in garnets (REEs and majors) and different mineral assemblages associated with core and rim compositions indicate a poly-phase metamorphic history. We propose that the Grt rim1 with its high X_{Grs} content relates to HP conditions during garnet rim growth. Rim2 must have grown subsequent to the HP event at lower PT conditions prior to garnet consumption.

Estimation of metamorphic P-T conditions

P-T conditions were estimated by means of pseudosection modeling substantiated by conventional geothermobarometry. Based on petrography, major element and REE distribution patterns of garnet, a polymetamorphic history can be concluded.

(1) First metamorphic event is represented by garnet cores, which typically contain inclusions of amphibole, plagioclase, and ilmenite \pm quartz \pm clinozoisite. Observed snowball textures in the cores indicate syndeformative garnet growth. PT estimations of this metamorphic event has been specified by intersection of garnet core isopleths (X_{Grs} , X_{Alm} , X_{Prp}) and X_{Mg} isopleths of amphibole in calculated bulk-rock pseudosections. Along with garnet-hornblende geothermometry of amphibole inclusions in garnet core, an amphibolite to lower granulite facies event can be concluded with 0.7 – 1.0 GPa and 630 – 730 °C with a stable mineral assemblage of amphibole, plagioclase, garnet, clinopyroxene and ilmenite. The first metamorphic event is solely represented by the garnet cores with mineral inclusions. Garnet cores do not exhibit any pronounced zonation. Thus, with the lack of further PT information no PT-path can be constructed for the first metamorphic event. PT conditions of initial garnet cores representing a pre eclogites metamorphic event are displayed in Fig. 55.

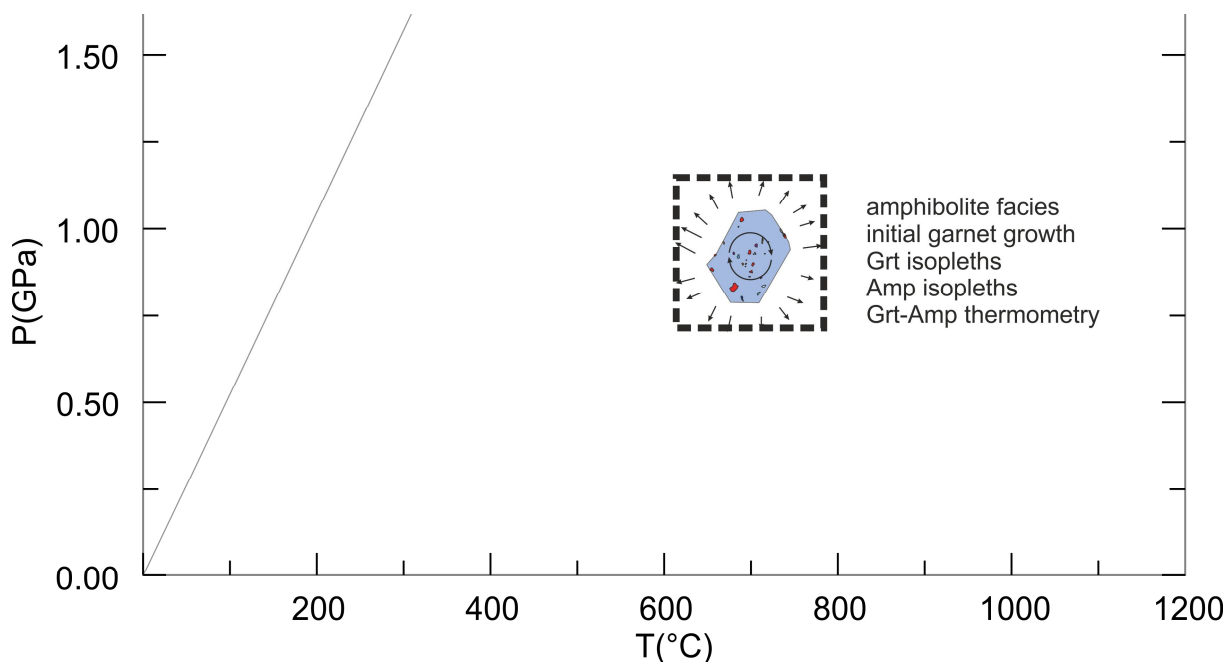
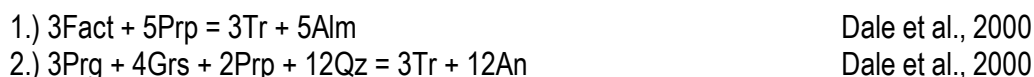


Fig. 55 PT diagram displaying first metamorphic event represented solely by garnet core. Isopleth geothermobarometry of garnet endmembers and X_{Mg} in amphibole and amphibole-garnet geothermometry yield a PT window of 0.7-1.0GPa and 630-730°C.

(2) A second metamorphic event of eclogitic conditions is represented by garnet rim and omphacitic clinopyroxene. To constrain PT conditions, pseudosections for garnet-rim growth were chemically adjusted in consideration of elements being locked into cores. Garnet rim isopleths (X_{Grs} , X_{Alm} , X_{Prp}) and omphacite isopleths (X_{Mg} , X_{Na}) intersect at 1.7 – 2.1 GPa and 570 – 650 °C, representing typical PT conditions of a eclogites facies metamorphic peak. That is substantiated by Cpx-Grt FeMg-1 geothermobarometry (Krogh, 2000) of garnet rim and omphacitic clinopyroxene found in matrix, yielding temperatures of 500 to 650°C.

Subsequent exhumation and hydration contributed to symplectitic clinopyroxene, amphibole growth, reaction bands between clinopyroxene and garnet, and consumption of garnet. A late retrograde stage is described by the formation of low grade minerals such as prehnite and pumpellyite. To evaluate PT conditions of retrogression, thermobarometric calculations and multi equilibrium geothermobarometry were used. For microtextural domains in the garnet coronae, consisting of plagioclase, amphibole and garnet, local equilibrium is assumed. Therefore strong to hardly developed garnet coronae have been analyzed to constrain PT conditions of the retrograde path by applying the Grt-Amp FeMg- thermometer and the Grt-Amp-Pl barometer (Prg-Tr reaction) after Dale et al., 2000, reaction 1-2.



Narrow coronas, of less retrogressed samples yield temperatures from 670 to 800°C and pressures from 0.8 to 1.3 GPa, representing an early retrograde stage. Coronae of stronger retrogressed grains yield lower conditions of 450-650°C and 0.4 – 0.6 GPa (Fig. 56). Further reactions that could contribute to the observed reaction bands between Cpx and Grt were calculated with winTWQ (Berman, 1991). Activities of mineral endmembers were determined by the activity-composition calculation program winCMP using nonideal activity models for garnet (Berman, 1990), amphibole (Mader et al., 1994) and plagioclase (Fuhrman and Lindsley, 1988).

Calculated reactions 3-10 are listed below and point at temperatures from 600 to 800°C.

- | | |
|---|----------|
| 3.) $12\text{Ts} + 6\text{Prg} = 19\text{Prp} + 6\text{Jd} + 11\text{Gr}_s + 3\text{Di} + 18\text{H}_2\text{O}$ | TWQ 1.02 |
| 4.) $3\text{Prg} + 9\text{Ts} = 8\text{Gr}_s + 3\text{Jd} + 13\text{Prp} + 3\text{Qz} + 12\text{H}_2\text{O}$ | TWQ 1.02 |
| 5.) $5\text{Qz} + \text{Tr} + 3\text{Prg} = 3\text{Prp} + 3\text{Jd} + 8\text{Di} + 4\text{H}_2\text{O}$ | TWQ 1.02 |
| 6.) $5\text{An} + 9\text{Tr} + 7\text{Prg} = 12\text{Prp} + 7\text{Jd} + 37\text{Di} + 16\text{H}_2\text{O}$ | TWQ 1.02 |
| 7.) $21\text{Ts} + 3\text{Tr} = 16\text{Gr}_s + 26\text{Prp} + 24\text{Qz} + 24\text{H}_2\text{O}$ | TWQ 1.02 |
| 8.) $8\text{Prg} + 5\text{Ts} + 11\text{Tr} = 48\text{Di} + 8\text{Jd} + 18\text{Prp} + 24\text{H}_2\text{O}$ | TWQ 1.02 |
| 9.) $12\text{Qz} + 6\text{Prg} = 5\text{Prp} + 6\text{Jd} + \text{Gr}_s + 9\text{Di} + 6\text{H}_2\text{O}$ | TWQ 1.02 |
| 10.) $3\text{An} + 3\text{Ts} + 3\text{Prg} = 7\text{Prp} + 3\text{Jd} + 5\text{Gr}_s + 6\text{H}_2\text{O}$ | TWQ 1.02 |

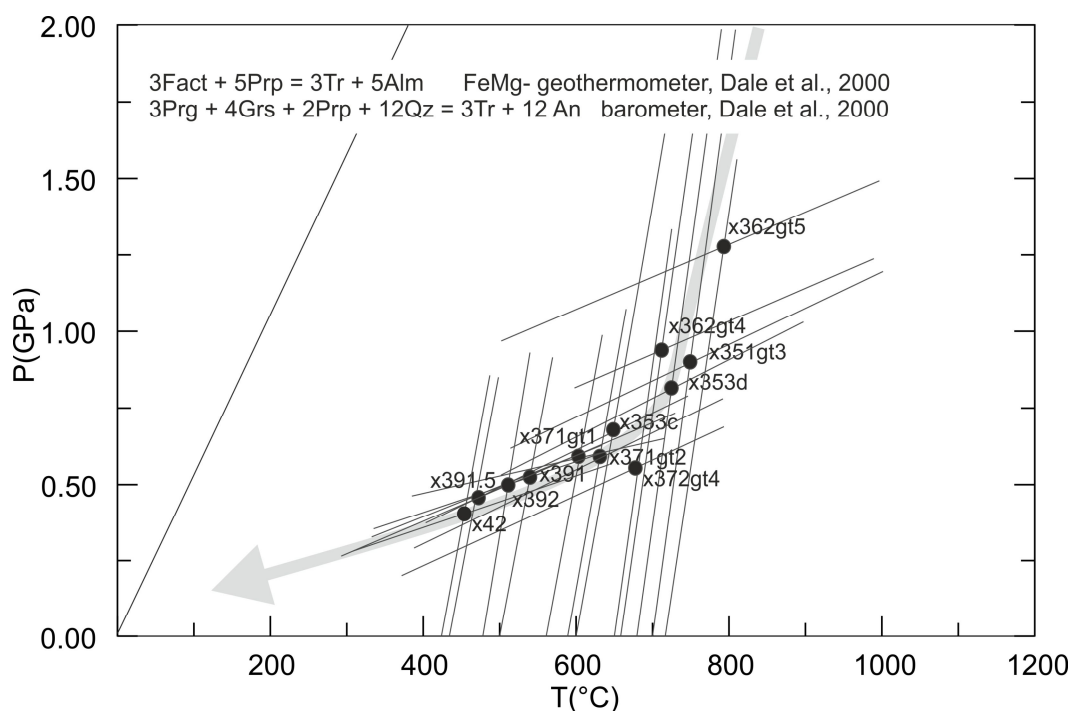


Fig. 56 P-T estimates of Pl-Amp coronae around Grt by using the Grt-Amp FeMg- thermometer and the Grt-Amp-Pl barometer (Prg-Tr reaction) after Dale et al., 2000. Each point represents the average value of multiple microprobe analyses taken at one micro domain.

PT estimates of retrograde Cpx-Pl-Amp symplectite assemblages range from 570 to 700°C and 0.5 to 0.7GPa (reactions 10-12).

- | | | |
|---|--------------------|--------------------------|
| 10.) $\text{Ed} + \text{Ab} = \text{Ri} + \text{An}$ | Hbl-Pl thermometer | Holland and Blundy, 1994 |
| 11.) $\text{Tr} + 4\text{Jd} + \text{Cats} = 3\text{Ab} + \text{Di} + \text{Prg}$ | | TWQ 1.02 |
| 12.) $2\text{Cats} + \text{Di} + \text{Jd} + \text{Ts} = \text{Prg} + 3\text{An}$ | | TWQ 1.02 |

Lowest conditions at late stage retrogression are presented by the formation of prehnite. Activities of mineral endmembers have been determined by the AXWin, i.e. (Tr=0.14, Ts=0.002, Prg=0.003, An=0.45, Di=0.61, Grs=0.03, Cats=0.21). Possible reactions leading to Prh in Grt corona (reaction 13) and Prh in Cpx-Pl-Amp-Prn (reactions 14-17) symplectite are listed below and point to temperatures between 200 – 350 °C for late stage retrogression.

- | | |
|---|---------|
| 13.) $2Prn = 1Grs + 1Qz + 1An + 2H_2O$ | PerpleX |
| 14.) $1Ts + 6Prh + 1Tr = 8An + 8Di + 8H_2O$ | PerpleX |
| 15.) $1Ts + 3Prh + 1Qz = 5An + 3Di + 4H_2O$ | PerpleX |
| 16.) $3Prh + 1Tr = 3An + 5Di + 1Qz + 4H_2O$ | PerpleX |
| 17.) $1Ts + 3Prh = 1Cats + 4An + 3Di + 4H_2O$ | PerpleX |

Results plotted in Fig. 57 suggest a clockwise P-T path for the second metamorphic event with eclogite facies conditions in field1. A short residence time at field2 was responsible for garnet rim2 growth, followed by early stage retrogression recorded by upper amphibolite facies decompression reactions in field3 (garnet breakdown, cpx-symplectite development) and late stage retrogression at low PT conditions in field4 (prehnite, pumpellyite formation).

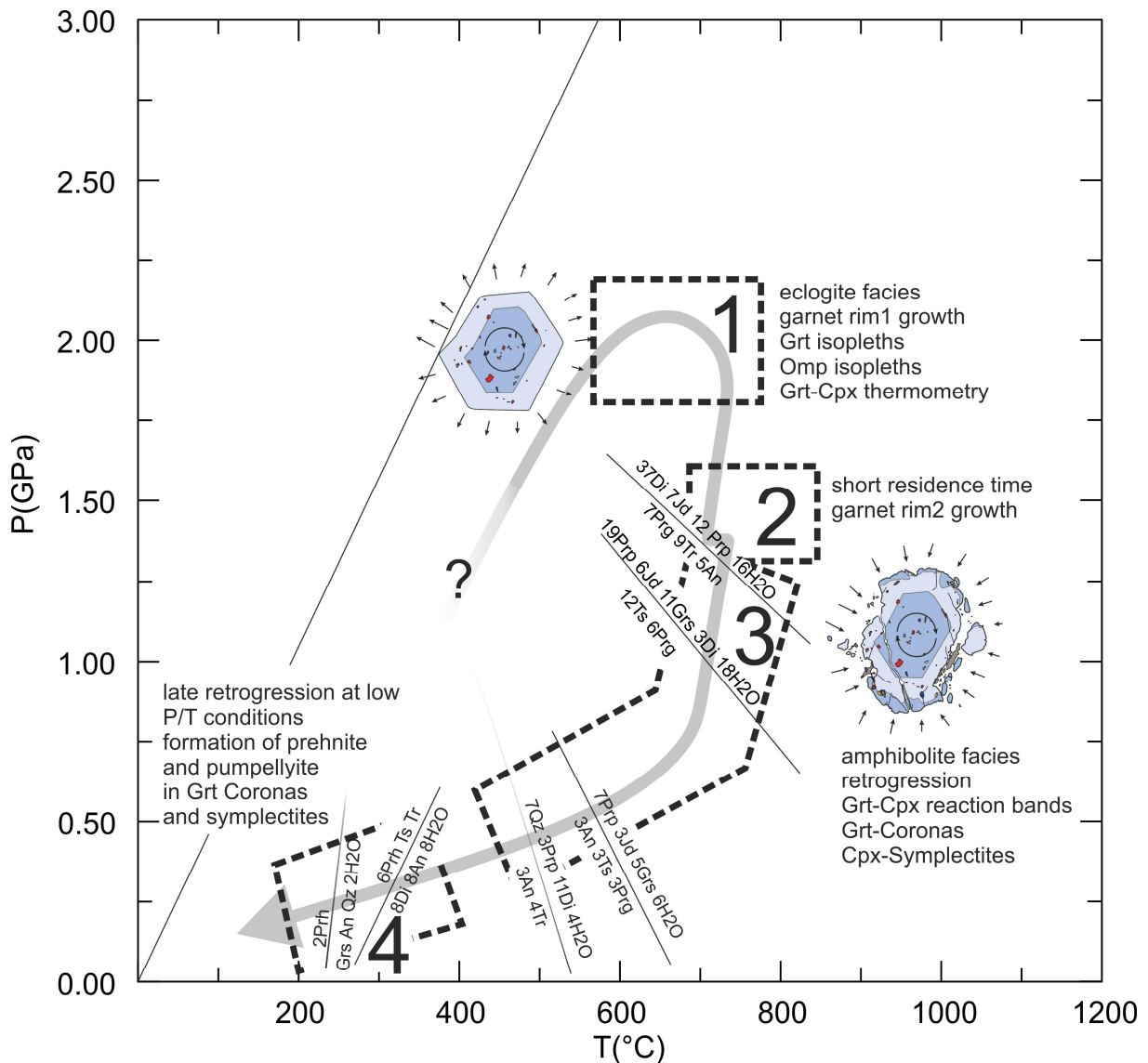


Fig. 57 PT estimates of Songshugou Grt-amphibolites for the second metamorphic event represented by garnet rim and matrix. **Field 1:** PT estimates from Grt core and Cpx isopleths geothermobarometry and Cpx-Grt geothermometry representing minimum peak conditions. **Field 2:** Short residence time in mid-crustal levels, growth of rim2. **Field 3:** retrograde stage, PT conditions estimated from Cpx-Pl-Amp symplectites, Grt-Cpx reaction bands and Grt-coronae (reactions 1-12). **Field 4:** late retrograde stage, PT conditions derived from Prn formation in Grt-coronae and symplectites.

(2) Tectonic framework.

“The Songshugou ophiolite represents a fragment of oceanic lithosphere that once separated the North Qinling and South Qinling terranes” (Dong et al., 2008). Obtained Sm-Nd whole rock ages of 1030 - 983 Ma represent the age of the basaltic oceanic crust protolith (Li et al., 1991; Liu et al., 2004, Dong et al., 2008), similar to the Sm-Nd age of the Heihe ophiolite (963 ± 10 Ma, Zhang et al., 2000) which outcrops in the western part of the Shangdan suture zone.

An amphibolite/lower granulite facies event is recorded in garnet cores, which may have taken place during Early Paleozoic. The modelled clockwise PT path for rim1 growth in this study is probably related to subduction at a collision regime, maybe the northward subduction of the Shangdan oceanic crust (Li Tang et al., 2016). Zircons of ophiolites along the Shangdan suture zone have been dated and yielded ages of 534-440 Ma for the northward subduction of the Shangdan oceanic crust. (Lu et al., 2003; Yang et al., 2006; Liu et al., 2007; Pei et al., 2007; Li 2008; Dong et al., 2011b). In North Qinling, HP to UHP metamorphism is widely observed at around 500 Ma. (Yang et al., 2003; Wang et al., 2011, Liu et al., 2013; Wang et al., 2014). Zircon, included in Grt amphibolites of the Songshuou metabasic unit, reveals similar ages of 485 – 510 Ma (Chen et al., 2004; Liu et al., 2009; Qian et al., 2013; Li et al., 2014b, Li Tang et al., 2016). Peak conditions of Songshugou Grt amphibolites (>18kbar, 550-650°C) represented by garnet rims and omphacitic clinopyroxene, probably belong to this subduction event. Subsequent post-peak decompression and retrogression contributing to retrograde textures such as symplectites after omphacite and coronae around garnet are commonly observed in eclogites (Eskola, 1921; Griffin and Raheim, 1973; Wilkerson et al., 1988; O'Brien et al., 1990; Droop et al., 1990; Zhao et al., 2001). A short residence time at midcrustal levels probably lead to formation of rim2, which was consumed partly together with rim1 by retrograde reactions Those characteristic retrograde textures together with the PT path point at decompression and later cooling possibly related to two stages of lifting in North Qinling at around 450Ma and 420Ma (Liu et al., 2013; Li Tang et al., 2016).

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