



**Petrogenesis of Volcanic Rocks in the Ekibastuz Region, Central Kazakhstan:
Constraints from Petrography and Geochemistry**

MSc in Geosciences

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ORIGINALITY STATEMENT

I, Ilyas Raiymkulov, hereby declare that this submission is my own work and to the best of my knowledge it contains no materials previously published or written by another person, or substantial proportions of material which have been accepted for the award of any other degree or diploma at Nazarbayev University or any other educational institution, except where due acknowledgement is made in the thesis.

Any contribution made to the research by others, with whom I have worked at NU or elsewhere, is explicitly acknowledged in the thesis.

I also declare that the intellectual content of this thesis is the product of my own work, except to the extent that assistance from others in the project's design and conception or in style, presentation, and linguistic expression is acknowledged.

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Abstract

A Ekibastuz is a region of central Kazakhstan that is part of the Central Asian Orogenic Belt (CAOB) of volcanic rocks of mafic to intermediate-felsic age ranges, dating between the Cambrian and the Devonian. This paper combines petrography with mineral chemistry (SEM–EDS), and whole-rock geochemistry to constrain the petrogenesis and tectonic environment of these rocks. Petrographic observations reveal that basalts, basaltic andesites, andesites, volcanoclastic rocks, and felsic volcanic rocks have predominantly porphyritic textures with assemblages of plagioclase, and variable amounts of clinopyroxene and amphibole, with alteration features of sericitization and chloritization. Information on mineral chemistry indicates that the albitic plagioclase compositions of Cambrian rocks and relatively higher Mg contents of mafic minerals of Lower Ordovician units, indicating more primitive compositions than younger rocks, and more evolved mineral assemblages, including K-bearing phases, of the Devonian rocks.

Systematic trends in increasing SiO_2 , decreasing MgO , FeO , and CaO and increasing Na_2O and K_2O , are observed, consistent with fractional crystallization. Patterns of trace elements normalized to ocean island basalt (OIB) are enriched in large ion lithophile elements (LILE) and depleted in highly field-strength elements (HFSE), especially Nb and Ta, characteristic of a subduction-related origin. The geochemical discrimination diagrams also show a change in the tholeiitic and calc-alkaline affinity and low-K to medium- to high-K change of composition with time. These geochemical features point to a gradual evolution of magma between rather primitive and more complex compositions.

The combined petrographic, mineral-chemical, and geochemical data indicate that magmatism evolved through several phases between the Cambrian and the Devonian, with an increasing arc maturity and magmatic differentiation. The data most consistently gives formation in a subduction related arc environment with earlier stages corresponding to an intra-oceanic arc environment and later stages representing more evolved magmatic conditions.

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1.0 Introduction

Arc magmatism, such as island arcs (IA) or continental arcs (ACM), is one of the characteristic features of orogenic belts, which form over the areas of subduction as a result of partial melting of the mantle wedge over the slab protruding downwards (Yan and Shi, 2011; Yamada et al., 2023; Degtyarev et al., 2020a). The magmas formed in these regions are commonly characterized by calc-alkaline geochemical patterns, which indicate melting of the mantle induced by fluids, plus fractional crystallization and fluctuating crustal fusion (Windley & Xiao, 2018; Yamada et al., 2023).

Mafic-intermediate magmas, such as basalt, basaltic andesites, and andesites, are prevalent in subduction and post-subduction tectonics (Burns and de Silva, 2023; Cassidy et al., 2015; Chen and Zhao, 2017; Chen et al., 2014; Chen et al., 2021; Chiaradia and Mu, 2011; Draut et al., 2009; Eichelberger, 1975; Eichelberger and Izbekov, 2000; Hamilton and Kröner, 1981; Jagoutz and Kelemen, 2015; Kent et al., 2013; Kuno, 1968; Lange et al., 2011; Reubi and Müntener, 2022). Lange et al. (2011) and Chen and Zhao (2017) provide summaries of the various mechanisms by which andesites form. These include crystal fractionation of hydrous basalts, partial melting of a hydrated mafic lower crust, magma mixing and mingling with rhyolites or dacites, and assimilation of the granitoid upper crust by basalt or basaltic andesites. Melekhova and Blundy (2024) link the origin of basaltic andesite in the Kamchatka arc to mantle melting, which they associate with primary magma. In subduction and post-subduction zones, andesites are often related to mafic rocks such as basalts or basaltic andesites (Burns and de Silva, 2023; Cassidy et al., 2015; Chiaradia and Mu, 2011; Cocker et al., 2022; Cole et al., 2001; Schmidt and Grunder, 2011; Snyder et al., 1997; Zhao et al., 2014). Many researchers conclude that magma mixing and mingling are also crucial processes in the formation of andesites and basaltic andesites (Morgavi et al., 2017; Burns and de Silva, 2023; Cassidy et al., 2015; Chiaradia and Mu, 2011; Cocker et al., 2022; Li et al., 2024; Cole et al., 2001; Schmidt and Grunder, 2011; Snyder et al., 1997; Zhao et al., 2014).

The geochemical and isotopic compositions of magmatic rocks and the compositions and textures of minerals (phenocrysts and groundmass) in porphyritic mafic and intermediate volcanic

rocks record significant magmatic processes and their subsequent post-magmatic modifications (Ubide et al., 2025; Li et al., 2024; Izbakov, P.).

The Central Asian Orogenic Belt (CAOB, also known as the Altaids) spans much of Central Asia and is one of the largest Phanerozoic accretionary orogenic assemblages in the world. The CAOB extends westward to Kazakhstan and eastward to the eastern parts of Russia and northern China (Windley & Xiao, 2018) (Figure 2).



Figure 1. Ekibastuz - Bozshakol study area location in Kazakhstan regional map

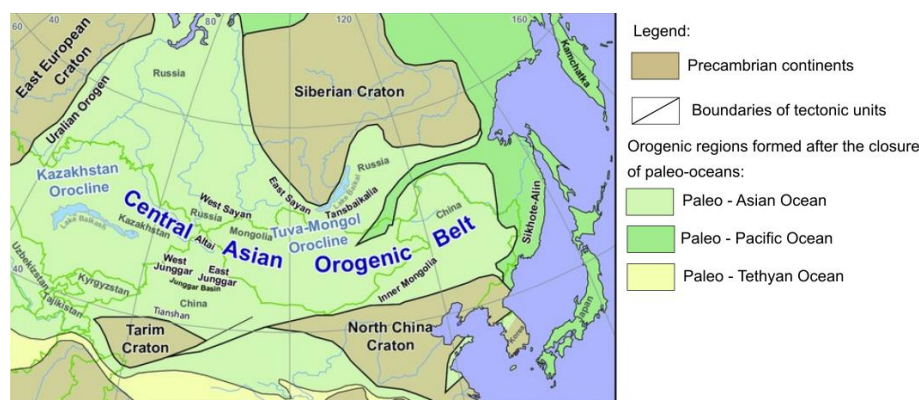


Figure 2. Central Asian Orogenic Belt (CAOB) schematic map (Modified after Windley & Xiao, 2018)

The Ekibastuz-Bozshakol area of central Kazakhstan in the CAOB is one such locality in this larger tectonic system where volcanic rocks of arc tectonics have been preserved in the different stratigraphic record. The volcanic series in this area, such as basaltic, basaltic-andesitic, andesitic, and dacitic-rhyolitic volcanics, are considered vestiges of early subduction-associated

magmatism that evolved along a continental boundary or intra-oceanic arc in the early to middle Paleozoic (Cambrian and Silurian) (Biske, 2015; Safonova et al., 2019, 2017; Shen et al., 2015; Degtyarev et al., 2020a). These processes occurred repeatedly on the CAO, closing oceanic basins and colliding and accreting terrains to create a big continental block. The IA successions, preserved in the belt, provide snapshots of the subduction process. Therefore, it is essential to study them to reconstruct the area's tectonic history (Figure 3).

The volcanic rocks in the Ekibastuz-Bozshakol region of central Kazakhstan are products of Paleozoic subduction-related magmatism in IA settings within the CAO of Kazakhstan (Shen et al., 2015). Their prevailing mafic to intermediate basalts and andesites, even rhyolitic (mafic to intermediate to felsic) compositions, and calc-alkaline affinities are characteristic of convergent plate margins (Shen et al., 2015). The compositional difference between mafic-intermediate rocks and felsic ones implies magma differentiation in an unstable arc system. In general, the Ekibastuz volcanic successions are fragments of the Paleozoic Island arc that formed as the Paleo-Asian Ocean closed (Safonova, 2011; Degtyarev et al., 2020; Liu et al., 2021; Han et al., 2018; Sun et al., 2022)

This research work explores mafic, intermediate, and felsic volcanic rocks in Central Kazakhstan, specifically in the Ekibastuz region, encompassing the Bozshakol and Ekibastuz local administrative areas of the current Pavlodar Region, Central East Kazakhstan, called "Ekibastuz." The rocks are mainly dominated by basalt, basaltic andesites, volcanoclastic and felsic volcanic deposits and are related to subduction magmatism during the Early to Middle Paleozoic (550–380 Ma). This section represents an important Paleozoic belt of the CAO, exposed in the area. Some of the world-class copper-gold-bearing ore deposits, e.g., “Bozshakol” (51°50'49" N 74°17'28" E (Figure 1)), are operated by KazMinerals, which is related to the subduction-related rocks of CAO. These volcanic and related rocks are normally organized in stratified layers. Volcanic formations, interlaced with pyroclastic materials, show periodic volcanic eruptions in an active tectonic setting. Despite their enormous economic importance, the petrogenesis and chronology of the Ekibastuz-Bozshakol volcanic formations have not been well established. The majority of interpretations are based on regional geological mapping and stratigraphic comparisons (Kacielson et al., 1972; Opravkhat et al., 1968; Revutskaya, 2003; Stebenev, 2004). Thus, detailed

petrographic, mineral-chemical, and whole-rock geochemical (major and trace elements) investigations have been carried out to determine the changing composition and tectonic implications of magmatic rocks.

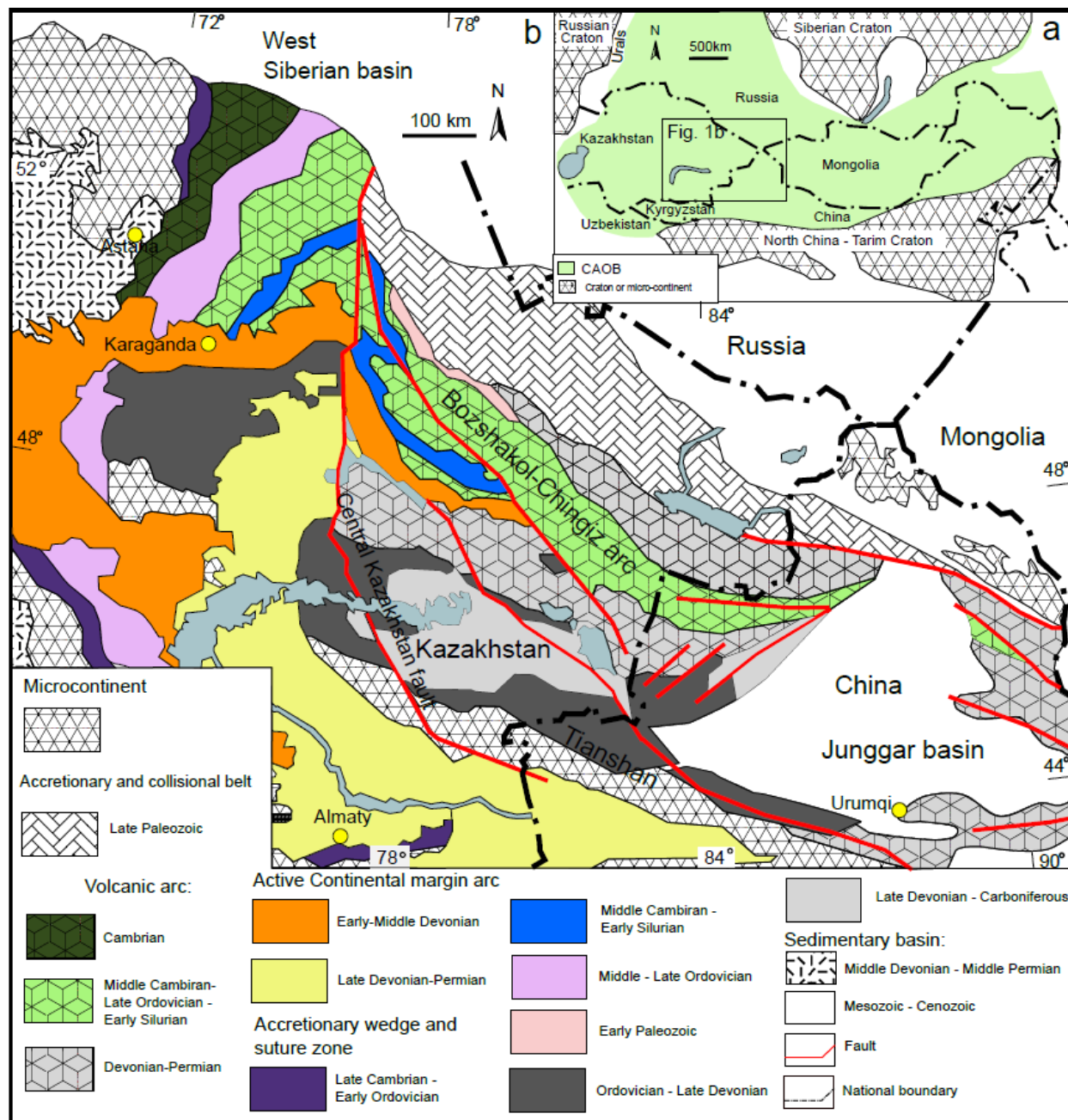


Figure 3. a) Central Kazakhstan in CAOB. b) Simplified geotectonic map of Kazakhstan and contiguous China (Modified after Shen et al., 2015)

1.1 Background/Problem Definition

Geological exploration in North Kazakhstan, including the Ekibastuz area, was initiated in the 1960s during the Kazakh Soviet Socialist Republic (Kazakh ASSR) within the USSR. Although previous geological mapping and exploration works already identified several volcanic formations in the Ekibastuz area, there is a lack of studies on the detailed petrographical and geochemical characteristics of the rocks. Previous works in the Ekibastuz region do not clearly specify how rocks were derived from magma sources. Moreover, the available data is outdated, largely descriptive, and provides a limited understanding of evolutionary processes and tectonic settings. Therefore, comprehensive petrographic and mineralogical studies, including mineral chemistry and geochemical studies, are paramount for establishing the magmatic evolution model of the study area. This research focuses mainly on the methodological gap, i.e., we use more modern (with certain limitations) geochemical tools to characterize minerals and rocks.

1.2 Objectives of the Thesis

1.2.1 Main Objectives

The main objective of this MSc thesis is to study the mineralogy, petrography, and geochemistry of various volcanic rocks exposed in the area. Though still secondary, the other objective is to correct the geological boundaries of formations in the existing geological map.

1.2.2 Specific Objectives

This research aims to study how magma type, nature, and composition change over time and space.

1.3 Scope of Work

The focus of this thesis is on petrographic, mineral-chemical, and whole-rock geochemical studies of selected volcanic rocks in the Ekibastuz-Bozshakol region, central Kazakhstan. The main goal of the research is to establish the petrogenesis of these volcanic rocks and assess their tectonic position within Paleozoic island-arc magmatism in the CAO. This study encompasses a detailed petrographic analysis of selected volcanic rocks to identify them. The mineralogy,

textures, and alteration patterns are described. Based on petrographic observations, crystallization sequences of different minerals and the tentative magmatic evolution are established. The selected rocks are subjected to mineral-chemical analyses by scanning electron microscopy with energy-dispersive spectroscopy (SEM-EDS) conducted on polished thin sections. Backscattered electron imaging is used to identify mineral phases and to observe the zoning patterns, reaction rims, and textural relationships. Major silicate phases were acquired as semi-quantitative mineral compositions to estimate crystallization variability and assess compositional variability among and within samples. A whole-rock major and selected trace element geochemical investigation was established using X-ray fluorescence (XRF). Based on these data, the volcanic rocks were classified, magmatic affinities were established, trends in fractional crystallization were determined, and tectonic settings were interpreted by utilizing existing geochemical discrimination diagrams and elemental ratios.

In general, the scope of work is limited to geochemical and petrographic characterization of volcanic rocks and interpreting the findings in the context of the CAO. However, it is not a comprehensive study of the region, but rather a sampling of selected representative volcanic units only. Therefore, this study has certain limitations, such as radiometric age determination (e.g., U-Pb zircon dating) and isotopic analysis (e.g., Sr-Nd-Pb isotopes), and finer structural and tectonophysical studies have not been performed. Although the findings can contribute to a more profound understanding of Paleozoic arc magmatism in central Kazakhstan, they can also serve as the basis for further research that incorporates geochronological and isotopic constraints.

2.0 Literature review

The literature review stage of this study will delve into all aspects of the investigations conducted in the Ekibastuz region. The occurrences of similar rocks in arc settings, the regional geology of the area, and their geological characteristics, as well as the precise revision of the Ekibastuz region, are carried out.

2.1 Subduction-related magmatism, examples, and their study

Volcanic rocks are one of the most fundamental aspects of understanding the crustal growth and geodynamic evolution in subduction-related settings at convergent plate boundaries, i.e., in

arc settings or orogenesis. The fluid, released by the dehydration of hydrous minerals such as phlogopite and amphiboles and pore water of the subducting slab, causes the initiation of partial melting of the mantle wedge and thus generates magmas with their own unique geochemical properties (Yan and Shi, 2011) (Figure 5). The subduction-related (arc) volcanic sequences usually range from basaltic to andesitic to rhyolitic composition in modern and ancient arc systems (Gill, 1981; Miyashiro, 1974; Chen et al., 2022; Kelemen et al., 2003). The modern continent arc (ACM), such as the Cascades, Andes, and Eastern Aleutians; and the island arc (IA) settings, e.g., the Japan arc, Marianas, Tonga-Kermadec, Scotia, and Western Aleutians (Figure 4), provide a key for modern and ancient orogenic belts.

In general, the compositional spectrum of IA volcanic rocks ranges between basalt and basaltic andesite to andesite, while dacite and rhyolite are less common than in the ACM (Yan and Shi, 2011; Yamada et al., 2023). This indicates the comparatively narrow oceanic crust that restricts magma differentiation and crustal assimilation (Yan and Shi, 2011). Geochemically, the IA volcanic rocks are usually enriched in large-ion lithophile elements (LILE) and depleted in high-field-strength elements (HFSE), specifically in Nb and Ta, depending on slab-derived fluids (Miyashiro, 1974; Gill, 1981; Kelemen et al., 2003) (Figure 7). These chemical features characterize arc magmas in relation to intraplate magmatism and serve as diagnostic tools of subduction-related events (Kelemen et al., 2003).

Although there are several IAs, e.g., Tonga-Kermadec, Japan, and Kuril, the Philippines IA system, including the Kyushu-Palau Ridge (KPR), is one of the prime examples, representing a classic intra-oceanic IA. According to Yan and Shi (2011), KPR was formed as a part of the Philippine Sea Plate, where volcanic rocks are predominantly represented by basalts, basaltic andesites, and andesites. These magmas have rather a primitive character due to their extraction from a metasomatized mantle wedge, which had little contribution of continental crust. There are cases where the IA system transitions to the back-arc setting, e.g., the Japan arc system formed by the Pacific plate subduction beneath the modern Eurasian plate (Yan and Shi, 2011; Yamada et al., 2023). Yamada et al. (2023) investigated the southwest Japan arc, providing evidence of the back-arc spreading in the Toyama basin, where the transition from rhyolitic to andesitic and back to rhyolitic magmatism occurred during the Oligocene-Miocene periods (Figure 6) (Yamada et al., 2023; Yan and Shi, 2011).

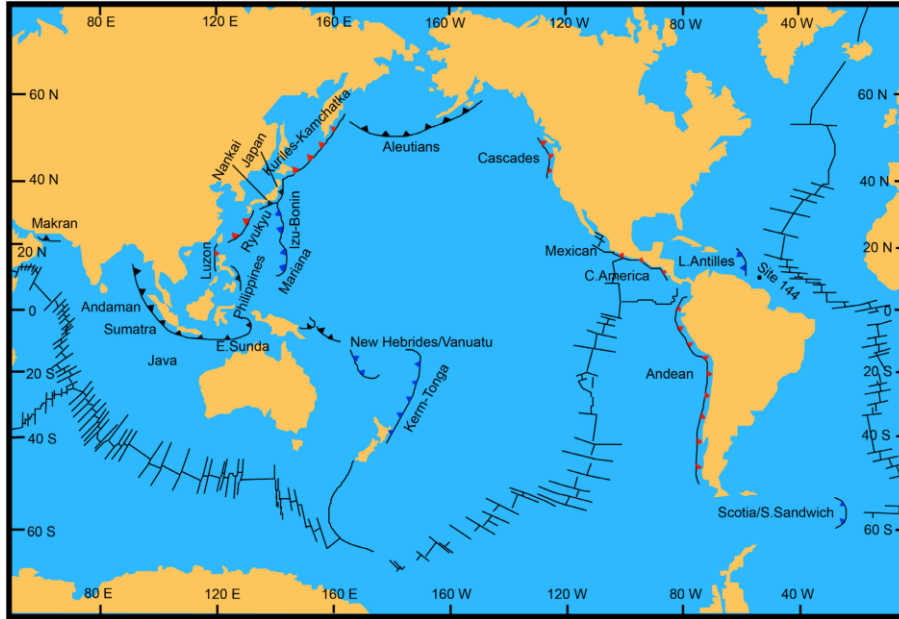


Figure 4. Principal oceanic subduction zones associated with orogenic volcanism and plutonism. Trenches with Red and blue triangles denote the continental arc and oceanic arc and trenches with black triangles denote the arcs (Chen et al., 2022).

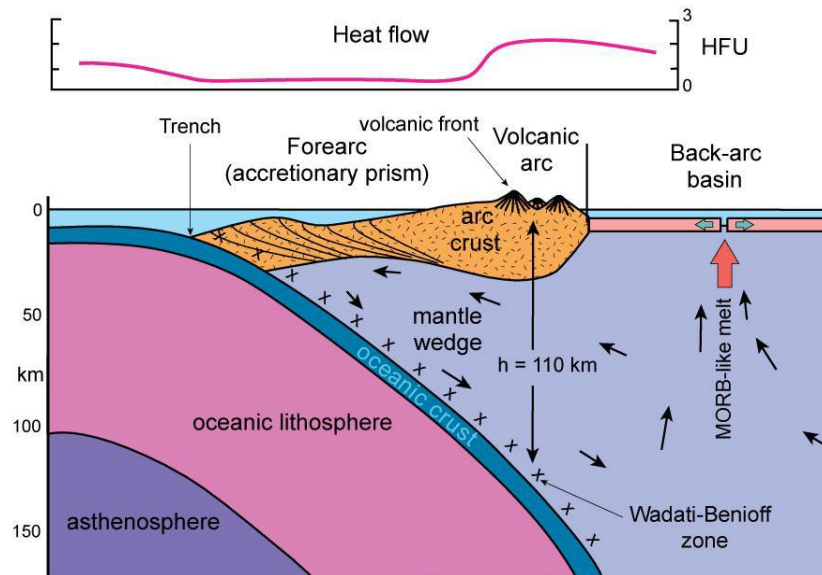


Figure 5. Schematic cross-section of a typical island arc (Winter, 2014)

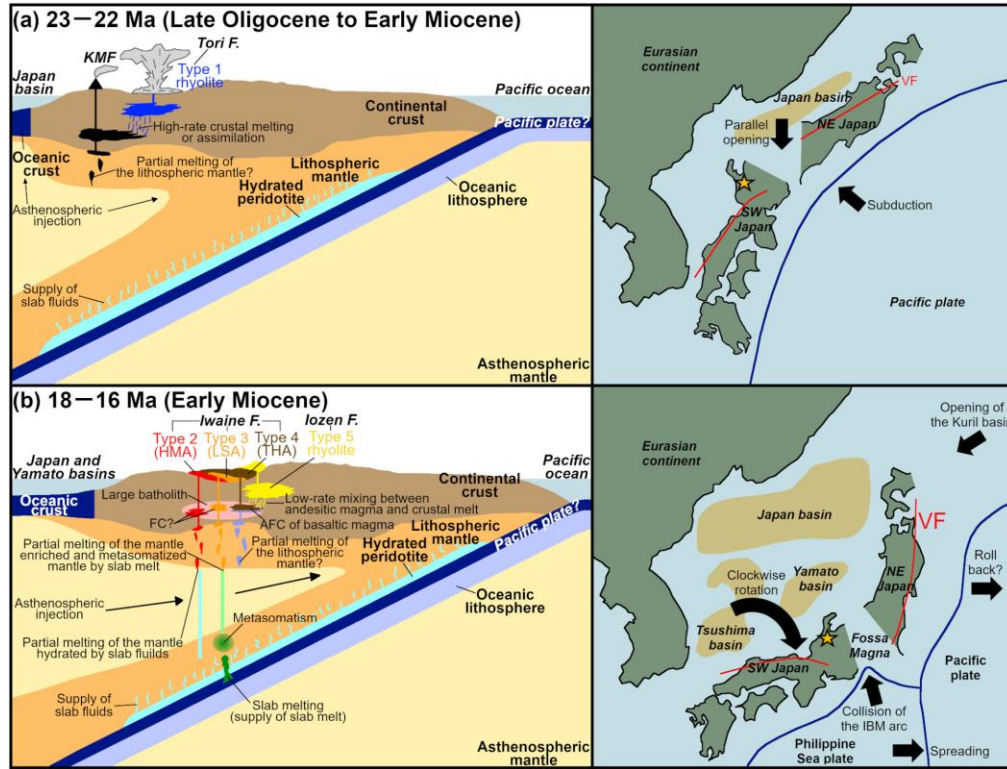


Figure 6. Schematic illustration of temporal change of arc volcanism in the Toyama basin during the Japan Sea opening in (a) 23–22 Ma (Late Oligocene to Early Miocene) and (b) 18–16 Ma (Early Miocene). Stars indicate the location of the study area, the Nanto area. AFC, assimilation and fractional crystallization; FC, fractional crystallization; HMA, high magnesian andesite; KMF, Kamiwazumi and Matsunagi Formations; LSA, low-SiO₂ adakite; THA, tholeiitic andesite; VF, volcanic front (Yamada et al., 2023)

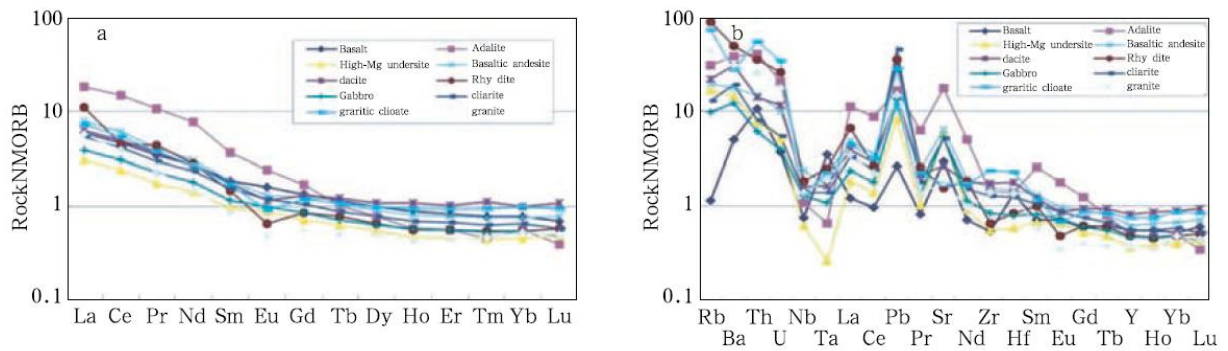


Figure 7. NMORB-normalized trace element spider diagram (a) and NMORB-normalized REE distributional pattern diagram (b) of Paleogene igneous rocks in the SW Japan arc [data from Imaoka et al. (2011)]. NMORB data are from Sun and McDonough (1989); similarly, hereinafter (Yan and Shi, 2011)

2.2 Regional geological setting of the study area

The Ekibastuz region (Central Kazakhstan) is a part of the CAOBS, also known as the “Altaids” (Sengor et al., 1993; Sengor & Natal’in, 1996), that is one of the largest Phanerozoic accretionary orogenic systems on Earth. The CAOBS extends from the North China Craton in a north-south direction and between the Siberian Craton and the Tarim Craton in a southern-northern direction (Windley and Xiao, 2018; Han and Zhao, 2017) (Figures 2 and 8). The CAOBS is formed during the Neoproterozoic and Paleozoic eras through prolonged interaction between oceanic and continental lithospheres (Windley, 2007; Windley and Xiao, 2018; Han and Zhao, 2017; Jahn et al., 2004; Xiao and Santosh, 2014; Safonova et al., 2017). The Altaids are formed during the closure of the Paleo-Asian Ocean (PAO) (Figure 9), having characteristic island arcs, accretionary complexes, fragments of continental crusts, and other subduction-related processes (Safonova, 2011; Degtyarev et al., 2020; Liu et al., 2021; Han et al., 2018; Sun et al., 2022).

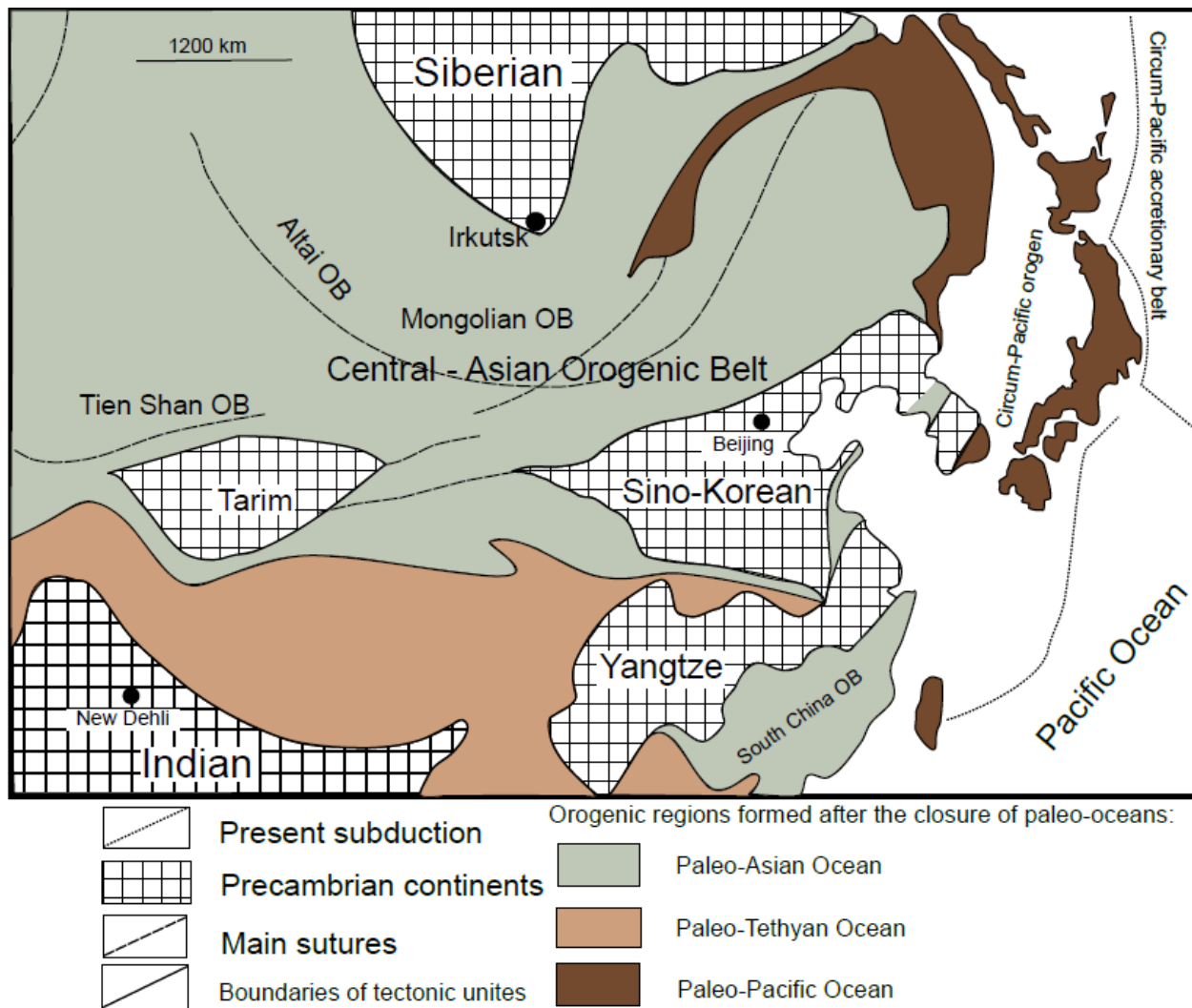


Figure 8. Simplified tectonic scheme of Central and East Asia showing the main orogens formed after the closure of paleo-oceans and the approximate location of local orogenic belts - OB (modified after Safonova et al., 2011).

The Kazakhstani continent plays a pivotal role in the COAB as a principal tectonic unit by the accretion of several Paleozoic IAs and related magmatic complexes (Degtyarev et al., 2020) and can be described as a collage of assembled volcanic arcs and accretionary systems during the Paleozoic era (541–252 Ma). The given arcs are associated with the subduction of oceanic lithosphere beneath the continental margins (Figure 9).

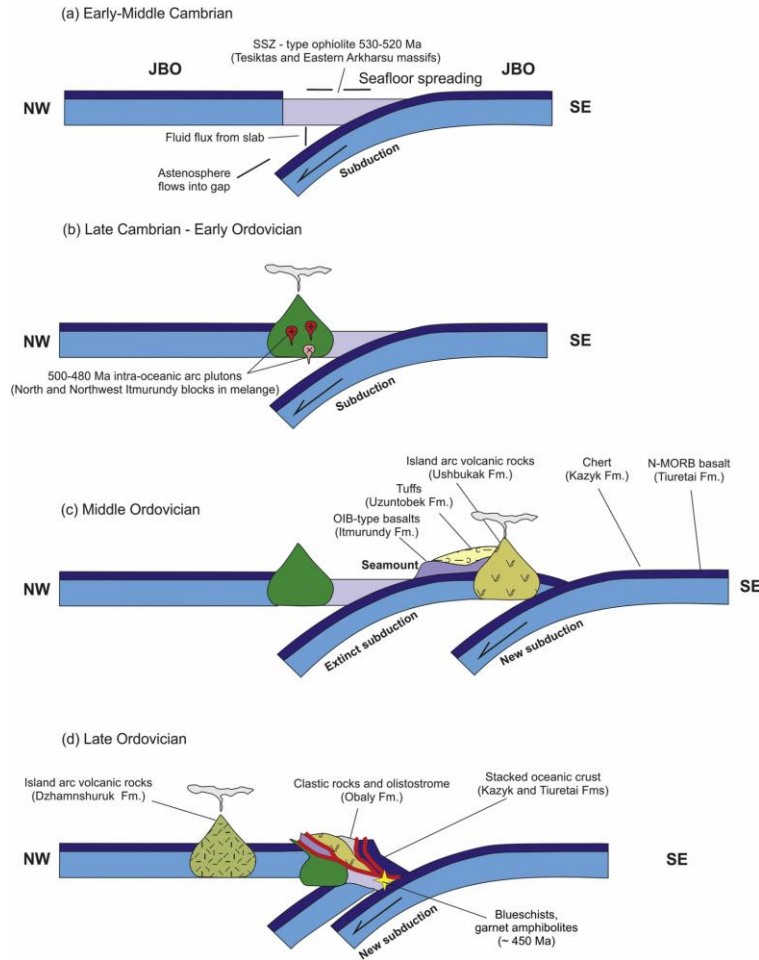


Figure 9. A model of the subduction-accretionary evolution in the North-Balkhash Zone during the early Paleozoic.

a) initiation of subduction with formation of SSZ ophiolites at 530 Ma (Tesiktas and Eastern Arkharsu); b) Late Cambrian arc magmatism (North Itmurundy); c) arrival of the seamount (Itmurundy Fm. formed just before its docking) to the subduction zone with initiation immediately afterwards of the new subduction and new magmatic arc (Ushbulak Fm.); d) continuing new subduction and arcward stacking of diverse assemblages (Itmurundy OIB, Obaly clastics, Ushbulak IA, Kazyk cherts, and Tiuretai N-MORB basalt) within the North-Balkhash accretionary wedge. JBO – Junggar-Balkhash Ocean (Degtyarev et al., 2020a)

2.2.1 The formation of the Central Asian Orogenic Belt (CAOB)

The closure of the PAO is directly linked and responsible for the formation of the CAOB (Safonova et al., 2017; Song et al., 2024; Safonova, 2011; Degtyarev et al., 2020; Liu et al., 2021; Han et al., 2018; Sun et al., 2022). The PAO existed in the geological time range from the Neoproterozoic to the Paleozoic period, representing an oceanic segment that separated several

continental blocks, including the CAO (Buslov et al., 2001; Safonova et al., 2017; Song et al., 2022; Liu et al., 2021; Windley et al., 2007; Song et al., 2024; Wan et al., 2018; Xiao et al., 2020). The merger of CAO and the ultimate closure of the PAO remain controversial, as their geochronology and mechanisms are still being examined. More recent studies indicate that geochronology of CAO formation differs and that subduction and accretion processes also occurred during the Permian-Triassic periods (Wan et al., 2018; Xiao et al., 2020).

The formation of the PAO is also debatable, since some scientists believe that it originated from the breakup of the Rodinia supercontinent during the late Neoproterozoic (Buslov et al., 2001; Xiao et al., 2020), and there is also the idea that it formed as a consequence of the Nuna supercontinent breakup (Wan et al., 2018). The initial stage of the ocean formation was at 1.35 Ga as a result of the rifting and separation of the Siberian and North Chinese cratons. The paleomagnetic and zircon age data show that the Siberia and North China cratons share similar zircon age peaks, which can have similar crustal evolution or tectonic connections (Wan et al., 2018). The other suggestion on how the PAO was opened is that the ocean was created in the late Neoproterozoic by the rifting of the Baltica-Siberia supercontinent (Sengor et al., 1993, 2014). The Rodinia supercontinent disassembly is disputable since, after paleomagnetic reconstruction of Rodinia by Li et al. (2008) and the reconstruction of the global full plate model during the Neoproterozoic (Merdith et al., 2017), it is revealed that the Siberian craton was not attached to other cratons during Rodinia assembly (Wan et al., 2018).

The final stages of PAO closure remained debatable, since the time ranges and mechanisms of closure have different hypotheses. Recent studies by Song et al. (2024) show that geological evidence of the Permian-Early Triassic (260-230 Ma) periods of PAO closure is supported by the presence of ophiolitic mélanges and accretionary complexes in the south CAO. These mélanges contain Permian gabbro, basalt, and radiolarian chert, suggesting that the subduction and oceanic spreading continued until the late Paleozoic-Early Mesozoic eras. The mechanism of the PAO closure can be partially explained by the reconstruction of Pangea (Figure 10). The other reconstruction of PAO closure reveals the mechanism, which is related to the early Cambrian to early Permian (540 - 290 Ma) time range rather than the Permian - early Triassic. The geodynamical schematic representation (Figure 11) is suggested by geochemical and isotope data

(Safonova et al., 2017; Jahn et al., 2000; Windley et al., 2007; Xiao and Santosh, 2014; Liu et al., 2017).

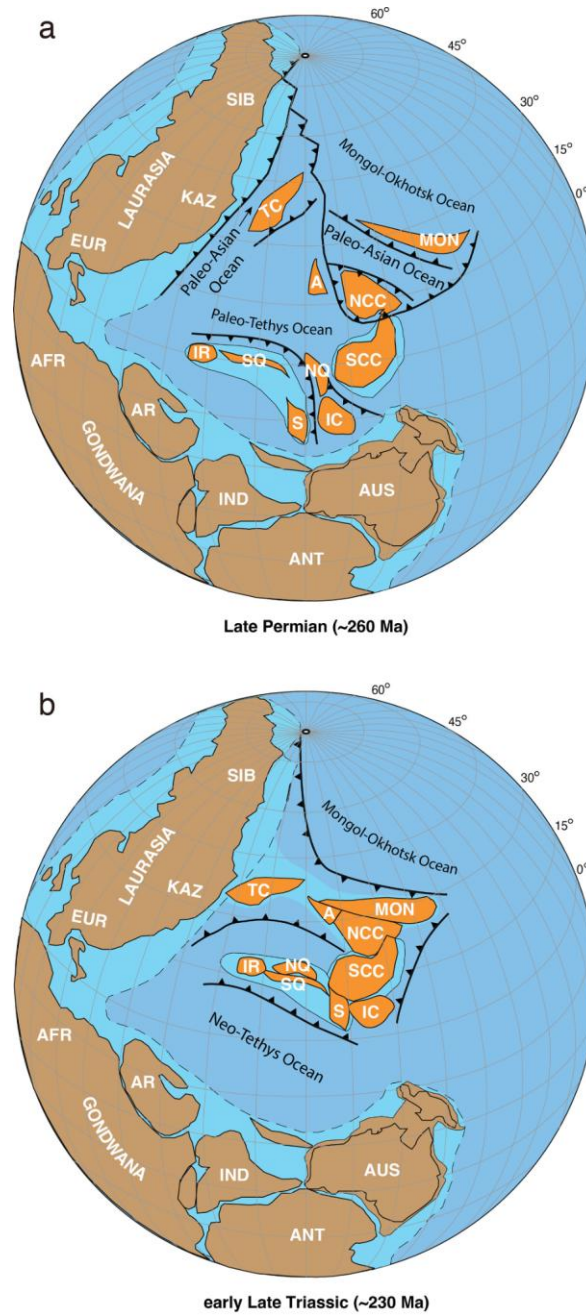


Figure 10. Schematic paleogeographic reconstruction of Pangea showing the final closure of the PAO and assembly of East Asian blocks (Song et al., 2024). (a) The East Asian blocks were separated from Pangea during the Permian. (b) The East Asian blocks joined Pangea after the closure of the Paleo-Asian Ocean and the east Paleo-Tethys Ocean in the middle to late Triassic. A = Alxa; ANT = Antarctic; AUS = Australia; AR = Arabia; AFR = Africa; EUR =

Europe; IC = Indochina; IND = India; IR = Iran; KAZ = Kazakhstan; MON = Mongolia; NCC = North China Craton; NQ = North Qiangtang; SQ = South Qiangtang; S = Sibumasu; SCC = South China Craton; SIB = Siberia; TC = Tarim Craton.

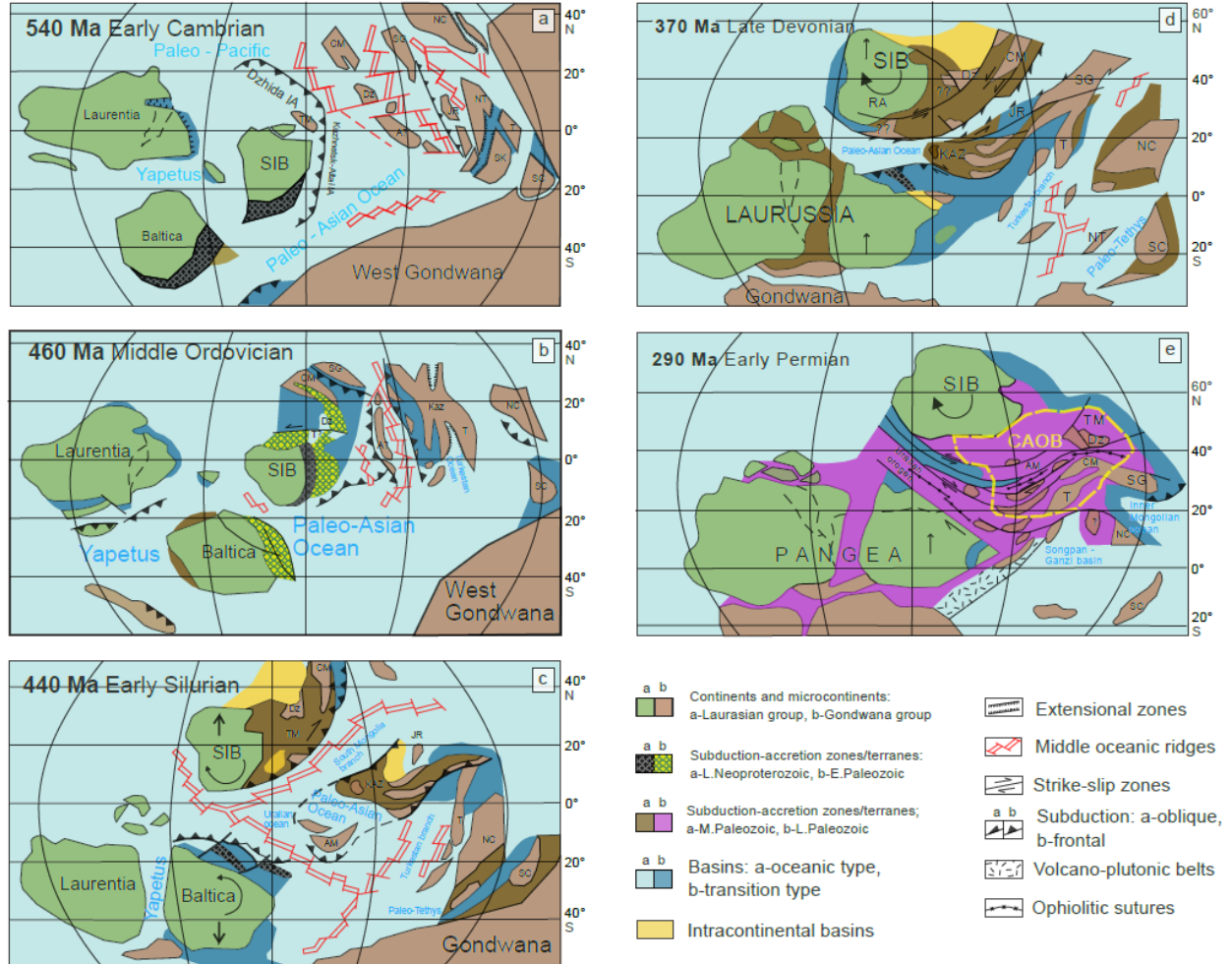


Figure 11. Geodynamic reconstruction of the Paleo-Asian Ocean based on geological, paleomagnetic, and petrologic data (Modified after Safonova et al., 2017). Abbreviations for continental blocks: CM, Central Mongolian; Dz, Dzabkhan (Baydrag); JR, Junggar; Kaz, Kazakhstan; NC, North China; NT, North Tianshan; SC, South China; SG, South Gobi; SIB, Siberian Craton; T, Tarim; TM, Tuva-Mongolian. Subduction-accretion zones: AM, Altai-Mongolian; GA, Gorny Altai; RA, Rudny Altai; IA, island arc.

2.3 Geology of the Ekibastuz-Bozshakol Area

Ekibastuz-Bozshakol study area is interpreted as a part of accretionary orogenic system within the COAB. The given interpretation is supported by the presence of volcanic and

volcaniclastic sequences of Cambrian – Devonian age, arc-related intrusive rocks, which range from gabbro to granodiorite, along with geochemical evidence of LILE enrichment and HFSE depletion (Figure 12). At the scale of the study area, a proximal continental margin has no clear evidence, and the lithological and geochemical properties are most compatible with an intra-oceanic arc environment. Subduction is thus construed in broad strokes with oceanic lithosphere of the Paleo-Asian Ocean subducting beneath an overriding oceanic plate. The polarity and direction of subduction, however, are not directly constrained by the available geological and geochemical data, and are therefore only presented schematically, not in a uniquely defined kinematic model. (Safonova et al., 2017, 2019; Shen et al., 2015).

Geochemical and geological studies of the Bozshakol-Ekibastuz region revealed mafic-intermediate volcanic rocks, such as basalts, basaltic andesites, and andesites, which are typical of this IA setting (Safonova et al., 2011, 2016; Shen et al., 2015). These rocks display calc-alkaline affinities and geochemical signatures that are common for subduction-related magmatism, such as Nb and Ta depletion (HFSE) and enrichment in large-ion lithophile elements (LILE) (Safonova et al., 2011, 2016; Shen et al., 2015) (Figure 12).

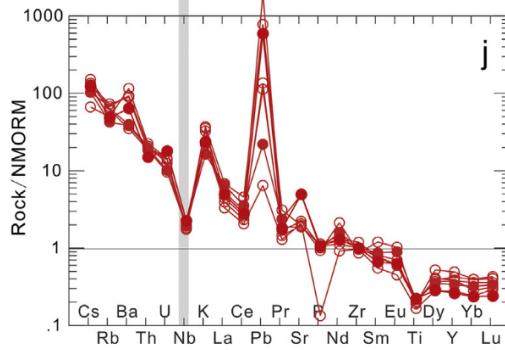
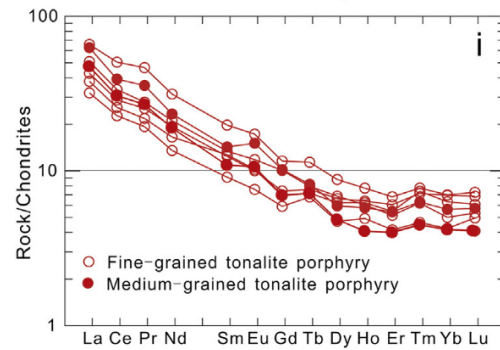
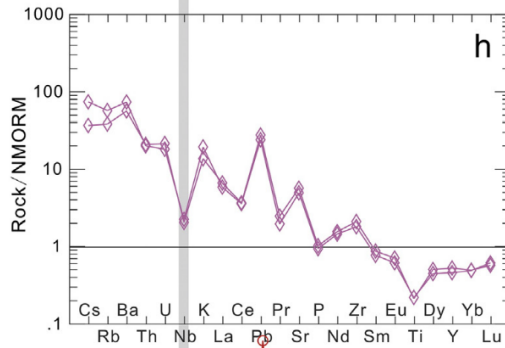
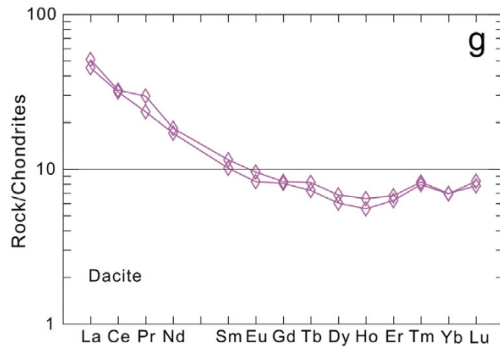
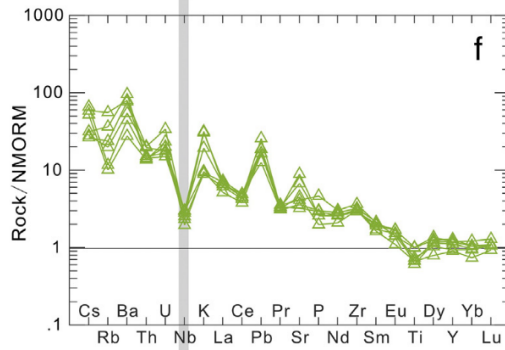
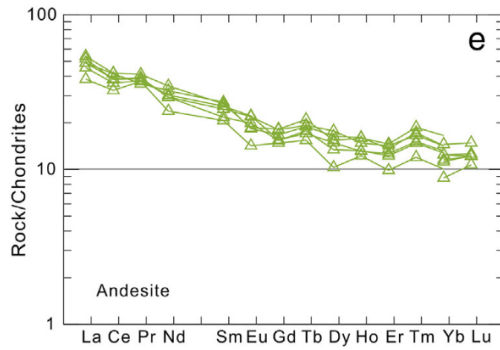
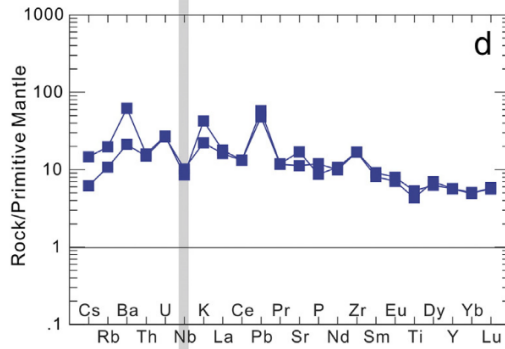
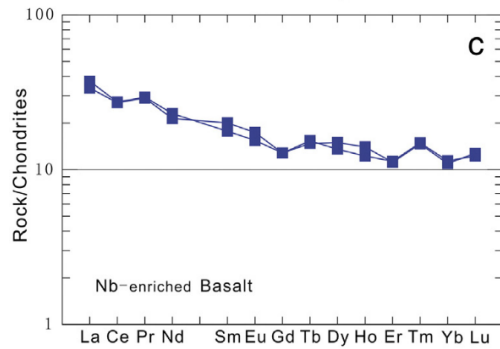
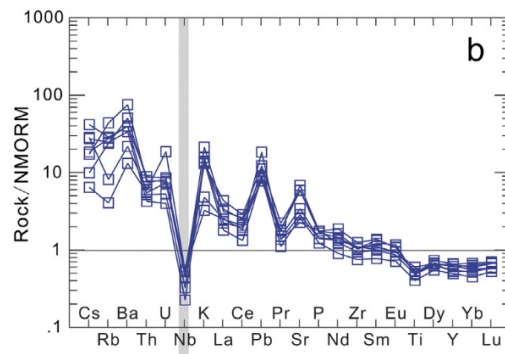
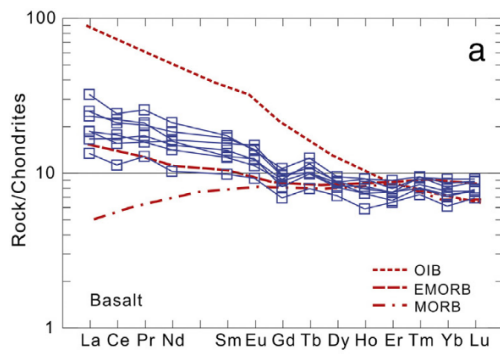


Figure 12. Chondrite normalized (Nakamura, 1974) REE and trace element (Sun and McDonough, 1989) patterns for the igneous rocks in the Bozshakol area (Shen et al., 2015).

2.3.1 Tectonic settings of the study area

There are three major structures: the Maikan-Ekibastuz anticlinorium of Upper Proterozoic, and two Caledonian synclinoria—Bozshakol and Maikan—in the area (Figure 13)

The core of the anticlinorium is composed of rocks of the Upper Proterozoic, which are intruded by Sinian ultrabasic intrusions. A large fault, parallel to its axis, limits the core of the anticlinorium (Kacielson et al., 1971; Revutskaya, 2003; Stebenev, 2004). This anticlinorium separates two synclinoria: Bozshakol and Maikan, which resulted in Caledonian time. The Bozshakol synclinorium is composed of Sarianian, Caledonian, and Hercynian phases. The basal sequence of the Bozshakol synclinorium is composed of Upper Cambrian rocks, which are overlain by sediments of various ages, including those related to the Alpine tectonic event. Maikan synclinorium is composed of the same/similar rocks/structural units as Bozshakol. The Bozshakol and Maikan synclinoria are Caledonian.

There are two major trends in the faults: 1) Northeast-striking faults and 2) Northwest-striking faults.

The oldest faults, the N-E faults, are upper Proterozoic and Sinian and are steeply dipping, associated with the Maikan-Ekibastuz anticlinorium. The faults are steeply dipping normal and reverse faults, with only a few thrust faults (Kacielson et al., 1971; Revutskaya, 2003; Stebenev, 2004). Most of the ultrabasic intrusions are associated with these events. The northwest-striking faults are younger and are of Hercynian age. The faults are normal and reverse, steeply dipping faults with hundreds of meters of displacement. Several grabens are associated with these faults, which are filled with Carboniferous sediments (Figure 13).

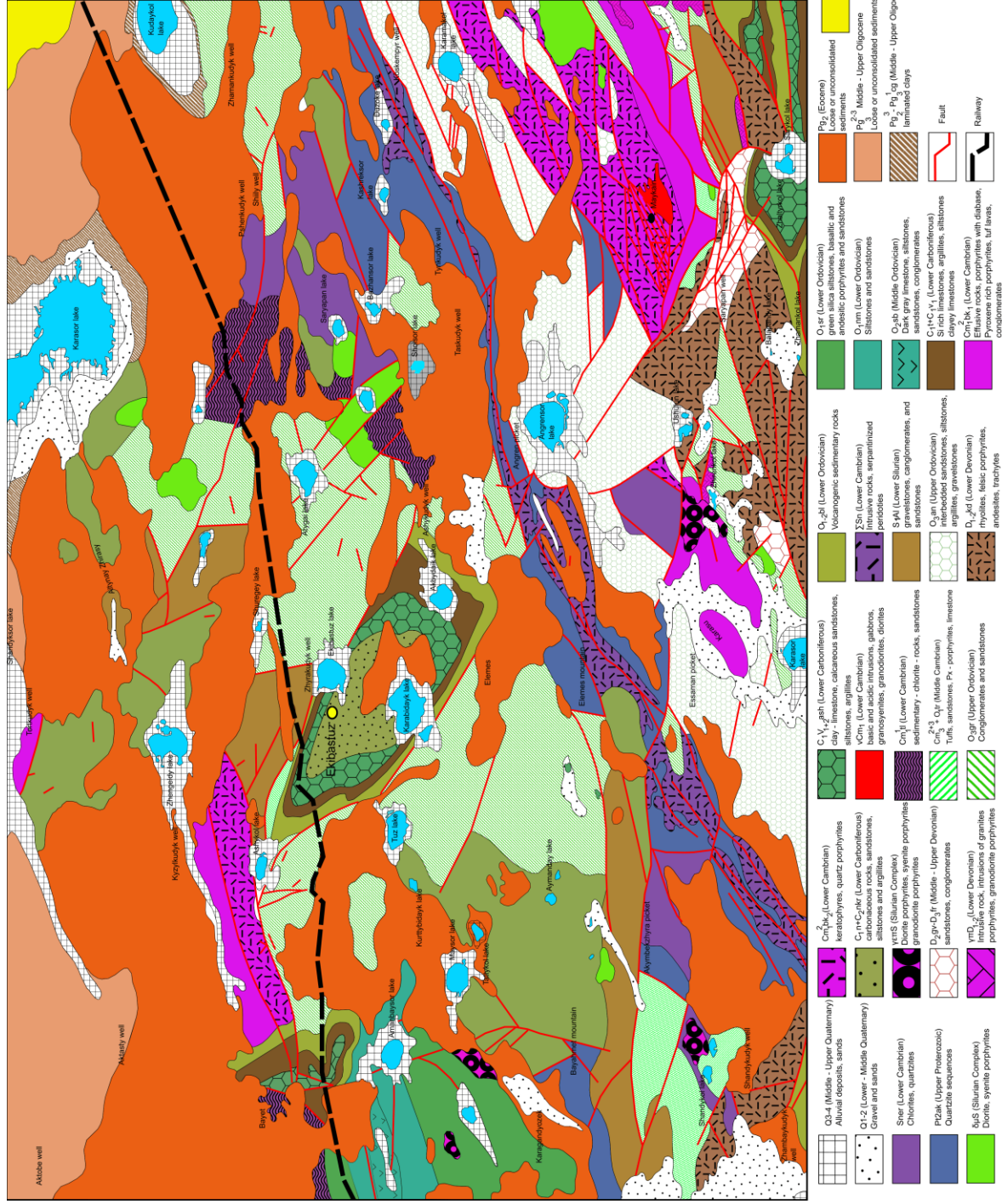


Figure 13. Geological Map of the Ekibastuz Area (Sheet “M-43-III”), Scale 1:200000 (Modified after Vydrin et al., 1969).

Thus, pre-Paleozoic, Caledonian, and Hercynian tectonic events, particularly the Sinian, Salarian, and Caledonian, shape the area's history.

2.3.2 Major plutonic and volcanic rocks in the area

The oldest magmatic rocks are found in the Erementau series (Sn_{er}) and are intermediate and basic extrusive rocks, prolonged in the central part of the Ekibastuz's geological map (Figure 13). The ultrabasic intrusions associated with the Maikan Ekibastuz anticlinorium were formed at the end of the Sinian. At the start of the Lower Cambrian during the Salarian time, the Sinian anticlinorium uplifted (Kacielson et al., 1971; Revutskaya, 2003; Stebenev, 2004). Intense erosion allowed sedimentation, together with some effusive and chemogenic deposits of the Lower Cambrian. In the Lower Cambrian, during the Salarian tectonic event, the Bozshakol spilite-keratophyr was formed. The magmatic rocks of the Bozshakol events are diabase porphyry, porphyrites rich in pyroxenes, porphyritic dacites, trachytic porphyry, and amygdaloidal lavas (Kacielson et al., 1971; Revutskaya, 2003; Stebenev, 2004). These effusive rocks are accompanied by tuff lava, tuff breccia, lithoclastic tuff, and conglomerate tuff. At the end of the Lower Cambrian, the N-E striking folds were formed in the Sinian anticlinorium. This event ended with the formation of gabbroic magma (Maikan Massif). During the start of the Caledonian tectonic event, intermediate and basic volcanism (basaltic and andesitic porphyry) occurred in the Early Ordovician. Late Ordovician volcanism yields rocks of tuffaceous agglomerates, intermediate and mafic porphyritic rocks, and tuffs (Svishev et al., 1967; Stebenev et al., 2004; Revutskaya, 2003).

Among the Silurian volcanics, andesite–basalt, including pyroxene and diabase porphyrites, amygdaloidal porphyrites, hornblende porphyrites, trachytes, and albite-bearing tuff lavas, are common (Kacielson et al., 1971; Revutskaya, 2003). Lithoclastic and crystal–clastic tuffs, tuffaceous sandstones, and conglomerates are also associated with these Silurian effusives.

In the lower and middle Devonian times, the area was in a continental regime, and there was an eruption of mainly acidic volcanic rocks, i.e., rhyolites, quartz-feldspar porphyrites,

trachytes, felsite porphyrites, liparites, andesites, and porphyrites with the formation of some subvolcanic, medium-grained sandstones and tuffogenic conglomerates (Kacielson et al., 1971; Revutskaya, 2003; Stebenev et al., 2004; Svished et al., 1967).

3.0 Methodology

In the section provided for the project, we will describe all aspects of sample preparation and the subsequent use of petrographic, SEM-EDS, and geochemical analyses in detail, including whole-rock preparation, analytical equipment settings, and software adjustments.

3.1 Rock samples

Different magmatic rocks (volcanics) of the area were selected for petrography, mineral chemistry, and whole rock geochemistry. The location of the samples with respect to the published geological map is illustrated (Figure 14), where the prefix “S” corresponds to the "EK," i.e., S5 is the station where sample EK005/25 was collected. A summary of the different studies for any particular sample is provided in Table 1.

Table 1. The summary of studies for all samples

Sample name	Petrography	SEM-EDS	XRF (Block 6)	XRF (C4)	Age	Rock type
EK009/25	+	-	+	-	O1-2bl	Granodiorite
EK016/25	+	-	+	+	O1-Sr	Basalt porphyry
EK017/25	+	+	+	+	O1-Sr	Basalt porphyry
EK019/25	+	-	+	+	O1-2bl	Basaltic andesite
EK044/25	+	-	+	+	O1-2bl	Porphyritic Andesite
EK045a/25	+	+	+	+	O ₃ An	Andesite
EK048/25	+	-	+	+	Cambrian	Keratophyre
EK049/25	+	-	+	+	Cambrian	Basaltic andesite
EK050/25	+	-	+	-	Cambrian	Andesite

EK055/25	+	+	+	+	Gamma S	Granodiorite
EK059/25	+	-	+	-	Cambrian	Keratophyre
EK065/25	+	-	+	-		Andesite clast from volcanoclastic rock
EK068/25	+	-	+	+	D1-2	Rhyolite
EK071/25	+	+	+	+	D1-2	Vesicular andesite
EK076/25	+	-	+	-	D1-2	Basaltic andesite
EK083/25	+	-	+	-	D1-2	Basaltic andesite
EK086/25	+	-	+	+	Pt2ak	Aphanitic to porphyritic basalt
EK095/25	+	+	-	-	S1A1	Strongly porphyritic andesite
EK096/25	+	-	+	-	O3Gr	Basaltic andesite
EK098/25	+	-	+	+	O1-2bl	Dacite to rhyolite
EK100/25	+	+	+	-	O1-2bl	PL phyrlic andesite
EK102/25	+	+	+	-	O1-2bl	PL phyrlic andesite
EK140/25	-	-	+	-	O3Gr	Andesite
EL24001K3	-	-	+	-		Diorite
EK005/25	+	-	-	+	Pt2ak	
EK137/25	+	-	-	-	Cambrian Bozshakol 2	Matrix of volcanoclastic rock
EK165/25	+	-	-	+	O3 An	Matrix of Breccia

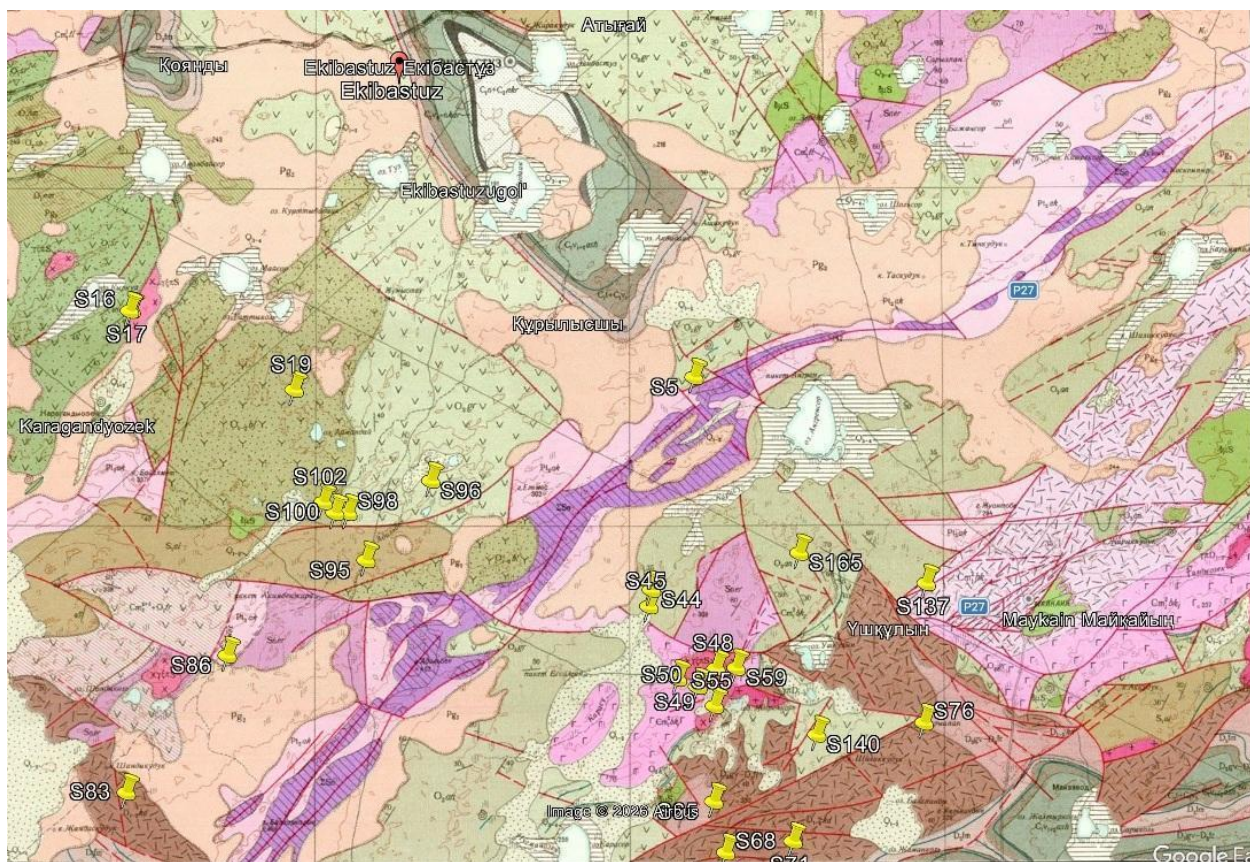


Figure 14. Geological map of the study area showing location of the collected samples

3.2 Justification of the selected methods

The section below briefly explains why these methods—petrography, SEM-EDS, and XRF—were selected for this study. Transmitted light petrography is a standard yet reliable technique for identifying minerals, their textures, and rocks, which helps in choosing rocks for further mineral-chemical and geochemical analyses. SEM-EDS offers data that must be used to reveal mineral chemistry of the rocks. This information is interpreted as mineral-scale chemical data and textures to understand crystallization processes and to link mineral chemistry with bulk-rock geochemistry. XRF enables precise identification of the whole-rock major and trace element compositions, which are vital for rock classification, magma series identification, and tectonic interpretation.

3.2.1 Thin Sections Preparation

Whole rock samples were collected and cut into billets using a “Cutting & Slabbing Saw 1.02.04” by the “BROTLAB” company and then further cut with a “Slicing Machine 10215” by the “BROTLAB” company to reduce the thickness to 400 microns. The next step is to polish the shaped rock sample (billet) with a diamond polishing machine, “Bench Polishing Machine 10320,” by the “BROTLAB” company to avoid Fe contamination after cutting. The polishers are diamond-made, and the polishing and decontamination process is based on a physical abrasive cut. After the rock is cut and diamond-polished, the right-shaped rocks should be glued with glass. The gluing procedure operates using “HQ glue 2-component epoxy” by “BROTLAB” and is placed into an oven; the adhesion procedure stands up to 12-13 hours and 60°C. After the gluing process, rocks should be ground until a 40–50-micron thickness and polished using “Automatic Polishing 10317” by the “BROTLAB” company with “GEL DIAMANTE GDSP 0600 and GDSP 0300” polishing gel, 6 μ and 3 μ grain size. The listed techniques are required to prepare thin sections fully.

All thin sections were carbon-coated before subjecting them to SEM-EDS analyses. C-coating is needed to apply non-conductive samples to avoid electrical charging, improve the signal quality, and to reduce analytical errors during SEM-EDS analysis. All samples were coated using the “Carbon Turbo Coater” by “Acar Scientific” (Figure 15b). The main parameters during sputtering were a voltage of 5V and a time of 10 seconds.

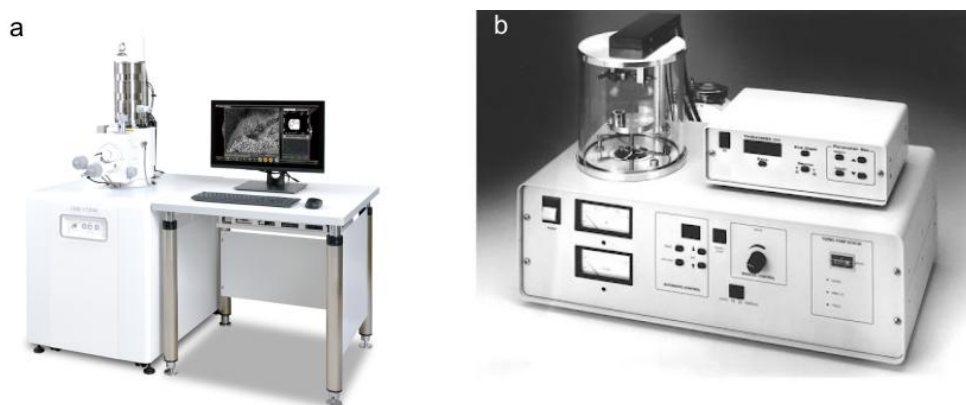


Figure 15. a) SEM-EDS “JEOL JSM-IT200”; b) Sputter “Carbon Turbo Coater” by “Acar Scientific.”

3.2.2 SEM-EDS and Petrography analysis

Minerals were subjected to qualitative mineral chemical analyses using energy-dispersive scanning electron microscopy with energy-dispersive spectroscopy (SEM-EDS) using “JSM-IT200” by the “JEOL” company (Figure 15a). The used 20kV, working distance (WD) of 9 to 11mm, Std.-PC 60, and high-vacuum mode while operating the SEM. The following oxides were acquired during EDS analyses: $SiO_2, TiO_2, Al_2O_3, Cr_2O_3, TiO_2, FeO, MnO, MgO, CaO, Na_2O, K_2O$.

3.2.3 Mineral Chemistry: Cation calculation and XMg

Major – element compositions of pyroxenes and amphiboles were used to calculate cation proportions and Mg-number (XMg). Weight percentage of oxides were converted to molar proportions, by dividing the oxide concentration by its molecular mass. Furtherly, molar amounts used to calculate cation proportions and, normalized to a fixed number of oxygens for pyroxenes (6 oxygens per formula unit) and amphiboles (23 oxygens per formula unit). The XMg was calculated using molar proportions of Mg and total iron according to the following equation 1.

$$XMg = \frac{Mg}{Mg+Fe^{2+}} \quad (1)$$

Where the molar proportions were calculated as:

$$Mg = MgO/40.304 \text{ and } Fe = FeO/71.844$$

Calculated XMg values for pyroxene ranges from 0.57 to 0.86 (Table B5), which indicates predominantly Mg-rich compositions. Whereas amphibole XMg values (Table C3) range from 0.62 to 0.73, which indicates moderate Mg-Fe compositions.

3.3 Geochemistry (XRF)

Major elements were analyzed using X-ray fluorescence (XRF) at two sessions: a) at the SMG lab and b) at the core facility of NU. XRF from the SMG lab represents the pressed powder pellet analysis, whereas the core facility XRF uses the fused glass bead technique. Both methods require different sample preparation stages and provide different geochemical results.

3.3.1 XRF Sample Preparation

The geochemical sample preparation involved the following procedures. The rocks were cut, and all weathered materials were removed before crushing them. Rocks were crushed using a tungsten carbide mortar and pestle (Figure 16a). During crushing, special attention was given to chemical and physical cleaning protocols to avoid contamination. Before and after use of the mortar and pestle, quartz sand is crushed to decontaminate equipment physically until a fine grain size is achieved by mechanical abrasion. Then the mortar and pestle were cleaned with water, followed by ethanol.

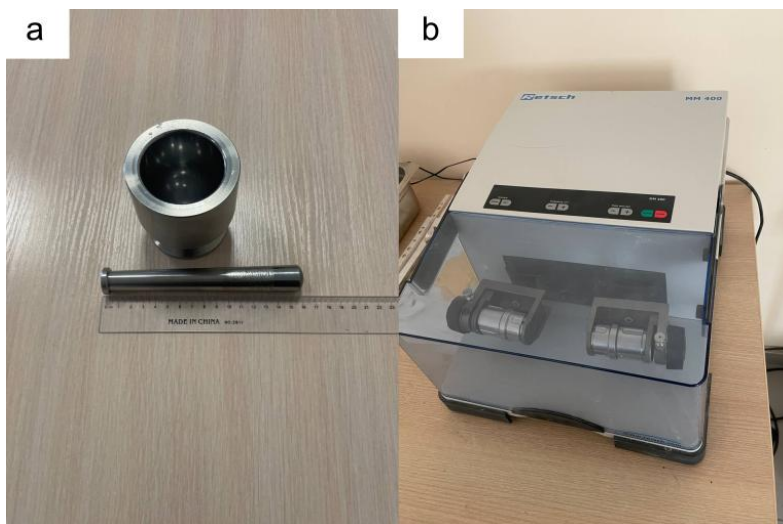


Figure 16. a) Mortar and pestle made from tungsten carbide (WC); b) ball mill “Restch MM 400.”

After the rock-crushing procedure, the next step is pulverizing. The pulverizing process was carried out using ball mill equipment “Retsch MM 400” (Figure 16b), where jars and balls were made from tungsten carbide (WC). The main parameters were 30 rpm and a 30-minute time cycle. Each sample was taken in at least two cycles. The number of cycles differed from one rock to another based on rock types. Before and after every sample, jars and balls were sent to physical and chemical cleaning procedures using quartz sand, abrasive decontamination, and ethanol rinsing.

The whole rock's major and trace elements were measured in this study using XRF machines available at two facilities: a) SMG of NU; b) Core facility—C4. Compressed powder was used in the XRF of SMG, whereas the fused glass beads were used in C4. Before preparing the glass beads, rock powders were heated in a muffle, “ELF 1100” by Carbolite Gero laboratory

chamber furnace (Figure 18a), in ceramic crucibles to determine loss on ignition (LOI). Carefully weighted rock powder samples were subjected to heating at 1050 °C for 2 hours. The samples were then cooled in a vacuum glass desiccator (Figure 18b), and the dry sample was weighed using the “Explorer EX124ZH/AD” analytical balance by the “Ohaul” company (Figure 18c).

Then the samples were fused to make glass beads. During fusion, a “sandwich” (Figure 17) system of fluxes and samples was adopted, which consisted of 0.5 grams of dried samples and 10 grams of lithium tetraborate ($\text{Li}_2\text{B}_4\text{O}_7$) and lithium metaborate (LiBO_2) fluxes. The mixture consisted of 67% lithium tetraborate and 33% lithium metaborate. The mixture was placed into platinum crucibles and placed into the fusion furnace “XRFuse 6” for glass bead preparation by the “XRF Scientific Ltd.” company (Figure 18d). The fusion parameters used were: Temperature: 1070°C. preheat time: 2 minutes; melt time: 5 minutes; shake time: 3 minutes. Stand time - 2 minutes 10 seconds; stage Cooling time: 1 minute; Stage 2 cooling time: 8 minutes; Shake angle: 45 °; Shake speed: 90%. An example of the glass bead is illustrated in Figure 18f.

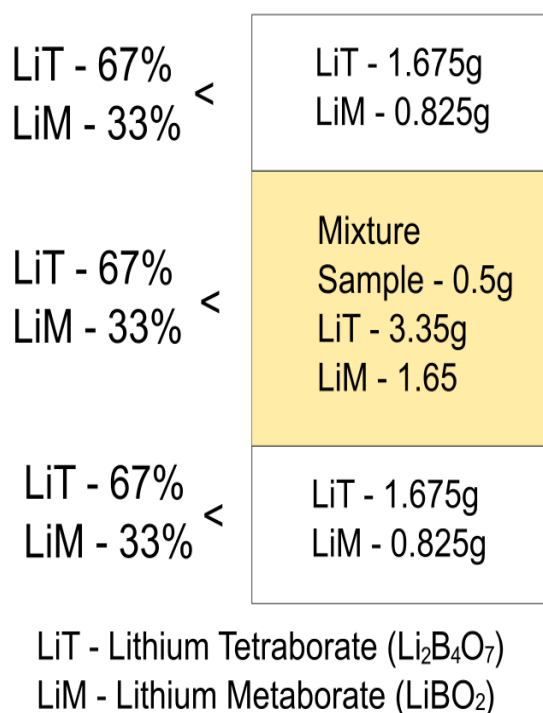


Figure 17. Sample and flux “sandwich” mixture



Figure 18. a) Carbolite Gero ELF 1100 laboratory chamber furnace. b) Vacuum desiccator for fused glass beads XRF analysis; c) Balance Ohaus Explorer EX124ZH/AD. d) XRFuse 6 fusion furnace by “XRF Scientific Ltd.”; e) PANalytical Axios mAX XRF Spectrometer; f) Ready glass bead after the fusion

3.3.2 XRF installation and use

The XRF use starts after all samples are crushed and pulverized. The equipment used for pressed powder pellet XRF analysis is the “Malvern Panalytical Epsilon 4” (Figure 19). The multifunctional benchtop allows elemental analysis from fluorine (F) to americium (Am) in ppm and wt% content ranges. For this project, the settings for analysis were chosen as “basic” and automatic range detection of chemical content, from wt% to part per million (ppm), and the elemental screening was “Omnian.” The machine can analyze up to 10 samples simultaneously;

the average time required to run 10 samples is 2 hours and 15 minutes.

“Epsilon software” is software for the Microsoft Windows 11 system by the “Malvern Panalytical” company.

In order to check the accuracy of the given pressed powder pellet XRF method, pure quartz sand was probed with resulting in the SiO₂ concentration 98.5 wt% (Table F3) and precision values (Table F4) for duplicated EK059/25 sample.



Figure 19. “Malvern Panalytical Epsilon 4” multifunctional XRF machine

In the core facility of NU, i.e., at C4, the samples were analyzed by using the “PANalytical Axios mAX XRF Spectrometer” (Figure 18e). The XRF spectrometer was set up at 20 kV voltage and 100 mA current. The machine was calibrated with Omnian calibration.

3.3.3 XRF Data normalization, Precision and Accuracy

Major and trace element composition data that were obtained from XRF were normalized considering loss in ignition (LOI) and contamination during the fused glass beads preparations. The LOI represents mass loss, which is associated with volatile components and was determined by heating the samples’ powder in 1050 degree centigrade for 3 hours in muffle furnace (Figure 18a). On the other hand, the small Br contamination was due to the used flux during fused glass bead preparation. The Br contamination was excluded from the composition of rocks since it is not from the rock’s composition. Therefore, all measurements should be normalized, excluding

LOI and Br effects, using the following equations 2 and 3 and only those data are used for geochemical interpretation. The normalized XRF, major oxides, and LOI are listed in Table E1.

$$X_{norm} = \left(\frac{X_{measured}}{100 - LOI - Br} \right) * 100 \quad (2)$$

- X_{norm} = normalized elements dataset
- $X_{measured}$ = initially measured elements dataset

$$LOI = \frac{(Weight_{wet} - Weight_{dry}) * 100}{Weight_{wet}} \quad (3)$$

- $Weight_{wet}$ = Weight of the wet sample
- $Weight_{dry}$ = Weight of the dry sample

During the sample preparation for fused glass beads XRF data (C4), 2 samples were duplicated, EK049/25 and EK098/25, to measure analytical precision. EK049/25D and EK098/25D were used to estimate the relative difference between repeated measurements (Table E2). The following equation (4) represents the precision calculation procedure.

$$\frac{X_{original} - X_{duplicate}}{X_{original}} * 100 \quad (4)$$

- $X_{original}$ = initial measured sample
- $X_{duplicate}$ = duplicated sample measurement

Finally, the analytical accuracy of the fused glass beads' XRF measurements was evaluated using the “BCR-2” sample, a certified reference sample, provided by the United States Geological Survey (USGS) (Jochum et al., 2016). In this study, the measured major oxide values of the “BCR-2” standard sample were compared to reference values from Jochum et al. (2016) to assess the accuracy of the fused glass beads XRF measurements (Table G1).

To assess the analytical accuracy using the “BCR-2” sample, the measured XRF values were compared to the reference values (Jochum et al., 2016) using Equation 5.

$$\frac{X_{measured}}{X_{reference}} * 100 \quad (5)$$

$X_{reference}$ = Reference value for BCR-2 value from Jochum et al, 2016

$X_{measured}$ = Measured and normalized fused glass beads XRF data

The results for the analytical accuracy procedure are listed in Table G1.

3.3.4 Alteration Assessment using AI – CCPI systematics

The degree of hydrothermal alteration of the studied rocks was conducted using alteration indexes such as Ishikawa Alteration Index (AI) and Chlorite – Carbonate – Pyrite Index (CCPI), following the approach of Large et al., (2001). The calculated AI values range from 8.4 to 100, whereas CCPI values range from 20.74 to 92.35, which indicate the various alteration intensities among the investigated samples (Table F1).

For Ishikawa Alteration Index (AI), the following Equation 6 was used to calculate alteration index values.

$$AI = \frac{K_2O + MgO}{K_2O + MgO + Na_2O + CaO} * 100 \quad (6)$$

For Chlorite – Carbonate – Pyrite Index (CCPI), it is necessary to use FeO values, in this study, all major oxide studies from XRF have Fe₂O₃ values, the following Equations 7 and 8 will represent the conversion Fe₂O₃ into FeO for further CCPI calculations.

$$\frac{2 * MW (FeO)}{MW (Fe_2O_3)} = \frac{2 * 71.844}{159.69} = 0.8998 \quad (7)$$

Where:

- MW = molecular weight
- 0.8998 = conversional factor

$$CCPI = \frac{MgO + FeO}{MgO + FeO + Na_2O + K_2O} * 100 \quad (8)$$

The LOI variation diagrams (Figure H1) show relationships between LOI and selected major and trace elements. The Na₂O and K₂O plot represents scattered trend with K₂O higher values than Na₂O (Figure H1a). The Rb and Ba diagram (Figure H1b) also reveals broad distribution, with Ba concentrations significantly higher than Rb. The Sr diagram demonstrates strong variability with several elevated Sr concentration samples (Figure H1c).

4.0 Results

4.1 Petrography

In this part of the project, all petrographic observations were conducted using an optical microscope, the “Axioscope 5” by the “ZEISS” company, and the “ZEISS LabScope” software program. All mineral abbreviations used are after Whitney and Evans (2010).

4.1.1 Cambrian

The investigated Cambrian rocks correspond to the second type of basalt of the Bozshakol Group (Shen et al., 2015). In the hand specimen, they are black porphyritic volcanic rock (samples EK048/25, EK049/25, EK050/25, and EK059/25) (Figure 20).

Microscopically, rocks contain numerous large, twinned pl phenocrysts (of dimensions) with a groundmass composed mostly of small pl. They mostly have a porphyritic texture. In Figure 20a, the larger plagioclase phenocrysts are surrounded by microlitic plagioclase-dominant grains and disseminated opaque minerals, which are sericitized (Ser). Sericite has light yellow-brown interference colors and is colorless in ppl. There are big plagioclase phenocrysts. A few grains of chloritized Hbl are present, while epidote after pl is common. Opaque minerals are present in accessory amounts. Sometimes, volcanoclastic rocks metamorphosed to greenschist with actinolite are also observed (EK049/25) (Figure 20e).

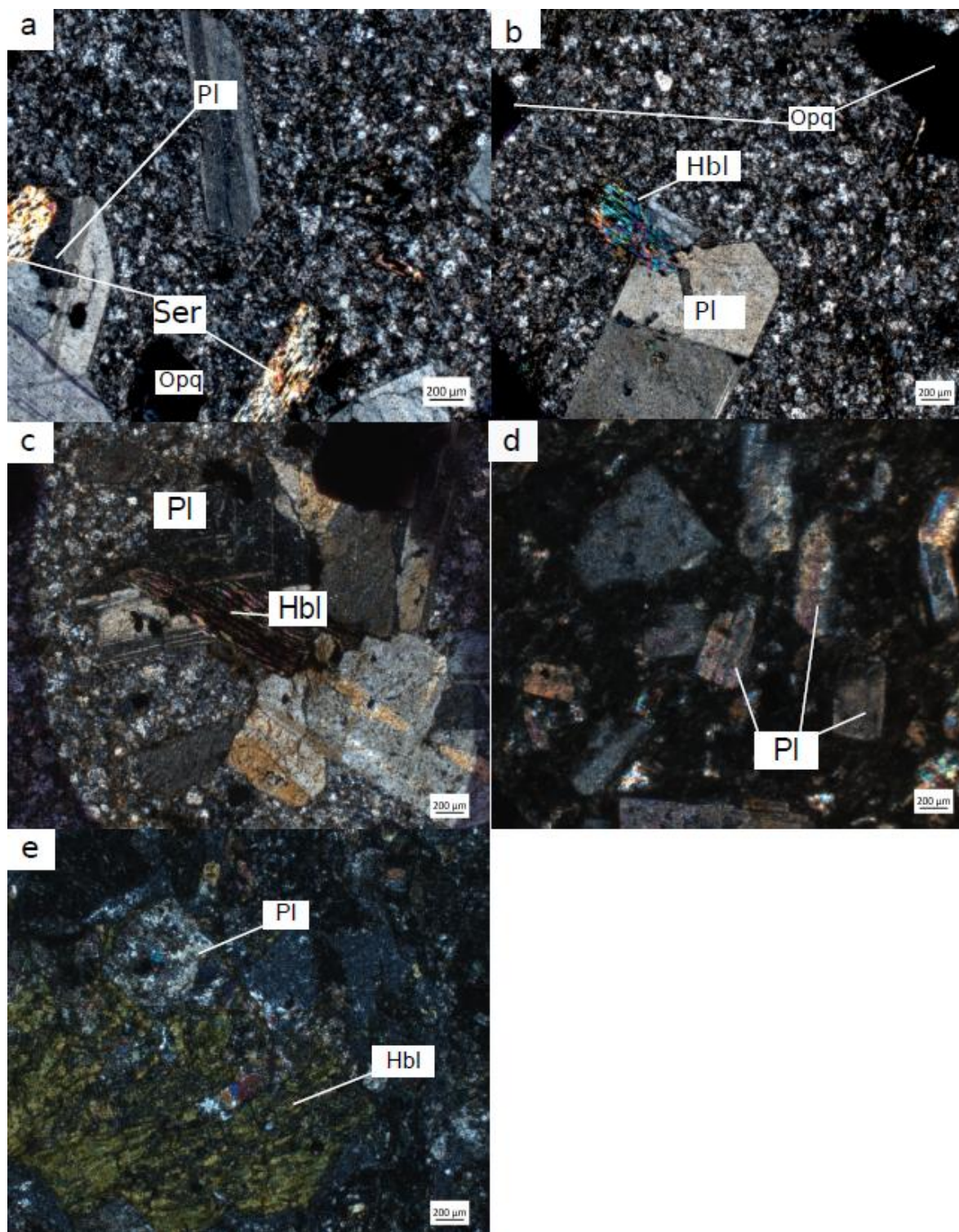


Figure 20. Photomicrographs of a) and b) EK048/25 with Pl phenocrysts with sericitization (Ser) and opaque minerals, porphyritic texture. c) EK050/25 Hbl and Pl phenocrysts, porphyritic texture. d) EK059/25, porphyritic texture, Pl, Hbl and Opq phenocrysts; e) EK049/25 Hbl and Pl phenocrysts with microlitic Pl groundmass

4.1.2 Lower Ordovician, O₁Sr

The Lower Ordovician (O₁Sr) volcanic formations are represented by basalt porphyry (EK016/25 and EK017/25).

Both EK016/25 and EK017/25 show porphyritic textures (ophitic in places) with bigger Px and smaller Pl phenocrysts. The Cpx phenocrysts are euhedral to subhedral (Figure 21a-d). Sometimes the Cpx phenocrysts are optically zoned and twinned, which is pervasive even in ppl. Sporadically, Px includes Pl (ophitic texture) and Fe-Ti oxides. Pl is epidotized, and they are smaller than Cpx phenocrysts. Rare Opx crystals are also present. Sometimes Pxs are completely chloritized. Fine-grained aggregates of minerals rimming the Cpx phenos in the form of corona textures indicating disequilibrium growth of Px are also observed. Volcanic ash is observed in the groundmass. Opaque minerals are found as accessory minerals (Figure 21e and f).

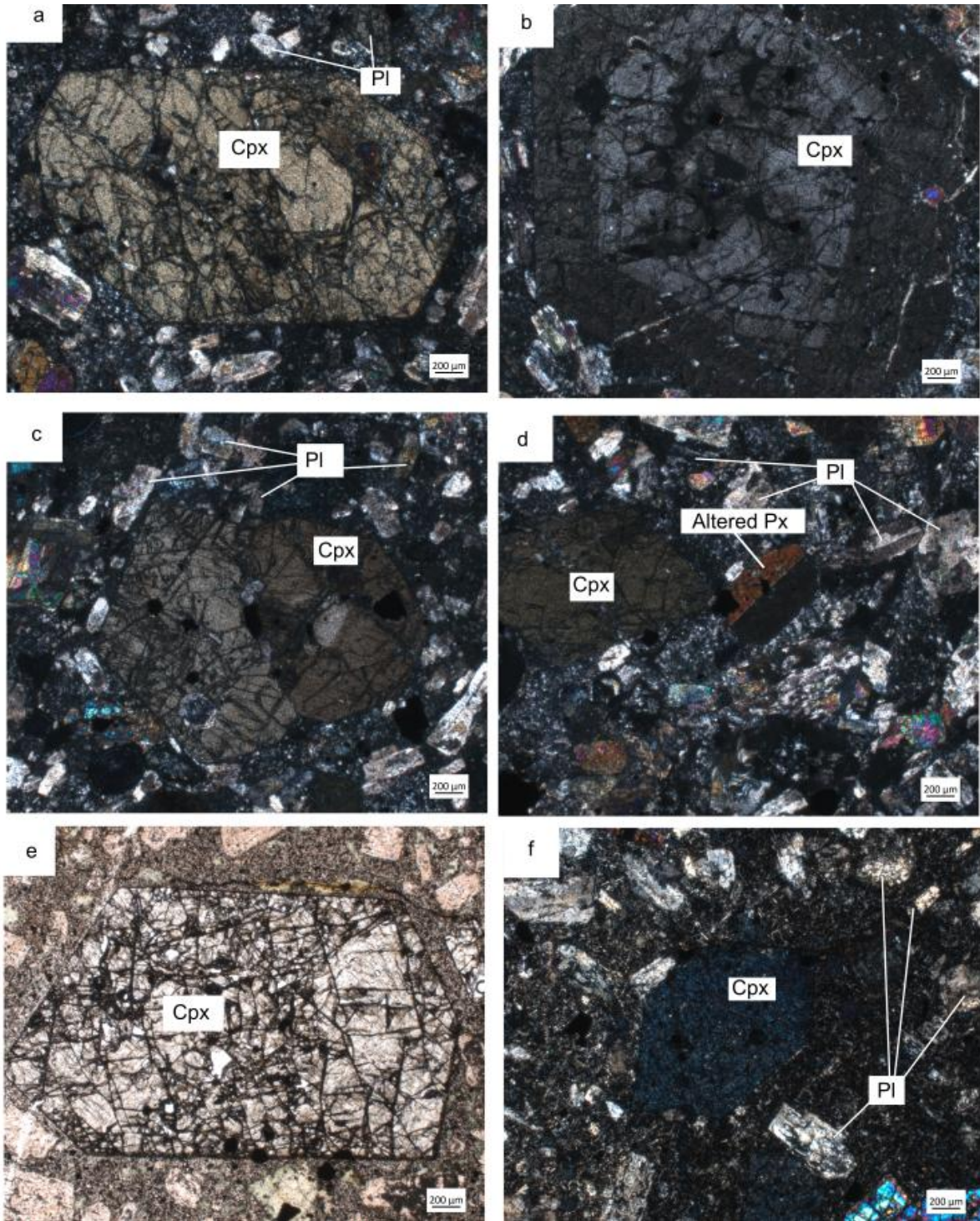


Figure 21. Photomicrographs of a) - d) zoned twinned Cpx in b) basalt with porphyritic texture, having Px and Pl phenocrysts (EK016/25); e) and f) reaction rim around Cpx phenocrysts (EK017/25).

4.1.3 Lower-Middle Ordovician (O₁₋₂)

The lower to middle Ordovician volcanic sequence is represented by porphyritic basaltic andesites with Hbl, Pl, and Px phenocrysts (EK019/15, EK098/25, EK100/25, and EK102/25); and volcanoclastic rocks with basaltic and andesitic clasts (EK044/25).

The sample EK019/25 represents Px-phyric basaltic andesite, which contains a significant amount of chloritized Px and a subordinate amount of Pl phenocrysts (Figure 22). Sporadically, Hbl after Px is also observed. The rock has metamorphosed to the greenschist facies. EK102/2 is also a porphyritic basaltic andesite with Hbl and Pl phenocrysts (Figures 23e and f). Hornblende phenocrysts are euhedral and twinned (Figure 23e). Plagioclase is sericitized. The groundmass mainly consists of Pl, with lesser amounts of Hbl and opaque minerals. The other basaltic andesite sample, EK100/25, is composed of Cpx, Hbl, and Pl phenocrysts (Figure 24). Hornblende phenocrysts are mostly fresh and euhedral. Cpx is twinned. Pl is sericitized. Mafic minerals, both in phenocrysts and the groundmass, are chloritized. A significant amount of opaque minerals is observed, while epidote is common after Pl. The other basaltic andesite sample (EK096/25) with Hbl, Pl, and Px phenocrysts has minerals that are mostly altered, and a significant amount of volcanic ash is present. The volcanoclastic rock in this formation (EK044/25) contains basaltic clasts with Px and Pl phenocrysts. Some plagioclase crystals in these volcanoclastic rocks are zoned and twinned and have overgrown corroded cores and are sericitized. The mafic minerals are chloritized (Figure 23a-d).

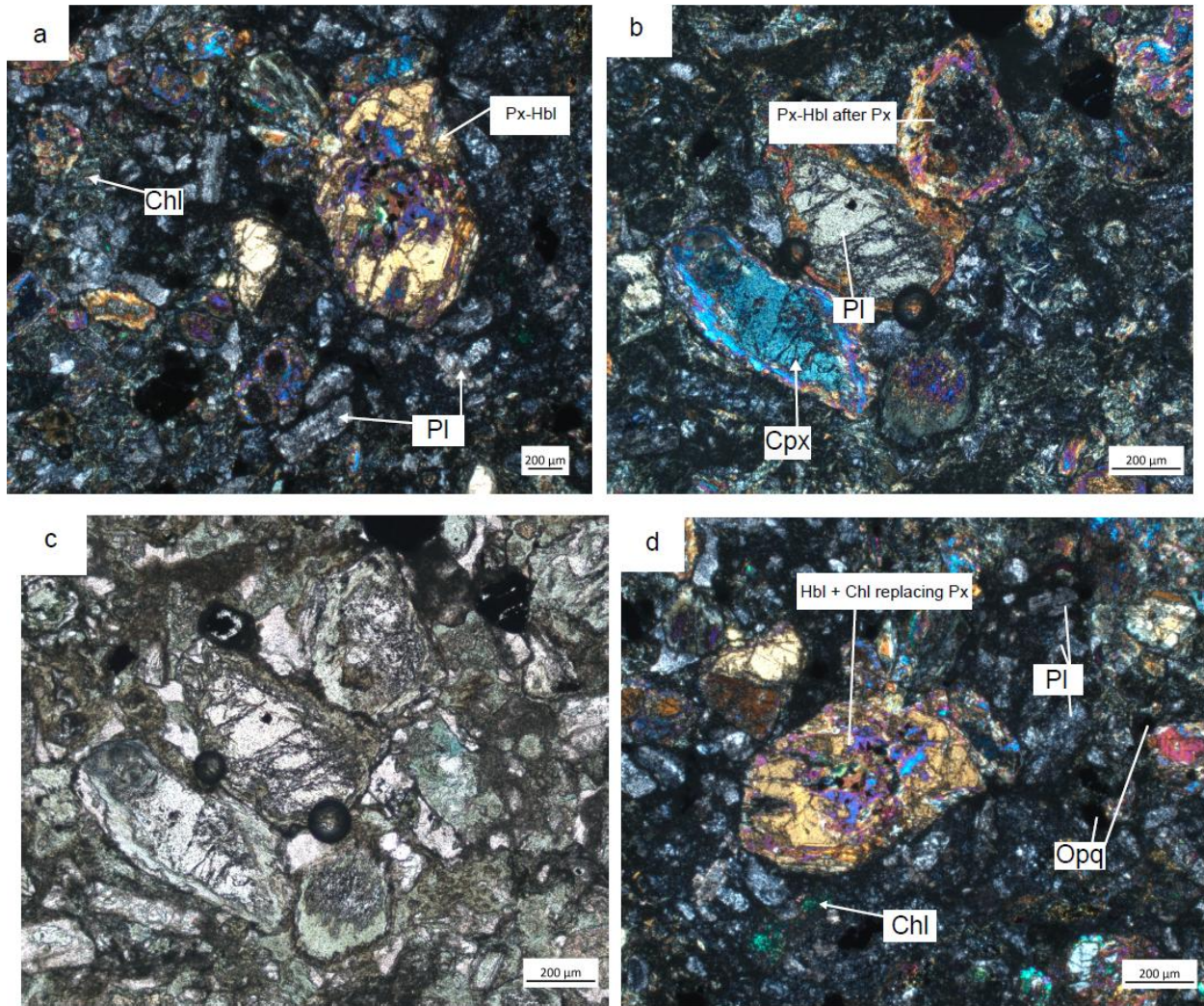


Figure 22. Photomicrographs of the EK019/25 chloritized Px in basaltic andesite, Opq, Hbl, and Cpx phenocrysts, porphyritic texture.

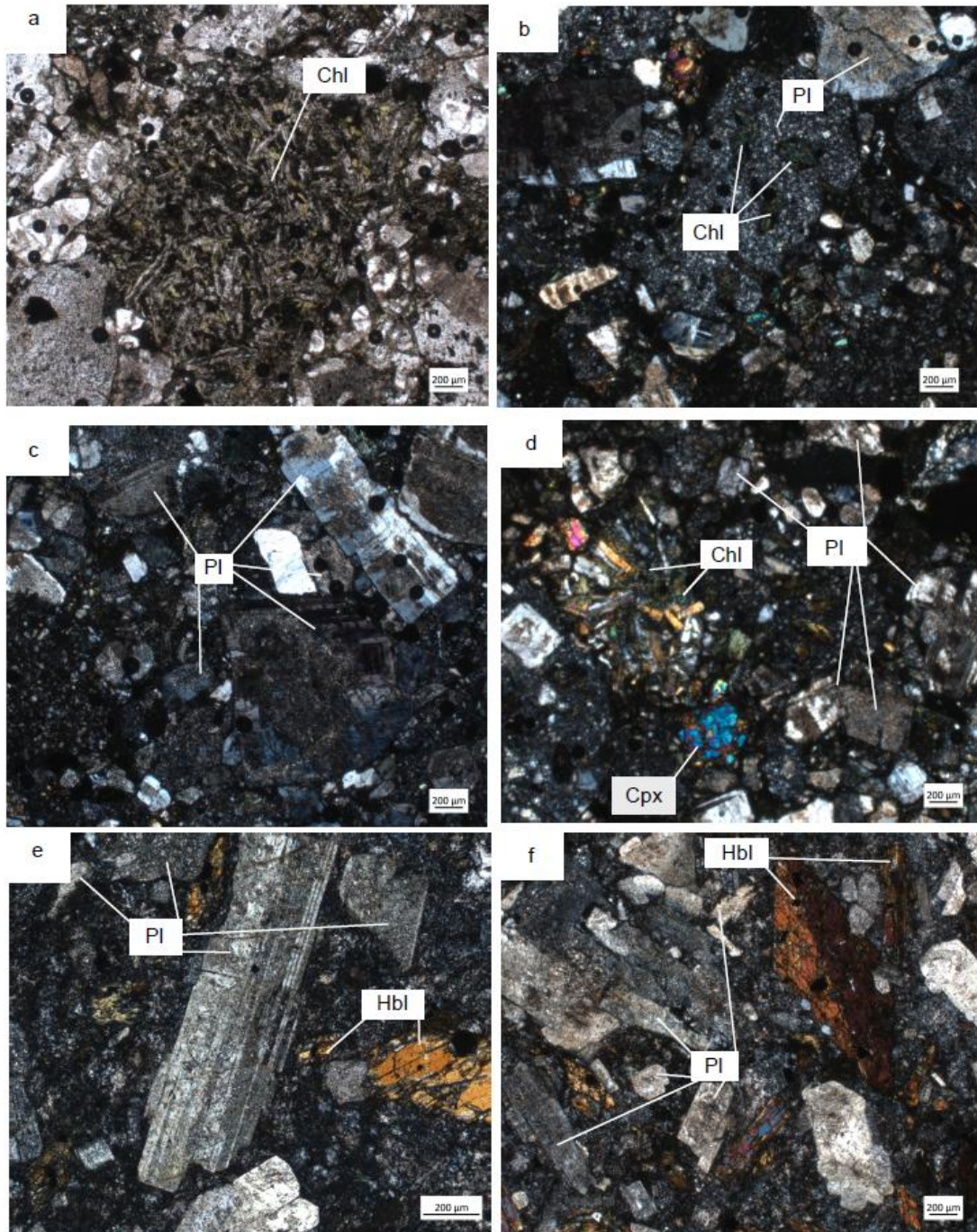


Figure 23. Photomicrographs a)-d) of a volcaniclastic rock (EK044/25) showing basaltic, Pl, Hbl, and Px clasts; e) and f) a porphyritic basaltic andesite with Pl and Hbl phenocrysts (EK102/25).

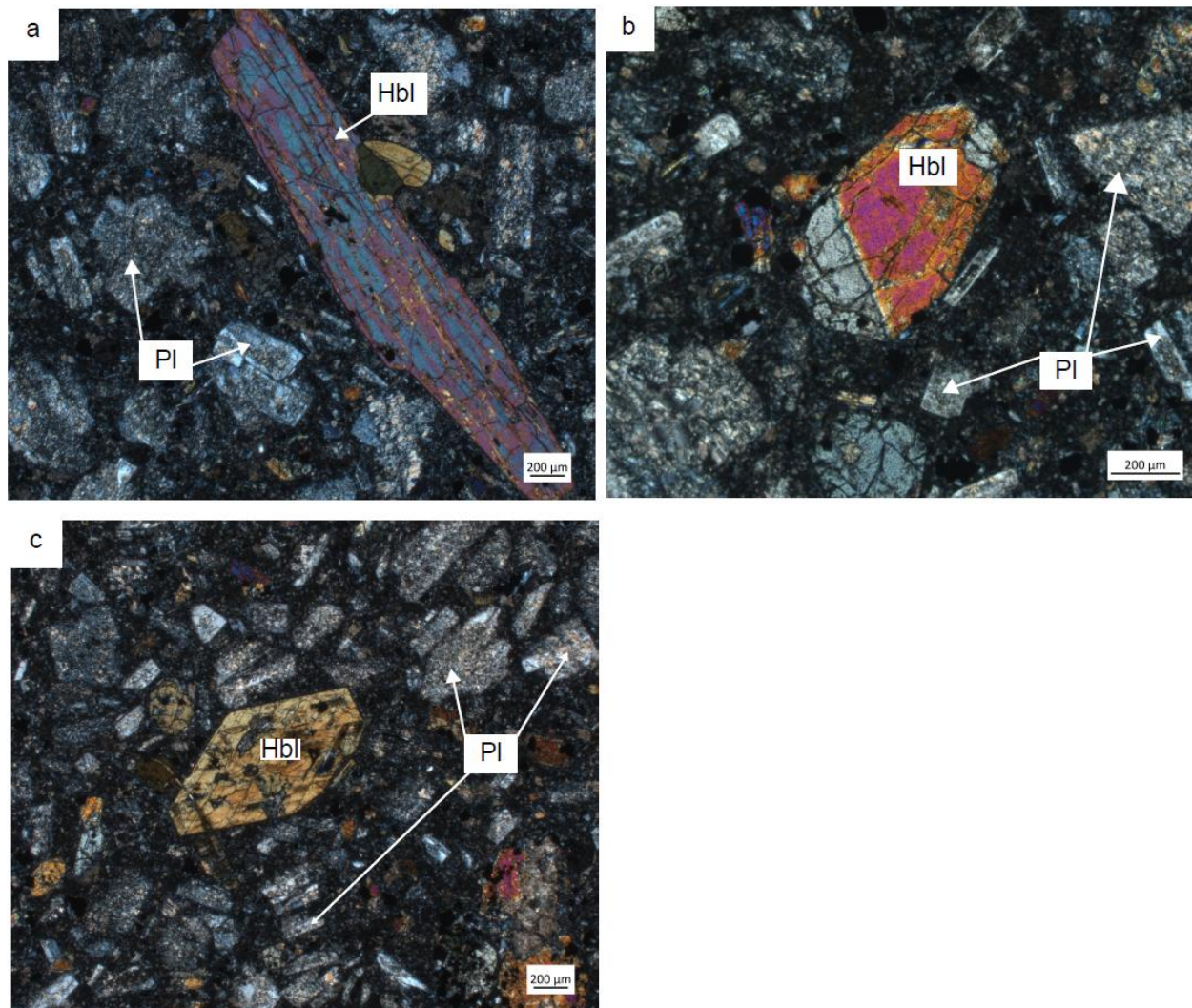


Figure 24. Porphyritic basaltic andesite with Cpx, Hbl, and Pl phenocrystal (EK100/25). Note that the mafic minerals are fresh

4.1.4 Upper Ordovician (O₃)

Upper Ordovician volcanic rocks are represented by highly altered andesites (EK045a/25) and some volcaniclastic rocks (EK096/25) with Pl, Hbl, and lithic clasts (Figure 25).

The sample EK045a/25 is a highly altered porphyritic andesite with Pl and sporadic Hbl phenocrysts. Plagioclase is sericitized while Hbl is chloritized and also altered to Fe-Ti oxides. The size of the Pl phenocrysts is bigger than in other studied samples. The altered Hbl still preserves its original euhedral shape. The modal amount of Pl phenocrysts is greater than Hbl

(Figure 25a and b). A studied volcanoclastic rock (EK096/25) contains clasts of plagioclase and Hbl, as well as lithic clasts of andesite (Figures 25c - f).

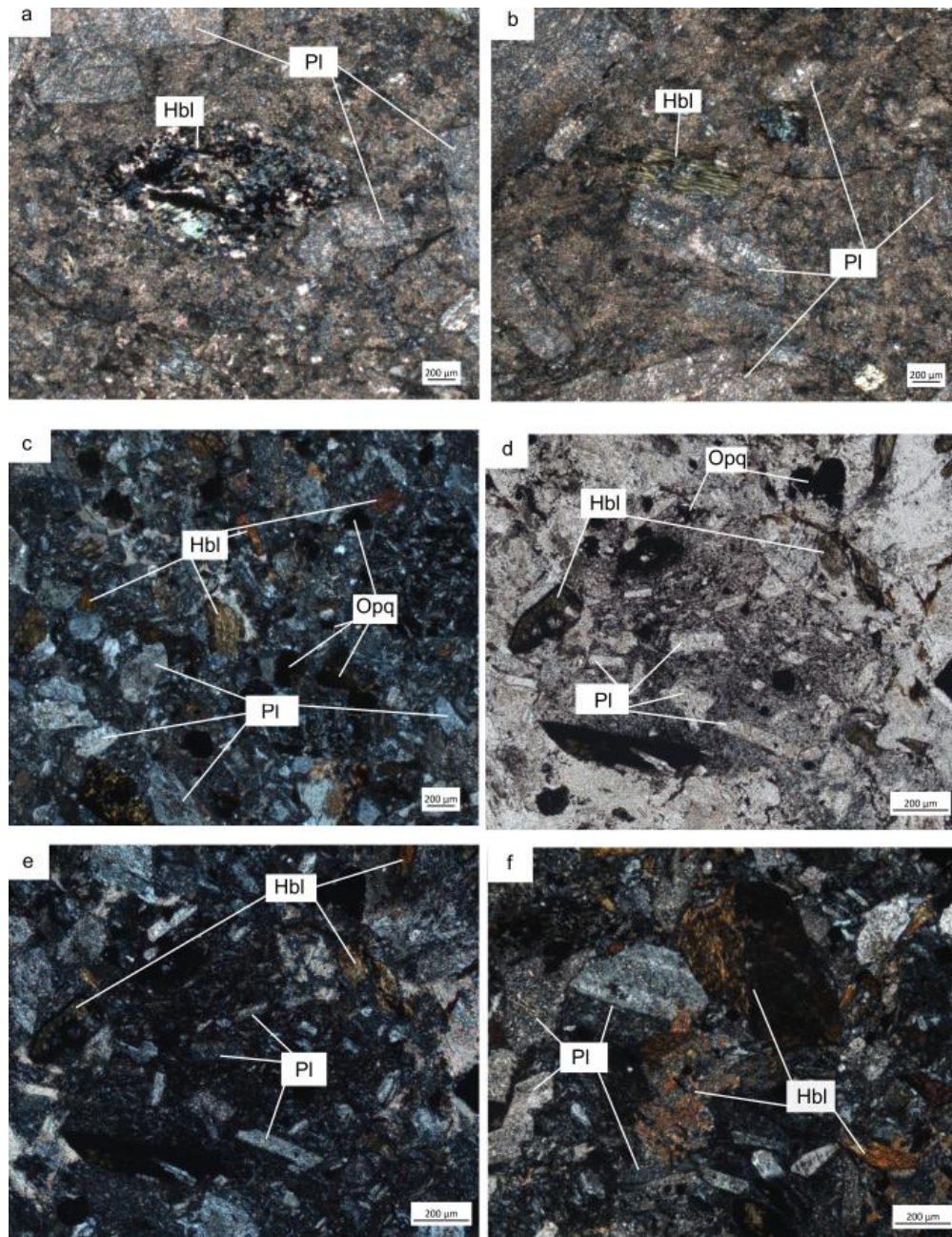


Figure 25. a) - b) Hbl and Pl phenocrysts (EK045a/25); c) - f) Hbl and Pl, and a basaltic clast in a volcanoclastic rock (EK096/25)

4.1.5 Devonian (D_{1-2Kd})

The volcanic rocks of the Devonian are represented mostly by aphyric andesite with quartz and zeolite amygdules (EK083/25); dacite to rhyolite (EK071/25); the volcanoclastic rocks (EK065/25 is the andesite clast from the volcanoclastic rock); and rhyolite (EK068/25) (Figures 26 and 27).

The sample EK083/25 is represented by andesite with Qtz amygdules. There are larger and more numerous sericitized Pl, as well as a significant amount of volcanic ash. The rocks show porphyritic textures. The large Pl phenocrysts are surrounded by finer Pl microlitic groundmass and opaque minerals. Plagioclase phenocrysts (with albite twinning) are abundant and sometimes are sericitized (Figure 26a). The sample (EK071/25) petrographically corresponds to a porphyritic dacite to rhyolite composition with Pl phenocrysts. Amygdules filled with quartz and zeolites and a significant amount of volcanic ash are also observed (Figures 27a-d). An andesitic clast in volcanoclastic rock (EK065/25) has a porphyritic texture where Pl (with albite twinning) and Hbl (chloritized) phenocrysts are surrounded by finer Pl microlitic groundmass. The sample has a significant amount of Opq and some volcanic ash (Figure 27e-h). EK068 is a rhyolite with a porphyritic texture, with quartz phenocrysts (Figure 26b). The groundmass is composed mostly of quartz and feldspars. Opaque minerals are disseminated throughout the groundmass and also are observed in tiny cracks (veinlets).

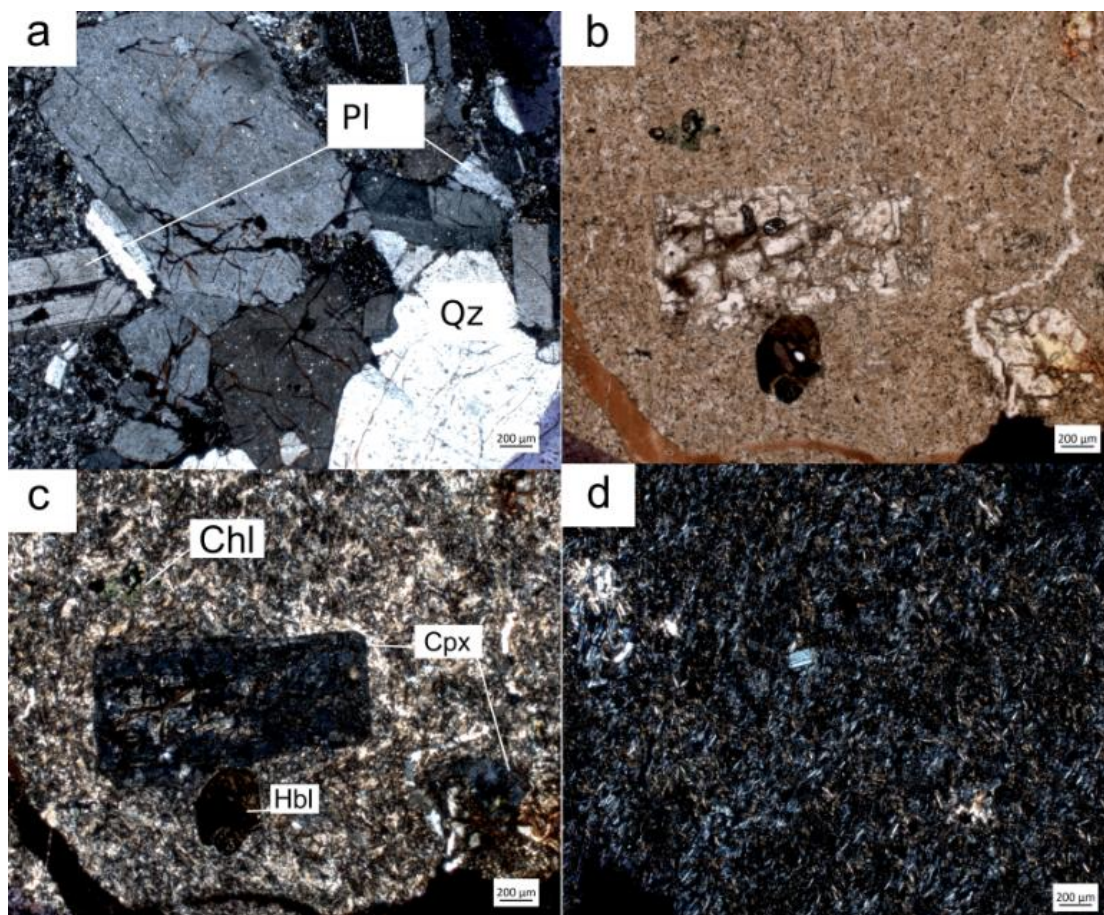


Figure 26. Photomicrographs of a) EK083/25 with Pl and b) Qtz phenocrysts EK068/25 and c) Chloritized Hbl phenocrysts, porphyritic texture; d) EK076/25, Pl-dominant groundmass, pilotaxitic texture.

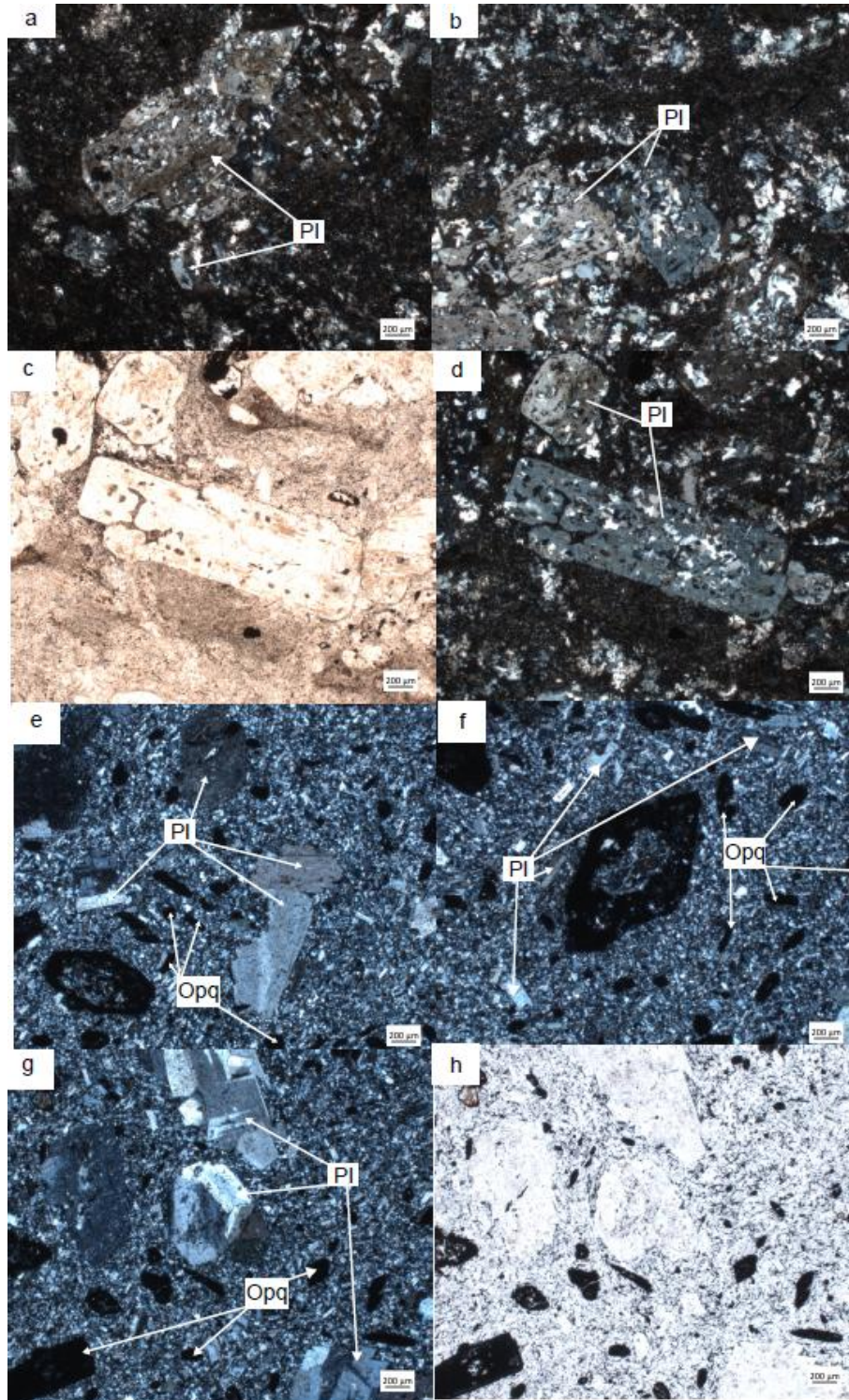


Figure 27. Photomicrographs of a) - d) Pl phyric dacite - rhyolite, porphyritic texture (EK071/25); e) - h) andesite clast from volcanoclastic rock with dominant Pl and Hbl (chloritized and altered to Fe-Ti oxides) phenocrysts (EK065/25)

4.1.6 Silurian Intrusives

The studied rocks from the Silurian period are altered granodiorite porphyry (Samples EK009/25 and EK055/25) (Figure 28). These rocks are composed of Pl and altered Hbl with Kfs, Qtz epidote, calcite, and opaque minerals. Plagioclase are sericitized.

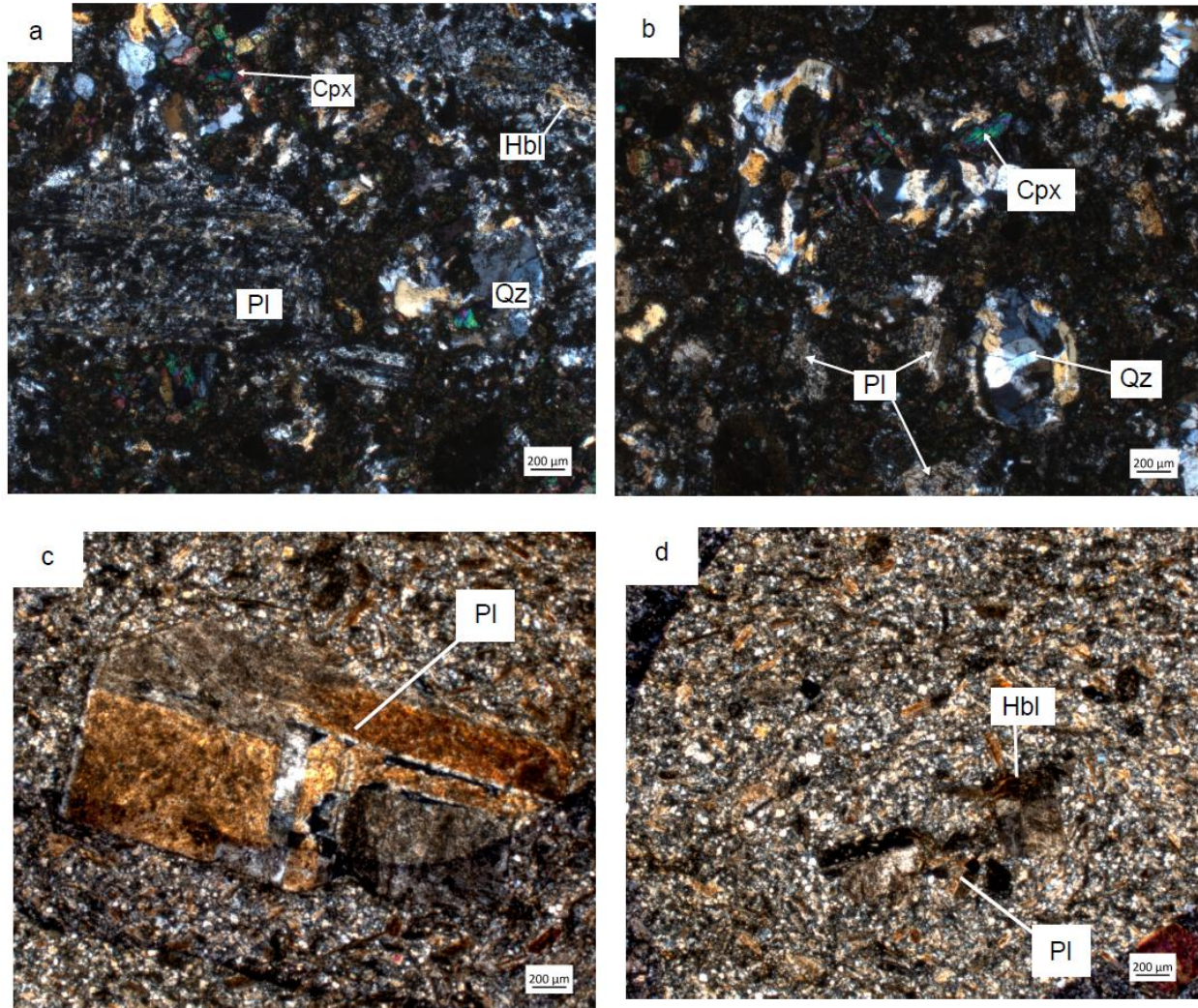


Figure 28. Photomicrographs of a) and b) EK009/25 with Pl, Qtz, Hbl, and Cpx phenocrysts and porphyritic texture; c) and d) EK055/25 with dominant Pl phenocrysts and Hbl inclusions.

4.2 Mineral Chemistry (SEM-EDS)

4.2.1 Feldspars

The plagioclase composition from the Lower Ordovician basaltic andesite (from EK017/25, EK096/25, EK100/25, and EK102/25) varies from $Ab_{45.1}An_{42.2}Or_{12.7}$ to $Ab_{98.8}An_{0.9}Or_{0.5}$ (Tables A4, A6, A1, and A7), while Pl from the Upper Ordovician andesite (EK045a/25) shows composition varying from $Ab_{7.6}An_{90.5}Or_{1.9}$ to $Ab_{96.5}An_{1.5}Or_{2.0}$ (Table A5). On the other hand, Silurian granodiorite porphyry (EK055/25) has more albitic Pl composition, varying from $Ab_{93.8}An_{2.2}Or_{4.1}$ to $Ab_{94.7}An_{4.3}Or_{1.0}$, the rim being richer in the Kfs component. Additionally, there is Kfs having a composition of $Ab_{5.4}An_{2.3}Or_{92}$ in granodiorite (Table A3). Alkali feldspar from vesicular rhyolite in the Devonian felsic sequence (EK071/25) has a feldspar composition that varies from $Ab_{3.1}An_{0.2}Or_{96.8}$ to $Ab_{10.4}An_{0.4}Or_{98.2}$ (Table A4) (Figure 29).

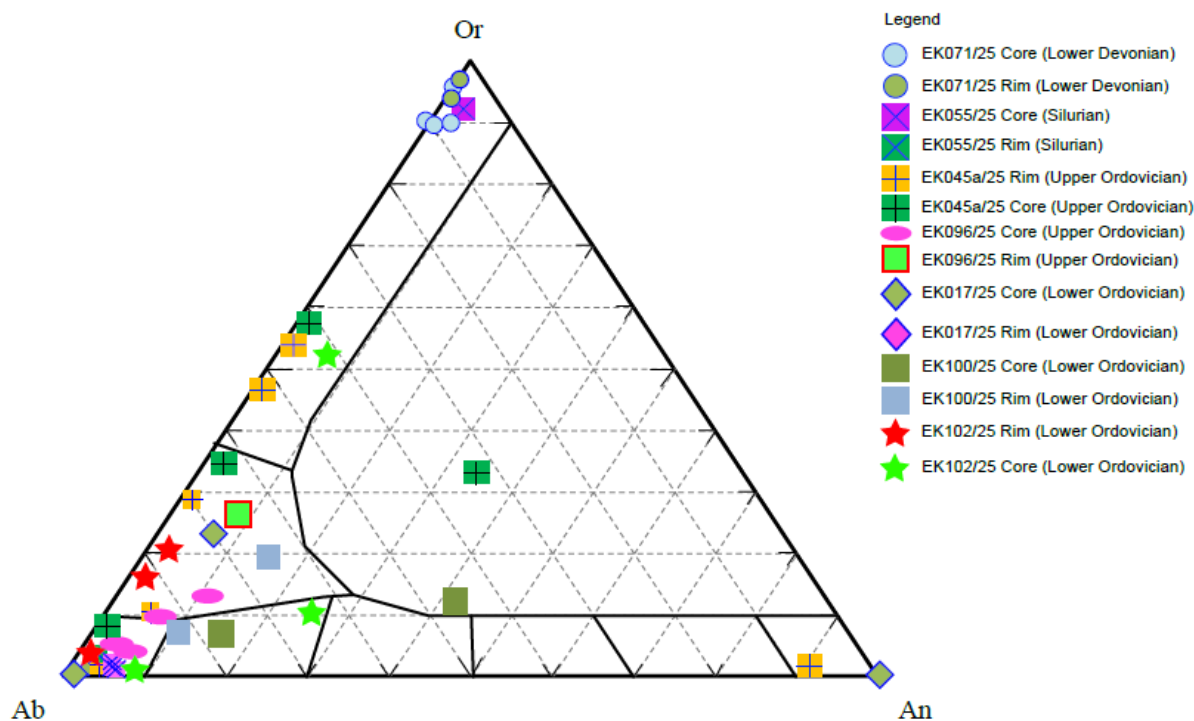


Figure 29. Feldspar compositions of the studied rocks in an Or-Ab-An triangular plot (note: the highest anorthite content in andesite is from the Upper Ordovician (EK045a/25) and high Or content in the Lower Devonian felsic rock (EK071/25).

4.2.3 Pyroxenes

The composition of Px from the Lower Ordovician rocks is dominated by augite (Cpx), with its composition varying from $\text{Wo}_{40.8}\text{En}_{46.5}\text{Fs}_{12.7}$ to $\text{Wo}_{45.5}\text{En}_{39.6}\text{Fs}_{15}$ in EK100/25 (Table B1), while the Px composition in other Lower Ordovician rocks (sample EK017/25) ranges from $\text{Wo}_{10.2}\text{En}_{60.8}\text{Fs}_{29}$ to $\text{Wo}_{49.3}\text{En}_{35.5}\text{Fs}_{15.2}$ (Table B2). Some rims are richer in Fe and Mg and have a low Ca content, indicating the presence of Opx (pigeonite). On the other hand, Px in the upper Ordovician (EK096/25) is represented mostly by Cpx with composition varying from $\text{Wo}_{24.4}\text{En}_{58.7}\text{Fs}_{16.9}$ to $\text{Wo}_{39.4}\text{En}_{12.9}\text{Fs}_{47.7}$ (Table B4). Notably, Px composition from Silurian intrusive (EK055/25) is mostly Opx (composition varying from $\text{Wo}_{0.15}\text{En}_{66.5}\text{Fs}_{33.25}$ to $\text{Wo}_{0.48}\text{En}_{61.11}\text{Fs}_{38.41}$) (Table B3) (Figure 30).

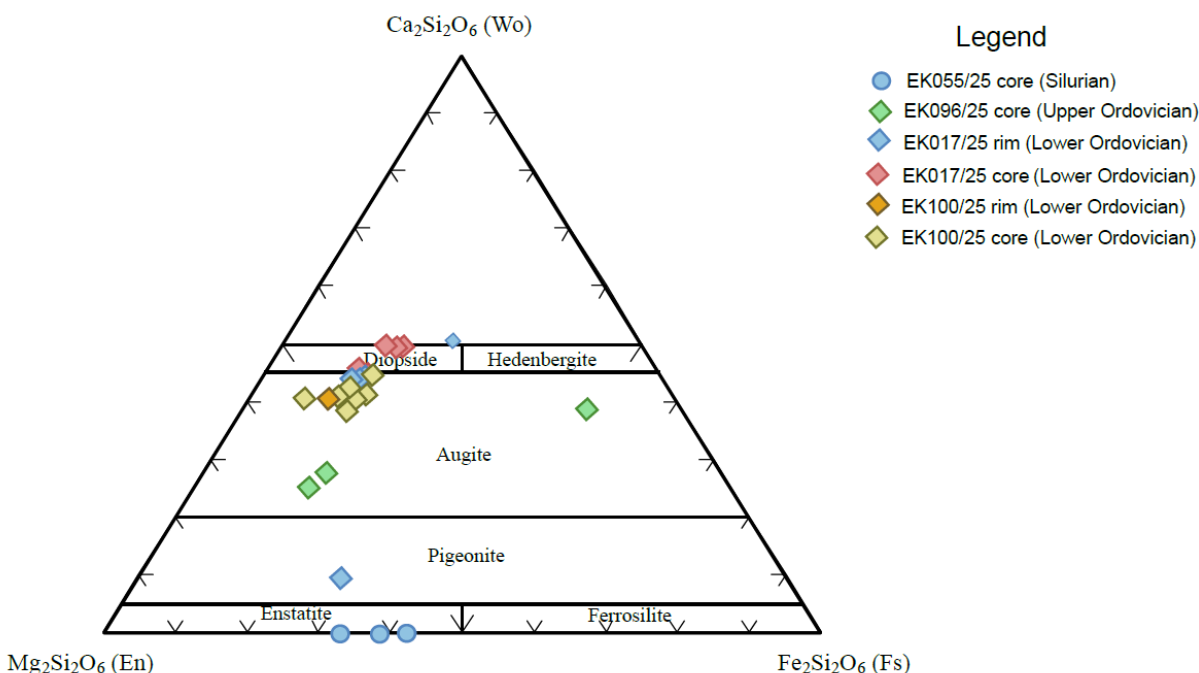


Figure 30. Compositions of Px from the volcanic rocks from the studied area in the Wo-En-Fs diagram after Morimoto et al. (1988). (Note: mainly clinopyroxene, although there is orthopyroxene in the Silurian intrusive).

4.2.4 Amphibole

The amphibole composition from Lower Ordovician volcanic rocks (EK100/25 and EK102/25) straddles primarily the magnesio - hornblende to pargasite boundary. However, a single analysis of amphibole core from EK100/25 plots into Tschermakite composition (Figure 31) (Tables C1 and C2).

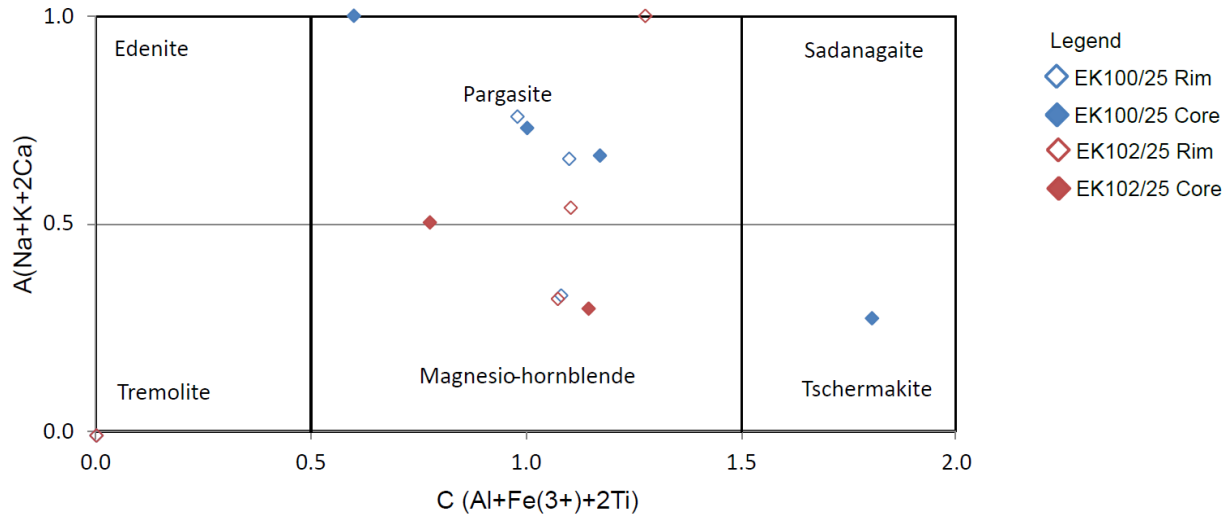


Figure 31. Amphibole compositions of the volcanic rocks from the studied area in the Ca-amphibole diagram classification (Hawthorne et al., 2012).

4.2.5 Mica

An Upper Ordovician andesite (EK045a/25) contains some mica with X-phlogopite 48%, X-siderophyllite 0.3%, and X-annite 49% (Figure 32) (Table D1).

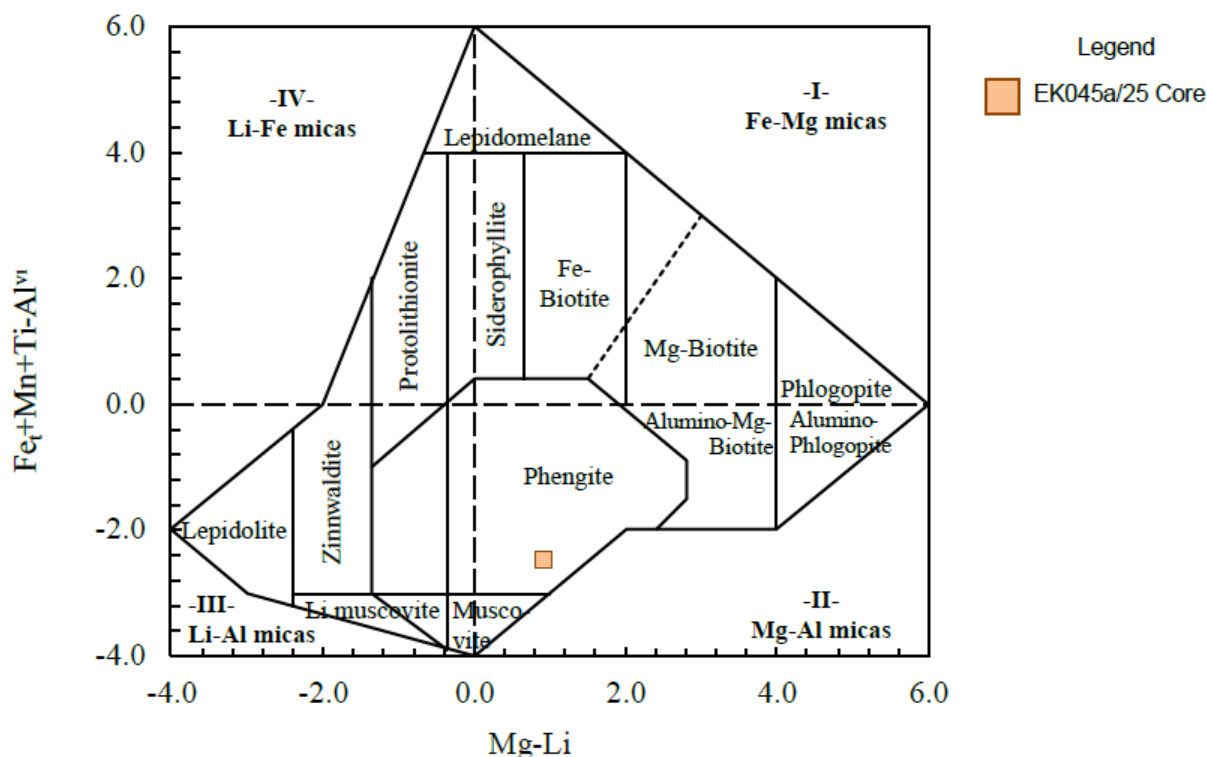


Figure 32. Compositions of mica from the sample EK045a/25 (Tischendorf et al., 1997).

4.3 Whole rock major and trace element geochemistry

The major elements of the studied rocks analyzed on fused glass beads in the core facility of Nazarbayev University are presented in Table E1, while the major as well as the selected trace elements acquired on the pressed pellet at the School of Mining and Geosciences of Nazarbayev University (NU SMG) are listed in Tables F1 and F2.

The SiO₂ contents for these rocks in pressed powder pellets vary from 43.86 wt% (EK019/25) to 75.06 wt% (EK068/25) (Table F1); in fused glass beads, the lowest SiO₂ content is in EK083/25 with 55 wt%, and the highest value is in EK068/25 with 78.17 wt% (Table E1). The range of MgO is from 0.17 wt% (EK068/25) to 6.88 wt% (EK019/25); EK019/25 rock has the highest MgO content (Table F1). In the fused glass beads, the lowest MgO content is in EK068/25 with 0.16 wt%, and the highest value is in EK019/25 with 6.11 wt% (Table E1). The variation in the total alkalis (K₂O + Na₂O) is from 2.36 wt% in EK019/25 to 8.39 wt% in EK071/25 (Table E1). The highest CaO value in pressed powder pellets varies from 0.64 wt% (EK059/25) to 14.56

wt% in EK019/25 (Table F1); in the fused glass beads, the values are from 0.16 wt% in EK071/25 to 12.12 wt% in EK019/25 (Table E1). The content of TiO₂ in pressed powder pellets varies from 0.59 wt% in EK049/25 to 1.64 wt% in EK083/25 (Table F1); in the fused glass beads, the lowest value is in EK049/25 with 0.46 wt%, and the highest values are in EK044/25 with 1.02 wt% (Table E1).

In the total alkali-silica (TAS) diagram of Middlemost (1994), the samples from fused glass beads and pressed powder pellets have the general trend of the rocks' composition being intermediate-felsic (Figures 33a and 33b). The samples mostly have rhyolite, basaltic andesite, and dacite compositions. However, some samples are placed in trachy-dacite to tephrite compositions (Figure 33a). Whereas the Zr/TiO₂ versus Nb/Y classification diagram (Winchester and Floyd, 1977) analyzed plots for altered volcanic rocks (Figure 33c) within sub-alkaline basalt, basaltic andesite, and rhyolite. The Lower Ordovician basaltic andesite, diorite, and rhyolite samples group within the andesite – basaltic andesite compositional range, meanwhile the Cambrian keratophyre samples mainly plot on the trachyandesite part. Devonian samples reveal the widest compositional range, which extends from andesite – dacite to rhyolite composition. The rhyolite (EK068/25) sample clearly cluster to the rhyolite field, while dacite – rhyolite sample (EK098/25) occupies the dacite – rhyodacite part.

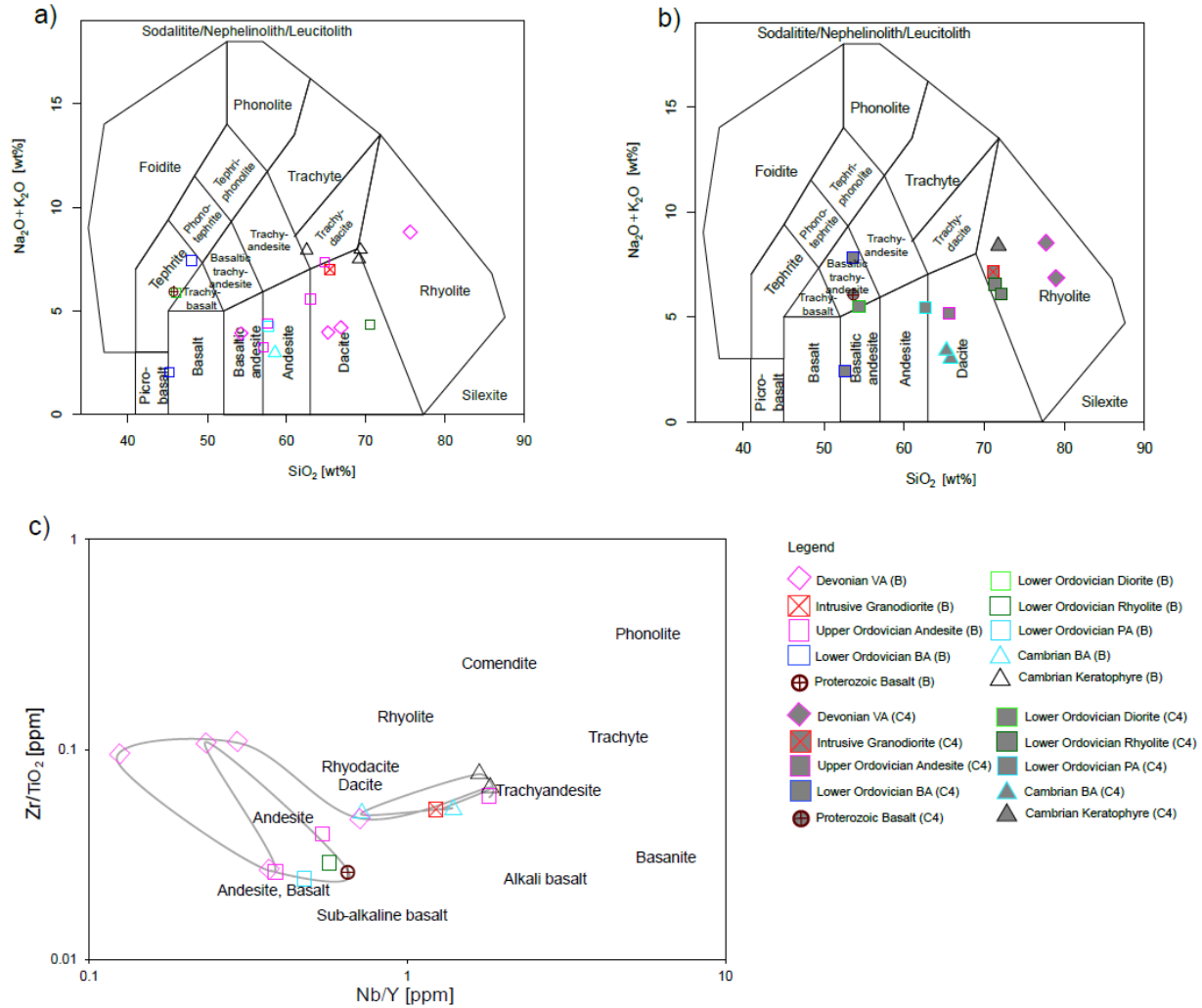


Figure 33. TAS classification for the studied rocks, based on measurements done at (a) C4; b) Block 6 (Middlemost, 1994); c) Nb/Y vs. Zr/TiO₂ classification diagram (Winchester and Floyd, 1977)

The AFM diagrams (Figures 34a and 34a') (Irvine and Baragar, 1971) illustrate the distribution of both pressed powder pellets (Figure 34a) and fused glass bead (Figure 34a') datasets in the triangular A-F-M system. Most of the samples are plotted in the calc-alkaline field while using data obtained from analyses done in fused glass beads, except Proterozoic basalt and Lower Ordovician basaltic andesite (BA) (Figure 34a'), which show tholeiitic nature, whereas while using data acquired in pressed powder pellets, the rocks show both tholeiitic and calc-alkaline natures (Figure 34a).

The SiO₂ vs. FeOt/MgO diagrams (Miyashiro, 1974) (Figures 34b and 34b') represent the ratio of FeO [total]/MgO with silica after Miyashiro (1974). The studied rocks show both

tholeiitic and calc-alkaline natures, tholeiitic being dominant. Notably, the Devonian felsic rock shows a calc-alkaline nature. On the other hand, in the fused glass beads (C4) dataset, the points reveal broader vertical spread; however, Lower Ordovician rhyolite and Devonian volcanoclastic andesite (VA) have anomalously high content of FeOt/MgO values. The pressed powder pellets dataset (B6) represents the same trends.

The SiO₂ vs. K₂O diagrams (Figures 34c and 34c') show distribution in the tholeiitic, calc-alkaline, high-calc-alkaline, and shoshonite series. The general trend represents wide variation in both SiO₂ (wt%) and K₂O (wt%). Notably, there is an anomalously high content of K₂O in andesitic clasts in Devonian volcanoclastic andesite in pressed powder pellets (B6), while the data from fused glass beads (C4) show similar behavior.

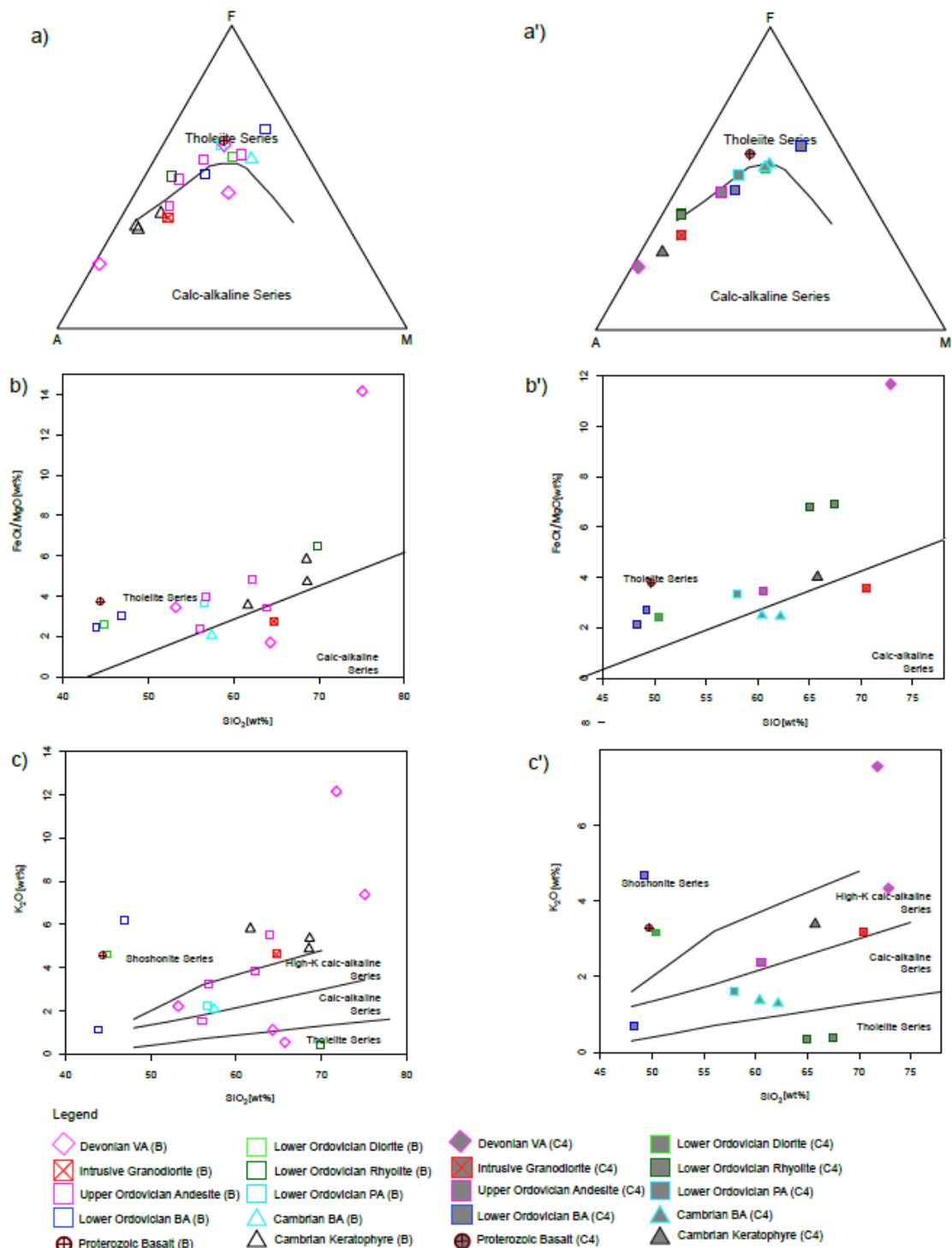


Figure 34. XRF major oxides classification diagrams, including C4 and Block 6 measurements: a) AFM plot from C4 (Irvine and Baragar, 1971); a') AFM plot from B6 (Irvine and Baragar, 1971); b) SiO₂ vs. FeO/MgO from C4 (Miyashiro, 1974); b') SiO₂ vs. FeO/MgO from B6 (Miyashiro, 1974). c) SiO₂ vs. K₂O (Peccerillo and Taylor, 1976) from C4; c') SiO₂ vs. K₂O (Peccerillo and Taylor, 1976) from B6

There are negative correlations of MgO, FeO_t, CaO, and TiO₂ with respect to SiO₂. Na₂O and K₂O exhibit poor positive correlation, while P₂O₅ and Al₂O₃ do not show any correlations with SiO₂ (Figure 35). The Ordovician mafic rocks have the highest concentrations of MgO, FeO, CaO, and TiO₂, while there are relatively higher concentrations of SiO₂ in the Devonian rocks (Figure 35).

The Zr versus trace elements variation diagram (Figure 36) represents relationships between Zr and selected compatible and incompatible trace elements for volcanic and intrusive rocks exposed in the study area. The given diagrams include Cr, Ni, Sr, Y, Ba, Nb, Th and Pb against Zr concentration from XRF block 6. The Cr and Ni diagrams mainly display negative correlation with increasing Zr, the highest Cr and Ni concentrations occur in Cambrian basaltic andesite and Proterozoic basalt samples. Rb generally increases with increasing Zr, precisely Devonian volcanic samples reveal the highest Zr concentrations. Strontium values show scattered trends, ranging from low concentrations in some evolved felsic rocks to high concentration in Cambrian keratophyre and Upper Ordovician andesite samples. Y and Ba concentrations generally increase with increasing Zr, whereas Nb concentrations show moderate enrichment with increasing Zr. Thorium cluster in relatively narrow ranges, meanwhile Pb concentrations display a strong scattering trend.

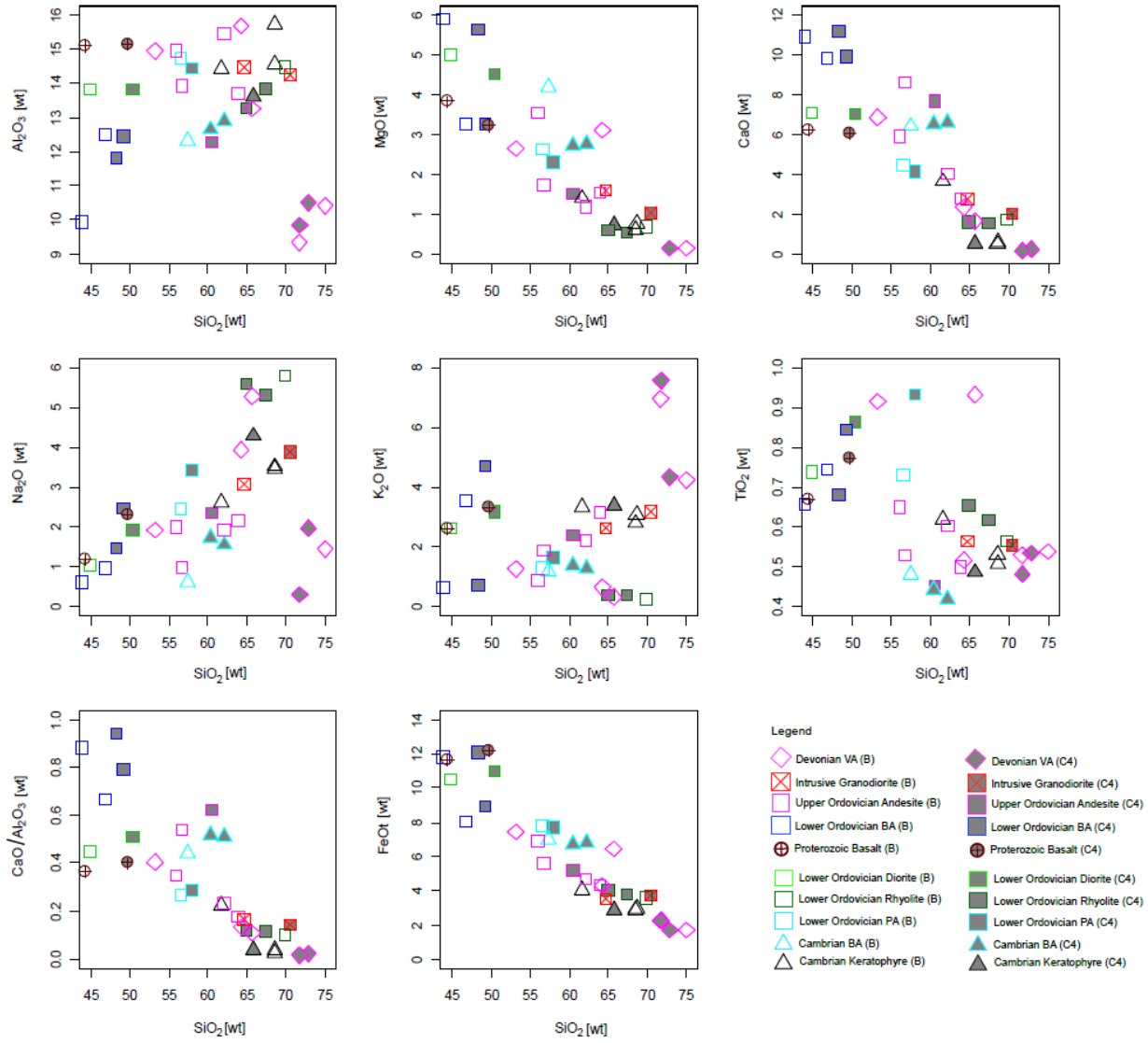


Figure 35. SiO_2 [wt%] vs. major oxides [wt%] plots (analyses done both in C4 and Block 6)

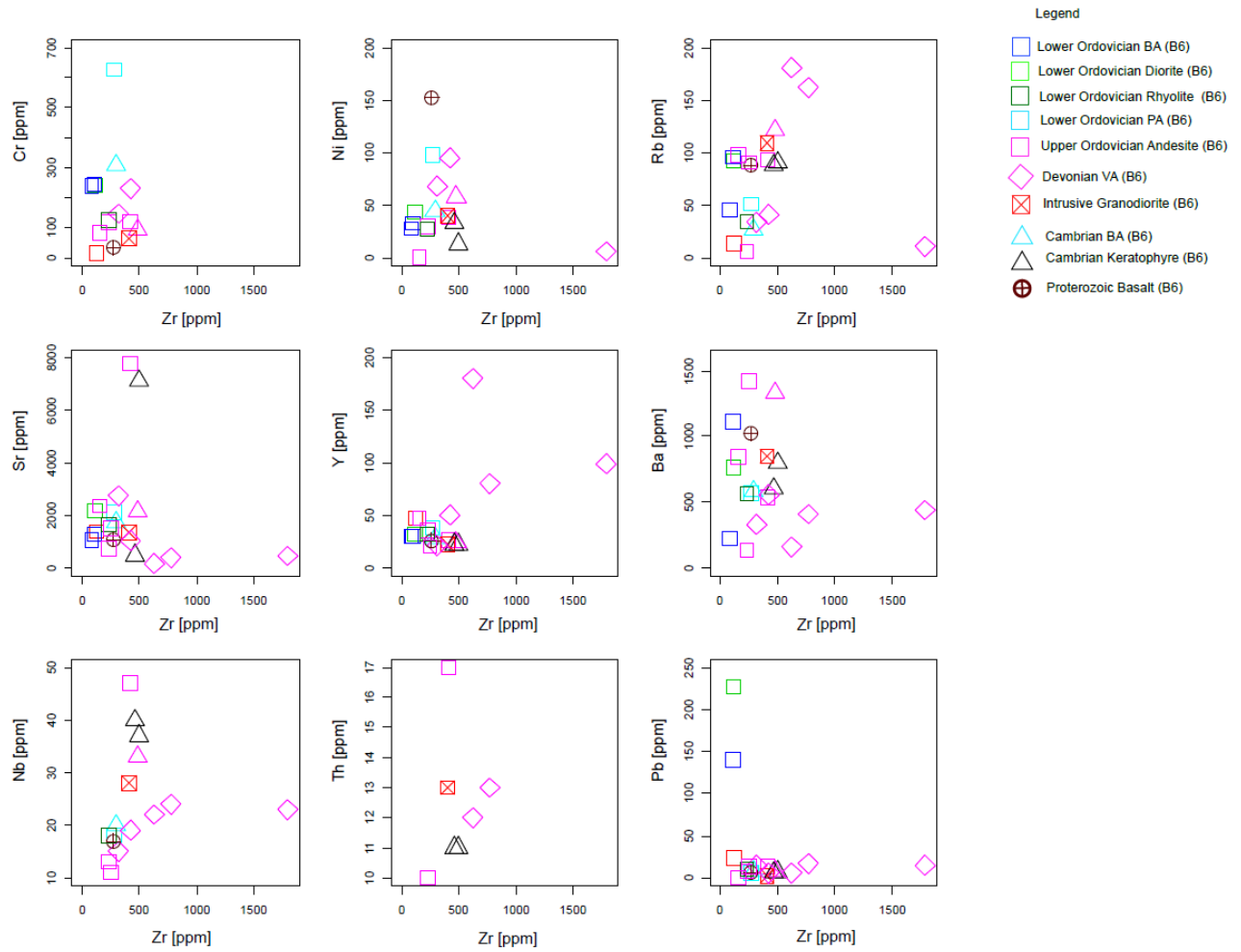


Figure 36. Zr [ppm] vs. selected trace elements [ppm] plots for the studied rocks based on analyses done in B6

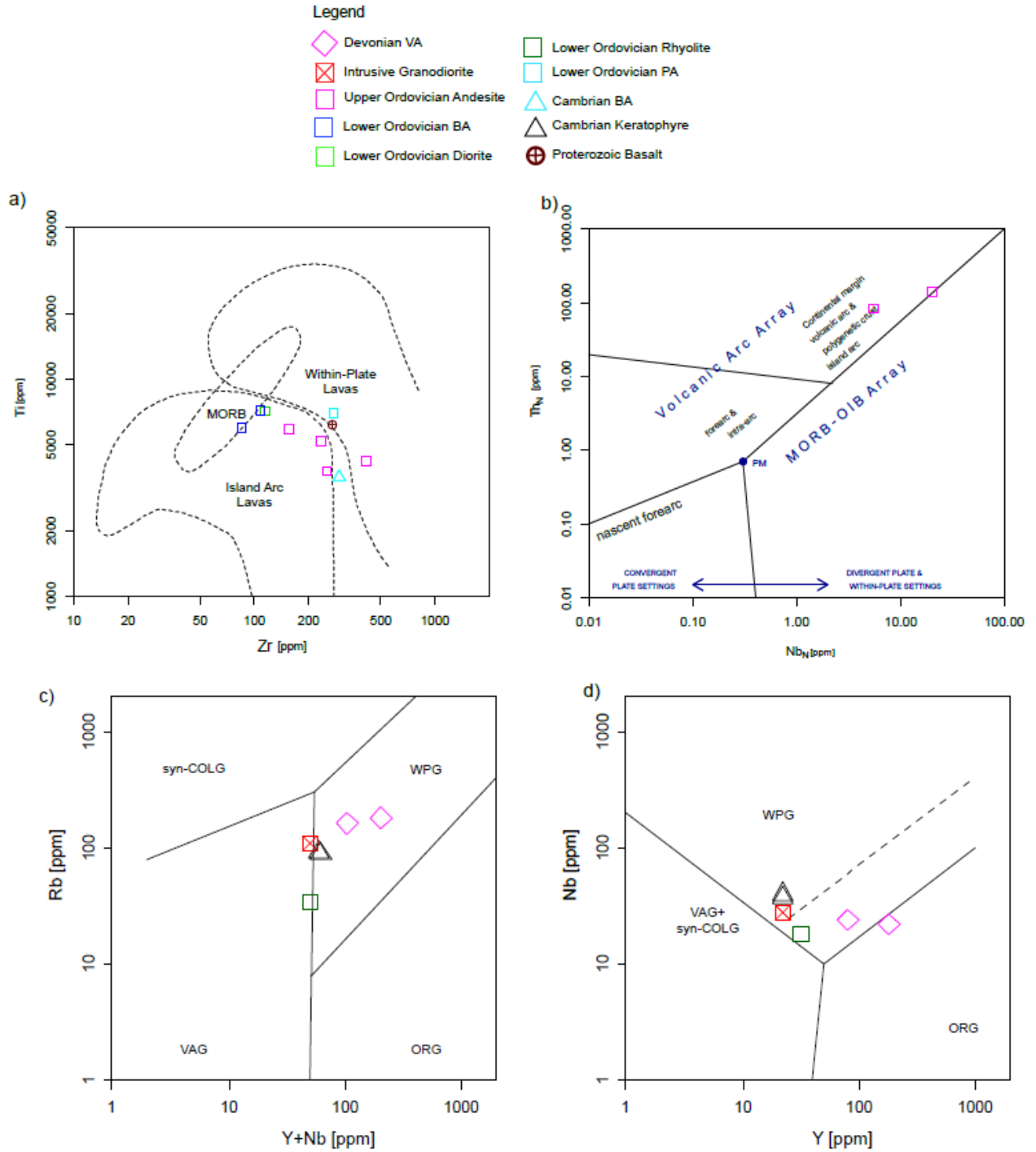


Figure 37. a) Zr vs. Ti (Pearce, 1982); b) Th [N] vs. Nb [N] (Saccani, 2015); c) Y+Nb vs. Rb (Pearce et al., 1984); d) Y vs. Nb (Pearce et al., 1984) discrimination diagrams for the studied rocks.

In the Ti vs. Zr discrimination diagram of Pearce [1982], the upper Ordovician and Devonian rocks plot in the field of within-plate volcanics, while all others fall in the field of island

arc and MORB for mafic rocks (Figure 37a). Moreover, all rocks plot in the continental margin, volcanic arc, and island arc fields in the Th(N) vs. Nb(N) diagram (Figure 37b). The Y+Nb vs. Rb (Pearce et al., 1984) (Figure 37c) and Y vs. Nb (Pearce et al., 1984) (Figure 37d) represent tectonic discrimination diagrams for rocks with felsic composition exposed in the study area, since the limited Ta concentrations in the rocks, only these two diagrams were chosen to reveal felsic rocks tectonic discriminaiton. On the Rb versus (Y+Nb) the felsic samples plot mainly within the volcanic arc granite (VAG) and syn-collisional granite (syn – COLG) fields, however some samples extend towards within – plate granite (WPG) part (Figure 37c). The same trends are similar to the Nb versus Y diagram, where felsic rocks are in VAG + syn – COLG, with some Devonian felsic samples in the WPG part (Figure 37d).

In the OIB-normalized trace elements, there are negative anomalies of Nb and Ti (Figure 38b). In Figure 38b, the rocks show almost similar concentrations of trace elements to those of OIB; nonetheless, the studied rocks have increased amounts of Pb, Sr, Zr, and Y (Figure 38b).

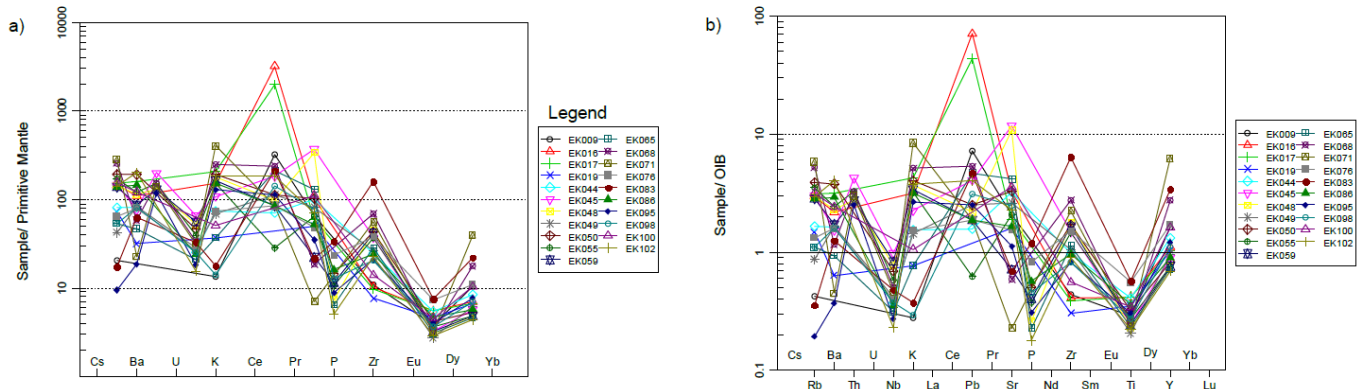


Figure 38. Primitive mantle (a) and OIB-normalized trace element patterns of the studied rocks (b). Normalizing values are after Sun and McDonough (1989)

5.0 Discussion

5.1 Transition from Mafic to Felsic from Cambrian to Devonian

The result of the study indicates that magmatism changed in space and time from mafic-intermediate (intra-oceanic subduction) (Safonova et al., 2011, 2017, 2019; Shen et al., 2015; Degtyarev et al., 2020a, b; Simonov et al., 2010) to felsic (mature arc related to the continent

formation) from the Cambrian to the Devonian (Kacielson et al., 1972). Below is the summary of evidence as seen in the petrography, mineral chemistry, and whole rock geochemistry of the rocks.

5.1.1 Petrographic evidence

Among the studied rocks, the keratophyric rocks (Na-rich rocks) of Cambrian age (samples EK048/25, EK049/25, and EK059/50) are the oldest volcanic rocks (Figure 20). These volcanic rocks were formed during the early stage of the IA formation because of the intra-oceanic subduction because of the low-degree partial melting of the Na-metasomatized depleted mantle as observed by Chakraborty et al (2021). The magmatism changed to a more mafic composition in the lower Ordovician as evidenced by the basaltic compositions of EK016/25 and EK017/25. In the lower to middle Ordovician, the volcanic composition shifted to mafic-intermediate, as indicated by the basaltic andesitic compositions of the rocks (EK019/15, EK096/25, EK100/25, and EK102/25) (Figures 22 - 25). Besides, some minor volcanoclastic rocks are also observed where the clasts are mainly made up of basalt (EK044/25). Then the magmatism shifted towards intermediate during the upper Ordovician as demonstrated by the andesites (EK045a/25) and some volcanoclastic rocks (EK096/25) with pl, hbl, and lithic clasts. The Devonian volcanism is completely different from those earlier as recorded by the appearance of felsic lavas (dacite to rhyolite (EK071/25) and rhyolite (EK068/25), with minor intermediate rocks that are also mostly aphyric as well as contain some amygdules (EK083/25) (Figure 26a). The clasts in the Devonian volcanoclastic rocks are represented by andesites (EK065/25). It is important to note that while changing the volcanic environment from oceanic (Ordovician) to continental (Devonian), there were minor intrusives in the area (e.g., granodiorite porphyry EK009/25 and EK055/25) during the Silurian (Figure 28); however, these intrusions are present as satellite bodies. Hence, petrographic studies show the more evolved rock types with time, which I relate to the maturity of the arc formation rather than cause by differentiation. Nonetheless, the change of mafic- to intermediate composition of volcanic rocks from Lower to Upper Ordovician can be due to differentiation in the chamber, as suggested by Nicholls and Ringwood (1972).

5.1.2 Evidence from mineral chemistry

The increased whole-rock silica content and the albite-rich plagioclase in Cambrian volcanics are consistent with the finding that they are keratophyre; however, the silica content and petrography do not support the idea that they are quartz keratophyre (Table A1). The pyroxene composition from the Lower Ordovician rocks (EK095/25) is richer in Mg than the Px composition from the middle Ordovician rocks that support a shift from mafic to more evolved magma composition from the Lower to Middle-Upper Ordovician (Figure 30). The Silurian (EK055/25) granodiorite porphyry, having quartz and K-feldspar, is richer in silica, and the plagioclase has an albitic composition. The chloritization of the Hbl supports extensive hydrothermal alteration (Figure 31). Presence of Kfs in the Devonian rocks (Figure 29) supports that the magmatism shifted towards felsic, supporting a shift towards matured arc as also indicated by petrography of rocks.

5.1.3 Evidence from Geochemistry

The Zr/TiO₂ vs. Nb/Y diagram (Winchester and Floyd, 1977) (Figure 33c) additionally demonstrates a compositional evolution from basaltic andesite and andesite compositions toward dacite, rhyodacite and rhyolite compositions. Cambrian and Lower Ordovician rocks are mainly basaltic andesite to andesite, while Devonian samples extent into more felsic compositions. The given trend may reflect continued fractional crystallization, crustal assimilation and increasing arc maturity during the magmatic evolution.

The shift of the tholeiitic to calc-alkaline trend of the studied rocks on the AFM diagram of Irvine and Baragar (1971) (Figures 34a and 34a')—the relatively younger samples being calc-alkaline is assumed to be due to the maturity of the arc (Tanuichi et al., 2020; Eichelberger, 1975). The similar trend is also observed in the SiO₂-FeO_t/MgO diagram (Miyashiro, 1974) (Figure 37b'). The composition variation of the investigated rocks is also further seen in the SiO₂-K₂O diagram (Peccerillo & Taylor, 1976) (Figures 34c and 34c'). The range includes low-K tholeiitic, medium-K calc-alkaline, and high-K calc-alkaline, with some specimens even having the shoshonitic character. Such an occurrence of high-K in young rocks may also indicate arc maturity (Figure 34c').

The Zr versus trace elements variation diagrams (Figure 36) also demonstrate progressive magma differentiation and compositional evolution of the rocks. Such compatible elements as Cr

and Ni mainly decrease with increasing Zr, reflecting fractional crystallization of mafic minerals, including clinopyroxene and amphibole during magma evolution. Whereas incompatible elements such as Rb, Nb, Th and Y reveal increasing trends with increasing Zr concentrations, indicating progressive enrichment of evolved melts, particularly in Devonian felsic volcanic rocks.

The negative anomaly of Ta and Ti in the normalized trace element plots with a slight elevated concentration of LILE (Figure 38) indicates the subduction-related origin of the studied rocks, which is also supported by the tectonic discrimination diagrams (Figures 37). However, there are several geochemical points that also support the change of oceanic arc to continental margin (arc maturity), as discussed below. Similarly, the felsic rocks plot dominantly within the volcanic arc granite (VAG) and syn – collisional granite (syn – COLG) on the (Pearce et al., (1984) (Figure 37c and d) supporting the interpretation of evolved calc-alkaline arc magmatism associated with progressive continental arc development.

6. Conclusion

The study investigated the petrography, mineral chemistry, and whole-rock geochemical composition of volcanic rocks from the Ekibastuz–Bozshakol study area, in central Kazakhstan. The studied volcanic successions range in age from the Cambrian to the Devonian, including basalts, basaltic andesites, andesites, volcanoclastic rocks, and felsic volcanic rocks (dacite and rhyolite). This study constrains their petrogenesis and tectonic settings within the Central Asian Orogenic Belt (CAOB).

Based on the petrographic observations Cambrian rocks have mainly porphyritic texture and are dominated by plagioclase phenocrysts and pl-rich microlitic groundmass. Mafic minerals such as hornblende and clinopyroxene are almost absent although few chloritized hornblendes are observed. These rocks are altered in some extent, e.g., there is sericitization of plagioclase, and chloritization of mafic phases. The Lower Ordovician rocks are represented by porphyritic basalts with clinopyroxene and plagioclase abundant phenocrysts with preserved ophitic textures. In contrast, the lower–middle Ordovician volcanic rocks have mainly basaltic andesite composition, with plagioclase, hornblende, and clinopyroxene phenocrysts. Volcanoclastic rocks are also present with basaltic and andesitic clasts. The Upper Ordovician rocks are represented by altered andesites and volcanoclastic rocks, including plagioclase and hornblende phenocrysts. Interestingly, the

Devonian rocks are characterized by more felsic composition, including dacitic to rhyolitic compositions, containing amygdules. Such petrographic features of the rocks indicate progressive change in magma composition from mafic in the Ordovician to felsic in Devonian.

Mineral chemistry provides additional constraints on magmatic evolution. The Cambrian rocks contain albite-rich plagioclase compositions, coherent with keratophyric volcanic rocks. In the Lower Ordovician rocks, high Mg contents in pyroxene composition compared with younger units suggest that these magmas are more primitive. The younger volcanic rocks show more evolved mineral assemblages and represent the evidence of hydrothermal alteration, with several samples particularly through chloritization of hornblende and alteration of mafic minerals. Silurian intrusive rocks that are represented by granodiorite porphyries with higher silica-rich magmatic compositions.

The whole-rock geochemical data confirms the subduction-related origin of the volcanic rocks. Trace elements show negative Ti and Ta anomalies with enrichment in large-ion lithophile elements (LILE); the listed geochemical patterns are the signatures of arc-related magmatism. The major elements diagrams reveal the predominantly tholeiitic to calc-alkaline magma series. The AFM diagrams by Irvine and Baragar (1971) also display the shift from tholeiitic composition in older rocks to calc-alkaline composition in younger rocks. The same trends are present in the FeO_t/MgO diagram by Miyashiro (1974). Furthermore, the compositional variations show transition from low-K tholeiitic mafic to medium-high-K calc-alkaline felsic progressively towards young in the silica vs. K₂O diagram of Peccerillo and Taylor (1976). Thus, the geochemistry of the studied rocks supports the compositional evolution of magma in subduction-related arc systems, where the area was mostly in IA setting until Silurian. The more felsic composition of Devonian rocks also indicate area was also in IA setting, however, these Devonian rocks are products of remelting of earlier magmatism as observed in Izu-Bonin arc (Heywood et al., 2020).

Hence, these studies (petrographic, mineral-chemical, and geochemical data) suggest that magmatism in the Ekibastuz region evolved through several stages from the Cambrian to the Devonian. The Cambrian rocks represent early IA magmatism, associated with intra-oceanic subduction processes. The Ordovician volcanic rocks with mafic to intermediate composition reflect the more mature IA systems. During the Devonian period, volcanic activity shifted toward

more evolved composition (dacite to rhyolite), which indicates further magmatic differentiation and more post collisional volcanic regimes.

The illustration below show the prolonged history of subduction-related magmatism within CAO B in Ekibastuz area (Figure 39).

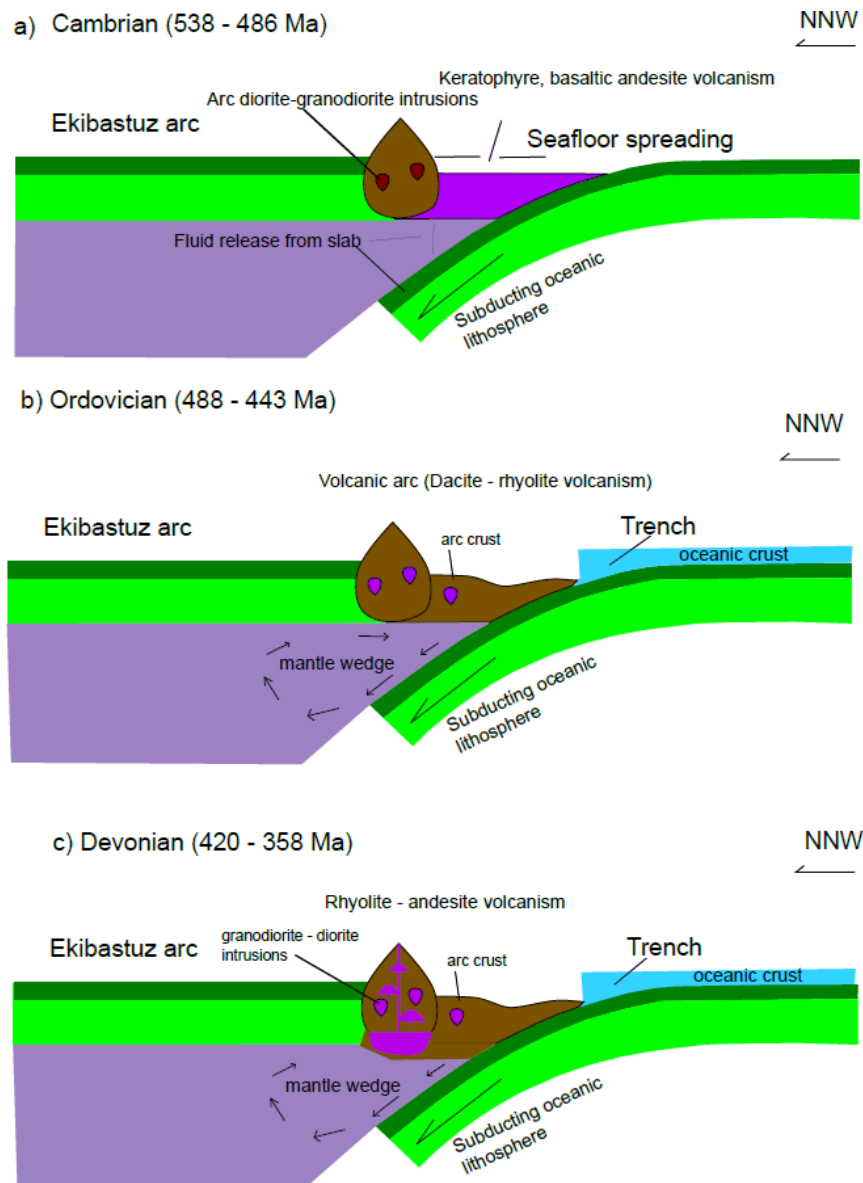


Figure 39. Schematic representation of Ekibastuz region magmatism evolution; a) initial island arc setting associated with IAO during Cambrian period; b) mature island arc with evolved composition (dacite to rhyolite); c) the eventual tectonic evolution during Devonian period, with more continental regime tectonic shifting (modified after Degtyarev et al., 2020a).

7. Recommendations

Since the current studies in this research has limitations, there are certain recommendations for future study e.g., more robust geochemical data, including inductive coupled plasma spectrometry (ICP-MS and/or ICP-OES). The use of such geochemical approaches would enhance geochemical datasets, including more precise trace elements and rare earth elements (REE). The further interpretation of these datasets will expand the understanding of the study area's tectonic settings. Moreover, the radiometric age dating (e.g., U-Pb zircon dating) and isotopic analysis (e.g., Sr-Nd-Pb isotopes) were not performed in this study; such investigations will further enhance the understanding of the study area, contributing to the studies of the CAO B and arc magmatism in the Ekibastuz-Bozshakol study area.

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9. Appendices

Appendix A: Mineral chemical composition of feldspars obtained using SEM-EDS

Table A1: SEM-EDS feldspars composition for EK100/25

Sam ple	SiO ₂ [wt %]	TiO ₂ [wt %]	Al ₂ O ₃ [wt %]	Cr ₂ O ₃ [wt %]	FeO _t [wt %]	Mn O [wt %]	Mg O [wt %]	CaO [wt %]	Na ₂ O [wt %]	K ₂ O [wt %]	P ₂ O ₅ [wt %]	Ab [mol %]	An [mol %]	Or [mol %]
EK1 00/2 5 rim	63.6 9	0.14	21.4 1	-	0.65	-	0.28	3.31	7.29	3.23	-	64.8	16.3	18.9
EK1 00/2 5 grou ndm ass	62.3 1	1.64	19.6 8	0.11	0.59	0.04	0.35	3.74	9.64	1.14	0.76	77.4	16.6	6
EK1 00/2 5 rim	60.6 7	0.11	19.3 8	-	4.04	0.17	3.99	2	8.66	0.98	-	83.2	10.6	6.2

EK100/25 groundmass	62.1	0.09	23.23	0.03	0.48	-	0.24	7.51	4.43	1.89	-	45.1	42.2	12.7
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Table A2. SEM-EDS plagioclase composition for EK017/25

Sample	SiO ₂ [wt %]	TiO ₂ [wt %]	Al ₂ O ₃ [wt %]	Cr ₂ O ₃ [wt %]	FeO _T [wt %]	MnO [wt %]	MgO [wt %]	CaO [wt %]	Na ₂ O [wt %]	K ₂ O [wt %]	P ₂ O ₅ [wt %]	Ab [mol %]	An [mol %]	Or [mol %]
EK017/25 rim	66.84	0.04	20.36	-	0.09	0.07	-	0.82	11.68	0.11	-	95.7	3.7	0.6
EK017/25 core	66.75	-	19.7	0.03	1.08	-	0.59	0.48	11.15	0.23	-	96.4	2.3	1.3
EK017/25 rim	66.38	0.03	20.31	-	0.31	0.15	0.14	0.58	11.82	0.27	-	96	2.6	1.4
EK017/25 rim	63.67	0.16	20	0.08	1.96	-	1.63	1.15	10.9	0.15	0.3	93.7	5.5	0.8
EK017/25 core	67.66	0.1	19.61	-	0.06	0.01	0.06	0.2	12.2	0.09	-	98.6	0.9	0.5
EK017/25 rim	52.92	0.37	20.17	-	8.72	0.76	7.34	0.91	5.69	2.8	0.32	70.813	6.258	22.928

Table A3. SEM-EDS feldspars composition for EK055/25

Sample	SiO ₂ [wt %]	TiO ₂ [wt %]	Al ₂ O ₃ [wt %]	Cr ₂ O ₃ [wt %]	FeO _T [wt %]	MnO [wt %]	MgO [wt %]	CaO [wt %]	Na ₂ O [wt %]	K ₂ O [wt %]	P ₂ O ₅ [wt %]	Ab [mol %]	An [mol %]	Or [mol %]
EK055/27	66.67	0.1	20.38	0.08	0.08	-	-	0.95	11.54	0.18	0.02	94.7	4.3	1

5 core														
EK0 55/2 5 core	65.9 5	0.01	20.8 7	0.01	0.09	0.08	0.02	0.85	11.5 5	0.35	0.22	94.3	3.8	1.9
EK0 55/2 5 core	66.7 5	0.08	20.4 4	-	0.13	-	-	1.1	11.3 9	0.11	-	94.4	5	0.6
EK0 55/2 5 rim	69.2 4	-	18.5 6	-	0.06	-	-	0.46	10.9 6	0.72	-	93.8	2.2	4.1
EK0 55/2 5 rim	64.3 2	0.28	17.7 3	-	0.09	0.01	0.18	0.48	0.62	16.0 6	0.24	5.4	2.3	92.2

Table A4. SEM-EDS feldspars composition for EK071/25

Sam ple	SiO2 [wt %]	TiO 2 [wt %]	Al2 O3 [wt %]	Cr2 O3 [wt %]	FeOt [wt %]	Mn O [wt %]	Mg O [wt %]	CaO [wt %]	Na2 O [wt %]	K2O [wt %]	P2O 5 [wt %]	Ab [mol %]	An [mol %]	Or [mol %]
EK0 71/2 5 core	69.3 5	0.34	15.5 3	-	0.29	0.05	-	0.07	1.02	13.3 5	-	10.4	0.4	89.2
EK0 71/2 5 core	66.4	-	17.2 9	-	0.03	0.13	-	0.15	0.47	15.5 4	-	4.4	0.8	94.9
EK0 71/2 5 core	74.2	0.09	13.3 6	0.06	0.09	0.32	-	0.23	0.78	10.7 5	0.12	9.8	1.6	88.6
EK0 71/2 5 core	73.8 1	0.23	12.3 1	-	2.06	-	-	0.5	0.57	10.2 3	0.31	7.5	3.6	88.8
EK0 71/2 5 grou	67.7 5	0.23	16.3 5	0.2	0.79	-	0.02	0.03	0.3	14.3 3	-	3.1	0.2	96.8

ndm ass														
EK0 71/2 5 grou ndm ass	66.6 1	0.22	17.0 5	0.2	0.37	-	-	0.1	0.6	14.8 5	-	5.8	0.5	93.7

Table A5. SEM-EDS feldspars composition for EK045a/25

Sam ple	SiO2 [wt %]	TiO 2 [wt %]	Al2 O3 [wt %]	Cr2 O3 [wt %]	FeOt [wt %]	Mn O [wt %]	Mg O [wt %]	CaO [wt %]	Na2 O [wt %]	K2O [wt %]	P2O 5 [wt %]	Ab [mol %]	An [mol %]	Or [mol %]
EK0 45/2 5 core	64.8 5	0.01	22.0 5	-	0.31	0.01	0.14	0.14	10.8 4	1.37	0.28	91.7	0.7	7.6
EK0 45/2 5 rim	60.1 5	-	25.4 9	-	0.89	0.05	0.35	0.05	8.01	4.7	0.31	72	0.2	27.8
EK0 45/2 5 core	53.7 7	0.03	27	0.02	1.39	0.1	0.64	7.34	3.8	5.69	0.23	32.8	35	32.3
EK0 45/2 5 rim	63.5 9	0.04	23.1 5	0.03	0.55	0.01	0.33	0.76	9.59	1.74	0.21	86	3.8	10.3
EK0 45/2 5 rim	75.2 5	0.27	13.8 3	-	1.37	0.11	1.16	0.21	7.43	0.23	0.15	96.5	1.5	2
EK0 45/2 5 rim	62.1 3	0.02	20.2 2	0.06	3.11	-	1.78	1.91	10.2 5	0.35	0.16	88.9	9.1	2
EK0 45/2 5 core	55.6 1	0.13	29.6 5	0.02	1.81	-	0.86	0.13	3.97	7.46	0.37	44.4	0.8	54.8
EK0 45/2 6	61.1 6	0.06	24.8 2	-	0.97	-	0.37	0.3	7.78	4.27	0.27	72.3	1.5	26.1

5 rim														
EK0 45/2 5 rim	72.2 8	0.05	18.1	0.01	1.57	0.03	1.18	0.1	2.76	3.71	0.22	52.5	1.1	46.4
EK0 45/2 5 core	59.3	0.07	27.3 9	-	0.88	-	0.37	0.12	6.37	5.22	0.28	64.5	0.7	34.8
EK0 45/2 5 rim	62.1 3	0.02	20.2 2	0.06	3.11	-	1.78	1.91	10.2 5	0.35	0.16	88.9	9.1	2
EK0 45/2 5 core	55.6 1	0.13	29.6 5	0.02	1.81	-	0.86	0.13	3.97	7.46	0.37	44.4	0.8	54.8
EK0 45/2 5 rim	61.1 6	0.06	24.8 2	-	0.97	-	0.37	0.3	7.78	4.27	0.27	72.3	1.5	26.1
EK0 45/2 5 rim	72.2 8	0.05	18.1	0.01	1.57	0.03	1.18	0.1	2.76	3.71	0.22	52.5	1.1	46.4
EK0 45/2 5 core	59.3	0.07	27.3 9	-	0.88	-	0.37	0.12	6.37	5.22	0.28	64.5	0.7	34.8

Table A6. SEM-EDS feldspars composition for EK096/25

Sam ple	SiO2 [wt %]	TiO 2 [wt %]	Al2 O3 [wt %]	Cr2 O3 [wt %]	FeOt [wt %]	Mn O [wt %]	Mg O [wt %]	CaO [wt %]	Na2 O [wt %]	K2O [wt %]	P2O 5 [wt %]	Ab [mol %]	An [mol %]	Or [mol %]
EK0 96/2 5 core	67.2 3	-	20.0 1	-	0.11	0.01	0.04	0.61	11.6	0.17	0.22	96.3	2.8	0.9
EK0 96/2 5 core	61.5 6	0.01	24.4 6	0.01	0.2	0.05	0.3	2.09	8.56	2.43	0.32	75.7	10.2	14.1

EK0 96/2 5 core	78.5 6	-	12.6 8	0.05	0.14	0.03	0.26	0.68	7.01	0.06	0.53	94.4	5.1	0.5
EK0 96/2 5 core	63.0 9	0.03	23.5 4	0.02	0.04	-	-	1.53	9.85	1.64	0.27	83.7	7.2	9.2
EK0 96/2 5 rim	60.5 2	0.02	23.5 3	-	2.32	0.03	0.97	1.68	6.76	3.85	0.32	66.1	9	24.7
EK0 96/2 5 rim	60.5 2	0.02	23.5 3	-	2.32	0.03	0.97	1.68 0	6.76	3.85	0.32	66.1	9	24.7

Table A7. SEM-EDS feldspars composition for EK102/25

Sam ple	SiO2 [wt %]	TiO 2 [wt %]	Al2 O3 [wt %]	Cr2 O3 [wt %]	FeOt [wt %]	Mn O [wt %]	Mg O [wt %]	CaO [wt %]	Na2 O [wt %]	K2O [wt %]	P2O 5 [wt %]	Ab [mol %]	An [mol %]	Or [mol %]
EK1 02/2 5 rim	64.9 1	0.07	21.4 9	-	0.46	-	0.1	0.84	9.37	2.63	0.13	81	4	15
EK1 02/2 5 core	65.6 7	-	20.7 3	0.07	0.03	-	-	1.8	11.3 8	-	0.31	92	8	0
EK1 02/2 5 rim	65.4 4	0.01	20.7 6	-	0.12	0.76	0.08	0.76	11.2	0.5	0.37	93.7	3.5	2.8
EK1 02/2 5 grou ndm ass	61.9 3	0.05	25.7 3	0.05	0.49	0.03	0.24	0.57	7.43	3.2	0.29	75.4	3.2	21.4
EK1 02/2 5 core	58.2 5	0.05	25.4 8	0.03	0.66	0.02	0.16	5.45	7.73	1.97	0.2	64.2	25	10.8

EK1 02/2 5 core	62.0 3	0.1	23.6 1	-	0.61	0.03	0.35	0.82	4.36	8	0.09	43.2	4.5	52.2
EK1 02/2 5 core	62.0 3	0.1	23.6 1	-	0.61	0.03	0.35	0.82	4.36	8	0.09	43.3	4.5	52.2

Appendix B: Mineral chemical composition of pyroxenes obtained using SEM-EDS

Table B1. SEM-EDS pyroxene composition for EK100/25

Sam ple	SiO ₂ [wt %]	TiO ₂ [wt %]	Al ₂ O ₃ [wt %]	Cr ₂ O ₃ [wt %]	FeO _t [wt %]	Mn O [wt %]	Mg O [wt %]	CaO [wt %]	Na ₂ O [wt %]	K ₂ O [wt %]	P ₂ O ₅ [wt %]	Wo [mol %]	En [mol %]	Fs [mol %]
EK1 00/2 5 core	53.5	0.29	2.98	0.33	4.78	0.4	16.8 3	20.1	0.67	0.09	-	42.5	49.6	7.9
EK1 00/2 5 core	53.2 5	0.63	2.21	0.08	7.26	0.4	14.8 7	20.3 3	0.79	0.18	-	43.5	44.3	12.1
EK1 00/2 5 core	53.1	0.25	2.96	0.26	6.61	0.4	15.6 3	19.9 1	0.8	0.08	-	42.5	46.5	11
EK1 00/2 5 core	53.9 8	0.18	2.32	0.65	7.02	0.41	15.1	19.8	0.54	-	-	42.8	45.4	11.8
EK1 00/2 5 rim	53.3 4	0.23	2.98	0.01	6.6	0.28	16.1 2	19.8 8	0.45	-	0.11	41.9	47.3	10.9
EK1 00/2 5 core	54.6 7	0.45	2.62	0.04	7.02	0.4	15.1 2	18.8 3	0.76	0.07	-	41.5	46.4	12.1
EK1 00/2 5	52.2 7	0.66	3.13	-	8.73	0.47	14.7 4	19.5 9	0.41	-	-	41.8	43.7	14.5

core														
EK100/25 core	53.65	0.16	1.99	0.05	7.76	0.37	15.99	19.51	0.34	0.07	0.12	40.8	46.5	12.7
EK100/25 core	51.37	0.52	2.47	0.09	9.17	0.37	13.6	21.73	0.46	0.07	0.14	45.5	39.6	15

Table B2. SEM-EDS pyroxene composition for EK017/25

Sample	SiO ₂ [wt %]	TiO ₂ [wt %]	Al ₂ O ₃ [wt %]	Cr ₂ O ₃ [wt %]	FeO _t [wt %]	MnO [wt %]	MgO [wt %]	CaO [wt %]	Na ₂ O [wt %]	K ₂ O [wt %]	P ₂ O ₅ [wt %]	Wo [mol %]	En [mol %]	Fs [mol %]
EK017/25 rim	53.18	0.8	2.96	-	7.93	0.39	14.07	20.1	0.57	-	-	43.8	42.7	13.5
EK017/25 core	51.21	0.81	2.59	-	9.18	0.35	12	23.18	0.51	0.1	0.06	43.8	42.7	13.5
EK017/25 rim	50.99	0.97	3.98	0.04	9.23	0.3	13.6	20.53	0.21	0.07	0.08	49.3	35.5	15.2
EK017/25 core	51.02	0.71	3.31	-	8.24	0.36	13.55	21.74	0.9	0.12	0.06	44	40.6	15.4
EK017/25 rim	51.36	0.61	3.52	-	8.63	0.34	13.6	21.11	0.75	0.07	-	46.2	40.1	13.7
EK017/25 core	49.13	1	3.19	0.05	10.16	0.56	12.14	23.33	0.42	0.04	-	45.1	40.5	14.4
EK017/25 core	51.79	0.67	3.26	0.09	8.27	0.29	13.87	21.5	0.23	0.04	-	48.5	35.1	16.5

EK0 17/2 5 grou ndm ass	51.6 5	0.68	3.54	0.05	8.84	0.1	13.5 3	21.1 2	0.42	0.05	0.03	45.5	40.8	13.7
EK0 17/2 5 core	42.1 4	11.8 5	9.71	-	8.01	0.45	9.38	18.4 6	0.01	-	-	45.1	40.2	14.7
EK0 17/2 5 rim	43.0 4	0.04	16.9 3	-	15.4 7	1.54	18.2 1	4.23	0.38	0.15	-	48.9	34.6	16.6
EK0 17/2 5 rim	32.6	-	22.3	-	24.3 1	2.17	18	0.5	0.09	0.03	-	10.2	60.8	29

Table B3. SEM-EDS pyroxene composition for EK055/25

Sam ple	SiO2 [wt %]	TiO 2 [wt %]	Al2 O3 [wt %]	Cr2 O3 [wt %]	FeOt [wt %]	Mn O [wt %]	Mg O [wt %]	CaO [wt %]	Na2 O [wt %]	K2O [wt %]	P2O 5 [wt %]	Wo [mol %]	En [mol %]	Fs [mol %]
EK0 55/2 5 core	33.5 2	0.1	21.4 2	0.11	22.6 9	1.03	20.2 5	0.22	0.48	0.18	-	0.48	61.1 1	38.4 1
EK0 55/2 5 core	34.5 1	0.16	23.3 6	-	19.4 5	0.37	21.7 6	0.07	0.11	0.14	0.07	0.15	66.5 0	33.3 5
EK0 55/2 5 core	33.7 4	0.15	22.4 1	-	24.7 7	0.9	18.7 4	0.18	0.14	-	0.07	0.39	57.2 0	42.4 1

Table B4. SEM-EDS pyroxene composition for EK096/25

Sam ple	SiO2 [wt %]	TiO 2 [wt %]	Al2 O3 [wt %]	Cr2 O3 [wt %]	FeOt [wt %]	Mn O [wt %]	Mg O [wt %]	CaO [wt %]	Na2 O [wt %]	K2O [wt %]	P2O 5 [wt %]	Wo [mol %]	En [mol %]	Fs [mol %]
EK0 95/2 5	51.5 2	1.45	9.38	0.1	8.56	0.59	16.6 3	9.63	1.66	1.66	0.07	24.4	58.7	16.9

core														
EK095/25 core	57.17	3.67	16.86	0.07	7.37	0.06	1.12	4.75	8.38	8.38	0.02	39.4	12.9	47.7
EK095/25 core	3.67	2.33	8.94	0.08	9.74	0.31	15.84	10.88	2.18	2.18	0.21	26.8	54.4	18.8

Table B5: Values for cation calculation and XMg for pyroxenes

Sample	Position	SiO ₂ (wt%)	FeOt (wt%)	MgO (wt%)	XMg
EK100/25	core	53.50	4.78	16.83	0.86
EK100/25	core	53.25	7.26	14.87	0.78
EK100/25	core	53.10	6.61	15.63	0.81
EK100/25	core	53.98	7.02	15.10	0.80
EK100/25	rim	53.34	6.60	16.12	0.83
EK100/25	core	54.67	7.02	15.12	0.80
EK100/25	core	52.27	8.73	14.74	0.75
EK100/25	core	53.65	7.76	15.99	0.79
EK100/25	core	51.37	9.17	13.60	0.72
EK017/25	rim	53.18	7.93	14.07	0.76
EK017/25	core	51.21	9.18	12.00	0.70
EK017/25	rim	50.99	9.23	13.60	0.74
EK017/25	core	51.02	8.24	13.55	0.77
EK017/25	rim	51.36	8.63	13.60	0.76
EK017/25	core	49.13	10.16	12.14	0.68
EK017/25	core	51.79	8.27	13.87	0.78
EK017/25	groundmass	51.65	8.84	13.53	0.75
EK017/25	core	42.14	8.01	9.38	0.68
EK017/25	rim	43.04	15.47	18.21	0.73
EK017/25	rim	32.60	24.31	18.00	0.57
EK055/25	core	33.52	22.69	20.25	0.61
EK055/25	core	34.51	19.45	21.76	0.67
EK055/25	core	33.74	24.77	18.74	0.57
EK095/25	core	51.52	8.56	16.63	0.78
EK095/25	core	57.17	7.37	1.12	0.21
EK095/25	core	3.67	9.74	15.84	0.74

Appendix C: Mineral chemical composition of amphibole obtained using SEM-EDS

Table C1. SEM-EDS amphibole composition for EK100/25

Sample	SiO ₂ [wt%]	TiO ₂ [wt%]	Al ₂ O ₃ [wt%]	Cr ₂ O ₃ [wt%]	FeOt [wt%]	MnO [wt%]	MgO [wt%]	CaO [wt%]	Na ₂ O [wt%]	K ₂ O [wt%]	P ₂ O ₅ [wt%]

EK10 0/25 rim	46.71	0.1	11.04	0.06	15.29	0.43	17.48	8.44	0.34	0.11	-
EK10 0/25 core	43.77	0.35	11.08	-	10.76	0.55	14.36	8.70	4.80	1.42	0.15
EK10 0/25 rim	46.57	0.26	7.2	-	10.97	0.47	16.43	13.44	0.45	0.17	-
EK10 0/25 core	43.16	1.75	11.59	0.009	11.67	0.07	13.40	11.02	2.63	0.67	-
EK10 0/25 rim	42.28	2.88	11.51	0.08	11.89	0.14	13.01	10.74	2.50	0.7	0.22
EK10 0/25 rim	42.99	0.08	16.49	-	8.87	0.45	10.3	8.43	4.13	1.47	3.02
EK10 0/25 rim	42.86	1.67	11.67	-	11.84	0.27	13.22	11.13	2.61	0.69	-
EK10 0/25 core	43.04	2.26	11.16	-	12.07	0.48	13.11	10.58	2.53	0.62	0.11
EK10 0/25 core	40.7	0.02	11.59	0.21	15.23	0.61	18.33	8.36	0.56	0.18	0.26

Table C2. SEM-EDS amphibole composition for EK0102/25

Sample	SiO ₂ [wt%]	TiO ₂ [wt%]	Al ₂ O ₃ [wt%]	Cr ₂ O ₃ [wt%]	FeO _t [wt%]	MnO [wt%]	MgO [wt%]	CaO [wt%]	Na ₂ O [wt%]	K ₂ O [wt%]	P ₂ O ₅ [wt%]
EK01 02/25 core	42.19	1.81	10.52	0.02	15.66	0.55	14.18	9.14	1.16	0.68	0.04
EK01 02/25 rim	47.85	0.31	11.09	0.16	10.55	0.36	1.48	21.91	0.73	1.44	0.06
EK01 02/25 core	47.37	1.67	9.16	0.07	10.74	0.37	13.99	9.84	1.99	0.64	0.11

EK01 02/25 rim	44.59	3.93	8.90	0.11	10.81	0.36	12.70	12.05	1.70	0.67	0.14
EK01 02/25 core	45.46	1.77	8.57	0.10	11.38	0.45	13.81	11.31	1.88	0.69	0.54

Table C3. Values for cation calculation and XMg for amphiboles

Sample	Position	SiO ₂ (wt%)	FeOt (wt%)	MgO (wt%)	XMg
EK100/25	rim	46.71	15.29	17.48	0.67
EK100/25	core	43.77	10.76	14.36	0.70
EK100/25	rim	46.57	10.97	16.43	0.73
EK100/25	core	43.16	11.67	13.40	0.67
EK100/25	rim	42.28	11.89	13.01	0.66
EK100/25	rim	42.99	8.87	10.30	0.67
EK100/25	rim	42.86	11.84	13.22	0.67
EK100/25	core	43.04	12.07	13.11	0.66
EK100/25	core	40.70	15.23	18.33	0.68
EK0102/25	core	42.19	15.66	14.18	0.62
EK0102/25	rim	47.85	10.55	1.48	0.20
EK0102/25	core	47.37	10.74	13.99	0.70
EK0102/25	rim	44.59	10.81	12.70	0.68
EK0102/25	core	45.46	11.38	13.81	0.68

Appendix D: Mineral chemical composition of mica obtained using SEM-EDS

Table D1. SEM-EDS mica composition for EK045a/25

Sam ple	SiO ₂ [wt %]	TiO ₂ [wt %]	Al ₂ O ₃ [wt %]	Cr ₂ O ₃ [wt %]	FeOt [wt %]	Mn O [wt %]	Mg O [wt %]	CaO [wt %]	Na ₂ O [wt %]	K ₂ O [wt %]	P ₂ O ₅ [wt %]	Phlo gopit e [mol %]	Side roph yllite [mol %]	Anni te [mol %]
EK0 45a/ 25 core	63.1 5	-	18.4 7	0.05	8.87	0.05	4.64	0.23	1.54	2.85	0.16	0.48	0.03	0.49

Appendix E: Whole-rock chemical composition from XRF analysis in C4

Table E1. Whole-rock major oxides composition in XRF C4 data measurements

Sample	SiO ₂ [wt%]	Al ₂ O ₃ [wt%]	Fe ₂ O ₃ [wt%]	MgO [wt%]	CaO [wt%]	Na ₂ O [wt%]	K ₂ O [wt%]	N ₂ O+K 2O [wt%]	TiO ₂ [wt%]	P ₂ O ₅ [wt%]	LOI
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EK016	55.27	15.15	13.42	4.95	7.70	2.10	3.48	5.58	0.95	0	3.9
BCR-2	55.06	12.54	16.48	2.49	7.23	2.29	1.79	4.08	2.31	0	5.9
EK017	54.57	13.78	10.99	3.61	10.96	2.74	5.20	7.94	0.94	0	3.7
EK019	52.46	12.83	14.62	6.11	12.12	1.60	0.76	2.36	0.74	0	2.8
EK044	63.75	15.87	9.41	2.52	4.55	3.75	1.79	5.54	1.02	0	3.2
EK045a	71.49	14.51	6.81	1.78	9.06	2.79	2.80	5.59	0.53	0	8.6
EK048	71.42	14.78	3.47	0.78	0.57	4.65	3.68	8.33	0.53	0	2.0
EK049	67.59	14.02	8.19	3.00	7.17	1.69	1.40	3.09	0.46	0	3.8
EK049 D	63.82	13.36	7.89	2.87	6.91	1.83	1.45	3.28	0.47	0	3.8
EK055	72.58	14.66	4.23	1.07	2.09	4.00	3.27	7.27	0.57	0	2.9
EK068	78.17	11.27	2.02	0.16	0.26	2.11	4.65	6.76	0.57	0	1.6
EK071	76.61	10.50	2.68	0.00	0.16	0.32	8.08	8.39	0.51	0	1.3
EK086	55.00	16.74	14.97	3.56	6.71	2.56	3.65	6.21	0.85	0	4.6
EK098	70.21	14.34	4.83	0.64	1.74	6.04	0.39	6.43	0.71	0	1.7
EK098 D	71.32	14.62	4.49	0.58	1.66	5.60	0.40	6.00	0.65	0	1.7

Table E2. Precision procedure for duplicated samples for fused glass beads XRF (C4)

Sample	SiO ₂ [wt%]	Al ₂ O ₃ [wt%]	Fe ₂ O ₃ [wt%]	MgO [wt%]	CaO [wt%]	Na ₂ O [wt%]	K ₂ O [wt%]	TiO ₂ [wt%]	P ₂ O ₅ [wt%]
EK049/25D	2.86	1.95	0.83	1.66	0.86	-11.51	-6.27	-5.72	0
EK098/25D	-3.82	-4.24	5.09	6.28	2.49	5.24	-4.13	5.65	0

Appendix F: Whole-rock chemical composition from XRF analysis in Block 6

Table F1. Whole-rock major oxides composition in XRF block 6 data measurements

Sample	SiO ₂ [wt%]	Al ₂ O ₃ [wt%]	Fe ₂ O ₃ [wt%]	MgO [wt%]	CaO [wt%]	Na ₂ O [wt%]	K ₂ O [wt%]	TiO ₂ [wt%]	P ₂ O ₅ [wt%]	AI	CCPI
EK009/25	59.81	13.5	11.22	1.28	10.72	1.18	0.4	0.83		12.37	87.80
EK016/25	44.81	15.13	16.74	5.82	9.45	1.1	4.61	1.19		49.71	78.53
EK017/25	46.81	14	12.71	3.81	13.09	1.06	6.18	1.2		41.38	67.80
EK019/25	43.86	11.79	18.79	6.88	14.56	0.86	1.11	1		34.13	92.35
EK044/25	56.52	15.91	12.36	3.06	5.94	1.93	2.23	1.17		40.20	77.32
EK045/25	56.73	15.21	8.86	2.01	11.52	1.07	3.25	0.7		29.47	69.79
EK048/25	68.61	15.77	4.7	0.9	0.78	2.52	5.35	0.65	0.16	65.45	39.46
EK049/25	57.41	13.84	11.05	4.89	8.54	0.85	2.07	0.59		42.57	83.55
EK050/25	61.66	15.63	6.42	1.63	4.85	2.02	5.8	0.91	0.31	51.96	48.64
EK055/25	64.67	15.68	5.62	1.85	3.65	2.29	4.62	0.78	0.23	52.14	49.99
EK059/25	68.54	16.76	4.59	0.71	0.64	2.55	4.87	0.7	0.25	63.63	39.48
EK065/25	64.27	16.72	6.8	3.62	3.13	2.79	1.11	0.67	0.14	44.41	71.40
EK068/25	75.06	12.21	2.68	0.17		1.34	7.4	0.72		84.96	22.80
EK071/25	71.73	11.29	3.54				12.17	0.7		100.00	20.74
EK076/25	53.19	16.09	11.79	3.08	9.12	1.62	2.21	1.6	0.51	33.00	78.14
EK083/25	65.7	14.64	10.26		2.2	3.58	0.54	1.64	0.73	8.54	69.14
EK086/25	44.36	16.23	18.49	4.46	8.23	1.18	4.58	1.03	0.35	49.00	78.55
EK095/25	62.15	16.53	7.44	1.38	5.37	1.62	3.85	0.87	0.19	42.80	59.61
EK098/25	69.82	15.69	5.69	0.79	2.26	3.87	0.42	0.78	0.28	16.49	57.94
EK100/25	55.97	16.11	10.96	4.14	7.87	1.66	1.52	0.98		37.26	81.49

EK102/25	63.87	15.03	6.86	1.8	3.71	1.75	5.49	0.63	0.11	57.18	52.41
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Table F2. Whole-rock trace elements composition in XRF block 6 data measurements

Sample	V [pp m]	Cr [pp m]	Ni [pp m]	Cu [pp m]	Zn [pp m]	Rb [pp m]	Sr [pp m]	Y [pp m]	Zr [pp m]	Nb [pp m]	Ba [pp m]	Pb [pp m]	Th [pp m]	Au [pp m]
EK009/ 25	498	15		99	537	13	138 0	47	123			23		
EK016/ 25	724	242	43	107	766	92	218 0	32	115		764	227		
EK017/ 25	668	246	33	416	476	96	126 0	30	108		111 0	140		
EK019/ 25	866	238	28	452	224	46	105 0	30	85		222			
EK044/ 25	542	626	98	100	149	51	212 0	38	275	18	567	5		
EK045/ 25	390	119	38	175	116	93	778 0	26	417	47	536	13	17	3.6
EK048/ 25	70		13	39	116	91	713 0	22	499	37	801	7	11	
EK049/ 25	418	307	44	171	133	27	172 0	28	294	20	581	8		
EK050/ 25	177	92	58	60	131	121	216 0	24	481	33	133 0	8		2.1
EK055/ 25	184	63	40	39	100	109	136 0	22	407	28	848	2	13	
EK059/ 25	64		33	34	191	88	470	22	465	40	602	6	11	
EK065/ 25	211	147	68	53	191	34	275 0	21	316	15	327	15		
EK068/ 25	50				178	162	389	80	772	24	408	17	13	
EK071/ 25					26	181	149	180	626	22	158	6	12	
EK076/ 25	413	231	95	120	142	41	102 0	50	423	19	555	6		
EK083/ 25	202		6	18	144	11	452	99	179 0	23	439	15		
EK086/ 25	218	33	152	48	121	88	109 0	26	270	17	102 0	6		
EK095/ 25	239	117	30	69	55	6	739	35	232	13	129	8	10	
EK098/ 25	488	126	27	63	137	34	163 0	32	230	18	564	10		1.5
EK100/ 25	878	82	0	373	238	98	234 0	47	156		844	0		
EK102/ 25	245			223	79	91	150 0	20	253	11	142 0	13		

Table F3. Test samples XRF Block 6 values

Sample	Na2O [wt%]	MgO [wt%]	Al2O3 [wt%]	SiO2 [wt%]	P2O5 [wt%]	CaO [wt%]	K2O [wt%]	TiO2 [wt%]
Quartz sand	-	-	0.861	98.536	-	-	-	-
EK059/25	2.552	0.708	16.756	68.536	0.251	0.642	4.868	0.700
EK059/25D	2.573	0.722	16.782	68.720	0.244	0.626	4.812	0.710

Table F4. Precision values for XRF Block 6 samples

Precision	Na2O [%]	MgO [%]	Al2O3 [%]	SiO2 [%]	P2O5 [%]	CaO [%]	K2O [%]	TiO2 [%]
EK059/25	-0.82	-1.98	-0.16	-0.27	2.79	2.49	1.15	-1.43

Appendix G: USGS “BCR-2” (Jochum et al., 2016) reference values

Table G1. Major Oxides values from Jochum et al, 2016, for reference sample “BCR-2”

Sample	Na2O [wt%]	MgO [wt%]	Al2O3 [wt%]	SiO2 [wt%]	K2O [wt%]	CaO [wt%]	TiO2 [wt%]	MnO [wt%]	Fe2O3 [wt%]
BCR-2 reference value	3.12	3.59	13.48	54	1.77	7.11	2.26	0.19	13.77
BCR-2 measured and normalize d	2.29	2.49	12.54	55.06	1.79	7.23	2.31	0.19	16.48
Accuracy	73.41	69.23	93.01	101.96	100.81	101.68	102.16	95.26	119.68

Appendix H: Supplementary geochemical diagrams

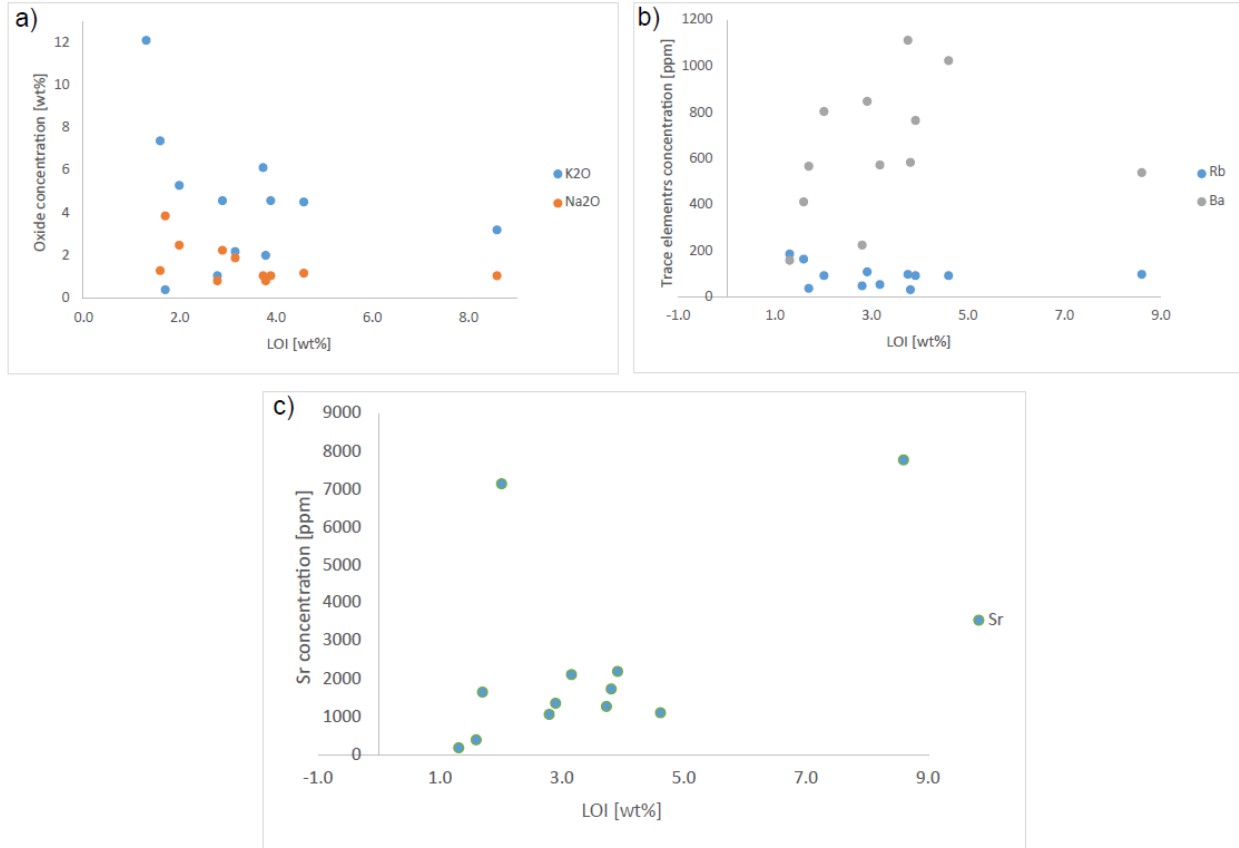


Figure H1. a) LOI [wt%] vs. selected oxides concentrations [wt%]; b) LOI [wt%] vs. Rb and Ba concentration [ppm]; c) LOI [wt%] vs. Sr concentration [ppm] to assess alteration effect of the rocks (see text for the explanation)