## 博士論文

Petrogenesis of Triassic gabbros and associated basalts from Chukotka (NE Russia): implications for eastern margin of Siberian LIP

(極東ロシア Chukotka、三畳紀はんれい岩および玄武 岩の起源~シベリア・トラップ東縁としての意義)

DESTA Minyahl Teferi

平成27年

#### SUMMARY

The PhD thesis consists of two parts and describes the comparative geochemical and petrological study of the Siberian LIP (~250 Ma) and Ethiopian LIP (~30 Ma) to consider their mantle and crustal processes in view of magmatic diversity among those LIPs. These two LIPs display contrasting high field strength elements (HFSEs) and petrographic features. The majority of the erupted low-Ti basalts of Siberian LIP are characterized by HFSE depleted trace element distribution patterns similar to island-arc-basalt, whereas the Ethiopian LIP basalts are HFSE-enriched and closly resemble OIB. Moreover, the hydrous nature of the mantle source for the Siberian LIP is evident from the presence of primary hydrous minerals such as in the gabbro, meimechite and ferropicrite rocks; however, the Ethiopian LIP is originated from anhydrous source.

The first chapter of this thesis studies the petrogenesis of Triassic gabbros and associated basalts of Chukotka, NE Russia, aming to find the eastern marginal extension of Siberian LIP. Our findings also provide additional constraints for the much debated origin of the Arctic Alaska-Chukotka microplate (AACM). We have identified two types of mafic rocks in this study, i.e. island-arc basalt (IAB)-type amphibole bearing gabbros (such as pyroxene-hornblende gabbro, hornblende gabbro, hornblende-pyroxene gabbro) and basalts (with ankaramites, pyroxene-phyric basalt, lamprophyre, and basaltic andesites sub-type) and OIB-type gabbros (include rare to no amphiboles). These gabbroic and associated basaltic rocks are mainly thoiliitic with both intra-plate and islandarc basalt geochemical features. In the primitive mantle normalized trace element patterns, IAB-type gabbroic and basaltic rocks are characterized by depletion in HFSE (Nb, Ta, Zr and Hf) and enrichment in LILE, and resemble arc-type igneous rocks. OIB-type gabbroic rocks can be distinguished from the rest of the studied samples by the absence of HFSE depletion, but show strong negative Sr anomalies. The positive Ti anomaly in the OIB-type gabbros can be attributed to high content of ilmenite in these rocks. Geochemical data suggest partial melting of the subduction-modified, metasomatized enriched mantle wedge of garnet lherzolite to produce the parental melt of the IAB-type gabbroic and basaltic rocks of Chukotka. The composition of the mantle source and degree of partial melting that produced the parental magmas of these rocks, determined by using REE abundance and ratios, indicate that IAB-type gabbroic and basaltic melts were generated at about 10-30% partial melting of hydrous garnet lherzolite. The geochemical similarity of the studied IAB-type gabbroic and basaltic rocks of Chukotka with Bel'kov Island dolerite and low-Ti Nadezhdinsky suit (Noril'sk region) in terms of the presence of dominant hydrous minerals and negative HFSE anomalies, it is possible that the eastern Chukotka was placed closer to the Siberian LIP in Triassic, and the Triassic mafic magmatism in Chukotka represents a marginal part of the Siberian LIP. Therefore, our finding gives an additional evidence for the recently suggested subduction related origin of the Siberian LIP.

The second chapter of this thesis presents the first finding of ferropicrite lava from the Ethiopian LIP (~30 Ma) in association with ultratitaniferous transitional basalt and picrites of the second high-Ti (HT2) series. The major and trace element data of the Ethiopian ferropicrite is compatible with the eclogitic source that has possibly represents the recycled oceanic crust components in the upwelling Afar plume head. The occurrence of this ferropicrite further supports the involvement of deep plume sources during Ethiopian LIP magmatism.

#### TABLE OF CONTENTS

SUMMARYI
TABLE OF CONTENTSIII
LIST OF FIGURESVIII
LIST OF TABLESXVIII
ACKNOWLEDGMENTSXXI
1. PETROGENESIS OF TRIASSIC GABBROS AND ASSOCIATED BASALTS FROM CHUKOTKA
(NE RUSSIA): IMPLICATIONS FOR EASTERN MARGIN OF SIBERIAN LIP1
1.1 ABSTRACT1
1.2 GENERAL INTRODUCTION2
1.2.1 Objective4
1.2.2 Analytical Techniques4
1.3 GEOLOGICAL SETTING5
1.4 PETROGRAPHY11
1.4.1 Gabbroic rocks11
1.4.1.1 Clinopyroxene11
1.4.1.2 Amphibole13
1.4.1.3 Plagioclase13

	1.4.1.4	Biotite	13
	1.4.1.5	Opaque	13
	1.4.2 Basal	ic rocks	14
	1.4.2.1	Clinopyroxene	14
	1.4.2.2	Plagioclase	15
	1.4.2.3	Amphibole	15
	1.4.2.4	Opaque	17
1.5	RESULTS		17
	1.5.1 Whol	-rock major and trace element composition	17
	1.5.2 Mine	al Chemistry	26
	1.5.2.1	Major element chemistry of minerals in gabbroic rocks	26
	1.5	.2.1.1 Clinopyroxene	26
	1.:	.2.1.2 Amphibole	32
	1.:	.2.1.3 Plagioclase	36
	1.	.2.1.4 Biotite	38
	1.	.2.1.5 Opaque minerals	39
	1.5.2.2	Major element chemistry of minerals in basaltic rocks	39
	1.	.2.2.1 Clinopyroxene	39

		1.5.2.2.2	Amphibole47
		1.5.2.2.3	Plagioclase
		1.5.2.2.4	Biotite53
		1.5.2.2.5	Opaque minerals53
	1	.5.2.3 Trace	elements in clinopyroxene and amphibole53
		1.5.2.3.1	Clinopyroxene in gabbroic rocks53
		1.5.2.3.2	Clinopyroxene in basaltic rocks54
		1.5.2.3.3	Amphiboles in gabbroic rocks58
		1.5.2.3.4	Amphiboles in basaltic rocks58
1.6	DIS	CUSSION	
	1.6.1	Parental ma	gma61
	1.6.2	Fractional c	rystallization63
	1.6.3	Crustal cont	tamination65
	1.6.4	Nature of m	antle source67
	1.6.5	Mantle melt	ing conditions71
	1.6.6	Pressure and	l temperature constraints74
	1.6.7	Evaluation (	of tectonic setting76
	1.6.8	Comparison	with the Noril'sk basalts of the Siberian LIP78

1.6.8.1. Hydrous nature78
1.6.8.2. HFSE depletion
1.7. CONCLUSIONS85
<b>1.8. REFERENCES87</b>
2. FERROPICRITE FROM THE LALIBELA AREA IN THE ETHIOPIAN LARGE IGNEOUS
PROVINCE109
2.1 ABSTRACT109
2.2 INTRODUCTION111
2.3 GEOLOGICAL SETTING113
2.4 ANALYTICAL METHODS115
2.5 WHOLE ROCK CHEMISTRY
2.5.1 Major and trace elements117
2.6 PETROGRAPHY AND MINERAL CHEMISTRY120
2.6.1 Petrography120
2.6.2 Mineral chemistry124
2.6.2.1 Olivine124
2.6.2.2 Cr-spinel125
2.6.2.3 Clinopyroxene129

	2.0	6.2.4 Plagioclase	132
2.7	DISCUS	SSION	134
	2.7.1	Olivine Fo and NiO showing mantle-derived melt	134
	2.7.2	Primary bulk-rock nature of the melt	135
	2.7.3	Temperature estimates	136
	2.7.4	High degree melting of the source mantle	137
	2.7.5	Cr/Al relationship between spinel and bulkrock: indicator of source lithology	138
	2.7.6	High-pressure melting of the source mantle	139
	2.7.7	Bulk-rock high Fe/Mn and Ni/Cr ratios: a core-mantle issue?	140
	2.7.8	Eclogite vs. peridotite as the source for Ethiopian ferropicrite	141
	2.7.9	Reversely zoned clinopyroxene; reaction with peridotitic mantle	142
	2.7.10	Experimental constraints for the source lithology	143
	2.7.11	Hydrous mantle melting?	144
2.8	CONCI	LUSIONS	145
2.9	REFER	ENCES	146

#### LIST OF FIGURES

Figure 1.1: (A) A position of the AACM among major geological structures of Arctic region (modified after
Miller et al., 2006). Abbreviations: WSB, West Siberian Basin, SAS, South Anyui suture; LI,
Lisburn Hills; WI, Wrangel Island; WHA, Wrangel, Herald Arch; KB, Kolyuchinskaya Bay; NSA,
New Siberian Archipelago; CR, Chersky Range; BR, Brooks Range; AN, Angayucham belt. (B)
General geology of Chukotka microplate after Ledneva et al. (2014) and position of study area.
Abbreviations: AACM, Arctic Alaska-Chukotka microplate; OChVB, Okhotsk-Chukotka volcanic
belt; VT, Vel'may terrane
Figure 1.2: Sketch geological map of the Chukotka peninsula showing the sampling location of the Triassic
basaltic and gabbroic rocks9
Figure 1.3: (A) Field photographs showing the occurrence of the studied gabbros as plat formal edifice tabular
hills behind the field vehicle. (B) Fine grained gabbroic dike occurring within coarse grained

hills behind the field vehicle. (B) Fine grained gabbroic dike occurring within coarse grained melanocratic gabbro. (C) Details display coarse grained IAB-type hornblende gabbro. (D) OIB-type gabbro cut by felsic veins. (E) Pillow lava of basalt that is closely associated with dolerite and gabbro in the S4 area. (F) Hand specimen of hornblende basaltic andesite showing large brown amphibole phenocrysts with a size as large as 1 cm (the coin is 22 mm in diameter)......10
Figure 1.4: Photomicrographs of the Triassic gabbroic rocks of Chukotka (Crossed-nicols). (A) Coarse grained

hornblende-gabbro (IAB-type) showing euhedral crystals of amphibole in contact with

#### K<sub>2</sub>O (wt. %) for Triassic mafic rocks of Chukotka, NE Russia. The shaded area displays the bulk-rock

composition of gabbroic rocks reported by Ledneva et al. (2014)
Figure 1.8: Variation diagrams of trace elements (ppm) vs. MgO (wt. %) for the Triassic mafic rocks of
Chukotka21
Figure 1.9: Primitive mantle-normalized trace element and REE patterns for the gabbroic (A, B) and basaltic
rocks (C, D) of Chukotka, NE Russia. Mantle-normalization values are from McDonough and Sun
(1995). Multi-element and REE patterens of OIB and N-MORB (Sun and McDonough, 1989) are
shown for comparison. Logarithmic scale
Figure 1.10: Pyroxene quadrilateral diagram showing the composition of pyroxene from the gabbroic rocks in
the Chukotka area, NE, Russia. Nomenclature (after Morimoto et al., 1988)27
Figure 1.11: Major element chemistry of clinopyroxene crystals from the gabbroic rocks of Chukotka. The
shaded circle showing clinopyroxene composition of gabbroic rocks reported by Ledneva et al.
(2014)
Figure 1.12: Plot of Al <sup>(IV)</sup> versus cations in A-site for hornblende in the studied rocks (nomenclature from Leak,
1978) <b>32</b>
Figure 1.13: Major element chemistry of amphibole from gabbroic rocks of Chukotka, NE Russia
Figure 1.14: An-Ab-Or triangular diagram showing the compositions of plagioclase from gabbroic rocks of
Chukotka. An, Anorthite; Ab, Albite; Or, Orthoclase
Figure 1.15: Pyroxene quadrilateral diagram showing the composition of pyroxene (after Morimoto et al., 1988)

from the basaltic rocks in the Chukotka area, NE, Russia40
Figure 1.16: Major element chemistry of clinopyroxene phenocrysts from the basaltic rocks of Chukotka41
Figure 1.17: (A) BSE-image of clinopyroxene phenocryst. (B-G) Compositional variations (TiO <sub>2</sub> , Al <sub>2</sub> O <sub>3</sub> , FeO,
MgO, CaO and Cr <sub>2</sub> O3) from core to rim traverse for oscillatory zoneed clinopyroxene phenocryst
of ankaramite rock (Cpx2, Sample #70; Table 1.7)42
Figure 1.18: Major element chemistry of amphibole from basaltic rocks of Chukotka
Figure 1.19: (A) BSE image of basaltic andesite with euhedral amphibole phenocryst showing oscillatory
zoning. White filled circles indicate analyses point. The white circle is a damge due to LA-ICP-
MS analyses. (B-E) Compositional variations (TiO <sub>2</sub> , Al <sub>2</sub> O <sub>3</sub> , FeO, and MgO) from core to rim
traverse for a oscillatory zoning of amphibole phenocryst of basaltic andesite (Hb7, Sample #55;
Table 1.5). Ilm, Ilmenite         48
Figure 1.20: An-Ab-Or triangular diagram showing the compositions of plagioclase from basaltic rocks of
Chukotka. An, Anorthite; Ab, Albite; Or, Orthoclase52
Figure 1.21: Primitive mantle normalized multi-element (A) and REE (B) patterns for the clinopyroxenes from
the gabbroic rocks of Ckukotka. Mantle-normalization values are from McDonough and Sun
(1995). (C) and REE (D) patterns for the clinopyroxenes from the basaltic rocks of Ckukotka.
Mantle–normalization values are from McDonough and Sun (1995)55

Figure 1.22: Primitive mantle normalized multi-element (A, C) and REE (B, D) patterns for the amphiboles

from the gabbroic (A, B) and basaltic (C, D) rocks of Ckukotka	. Mantle-normalization values are
	-
from McDonough and Sun (1995).	

Figure 1.26: (A) Nb/Yb vs. Zr/Yb after Pearce and Peate (1995), (B) Zr/Y vs. Nb/Y after Fitton et al. (1997)

- Figure 1.27: (A) (Ta/La)<sub>PM</sub> vs. (Hf/Sm)<sub>PM</sub> diagram (LaFlèche et al., 1998). Subscript PM denotes the primitive mantle-normalized. Primitive mantle-normalizing values from (McDonough and Sun, 1995). (B) Th/Zr vs. Nb/Zr diagrams for the gabbroic and basaltic rocks of Chukotka, NE Russia. Field for

Kamchatka lavas are after Kepezhinskas et al. (1997).....70

Figure 1.28: Plots of Sm/Yb vs. La/Sm (A) and Sm/Yb vs. Sm (B) for the IAB-type gabbroic and basaltic rocks of Chukotka, NE Russia (after Zhao and Zhou, 2007). Mantle array (heavy line) defined by depleted MORB mantle (DMM, McKenzie and O'Nions, 1991) and primitive mantle (PM, Sun and McDonough, 1989). Melting curves for spinel lherzolite (Ol<sub>53</sub>+Opx<sub>27</sub>+Cpx<sub>17</sub>+Sp<sub>11</sub>) and garnet peridotite (Ol<sub>60</sub>+Opx<sub>20</sub>+Cpx<sub>10</sub>+Gt<sub>10</sub>) with both DMM and PM compositions are after Aldanmaz et al. (2000). Newly, and the provide the decrease of the period provide the provide the spinel line of the period.

al. (2000). Numbers along lines represent the degree of the partial melting......72

Figure 1.30: Al<sup>(IV)</sup> versues Al<sup>(VI)</sup> diagram for amphiboles from the gabbroic anad basaltic rocks of Chukotka, NE

Russsia. Ratios and fields are from Fleet and Barnett, 1978)	
--	--

Figure 1.31: (A) and (B) Alz (percentage of tetrahedral sites occupied by Al) vs. TiO2 in clinopyroxene (Loucks, 1990) from gabbroic and basaltic rocks respectively. (C) Relationship between anorthite (An) content of plagioclase and Mg-number (=Mg/Fe+Mg)) of coexisting clinopyroxene in the mafic rocks of Chukotka. The fields for island arc basalts (IAB) and mid-ocean ridge basalts (MORB) are from Ishiwatari et al. (1990). (D) 2Nb-Zr/4-Y tectonic environment discrimination diagram for the studied mafic rocks of Chukotka (after Meschede, 1986). AI + AII: within-plate

Figure 1.32: (A) (La/Nb)<sub>N</sub> vs. (Th/Ta)<sub>N</sub> (after Neal et al., 2002), where N denotes normalized to primitive mantle (McDonough and Sun, 1995) and (B) Nb/Yb vs. Th/Yb diagram discriminating rocks enriched by input from subduction componenet, crustal contamination, and deep crustal recycling (modified after Pearce, 2008). SZE: subduction zone enrichment, CC: continental contamination, WPE: within-plate enrichment. The field of Siberian LIP is from Wooden et al. (1993) and Krivolutskaya et al. (2009); Bel'kov Island, Kuz'michov and Pease (2007); Central Atlantic magmatic province (CAMP), Callegaro et al. (2013); Ethiopian LIP, Beccaluva et al. (2009) and Desta et al., 2014; Etendeka, Gibson et al. (2000); Karoo LIP, Luttinen et al. (2010); Kamchatka arc, Churikova et al. (2001); Mariana arc, Tamura et al. (2014); East Pacific Rise, Turner et al. (2011); Hawaiian-Emperor Chain, Huang et al. (2005) are shown for comparison. Upper crust (UC) and lower crustal (LC) values are from Rudnick and Gao, (2003). NMORB, EMORB and OIB are from Sun and McDonough (1989).

Figure 2.1: Sketch map of the Ethiopian large igneous province (LIP) including the Yemen conjugate margin, modified after Beccaluva et al. (2009) and Natali et al. (2011). Oligocene (~30 Ma) volcanic rocks: LT, Low-Ti tholeiitic basalts; HT1, High-Ti tholeiitic basalts; HT2, very High-Ti transitional basalts and picrites. Location of ferropicrite from the Dilb road section reported in this study is indicated by star. Miocene to Quaternary volcanic rocks in the Main Ethiopian Rift (MER), are not shown. CFB:

- Figure 2.5: Photomicrographs of Ethiopian ferropicrite and picritic ferrobasalt. (a) Crossed polarized light showing porphyritic texture with abundant magnesian olivine phenocrysts. (b) Back-scattered electron images of olivine phenocrysts and spinel inclusions. Subhedral to euhedral olivine phenocrysts are set in a microcrystalline groundmass. (c) Crossed polarized light images of clinopyroxene with reverse zoning, Cpx3 of Sample 1 and (d) that with resorbed texture, Cpx1 of Sample 2. Small circles in the clinopyroxene phenocrysts show ICP-MS analytical points (Table

- Figure 2.8: Bulk rock Cr/Al vs Spinel Cr/Al ratios for the Ethiopian ferropicrite and picritic ferrobasalts. Dashed arrows indicate the possible eclogitic and peridotitic sources. Data sources: Ethiopian LIP low-Ti and HT2 suits (Beccaluva et al., 2009); Abitibi komatiite (Barnes, 1985); Pioneer komatiite (Stiegler et al., 2012); Gorgona komatiite (Dietrich et al., 1981); Emeishan picrites (Kamenetsky et al., 2012);

- Figure 2.9: Pyroxene quadrilateral diagram showing the composition of pyroxene (after Morimoto et al., 1988) from the ferropicrite and picritic ferrobasalts in the Lalibela area. The circlualr area displays the composition of clinopyroxene in the picrite of Ethiopian LIP (Beccaluva et al. 2009)......129
- Figure 2.10: Plots of Mg# versus TiO<sub>2</sub> (a) and Cr<sub>2</sub>O<sub>3</sub> (b) for the ferropicrite and picritic ferrobasalt of Ethiopian LIP. For comparison, clinopyroxenes from the high-Ti 2 picrite (Beccaluva et al., 2009) are also plotted. Dashed arrow represents the core to rim reverse zoning trend within a single crystal.....130

#### LIST OF TABLES

Table 1.1: Major and trace element compositions for the basaltic and gabbroic rocks of Chukotka, NE,
Russia24
Table 1.2: Bulk-rock trace element analyses of mafic rocks of Chukotka, NE Russia
Table 1.3: Representative electron-microprobe analyses of clinopyroxene crystals in gabbroic rocks of Chukotka,
NE Russia. *Total Fe expressed as FeO; Mg#= 100×Mg (Mg+Fe <sup>2+</sup> ). Abbreviations: Wo,
wollastonite; En, enstatite; Fs, ferrosilite
Table 1.4: Representative electron-microprobe analyses of hornblende crystals in gabbroic rocks of Chukotka,
NE Russia34
Table 1.5: Average electron microprobe analyses of plagioclase and alkali feldspar from the basaltic and
gabbroic rocks of Chukotka, NE Russia. Abbreviations: An, Anorthite; Ab, Albite; Or, orthoclase; n,
number of analyses used for the average; n, number of analyses used for the average
Table 1.6: Electron-microprobe analyses of biotite from the basaltic and gabbroic rocks of Chukotka, NE
Russia
Table 1.7: Representative electron-microprobe analyses of clinopyroxene phenocrysts and microphenocrysts in
basaltic rocks of Chukotka, NE Russia. *Total Fe expressed as FeO; Mg#= 100×Mg (Mg+Fe <sup>2+</sup> ).
Abbreviations: Wo, wollastonite; En, enstatite; Fs, ferrosilite43
Table 1.8: Representative electron-microprobe analyses of hornblende phenocrysts and microphenocrysts in

basaltic rocks of Chukotka, NE Russia. *Total Fe as FeO; Mg#= 100×Mg (Mg+Fe <sup>2+</sup> )49
Table 1.9: Trace element analyses (ppm) of clinopyroxenes from gabbroic rocks of Chukotka, NE Russia.
Abbreviations: Cpx, clinopyroxene; n.d. not detected
Table 1.10: Trace element analyses (ppm) of clinopyroxenes from basaltic rocks of Chukotka, NE Russia.
Abbreviations: Cpx, clinopyroxene; n.d. not detected
Table 1.11: Trace element compositions of amphiboles in the IAB-type gabbros and basalts of Chukotka, NE
Russia60
Table 2.1: Whole rock chemistry of the ferropicrite and picritic ferrobasalts from the Lalibela area, Ethiopian
LIP. *Total iron as FeO. Mg# (=Mg/Mg+ $Fe_{Total}$ ) ×100; LOI = Loss on ignition116
Table 2.2: Representative analyses of olivine phenocrysts in ferropicrite and picritic ferrobasalt rocks from
Lalibela area, Ethiopian LIP. *Total Fe as FeO122
Table 2.3: Representative, analyses of spinel inclusions in olivine phenocrysts. *Total Fe as FeO; Cr#=100Cr/
(Cr+Al); $Mg\#=100Mg/(Mg+Fe^{2+})$ ; $Fe^{3+}\#=100Fe^{3+}/(Cr+Al+Fe^{3+})$ . Abbreviations: n.d. not detected;
Spl, spinel; Ol, olivine; Gm, groundmass126
Table 2.4: Representative, analyses of clinopyroxene phenocrysts and microphynocrysts of ferropicrite and
picritic ferrobasalt rocks from Ethiopian LIP. *Total Fe as FeO; Mg#=100Mg/(Mg+Fe <sup>2+</sup> ).
Abbreviations: Cpx, clinopyroxene; Wo, wollastonite; En, enstatite; Fs, ferrosilite; gm, groundmass;

## Table 2.5: Representative trace element analyses of clinopyroxenes (LA-ICP-MS; values in ppm) from

ferropicrite and picritic ferrobasalt rocks. Abbreviations: Cpx, clinopyroxene; n.d. not detected....133

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### **CHAPTER 1**

# Petrogenesis of Triassic gabbros and associated basalts from Chukotka (NE Russia): implications for eastern margin of Siberian LIP

#### 1.1. ABSTRACT

The Triassic gabbroic intrusions and associated basaltic lavas from Chukotka contain abundant hornblende, and are mainly tholeiitic with both OIB-type and island-arc basalt (IAB)-type geochemical signatures. Mgnumber (Mg#=100×Mg/ (Mg+Fe<sup>2+</sup>)) ranges from 48 to 66 for IAB-type gabbros, around 40 for OIB-type gabbros, 63-65 for ankaramites (IAB-type), 57 for pyroxene phyric basalt (IAB-type), 51-54 for lamprophyres (IAB-type) and 43-50 for basaltic andesite (IAB-type). TiO<sub>2</sub> contents of the studied samples are low (<2 wt. %) except for OIB-type gabbros (4.3-5.3 wt. %). Gabbroic rocks generally have lower K<sub>2</sub>O and Na<sub>2</sub>O than the volcanic rocks. OIB-type gabbros are typically enriched in FeO<sup>\*</sup> (16-18 wt. %) as compared to IAB-type gabbros (10-14 wt. %), and IAB-type basaltic rocks (ankaramites ~10 wt. %, lamprophyres ~14, pyroxene-phyric basalt 11 wt. %, and basaltic andesite 9-10 wt. %). In the primitive mantle normalized trace element patterns, IAB-type gabbroic and basaltic rocks are characterized by depletion in HFSE (Nb, Ta, Zr and Hf) and enrichment in LILE, and resemble arc-type igneous rocks. OIB-type gabbroic rocks can be distinguished from the rest of the studied samples by the absence of HFSE depletion, but show strong negative Sr anomalies. The positive Ti anomaly in the OIB-type gabbros can be attributed to high content of ilmenite in these rocks. The composition of the mantle source and degree of partial melting that produced the parental magmas of these rocks, determined by using REE abundance and ratios, indicate that IAB-type gabbroic and basaltic melts were generated at about 10-30% partial melting of hydrous garnet lherzolite. Trace element characteristics of IAB-type gabbroic rocks and basalts are compatible with their magmas derived from subduction influenced melts, whereas OIB-type gabbros show within-plate geochemical characteristics. IAB-type gabbroic and basaltic rocks display similar geochemical features with the low-Ti Nadezhdinsky suit (Noril'sk region) and Bel'kov dolerite (New Siberian Islands) of Siberian LIP in view of HFSE depletion and high H<sub>2</sub>O content of the magma to crystallize abundant hornblende not only in gabbros but also as phenocrysts in basalts.

Keywords: Island-arc geochemistry, intra-plate geochemistry, ankaramite, hornblende basalt, HFSE

#### **1.2. GENERAL INTRODUCTION**

The Arctic Alaska-Chukotka microplate (AACM) is the key element in the tectonic evolution of Amerasian Basin (Miller et al., 2006). In the north it is bounded by the Arctic Alaskan and Russian outer shelf edges. Its southern boundary is defined by a belt of arc and an ophiolitic rocks that includes the Angayucham terrane of the southern Brooks Range (Moore et al., 1994) and South Anyui zone of western Chukotka (Sokolov et al., 2002). Eastern Chukotka is interpreted as a part of this microplate which is formed during the Cretaceous opening of the Amerasian basin. Geophysical data sets and seismic reflection based stratigraphic correlations support to the suggested rifting model or "rotational model" for the formation of Amerasian basin (Grantz et al. 1998; Lawver et al. 2002). This model proposes that early Cretaceous rifting rotated a continental mass, now it is known as Arctic Alaska-Chukotka microplate, southward from the Arctic margin of Canada. On the other hand, Miller et al. (2006) proposed that AACM is rifted from the Siberian craton, which is supported by U-Pb dates of detrital zircons from the Triassic terrigenous sedimentary rocks of eastern Chukotka, Wrangel Island, and the Lisburne Hills in the Arctic Alaska region indicating that the youngest detrital zircon population has a Permo-Triassic age similar to the basaltic rocks of the eastern Urals, Tunguska and Taimyr provinces of the Siberian large igneous province (LIP). Kuz'michov and Pease (2007) also reported that the hypabyssal mafic rocks (dolerites) of the New Siberian Archipelago (Bel'kov Island) have similar age  $(252\pm 2 \text{ Ma, U-Pb TIMS})$  ages of igneous zircons), petrographic features and geochemical signatures with the moderately alkaline basalts in the Noril'sk district, Siberia. As a result, Miller et al., (2006) and Kuz'michov and Pease (2007) concluded that the eastern Chukotka along with other parts of AACM, was closer to the Siberian craton than to Arctic Canada, or that it may even have constituted a part of the Siberian platform, respectively. Recent investigations have shown that hypabyssal mafic rocks and basalts with inter-pillow cherts and terrigenous sedimentary rocks spacially associated with them occur in the vicinity of the Kolyuchinskaya Bay in eastern Chukotka, and that the trace element patterns and Sr- and Nd-isotope compositions of these sedimentary and volcanic associations are similar to the tholeiitic flood basalts of the main plateau stage of the Siberian LIP (Ledneva et al., 2011). Moreover, the gabbroic rocks of western Chukotka (such as in the area of Keperveem, Malyi Anyui and Raucha Uplifts; Fig. 1.1B) and the Siberian trap basalts are highly similar in terms of the geochemistry of their major oxides (Gel'man, 1963; Degtyaryov, 1975). Small bodies of gabbroic intrusions (dikes and sills) are also widespread in the Permianlower Triassic and lower-middle Triassic shelf and continental slope sedimentary sequences (Ledneva et al., 2014).

#### 1.2.1. Objectives

The mafic intrusive and extrusive rocks occur in the eastern Chukotka and are assumed to be of Permo-Triassic to Early-Middle Triassic age. This study is primarily aiming to find the possible eastern marginal extension of Siberian large igneous province (Permo-Triassic, ~250 Ma) and compared its petrology and geochemistry with the central Siberian plateau. Here, we present XRF whole rock geochemical analyses, electron microprobe analyses of hornblende, clinopyroxene, plagioclase and Fe-Ti oxide, LA-ICP-MS analyses of bulk-rock, hornblende and clinopyroxene for the Triassic gabbros and associated basaltic rocks of Chukotka in order to place constraints on the origin of their parental magmas, and to fingerprint their geochemical signatures. We compared our results with the previously published data from Siberian LIP in search for genetic relationships between these igneous provinces. Our findings also provide additional constraints for the much debated origin of the AACM.

#### 1.2.2. Analytical Techniques

The samples were collected by the Prof. Akira Ishiwatari from outcrops in the course of his Japanese-Russian joint field work for ophiolite in 2009 in the Chukotka area, northeast Russia. Electron microprobe analyses were conducted on hornblende, clinopyroxene, plagioclase and Fe $\pm$ Ti oxide minerals in polished thin section, using

an energy dispersive X-ray spectrometer Oxford Link ISIS equipped on the JEOL JSM-5410 Scanning electron microscope (SEM) at the Earth Science department, Tohoku University. The reader is referred to Erdenesaihan et al. (2013) and Desta et al. (2014) for analytical details about electron microprobe technique. Major and some trace elements (V, Cr, Ni, Rb, Sr, Ba, Y, Zr, Nb) were obtained using X-ray fluorescence spectrometer (XRF-RIX 2100) on fused glass discs at the aforementioned department, Tohoku University. The loss on ignition (LOI) was determined following the procedure described by Desta et al. (2014). The trace element analysis of whole rock and mafic minerals (i.e. clinopyroxene and amphibole) have been carried out by a laser ablation (193 nm ArF exciemer: MicroLas GeoLas Q-plus)-inductively coupled plasma spectrometer Agilent 7500S (LA-ICPMS) at Kanazawa University (Ishida et al., 2004). Detailed LA-ICPMS analytical procedures have been reported by Erdenesaihan et al. (2013) and Desta et al. (2014).

#### **1.3. GEOLOGICAL SETTING**

The study area (Fig. 2.1B) is situated within the Arctic Alaska-Chukotka microplate (AACM) or Chukotka microcontinent (Parfenov et al., 1993). The AACM is composed of a Neoprotrozoic crystalline basement (Natal'in et al., 1999, Amato, et al., 2009), and overlain by Carboniferous and Permian platform strata (P'yankov, 1981; Natal'in et al., 1999). These units are, in turn, overlain by a Permo-Triassic to upper Triassic terrigenous continental shelf sedimentary sequence (Tuchkova et al., 2009) and a Jurassic volcanic-terrigenous foreland sedimentary package (Vatrushkina and Tuchkova, 2014).

To the south, the AACM is bounded by the South Anyui Suture (SAS) zone, which was formed by the closure

of a late Jurassic-early Cretaceous oceanic basin and the collision of the North Asian craton with AACM (Seslavinsky, 1979; Parfenov, 1984). This suture zone is buried under the Cretaceous Okhotsk-Chukotka volcanic belt (Tikhomirov et al., 2012).

In the western part of Chukotka it is marked by Mesozoic terrigenous turbidite and fragments of ophiolite sequences (Sokolov et al., 2002). In the eastern Chukotka the position of SAS attributed to the Velmai terrane (Parfenov et al., 1993; Nokleberg et al., 1998; Sokolov et al., 2009).

In the study area the gabbroic intrusions occur as flat-lying tabular bodies ranging in thickness from a few meters to few hundred meters, and are mainly confined to the upper Permian-lower Triassic and lower-middle Triassic strata of the AACM cover (Fig. 1.1). However, the upper Triassic sedimentary units overlying these older sequences are devoid of tabular bodies of gabbroic intrusions (Til'man and Sosunov, 1960; Gel'man, 1963; Degtyaryov, 1975). In the western Chukotka these intrusions extend for ~350 km (the Keperveem and Raucha Uplifts); in central and eastern Chukotka they are traced to a distance of ~ 900 km (the vicinity of Cape Schmidt and the interfluves of the Amguema and Vel'may rivers and the Kolyuchinskaya Bay area) (Fig. 1.1B; Ledneva et al., 2014). These gabbroic rocks were recognized as parts of a large regional complex (Til'man and Sosunov, 1960; Gel'man, 1963) named as the Amguema-Anyui Igneous Province (Degtyaryov, 1975). The Permo-Triassic to early-middle Triassic age of these intrusion is proven by: (1) their stratigraphic position within the Permian-lower Triassic and lower-middle Triassic terrigenous sediments, contemporaneous joint deformation of gabbroic bodies and their country rocks (Til'man and Sosunov, 1960; Gel'man, 1963); (2) bulk-rock K-Ar determinations

of 250, 231 and 223 Ma (Ivanov and Milov, 1975; Degtyaryov, 1975) and (3) and the U-Pb TIMS igneous zircon age of 252±4 Ma obtained for the Kolyuchinskaya Bay gabbro (Sokolov, et al., 2009). The gabbroic intrusions described by Ledneva et al. (2014) are characterized by intra-plate basaltic geochemical features.

However, our mineralogical and geochemical data confirm the presence of both island-arc basalt (IAB)-type and OIB-type mafic intrusions in the Triassic system of Chukotka. These two gabbro types were likely derived from two different mantle sources. Our OIB-type gabbros are analogous to those described by Ledneva et al. (2014) in terms of petrography and geochemistry. In the study area, these OIB-type and IAB-type gabbroic rocks and associated IAB-type basaltic units (i.e. ankaramites, pyroxene-phyric basalts, lamprophyres and basaltic andesites) are commonly occurring together and are exposed as platformal edifice (Fig. 1.3A). The basaltic lavas rarely exhibit pillow structure (at S4 of Fig. 1.2, See Fig. 1.3E). They are commonly interbedded with sandstone, siltstone, and mudstone and bedded tuff. The most magnesian samples (i.e. ankaramites, Sample#69, #70, and #71) of this study come from the sampling locality 4 (Fig.1.2; Tables 1.1 and 1.2; N66°45'26″, W177°17'31″).



**Figure 1.1:** (A) A position of the AACM among major geological structures of Arctic region (modified after Miller et al., 2006). Abbreviations: SAS, South Anyui suture; LI, Lisburn Hills; WI, Wrangel Island; WHA, Wrangel, Herald Arch; KB, Kolyuchinskaya Bay; NSA, New Siberian Archipelago; CR, Chersky Range; BR, Brooks Range; AN, Angayucham belt. (B) General geology of Chukotka microplate after Ledneva et al. (2014) and position of study area. Abbreviations: AACM, Arctic Alaska-Chukotka microplate; OChVB, Okhotsk-Chukotka volcanic belt; VT, Vel'may terrane.



Figure 1.2: Sketch geological map of the Chukotka peninsula showing the sampling location of the Triassic

basaltic and gabbroic rocks.



**Figure 1.3:** (A) Field photographs showing the occurrence of the studied gabbros as plat formal edifice tabular hills behind the field vehicle. (B) Fine grained gabbroic dike occurring within coarse grained melanocratic gabbro. (C) Details showing coarse grained IAB-type hornblende gabbro. (D) OIB-type gabbro cut by felsic veins. (E) Pillow lava of basalt that is closely associated with dolerite and gabbro in the S4 area. (F) Hand specimen of hornblende basaltic andesite showing large brown amphibole phenocrysts with a size as large as 1 cm (the coin is 22 mm in diameter).

#### **1.4. PETROGRAPHY**

#### 1.4.1. Gabbroic rocks

We have identified two types of gabbroic bodies in this study, i.e. IAB-type amphibole bearing gabbroic rocks such as pyroxene-hornblende gabbro, hornblende gabbro, hornblende-pyroxene gabbro and OIB-type gabbros (include rare to no amphiboles).

IAB-type gabbros display a notable grain size variation; from medium grained (subordinately fine grained) to coarse crystals with size reaching about 20 mm (Fig. 1.4). They have a granular texture with hornblende, pyroxene and plagioclase. However, in some samples plagioclase minerals are altered to chlorite, epidote and probably sericite. Magnetite mineral occurs dominantly with variable size and shape (Fig. 1.4A-D). Rare apatite grains are also observed as accessory minerals in IAB-type pyroxene-hornblende gabbro.

OIB-type gabbros consist mainly of clinopyroxene, plagioclase (locally transformed to sericite) and ilmenite (Fig. 1.4E and F). They are massive fine- to medium grained rocks and are mainly display hypidiomorphicgranular texture. In general, olivine and orthopyroxene crystals are absent in both types of gabbros.

#### 1.4.1.1. Clinopyroxene

Clinopyroxene shows a characteristic subhederal to irregular shape and enclosed within the calcic amphibole oikocrysts in IAB-type gabbros. Their color varies from light-yellow, colorless, pale green to pinkish. Clinopyroxene in OIB-type gabbros forms elongated, subhedral to anhedral shape.



**Figure 1.4:** Photomicrographs of the Triassic gabbroic rocks of Chukotka (Crossed-nicols). (A) coarse grained hornblende-gabbro (IAB-type) showing euhedral crystals of amphibole in contact with altered plagioclase, (B) fine grained hornblende gabbros (IAB-type), (C) and (D) poikilitic texure in IAB-type gabbros, (E) and (F) OIB-type gabbros showing ophitic texture and ilmenite grains. Cpx, clinoopyroxene; Amp, amphibole; Pl, plagioclase; Mag, magnetite; Ilm, ilmenite.

#### 1.4.1.2. Amphibole

Amphiboles are the dominant ferromagnesian minerals in the IAB-type gabbroic rocks. The colour of hornblende minerals varies from light brown to green. They generally display sub-hedral to anhedral shape, but shows good cleavage (Fig. 1.4A). They usually occur as oikocrysts and enclose relatively small sized pyroxenes, plagioclase, opaque minerals and rarely apatite. Their grain size varies from 1 to 20 mm.

#### 1.4.1.3. Plagioclase

Plagioclase is not well preserved (partly to completely altered) in gabbros and is replaced by sericite minerals. However, few relict plagioclases from IAB-type gabbros are analyzed. They are usually twinned, but zoned plagioclase is rare. Plagioclase in OIB-type gabbros forms euhedral and sub-hedral tabular crystals and display ploysynthetic twinning where they are fresh.

#### 1.4.1.4. Biotite

Biotite is rarely present in IAB-type gabbros (mainly found in pyroxene-hornblende gabbro). They occur as a minor phase and inter-layered with chlorite minerals. Their grain size varies from 1.4 mm to 2 mm.

#### 1.4.1.5. Opaque

Opaque minerals such as magnetite and titano-magnetite are predominant in IAB-type gabbroic rocks, whereas ilmenite is common in the OIB-type gabbroic rocks (Fig. 1.4E and F). The size of titano-magnetite in the coarse grained hornblende gabbro (Sample #60; IAB-type) reaches as large as 2 mm. Opaque minerals are also occurring as inclusion within the amphibole minerals.
## 1.4.2. Basaltic rocks

Two groups of volcanic rocks are recognized based on their texture and whole-rock chemical analysis: (1) basaltic rocks such as ankaramites (Sample #69, #70 and #71) and pyroxene-phyric basalt (Sample #67) with clinopyroxene as a main phenocryst phase, and (2) basaltic andesites (Sample #55 and #56) containing hornblende and few clinopyroxene phenocryts (Fig. 1.5). We have also identified two lamprophyre samples based on their high modal abundance of amphibole phenocryst (Sample #74 and #77) (hereafter we explained these samples as basaltic rocks for the sake of simplicity). Basaltic rocks show sub-ophitic, porphyritic, glomeroporphyritic and glassy textures. The most common texture is porphyritic with phenocrysts of amphibole (mainly in lamprophyres), clinopyroxene and plagioclase minerals (Fig. 1.5). Rapid crystallization is indicated by the occurrence of glass (altered) in the groundmass of pyroxene-phyric basalt. The modal abundances of phenocrysts are in the range of 5-40%. Plagioclase phenocrysts occur in the hornblende basaltic and esite ( $\sim$ 5%). Clinopyroxenes are the main phenocrysts in ankaramite (~40 vol. %) and pyroxene phyric basaltic rocks (~25 vol. %). The most common groundmass minerals include plagioclase, amphibole, Fe-Ti oxide, rare biotite, quartz and pyroxene. All these basaltic rocks display island-arc basalt type trace element patterns.

## 1.4.2.1. Clinopyroxene

Clinopyroxene occur as elongated and prismatic crystals in basaltic rocks. Its shape varies from euhedral to anhedral (irregular). Clinopyroxene phenocrysts varies in size and reaches as large as 4.5 mm in basaltic andesite, 2.5 mm in pyroxene-phyric basalt and 3.5 mm in ankaramites, and 2.5 mm in lamprophyres (Fig. 1.5). The color in a thinsection varies from light green, pinkish, to light yellow and pale brown. Some of these crystals show normal or oscillatory zoning and resorbed texture. They also occur as broken pieces in the pyroxene-phyric basalt and they exhibits well developed zoning (Fig. 1.5C and D). Clinopyroxene phenocrysts in basaltic andesite also display oscillatory zoning and locally contain plagioclase and ilmenite inclusion. Clinopyroxene phenocrysts in basaltic andesite are ubiquitously resorbed and are commonly twinned (e.g. in Sample #56).

### 1.4.2.2. Plagioclase

Plagioclase in most basalt is not well preserved, but some in basaltic andesite and lamprophyre have survived. They occur as phenocrysts and groundmass in basaltic andesite and as only groundmass in ankaramites and lamprophyres. Albite-rich plagioclase occurs as fresh phenocryst in the basaltic andesite, where as anorthite-rich plagioclase likely more affected by alteration.

# 1.4.2.3. Amphibole

Amphibole minerals occur in the ankaramite rocks only as groundmass, and as phenocrysts in the basaltic andesites and lamprophyres. They occur as elongated anhedral (rounded) and euhedral phenocrysts in basaltic andesite, but as they occur as subhedral and needle-like crystals in the lamprophyres. Amphibole phenocrysts are commonly glomerocrystic in lamprophyre samples. Their size reaches as large as 1cm in hornblende basaltic andesite (Fig. 1.3F). Some of the amphiboles from basaltic andesite (Sample #56; Fig. 1.5B) display resorption both in the core and along their margins. Their colour ranges from pale brown to dark brown. The euhedral amphibole phenocrysts in the basaltic andesite show clear oscillatory zoning (e.g. in Sample #55). In hornblende

basaltic andesite they occur in association with alkali feldspar and clinopyroxene phenocrysts. Amphibole

phenocryts in the basaltic andesite locally exhibit twinning.



**Figure 1.5:** Backscatter electron (BSE) images illustrating the petrographic characteristics of the basaltic rocks. (A-B) Brown hornblende phenocrysts in basaltic andesites (Sample #55 and #56 respectively) displaying oscillatory zoning (A) and resorbed texture (B). (C) Fragment of clinopyroxene phenocryst with broken side in pyroxene-phyric basalt (Sample #67), showing evidence of incipient melting. (D) Open nicol view of ankaramite (Sample #69) showing porphyritic texture. (E-F) Lampropyre (Sample #77) exhibiting a cluster of euhedral to sub-hedral phenocrysts of clinopyroxene and hornblende (BSE image, E; open nicol view, F). Amp, amphibole; Cpx, clinopyroxene; Plg, plagioclase; Ti-Mag, Ti-Magnetite.

## 1.4.2.4. Opaque

Opaque minerals such as iron-sulfide and magnetite are investigated from the pyroxene-phyric basalt and ankaramites and lamprophyres, respectively. They are irregular shaped or subhedral and occur as interstitial grains in hornblende and clinopyroxene phenocryst. They have variable crystal size, but mostly as large as 0.5 mm in lamprophyre, 0.2 mm in ankaramite and 0.065mm in pyroxene-phyric basalt. Ilmenite is present as an inclusion in amphibole and clinopyroxene phenocrysts and groundmass in basaltic andesite samples.

# **1.5. RESULTS**

### 1.5.1. Whole-rock major and trace element composition

Representative, major element chemical data for the Triassic gabbroic and basaltic rocks of Chukotka are presented in Table 1.1. All the analyzed samples are tholeiitic in composition, although, one basaltic and one basaltic andesite samples plot on the dividing line between the calc-alkaline and tholeiitic fields on the SiO<sub>2</sub>-FeO<sub>Total</sub>/MgO diagram of Miyashiro (1974) (Fig. 1.6A). In the AFM diagram of Irvine and Baragar (1971), the studied samples plot above and on the demarcating line, showing a tholeiitic affinity, and following an iron enrichment trend (Fig. 1.6B). These rocks have Nb/Y ratios of 0.09-0.59, plotting in the sub-alkaline basalt field on the Nb/Y versus Zr/Ti diagram of Winchester and Floyd (1977) and Pearce (1996) (Fig. 1.6C), except one sample of OIB-type gabbro falling in the alkaline field. Variation diagrams for major element oxides against MgO wt. % are presented in Fig. 1.7A-F. Mg-number (Mg#=100×Mg/ (Mg+Fe<sup>2+</sup>)) range from 48 to 66 for IAB-

type gabbros, around 40 for OIB-type gabbros, 63-65 for ankaramites (IAB-type), 57 for pyroxene phyric basalt (IAB-type), 51-54 for lamprophyres (IAB-type), and 43-50 for basaltic andesite (IAB-type) rocks (Table 1.1).



**Figure 1.6:** Classification diagrams for the mafic rocks of Chukotka: (A) FeOt/MgO versues SiO<sub>2</sub> (wt. %) diagram (after Miyashiro, 1974). (B) AFM (Na<sub>2</sub>O+K<sub>2</sub>O-FeO<sub>Total</sub>-MgO) triangle diagram; (C) immobile element ratios such as Nb/Y vs Zr/Ti distinguishing subalkaline and alkaline basalts (Winchester and Floyd 1977, modified by Pearce, 1996).

The low to intermediate Mg-number of the studied samples suggests that these rocks do not represent primary, mantle-derived melts. This is consistent to the low concentrations of compatible trace element (such as Cr and Ni) in the studied samples.

The TiO<sub>2</sub> contents of all the studied samples are low (<2 wt. %) except OIB-type gabbros (4.3-5.3 wt. %). IAB-type gabbros have higher CaO contents (13-19 wt. %) (Except Sample #78, ~7 wt. %) compared to OIB-type gabbros (5-9 wt. %). OIB-type gabbros typically enriched in FeO<sup>\*</sup> (16-18 wt. %) as compared to IAB-type gabbros (10-14 wt. %), and IAB-type basaltic rocks (~10 wt. %, ankaramites; 11 wt. %, pyroxene-phyric basalt; ~14 wt. %, lamprophyres and basaltic andesite samples 9-10 wt. %). Ankaramites have higher CaO/Al<sub>2</sub>O<sub>3</sub> (0.99-1.04) ratios compared to pyroxene-phyric basalt, lamprophyres and basaltic andesites (0.83, 0.82-0.86 and 0.43-0.44, respectively). Moreover, ankaramite samples have high Cr/Ni (6.5-7.6), and Sc/Ni (~0.9) ratios, characteristic of arc ankaramites (Bardsell and Berry, 1990). Considering the above points Sample #75 (IAB-type gabbros) show similar characteristics to ankaramite samples, thus it may represent the intrusive equivalent of ankaramite lava. Gabbroic rocks generally have lower K<sub>2</sub>O and Na<sub>2</sub>O than the volcanic rocks. The Na<sub>2</sub>O concentrations in the studied samples increases with deceasing MgO content, whereas the K<sub>2</sub>O content of gabbroic rocks (except basaltic rocks) show more scattered trend (Fig. 1.7E and F).

Trace element compositions of the analysed samples are provided in Tables 1.1 and 1.2. Variation diagrams (Fig. 1.8A-F) show that the compatible elements (Ni and Cr) decrease with decreasing MgO. The Ni content of the studied samples are low, and even the most mafic ankaramite have low Ni (~81 ppm) at high Cr (>500 ppm).



**Figure 1.7:** Plots of MgO (wt. %) vs  $TiO_2$  (wt. %),  $Al_2O_3$  (wt. %), FeOt (wt. %), CaO (wt. %), Na<sub>2</sub>O (wt. %) and K<sub>2</sub>O (wt. %) for Triassic mafic rocks of Chukotka, NE Russia. The shaded area displays the bulk-rock composition of gabbroic rocks reported by Ledneva et al. (2014).

Incompatible elements (Such as Zr and Nb) are very low in abundance for IAB-type gabbros and basalts but are high in OIB-type gabbros and basaltic andesite and increase with decreasing MgO. ΣREE is low in IAB-type gabbroic rocks (32-72 ppm), ankaramite (~38 ppm), pyroxene-pyric basalt (~63 ppm), and lamprophyres (52-56 ppm) but is high in basaltic andesites (~174 ppm) and OIB-type gabbros (138-175 ppm).



Figure 1.8: Variation diagrams of trace elements (ppm) vs. MgO (wt. %) for the Triassic mafic rocks of Chukotka.

In the primitive mantle normalized multi-trace elements plot normalized to the primitive mantle (Fig. 1.9), analysed IAB-type gabbroic and basaltic rocks are characterized by depletion of high field strength elements (HFSE) such as Nb, Ta, Zr and Hf relative to the neighbouring elements, similar to those of arc-type igneous rocks (Rudnick, 1995; Taylor and McLennan, 1995). They are depleted in HREE compared with N-MORB. In addition, these rocks exhibit depletion in Rb and Th relative to Ba and U, respectively, and show positive anomalies of Ba and K (and Pb in one IAB-type gabbro sample). However, the concentrations of Th and U in IAB-type gabbros are variable. All the analyzed IAB-type gabbroic and basaltic rocks have  $Th_N/La_N < 1$ , and two samples (Sample #75 of IAB-type gabbro and Sample #69 of basaltic rocks) have Th<sub>N</sub>/La<sub>N</sub>~1.2. The most basic intrusive rock (Sample #75 of IAB-type gabbros) is depleted in LREE compared to MREE similar to NMORB, but the former is more depleted in HREE (Fig. 1.9B). We see strong positive Sr anomalies in IAB-type gabbroic and basaltic rocks, whereas negative Sr anomalies in OIB-type gabbros. On the primitive mantle normalized REE plot (Fig. 1.9D), the hornblende basaltic andesites display elevated trace element and total REE concentration compared to the basaltic rocks. Basaltic andesites share similar patterns of depletion in HFSE (Nb, Ta) to those displayed by basaltic rocks. However, they do not show negative Zr and Hf anomalies (Fig. 1.9C). Basaltic andesite rocks show enrichment in Th ((Th/La)<sub>N</sub> >1.5) and U relative to HFSE (Nb/U=7.8-9.3). Moreover, they exhibit strong LREE enrichment ( $(La/Yb)_N = 7.38-7.74$ ), with a slightly concave-upward heavy REE (HREE) distribution and have slight negative Eu anomalies (Eu/Eu\* ~0.85) (Fig. 1.9D).

OIB-type gabbroic rocks can be distinguished from the rest of the studied samples based on the absence of

HFSE depletion, but show strong negative Sr anomalies. Moreover, their HFSE are slightly enriched relative to  $LREE ((La/Nb)_N = 0.69-1.01)$  (Fig. 1.9C) and Nb/U=33-58. The positive Ti anomaly in the OIB-type gabbros can



be attributed to their high content of ilmenite.

Rock	Ankaraı	mites	Px- phyric basalt	Lampro	ophyres	Bas ande	altic sites	IAB-type gabbros								OIB	-type gab	bros		
Sample	#69	#71	#67	#74	#77	55	#56	#57	#58	#62	#63	#66	#72	#73	#75	#76	#78	#81	#84	#85
Lat.(N)	66° 45′26″	66° 45′26″	66° 45′40″	66° 45′13″	66° 45′10″	66° 43′22″	66° 43′22″	66° 44′24″	66° 44′22″	66° 44'10''	66° 44′10″	66° 45′0″	66° 45′17″	66° 45′13″	66° 45′10″	66° 45′10″	66° 45′10″	66° 46′52″	66° 47'17''	66° 56'37″
Lon (W)	177° 17′31″	177° 17′31″	177° 17′45″	177° 17′30″	177° 17′15″	177° 1 <i>7'42''</i>	177° 17'42''	177° 23'47''	177° 23'46''	177° 24'4''	177° 24'4''	177° 20′51″	177° 17′28″	177° 17′30″	177° 17′15″	177° 17′15″	177° 17'26''	177° 21′37″	177° 22'7''	177° 40'25''
Major oxi	ides (wt.%	: determ	ined by X	(RF)	1715	1742	1/42	2347	2340	244	244	20.51	1720	17.50	1715	1/15	1720	2157	221	40.25
SiO	47.92	47.64	47.61	43.79	43.74	54.12	54.23	39.97	39.18	38.62	40.70	39.27	44.58	38.88	47.64	45.26	50.97	53.71	49.74	45.20
TiO <sub>2</sub>	0.79	0.74	0.92	1.36	1.60	1.67	1.29	1.70	1.67	1.41	1.22	1.35	1.06	1.75	0.82	0.77	1.58	2.47	4.31	5.32
$Al_2O_3$	12.43	11.40	13.43	14.18	14.35	15.83	15.92	18.80	8.31	18.46	18.36	18.76	12.00	12.54	8.41	13.02	15.16	13.40	13.11	12.77
FeO <sup>*</sup>	10.30	10.27	11.21	13.78	13.54	10.04	8.68	14.27	16.94	12.65	13.01	13.51	12.69	15.23	10.17	10.48	11.93	14.00	15.99	17.54
CaO	12.31	11.90	11.17	11.67	12.32	6.99	6.92	15.58	19.18	14.94	15.39	13.27	14.99	13.88	17.36	14.85	6.96	4.57	7.60	9.84
MgO	9.94	10.70	8.37	8.06	8.78	5.58	3.61	8.77	10.28	7.14	6.71	6.22	8.38	9.82	11.34	9.59	4.12	3.17	5.90	6.61
MnO	0.22	0.20	0.22	0.27	0.31	0.15	0.11	0.15	0.16	0.17	0.18	0.17	0.19	0.22	0.19	0.17	0.21	0.21	0.27	0.21
K <sub>2</sub> O	1.27	0.94	1.45	1.20	1.21	2.29	1.55	0.55	0.05	0.76	0.58	1.01	1.22	0.92	0.80	1.59	0.94	0.19	0.24	0.71
Na <sub>2</sub> O	2.09	1.79	1.96	1.97	2.44	2.12	3.01	1.12	0.34	1.52	1.23	1.76	1.46	1.23	1.24	1.20	4.09	4.64	4.03	2.11
$P_2O_5$	0.11	0.05	0.30	0.14	0.12	0.28	0.26	0.02	0.01	0.21	0.76	0.03	0.10	0.03	0.07	0.02	0.10	0.52	0.34	0.21
Total	98.53	95.63	97.88	97.95	99.92	100.17	96.54	102.52	96.12	95.55	99.59	95.35	98.07	94.50	99.14	96.95	96.06	97.41	103.31	102.48
Mg#	63.2	65.0	57.1	51.1	53.6	49.8	42.6	52.3	51.9	50.2	47.9	45.1	54.1	53.5	66.5	61.9	38.1	28.7	39.7	40.2
LOI	3.56		3.18	1.53	3.10	0.94	1.00				1.01		1.18		0.98				1.60	1.19
Trace eler	ments (pp	m; detern	nined by 2	XRF)																
V	316	296	325	522	580	224	159	578	622	434	426	468	464	669	334	327	404	189	517	731
Cr	466	530	286	102	62	59	35	18	23	30	24	20	109	29	358	364	27	4.	5.2	1.7
Ni	67	81	72	32	27	18	6.5	26	45	23	14	13	28	52	56	48	6.	1.	15	n.d
Rb	20	14	28	36	27	156	88	6.7	0.9	8.	8.	13	28	12	16	39	219	5.	11	33
Sr	380	312	460	534	524	547	521	969	203	1077	1188	839	481	449	259	628	615	111	161	215
Ba	243	177	324	246	605	691	455	149	56.	306	276	375	311	159	220	533	416	98	165	309
Y	16	14	18	20	20	35	32	13	14	21	19	14	16	18	14	10	32	78	43	47
Zr	34	21	63	54	52	208	212	40	30	20	46	27	48	24	40	15	64	483	282	216
Nb	2.4	2.6	3.7	2.9	2.9	10.5	10.4	2.5	1.9	3.9	3.2	3.2	3.1	2.4	2.6	2.1	3.4	46	26	13.6

 Table 1.1: Major and trace element compositions for the basaltic and gabbroic rocks of Chukotka, NE, Russia.

\*Total Fe as FeO; n.d., not determined; LOI, loss on ignition.

Rock	Ankara- mite	Px- phyric basalt	Lampro	ophyres	Basaltic a	andesites		IAB-type	gabbros		OIB-typ	e gabbros
Sample	#69	#67	#74	#77	#55	#56	#57	#72	#75	#6	#84	#85
Lat. (N)	66° 45′26″	66° 45′40″	66° 45'13''	66° 45'10″	66° 43′22″	66° 43′22″	66° 44′24″	66° 45′17″	66° 45'10''	<b>6</b> 6° 44′10″	66° 47′17″	66° 56′37″
Lon. (W)	177° 17′31″	177° 17'45''	177° 17′30″	177° 17′15″	177° 17′42″	177° 17'42''	177°23′47″	177° 17′28″	177° 17′15″	177°24'4″	177°22′7″	177° 40′25″
Determin	ed by LA-I	CP-MS										
Sc	58.4	48.9	92.3	92.3	25.5	20.4	62.7	82.7	103.2	33.7	34.9	49.4
Ti	8200	9200	12200	13000	13400	11400	14000	10400	8400	11700	27800	34200
V	390	395	552	624	273	213	602	543	401	505	468	614
Cr	498	264	110	64.9	69.5	36.4	6.0	119	403	16.2	7.3	5.5
Co	38.6	38.7	30.4	41.9	18.2	14.1	48.0	46.	41.8	32.2	41.4	47.9
Ni	65.6	65.3	36.0	30.9	18.5	12.1	30.6	33.9	53.4	19.1	23.4	11.9
Rb	16.9	22.5	29.9	22.2	123.5	70.5	4.3	22.3	12.6	6.9	7.6	26.4
Sr	388	482	608	553	536	540	1045	549	274	1403	155	213
Y	12.7	16.8	18.9	18.1	28.5	30.4	11.0	15.9	12.7	17.2	39.5	44.3
Zr	25	53	47	41	186	210	21	41	34	27	269	208
Nb	1.4	2.5	2.0	1.7	12.8	13.4	1.0	2.1	1.3	2.2	40.5	19.8
Cs	0.25	1.57	2.19	0.97	33.4	12.59	0.40	1.97	0.47	3.61	2.05	5.30
Ва	261	345	250	653	. 661	423	143	367	231	316	112	264
La	4.9	8.5	6.5	5.5	34.1	34.9	2.2	6.9	5.0	8.4	27.8	19.7
Ce	10.9	19.7	15.2	13.7	67.2	65.9	6.8	15.5	11.0	21.0	59.9	42.4
Pr	1.6	2.9	2.4	2.2	8.3	8.2	1.3	2.4	1.7	3.4	8.1	6.0
Nd	8.3	14.9	13.1	12.1	34.6	34.1	8.3	12.5	9.2	18.6	37.7	28.6
Sm	2.4	3.8	3.9	3.8	7.0	7.1	2.9	3.6	2.8	5.0	8.9	7.3
Eu	0.9	1.3	1.2	1.4	1.8	1.9	1.1	1.2	0.9	1.8	2.9	2.5
Gd	2.6	3.7	4.3	4.2	6.3	6.4	3.2	3.7	3.0	5.0	8.9	8.3
Tb	0.4	0.5	0.6	0.6	0.9	0.9	0.4	0.5	0.4	0.7	1.3	1.2
Dy	2.5	3.3	3.9	3.8	5.5	5.8	2.6	3.3	2.6	3.8	8.4	8.7
Но	0.5	0.6	0.7	0.7	1.1	1.1	0.4	0.6	0.5	0.7	1.6	1.7
Er	1.4	1.8	2.1	1.9	3.0	3.2	1.1	1.7	1.3	1.8	4.2	4.9
Tm	0.2	0.3	0.3	0.3	0.4	0.5	0.1	0.2	0.2	0.2	0.6	0.7
Yb	1.3	1.8	1.9	1.7	3.0	3.2	0.9	1.5	1.2	1.4	4.0	5.0
Lu	0.2	0.2	0.3	0.2	0.4	0.5	0.1	0.2	0.2	0.2	0.5	0.7
Hf	0.86	1.58	1.60	1.52	4.77	5.43	1.00	1.49	1.24	1.19	6.77	5.65
Та	0.09	0.16	0.12	0.12	0.81	0.89	0.05	0.16	0.12	0.15	2.69	1.38
Pb	1.34	2.37	0.93	1.60	11.33	7.01	1.48	1.08	0.86	1.12	3.25	2.10
Th	0.75	0.93	0.66	0.52	7.44	9.38	0.10	0.77	0.74	0.22	2.84	2.40
U	0.35	0.57	0.29	0.28	1.38	1.72	0.03	0.32	0.31	0.06	0.69	0.61
Eu/Eu*	1.07	1.03	0.91	1.08	0.85	0.84	1.06	1.04	1.00	1.07	0.99	0.98
$\Sigma$ REE	38.1	63.3	56.4	52.1	174	174	31.4	53.8	40.0	72.0	175	138
La/Sm	2.04	2.24	1.67	1.45	4.87	4.92	0.76	1.92	1.79	1.68	3.12	2.69
Sm/Yb	1.85	2.11	2.05	2.24	2.33	2.22	3.22	2.40	2.33	3.57	2.23	1.46
Dy/Yb	1.92	1.83	2.05	2.24	1.83	1.81	2.89	2.20	2.17	2.71	2.10	1.74
(La/Nb)	3.62	3.42	3.35	3.24	2.71	2.64	2.33	3.32	3.84	3.82	0.69	1.01
(Th/Ta)	4.03	2.69	2.57	1.97	4.25	4.89	0.90	2.25	2.94	0.69	0.45	0.80

 Table 1.2: Bulk-rock trace element analyses of mafic rocks of Chukotka, NE Russia.

Note:  $Eu/Eu*=EuN/\sqrt{SmN \times GdN}$ ; subscript N denotes normalized to Primitive mantle (McDonough and Sun, 1995).

## 1.5.2. MINERAL CHEMISTRY

## 1.5.2.1. Major element chemistry of minerals in gabbroic rocks

## 1.5.2.1.1. Clinopyroxene

The chemical composition of clinopyroxene grains from IAB-type and OIB-type gabbroic rocks are listed in Table 1.3. In the conventional classification diagram (Morimoto et al. 1988), clinopyroxenes of IAB-type gabbros ranges from augite to diopside, but some compositions plot above the 50% Ca line, whereas those in OIB-type gabbros mainly ploted in the augite field (Fig. 1.10). Generally, on a pyroxene quadrilateral diagram the clinopyroxene compositions of IAB-type gabbros exhibit an alkaline trend (Wo increase with Fs) whereas clinopyroxenes from OIB-type gabbros follow a tholeiitic trend (Wo decrease with En). Clinopyroxenes in IABtype gabbroic rocks show lower TiO<sub>2</sub> (0.17-1.25 wt. %, average 0.70 wt. %) and higher CaO (22.0-25.1 wt. %, average 22.9 wt. %) and Mg# (76.9-90.2, average 78.3) than those in OIB-type gabbros (0.7-2.7, average 1.0 wt. %; 18.3-21.1, average 20.1 wt.% and 53.2-70.6, average, 63.6, respectively; Fig. 1.11). Clinopyroxene in one IAB-type gabbro sample (Sample #78) has lower CaO (16.9-19.5 wt. %) than other clinopyroxene. The clinopyroxenes from both IAB-type and OIB-type gabbroic rocks are characterized by Ti contents decreasing with Al (Fig. not shown). However, the Ti/Al ratios in clinopyroxenes of the IAB-type gabbros clinopyroxenes are lower than those in the OIB-type gabbros.



**Figure 1.10:** Pyroxene quadrilateral diagram showing the composition of pyroxene from the gabbroic rocks in the Chukotka area, NE, Russia. Nomenclature (after Morimoto et al. 1988).



**Figure 1.11**: Major element chemistry of clinopyroxene crystals from the gabbroic rocks of Chukotka. The shaded circle showing clinopyroxene composition of gabbroic rocks reported by Ledneva et al. (2014).

Rock	IAB-type gabbros #60 #62																
Sample			#5	57				#.	58			#60			#6	52	
Mineral	Cpx1	Cpx2	Cpx3	Cpx4	Cpx5	Срхб	Cpx1	Cpx2	Cpx3	Cpx4	Cpx1	Cpx2	Cpx3	Cpx1	Cpx4	Cpx5	Срх6
	core	core	core	core	core	core	core	core	core	core	core	core	core	core	core	core	core
SiO <sub>2</sub>	46.88	47.11	44.14	47.71	48.47	49.01	48.07	47.15	49.44	49.54	47.83	47.97	48.8	48.89	50.24	51.87	49.81
TiO <sub>2</sub>	1.21	1.07	1.06	1.06	1.04	0.83	1.24	1.11	1.06	0.75	1.03	0.99	0.78	0.84	0.62	0.66	0.77
$Al_2O_3$	6.45	6.18	5.88	5.62	5.71	4.65	6.25	5.78	5.57	4.92	5.61	5.34	4.58	4.24	3.6	3.89	3.62
$Cr_2O_3$	0	0.08		0.06	0.06	0.11	0.05	0.05		0.04	0.03	0.02	0.05	0.12	0.07	0.45	0.11
FeO	6.65	6.8	6.06	6.49	6.94	6.76	7.76	7.5	7.77	6.79	6.83	6.61	6.59	6.91	6.79	6.75	6.83
Mno	0.17	0.06	0.12	0.11	0.09	0.15	0.03	0.08	0.11	0.12	0.17	0.06	0.14				
MgO	12.45	12.71	12	12.85	13.19	13.25	12.69	12.5	13.25	13.6	13.02	13.17	13.16	12.88	13.45	13.93	13.32
CaO	23.93	23.94	22.22	24.14	24.08	23.84	23.88	23.58	24.28	22.88	23.37	23.44	23.3	23.23	23.68	24.17	23.3
Na <sub>2</sub> O	0.2	0.17	0.2	0.22	0.18	0.2	0.17	0.25	0.23	0.29	0.31	0.37	0.35	0.39	0.34	0.36	0.37
Total	97.94	98.12	91.68	98.26	99.76	98.8	100.14	98	101.71	98.93	98.2	97.97	97.75	97.5	98.79	102.08	98.13
Cations (	0=6)																
Si	1.791	1.796	1.798	1.814	1.816	1.851	1.799	1.805	1.822	1.86	1.819	1.826	1.859	1.869	1.892	1.888	1.889
Al	0.29	0.278	0.282	0.252	0.252	0.207	0.276	0.261	0.242	0.218	0.251	0.24	0.206	0.191	0.16	0.167	0.162
Ti	0.035	0.031	0.033	0.03	0.029	0.023	0.035	0.032	0.029	0.021	0.03	0.028	0.022	0.024	0.017	0.018	0.022
Al	0.29	0.278	0.282	0.252	0.252	0.207	0.276	0.261	0.242	0.218	0.251	0.24	0.206	0.191	0.16	0.167	0.162
Cr <sup>3+</sup>	0	0.002		0.002	0.002	0.003	0.001	0.002		0.001	0.001	0.001	0.001	0.004	0.002	0.013	0.003
Fe <sup>2+</sup>	0.213	0.217	0.206	0.207	0.217	0.213	0.243	0.24	0.239	0.213	0.217	0.211	0.21	0.221	0.214	0.206	0.217
Mn	0.005	0.002	0.004	0.003	0.003	0.005	0.001	0.003	0.003	0.004	0.005	0.002	0.004				
Mg	0.709	0.722	0.729	0.728	0.736	0.746	0.708	0.713	0.728	0.761	0.738	0.747	0.747	0.734	0.755	0.756	0.753
Ca	0.979	0.978	0.97	0.984	0.967	0.965	0.958	0.967	0.959	0.92	0.952	0.956	0.951	0.952	0.956	0.943	0.947
Na	0.015	0.013	0.016	0.016	0.013	0.015	0.013	0.018	0.017	0.021	0.023	0.027	0.026	0.029	0.025	0.025	0.028
Total	4.037	4.039	4.038	4.036	4.035	4.028	4.034	4.041	4.039	4.019	4.036	4.038	4.026	4.024	4.021	4.016	4.021
Mg#	76.89	76.89	77.97	77.86	77.23	77.79	74.45	74.82	75.28	78.13	77.28	77.97	78.06	76.86	77.92	78.58	77.63
Wo	51.49	51.02	50.92	51.28	50.36	50.16	50.18	50.36	49.79	48.57	49.92	49.95	49.84	49.92	49.66	49.50	49.40
En	37.29	37.66	38.28	37.93	38.33	38.77	37.09	37.14	37.79	40.18	38.69	39.03	39.15	38.49	39.22	39.68	39.28
Fs	11.22	11.32	10.81	10.79	11.30	11.07	12.73	12.50	12.41	11.25	11.38	11.02	11.01	11.59	11.12	10.81	11.32

Table 1.3: Representative electron-microprobe analyses of clinopyroxene crystals in gabbroic rocks of Chukotka, NE Russia.

\*Total Fe expressed as FeO;  $Mg\#=100 \times Mg$  ( $Mg+Fe^{2+}$ ). Abbreviations: Wo, wollastonite; En, enstatite; Fs, ferrosilite.

 Table 1.3: (Continued)

Rock								IAI	B-type gab	bros							
Sample			#	63				#	64					#72			
Mineral	Cpx1	Cpx2	Cpx3	Cpx4	Срх6	Cpx7	Cpx2	Cpx3	Cpx4	Cpx5	Cpx1	Cpx2	CI	px3	Cpx4	Cpx5	Срхб
	core	core	core	core	core	core	core	core	core	core	core	core	core	rim	core	core	core
SiO <sub>2</sub>	49.25	50.55	50.52	51.18	51.67	53.67	50.92	50.3	50.92	49.91	49.68	53.16	49.99	53.25	53.32	50.93	52.3
TiO <sub>2</sub>	0.71	0.67	0.74	0.75	0.53	0.5	0.75	0.71	0.65	0.76	0.59	0.32	0.43	0.3	0.17	0.23	0.17
$Al_2O_3$	3.42	3.03	3.64	3.61	2.92	2.44	3.05	3.5	3.25	3.85	4.35	1.24	2.92	1.75	0.68	1.4	0.88
$Cr_2O_3$	0.09	0.02	0.04	0.07	0.03	0.01		0.14	0.09	0.08	0.08	0.05	0.08	0.04	0.09	0.07	0.12
FeO	6.78	6.85	6.62	7.43	6.51	7.37	5.76	6.4	6.52	6.34	7.72	7.42	6.61	7.7	7.92	7.72	6.4
Mno	0.26	0.24	0.37	0.28	0.27	0.42	0.18	0.25	0.29	0.2	0.09	0.37	0.25	0.12	0.27	0.34	0.17
MgO	13.25	13.77	13.5	13.79	14.28	14.59	13.86	13.69	13.89	13.39	13.51	14.01	14	14.58	14.07	13.28	14.04
CaO	23.02	23.08	23.56	23.75	23.64	24.11	24.91	23.9	23.77	23.78	23.25	23.42	23.68	23.67	23.64	24.28	23.94
Na <sub>2</sub> O	0.39	0.41	0.37	0.42	0.42	0.36		0.26	0.31	0.25	0.27	0.49	0.04	0.32	0.43	0.3	0.33
Total	97.17	98.62	99.36	101.28	100.27	103.47	99.43	99.15	99.69	98.56	99.54	100.48	98	101.73	100.59	98.55	98.35
Cations (	O=6)																
Si	1.889	1.907	1.892	1.886	1.914	1.93	1.902	1.888	1.899	1.883	1.865	1.969	1.9	1.947	1.977	1.939	1.975
Al	0.155	0.135	0.161	0.157	0.127	0.103	0.134	0.155	0.143	0.171	0.192	0.054	0.131	0.076	0.03	0.063	0.039
Ti	0.02	0.019	0.021	0.021	0.015	0.013	0.021	0.02	0.018	0.021	0.017	0.009	0.012	0.008	0.005	0.007	0.005
Al	0.155	0.135	0.161	0.157	0.127	0.103	0.134	0.155	0.143	0.171	0.192	0.054	0.131	0.076	0.03	0.063	0.039
$Cr^{3+}$	0.003	0.001	0.001	0.002				0.004	0.003	0.002	0.002	0.001	0.002	0.001	0.003	0.002	0.004
Fe <sup>2+</sup>	0.218	0.216	0.207	0.229	0.202	0.222	0.18	0.201	0.203	0.2	0.242	0.23	0.21	0.235	0.246	0.246	0.202
Mn	0.009	0.008	0.012	0.009	0.008	0.013	0.006	0.008	0.009	0.006	0.003	0.012	0.008	0.004	0.008	0.011	0.006
Mg	0.758	0.774	0.753	0.758	0.788	0.782	0.772	0.766	0.772	0.753	0.756	0.773	0.793	0.795	0.778	0.753	0.79
Ca	0.946	0.933	0.946	0.938	0.938	0.929	0.997	0.961	0.95	0.961	0.935	0.929	0.964	0.927	0.939	0.99	0.968
Na	0.029	0.03	0.027	0.03	0.03	0.025		0.019	0.023	0.019	0.019	0.035	0.003	0.023	0.031	0.022	0.024
Total	4.027	4.023	4.02	4.03	4.022	4.017	4.012	4.022	4.02	4.016	4.029	4.011	4.021	4.015	4.014	4.031	4.009
Mg#	77.66	78.18	78.44	76.80	79.60	77.89	81.09	79.21	79.18	79.01	75.75	77.07	79.06	77.18	75.97	75.37	79.64
Wo	49.22	48.52	49.63	48.73	48.65	48.06	51.15	49.84	49.35	50.21	48.37	48.08	49.01	47.37	47.83	49.77	49.39
En	39.44	40.25	39.51	39.38	40.87	40.45	39.61	39.73	40.10	39.34	39.11	40.01	40.31	40.62	39.63	37.86	40.31
Fs	11.34	11.23	10.86	11.89	10.48	11.48	9.24	10.43	10.55	10.45	12.52	11.90	10.68	12.01	12.53	12.37	10.31

 Table 1.3: (Continued)

Rock								IAB-ty	pe gabbros							
Sample		#75					#76						#	78		<u> </u>
Mineral	C	px1	Cpx3	Cpx1	Cpx2	Cpx3	Cpx4	Cpx5	Срхб	Cpx8	Cpx1	CĮ	ox2	Cpx4	CĮ	ox5
	core	rim	core	core	core	core	Core	core	core	core	core	core	rim	core	core	rim
SiO <sub>2</sub>	52.69	51.87	52.83	51.19	52	51.92	49.99	53.11	51.12	53.66	51.01	52.46	52.23	52.94	53.98	52.76
TiO <sub>2</sub>	0.23	0.25	0.26	0.49	0.24	0.35	0.71	0.26	0.32	0.19	0.51	0.89	0.87	0.76	0.48	0.7
$Al_2O_3$	1.88	1.84	1.79	2.84	1.75	1.55	3.38	1.57	2.22	1.11	2.99	3.25	3.18	3.15	4.03	3.27
$Cr_2O_3$	0.34	0.15	0.11	0.11	0.45	0.12	0.11	0.16	0.49	0.51	0.11	0.07	0.08		0.3	0.02
FeO	4.59	7.32	6.74	6.02	4.71	6.74	6.81	6.53	4.38	3.27	9.54	9.52	9.12	7.79	3.61	6.65
Mno	0.11	0.23	0.19	0.2	0.08	0.25	0.18	0.16	0.12	0.03	0.12	0.2	0.22	0.24	0.07	0.28
MgO	15.99	14.71	14.92	14.42	15.73	14.64	13.69	15.16	15.67	16.92	15.64	15.91	15.5	16.16	17.95	16.35
CaO	23.99	22.75	23.54	23.81	23.19	22.73	22.85	23.31	23.4	24.28	17.26	18.21	18.85	19.54	17.69	16.99
Na <sub>2</sub> O	0.03	0.3	0.09	0.1	0.1	0.27	0.42	0.33			0.36	0.28	0.24	0.2	0.23	0.25
Total	99.85	99.42	100.47	99.18	98.25	98.57	98.14	100.59	97.72	99.97	97.54	100.79	100.29	100.78	98.35	97.29
Cations (	O=6)															
Si	1.94	1.94	1.948	1.913	1.945	1.953	1.895	1.954	1.924	1.961	1.932	1.923	1.925	1.931	1.961	1.966
Al	0.082	0.081	0.078	0.125	0.077	0.069	0.151	0.068	0.098	0.048	0.133	0.14	0.138	0.135	0.172	0.143
Ti	0.006	0.007	0.007	0.014	0.007	0.01	0.02	0.007	0.009	0.005	0.014	0.025	0.024	0.021	0.013	0.02
Al	0.082	0.081	0.078	0.125	0.077	0.069	0.151	0.068	0.098	0.048	0.133	0.14	0.138	0.135	0.172	0.143
$Cr^{3+}$	0.01	0.004	0.003	0.003	0.013	0.004	0.003	0.005	0.015	0.015	0.003	0.002	0.002		0.009	0.001
Fe <sup>2+</sup>	0.141	0.229	0.208	0.188	0.148	0.212	0.216	0.201	0.138	0.1	0.302	0.292	0.281	0.238	0.11	0.207
Mn	0.004	0.007	0.006	0.006	0.002	0.008	0.006	0.005	0.004	0.001	0.004	0.006	0.007	0.007	0.002	0.009
Mg	0.878	0.82	0.82	0.803	0.877	0.821	0.774	0.832	0.879	0.922	0.883	0.869	0.851	0.879	0.972	0.908
Ca	0.946	0.911	0.93	0.953	0.929	0.916	0.928	0.919	0.944	0.951	0.7	0.715	0.744	0.764	0.689	0.678
Na	0.002	0.022	0.007	0.007	0.007	0.019	0.031	0.024			0.026	0.02	0.017	0.014	0.016	0.018
Total	4.009	4.021	4.007	4.012	4.005	4.012	4.024	4.015	4.011	4.003	3.997	3.992	3.989	3.989	3.945	3.951
Mg#	86.16	78.17	79.77	81.03	85.56	79.48	78.18	80.54	86.43	90.22	74.51	74.85	75.18	78.69	89.83	81.43
Wo	48.14	46.48	47.50	49.02	47.54	47.00	48.38	47.08	48.14	48.20	37.14	38.11	39.66	40.62	38.90	37.81
En	44.68	41.84	41.88	41.31	44.88	42.12	40.35	42.62	44.82	46.73	46.84	46.32	45.36	46.73	54.88	50.64
Fs	7.18	11.68	10.62	9.67	7.57	10.88	11.26	10.30	7.04	5.07	16.02	15.57	14.98	12.65	6.21	11.54

 Table 1.3: (Continued)

Rock									OIB-type	e gabbros								
Sample		#	81			#84				#8	85					#86		
Mineral	Cpx1	Cpx2	Cpx3	Cpx4	Cpx7	Cpx8	Cpx9	Cpx1	Cpx2	Cpx3	Cpx4	Срх6	Cpx7	Cpx1	Cpx2	Cpx3	Cpx4	Cpx5
	core	core	core	core	core	core	core	core	core	core	core	core	core	core	core	core	core	core
SiO <sub>2</sub>	50.17	51.4	50.98	51.43	50.83	48.49	48.92	51.96	53.36	51.72	52.47	51.83	49.55	48.79	50.53	52.56	50.09	51.81
TiO <sub>2</sub>	1.25	0.66	1.03	0.81	1.13	1.91	1.8	0.79	0.25	0.82	0.89	0.98	0.8	2.93	0.32	0.29	0.29	0.43
$Al_2O_3$	2.31	1.16	1.87	1.36	1.88	3.67	3.66	1.49	0.5	1.84	2	1.59	3.27	1.34	1.11	0.79	0.69	1.38
$Cr_2O_3$	0.1	0.04	0.11			0.03	0.03	0.03	0.03			0.07	0.05	0.08	0.1	0.03	0.02	0.01
FeO	13.17	15.83	13.43	13.63	10.39	10.61	10.26	12.12	15.33	14.67	14.41	13.19	15.08	12.15	12.5	12.66	12.69	12.13
Mno	0.28	0.43	0.4	0.28	0.23	0.18	0.15	0.35	0.37	0.37	0.48	0.56	0.29	0.33	0.22	0.48	0.32	0.41
MgO	12.94	12.96	13.22	13.91	14.02	12.85	12.78	13.3	11.08	12.17	12.14	11.65	12.03	11.31	11.32	11.68	10.94	12.27
CaO	18.71	17.62	18.69	17.54	19.78	20.62	20.8	19.32	20.78	19.51	20.29	21.44	18.24	21.71	21.27	22.38	22.42	20.82
Na <sub>2</sub> O	0.24	0.17	0.19	0.25	0.32	0.39	0.37	0.17	0.16	0.16	0.08	0.16	0.29	0.18	0.33	0.14	0.15	0.31
Total	99.17	100.27	99.92	99.21	98.58	98.75	98.77	99.53	101.86	101.26	102.76	101.47	99.6	98.82	97.7	101.01	97.61	99.57
Cations (	O=6)																	
Si	1.914	1.954	1.931	1.955	1.931	1.853	1.864	1.962	2	1.943	1.941	1.943	1.897	1.886	1.966	1.977	1.961	1.966
Al	0.104	0.052	0.084	0.061	0.084	0.165	0.165	0.066	0.022	0.081	0.087	0.07	0.147	0.061	0.051	0.035	0.032	0.062
Ti	0.036	0.019	0.029	0.023	0.032	0.055	0.052	0.022	0.007	0.023	0.025	0.028	0.023	0.085	0.009	0.008	0.009	0.012
Al	0.104	0.052	0.084	0.061	0.084	0.165	0.165	0.066	0.022	0.081	0.087	0.07	0.147	0.061	0.051	0.035	0.032	0.062
Cr <sup>3+</sup>	0.003	0.001	0.003	0		0.001	0.001	0.001	0.001			0.002	0.002	0.002	0.003	0.001	0.001	0
Fe <sup>2+</sup>	0.42	0.503	0.425	0.433	0.33	0.339	0.327	0.383	0.481	0.461	0.446	0.414	0.483	0.393	0.406	0.398	0.416	0.385
Mn	0.009	0.014	0.013	0.009	0.007	0.006	0.005	0.011	0.012	0.012	0.015	0.018	0.01	0.011	0.007	0.015	0.01	0.013
Mg	0.736	0.734	0.746	0.788	0.794	0.732	0.726	0.749	0.619	0.682	0.669	0.651	0.686	0.652	0.656	0.655	0.639	0.694
Ca	0.765	0.717	0.758	0.714	0.805	0.844	0.849	0.781	0.834	0.785	0.804	0.861	0.748	0.899	0.887	0.902	0.94	0.846
Na	0.018	0.013	0.014	0.018	0.023	0.029	0.027	0.012	0.012	0.011	0.006	0.011	0.022	0.014	0.025	0.01	0.012	0.023
Total	4.005	4.007	4.003	4.001	4.006	4.024	4.016	3.987	3.988	3.998	3.993	3.998	4.018	4.003	4.01	4.001	4.02	4.001
Mg#	63.67	59.34	63.71	64.54	70.64	68.35	68.95	66.17	56.27	59.67	60.00	61.13	58.68	62.39	61.77	62.20	60.57	64.32
Wo	39.82	36.69	39.29	36.90	41.73	44.07	44.64	40.83	43.12	40.72	41.90	44.70	39.02	46.24	45.51	46.14	47.12	43.95
En	38.31	37.56	38.67	40.72	41.16	38.22	38.17	39.15	32.01	35.37	34.86	33.80	35.79	33.54	33.66	33.50	32.03	36.05
Fs	21.86	25.74	22.03	22.38	17.11	17.70	17.19	20.02	24.87	23.91	23.24	21.50	25.20	20.22	20.83	20.36	20.85	20.00

# 1.5.2.1.2. Amphiboles

Amphiboles are the dominant ferro-magnesian minerals in the IAB-type gabbroic rocks of Chukotka. Most of the amphiboles from IAB-type gabbros are plotted in the pargasite compositional field whereas from OIB-type gabbros plotted in the magnesio-hornblende, actinolitic hornblende and edenite field (Fig. 1.12).



**Figure 1.12:** Plot of Al<sup>(IV)</sup> versus cations in A-site for hornblende in the studied rocks (nomenclature from Leake, 1978).

In the Al<sub>total</sub> versus Al<sup>iv</sup> variation diagram (Fig. not shown), amphibole minerals from IAB-type gabbroic rocks have higher content of Al<sub>total</sub> than those from OIB-type gabbroic rocks. It is important to note that amphiboles from the most magesian IAB-type gabbro (i.e. Sample #75) are higher in MgO (14.5-16.3 wt. %) compared to the rest of the studied samples, but it is similar to those in ankaramitic volcanic rocks (14.6-16.4 wt. %). Amphibole crystal from IAB-type gabbroic rocks have higher TiO<sub>2</sub> (2.3-3.1 wt. %) and Al<sub>2</sub>O<sub>3</sub> (11.1-14.8) content compared to those in OIB-type gabbros (0.5-0.9 wt. %, 4.9-6.6 wt. %; respectively; Fig. 1.13A and B). Mg-numbers in amphibole are mostly lower than those of clinopyroxene from the basaltic and gabbroic rocks and is interpreted as a late magmatic mineral.



Figure 1.13: Major element chemistry of amphibole from gabbroic rocks of Chukotka, NE Russia.

Rock								IAE	-type gabb	oros							
Sample			#:	57					#6	53					#64		
Minera	Hb1	Hb2	Hb3	Hb4	Hb5	Hb6	Hb2	Hb3	Hb4	Hb5	Hb6	Hb7	Hb1	Hb2	Hb3	Hb4	Hb5
Positio	core	core	core	core	core	core	core	core	core								
SiO <sub>2</sub>	38.71	39.24	39.94	38.7	40.19	40.37	40.96	41.71	42.12	42.08	41.13	41.21	39.57	40.65	41.24	40.99	42.76
TiO <sub>2</sub>	2.37	2.35	2.52	2.32	2.53	2.43	2.65	2.77	2.62	2.5	2.6	2.76	2.54	2.58	2.48	2.54	2.69
$Al_2O_3$	14.47	14.79	14.77	13.93	14.78	14.15	12.99	12.53	12.92	13.15	13.43	13.33	13.44	13.35	13.23	13.54	14
$Cr_2O_3$				0.004			0.04	0.1	0.06		0.1	0.02	0.02	0.05	0.03	0.01	0.07
FeO	9.81	10.33	10.41	10.06	10.44	10.11	11.64	12.14	12.04	11.37	11.77	12.02	10.99	11.29	11.22	10.71	11.58
MnO	0.07	0.15	0.19	0.02	0.06	0.17	0.29	0.25	0.26	0.27	0.18	0.31	0.14	0.15	0.14	0.18	0.22
MgO	13.15	13.29	13.97	13.3	13.88	14.07	13.16	13.34	13.49	13.84	13.14	13.12	12.93	13.29	13.6	13.58	14
CaO	12.59	12.5	12.89	12.48	13	12.95	12.4	12.34	12.30	12.09	12.63	12.72	12.16	12.53	12.51	12.47	12.72
Na <sub>2</sub> O	2.56	2.83	2.72	2.6	2.76	2.65	3.02	3.07	3.12	3.4	3.06	3.03	2.9	3.06	2.95	3.01	3.23
K <sub>2</sub> O	1.08	1.18	1.25	1.16	1.21	1.18	0.95	0.83	0.84	0.98	0.96	0.99	0.95	0.92	1.04	1.03	1.08
Total	94.81	96.66	98.66	94.574	98.85	98.08	98.1	99.08	99.77	99.68	99	99.51	95.64	97.87	98.44	98.06	102.35
Cations (	O=23)																
Si	5.893	5.877	5.862	5.915	5.882	5.947	6.065	6.117	6.122	6.11	6.036	6.028	5.997	6.024	6.068	6.043	6.049
Ti	0.271	0.265	0.278	0.267	0.278	0.269	0.295	0.305	0.287	0.273	0.287	0.304	0.29	0.287	0.274	0.281	0.286
Al	2.595	2.61	2.556	2.51	2.55	2.458	2.267	2.165	2.214	2.251	2.323	2.298	2.401	2.332	2.294	2.352	2.334
Cr <sup>3+</sup>				0.005			0.005	0.011	0.007		0.011	0.002	0.002	0.006	0.004	0.001	0.008
Fe <sup>2+</sup>	1.249	1.294	1.278	1.285	1.278	1.245	1.442	1.489	1.464	1.381	1.445	1.47	1.392	1.399	1.381	1.32	1.37
Mn	0.009	0.019	0.024	0.002	0.008	0.022	0.037	0.032	0.032	0.033	0.022	0.039	0.017	0.019	0.017	0.023	0.027
Mg	2.984	2.967	3.057	3.031	3.029	3.089	2.903	2.916	2.923	2.994	2.875	2.861	2.921	2.935	2.982	2.983	2.952
Ca	2.054	2.006	2.027	2.045	2.038	2.044	1.967	1.94	1.915	1.882	1.985	1.993	1.975	1.99	1.972	1.97	1.928
Na	0.757	0.822	0.775	0.771	0.784	0.758	0.867	0.873	0.88	0.956	0.871	0.86	0.852	0.879	0.841	0.86	0.887
K	0.21	0.225	0.234	0.227	0.227	0.222	0.18	0.155	0.155	0.181	0.179	0.185	0.183	0.174	0.196	0.193	0.195
Total	16.022	16.085	16.091	16.058	16.074	16.054	16.028	16.003	15.999	16.061	16.034	16.04	16.03	16.045	16.029	16.026	16.036
Mg#	70.49	69.63	70.52	70.23	70.33	71.27	66.81	66.20	66.63	68.43	66.55	66.06	67.73	67.72	68.35	69.32	68.30

Table 1.4: Representative electron-microprobe analyses of hornblende crystals in gabbroic rocks of Chukotka, NE Russia

Table	1.4: (	(Continued)	)
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Rock					IAB-type	e gabbros							OIE	B-type gabb	oros		
Sample		#7	72			#7	'5		#	76		#85			#8	36	
Minera	Hb1	Hb2	Hb3	Hb4	Hb1	Hb2	Hb3	Hb4	Hb1	Hb3	Hb2	Hb3	Hb4	Hb1	Hb2	Hb3	Hb4
Positio	core	core	core	core	core	core	core	core	core	core	core	core	core	core	core	core	core
SiO <sub>2</sub>	42.38	42.41	41.65	42.42	42.22	45.54	42.52	42.51	41.3	42.62	49.08	47.72	49.32	46.19	49.98	48.13	49.61
TiO <sub>2</sub>	2.37	2.44	2.62	2.62	2.89	0.31	3.07	2.59	2.59	2.31	1.43	1.2	1.12	0.6	0.49	0.58	0.97
$Al_2O_3$	12.22	11.08	12.42	12.67	12.52	11.14	12.79	12.51	12.14	11.82	5.66	6.61	5.53	8.24	5.38	6.36	4.89
$Cr_2O_3$	0.08	0.08	0.05	0.03	0.06	0.02		0.09	0.07	0.02		0.03	0.03		0.12	0.08	0.03
FeO	13.43	13.91	13.79	12.98	10.53	10.95	11.34	11.2	11.94	11.55	19.85	21.46	17.79	20.34	19.06	19.09	17.13
MnO	0.14	0.13	0.11	0.09	0.2	0.17	0.15	0.16	0.2		0.16	0.15	0.27	0.13	0.23	0.2	0.17
MgO	13.17	12.66	12.78	13.22	14.53	16.34	14	14.55	12.78	13.46	10.77	10.01	11.9	10.11	11.57	11.11	12.07
CaO	12.09	12.27	12.18	12.28	11.7	12.33	12.34	12.29	12.14	12.19	11.76	10.73	12.08	11.71	12.05	11.77	11.66
Na <sub>2</sub> O	2.97	2.65	2.87	3.12	3.14	2.48	2.92	2.86	2.73	2.8	2	1.73	1.91	1.41	0.99	1.3	1
K <sub>2</sub> O	1.13	1.18	1.13	1.17	1.06	0.91	1.07	1.06	1.09	1.02	0.66	0.63	0.76	0.56	0.39	0.47	0.38
Total	99.98	98.81	99.6	100.6	98.85	100.19	100.2	99.82	96.98	97.79	101.37	100.27	100.71	99.29	100.26	99.09	97.91
Cations (	O=23)																
Si	6.187	6.283	6.122	6.144	6.15	6.501	6.134	6.151	6.185	6.292	7.142	7.057	7.168	6.885	7.283	7.126	7.337
Ti	0.26	0.272	0.289	0.286	0.317	0.033	0.333	0.282	0.292	0.256	0.156	0.134	0.122	0.067	0.053	0.065	0.108
Al	2.102	1.935	2.152	2.163	2.15	1.874	2.175	2.134	2.143	2.056	0.97	1.152	0.947	1.448	0.924	1.11	0.852
$Cr^{3+}$	0.009	0.009	0.006	0.004	0.007	0.002		0.01	0.008	0.002		0.003	0.003		0.014	0.009	0.004
Fe <sup>2+</sup>	1.639	1.723	1.695	1.572	1.283	1.307	1.368	1.355	1.495	1.426	2.415	2.654	2.163	2.536	2.323	2.364	2.119
Mn	0.017	0.017	0.013	0.012	0.025	0.02	0.018	0.02	0.025		0.019	0.019	0.033	0.017	0.028	0.026	0.021
Mg	2.866	2.795	2.8	2.855	3.154	3.477	3.011	3.138	2.853	2.962	2.336	2.206	2.577	2.247	2.513	2.452	2.661
Ca	1.891	1.947	1.918	1.905	1.825	1.886	1.907	1.905	1.948	1.932	1.834	1.701	1.881	1.869	1.881	1.868	1.847
Na	0.841	0.762	0.818	0.877	0.887	0.686	0.816	0.801	0.794	0.801	0.566	0.496	0.539	0.407	0.281	0.373	0.286
Κ	0.21	0.223	0.212	0.216	0.197	0.166	0.197		0.207	0.192	0.123	0.119	0.141	0.107	0.072	0.089	0.071
Total	16.022	15.966	16.025	16.034	15.995	15.952	15.959	15.796	15.95	15.919	15.561	15.541	15.574	15.583	15.372	15.482	15.306
Mg#	63.62	61.86	62.29	64.49	71.08	72.68	68.76	69.84	65.62	67.50	49.17	45.39	54.37	46.98	51.96	50.91	55.67

## 1.5.2.1.3. Plagioclase

*Plagioclase* crystals composition in the IAB-type gabbroic rock varying from  $An_{100-46} Ab_{0-54}$  (i.e. anorthite to andesine), whereas in OIB-type gabbroic rocks  $An_{1-57}Ab_{99-42}Or_{0-25}$  (i.e. labradorite to alkali-feldspars) (Fig. 1.14). However, rare orthoclase crystals are also present in IAB-type gabbros (Sample #75). Representative plagioclase compositions are given in Table 1.5.



**Figure 1.14:** An-Ab-Or triangular diagram showing the compositions of plagioclase from gabbroic rocks of Chukotka. An, Anorthite; Ab, Albite; Or, Orthoclase.

Rock Type	Lampr	ophyres	Basaltio	c andesites			IAB-type	e gabbros			OIB-type gabbro
Sample	#74	#77	#55	#56	#62	#63	#64	#72	#75	#76	#85
n:	4	4	6	3	5	5	5	3	4	3	3
SiO <sub>2</sub>	56.89	59.38	52.58	51.17	46.04	46.58	44.79	57.13	53.92	51.44	54.98
$Al_2O_3$	26.71	28.34	30.26	30.50	33.02	34.30	34.54	27.09	32.66	29.99	27.68
FeO	0.70	1.05	0.21	0.47	0.55	0.60	0.51	0.40	0.93	0.44	1.02
CaO	8.60	1.12	13.08	13.57	17.26	18.19	18.89	9.46	2.40	13.36	10.88
Na <sub>2</sub> O	4.85	6.75	3.79	3.03	1.27	1.02	0.50	5.41	3.68	3.53	4.83
K <sub>2</sub> O	1.98	5.65	0.31	0.47	0.03	0.02	0.02	0.68	8.56	0.16	0.37
Total	99.81	100.59	100.22	99.21	98.24	100.78	99.30	100.17	99.71	98.97	99.89
Cations (O=8)											
Si	2.566	2.643	2.376	2.347	2.155	2.129	2.083	2.562	2.460	2.359	2.489
Al	1.427	1.496	1.616	1.648	1.822	1.847	1.893	1.434	1.758	1.624	1.476
Fe	0.027	0.039	0.007	0.018	0.022	0.023	0.020	0.015	0.035	0.017	0.039
Ca	0.421	0.053	0.637	0.667	0.866	0.890	0.941	0.456	0.116	0.659	0.528
Na	0.422	0.575	0.330	0.270	0.116	0.091	0.045	0.470	0.324	0.313	0.424
Κ	0.113	0.326	0.018	0.028	0.002	0.001	0.003	0.038	0.500	0.009	0.021
Total	4.975	4.988	4.983	4.978	4.981	4.982	4.983	4.975	5.002	4.981	4.977
An	44.08	5.94	64.92	69.10	88.07	90.62	95.36	47.24	10.06	67.05	54.23
Ab	44.55	48.90	33.30	28.00	11.76	9.24	4.54	48.75	19.42	32.03	43.61
Or	11.37	45.16	1.78	2.89	0.16	0.14	0.10	4.01	70.53	0.92	2.16

Table 1.5: Average electron microprobe analyses of plagioclase and alkali feldspar from the basaltic and gabbroic rocks of Chukotka, NE Russia.

Abbreviations: An, Anorthite; Ab, Albite; Or, orthoclase; n, number of analyses used for the average; n, number of analyses used for the average.

# 1.5.2.1.4. Biotite

Biotite from IAB-type gabbroic rocks have Mg# [=  $100*Mg/(Mg+Fe^{2+})$ ] between 64-66 whereas biotite from OIB-type gabbros has Mg# about 30. In the Mg# [=  $100*Mg/(Mg+Fe^{2+})$ ] vs Al classification diagram biotite from IAB-type gabbro fall in the phlogopite compositional field, but those from OIB-type gabbro plotted in annite (Fig. not shown). Biotite crystals lie in the magmatic biotite domain of the FeO\* (=FeO<sup>total</sup>+MnO)- $10\times$ TiO<sub>2</sub>-MgO diagram (Fig. not shown; Nachit et al., 2005).

Rock	IAB-type gal	obro	OIB-type gabbro		В	asaltic andesit	te	
Sample	#7	72	#85			#56		
Mineral	Bi1	Bi2	Bil	Bi1	Bi2	Bi3	Bi4 gm	Bi5
SiO <sub>2</sub>	39.78	39.54	37.63	44.34	43.15	41.57	43.27	40.33
TiO <sub>2</sub>	4.89	4.79	4.95	0.66	0.59	0.62	0.84	0.43
$Al_2O_3$	15.5	15.27	13.39	15.49	12.94	14.24	13.26	15.49
$Cr_2O_3$	0.08	0.07	0.06	0.02	0.07	0.02	0.01	0.08
FeO	14.99	14.65	28.13	19.02	20.93	21.85	20.34	22.83
MnO			0.12	0.00	0.00	0.00	0.00	0.00
MgO	15.16	15.95	6.65	10.93	12.21	12.45	12.45	13.50
CaO	0.03		0.00	0.10	1.34	0.25	1.01	0.29
Na <sub>2</sub> O	0.2	0.17	0.06	0.05	0.06	0.04	0.03	0.08
K <sub>2</sub> O	9.37	9.56	9.00	9.38	8.71	8.95	8.78	6.97
Total	100	100	100	100	100	100	100	100
Si	5.619	5.588	5.678	6.276	6.208	6.012	6.199	5.805
Ti	0.52	0.509	0.562	0.071	0.064	0.068	0.091	0.047
Al	2.58	2.544	2.382	2.584	2.194	2.427	2.239	2.628
Cr	0.009	0.008	0.007	0.002	0.008	0.002	0.002	0.01
Fe	1.771	1.732	3.55	2.251	2.518	2.643	2.437	2.748
Mn			0.016					
Mg	3.192	3.361	1.496	2.306	2.62	2.684	2.659	2.896
Ca	0.005			0.015	0.207	0.039	0.155	0.043
Na	0.055	0.047	0.018	0.015	0.016	0.011	0.01	0.023
K	1.688	1.724	1.732	1.694	1.598	1.65	1.604	1.28
Total	15.439	15.513	15.441	15.214	15.433	15.536	15.396	15.48
Mg#	0.64	0.66	0.30	0.51	0.51	0.50	0.52	0.51

Table 1.6: Electron-microprobe analyses of biotite from the basaltic and gabbroic rocks of Chukotka, NE Russia.

#### 1.5.2.1.5. Opaque minerals

Opaque phases in the IAB-type gabbroic rocks include magnetite and titano-magnetite. The  $TiO_2$  content of magnetite varies from 0.17 to 0.43 wt. %. Titano-magnetite contains  $TiO_2$  ranging from 3.39 to 5.09 wt. %. Opaque minerals in OIB-type gabbros are mainly ilmenite with  $TiO_2$  content ranging from 49.3 to 51.1 wt. %.

#### 1.5.2.2. Major element chemistry of minerals in basaltic rocks

On the basis of petrography and mineral chemistry two distinct groups of lava are identified i.e. basaltic rocks (phyroxene-phyric basalt, ankaramites and lamprophyres) and hornblende bearing basaltic andesites. Both groups of lava are characterized by island-arc basalt (IAB)-type geochemical features. Orthopyroxene and olivine grains are not observed in the studied samples.

## 1.5.2.2.1. Clinopyroxene

In the conventional classification diagram (Morimoto et al., 1988), clinopyroxene from basaltic rocks is diopsidic in composition ( $Wo_{45-50}En_{36-50}Fs_{4-14}$ ; Fig. 1.15), with the averaged TiO<sub>2</sub> contents ranging from 0.23 to 0.85 wt. % and Al<sub>2</sub>O<sub>3</sub> from 1.83 to 4.84 wt. %, whereas clinopyroxene in basaltic andesite is augite ( $Wo_{29-42}En_{31-40}Fs_{17-37}$ ) with 0.59-0.77 wt. % TiO<sub>2</sub> and 2.22-2.71 wt. % Al<sub>2</sub>O<sub>3</sub> (Table 1.7).



**Figure 1.15:** Pyroxene quadrilateral diagram showing the composition of pyroxene (after Morimoto et al., 1988) from the basaltic rocks in the Chukotka area, NE, Russia.

Clinopyroxene in basalts is higher in CaO than those of basaltic andesite. The Mg# [=  $100 \times Mg/(Mg+Fe^{2^+})$ ] of clinopyroxene in ankaramites ranges from 85.3 to 92.4 (average 87.1), pyroxene-phyric basalt from 72.4 to 91.2 (average 84.5), lamprophyres from 80.5 to 93.1 (average 86.6) and basaltic andesites ranges from 45.5 to 70.6 (average 57.9) (Table 1.7; Fig. 1.16). Clinopyroxene crystals have high Al<sup>VI</sup>/Al<sup>IV</sup> ratios (generally >0.25). TiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> content of clinopyroxene in basalts displays a negative correlation with Mg#, whereas those in basaltic andesites have positive correlation (Fig. 1.16). Clinopyroxene in basaltic andesites has higher content of FeO<sup>\*</sup> (10.7-16.4 wt. %) than that in basalts (4.6-7.7 wt. %). Clinopyroxene of ankaramites have relatively high Cr<sub>2</sub>O<sub>3</sub> (as high as 0.79 wt. %) compared to the other clinopyroxenes. In general, the Cr<sub>2</sub>O<sub>3</sub> content of clinopyroxene in basalts (mainly in pyroxene-phyric basalt) show strong normal zoning with a general ferrosilite (Fs) increase from core to rim. However, few clinopyroxene phenocrysts from pyroxene-

phyric basalt shows reverse Fe enrichment from core to rim. Sometimes oscillatory-zoned clinopyroxene is observerd in ankaramites (e.g. Sample #70; Fig. 1.17). In general, the compositional difference between core and rim of clinopyroxenes follows the normal pyroxene fractionation trend: the cores are richer in Mg, Si and Cr and poorer in Fe, Ti and Al.



Figure 1.16: Major element chemistry of clinopyroxene phenocrysts from the basaltic rocks of Chukotka.



**Figure 1.17:** (A) BSE-image of clinopyroxene phenocryst. (B-G) Compositional variations (TiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, FeO, MgO, CaO and Cr<sub>2</sub>O3) from core to rim traverse for oscillatory zoned clinopyroxene phenocryst of ankaramite rock (Cpx2, Sample #70; Table 1.7).

Rock								Bas	altic andes	ites							
Sample			#55								#:	56					
Mineral	Px1gm	Px2	Px3	Px5	Px6	Px1	Px1	Px1	Px2	Px2	Px2	Px2	Px2	Px2	Px2	Px3	Px4gm
				core	rim	core	rim1	rim2	core	rim1	rim2	rim3	rim4	rim5	rim6		
SiO <sub>2</sub>	49.39	53.97	52.69	53.19	53.16	52.36	51.5	52.5	51.96	51.93	52.26	52.46	50.71	49.84	50.56	50.47	52.16
TiO <sub>2</sub>	2.55	0.07	0.1	0.14	0.08	0.48	0.87	0.64	0.77	0.69	0.7	0.76	0.96	1.53	0.76	0.49	0.55
$Al_2O_3$	4.01	2.05	2.52	2.63	2.32	1.52	2.85	1.57	2.21	1.68	1.51	1.36	3.1	4.24	1.74	3.18	1.7
$Cr_2O_3$	0.17	0.02	0.03	0.05	0.1	0.09	0.12	0.15	0.07	0.15	0.19	0.15	0.15	0.06	0.05	0.06	0.15
FeO	20.03	19.03	20.48	19.94	19.13	14.83	12.21	12.42	10.43	13.59	12.84	13.23	12.18	11.04	13.66	13.53	13.96
MnO				0.39	0.33	0.26	0.25	0.42	0.25	0.39	0.31	0.38	0.27	0.24	0.24	0.33	0.34
MgO	9.37	12.25	11.46	11.32	11.8	12.56	13.2	13.53	14.02	13.38	13.69	13.47	13.23	13.04	13.2	12.96	13.09
CaO	13.64	12.88	12.63	12.59	12.61	19.11	19.9	20.1	20.74	18.8	19.71	19.75	19.43	20.08	18.11	18.45	19.13
Na <sub>2</sub> O	0.58	0.28	0.26			0.26	0.34	0.15	0.1	0.19	0.19	0.15	0.11	0.16	0.16	0.32	0.27
Total	99.74	100.55	100.17	100.25	99.53	101.47	101.24	101.48	100.55	100.8	101.4	101.71	100.14	100.23	98.48	99.79	101.35
Cations (	0=6)																
Si	1.902	2.024	2.001	2.011	2.019	1.96	1.917	1.95	1.934	1.947	1.945	1.95	1.906	1.868	1.941	1.912	1.949
Ti	0.074	0.003	0.003	0.004	0.002	0.013	0.024	0.018	0.022	0.019	0.02	0.021	0.027	0.043	0.022	0.014	0.016
Al	0.182	0.091	0.113	0.117	0.104	0.067	0.125	0.069	0.097	0.074	0.066	0.06	0.137	0.187	0.079	0.142	0.075
$Cr^{3+}$	0.005	0.001	0.001	0.001	0.003	0.003	0.004	0.005	0.002	0.004	0.006	0.004	0.005	0.002	0.002	0.002	0.004
Fe <sup>2+</sup>	0.645	0.597	0.65	0.631	0.608	0.464	0.38	0.386	0.325	0.426	0.4	0.411	0.383	0.346	0.439	0.429	0.436
Mn					0.011	0.008	0.008	0.013	0.008	0.012	0.01	0.012	0.009	0.008	0.008	0.011	0.011
Mg	0.538	0.685	0.648	0.638	0.668	0.701	0.732	0.749	0.778	0.748	0.76	0.746	0.741	0.729	0.756	0.732	0.729
Ca	0.563	0.518	0.514	0.51	0.513	0.766	0.793	0.8	0.827	0.755	0.786	0.787	0.783	0.806	0.745	0.749	0.766
Na	0.043	0.02	0.019			0.019	0.024	0.011	0.007	0.014	0.014	0.011	0.008	0.012	0.012	0.024	0.02
Total	3.952	3.939	3.949	3.912	3.928	4.001	4.007	4.001	4	3.999	4.007	4.002	3.999	4.001	4.004	4.015	4.006
Mg#	45.48	53.43	49.92	50.28	52.35	60.17	65.83	65.99	70.53	63.71	65.51	64.48	65.92	67.81	63.26	63.05	62.58
Wo	32.25	28.78	28.37	28.67	28.68	39.67	41.63	41.34	42.85	39.14	40.39	40.48	41.06	42.85	38.40	39.21	39.67
En	30.81	38.06	35.76	35.86	37.34	36.30	38.43	38.71	40.31	38.78	39.05	38.37	38.86	38.76	38.97	38.32	37.75
Fs	36.94	33.17	35.87	35.47	33.99	24.03	19.95	19.95	16.84	22.08	20.55	21.14	20.08	18.39	22.63	22.46	22.58

Table 1.7: Representative electron-microprobe analyses of clinopyroxene phenocrysts and microphenocrysts in basaltic rocks of Chukotka, NE Russia.

\*Total Fe expressed as FeO;  $Mg\#=100 \times Mg$  ( $Mg+Fe^{2+}$ ). Abbreviations: Wo, wollastonite; En, enstatite; Fs, ferrosilite; n, number of analyses used for average.

Rock	Pyroxene-phyric basalt																
Sample									#67								
Minral	Ср	x1	Cpx2	Ср	x3	Cpx4		Cpx5		Срхб		Cpx8		Cpx9		Cpx10	
	core	rim		core	rim												
SiO <sub>2</sub>	52.92	53.26	50.63	52.11	52.82	52.77	49.94	50.68	48.88	50.88	50.8	49.51	47.91	51.34	48.71	53.22	48.88
TiO <sub>2</sub>	0.28	0.3	0.71	0.27	0.47	0.28	0.67	0.56	0.7	0.57	0.57	0.6	0.76	0.44	0.68	0.25	0.83
$Al_2O_3$	1.33	1.41	3.64	2.07	2.35	1.87	3.07	3.39	4.69	3.36	1.83	3.89	9.28	3.06	4.11	1.16	5.09
$Cr_2O_3$	0.42	0.39	0.08	0.18	0.18	0.18	0.04	0.16	0.06	0.07		0.12	0.07	0.35	0.15	0.22	0.11
FeO	3.64	3.52	6.52	4.61	4.67	4.34	7.27	5.89	7.74	5.28	7.55	6.41	7.44	5.49	6.6	3.52	6.16
MnO	0.05	0.13	0.11	0.09	0.04	0.11	0.13	0.13	0.11	0.16	0.38	0.14	0.15	0.12	0.1	0.09	0.12
MgO	16.73	16.9	14.57	15.8	16.11	16.27	13.86	14.88	13.54	15.07	14.39	14.31	10.94	15.22	13.9	16.63	14.06
CaO	23.88	23.73	23.22	23.49	23.96	24.1	22.37	23.09	22.72	23.42	21.04	23.01	20.61	23.06	22.57	23.63	22.79
Na <sub>2</sub> O	0.04	0.01	0.14	0.05		0.05	0.25	0.07	0.13	0.12	0.34	0.09	0.81	0.04	0.17		0.1
Total	99.29	99.65	99.62	98.67	100.6	99.97	97.6	98.85	98.57	98.93	96.9	98.08	97.97	99.12	96.99	98.72	98.14
Cations (	O=6)																
Si	1.951	1.953	1.885	1.94	1.928	1.939	1.903	1.896	1.852	1.898	1.946	1.874	1.808	1.91	1.867	1.968	1.846
Ti	0.008	0.008	0.02	0.007	0.013	0.008	0.019	0.016	0.02	0.016	0.016	0.017	0.022	0.012	0.019	0.007	0.023
Al	0.058	0.061	0.16	0.091	0.101	0.081	0.138	0.149	0.209	0.148	0.083	0.173	0.413	0.134	0.186	0.051	0.227
Cr <sup>3+</sup>	0.012	0.011	0.002	0.005	0.005	0.005	0.001	0.005	0.002	0.002		0.004	0.002	0.01	0.005	0.007	0.003
Fe <sup>2+</sup>	0.112	0.108	0.203	0.144	0.143	0.133	0.232	0.184	0.245	0.165	0.242	0.203	0.235	0.171	0.212	0.109	0.195
Mn	0.002	0.004	0.003	0.003	0.001	0.004	0.004	0.004	0.004	0.005	0.012	0.004	0.005	0.004	0.003	0.003	0.004
Mg	0.919	0.924	0.809	0.876	0.877	0.891	0.788	0.83	0.764	0.838	0.822	0.807	0.615	0.844	0.794	0.917	0.792
Ca	0.943	0.932	0.927	0.937	0.937	0.949	0.914	0.925	0.922	0.936	0.864	0.934	0.833	0.919	0.927	0.936	0.922
Na	0.003	0.001	0.01	0.003		0.004	0.018	0.005	0.01	0.009	0.025	0.007	0.06	0.003	0.013		0.007
Total	4.008	4.002	4.019	4.006	4.005	4.014	4.017	4.014	4.028	4.017	4.01	4.023	3.993	4.007	4.026	3.998	4.019
Mg#	89.14	89.54	79.94	85.88	85.98	87.01	77.25	81.85	75.72	83.55	77.26	79.90	72.35	83.15	78.93	89.38	80.24
Wo	47.77	47.45	47.81	47.88	47.88	48.10	47.26	47.71	47.75	48.27	44.81	48.05	49.49	47.52	47.96	47.71	48.30
En	46.56	47.05	41.72	44.76	44.81	45.16	40.74	42.81	39.56	43.22	42.63	41.51	36.54	43.64	41.08	46.74	41.49
Fs	5.67	5.50	10.47	7.36	7.31	6.74	12.00	9.49	12.69	8.51	12.55	10.44	13.96	8.84	10.97	5.56	10.21

# Table 1.7: (Continued)

Table 1	1.7:	(Continu	ied)
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Rock									Ank	aramites								
Sampl	Sampl #69						#70						#71					
Minera	Cpx1	Cpx 2 Cpx4 Cpx5					Cpx2			Cpx2								
	core	core	rim	core	rim	core	core	inner	inner	inner	outer	core	inner	inner	inner	inner	outer	
SiO <sub>2</sub>	52.82	53.31	52.63	54.28	52.55	54.88	53.53	53.88	52.96	54.49	50.6	52.4	53.44	52.22	53.55	51.59	53.8	
TiO <sub>2</sub>	0.22	0.26	0.38	0.07	0.27	0.73	0.25	0.1	0.25	0.09	0.5	0.21	0.09	0.22	0.1	0.23	0.09	
$Al_2O_3$	1.91	1.66	2.51	0.78	2.54	2.25	2	1.06	2.36	0.9	3.52	1.42	0.92	1.93	1.15	2.22	1.08	
$Cr_2O_3$	0.41	0.52	0.34	0.5	0.36	0.08	0.7	0.68	0.34	0.7	0.08	0.4	0.56	0.45	0.68	0.45	0.56	
FeO	4.79	4.14	5.13	2.96	5.23	14.6	4.06	2.88	4.45	2.62	7.78	3.62	2.79	4.39	3.07	4.45	3.13	
MnO	0.1	0.11	0.05	0.19	0.09	0.66	0.16	0.04	0.07	0.03	0.09	0.07	0.07		0.05	0.05	0.03	
MgO	16.33	16.74	16.35	17.45	15.78	15.64	16.59	17.4	16.51	17.73	14.7	16.7	17.4	16.29	17.15	16.15	17.29	
CaO	23.47	23.91	23.33	23.88	24.27	11.29	23.49	23.28	23.38	23.51	22.0	22.7	22.86	23.26	23.15	22.91	23.1	
Na <sub>2</sub> O						0.41					0.07		0.07	0.07		0.03		
Total	100.0	100.6	100.7	100.1	101.0	100.54	100.7	99.32	100.3	100.07	99.5	97.6	98.2	98.83	98.9	98.08	99.08	
Cations	(0=6)																	
Si	1.939	1.942	1.921	1.975	1.918	2.014	1.944	1.972	1.934	1.977	1.89	1.96	1.977	1.938	1.97	1.93	1.975	
Ti	0.006	0.007	0.01	0.002	0.008	0.02	0.007	0.003	0.007	0.002	0.01	0.00	0.003	0.006	0.003	0.006	0.002	
Al	0.083	0.071	0.108	0.034	0.109	0.097	0.086	0.046	0.102	0.039	0.15	0.06	0.04	0.084	0.05	0.098	0.047	
$Cr^{3+}$	0.012	0.015	0.01	0.014	0.01	0.002	0.02	0.02	0.01	0.02	0.00	0.01	0.016	0.013	0.02	0.013	0.016	
Fe <sup>2+</sup>	0.147	0.126	0.157	0.09	0.16	0.448	0.123	0.088	0.136	0.079	0.24	0.11	0.086	0.136	0.094	0.139	0.096	
Mn	0.003	0.003	0.002	0.006	0.003	0.021	0.005	0.001	0.002	0.001	0.00	0.00	0.002		0.002	0.002	0.001	
Mg	0.894	0.909	0.889	0.947	0.859	0.856	0.898	0.949	0.899	0.959	0.82	0.93	0.959	0.901	0.941	0.901	0.946	
Ca	0.923	0.933	0.912	0.931	0.949	0.444	0.914	0.913	0.915	0.914	0.88	0.90	0.906	0.925	0.913	0.918	0.908	
Na						0.029					0.00		0.005	0.005		0.002		
Total	4.007	4.006	4.009	3.999	4.016	3.931	3.997	3.992	4.005	3.991	4.01	3.99	3.994	4.008	3.993	4.009	3.991	
Mg#	85.88	87.83	84.99	91.32	84.30	65.64	87.95	91.51	86.86	92.39	77.2	89.1	91.77	86.88	90.92	86.63	90.79	
Wo	46.99	47.41	46.58	47.31	48.22	25.40	47.23	46.82	46.92	46.82	45.2	46.5	46.44	47.15	46.87	46.88	46.56	
En	45.52	46.19	45.40	48.12	43.65	48.97	46.41	48.67	46.10	49.13	42.2	47.6	49.15	45.92	48.31	46.02	48.51	
Fs	7.49	6.40	8.02	4.57	8.13	25.63	6.36	4.51	6.97	4.05	12.4	5.79	4.41	6.93	4.83	7.10	4.93	

Rock					Lamprophyres				
Sample	#:	59	#	74			#77		
Mineral	Cpx1	Cpx5	Cpx1	Cpx2	Cp	ox1	Cpx2	Cpx3	Cpx4
	core	core	core	core	core	rim	core	core	core
SiO <sub>2</sub>	52.04	50.68	49.9	46.87	49.18	50.02	48.45	49.88	48.79
TiO <sub>2</sub>	0.52	0.89	0.8	0.11	0.82	0.67		0.80	1.00
$Al_2O_3$	2.45	4.66	4.58	2.26	4.76	3.68	4.94	4.72	6.10
$Cr_2O_3$	0.51	0.31	0.13	0.18	0.06	0.22	0.07	0.09	0.02
FeO	4.39	5.8	6.3	8.42	6.80	6.09	8.58	7.02	8.82
MnO	0.03	0.14	0.14	0.45	0.19	0.02	0.15	0.11	0.16
MgO	15.91	14.69	13.77	12.8	13.80	14.51	12.66	14.03	12.67
CaO	23.47	24.02	23.65	24.22	24.01	23.67	23.03	23.88	23.83
Na <sub>2</sub> O	0.04	0.11	0.12	0.03	0.130	0.080	0.240	0.070	0.140
Total	99.36	101.3	99.39	95.34	99.750	98.960	99.070	100.600	101.530
Cations (O=6	)								
Si	1.923	1.854	1.864	1.867	1.840	1.876	1.837	1.848	1.808
Ti	0.015	0.024	0.022	0.003	0.023	0.019	0.027	0.022	0.028
Al	0.107	0.201	0.201	0.106	0.210	0.163	0.221	0.206	0.266
Cr <sup>3</sup> +	0.015	0.009	0.004	0.006	0.002	0.006	0.002	0.003	0.001
Fe <sup>2+</sup>	0.136	0.177	0.197	0.281	0.213	0.191	0.272	0.218	0.273
Mn	0.001	0.004	0.004	0.015	0.006	0.001	0.005	0.003	0.005
Mg	0.876	0.801	0.767	0.76	0.77	0.811	0.716	0.775	0.699
Ca	0.929	0.942	0.947	1.034	0.963	0.951	0.936	0.948	0.946
Na	0.003	0.008	0.009	0.002	0.01	0.006	0.018	0.005	0.01
Total	4.005	4.02	4.015	4.074	4.037	4.024	4.034	4.028	4.036
Mg#	86.56	81.90	79.56	73.01	78.33	80.94	72.47	78.05	71.91
Wo	47.86	49.06	49.56	49.83	49.49	48.69	48.65	48.84	49.32
En	45.14	41.72	40.14	36.63	39.57	41.53	37.21	39.93	36.44
Fs	7.01	9.22	10.31	13.54	10.95	9.78	14.14	11.23	14.23

Table 1.7: (Continued)

## 1.5.2.2.2. Amphibole

Amphibole phenocrysts in the basalts and basaltic andesite have high CaO contents (11.3-12.8 wt. %; Table 1.8) and thus are calcic amphiboles (Leake 1978). According to Leake et al. (1978)  $AI^{(IV)}$  versus (Na+K)<sub>A</sub> amphibole classification diagram (Fig. 1.12), amphiboles from basalts are plotted in the pargasite, pargasitic hornblende and edenitic hornblende field, whereas those from basaltic andesite are plotted in the pargasite field.. The ankaramite rocks contain groundmass amphiboles with edenitic (Na+K, 0.51-0.53; Si, >6.5) composition. The Mg# of amphibole in basaltic rocks is higher (lamprophyre ranges from 61 to 72, ankaramite from 73 to 74) compared to those in basaltic andesites (61-71) (Fig. 1.18). Amphiboles in lamprophyres exhibit higher content of  $Al_2O_3$ (13.6-16.0 wt. %, average, 14.6 wt. %) and CaO (10.0-13.2 wt. %, average, 12.5 wt. %) than those of basaltic andesite  $Al_2O_3$  12.3~13.1 wt. %, average, 12.0 wt. %; CaO 11.4-11.6 wt. %, average, 11.5 wt. %).



Figure 1.18: Major element chemistry of amphibole from basaltic rocks of Chukotka.

However, those in ankaramite show CaO ~11.2 wt. % and lower in  $Al_2O_3 \sim 10$  wt. %. The TiO<sub>2</sub> concentration of amphiboles in basaltic andesites ranges from 4.12 to 4.74 wt. %, lamprophyres from 0.36-3.1 wt. % and ankaramite from 2.04-2.24 wt. %. Some of the amphibole phenocryts in basaltic andesite are characterized by oscillatory zoing (Fig. 1.19).



**Figure 1.19:** (A) BSE image of basaltic andesite with euhedral amphibole phenocryst showing oscillatoryzoning. White filled circles indicate analyses point. The white circle is a damge due to LA-ICP-MS analyses. (B-E) Compositional variations (TiO<sub>2</sub>,  $Al_2O_3$ , FeO, and MgO) from core to rim traverse for a oscillatory zoning of amphibole phenocryst of basaltic andesite (Hb7, Sample #55; Table 1.8). Ilm, Ilmenite.

Rock								Bas	altic andes	ites							
Sample						#55			#56								
Mineral	ral Hb1		Hb7			Н	Hb8 Hb10				H	<b>b</b> 1	Hb2		Hb3		
Position	core	rim	core	rim1	rim2	rim3	core	rim	core	rim1	rim2	core	rim	core	core	rim1	rim2
SiO <sub>2</sub>	42.35	41.82	42.74	41.92	42.6	42.16	42.35	42.42	42.82	42.65	42.49	43.34	42.25	42.7	42.64	42.4	42.57
TiO <sub>2</sub>	4.03	4.23	4.11	4.23	3.91	4.26	4.41	4.38	4.33	4.11	4.29	3.88	4.7	4.67	4.44	4.36	4.82
$Al_2O_3$	11.8	11.77	11.72	13.32	12.07	11.91	12.6	13.21	11.75	13.32	13.06	11.94	12.65	12.4	12.13	12.14	13.24
$Cr_2O_3$	0.06	0.11	0.02	0.09	0.03	0.06	0.03	0.08	0.13	0.11	0.13	0.13	0.15	0.21	0.09	0.16	0.28
FeO	15.89	14.26	15.75	12.22	15.85	14.86	12.64	12.42	14.5	12.06	12.26	15.24	11.21	12	12.74	13.73	10.98
MnO														0.18	0.16	0.1	0.05
MgO	11.04	11.57	11.15	12.93	10.39	11.48	12.84	12.87	11.85	13.36	13.11	11.69	13.12	13.16	12.45	12.15	13.71
CaO	11.11	11.14	11.39	11.7	10.63	11.33	11.21	11.76	11.48	11.48	11.51	11.3	11.76	11.69	11.43	11.41	11.81
Na <sub>2</sub> O	2.84	2.7	2.81	2.71	3.12	2.8	2.84	2.74	2.79	2.81	2.77	2.81	2.78	2.85	2.6	2.77	2.82
K <sub>2</sub> O	1.08	1.09	1.11	1.01	1.13	1.06	0.9	0.99	1.08	1.02	0.94	0.96	1.02	0.99	1.09	0.99	1.01
Total	100.20	98.69	100.80	100.13	99.73	99.92	99.82	100.87	100.73	100.92	100.56	101.29	99.64	100.85	99.77	100.21	101.29
Cations (0	D=23)																
Si	6.213	6.191	6.229	6.058	6.268	6.179	6.138	6.085	6.212	6.099	6.105	6.255	6.112	6.126	6.195	6.163	6.051
Ti	0.444	0.471	0.45	0.46	0.433	0.47	0.48	0.473	0.472	0.441	0.464	0.421	0.511	0.504	0.485	0.476	0.515
Al	2.04	2.053	2.013	2.269	2.093	2.058	2.153	2.234	2.008	2.245	2.211	2.03	2.157	2.097	2.077	2.08	2.218
Cr <sup>3+</sup>	0.007	0.013	0.002	0.01	0.004	0.007	0.003	0.009	0.014	0.013	0.014	0.015	0.018	0.024	0.01	0.018	0.032
Fe <sup>2+</sup>	1.950	1.765	1.919	1.476	1.949	1.821	1.533	1.489	1.758	1.442	1.473	1.839	1.356	1.44	1.548	1.669	1.306
Mn														0.022	0.02	0.012	0.006
Mg	2.414	2.553	2.422	2.785	2.278	2.509	2.773	2.752	2.563	2.848	2.808	2.514	2.829	2.814	2.696	2.633	2.905
Na	0.808	0.775	0.793	0.759	0.89	0.795	0.797	0.762	0.786	0.78	0.772	1.747	1.822	1.798	1.779	1.778	1.798
Ca	1.746	1.767	1.779	1.811	1.676	1.779	1.741	1.807	1.784	1.759	1.772	0.785	0.78	0.791	0.731	0.781	0.777
K	0.202	0.207	0.206	0.186	0.213	0.199	0.166	0.18	0.199	0.185	0.172	0.177	0.188	0.181	0.201	0.184	0.182
Total	15.82	15.79	15.81	15.81	15.80	15.82	15.78	15.79	15.79	15.81	15.79	15.78	15.77	15.79	15.74	15.79	15.79
Mg#	55.32	59.12	55.79	65.36	53.89	57.94	64.39	64.89	59.31	66.38	65.59	57.75	67.59	66.14	63.52	61.20	68.98

Table 1.8: Representative electron-microprobe analyses of hornblende phenocrysts and microphenocrysts in basaltic rocks of Chukotka, NE Russia

\*Total Fe as FeO; Mg#=  $100 \times Mg (Mg+Fe^{2+})$ .
Table 1.8: (Continued)

Rock							Ankaramite	S					
Sample			#69				#	ŧ70		#71			
Mineral	Hb1 gm	Hb2 gm	Hb3 gm	Hb4 gm	Hb5 gm	Hb1 gm	Hb2 gm	Hb3 gm	Hb4 gm	Hb1 gm	Hb2 gm	Hb4 gm	Hb5 gm
SiO <sub>2</sub>	43.67	44.34	42.9	44.84	46.11	45.37	43.76	44.61	43.65	44.58	45.67	44.5	46.08
TiO <sub>2</sub>	1.7	2.07	1.81	2.31	1.75	1.98	2.68	1.78	1.97	1.17	1.92	2.03	1.42
$Al_2O_3$	11.86	11.29	12.12	10.73	9.31	9.97	11.4	10.38	11.23	11.54	10.02	10.97	9.95
$Cr_2O_3$		0.11	0.06	0.03	0.05	0.04		0.02	0.12	0.14	0.04	0.05	0.07
FeO	12.07	11.71	12.02	11.84	12.23	10.53	11.09	11.93	11.35	11.61	10.26	10.99	11.14
MnO	0.49	0.35	0.43	0.45	0.56	0.5	0.33	0.49	0.39	0.48	0.44	0.43	0.43
MgO	14.96	15.18	14.78	15.58	15.38	16.36	15.26	14.72	15.05	14.59	16.17	15.46	16.05
CaO	11.15	11.49	11.24	11.37	11.38	10.39	11.25	11.02	11.17	11.67	10.96	11.2	10.79
Na <sub>2</sub> O	2.98	3.1	3.15	2.97	2.84	3.04	3.01	2.83	2.97	2.72	3.09	3.05	3.01
K <sub>2</sub> O	0.8	0.81	0.8	0.82	0.64	0.61	0.71	0.74	0.82	0.84	0.66	0.74	0.63
Total	99.68	100.45	99.31	100.94	100.25	98.79	99.49	98.52	98.72	99.34	99.23	99.42	99.57
Cations (O	=23)												
Si	6.317	6.357	6.241	6.395	6.614	6.543	6.313	6.509	6.359	6.448	6.557	6.416	6.606
Ti	0.185	0.224	0.198	0.248	0.189	0.214	0.291	0.195	0.216	0.127	0.208	0.22	0.153
Al	2.022	1.908	2.079	1.804	1.574	1.695	1.939	1.785	1.927	1.967	1.695	1.864	1.681
Cr <sup>3+</sup>		0.012	0.007	0.003	0.006	0.004		0.002	0.014	0.016	0.004	0.006	0.008
Fe <sup>2+</sup>	1.46	1.404	1.463	1.413	1.468	1.271	1.338	1.456	1.383	1.404	1.232	1.325	1.335
Mn	0.06	0.043	0.053	0.055	0.068	0.061	0.04	0.061	0.048	0.059	0.053	0.052	0.052
Mg	3.227	3.245	3.206	3.311	3.288	3.518	3.281	3.2	3.269	3.145	3.46	3.323	3.43
Na	1.728	1.765	1.752	1.738	1.748	1.605	1.739	1.723	1.744	1.809	1.686	1.73	1.657
Ca	0.835	0.861	0.888	0.822	0.79	0.851	0.842	0.8	0.838	0.764	0.86	0.853	0.835
Κ	0.147	0.147	0.148	0.149	0.117	0.112	0.13	0.137	0.152	0.155	0.121	0.135	0.115
Total	15.98	15.97	16.04	15.94	15.86	15.87	15.91	15.87	15.95	15.89	15.88	15.92	15.87
Mg#	68.85	69.80	68.67	70.09	69.13	73.46	71.03	68.73	70.27	69.14	73.74	71.49	71.98

<b>Table 1.8:</b> (Co	ontinued)
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Rock	k Lamprophyres																
Sample	#59							#74				#77					
Minera	Hb1	Hb4	Hb5	Hb7	Hb1	Н	b2	Hb5	Hb6	Hb7	Hb10	Hb1	Н	b2		Hb4	
Positio	core	core	core	core	core	core	rim	core	core	core	core	core	core	rim	core	rim1	rim2
SiO <sub>2</sub>	37.72	39.94	39.72	41.51	40.21	39.6	40.44	39.98	39.68	39.38	40.14	40.27	40.93	40.56	41.16	41.4	42.7
TiO <sub>2</sub>	2.98	2.82	3.12	2.58	2.28	1.76	2.34	2.29	2.34	2.26	2.28	2.21	2.27	2.24	2.2	2	2.01
$Al_2O_3$	15.24	15.25	15.32	14.49	14.54	14.79	14.64	14.66	15.12	15.74	14.54	14.48	14.62	14.79	14.54	14.47	12.76
$Cr_2O_3$	0.03	0.1	0.05	0.02		0.1				0.04				0.12	0.01	0	0.04
FeO	10.42	11.01	10.92	12.43	10.72	12.27	9.97	9.86	11.3	10.36	10.23	11.56	11.96	11.6	10.77	11.96	12.19
MnO	0.17	0.06	0.17	0.28	0.03	0.09	0.14	0.09	0.16	0.15	0.07	0.11	0.06	0.06	0.16	0.16	0.15
MgO	12.8	13.75	13.67	13.54	13.41	15.95	14.22	14.07	12.89	13.43	13.89	13.71	13.94	13.81	14.66	13.6	13.82
CaO	12.12	12.69	12.65	12.62	12.54	9.77	12.73	12.61	12.68	12.79	12.6	12.65	12.84	12.72	12.98	13.03	13.05
Na <sub>2</sub> O	2.8	2.88	3.11	2.99	2.7	2.41	2.65	2.67	2.81	2.77	2.65	2.55	2.58	2.89	2.82	2.64	2.28
$K_2O$	0.82	0.72	0.75	0.77	0.96	0.92	1	1.06	1.02	1.05	1.04	1.07	1.05	1.08	1.12	0.91	1.02
Total	95.1	99.22	99.48	101.23	97.39	97.66	98.13	97.29	98	97.97	97.44	98.61	100.25	99.87	100.42	100.17	100.02
Cations (	O=23)																
Si	5.743	5.822	5.783	5.957	5.96	5.853	5.932	5.918	5.873	5.81	5.939	5.923	5.925	5.896	5.928	5.992	6.184
Ti	0.341	0.309	0.342	0.278	0.254	0.196	0.258	0.255	0.26	0.251	0.254	0.245	0.247	0.245	0.238	0.218	0.219
Al	2.735	2.621	2.628	2.451	2.54	2.577	2.531	2.557	2.638	2.736	2.535	2.511	2.494	2.533	2.468	2.469	2.178
Cr <sup>3+</sup>	0.004	0.012	0.006	0.002		0.012				0.005				0.014	0.001	0	0.005
Fe <sup>2+</sup>	1.327	1.342	1.329	1.492	1.328	1.517	1.224	1.221	1.399	1.278	1.266	1.422	1.449	1.41	1.298	1.448	1.477
Mn	0.022	0.008	0.021	0.034	0.003	0.011	0.017	0.011	0.02	0.019	0.009	0.014	0.007	0.008	0.019	0.02	0.019
Mg	2.905	2.986	2.966	2.896	2.963	3.513	3.109	3.103	2.845	2.954	3.063	3.005	3.008	2.991	3.147	2.933	2.983
Na	1.977	1.981	1.973	1.94	1.991	1.548	2.002	2	2.012	2.021	1.997	1.994	1.992	1.982	2.003	2.02	2.025
Ca	0.827	0.814	0.879	0.833	0.777	0.691	0.754	0.767	0.806	0.792	0.759	0.728	0.723	0.815	0.787	0.741	0.64
Κ	0.159	0.133	0.139	0.142	0.181	0.173	0.187	0.2	0.193	0.198	0.196	0.201	0.195	0.2	0.205	0.168	0.189
Total	16.04	16.028	16.066	16.025	15.997	16.091	16.014	16.032	16.046	16.064	16.018	16.043	16.04	16.094	16.094	16.009	15.919
Mg#	68.64	68.99	69.06	66.00	69.05	69.84	71.75	71.76	67.04	69.80	70.76	67.88	67.49	67.96	70.80	66.95	66.88

# 1.5.2.2.3. Plagioclase

Plagioclase feldspar and minor k-feldspar occur in most of studied volcanic rocks. The k-feldspar is orthoclase (mainly in Sample #69, #70, #74 and #77), whereas plagioclase has composition of  $An_{1.4-13.7}Ab_{80.9-98.3}Or_{0.2-6.6}$  in basaltic rocks (except Sample #74 which has higher  $An_{65.2-73.6}$  contents) and  $An_{56-85}Ab_{14-69}Or_{0.6-5}$  in hornblende basaltic andesite (Fig. 1.20). Plagioclase in basaltic rocks may mostly be the product of albitization (secondary alteration).



**Figure 1.20:** An-Ab-Or triangular diagram showing the compositions of plagioclase from basaltic rocks of Chukotka. An, Anorthite; Ab, Albite; Or, Orthoclase.

#### 1.5.2.2.4. Biotite

*Biotites* in the basaltic andesite (Sample #56) have a compositional range of Mg# (0.51-0.53; Table 1.6) and the alumina saturation index (ASI= Al/Ca+Na+K) ranges from 0.42 to 1.95. All these biotites are not primary magmatic and in the ternary FeO\* (=FeO<sub>total</sub>+MnO)-10TiO<sub>2</sub>-MgO discrimination diagram (Fig. not shown) they plot in the re-equilibriated biotite field, suggesting their chemical compositions are likely influenced by late-magmatic hyrdrothermal fluid (Nachit et al., 2005).

# 1.5.2.2.5. Opaque minerals

Opaque minerals from the pyroxene-phyric basalt are predominantly iron-sulphide minerals. Lamprophyres includes both Ti-bearing ( $0.3 < TiO_2 < 19.5$  wt. %) and Ti-free magnetite. Ti- magnetite also contains minor  $Cr_2O_3$  (0.03-0.16 wt. %) and  $Al_2O_3$  (0.21-4.44 wt. %).

### 1.5.2.3. Trace elements in clinopyroxene and amphibole

Representative, clinopyroxene and amphibole trace element compositions of the studied samples are reported in Tables 1.9 1.10 and 1.11, although amphiboles from OIB-type gabbro are not analyzed.

## 1.5.2.3.1. Clinopyroxene in gabbroic rocks

Clinopyroxenes in IAB-type gabbroic rocks are characterized by enrichment in LREE ((Ce/Yb)<sub>N</sub> =1.69-2.62; where N refers to primitive mantle normalization) and MREE ((Eu/Yb)<sub>N</sub>=2.8-3.3) relative to HREE as compared

to those in OIB-type gabbro (~1.69 and 2.1 respectively). No significant Eu anomaly was observed for clinopyroxenes from both IAB-type and OIB-type gabbroic rocks (Eu/Eu\*=0.97-1 and 0.91-0.96 respectively). Clinopyroxenes of IAB-type gabbros have higher  $(La/Nb)_N$  than clinopyroxenes from OIB-type gabbros. As a result, the primitive-mantle normalized trace element patterns of the clinopyroxenes from IAB-type gabbros are distinctive in their deep negative Nb anomalies (Fig. 1.21A). The concentration of LILE (Cs, Rb, Ba) in clinopyroxens of OIB-type gabbroic rocks are higher than those in IAB-type gabbros, but significant depletion of Sr is detected in the former.

# 1.5.2.3.2. Clinopyroxene in basaltic rocks

Basalts show trace element compositions of clinopyroxene characterized by negative anomalies of HFSE (Nb, Ta, Zr) and LILE (Ba, Rb). In addition, these phenocrysts exhibit variable concentrations of Cs, Th and U (Fig. 1.21C). The negative anomalies of the aforementioned incompatible trace elements also exhibited in clinopyroxenes from basaltic andesite, but the concentrations are higher than those in basalts. The primitive mantle-normalized REE patterns (Fig. 1.21D) of clinopyroxenes in both basalt and basaltic andesite samples are characterized by similar depletion in LREE (La/Sm)<sub>N</sub>=0.19-0.34; 0.22-0.26 respectively) relative to MREE. However, clinopyroxene in basaltic andesite is characterized by HREE enrichment ((Eu/Yb)<sub>N</sub>=0.75-0.79) relative to MREE and display slight negative Eu anomalies (Eu/Eu\*(=EuN/ $\sqrt{SmN \times GdN}$ )). This REE signature is significantly different from that of the clinopyroxenes in basaltic rocks. In basalts, clinopyroxene contains high

Cr contents (up to 1181 ppm in pyroxene-phyric basalt, 3347 ppm in ankaramite and 435 ppm in lamprophyre) and Ni (up to 131 ppm in pyroxene phyric basalt, 124 ppm in ankaramite and 38 ppm in lamprophyre). These values drop to less than 200 ppm of Cr and 20 ppm of Ni in basaltic andesite (Table 1.9).



**Figure 1.21**: Primitive mantle normalized multi-element (A) and REE (B) patterns for the clinopyroxenes from the gabbroic rocks of Ckukotka. Mantle–normalization values are from McDonough and Sun (1995). (C) and REE (D) patterns for the clinopyroxenes from the basaltic rocks of Ckukotka. Mantle–normalization values are from McDonough and Sun (1995).

Rock type		IAB-ty	pe gabbros	OIB-type gabbros			
Sample		#60		#57	_	#84	
Mineral	Cpx1	Cpx2	Cpx1	Cpx2	Cpx1	Cpx2	
Determined by	LA-ICP-MS						
Sc	116.0	110.1	71.1	76.9	148.5	90.0	
Ti	4261	4497	6593	4897	15298	6335	
V	253	247	381	285	797	459	
Cr	2.8	2.8	n.d.	0.6	11.8	4.4	
Co	34.7	33.6	32.7	33.4	60.6	52.3	
Ni	29	26	11	14	35	19	
Rb	0.008	0.010	0.018	0.005	0.769	1.047	
Sr	73.4	59.6	98.6	79.2	25.1	24.1	
Y	12.6	11.5	18.5	12.4	28.7	19.1	
Zr	34.5	36.6	34.0	25.5	90.3	36.6	
Nb	0.05	0.05	0.07	0.04	1.15	0.21	
Cs	0.005	n.d.	0.002	0.004	0.773	0.517	
Ba	0.03	0.01	0.20	0.05	3.35	13.67	
La	2.70	2.27	1.90	1.70	3.72	2.40	
CE	10.37	9.05	9.23	7.33	16.15	10.51	
Pr	1.81	1.63	1.95	1.40	2.87	1.87	
Nd	10.36	9.39	13.30	8.74	16.43	10.65	
Sm	3.31	3.03	4.90	3.17	5.61	3.65	
Eu	1.06	0.99	1.71	1.10	1.90	1.19	
Gd	3.36	3.04	5.48	3.49	6.49	4.35	
Tb	0.47	0.43	0.76	0.49	1.01	0.68	
Dy	2.87	2.60	4.64	2.96	6.37	4.28	
Но	0.51	0.47	0.84	0.52	1.19	0.78	
Er	1.31	1.20	1.96	1.32	3.08	2.00	
Tm	0.18	0.16	0.25	0.16	0.41	0.26	
Yb	1.10	1.01	1.52	1.07	2.66	1.75	
Lu	0.16	0.14	0.19	0.14	0.34	0.23	
Hf	1.66	1.67	1.97	1.54	3.91	1.66	
Та	0.01	0.02	0.02	0.01	0.12	0.03	
Pb	0.11	0.11	0.12	0.10	0.43	0.22	
Th	0.120	0.114	0.11	0.12	0.09	0.03	
U	0.069	0.053	0.071	0.054	0.033	0.008	

Table 1.9: Trace element analyses (ppm) of clinopyroxenes from gabbroic rocks of Chukotka, NE Russia.

Abbreviations: Cpx, clinopyroxene; n.d. not detected.

Rock		Ankaramite	e		Pyroxene-j	phyic basal	Lampi	ophyre	Basaltic andesite		
Sample		#69			#	67		#	77	#55	
Mineral	Cpx1	Cp	ox2	Cp	ox1	Cl	px3	Cpx1		Cpx2	
	core	core	rim	core	rim	core	rim	core	rim	core	
Determin	ed by LA-l	ICP-MS									
Sc	91.4	87.0	100.6	98.3	126.0	117.7	125.9	173.0	123.7	32.6	
Ti	1156	1048	1251	3154	4079	2706	2351	3671	4044	3258	
V	119	110	133	293	355	250	205	269	346	305	
Cr	2767	3077	3348	15	545	736	1096	435	20	188	
Co	33.6	35.0	35.2	44.2	43.9	44.2	43.5	33.6	37.9	38.4	
Ni	121	125	114	74	86	107	114	54	22	18	
Rb	0.003	0.001	0.007	0.005	0.015	0.001	0.003	n.d.	0.016	0.587	
Sr	41.5	42.8	42.8	60.54	70.5	54.4	42.5	53.4	54.3	12.7	
Y	2.33	2.10	3.35	8.27	12.12	5.76	4.83	6.82	10.34	9.76	
Zr	1.08	0.91	1.79	12.50	20.49	7.55	5.50	8.35	13.71	12.92	
Nb	0.04	0.04	0.05	0.02	0.04	0.02	0.02	0.01	0.02	3.94	
Cs	n.d.	0.001	0.005	0.008	n.d.	0.000	0.001	n.d.	0.098	1.785	
Ba	0.03	0.01	0.14	0.14	0.04	0.00	0.01	0.01	0.13	2.90	
La	0.15	0.13	1.04	0.88	1.39	0.49	0.32	0.44	0.67	0.49	
Ce	0.75	0.66	3.11	4.35	6.79	2.48	1.78	2.38	3.40	2.81	
Pr	0.14	0.13	0.43	0.88	1.35	0.51	0.38	0.52	0.73	0.61	
Nd	1.05	0.91	2.09	5.71	8.72	3.34	2.47	3.54	5.01	3.51	
Sm	0.47	0.39	0.66	2.16	3.14	1.32	1.02	1.42	2.00	1.38	
Eu	0.17	0.15	0.25	0.72	1.05	0.46	0.37	0.54	0.75	0.35	
Gd	0.55	0.43	0.80	2.30	3.38	1.42	1.14	1.69	2.37	1.52	
Tb	0.09	0.07	0.11	0.32	0.46	0.22	0.17	0.25	0.37	0.26	
Dy	0.55	0.49	0.76	1.90	2.76	1.32	1.09	1.58	2.40	1.76	
Но	0.10	0.09	0.14	0.36	0.50	0.24	0.18	0.28	0.43	0.35	
Er	0.27	0.22	0.37	0.88	1.31	0.63	0.51	0.71	1.13	1.03	
Tm	0.03	0.02	0.05	0.12	0.18	0.08	0.07	0.09	0.15	0.16	
Yb	0.21	0.18	0.28	0.77	1.06	0.53	0.44	0.54	0.92	1.35	
Lu	0.03	0.02	0.04	0.10	0.15	0.07	0.06	0.07	0.12	0.23	
Hf	0.06	0.06	0.11	0.64	1.14	0.41	0.33	0.49	0.71	0.51	
Та	0.00	0.00	n.d.	0.00	0.01	0.00	0.00	0.00	0.00	0.14	
Pb	0.12	0.14	0.07	0.05	0.04	0.06	0.04	0.05	0.08	1.02	
Th	0.00	0.00	0.16	0.01	0.02	0.00	n.d.	0.00	0.01	0.75	
U	n.d.	0.000	0.047	0.003	0.009	0.002	0.000	0.001	0.007	0.553	

Table 1.10: Trace element analyses (ppm) of clinopyroxenes from basaltic rocks of Chukotka, NE Russia.

Abbreviations: Cpx, clinopyroxene; n.d. not detected.

#### 1.5.2.3.3. Amphiboles in gabbroic rocks

In the spider diagram (Fig. 1.22A), amphiboles from IAB-type gabbros exhibit negative anomalies for Th, U, Pb, Zr and enrichment in LILE (Ba and Sr). In the primitive mantle-normalized REE patterns (Fig. 1.22B) they are characterized by LREE enrichment relative to HREE ((La/Yb)<sub>N</sub>=1.4-1.8). REE patterns do not show Eu anomaly (Eu/Eu\*=1.04-1.11).

#### 1.5.2.3.4. Amphiboles in basaltic rocks

The trace element characteristics of amphibole further emphasize the existence of two types among basaltic rocks in the Chukotka area. The primitive mantle-normalized REE pattern (Fig. 1.22D) of amphiboles from both basalts and basaltic andesite are convex-upward shaped with lower LREE ( $La_N/Sm_N$ ; 0.22-0.24, 0.48-0.53 respectively) and HREE. This shape is typical of deep cumulates from basaltic melts (Irving and Frey, 1984). Amphiboles from basaltic andesite have higher HFSE (Nb, Ta) and total REE contents as compared to those in basalts. Moreover, these phenocrysts show a remarkable negative Eu anomaly (Eu/Eu\*= 0.51-0.71) in the primitive mantle–normalized REE pattern. Amphiboles of basalts are highly enriched in Sr, but slight negative anomaly is detected for those from basaltic andesite. The incompatible element pattern of amphiboles from both basalts and basaltic andesites (Fig. 1.22C) reveals a strong depletion in Th, U and Zr relative to the neighbouring elements. However, the concentrations of the aforementioned elements are still higher in amphiboles from basaltic andesite. The Ni and Cr contents of amphiboles are very low; 55-78 ppm and 3.9-79 ppm in basalt (Sample #77) and 36-39 ppm and 125-319 ppm in basaltic andesite (Sample #55), respectively (Table 1.11).



**Figure 1.22**: Primitive mantle normalized multi-element (A, C) and REE (B, D) patterns for the amphiboles from the gabbroic (A, B) and basaltic (C, D) rocks of Ckukotka. Mantle–normalization values are from McDonough and Sun (1995).

Rock type		IAB-type	e gabbros		L	amprophyre		Basaltic andesite			
Sample	#:	57	#6	0		#77			#55		
Mineral	Hb1	Hb2	Hb1	Hb2	Hb1	Hb	2	Hb1	Hb	2	
					Core	Core	Rim	Core	Core	Rim	
Determined	by LA-ICI	P-MS									
Sc	76.5	67.6	110.3	111.5	160.0	148.4	148.0	83.6	84.5	99.4	
Ti	12023	12498	11944	12292	11714	11736	11671	22453	21469	22629	
V	467	509	501	478	608	638	641	1514	870	1329	
Cr	13.1	0.5	1.9	4.8	78.9	10.2	3.8	318.6	125.3	303.5	
Co	60.2	62.2	58.4	64.2	61.9	63.3	63.6	51.7	52.4	52.3	
Ni	45.5	39.3	51.5	64.5	78.0	52.2	54.7	35.5	35.6	38.8	
Rb	7.3	8.2	6.9	7.4	3.6	3.5	3.7	5.3	4.5	4.7	
Sr	515	685	598	447	424	423	453	302	271	284	
Y	16.8	14.7	15.4	16.3	12.3	12.4	12.9	32.2	51.2	54.4	
Zr	32.5	22.3	27.9	32.5	15.0	15.5	16.8	53.8	77.3	81.2	
Nb	2.9	1.5	2.0	2.6	0.6	0.6	0.6	6.3	14.1	13.8	
Cs	0.032	0.003	0.189	0.170	0.019	0.013	0.039	0.028	0.004	0.012	
Ba	272	208	288	285	143	147	165	217	244	263	
La	3.18	2.22	3.02	3.33	0.93	0.95	1.04	5.34	9.58	10.56	
Ce	13.04	9.24	11.64	12.67	4.55	4.70	5.06	23.02	41.07	45.06	
Pr	2.34	1.79	2.12	2.22	0.98	0.98	1.06	4.00	7.07	7.68	
Nd	14.11	11.25	12.77	13.06	6.55	6.71	7.15	22.07	39.37	41.87	
Sm	4.61	3.91	4.18	4.38	2.61	2.62	2.77	6.96	11.76	12.55	
Eu	1.61	1.44	1.51	1.50	1.01	1.00	1.07	1.64	2.04	2.10	
Gd	4.77	4.02	4.60	4.45	3.06	3.00	3.24	7.28	12.13	12.50	
Tb	0.64	0.56	0.63	0.60	0.44	0.45	0.45	1.05	1.77	1.85	
Dy	3.83	3.40	3.58	3.68	2.81	2.82	2.97	6.87	11.24	11.61	
Но	0.71	0.59	0.62	0.65	0.52	0.54	0.55	1.28	2.14	2.15	
Er	1.69	1.51	1.53	1.63	1.28	1.32	1.34	3.34	5.59	5.59	
Tm	0.21	0.18	0.20	0.20	0.16	0.16	0.17	0.43	0.72	0.74	
Yb	1.37	1.09	1.15	1.34	0.94	0.99	1.06	2.84	4.61	4.70	
Lu	0.17	0.14	0.15	0.17	0.13	0.13	0.13	0.36	0.59	0.60	
Hf	1.48	1.13	1.24	1.47	0.80	0.82	0.92	2.31	3.43	3.38	
Та	0.17	0.08	0.10	0.15	0.03	0.03	0.04	0.28	0.65	0.59	
Pb	0.39	0.40	0.79	0.57	0.38	0.14	0.23	1.66	1.48	1.60	
Th	0.077	0.079	0.098	0.110	0.009	0.011	0.008	0.079	0.123	0.144	
U	0.033	0.061	0.053	0.061	0.006	0.003	0.004	0.028	0.041	0.050	

 Table 1.11: Trace element composition of amphiboles in the IAB-type gabbros and basalts of Chukotka, NE Russia.

## **1.6. DISCUSSION**

#### 1.6.1. Parental magma

The trace element composition of parental melts in equilibrium with clinoyroxens from the studied samples have been calculated using clinopyroxene/melt partition coefficients after Hart and Dunn, (1993), Adam and Green, (2006), and Tiepolo (1999). On the primitive mantle normalized trace element diagram (Fig. 1.23), the calculated melt from clinopyroxene in IAB-type gabbros exhibits a marked enrichment of Th, U and LREE over HREE ((La/Yb)<sub>N</sub>) average is 10.24) and depletion of HFSE (Nb, Ta, Zr). These geochemical features are a characteristic of subduction zone magmatism (Pearce and Peate, 1995) or crustal contamination (Rudnick and Gao, 2003). Given that these magmas have not signifificantly contaminated by crustal materials as discussed below, the negative Nb-Ta anomalies may be reflect the primary feature mantle source that was previously metasomatized by a subduction related component (Pearce et al., 2005). The general trace element patterns of calculated melt are similar to basalts in terms of strong depletion of HFSE, but higher contents of overall trace elements for the former. These similarities of trace element patterns between calculated melts for IAB-type gabbros and bulk rock composition of basalts may suggest that they are genetically related but the relatively higher concentration of the calculated melt suggesting that it was slightly more evolved. This interpretation is consistent with the absence of olivine in the IAB-type gabbros, indicating the evolved nature of the parental melt. On the other hand, we do not observe negative anomalies of HFSE in calculated melt in equilibrium with clinopyroxene in OIB-type gabbros, suggesting that OIB-type gabbros are not genetically related to IAB-type

gabbros, basalts and basaltic andesites.



**Figure 1.23**: Primitive mantle normalized multi-element patterns for the calculated liquid in equilibrium with clinopyroxene compared with volcanic rock trace element composition. Normalization factors for the calculated liquid are after Hart and Dunn (1993), Tiepolo (1999), and Adam and Green (2006). The bulk-rock composition of basalts also plotted for comparison. Mantle-normalization values are from McDonough and Sun (1995). CL, calculated liquid.

Ankaramites of Chukotka (Sample #69 and #71) have Mg# 63-65, Cr-contents 466-530 ppm, and Nicontents of 67-81ppm. They are also characterized by very low REE abundance with a strong depletion of HFSE. They include high-Mg clinopyroxene (Mg#  $\leq$ 93), although olivine is absent. Moreover, they are characterized by high CaO/Al<sub>2</sub>O<sub>3</sub> ~1.04, which are common features of primitive or parental arc-ankaramite (Della-Pasqua and Varne, 1997). Hence, these features make them a likely candidate for a near-primary mantle melt. High MgO, high CaO lavas and melt inclusions akin to ankaramites have been reported from many active island-arc systems (Barsdell and Berry, 1990; Della-Pasqua and Varne, 1997; Schiano et al., 2000). Several experimental modelling has revealed that melting of MORB-sourced upper mantle peridotite cannot produce primitive ankaramite (Schiano et al., 2000; Kogisio and Hirschmann 2001). Della-Pasqua and Varne (1997) and Green et al. (2004) suggested that ankaramites can be formed by melting of CO<sub>2</sub> metasomatized mantle, or by fusion of clinopyroxenites or wehrlites with in the mantle or at the base of the crust (Barsdell and Berry, 1990; Schiano et al., 2000; Kogisio and Hirschmann 2001). Therefore, the petrological and geochemical constraints suggest that the Chukotka ankaramite magma was probably formed by hydrous melting of the clinopyroxenerich source as evidenced by the occurrence of amphibole.

## 1.6.2. Fractional crystallization

Primary basaltic magma resulting from partial melting of mantle peridotite source must have Mg# in the range of 68-75 (Green, 1976; Hanson and Langmuir, 1978). The studied basaltic and gabbroic rocks display different evolutionary trends, suggesting that they followed different paths of fractional crystallization or accumulation. A negative correlation between MgO and FeO<sup>\*</sup> for the basalts and IAB-type gabbros suggests no fractionation of olivine, this interpretation is supported by the absence of this mineral in these rocks. The positive correlation between CaO and MgO in the OIB-type gabbros (Fig. 1.7) suggests fractionation of clinopyroxene. Furthermore, the positive correlations of Cr against MgO for the studied samples suggest the role of clinopyroxene fractionation. The lack of negative Eu anomalies and the progressive increase in Al<sub>2</sub>O<sub>3</sub> with decreasing MgO for basalts and gabbros suggests an absence of significant plagioclase fractionation (Fig. 1.7B). However, slight negative Eu anomalies indicate fractionation of plagioclase in the basaltic andesite. This interpretation is supported by the presence of marked negative Eu anomalies exhibited by hornblende phenocrysts in basaltic andesite (Fig. 1.22D). Moreover, IAB-type gabbroic and basaltic rocks do not have obvious Eu anomalies in the primitive mantle–normalized REE diagram (Fig. 1.22), suggesting that plagioclase were not important fractionating phase for IAB-type gabbroic and basaltic rocks of Chukotka. Most of the studied samples (except OIB-type gabbros) show trends of decreasing Dy/Yb with differentiation index (SiO<sub>2</sub>) (Fig. 1.24A), this is interpreted as significant amphibole fractionation (Davidson et al. 2007; Smith, 2014), because amphibole incorporates preferentially MREE compared to HREE (Tiepolo et al. 2007).



**Figure 1.24:** (A, B) Plots of SiO<sub>2</sub> (wt. %) vs. Dy/Yb and Zr/Sm. Variation of Dy/Yb and Zr/Sm primarily attributed to amphibole fractionation. However, clinopyroxene fractionation may also exert an influence on these ratios. Fractionation trends for amphibole are after Davidson et al. (2007). The geochemical data of Bel'kov Island dolerite (Siberian LIP; after Kuz'michov and Pease, 2007) and eastern Chukotka gabbros (Ledneva et al. 2014) also shown for comparison.

However, this interpretation is arguing against the absence of saucer-shaped REE patterns in the studied basaltic rocks (Fig. 1.9), which would be expected due to amphibole fractionation that observed in some arc lavas (e.g. Jolly et al., 2002; Figueroa et al., 2009).

As shown, in Fig. 1.9B, the REE patterns of the basaltic andesite is slightly concave-upward shaped, a feature classically attributed to amphibole fractionation (Green and Pearson, 1985) and confirmed by the presence of amphibole phenocrysts in these rocks. In addition, variation of Zr/Sm ratio is also often attributed primarily to amphibole fractionation (Fig. 1.24B). However, augite fractionation (Thirlwall et al., 1994) and magnetite fractionation (Tribuzio et al., 1999) may also exert an influence on the Zr/Sm ratios.

### 1.6.3. Crustal contamination

When continental basaltic magmas rise from their sources in the mantle through the continental crust, they often experience contamination (Watson, 1982; Arndt and Chrisensen, 1992; Hawkesworth et al., 1984; 1992; Mahoney, 1988; Carlson, 1991; Hergt et al., 1991). HFSE ratios are important indicators of crustal contamination in an open magma system. As shown in Fig. 1.31A IAB-type gabbroic and basaltic rocks (excepting OIB-type gabbros) are characterized by  $(Th/Ta)_N$  and  $(La/Nb)_N$  ratios >1, suggesting that the significant contribution of crustal material in their genesis (Neal et al., 2002). However, these rocks have obvious negative Zr-Hf anomalies in the primitive mantle-normalized trace element diagram (Fig. 1.9), arguing against significant crustal contamination because minor crustal contamination will increase the Zr-Hf contents due to the enrichment of

these elements in crustal material (Wedepohl, 1995). In addition, the Nb/La ratios for IAB-type gabbroic and basaltic rocks remain constant irrespective of  $SiO_2$  content (Fig. 1.25), contradicting to the trend that would expect for crustal contamination. Thus, the observed negative Zr-Hf anomalies may suggest that they originated from a mantle source metasomatized by slab derived fluid because Zr and Hf are immobile in fluid-dominated subduction processes (Münker et al., 2004). On the other hand, the depletion of Zr and Hf by amphibole fractionation is likely (Hollings and Kerrich, 2000), which is consistent with the presence of abundant amphibole crystals in these rocks. The involvement of crustal material for OIB-type gabbros is not supported by (1) relatively enrichment in Nb and Ta with Nb/La ratios of 0.99-1.43, and (2) its high  $TiO_2$  and FeO\* contents. Trace element ratios such as Th/Yb, Nb/Yb and Ta/Yb can be used as geochemical indicator mainly for understanding the nature of crustal inputs during magma genesis manifested in terms of subduction, crustal contamination and crustal recycling (Pearce and Peate, 1995; Pearce, 2008). In the Th/Yb vs Nb/Yb diagram (Fig. 1.32B) (Pearce, 2008) the IAB-type gabbros and basaltic rocks show a characteristic feature of arc setting with a prominent signature of slab dehydration and mantle enrichment, which in turn indicate the important role of subduction zone fluids enriched in Th in their petrogenesis. The IAB-type gabbros and basaltic rocks plot above MORB-OIB field in Fig. 1.31B, (except for OIB-type gabbroic samples that plot close or in the mantle array field), suggesting that their magma had an input from enriched subducted material (Pearce, 2008). The above lines of evidence suggest that crustal contamination was not important during the magma evolution.



Figure 1.25: SiO<sub>2</sub> (wt. %) vs. Nb/La diagram showing the crustal contamination.

### 1.6.4. Nature of mantle source

The incompatible element patterns defined by negative anomalies at Nb, Ta and Ti are characteristic features of HFSE depleted rocks generated by subduction zone magmatic processes. The depletion of HFSE, mainly Nb– Ta relative to LILE can be ascribed to three processes: (1) addition of LILE-enriched, Nb–Ta poor fluid released from the subducted slab to the mantle wedge, (2) the preferential retention of Nb–Ta in amphibole and rutile relative to the other phases in the subducted slab or mantle source, and (3) contamination of mantle-derived magma by crustal components (Rollinson 1993; Weyer et al., 2003; Wilson, 2007). Moreover, the depletion in HFSEs may have been caused by previous melt extraction in a back-arc basin (Woodhead et al., 1993; 1998; Elliott et al., 1997) or in arc settings (Grove et al., 2002). The absence of negative spike at Nb and Ta in the OIB- type gabbroic rocks precludes the major role of crustal contamination and/or subduction-related magmatic sources in their origin. The nature of the mantle source rocks can further be constrained by the trace element ratios such as Nb/Yb, Zr/Yb, and Th/Yb (Pearce and Peate, 1995). In the Nb/Yb vs. Th/Yb relationship (Fig. 1.32B), where our IAB-type gabbroic and basaltic rocks (except OIB-type gabbros) plot above the MORB-OIB array (Pearce and Peate, 1995), suggesting a subduction component in their source regions because fluid/melt released from a subducted slab is known to result in high Th and low Nb in the upper mantle wedge (Pearce et al. 1995). The Zr/Yb vs Nb/Yb diagram (Pearce and Peate, 1995) can be used to define a mantle array (Fig. 1.26A). Data points plotted above the upper boundary of the array can be interpreted as Zr derived from the subducted slab, accumulated zircon, or have undergone crustal contamination (Pearce and Peate, 1995). The studied basalts and gabbroic rocks of Chukotka plot within the mantle array (except basaltic andesite samples that falls above the upper boundary of array); hence we interpreted that slab-derived fluid, not melt, contributed to the magma source. The Nb/Y vs. Zr/Y diagram (Fitton et al., 1997) can be used to distinguish MORB-source mantle from more enriched source; arc magmas derived from depleted MORB-source plot below the lower boundary of the 'Iceland array', whereas those derived from more enriched sources plot with in the Iceland array (Fig. 1.26B). All the studied basaltic and gabbroic rocks of Chukotka (except basaltic andesite samples) fall within the Iceland array, suggesting that they are derived from enriched MORB-source mantle that was affected by subduction zone processes as mentioned above.



**Figure 1.26**: (A) Nb/Yb vs. Zr/Yb after Pearce and Peate (1995) and (B) Zr/Y vs. Nb/Y after Fitton et al. (1997) showing separation of MORB-source and enriched, plume-like mantle sources

The enrichment of LILEs and depletion of HFSEs of the Chukotka IAB-type gabbroic and basaltic rocks may reflect the metasomatism of mantle sources by the influx of slab-drived fluids; because crustal contamination possibility is excluded as discussed above (see Section 1.6.3). The metasomatism characteristics of mantle source for the basaltic and gabbroic rocks of Chukotka can be examined using a plot of (Ta/La)<sub>PM</sub> vs. (Hf/Sm)<sub>PM</sub> (LaFlèche et al., 1998) and Th/Zr vs. Nb/Zr (Kepezhinskas et al. (1997). As shown in the Fig. 1.27A, the data points of IAB-type gabbros and basalts plot into fluid-related metasomatism. Similarly, the Th/Zr vs. Nb/Zr diagram (Fig. 1.27B) also shows that the matle source for IAB-type gabbros and basaltic was metasomatizd by fluids, whereas for OIB-type gabbros was probably related to melt enrichment.



**Figure 1.27:** (A)  $(Ta/La)_N$  vs.  $(Hf/Sm)_N$  diagram (LaFlèche et al., 1998). Subscript N denotes the primitive mantle-normalized. Primitive mantle-normalizing values from (McDonough and Sun, 1995). (B) Th/Zr vs. Nb/Zr diagram (after Kepezhinskas et al. (1997) for the gabbroic and basaltic rocks of Chukotka, NE Russia.

This interpretation is also supported by the multiple formations of hydrous minerals, such as amphibole, in IABtype gabbros, which implies that magmas of the Chukotka IAB-type gabbroic and basaltic rocks were drived from a "wet" source. The basaltic andesite samples exhibit the ratios of Th/Ce>0.1, indicating minor contributions from melting of pelagic sediment of the subducted oceanic lithosphere (Hawkesworth et al., 1997). HFSE and HREE have not been mobilized from the slab to mantle wedge. Therefore, we suggest that the IABtype gabbroic and basaltic rocks (except OIB-type gabbros) were derived from a mantle source strongly modified by fluids released by subducted slab, although minor contribution of sediment melt in basaltic andesite cannot be ruled out.

### 1.6.5. Mantle melting conditions

Trace element data (mainly rare-earth element compositions) can provide important constraints in understanding the mantle melting conditions because their relative abundances in mantle derived melts are strongly dependent on the degree of partial melting and the nature of aluminous phases (spinel or garnet) in the mantle source (Lassiter et al., 1995; Aldanmaz et al., 2000; Reichow et al., 2005; He et al., 2010). HREE especially Yb has high garnet/melt partition coefficient (D<sub>garnet/melt</sub>=6.6) and is compatible in garnet, whereas La (LREE) and Sm has low garnet/melt partition coefficients (D<sub>garnet/melt</sub>= 0.0016 and 0.25 respectively) and are less compatible (Johnson, 1994; Green, 2006). Sm and Yb have similar partition coefficients during partial melting of spinel lherzolite mantle source, thus the Sm/Yb ratio does not change during the partial melting, whereas, it may decrease La/Sm ratios and Sm contents of the melts (Aldanmaz et al., 2000). On the other hand, partial melting of garnet lherzolite mantle source with residual garnet will produce a more steep-slope trend on a Sm/Yb versus La/Sm (Fig. 1.28).



**Figure 1.28**: Plots of Sm/Yb vs. La/Sm (A) and Sm/Yb vs. Sm (B) for the IAB-type gabbroic and basaltic rocks of Chukotka, NE Russia (After Zhao and Zhou, 2007). Mantle array (heavy line) defined by depleted MORB mantle (DMM, McKenzie and O'Nions, 1991) and primitive mantle (PM, Sun and McDonough, 1989). Melting curves for spinel lherzolite ( $Ol_{53}+Opx_{27}+Cpx_{17}+Sp_{11}$ ) and garnet peridotite ( $Ol_{60}+Opx_{20}+Cpx_{10}+Gt_{10}$ ) with both DMM and PM compositions are after Aldanmaz et al. (2000). Numbers along lines represent the degree of the partial melting.

IAB-type gabbroic and basaltic rocks have Sm/Yb ratios higher than the spinel+garnet lherzolite melting curve, but lower than the garnet lherzolite melting. We excluded the composition of the OIB-type gabbros and basaltic andesites because they are relatively fractionated rocks. Thus, the composition of the mantle source and degree of partial melting that produced the parental magma of these rocks, indicate that IAB-type gabbroic and basaltic melts were generated at about 10-30% partial melting of garnet lherzolite.

In the Tb/Yb versus La/Yb diagram (Fig. 1.29), a high level of MREE/HREE enrichment of the IAB-type gabbros and basaltic rocks can be attributed to large amout of (2-7%) of residual garnet in their source.



**Figure 1.29:** Tb/Yb versus La/Yb for the basaltic and gabbroic rocks of Chukotka (after Wei et al., 2014) and non-modal bach melting (Shaw, 1970) of a lherzolite mantle source showing the role of garnet and spinel in the melting region.

According to Stolper and Newman (1994) the increasing amounts of slab-derived fluid in the mantle wedge would lower the solidus and resulting in higher degree of melting. The IAB-type gabbros and basalts demonstrating highest percent of melts in the Sm/Yb versus La/Sm diagram (Fig. 1.28), consistent with the fluid dominated mantle sources.

## **1.6.6.** Pressure and Temperature constraints

The physical conditions of crystallizations such as pressure and temperature estimate can be obtained based on compositions of phases with in the gabbro. Equilibrium pressure was estimated using classical Al content in hornblende geobarometers (Hammarstrom and Zen 1986; Hollister et al. 1987; Johnson and Rutherford 1989; Blundy and Holland 1990), because the Al content in amphiboles is a sensitive indicator of pressure and temperature condition of crystallization. Calculated pressures show a range of 6.6-9.8 kbar within IAB-type gabbros but range as low as 1.0-1.9 kbar for OIB-type gabbros when applying the Hammarstrom and Zen (1986), Hollister et al. (1987) and Blundy and Holland (1990) methods. The obtained pressure for amphibole crystallization in IAB-type gabbros (average 7.4 kbar) and OIB-type gabbros (average 1.3 kbar) indicating an intrusion depth of about 24 km and 4.3 km respectively. The geobarometer of Johnson and Rutherford (1989) gave a pressure estimate lower by about 2 kbar for amphibole in IAB-type gabros, whereas about 0.2 kbar for amphibole in OIB-type gabbros. Application of Al in hornblende geobarometer (Schmidt 1992) for amphiboles from basaltic rocks yield different pressure estimates: 6.5-7.8 kbar for basaltic andesite, 7.4-10.0 kbar for lamprophyre, and generally lower for groundmass amphiboles from ankaramite and pyroxene pyric basalt (4.5-6.6 kbar). However, pressure estimates may be affected by ion substitutions in hornblende, oxygen fugacity and

fluid composition. Hornblende Al content will also vary as a function of temperature (Spear 1981; Hammarstrom and Zen 1986; Holland and Blundy 1994; Anderson and Smith 1995). On the other hand, the Ti/Al ratios in the IAB-type gabbros clinopyroxenes are lower than those in the OIB-type gabbros. These may suggest that the clinopyroxenes from IAB-type gabbros have higher pressure of crystallization than those from OIB-type gabbros.

Moreover, qualitative estimate can be also obtained from the ratio of  $AI^{(IV)}/AI^{(VI)}$  in amphibole, as proposed by (Fleet and Barnett, 1978). The amphiboles in the basaltic and gabbroic rocks of Chukotka plot in the low-pressure Ca-amphibole field on the  $AI^{(IV)}$  vs.  $AI^{(VI)}$  diagram (Fig. 1.30). Fleet and Barnett (1978) have proposed that the  $AI^{(IV)}/AI^{(VI)}=2$  ratio correspondes to about 5kbar pressureof Rease (1974), however, these preesure estimates are generally lower than those estimated by quantitative methods.



**Figure 1.30:** Al<sup>(IV)</sup> versues Al<sup>(VI)</sup> diagram for amphiboles from the gabbroic anad basaltic rocks of Chukotka, NE Russsia. Ratios and fields are from Fleet and Barnett, 1978).

Equilibration temperatures for amphiboles were calculated using the amphibole geothermobarometer of Ridolfi et al. (2010). Results show temperature values that range from 940-1006°C for basaltic andesites, 900-1080°C for basaltic rocks, 930-1001°C for IAB-type gabbros and 720-800°C for OIB-type gabbros. Ridolfi et al. (2010) reported uncertainities of  $\pm 22$ °C for the amphibole geothermometer. These temperature estimates are generally lower than the crystallization temperature of a normal basaltic magma (>1200 °C) (Lee et al., 2009).

### 1.6.7. Evaluation of tectonic setting

The Al<sub>Z</sub>/TiO<sub>2</sub> ratios (where Al<sub>Z</sub> indicates the percentage of tetrahedral sites occupied by Al) in clinopyroxene are an effective indicators for discriminating the tectonomagmatic affiliations of gabbros (Loucks, 1990). Clinopyroxenes from subduction-related yield an Al<sub>z</sub>/TiO<sub>2</sub> ratio that is twice as steep that of reft-related magams, mainly because that the former form under high water and oxygen fugacity condition (Loucks, 1990). Clinopyroxene of IAB-type gabbros and basalts are clearly follow the trend defined by volcanic rocks and cumulates from island are magmas (Loucks, 1990; Himmelberg and Loney, 1995; Krause et al., 2007), whereas those of OIB-type gabbros follow rift cumulate trend (Fig. 1.31A). The relationship between anorthite (An) content of plagioclase and Mg-number (Mg#) of clinopyroxene (Fig. 1.31C; Ishiwatari et al., 1990) also indicate an island are basalt affinity for the IAB-type gabbroic and basaltic rocks (Except lamprophyre which is plotted in the MORB field). In terms of 2Nb-Zr/4-Y variations (Fig. 1.31D), all the IAB-type gabbroic and basaltic rocks (except for OIB-type gabbros and basaltic andesites) exhibit an affinity for volcanic are basalts (VAB), which supports an arc-related tectonic environment for their generation in the former.



**Figure 1.31:** (A) and (B) Alz (percentage of tetrahedral sites occupied by Al) vs. TiO<sub>2</sub> in clinopyroxene (Loucks, 1990) from gabbroic and basaltic rocks respectively. (C) Relationship between anorthite (An) content of plagioclase and Mg-number (=Mg/Fe+Mg)) of coexisting clinopyroxene in the mafic rocks of Chukotka. The fields for island arc basalts (IAB) and mid-ocean ridge basalts (MORB) are from Ishiwatari et al. (1990). (D) 2Nb-Zr/4-Y tectonic environment discrimination diagram for the studied mafic rocks of Chukotka (after Meschede, 1986). AI + AII: within-plate basalt; B: MORB; D: N-MORB; C + D: magma series at destructive plate margins.

Moreover, in the  $(La/Nb)_N$  vs  $(Th/Ta)_N$  diagram, the studied basaltic rocks and IAB-type gabbros (except OIB-type gabbros) have trace element compositions similar to island-arc basalts, particularly similar to the eastern volcanic front lava of Kamchatka arc (Churikova et al., 2001), also suggesting subduction related environment (Fig. 1.32A).

# 1.6.8. COMPARISON WITH THE NORIL'SK BASALTS OF THE SIBERIAN LIP

### 1.6.8.1. Hydrous nature

Most Siberian trap basalts are known to have erupted during a very short time interval at the Permian-Triassic boundary (252-250 Ma) (Kamo et al., 2003; Reichow et al., 2009). Based on the U-Pb and  $^{40}$ Ar/<sup>39</sup>Ar geochronologic data, however, Ivanov et al. (2013) shown that the Siberian LIP magmatism had two pulses at the Permo-Triassic boundary and in the Middle Triassic. Siberian LIP represents one of the largest Phanerozoic continental LIPs with an area and volume of about  $7 \times 10^{6}$  km<sup>2</sup> and  $4 \times 10^{6}$  km<sup>3</sup>, respectively (Masaitis, 1983; Ivanov, 2007). It makes up of volumetrically dominant low-Ti tholeiitic rocks with subordinate amount of rocks with acidic, intermediate and ultrabasic alkaline composition (Lightfoot et al., 1993; Wooden et al., 1993; Fedorenko et al., 1996; Reichow et al., 2005; Ivanov, 2007; Krivolutskaya and Rudakova, 2009). Geochemical studies of volcanic and gabbroic rocks from several localities of the broad region of Siberian LIP have been documented. Among such regions are classical Nori'sk lava sequence (Sharma et al., 1991; Lightfoot et al., 1993; Wooden et al., 1993; Fedorenko et al., 1996; Walker et al., 1997; Al'mukhamedov et al., 2004), Putorana plateau (Sharma et al., 1991; Basu et al., 1998; Ryabchikov et al., 2001; Al'mukhamedov et al., 2004), Maymecha-Kotuy area (Arndt et al., 1995; Basu et al., 1995; Fedorenko and Czamanske, 1997; Fedorenko et al., 2000; Al'mukhamedov et al., 2004), Tunguska Syncline (DePaolo and Wasserburg 1979) and the west Siberian basin (Medvedev et al., 2003; Reichow et al., 2005).

In general, magmatic activity within the Siberian LIP divided into three stages (Wooden et al., 1993; Al'mukhamedov et al., 1999). The early rift stage dominated by variably differentiated subalkaline volcanic rocks ranging from high-Fe mantle melt (ferropicrites) like other LIPs (e.g. Parana-Etendeka, Tuff et al., 2005; Ethiopia, Desta et al., 2014) to evolved silica saturated basalts and basaltic andesites and characterized by variable trace element abundances similar to ocean island basalts. In general, the rift stage volcanic deposits reach a maximum thickness of 1 km below Nadezhdinsky suite of Noril'sk region (Al'mukhamedov et al., 2004). The main plateau stage, defined by voluminous extrusion of low-Ti tholeiitic flood basalts above the Nadezhdinsky suite reaching a maximal thickness of ~2.5 km (e.g. Al'mukhamedov et al., 2004) and show very uniform major and trace element composition (Reichow et al., 2005). The final stage is dominated by alkaline magmatism such as meimechite (Fedorenko and Czamanske, 1997; Arndt et al., 1998; Elkins-Tanton et al., 2007).

Moreover, the occurrences of Siberian LIP in the Arctic region were reported in the Taimyr Peninsula, in the islands of Kara Sea (Vernikovsky, et al., 2003; Dobretsov, et al., 2008) and in the New Siberian Islands (Kuz'michov and Pease, 2007). Gabbros and associated lavas from the eastern Chukotka in the Kolyuchinskaya Bay area show geochemical feature similar to intra-plate basalts and in general some tholeiitic basalts of Siberian

LIP (Ledneva et al., 2011). Recently, Ledneva et al. (2014) also reported gabbroic rocks with intraplate type geochemistry from southwest of Kolyuchinskaya Bay (these rocks are analogous to our OIB-type gabbros and some of them were sampled from the same localities i.e. S5 and S6 in Fig. 1.2).

A number of different models have been proposed to explain the origin of Siberian LIP (For a detailed review, see Ivanov, 2007). In general, the plume model is suggested for the origin of Siberian LIP on the basis of major, trace and radiogenic isotope data (e.g. Sharma et al., 1992; Arndt et al., 1993; Wooden et al., 1993; Saunders et al., 2005, Reichow et al., 2005, 2009). However, the plume model has been criticized by Czamanske et al. (1998) on the basis of uplift/subsidence history. Recently, an alternative subduction related model or "wet" mantle source is suggested by Ivanov (2007) for the Siberian LIP considering the following points: (1) the tectonic position of Siberian LIP in a back-arc setting of Permian subduction system in the Mongolian-Okhotsk belt, (2) the majority of low-Ti basalts show island-arc basalt type trace element patterns, and (3) the presence of primary mica in volcanic rocks. The presence of hydrous minerals is reported from several localities of Siberian LIP: amphibole and biotite in Noril'sk I intrusion (Renne 1995), biotite in meimechite from Maymecha-Kotuy region (Fedorenko and Czamanske 1997); biotite in the olivine gabbro from west Siberian basin (Reichow et al., 2002); biotite in dolerite sills of Angara-Taseevskaya (Ivanov 2007); amphibole and biotite in the dolerite of New Siberian Islands (Kuz'michov and Pease 2007). However, it is important to note that amphibole is rarely a phenocryst in arc basalts (Davidson et al., 2007) and their scarcity can be attributed to its instability at low pressures (e.g. Rutherford and Devine, 1988; Romick et al., 1992). Ivanov and Litasov (2014) have shown that

the influence of the subduction related deep water cycle on the Siberian LIP on the basis of experimental data and numerical calculations. The above lines of evidence support the hydrous nature of the Siberian LIP.

The hydrous nature of the IAB-type gabbroic and basaltic rocks of Chukotka is evident from its high Ca content of clinopyroxene and crystallization of abundant magmatic amphibole. High water-pressure ( $P_{H2O}$ ) conditions in the magma are suggested by the occurrence of Ca-rich clinopyroxene (Johannes, 1978). High  $P_{H2O}$  could also cause plagioclase to be Ca-rich (Johannes, 1978), which is consistent with the presence of An-rich plagioclase crystals from IAB-type gabbros (Fig. 1.31C). In addition, Arculus and Wills (1980) described that hydrous basaltic melts crystallize more Ca-rich (anorthitic) plagioclase than anhydrous melts.

### 1.6.8.2. HFSE depletion

Basalts of the Nadezhdinsky suite belong to a particular sub-type of the low-Ti rock series (Fedorenko et al., 1996), which is characterized by pronounced negative anomalies of HFSE (e.g. Nb, Ti) compared to the rest of volcanic suites of Siberian traps and are attributed to crustal contamination (e.g., Arndt et al., 1993; Wooden et al., 1993) or melting of the lithospheric mantle (Lightfoot et al., 1993; Hawkesworth et al., 1995). Multi-element diagrams for the Triassic basalts and gabbros of Chukotka are compared with averaged data for the Siberian LIP from the Noril'sk region (Fig. 1.9). Trace element patterns for the basalts and IAB-type gabbros resemble to the low-Ti Nadezdinsky suite of Noril'sk region in terms of depletion in HFSE (i.e. Nb, Ta, Zr, P), which may suggest similar condition of formation. However, our samples show a more pronounced HFSE depletion and higher (La/Nb)<sub>N</sub> ratios (Figs. 1.9 and 1.32A, respectively) which are remarkably similar with the eastern volcanic front basalts of the Kamchatka arc (Churikova et al., 2001). The degree of HFSE depletion in our samples is lower compared to intra-oceanic convergent margin lavas (i.e. Mariana arc, Tamura et al., 2014). It is important to mention that the major continental LIPs, e.g. Siberian LIP (Wooden et al., 1993; Krivolutskaya and Rudakova, 2009), Central Atlantic magmatic province (Callegaro et al., 2013), and Karoo LIP (Luttinen et al., 2010) are characterized by elevated (La/Nb)<sub>N</sub> ratios similar to island-arc basalts (Fig. 1.32).

Such arc-like features of continental LIPs have been attributed to a sudden reactivation of dormant arc or backarc sources trapped under continental-plate sources (Puffer, 2001). The island-arc basalt like trace element pattern of the low-Ti basalts of Siberian LIP have been usually attributed to the signature of lithospheric contamination (e.g. Lightfoot et al., 1993; Reichow et al., 2005).

On the other hand, Puffer (2001) discussed the geochemical similarity between low-Ti Siberian LIP and island-arc basalts in terms of depletion of HFSE and enrichment of LILE, which indicates their mantle source, is similar to mantle wedge of active continental margins.

OIB-type gabbros have (La/Nb)<sub>N</sub> between 0.7 and 1.0 and (Th/Ta)<sub>N</sub> between 0.5 and 0.8 (Fig. 1.32) similar to typical plume related LIPs, e.g. Ethiopian LIP (Beccaluva et al., 2009; Desta et al., 2014) and Hawaiian-Emperor Chain basalts (Huang et al., 2005), which can be interpreted as insignificant contribution of continental material in their source. Similarly, in terms of Th/Yb vs. Nb/Yb relations (Fig. 1.32B) (Pearce, 2008) OIB-type gabbroic samples like typical plume related LIPs e.g. Ethiopian LIP (Beccaluva et al., 2009; Desta et al., 2014) and Etendeka magmatism (Gibson et al., 2000) and Hawaiian-Emperor Chain basalts (Huang et al., 2005) plot close to or with in the oceanic mantle array, which may indicate no influence of lithospheric component in their genesis.

However, the Nadezhdinsky suit (Siberian LIP) (Wooden et al., 1993), Central Atlantic magmatic province (Callegaro et al., 2013), Karoo LIP (Luttinen et al., 2010) clearly displaced from the oceanic mantle array field to higher Th/Yb ratios (Fig. 1.32B), which can be explained by crustal contamination or subduction zone enrichment (Pearce and Peate, 1995). In the case of IAB-type gabbros and basaltic rocks of Chukotka, the displacement of data above the mantle array is attributed to enrichment by fluids. Ivanov et al. (2008) and Ivanov and Litasov (2014) discussed the similarity of the calculated initial melt compositions of the southeastern Siberian flood basalt province (Angara-Taseevskaya dolerite sills) with the initial melt compositions of the modern arc of Eastern Kamchatka (Portnyagin et al., 2007) in terms of trace elements, suggesting a similar subduction-related processes are responsible for their origin. Ivanov and Litasov (2014) concluded that the Siberian LIP is formed in a far back-arc region of the Mongolia-Okhotsk subduction system and the influence of subduction in the trace element budget of flood basalts reduces away from subduction zone (e.g. presence of rocks with OIB signature such as meimechite from the northernmost Maymecha-Kotuy region). However, meimechite and picritic lavas are not known in Chukotka like that of Siberian LIP.



**Figure 1.32:** (A)  $(La/Nb)_N$  vs.  $(Th/Ta)_N$  (after Neal et al., 2002), where N denotes normalized toprimitivemantle (McDonough and Sun, 1995) and (B) Nb/Yb vs. Th/Yb diagram discriminating rocks enriched by input from subduction componenet, crustal contamination, and deep crustal recycling (modified after Pearce, 2008). SZE: subduction zone enrichment, CC: continental contamination, WPE: within-plate enrichment. The field of Siberian LIP is from Wooden et al. (1993) and Krivolutskaya et al. (2009); Bel'kov Island, Kuz'michov and Pease (2007); Central Atlantic magmatic province (CAMP), Callegaro et al. (2013); Ethiopian LIP, Beccaluva et al. (2009) and Desta et al., 2014; Etendeka, Gibson et al. (2000); Karoo LIP, Luttinen et al. (2010); Kamchatka arc, Churikova et al. (2005) are shown for comparison. Upper crust (UC) and lower crustal (LC) values are from Rudnick and Gao, (2003). NMORB, EMORB and OIB are from Sun and McDonough (1989).

The vast distribution of the Paleozoic accretionary complexes in Mongolia with oceanic sediments, oceanic plateau fragments with a trace of forearc magmatism evidences for a long term, wide scale operation of the subduction system (Erdenesaihan et al., 2013).

In summary, the Triassic mafic rocks of Chukotka may represent the eastern margin of Siberian LIP based on the following points: (1) the presence of both OIB and IAB-like (i.e. depletion of HFSE) mafic rocks throughout Chukotka like that of Siberian LIP, (2) the hydrous nature of Siberian magma to crystallize hydrous minerals, (3) plat formal field occurrence of the studied rocks and (4) the geochemical and petrological similarity between the IAB-type gabbros of Chukotka and the Bel'kov Island dolerites suggests that the eastern Chukotka was closer to the Siberian margin during Triassic and later tectonically rifted and moved to the current position.

# **1.7. CONCLUSIONS**

IAB-type gabbroic suite is genetically related to the associated basaltic rocks and represents the slowly cooled, tabular-shaped intrusion of mafic magma. Mineral and bulk rock chemical characteristics of IAB-type gabbroic rocks and basalts are compatible with magmas from subduction zone geotectonic setting, whereas OIB-type gabbros show within plate magma characteristics. Geochemical data suggest partial melting of the subductionmodified, metasomatized enriched mantle wedge of garnet lherzolite to produce the parental melt of the IABtype gabbroic and basaltic rocks of Chukotka. The parental magma of the IAB-type gabbroic and basaltic rocks formed by about 10-30% partial melting of garnet lherzolite. The near-primary nature of the ankaramite of
Chukotka reflected on its high Mg# (63-65), Cr contents (466-530 ppm), Ni-contents (67-81 ppm) and occurrenc of high-Mg clinopyroxene phenocrysts (Mg#  $\leq$ 93). The geochemical similarity of the studied IAB-type gabbroic and basaltic rocks of Chukotka with Bel'kov dolerite and low-Ti Nadezhdinsky suit (Noril'sk region) in terms of the presence of dominant hydrous minerals and negative HFSE anomalies, it is possible that the eastern Chukotka was placed closer to the Siberian LIP in Triassic, and the Triassic mafic magmatism in Chukotka represents a marginal part of the Siberian LIP.

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# **CAPTER 2**

# Ferropicrite from the Lalibela area in the Ethiopian large igneous province

Minyahl Teferi DESTA\*, Dereje AYALEW\*\*, Akira ISHIWATARI \*\*\*\*,

Shoji ARAI \*\*\*\* and Akihiro TAMURA \*\*\*\*

<sup>\*</sup>Department of Earth Science, Graduate School of Science, Tohoku University, Aoba, Sendai 980-8578, Japan

\*\*School of Earth Sciences, Addis Ababa University, P.O.Box 1176, Addis Ababa, Ethiopia

\*\*\*\*Center for Northeast Asian Studies, Tohoku University, Kawauchi 41 Aoba-ku, Sendai 980-8576, Japan

\*\*\*\* Department of Earth Sciences, Faculty of Science, Kanazawa University, Kanazawa 920-1192, Japan

# 2.1 ABSTRACT

Ferropicrite (FeO\*=14.0 wt. % and MgO=13.9 wt. %) and picritic ferrobasalt (FeO\*=14.7 wt. % and MgO=10.8 wt. %) lava flows are found near Lalibela in the Oligocene (~30 Ma) Ethiopian large igneous province (LIP) in association with ultratitaniferous transitional basalt and picrites of the second high-Ti (HT2) series. The dominant phenocryst in the studied samples is Mg-rich olivine (up to  $Fo_{88.9}$ ) with high CaO contents (to 0.42

wt. %) without any kink band structure, indicating that the olivines are crystallized from a magnesian melt. Spinel microphenocrysts and inclusions in olivine are characterized by extremely high Cr# (79-84), moderate Mg# (18-51), moderate Fe<sup>3+</sup># (11-39) and high TiO<sub>2</sub> (3.6-14.8 wt. %). The clinopyroxene phenocrysts are Mg#=74-88, TiO<sub>2</sub>=0.84-1.82 wt. %, and Al<sub>2</sub>O<sub>3</sub>=1.2-3.2 wt. % in the cores. The REE contents of clinopyroxenes display enrichment in LREE ( $La_N/Yb_N=1.2-1.9$ ) and MREE ( $Eu_N/Yb_N=3.3-4.3$ ) relative to HREE. Relative depletion of HFSE (e.g. Nb and Zr) is also observed. In general, these trace element characteristics of clinopyroxene are similar to those of the HT2 basalts. Some of the clinopyroxene crystals show strong reverse zoning with abrupt increase in Cr, Ni and Mg# from core to rim, which may be resulted from reaction of melt with mantle peridotite during magma ascent. Bulk rock chemistry of the studied samples exhibits very low Al<sub>2</sub>O<sub>3</sub>/TiO<sub>2</sub> (1.8-2.2) and high Zr/Y (8.2-10.2) ratios. These may indicate the important role for garnet during melting and that the lavas were formed by a small degree of partial melting which apparently contradicts to the high Cr# of spinel. In view of low Cr/Al ratio of the bulk rock, the high Cr# of spinel suggests very high temperature of the magma (and the mantle plume). The origin of these ferropicrite and picritic ferrobasalt could be attributed to high pressure partial melting of peridotite-eclogite (pyroxenite) mixture that possibly incorporated recycled oceanic crust components.

Keywords: Ferropicrite, Cr-spinel, large igneous province, Oligocene, Lalibela, eclogitic source

# **2.2. INTRODUCTION**

Ferropicrites are subalkaline or mildly alkaline primitive rocks that were reported for the first time from the Paleoproterozoic Pechenga volcanic belt of the Kola Peninsula by Hanski and Smolkin (1989), who defined ferropicrite as an MgO rich volcanic rock with FeO\* higher than 14 wt. %. Ferropicrites may have similar MgO contents to komatilites (~19 wt. %) but significantly higher  $TiO_2$  contents (>1 wt. %) like meimechite (Le Bas, 2000). The geochemical characteristics of ferropicrites and meimechites indicates their derivation by lower degree of partial melting at higher pressure as compared to common continental flood basalt picrites that originate as more homogenized and voluminous melting at lower pressures (Gibson, 2002). For the last two decades, a number of ferropicritic whole-rock compositions have been reported from the Precambrian volcanic belts e.g. Slave and Superior Provinces (Goldstein and Francis, 2008; Francis et al., 1999) and from the Phanerozoic continental flood basalt provinces (CFB) (Siberian Traps, Karoo, Paraná-Etendeka, North Atlantic, Emeishan; Wooden et al., 1993; Gibson et al., 2000; Riley et al., 2005; Zhang et al., 2006). Ichiyama et al. (2006) reported ferropicritic; highly magnesian olivine cumulates from a Permian accreted oceanic plateau, southwestern Japan.



**Figure 2.1:** Sketch map of the Ethiopian large igneous province (LIP) including the Yemen conjugate margin, modified after Beccaluva et al. (2009) and Natali et al. (2011). Oligocene (~30 Ma) volcanic rocks: LT, Low-Ti tholeiitic basalts; HT1, High-Ti tholeiitic basalts; HT2, very High-Ti transitional basalts and picrites. Location of ferropicrite from the Dilb road section reported in this study is indicated by star. Miocene to Quaternary volcanic rocks in the Main Ethiopian Rift (MER), are not shown. CFB: Continental flood basalt.

Recently, several petrogenetic models are provided for the origin of ferropicrite. Gibson (2002) describes the significance of recycled oceanic crust as a "re-fertilizer" of peridotite in the starting mantle plume head. Ichiyama et al. (2006) and Tuff et al. (2005) also suggested analogous models with recycled eclogitic or

pyroxenitic mantle source, respectively. On the basis of silicate liquid immiscibility study, Jakobsen et al. (2005) interpreted that ferropicrites could also form by mixing of evolved, immiscible Fe-rich liquid with picritic mantle melts. More recently, Sobolev et al. (2007) described that iron-rich source regions in the mantle can be produced by pyroxenite veining. Generally, ferropicrites are attributed to anomalously hot mantle sources and mantle plumes (Hanski and Smolkin, 1995; Goldstein and Francis, 2008).

Picritic lavas from Ethiopian LIP are representative of the second high-Ti (HT2) series, as described by Pik et al. (1998) and Beccaluva et al. (2009) and are overlain by rhyolitic ignimbrite of 30 Ma age (Hofmann et al., 1997). In previous literatures the occurrence of Fe-rich picrite in Ethiopian large igneous province (LIP) has been unrecognized.

In this study, we report the results of the mineral chemistry and whole rock geochemistry of ferropicrite (Sample 1) and picritic ferrobasalt (Samples 2 and 3) rocks from the eastern part of Ethiopian large igneous province in order to obtain insight into the characteristics of their mantle source. Ferropicrite and picritic ferrobasalt samples were obtained from the Dilb road section of the Lalibela area, eastern portion of Ethiopian LIP (Fig. 2.1).

### 2.3. GEOLOGICAL SETTING

The Oligocene Ethiopian LIP represents one of the youngest, best exposed sequences of mafic and felsic volcanic rocks, associated with incipient lithospheric breakup (extensional tectonics) and plume impingement

(Marty et al., 1996). It is dissected by the Main Ethiopian Rift (MER)-Red Sea-Gulf of Aden rift system (with the Afar R-R-R-triple junction), which indicates the close association of magmatism and lithospheric extension and hence satisfy the plume theory. In addition, the tectonomagmatic and geophysical studies shows that the existence of deep mantle plume (Ritsema et al., 1999; Courtillot et al., 2003). The present remnants of Ethiopian flood volcanism cover an area of at least  $6 \times 10^6$  km<sup>2</sup> and have a total volume of about  $\sim 3.5 \times 10^5$  km<sup>3</sup> (Mohr & Zanettin, 1988). Rochette et al. (1998) estimated as the original volume reached up to  $10^6$  km<sup>3</sup>. This voluminous basaltic magmatism was emplaced in a rather short time interval ~30±1 Ma (Hofmann et al., 1997) and successively followed by a number of huge shield volcanoes (Piccirillo et al., 1979). These shield volcanoes are a conspicuous feature of the Ethiopian LIP and distinguish it from other LIPs, such as Deccan and Karoo (Kieffer et al., 2004) and Siberia. The ferropicrite and picritic ferrobasalt of this study is considered as a part of the main flood basalt volcanism (~30 Ma). Ayalew et al. (2002) and Ayalew and Ishiwatari (2011) described the presence of significant volume of rhyolite (up to 20 %) with a maximum thickness of ca. 500 m mostly on the upper part of the Ethiopian continental flood basalt sequence. The final phase of volcanism (i.e. Pliocene to present) mostly concentrated along the Main Ethiopian Rift and Afar region. However, volumetrically small volcanic rocks as old as 45-40 Ma are found in southern and south-western Ethiopia (George et al., 1998). All the Ethiopian plateau rocks rest either directly over the Neoprotrozoic crystalline basement or over the Mesozoic sedimentary sequences. According to Pik et al. (1998) and Beccaluva et al. (2009), the Northern Ethiopian plateau basalts are classified into three magma types based on their  $TiO_2$  content (Fig.2.1): Low-Ti tholeiites (LT) distributed in the northwestern areas; the first high-Ti lavas (HT1) in the eastern areas and ultratitaniferous transitional basalt and picrites of the second high-Ti (HT2) series, which are concentrated in the Lalibela area close to the Afar depression. The lava piles in the Lalibela area reaches up to ~1800 m thick, consisting of basaltic and picritic units capped by rhyolitic ignimbrite. The HT2 picrites are geographically localized in the high-Ti sub-province and the ferropicrite and picritic ferrobasalt rocks occur associated with HT2 basalt and picrite series. Ferropicrites constitute volumetrically minor parts of Ethiopian LIP and they typically form thin flows at or near the base of thick lava piles in the Lalibela area.

# 2.4. ANALYTICAL METHODS

The major element analysis of the constituent minerals of these samples was determined by electron probe micro analyser (EPMA) using energy dispersive X-ray spectrometer Oxford Link ISIS equipped on the JEOL JSM-5410 Scanning electron microscope (SEM) at the Earth Science department laboratory of Tohoku University, Japan. The operating conditions were at 15 kV acceleration voltage and a beam current of 1 nA. A number of natural standards were applied for calibration, and the data were corrected with ZAF quantitative procedure. Major and some trace elements for the whole-rock analyses (such as V, Cr, Ni, Rb, Sr, Ba, Y, Zr, Nb) were carried out by X-ray fluorescence spectrometer (XRF-RIX 2100) at the aforementioned department, Tohoku University. Three glass beads were prepared by using fusion procedure, which consists of heating a 1:5 mixture of sample and flux (Li<sub>2</sub>B<sub>4</sub>O<sub>7</sub>) at ~1050 °C. The Loss on Ignition (LOI) is determined by weighing a 1 gram of rock powder before and after ignition at 750  $^{\circ}$ C for 6 hours. Trace element concentrations of clinopyroxene in ferropicrite and picritic ferrobasalts were determined by a laser ablation (193 nm ArF excimer: MicroLas GeoLas Q-plus)-inductively coupled plasma spectrometer Agilent 7500S (LA-ICP-MS) at Kanazawa University (Ishida et al., 2004). The analysis was conducted by ablating spot of 50-60 µm in diameter at laser power of 8 J/cm<sup>2</sup>. NIST SRM 612 glass was used as a standard. The trace element concentration of NIST SRM 612 was selected from Pearce et al. (1997). <sup>29</sup>Si was used as internal standard for pyroxene, with concentration of SiO<sub>2</sub> determined by EPMA.

 Table 2.1: Whole rock chemistry of the ferropicrite and picritic ferrobasalts from the Lalibela area, Ethiopian LIP.

Rock	Ferropicrite	Picritic ferrobasalts	
Sample	1	2	3
Major elements (wt. %)			
SiO <sub>2</sub>	45.82	43.04	44.03
TiO <sub>2</sub>	3.84	4.74	5.04
Al <sub>2</sub> O <sub>3</sub>	8.58	8.65	9.23
FeO*	14.00	14.50	14.70
CaO	10.00	9.87	10.63
MgO	13.92	10.05	10.81
MnO	0.18	0.18	0.18
$K_2O$	0.76	0.90	0.76
Na <sub>2</sub> O	1.82	1.89	2.02
$P_2O_5$	0.35	0.62	0.58
Total	99.27	94.44	97.98
LOI	-0.01	1.58	0.10
Mg#	63.9	55.3	56.7
Trace elements (ppm)			
V	407	463	490
Cr	195	40.8	18.2
Ni	501	389	356
Rb	16.1	20.3	9.6
Sr	415	503	567
Ba	210	268	282
Y	34.4	38.9	37.2
Zr	283	359	378
Nb	23.6	31.0	31.9

\*Total iron as FeO. Mg# (=Mg/Mg+ Fe<sub>Total</sub>)  $\times$  100; LOI = Loss on ignition.

#### 2.5. WHOLE ROCK CHEMISTRY

#### 2.5.1. Major and trace elements

Table 2.1 shows whole-rock analyses of the ferropicrite and picritic ferrobasalt from the Lalibela area. The studied samples are characterized by high TiO<sub>2</sub> (3.8-5.1 wt. %) and FeO\* (total Fe as FeO) (14.0-14.7 wt. %) (Fig. 2.2). The FeO\* content is within the range of ferropicrites of other LIPs (Superior Province, Pechenga, Siberia, Paraná-Etendeka and Japan). The Fe/Mn ratios of the bulk rock range from 78 to 82, which is higher than those reported for the Ethiopian picritic lava (70-76; Rogers et al., 2010). The Ni/Cr ratio is also high (0.4 in ferropicrite). The MgO content ranges from 10.5 to 13.8 wt. % and Sample 1 satisfies the definition of picrite (> 12 wt. % MgO) (Le Bas, 2000). A general decrease of Ni (500 to 350 ppm) with decreasing Mg# (64 to 56) implies removal of olivine through evolution from ferropicritic to ferro-basaltic composition. They show enrichment of high field strength elements (HFSE), e.g. P<sub>2</sub>O<sub>5</sub> (0.35-0.64 wt. %), Nb (24-32 ppm), Y (34-39 ppm) and TiO<sub>2</sub> (3.8-5.1 wt. %) and their increase with decreasing MgO (Figs. 2.2 and 2.3). They are further characterized by very high V (407-490 ppm) content. The content of Zr (283-378 ppm) in the Ethiopian ferropicrite is very high and is comparable to that of Siberian ferropicrite, but the latter is characterized by higher Nb/Y ratio. Figure 2.4 shows the variations of Al<sub>2</sub>O<sub>3</sub>/TiO<sub>2</sub> with respect to Zr/Y ratios for the ferropicrite and picritic ferrobasalt. In comparison with other ferropicrites (Superior Province, Pechenga, Paraná-Etendeka and Japan) the Ethiopian ferropicrite and picritic ferrobasalt exhibit low Al<sub>2</sub>O<sub>3</sub>/TiO<sub>2</sub> ratio close to Siberian ferropicrite (~2.2) and are similar to HT2 basalt and picrite (Beccaluva et al., 2009).



**Figure 2.2:** Major element variations with respect to MgO of the ferropicrite and picritic ferrobasalt rocks. For comparison, Ethiopian LIP (LT, low-Ti basalt; HT1, high-Ti 1 basalt; HT2, high-Ti 2 basalt and picrite; Beccaluva et al., 2009), ferropicrites from Superior Province (Goldstein and Francis, 2008), Pechenga (Hanski and Smolkin, 1995), Siberia (Arndt et al., 1995), Paraná-Etendeka (Gibson et al., 2000), Japan (Ichiyama et al., 2006), the composition of a picritic melt produced from  $GA1_{50}MPY90_{50}$  at 3.5 GPa (Yaxley & Green, 1998) and 97SB68 starting composition of Tuff et al. (2005) experiment.



**Figure 2.3:** Trace element variation with respect to MgO of Ethiopian ferropicrite and picritic ferrobasalt. Symbols and data sources are as in figure 2.2.

According to the Pik et al. (1998) classification of the Ethiopian LIP based on Ti/Y ratio, the studied samples falls in the HT1 compositional field (not shown). The high FeO\* content of these samples are similar to the first high-Ti basalts (HT1) of Adigrat area (Beccaluva et al., 2009). However, the latter is characterized by lower MgO (< 10 wt. %), CaO/Al<sub>2</sub>O<sub>3</sub> (~ 0.5) and Ni ( $\leq$  110 ppm), supporting HT2 affiliation of our samples.



**Figure 2.4:** Bulk-rock  $Al_2O_3/TiO_2$  vs Zr/Y plot for the Ethiopian ferropicrite and picritic ferrobasalt. Data sources are as in fig. 2.2. The arrow assumes a single peridotitic source.

## 2.6. PETROGRAPHY AND MINERAL CHEMISTRY

# 2.6.1. Petrography

Ferropicrite and picritic ferrobasalts examined in this study shows porphyritic texture with phenocryst phases of olivine (15-30 vol. %) and augitic clinopyroxene (10-25 vol. %) (Fig.2.5). Minor plagioclase microphenocrysts occur in one of the studied samples. Chrome-spinels are included in olivine and rarely occur as microphenocrysts set in the groundmass, which comprises a mixture of plagioclase, clinopyroxene, and ilmenite. Olivine phenocrysts typically show hexagonal euhedral shape (Fig. 2.5a, b) with irregular cracks and slight iddingsite alteration along the cracks. Some of the faces on olivine crystal are curved and embayed. Smaller olivines (~2 mm) are generally rounded and exhibit a rim of distinctive red tarnish of iddingsite formed by oxidation of olivine. Some olivine crystals are completely replaced by iddingsite. Deformed, kink-banded crystals are absent. Clinopyroxenes occur as euhedral, elongated pinkish phenocrysts (<4 mm) which are partially embayed and resorbed (Fig. 2.5c and d). In places, olivine and clinopyroxene occur together as glomerocrysts up to 7 mm in size in which olivines appear to be interstitial between clinopyroxenes. Ilmenites (up to 0.2 mm) are also included in some clinopyroxene phynocrysts. Representative compositions of the main mineral phases are shown in Tables 2.2-2.5.



**Figure 2.5:** Photomicrographs of Ethiopian ferropicrite and picritic ferrobasalt. (a) Crossed polarized light showing porphyritic texture with abundant magnesian olivine phenocrysts. (b) Back-scattered electron images of olivine phenocrysts and spinel inclusions. Subhedral to euhedral olivine phenocrysts are set in a microcrystalline groundmass. (c) Crossed polarized light images of clinopyroxene with reverse zoning, Cpx3 of Sample 1 and (d) that with resorbed texture, Cpx1 of Sample 2. Small circles in the clinopyroxene phenocrysts show ICP-MS analytical points (Table 2.5). Ol, olivine; Cpx, clinopyroxene; Sp, spinel.
Sample				Ferro	picrite				Picritic ferrobasalt 1           Ol1         Ol3         Ol4         Ol5           Core         core         rim         core         rim         core         rin           41.17         42.12         40.73         41.01         40.44         40.44         41.0           14.80         10.63         11.91         10.52         12.75         13.19         13.8           0.16         0.18         0.18         0.14         0.22         0.19         0.1           45.17         48.00         46.19         47.18         44.90         44.86         45.3           0.37         0.31         0.31         0.28         0.31         0.30         0.30						
Mineral	Ol1	(	012	0	13	Ol4	O15	Ol6	Ol1	0	13	0	014	0	15
	Core	core	Rim	core	rim	core	core	core	Core	core	rim	core	rim	core	rim
SiO <sub>2</sub>	39.03	41.68	40.00	40.94	39.08	40.48	40.03	41.80	41.17	42.12	40.73	41.01	40.44	40.44	41.08
FeO*	19.48	12.39	16.33	11.41	18.59	11.19	17.27	10.82	14.80	10.63	11.91	10.52	12.75	13.19	13.83
MnO	0.24	0.16	0.26	0.20	0.30	0.18	0.14	0.18	0.16	0.18	0.18	0.14	0.22	0.19	0.14
MgO	39.35	46.96	42.32	46.55	40.28	46.00	42.09	48.24	45.17	48.00	46.19	47.18	44.90	44.86	45.33
CaO	0.29	0.34	0.32	0.42	0.34	0.37	0.29	0.32	0.37	0.31	0.31	0.28	0.31	0.30	0.30
NiO	0.27	0.22	0.25	0.25	0.39	0.27	0.26	0.11	0.34	0.30	0.44	0.30	0.30	0.25	0.40
Total	98.66	101.75	99.48	99.77	98.98	98.49	100.08	101.47	102.01	101.54	99.76	99.43	98.92	99.23	101.08
Cations (O=	=4)														
Si	1.016	1.015	1.016	1.014	1.012	1.015	1.015	1.013	1.011	1.018	1.011	1.014	1.016	1.015	1.014
Fe <sup>2+</sup>	0.424	0.252	0.347	0.236	0.403	0.235	0.366	0.219	0.304	0.215	0.247	0.218	0.268	0.277	0.286
Mn	0.005	0.003	0.006	0.004	0.007	0.004	0.003	0.004	0.003	0.004	0.004	0.003	0.005	0.004	0.003
Mg	1.526	1.704	1.602	1.718	1.554	1.719	1.590	1.743	1.654	1.730	1.709	1.738	1.682	1.678	1.668
Ca	0.008	0.009	0.009	0.011	0.009	0.010	0.008	0.008	0.010	0.008	0.008	0.007	0.008	0.008	0.008
Total	2.984	2.986	2.984	2.983	2.985	2.983	2.982	2.987	2.982	2.981	2.989	2.980	2.979	2.986	2.986
Fo	77.73	86.57	81.61	87.23	78.79	87.38	80.84	88.28	83.91	88.42	86.83	88.41	85.69	85.31	84.91

Table 2.2: Representative analyses of olivine phenocrysts in ferropicrite and picritic ferrobasalt rocks from Lalibela area, Ethiopian LIP

\*Total Fe as FeO.

Table	e 2.2:	Continued
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Sample			Picritic fe	rrobasalt 2		
Mineral	Ol2	Ol	3	O15	0	16
	Core	Core	Rim	Core	Core	Rim
$SiO_2$	40.04	40.51	40.96	39.92	39.29	40.97
FeO*	14.40	14.69	14.52	13.23	16.48	17.26
MnO	0.11	0.23	0.24	0.19	0.23	0.24
MgO	43.74	43.82	44.32	43.59	40.87	42.70
CaO	0.40	0.37	0.36	0.33	0.37	0.36
NiO	0.31	0.29	0.45	0.29	0.28	0.21
Total	99.00	99.91	100.85	97.55	97.52	101.74
Cations (O=4)						
Si	1.014	1.018	1.017	1.020	1.020	1.019
Fe <sup>2+</sup>	0.305	0.309	0.301	0.283	0.358	0.359
Mn	n.d.	0.005	0.005	0.004	0.005	0.005
Mg	1.651	1.641	1.640	1.659	1.582	1.583
Ca	0.011	0.010	0.010	0.009	0.010	0.010
Total	2.981	2.983	2.983	2.980	2.980	2.981
Fo	83.84	83.53	83.84	84.88	80.91	80.91

### 2.6.2. Mineral chemistry

#### 2.6.2.1. Olivine

Olivine phynocrysts in the studied samples are homogenous and show a narrow compositional range (Fo<sub>78-88</sub>), which corresponds to the previously reported values from HT2 basalts and picrites (Fo<sub>77-90</sub>, Beccaluva et al., 2009). The Fo content of olivines from the Ethiopian ferropicrite and picritic ferrobasalt fall within the range of those in Archean and Phanerozoic ferropicrites (Fo<sub>83-84</sub> in Pechenga complex, Hanski and Smolkin, 1995; Fo<sub>85-88</sub> in Emeishan/Lijiang, Zhang et al., 2006). Generally, the largest olivines are the most magneisan, whereas smaller crystals are relatively Fe-rich. NiO in the Fo-rich olivine cores reaches 0.3 wt. % (Fig. 2.6).



**Figure 2.6:** Fo content vs NiO (wt. %) for olivines in ferropicrite and picritic ferrobasalt rocks from Ethiopian LIP. Those of the komatiites from Superior Province (Arndt et al., 1977); meimechite from Siberian traps (Elkins-Tanton et al., 2007), ferropicrites from Karoo & Ferrar provinces (Heinonen and Luttinen, 2008), Paraná-Etendeka provinces (Gibson et al., 2000) and picrites from Sorachi-Yezo (Ichiyama et al., 2012). The composition of olivines from the LT (low-Ti) and HT2 (high-Ti 2 basalt and picrites) of Ethiopian LIP (Beccaluva et al., 2009) are also shown for comparison.

The CaO contents range from 0.28 to 0.42 wt. %, indicating that they are not mantle xenocrysts (Simkin and Smith, 1970; Gurenko et al., 1996; Thompson and Gibson, 2000; Kawabata et al., 2011) and MnO contents vary between 0.14 and 0.24 wt. %.

### 2.6.2.2. Cr-spinel

The Cr-spinels are characterized by extremely high Cr# (100Cr/ (Cr+Al)) (up to 84), moderate Mg# (100Mg/ (Mg+Fe<sup>2+</sup>)) (18-51) and moderate Fe<sup>3+</sup># (100Fe<sup>3+</sup>/ (Cr+Al+Fe<sup>3+</sup>)) (11-39) (Table 2.3). The Cr<sub>2</sub>O<sub>3</sub> content varies from 14 to 49 wt. %. The TiO<sub>2</sub> contents of Cr-spinels are very high (3.6-14.8 wt. %) as compared to Cr-spinels in meimechite and depleted ferropicrites from Vestfjella (Heinonen and Luttinen, 2010). The Cr# of Cr-spinels from these ferropicrite and picritic ferrobasalt is as high as those in boninite and is distinctly higher than Crspinels in abyssal peridotites (Dick and Bullen, 1984), MORB (Sigurdsson and Schilling, 1976), picritic basalts (e.g. West Greenland; Larsen and Pedersen, 2000, Emeishan; Kamenetsky et al., 2012, Iceland; Sigurdsson et al., 2000, Sorachi-Yezo; Ichiyama et al., 2012) and ferropicrites from Pechenga (Hanski, 1992) and accreted oceanic plateau in Japan (Mino-Tamba belt; Ichiyama et al., 2006), (Figs. 2.7a and b). Figure 2.8 shows the relationship between Cr-spinel and bulk rock in their Cr/Al ratios of the studied samples and other related rocks. The high Cr/Al of the Cr-spinels and very low Cr/Al of the host rock is unique feature of the studied Ethiopian ferropicritic rocks.

Sample	Ferropicrite	e	Picritic ferr	obasalt 1			Picritic ferr	obasalt 2
Mineral	Spl1(ol1)	Spl4(ol3)	Spl1(ol1)	Spl2(ol3)	Spl3(ol4)	Spl5 gm	Spl2 (ol2)	Spl5 (ol5)
TiO <sub>2</sub>	14.81	9.60	6.22	3.81	3.60	3.75	7.08	5.99
$Al_2O_3$	8.02	5.52	5.85	6.85	6.44	5.90	6.12	4.74
$Cr_2O_3$	13.97	38.50	37.38	48.93	47.31	43.21	34.44	37.85
FeO*	51.77	32.61	39.39	30.74	30.62	39.50	39.07	43.86
MnO	0.34	0.24	0.16	0.19	0.17	0.32	0.16	0.26
MgO	5.80	9.47	9.18	7.79	11.08	3.74	8.27	4.86
Total	94.71	95.94	98.18	98.31	99.22	96.42	95.14	97.56
Cations (O	=4)							
Ti	0.398	0.253	0.160	0.099	0.090	0.102	0.188	0.161
Al	0.338	0.228	0.235	0.278	0.253	0.252	0.255	0.199
Cr	0.395	1.065	1.009	1.332	1.247	1.238	0.962	1.067
Fe <sup>3+</sup>	0.470	0.202	0.437	0.192	0.319	0.306	0.407	0.413
Fe <sup>2+</sup>	1.079	0.752	0.688	0.693	0.535	0.890	0.748	0.894
Mn	0.010	0.007	0.005	0.006	0.005	0.010	0.005	0.008
Mg	0.309	0.494	0.467	0.400	0.551	0.202	0.436	0.258
Total	2.999	3.001	3.001	3.000	3.000	3.000	3.001	3.000
Cr#	53.89	82.39	81.08	82.73	83.13	83.09	79.06	84.27
Mg#	22.28	39.65	40.44	36.59	50.74	18.49	36.81	22.40
Fe <sup>3+</sup> #	39.06	13.54	25.97	10.66	17.54	17.05	25.05	24.60

 Table 2.3: Representative analyses of spinel inclusions in olivine phenocrysts.

\*Total Fe as FeO; Cr#=100Cr/(Cr+Al); Mg#=100Mg/(Mg+Fe<sup>2+</sup>); Fe<sup>3+</sup>#=100Fe<sup>3+</sup>/(Cr+Al+Fe<sup>3+</sup>).

Abbreviations: n.d. not detected; Spl, spinel; Ol, olivine; Gm, groundmass.



**Figure 2.7:** Cr-spinel composition of the Ethiopian ferropicrite and low-Ti basalt and HT2 picrites (Beccaluva et al., 2009). Those of the picrites from Sorachi-Yezo (Ichiyama et al., 2012), Iceland (Sigurdsson et al., 2000), Tamba belt (Ichiyama et al., 2006), Emeishan (Kamenetsky et al., 2012), West Greenland (Larsen and Pedersen, 2000), Vestfjella meimechites and ferropicrite (Heinonen and Luttinen, 2010) and the ferropicrites from Pechenga (Hanski, 1992). The composition of MORB (Sigurdsson and Schilling, 1976), abyssal peridotites (Dick and Bullen, 1984) and boninite are also taken for comparison.



**Figure 2.8:** Bulk rock Cr/Al vs Spinel Cr/Al ratios for the Ethiopian ferropicrite and picritic ferrobasalts. Dashed arrows indicate the possible eclogitic and peridotitic sources. Data sources: Ethiopian LIP low-Ti and HT2 suits (Beccaluva et al., 2009); Abitibi komatiite (Barnes, 1985); Pioneer komatiite (Stiegler et al., 2012); Gorgona komatiite (Dietrich et al., 1981); Emeishan picrites (Kamenetsky et al., 2012); Siberian ferropicrite (Arndt et al., 1995); Karoo meimechite and ferropicrite (Heinonen and Luttinen, 2008, 2010); West Greenland picrite (Larsen and Pedersen, 2000); Hawaii picrite (Wilkinson and Hensel 1988); Tonga boninite (Sobolev and Danyushevsky, 1994); Sorachi-Yezo picrite (Ichiyama et al., 2012); Tango picrite (Ishiwatari and Imasaka, 2002); depleted (D-type) and enriched (E-type) picrites from Mikabu belt (Ichiyama et al., 2014); high magnesian andesite (HMA) and tholeiite lava Noto Peninsula (López and Ishiwatari, 2002); Mongolian high magnesian andesite and picrite (Erdenesaihan et al., 2013).

## 2.6.2.3. Clinopyroxene

Clinopyroxene phenocrysts are Mg#=74-88, TiO<sub>2</sub>=0.84-1.82 wt. %, and Al<sub>2</sub>O<sub>3</sub>= 1.2-3.2 wt. % in the cores. Clinopyroxenes are Mg-rich augite ( $Wo_{43.46}En_{41.48}Fs_{7-15}$ ; Fig 2.9) in composition. They commonly show normal zoning and it gives a trend of increasing Fe, Al, and Ti concentrations and decreasing Mg#, Si and Cr from core to rim (Fig. 2.10).



**Figure 2.9:** Pyroxene quadrilateral diagram showing the composition of pyroxene (after Morimoto et al., 1988) from the ferropicrite and picritic ferrobasalts in the Lalibela area. The circlualr area displays the composition of clinopyroxene in the picrite of Ethiopian LIP (Beccaluva et al. 2009).



**Figure 2.10:** Plots of Mg# versus  $TiO_2$  (a) and  $Cr_2O_3$  (b) for the ferropicrite and picritic ferrobasalt of Ethiopian LIP. For comparison, clinopyroxenes from the high-Ti 2 picrite (Beccaluva et al., 2009) are also plotted. Dashed arrow represents the core to rim reverse zoning trend within a single crystal.

Sample		1 Ferro	opicrite			2 Pi	critic ferroba	salt				3 Picritic fe			
Mineral	Срх	:1	Ср	x3	Сру	x1	Cpx1gm	Ср	x3	Сря	x1	Срх	x2	Сря	x3
	Core	Rim	Core	Rim	Core	Rim	Core	Core	Rim	core	rim	core	rim	core	rim
SiO2	53.87	50.45	50.74	52.46	51.78	50.62	49.55	53.5	51.78	51.25	48.90	50.59	50.47	50.81	48.08
TiO <sub>2</sub>	0.84	1.68	1.64	1.67	1.70	1.77	1.83	1.08	1.80	1.34	2.21	1.82	1.77	1.68	2.39
$Al_2O_3$	1.25	2.50	2.71	2.74	2.55	2.62	2.82	1.22	2.76	1.75	3.49	3.21	3.18	2.98	4.14
Cr <sub>2</sub> O <sub>3</sub>	0.73	0.38	0.22	0.62	0.12	0.25	0.15	0.67	0.20	0.73	0.62	0.89	0.24	0.08	0.06
FeO*	4.37	7.13	7.65	6.02	7.97	7.08	9.24	4.83	8.05	5.03	6.80	6.23	7.16	6.96	8.39
MnO	0.16	0.20	0.07	0.14	0.16	0.13	n.d.	n.d.	n.d.	0.15	0.17	0.09	0.13	0.21	0.14
MgO	17.36	15.33	15.02	16.15	15.26	15.12	14.21	16.96	15.33	15.97	14.54	15.57	14.91	15.35	13.53
CaO	22.48	20.96	20.61	21.67	21.43	21.26	20.93	22.6	20.73	21.79	21.46	21.42	21.38	21.26	21.06
Total	101.06	98.63	98.66	101.47	100.97	98.85	98.73	100.86	100.65	98.01	98.19	99.82	99.24	99.33	97.79
Cations (O	)=6)														
Si	1.949	1.895	1.904	1.902	1.903	1.896	1.878	1.944	1.904	1.922	1.851	1.873	1.884	1.893	1.837
Ti	0.023	0.047	0.046	0.046	0.047	0.050	0.052	0.030	0.050	0.038	0.063	0.051	0.050	0.047	0.069
Al	0.053	0.111	0.120	0.117	0.111	0.116	0.126	0.052	0.120	0.077	0.156	0.140	0.140	0.131	0.187
Cr	0.021	0.011	0.007	0.018	0.003	0.007	0.004	0.019	0.006	0.022	0.018	0.026	0.007	0.002	0.002
Fe <sup>2+</sup>	0.132	0.224	0.240	0.182	0.245	0.222	0.293	0.147	0.248	0.158	0.215	0.193	0.224	0.217	0.268
Mn	0.005	0.006	0.002	0.004	0.005	0.004	n.d.	n.d.	n.d.	0.005	0.005	0.003	0.004	0.007	0.004
Mg	0.936	0.859	0.840	0.873	0.836	0.844	0.803	0.919	0.840	0.893	0.821	0.859	0.830	0.852	0.771
Ca	0.871	0.844	0.828	0.842	0.844	0.853	0.850	0.880	0.817	0.876	0.870	0.850	0.855	0.848	0.862
Total	3.990	3.997	3.985	3.984	3.994	3.992	4.006	3.991	3.985	3.991	3.999	3.992	3.994	3.997	4.000
Wo	44.9	43.8	43.4	44.4	43.8	44.5	43.7	45.2	42.9	45.5	45.7	44.7	44.8	44.2	45.4
En	48.3	44.6	44.0	46.0	43.4	44.0	41.3	47.2	44.1	46.4	43.0	45.2	43.5	44.4	40.5
Fs	6.8	11.6	12.6	9.6	12.7	11.6	15.1	7.5	13.0	8.2	11.3	10.1	11.7	11.3	14.1
Mg#	87.63	79.31	77.78	82.71	77.34	79.2	74.33	86.22	77.25	84.98	79.22	81.67	78.78	79.72	74.19

Table 2.4: Representative, analyses of clinopyroxene phenocrysts and microphynocrysts of ferropicrite and picritic ferrobasalt rocks from Ethiopian LIP.

\*Total Fe as FeO; Mg#=100Mg/(Mg+Fe<sup>2+</sup>).

Abbreviations: Cpx, clinopyroxene; Wo, wollastonite; En, enstatite; Fs, ferrosilite; gm, groundmass; n.d., not detected.

However, some of the studied clinopyroxene crystals are very rich in Cr (up to 6240 ppm) and display very strong reverse zoning with significant increase of compatible elements (such as Cr and Ni; Tables 2.4 and 2.5) and decreasing REEs from core to rim. This unusual, significant reverse zoning provides insight in to the origin of these lavas (see Section 2.79). The trace element composition of clinopyroxenes of ferropicrite and picritic ferrobasalt rocks resembles those of HT2 basalt (Beccaluva et al., 2009), but they are enriched in total REE contents than those of iron-poor picrites. The REE contents of clinopyroxenes display enrichment in LREE (La<sub>N</sub>/Yb<sub>N</sub>=1.2-1.9) and MREE (Eu<sub>N</sub>/Yb<sub>N</sub>=3.3-4.3) relative to HREE. The primitive mantle-normalized pattern (Fig. 2.10) of clinopyroxene is characterized by low contents of Pb, Zr and LILE (e.g. Ba, Rb, Sr) relative to the neighboring elements, which is consistent with the low  $D_{LILE}^{Cpx/liq}$  (Tuff and Gibson, 2007). Slight depletion of HFSE (e.g. Nb and Ta) is also observed relative to LREE (La and Ce). There is no significant negative Eu anomaly (Eu/Eu\*=0.95-1).

# 2.6.2.4. Plagioclase

Plagioclase microphenocrysts have labradorite composition  $(An_{62}Ab_{36}Or_2)$  while plagioclase in groundmass is andesine  $(An_{41}Ab_{54}Or_4)$ , consistent with its late crystallization. The opaque minerals in the groundmass are mainly ilmenite.

Sample	1 Ferro	opicrite		2 Picritic ferrobasalt 3 Picritic ferro			3 Picritic ferrobasalt			
Mineral	Ср	ox3	Ср	x1	CI	ox2	Cl	ox1	Cŗ	ox2
	Core	Rim	Core	Rim	Core	Rim	Core	Rim	Core	Rim
Sc	64.3	62.2	64.2	66.1	81.1	73.1	68.4	68.4	58.9	61.1
Ti	7480	7840	10050	10010	11140	10600	8580	8690	7110	9750
V	449	313	471	419	391	402	247	252	202	314
Cr	886	4240	809	2040	2550	2440	6240	5850	2120	2320
Co	52.6	44.9	49.0	49.3	47.4	48.4	39.2	39.1	41.7	42.0
Ni	262	358	255	305	300	295	374	347	375	364
Rb	0.004	0.043	0.02	0.1	0.01	0.01	0.01	0.001	0.004	0.01
Sr	49.9	46.9	73.5	70.0	68.3	65.7	58.6	62.1	56.1	77.7
Y	14.6	11.2	18.0	15.5	14.2	16.8	11.0	11.3	10.6	14.1
Zr	35.0	25.7	62.4	54.4	53.5	60.7	30.2	31.8	24.0	45.9
Nb	0.1	0.2	0.3	0.3	0.3	0.3	0.2	0.2	0.1	0.2
Cs	n.d.	0.002	n.d.	0.010	n.d.	0.0003	n.d.	0.002	n.d.	n.d.
Ba	0.02	0.64	0.23	0.33	0.03	0.05	0.02	0.03	0.01	0.02
La	2.2	1.4	3.3	2.8	2.7	2.8	2.1	2.3	1.6	2.6
Ce	10.7	7.2	15.9	13.7	12.6	13.5	9.3	10.4	7.6	12.8
Pr	2.1	1.4	2.9	2.6	2.4	2.5	1.7	1.9	1.5	2.4
Nd	12.2	8.3	17.5	15.0	13.9	15.0	10.0	11.0	8.8	13.9
Sm	4.0	2.8	5.5	4.8	4.6	5.1	3.3	3.6	3.0	4.5
Eu	1.3	0.9	1.8	1.6	1.5	1.6	1.1	1.2	1.0	1.5
Gd	4.3	3.1	5.7	4.9	4.6	5.2	3.5	3.8	3.3	4.5
Tb	0.6	0.5	0.8	0.7	0.6	0.7	0.5	0.6	0.5	0.7
Dy	3.6	2.7	4.5	3.9	3.6	4.0	2.9	3.1	2.7	3.7
Ho	0.6	0.5	0.8	0.7	0.6	0.7	0.5	0.5	0.4	0.6
Er	1.5	1.1	1.8	1.5	1.4	1.6	1.2	1.2	1.1	1.5
Tm	0.2	0.1	0.2	0.2	0.2	0.2	0.1	0.2	0.1	0.2
Yb	1.1	0.8	1.3	1.0	0.9	1.1	0.8	0.9	0.8	1.0
Lu	0.1	0.1	0.2	0.1	0.1	0.1	0.1	0.1	0.1	0.1
Hf	1.7	1.2	2.8	2.4	2.6	2.8	1.7	1.7	1.2	2.2
Та	0.02	0.02	0.05	0.04	0.04	0.04	0.03	0.03	0.01	0.04
Pb	0.05	0.05	0.1	0.06	0.04	0.03	0.05	0.05	0.05	0.04
Th	0.01	0.01	0.03	0.02	0.03	0.02	0.02	0.02	0.01	0.02
U	0.003	0.003	0.007	0.004	0.004	0.003	0.002	0.006	0.002	0.005

 Table 2.5: Representative trace element analyses (LA-ICP-MS; values in ppm) of clinopyroxenes from ferropicrite and picritic ferrobasalt rocks from Lalibela area, Ethiopian LIP

Abbreviations: cpx, clinopyroxene; n.d. not detected.



**Figure 2.11:** Primitive-mantle-normalized REE and trace element patterns for clinopyroxenes of ferropicrite and picritic ferrobasalt rocks from Lalibela area, Ethiopian LIP. Normalizing values are from McDonough and Sun (1995). For comparison, clinopyroxene compositions from low-Ti (a-b) and High-Ti 2 basalt and picrites (c-d) of Ethiopian LIP are also plotted after Beccaluva et al. (2009).

# 2.7. DISCUSSION

# 2.7.1. Olivine Fo and NiO showing primitive mantle-derived melt

Primitive rocks that are associated with continental flood basalt LIPs are scarce, but their presence provides important information on the parental sources of these voluminous mantle derived magma. The most MgO-rich olivine that we analyzed is Fo<sub>88.9</sub> (Table 2.2), which is higher than those of Paraná-Etendeka ferropicrite Fo<sub>85</sub>

(Gibson et al., 2000) and slightly lower than those of anhydrous fertile lherzolite (Fo<sub>90</sub>) (e.g. Ishiwatari, 1985). They are only slightly less forsteritic than the most magnesian olivine from HT2 picrites (Fo<sub>90</sub>) of Ethiopia (Beccaluva et al., 2009) and picrites from Karoo (Fo<sub>90</sub>, Cox and Jamieson, 1974). More magnesian olivines from Hokkaido, Japan (Fo<sub>94</sub>, Ichiyama et al., 2012) and West Greenland (Fo<sub>92</sub>, Pedersen, 1985) may represent higher potential temperature in the mantle. The magnesian and high NiO (up to 0.3 wt. %) characteristics of olivine (Fig. 2.6) support the primitive, mantle-derived nature of the Ethiopian ferropicrite.

# 2.7.2. Primary bulk-rock nature of the melt

To assess the hypothetical primary melt compositions for the Ethiopian ferropicrite, we have tested a modeling program (PRIMELT2) (Herzberg and Asimow, 2008); however the outcome is unreliable due to the possible pyroxenite source component suggested by PRIMELT2 model. We thus focused on the modeling of primary melts on the basis of olivine-liquid equilibrium (Putirka, 2008). The analyzed samples are characterized by primitive olivine (>  $Fo_{78}$ ; Table 2.2). The most Mg-rich olivine compositions ( $Fo_{88}$  in ferropicrite and  $Fo_{88-85}$  in picritic ferrobasalts) correspond to olivine that would crystallize from mantle derived melts. Assuming a  $K_D$ (Fe-Mg)<sup>ol-liq</sup> of 0.32 (Putirka, 2005),  $Fo_{85-88}$  would have been in equilibrium with a liquid with Mg# 64-71 and 15-19 wt.% MgO. These observations indicate that the Ethiopian ferropicrite (Mg# 64), 14 wt. % MgO and 14 wt. % FeO\*; Table 2.1 is likely to represent true Fe-rich mantle melt. Therefore, the high FeO\* content of Ethiopian ferropicrite is not an accumulation effect.

### 2.7.3. Temperature estimates

Gibson (2002) suggested that the ferropicritic liquid is generated by the partial melting of basalt plus peridotite mixture at >1450 °C and >4.5 GPa. The experimental result of Tuff et al. (2005) confirmed that a ferropicrite melts 100 % at 5 GPa and 1650 °C, which is similar to the solidus (5 GPa and 1625 °C) of silicaundersaturated garnet pyroxenite studied by Kogiso et al. (2003). These temperature are higher than the ambient upper mantle ( $T_p \sim 1280-1475$  °C; McKenzie and Bickle, 1988) and supports the derivation of ferropicrites from high temperature magma (and the plume). However, the available thermodynamic models are only compatible with peridotite sources (e.g. Herzberg and Asimow, 2008) and may not be applicable to estimate the physical conditions (pressure, mantle potential temperature) for pyroxene-rich sources. Considering the compositional similarity between the Ethiopian ferropicrite and 97SB68 in terms of MgO, FeO\* and Al<sub>2</sub>O<sub>3</sub> (Fig. 2.2), the melting condition of our ferropicrite may be close to that of the melting experiment conducted by Tuff et al. (2005) as noted above.

Application of olivine-spinel geothermometer (Fabriès, 1979) to the ferropicrite and picritic ferrobasalt rocks results in temperatures as high as 1090 °C for the most chromian spinel. This may represent closure temperature of Fe-Mg exchange between spinel inclusion and host olivine during cooling of the magma, and hence gives the lower limit of the magmatic temperature estimate.

In addition, the Cr content of spinel may provide a clue for the temperature of the magma from which it crystallized. The Cr content of the melt in equilibrium with spinel (Cr solubility) increases with increasing

temperature (Barnes, 1986). Effect of oxygen fugacity also matters, but co-existing ilmenite and absence of magnetite suggest low oxygen fugacity. The high Cr/Al spinel would have been expected to crystallize from the magma having high Cr/Al ratio, or the magmatic temperature was very high, and these in turn may indicate high degrees of melting, however, the bulk rock data of our samples shows very low content of Cr. Thus, it is likely that the observed high Cr/Al ratio of spinel is due to high magmatic temperature.

#### 2.7.4. High degree melting of the source mantle?

Cr-spinel is one of the liquidus phases in basaltic magma and its chemical variation may have significant inferences about the degree of melting and source regions of magma (Dick and Bullen, 1984; Arai, 1994). The Cr-spinel of Ethiopian ferropicrite is significantly higher in Cr# (average 78.7) than those of MORB, Emeishan high-Ti picrite (Kamenetsky et al., 2012), Pechenga ferropicrite (Hanski, 1992) and comparable to those of boninite (Fig. 2.7). The TiO<sub>2</sub> content of Cr-spinel is also very high (Fig. 2.7b), which is consistent with the high Ti characteristics of bulk rock chemistry of the studied samples. Moreover, the TiO<sub>2</sub> content of spinel is equal to or higher than those of LIP lavas (Kamenetsky et al., 2001). The high Cr/Al ratio of spinels from the Ethiopian ferropicrite and picritic ferrobasalts (Fig. 2.8) might indicate high degree of melting, but the bulk rock Cr/Al ratio is very low and is not proportional to that of spinel. Thus we propose very low Cr/Al of the source material (see Section 2.75). Removal of spinel in the early stage of magma evolution is another possibility (Fig. 2.8), but is unlikely in view of the very primitive nature of the magma. However, this interpretation apparently contradicts to the suggested small degree of partial melting (of peridotite source) on the basis of low Al<sub>2</sub>O<sub>3</sub>/TiO<sub>2</sub> and high Zr/Y ratios of bulk rock compositions (Fig. 2.4).

### 2.7.5. Cr/Al relationship between spinel and bulk rock: indicator of source lithology

Figure 2.8 shows the relationship between the bulk-rock Cr/Al and spinel Cr/Al ratios of the Ethiopian ferropicrite in comparison with mafic-ultramafic rocks of other igneous provinces. Based on this, the Cr/Al ratio of spinels of Ethiopian ferropicrite is similar to those of Archean komatiite (Stiegler et al., 2012), Siberian ferropicrite (Arndt et al., 1995), and boninite (Sobolev and Danyushevsky, 1994), although the bulk-rock Cr/Al ratio (<0.005) is significantly lower than those mentioned above.

The observed very low bulk-rock Cr/Al ratios in the Ethiopian ferropicrite and picritic ferrobasalts might be attributed to the removal of Cr-spinel in the early stage of magma evolution. However, primitive nature of the studied samples does not support extensive early stage crystal fractionation. On the other hand, Sorachi-Yezo picrites (Ichiyama et al., 2012), Mikabu D-type picrites (Ichiyama et al., 2014) and Abitibi komatiite (Barnes, 1985) shows high bulk rock Cr/Al but low spinel Cr/Al ratios, which might indicate the accumulation of spinel in the magma (Fig. 2.8). However, occurrence of high Fo olivines in these rocks is compatible with high degree melting of peridotitic mantle rather than olivine accumulation process in shallow magma chamber. Thus, bulk rock Cr/Al ratio of the primitive magmas may be mainly controlled by lithology of the source material in the mantle. For example, if the source is eclogite (or pyroxenite), bulk rock Cr/Al ratios of magma may not exceed 0.01, but if the source is peridotite, Cr/Al of the magma may be as high as 0.1 (Fig. 2.8). The very low Cr/Al ratio of the Ethiopian ferropicrite together with the others of low bulk-rock Cr/Al (such as those of Noto tholeiite and high magnesian andesite (HMA), López and Ishiwatari, 2002; Mongolia picrite and HMA, Erdenesaihan et al., 2013; Hawaii picrite, Wilkinson and Hensel, 1988) (Fig. 2.8) may suggest eclogitic source, which is supported by the lines of evidence as discussed later (see Section 2.7.8).

## 2.7.6. High-pressure melting of the source mantle

The increasing Zr/Y and decreasing Al<sub>2</sub>O<sub>3</sub>/TiO<sub>2</sub> ratios (Fig. 2.4) are generally attributed to increase of melting pressure or melt segregation depth and increasing stability of garnet in the residue (Walter, 1998). The Ethiopian ferropicrite and picritic ferrobasalts are characterized by higher Zr/Y and lower Al<sub>2</sub>O<sub>3</sub>/TiO<sub>2</sub> ratios than other ferropicritic rocks (e.g. Superior Province, Pechenga, Paraná-Etendeka and Mino-Tamba), indicating that their source region contained residual garnet and thus the partial melting took place in the garnet stability field. The low Al content in magmas such as ferropicrite (Tuff et al., 2005) and Al-depleted komatiites (Arndt et al., 2008; Robin-Popieul et al., 2012) is interpreted to indicate the presence of residual garnet in the mantle source. Compared to the Ethiopian ferropicrite, the ferropicrites of Siberia exhibit higher Zr/Y and lower Al<sub>2</sub>O<sub>3</sub>/TiO<sub>2</sub> ratios, suggesting higher melting pressure.

The high Ni content (501 ppm) along with the low Al<sub>2</sub>O<sub>3</sub> (~9 wt. %) of Ethiopian ferropicrite may also indicate that garnet was a residual phase in its mantle source. This interpretation is consistent with the high pressure experimental result on the Paraná-Etendeka ferropicrite produced by Tuff et al. (2005).

In addition, REE patterns of clinopyroxene phenocrysts from the studied samples show distinct convex upward patterns in chondrite-normalized diagrams (Fig. 2.10) with La<sub>N</sub>/Yb<sub>N</sub> (1.2-1.9) and Eu<sub>N</sub>/Yb<sub>N</sub> (3.3-4.3),

resembling those reported HT2 basalt and picrites of Ethiopia (Beccaluva et al., 2009). Therefore, the strong HREE fractionation supports the presence of garnet in the mantle source region.

### 2.7.7. Bulk-rock high Fe/Mn and Ni/Cr ratios: a core-mantle issue?

High Fe/Mn ratios of basalts could be resulted from core-mantle interaction. However, on the basis of high Fe/Mn and unradiogenic <sup>187</sup>Os/<sup>188</sup>Os content of the Ethiopian picrite, Roger et al. (2010) speculated that the entrapment of core material in the source of the Afar mantle plume is unlikely. Basaltic melts with high Fe/Mn (>60) ratio can be formed by partial melting of pyroxenite at the degree of melting less than 70 % (Kogiso and Hirschmann, 2001, Pertermann and Hirschmann, 2003, Kogiso et al., 2004) or of hydrous peridotite at the degree of melting greater than 50 % (Parman and Grove, 2004).

High fraction of clinopyroxene crystallization (> 30 %) could also produce a melt with high Fe/Mn ratio (Liu et al., 2008). In view of high MgO (> 10 wt. %) of the studied samples, such a high degree of crystallization is unrealistic. High Fe/Mn could be also resulted from the presence of residual garnet in the source (Herzberg, 2011), because  $D_{Mn}^{Garnet/liquid}$  is ~7 at low melt fraction (Pertermann and Hirschmann, 2003). High Ni content (500 ppm) and high Ni/Cr ratio of the Ethiopian ferropicrite (Table 2.1) may also suggest contribution of Fe-Ni metal in its magma genesis, but to attribute this to the core-mantle reaction must be too speculative.

### 2.7.8. Eclogite vs. peridotite as the source for Ethiopian ferropicrite

The genesis of ferropicritic rocks have been considered to be associated with mantle plume (Gibson, 2002). Sobolev et al. (2007) suggested that ~2 % to 30 % of recycled crust is involved in the mantle melting to form MORBs, OIBs, continental basalts and komatiites. On the basis of phase relation and bulk rock composition of the Paraná-Etendeka ferropicrite, Tuff et al. (2005) speculated that ferropicrite primary melt is unlikely to have been derived from partial melt of normal peridotite and melting of garnet pyroxenite source may have been significant. The occurrence of garnet liquidus phase with clinopyroxene at pressure  $\geq$  6 GPa, leading Tuff et al. (2005) to propose garnet pyroxenite as mantle source for the Paraná- Etendeka ferropicrite. Ichiyama et al. (2006) have suggested that suitable ferropicrite sources include recycled ferrobasalts and Fe–Ti gabbros (that should have been eclogitized in the source mantle). It is evident that ferropicrite liquid cannot originate in direct partial melting of ambient depleted peridotite (Stone, 1995).

Jakobsen et al. (2005) suggested a mixing between the peridotite-derived picritic melts with evolved Fe-rich basalts or immiscible liquids could result in a ferropicritic composition. However, liquid immiscibility and subsequent mixing process is unlikely cause for the generation of Ethiopian ferropicritic melt because of two reasons: (1) immiscibility tends to fade away with increasing pressure (Charlier and Grove, 2012); (2) such mixing process would be expected to produce significant disequilibrium textures, which are not observed among studied rocks.

The bulk rock Cr/Al ratio (Fig. 2.8) may provide important clue about the source material. The extremely

low bulk rock Cr/Al ratio of Ethiopian ferropicrite and picritic ferrobasalt rocks evidence that they cannot be formed from the partial melting of only peridotite mantle source as the other mafic-ultramafic rocks (e.g. Sorachi-Yezo picrites, Japan; D-type Mikabu picrite, Japan; Pioneer komatiite, South Africa). Thus, we suggest that the significant contribution of recycled eclogitic material for the origin of Ethiopian ferropicrite and picritic ferrobasalts.

### 2.7.9. Reversely zoned clinopyroxene; reaction with peridotitic mantle

The origin of reversely zoned clinopyroxenes with resorbed texture has been attributed to magma mixing in many literatures (e.g. Wass, 1979; Simonetti et al., 1996). Kay (1978) suggested that the reversely zoned clinopyroxene may indicate reaction between a silicic melt and peridotite in the upper mantle. Reversely zoned clinopyroxenes have been also reported from Cenozoic basalts (Wang et al., 2007) and late Jurassic high-Mg adakaites of China (Gao et al., 2004), and suggested the presence of pyroxenite in the mantle source. Some of the analyzed clinopyroxene crystals of Ethiopian ferropicrite and picritic ferrobasalts exhibit unusually strong reverse zoning, which have a rim with distinctly high Mg#, Cr and Ni (Tables 2.4 and 2.5; Fig. 2.9). These zoning may indicate a significant increase of Mg#, Cr and Ni in the melt by assimilation of mantle peridotite (i.e. an olivine consuming reaction) or mixing with the peridotite-origin magma during magma ascent. Thus, the presence of these unusual reversely zoned clinopyroxene crystals may further proves the origin of Ethiopian ferropicrite and picritic ferrobasalt rocks from eclogitic source, and their reaction with the peridotitic mantle.

### 2.7.10. Experimental constraints for the source lithology

According to Yaxley & Green (1998), partial melting of relatively fusible eclogite inclusions produces SiO<sub>2</sub>-rich melts that react with olivine in the host garnet peridotite and generate a secondary garnet pyroxenite source in upwelling mantle. Progressive melting of this "re-fertilized" source may yields silica-undersaturated, more mafic partial melt. Gibson (2002) suggested this "re-fertilized" source model to ferropicrite petrogenisis. Herzberg (2011) also discussed about the reaction between eclogite (pyroxenite)-origin melt and the host peridotite for the generation OIB.

Partial melting experiment of equal proportion of mixed basalt (GA1, in the form of coesite eclogite) and peridotite (MPY90) at 1500 °C and 3.5 GPa by Yaxley & Green (1998) and Yaxley (2000) yields a picritic melt that is close to Ethiopian ferropicrite composition. However,  $GA1_{50}MPY90_{50}$  has slightly higher MgO (16.5 wt. %) and  $Al_2O_3$  (11.7 wt. %), lower FeO\* (12.50 wt. %) as compared with Ethiopian ferropicrite (13.92 wt. %, 8.58 wt. % and 14.00 wt. %, respectively) (Fig. 2.2 a-c). Tuff et al. (2005) proposed a source composition similar to a 75 % basalt and 25 % peridotite mixture at  $\geq$ 5 GPa for the Paraná-Etendeka ferropicrite, but it is not supported by experimental data at this pressure. Likewise, we suggest that a higher pressure mixture of eclogiteperidotite (GA1<sub>75</sub>MPY90<sub>25</sub>) might be a plausible explanation to achieve the FeO\* content similar with Ethiopian ferropicrite.

The high  $TiO_2$  (>3 wt. %) content of the Ethiopian ferropicrite and picritic ferrobasalts may further support the important role of Ti-rich recycled oceanic crust (eclogite).

### 2.7.11. Hydrous mantle melting?

The significance of water for the origin of ferropicrite is poorly known. However, different suggestions are given in literatures, such as the parental melt have been hydrous (Hanski and Smolkin, 1995, Fiorentini et al., 2008; their interpretation is based on the presence of kaersutite and phlogopite) and anhydrous (Gibson, 2002).

Partial melting experiment at high pressures (5- 11 GPa) have been conducted on H<sub>2</sub>O-saturated mantle peridotite (KLB-1) by Kawamoto and Holloway (1997). At about 7.5 GPa the partial melt have lower SiO<sub>2</sub>, TiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, Na<sub>2</sub>O and significantly higher MgO (32 wt. %) than the Ethiopian ferropicrite, but similar FeO\*. Thus, partial melt of H<sub>2</sub>O saturated peridotite unlikely to be the source of Ethiopian ferropicrite. Moreover, the absence of primary magmatic hydrous mineral phases as phenocrysts, in the groundmass or as inclusions from the studied Ethiopian ferropicrite precludes its derivation from hydrous magma source.

In summary, the presence of ferropicrite in Ethiopian LIP may provide additional evidence for the high temperature and high pressure mafic magmatism of Afar plume during Oligocene (~30 Ma) and thus it may further proves for the high eruption temperature in Phanerozoic time. The origin of these ferropicrite and picritic ferrobasalt rocks could be attributed to high pressure partial melting of mantle peridotite that possibly incorporated recycled components (eclogite or garnet pyroxenite).

## 2.7.12. CONCLUSIONS

The ferropicrite and picritic ferrobasalt from Lalibela area show high Zr/Y and low Al<sub>2</sub>O<sub>3</sub>/TiO<sub>2</sub> ratios indicating higher pressure melting or smaller degree of partial melting, which apparently contradicts to the high Cr# of spinel in these rocks. The major and trace element data of the Ethiopian ferropicrite is compatible with the eclogitic source that has possibly represents the recycled oceanic crust components in the upwelling Afar plume head. The occurrence of ferropicrite further supports the involvement of deep plume sources during Ethiopian LIP magmatism. In view of low Cr/Al ratio of the bulk rock, the high Cr# of spinel may be due to the very high temperature of the magma that originated in the eclogitic source. The occurrence of clinopyroxene crystals with extreme reverse zoning characteristics may further support the origin of Ethiopian ferropicrite and picritic ferrobasalts from eclogitic source at depths and their later interaction with the mantle peridotite.

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