

Hydrothermal Alteration of Pyroxene in the Hellisheiði Geothermal Field, SW-Iceland

Helga Margrét Helgadóttir¹⁾, Hjalti Franzson¹⁾, Niels Óskarsson²⁾, Karl Grönvold²⁾ and Sigurður Steinþórsson²⁾

¹⁾ Iceland GeoSurvey (ISOR), Grensásvegur 9, IS-108, Reykjavík, Iceland

²⁾ University of Iceland, Faculty of Earth Science, Askja, Sturlugötu 7, 101 Reykjavík, Iceland

E-mail address: helga.m.helgadottir@isor.is

Keywords: Alteration, Pyroxene, dissolution, precipitation, geothermal, actinolite, chlorite, titanite, Iceland, Hellisheiði

ABSTRACT

Extensive drilling at the Hellisheiði geothermal field within the Hengill volcanic complex in SW-Iceland has yielded vast amount of data on hydrothermal alteration and alteration zones within an active rift-zone. The majority of rock formations in the area are of olivine-tholeiite composition and are mostly hyaloclastite formations formed subglacially. Basalt lava flows from interglacial periods and from the Holocene occupy the lowlands and are therefore less common in the volcanic centre. This study involved characterising the clinopyroxene in the Hellisheiði geothermal wells and their subsequent alteration by electron microprobe analyses. The intention was to compare the progressive alteration of buried lava flows, where temperatures have risen with increased burial depth, with the alteration of intrusive rocks that should record the primary alteration of the prevailing temperature conditions in their surroundings. The results suggest that the geothermal alteration of primary pyroxene in olivine tholeiite is dominated by dissolution-precipitation reactions. They also show that there is a significant difference in the composition of actinolite replacing pyroxene depending on the origin of the primary mineral within a lava flow or an intrusive rock. This is possibly attributed to the less oxidised intrusive rock but more significant, however, may be the different modes of alteration: in the lava flows the actinolite may form from the already altered pyroxene (via chlorite) whereas in the intrusive rocks it forms directly from the primary pyroxene.

1. INTRODUCTION

During the past few years, extensive drilling at the Hellisheiði geothermal field within the Hengill volcanic complex in SW-Iceland (Fig. 1) has yielded vast amount of data on hydrothermal alteration and alteration zones of a 2-3 km deep section through an active rift-zone. Although chemically dominated by monotonous olivine tholeiite basalt the rift-zone crust is composed of three lithofacies; lavas, hyaloclastite formations and dyke-intrusions. A simplified stratigraphical succession of these lithofacies may be shown as hyaloclastite ridges at the surface surrounded by Holocene lavas underlain by hyaloclastites from former glaciations as well as basaltic lava sequences from interglacials mingled in between. There are indications that the geothermal wells in the Hengill area may reveal lavas that have been exposed to over 200 kyrs of prograde hydrothermal alteration and possibly up to 300-400 kyrs (e.g. Franzson et al., 2010). The hypocrySTALLINE basalts of the hyaloclastite ridges are generally more altered than basaltic lavas at the same level. The basaltic dykes and occasional sills or minor intrusions are the least altered lithofacies, due to lower porosity in addition to generally shorter residence time (e.g. Franzson, 1994, 1998).

Alteration zones within the Hengill volcanic centre are as follows: zeolite-smectite zone (<200°C), mixed-layer-smectite zone (~200-230°C), chlorite zone (~230-240°C), chlorite-epidote zone (~240-280°C) and epidote-actinolite zone (>280°C). The depth and thickness of the alteration zones vary across the rift-zone section. The Hengill area has been formed by several volcanic cycles from various spreading epochs of the rift-zone. Olivine tholeiite lavas from large lava shields are the most prominent lava flows and voluminous hyaloclastite ridges, also mostly of olivine tholeiite composition, dominate the hyaloclastite formations. Even though olivine tholeiite is the most common rock type found in the Hengill system, rocks such as picrite and rhyolite are also observed in small volumes both on the surface and as intrusives in drill holes (e.g. Sæmundsson, 1995; Alfreðsson et al., 2008; Nielsson, 2011). An inevitable result of spreading epochs within the rift-zone is the formation of dyke swarms which influence the thermal structure of the rift-zone crust. The prevailing regional alteration zones may therefore have been affected by alternating short-lived thermal episodes. This has resulted in different depth of zone-boundaries across the rift-zone as well as different thickness of the zones (Fig. 2).

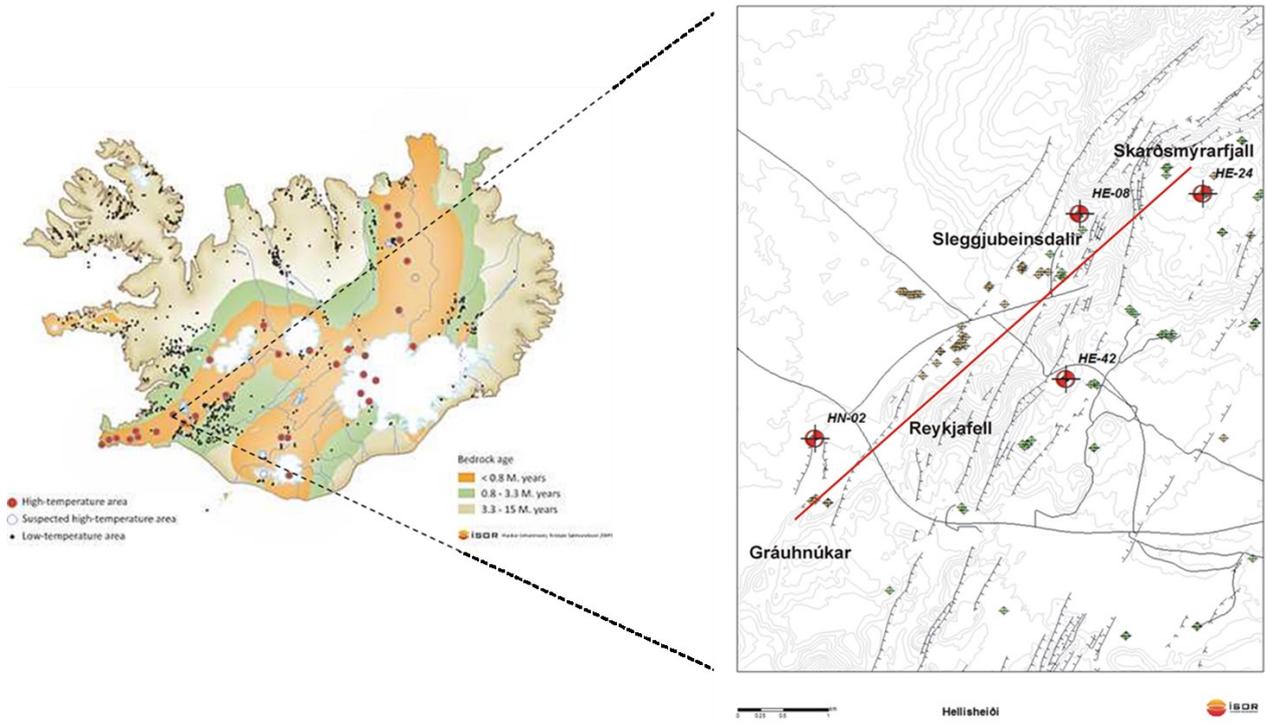


Figure 1. Hellisheiði geothermal field. Sampled wells are shown in red. The cross-section in figure 2 is indicated with a red line. Green dots represent the well-tops of production or exploration wells and the yellow dots represent reinjection wells.

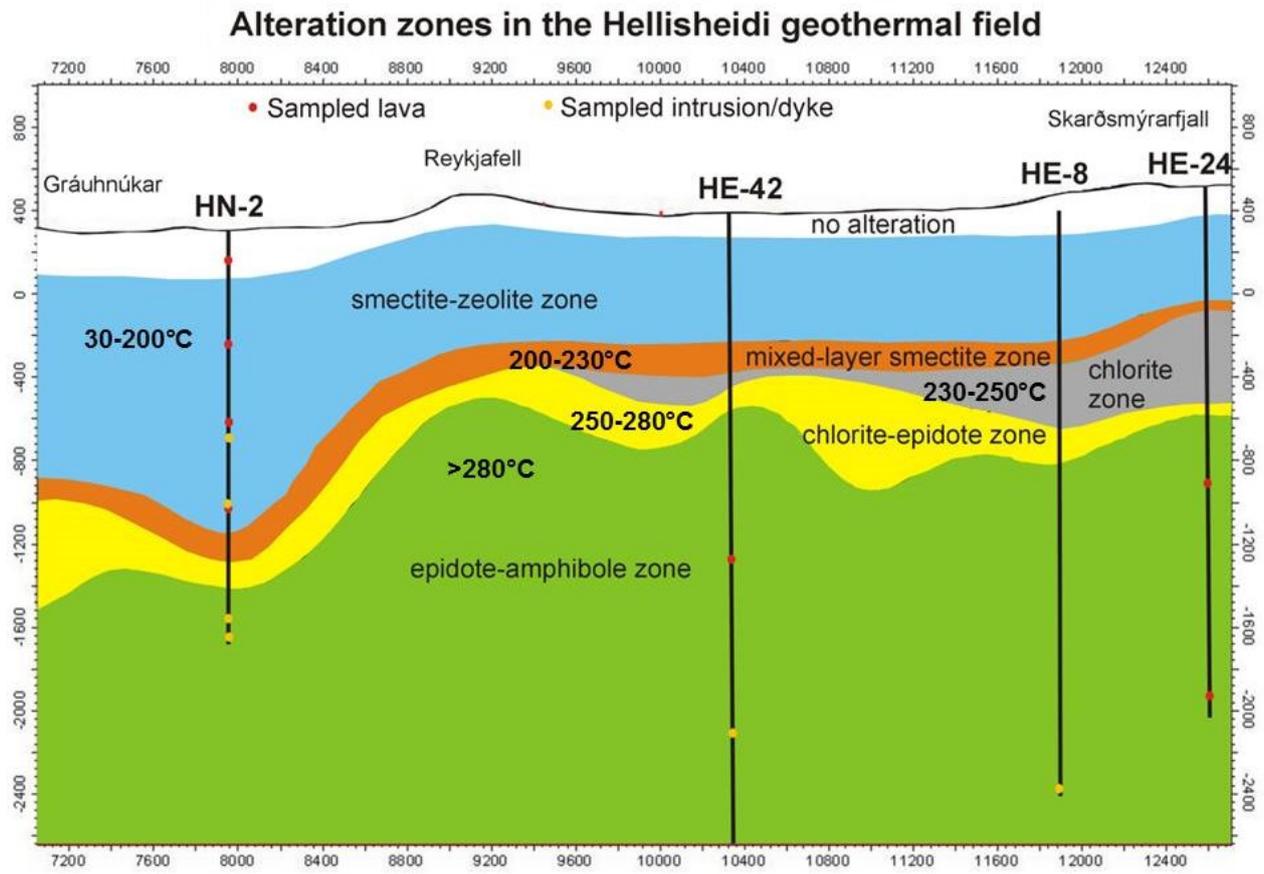


Figure 2. Alteration zones in the Hellisheiði geothermal field.

At all depths in the wells the extent of alteration is clearly recorded in the degree of alteration of the primary minerals of the basalt. Olivine tholeiites usually have simple mineralogy characterised by the early formation of olivine followed by the crystallisation of olivine and plagioclase and then the formation of clinopyroxene which dominates the groundmass together with olivine, plagioclase and titanomagnetite (e.g. Jakobsson, 1983). This leads to the characteristic ophitic to sub-ophitic textures of olivine tholeiites.

One approach estimating the degree of alteration is to focus on the alteration of the primary phases. This approach is different from defining the entire assembly of alteration minerals. If retrograde alteration has occurred the primary minerals and their reaction products are likely to reveal the maximum degree of alteration whereas the entire secondary mineral assemblage may also show phases characteristic of lower temperatures. This study involves characterising the primary clinopyroxene in the Hellisheiði geothermal wells and their subsequent alteration. Hydrothermal alteration of plagioclase in the Hengill area has already been studied in detail by Larsson et al. (2002). The main conclusion of that study was that secondary feldspars (Na- and K-feldspars) were formed by dissolution/precipitation reactions in and around plagioclase. Alteration of primary minerals in basalt in the area has also been studied through petrographic analysis (e.g. Franzson, 1994). The alteration of pyroxene is the main focus of this study with the aim to recognise the igneous clinopyroxenes and determine their alteration products within different alteration zones. On the one hand the alteration of this particular primary mineral in olivine-tholeiite lava flows is examined to determine whether progressive alteration is discernible. All subsurface lava flows have gradually been buried beneath younger formations and have been altered accordingly. Chemical weathering at the surface is gradually followed by geothermal alteration as temperatures rise with increased burial depth. The question is whether this is noticeable in the alteration of the primary minerals. On the other hand the somewhat different geothermal alteration of dykes and intrusions is addressed. Fresh intrusive rocks cool down to the prevailing temperature conditions in their surroundings and start to alter accordingly. The fresh intrusions should therefore record the primary alteration of the current active heat source. Deuteric alteration may, however, complicate matters in both cases.

Petrographic analyses of the alteration of primary minerals in the Hellisheiði field have already been done (e.g. Helgadóttir, 2011). According to thin section studies the first signs of the alteration of pyroxene may be noted as shallow as in the smectite-zeolite zone but these signs are few. The alteration usually starts in the mixed-layer clay or chlorite zone where clay alteration of the pyroxene seems to occur. Extensive alteration of pyroxene to actinolite does not occur until the epidote-actinolite zone (as the name implies) but pyroxene seems to be rather resistive towards alteration.

2. GEOLOGICAL SETTINGS

The Hengill volcanic complex is located at a triple junction where the active rift zones of the Reykjanes Peninsula and the Western Volcanic Zone meet the South Iceland Seismic Zone, a seismically active transform zone. About 10 km wide NE-SW trending graben runs across the area, parallel to the hyaloclastite ridges of the area and the most prominent tectonic faults. The Hengill area is built up of volcanic rocks of late Quaternary and postglacial age (e.g. Sæmundsson, 1967). The majority of rock formations in the area are hyaloclastite formations (tuffs, breccias and pillow lavas) that formed sub-glacially. Basalt lava flows from interglacial periods and from the Holocene occupy the lowlands and are therefore less common in the volcanic centre. Some primitive rocks, like picrites, can be found in the Hengill system, as well as intermediate rocks and rhyolites, the latter two mostly as intrusives. Whole-rock chemical analyses from several locations in the Hengill area, however, indicate that the majority of the rocks are of olivine-tholeiite composition (e.g. Larson et al., 2002; Alfredsson et al., 2008; Nielsson, 2011). This study is focused on the Hellisheiði high-temperature field, in the southwestern part of the Hengill geothermal area. Part of the study area is in a retrograde state with regards to geothermal activity, located just outside the western rift margin of the Hengill volcanic complex (well HN-2 in Fig. 1).

3. SAMPLING AND METHODS

An advantage of using drill cuttings for examination of mineral assemblages is that the cuttings comprise a significant sampling of all there is to be found at a certain depth range. On the other hand the disadvantage of using drill cuttings is the difficulty in studying textural relationships between coexisting phases, especially if the cuttings are very fine-grained. Furthermore, each sample of the drill cuttings represents limited depth range instead of exact horizons. The presence of minerals derived from shallower depths can, for example, not be ruled out because of mixing within the well during drilling. The drilling process can also be somewhat destructive to the more delicate secondary minerals. These disadvantages are, however, less critical in the study of singular primary minerals since their reaction products, contained in veins and altered margins, remain in situ. Furthermore, if the samples have been carefully selected and the depth corrected (with regards to the delay of the cuttings reaching the surface and the geophysical logs), it is safe to assume that the samples represent given depths. The data can therefore be considered to show real assemblages at specific depths, especially from the upper part of the wells. In this study it was possible to sample from rather coarse cuttings which simplifies the determination of the types.

The samples in this study consist of olivine tholeiite lava flows (in one case possible hypocrySTALLINE basalt or pillow lava) on the one hand and of olivine tholeiite intrusions or dykes on the other. The aim of such a sample collection is to make it possible to examine the progressive alteration of the primary minerals which are buried deeper with time, experiencing increasing alteration. The alteration of intrusions or dykes involves a different process where fresh primary minerals usually experience the influence of the alteration zone in which they are emplaced without going through progressive alteration.

Most of the samples were picked from HN-2, west of the Gráuhnúkar area, a well situated just outside the western rim of the Hengill volcanic complex (Figs. 1 and 2). This would represent altered basaltic crust in a retrograde state since the formation temperatures of the well are slightly lower than the temperatures indicated by thermally dependent secondary minerals. This well does not have any deep lava flows so samples were also gathered from wells HE-8 in Sleggjubeinsdalir, HE-24 in Skarðsmýrarfjall and HE-42 in Stóra-Reykjafell (Figs. 1 and 2). Polished sections of the selected samples were prepared for the ARL-SEMQ-30 electron microprobe at the University of Iceland. Analysis of the selected pyroxene samples were run at 15 kV accelerating voltage and 20 nA sample current for 20 seconds. The diameter of the electron beam was set at 3 µm. The minerals were analysed by point analyses. The standards used were: quartz (Si), rutile (Ti), periclase (Mg), Corundum (Al), Diopside Chesterman (Si,Mg,Ca),

Magnetite synth (Fe), Ilmenite Sawyer (Ti, Mn), Hematite (Fe), Chromite 396 (Cr), Hornblende Kakanui (Na,Al,Ti) and Grunerite (Fe). Simultaneously backscattered electron images were acquired.

4. RESULTS

Clinopyroxene (augite in this case) tends to alter along rims and along fractures and cleavage planes of the crystal, indicating a crystallographic control on the alteration reaction (Spilde et al., 1993). Indications of this can be seen in Fig. 5. It has been suggested that augite minerals are stable at temperatures between 50°C and 150°C. At higher temperatures they start to become more sensitive towards alteration (Stefánsson et al., 2001). This is illustrated by the fact that pyroxene does not seem to alter to any significant extent until in the chlorite-epidote zone.

The primary pyroxene samples analysed come from variable depths and alteration zones (selected samples can be seen in Tables 1 and 2). Only one of the selected spots for sampling (at 2502-2508 m in HE-8) shows extensive alteration of the clinopyroxene to ferro-actinolite (and titanite and chlorite in minor amounts) (Fig. 3). The alteration degree of clinopyroxenes is much lower in all of the other samples.

The pyroxene composition of the samples in this study ranges from $Wo_{28}Fs_{39}En_{33}$ to $Wo_{48}Fs_{34}En_{18}$. Some of the variability in the composition of the clinopyroxene can probably be attributed to compositional zoning as well as fine-grained secondary minerals in the primary one, especially in the epidote-amphibole zone. This can also explain lower Ca content and lower oxide totals in some cases (Lonker et al., 1993).

When compared to pyroxene analyses from the high-temperature field at Reykjanes (Marks et al., 2010, 2011) it is interesting to note that the amount of Ti in the clinopyroxenes in the Hellisheiði field is somewhat higher (Fig. 3), the majority of the samples being titaniferous augite and titanaugite (Deer et al., 1992). The reason for this lies probably in the difference in evolution of the basalts. While the Reykjanes olivine tholeiites belong to relatively high MgO basalts (e.g. Jakobsson et al., 1978) the Hellisheiði rock suite contains more evolved basalts belonging to the Hengill volcanic centre. Sub-calcic titaniferous augite is the dominating late-forming pyroxene in slightly evolved tholeiites where MgO is about and below 6 wt% (Niels Óskarsson, personal communication, September, 2011).

Table 1. Representative clinopyroxene analyses (from lava flows).

Lava flows:						
	504 m (HN-2)	876 m (HN-2)	880 m (HN-2)	1294 m (HN-2)	1480 m (HE-24)	1608 m (HE-42)
	sme-zeol zone	sme-zeol zone	sme-zeol zone	sme-zeol zone	chl-ep zone	ep-amph zone
Analyses as oxides, wt%						
SiO ₂	51.06	53.16	52.04	51.38	48.87	49.53
TiO ₂	1.07	0.87	1.01	0.93	1.6	1.47
Al ₂ O ₃	1.5	2.54	1.87	2.19	5.55	4.69
FeO	15.47	7.48	11.62	18.4	9.85	13.17
MnO	0.34	0.33	0.56	0.42	0.43	0.4
MgO	13.22	13.9	15.63	11.71	13.63	11.84
CaO	16.09	20.9	17.7	14.98	19.58	18.65
Na ₂ O	0.26	0.27	0.32	0.37	0.27	0.01
Cr ₂ O ₃	0.04	0.12	0.06	0	0.18	0
Total	99.05	99.57	100.81	100.38	99.96	99.76
Structural formula based on 6 Oxygens						
Si	1.95	1.97	1.93	1.96	1.83	1.87
Al	0.07	0.11	0.08	0.10	0.24	0.21
Al (IV)	0.05	0.03	0.07	0.04	0.17	0.13
Al (VI)	0.02	0.08	0.01	0.05	0.07	0.08
Ti	0.03	0.02	0.03	0.03	0.05	0.04
Fe	0.49	0.23	0.36	0.59	0.31	0.42
Mn	0.01	0.01	0.02	0.01	0.01	0.01
Mg	0.75	0.77	0.86	0.66	0.76	0.67
Ca	0.66	0.83	0.70	0.61	0.79	0.76
Na	0.02	0.02	0.02	0.03	0.02	0.00
Cr	0.00	0.00	0.00	0.00	0.01	0.00
	2.00	2.00	2.00	2.00	2.00	2.00
M1	1.31	1.11	1.28	1.34	1.21	1.22
M2	0.68	0.85	0.73	0.64	0.80	0.76
	$En_{39}Fs_{26}Wo_{35}$	$En_{42}Fs_{13}Wo_{45}$	$En_{45}Fs_{19}Wo_{36}$	$En_{36}Fs_{31}Wo_{33}$	$En_{41}Fs_{17}Wo_{42}$	$En_{36}Fs_{23}Wo_{41}$
	augite	hedenbergite	augite	augite	augite	augite

Table 2. Representative pyroxene analyses (from intrusions).

Intrusions:												
	1284 m	1776 m	1782 m	1836 m	1928 m	2536 m	2536 m	2600 m	3055 m	3055 m	3055 m	
	(HN-2)	(HN-2)	(HE-24)	(HN-2)	(HN-2)	(HE-42)	(HE-42)	(HE-8)	(HE-42)	(HE-42)	(HE-42)	
	sme-zeol	sme-zeol	ep-amph									
	zone	zone	zone	zone	zone	zone	zone	zone	zone	zone	zone	
Analyses as oxides, wt%												
SiO ₂	49.74	51.96	53.07	48.56	50.58	52.3	50.85	49.86	49.18	50.18	49.45	53.83
TiO ₂	1.03	0.87	1.32	2.12	0.9	0.89	0.65	0.8	1.57	0.89	0.97	0.5
Al ₂ O ₃	3.08	2.82	2.29	5.4	1.56	1.36	3.83	5.5	5.46	1.97	2.64	2.35
FeO	16.06	9.33	12.08	10.58	19.56	13.72	8	5.6	10.7	13.57	16.33	6.97
MnO	0.56	0.34	0.33	0.27	0.57	0.46	0.36	0.3	0.36	0.71	0.91	0.35
MgO	11.64	14.41	11.34	12.07	9.93	13.6	15.57	15.47	12.26	14.65	11.42	16.84
CaO	17.6	20.21	19.61	20.75	16.35	16.84	20.38	21.1	20.53	17.67	18.06	19.38
Na ₂ O	0.12	0.36	0.3	0.14	0.3	0.29	0.22	0.2	0.41	0.24	0.27	0.13
Cr ₂ O ₃	0	0	0.03	0.08	0	0.01	0.08	1.08	0.09	0.02	0	0.03
Total	99.83	100.3	100.37	99.97	99.75	99.47	99.94	99.91	100.56	99.9	100.05	100.38
Structural formula based on 6 Oxygens												
Si	1.90	1.93	1.98	1.83	1.96	1.98	1.89	1.84	1.84	1.90	1.90	1.96
Al	0.14	0.12	0.10	0.24	0.07	0.06	0.17	0.24	0.24	0.09	0.12	0.10
Al (IV)	0.10	0.07	0.02	0.17	0.04	0.02	0.11	0.16	0.16	0.10	0.10	0.04
Al (VI)	0.04	0.05	0.08	0.07	0.03	0.04	0.05	0.08	0.08	-0.01	0.02	0.06
Ti	0.03	0.02	0.04	0.06	0.03	0.03	0.02	0.02	0.04	0.03	0.03	0.01
Fe	0.51	0.29	0.38	0.33	0.63	0.43	0.25	0.17	0.33	0.43	0.52	0.21
Mn	0.02	0.01	0.01	0.01	0.02	0.01	0.01	0.01	0.01	0.02	0.03	0.01
Mg	0.66	0.80	0.63	0.68	0.57	0.77	0.86	0.85	0.68	0.83	0.65	0.91
Ca	0.72	0.80	0.78	0.84	0.68	0.68	0.81	0.83	0.82	0.72	0.74	0.76
Na	0.01	0.03	0.02	0.01	0.02	0.02	0.02	0.01	0.03	0.02	0.02	0.01
Cr	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.03	0.00	0.00	0.00	0.00
M1	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00
M2	1.27	1.17	1.14	1.15	1.29	1.28	1.19	1.16	1.16	1.30	1.26	1.21
	0.73	0.83	0.81	0.85	0.70	0.70	0.83	0.85	0.85	0.74	0.76	0.77
$En_{35}Fs_{27}Wo_{38}$ $En_{42}Fs_{15}Wo_{43}$ $En_{35}Fs_{21}Wo_{44}$ $En_{37}Fs_{18}Wo_{45}$ $En_{30}Fs_{34}Wo_{36}$ $En_{41}Fs_{23}Wo_{36}$ $En_{45}Fs_{13}Wo_{42}$ $En_{46}Fs_{9}Wo_{45}$ $En_{37}Fs_{18}Wo_{45}$ $En_{42}Fs_{22}Wo_{36}$ $En_{34}Fs_{27}Wo_{39}$ $En_{48}Fs_{11}Wo_{40}$												
augite augite												

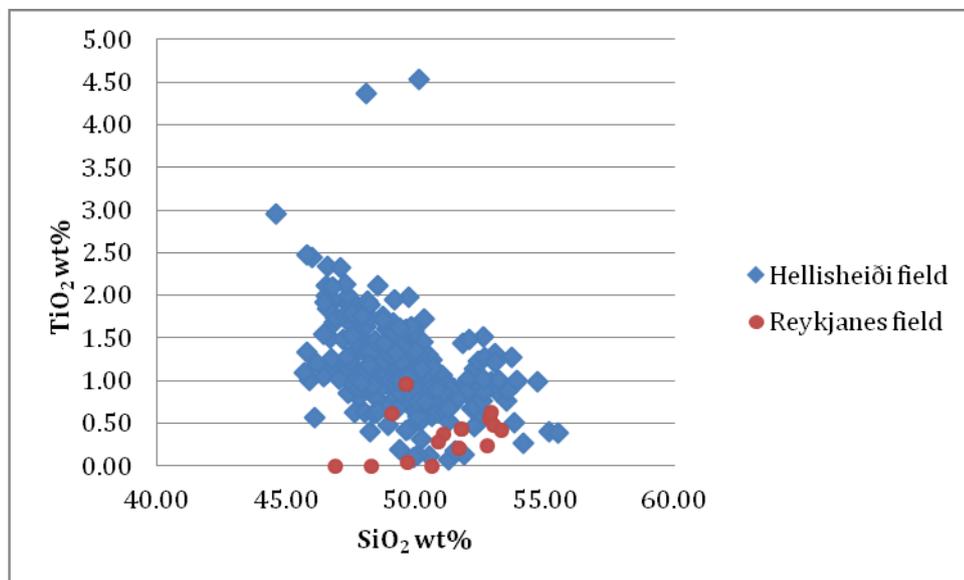


Figure 3. Comparison between wt% TiO₂ in pyroxenes in the Hellisheiði field and the Reykjanes field (from Marks et al., 2010 and 2011).

The alteration mineral replacing primary clinopyroxene is primarily chlorite in the chlorite-epidote facies. Titanite is also noted in one sample in the chlorite-epidote zone (lava flow at 1602 m in HE-42), but otherwise it is more common in the epidote-amphibole zone (Fig. 4). When the epidote-amphibole zone has been reached, actinolite and ferro-actinolite are the chief alteration minerals replacing augite (Fig. 5 and 6).

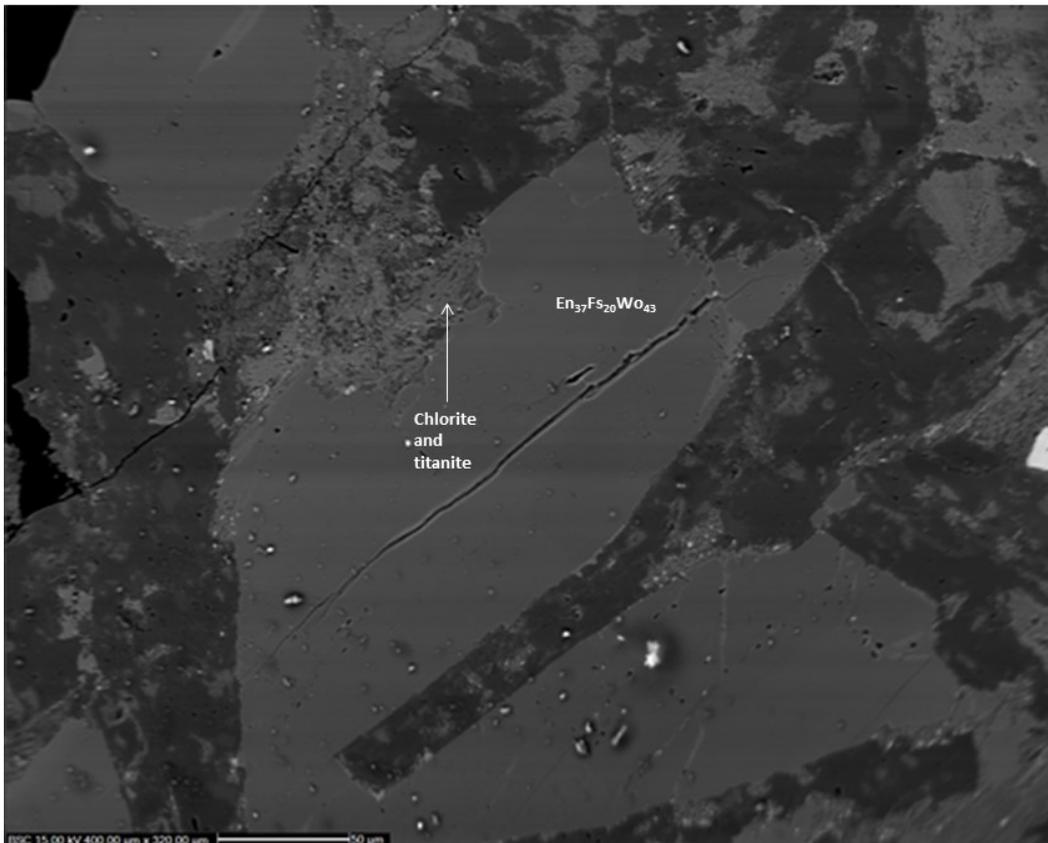


Figure 4. Sample from an intrusion at 1780-1786 m in HE-24. Alteration minerals replacing the augite are titanite and chlorite. Epidote-amphibole zone. The figure is approximately 480 μm wide. Backscattered image.

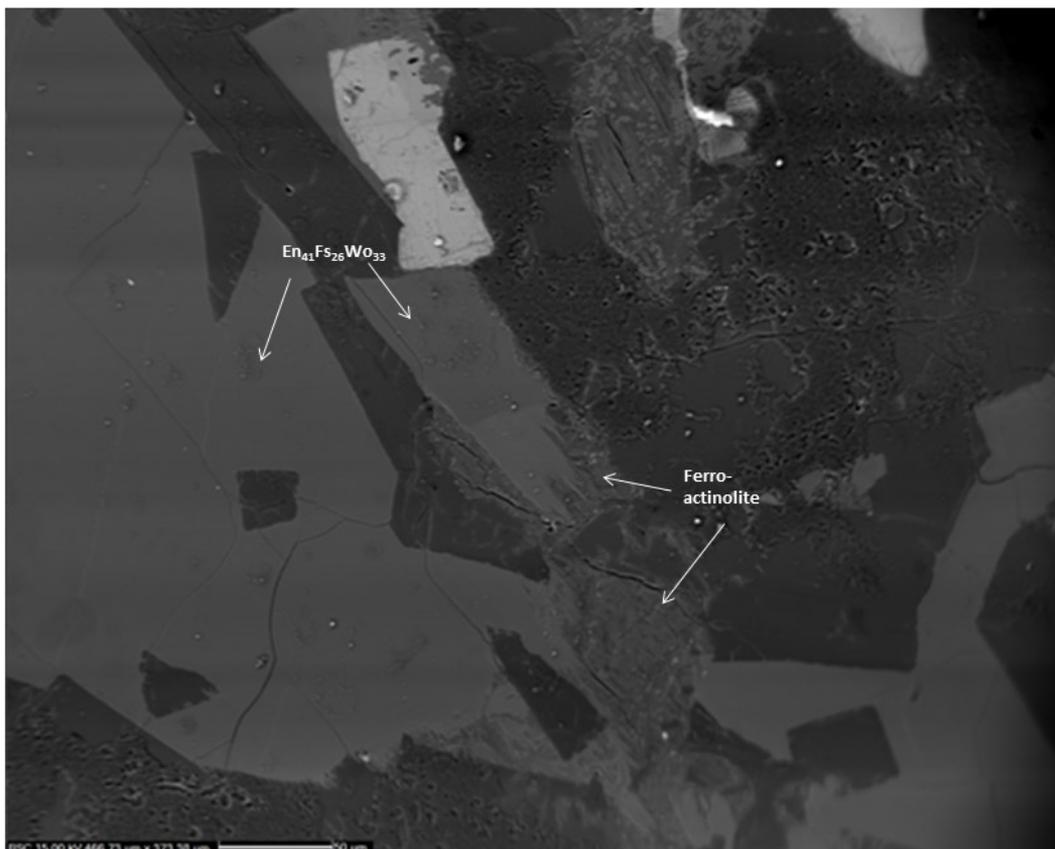


Figure 5. Sample from an intrusion at 1928 m in HN-2. Ferro-actinolite replacing augite along some of the edges and along some of the edges and cleavage plains. Backscattered image.

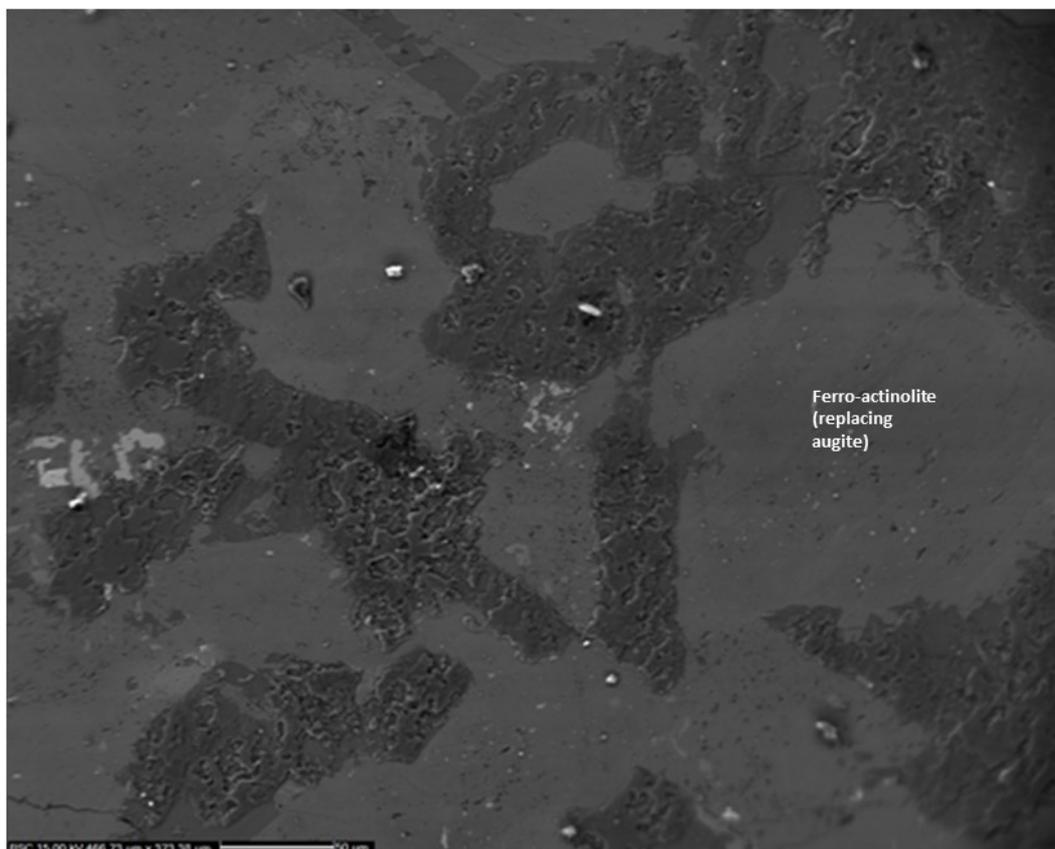


Figure 6. Ferro-actinolite replacing augite in a lava flow at 2502 m in HE-8. The figure is approximately 480 μm wide. Backscattered image.

Chlorite

Typical examples of chlorites which have replaced clinopyroxene can be seen in Table 3. Chlorite seems to have a lower Si-content in the lava flows than in the intrusions (Fig. 7). This correlates well with previous studies that indicate that chlorite grains in more permeable formations show lower Si-contents compared to chlorite in less permeable formations (e.g. Lonker et al., 1993). Generally, intrusions are much less permeable than lava flows which commonly also have higher proportion of vesicles. Some of the samples shown in Fig. 7 generally have rather high SiO_2 contents. This is believed to be caused by interstitial SiO_2 (perhaps originating from the dissolution of plagioclase), which can easily reside in between the chlorites.

Table 3. Representative chlorite analyses.

	Lava flows			Intrusions						
	2506 m (HE-8)	1602 m (HE42)	1480 m (HE-24)	1776 m (HN-2)	1784 m (HE-24)	1834 m (HN-2)	1928 m (HN-2)	2598 m (HE-8)	2538 m (HE-42)	3055 m (HE-42)
	Analysis as oxides, wt%									
SiO_2	30.69	28.44	28.71	30.82	31.4	29.35	29.23	27.96	30.32	37.24
TiO_2	0.07	0.08	0.01	0.05	0	0	0.04	0.03	0.15	0.05
Al_2O_3	18.6	16.78	21.47	18.35	18.45	16.23	13.8	20.32	17.54	12.83
FeO	22.58	32.42	25.34	34.01	23.37	27.3	29.97	26.57	22.51	18.39
MnO	0.18	0.28	0.57	0.33	0.2	0.34	0.17	0.5	0.28	0.42
MgO	14.91	11	13.72	7.02	15.69	13.83	11.63	12.55	17.68	19.06
CaO	0.19	0.3	0.23	0.47	0.21	0.44	0.44	0.36	0.36	1.45
Na_2O	0	0	0	0.39	0	0.3	0.24	0.02	0.06	0.49
Cr_2O_3	0	0	0.01	0	0.03	0	0	0.08	0	0
Total	87.22	89.3	90.06	91.44	89.35	87.79	85.52	88.39	88.9	89.93
	Number of Cations based on 28 Oxygens									
Si	6.33	6.09	5.83	6.43	6.34	6.23	6.49	5.85	6.16	7.27
Al	4.52	4.24	5.14	4.51	4.39	4.06	3.61	5.01	4.20	2.95
Al (IV)	1.67	1.91	2.17	1.57	1.66	1.77	1.51	2.15	1.84	0.73
Al (VI)	2.85	2.33	2.98	2.94	2.72	2.29	2.10	2.87	2.37	2.22
Ti	0.01	0.01	0.00	0.01	0.00	0.00	0.01	0.00	0.02	0.01
Fe	3.89	5.81	4.31	5.93	3.94	4.85	5.56	4.65	3.83	3.00
Mn	0.03	0.05	0.10	0.06	0.03	0.06	0.03	0.09	0.05	0.07
Mg	4.58	3.51	4.16	2.18	4.72	4.38	3.85	3.92	5.36	5.55
Ca	0.04	0.07	0.05	0.11	0.05	0.10	0.10	0.08	0.08	0.30
Na	0.00	0.00	0.00	0.16	0.00	0.12	0.10	0.01	0.02	0.19
Cr	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.00
Si+Al(IV)	8.00	8.00	8.00	8.00	8.00	8.00	8.00	8.00	8.00	8.00
M1	11.40	11.78	11.59	11.39	11.47	11.80	11.75	11.63	11.72	11.34

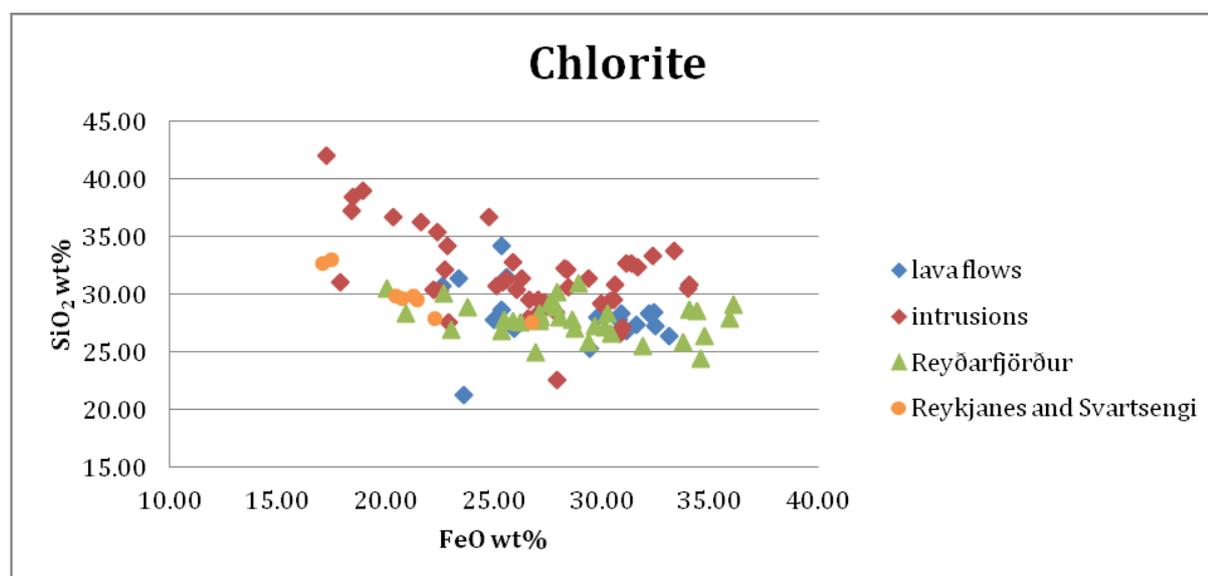


Figure 7. Wt% SiO₂ plotted against Wt% FeO (total Fe, calculated as FeO) in chlorites from lava flows and intrusions.

In Figure 7, wt% SiO₂ is plotted against wt% FeO (total iron calculated as FeO) for the chlorites in the Hellisheiði field and compared to chlorites from core samples of Tertiary age from Reyðarfjörður (data from Exley, 1982, Mehegan et al., 1982) and to chlorites from Reykjanes/Svartsengi (data from Lonker et al., 1993). The difference between the Hellisheiði data and data from Reykjanes/Svartsengi and Reyðarfjörður is that the chlorites in the Hellisheiði field are mostly formed by alteration of pyroxene although an occasional chlorite mineral can be attributed to fractures in the primary mineral. The chlorites from the other sites originate from variable sources such as vesicles and olivines. The most notable difference in Fig.7 is the amount of silica, which is considerably higher in some of the chlorites replacing clinopyroxene in the intrusives in the Hellisheiði field. Otherwise the chlorites from the lava flows as well as from some of the intrusives correlate well with the Reyðarfjörður and the Reykjanes/Svartsengi data.

Titanite

Titanite is found as an alteration mineral replacing clinopyroxene in numerous samples. It has been noted that titanite often occurs as fine-grained crystals that form discontinuous rims around minerals replaced by chlorite (Marks et al., 2010). This observation relates to the fact that the most abundant occurrence of titanomagnetite in olivine tholeiite is on grain boundaries of the major silicate phases. This illustrates the enrichment of titanium in the magma during the final stages of lava crystallisation. There are, however, indications that titanium is somewhat mobile during hydrothermal alteration as indicated by the observation that titanite replaces all of the primary minerals of basalts except olivine (i.e. clinopyroxene, plagioclase, Fe-Ti oxides and glass) (e.g. Lonker et al., 1993).

Amphibole

In the epidote-amphibole facies actinolite and ferro-actinolite start to replace primary clinopyroxenes. Representative amphibole compositions are shown in Table 4.

In Figure 8 wt% SiO₂ is plotted against wt% FeO from the amphiboles in lava flows compared to amphiboles from intrusions. A notable difference is observed in the range of FeO content, showing greater variation in the intrusions (ca. 15-27 wt%) compared to the lava flows (ca. 15-20 wt%). This is probably caused by the different oxidation state of the intrusions as compared to the relatively older lava pile. There is ample evidence that the oxidation of the rift-zone crust mainly takes place within its upper levels where oxygen-rich water has access to the strata. It may be argued that a basaltic intrusion at depth solidifies at less oxidised conditions. Accordingly its Fe₂O₃/FeO ratio is low as compared to the more oxidised surroundings of the intrusion. This higher relative abundance of FeO within the intrusion favours the formation of more FeO-rich actinolite.

An even greater difference is seen when FeO (total iron calculated as FeO) is plotted against Al₂O₃ where two distinct groups of actinolites seem to form (Fig. 9). The amphiboles found in the lava flows have higher wt% Al₂O₃ and lower wt% FeO at the same FeO concentrations (with a few minor exceptions). During the primary alteration of an intrusion in the epidote-actinolite zone the plagioclase is probably the only Al-source. Dissolution of plagioclase and the formation of albite and K-feldspar releases the anorthite component of the plagioclase (Ca and Al) and therefore aluminous epidote could be formed as a replacement mineral. The observed growth of Fe-poor epidote as a replacement mineral of plagioclase indicates that Al is preferentially taken up by the epidote. At the same time the abundance of FeO in the un-oxidized intrusion is high as compared to the lava pile (Figs. 8 and 9). Al-poor actinolite and Al-rich epidote pairs can, accordingly, be taken as an indication of primary alteration of intrusive rock in the epidote-actinolite zone. The few epidotes recognised in this study were found in an intrusion at 1826 m in HN-2, along with Al-poor ferro-actinolite.

More significant, however, may be the different modes of alteration of lava flows compared to intrusives. The progressive alteration of lava flows may lead to Al-rich actinolite forming from an already chlorite altered clinopyroxene in contrast to

intrusives where prevailing temperatures of the surrounding country rock lead to actinolite forming directly from the original pyroxene.

Table 4. Representative amphibole analyses.

	Intrusions:				Lava flows:		
	1776 m (HN-2)	1836 m (HN-2)	1928 m (HN-2)	2600 m (HE-8)	3055 m (HE-42)	1602 m (HE-42)	2506 m (HE-8)
Analyses as oxides, wt%							
SiO ₂	49.7	48.2	49.9	48.16	53.31	52.34	44.27
TiO ₂	0.02	0.05	0.1	0.39	0.22	0.6	0.88
Al ₂ O ₃	5.5	4.95	3.27	5.48	4.51	5.8	10.61
FeO	23.92	24.1	24.55	20.31	15.59	22.12	18.54
MnO	0.59	0.27	0.4	0.37	0.64	0.66	0.28
MgO	7.02	7.31	7.44	9.3	12.65	7.84	10.4
CaO	10.81	10.61	11.09	11.77	11.29	10.76	10.79
Na ₂ O	0.19	0.13	0.09	0.37	0.56	1	0.99
Cr ₂ O ₃	0.06	0.07	0	0	0	0.01	0.07
Total	97.81	95.69	96.84	96.15	98.77	101.13	96.83
Number of cations based on 23 Oxygens							
Si	7.52	7.49	7.67	7.35	7.66	7.57	6.68
Al	0.98	0.91	0.59	0.99	0.76	0.99	1.89
Al (IV)	0.48	0.51	0.33	0.65	0.34	0.43	1.32
Al (VI)	0.50	0.39	0.26	0.33	0.43	0.56	0.56
Ti	0.00	0.01	0.01	0.04	0.02	0.07	0.10
Fe	3.03	3.13	3.16	2.59	1.87	2.67	2.34
Mn	0.08	0.04	0.05	0.05	0.08	0.08	0.04
Mg	1.58	1.69	1.70	2.12	2.71	1.69	2.34
Ca	1.75	1.77	1.83	1.92	1.74	1.67	1.74
Na	0.06	0.04	0.03	0.11	0.16	0.28	0.29
Cr	0.01	0.01	0.00	0.00	0.00	0.00	0.01
Si+Al (IV)	8.00	8.00	8.00	8.00	8.00	8.00	8.00
M1	5.20	5.27	5.18	5.13	5.11	5.07	5.39
M2	1.81	1.80	1.85	2.03	1.90	1.95	2.03

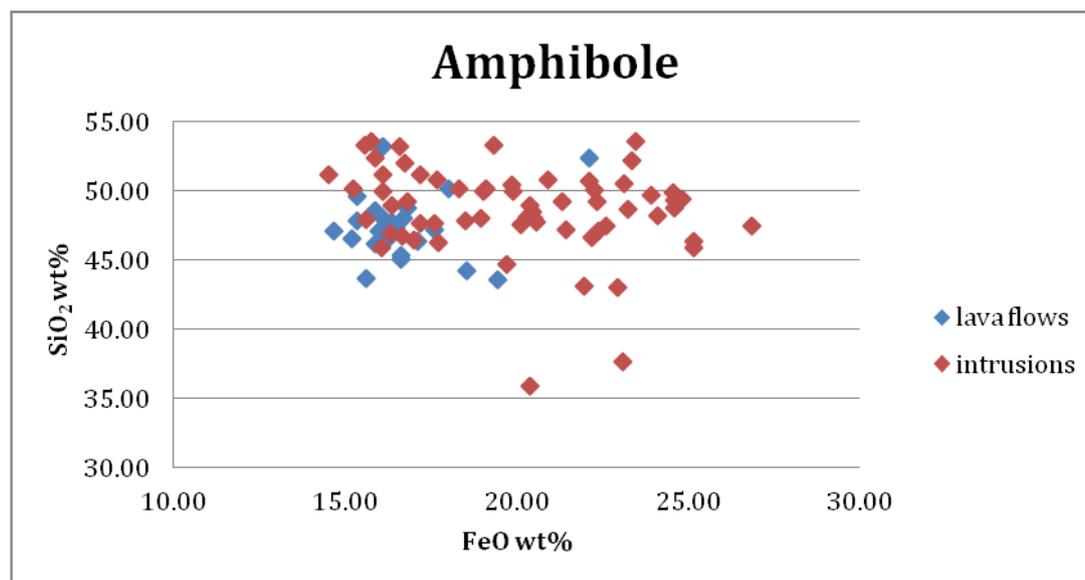


Figure 8. Amphibole alteration of clinopyroxene, wt% SiO₂ plotted against iron as wt% FeO.

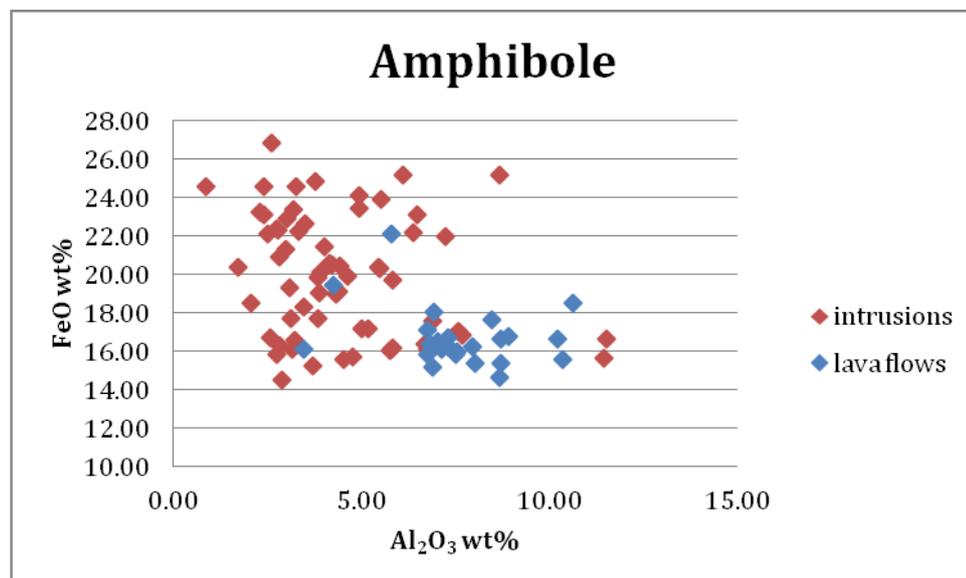


Figure 9. Amphibole alteration of clinopyroxene, iron as wt% FeO plotted against wt% Al_2O_3 .

4. CONCLUSIONS

Geothermal alteration of primary pyroxene in olivine tholeiite is dominated by dissolution/precipitation reactions. This is consistent with a previous study of plagioclase in the Hengill area (Larsson et al., 2002).

Clinopyroxene remains stable into the chlorite-epidote zone where it is replaced by chlorite in situ. In the epidote-actinolite zone clinopyroxene is transformed into actinolite in situ.

There is a significant difference in the composition of actinolite that forms from clinopyroxene within intrusions when compared to actinolite from the lava pile. The difference is attributed to progressive alteration in the lava pile (i.e. actinolite may also form from chlorite in the lava pile in contrast to forming directly from pyroxene in the intrusives) although it may also be caused by the less oxidised intrusive rock.

There is also a notable difference in the amount of SiO_2 in chlorites from intrusions when compared to chlorites from lava flows where it seems significantly lower. This is believed to stem from less permeability in the intrusives.

ACKNOWLEDGEMENTS

Sigurður Steinþórsson and Björn S. Harðarson are thanked for their invaluable comments. GEORG, Geothermal Research Group, is also thanked, having funded a part of the study. Reykjavík Energy readily allowed the use of their data for which it deserves gratitude.

REFERENCES

- Alfredsson, H.A., Hardarson, B.S., Franzson, H. and Gislason, S.R.: CO_2 sequestration in basaltic rock at the Hellisheidi site in SW Iceland: stratigraphy and chemical composition of the rocks at the injection site. *Mineralogical Magazine*, vol. 72 (1), (2008), 1-5.
- Deer, W.A., Howie, R.A. and Zussman, J.: *An Introduction to the Rock-Forming Minerals*. Second edition. Pearson Education Limited, (1992).
- Exley, R.A.: Electron microprobe studies of Iceland Research Drilling Project drill core high-temperature hydrothermal mineral geochemistry. *Journal of Geophysical Research*, vol. 87, no. B8, (1982), pp. 6489-6510.
- Franzson, H.: Nesjavellir. Alteration in a geothermal system. Orkustofnun report OS94021/JHD-06, (1994), 53 p. (In Icelandic).
- Franzson, H.: Reservoir Geology of the Nesjavellir High-Temperature Field in SW-Iceland. Proceedings 19th Annual PNOC-EDC Geothermal Conference, Manila, Philippines (1998), 13-20.
- Franzson, H., Árnason, K., Sæmundsson, K., Steingrímsson, B., Harðarson, B.S. and Gunnlaugsson, E.: The Hengill geothermal system, conceptual geological model. Proceedings World Geothermal Congress 2010, Bali, Indonesia, (2010), 9 p.
- Helgadóttir, H.M.: The Gráuhnúkar geothermal system, Hellisheidi: Geology and hydrothermal alteration. M.Sc. thesis. University of Iceland, (2011), 186 p.
- Jakobsson, S.: Icelandic rock types 2. Olivine-tholeiite. *Náttúrufræðingurinn*, **53**, (1983), 13-18. (In Icelandic).
- Larsson, D., Grönvold K., Oskarsson, N. and Gunnlaugsson E.: Hydrothermal alteration of plagioclase and growth of secondary feldspar in the Hengill Volcanic Centre, SW Iceland. *Journal of Volcanology and Geothermal Research*, vol. 114, (2002), 275-290.

- Lonker, S.W., Franzson, H. and Kristmannsdóttir H.: Mineral-fluid interactions in the Reykjanes and Svartsengi geothermal systems, Iceland. *American Journal of Science*, vol. 293, (1993), 605-670.
- Marks, N., Schiffman, P., Zierenberg, R.A., Franzson, H. and Fridleifsson, G.Ó.: Hydrothermal alteration in the Reykjanes geothermal system: Insights from Iceland deep drilling program well RN-17. *Journal of Volcanology and Geothermal Research* **189**, (2010), 172-190.
- Marks, N., Schiffman, P. and Zierenberg R.A.: High-grade contact metamorphism in the Reykjanes geothermal system: Implications for fluid-rock interactions at mid-oceanic ridge spreading centers. *Geochemistry, Geophysics, Geosystems*, vol. 12, (2011), 25 pp.
- Mehegan, J.M. and Robinson, P.T.: Secondary Mineralization and Hydrothermal Alteration in the Reydarfjordur Drill Core, Eastern Iceland. *Journal of Geophysical Research*, vol. 87, no. B8, (1982), pp. 6511-6524.
- Nielsson, Steinþór.: Geology and alteration in the Hverahlíð geothermal system in Hellisheiði. M.Sc. thesis. University of Iceland, (2011), 208 p. (In Icelandic).
- Spilde, M.N., Brearley, A.J. and Papike, J.J., 1993. Alteration of plagioclase and pyroxene phenocrysts in a fissure fumarole, Valley of Ten Thousand Smokes, Alaska. *American Mineralogist*, vol. 78, pp. 1066-1081.
- Stefánsson, A., Gíslason, S.R. and Arnórsson, S.: Dissolution of primary minerals in natural waters. II. Mineral saturation state. *Chemical Geology*, **172**, (2001), 251-276.
- Sæmundsson, K.: Vulkanismus und Tektonik des Hengill-Gebietes. *Acta nat. Isl.* II, no. 7, (1967), 101 p.
- Sæmundsson, K.: Geological map of the Hengill area 1:50,000. Orkustofnun, Reykjavík, (1995).