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1	Long or short silicic magma residence time beneath Hekla
2	volcano, Iceland?
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12	Abstract
 13 14 15 16 17 18 19 20 21 22 23 24 25 26 27 28 29 30 31 32 33 34 	Timescales of magma transfer and differentiation processes can be estimated when the magma differentiation mechanism is known. When conventional major- and trace-element analyses fail to distinguish between various processes of magma differentiation, isotope compositions can be useful. Lower Th isotope ratios in silicic relative to basaltic magmas at a given volcano, could either result from magma storage over a period of several tens of thousands of years of if the differentiation process was fractional crystallisation alone, or from crustal anatexis on a much shorter timescale. Recently mapped bimodal tephra layers from Mt. Hekla, Iceland, confirm lower (²³⁰ Th/ ²³² Th) and higher Th/U in silicic versus mafic magmas. Higher Th/U has been taken to indicate either apatite fractionation or partial crustal melting. In-situ trace element analysis of apatite and the enveloping glass in basaltic andesite, dacite and rhyolite was undertaken to examine its capacity to fractionate trace elements and their ratios. Both Th and U are compatible in apatite with a partition coefficient ratio D ^U /D Th of 1. Hence, apatite crystallization and separation from the melt has a negligible effect on Th/U in Hekla magmas. Partial melting of hydrothermally altered crust remains the preferred mechanism for producing silicic melt beneath Hekla. Ten to twenty percent partial melting of metabasaltic crust with 0.4-1.2 wt% H ₂ O produce dacite magma with 4-6% water. Absence of low δ^{18} O values in Hekla magmas compared to silicic magma formation, storage, differentiation and eruption at Hekla occurred over a timescale of less than a few centuries. Decreasing production of rhyolite and dacite during the Holocene lifetime of Hekla suggests changes in the crustal magma source and readjustment of the magma system with time.
35 36	
37	
38	Keywords Magma differentiation timescales, tephra, apatite, partition coefficients, Th/U

1 Introduction

2 An important research goal for better understanding volcanic behaviour is the evaluation of

3 how fast magma differentiates at depth and how quickly it ascents through the crust. The

4 timescales of magma transfer after a mixing event of two magma types, or thermal

- 5 perturbations, is often recorded in mineral zonation (e.g. Costa et al. 2020 and references
- 6 therein) whereas zircon-ages suggest several order of magnitude longer timescales (e.g.
- 7 Cooper & Reed 2008). Information on the timescale of magma differentiation derived from
- 8 U-series disequilibria on whole-rocks depends on a good understanding of the magma 9 fractionation process(es) and how different elements of the U-series respond (e.g.
- Condomines et al. 2003). The occurrence of low Th isotope ratio in more silicic magmas from
- 11 several active volcanoes such as Teide (Tenerife, Canary Islands), Snæfellsjökull and Hekla
- volcanoes (Iceland; Fig. 1a) have been interpreted as reflecting several tens to hundreds of
- 13 thousands of years of closed- or open-system fractional crystallisation of mafic magma before
- 14 the eruptions (Hawkesworth et al. 2000; Kokfelt et al. 2009; Chekol et al. 2011). Similarly,
- $^{238}\text{U}^{-230}$ Th radiosactive equilibrium in continental rhyolites from North America were
- 16 explained by inferring a crustal residence time of $> 10^5$ years (Reagan et al. 2003). These long
- 17 timescales have also been suggested from zircon compositions in rhyolite at the Yellowstone
- 18 caldera (Stelten et al. 2015) and in a silicic tephra from Hekla (Carley et al. 2011). In marked
- 19 contrast, the complete magma suite from basalt to rhyolite of Hekla volcano would have been
- 20 produced over a period that was one or two orders of magnitude shorter (hundreds to
- thousands of years) if the silicic magma result from crustal anatexis (Sigmarsson et al. 1992).
- 22 Therefore, estimations of time elapsed from magma generation to eruption depend on a
- 23 detailed knowledge of the magma generation, and thus of the differentiation mechanisms.
- 24 Magma differentiation processes generating silicic melt have been debated for a long time.
- 25 Fractional crystallisation, assimilation fractional crystallisation (AFC), melting of crustal
- silicic segregations or fluid-absent melting of hydrated metabasalts (amphibolites) have been
- 27 proposed to explain the abundance of silicic magmas in Iceland (see review by Jónasson 2007
- and references therein). All of these processes have been shown to be capable of producing
- silicic melts with the appropriate major-element composition, though their efficiency most
- 30 likely depends on the crustal thermal regime (Martin and Sigmarsson, 2007; Schattel et al.
- 2014). Silicic magma at Askja, Krafla and Torfajökull volcanoes, all of which have developed
- powerful geothermal systems, have different isotope ratios to contemporaneously erupted
- basalts, and are thus ascribed to crustal melting associated with an AFC process (Nicholson et
- al. 1991; Sigmarsson et al. 1991; Gunnarsson et al. 1998; Martin and Sigmarsson 2007;
- Zellmer et al. 2008; Chekol et al. 2011; Kuritani et al. 2011; Bindeman et al. 2012).
- 36 Elsewhere, such as at Hekla volcano, different magma types have less contrasting isotope
- 37 ratios with the exception of Th and a few heavy stable isotopes.
- 38 Identifying crustal melts and their proportions in mingled or mixed magma is straightforward
- 39 when the crust has a contrasting isotope composition compared to mantle derived basalts.
- 40 Such a discrimination is not straightforward for partial melts of young oceanic or oceanic
- 41 island crusts where classic radiogenic isotope ratios, such as those of Sr and Nd, remains
- 42 indistinguishable from the pristine mantle melts. This is because the low ratio of radioactive
- 43 versus radiogenic isotopes together with long half-life of the radioactive parent isotope lead to
- slow production of the radiogenic daughter isotope in a crust of young age. Such is the case of
- 45 the young Icelandic crust. Therefore, isotopes with a short half-life (such as that of 230 Th with

1 a half-life of only 75 kyrs) are needed to detect contributions from young mafic crust. Lower

2 Th isotope ratio in a metabasaltic crust that is a few million years old relative to recently

3 erupted basalts is thus an excellent tracer to decipher oceanic crustal contamination (e.g.

4 Nicholson et al. 1991; Sigmarsson et al. 1991). Recently, it has been proposed that the Hekla

5 silicic magma with low Th isotope ratios resulted from fractional crystallisation of basaltic

parental magma and "storage in a molten stage over tens of thousands of years" before its
eruptions (Geist et al. 2021) rather than being the product of crustal anatexis and rapid

8 transfer to the surface (Sigmarsson et al. 1992).

9 The Hekla magma suite is frequently chosen for testing the effects of terrestrial magma

10 differentiation on heavy stable isotope composition (e.g. Tuller-Ross et al. 2019). However, a

11 lack of consensus concerning the exact differentiation mechanism producing the Hekla

magma suite, namely whether the suite is co-genetic or not, hampers its value for studying
 magmatic processes. The disagreement appears to lie in the understanding of different tools

for identifying the differentiation processes in operation. The most important divergence in

15 view concerns the role of apatite during magma differentiation and the storage time of silicic

16 melts at depth. Can the observed increase in Th/U from basalt to rhyolite (Sigmarsson et al.

17 1992) simply be explained by extraction of apatite from the melt (Geist et al. 2021)? Or does

18 the higher Th/U in silicic Hekla magma reflect an origin from anatectic melting (Sigmarsson

19 et al. 1992)? Lower (230 Th/ 232 Th) in the silicic magma in the former case could be interpreted

as being the result of fractional crystallisation of basalt to produce the entire Hekla magma

suite, followed by a long storage time at depth (tens of thousands years). In the second case,

22 the silicic magma could have erupted shortly after anatexis with the rhyolite simply

23 originating from fractional crystallisation of the dacitic crustal melt.

In order to assess if apatite fractionation lowers Th/U in the derived melt, selected trace element partition coefficients between minerals and melt were measured in four rock types

chosen to represent the Hekla magma series. Moreover, additional field and geochemical data

have been integrated to discuss the different hypotheses proposed for the origin of the silicic
magma. It is shown that apatite fractionation from Hekla magma has a negligible effect on the

magma. It is shown that apatite fractionation from Hekla magma has a negligible effect on th
 Th/U in the fractionated melt. Furthermore, new Th isotope ratios in two-coloured tephra

30 layers confirm lower ratios in the more evolved magma. Rapid magma differentiation and

eruption is shown to be fully compatible with the lower Th isotope ratios in the silicic

32 magmas compared to the basalt and basaltic andesite magmas. Short timescales of magma

evolution concur with the well-known eruption history whereas long-term storage of silicic

34 melt somewhere beneath the volcano which is not involved in the numerous eruptions of the

whole magma suite, from basalt to rhyolite, is considered unlikely. Finally, the erupted

36 magma compositions are used to infer the nature of the crustal magma source and the partial

37 melting conditions during the formation of the silicic magma under Hekla.

38

39 Hekla magmas and samples

40 The Hekla volcanic system (Fig. 1a) is constructed on older crust at the junction between a

41 transform fault and a southward propagating rift into the metabasaltic crust (e.g. Sæmundsson

42 1979; Meyer et al. 1985, Óskarsson et al. 1982). Its basement is built up of Pleistocene

43 hyaloclastite ridges of basaltic composition and Mt. Hekla is only known to have produced

differentiated magma during the Holocene. Prehistoric Plinian eruptions of Hekla (Hekla-5, -4

- 1 and -3 eruptions) produced compositionally zoned tephra layers ranging from rhyolite at the
- 2 base to andesite and basaltic andesite tephra at the top, whereas basaltic andesite and basalt
- 3 are respectively erupted from Hekla proper and fissures around the volcano (e.g. Sigvaldason
- 4 1974; Larsen and Thorarinsson 1977; Jakobsson 1979; Sigmarsson et al. 1992; Sverrisdóttir
- 5 2007). Recent work on the prehistoric tephra stratigraphy has led to an increased
- 6 understanding of it (Larsen et al. 2019), yielding a better time series of the volcanic and
- 7 magmatic evolution of Mt. Hekla. After the Hekla-3 eruption (3000 years ago) a series of
- 8 two-coloured (or bimodal) tephra were erupted (Fig. 1b), followed by more mafic
- 9 compositions until historical times in Iceland (~ 870 CE). The first two historical eruptions
- 10 produced rhyodacite (Hekla-1 eruption; 1104 CE; Thorarinsson 1967) and dacite (1158 CE)
- 11 magmas. Since then, basaltic andesite to evolved iron-rich andesite (icelandite) have been the
- 12 dominant eruption products.

13 *The bimodal tephra suite*

- 14 The well-known silicic tephra layers from the Plinian Hekla-5, -4 and -3 eruptions (7100,
- 15 4250 and 3050 years ago, respectively) characterize the early history of Hekla activity (Fig.
- 16 2). Smaller silicic eruptions also produced compositionally zoned tephra layers such as the
- 17 HÖ eruption, approximately 6100 years ago (Gudmundsdóttir et al. 2011; Jónsson et al.
- 18 2020). Recently, Larsen et al. (2019) demonstrated a shift in the eruption mode of Hekla
- 19 which occurred approximately 3000 years ago, or soon after the large compositionally zoned
- 20 Hekla-3 Plinian eruption. From 3050 b2k (age before the year 2000 CE) the volcanic activity
- changed from infrequent large explosive eruptions to frequent smaller eruptions until the first
- historical eruption occurred, namely the Plinian 1104 CE, or Hekla-1, eruption. For a 600-
- 23 year period after the Hekla-3 eruption, nine two-coloured tephra layers were formed with a
- volumetrically smaller light coloured lower part (evolved iron-rich andesite) and a dominant
 dark upper unit of basaltic andesite composition (Fig. 1b). This was followed by a 500-years
- period of andesitic production with an increase in eruption of basaltic tephra towards the end
- of the prehistoric period prior to the Hekla-1 eruption. Eight units were selected from the four
- largest two-coloured tephra layers, H-X (2260 b2k), H-Y (2680 b2k), H-B (2800 b2k) and H-
- 29 C (2840 b2k), from which cm-sized pumice fragments were collected and analysed together
- 30 with twenty lavas and tephra from Sigmarsson et al. (1992). The sample suite represents the
- entire age range of products from the Hekla volcanic system.

32 Tephra for mineral-melt partition analysis

- Four tephra of lapilli size were collected for in-situ measurements of selected trace element 33 partition coefficients, namely basalt scoria from the Lambafit 1913 CE crater row (Moune et 34 al. 2007), basaltic andesite from the 1970 CE craters (Baldridge et al. 1973), the 1158 CE 35 dacitic tephra (Larsen et al. 1999) and a rhyolite from the first phase of the Hekla-3 eruption 36 (Larsen and Thorarinsson 1977). The samples were chosen to represent the range in magma 37 composition of the Hekla volcanic system. They correspond to tephra of different eruption 38 types, from scoria derived from a low-energy fire fountaining basalt fissure eruption to silicic 39 pumice of a Plinian eruption, which produced cubic kilometre of tephra. All the analytical 40 methods and results are given in Supplementary Information 1 and 2, respectively. 41
- 42
- 43 **Results**

1 Mineral-melt equilibrium assessment

- 2 Partition coefficients, or the distribution of an element between two phases in thermodynamic
- 3 equilibrium, can be measured if equilibrium conditions are met. Textural equilibrium between
- 4 minerals and glass was examined with a scanning electron microscope (SEM) and assessed
- 5 based on the sharpness of the crystal faces and signs of resorption in contact with the
- 6 surrounding glass (see Fig.1 in Supplementary Information 1). Once textural equilibrium had
- 7 been established, chemical equilibrium was evaluated using existing minerals-melt
- 8 equilibrium relationships. For olivine-, plagioclase- and pyroxene-melt equilibrium, the
- 9 criteria discussed in Putirka (2008 and references therein) was employed together with that of
- 10 Bacon and Hirschmann (1988) for coexisting FeTi-oxides.
- 11 Ninety-six olivine crystals, 148 plagioclases and 117 clinopyroxenes were analysed for major
- elements. No pyroxene was found in the 1970 basaltic andesite, but 30 FeTi-oxides could be
- 13 analysed. Limited chemical zonation was observed in most macrocrysts apart from the
- 14 plagioclase in H1970 which was normally zoned from An_{57} to An_{45} . The mineral composition
- 15 is within the published range for the 1913 basalt, the 1970 basaltic andesite and the H3
- rhyolite (Baldridge et al. 1972; Moune et al. 2007; Chekol et al. 2011; Portnyagin et al. 2012;
- 17 Lucic et al. 2016, Weber and Castro 2017; Geist et al. 2021). Olivine in the H1158 dacite was
- homogeneous with a median composition of $Fo_{23.6}$ (rim: Fo_{23-25} ; core: Fo_{23-24}). In contrast,
- both normal and reversed zoning was observed in H1158 plagioclase, ranging in composition
- from An_{56} to An_{36} . Similarly, clinopyroxene ranged in composition from Mg# 40-46 at the
- rim to Mg# 39-48 in the cores (median Mg# of 44 and 40, respectively) and thus mostly
- 22 displayed reverse zoning.
- 23 Major-element concentrations
- 24 Whole-rock major element concentrations were measured in ten new tephra and lavas. The
- results represent the melt composition because of the aphyric character of the Hekla products.
- 26 On the total alkali vs silica (TAS) diagram (Fig. 3) the analyses form a complete magma suite
- when plotted together with those previously published by Sigmarsson et al. (1992), Chekov et
- al. (2011) and Geist et al (2021). A linear correlation is observed from the more evolved
- 29 basalt to the rhyolite composition. In order to minimize inter-laboratory differences, only
- 30 whole-rock analyses from Clermont-Ferrand and Misasa laboratories are shown in Fig. 3,
- together with the recent results of Geist et al. (2021) and the detailed basalt study of
- Jakobsson (1979). Several Harker diagrams are displayed in Supplementary Information 3.
- 33 The most primitive basalts are pillow fragments from the Pleistocene hyaloclastite (Hek-4 and
- -10; Supplementary Information 2) that forms the basement upon which Hekla volcano is
- 35 constructed (MgO \leq 7.73%).
- 36 The variations in P_2O_5 concentrations with magma differentiation are shown against those of
- 37 MgO in figure 4 together with whole-rock lava values from the litterature (Jakobsson 1979;
- Chekol et al. 2011; Geist et al. 2021) and lapilli-sized tephra by Larsen et al. (2019) for
- 39 comparison. Historical basalt lavas fall on a slightly different curve compared to prehistoric
- 40 basalt, both of which reach the maximal P_2O_5 values of 1.4-1.6% in the relatively primitive
- 41 basaltic andesite of the Valagjá chasm (sample Hek-11 and Hek-11b; Table 1 in
- 42 Supplementary Information 2). From this peak two linear trends of falling P₂O₅ vs MgO are
- 43 observed. The main trend extends from the Valagjá basaltic andesite to the initial tephra of the
- 44 1947 eruption (sample H1947F in Supplementary Information 2 with MgO = 1.46%) and

1 olivine-hosted melt inclusions from dacite and rhyolite (Portnyagin et al. 2012; Lucic et al.

- 2 2016; not plotted for clarity). A secondary trend is formed by several basaltic andesites that
- 3 pre-date the H3 eruption (3000 a) originating from craters on the northern part of the Hekla
- 4 ridge and lavas close to the Older Valagjá crater.
- 5 *Trace-element concentrations*
- 6

7 Increasing SiO_2 and decreasing MgO concentrations are often used as differentiation index for

8 magma suites but highly incompatible elements amplify the variability of elemental

9 concentration during magma differentiation. While SiO_2 concentrations increase from 45% to

10 75% on an anhydrous basis from basalt to rhyolite (Fig. 3), the Th concentrations increase by

11 a factor of 6 (Fig. 5a). Thorium is therefore used to measure the evolution of the magma

12 composition. Variations of TiO_2 with Th concentrations are shown in Fig. 5b. A sharp 13 increase in TiO_2 is observed with increasing Th in the basalts up to a TiO_2 concentration

around 5 %. From there, TiO_2 concentrations falls from basaltic andesite to dacite and

15 rhyolite.

16 Forty-eight trace elements, analysed for 20 samples representing the whole Hekla magma

suite, complement the trace element analyses of Sigmarsson et al. (1992) and the study of the

18 most recent Hekla lavas by Chekol et al. (2011) and Geist et al. (2021). The multi-element

19 ICP-MS analyses yield that are results coherent with the ID-MS analyses for U and Th

20 concentrations albeit less precise (see Supplementary Information 2 and 4). Uranium and

other large-ion lithophile element concentrations (such as those of Cs and Rb; see

22 Supplementary Information 4) form an excellent linear correlation with Th, as expressed by

squared correlation coefficient, R^2 , higher than 0.96. Basalt to basaltic andesite lavas fall on a

line passing through the origin for light and middle Rare Earth Elements (LREE and MREE,

respectively) versus Th concentration diagrams. Smaller increase in LREE is observed from

- basaltic andesite to silicic magma while MREE decrease from basaltic andesite to dacite and
 then rise again in the most evolved rhyolite (Supplementary Information 4). Increasing Th/U
- with differentiation (Sigmarsson et al. 1992) is confirmed by the new results (Fig. 6). The

change in REE occurs at a Th concentration equal to 4 ppm whereas a rise in Th/U occurs at

30 Th of 5-6 ppm. Zirconium concentration deviates from the line defined by the basalts at a

31 similar Th concentrations to those of the REE. It varies by a factor of 5 in the silicic magmas

32 while Th differs by less than a factor of 2 (Fig. 6). Evolved andesite from the bimodal tephra

33 frequently deviate from the main evolution trends on concentration plots.

34 Samarium concentration in basalts correlate linearly with that of Th with a line extending

from the origin towards basaltic andesite at approximately 15 ppm of Sm (Fig. 7). From there

a flat trend connects basaltic andesite (via andesite) with dacite/rhyolite until a final rise is

observed in the most evolved rhyolite of the zoned H4 eruption (H4-5). The evolved andesite

from the bimodal tephra layers falls well below the general trend. Basalt and basaltic andesite

magmas have uniform Gd/Yb of 2.45-2.70, falling to approximately 2 in the andesite (Fig. 7).

40 The lowest ratio of 1.7 is measured in HY-A, an evolved andesite, but remain constant at 1.8-

41 1.9 in silicic magma from Hekla. Silicic magma from Torfajökull, Tindfjallajökull and

42 Snæfellsjökull (Martin and Sigmarsson 2007; Zellmer et al. 2008; Kokfelt et al. 2009;

43 Tomlinson et al. 2010) have Gd/Yb ranging from 1.54 to 2.2, similar to that of Hekla.

44

In-situ trace-element analyses and partition coefficients 1

- 2 A total of 111 laser-ablation analyses were performed on mineral and glass phases in H1913,
- H1970, H1158 and H3 tephra and 71 partition coefficients were calculated (Supplementary 3
- Information 5 and 6; Fig.8). In plagioclase, Sr is the only element of those analysed that is 4
- considered compatible ($D_{min/melt} > 1$), together with Eu ($D^{Eu} = 1.21$) in the silicic rocks. The 5
- D_{plag-melt} for Sr and Eu increase by up to an order of magnitude from the more primitive 6
- H1913-Lambafit basalt ($D^{Sr} = 1.53$ and $D^{Eu} = 0.14$) to the H1158 dacite ($D^{Sr} = 3.73$ and D^{Eu} 7
- =1.21). In clinopyroxene, Sc, Cr, Co and Ni are compatible together with a few REE in the 8
- more evolved H1158 dacite and H3 rhyolite, $D^{Sm} = 1.62-1.75$, $D^{Gd} = 1.93-1.96$ and $D^{Yb} =$ 9
- 1.59-1.70. Yttrium is also compatible in clinopyroxene from H1158 and H3 with $D^{Y} = 1.57$ -10
- 1.66. None of the elements measured are compatible in olivine, and the highest D calculated 11
- is that of Sc (~ 0.5). 12
- Primary emphasis was put on measuring the partition coefficients for apatite-melt pairs in 13
- Hekla and the mean D is found to be consistent from one rock type to another (Supplementary 14
- Information 5; Fig. 8a). Rubidium, Nb and Ba are incompatible in apatite, as is Zr to a lesser 15
- degree. The highest partition coefficients are observed for the MREE (Nd, Gd, Sm, Pr) then 16
- the LREE (La, Ce) and Y with the HREE (Yb and Lu) having the lowest D. Strontium has a 17
- somewhat lower D but Th and U are equally compatible in the apatite with D^{ap-melt} ranging 18
- from approximately 1 in the basaltic and esite $[D(Th) = 0.80 \pm 0.16 \text{ and } D(U) = 0.95 \pm 0.22$ 19
- (2σ)] to 2 in the rhyolite [D(Th) = 1.9 ± 0.4 and D(U) = 1.9 ± 0.4 (2σ)]. The D^{apt-melt} of this 20
- study agree with experimental results (Watson and Green 1981; Klemme and Dalpé 2003; 21 Prowatke and Klemme 2006; Fig. 8b). It is noteworthy that there is again a consistent increase
- 22 in D^{apt-melt} from the basaltic andesite through the dacite to the rhyolite by a factor of 23
- approximately 3 for each element. Apatite has D^U and DTh approaching a value of 2 and the
- 24
- ratio of DTh over D^U is always within error of 1 (Table 1). 25
- Thorium isotope ratios, Th/U and ²³⁰Th-²³⁸U disequilibria 26
- The Th/U of 3.2 in Recent Hekla basalts and basaltic andesite contrasts with increasing ratio 27
- of 3.4 in the dacite and 3.6-3.7 in the rhyolite. Zircon fractionation and accumulation 28
- observed in the zoned H4 eruption caused large variations in Th/U (Sigmarsson et al. 1992), 29
- whereas relatively high ratios are measured in two of the bimodal andesites (Fig.6b). 30
- Four pairs of evolved andesite or basaltic andesite from the sequence of bimodal tephra layers 31
- yielded significantly lower (²³⁰Th/²³²Th) and higher Th/U in the silicic part (Fig. 9 and 32
- Supplementary Information 2). As an example the light-coloured (Fig. 1b) silicic part of the 33
- HY tephra layer has $(^{230}\text{Th}/^{232}\text{Th})$ and Th/U of 0.936 (±0.008; 2SD) and 3.44 (± 1%), 34
- respectively, compared to $1.030 (\pm 0.014; 2SD)$ and 3.25 in the darker part. Two magma types 35
- of a contrasting composition are thus erupted in a single eruption. The evolved andesites of 36
- the bimodal tephra have relatively low (230 Th/ 232 Th) for a given Th concentration (Fig. 9). 37
- Moreover, these evolved andesites have significantly lower ²³⁰Th-excess over ²³⁸U than 38
- dacites or rhyolites from Hekla (Fig. 10). The new results confirm the already observed 39
- difference between silicic and more mafic magmas from Hekla (Sigmarsson et al. 1992). 40
- 41
- 42

1 Discussion

2 The Hekla magma suite revisited

3 Recently, studies of "non-traditional" stable isotopes of a number of elements have used

- 4 Hekla volcano as a case study for evaluating the effect of magma differentiation on the
- 5 systematics of a given isotope. Clearly, understanding of terrestrial fractionation is needed
- 6 before the physical and chemical processes occurring on a planetary scale can be discussed.
- 7 While isotopes of several elements either show no isotope fractionation at Hekla (e.g. Zn, Mo
- and K; Chen et al. 2013; Yang et al. 2015; Tuller-Ross et al. 2019), or non-systematic
 variations (e.g. Li and Tl isotopes; Schuessler et al. 2009; Prytulak et al. 2017a), other isotope
- systems (Fe, Si, V, Ti and Zr) display clear evolutionary trends (Schuessler et al. 2009;
- 11 Savage et al. 2011; Prytulak et al. 2017b; Deng et al. 2018; Inglis et al., 2019). The heavier
- 12 Fe, V, Ti and Si isotope ratios with magma differentiation have been suggested to reflect
- 13 either Rayleigh fractionation, redox variations (with FeTi-oxide fractionating Fe, V and Ti
- 14 isotopes) or thermogravitational differentiation (e.g. Zambardi et al. 2014 and references
- therein), whereas the possibility of crustal contamination is rarely explored. Similarly,
- 16 conflicting interpretations have arisen with respect to Zr isotope results in Hekla rocks, with
- 17 either isotopically light zircon being extracted during magmatic differentiation (Inglis et al.
- 18 2019) or isotopically heavy Zr being inherited from crustal anatexis (Ibañez-Mejia and Tissot
- 19 2019). The latter proposition is in accordance with the interpretation of B isotopes (Rose-
- 20 Koga and Sigmarsson, 2008). Therefore, the lack of consensus concerning the exact
- 21 differentiation mechanism operating beneath Hekla hampers accurate interpretation of several
- 22 heavy stable isotope systematics when applied to a magma suite.
- 23 Tight correlations of major- and trace-elements have been used as an argument for magma
- 24 differentiation by fractional crystallisation alone (e.g. Kokfelt et al. 2009; Geist et al. 2021).
- 25 However, melt and rhyolite-melt models of fractional crystallisation processes have failed to
- explain several major element variations, such as those of Fe_2O_3 and K_2O (Chekol et al. 2011)
- and Al_2O_3 and P_2O_5 , in the Hekla magma suite (Geist et al. 2021). Moreover, the analytical
- 28 precision of major- and trace-element measurements is not always good enough to distinguish
- between magma differentiation from a basaltic parent magma by fractional crystallization
- alone or by assimilation fractional crystallization (AFC) process with dominant magma
 mixing between silicic crustal melt and more mafic melts (e.g. Sigmarsson et al. 1992). The
- complication is illustrated by the TiO_2 vs Th concentration diagram (Fig. 5b), which could be
- used to support either interpretation. The divergent view on silicic magma formation at Hekla
- (e.g. Sigmarsson et al. 1992; Chekol et al. 2011; Portnyagin et al. 2012; Geist et al. 2021)
- centres around the role of apatite fractionation and its effect on trace element systematics
- 36 during magma differentiation together with interpretations of low Th isotope ratios in the
- 37 silicic magma.

38 Apatite fractionation

- Highest P₂O₅ concentrations are observed in the basaltic andesite of the Valagjá lava chasm
- 40 (Hek-11) and associated volcanic bomb (Hek-11bis), which tephrachronology shows to be
- older than the H3 eruption (3050 years ago) but younger than H4 (4250 years ago). Apatite
- 42 fractionation would cause a decrease of P_2O_5 in the derived melt, which coincides with the
- 43 transition from evolved basalt to basaltic andesite. However, the straight line of decreasing
- 44 P_2O_5 and MgO could also represent magma mixing. The decrease in P_2O_5 is different before

- 1 and after the H3 eruption as reflected by different slopes on Fig. 4 which might suggest either
- 2 more apatite fractionation in the past or different silicic end-members during magma mixing
- 3 or AFC.
- 4 Fractional crystallisation of apatite has been called upon to explain the REE patterns in
- 5 several magma suites such as that of Snæfellsjökull and Hekla volcanoes (Kokfelt et al. 2009;
- 6 Chekol et al. 2011). Apatite fractionation is known to deplete the residual melt in REE,
- 7 especially the MREE. Experimental studies have shown that D^{ap/melt} is higher for MREE than
- 8 light or heavy REE (Prowatke and Klemme 2006; Fig. 8). The deflection in REE
- 9 concentrations when examined against an index of magma differentiation for Hekla occurs at
- 10 a Th concentration equal to 4 ppm (Fig. 7). It appears to coincide with apatite fractionation,
- 11 starting at magma composition corresponding to the basaltic andesite of Valagjá with
- approximately 1.6 % P₂O₅ and Th close to 4 ppm (Figs. 4). However, the rise in Th/U starts
- 13 later in the magma evolution at a Th concentration of 5 to 6 ppm (Fig .6b).
- 14 Apatite partition coefficients
- 15 The measured $D^{ap-melt}$ confirm the correlations with SiO₂ concentrations, or the melt
- 16 polymerization, as experimentally observed (e.g. Prowatke and Klemme, 2006; Fig. 8b). The
- 17 partition coefficients are thus strongly composition dependent. For example D_{Sm} between
- clinopyroxene and melt increases by a factor of 4 from 0.41 (\pm 0.04; 2 σ) in the 1913 CE
- basalt to 1.75 (\pm 0.22; 2 σ) in the H3 rhyolite and that of apatite-melt reaches values as high as
- 20 40 for the MREE.
- 21 The new partition coefficients allow better quantification of the differentiation process as
- 22 illustrated by the Sm vs Th diagram (Fig. 7). The best-fit linear correlation between Sm and
- 23 Th concentrations in basalts passes through the origin with a slope corresponding to a bulk
- 24 D_{Sm} of 0.002, readily explained by small proportions of clinopyroxene in the crystallising
- assemblage. Slightly decreasing Sm concentrations from basaltic and esites (Th = 4 ppm) to
- Hek-8 dacite (Th = 7.75 ppm) and an abrupt decrease to evolved and esite HY-A (Th = 6.68
- 27 ppm) would correspond to bulk D_{Sm} of 1.15 and 1.7, respectively, with an increase in apatite
- fraction in the crystallising assemblage from 5 to 8%. The final rise in Sm from dacite torhyolite could then indicate the end of apatite fractionation. Fractional crystallisation of
- clinopyroxene and significant fraction of apatite could thus, in principle, account for the Sm -
- 31 Th systematics in Hekla products, although it can by no means be used as proof for that
- process. Indeed, the flat trend around 15 ppm Sm from basaltic andesite through andesite and
- dacite towards rhyolite (from 4 to 10.5 ppm Th) is equally well explained by binary mixing
- 34 and/or AFC with a small mass of crystal fractionation relative to melt assimilant.
- 35 Further assessment of the fractional crystallisation mechanism for magma composition
- varying from basaltic andesite to dacite can be obtained from the measured D^{ap-melt} for Gd, Yb
- and Th. Five percent apatite in the fractionating mineral assemblage has been suggested from
- 38 major-element modelling (Chekol et al. 2011). Apatite is the only mineral, in the present case,
- that incorporates Th with a $D^{ap-melt}$ of 0.8 in the basaltic and esite. From these parameters, 50%
- 40 fractional crystallisation of basaltic andesite with 4 ppm Th would produce dacitic magma
- with 7.8 ppm Th. With D^{ap-melt} in the basaltic andesite of 13 for Gd and 4.9 for Yb
 (Supplementary Information 5), and assuming an average D^{cpx-melt} for basaltic andesite from
- (Supplementary Information 5), and assuming an average D^{cpx-melt} for basaltic andesite fron
 those measured in the basalt and dacite and further assuming that clinopyroxene makes up
- half the mass of the fractionating phases, the Gd concentrations would decrease from 16.1 in

- 1 basaltic andesite (with 4 ppm Th) to 8.87 ppm, whereas Yb would only slightly decrease from
- 2 6.29 ppm to 6.19 ppm. This would lead to a decrease in Gd/Yb from 2.6 to 1.43, which is
- 3 significantly lower than that found in Hekla silicic magma (Fig. 7). In addition, the calculated
- 4 Gd and Yb concentrations in the hypothetical dacite are too low compared to those measured
- 5 in Hekla dacites, which have values of 14.6 15.1 ppm for Gd and 7.33 8.66 ppm for Yb.
- 6 Lowering the proportions of clinopyroxene fractionation to only 10%, for the sake of
- 7 argument, yields Gd and Yb concentrations (12.4 and 8.51 ppm, respectively) closer to the
- 8 observed values but still results in a Gd/Yb of 1.43, which is significantly lower than the
- 9 actual value. A simple fractional crystallization model thus underestimates MREE
- 10 concentrations and their ratios in the derived melt compared to those measured in Hekla
- 11 dacite.
- 12 The strongest argument against major apatite fractionation is the indistinguishable D^{U} and D^{Th}
- between apatite and melt, which clearly eliminates the theory that apatite fractionation could
- 14 explain the higher Th/U in the silica rich magma of Hekla. Therefore, fractional crystallisation
- 15 of parental basalt cannot explain all the trace element systematics of the Hekla magma suite.

16 Source of silicic Hekla magmas

- 17 Silicic magmas from the rift-zone in Iceland are characterized by low δ^{18} O whereas those far
- from the rift-axis have higher δ^{18} O (Martin and Sigmarsson 2007; Schattel et al. 2014 and
- 19 references therein). Less intense basaltic magmatism away from the rift-zones leads to a lower
- 20 geothermal gradient and cooler crust that causes incoming basalts to loose heat and
- 21 differentiate mainly via fractional crystallisation to produce silicic derivatives (e.g.
- 22 Öræfajökull and Eyjafjallajökull volcanoes; Selbekk and Trønnes 2007; Sigmarsson et al.
- 23 2011). In contrast, hotter crust from intense basaltic magmatism is expected at the rift-axis,
- 24 which is consequently easier to partially melt. High permeability of the intensively fractured
- crust in rift-zones leads to hydrothermal alteration of the dominant basaltic lavas and intrusive
- rocks. The oxygen isotope composition of the altered bulk crust depends on several factors
 such as alteration temperature, secondary mineral fractionations of O-isotopes, degree of
- such as alteration temperature, secondary mineral fractionations of O-isotopes, degree of
 hydration and degree of metamorphism together with the composition of the thermal water,
- which in Iceland ranges from δ^{18} O of -20.8 to +2.3 ‰ (SMOW; Stefánsson et al. 2017).
- 30 Consequently, hydrothermally altered basalts have large range of δ^{18} O or from -11 to +6 ‰
- (Hattori and Muehlenbachs 1982). Mount Hekla, being located on a flank zone with no
- extensional tectonics, produces dacite and rhyolite with relatively high δ^{18} O compared to rift-
- zone rhyolites (e.g. Muehlenbachs et al. 1974; Sigmarsson et al. 1992; Bindeman et al. 2012;
- Geist et al. 2021). The water content of the crustal source for Hekla silicic rocks can be
- estimated from the olivine-hosted melt inclusions of Portnyagin et al. (2012) and Lucic et al.
- 36 (2016). Dacite melts within Fo₂₅ olivine were shown to contain approximately 4% H₂O. If the
- dacite were formed by 10-20% dehydration melting of amphibolite under fluid-absent
- conditions (Thy et al. 1990; Sigmarsson et al. 1992) then the water content of that amphibolite
- source would only have to be 0.4-0.8% since water behaves incompatibly with respect to
- 40 "water-free" residual minerals after amphibole breakdown. Such a low water content would
- 41 be expected if the hydrothermal alteration occurred at a relatively low water-rock ratio
- 42 (Hattori and Muehlenbachs 1982), explaining why the silicic rocks of Hekla do not have very
- 43 low δ^{18} O.

- Zircons extracted from a single Hekla tephra layer (most likely that of the H3 eruption) by 1
- Carley et al. (2011) exhibit complex compositional zonation, have an order of magnitude 2
- variation in REE concentrations and δ^{18} O that varies from 1.8 to 4.8‰ (SMOW) suggesting 3
- an entrained crystal cargo of diverse origin (Bindeman et al. 2012). These zircons also span a 4 surprising range in Th isotope ratio with (²³⁰Th/²³²Th) ranging from 0.18 to 2.22. None of
- 5 these zircons have reached radioactive equilibrium between ²³⁸U and ²³⁰Th and must therefore 6
- 7 be younger than ~400 ka. The zircon results demonstrate important crustal heterogeneity
- 8 beneath Hekla and they record crystal ages of several tens to hundreds of thousands of years
- 9 beneath Hekla volcano, possibly from silicic segregations present within the old metabasaltic
- crust and defrosted by thermal pulses from the southward propagating rift (Sigurdsson 1977; 10
- Gunnarsson et al. 1998). At first glance, this timescale is comparable to that discussed by 11
- Chekol et al. (2011) for the production of andesite from a basaltic parent. However, such a 12
- long timescale is inconsistent with the eruption history of the silicic Hekla magma. It calls for 13
- isolated silicic magma pockets to have remained molten over tens to hundreds of thousands of 14
- years, beneath the volcano but to have escaped ascending basalt, basaltic andesite or andesite 15 during the entire volcanic history of Hekla, which appears rather fortuitous. Elsewhere, 16
- zircons have been suggested to be recycled between solidification and defrosting (Cooper and 17
- Kent, 2014) in mature magma systems, which is an unlikely scenario for Hekla due to its 18
- aphyric magma and young age. Therefore, these heterogeneous zircons are most likely 19
- xenocrysts and do not convey much information about the formation of the silicic magma. 20
- 21 The rarity of crystals in Hekla magmas and the absence of complex zoning in those present
- (e.g. Sigvaldason 1974; Geist et al. 2021) is best explained by crustal melting and dominant 22
- melt mixing at the origin of Hekla evolved magmas (Fig. 9). 23
- Radioactive disequilibrium and time constraints 24
- Decreasing $(^{230}\text{Th}/^{232}\text{Th})$ and $(^{238}\text{U}/^{232}\text{Th})$ with magma differentiation for the entire Hekla 25
- magma suite is shown in Fig. 10. If the whole suite were generated by fractional 26
- crystallisation alone, a period of 130 thousand years would be needed to decrease the 27
- (²³⁰Th/²³²Th) from 1.08 (the highest ratio in basalts) to 0.94 (lowest ratio in evolved andesite). 28
- The dacite and rhyolite would have to remain for $10^4 10^5$ years at depth, which is clearly not 29
- supported by the volcanic history of Mt. Hekla. Therefore, the lower $(^{230}\text{Th}/^{232}\text{Th})$ in the 30
- silicic magma of Hekla is best explained by metabasaltic crustal anatexis (Sigmarsson et al. 31
- 1991). 32
- The tectonic situation of Hekla volcano, namely at the intersection of a transform fault and a 33
- propagating rift segment (Saemundsson 1979), suggests a source of relatively fertile 34
- metabasaltic crust generated and hydrothermally altered at a rift-axis, and metamorphosed as 35
- a consequence of isostasy from the loading of volcanic products and plate spreading (e.g. 36
- Óskarsson et al., 1982). To produce ²³⁰Th excesses, or (²³⁰Th/²³⁸U) higher than 1, with partial 37
- melting of metabasaltic crust, or amphibolite, a residual mineral phase during melting is 38
- needed that is capable of retaining U relative to Th. The most likely candidate is a Ti-bearing 39
- phase (hemoilmenite-ulvospinel solid solutions or rutile) with higher D^U than DTh. Klemme et 40 al. (2006) measured partition coefficients between FeTi-oxides and melt and found that D^U
- 41 was less than or equal to 0.01 and that of DTh an order of magnitude lower. Such low partition
- 42 coefficients cannot explain (²³⁰Th /²³⁸U) of 1.10-1.20 in silicic magma generated by 10 to 43
- 20% dehydration melting of amphibolite. The melting degree would have to be an order of 44
- magnitude smaller to yield a reasonable residue with 5-20% FeTi-oxides. In addition, a melt 45

- 1 fraction of only 1% would yield high-silica rhyolite rather than dacite. Dacitic melt with
- 2 $(^{230}\text{Th}/^{238}\text{U})$ of 1.10 to 1.20 can be generated by 10-20% amphibolite melting if the
- 3 proportions of rutile in the residue are between 0.5 and 2.5%, assuming rutile-melt D^U of 2
- 4 and D^{Th} of 0. Indeed, Klemme et al. (2005) found D^{Th} to be less than 0.004 for rutile whereas
- 5 that of D^U was frequently higher than 1 and even reached 3.8 in their melting experiments.
- 6 Residual rutile after 20% melting of a mafic crust with Nb/La of 1.3 yields dacite with Nb/La
- of 0.93 (assuming 0.5% rutile in the residue and D^{Nb} and D^{La} between rutile and melt of 20
- 8 and 0.003, respectively) as observed at Hekla (range: 0.9-1.1). Thus residual rutile is the most
- 9 likely cause of the 10-20% ²³⁰Th excess over ²³⁸U in the silicic rocks of Hekla, and their
- 10 formation must occur in the deepest part of the crust due to the pressure dependent stability of
- rutile (Xiong et al. 2005; Angiboust and Harlov 2017). Melt inclusions (Portnyagin et al.
 2012; Lucic et al. 2016) reveal H₂O contents as high as 5-6 wt %, which suggest an elevated
- 12 crystallisation pressure for the olivine to explain the high water solubility in the entrapped
- 14 silicic melt. Furthermore, high volatile solubility results in low enough viscosity and density
- 15 to generate the buoyant force for the crustal melt to migrate to higher level where the final
- 16 phase equilibria of the silica-rich magma took place (5-6.6 km according to the melting
- 17 experiments of Weber and Castro 2017).
- 18 The crustal melt produced over the Holocene cannot have had a constant composition as
- 19 demonstrated by variable $(^{230}\text{Th}/^{232}\text{Th})$ in the evolved andesite, dacites and rhyolites (Fig. 9).
- 20 Lower SiO₂ and Th concentrations as well as lower (230 Th/ 232 Th) and (230 Th/ 238 U), compared
- to earlier formed dacites, occur in the evolved andesite of the bimodal tephra that were
- erupted soon after the H3 eruption. Between H3 (3050 BP) and H1 (1104 CE) basaltic
- andesite became the dominant magma type produced by Hekla (Larsen et al. 2019; Fig. 2).
- From 3050 BP to approximately 2100 BP, ten eruptions emitted both evolved andesite and
- 25 basaltic andesite forming the bimodal tephra layers, with no evidence for magma mingling
- between the two magma types (Fig. 1b). The composition of these younger evolved andesites
- suggests a separate crustal source, with lower $(^{230}\text{Th}/^{232}\text{Th})$ in the crustal melt. That source
- would have produced higher melt fractions (to explain lower SiO_2 and Th concentrations as
- 29 well as lower 230 Th excess over 238 U; Fig. 10). The increased eruption frequency of the
- basaltic andesite after the H3 eruption implies a greater flux of hot mafic magma into the
 magma system and consequently increased latent heat from basalt crystallisation forming the
- basaltic andesite. Both these factors would facilitate a larger degree of crustal melting if other
- parameters remained constant. Melting experiments studying the phase equilibria of these
- evolved andesites are needed to better understand whether the crustal source was at a different
- 35 level than for the previous magmas.
- 36 *Field evidence on time constraints*
- 37
- The elevated H_2O and F concentrations in Hekla melts at depth (Moune et al. 2007;
- Portnyagin et al. 2012) and the nearly aphyric character of the erupted magma does not
- 40 indicate a gas-filter pressing mechanism to separate silicic melt from crystals. Rather the high
- 41 volatile solubility suggests a relatively low viscosity of buoyant melt and both rapid and
- 42 efficient separation from the solid residue after partial crustal melting. The lack of magma
- 43 mingling in the two-coloured tephra implies separate magma storage for the bimodal magmas
- 44 and a short contact time between the two magmas before eruptions. The time interval between
- 45 these "two-magma" eruptions range from only 30 to 200 yrs. (Larsen et al. 2019) showing

- 1 that silicic magma was generated by crustal melting beneath Hekla on a decadal timescale and
- 2 erupted without accumulation into a large magma body as suggested, for example, before
- 3 caldera-forming eruptions, such as the Minoan eruption on Santorini (Druitt et al. 2012).
- 4 Further field studies are needed to establish the length of the quiescent period before the large
- 5 zoned Plinian eruptions H3 and H4, when compositionally stratified magma chambers were
- 6 emptied. Judging from the repose time preceding the last rhyodacite eruption in 1104 CE (H1
- 7 tephra) at least 200-250 years are needed for the accumulation of silicic magma beneath
- 8 Hekla before a large explosive eruption.
- 9

10 Conclusion

11 The principal conclusions of this study are the following:

- The partition coefficients of U and Th between apatite and melt are identical.
- Therefore, apatite fractionation cannot explain the higher Th/U in the silicic magma
 from Hekla compared to the basalt and basaltic andesite.
- The higher Th/U and lower Th isotope ratios in the silicic magma are best explained
 by partial melting of a metabasaltic crust and rapid magma ascent through the crust.
- The diverse composition of the Hekla evolved andesite and dacite, the bimodal tephra
 versus those produced during the large Plinian eruption, suggest a heterogeneous
 crustal source and variable crustal melt fractions.
- The short quiescent time between the prehistoric eruptions and the lack of magma mingling after the H3 eruption suggest that the time elapsed between crustal melting episodes and eruptions is in the range of only 10-100 years.
- The time needed for establishing of larger magma reservoirs before the zoned Plinian eruptions is only a few hundred years. The lifetime of the magma reservoirs appears to have shortened with time, becoming only a few tens to a hundred years during the historical period.
- Although Hekla appears to produce more mafic magma with time, the magma system
 has not yet developed a high-level magma chamber, suggesting that partial melting of
 the lower to middle crust has given rise to the explosive silicic magma.
- 30
- 31

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17 Table legend.

- 18 Table 1. Mean partition coefficients between minerals and melt for Th and U.
- 19

20 Figure legends.

- Fig. 1. Left panel shows a digital elevation map of Hekla volcano and the Valagjá chasm. In
- the right panel the peculiar sharp boundary between evolved andesite and basaltic andesite isshown for the HY bimodal tephra layer.
- Fig. 2. Simplified stratigraphic column for tephra layers from Hekla volcano. Note that basalt
- units are not shown. Historical dates are given as CE (Common Era) and prehistoric dates as
- 26 before 2000 CE (b2k). Different colours are shown in the on-line version with yellow as
- 27 rhyolite, orange as dacite and blue for andesite-basaltic andesite tephra.
- Fig. 3. The sum of sodium and potassium oxides plotted against silica oxide concentrations
- 29 (TAS diagram) for Hekla lavas and tephra. Results from Jakobsson (1979), Sigmarsson et al.
- 30 (1992), Chekol et al. (2011) and Geist et al. (2021) are plotted together with results of this
- 31 study. All results have been recalculated on an anhydrous basis.
- Fig. 4. Concentrations of P_2O_5 in historical basalts are higher than in prehistoric basalts for a
- 33 given MgO. In contrast, P_2O_5 decreases faster in older basaltic and esite from the northern part
- of the Hekla ridge and craters further north along the same strike (Fig. 1) relative to basaltic
- andesite and andesite younger than the H3 eruption (ca. 3000 a). Two double-headed arrows
- indicate either apatite fractionation or magma mixing of basaltic andesite with differentiated
- magma components, with the older one (between Valagjá and Older Valagjá) being of less
- evolved composition. Results from Jakobsson (1979), Sigmarsson et al. (1992), Chekol et al.

- 1 (2011) and Larsen et al. (2019) are plotted together with those of this study. See text for
- 2 further discussion.
- Fig. 5 a) Thorium vs SiO₂ concentrations in Hekla volcanics. The over five-fold rise in Th
- 4 corresponds to only a 1.6 times increase in SiO₂ concentrations demonstrating that fine details
- 5 of magma differentiation are better represented by Th variations than by variations in silica.
- 6 Only Th measured by ID-MS are plotted together with results from Sigmarsson et al. (1992;
- 7 filled circles) and those of Chekol et al. (2011; empty circles). b) Titanium oxide vs Th
- 8 concentrations in Hekla volcanics. Onset of FeTi-oxide fractionation in the basalts is marked
- 9 by the spike in TiO_2 concentrations. The decreasing TiO_2 with differentiation (increasing Th)
- 10 can be explained by either progressive fractional crystallisation or by magma mixing of
- 11 different components. Such a mixing line is drawn from the basaltic andesite through andesite
- 12 towards the dacite.
- 13 Fig. 6. a) Zirconium versus Th concentrations. The observed differences between the new
- results and those of Sigmarsson et al. (1992) reflects the different analytical methods (isotope
- 15 dilution mass spectrometry, ICP-MS multi-element analysis and XRF on pressed pellets) used
- 16 in three separate laboratories. Open headed arrows depict fractional crystallisation from basalt
- to basaltic andesite and from dacite to rhyolite. Binary magma mixing between basaltic
- 18 and esite and dacite is indicated by the double-headed arrow. Zircon fractionation and
- 19 accumulation controls the zirconium concentration in products from the H4 eruption. Also
- 20 notable is the peculiarity of the evolved andesite from the bimodal tephra layers (HY-A and
- 21 HX-A). b) Only U and Th results obtained by isotope dilution mass spectrometry are plotted.
- 22 The Th/U in basalt and basaltic and esite is uniform at \sim 3.2 up to Th \sim 5-6 ppm, from where the
- ratio increases to ~3.5. Redistribution of zircon in the H4 zoned eruption causes Th/U to vary
- between 3.04 and 3.73.
- Fig.7. Rare Earth Element variations examined with increasing magma differentiation in the
- Hekla magma suite. Analytical errors on the REE concentrations are shown as 3%. Range of
- 27 Gd/Yb in Icelandic silicic magmas is shown as well. See text for further discussion.
- Fig. 8. a) Mean partition coefficients between apatite and melt for intermediate to silicic
- 29 magma from Hekla. Note the consistent increase in D from basaltic andesite through dacite to
- 30 rhyolite. b) Increasing D^{ap-melt} with sillica content of the melt. Filled symbols are averages
- from this study; associated error is in most cases smaller than the size of symbols (see
- 32 Supplementary Information 5). The D^{ap-melt} of U and Th are within analytical error and thus
- overlap each other. Open symbols are experimental apatite/melt partition coefficient from
- published studies (Watson and Green 1981; Klemme and Dalpé 2003; Prowatke and Klemme
- 2006; Hammouda et al. 2010) and the calculated exponential best fits are shown as dashed
- 36 lines for comparison with the new results.
- Fig. 9. Thorium isotopes in Recent Hekla magmas plotted against Th concentration and
- $1/(^{232}\text{Th})$ (in grams per disintegration per minute (dpm)). Identical ($^{230}\text{Th}/^{232}\text{Th}$) in basalt and
- 39 the most primitive basaltic andesite reflects fractional crystallisation (FC). Decreasing
- 40 $(^{230}\text{Th}/^{232}\text{Th})$ from basaltic andesite through andesite towards dacite strongly suggests magma
- 41 mixing with limited crystal-melt separation causing the observed scatter. Fractional
- 42 crystallisation of dacite produces rhyolite. Evolved andesite from the bimodal tephra sequence
- 43 are explained by crustal melt of different composition than for the other dacites. See text for
- 44 further discussion.

- 1 Fig. 10. Equiline diagram schematically displaying the mantle source and the metabasaltic
- 2 crust in U-Th radioactive equilibrium ($(^{230}Th) = (^{238}U)$) together with the approximate fields
- 3 for rift-zone basalts Kokfelt et al. (2006 and references therein) and partial metabasalt melts.
- 4 Ageing and metamorphism of basalts, produced by mantle melting and erupted in the rift-
- 5 zone, together with isostasy and crustal spreading form amphibolite crust that upon
- 6 dehydration melting produces the Hekla silicic magmas (Sigmarsson et al. 1991). The spread
- of results for silicic magma on the diagram suggest a heterogeneous crustal source. Excess
 ²³⁰Th over ²³⁸U results from dehydration crustal melting and subsequent zircon fractionation
- as observed for the rhyolites. The maximum time needed for 230 Th decay alone is also
- 10 indicated. See text for further discussion.
- 11
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- 14 Supplementary Information
- 15 **1- Methods and analytical technics**
- 16 2- Analytical results (Major and trace element concentrations, U and Th
- 17 concentrations by isotope dilution and (²³⁰Th/²³²Th) measurement results)
- 18 **3- Harker diagrams**
- 19 **4- Trace element plots**
- 20 **5- Measured partition coefficients**
- 21 **6-** In-situ trace element results





Eruption units of Hekla volcano







Th (ppm)





Th (ppm)















































Supplementary Information 1

To the paper "Long or short silicic magma residence time beneath Hekla volcano, Iceland?" by Sigmarsson et al. (2022)

Methods

All rock samples, free of any weathered surface, were cleaned in deionized water, disintegrated in a jaw crusher and powdered in an agate mill. For separation of the rare minerals in Hekla products, crushed tephra was hand sieved and the size fraction between 180 and 250 µm collected. Hand magnet covered with paper collected grains with Fe-Ti oxides whereas less magnetized grains were poured into a funnel with heavy liquid for density separation. Combination of the heavy liquids LST Fastfloat (diluted sodium heteropolytungstates), bromoform and diiodomethane (density of 2.71, 2.84 and 3.31 g/ml, respectively) was used for mineral separation and the slightly- to non-magnetized grains were further purified with a Frantz magnetic separator.



Figure 1. Back-scattered electron (BSE) images of a) H3 rhyolitic tephra showing an anhedral olivine crystal with a thin border of glass, euhedral Fe-Ti oxides and a few small apatite crystals, both within a melt inclusion, together with sulphide bleb, which also occurs bordering the mineral. Scale bar 200 µm. b) H1158 dacitic tephra grain with euto subhedral olivine surrounded by glass. Apatite occurs both as inclusions and in embayments of the phenocryst. Scale bar 10 µm. c) H1970 basaltic andesite

tephra showing euhedral olivine and plagioclase phenocrysts along with small apatite inclusions enclosed in a microlite-poor glass. Scale bar 100 μ m. d) H1913-Lambafit basalt showing a grain of microlite-free glass as well as grains of microlite dominated groundmass and plagioclase phenocrysts. Scale bar 300 μ m. Abbreviations: ol = olivine, plg = plagioclase, Fe-Ti ox = Fe-Ti oxides, apt = apatite and GR = groundmass.

Electron Probe Micro Analyses (EPMA)

The tephra grains were mounted into epoxy plugs, polished and subsequently coated with carbon for Electron Probe Micro Analysis (EPMA) of major-element compositions in glass and mineral phases (Fig. 1). A JEOL JXA-8230 microprobe at the Institute of Earth Sciences (University of Iceland) was used for H1970 and H1158 pumices, while the H3 and H1913-Lambafit tephra were analysed at the Laboratoire Magmas et Volcans, Université Clermont-

Auvergne, France with a CAMECA SX100 instrument. For the EPMA both natural and synthetic standards were used. Secondary standards were run at the beginning and end of each analytical session: glass A99 and Astimex obsidian, plagioclase (Astimex Standards Ltd.) and olivine (OL SPM). Fifteen kV acceleration voltage and focused beam was used except for glass analyses, where the beam was defocused to 10 μ m. Probe current of 10 nA was employed for plagioclase and glass analyses and 20 nA for other mineral phases.

Laser Ablation Inductively Coupled Plasma Mass Spectrometer (LA-ICP-MS)

Minor and trace element concentrations in glass, olivine, clinopyroxene, plagioclase and apatite were acquired with a LA-ICP-MS instrument at the Laboratoire Magmas et Volcans, Université Clermont-Auvergne, France; Resonetics M50 EXCIMER laser (193 nm), coupled to a Thermo Element XR mass-spectrometer. Each analysis consisted of background measurements for 20 seconds before the laser ablation and data accumulation for 90 seconds. Appropriate standards, GSE, GSD, BCR, SRM NIST610 and SRM NIST612, were measured at the beginning and the end of each analytical session. The laser beam diameter was set at 7 μm, 9 μm and 12 μm for glass, 4 μm for apatite and to 12 μm, according to mineral grain size, for olivine, plagioclase and clinopyroxene (Fig. 2). Laser frequency of 1 and 2 Hz was utilized and the laser fluence was 2.8 J/cm². Trace elements acquired for apatite and glass pairs were Li, Al, Sr, Y, Ba, La, Ce, Pr, Nd, Sm, Gd, Yb, Lu, Th and U. For olivine, plagioclase, clinopyroxene and associated glass the elements were Li, Mg, Al, Sc, Cr, Ni, Sr, Y, Ba, Ce, Sm, Eu, Gd, Yb, Hf, Ta and Th. The raw analyses were reduced with the GLITTER software (van Achterbergh et al., 2001), using CaO and MgO concentrations (measured earlier by electron microprobe) as internal standards for Ca-rich phases (glass, apatite, plagioclase and clinopyroxene) and olivine, respectively.



Figure 2. a) Embayment in olivine growing around a relatively large apatite crystal with a second one in a melt inclusion in H1158 dacite. Both apatite crystals show euhedral habits. Scale bar is 100 µm long.



b) Example of laser-ablation craters in plagioclase, apatite and glass of Hekla 1970 CE basaltic andesite. Two 7 µm spots on the glass (#11 and 12) and two on a plagioclase (#13 and 14) were used to calculate D for Sr and Ba. Limited size of apatite as can be seen from the craters #7 and 8 requested the use of laser spots as small as 4 µm in diameter. Shown are several D determinations for this single grain, whereas average results from several mineral-melt pairs are discussed in the text. Scale bar is 100 µm long.

Whole-rock analyses

Approximately 100 mg of sample powder were fluxed with lithium metaborate (LiBO₂, proportions 1:3) in a carbon crucible using an induction furnace. The melt-pearl was immediately dissolved in 1 M HNO₃ and diluted 2000 times before ICP-AES analysis of major element concentrations. Fifteen samples from an earlier study (Sigmarsson et al., 1992) were selected for P₂O₅ concentration analysis; four of which were duplicated within 6%. For trace element analyses, another 100 mg of powder of each of the most evolved andesites, dacites and rhyolites was also fluxed with ammonium bifluoride (NH₄HF₂, proportions 1:4) and dissolved, whereas basalt and basaltic andesite powders were dissolved in a concentrated HF-HNO₃ mixture, evaporated to near dryness and re-dissolved in 7M HNO₃ and subsequently diluted in HNO₃ 0.4M to reach a total dilution factor of 5000. Analyses were performed on a quadrupole ICP-MS (Agilent 7500) instrument using reaction cell (He mode) to reduce interferences on masses ranging from 45 amu (Sc) to 75 amu (As). The signal was calibrated externally with a reference basaltic standard (BHVO-2) and the silicic standard RMG, both processed in the same way as the samples. Data reduction was achieved by

employing the GeoReM preferred values (http://georem.mpch-mainz.gwdg.de/). Both standards and pure HNO₃ 0.4M were measured every four samples. The external reproducibility of the method, as estimated by the repeated running of different standards (BCR-2, BIR, BEN, A-THO) is better than 5% (2σ) for most lithophile elements and <15% for chalcophile elements.

Uranium and Th concentrations were determined by isotope dilution and thermal ionization mass spectrometry, whereas the Th-isotope ratio was analysed either by α -spectrometry or a multi-collector ICP mass spectrometer (MC-ICP-MS) using conventional and more recent methods (Sigmarsson et al., 1992; Carpentier et al., 2016 and references therein). Nine stainless-steel discs with electroplated Th from Sigmarsson et al. (1992) were recounted, and combined with earlier results, for improved precision of (²³⁰Th/²³²Th) and ten new samples were analysed by the MC-ICP-MS (Neptune Plus). The measured atomic ratio of ²³²Th/²³⁰Th was converted to (²³⁰Th/²³²Th) activity ratio (= [λ^{230} Th/ λ^{232} Th] / [²³²Th/²³⁰Th]) using the following decay constants: λ^{232} Th = 4.9313 10⁻¹¹ and λ^{230} Th = 9.17055 10⁻⁶ (yrs⁻¹; Chen et al. 2013). All Th isotope results discussed are values at the time of eruption. Post-eruptional decay correction for ²³⁰Th decay was only needed for the prehistoric rhyolites of the H5 and H4 eruptions.

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Major element composition of the Hekla magma suite in weight %. Samples with prefix H17 and Hek-11 are new results together with the P2O5 concentrations on samples from Sigmarsson et al. (1992).

Dissolved water concentration at depth were estimated from H₂O/K₂O of 2 for mafic to intermediate compositions H1300L-Hek 4) but 2.3 for the more evolved compositions (H5A- Hek25) (Moune et al. 2007; Portnyagin et al. 2012; Lucic et al. 2016).

														H ₂ O from
Sample no	. Rock type	SiO ₂	TiO ₂	Al_2O_3	FeO ^{total}	MnO	MgO	CaO	Na₂O	K ₂ O	$P_{2}O_{5}$	H ₂ O	Sum	K ₂ O
H5A		72.7	0.15	12.8	2.20	0.08	0.13	1.68	4.77	2.56	0.05	3.08	100.2	5.89
H4-7	Rhyolite	72.6	0.15	13.3	2.19	0.09	0.09	1.29	5	2.96	0.00		97.7	6.81
H4-5		72.0	0.14	12.6	2.12	0.09	0.07	1.44	4.79	2.71	0.00	2.94	98.9	6.23
H4-3		66.3	0.52	14.8	7.43	0.25	0.37	3.53	5.16	2.08	0.00		100.4	4.78
H4-2		62.0	0.78	14.3	9.44	0.29	0.91	4.52	4.48	1.55	0.32	0.08	98.7	3.57
H4-T		59.8	1.13	15.3	10.5	0.27	1.65	5.21	4.37	1.54	0.53	0.11	100.4	3.54
H2	Dacite	68.6	0.29	14.0	3.98	0.12	0.3	2.49	5.03	2.18	0.08	1.9	99.0	5.01
H1104A		68.4	0.36	14.1	4.56	0.14	0.28	2.63	5.27	2.33	0.10	0.88	99.1	5.36
Hek 8		64.7	0.64	14.6	7.26	0.21	0.76	3.78	4.99	1.87	0.21	0.11	99.1	4.30
H1947F		61.5	0.99	14.8	8.3	0.23	1.46	4.50	4.72	1.74	0.36	- 0.17	98.5	3.99
H1947A	Andesite	61.0	1.14	14.9	9.06	0.24	1.65	5.11	4.55	1.48	0.48	0.11	99.7	3.40
H1300M		60.3	1.08	14.8	9.37	0.25	1.58	5.12	4.47	1.47	0.44	0	98.9	3.38
Hek-25		57.6	1.46	15.1	10.9	0.28	2.15	5.82	4.34	1.43	0.75	0.07	99.9	3.29
H1300L		55.1	1.72	14.9	11.6	0.29	2.68	6.4	4.32	1.36	0.98	0.08	99.4	2.72
H1846L		54.8	1.89	14.8	12.0	0.29	2.9	6.73	4.08	1.27	1.05	0.16	100.0	2.54
H1970-14 ^b		55.0	1.96	14.9	11.8	0.29	2.94	6.84	4.03	1.22	1.02	0.16	100.2	2.44
H17-4	3as.Andesit€	54.7	2.11	14.5	11.9	0.27	3.11	6.66	3.83	1.19	0.68	- 0.32	98.7	2.37
H17-1		53.2	2.27	14.4	12.2	0.27	3.25	6.88	3.79	1.11	0.79	0.04	98.2	2.22
H17-2		52.4	2.33	14.4	12.3	0.29	3.52	7.22	3.51	1.13	1.31	0.19	98.6	2.26
Hek 11		52.7	2.42	14.2	12.1	0.28	3.48	7.27	3.58	1.12	1.44	- 0.17	98.3	2.23
Hek 11B		52.1	2.61	14.1	12.5	0.28	3.73	7.63	3.66	1.12	1.57	- 0.65	98.6	2.25
H17-3		50.2	3.13	14.0	13.5	0.29	4.13	7.81	3.48	1.03	0.82	- 0.38	97.9	2.06
H1554		49.7	3.32	13.9	13.8	0.29	4.34	8.14	3.49	1.03	0.95	- 0.47	98.5	2.07
Hek 9		47.4	4.38	13.2	15.3	0.28	5.05	8.98	2.97	0.79	0.70	- 0.64	98.3	1.59
Hek 18 ^ª	Basalte	47.3	4.66	13.2	15.3	0.25	5.17	9.23	3.03	0.67	0.61	0.35	99.8	1.34
Hek 16		45.6	4.68	13.2	15.7	0.26	5.65	9.66	2.79	0.67	0.56	- 0.63	98.1	1.34
Hek 28		46.2	3.54	14.1	16.4	0.26	6.18	9.92	2.9	0.56	0.42	0.12	100.6	1.12
Hek 10		46.0	2.82	15.0	14.4	0.22	7.32	10.8	2.56	0.44		0.14	99.7	0.88
Hek 4		46.0	2.37	16.0	13.0	0.2	7.73	11.2	2.42	0.4	0.27	0.14	99.7	0.80

Trace element concentrations of the Hekla magma suite. ICP-MS results.

Sample#	Li	Ве	Sc	Ti	V	Cr	Со	Ni	Cu	Ga	Rb	Sr	Y	Zr	Nb	Мо	Cd	Sn	Sb	Cs
Hek-4	4.54	0.90	31.0	14424	333	48.4	73.8	117	141	22.0	7.08	385	23.7	135	19.3	0.84	0.06	1.37	0.05	0.08
Hek-28	7.33	1.36	34.1	21760	467	29.0	83.3	66.33	186	26.4	10.3	361	36.0	209	29.1	1.25	0.07	1.81	0.06	0.12
Hek-35	7.57	1.49	33.9	22691	465	24.9	61.4	64.37	179	26.2	10.9	356	39.1	226	31.8	1.29	0.07	1.95	0.06	0.12
Hek-18	8.34	1.65	35.2	27605	368	8.3	51.6	11.22	32.6	26.3	12.2	364	45.6	264	41.4	1.49	0.09	2.12	0.07	0.17
H17-1	15.5	2.8	22.1	13928	135	8.95	26.7	22.2	41.0	28.2	22.1	373	71.6	498	55.3	2.43	0.283	3.47	0.08	0.282
Hek-11	12.8	2.59	23.9	14566	90.7	0.586	21.1	0.51	13.7	29.2	22.1	377	75.1	427	57.0	2.51	0.13	3.10	0.12	0.27
HY-b	15.4	2.87	23.1	12945	83.5	1.93	23.2	3.12	17.1	30.6	24.4	393	74.8	444	60.9	2.66	0.13	3.42	0.14	0.29
H1846-L	14.5	2.95	22.9	11565	51.4	2.95	15.4	0.39	10.4	31.1	25.4	394	75.6	460	66.6	2.95	0.14	3.40	0.15	0.29
H-2000	14.6	2.91	24.7	13151	70.9	1.10	55.7	0.60	14.8	32.0	25.7	394	76.4	458	66.8	2.96	0.15	3.43	0.16	0.30
НХ-В	15.3	2.93	18.8	12260	91.7	0.486	20.2	2.94	26.4	28.7	25.5	383	74.4	443	59.2	2.46	0.185	3.84	0.10	0.34
H1300-L	15.1	3.08	22.4	10893	32.9	1.51	15.1	0.37	13.4	31.7	26.8	393	76.9	474	67.8	2.96	0.14	3.58	0.15	0.31
Н4-Т	20.6	3.26	21.7	7122	10.5	3.42	10.3	1.20	18.2	30.7	31.8	342	75.9	670	60.9	3.33	0.17	3.85	0.17	0.39
H1947-A	19.5	3.47	19.3	7395	17.1	1.97	8.7	1.19	40.2	32.1	34.5	366	74.4	542	70.2	3.37	0.16	9.20	0.23	0.42
H1300-M	19.4	3.61	20.6	7038	18.1	2.28	34.8	2.54	18.0	32.1	34.8	354	77.8	565	72.1	3.55	0.17	4.33	0.21	0.42
HX-A	23.4	3.23	14.4	6767	37	0.833	12.6	1.92	28.1	27.9	35.3	336	69.5	493	54.6	2.89	0.194	4.41	0.14	0.52
H1947F	22.3	3.8	17.2	6244	9.44	1.99	7.06	6.31	11.0	31.0	36.2	345	81.8	588	75.9	3.36	0.249	5.15	0.17	0.49
HY-a	22.2	2.91	13.2	5666	35.0	1.04	10.5	2.99	31.4	24.2	35.9	296	57.3	432	44.5	2.68	0.16	3.84	0.15	0.55
H4-3	25.5	4.19	21.5	3206	3.27	0.519	1.93	2.96	19.6	28.6	40.5	263	89.7	1166	73.4	4.12	0.40	4.89	0.14	0.53
Hek-8	24.9	4.11	15.2	4018	0.898	2.67	3.54	0.27	15.5	29.4	42.4	293	81.2	655	73.7	3.89	0.24	3.94	0.16	0.54
H3 Haf	29.0	4.45	11.1	2116	0.682	0.327	23.4	0.51	17.3	27.5	49.8	230	86.9	602	73.7	4.20	0.23	30.0	0.18	0.67
H1104-A	28.1	4.43	11.3	2470	0.795	0.031	24.0	0.68	15.1	29.0	50.5	239	82.5	674	75.6	4.27	0.26	5.69	0.19	0.68
H4-7	35.8	5.02	4.88	895	4.90	1.09	24.8	2.03	20.3	26.5	61.7	112	96.6	326	90.1	4.78	0.18	7.57	0.24	0.81
H5-A	36.1	4.34	6.16	939	4.54	3.56	1.30	4.35	16.3	25.0	58.8	137	84.0	281	73.6	4.21	0.15	6.86	0.21	0.79
H4-5	36.1	5.18	4.45	917	2.69	0.865	25.5	1.19	15.4	28.1	60.6	124	96.4	292	91.8	4.85	0.17	7.42	0.23	0.80

Sample#	Ва	La	Ce	Pr	Nd	Sm	Eu	Tb	Gd	Dv	Но	Er	Tm	Yb	Lu	Hf	Та	W	TI	Pb	Th	U	Mill type
Hek-4	107	14.0	32.8	4.51	20.3	4.90	1.72	0.78	5.16	4.69	0.90	2.37	0.314	1.97	0.278	3.42	1.31	83.8	0.014	1.15	1.14	0.336	WC
Hek-28	150	21.2	49.4	6.73	29.9	7.26	2.47	1.15	7.58	6.86	1.32	3.63	0.495	3.09	0.438	5.14	1.95	113	0.018	1.56	1.69	0.509	WC
Hek-35	159	23.0	54.4	7.29	32.4	7.79	2.63	1.25	8.32	7.44	1.45	3.94	0.531	3.35	0.481	5.55	1.96	0.30	0.019	1.65	1.84	0.557	Agat
Hek-18	185	27.5	65.7	8.68	39.0	9.27	3.17	1.47	9.76	8.74	1.69	4.57	0.606	3.86	0.551	6.46	2.62	0.36	0.065	1.73	2.12	0.632	Agat
H17-1	290	45.1	106	13.5	58.7	13.5	4.05	2.12	13.7	12.2	2.42	6.57	0.923	5.81	0.884	11.5	2.88	0.57	0.053	3.01	4.06	1.25	Agat
Hek-11	302	49.3	115	15.3	67.7	15.9	4.74	2.34	16.1	13.9	2.71	7.29	0.975	6.29	0.896	10.2	3.36	0.60	0.066	3.54	4.09	1.19	Agat
HY-b	326	49.7	116	15.2	66.2	15.4	4.74	2.32	15.6	13.6	2.64	7.24	0.977	6.30	0.893	10.6	3.63	19.9	0.054	3.60	4.34	1.26	wc
H1846-L	346	52.5	120	15.5	67.4	15.4	4.82	2.36	15.8	13.9	2.72	7.36	1.01	6.36	0.910	11.0	3.73	0.75	0.057	3.66	4.48	1.33	Agat
H-2000	345	52.5	119	15.6	67.4	15.4	4.80	2.35	15.9	14.0	2.70	7.36	1.01	6.36	0.901	10.9	4.01	283	0.060	3.74	4.56	1.34	wc
НХ-В	320	49.2	114	14.4	62.2	14.4	4.31	2.20	14.5	12.9	2.53	6.83	0.968	6	0.911	10.6	3.11	0.67	0.382	3.41	4.65	1.37	Agat
H1300-L	359	54.2	123	15.9	68.9	15.7	4.87	2.38	16.0	14.2	2.78	7.55	1.04	6.60	0.945	11.5	3.82	0.77	0.093	3.91	4.80	1.41	Agat
Н4-Т	406	56.4	123	15.4	64.9	14.6	4.48	2.21	14.6	13.3	2.64	7.44	1.06	6.93	1.040	15.2	3.53	0.79	0.343	4.70	5.95	1.74	Agat
H1947-A	433	57.6	124	15.6	65.0	14.6	4.43	2.21	14.5	13.3	2.65	7.39	1.04	6.73	0.987	13.1	3.96	0.93	0.200	8.31	6.19	1.77	Agat
H1300-M	436	59.6	130	16.2	67.5	15.1	4.53	2.30	15.1	14.0	2.78	7.71	1.09	7.02	1.03	13.7	4.24	105	0.116	4.94	6.27	1.80	WC
HX-A	402	51.3	113	13.6	55.3	12.3	3.62	1.92	12.2	11.4	2.29	6.44	0.930	5.97	0.909	11.9	2.89	0.91	0.118	4.49	6.30	1.85	Agat
H1947F	439	61.6	133	16.2	66.8	14.9	4.33	2.32	14.7	13.7	2.74	7.66	1.10	7.04	1.07	14.1	3.70	0.97	0.101	5.04	6.44	1.93	Agat
HY-a	394	48.1	102	12.0	48.1	10.5	2.89	1.63	10.3	9.82	1.95	5.57	0.81	5.18	0.81	10.4	2.85	0.94	0.238	4.48	6.70	1.93	Agat
H4-3	479	68.2	145	17.4	70.7	15.5	4.01	2.44	15.1	14.7	3.00	8.74	1.32	8.66	1.38	25.2	4.22	1.22	0.122	5.16	7.77	2.44	Agat
Hek-8	494	64.7	138	16.6	67.3	14.7	4.03	2.30	14.6	14.1	2.81	7.89	1.16	7.33	1.14	15.9	4.45	1.32	0.105	5.23	7.78	2.35	Agat
H3 Haf	568	72.3	151	17.7	69.9	15.1	3.41	2.38	14.7	14.4	2.90	8.28	1.24	7.93	1.22	15.2	4.67	63.1	0.164	6.23	9.09	2.65	WC
H1104-A	567	69.9	146	17.2	68.5	14.9	3.59	2.29	14.4	14.0	2.80	7.91	1.18	7.54	1.14	16.8	4.75	54.3	0.149	6.11	9.22	2.68	WC
H4-7	670	65.7	143	16.9	67.8	15.5	2.67	2.61	15.8	16.1	3.22	9.23	1.35	8.65	1.26	11.4	5.58	83.4	0.253	7.98	10.6	3.16	WC
H5-A	636	70.0	146	16.8	65.7	14.2	2.56	2.27	14.0	14.0	2.81	8.01	1.17	7.57	1.12	9.53	4.74	1.87	2.35	7.83	10.7	3.03	Agat
H4-5	665	90.7	185	21.4	83.0	17.4	2.88	2.69	16.5	16.1	3.20	9.11	1.31	8.39	1.24	10.2	5.53	103.32	0.18	15.37	11.2	3.00	wc

Uranium and Th concentrations and Th isotope ratios in Hekla volcanics.

Results from Sigmarsson et al. (1991, 1992) together with additional recounted 230 Th/ 232 Th and new MC-ICP-MS measurements. Concentrations measured by isotope dilution mass spectrometry. All new results are in italics. Age is given as calibrated age before 2000 or as eruption date CE.

Sample	Eruption		D .(Bash a sa	U	Th	T L (1)	,238. , ,232	,230	232 、	
number	unit ¹	Age	Ref.	Rock type	(ppm)	(ppm)	Th/U	(²⁰⁰ U/ ²⁰² Th)	(Th/	Th)	Sample locality
Hekla volcano										1σ error	
H5-A	Hekla-5	7100 yrs	1	Rhyolite	2.76	10.20	3.700	0.820	0.973	± 0.005	Sauðafell
Н5-В	Hekla-6	7100 yrs	1	Rhyolite	2.78	10.10	3.630	0.836	0.964	± 0.005	н
H4-7	Hekla-5	4250 yrs	1.2	Rhyolite	3.03	10.40	3.430	0.885	0.970	± 0.010	Sigalda
H4-5	Hekla-4	4250 yrs	1.2	Rhyolite	2.99	11.20	3.730	0.813	0.956	± 0.009	п
H4-3	Hekla-4	4250 yrs	1.2	Dacite	2.49	7.85	3.150	0.963	0.970	± 0.010	н
H4-2	Hekla-4	4250 yrs	1.2	Andesite	2.22	6.76	3.040	0.998	0.978	± 0.009	н
Н4-Т	Hekla-4	4250 yrs	1.2	Andesite	1.79	5.78	3.230	0.939	0.994*	± 0.006	
H2	Hekla-S	3850 yrs	3	Dacite	2.56	8.90	3.480	0.872	0.977	± 0.009	Ofan á Kothrauni
Н3-В	Hekla-3	3050 yrs	1.2	Dacite	2.64	9.20	3.490	0.869	0.990	± 0.010	
H3-Haf	Hekla-3	3050 yrs	1.2	Dacite	2.59	9.08	3.510	0.864			Haf
Н3-Т	Hekla-3	3050 yrs	1.2	Dacite	2.12	7.13	3.360	0.903	0.980	± 0.010	
НС-Т	Hekla-C	2840 yrs	4	Basaltic andesite	1.34	4.36	3.250	0.934	1.034	± 0.008	Helliskvísl
НС-В	Hekla-C	2840 yrs	4	Andesite	2.00	6.62	3.310	0.917	0.991**		"
НВ-Т	Hekla-B	2800 yrs	4	Basaltic andesite	1.33	4.30	3.230	0.939	1.025	± 0.007	
HB-B	Hekla-B	2800 yrs	4	Andesite	1.96	6.39	3.260	0.931	0.986**		"
HY-b ²	Hekla-Y	2680 yrs	4	Basaltic andesite	1.30	4.21	3.250	0.934	1.030	± 0.007	Frostastaðavatn
HY-a ²	Hekla-Y	2680 yrs	4	Andesite	1.94	6.68	3.440	0.882	0.939	± 0.005	"
HY-aa	Hekla-Y	2680 yrs	4	Andesite	1.95	6.73	3.45	0.879	0.93	± 0.007	N of Hrafntinnuhraun
HX-b	Hekla-X	2260 yrs	4	Basaltic andesite	1.38	4.57	3.310	0.917	1.014	± 0.010	Frostastaðavatn "
HX-a	Hekla-X	2260 yrs	4	Andesite	1.81	6.15	3.400	0.892	0.947	± 0.009	"
H1104-A	Hekla-1104	1104 CE	5	Dacite	2.66	9.34	3.510	0.864	0.973*	± 0.004	Haf
H1104m	Hekla-1104	1104 CE	5	Dacite	2.57	9.03	3.520	0.862	0.970	± 0.010	Haf
H1158-A	Hekla-1158	1158 CE	6	Dacite	2.33	7.90	3.390	0.895	0.986	± 0.005	Skjólkviar
H1158	Hekla-1158	1158 CE	6	Dacite	2.32	7.80	3.360	0.903	0.007*		Skjölkviar
нек-8	Haanraun	1158 CE?	/	Dacite	2.31	7.75	3.360	0.903	0.987*	± 0.007	Haanraun
Hek-25	Erranvoisnraur	1200 CE ?	F	Andesite	1.02	5.29	3.270	0.928	1 000	+ 0.010	Ch Sälvahraun
	Hekia-1300	1300 CE	5	Andesite	1.83	0.00	3.320	0.914	1.000	± 0.010	Un Solvanraun
H1300-1	1200 Java	1300 CE	5	Andesite Basaltia andosito	1.78	5.88	3.300	0.919	1.000	± 0.010	Suðurbraun
	1300 lava	1300 CE	5	Basaltic andesite	1.47	4.77	2 260	0.930	1.020*	± 0.000	Norðurhraun
H1590L	1509 lava	1509 CE	5	Andosite	1.40	4.70 6.44	2 220	0.931	1.021		Hollo
H1510-A	Hekla-1510	1510 CE	5	Andesite	1.95	6 39	3 320	0.914			Svikatorfa
H1510-R	Hekla-1510	1510 CE	5	Andesite	1.52	6.00	3 380	0.898	1 014	+ 0 007	Kothraun
H1636	Hekla-1636	1636 CF	5	Andesite	1.62	5.28	3.260	0.931	1.030	+ 0.010	F off Lambafitiahraun
H1693L	1693 Java	1693 CF	5	Andesite	1.67	5.52	3.300	0.919	2.000	- 0.010	In between Rauðöldur
H1693-B	Hekla 1693	1693 CE	5	Andesite	1.67	5.50	3.290	0.922	1.018	+ 0.007	Haf?
H1766-A	Hekla 1766	1766 CE	5	Andesite	1.78	5.83	3.280	0.925	1.030	± 0.010	Búrfellsháls
H1768L	1766 lava	1767 CE	5	Basaltic andesite	1.40	4.53	3.220	0.942	1.04*	± 0.006	Sunnan Háahrauns
H1845-a	Hekla-1845	1845 CE	5	Andesite	1.80	6.10	3.380	0.898	0.962	± 0.010	N af Hrafntinnuhrauni
H1846-L	1846 lava	1845 CE	5	Basaltic andesite	1.41	4.55	3.240	0.936	1.040	± 0.010	Close to old Næfurholt
H1947-A	Hekla-1947	1947 CE	8	Andesite	1.84	5.94	3.240	0.936	1.000	± 0.008	Vestman Islands
H1947-La	1947 lava	1947 CE	8	Basaltic andesite	1.51	4.81	3.210	0.945	1.020	± 0.010	At Rauðöldur
H1970-8	Hekla-1970	1970 CE	9	Xenolith	3.79	12.80	3.360	0.903	0.921	± 0.003	Skjólkvíar
H1970-72	Hekla-1970	1970 CE	9	Dacite	2.47	8.33	3.370	0.900	0.97*	± 0.010	н
H1970-14	Hekla-1970	1970 CE	9	Basaltic andesite	1.36	4.48	3.290	0.922	1.050	± 0.010	н
H1980	Hekla-1980	1980 CE	10	Basaltic andesite	1.41	4.57	3.250	0.934	1.023	± 0.005	Rángárbotn
H81L	1981 lava	1981 CE	10	Basaltic andesite	1.41	4.58	3.240	0.936			Hekla slope
H1991	Hekla-1991	1991 CE	11	Basaltic andesite	1.36	4.43	3.250	0.934			Landmannaleið
H2000	Hekla-2000	2000 CE	12	Basaltic andesite	1.39	4.52	3.250	0.934			н
Vicinity of Heklo	7										
Hek-9	Lava 012	1913 CE	13	Basalt	0.745	2.38	3.19	0.951	1.06*	± 0.007	S off Mundafell
Hek-18	Lava 075	1878 CE	13	Basalt	0.650	2.07	3.190	0.951	1.06*	± 0.007	Nýjahraun
Hek-1554	Lava 447	1554 CE	13	Basalt	0.965	3.1	3.21	0.945	1.053		Pálssteinshraun
duplicate				Basalt					1.053		
H1725	Lava 252	1725	13	Basalt	0.600	1.9	3.18	0.954			

r and Rauðölduhnjúkur

Hek-17	Lava 235	< 1500 yrs	13.14	Basalt	0.505	1.62	3.22	0.942	1.08*	± 0.007	Helliskvíslarhraun
Hek-14	Lava 033 (HH6)	< 1500 yrs	13.14	Basalt	0.446	1.41	3.17	0.957			Stakahraun
Hek-15	Lava 014 (HH7)	< 1500 yrs	13.14	Basalt	0.537	1.73	3.22	0.942	1.11	± 0.020	Taglgígahraun
Hek-21	Lava 069 (Sölva	< 1500 yrs	13.14	Basaltic andesite	1.16	3.75	3.22	0.942	1.04	± 0.010	Sölvahraun
Hek-26	Lava 482	unknown	13	Basaltic andesite	1.22	3.9	3.2	0.948	1.06	± 0.010	Under 1970CE lava at Sauða
Hek-1	Lava 239	< 2000 yrs	13	Basalt	0.827	2.64	3.19	0.951	1.06	± 0.010	Eldiviðarhraun
Hek-27	Lava 230	< 3000 yrs	13	Basalt	0.883	2.82	3.200	0.948	1.060	± 0.010	Rauðkembingahraun
Hek-11	Valagjá 017	< 4250 yrs	15	Basaltic andesite	1.24	3.98	3.22	0.942	1.02	± 0.010	Valagjá
Hek-29	Lava HH8	< 5500 yrs	16	Basalt	0.543	1.75	3.22	0.942			Old cross-road to Sigalda
Hek-2	Lava 109	~ 7000 yrs	13	Basalt	0.537	1.72	3.2	0.948	1.067**		Bæjarhraun
duplicate	Lava 109	~ 7000 yrs	13	Basalt					1.065**		Bæjarhraun
Hek-28	Lava 107	> 7000 yrs	13	Basalt	0.519	1.66	3.190	0.951	1.066*	± 0.007	Krókahraun
Hek-30	Hekla ridge	unknown	15	Basaltic andesite	1.35	4.35	3.22	0.942			Crater rim on N Hekla ridge
H17-2	Rauðaskál crat	unknown	15	Basaltic andesite	1.24	3.95	3.20	0.949			Rauðaskál at Skjólkvíar
H17-3		unknown	15	Basalt	1.01	3.22	3.18	0.953	1.046**		S off Rauðuskál
duplicate									1.046**		
Hek-4	Selsundsfjall	Pleistocene	7, 13	Basalt	0.329	1.08	3.280	0.925	1.060	± 0.010	Selsundsfjall
Hek-5	Bjólfell	Pleistocene	7, 13	Basalt	0.310	1.04	3.35	0.906	1.09	± 0.010	Bjólfell
Hek-10	Mundafell	Pleistocene	7	Basalt	0.382	1.23	3.220	0.942	1.120	± 0.010	Mundafell pillow fragment
Hek-13	Móhnjúkar	Pleistocene	7	Basalt	0.328	1.09	3.32	0.914	1.11	± 0.010	N Móhnjúkar pillow fragmer
Hek-19	Valahnjúkur	Pleistocene	7	Basalt	0.332	1.07	3.22	0.942			Valahnjúkur pillow fragment
Hek-32	Hestalda	Pleistocene	7	Basalt	0.332	1.08	3.26	0.931	1.08	± 0.015	Hestalda pillow fragment
Hek-33	Litla Hekla	Pleistocene	7	Basalt	0.319	1.14	3.580	0.847			Litla-Hekla

¹tephra has Hekla prefix

²HY-a and -b initially mapped as HZ-a and -b and published as such by Sigmarsson et al. (1991)

* lpha recount

**new MC-ICP-MS results. 2σ uncertainty < 1%

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. Iceland GeoSurvey, Iceland Power Company and Ministry for the Environment and Natural Resources.











Online resource 5 for CMP paper: **The Hekla magma suite revisited** Olgeir Sigmarsson (o.sigmarsson@opgc.fr; olgeir@hi.is), Ingibjörg A. Berg

								Partit	ion coefficien	ts D (min	/melt)																
			Plagio	oclase					Срх				Olivine	9			Apatite							Melt on	nly concentrati	on (ppm)	
Element	H1913 mean 1 c	σ error	H1970 mean 1	1 σ error	H1158 mean	1 σ error	H1913 mean 1 c	o error	H1158 mean 1 c	o error	H3 mean 1	σ error	H1970 mean 1 σ	error	H1970 mean 1σ	error	H1158 mean 1 o	error	H3 mean 1 d	σ error	H1913	1σ error	H1970	1σ	error H1158	3 1 c	Jerror H3
Li7	0.8	0.1	2		1 0.3	36 0.03	3 0.43	0.06	0.16	0.02	0.24	0.10	0.11	0.03							7.	0 0	.5	60	6	27	2
Sc45	0.03	0.01	0.12	0.0	4 0.0	0.02	2 3.8	0.2	13.1	0.8	29	3	0.54	0.04							3	0	1	24	1	16.1	0.8
Cr53							100	33														8	2			22	5
Co59	0.021	0.003	3		0.2	20 0.05	5 1.13	0.05	8.3	0.8											5	0	2			1.9	0.2
Ni60	0.21	0.09)				7.69	1.95													2	3	4 12	.06	5.67	12	4
Rb85																	0.02	0.01								48	9
Sr88	1.53	0.09	2.6	0	1 3	.7 0.2	2 0.075	0.004	0.14	0.01	0.15	0.01	0.006	0.001	1.84	0.09	2.4	0.3	2.7	0.2	42	.6 1	.8 3	327	11	233	19
Y89	0.005	0.001	0.022	0.00	2 0.00	0.002	1 0.66	0.03	1.66	0.08	1.57	0.08	0.018	0.002	9.1	0.5	17	2	26	2	3	9	1	72	3	77	5
Zr90																	0.12	0.05								581	121
Nb93	0.0013	0.0004	ŀ		0.000	0.0002	2 0.032	0.002	0.011	0.001							0.01	0.01			3	4	1			73	6
Ba137	0.33	0.02	0.32	0.0	3 0.2	26 0.02	1 0.028	0.002	0.005	0.0004			0.002	0.001	0.03	0.01	0.02	0.01	0.05	0.02	18	0	8 3	367	21	529	48
La139	0.042	0.003	3		0.06	56 0.003	3 0.083	0.004	0.26	0.01					7.1	0.4	13	2	20	2	28.	5 0	.9	57	3	66	5
Ce140	0.030	0.002	0.043	0.00	3 0.04	15 0.002	2 0.13	0.01	0.47	0.02	0.41	0.02	0.010	0.001	8.7	0.4	16	3	27	2	6	8	2 1	129	5	143	13
Pr141															9.9	0.5	20	3	35	3			1	7.0	0.7	17	2
Nd146															12.1	0.8	25	5	37	3				73	4	67	11
Sm147	0.015	0.004	0.04	0.0	1 0.02	21 0.004	4 0.41	0.02	1.62	0.09	1.7	0.1	0.05	0.01	13	1	24	4	38	5	10.	1 0	.4 1	7.0	0.9	16	2
Eu153	0.14	0.01	0.37	0.0	4 1.2	21 0.08	8 0.43	0.03	1.05	0.07	0.98	0.08	0.02	0.01							3.	4 0	.1	5.1	0.3	3.6	0.2
Gd157			0.05	0.0	2 0.0	0.02	1 0.54	0.04	1.9	0.1	1.96	0.15			13	1	25	5	41	8	10.	0 0	.5	17	1	16	2
Yb172	0.02	0.01	L		0.00	0.003	3 0.69	0.05	1.6	0.1	1.70	0.15	0.06	0.02	4.9	0.4	9	2	13	2	3.	1 0	.2	6.8	0.4	7.7	0.9
Hf178	0.06	0.02	0.03	0.0	1		0.44	0.06	0.4	0.1	0.38	0.03	0.02	0.01							5.	8 0	.3 1	2.1	0.6	15.4	0.8
Ta181			0.03	0.0	1 0.00	0.002	2 0.05	0.03	0.02	0.03	0.010	0.004									2.	1 0	.1	4.1	0.2	3.9	0.2
Lu175							0.72	0.01	1.698	0.003					4.3	0.4	7	1	8	1	0.4	2 0.0)2	1.1	0.1	1.2	0.2
Th232			0.006	0.00	3 0.00	0.000	5 0.032	0.004	0.024	0.002	0.004	0.001	0.001	0.001	0.80	0.06	1.3	0.2	1.9	0.2	2.	5 0	.2	5.0	0.2	8.6	0.8
U238	0.005	0.002	2		0.00	0.002	2 0.028	0.004	0.023	0.002					0.95	0.11	1.4	0.2	1.9	0.2	0.7	4 0.0)5	1.5	0.1	2.4	0.2
DTh/DU					0.2	21 0.13	3 1.13	0.41	1.05	0.26					0.84	0.23	0.95	0.38	0.97	0.32							

Analytical error calculated for each measured partition coefficient,

D = mineral/melt as:

$$\Delta D = |D| * \sqrt{(\frac{\delta mineral}{mineral})^2 + (\frac{\delta melt}{melt})^2}$$

Average propagated error for each sample is listed in the Table.

3		1σ error	
	39		9
	10.5		0.9
	32		13
	161		7
	74		3
	600		26
	75		6
	151		7
	18		1
	76		7
	15		1
	3.1		0.2
	14		1
	7.6		0.6
	10.4		0.5
	4.1		0.2
	1.6		0.2
	9.3		0.6
	3.4		0.3