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Abstract: Major and trace element compositions of amphibole in igneous
environments commonly reflect evolving magma compositions. In this study,
we use the amphibole-group minerals from the Strange Lake, REE-enriched
peralkaline granitic pluton to gain insights into the evolution of the
magma. This 1240 Ma old pluton consists of two main intrusive facies, an
early hypersolvus granite, which occurs as separate northern and southern
intrusions, and a more evolved transsolvus granite. In the hypersolvus
granite the amphibole is a late interstitial phase, whereas in the
transsolvus granite, it is present as phenocrysts. The amphibole
compositions vary from calcic-sodic (ferro-ferri-katophorite) in the
southern hypersolvus granite to sodic (arfvedsonite, ferro-ferri-
leakeite) in the other, more evolved granitic units. High Na, Si, Li, and
low Al and Ca concentrations in the amphibole phenocrysts of the
transsolvus granite indicate formation from a more evolved magma compared
to the hypersolvus granite, despite the fact that these crystals formed
early. We interpret the increasing Fe^{3+}/Fe^{2+} ratios in the amphibole of
the hypersolvus granite to reflect crystal chemical effects (Na/Ca-ratio)
and increasingly oxidizing conditions in the magma, whereas in the
phenocrysts of the transsolvus granite, the increasing ratio was the
product of increasing proportions of F^- and OH^- in the melt. The
amphiboles of all the granite units have elevated Nb, Zr, Hf and REE
concentrations compared to the bulk rock, suggesting that these elements
are compatible in amphibole. By contrast the much lower Ti concentration
was due to saturation of the magma in sodium-titanosilicates. The
amphibole REE concentrations vary greatly among the granite units.
Amphibole of the southern and northern hypersolvus granite contains 0.16
and 0.07 wt. % ∑REE+Y, on average, respectively, and in the transsolvus
granite, the average ∑REE content is only 0.01 wt. %, despite the more
evolved nature of its host transsolvus granite. We intrepret this
compositional difference to be due to the fact that the latter represents
phenocrysts, which crystallised early, whereas the hypersolvus
arfvedsonite is a late interstitial phase. Chondrite-normalized REE
profiles emphasise the wide range in LREE-, and the narrow range in HREE-
concentrations of the amphiboles. The variations in the LREE-profiles
reflect the variable crystallization of primary LREE-bearing phases,

including monazite-(Ce), pyrochlore group minerals and gagarinite-(Ce), prior to or contemporaneous with the amphibole, as well as the exsolution of a LREE-rich fluoride melt. The LREE are incompatible in the amphibole structure (apparent D < 0.01) and are preferably accommodated by the octahedral C-site, whereas the HREE occupy the B-site. The chondrite-normalized HREE profiles are steep and display an increasing relative enrichment that culminates in compatible behavior for Yb and Lu (apparent D >1). Owing to their small ionic radius and their compatibility with the amphibole structure, HREE concentrations were more controlled by partitioning (crystal chemical effects) than by the concentrations in the corresponding magma. Large proportions of the bulk HREE content (up to 70 %) reside in the amphibole, and their later release through hydrothermal replacement helps to explain the extreme and unusual HREE enrichment of the Strange Lake pluton.

RESPONSE TO EDITOR AND REVIEWERS

We are encouraged that Editor Nelson Eby and the two reviewers consider our manuscript merits publication after moderate revision. Below, we systematically address the minor points raised by the editor and reviewer #1, and then the more specific points raised by reviewer #2.

EDITOR COMMENTS

1) Sections need to be numbered.

Sections have been numbered.

2) Line 23 - NEVER cite "in prep" in a manuscript. Citation found in a number of places. Remove.

Citations removed.

3) Starting on line 229, multiple repeats of the same line. Same problem starting on line 247.

Repetitions removed

4) How was the Fe2+/Fe3+ ratio calculated.

The ratio was calculated from apfu numbers, which were obtained from the formula calculations.

5) Tables 2 - 5 - better to give all the analyses in supplemental data tables rather than averages which are essentially useless information.

We have added values for the median and median absolute deviation to the tables to address this concern and provided the full dataset in supplemental tables.

6) Mayer et al. reference incomplete.

Reference corrected.

REVIEWER #1

General comments of reviewer #1:

The manuscript is well written, data are of high quality and results are supported by data. Discussion is rigorous and methods are correct. In general, the manuscript does not bring much new knowledge on amphibole crystal chemistry and on magma evolution in peralkaline systems. However, I consider the manuscript an important contribution for the international scientific community and worth to be published in Lithos because it is a positive attempt to link amphibole crystal chemistry to igneous evolution of peralkaline melts. The manuscript is probably too long and would benefit, in order to increase its readability, of a significant shortening. I thus suggest to the authors to operate a shortening of the text in all sections. The number of figures is also excessive and should be shortened (figure 6, 9, 10, 11a for example are not strictly necessary). I consider the manuscript worth of publication after minor to moderate revision.

We have been able to make a minor reduction in the overall length of the manuscript and have removed Figures 9 and 11a. However, we consider Figure 6 and 10 necessary to support our conclusions. The figure numbers have been adapted (new total of 15 figures).

The authors should also consider to revise the conclusions based on the core to rim variations observed in amphibole phenocrysts because the trends they describe are in most cases very poorly constrained. For most of the elements there is complete overlap between core and rim.

We disagree. Although there is some overlap between core and rim concentrations, there is still an obvious trend to more evolved compositions (see Fig. 6 and Table 5) in the phenocryst rims.

Additional comments

Line 23. Remove this sentence because it refers to a paper in progress.

The first part of the sentence was removed. However, the second part is necessary in order to provide a quick overview of the main findings of the study.

Line 65-66. Remove this sentence because it refers to a paper in progress.

Sentence deleted.

Line 168. Remove this sentence because it refers to a paper in progress.

Sentence deleted.

Lines 225-243. Check repetitions.

Repetitions deleted.

Lines 248-263. Check repetitions.

Repetitions deleted.

Lines 482-486. Remove this sentence because it refers to a paper in progress.

The first part of the sentence was removed.

Lines 488-489. This sentence is generic. In Ca-amphiboles Ti is generally compatible, the authors should specify which system they are referring to.

Sentence rephrased.

Line 514. Remove reference to work in progress.

Reference removed.

Line 532. "in" not necessary

Word removed.

Lines 614-615. This sentence should be better explained. In general, with the increasing of melt evolution (polymerization) network modifiers elements (such as REE) become more compatible in amphibole. Here authors suggest the opposite.

Sentence rephrased.

Lines 623-625. Not clear conclusion I suggest to remove this sentence.

The sentence is needed to provide linkage to the next paragraph. It has been rephrased, however, in order to make our point more clearly.

Lines 703-705. How quenching can modify the REE incorporation? More details are needed or the sentence should be removed.

The first part of the sentence was removed.

REVIEWER #2

General comments of reviewer #2:

I enjoyed reading this paper, which is well-written, but would like to have seen more context for your research, including more discussion of previous work and more clearly-developed science questions. I am surprised by the introduction of different granite terminology from all previous workers with no real explanation as to why you have made the change, and I would like to see some more petrographical descriptions to underpin the mineral chemistry.

These concerns are all addressed in the course of the following section.

Specific comments

Introduction, general: I agree that an extensive introduction to the REE as critical metals is not needed here, because the literature on this is pretty voluminous. However, I would like to see a few sentences explaining the economic value of the REE (and Nb and Zr) and something about the wider distribution and types of deposits, with some relevant references. This seems particularly appropriate as the project has been sponsored by Quest Rare Minerals.

We disagree. The focus of this manuscript is the nature of amphiboles from alkaline systems and their ability to host some of the HFSE rather than the economic value of the REE in general. Moreover, publications by our group have provided this information for Strange Lake, e.g., Gysi et al. (2016) published in the journal Economic Geology.

Intro, line 18: I find the phrase 'This magma ultimately produced a large REE/HFSE resource' a bit odd, partly because hydrothermal fluids that may or may not have been derived from the magma played quite a significant role in the formation of the Strange Lake deposit. I'd suggest rewording.

Sentence rephrased.

Intro, line 19: Resources are most commonly described in terms of total rare earth oxides - TREO (or in the case of Strange Lake, TREO + Y) - or sometimes as RE2O3. Not REEO3 please - this is incorrect.

Corrected.

Intro, line 21: You are referring to the current study, so I think you mean 'are used' not 'were used'. I was somewhat confused at first by this paragraph, which jumps from the results of this study, to published resource data, and then back to this study. Make sure your own work is distinct from previously published work.

Sentence rephrased.

Intro, line 23: Throughout the paper you refer to Siegel et al. (in prep) - please don't do this, as it is not a reference that the reader will be able to find. Remove all references to papers in prep - the current paper should be able to stand on its own, as you are publishing it first.

Reference removed.

Background, line 33: Note spelling of riebeckite

Corrected.

Background, line 51-52: Please cite some other papers here describing Strange Lake. Where were the different granites first described?

The words 'this study' were added to the sentence in order to clarify that the division of the hypersolvus granite into two units and the occurrence of a transsolvus granite (instead of subsolvus granite as described in earlier studies) are the result of this study and Siegel et al. (in prep.).

Background, line 55: I don't agree with the suggestion that the high concentration of REE in these pegmatites is rarely observed elsewhere. There are many magmatic-hosted REE deposits, some associated with pegmatites Ambohimirahavavy in Madagascar and Tamazeght in Morocco are some examples of alkaline intrusions with REE-enriched pegmatites. Please make sure you cite references for some of the other extensive research in similar magmatic-hydrothermal systems.

We are aware that there are other highly REE enriched magmatic-hydrothermal deposits. However, as the focus of the manuscript is the amphibole chemistry, we only cited work that uses amphibole compositions for understanding the deposit evolution. Also, Strange Lake is special because of its extreme HREE enrichment, something that is rarely observed elsewhere.

Background, line 64 "which accumulated in the highly evolved residual melts" - it's not clear what you are referring to here.

Clarified.

Intro and background, general: So much has already been written about Strange Lake and especially the interaction of magmatic and hydrothermal processes to generate the alteration, that I think you should state very clearly in this section why it is also important to study the magmatic minerals, and what questions you aim to answer in this work. This might only be a couple of sentences, but I think it would strengthen the paper.

We believe that we have addressed the importance of the amphibole study, which is clearly explained in lines 15 onwards.

Geologic setting, line 76-82: Could this background geology be shown on Fig 1, for example the extent of the Nain Plutonic Suite on the inset?

This would require an additional figure, as the Nain Plutonic Suite is too small to be visible on the inset in Fig. 1. Thus, Gower and Krogh, (2002) and Miller (1996) are cited where Strange Lake is shown in the context of the NPS.

Geologic setting, line 83: 'is hosted by' is ambiguous - do you mean 'intrudes'?

Rephrased.

Geologic setting, line 84: It would be nice to see reference here to some of the more recent research in the area, such as the Misery syenite for example, to give more context.

A reference to the Misery Lake intrusion has been added.

Geologic setting, line 90: again, 'other host' is unclear; wording such as 'country rock for the northern part of....' would be better

Rephrased.

Geologic setting, line 96: On what basis is it known to be the earliest phase of the pluton? Cite a reference. Overall this section needs more references, as you are describing previous work.

Reference added. Most of information on the Strange Lake pluton given in this section was gathered during the course of this study.

Geologic setting, line 98: On the map it looks like the central and southern part of the pluton, not just the central part

Rephrased.

Geologic setting, line 102: How small is small? 1m, 100m, 1 km?

This is not possible to define as there is very limited outcrop. The word 'smaller' refers to the previous sentence 'occupies the major part of the pluton'.

Geologic setting, line 105-106: Is this porphyritic granite shown on Fig. 1? I wonder if it might be the area shown as 'quench zone'? Make sure the map and text match

The term 'quench zone' has been replaced by 'dark grey granite' in Fig. 1.

Strange Lake Pluton, general: I compared your Fig. 1 with the map in Vasyukova and Williams-Jones 2016 and was surprised to see that the map is the same but the key is different. Your map indicates that most of the pluton is transsolvus granite, whilst hers shows it as subsolvus granite. A bit more checking shows that Gysi and Williams-Jones (2013) used a different map, but again

had the largest area as subsolvus granite, as did Salvi and Williams-Jones (2006), Boily and Williams-Jones (1994) - and all other workers. You may disagree with them all and have very good reasons for using a different classification of the granites, but you should explain why, and cite their work.

A clarification and citation of previous work was added to the text.

The terminology of the granite units was revised during the course of this study based on a careful petrological examination. A manuscript that explains new granite definitions is about to be submitted for publication.

Geologic setting, line 110-111: Divided by who? Is this your work? If so, make it clear that this subdivision is part of this study. If not, cite a reference. Note that by definition granite cannot be fine-grained - are you referring to a microgranite (medium-grained)? Please clarify this.

The subdivision is part of this study (clarified in text).

The term granite has been replaced by microgranite.

Geologic setting, line 124: What forms remnants in what?

Sentence rephrased.

Geologic setting, line 127: Try to ensure that your figures appear in the order they are referenced in the text - so 2d should not be referenced before 2c.

Figures 2c and d have been exchanged in the figure and text.

Geologic setting, line 138: What size are these enclaves? cm-scale, m-scale or larger? What are they made of, and what is the nature of their contacts? Either provide more description, or cite a reference in which they are described.

A more detailed description of the appearance of the enclaves was added. Their mineralogical composition had been described previously in line 177 ff.

Transsolvus granite, general: As mentioned above, most other workers distinguished a subsolvus granite which was highly altered, but lacked perthitic feldspar. You have used different terminology, implying that perthitic feldspar is present throughout the intrusion, and that there is an unaltered hypersolvus granite in the central part which becomes progressively more altered outwards. However the reason for this different terminology is not clearly described or explained, and in the section on the transsolvus granite it is not clear which parts of the description apply to the fresher core and which to the more altered part. This descriptive section really needs to be rewritten which reference to previous work, and a clear explanation of where and why your subdivisions of the pluton diverge from those of other workers.

See response to comment 'Strange Lake Pluton, general'

Geologic setting, line 163-173: Where is this porphyritic granite? It is not shown on Fig. 1. Is the intruding transsolvus granite part of the main transsolvus granite or something different? Please clarify as part of the rewrite of this section. Note that the enclaves should be described where they are first introduced.

The term quench zone in Figure 1 has been replaced by dark porphyritic microgranite. The description of the enclaves has been expanded.

Methods, material: It would be helpful if sample numbers were added to Fig. 1. I note that only averages are presented in the tables, but would suggest that the full datasets are made available as supplemental data. I would prefer to see a little more information about when the bulk-rock samples were analysed, what methods were used - is this sodium peroxide or lithium metaborate fusion? - and what QC was done (duplicate analyses etc.)

The full datasets are now reported as supplemental data. We have also added the median and median absolute deviation (mad) for the bulk rock and amphibole analyses (Tables 1, 4)

We consider the analytical information provided for the bulk rock analysis as sufficient.

Results, general: This section starts straight into the details of amphibole chemistry, with no description of the petrography of the samples that you are working on. You have studied a lot of samples, and whilst there is some general overview in the geologic setting section, it would be useful to give a brief petrographical summary of the actual samples that have been analysed, which will make the mineral chemistry easier to understand. For example, petrographic differences between the fine-grained and pegmatitic/oikocrystic variants of the southern hypersolvus granite have not been described in the geologic setting.

We consider that descriptions of the samples used in the study would unnecessarily lengthen the manuscript. All the granite types are described petrographically in the section 'geologic setting'. We have, however, added a more detailed description of the pegmatitic/oikocrystic samples of the southern hypersolvus granite in the geologic setting.

Results, line 224-243: In the pdf that I received, these lines are simply a continuous repeat of the references. This may be a problem in pdf creation, but needs to be checked. Lines 247-263 are the same.

Repetitions removed.

Results, line 284-286: What about tables 2 and 4? Tables should be numbered in the order they are cited in the text. You have presented whole-rock data for your samples but they are not separately described in the results section, and the major element data are not discussed at all. I

would recommend adding a brief stand-alone description of these data to provide context for the mineral chemistry.

A separate description of the major and trace element compositions of the samples used in this study was added in the results section (5.1). The table numbers have been adjusted and now appear in the order that they are cited in the text.

Results, line 291-292: You might want to state that here you have alkali feldspar phenocrysts, so it's a reasonable assumption that alkali feldspar fractionation was the main control - and so lower Al amphiboles are more evolved. It may seem obvious to you, but it can be useful to make the basis for your assumptions clear.

Information added as recommended.

Results, line 327: You haven't mentioned F (fig. 5h).

A statement on amphibole fluorine contents was added.

Results, line 328-337: Why did you choose to only plot cores and rims for the transsolvus granite - because this is the only unit with zoned phenocrysts? How large are these amphiboles? You state in the geologic setting that they form prismatic phenocrysts, but as mentioned above you have not described your samples in detail. A summary of basic petrographical information is necessary to underpin the mineral chemistry. Also note that on Fig. 6 core-rim pairs from the same crystal are not identified, so it is difficult to see if there is systematic variation. You might want to consider whether this would be useful.

Indeed the transsolvus granite is the only unit with amphibole phenocrysts. The size of these phenocrysts can be estimated from Figures 2c and 3c. We consider our sample description to be sufficient; additional description would unnecessarily extend the length of the manuscript.

The display of core-rim pairs for individual samples in Fig. 6 was considered, however too few analyses were performed to enable showing the differences within a sample. We consider that the displayed core-rim differences are sufficient to make the point that the rims are more evolved than the cores.

Results, line 344: 'average' - is this the mean value? I would guess so but it should be stated. It is interesting that the amphiboles in the fine-grained southern hypersolvus granite seem to be major contributors for the bulk-rock REE whereas in other variants other REE minerals are likely more important. As above, a petrographical description of the different variants, including discussion of their REE mineralogy, is needed to provide context here.

The 'average' is the median value, and this has been added in the text. As stated above, a detailed petrographical description of the granite variants is provided in the 'geologic setting' section.

Results, line 368: I'm not convinced by 'conspicuous exceptions' here. At least some of the rock types mentioned contain pyrochlore group minerals and zircon, and these would certainly accommodate Nb, Zr and Hf. Again, this discussion needs to be linked more clearly to the petrography of the analysed samples. In general, it looks as though the amphibole may be the major hosts of many trace elements in the southern hypersolvus granites, but less so in all other variants.

We agree that most of the Nb, Zr and Hf is preferentially accommodated by zircon, monazite-(Ce) and the pyrochlore group minerals at Strange Lake. The sentence has been modified accordingly. The 'conspicuous exceptions' statement is only to point out that the amphibole is also an important host for these elements in all granite units (see Figs. 7 b, d, f).

Results, line 379: If you are going to discuss lithium it should also be included in the figures.

The lithium (vs. Fe3+) content is displayed in Figure 11 (former Fig. 12).

Results, line 383: As individual samples are neither plotted for Li nor included in the table, there is no evidence for the extensive variation between different samples and crystals, except the fact that errors (presumably representing the range of values) are large. Plotting Li would help with this, as would including the full dataset as supplemental data.

As stated above, the lithium (vs. Fe^{3+}) content and its distribution among granite units is displayed in Figure 11 (former Fig. 12).

Discussion, line 399: Ferro-ferri-katophorite has only been described in the southern hypersolvus granite but is important for its high REE concentrations and seems to be the main REE-bearing mineral in this granite type, yet is only mentioned here as "minor (fluoro)-katophorite" - it would be very useful to see some clearer discussion of modal abundances of the different amphiboles in the rock.

Determining the modal abundances of the different amphibole is effectively impossible because they can only be distinguished on the basis of electron microprobe analyses. We have added the number of analyses (n) for each amphibole type measured per granite unit in the text.

Discussion, line 439: Please quote some of the many references giving evidence for exsolution of a hydrous fluid, for example the papers of Salvi and Williams-Jones. The existing models for the evolution of the Strange Lake pluton and mineral deposit should have already been discussed in more detail in the geologic setting section.

References have been added.

Discussion, line 445: What is the evidence that the enclaves represent the quenched margin of the transsolvus granite?

The sentence has been replaced by a more accurate and data-supported statement.

Discussion, line 459-460: Here you suggest a progressive change from the southern to the northern hypersolvus granite, but in line 428-429 you suggested that they are derived from separate magma batches. Certainly they are chemically quite different. It would be useful to include some discussion of their likely relationship - cogenetic or not? to provide context for the detailed chemistry.

The northern and southern hypersolvus granites do, indeed, represent two separate magma batches. The sentence has been changed accordingly.

Discussion, line 475-476: Here you say that the amphibole in the transsolvus granite occurs as phenocrysts, therefore crystallised too deep to have experienced fluid exsolution. However in line 438 you note depleted Na in the rims of these phenocrysts and suggest that this is due to fluid exsolution. These two statements seem to me to be contradictory and to need rethinking. Looking back at some published papers (e.g. Salvi & Williams-Jones 2006), I note that fluid exsolution is likely to have occurred below the temperatures of amphibole crystallisation, but to have caused alteration of amphiboles including Na-depletion - it would be useful for you to consider this previous work in your discussion.

We agree that the two statements contradict each other. We have rephrased the statements in both sections based on recent research indicating that the amphibole rims may have continued to crystallize after emplacement, during which the magma experienced degassing and oxidation.

Discussion, line 500: It's not entirely clear to me what has been done here - in line 495 you suggest that you used a spreadsheet to estimate the proportion of amphibole in each unit; is the 14 wt% amphibole mentioned in line 500 based on the calculations in this spreadsheet, or is it based on actual estimation from your thin sections? If the former, was it checked with the real samples? I may have misunderstood, in which case my apologies, but I think this could be written a bit more clearly.

The proportion of 14 wt. % amphibole is based on calculations using the MINSQ spreadsheet mentioned in line 500, and is in good agreement with visual estimates of several thin sections (~15 wt. %).

Discussion, line 548: You might want to make reference to, or comparison with the Pitinga rare-metal deposit, which is very similar to Strange Lake but even more lithium-enriched.

Although the Pitinga rare metal deposit may be lithium enriched, no study of the lithium content of the amphibole of this deposit has been reported and thus there seems no reason for referring to this deposit.

Discussion, line 624: It seems likely that as the magma evolved, another phase began to crystallise that preferentially incorporated the REE, for example allanite or monazite? The REE would be more compatible in this phase than in amphibole, thus leading to lower contents in

amphibole in all but the earliest hypersolvus granite. Ah - I see that you actually state this in line 689 - it might be worth proposing this earlier?

We consider that the issue has been addressed sufficiently.

Discussion, line 664-667: As you establish in the next paragraph, amphibole typically contains <10 % of the bulk-rock REE - perhaps not the 'significant proportion' stated here?

We disagree, the amphibole hosts up to 70 wt. % of the bulk HREE in some units.

Conclusions, general: Overall the conclusions are good, and well-developed from the evidence presented here. I note that you now describe a smooth process of evolution of the different granitic types, without mention of the possibility of different magma batches forming the two hypersolvus granites. Strange Lake is interesting because of the interplay of the magmatic and hydrothermal processes, and you have clearly demonstrated the magmatic background, but your final sentence is the key one. I think this paper could discuss the understanding of those hydrothermal processes just slightly more, as context for the importance of the magmatic story.

A statement to the effect that the intrusion of the hypersolvus granite occurred as two separate magma batches (south and north) has been added to the text. The focus of the paper is the magmatic evolution of Strange Lake. We therefore consider that the existing discussion of hydrothermal processes is sufficient.

Figure 1: Note spelling of quartz in key

Corrected.

The amphiboles of the REE-rich A-type peralkaline Strange Lake pluton – Fingerprints of magma evolution

Lithos

Karin Siegel, Anthony E. Williams-Jones, Vincent J. van Hinsberg

1

2 **ABSTRACT**

3 Major and trace element compositions of amphibole in igneous environments commonly reflect

4 evolving magma compositions. In this study, we use the amphibole-group minerals from the

5 Strange Lake, REE-enriched peralkaline granitic pluton to gain insights into the evolution of the

6 magma. This 1240 Ma old pluton consists of two main intrusive facies, an early hypersolvus

7 granite, which occurs as separate northern and southern intrusions, and a more evolved

8 transsolvus granite. In the hypersolvus granite the amphibole is a late interstitial phase, whereas

9 in the transsolvus granite, it is present as phenocrysts. The amphibole compositions vary from

10 calcic-sodic (ferro-ferri-katophorite) in the southern hypersolvus granite to sodic (arfvedsonite,

11 ferro-ferri-leakeite) in the other, more evolved granitic units. High Na, Si, Li, and low Al and Ca

12 concentrations in the amphibole phenocrysts of the transsolvus granite indicate formation from a

13 more evolved magma compared to the hypersolvus granite, despite the fact that these crystals

14 formed early. We interpret the increasing Fe^{3+}/Fe^{2+} ratios in the amphibole of the hypersolvus

15 granite to reflect crystal chemical effects (Na/Ca-ratio) and increasingly oxidizing conditions in

16 the magma, whereas in the phenocrysts of the transsolvus granite, the increasing ratio was the

17 product of increasing proportions of F^- and OH^- in the melt. The amphiboles of all the granite

18 units have elevated Nb, Zr, Hf and REE concentrations compared to the bulk rock, suggesting

19 that these elements are compatible in amphibole. By contrast the much lower Ti concentration

20 was due to saturation of the magma in sodium-titanosilicates. The amphibole REE

21 concentrations vary greatly among the granite units. Amphibole of the southern and northern

22 hypersolvus granite contains 0.16 and 0.07 wt. % $\sum$REE+Y, on average, respectively,

23

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24   and in the transsolvus granite, the average ∑REE content is only 0.01 wt. %, despite the more

25   evolved nature of its host transsolvus granite. We intrepret this compositional difference to be

26   due to the fact that the latter represents phenocrysts, which crystallised early, whereas the

27   hypersolvus arfvedsonite is a late interstitial phase. Chondrite-normalized REE profiles

28   emphasise the wide range in LREE-, and the narrow range in HREE-concentrations of the

29   amphiboles. The variations in the LREE-profiles reflect the variable crystallization of primary

30   LREE-bearing phases, including monazite-(Ce), pyrochlore group minerals and gagarinite-(Ce),

31   prior to or contemporaneous with the amphibole, as well as the exsolution of a LREE-rich

32   fluoride melt. The LREE are incompatible in the amphibole structure (apparent $D < 0.01$) and are

33   preferably accommodated by the octahedral C-site, whereas the HREE occupy the B-site. The

34   chondrite-normalized HREE profiles are steep and display an increasing relative enrichment that

35   culminates in compatible behavior for Yb and Lu (apparent $D > 1$). Owing to their small ionic

36   radius and their compatibility with the amphibole structure, HREE concentrations were more

37   controlled by partitioning (crystal chemical effects) than by the concentrations in the

38   corresponding magma. Large proportions of the bulk HREE content (up to 70 %) reside in the

39   amphibole, and their later release through hydrothermal replacement helps to explain the extreme

40   and unusual HREE enrichment of the Strange Lake pluton.

41

42   **KEYWORDS**

43   Amphibole, REE, Strange Lake, Peralkaline granite, Magma evolution

The amphiboles of the REE-rich A-type peralkaline Strange Lake pluton – Fingerprints of magma evolution

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Highlights

- Amphibole compositions reflect magmatic evolution of Strange Lake pluton

- Compositions run from calcic-sodic over sodic to sodic-lithic members with evolution

- Fe^{3+} concentration result of Na/Ca ratio, fO_2 and OH^- and F^- melt concentrations

- Incompatible LREE coupled to Ca concentration (B-site); HREE compatible with C-site

- Significant proportion of Strange Lake bulk HREE content carried by amphibole

THE AMPHIBOLES OF THE REE-RICH A-TYPE PERALKALINE STRANGE LAKE PLUTON – FINGERPRINTS OF MAGMA EVOLUTION

Lithos

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1. INTRODUCTION

2   Our understanding of the genesis of intra-plate rift-generated intrusions that produce A-type

3   granites is still incomplete. In particular, the reasons for the extremely high REE-, F- and other

4   HFSE-concentrations in many of these peralkaline rocks are poorly known. In addition to the

5   need for a highly fertile magma source, magmatic evolution by fractional crystallization appears

6   to play a critical role in the enrichment of these elements (e.g., Kovalenko et al., 1995; Mungall

7   and Martin, 1996). The chemistry of a major mineral, such as amphibole, which adapts to its *P-*

8   *T-X* environment, and is capable of hosting most cation sizes and charges, can potentially record

9   this and any other processes that might have operated in the magma chamber. As a phenocryst,

10   the amphibole would record the conditions prior to intrusion, and as a late crystallizing phase,

11   the in-situ crystal fractionation processes.

12   The well-known ability of minerals of the amphibole super-group to accommodate a wide

13   variety of elements with highly variable ionic radius and charge, including alkali elements, high

14   field strength elements (HFSE) and the rare earth elements (REE), makes it an ideal monitor of

15   magma evolution (Abdel-Rahman, 1994; Marks et al., 2004). In this study, we use the

16   occurrence and composition of amphibole-group minerals in the Strange Lake pluton, Québec-

17   Labrador, Canada, to trace the evolution of a peralkaline granitic magma that is unusually

18   enriched in the REE, Zr and Nb. This magma was the source of a large REE/HFSE resource

19   (indicated resources: 278 million tons grading 0.93 wt. % REE_2O_3, 0.18 wt. % Nb_2O_5 and 1.92

20   wt. % ZrO_2; Quest Rare Minerals Ltd., 2012) that is currently being considered for exploitation.

21   In this study, the Na, Ca, Li, Fe^{3+} and REE contents of the amphibole-group minerals are used to

22   gain information on the composition of the magma and conditions prior to, during and after its

23   emplacement. The results show that fractional crystallization of a perthitic alkali feldspar, gravity

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24   settling of REE-minerals and zircon as well as the exsolution of a LREE-rich fluoride melt

25   played a major role in the evolution of the magma and in concentrating the ore elements. They

26   also show that the amphibole-group minerals host a significant proportion of the REE, and were

27   the principal carriers of the HREE in some parts of the pluton.

2. BACKGROUND INFORMATION

29   A number of studies have traced evolutionary trends in alkaline rock suites using the crystal

30   chemistry of the dominant mafic minerals (Davidson, 1982; Marks et al., 2004). In peralkaline

31   rocks, which are defined by a molar excess of alkalis in respect to aluminum, the mafic minerals

32   are usually of a sodic nature, e.g., amphiboles, such as arfvedsonite and riebeckite, or pyroxenes

33   such as aegirine. The amphiboles of alkaline complexes generally trend from calcic through

34   sodic-calcic to sodic members with differentiation, reflecting the increasing alkalinity of the melt

35   from which they crystallized (Giret et al., 1980; Piilonen et al., 2013). They also display

36   significant variations in REE and HFSE concentrations with magmatic differentiation, as shown,

37   for example, by Marks et al. (2004) for the Gardar alkaline province (SW-Greenland). Similar

38   conclusions have been reached for amphibole phenocrysts in alkaline basalts from the Rhine

39   graben valley, Germany (Mayer et al., 2014).

40   Lithium has proven to be a particularly important constituent of alkali amphiboles (Camara et al.,

41   2010; Hawthorne et al., 1993). Owing to its incompatible character in common rock-forming

42   minerals, its concentration in amphibole may reflect the degree of melt differentiation. This case

43   has been made for lithium-bearing amphiboles from Hurricane Mountain, New Hampshire,

44   where the amphiboles vary from early Li-rich leakeite to late Li-poor riebeckite (Hawthorne et

45   al., 1996). The progressive depletion in lithium in crystals growing into miarolitic cavities in

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46 granitic pegmatites is consistent with the idea that a highly evolved melt with a high Li content

47 formed the earlier leakeite, and that progressive fluid exsolution resulted in the removal of

48 lithium and the growth of Li-poor riebeckite.

49 The 1240 Ma Strange Lake pluton (Miller et al., 1997) is an extraordinary example of hyper-

50 REE-, Zr-, and Nb- enrichment in a peralkaline granite, and is composed of a sequence of

51 granitic intrusions, two earlier hypersolvus granites and a later transsolvus granite (this study).

52 The last of these intrusions is host to numerous NYF-type pegmatites with extremely high

53 concentrations of REE, particularly the heavy REE (HREE), Zr and Nb. Most of the previous

54 studies of the pluton have focused on the hydrothermal alteration and the rare-metal mineralized

55 pegmatites (Gysi et al., 2016; Gysi and Williams-Jones, 2013; Kerr and Rafuse, 2012; Salvi and

56 Williams-Jones, 1990; 1992; 1996; 1997; 2006; Vasyukova et al., 2016). Several studies,

57 however, have addressed its magmatic evolution. Boily and Williams-Jones (1994) proposed that

58 the REE-enrichment was due to a combination of fractional crystallization, and the

59 heterogeneous distribution of F-rich residual melts, in which the REE and HFSE were

60 transported as fluoro-complexes. Vasyukova and Williams-Jones (2014; 2016) provided

61 evidence for the early separation of a REE- and Y-rich immiscible fluoride melt from the silicate

62 melt, which accumulated in the highly evolved residual melts that formed the mineralized

63 pegmatites.

64 Previous studies of the mafic minerals of the Strange Lake pluton concluded that the amphiboles

65 are enriched in Li and Zn, are associated with Ti-silicates and crystallized under relatively low

66 $f\mathrm{O}_2$ (Pillet et al., 1993; Roelofsen, 1997). Hawthorne et al. (2001) showed that Li is an essential

67 component of the amphiboles and identified lithian arfvedsonite and lithian manganoan

68 arfvedsonite.

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3. GEOLOGIC SETTING

The Strange Lake pluton is part of the Nain Plutonic AMCG suite, which comprises anorthosites, mangerites, charnockites and granites (Miller, 1996; Gower and Krogh, 2002). Rocks of the Nain suite were emplaced along the boundary between the Archean Nain province and the Archean to Early Paleoproterozoic Churchill province (Emslie et al., 1994), more recently referred to as the Core Zone (James and Dunning, 2000). The Nain Plutonic Suite covers an area of ~19,000 km^2, and was emplaced between 1460 and 1240 Ma, with the Strange Lake pluton (1240 ± 2 Ma) representing the youngest intrusive body (Gower and Krogh, 2002).

To the south and west, the Strange Lake pluton intrudes the Napeu Kainiut quartz monzonite, which is interpreted to represent a satellite body of the Mistastin batholith (Miller et al., 1997). The Napeu Kainiut intrusion, which is composed mainly of quartz, K-feldspar, plagioclase and biotite, also occurs within the Strange Lake pluton as xenoliths and large roof pendants. The Mistastin batholith consists of pyroxene- and fayalite-bearing Rapakivi-textured granites, which were cut by younger biotite-hornblende-bearing granites and minor syenitic intrusions, such as the Misery Lake syenite, which hosts abundant REE mineralization (Petrella et al., 2014). Dated at 1420 Ma (Emslie and Stirling, 1993), the Mistastin batholith represents one of the oldest members of the Nain Plutonic Suite. The other host rock to the Strange Lake pluton is an Archean to Paleoproterozoic gneiss complex belonging to the Core Zone (Churchill Province), comprising quartzofeldspathic augen-gneiss, banded biotite gneiss and minor garnet-bearing paragneiss and mafic gneiss.

3.1 The Strange Lake Pluton

90   The circular (in outcrop), ~ 6 km in diameter, Strange Lake pluton is located on the border

91   between Québec and Labrador, and consists of a sequence of alkaline granitic intrusive units

92   (Fig. 1). The earliest phase of the pluton is a hypersolvus granite (Pillet et al., 1992), its

93   formation at conditions above those for the alkali feldspar solvus (Tuttle and Bowen, 1958). The

94   hypersolvus granite occurs in the center and southern part of the pluton, and has been subdivided

95   into a northern and a southern unit, based on bulk rock and mineral compositional differences.

96   The third major unit, formerly classified as subsolvus granite (Boily and Williams-Jones, 1994;

97   Salvi and Williams-Jones, 1996; Gysi and Williams-Jones, 2013), is now classified as

98   transsolvus granite, and contains perthite phenocrysts as well as separate albite and K-feldspar

99   crystals in the groundmass. It occupies much of the pluton, and has been strongly affected by

100 hydrothermal activity. A smaller, unaltered part of the transsolvus granite is exposed in the

101 center of the pluton and provided the samples for this study. The transsolvus granite commonly

102 contains dark grey, fine-grained ovoid enclaves and barren pegmatite pockets; the altered

103 transsolvus granite is host to highly REE/HFSE-enriched pegmatites. A dark grey porphyritic

104 microgranite with a fine-grained matrix occurs in contact with remnants of country rock within

105 the pluton and is interpreted to represent quenched hypersolvus granite. The enclaves in the

106 transsolvus granite, some of which are compositionally similar to the hypersolvus granite, are

107 interpreted to represent fragments of this quenched material; the other fragments represent

108 quenched transsolvus granite. The pluton is surrounded by a purple to dark red fluorite-hematite

109 breccia, delineating a ring-fault that contains angular fragments of the host rocks.

110 **3.2 Hypersolvus granite**

111 The hypersolvus granite has been subdivided into an equigranular and fine-grained northern part

112 and a variably textured fine- to coarse-grained southern part (this study). Locally, the southern

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113   hypersolvus granite is coarse-grained and displays poikilitic to pegmatitic textures, which are

114   also observed in drill core of the northern hypersolvus granite (not sampled). These poikilitic

115   textured samples contain anhedral arfvedsonite oikocrysts enclosing smaller crystals of perthitic

116   alkali feldspar, whereas the pegmatitic samples are coarse-grained and contain comb-textured

117   arfvedsonite, quartz, K-feldspar and minor proportions of alkali zirconosilicate minerals. Both

118   the northern and southern hypersolvus granite units are composed of perthitic feldspar, quartz,

119   and sodic amphibole. Minor microcline and albite are present in the groundmass, either

120   reflecting evolution of the magma to conditions in the two-feldspar stability field or subsolidus

121   hydrothermal crystallization. A number of alkali feldspar crystals of the southern hypersolvus

122   granite contain inclusions of fibrous astrophyllite. The quartz and sodic amphibole both occur

123   interstitially to the perthite, and the amphibole appears to have crystallized later than the quartz

124   (Fig. 2a). In most of the southern hypersolvus granite samples, the amphibole exhibits swapped

125   margins with perthite (Fig. 2b). The amphibole contains numerous inclusions of fluorite and a Y-

126   rich fluorite-fluocerite solid solution, particularly in the cores of crystals (Fig. 3a). In addition to

127   the silicates mentioned above, a variety of interstitial zirconosilicate minerals, e.g., vlasovite,

128   elpidite, dalyite and catapleiite replaced primary zircon (remnants of zircon in crystal cores).

129   Titanosilicates occur mostly in the northern hypersolvus granite, and locally replaced the sodic

130   amphibole. These minerals comprise dark red aenigmatite ($Na_2Fe^{2+}{}_5TiSi_6O_{20}$) and yellow fibrous

131   astrophyllite ($(K,Na)_3(Fe^{2+})_7Ti_2Si_8O_{26}(OH)_4$) (Figs. 2c, 3b). The primary REE-minerals of both

132   the northern and southern hypersolvus granite are monazite-(Ce) and fluornatropyrochlore. The

133   monazite-(Ce) crystals are small and euhedral, and occur as inclusions in the perthitic alkali

134   feldspar. Fluor-natropyrochlore is more abundant, and occurs as pyramidal crystals in the

135   groundmass, or as inclusions in the alkali feldspar. The oikocrystic and pegmatitic textured

136 samples contain a much smaller proportion of primary REE minerals than the fine-grained

137 varieties of the same unit. Fluorite is an abundant accessory mineral and forms small to large,

138 rounded, translucent to purple inclusions in sodic amphibole or is disseminated interstitially

139 through the rock. It is usually rimmed by the Y-rich fluorite-fluocerite solid solution, which is

140 brighter in BSE images (Fig. 3a). Locally, gagarinite-(Y) occurs in association with fluorite and

141 the fluorite-fluocerite solid solution, and is interpreted to be secondary.

3.3 Transsolvus granite and enclaves

143 The transsolvus granite unit, which contains abundant fine-grained, dark grey ellipsoidal

144 enclaves, surrounds and partially intruded the hypersolvus granite. The unaltered part of this

145 intrusion at the center of the pluton is composed of the same major minerals as the hypersolvus

146 granite, i.e., perthitic alkali feldspar, arfvedsonite and quartz. However, in contrast to the

147 hypersolvus granite, microcline and albite form an essential part of the groundmass, indicating

148 that the transsolvus granite crystallized at a lower temperature and/or higher pH_2O than the

149 hypersolvus granite (Tuttle and Bowen, 1958). Amphibole in this granitic facies forms prismatic

150 phenocrysts that locally contain inclusions of microcline and albite (Fig. 3c), but in contrast to

151 amphibole in the hypersolvus granite, they rarely contain fluorite inclusions. Locally, the

152 amphibole has been replaced by aegirine (Fig. 2d) and, in the more heavily altered parts of the

153 pluton, hematite. Quartz forms round crystals that display a snowball texture, in which primary

154 albite nucleated on the faces of the crystal. Alkali zirconosilicates, such as vlasovite and elpidite,

155 occur intersitially, and usually occupy a larger proportion of the rock volume than in the

156 hypersolvus granite. Narsarsukite ($Na_2(Ti,Fe^{3+})Si_4(O,F)_{11}$), the sole sodium-titanosilicate, occurs

157 as large tabular beige poikilitic crystals, and is observed in the dark grey enclaves and in a

158 number of transsolvus granite samples. Titanite has been reported to occur in the altered parts

159 (Birkett et al., 1996), and is an abundant phase in the pegmatites of the transsolvus granite (Gysi

160 et al., 2016). The primary REE minerals are fluornatropyrochlore, monazite-(Ce) and gagarinite-

161 (Ce), which was replaced by bastnäsite-(Ce). Fluorbritholite-(Ce) occurs sparsely and

162 interstitially in association with fluorite. Fluorite occurs as a late magmatic, interstitial

163 (translucent) or hydrothermal (purple) phase, and is less abundant than in the hypersolvus

164 granite. The transsolvus granite hosts a large number of NYF-type pegmatites with border zones

165 of K-feldspar, quartz, sodic amphibole and alkali zirconosilicates, and a strongly altered core

166 with quartz, fluorite and exotic REE minerals, as well as zircon and pyrochlore (Gysi and

167 Williams-Jones, 2013). These pegmatites host the bulk of the rare metal mineralization in the

168 deposit and have been the target of recent mineral exploration.

169 A dark grey, porphyritic microgranite exposed within the Strange Lake pluton contains perthitic

170 alkali feldspar phenocrysts, quartz eyes and fine-grained subhedral to phenocrystic arfvedsonite

171 in the groundmass (Fig. 3d). Locally, this unit was intruded by a leucocratic transsolvus granite,

172 which, texturally and mineralogically, is similar to the dark grey enclaves observed in the

173 transsolvus granite. This unit has a bulk composition slightly less evolved than, and a mineralogy

174 similar to that of the transsolvus granite. The fine-grained, dark grey enclaves hosted by the

175 transsolvus granite are ellipsoidal in shape, range from a few cm up to 50 cm in diameter and

176 have sharp edge contacts in most cases. These enclaves are composed of perthitic alkali feldspar

177 phenocrysts embedded in a matrix of fine-grained quartz, microcline, albite and finely distributed

178 subhedral and locally phenocrystic sodic amphibole, which gives them their dark appearance.

179 **4. METHODS**

180 **4.1 Material**

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181   The major and trace element compositions of the amphibole-group minerals were determined in

182   22 least-altered rock samples. All granite types occurring in the unaltered portion of the Strange

183   Lake pluton were considered (Fig. 1). Bulk-rock compositions of the samples were provided by

184   Quest Rare Minerals Ltd., and represent the results of analyses by Actlabs using XRF (X-ray

185   fluorescence) for Nb, ISE-MS (ion selective electrode) for F, fusion-ICP-OES for major

186   elements and fusion ICP-MS for most trace elements.

187   **4.2 Electron-microprobe analyses**

188   The composition of the amphibole-group minerals in 30μm thick, carbon-coated polished thin

189   sections was determined using a JEOL JXA-8900L electron microprobe (EMP) at the

190   Department of Earth and Planetary Sciences, McGill University. The beam current was 20 nA,

191   the acceleration voltage 20 kV, and the beam diameter 10 μm. Counting times and standards

192   used for analyses as well as detection limits based on repeated standard analyses are listed in the

193   appendix. To ensure analysis of the same spots by both EMP and LA-ICP-MS (see below),

194   backscattered electron micrographs (BSE) of the analyzed grains were taken.

195   **4.3 Laser-ablation analyses**

196   Laser ablation ICP–MS (LA-ICP-MS) analyses were conducted on 16 samples using a

197   NewWave 213 nm Nd-YAG laser-ablation system and a Thermo Finnigan iCapQc quadrupole

198   ICP-MS at the Department of Earth and Planetary Sciences, McGill University. Six samples

199   were analysed at Université du Québec à Montreal (UQAM) using a Photon Machine G2 short-

200   pulse (4ns) laser-ablation system (193 nm excimer) and a Nu AttoM high-resolution magnetic

201   sector ICP-MS. The amphibole-group minerals were analyzed for selected major and trace

202   elements in the same 30 μm-thick polished sections. NIST SRM 610 glass was used as the

203 primary standard, and EMP data for both Si and Ti were used as internal references. The

204 analyses were performed with a 5 Hz repetition rate, on material ablated from a 20 μm diameter

205 pit. Data reduction was carried out using the software, Iolite, version 2.5. The estimated

206 precision is 5-10 % for each element.

4.4 Amphibole formulae

208 The amphibole-group mineral formulae were calculated on the basis of O + OH + F = 24 atoms

209 per formula unit (apfu) and OH = 2-2Ti, using the amount of Ti^{4+} as a proxy for the (maximum)

210 oxy-component in the mineral structure (Hawthorne et al., 2012). The formula calculation was

211 performed following the latest IMA 2012 recommendations (Hawthorne et al., 2012; Oberti et

212 al., 2012) using the Excel spreadsheet of Locock (2014). On the basis of a preliminary formula

213 calculation after Leake et al. (1997), the following cation normalization schemes were chosen:

214 Si-Ca+Li ≤ 15, Si-Na ≥ 15 and Si-K ≤ 16. As some fluorite inclusions in the amphibole from the

215 hypersolvus granite were too small to be detected by imaging, analyses returning high

216 concentrations of both Ca (> 3 wt. %) and F (> 2 wt. %) were removed from the dataset.

5. RESULTS

5.1 Bulk rock compositions

219 The average (median) major and trace element bulk-rock compositions of the unaltered Strange

220 Lake granites are reported in Table 1. The agpaitic indices (molar [Na+K]/Al]) of all units are >1

221 and hence classify the rocks as peralkaline. The granites generally have low Ca and Mg and high

222 alkali, Fe, F, Zn, Rb, Zr, Nb and REE concentrations. The evolution of the granites is reflected

223 by decreasing Al, and increasing Si, Fe and incompatible element concentrations (i.e., REE, Nb,

224 Zr). The agpaitic index also increases with evolution. The fine-grained southern hypersolvus

225 granite, based on the above mentioned element concentrations, is interpreted to represent the

226 least evolved rock unit. The oikocrystic / pegmatitic textured members of this unit has higher Si

227 and Fe concentrations, a higher agpaitic index and slightly elevated REE and Zr concentrations.

228 The concentrations of the HFSE (REE, Th, U, Nb, Zr, Hf) in the northern hypersolvus granite are

229 higher, whereas Al concentrations are lower than those in the southern hypersolvus granite,

230 suggesting that it is more evolved. The transsolvus granite generally has high Si, REE, Zr, Nb,

231 Rb and F concentrations and significantly lower Al and Ca concentrations than the hypersolvus

232 granite, and is considered to be the most evolved member of the suite. The dark grey enclaves

233 hosted in the transsolvus granite have high Al, K and Ca, and low Na, Fe, Ti, Zr and Nb

234 concentrations compared to the other granite types. Their REE concentrations are lower than

235 those of their host, but higher than those of the hypersolvus granites.

236 **5.2 Formula assignments**

237 The amphibole-group minerals have the general structural formula, $AB_2C_5T_8O_{22}W_2$. The A-site

238 of the Strange Lake amphiboles is occupied by Na^+ and minor K^+, and the B-site by Na^+ and

239 Ca^{2+}, which assigns them to the alkali group. The octahedral C-site is occupied by Ti^{4+}, Zr^{4+},

240 Al^{3+}, REE^{3+}, Fe^{3+}, Zn^{2+}, Mn^{2+}, Fe^{2+}, Mg^{2+} and Li^+. The tetrahedral T-site is occupied by Si^{4+},

241 $^TAl^{3+}$ and in some cases $^TTi^{4+}$. The W-site is dominated by the anions F^-, Cl^- and OH^-, which

242 assigns the amphiboles to the hydroxy-fluoro-chloro-group, where $^WF > {^W}OH$, ^WCl, and a

243 "fluoro"-prefix is assigned to the amphibole name, which was the case for the majority of the

244 crystals analyzed (see Table 2). In the matter of nomenclature, we have followed the latest IMA

245 recommendations (Hawthorne et al., 2012; Oberti et al., 2012).

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246 The C-site has a consistent under-occupancy (< 5 apfu), whereas the A-site has an over-

247 occupancy (> 1 apfu) (see Table 2). Despite using a variety of calculation procedures

248 (Hawthorne et al., 2012; Leake et al., 1997; Oberti et al., 2012), normalization schemes, and

249 varying the Fe^{2+}/Fe^{3+} ratios and oxo-components, we were unable to reduce the under-occupancy

250 and over-occupancy of the C- and A-sites, respectively. This issue has been reported to be

251 common for alkali amphiboles in peralkaline rocks, such as arfvedsonite or riebeckite, by other

252 researchers, who have deemed it to be an irresolvable artefact (Czamanske and Dillet, 1988;

253 Hawthorne, 1976; Hawthorne et al., 1993). Hawthorne (1976) suggested that some of the B-site

254 cations, notably Ca^{2+}, theoretically could be accommodated in the C-site on the basis of bond-

255 length constraints. This would result in a total C-site occupation closer to 5 apfu, and shift the

256 excess A-site cations to the B-site.

257 The occupancy of the A- and B-sites determines whether the amphiboles analyzed belong to the

258 sodic subgroup (arfvedsonite, leakeite) or the sodic-calcic subgroup (katophorite), in which ^{B}Ca

259 > 0.5. Ferro-ferri-katophorite was identified in the least evolved fine- to medium-grained

260 samples of the southern hypersolvus granite, exclusively. All the other amphiboles belong to the

261 sodic subgroup, and in the cases of a calculated Fe^{2+}/Fe^{3+} ratio of 1.1 to 2.3, have been classified

262 as arfvedsonite. The solid solution between the endmembers, arfvedsonite and katophorite, is

263 displayed in Figure 4a. In principle, the location of endmember arfvedsonite could lie anywhere

264 on the Na-K axis, as a potassic endmember has not been shown to exist in nature. The occupancy

265 of the C-site divides the sodic amphibole subgroup into arfvedsonite and ferro-ferri-leakeite; the

266 latter has ^{C}Li > 0.5 apfu and a Fe^{2+}/Fe^{3+} ratio between 0.7 and 1.3. Ferro-ferri-leakeite is the

267 principal amphibole in the transsolvus granite but also occurs in the northern hypersolvus

268 granite. The fluoride-rich-variety (ferro-ferri-fluor-leakeite) was detected mainly in the

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269   transsolvus granite and its enclaves, whereas the fluoride-poor variety occurs predominantly in

270   the northern hypersolvus granite. The composition of the analyzed solid-solution between the

271   endmembers, arfvedsonite and ferro-ferri-leakeite, is displayed in Figure 4b. The slope of the

272   trend from the arfvedsonite to leakeite endmembers indicates an increase in Fe^{3+} with increasing

273   Li^+. The end-member stoichiometric formulae of the amphibole-group minerals present in the

274   unaltered granites of the Strange Lake pluton are listed in Table 3.

275   **5.3 Major elements**

276   The major element compositions of the analyzed amphibole are reported in Table 4 (mean

277   values) and illustrated in Figure 5 relative to their Al content. Aluminum was chosen because the

278   Al content of amphibole is commonly a reliable indicator of the differentiation of the

279   corresponding magma, if alkali feldspar fractionation (perthite phenocrysts) was the major

280   control on magma evolution (Hawthorne et al., 2001; Piilonen et al., 2013). As shown in Figure

281   5a, the Ca content decreases with decreasing Al content in a ratio slightly greater than 1:1, and is

282   highest and shows the greatest range (~ 0.3 to 0.6 apfu) in the amphibole of the fine-grained

283   granite from the southern hypersolvus granite. The Ca content is lower in the pegmatitic and

284   oikocrystic textured samples of the same unit (0.1 to 0.35 apfu). Amphibole of the northern

285   hypersolvus granite has a much lower Ca concentration, between 0.05 and 0.2 apfu. The lowest

286   Ca concentrations are for amphibole in the enclaves and the transsolvus granite (≤ 0.1 apfu) (Fig.

287   5a). Sodium exhibits the opposite trend to Ca, with concentrations increasing with decreasing Al

288   content. In the fine- to medium-grained samples of the southern hypersolvus granite, Na-contents

289   are relatively low, between 2.1 and 2.6 apfu, whereas in the oikocrystic to pegmatitic samples,

290   the Na contents are consistently higher, between 2.6 and 2.9 apfu, and are similar to those of the

291   amphibole from the northern hypersolvus granite, the enclaves and the transsolvus granite (Fig.

14

292   5b). The Ti content of amphibole in the fine- to medium-grained samples of the southern

293   hypersolvus granite has a similar range to that in the northern hypersolvus granite, i.e., from 0.08

294   to 0.22 apfu versus 0.1 to 0.21 apfu, but because of the much lower Al content of the amphibole

295   in the northern hypersolvus granite samples, the two datasets display separate Ti-Al trends (Fig.

296   5c). Amphiboles in the oikocrystic to pegmatitic samples of the southern hypersolvus granite, the

297   transsolvus granite and the enclaves all have relatively low Ti contents (0.06 to 0.16 apfu) (Fig.

298   5c). Silica in amphibole behaves similarly to Na, increasing in concentration with decreasing Al

299   concentration. The lowest silica concentrations are those of the fine- to medium-grained samples

300   of the southern hypersolvus granite (7.4 to 7.7 apfu) (Fig. 5d); the oikocrystic to pegmatitic

301   samples display the largest range in amphibole Si content, from 7.4 to 8.0 apfu. Amphibole in the

302   northern hypersolvus granite, the enclaves and the transsolvus granite has Si contents from 7.7 to

303   7.9, 7.6 to 7.9 and 7.6 to 8 apfu, respectively (Fig. 5d). Manganese contents of amphibole are

304   highest in the northern hypersolvus granite (0.09 − 0.12) and show the greatest range in the

305   transsolvus granite (0.06 − 0.12) (Fig. 5e). They are broadly similar for amphibole from the

306   enclaves and the southern oikocrystic to pegmatitic hypersolvus granite (0.07 − 0.10), and range

307   from 0.08 to 0.11 for amphibole from the fine-grained southern hypersolvus granite. The

308   calculated Fe^{2+}/Fe^{3+} ratios correlate weakly with the Al concentrations. Amphibole from the fine-

309   grained southern hypersolvus granite generally has the highest Fe^{2+}/Fe^{3+} ratio; amphibole from

310   the enclaves, the northern hypersolvus granite and many of the transsolvus granite samples has a

311   low ratio (Fig. 5f). Zinc concentrations are slightly elevated for the amphibole from the fine-

312   grained samples of the southern hypersolvus granite (avg. 0.08 apfu) and the enclaves (avg. 0.07

313   apfu), compared to the amphibole of the northern hypersolvus granite, the transsolvus granite

314   and the oikocrystic and pegmatitic samples of the southern hypersolvus granite (all avg. 0.05

15

315   apfu) (Fig. 5g). Fluorine concentration is highest in the amphibole of the transsolvus granite (1.0

316   - 1.4 apfu), lowest for the crystals of the (fine-grained) southern hypersolvus granite (0.2 – 0.8

317   apfu) and is intermediate (avg. ~ 1 apfu) for all the other granite units.

318   The amphibole phenocrysts of the transsolvus granite differ only slightly in composition from

319   core to rim (Fig. 6; Table 5). The phenocryst cores have total Al and Si contents averaging 0.06

320   (apfu) and 7.9 (apfu), respectively, a considerable range in Ca concentration (~0.1 to 0.5 apfu,

321   avg. 0.03 apfu), Na and K contents averaging 2.8 and 0.33 apfu, respectively, a Fe^{3+} content

322   averaging 1.8 apfu, a Mg content averaging 0.03 apfu, a total Ti content of 0.09 apfu (avg.), Mn

323   and Zn contents averaging 0.07 and 0.05 apfu (avg.), respectively, and a F content averaging 1.2

324   apfu. The phenocryst rims have lower concentrations of Al (avg. 0.06 apfu), Si (7.7 apfu), Ca

325   (avg. 0.02 apfu), Na (avg. 2.8 apfu), Mg (avg. 0.02) and F (avg. 1.1 apfu), and higher

326   concentrations of total Fe^{3+} (avg. 2.2 apfu), K (avg. 0.4 apfu), total Ti (0.1 apfu), Mn and Zn

327   (avg. 0.09 and 0.07 apfu, respectively).

328   **5.4 The REE and other trace elements**

329   The shapes of the chondrite-normalized amphibole REE profiles (Sun and McDonough, 1989)

330   are similar for all the granite units and, in general, are characterized by relatively flat light and

331   middle REE parts, a marked negative Eu-anomaly (Eu/Eu* = 0.04-0.66) and an enrichment in

332   the HREE (Fig. 7). However, the absolute REE concentrations differ considerably. The

333   amphiboles of the fine-grained samples of the southern hypersolvus granite have the highest total

334   REE concentration, on average (median value) 0.16 ± 0.03 wt. % (Table 4). By contrast,

335   oikocrystic to pegmatitic samples of the same unit have much lower amphibole REE

336   concentrations, on average, 0.04 ± 0.01 wt. %. The total REE concentrations of amphibole in the

337 northern hypersolvus granite are intermediate between those of the fine-grained and oikocrystic

338 to pegmatitic southern hypersolvus granite, averaging 0.07 ± 0.02 wt. %. Amphiboles of the

339 transsolvus granite and its enclaves have much lower total REE concentrations, averaging 0.01 ±

340 0.002 wt. % and 0.04 ± 0.01 wt. %, respectively (Table 4). The amphibole REE concentrations

341 are between 10^2 and 10^3 times the chondrite values (Fig. 7c, e).

342 The contents of the individual REE in the amphiboles are significantly lower (in the case of the

343 light REE (LREE), more than an order of magnitude lower) than their respective bulk host rock

344 concentrations, except for the heaviest of the REE, Yb and Lu, which are significantly higher

345 (Fig. 7). In the case of the fine-grained southern hypersolvus granite, the exception extends to the

346 middle REE and for Yb and Lu the content in amphibole is about four times higher than the bulk

347 rock content (Fig. 7a). The concentrations of Yb and Lu of the amphiboles from the northern

348 hypersolvus granite exceed the bulk rock concentrations to a similar degree (Fig. 7c). The largest

349 difference between amphibole and bulk rock REE concentrations is exhibited by the transsolvus

350 granite, which has considerably higher concentrations in the bulk rock except for Yb and Lu; the

351 amphibole in this unit also shows the steepest chondrite-normalized rise in HREE concentration

352 (Fig. 7e). The amphiboles in the dark-grey enclaves hosted by this unit have elevated light to

353 middle REE compositions compared to that of amphibole in the transsolvus granite, whereas the

354 Tm, Yb and Lu concentrations are within the range of their host (Fig. 7e).

355 As is the case for the REE, the contents of most of the other trace elements are considerably

356 lower in the amphibole-group minerals than in the average bulk-rock (other than in the southern

357 fine- to medium-grained hypersolvus granite). Conspicuous exceptions are Nb, Zr and Hf, which

358 in addition to being present in zircon, monazite-(Ce) and the pyrochlore group minerals, are also

359 accommodated by the amphibole. The chondrite-normalized trace element profiles for the

360 amphiboles in all granite units have negative Ba, U, K, Pb, Sr, Eu, Ti and Y anomalies, and

361 positive Th, Nb, Ta, Sn, REE, Zr and Hf anomalies, whereas the average bulk rock has negative

362 Ba, K, Pb, Sr, Eu, and Ti and positive Th, U, Nb, Ta, REE, Zr, Hf and Y anomalies (Fig. 7).

363 Thus, although the behavior of most elements in the amphibole is similar to that in the host rock,

364 U and Y show opposite behavior, i.e., their concentrations are anomalously low in the amphibole

365 and high in the bulk rock. Zirconium concentrations are lowest in amphibole from the southern

366 hypersolvus granite (avg. 0.07 to 0.12 wt. %), and reach more than double these concentrations

367 in amphibole from the northern hypersolvus granite (~0.26 wt. %). Concentrations are

368 intermediate between these extremes in the amphibole of the transsolvus granite (~0.14 wt. %)

369 and enclaves (~0.21 wt. %). Lithium concentrations, on average, are lowest in amphibole of the

370 southern hypersolvus granite (avg. 0.15 to 0.16 wt. %), significantly higher in amphibole of the

371 northern hypersolvus granite (avg. 0.31 wt. %) and by far the highest in amphibole of the

372 transsolvus granite (avg. 0.58 wt. %) and enclaves (avg. 0.48 wt. %). However, they vary greatly

373 among samples, and, to a lesser extent, among crystals in the same sample (see Table 4).

374 Differences in the chondrite-normalized REE profile are particularly marked among the five

375 amphibole types identified in this study. Sodium- and calcium-rich ferro-ferri-katophorite as well

376 as arfvedsonite have the highest total REE concentrations; their average La_N/Yb_N ratios are 0.23

377 and 0.49, respectively (Fig. 8). Fluoro-arfvedsonite and Li-rich ferro-ferri-leakeite both have

378 intermediate REE concentrations and a more prominent HREE enrichment with an average

379 La_N/Yb_N ratio of 0.09 and 0.14, respectively. Ferro-ferri-fluoro leakeite has by far the lowest

380 total REE concentration, and it exhibits the strongest relative HREE enrichment with an average
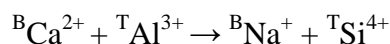
381 La_N/Yb_N ratio of. 0.04.

382 **6. DISCUSSION**

18

6.1 Amphibole composition as a tracer of granite differentiation

The variations in the major and trace element chemistry of amphibole in the Strange Lake pluton are interpreted to reflect the evolution of the granitic melt. The earliest intrusive phase was the hypersolvus granite, which has been subdivided into a southern and a northern part on the basis of compositional and mineralogical differences. In both units, the amphiboles, mainly (fluoro)-arfvedsonite (n=49) and minor (fluoro)-katophorite (n=6), occur interstitially to perthite and quartz, and thus were the last of the main rock-forming minerals to crystallize. By contrast, in the more evolved transsolvus granite, the amphibole, mostly fluoro-arfvedsonite and ferro-ferri-(fluoro)-leakeite (n=55), occurs as phenocrysts together with minor perthite, and therefore crystallized prior to the emplacement of this granite facies. This difference in the timing of crystallization of the amphibole, as we will show below, played a crucial role in determining the extent to which incompatible elements, such as the REE and other HFSE, were incorporated in its crystal structure.

6.2 Magma evolution monitored by A-and B-site occupancy

In the hypersolvus granite, the A- and B-sites are occupied mainly by Na, but also by considerable Ca in some samples of the southern hypersolvus granite (see Fig. 4a). The high density of fluorite inclusions also suggests that the early melt was relatively rich in Ca. The occupation of the B-site by the bivalent Ca ion was balanced by Al^{3+} at the T-site. With increasing degree of differentiation, Na^+ substituted for Ca^{2+} and Si^{4+} for Al^{3+} (see Figs. 5a, b, d). This coupled substitution can be expressed by the reaction:

$$^{B}Ca^{2+} + {}^{T}Al^{3+} \rightarrow {}^{B}Na^+ + {}^{T}Si^{4+}$$

19

404 A similar correlation of decreasing Ca and increasing Si in amphibole with magmatic evolution

405 has been documented for silica-undersaturated alkaline intrusive suites, namely Ilímaussaq in

406 southern Greenland (Marks et al., 2004), the Khibiny complex in the Kola Peninsula of Russia

407 (Konopleva et al., 2008), and the alkaline pegmatites of the silica-undersaturated to -saturated

408 Larvik plutonic suite of the Oslo Rift in Southern Norway (Piilonen et al., 2013). In these three

409 locations, the amphibole composition evolved from calcic to sodic-calcic to sodic varieties with

410 increasing degree of differentiation, reflecting the increasing alkalinity of the corresponding

411 magma.

412 As the Ca content is highest in amphibole of the fine- to medium-grained southern hypersolvus

413 granite (see Fig. 5a), we interpret this unit to be the earliest and least evolved intrusive facies of

414 the Strange Lake pluton. The much lower content of Ca in amphibole of the oikocrystic to

415 pegmatitic textured granites from the same unit is consistent with the interpretation that these

416 rocks crystallized from residual melts. Consistent with these interpretations, the northern

417 hypersolvus granite, in which amphibole has a relatively low Ca (and Al) concentration,

418 represents the intrusion of a separate and more evolved batch of magma.

419 The amphibole of the transsolvus granite generally has low Ca- and Al-, as well as high Na- and

420 Si-concentrations (see Fig. 5a, b, d), which all point towards a significantly more evolved melt.

421 As the amphibole of this unit crystallized early (it occurs as phenocrysts), as opposed to the

422 hypersolvus granite, the transsolvus granitic melt was more evolved from the outset. The

423 evolution of this melt is monitored by the compositional differences between phenocryst cores

424 and rims. For example, Ca, Na and Al concentrations decrease from core to rim (see Fig. 6,

425 Table 4). Decreasing Ca and Al concentrations mirror the evolution to a more alkaline magma

426 composition, which was caused by alkali feldspar fractionation (Boily and Williams-Jones,

20

427   1994). The unexpected depletion of Na in the rims, however, is likely an artefact of the

428   exsolution of a Na-rich fluid at a later stage of crystallization (Salvi and Williams-Jones, 1996;

429   Roelofsen, 1997; Gysi et al., 2016), and/or the onset of albite crystallization. Not surprisingly,

430   given the generally very low Ca and Al contents (close to zero) (Fig. 5a) and very high Na (Fig.

431   5b) content of the amphibole, compared to those of the hypersolvus granite, the transsolvus

432   granite is the most evolved of the intrusive units considered in this study. The enclaves in this

433   unit contain amphibole with slightly higher Ca, and Al, and lower K and F concentrations than

434   the crystals in the host granite (see Fig. 5), which points to a slightly less evolved composition.

435   Nonetheless, their close compositional resemblance to the crystals of the transsolvus granite,

436   indicates that they may be part of the same intrusion.

437   **6.3 Magma evolution monitored by the C-site occupation**

438   *6.3.1 Implications of the Fe^{2+}/Fe^{3+} ratio*

439   The C-site of the amphibole-group minerals in the Strange Lake complex mainly hosts Fe^{2+} and

440   Fe^{3+}, but also Li^+, Mg^{2+}, Mn^{2+}, Zn^{2+}, Ti^{4+} and Zr^{4+} in significant proportions. The Fe^{2+}/Fe^{3+} ratio

441   of a magma is controlled by the fO_2, and may be recorded by the amphibole composition.

442   However, Fe^{3+} also becomes more or less compatible in the amphibole structure depending on its

443   overall composition, and the exchange vectors that operate. In particular, the incorporation of Na

444   at the expense of Ca is charge-balanced by 3+ elements in the exchange vector: Ca + (Mg, Fe^{2+})

445   = Na + (Al, Fe^{3+}). When Al contents are depleted in the melt (e.g., increasing peralkalinity), Fe^{3+}

446   becomes progressively more important in this exchange vector. In this case, the amphibole

447   Fe^{2+}/Fe^{3+} ratio will vary with the Na/Ca ratio in rocks with the same major mineral paragenesis.

448   In the late amphibole of the hypersolvus granite, Fe^{2+}/Fe^{3+} ratios of the northern unit are lower

and have higher Na/Ca ratios than the amphibole of the southern unit (Fig. 9), which suggests

that incorporation of Fe^{3+} in the structure, to some degree, was tied to the lower Ca content of the

amphibole. However, as the correlation between Fe^{2+}/Fe^{3+} and Na/Ca is not 1:1, it is likely that

there was an additional effect on the Fe^{2+}/Fe^{3+} ratio, e.g., oxidation. Oxidation of a magma

commonly occurs following fluid exsolution from the magma, due to decomposition of H_2O to

H_2 and $\frac{1}{2}O_2$, and the subsequent loss of the much faster diffusing H_2 (Czamanske and Wones,

1973). As the amphibole crystallized late in this facies, it can be inferred that the cooling

intrusion had experienced some degassing and subsequent fluid loss at this point. Even in the

freshest units (e.g., the hypersolvus granite) of the Strange Lake pluton, there is evidence of

H_2O-saturation at a late stage of in-situ evolution, e.g., the albitization of K-feldspar, the

hydrothermal alteration of primary REE-minerals and the crystallization of hydrothermal REE-

phases, such as gagarinite-(Y) after fluorite (Gysi et al., 2016; Vasyukova and Williams-Jones,

2016).

The amphibole of the transsolvus granite and enclaves generally has a low Fe^{2+}/Fe^{3+} ratio (see

Fig. 5f). In addition, the phenocrysts rims have elevated Fe^{3+} concentrations compared to their

cores (see Fig. 6c) which can be related to increasing fO_2. The amphibole rims may have

continued to crystallize after emplacement, when the magma experienced degassing and

oxidation. In addition, some correlation between Fe^{2+}/Fe^{3+} and Na/Ca suggests that crystal

chemical effects (high Na/Ca ratio), partially caused the low Fe^{2+}/Fe^{3+} ratio (Fig. 9). However, as

the correlations are not 1:1, this indicates that a process, in addition to crystal chemical effects

and oxidation, caused the high Fe^{3+} content. In peralkaline igneous systems, high concentrations

of F^- and OH^- in the melt allow more Fe^{3+} to be present at a given fO_2 (Birkett et al., 1996; Giehl

et al., 2013). The high proportion of Fe^{3+} in the amphibole was likely caused by an increasing

22

472 proportion of anions, notably F⁻ and OH⁻ in the evolving melt. This is manifested by significantly

473 higher F concentrations in the amphibole phenocrysts, compared to the amphiboles of the

474 hypersolvus granite (see Table 3).

6.3.2 Titanium, manganese and zinc concentrations

476 The titanium concentration of the amphibole-group minerals in alkaline rocks is an important

477 indicator of the melt evolution owing to the incompatible nature of Ti. Indeed Ti^{4+} was

478 preferentially incorporated into the late crystallizing amphibole of the hypersolvus granite and

479 much less so in the phenocrysts of the transsolvus granite (see Fig. 5c). From bulk rock

480 compositions, we know that both the southern and northern hypersolvus granitic magmas were

481 relatively enriched in TiO_2 (on average, 0.3 wt. % in both units). However, the amphibole of the

482 southern unit has a much higher TiO_2 concentration (avg. 1.5 wt. %) than the northern unit

483 (avg.1.1 wt. %).

484 The proportion of the amphibole in each granite unit was estimated using the MINSQ excel

485 spreadsheet of Herrmann and Berry (2002), which applies a least squares method to bulk rock

486 and mineral compositions in order to determine the normative mineralogy of a sample.

487 Proportions of the bulk TiO_2 contributed by the mineral group were estimated from the

488 amphibole proportion and the TiO_2 content. The fine-grained southern hypersolvus granite

489 contains ~14 wt. % amphibole, which hosts ~70 % of the bulk TiO_2. The northern hypersolvus

490 granite contains only ~11 wt. % amphibole, which hosts about 40 % of the bulk TiO_2. The

491 remaining titanium is concentrated in aenigmatite and astrophyllite, sodium-titanosilicate

492 minerals, which are present almost exclusively in the northern hypersolvus granite (see Fig. 2d).

493 In the southern hypersolvus granite, the missing 30 % is concentrated mostly in secondary

494   astrophyllite, which occurs as inclusions in the alkali feldspar. Both the transsolvus granite and

495   its enclaves have bulk rock Ti concentrations of ~0.2 wt. % and significantly lower

496   concentrations in amphibole (0.7 and 0.9 wt. %, respectively). As the amphibole is a phenocryst

497   phase, it did not incorporate the relatively incompatible Ti^{4+}. However, a slight increase in total

498   Ti concentration from phenocryst cores to rims (avg. 0.09 to 0.1 apfu) is consistent with the

499   internal evolution of this unit. In both the transsolvus granite and its enclaves, about 58 % of the

500   bulk TiO_2 is hosted by the amphibole. The transsolvus granite has an elevated proportion of

501   amphibole (~18 wt. %), whereas the enclaves contain much lower proportions of the mineral

502   (~12 wt. %), due to density separation that occurred in the magma chamber. The remaining TiO_2

503   in this unit is concentrated mostly in the Na-Ti-silicate, narsarsukite.

504   Several studies have reported a strong positive correlation between Ti^{4+} and O^{2-} concentrations in

505   amphibole, which is reflected in the relationships, $^{C}Ti = Ti$ and $O^{2-} = 2Ti^{4+}$ with the limit of ^{W}[2-

506   (OH, F, Cl)]. This means, that if the F, Cl and Ti concentrations of the amphibole are measured,

507   and a maximum of 2 apfu for the W-site is assigned, the OH- (and O-) proportion can be

508   estimated using the relationship OH = 2 − (2Ti − F − Cl) (Hawthorne et al., 2012; King et al.,

509   1999; Leake, 1968; Oberti et al., 2012). Following this protocol, hydroxyl (OH^{-}) and oxygen (O^{2-}

510   ) are essential components of the amphibole from the southern hypersolvus granite (>1 apfu)

511   (Fig. 10), whereas in the other, more evolved granite units, F^{-} is the dominant W-site anion (see

512   Figs. 5h, 11b). Abundant fluorite inclusions in the amphibole of this unit (see Fig. 3a) indicate

513   that fluorite saturated prior to the amphibole. This suggests that in the early and least evolved

514   magma, the late amphibole crystallized from a water-rich, F-poor, residual magma. In the

515   northern hypersolvus residual granitic melt, more F^{-}, in addition to oxygen, was available to be

516   incorporated in the amphibole (see Figs. 5h, Fig. 10). In both hypersolvus granite units (south

517 and north), high Ti^{4+} concentrations required significant proportions of O^{2-} (0.2 to 0.45 apfu) to

518 balance the higher charge of the C site. The phenocrysts of the transsolvus granite have high

519 proportions of F^-, and low proportions of O^{2-} and OH^- occupying the W-site (see Fig. 5h, Fig.

520 10). This implies a highly F-enriched melt from the outset (phenocryst cores).

521 Elevated Mn-concentrations in the amphibole of the northern hypersolvus granite compared to

522 those of amphibole in the fine-grained samples of the southern unit (see Fig. 5e) point to a

523 progressive increase in Mn^{2+} concentration with hypersolvus granite evolution. The relatively

524 incompatible behavior of Mn^{2+} compared to Fe^{2+} was likely caused by the larger ionic radius of

525 $^CMn^{2+}$ (r=0.83Å) over Fe^{2+} (r=0.78Å) (Hawthorne et al., 2001; Shannon, 1976). Amphibole Zn^{2+}

526 concentrations decrease with hypersolvus granite differentiation (see Fig. 5g), due either to the

527 co-crystallization of another Zn-bearing phase or the progressive replacement of the relatively

528 compatible Zn^{2+} ion by more incompatible cations, such as Fe^{3+}. The amphibole phenocrysts of

529 the transsolvus granite generally have low but highly variable Mn^{2+}- and Zn^{2+}-concentrations,

530 from 0 to 0.12 apfu, and 0.02 to 0.14 apfu, respectively. The latter is due to the much higher Mn

531 and Zn concentrations of the phenocryst rims compared to the cores (see Table 4), which reflects

532 increasing evolution of the magma. A progressive build-up in both Mn and Zn in the Strange

533 Lake amphiboles with evolution was reported by Hawthorne et al. (2001), whereas we observe

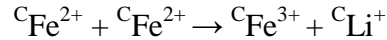534 this trend separately for each granite unit.

6.3.3 The role of lithium

536 Lithium is a significant component of the Strange Lake amphiboles and has been reported to be

537 an important constituent in alkali amphiboles of highly evolved alkaline rocks elsewhere (e.g.,

538 Hawthorne et al., 1993; Hawthorne et al., 1996; Marks et al., 2004). Owing to the incompatibility

539   of lithium in common rock-forming minerals, its concentration reflects the degree of melt

540   differentiation. The amphiboles of the Strange Lake pluton have an average Li concentration of

541   0.3 apfu, but concentrations reach > 1.0 apfu in some transsolvus granite samples. Lithium

542   concentrations of >0.5 apfu classify a sodic amphibole as ferro-ferri-(fluoro)-leakeite, which is

543   the case for most of the amphibole in the more evolved units. Hawthorne et al. (2001), who

544   reported Li concentrations of up to 0.4 apfu for amphibole in the most evolved members of the

545   Strange Lake pluton, concluded that the elevated Li concentration was due to its high content in

546   the magma rather than the structure of the mineral. The generally low content of Li in amphibole

547   of both the southern and northern hypersolvus granite (avg. 0.16 and 0.31 wt. %, respectively)

548   compared to the transsolvus granite (avg. 0.58 wt. %) (see Table 4), despite the fact that

549   amphibole in the hypersolvus granite was a late crystallizing phase, suggests that the hypersolvus

550   granite magma was relatively poor in Li. In contrast, the occurrence of ferro-ferri-(fluoro)-

551   leakeite as phenocrysts in the transsolvus granite suggests that the corresponding magma was

552   more evolved. Of significance in this regard is the large range in Li-concentrations of the

553   amphibole phenocrysts (0.1 to 1.2 apfu) (Fig. 11), which suggests that they record a large part of

554   the evolution of the magma, a conclusion that is supported by the elevated Li concentrations of

555   crystal rims relative to their cores (see Fig. 6d).

556   As noted earlier, the Li^+ concentration of the amphiboles correlates positively with the C-site

557   occupancy ($R^2 \sim 0.8$), and hence knowledge of the concentration of this ion is essential to reliably

558   evaluate the amphibole formula. In particular, the calculation of the Fe^{3+} concentration, which is

559   highly dependent on Li^+ for charge balance, can only be performed accurately if the Li^+

560   concentration is known (Hawthorne et al., 1993). The lithium concentration in the amphiboles

561   correlates strongly with the Fe^{3+} concentration ($R^2=0.92$ for the transsolvus granite, $R^2=0.83$ for

562 the hypersolvus granite) (Fig. 11), and, with increasing degree of evolution, can be expressed by

563 the coupled substitution reaction

564 $$^C Fe^{2+} + {}^C Fe^{2+} \rightarrow {}^C Fe^{3+} + {}^C Li^+$$

565 The progressive increase in Li^+ and Fe^{3+} with evolution is consistent with the increase in fO_2 in

566 the hypersolvus granite, and also with the increase in melt F^- and OH^- in the transsolvus granite,

567 both of which were discussed earlier.

568 **6.4 Distribution of the REE and other trace elements**

569 The trace element composition of amphibole-group minerals is a function of the magma

570 composition and the structure of the mineral (i.e., the preference of its sites for ions of a

571 particular size and charge). In the Strange Lake granites, for example, the negative Ba, Pb, Sr,

572 and Eu anomalies in both the amphibole and bulk rock are likely due to voluminous plagioclase

573 fractionation early in the crystallization history. This process is interpreted to have produced the

574 large Mesoproterozoic anorthosite complexes of the Nain Plutonic Suite (Emslie et al., 1994;

575 McLelland et al., 2010). Consistently low Rb concentrations, and negative U and Y anomalies in

576 the amphibole, but not in bulk rock, on the other hand, are interpreted to have been caused by

577 within-pluton-fractionation of K-feldspar (substitution of Rb for K) and of Y- and U-rich

578 minerals, such as gagarinite-(Y), the fluorite-fluocerite solid solution and small amounts of U-

579 bearing thorite.

580 The behavior of the REE in amphibole-group minerals is governed by a combination of crystal

581 chemical constraints and magmatic processes. Several studies have concluded that the trace

582 element composition of amphibole is dependent on the major element distribution, and, to a

583 lesser extent, on the P, T and fO_2 conditions (Bottazzi et al., 1999; Dalpé and Baker, 2000). In

27

584   the Gardar Province (Ilímaussaq, Puklen and Grønnedal-Ika intrusions), for example, Ca-rich

585   amphibole- group minerals are strongly enriched in the LREE (order of magnitude), compared to

586   the Na-rich members of the same mineral group (Marks et al., 2004). Consistent with this

587   observation, the Ca-rich ferro-ferri-katophorite at Strange Lake is enriched in the REE by 10^2 to

588   10^3 times the chondrite values, whereas the Na-rich fluor-arfvedsonite and ferro-ferri-(fluoro)-

589   leakeite have much lower total REE concentrations, and show a stronger relative enrichment in

590   the HREE (see Fig. 8).

591   The Ca-rich amphiboles are members of the earlier, less evolved hypersolvus granite, in which

592   they crystallized as a late, interstitial phase from a small proportion of residual liquid. The

593   residual liquid of this overall less evolved unit was relatively enriched in incompatible elements

594   such as the REE, whereas the amphibole phenocrysts of the more evolved transsolvus granite

595   crystallized from a relatively 'dilute' magma with low incompatible element concentrations. In

596   contrast, the amphiboles of the Gardar Province all are late, near solidus phases in all rock types

597   that have been investigated, e.g., augite-syenites, alkali granites, agpaites and nepheline syenites

598   (Markl et al., 2001; Marks et al., 2004). Thus, the fact that the LREE are tied to Ca-rich

599   amphiboles implies that another factor, in addition to the magma composition, may have been

600   important in accommodating the REE in the crystal structure. Rare earth element concentrations

601   in the Strange Lake amphiboles correlate positively with Al^{3+} (R^2=0.59) and Ca^{2+} (R^2 = 0.61)

602   concentrations, and negatively with Na^+ (R^2= 0.57), F^- (R^2 = 0.51) (Fig. 12) and Si^{4+}

603   concentrations. This suggests that overall the REE become less compatible in the amphibole

604   structure with increasing degree of magma evolution, or alternatively, that the nature of the

605   major elements in the mineral structure control the accommodation of the REE.

606   Interestingly, the amphiboles of the oikocrystic and pegmatitic samples of the southern

607   hypersolvus granite have much lower REE concentrations (avg. ~0.04 wt. %) than their host

608   (avg. 0.16 wt. %), but similar to those of amphiboles in the northern hypersolvus granite (avg.

609   ~0.07 wt. %) (see Table 3). In the latter amphiboles, however, the Al and Ca contents are

610   significantly lower (0.5 vs 1.0 wt. % Al_2O_3 and 0.5 vs. 1.1 wt. % CaO). This is consistent with

611   the interpretation that the oikocrystic and pegmatitic granites crystallized from volatile-rich melt

612   pockets that evolved in-situ, and is further evidence that the northern hypersolvus granite

613   evolved from the southern hypersolvus granite. The decoupling of REE concentrations from

614   those of Ca and Al observed in these two rock units speaks to a factor other than the degree of

615   magma evolution in controlling the incorporation of the REE in amphibole.

616   **6.5 REE inter-site partitioning**

617   Previous studies have concluded that the REE in the amphibole structure are distributed over the

618   B and C sites and that this distribution depends on the nature of the major elements that reside in

619   these sites (Bottazzi et al., 1999; Tiepolo et al., 2007; Tiepolo et al., 2000). These conclusions

620   were reached from studies of the partitioning of the REE between amphibole and melt, with the

621   D_{REE} showing systematic behavior controlled by the B and C site dimensions (*cf.* Blundy and

622   Wood, 2003). Unfortunately, these data do not extend to the amphibole compositions

623   encountered at Strange Lake. In order to obtain a first-order estimate of the localization of the

624   REE in sodic amphibole, apparent mineral-melt partition coefficients were calculated from the

625   bulk rock and median sodic amphibole compositions of transsolvus granite sample 204720.

626   Amphibole was the first major phase to crystallize in this sample, but inclusions of pyrochlore

627   group minerals and monazite-(Ce) indicate that these minerals had likely already saturated. The

628   median compositions of these minerals at their respective modes were subtracted from the bulk

629 composition to obtain an estimate of the melt composition at the time of amphibole

630 crystallization. This assumes that sample 204720 acted as a closed system, that it represents a

631 melt composition, that all pyrochlore group minerals and monazite-(Ce) crystallized prior to

632 amphibole, and that all amphibole formed at the same time. However, deviations from these

633 assumptions mainly impact the absolute D values, whereas their systematics are unaffected.

634 A plot of the partition coefficients against the radii of the REE (6-fold and 8-fold coordinated

635 radii for the C and B-sites, respectively, as given in Shannon 1976) is shown in Fig. 13. The

636 LREE in the sodic amphiboles from Strange Lake are most compatible with the B-site (Fig. 13),

637 as also has been shown for calcic and sodic-calcic amphiboles (Bottazzi et al., 1999). The

638 lightest of the lanthanides, La and Ce, which have ionic radii of 1.16 Å and 1.14 Å (at 8-fold

639 coordination) are closest to the ideal radius of the B-site and are thus preferentially incorporated.

640 For reference, the major elements occupying this site are Na and Ca, which with ionic radii of

641 1.12 Å and 1.18 Å, respectively, are slightly smaller or larger than the ideal radius. The HREE,

642 which have ionic radii between 0.86 to 0.94 Å, on the other hand, are compatible with the 6-fold

643 coordinated C-site, and their compatibility increases exponentially with increasing atomic

644 number (Fig. 13). Thus, the 'heaviest' of the REE, Yb and Lu are preferentially incorporated in

645 the crystal structure ($D^{amph-bulk}_{Yb, Lu}$ >1.0), which, indeed, is what is observed in the chondrite-

646 normalized REE profiles (Fig. 7). The middle REE, e.g., Gd, has the lowest apparent partition

647 coefficient as its radius is furthest from that of the ideal radii of both the B and C sites and hence

648 fits in neither site (in Fig. 13 it is shown at its 6-fold coordinated radius). The apparent D values

649 also suggest that $D_{LREE} < D_{HREE}$, in agreement with Tiepolo et al. (2000), who showed that the

650 LREE are incompatible in amphibole ($D^{amph/l}_{La}$ = 0.06 to 0.5), whereas the HREE are relatively

651 compatible ($D^{amph/l}_{Yb}$ = 0.25 to 2.0). The apparent (calculated) $D^{amph-bulk}$ and ionic radii at 6- and

652 8-fold coordination are given in Table 6.

6.6 The role of amphibole in concentrating HREE in the pluton

654 A significant proportion of the bulk REE content of the Strange Lake granites is contained in

655 amphibole. Indeed, the REE content of amphibole in both fine-grained and oikocrystic and

656 pegmatitic samples of the southern hypersolvus granite is similar to or exceeds that of the bulk

657 rock, except for La and Ce; the contents of the heaviest of the REE, Yb and Lu, are four times

658 higher than in the bulk rock.

659 Proportions of the bulk REE hosted by the mineral group were estimated from the proportion of

660 the amphibole in each granite facies and the REE contents of the corresponding amphiboles. The

661 amphibole of the southern hypersolvus granite (fine-grained) (~ 14 wt. %) contains about 10 %

662 of the bulk LREE (avg. 0.1 wt. %) and more than 35 % of the bulk HREE (avg. 0.01 wt. %) (Fig.

663 14). In the case of Yb and Lu, the proportions increase to 55 and 70 wt. %, respectively. In the

664 northern hypersolvus granite, REE concentrations are considerably lower than the bulk rock

665 concentrations, except for Tm, Yb and Lu. On average, 2 % of the bulk LREE (avg. 0.15 wt. %),

666 and 17 % of the bulk HREE (avg. 0.02 wt. %) are hosted by amphibole in this unit (~11 wt. %)

667 (Fig. 14). As the bulk rock LREE concentrations of this unit are relatively high (~10^3 times

668 chondrite values), this points to a major LREE bearing phase, e.g., monazite-(Ce), and/or

669 pyrochlore group minerals having crystallized prior to the amphibole or that there was another

670 sink for the LREE. The latter would be consistent with the findings of Vasyukova and Williams-

671 Jones (2014, 2016) that the hypersolvus granite magma saturated with (exsolved) a fluoride

672 liquid into which the LREE partitioned preferentially.

31

673 Amphibole proportions in the transsolvus granite are relatively high (~18 wt. %), whereas their

674 REE concentrations are particularly low (> 1 and < 100 times the chondrite value). In this unit,

675 only 0.1% of the bulk LREE (avg. 0.28 wt. %) and 4 % of the HREE (avg. 0.03 wt. %), on

676 average, are hosted by the amphibole (Fig. 14). As the amphiboles occur as phenocrysts in the

677 transsolvus granite, they largely record information about the pre-emplacement composition of

678 the magma. Given the low LREE content of the amphibole, it is possible that an early

679 fractionating phase depleted the melt in the LREE. These phases were monazite-(Ce) and

680 gagarinite-(Ce), which crystallized prior to or contemporaneously with the amphibole.

681 As mentioned earlier, some of the enclaves hosted by the transsolvus granite are interpreted to

682 represent the quenched margin of this intrusion. Accordingly, amphibole phenocrysts in these

683 enclaves and the host intrusion should have similar compositions. Indeed, their major element

684 concentrations match closely those of the transsolvus granite (see Fig. 5). However, the light and

685 middle REE contents of the amphiboles from the enclaves are generally higher than those of

686 amphiboles in their host (see Fig. 7e); the chondrite-normalized profiles of the bulk enclaves are

687 parallel to those of the bulk host granite, but their absolute values are slightly lower. The

688 consistently higher light and middle REE concentrations of amphibole in the enclaves compared

689 to their host could indicate that the amphibole crystallized from a melt relatively enriched in

690 these elements. However, much of the amphibole in the enclaves crystallized after emplacement

691 (quenching), which means that it crystallized from the very first and least evolved transsolvus

692 granite magma (lower bulk REE profile, see Fig. 7e). We therefore suggest that amphibole in the

693 enclaves crystallized slightly later than the phenocrysts in the magma chamber (transsolvus

694 granite), resulting in an amphibole more enriched in the REE.

32

The amphibole in the more altered localities of the transsolvus granite was replaced extensively by aegirine and/or hematite during hydrothermal alteration (Gysi and Williams-Jones, 2013; Gysi et al., 2016; Salvi and Williams-Jones, 1990, 1996; Vasyukova et al., 2016). As the REE content of the aegirine is orders of magnitude lower than that of the amphibole, it is very likely that the replacement of amphibole by aegirine (and hematite) led to the release of the REE, particularly the HREE to the hydrothermal fluid and the development of potentially exploitable zones of HREE mineralization.

7. CONCLUSIONS

We have shown that the major and trace-element compositions of amphiboles of the Strange Lake granite complex reflect the magmatic evolution of the pluton. The differentiation of the magma proceeded from the southern hypersolvus granite to the more evolved northern hypersolvus granite, two separate intrusions which both contain amphibole as a late, interstitial phase (Fig. 15a). The most evolved unit, a transsolvus granite, contains early crystallizing amphibole in the form of phenocrysts (Fig. 15b). Amphibole compositions vary from calcic-sodic (ferro-ferri-katophorite) in the least evolved southern hypersolvus granite to sodic members ((fluoro)-arfvedsonite, ferro-ferri-(fluoro)-leakeite) in the other, more evolved granites. The increasing Fe^{3+} concentration in amphibole with hypersolvus granite evolution was a result of crystal chemical effects (Na/Ca proportion) and increasing fO_2 through degassing. The same trend in the phenocrysts of the transsolvus granite implies a higher compatibility of Fe^{3+} with increasing Na/Ca proportions and an increase in OH^- and F^- concentrations in the evolving melt. Variations in Ti-concentrations indicate the presence of Na-Ti-silicates, such as aenigmatite, astrophyllite and narsarsukite, which replaced the amphibole to varying degrees in each unit. In the transsolvus granite, magma evolution is manifested by increasing Ti, Mn and Zn

718 concentrations from amphibole cores to rims. The phenocrysts of the transsolvus granite also

719 contain significant Li (ferro-ferri-fluoro-leakeite) that correlates positively with Fe^{3+}, indicating

720 that this most evolved melt was already enriched in Li at an early stage.

721 The amphiboles of all units are enriched in Nb, Zr and Hf and the HREE compared to the bulk

722 rock, reflecting a combination of magmatic compositional and crystal chemical effects. In the

723 hypersolvus granite, the late crystallization of amphiboles from a small proportion of residual

724 magma resulted in high incompatible element concentrations, whereas the early crystallization of

725 amphiboles in the transsolvus granite ensured relatively low concentrations of these elements,

726 despite the overall more evolved nature of the magma. The concentrations of the relatively

727 incompatible LREE ($D_{arf\text{-}bulk} < 0.01$) are positively coupled to the amphibole Ca concentration,

728 with the LREE preferentially incorporated in the larger B-site. The HREE were preferred by the

729 C-site and increased in compatibility ($D_{arf/bulk} > 0.1$) with increasing atomic number and

730 decreasing ionic radius. Variations in the LREE concentrations of the amphiboles were

731 controlled by the relative timing of crystallization of amphibole and the presence of primary

732 LREE minerals, such as monazite-(Ce), pyrochlore group minerals and gagarinite-(Ce), as well

733 as the exsolution of a LREE-rich fluoride melt. The uptake of the HREE by amphibole was

734 controlled by their relative compatibility in the structure of this mineral due to their smaller radii.

735 A significant proportion of the bulk HREE content of the Strange Lake granites was carried by

736 the amphibole, which during subsequent hydrothermal alteration was released to the fluid and

737 contributed to the development of potentially exploitable HREE mineralization.

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750 **REFERENCES**

751 Abdel-Rahman, A. F. M., 1994, Alkali Amphibole: A Potential Source of Rare Earth Elements in

752   Felsic Alkaline Rocks: Exploration and Mining Geology, v. 3, no. 2, p. 81-94.

753 Birkett, T. C., Trzcienski, W. E., and Stirling, J. A. R., 1996, Occurrence and compositions of

754   some Ti-bearing minerals in the Strange Lake intrusive complex, Quebec-Labrador

755   boundary: Canadian Mineralogist, v. 34, p. 779-801.

756 Blundy, J., and Wood, B., 2003, Partitioning of trace elements between crystals and melts: Earth

757   and Planetary Science Letters, v. 210, no. 3-4, p. 383-397.

758 Boily, M., and Williams-Jones, A. E., 1994, The role of magmatic and hydrothermal processes in

759   the chemical evolution of the Strange Lake plutonic complex, Quebec-Labrador:

760   Contributions to Mineralogy and Petrology, v. 118, no. 1, p. 33-47.

761 Bottazzi, P., Tiepolo, M., Vannucci, R., Zanetti, A., Brumm, R., Foley, S. F., and Oberti, R.,

762   1999, Distinct site preferences for heavy and light REE in amphibole and the prediction

763   of D-Amph/L(REE): Contributions to Mineralogy and Petrology, v. 137, no. 1-2, p. 36-

764   45.

765 Camara, F., Hawthorne, F. C., Ball, N. A., Bekenova, G., Stepanov, A. V., and Kotel'nikov, P.

766   E., 2010, Fluoroleakeite, $NaNa_2(Mg_2Fe_2^{3+}Li)Si_8O_{22}F_2$, a new mineral of the

767   amphibole group from the Verkhnee Espe deposit, Akjailyautas Mountains, Eastern

768   Kazakhstan District, Kazakhstan: description and crystal structure: Mineralogical

769   Magazine, v. 74, no. 3, p. 521-528.

770 Czamanske, G. K., and Dillet, B., 1988, Alkali amphibole, tetrasilicic mica, and sodic pyroxene

771   in peralkaline siliceous rocks, Questa Caldera, New Mexico: American Journal of

772   Science, v. 288-A, no. 1988, p. 358-392.

773   Czamanske, G. K., and Wones, D. R., 1973, Oxidation during Magmatic Differentiation,

774   Finnmarka Complex, Oslo Area, Norway .2. Mafic Silicates: Journal of Petrology, v. 14,

775   no. 3, p. 349-380.

776   Dalpé, C., and Baker, D. R., 2000, Experimental investigation of large-ion-lithophile-element-,

777   high-field-strength-element- and rare-earth-element-partitioning between calcic

778   amphibole and basaltic melt: the effects of pressure and oxygen fugacity: Contributions

779   to Mineralogy and Petrology, v. 140, no. 2, p. 233-250.

780   Davidson, A., 1982, Petrochemistry of the Blachford Lake Complex near Yellowknife,

781   Northwest Territories.: Maurice, E. T. (ed.) Uranium in Granites. Geological Survey of

782   Canada, p. 71-79.

783   Emslie, R. F., Hamilton, M. A., and Theriault, R. J., 1994, Petrogenesis of a Midproterozoic

784   anorthosite-mangerite-charnockite-granite (AMCG) complex - isotopic and chemical

785   evidence from the Nain Plutonic Suite: Journal of Geology, v. 102, no. 5, p. 539-558.

786   Emslie, R. F., and Stirling, J. A. R., 1993, Rapakivi and Related Granitoids of the Nain Plutonic

787   Suite - Geochemistry, Mineral Assemblages and Fluid Equilibria: Canadian Mineralogist,

788   v. 31, p. 821-847.

789   Giehl, C., Marks, M., and Nowak, M., 2013, Phase relations and liquid lines of descent of an

790   iron-rich peralkaline phonolitic melt: an experimental study: Contributions to Mineralogy

791   and Petrology, v. 165, no. 2, p. 283-304.

792   Giret, A., Bonin, B., and Leger, J. M., 1980, Amphibole Compositional Trends in Oversaturated

793   and Undersaturated Alkaline Plutonic Ring-Complexes: Canadian Mineralogist, v. 18, p.

794   481-495.

795   Gower, C. F., and Krogh, T. E., 2002, A U-Pb geochronological review of the Proterozoic

796   history of the eastern Grenville Province: Canadian Journal of Earth Sciences, v. 39, no.

797   5, p. 795-829.

798   Gysi, A. P., and Williams-Jones, A. E., 2013, Hydrothermal mobilization of pegmatite-hosted

799   REE and Zr at Strange Lake, Canada: A reaction path model: Geochimica et

800   Cosmochimica Acta, v. 122, no. 2013, p. 324-352.

801   Gysi, A. P., Williams-Jones, A. E., and Collins, P., 2016, Lithogeochemical Vectors for

802   Hydrothermal Processes in the Strange Lake Peralkaline Granitic REE-Zr-Nb-Deposit:

803   Economic Geology and the Bulletin of the Society of Economic Geologists, v. 111, p.

804   1241-1276.

805   Hawthorne, F. C., 1976, The crystal chemistry of amphiboles: V. the structure and chemistry of

806   arfvedsonite: Canadian Mineralogist, v. 14, p. 346-356.

807   Hawthorne, F. C., Oberti, R., Cannillo, E., Ottolini, L., Roelofsen, J. N., and Martin, R. F., 2001,

808   Li-bearing arfvedsonitic amphiboles from the Strange Lake peralkaline granite, Quebec:

809   Canadian Mineralogist, v. 39, p. 1161-1170.

810   Hawthorne, F. C., Oberti, R., Harlow, G. E., Maresch, W. V., Martin, R. F., Schumacher, J. C.,

811   and Welch, M. D., 2012, Nomenclature of the amphibole supergroup: American

812   Mineralogist, v. 97, no. 11-12, p. 2031-2048.

813   Hawthorne, F. C., Oberti, R., Ottolini, L., and Foord, E. E., 1996, Lithium-bearing fluor-

814   arfvedsonite from Hurricane Mountain, New Hampshire: A crystal-chemical study:

815   Canadian Mineralogist, v. 34, p. 1015-1019.

816   Hawthorne, F. C., Ungaretti, L., Oberti, R., Bottazzi, P., and Czamanske, G. K., 1993, Li - an

817   Important Component in Igneous Alkali Amphiboles: American Mineralogist, v. 78, no.

818   7-8, p. 733-745.

819   Herrmann, W., and Berry, R. F., 2002, MINSQ - a least squares spreadsheet method for

820   calculating mineral proportions from whole rock major element analyses: Geochemistry:

821   Exploration, Environment, Analysis, v. 2, no. 4, p. 361-368.

822   James, D. T., and Dunning, G. R., 2000, U-Pb geochronological constraints for paleoproterozoic

823   evolution of the core zone, southeastern Churchill Province, northeastern laurentia:

824   Precambrian Research, v. 103, no. 1-2, p. 31-54.

825   Kerr, A., and Rafuse, H., 2012, Rare-earth element (REE) geochemistry of the Strange Lake

826   deposits: Implications for resource estimation and metallogenic models.: Current

827   Research (2012) Newfoundland and Labrador Department of Natural Resources, v. 1, p.

828   39-60.

829   King, P. L., Hervig, R. L., Holloway, J. R., Vennemann, T. W., and Righter, K., 1999, Oxy-

830   substitution and dehydrogenation in mantle-derived amphibole megacrysts: Geochimica

831   Et Cosmochimica Acta, v. 63, no. 21, p. 3635-3651.

832   Konopleva, N. G., Ivanyuk, G. Y., Pakhomovsky, Y. A., Yakovenchuk, V. N., Men'shikov, Y.

833   P., and Korchak, Y. A., 2008, Amphiboles of the Khibiny alkaline pluton, Kola

834   Peninsula, Russia: Geology of Ore Deposits, v. 50, no. 8, p. 720-731.

835   Kovalenko, V. I., Tsaryeva, G. M., Goreglyad, A. V., Yarmolyuk, V. V., Troitsky, V. A., Hervig,

836   R. L., and Farmer, G. L., 1995, The Peralkaline Granite-Related Khaldzan-Buregtey

837   Rare-Metal (Zr, Nb, Ree) Deposit, Western Mongolia: Economic Geology and the

838   Bulletin of the Society of Economic Geologists, v. 90, no. 3, p. 530-547.

839   Leake, B. E., 1968, A Catalog of Analyzed Calciferous and Subcalciferous Amphiboles Together

840   with Their Nomenclature and Associated Minerals: Geological Society of America,

841   Special Papers 1968, v. 98, p. 1-44.

842   Leake, B. E., Woolley, A. R., Arps, C. E. S., Birch, W. D., Gilbert, M. C., Grice, J. D.,

843   Hawthorne, F. C., Kato, A., Kisch, H. J., Krivovichev, V. G., Linthout, K., Laird, J.,

844   Mandarino, J. A., Maresch, W. V., Nickel, E. H., Rock, N. M. S., Schumacher, J. C.,

845   Smith, D. C., Stephenson, N. C. N., Ungaretti, L., Whittaker, E. J. W., and Guo, Y. Z.,

846   1997, Nomenclature of amphiboles: Report of the subcommittee on amphiboles of the

847   International Mineralogical Association, Commission on New Minerals and Mineral

848   Names: Canadian Mineralogist, v. 35, p. 219-246.

849   Locock, A. J., 2014, An Excel spreadsheet to classify chemical analyses of amphiboles following

850   the IMA 2012 recommendations: Computers & Geosciences, v. 62, p. 1-11.

851   Ltd., Q. R. M., 2012, Quest announces that a revised resource estimate for the Strange Lake B-

852   Zone REE deposit shows a doubling of tonnage, http://questareminerals.com/news.php,

853   Volume 2016: Toronto, Quest Rare Minerals Ltd.

854   Markl, G., Marks, M., Schwinn, G., and Sommer, H., 2001, Phase equilibrium constraints on

855   intensive crystallization parameters of the Ilimaussaq complex, South Greenland: Journal

856   of Petrology, v. 42, no. 12, p. 2231-2258.

857   Marks, M., Halama, R., Wenzel, T., and Markl, G., 2004, Trace element variations in

858   clinopyroxene and amphibole from alkaline to peralkaline syenites and granites:

859   implications for mineral-melt trace-element partitioning: Chemical Geology, v. 211, no.

860   3-4, p. 185-215.

861 Mayer, B., Jung, S., Romer, R. L., Pfander, J. A., Klugel, A., Pack, A., and Groner, E., 2014,

862   Amphibole in alkaline basalts from intraplate settings: implications for the petrogenesis

863   of alkaline lavas from the metasomatised lithospheric mantle: Contributions to

864   Mineralogy and Petrology, v. 167, no. 989.

865 McLelland, J. M., Selleck, B. W., Hamilton, M. A., and Bickford, M. E., 2010, Late- to post-

866   tectonic setting of some major proterozoic anorthosite - mangerite - charnockite - granite

867   (AMCG) suites: Canadian Mineralogist, v. 48, no. 4, p. 729-750.

868 Miller, R. R., 1996, Structural and textural evolution of the Strange Lake peralkaline rare-

869   element (NYF) granitic pegmatite, Quebec-Labrador: Canadian Mineralogist, v. 34, p.

870   349-371.

871 Miller, R. R., Heaman, L. M., and Birkett, T. C., 1997, U-Pb zircon age of the Strange Lake

872   peralkaline complex: Implications for Mesoproterozoic peralkaline magmatism in north-

873   central Labrador: Precambrian Research, v. 81, no. 1-2, p. 67-82.

874 Mungall, J. E., and Martin, R. F., 1996, Extreme differentiation of peralkaline rhyolite, Terceira,

875   Azores: A modern analogue of Strange Lake, Labrador?: Canadian Mineralogist, v. 34, p.

876   769-777.

877 Oberti, R., Cannillo, E., and Toscani, G., 2012, How to name amphiboles after the IMA2012

878   report: rules of thumb and a new PC program for monoclinic amphiboles: Periodico Di

879   Mineralogia, v. 81, no. 2, p. 257-267.

880 Petrella, L., Williams-Jones, A. E., Goutier, J., and Walsh, J., 2014, The Nature and Origin of the

881   Rare Earth Element Mineralization in the Misery Syenitic Intrusion, Northern Quebec,

882   Canada: Economic Geology, v. 109, no. 6, p. 1643-1666.

883   Piilonen, P. C., Mcdonald, A. M., Poirier, G., Rowe, R., and Larsen, A. O., 2013, Mafic Minerals

884   of the Alkaline Pegmatites in the Larvik Plutonic Complex, Oslo Rift, Southern Norway:

885   Canadian Mineralogist, v. 51, no. 5, p. 735-770.

886   Pillet, D., Chenevoy, M., and Belanger, M., 1992, Petrology of Peralkaline Granite from Lake

887   Brisson (Central Labrador, Nouveau-Quebec) .1. Intrusion and Chemical Evolution:

888   Canadian Journal of Earth Sciences, v. 29, no. 2, p. 353-372.

889   -, 1993, Petrology of Peralkaline Granite from Lake Brisson (Quebec-Labrador) .2. Mineralogy

890   and Modes of Crystallization: Canadian Journal of Earth Sciences, v. 30, no. 12, p. 2423-

891   2435.

892   Roelofsen, J. N., 1997, The primary and secondary mafic silicates of two alkaline anorogenic

893   complexes: Strange Lake (Québec-Labrador) and Amba Dongar (Gujarat, India) [Ph.D.:

894   McGill University, 321 p.

895   Salvi, S., and Williams-Jones, A. E., 1990, The Role of Hydrothermal Processes in the Granite-

896   Hosted Zr, Y, Ree Deposit at Strange Lake, Quebec Labrador - Evidence from Fluid

897   Inclusions: Geochimica et Cosmochimica Acta, v. 54, no. 9, p. 2403-2418.

898   Salvi, S., and Williams-Jones, A. E., 1992, Reduced Orthomagmatic C-O-H-N-Nacl Fluids in the

899   Strange Lake Rare-Metal Granitic Complex, Quebec Labrador, Canada: European

900   Journal of Mineralogy, v. 4, no. 5, p. 1155-1174.

901   Salvi, S., and Williams-Jones, A. E., 1996, The role of hydrothermal processes in concentrating

902   high-field strength elements in the Strange Lake peralkaline complex, northeastern

903   Canada: Geochimica et Cosmochimica Acta, v. 60, no. 11, p. 1917-1932.

904 Salvi, S., and Williams-Jones, A. E., 1997, Fischer-Tropsch synthesis of hydrocarbons during

905   sub-solidus alteration of the Strange Lake peralkaline granite, Quebec/Labrador, Canada:

906   Geochimica Et Cosmochimica Acta, v. 61, no. 1, p. 83-99.

907 Salvi, S., and Williams-Jones, A. E., 2006, Alteration, HFSE mineralisation and hydrocarbon

908   formation in peralkaline igneous systems: Insights from the Strange Lake Pluton, Canada:

909   Lithos, v. 91, p. 19-34.

910 Shannon, R. D., 1976, Revised Effective Ionic-Radii and Systematic Studies of Interatomic

911   Distances in Halides and Chalcogenides: Acta Crystallographica Section A, v. 32, no.

912   Sep1, p. 751-767.

913 Sun, S. S., and McDonough, W. F., 1989, Chemical and isotopic systematics of oceanic basalts:

914   implications for mantle composition and processes: Geological Society, London, Special

915   Publications, v. 42, p. 313-345.

916 Tiepolo, M., Oberti, R., Zanetti, A., Vannucci, R., and Foley, S. F., 2007, Trace-element

917   partitioning between amphibole and silicate melt: Amphiboles: Crystal Chemistry,

918   Occurrence, and Health Issues, v. 67, p. 417-451.

919 Tiepolo, M., Vannucci, R., Bottazzi, P., Oberti, R., Zanetti, A., and Foley, S., 2000, Partitioning

920   of rare earth elements, Y, Th, U, and Pb between pargasite, kaersutite, and basanite to

921   trachyte melts: Implications for percolated and veined mantle: Geochemistry Geophysics

922   Geosystems, v. 1.

923 Tuttle, O. F., and Bowen, N. L., 1958, Origin of granite in the light of experimental studies in the

924   system $NaAlSi_3O_8$-$KAlSi_3O_8$-SiO_2-H_2O, Geological Society of America, Memoir 74, 146

925   p.:

926 Vasyukova, O., and Williams-Jones, A. E., 2014, Fluoride–silicate melt immiscibility and its role

927   in REE ore formation: Evidence from the Strange Lake rare metal deposit, Que´bec-

928   Labrador, Canada: Geochimica et Cosmochimica Acta, v. 139, no. 2014, p. 110-130.

929 -, 2016, The evolution of immiscible silicate and fluoride melts: Implications for REE ore-

930   genesis: Geochimica et Cosmochimica Acta, v. 172, p. 205-224.

931 Vasyukova, O. V., Williams-Jones, A. E., and Blamey, N. J. F., 2016, Fluid evolution in the

932   Strange Lake granitic pluton, Canada: Implications for HFSE mobilization: Chemical

933   Geology, v. 444, p. 83-100.

934

FIGURE CAPTIONS

936 Fig. 1: A geological map of the Strange Lake pluton showing the distribution of the major

937 lithological units. Locations of the samples used in this study are indicated.

938 Fig. 2: Thin section photomicrographs showing a) amphibole in hypersolvus granite (Arf),

939 occupying interstices between alkali-feldspar (perthite) (Afs) and quartz (Qtz) (ppl view), b)

940 amphibole in hypersolvus granite showing swapped margin texture with alkali-feldspar (ppl), c)

941 interstitial amphibole in the northern hypersolvus granite that has been largely replaced by

942 aenigmatite (red) (Aen) and astrophyllite (orange) (Ast) (xpl) and d) a Li-bearing amphibole

943 (Lea) phenocryst in transsolvus granite that has been partly replaced by aegirine (Aeg) along its

944 rim (ppl).

945 Fig. 3: Backscattered electron images of Strange Lake amphibole-group minerals showing a)

946 arfvedsonite with one large and numerous small fluorite (Fl) and fluorite-fluocerite solid solution

947 (Fl-Flc) (brighter) inclusions (hypersolvus granite), b) amphibole interstitial to perthitic alkali

948 feldspar and quartz (hypersolvus granite), replaced by fibrous astrophyllite along the rim, c) an

949 euhedral Li-bearing alkali amphibole (ferro-ferri-fluoro-leakeite) crystal (transsolvus granite)

950 containing numerous microcline (Mc) and albite (Ab) inclusions and, d) small subhedral

951 amphibole crystals among K-feldspar (Ksp) and quartz crystals (enclave).

952 Fig. 4: Ternary diagrams showing a) the A-and B-site occupancy of the sodic-calcic to sodic

953 amphibole-group minerals of the Strange Lake pluton (in apfu) (note that theoretically,

954 endmember arfvedsonite can have any composition along the Na-K tie-line), and b) the C-site

955 occupation of the amphibole-group minerals. The diagram (b) organizes the compositional data

956 according to the valence state of the cations, where $R^+ = {}^CLi^+$, $R^{2+} = Fe^{2+}$, Mn^{2+}, Mg^{2+}, Zn^{2+} and

957 $R^{3+} = Fe^{3+}$, $^{C}Al^{3+}$. The endmember compositions of katophorite (sodic-calcic), arfvedsonite and

958 leakeite (sodic) are indicated on the diagrams. In the legend "fgr" (southern hypersolvus granite)

959 refers to the fine-grained rocks of the unit, whereas "peg" stands for the oikiocrystic to

960 pegmatitic textured rocks.

961 Fig. 5: Binary diagrams showing major and minor element concentrations of amphibole in atoms

962 per formula unit (apfu), all as a function of Al concentration (X-axis). The decreasing Al content

963 monitors the differentiation of the magma.

964 Fig. 6: Binary diagrams showing the changing concentration (apfu) of selected elements as a

965 function of Al concentration (dashed arrows) from the cores to rims of amphibole phenocrysts in

966 the transsolvus granite.

967 Fig. 7: Chondrite-normalized REE- and trace element profiles of the Strange Lake amphibole-

968 group minerals displayed with the average bulk rock profiles of the respective units. a) REE- and

969 b) trace element spider diagram for the southern hypersolvus granite; c) REE- and d) trace

970 element spider diagram for the northern hypersolvus granite; and e) REE- and f) trace element

971 spider diagram for the transsolvus granite and enclaves. The chondrite values are from Sun and

972 McDonough, 1989.

973 Fig. 8: Chondrite-normalized REE-spider diagrams showing the average distribution of the

974 elements corresponding to the amphibole species identified in the Strange Lake pluton. The

975 chondrite values are from Sun and McDonough, 1989.

976 Fig. 9: Binary diagram showing the amphibole Fe^{2+}/Fe^{3+} ratio as a function of the Na/Ca ratio in

977 both, hypersolvus and transsolvus granite indicating a (low degree) coupled behavior of the

978 ratios in rocks with the same major phase paragenesis.

979 Fig. 10: Bar diagram showing the (average) relative proportion of the anions occupying the W-

980 site for each granite unit.

981 Fig. 11: Binary diagram illustrating the positive correlation between Fe^{3+} and Li^+ in amphibole

982 from the different granite facies. Linear trend lines and correlation coefficients have been added

983 to distinguish amphibole in the hypersolvus granite from that in the transsolvus granite. Lithium

984 concentrations are consistently lower in the hypersolvus granite than in the transsolvus granite.

985 Fig. 12: Binary diagrams showing the total REE concentration in amphibole of the different

986 granite facies as a function of the concentration of selected major elements. Also shown are the

987 corresponding trend lines and correlation coefficients (R^2).

988 Fig. 13: Diagram showing the ionic radii of the REE either in 6-fold (C-site) or 8-fold (B-site)

989 coordination versus the apparent partition coefficient $D_{arf-bulk}$ (median REE content of amphibole

990 / REE content of the bulk rock, sample 204720), plotted with error bars (median absolute

991 deviation). Also shown is a Lattice-Strain Theory fit through these data (solid line).

992 Fig. 14: Chart comparing the relative proportions of the bulk rock REE concentrations hosted by

993 amphibole (average values) for each granite facies (see text for details). The chart for the

994 southern hypersolvus granite only considers fine-grained samples.

995 Fig. 15: Cartoons showing the evolution of amphibole in the context of the textural development

996 of a) hypersolvus and b) transsolvus granite, from liquidus to solidus stages and the subsolidus

997 Na-alteration that affected the transsolvus granite. Crystallization temperature-, pressure- and

998 oxygen fugacity ranges are given, and were taken from the studies of the Strange Lake pluton by

999 Salvi and Williams-Jones (1992) and Vasyukova et al. (2016). The fO$_2$ ranges are indicated in

47

1000   respect to the iron oxide buffers, MH (magnetite-hematite), QFM (quartz-fayalite-magnetite) and

1001   QIF (quartz-iron-fayalite).

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fingerprints of magma evolution. Lithos 288:156-174.
doi: 10.1016/j.lithos.2017.07.012.

Tables

Table 1: Average (median) bulk rock major and trace element compositions of the unaltered granites from the center of the Strange Lake pluton (*fgr = fine grained samples, +oik/peg = oikocrystic and pegmatitic samples)

Unit	Hypersolvus granite S fgr*		Hypersolvus granite S oik/peg+		Hypersolvus granite N		Transsolvus granite		Enclaves	
Samples	*7*		*8*		*12*		*24*		*12*	
		+/-		+/-		+/-		+/-		+/-
SiO_2 *wt. %*	69.04	0.89	70.57	0.56	70.68	0.36	71.28	0.53	69.36	0.60
Al_2O_3	11.88	0.26	10.57	0.17	11.74	0.21	10.27	0.39	11.97	0.25
Fe_2O_3	5.78	0.31	6.72	0.52	4.89	0.08	5.98	0.47	5.05	0.10
MnO	0.10	0.01	0.11	0.01	0.10	0.01	0.12	0.01	0.09	0.02
MgO	0.04	0.01	0.02	0.01	0.05	0.01	0.03	0.01	0.04	0.02
CaO	0.73	0.19	0.37	0.11	0.57	0.03	0.45	0.18	0.83	0.15
Na_2O	4.92	0.17	5.11	0.05	5.09	0.10	5.08	0.35	3.60	0.98
K_2O	4.93	0.21	4.48	0.09	4.74	0.11	4.32	0.31	7.60	1.61
TiO_2	0.28	0.03	0.21	0.03	0.27	0.01	0.21	0.05	0.15	0.04
Nb_2O_5	0.03	0.01	0.05	0.01	0.06	0.005	0.05	0.02	0.02	0.02
P_2O_5	0.02	0.00	0.02	-	0.02	0.01	0.01	0.01	-	-
F	0.44	0.02	0.37	0.09	0.46	0.04	0.51	0.06	0.49	0.07
TREO	0.17	0.03	0.19	0.02	0.24	0.03	0.48	0.06	0.25	0.03
LREO	0.12	0.02	0.13	0.02	0.16	0.02	0.33	0.04	0.16	0.02
HREO+Y	0.05	0.005	0.06	0.01	0.08	0.01	0.11	0.04	0.09	0.01
LOI	0.72		0.47		0.70		0.72		0.83	
Total	98.53		99.19		99.14		99.20		99.68	
Agp index	1.13	0.02	1.23	0.02	1.15	0.03	1.27	0.03	1.17	0.02
Be *(ppm)*	36	8	40	14	53	11	54	22	31	7
Zn	285	40	545	30	465	60	585	90	465	145
Ga	45	3	52	3	44	1	60	3	48	5
Rb	417	23	436	31	522	47	672	99	925	241
Sr	18	5	15	5	21	7	21	8	21	5
Y	266	17	293	36	392	74	616	196	556	48
Zr	2413	667	2504	469	3656	268	4984	1917	1488	1126
Ba	76	13	43	8	85	18	43	15	58	14
La	228	33	221	35	305	51	630	81	286	47
Ce	464	73	485	72	629	79	1235	170	589	88
Pr	56	14	60	7	73	10	149	20	74	10
Nd	191	42	207	27	240	35	527	52	282	23
Sm	39	10	51	6	49	6	115	16	68	5
Eu	2	0.4	3	0.4	3	0.4	6	1	4	0.2
Gd	33	5	44	7	45	7	100	18	66	7
Tb	6	1	8	1	10	1	17	4	12	1
Dy	44	7	53	8	69	12	103	29	72	10
Ho	10	2	11	2	15	2	21	7	14	3
Er	33	6	36	7	50	6	64	24	37	10
Tm	5	1	6	1	8	1	9	4	5	2
Yb	36	3	42	9	57	4	58	29	25	10
Lu	6	0.4	7	1	9	1	8	4	4	1

49

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Hf	69	12	67	12	97	15	136	47	42	31
Ta	14	1	20	4	28	4	25	13	7	5
Pb	94	17	169	53	137	38	187	73	38	21
Th	54	9	69	20	88	15	84	40	23	17
U	10	3	14	3	19	2	17	8	4	3

1006

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1007 Table 2: Average calculated formulae and cation assignments (in apfu) of amphibole group

1008 minerals, based on 24 oxygens. Ideal site occupation is noted in brackets. The rock units are: HS

1009 S fgr (hypersolvus granite south, fine grained), HS N (hypersolvus granite north), EN (enclaves),

1010 TS (transsolvus granite).

Species	Arfved sonite	Fluor-arfvedsonite	Ferro-ferri-leakeite	Ferro-ferri-fluoro-leakeite	Ferro-ferri-kato-phorite
Unit	HS S	all units	HS N	HS N, TS	HS S fgr
Analyses	*n=12*	*n=56*	*n=5*	*n=70*	*n=6*
Formula Assignments					
Si	7.64	7.83	7.64	7.74	7.53
Al	0.23	0.10	0.11	0.07	0.36
Ti	0.09	0.09	0.11	0.09	0.11
Fe^{3+}	0.10	0.03	0.15	0.12	-
T (8)	8.00	8.00	8.00	8.00	8.00
Ti	0.09	0.06	-	0.03	0.10
Zr	0.01	0.01	0.02	0.01	-
Al	0.10	0.05	-	-	-
REE	0.02	0.01	0.01	-	0.03
Fe^{3+}	1.66	1.70	1.99	2.01	1.36
Zn	0.08	0.04	0.11	0.05	0.06
Mn^{2+}	0.09	0.10	0.09	0.08	0.10
Fe^{2+}	2.62	2.49	1.96	2.00	3.02
Mg	0.06	0.04	0.05	0.02	0.09
Li	0.29	0.31	0.71	0.74	0.15
C (5)	4.87	4.75	4.94	4.92	4.91
Li	-	-	0.07	0.08	-
Ca	0.23	0.10	0.09	0.03	0.57
Na	1.77	1.90	1.87	1.95	1.43
B (2)	2.00	2.00	2.00	2.00	2.00
Na	0.79	0.89	0.87	0.86	0.69
K	0.28	0.31	0.31	0.33	0.26
A (0-1)	1.07	1.20	1.18	1.19	0.95
OH	1.05	0.70	0.93	0.61	1.14
F	0.72	1.07	0.85	1.20	0.44
Cl	0.01	-	-	-	0.01
O	0.23	0.22	0.21	0.19	0.41
W (2)	2.00	2.00	2.00	2.00	2.00

1011

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1012 Table 3: List of amphibole and titanium bearing minerals identified in the unaltered Strange Lake

1013 granites with their endmember structural formulae

Mineral name	Formula
Amphibole-group minerals	
(Fluoro)-arfvedsonite	$NaNa_2(Fe^{2+}_4Fe^{3+})Si_8O_{22}(OH,F)_2$
Ferro-ferri-(fluoro)-katophorite	$Na(NaCa)(Fe^{2+}_4Fe^{3+})Si_7AlO_{22}(OH,F)_2$
Ferro-ferri-(fluoro)-leakeite	$NaNa_2(Fe^{2+})_2(Fe^{3+})_2LiSi_8O_{22}(OH,F)_2$
Clinopyroxenes	
Aegirine	$NaFe^{3+}Si_2O_6$
Titano-silicates and Ti-oxide mineral	
Aenigmatite	$Na_2Fe^{2+}_5TiSi_6O_{20}$
Astrophyllite	$(K,Na)_3(Fe^{2+})_7Ti_2Si_8O_{26}(OH)_4$
Narsarsukite	$Na_2(Ti,Fe^{3+})Si_4(O,F)_{11}$
Titanite	$CaTiSiO_5$
Ilmenite	$Fe^{3+}TiO_3$

1014

Unit	Hypersolvus granite S fgr*		Hypersolvus granite S oik/peg[+]		Hypersolvus granite N		Enclaves		Transsolvus granite	
Analyses	*n=13*		*n=19*		*n=39*		*n=9*		*n=72*	
		+/-		+/-		+/-		+/-		+/-
SiO_2 *wt. %*	48.29	0.51	49.97	0.80	50.71	0.19	50.71	0.93	51.02	0.52
Al_2O_3	1.47	0.30	0.99	0.15	0.50	0.08	0.36	0.01	0.34	0.05
TiO_2	1.45	0.30	0.84	0.12	1.09	0.14	0.92	0.08	0.71	0.09
FeO	33.67	0.42	33.80	0.41	32.06	0.27	31.78	0.22	32.47	0.38
MgO	0.72	0.05	0.64	0.05	0.85	0.03	0.71	0.08	0.56	0.04
MnO	0.34	0.07	0.10	0.08	0.22	0.03	0.09	0.03	0.08	0.03
ZnO	0.62	0.16	0.24	0.05	0.45	0.04	0.60	0.11	0.30	0.05
ZrO_2	0.04	0.02	0.06	0.03	0.17	0.04	0.13	0.03	0.11	0.03
Nb_2O_5	0.07	0.02	0.02	0.01	0.02	0.02	0.02	0.01	0.01	0.004
Na_2O	7.25	0.54	9.18	0.20	9.36	0.09	9.34	0.19	9.57	0.13
K_2O	1.27	0.15	1.28	0.12	1.59	0.11	1.73	0.09	1.65	0.09
CaO	2.79	0.69	1.11	0.50	0.47	0.08	0.13	0.05	0.13	0.03
F	1.29	0.31	1.97	0.27	2.08	0.12	2.05	0.18	2.56	0.15
Cl	0.03	0.01	0.02	0.01	0.01	0.01	-	-	0.01	0.005
Total	99.18		100.5		99.87		98.84		99.93	
Li *(ppm)*	1613	772	1450	615	3099	549	4802	931	5775	1260
Rb	58.8	17.8	20.9	6.3	61.8	9.4	88.7	15.5	84.3	18.6
Sr	23.3	6.8	8.5	3.0	11.7	3.7	4.0	1.4	1.4	0.5
Y	471	145	70.9	26.0	107	27	92.0	32.0	27.7	5.5
Zr	1208	653	647	124	2648	450	2073	234	1356	339
Sn	160	80.3	21.3	8.9	156	49	90.1	36.2	137	41
La	96.0	11.2	31.9	9.5	32.4	5.9	24.1	8.5	2.8	1.2
Ce	282	24	91.6	14.7	85.9	22.6	45.3	9.7	6.6	2.8
Pr	44.4	4.9	13.5	2.8	13.7	4.3	6.9	1.6	1.0	0.4
Nd	218	25	60.1	15.7	62.3	20.5	32.5	8.0	4.7	2.2
Sm	59.7	7.3	13.8	2.7	11.6	4.5	6.2	1.3	0.91	0.47
Eu	4.0	0.3	0.85	0.22	0.68	0.30	0.37	0.17	0.05	0.02
Gd	50.0	5.8	9.6	2.0	7.6	3.1	9.3	3.9	0.67	0.33
Tb	10.6	1.5	1.7	0.5	1.6	0.6	1.7	0.7	0.21	0.08
Dy	71.7	13.8	12.4	2.3	18.3	5.7	11.4	3.0	2.6	0.6
Ho	17.1	3.7	3.1	0.5	7.7	1.8	3.2	0.9	1.2	0.3
Er	69.7	21.2	15.1	2.9	48.5	12.3	14.9	1.2	8.1	1.4
Tm	14.2	4.4	4.3	1.0	17.5	4.8	4.6	0.8	2.7	0.5
Yb	144	52	53.1	11.8	215	53	52.4	5.7	35.9	6.3
Lu	29.5	11.6	11.7	2.6	50.1	11.5	12.8	3.1	8.6	1.9
Hf	60.3	35.8	27.5	7.0	130	25	85.0	20.6	63.6	17.6
Ta	9.0	1.7	2.2	0.4	2.9	0.8	1.9	0.6	1.1	0.3
Pb	77.9	8.0	8.9	5.1	34.5	10.5	10.7	4.6	5.8	1.7
Nb	468	116	124	51	214	34	109	20	92.4	13.8
Ba	10.5	6.3	3.4	2.5	6.0	2.4	1.9	0.9	0.43	0.26
Th	1.7	1.4	0.75	0.66	0.51	0.47	2.9	2.5	0.02	0.02
U	0.13	0.10	0.13	0.11	0.03	0.03	0.16	0.15	0.01	0.01

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| TREE+Y | 1634 | 297 | 395 | 91 | 708 | 174 | 389 | 117 | 110 | 19 |

1018

1019   Table 5: Average (median) core and rim compositions (in apfu) with median absolute deviation

1020   (+/-) of selected phenocrysts from the transsolvus granite

Location	Core		Rim	
Analyses	*n=24*		*n=7*	
		+/-		+/-
^{T}Si *(apfu)*	7.906	0.102	7.716	0.039
^{T}Al	0.059	0.006	0.059	0.003
^{T}Ti	0.072	0.010	0.083	0.008
^{T}Fe^{3+}	0.143	0.030	0.135	0.025
^{C}Ti	0.084	0.016	0.001	-
^{C}Zr	0.008	0.003	0.008	0.002
^{C}Al	0.052	0.019	-	-
^{C}REE	0.002	0.001	0.002	-
^{C}Fe^{3+}	1.763	0.215	2.022	0.007
^{C}Zn	0.034	0.006	0.072	0.015
^{C}Mn^{2+}	0.072	0.004	0.081	0.007
^{C}Fe^{2+}	2.441	0.321	1.952	0.058
^{C}Mg	0.026	0.006	0.014	0.001
^{C}Li	0.407	0.232	0.825	0.044
^{B}Li	0.051	0.024	0.066	0.024
^{B}Ca	0.024	0.006	0.019	0.005
^{B}Na	1.973	0.009	1.964	0.017
^{A}Na	0.867	0.042	0.838	0.037
^{A}K	0.317	0.011	0.347	0.050
^{W}F	1.205	0.057	1.027	0.122
total Ti	0.156	0.026	0.083	0.008
total Al	0.111	0.025	0.059	0.003
total Fe^{3+}	0.074	0.011	2.164	0.046
total Na	1.906	0.245	2.769	0.040
total Li	8.034	0.006	0.860	0.071
total Fe	0.156	0.020	0.825	0.044
Fe^{2+}/Fe^{3+}	2.449	0.324	2.134	0.040

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fingerprints of magma evolution. Lithos 288:156-174.
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1022   Table 6: Apparent melt-arfvedsonite partition coefficients ($D_{arf-bulk}$), ionic radius 'r' in 6- and 8-

1023   fold coordination, ideal radius (r) for each element and median absolute deviation (MAD)

	$D_{arf-bulk}$	r_{6-fold}	r_{8-fold}	r	MAD[*]
La	0.006	1.03	1.16	1.2	0.005
Ce	0.005	1.01	1.14	1.1	0.003
Pr	0.005	0.99	1.13	1.1	0.003
Nd	0.008	0.98	1.11	1.1	0.004
Sm	0.006	0.96	1.08	1.1	0.002
Eu	0.006	0.95	1.07	1.1	0.004
Gd	0.006	0.94	1.05	0.9	0.003
Tb	0.014	0.92	1.04	0.9	0.002
Dy	0.027	0.91	1.03	0.9	0.005
Ho	0.075	0.90	1.02	0.9	0.011
Er	0.201	0.89	1.00	0.9	0.016
Tm	0.657	0.88	0.99	0.9	0.053
Yb	1.664	0.87	0.99	0.9	0.165
Lu	3.261	0.86	0.98	0.9	0.321
Y	0.043	0.90	1.02	0.9	0.006

1024

1025   [*]The Median Absolute Deviation (MAD) is reported (plotted as error bars in Fig. 14) instead of the standard deviation, as the
1026   median amphibole concentration was used instead of the mean concentration.

1027

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1028 Appendix A: Standards, counting time and detection limits used for electron microprobe

1029 analyses (EMPA) of the amphibole group minerals

Element	Standard	Counting time (s)	Detection limit (ppm)
Na	Albite	20	267
Fe	Hematite	20	264
Mn	Spessartine	20	413
Ti	Rutile	20	370
Zr	Zircon	20	653
Si	Diopside	20	363
Ca	Diopside	20	243
Mg	Diopside	20	266
Al	Orthoclase	20	216
K	Orthoclase	20	205
Cl	Vanadinite	20	218
F	Fluorite	100	1501
Zn	Willemite	20	427

1030

1031 Detection limits and standard deviations (2 σ) represent average detection limits calculated from repeated analyses of standards
1032 during the analytical runs.

THE AMPHIBOLES OF THE REE-RICH A-TYPE PERALKALINE STRANGE LAKE PLUTON – FINGERPRINTS OF MAGMA EVOLUTION

Lithos

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1. INTRODUCTION

Our understanding of the genesis of intra-plate rift-generated intrusions that produce A-type granites is still incomplete. In particular, the reasons for the extremely high REE-, F- and other HFSE-concentrations in many of these peralkaline rocks are poorly known. In addition to the need for a highly fertile magma source, magmatic evolution by fractional crystallization appears to play a critical role in the enrichment of these elements (e.g., Kovalenko et al., 1995; Mungall and Martin, 1996). The chemistry of a major mineral, such as amphibole, which adapts to its *P-T-X* environment, and is capable of hosting most cation sizes and charges, can potentially record this and any other processes that might have operated in the magma chamber. As a phenocryst, the amphibole would record the conditions prior to intrusion, and as a late crystallizing phase, the in-situ crystal fractionation processes.

The well-known ability of minerals of the amphibole super-group to accommodate a wide variety of elements with highly variable ionic radius and charge, including alkali elements, high field strength elements (HFSE) and the rare earth elements (REE), makes it an ideal monitor of magma evolution (Abdel-Rahman, 1994; Marks et al., 2004). In this study, we use the occurrence and composition of amphibole-group minerals in the Strange Lake pluton, Québec-Labrador, Canada, to trace the evolution of a peralkaline granitic magma that is unusually enriched in the REE, Zr and Nb. This magma was the source of a large REE/HFSE resource (indicated resources: 278 million tons grading 0.93 wt. % REE_2O_3, 0.18 wt. % Nb_2O_5 and 1.92 wt. % ZrO_2; Quest Rare Minerals Ltd., 2012) that is currently being considered for exploitation. In this study, the Na, Ca, Li, Fe^{3+} and REE contents of the amphibole-group minerals are used to gain information on the composition of the magma and conditions prior to, during and after its emplacement. The results show that fractional crystallization of a perthitic alkali feldspar, gravity

2

24 settling of REE-minerals and zircon as well as the exsolution of a LREE-rich fluoride melt

25 played a major role in the evolution of the magma and in concentrating the ore elements. They

26 also show that the amphibole-group minerals host a significant proportion of the REE, and were

27 the principal carriers of the HREE in some parts of the pluton.

28 **2. BACKGROUND INFORMATION**

29 A number of studies have traced evolutionary trends in alkaline rock suites using the crystal

30 chemistry of the dominant mafic minerals (Davidson, 1982; Marks et al., 2004). In peralkaline

31 rocks, which are defined by a molar excess of alkalis in respect to aluminum, the mafic minerals

32 are usually of a sodic nature, e.g., amphiboles, such as arfvedsonite and riebeckite, or pyroxenes

33 such as aegirine. The amphiboles of alkaline complexes generally trend from calcic through

34 sodic-calcic to sodic members with differentiation, reflecting the increasing alkalinity of the melt

35 from which they crystallized (Giret et al., 1980; Piilonen et al., 2013). They also display

36 significant variations in REE and HFSE concentrations with magmatic differentiation, as shown,

37 for example, by Marks et al. (2004) for the Gardar alkaline province (SW-Greenland). Similar

38 conclusions have been reached for amphibole phenocrysts in alkaline basalts from the Rhine

39 graben valley, Germany (Mayer et al., 2014).

40 Lithium has proven to be a particularly important constituent of alkali amphiboles (Camara et al.,

41 2010; Hawthorne et al., 1993). Owing to its incompatible character in common rock-forming

42 minerals, its concentration in amphibole may reflect the degree of melt differentiation. This case

43 has been made for lithium-bearing amphiboles from Hurricane Mountain, New Hampshire,

44 where the amphiboles vary from early Li-rich leakeite to late Li-poor riebeckite (Hawthorne et

45 al., 1996). The progressive depletion in lithium in crystals growing into miarolitic cavities in

3

46 granitic pegmatites is consistent with the idea that a highly evolved melt with a high Li content

47 formed the earlier leakeite, and that progressive fluid exsolution resulted in the removal of

48 lithium and the growth of Li-poor riebeckite.

49 The 1240 Ma Strange Lake pluton (Miller et al., 1997) is an extraordinary example of hyper-

50 REE-, Zr-, and Nb- enrichment in a peralkaline granite, and is composed of a sequence of

51 granitic intrusions, two earlier hypersolvus granites and a later transsolvus granite (this study).

52 The last of these intrusions is host to numerous NYF-type pegmatites with extremely high

53 concentrations of REE, particularly the heavy REE (HREE), Zr and Nb. Most of the previous

54 studies of the pluton have focused on the hydrothermal alteration and the rare-metal mineralized

55 pegmatites (Gysi et al., 2016; Gysi and Williams-Jones, 2013; Kerr and Rafuse, 2012; Salvi and

56 Williams-Jones, 1990; 1992; 1996; 1997; 2006; Vasyukova et al., 2016). Several studies,

57 however, have addressed its magmatic evolution. Boily and Williams-Jones (1994) proposed that

58 the REE-enrichment was due to a combination of fractional crystallization, and the

59 heterogeneous distribution of F-rich residual melts, in which the REE and HFSE were

60 transported as fluoro-complexes. Vasyukova and Williams-Jones (2014; 2016) provided

61 evidence for the early separation of a REE- and Y-rich immiscible fluoride melt from the silicate

62 melt, which accumulated in the highly evolved residual melts that formed the mineralized

63 pegmatites.

64 Previous studies of the mafic minerals of the Strange Lake pluton concluded that the amphiboles

65 are enriched in Li and Zn, are associated with Ti-silicates and crystallized under relatively low

66 fO$_2$ (Pillet et al., 1993; Roelofsen, 1997). Hawthorne et al. (2001) showed that Li is an essential

67 component of the amphiboles and identified lithian arfvedsonite and lithian manganoan

68 arfvedsonite.

3. GEOLOGIC SETTING

The Strange Lake pluton is part of the Nain Plutonic AMCG suite, which comprises anorthosites, mangerites, charnockites and granites (Miller, 1996; Gower and Krogh, 2002). Rocks of the Nain suite were emplaced along the boundary between the Archean Nain province and the Archean to Early Paleoproterozoic Churchill province (Emslie et al., 1994), more recently referred to as the Core Zone (James and Dunning, 2000). The Nain Plutonic Suite covers an area of ~19,000 km^2, and was emplaced between 1460 and 1240 Ma, with the Strange Lake pluton (1240 ± 2 Ma) representing the youngest intrusive body (Gower and Krogh, 2002).

To the south and west, the Strange Lake pluton intrudes the Napeu Kainiut quartz monzonite, which is interpreted to represent a satellite body of the Mistastin batholith (Miller et al., 1997). The Napeu Kainiut intrusion, which is composed mainly of quartz, K-feldspar, plagioclase and biotite, also occurs within the Strange Lake pluton as xenoliths and large roof pendants. The Mistastin batholith consists of pyroxene- and fayalite-bearing Rapakivi-textured granites, which were cut by younger biotite-hornblende-bearing granites and minor syenitic intrusions, such as the Misery Lake syenite, which hosts abundant REE mineralization (Petrella et al., 2014). Dated at 1420 Ma (Emslie and Stirling, 1993), the Mistastin batholith represents one of the oldest members of the Nain Plutonic Suite. The other host rock to the Strange Lake pluton is an Archean to Paleoproterozoic gneiss complex belonging to the Core Zone (Churchill Province), comprising quartzofeldspathic augen-gneiss, banded biotite gneiss and minor garnet-bearing paragneiss and mafic gneiss.

3.1 The Strange Lake Pluton

90   The circular (in outcrop), ~ 6 km in diameter, Strange Lake pluton is located on the border

91   between Québec and Labrador, and consists of a sequence of alkaline granitic intrusive units

92   (Fig. 1). The earliest phase of the pluton is a hypersolvus granite (Pillet et al., 1992), its

93   formation at conditions above those for the alkali feldspar solvus (Tuttle and Bowen, 1958). The

94   hypersolvus granite occurs in the center and southern part of the pluton, and has been subdivided

95   into a northern and a southern unit, based on bulk rock and mineral compositional differences.

96   The third major unit, formerly classified as subsolvus granite (Boily and Williams-Jones, 1994;

97   Salvi and Williams-Jones, 1996; Gysi and Williams-Jones, 2013), is now classified as

98   transsolvus granite, and contains perthite phenocrysts as well as separate albite and K-feldspar

99   crystals in the groundmass. It occupies much of the pluton, and has been strongly affected by

100   hydrothermal activity. A smaller, unaltered part of the transsolvus granite is exposed in the

101   center of the pluton and provided the samples for this study. The transsolvus granite commonly

102   contains dark grey, fine-grained ovoid enclaves and barren pegmatite pockets; the altered

103   transsolvus granite is host to highly REE/HFSE-enriched pegmatites. A dark grey porphyritic

104   microgranite with a fine-grained matrix occurs in contact with remnants of country rock within

105   the pluton and is interpreted to represent quenched hypersolvus granite. The enclaves in the

106   transsolvus granite, some of which are compositionally similar to the hypersolvus granite, are

107   interpreted to represent fragments of this quenched material; the other fragments represent

108   quenched transsolvus granite. The pluton is surrounded by a purple to dark red fluorite-hematite

109   breccia, delineating a ring-fault that contains angular fragments of the host rocks.

110   **3.2 Hypersolvus granite**

111   The hypersolvus granite has been subdivided into an equigranular and fine-grained northern part

112   and a variably textured fine- to coarse-grained southern part (this study). Locally, the southern

hypersolvus granite is coarse-grained and displays poikilitic to pegmatitic textures, which are also observed in drill core of the northern hypersolvus granite (not sampled). These poikilitic textured samples contain anhedral arfvedsonite oikocrysts enclosing smaller crystals of perthitic alkali feldspar, whereas the pegmatitic samples are coarse-grained and contain comb-textured arfvedsonite, quartz, K-feldspar and minor proportions of alkali zirconosilicate minerals. Both the northern and southern hypersolvus granite units are composed of perthitic feldspar, quartz, and sodic amphibole. Minor microcline and albite are present in the groundmass, either reflecting evolution of the magma to conditions in the two-feldspar stability field or subsolidus hydrothermal crystallization. A number of alkali feldspar crystals of the southern hypersolvus granite contain inclusions of fibrous astrophyllite. The quartz and sodic amphibole both occur interstitially to the perthite, and the amphibole appears to have crystallized later than the quartz (Fig. 2a). In most of the southern hypersolvus granite samples, the amphibole exhibits swapped margins with perthite (Fig. 2b). The amphibole contains numerous inclusions of fluorite and a Y-rich fluorite-fluocerite solid solution, particularly in the cores of crystals (Fig. 3a). In addition to the silicates mentioned above, a variety of interstitial zirconosilicate minerals, e.g., vlasovite, elpidite, dalyite and catapleiite replaced primary zircon (remnants of zircon in crystal cores). Titanosilicates occur mostly in the northern hypersolvus granite, and locally replaced the sodic amphibole. These minerals comprise dark red aenigmatite ($Na_2Fe^{2+}_5TiSi_6O_{20}$) and yellow fibrous astrophyllite (($K,Na)_3(Fe^{2+})_7Ti_2Si_8O_{26}(OH)_4$) (Figs. 2c, 3b). The primary REE-minerals of both the northern and southern hypersolvus granite are monazite-(Ce) and fluornatropyrochlore. The monazite-(Ce) crystals are small and euhedral, and occur as inclusions in the perthitic alkali feldspar. Fluor-natropyrochlore is more abundant, and occurs as pyramidal crystals in the groundmass, or as inclusions in the alkali feldspar. The oikocrystic and pegmatitic textured

7

136 <mark>samples contain a much smaller proportion of primary REE minerals than the fine-grained</mark>

137 <mark>varieties of the same unit.</mark> Fluorite is an abundant accessory mineral and forms small to large,

138 rounded, translucent to purple inclusions in sodic amphibole or is disseminated interstitially

139 through the rock. It is usually rimmed by the Y-rich fluorite-fluocerite solid solution, which is

140 brighter in BSE images (Fig. 3a). Locally, gagarinite-(Y) occurs in association with fluorite and

141 the fluorite-fluocerite solid solution, and is interpreted to be secondary.

142 **3.3 Transsolvus granite and enclaves**

143 The transsolvus granite unit, which contains abundant fine-grained, dark grey ellipsoidal

144 enclaves, surrounds and partially intruded the hypersolvus granite. The unaltered part of this

145 intrusion at the center of the pluton is composed of the same major minerals as the hypersolvus

146 granite, i.e., perthitic alkali feldspar, arfvedsonite and quartz. However, in contrast to the

147 hypersolvus granite, microcline and albite form an essential part of the groundmass, indicating

148 that the transsolvus granite crystallized at a lower temperature and/or higher pH_2O than the

149 hypersolvus granite (Tuttle and Bowen, 1958). Amphibole in this granitic facies forms prismatic

150 phenocrysts that locally contain inclusions of microcline and albite (Fig. 3c), but in contrast to

151 amphibole in the hypersolvus granite, they rarely contain fluorite inclusions. Locally, the

152 amphibole has been replaced by aegirine (Fig. <mark>2d</mark>) and, in the more heavily altered parts of the

153 pluton, hematite. Quartz forms round crystals that display a snowball texture, in which primary

154 albite nucleated on the faces of the crystal. Alkali zirconosilicates, such as vlasovite and elpidite,

155 occur intersitially, and usually occupy a larger proportion of the rock volume than in the

156 hypersolvus granite. Narsarsukite ($Na_2(Ti,Fe^{3+})Si_4(O,F)_{11}$), the sole sodium-titanosilicate, occurs

157 as large tabular beige poikilitic crystals, and is observed in the dark grey enclaves and in a

158 number of transsolvus granite samples. Titanite has been reported to occur in the altered parts

(Birkett et al., 1996), and is an abundant phase in the pegmatites of the transsolvus granite (Gysi et al., 2016). The primary REE minerals are fluornatropyrochlore, monazite-(Ce) and gagarinite-(Ce), which was replaced by bastnäsite-(Ce). Fluorbritholite-(Ce) occurs sparsely and interstitially in association with fluorite. Fluorite occurs as a late magmatic, interstitial (translucent) or hydrothermal (purple) phase, and is less abundant than in the hypersolvus granite. The transsolvus granite hosts a large number of NYF-type pegmatites with border zones of K-feldspar, quartz, sodic amphibole and alkali zirconosilicates, and a strongly altered core with quartz, fluorite and exotic REE minerals, as well as zircon and pyrochlore (Gysi and Williams-Jones, 2013). These pegmatites host the bulk of the rare metal mineralization in the deposit and have been the target of recent mineral exploration.

A dark grey, porphyritic microgranite exposed within the Strange Lake pluton contains perthitic alkali feldspar phenocrysts, quartz eyes and fine-grained subhedral to phenocrystic arfvedsonite in the groundmass (Fig. 3d). Locally, this unit was intruded by a leucocratic transsolvus granite, which, texturally and mineralogically, is similar to the dark grey enclaves observed in the transsolvus granite. This unit has a bulk composition slightly less evolved than, and a mineralogy similar to that of the transsolvus granite. The fine-grained, dark grey enclaves hosted by the transsolvus granite are ellipsoidal in shape, range from a few cm up to 50 cm in diameter and have sharp edge contacts in most cases. These enclaves are composed of perthitic alkali feldspar phenocrysts embedded in a matrix of fine-grained quartz, microcline, albite and finely distributed subhedral and locally phenocrystic sodic amphibole, which gives them their dark appearance.

4. METHODS

4.1 Material

181   The major and trace element compositions of the amphibole-group minerals were determined in

182   22 least-altered rock samples. All granite types occurring in the unaltered portion of the Strange

183   Lake pluton were considered (Fig. 1). Bulk-rock compositions of the samples were provided by

184   Quest Rare Minerals Ltd., and represent the results of analyses by Actlabs using XRF (X-ray

185   fluorescence) for Nb, ISE-MS (ion selective electrode) for F, fusion-ICP-OES for major

186   elements and fusion ICP-MS for most trace elements.

187   **4.2 Electron-microprobe analyses**

188   The composition of the amphibole-group minerals in 30μm thick, carbon-coated polished thin

189   sections was determined using a JEOL JXA-8900L electron microprobe (EMP) at the

190   Department of Earth and Planetary Sciences, McGill University. The beam current was 20 nA,

191   the acceleration voltage 20 kV, and the beam diameter 10 μm. Counting times and standards

192   used for analyses as well as detection limits based on repeated standard analyses are listed in the

193   appendix. To ensure analysis of the same spots by both EMP and LA-ICP-MS (see below),

194   backscattered electron micrographs (BSE) of the analyzed grains were taken.

195   **4.3 Laser-ablation analyses**

196   Laser ablation ICP–MS (LA-ICP-MS) analyses were conducted on 16 samples using a

197   NewWave 213 nm Nd-YAG laser-ablation system and a Thermo Finnigan iCapQc quadrupole

198   ICP-MS at the Department of Earth and Planetary Sciences, McGill University. Six samples

199   were analysed at Université du Québec à Montreal (UQAM) using a Photon Machine G2 short-

200   pulse (4ns) laser-ablation system (193 nm excimer) and a Nu AttoM high-resolution magnetic

201   sector ICP-MS. The amphibole-group minerals were analyzed for selected major and trace

202   elements in the same 30 μm-thick polished sections. NIST SRM 610 glass was used as the

203 primary standard, and EMP data for both Si and Ti were used as internal references. The

204 analyses were performed with a 5 Hz repetition rate, on material ablated from a 20 μm diameter

205 pit. Data reduction was carried out using the software, Iolite, version 2.5. The estimated

206 precision is 5-10 % for each element.

<mark>4.4</mark> Amphibole formulae

208 The amphibole-group mineral formulae were calculated on the basis of O + OH + F = 24 atoms

209 per formula unit (apfu) and OH = 2-2Ti, using the amount of Ti^{4+} as a proxy for the (maximum)

210 oxy-component in the mineral structure (Hawthorne et al., 2012). The formula calculation was

211 performed following the latest IMA 2012 recommendations (Hawthorne et al., 2012; Oberti et

212 al., 2012) using the Excel spreadsheet of Locock (2014). On the basis of a preliminary formula

213 calculation after Leake et al. (1997), the following cation normalization schemes were chosen:

214 Si-Ca+Li ≤ 15, Si-Na ≥ 15 and Si-K ≤ 16. As some fluorite inclusions in the amphibole from the

215 hypersolvus granite were too small to be detected by imaging, analyses returning high

216 concentrations of both Ca (> 3 wt. %) and F (> 2 wt. %) were removed from the dataset.

<mark>5.</mark> RESULTS

<mark>5.1 Bulk rock compositions</mark>

219 <mark>The average (median) major and trace element bulk-rock compositions of the unaltered Strange</mark>

220 <mark>Lake granites are reported in Table 1. The agpaitic indices (molar [Na+K]/Al]) of all units are >1</mark>

221 <mark>and hence classify the rocks as peralkaline. The granites generally have low Ca and Mg and high</mark>

222 <mark>alkali, Fe, F, Zn, Rb, Zr, Nb and REE concentrations. The evolution of the granites is reflected</mark>

223 <mark>by decreasing Al, and increasing Si, Fe and incompatible element concentrations (i.e., REE, Nb,</mark>

224 <mark>Zr). The agpaitic index also increases with evolution. The fine-grained southern hypersolvus</mark>

11

granite, based on the above mentioned element concentrations, is interpreted to represent the least evolved rock unit. The oikocrystic / pegmatitic textured members of this unit has higher Si and Fe concentrations, a higher agpaitic index and slightly elevated REE and Zr concentrations. The concentrations of the HFSE (REE, Th, U, Nb, Zr, Hf) in the northern hypersolvus granite are higher, whereas Al concentrations are lower than those in the southern hypersolvus granite, suggesting that it is more evolved. The transsolvus granite generally has high Si, REE, Zr, Nb, Rb and F concentrations and significantly lower Al and Ca concentrations than the hypersolvus granite, and is considered to be the most evolved member of the suite. The dark grey enclaves hosted in the transsolvus granite have high Al, K and Ca, and low Na, Fe, Ti, Zr and Nb concentrations compared to the other granite types. Their REE concentrations are lower than those of their host, but higher than those of the hypersolvus granites.

5.2 Formula assignments

The amphibole-group minerals have the general structural formula, $AB_2C_5T_8O_{22}W_2$. The A-site of the Strange Lake amphiboles is occupied by Na^+ and minor K^+, and the B-site by Na^+ and Ca^{2+}, which assigns them to the alkali group. The octahedral C-site is occupied by Ti^{4+}, Zr^{4+}, Al^{3+}, REE^{3+}, Fe^{3+}, Zn^{2+}, Mn^{2+}, Fe^{2+}, Mg^{2+} and Li^+. The tetrahedral T-site is occupied by Si^{4+}, $^TAl^{3+}$ and in some cases $^TTi^{4+}$. The W-site is dominated by the anions F^-, Cl^- and OH^-, which assigns the amphiboles to the hydroxy-fluoro-chloro-group, where $^WF > {}^WOH$, ^WCl, and a "fluoro"-prefix is assigned to the amphibole name, which was the case for the majority of the crystals analyzed (see Table 2). In the matter of nomenclature, we have followed the latest IMA recommendations (Hawthorne et al., 2012; Oberti et al., 2012).

246   The C-site has a consistent under-occupancy (< 5 apfu), whereas the A-site has an over-

247   occupancy (> 1 apfu) (see Table 2). Despite using a variety of calculation procedures

248   (Hawthorne et al., 2012; Leake et al., 1997; Oberti et al., 2012), normalization schemes, and

249   varying the Fe^{2+}/Fe^{3+} ratios and oxo-components, we were unable to reduce the under-occupancy

250   and over-occupancy of the C- and A-sites, respectively. This issue has been reported to be

251   common for alkali amphiboles in peralkaline rocks, such as arfvedsonite or riebeckite, by other

252   researchers, who have deemed it to be an irresolvable artefact (Czamanske and Dillet, 1988;

253   Hawthorne, 1976; Hawthorne et al., 1993). Hawthorne (1976) suggested that some of the B-site

254   cations, notably Ca^{2+}, theoretically could be accommodated in the C-site on the basis of bond-

255   length constraints. This would result in a total C-site occupation closer to 5 apfu, and shift the

256   excess A-site cations to the B-site.

257   The occupancy of the A- and B-sites determines whether the amphiboles analyzed belong to the

258   sodic subgroup (arfvedsonite, leakeite) or the sodic-calcic subgroup (katophorite), in which ^{B}Ca

259   > 0.5. Ferro-ferri-katophorite was identified in the least evolved fine- to medium-grained

260   samples of the southern hypersolvus granite, exclusively. All the other amphiboles belong to the

261   sodic subgroup, and in the cases of a calculated Fe^{2+}/Fe^{3+} ratio of 1.1 to 2.3, have been classified

262   as arfvedsonite. The solid solution between the endmembers, arfvedsonite and katophorite, is

263   displayed in Figure 4a. In principle, the location of endmember arfvedsonite could lie anywhere

264   on the Na-K axis, as a potassic endmember has not been shown to exist in nature. The occupancy

265   of the C-site divides the sodic amphibole subgroup into arfvedsonite and ferro-ferri-leakeite; the

266   latter has ^{C}Li > 0.5 apfu and a Fe^{2+}/Fe^{3+} ratio between 0.7 and 1.3. Ferro-ferri-leakeite is the

267   principal amphibole in the transsolvus granite but also occurs in the northern hypersolvus

268   granite. The fluoride-rich-variety (ferro-ferri-fluor-leakeite) was detected mainly in the

269   transsolvus granite and its enclaves, whereas the fluoride-poor variety occurs predominantly in

270   the northern hypersolvus granite. The composition of the analyzed solid-solution between the

271   endmembers, arfvedsonite and ferro-ferri-leakeite, is displayed in Figure 4b. The slope of the

272   trend from the arfvedsonite to leakeite endmembers indicates an increase in Fe^{3+} with increasing

273   Li^+. The end-member stoichiometric formulae of the amphibole-group minerals present in the

274   unaltered granites of the Strange Lake pluton are listed in Table 3.

275 **5.3 Major elements**

276   The major element compositions of the analyzed amphibole are reported in Table 4 (mean

277   values) and illustrated in Figure 5 relative to their Al content. Aluminum was chosen because the

278   Al content of amphibole is commonly a reliable indicator of the differentiation of the

279   corresponding magma, if alkali feldspar fractionation (perthite phenocrysts) was the major

280   control on magma evolution (Hawthorne et al., 2001; Piilonen et al., 2013). As shown in Figure

281   5a, the Ca content decreases with decreasing Al content in a ratio slightly greater than 1:1, and is

282   highest and shows the greatest range (~ 0.3 to 0.6 apfu) in the amphibole of the fine-grained

283   granite from the southern hypersolvus granite. The Ca content is lower in the pegmatitic and

284   oikocrystic textured samples of the same unit (0.1 to 0.35 apfu). Amphibole of the northern

285   hypersolvus granite has a much lower Ca concentration, between 0.05 and 0.2 apfu. The lowest

286   Ca concentrations are for amphibole in the enclaves and the transsolvus granite (≤ 0.1 apfu) (Fig.

287   5a). Sodium exhibits the opposite trend to Ca, with concentrations increasing with decreasing Al

288   content. In the fine- to medium-grained samples of the southern hypersolvus granite, Na-contents

289   are relatively low, between 2.1 and 2.6 apfu, whereas in the oikocrystic to pegmatitic samples,

290   the Na contents are consistently higher, between 2.6 and 2.9 apfu, and are similar to those of the

291   amphibole from the northern hypersolvus granite, the enclaves and the transsolvus granite (Fig.

292   5b). The Ti content of amphibole in the fine- to medium-grained samples of the southern

293   hypersolvus granite has a similar range to that in the northern hypersolvus granite, i.e., from 0.08

294   to 0.22 apfu versus 0.1 to 0.21 apfu, but because of the much lower Al content of the amphibole

295   in the northern hypersolvus granite samples, the two datasets display separate Ti-Al trends (Fig.

296   5c). Amphiboles in the oikocrystic to pegmatitic samples of the southern hypersolvus granite, the

297   transsolvus granite and the enclaves all have relatively low Ti contents (0.06 to 0.16 apfu) (Fig.

298   5c). Silica in amphibole behaves similarly to Na, increasing in concentration with decreasing Al

299   concentration. The lowest silica concentrations are those of the fine- to medium-grained samples

300   of the southern hypersolvus granite (7.4 to 7.7 apfu) (Fig. 5d); the oikocrystic to pegmatitic

301   samples display the largest range in amphibole Si content, from 7.4 to 8.0 apfu. Amphibole in the

302   northern hypersolvus granite, the enclaves and the transsolvus granite has Si contents from 7.7 to

303   7.9, 7.6 to 7.9 and 7.6 to 8 apfu, respectively (Fig. 5d). Manganese contents of amphibole are

304   highest in the northern hypersolvus granite (0.09 − 0.12) and show the greatest range in the

305   transsolvus granite (0.06 − 0.12) (Fig. 5e). They are broadly similar for amphibole from the

306   enclaves and the southern oikocrystic to pegmatitic hypersolvus granite (0.07 − 0.10), and range

307   from 0.08 to 0.11 for amphibole from the fine-grained southern hypersolvus granite. The

308   calculated Fe^{2+}/Fe^{3+} ratios correlate weakly with the Al concentrations. Amphibole from the fine-

309   grained southern hypersolvus granite generally has the highest Fe^{2+}/Fe^{3+} ratio; amphibole from

310   the enclaves, the northern hypersolvus granite and many of the transsolvus granite samples has a

311   low ratio (Fig. 5f). Zinc concentrations are slightly elevated for the amphibole from the fine-

312   grained samples of the southern hypersolvus granite (avg. 0.08 apfu) and the enclaves (avg. 0.07

313   apfu), compared to the amphibole of the northern hypersolvus granite, the transsolvus granite

314   and the oikocrystic and pegmatitic samples of the southern hypersolvus granite (all avg. 0.05

15

315 apfu) (Fig. 5g). <mark>Fluorine concentration is highest in the amphibole of the transsolvus granite (1.0</mark>

316 <mark>- 1.4 apfu), lowest for the crystals of the (fine-grained) southern hypersolvus granite (0.2 − 0.8</mark>

317 <mark>apfu) and is intermediate (avg. ~ 1 apfu) for all the other granite units.</mark>

318 The amphibole phenocrysts of the transsolvus granite differ only slightly in composition from

319 core to rim (Fig. 6; Table <mark>5</mark>). The phenocryst cores have total Al and Si contents averaging <mark>0.06</mark>

320 (apfu) and <mark>7.9</mark> (apfu), respectively, a considerable range in Ca concentration (~0.1 to 0.5 apfu,

321 avg. 0.03 apfu), Na and K contents averaging <mark>2.8 and 0.33</mark> apfu, respectively, a Fe^{3+} content

322 averaging <mark>1.8</mark> apfu, a Mg content averaging <mark>0.03</mark> apfu, a total Ti content of <mark>0.09</mark> apfu (avg.), Mn

323 and Zn contents averaging <mark>0.07 and 0.05</mark> apfu (avg.), respectively, and a F content averaging <mark>1.2</mark>

324 apfu. The phenocryst rims have lower concentrations of Al (avg. <mark>0.06</mark> apfu), Si (<mark>7.7</mark> apfu), Ca

325 (avg. <mark>0.02</mark> apfu), Na (avg. <mark>2.8</mark> apfu), Mg (avg. <mark>0.02</mark>) and F (avg. 1.1 apfu), and higher

326 concentrations of total Fe^{3+} (avg. <mark>2.2</mark> apfu), K (avg. <mark>0.4</mark> apfu), total Ti (<mark>0.1</mark> apfu), Mn and Zn

327 (avg. <mark>0.09 and 0.07 apfu</mark>, respectively).

328 **<mark>5.4</mark> The REE and other trace elements**

329 The shapes of the chondrite-normalized amphibole REE profiles (Sun and McDonough, 1989)

330 are similar for all the granite units and, in general, are characterized by relatively flat light and

331 middle REE parts, a marked negative Eu-anomaly (Eu/Eu* = 0.04-0.66) and an enrichment in

332 the HREE (Fig. 7). However, the absolute REE concentrations differ considerably. The

333 amphiboles of the fine-grained samples of the southern hypersolvus granite have the highest total

334 REE concentration, on average <mark>(median value) 0.16 ± 0.03 wt. %</mark> (Table <mark>4</mark>). By contrast,

335 oikocrystic to pegmatitic samples of the same unit have much lower amphibole REE

336 concentrations, on average, <mark>0.04 ± 0.01 wt. %.</mark> The total REE concentrations of amphibole in the

337 northern hypersolvus granite are intermediate between those of the fine-grained and oikocrystic

338 to pegmatitic southern hypersolvus granite, averaging 0.07 ± 0.02 wt. %. Amphiboles of the

339 transsolvus granite and its enclaves have much lower total REE concentrations, averaging 0.01 ±

340 0.002 wt. % and 0.04 ± 0.01 wt. %, respectively (Table 4). The amphibole REE concentrations

341 are between 10^2 and 10^3 times the chondrite values (Fig. 7c, e).

342 The contents of the individual REE in the amphiboles are significantly lower (in the case of the

343 light REE (LREE), more than an order of magnitude lower) than their respective bulk host rock

344 concentrations, except for the heaviest of the REE, Yb and Lu, which are significantly higher

345 (Fig. 7). In the case of the fine-grained southern hypersolvus granite, the exception extends to the

346 middle REE and for Yb and Lu the content in amphibole is about four times higher than the bulk

347 rock content (Fig. 7a). The concentrations of Yb and Lu of the amphiboles from the northern

348 hypersolvus granite exceed the bulk rock concentrations to a similar degree (Fig. 7c). The largest

349 difference between amphibole and bulk rock REE concentrations is exhibited by the transsolvus

350 granite, which has considerably higher concentrations in the bulk rock except for Yb and Lu; the

351 amphibole in this unit also shows the steepest chondrite-normalized rise in HREE concentration

352 (Fig. 7e). The amphiboles in the dark-grey enclaves hosted by this unit have elevated light to

353 middle REE compositions compared to that of amphibole in the transsolvus granite, whereas the

354 Tm, Yb and Lu concentrations are within the range of their host (Fig. 7e).

355 As is the case for the REE, the contents of most of the other trace elements are considerably

356 lower in the amphibole-group minerals than in the average bulk-rock (other than in the southern

357 fine- to medium-grained hypersolvus granite). Conspicuous exceptions are Nb, Zr and Hf, which

358 in addition to being present in zircon, monazite-(Ce) and the pyrochlore group minerals, are also

359 accommodated by the amphibole. The chondrite-normalized trace element profiles for the

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360   amphiboles in all granite units have negative Ba, U, K, Pb, Sr, Eu, Ti and Y anomalies, and

361   positive Th, Nb, Ta, Sn, REE, Zr and Hf anomalies, whereas the average bulk rock has negative

362   Ba, K, Pb, Sr, Eu, and Ti and positive Th, U, Nb, Ta, REE, Zr, Hf and Y anomalies (Fig. 7).

363   Thus, although the behavior of most elements in the amphibole is similar to that in the host rock,

364   U and Y show opposite behavior, i.e., their concentrations are anomalously low in the amphibole

365   and high in the bulk rock. Zirconium concentrations are lowest in amphibole from the southern

366   hypersolvus granite (avg. 0.07 to 0.12 wt. %), and reach more than double these concentrations

367   in amphibole from the northern hypersolvus granite (~0.26 wt. %). Concentrations are

368   intermediate between these extremes in the amphibole of the transsolvus granite (~0.14 wt. %)

369   and enclaves (~0.21 wt. %). Lithium concentrations, on average, are lowest in amphibole of the

370   southern hypersolvus granite (avg. 0.15 to 0.16 wt. %), significantly higher in amphibole of the

371   northern hypersolvus granite (avg. 0.31 wt. %) and by far the highest in amphibole of the

372   transsolvus granite (avg. 0.58 wt. %) and enclaves (avg. 0.48 wt. %). However, they vary greatly

373   among samples, and, to a lesser extent, among crystals in the same sample (see Table 4).

374   Differences in the chondrite-normalized REE profile are particularly marked among the five

375   amphibole types identified in this study. Sodium- and calcium-rich ferro-ferri-katophorite as well

376   as arfvedsonite have the highest total REE concentrations; their average La_N/Yb_N ratios are 0.23

377   and 0.49, respectively (Fig. 8). Fluoro-arfvedsonite and Li-rich ferro-ferri-leakeite both have

378   intermediate REE concentrations and a more prominent HREE enrichment with an average

379   La_N/Yb_N ratio of 0.09 and 0.14, respectively. Ferro-ferri-fluoro leakeite has by far the lowest

380   total REE concentration, and it exhibits the strongest relative HREE enrichment with an average
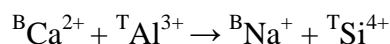
381   La_N/Yb_N ratio of. 0.04.

382   **6. DISCUSSION**

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Siegel K, Williams-Jones AE, van Hinsberg VJ (2017) The amphiboles of the REE-rich A-type peralkaline Strange Lake pluton – fingerprints of magma evolution. Lithos 288:156-174.
doi: 10.1016/j.lithos.2017.07.012.

6.1 Amphibole composition as a tracer of granite differentiation

The variations in the major and trace element chemistry of amphibole in the Strange Lake pluton are interpreted to reflect the evolution of the granitic melt. The earliest intrusive phase was the hypersolvus granite, which has been subdivided into a southern and a northern part on the basis of compositional and mineralogical differences. In both units, the amphiboles, mainly (fluoro)-arfvedsonite (n=49) and minor (fluoro)-katophorite (n=6), occur interstitially to perthite and quartz, and thus were the last of the main rock-forming minerals to crystallize. By contrast, in the more evolved transsolvus granite, the amphibole, mostly fluoro-arfvedsonite and ferro-ferri-(fluoro)-leakeite (n=55), occurs as phenocrysts together with minor perthite, and therefore crystallized prior to the emplacement of this granite facies. This difference in the timing of crystallization of the amphibole, as we will show below, played a crucial role in determining the extent to which incompatible elements, such as the REE and other HFSE, were incorporated in its crystal structure.

6.2 Magma evolution monitored by A-and B-site occupancy

In the hypersolvus granite, the A- and B-sites are occupied mainly by Na, but also by considerable Ca in some samples of the southern hypersolvus granite (see Fig. 4a). The high density of fluorite inclusions also suggests that the early melt was relatively rich in Ca. The occupation of the B-site by the bivalent Ca ion was balanced by Al^{3+} at the T-site. With increasing degree of differentiation, Na^+ substituted for Ca^{2+} and Si^{4+} for Al^{3+} (see Figs. 5a, b, d). This coupled substitution can be expressed by the reaction:

$$^{B}Ca^{2+} + {}^{T}Al^{3+} \rightarrow {}^{B}Na^{+} + {}^{T}Si^{4+}$$

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404 A similar correlation of decreasing Ca and increasing Si in amphibole with magmatic evolution

405 has been documented for silica-undersaturated alkaline intrusive suites, namely Ilímaussaq in

406 southern Greenland (Marks et al., 2004), the Khibiny complex in the Kola Peninsula of Russia

407 (Konopleva et al., 2008), and the alkaline pegmatites of the silica-undersaturated to -saturated

408 Larvik plutonic suite of the Oslo Rift in Southern Norway (Piilonen et al., 2013). In these three

409 locations, the amphibole composition evolved from calcic to sodic-calcic to sodic varieties with

410 increasing degree of differentiation, reflecting the increasing alkalinity of the corresponding

411 magma.

412 As the Ca content is highest in amphibole of the fine- to medium-grained southern hypersolvus

413 granite (see Fig. 5a), we interpret this unit to be the earliest and least evolved intrusive facies of

414 the Strange Lake pluton. The much lower content of Ca in amphibole of the oikocrystic to

415 pegmatitic textured granites from the same unit is consistent with the interpretation that these

416 rocks crystallized from residual melts. Consistent with these interpretations, the northern

417 hypersolvus granite, in which amphibole has a relatively low Ca (and Al) concentration,

418 represents the intrusion of a separate and more evolved batch of magma.

419 The amphibole of the transsolvus granite generally has low Ca- and Al-, as well as high Na- and

420 Si-concentrations (see Fig. 5a, b, d), which all point towards a significantly more evolved melt.

421 As the amphibole of this unit crystallized early (it occurs as phenocrysts), as opposed to the

422 hypersolvus granite, the transsolvus granitic melt was more evolved from the outset. The

423 evolution of this melt is monitored by the compositional differences between phenocryst cores

424 and rims. For example, Ca, Na and Al concentrations decrease from core to rim (see Fig. 6,

425 Table 4). Decreasing Ca and Al concentrations mirror the evolution to a more alkaline magma

426 composition, which was caused by alkali feldspar fractionation (Boily and Williams-Jones,

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427　1994). The unexpected depletion of Na in the rims, however, is likely an artefact of the

428　exsolution of a Na-rich fluid at a later stage of crystallization (Salvi and Williams-Jones, 1996;

429　Roelofsen, 1997; Gysi et al., 2016), and/or the onset of albite crystallization. Not surprisingly,

430　given the generally very low Ca and Al contents (close to zero) (Fig. 5a) and very high Na (Fig.

431　5b) content of the amphibole, compared to those of the hypersolvus granite, the transsolvus

432　granite is the most evolved of the intrusive units considered in this study. The enclaves in this

433　unit contain amphibole with slightly higher Ca, and Al, and lower K and F concentrations than

434　the crystals in the host granite (see Fig. 5), which points to a slightly less evolved composition.

435　Nonetheless, their close compositional resemblance to the crystals of the transsolvus granite,

436　indicates that they may be part of the same intrusion.

437　**6.3 Magma evolution monitored by the C-site occupation**

438　*6.3.1 Implications of the Fe^{2+}/Fe^{3+} ratio*

439　The C-site of the amphibole-group minerals in the Strange Lake complex mainly hosts Fe^{2+} and

440　Fe^{3+}, but also Li^+, Mg^{2+}, Mn^{2+}, Zn^{2+}, Ti^{4+} and Zr^{4+} in significant proportions. The Fe^{2+}/Fe^{3+} ratio

441　of a magma is controlled by the fO_2, and may be recorded by the amphibole composition.

442　However, Fe^{3+} also becomes more or less compatible in the amphibole structure depending on its

443　overall composition, and the exchange vectors that operate. In particular, the incorporation of Na

444　at the expense of Ca is charge-balanced by 3+ elements in the exchange vector: $Ca + (Mg, Fe^{2+})$

445　$= Na + (Al, Fe^{3+})$. When Al contents are depleted in the melt (e.g., increasing peralkalinity), Fe^{3+}

446　becomes progressively more important in this exchange vector. In this case, the amphibole

447　Fe^{2+}/Fe^{3+} ratio will vary with the Na/Ca ratio in rocks with the same major mineral paragenesis.

448　In the late amphibole of the hypersolvus granite, Fe^{2+}/Fe^{3+} ratios of the northern unit are lower

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449 and have higher Na/Ca ratios than the amphibole of the southern unit (Fig. 9), which suggests

450 that incorporation of Fe^{3+} in the structure, to some degree, was tied to the lower Ca content of the

451 amphibole. However, as the correlation between Fe^{2+}/Fe^{3+} and Na/Ca is not 1:1, it is likely that

452 there was an additional effect on the Fe^{2+}/Fe^{3+} ratio, e.g., oxidation. Oxidation of a magma

453 commonly occurs following fluid exsolution from the magma, due to decomposition of H_2O to

454 H_2 and $\frac{1}{2}O_2$, and the subsequent loss of the much faster diffusing H_2 (Czamanske and Wones,

455 1973). As the amphibole crystallized late in this facies, it can be inferred that the cooling

456 intrusion had experienced some degassing and subsequent fluid loss at this point. Even in the

457 freshest units (e.g., the hypersolvus granite) of the Strange Lake pluton, there is evidence of

458 H_2O-saturation at a late stage of in-situ evolution, e.g., the albitization of K-feldspar, the

459 hydrothermal alteration of primary REE-minerals and the crystallization of hydrothermal REE-

460 phases, such as gagarinite-(Y) after fluorite (Gysi et al., 2016; Vasyukova and Williams-Jones,

461 2016).

462 The amphibole of the transsolvus granite and enclaves generally has a low Fe^{2+}/Fe^{3+} ratio (see

463 Fig. 5f). In addition, the phenocrysts rims have elevated Fe^{3+} concentrations compared to their

464 cores (see Fig. 6c) which can be related to increasing fO_2. The amphibole rims may have

465 continued to crystallize after emplacement, when the magma experienced degassing and

466 oxidation. In addition, some correlation between Fe^{2+}/Fe^{3+} and Na/Ca suggests that crystal

467 chemical effects (high Na/Ca ratio), partially caused the low Fe^{2+}/Fe^{3+} ratio (Fig. 9). However, as

468 the correlations are not 1:1, this indicates that a process, in addition to crystal chemical effects

469 and oxidation, caused the high Fe^{3+} content. In peralkaline igneous systems, high concentrations

470 of F^- and OH^- in the melt allow more Fe^{3+} to be present at a given fO_2 (Birkett et al., 1996; Giehl

471 et al., 2013). The high proportion of Fe^{3+} in the amphibole was likely caused by an increasing

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472   proportion of anions, notably F^- and OH^- in the evolving melt. This is manifested by significantly

473   higher F concentrations in the amphibole phenocrysts, compared to the amphiboles of the

474   hypersolvus granite (see Table 3).

475   *6.3.2 Titanium, manganese and zinc concentrations*

476   The titanium concentration of the amphibole-group minerals in alkaline rocks is an important

477   indicator of the melt evolution owing to the incompatible nature of Ti. Indeed Ti^{4+} was

478   preferentially incorporated into the late crystallizing amphibole of the hypersolvus granite and

479   much less so in the phenocrysts of the transsolvus granite (see Fig. 5c). From bulk rock

480   compositions, we know that both the southern and northern hypersolvus granitic magmas were

481   relatively enriched in TiO_2 (on average, 0.3 wt. % in both units). However, the amphibole of the

482   southern unit has a much higher TiO_2 concentration (avg. 1.5 wt. %) than the northern unit

483   (avg.1.1 wt. %).

484   The proportion of the amphibole in each granite unit was estimated using the MINSQ excel

485   spreadsheet of Herrmann and Berry (2002), which applies a least squares method to bulk rock

486   and mineral compositions in order to determine the normative mineralogy of a sample.

487   Proportions of the bulk TiO_2 contributed by the mineral group were estimated from the

488   amphibole proportion and the TiO_2 content. The fine-grained southern hypersolvus granite

489   contains ~14 wt. % amphibole, which hosts ~70 % of the bulk TiO_2. The northern hypersolvus

490   granite contains only ~11 wt. % amphibole, which hosts about 40 % of the bulk TiO_2. The

491   remaining titanium is concentrated in aenigmatite and astrophyllite, sodium-titanosilicate

492   minerals, which are present almost exclusively in the northern hypersolvus granite (see Fig. 2d).

493   In the southern hypersolvus granite, the missing 30 % is concentrated mostly in secondary

494 astrophyllite, which occurs as inclusions in the alkali feldspar. Both the transsolvus granite and

495 its enclaves have bulk rock Ti concentrations of ~0.2 wt. % and significantly lower

496 concentrations in amphibole (0.7 and 0.9 wt. %, respectively). As the amphibole is a phenocryst

497 phase, it did not incorporate the relatively incompatible Ti^{4+}. However, a slight increase in total

498 Ti concentration from phenocryst cores to rims (avg. 0.09 to 0.1 apfu) is consistent with the

499 internal evolution of this unit. In both the transsolvus granite and its enclaves, about 58 % of the

500 bulk TiO_2 is hosted by the amphibole. The transsolvus granite has an elevated proportion of

501 amphibole (~18 wt. %), whereas the enclaves contain much lower proportions of the mineral

502 (~12 wt. %), due to density separation that occurred in the magma chamber. The remaining TiO_2

503 in this unit is concentrated mostly in the Na-Ti-silicate, narsarsukite.

504 Several studies have reported a strong positive correlation between Ti^{4+} and O^{2-} concentrations in

505 amphibole, which is reflected in the relationships, $^{C}Ti = Ti$ and $O^{2-} = 2Ti^{4+}$ with the limit of $^{W}[2-$

506 (OH, F, Cl)]. This means, that if the F, Cl and Ti concentrations of the amphibole are measured,

507 and a maximum of 2 apfu for the W-site is assigned, the OH- (and O-) proportion can be

508 estimated using the relationship $OH = 2 - (2Ti - F - Cl)$ (Hawthorne et al., 2012; King et al.,

509 1999; Leake, 1968; Oberti et al., 2012). Following this protocol, hydroxyl (OH$^-$) and oxygen (O^{2-}

510) are essential components of the amphibole from the southern hypersolvus granite (>1 apfu)

511 (Fig. 10), whereas in the other, more evolved granite units, F$^-$ is the dominant W-site anion (see

512 Figs. 5h, 11b). Abundant fluorite inclusions in the amphibole of this unit (see Fig. 3a) indicate

513 that fluorite saturated prior to the amphibole. This suggests that in the early and least evolved

514 magma, the late amphibole crystallized from a water-rich, F-poor, residual magma. In the

515 northern hypersolvus residual granitic melt, more F$^-$, in addition to oxygen, was available to be

516 incorporated in the amphibole (see Figs. 5h, Fig. 10). In both hypersolvus granite units (south

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and north), high Ti^{4+} concentrations required significant proportions of O^{2-} (0.2 to 0.45 apfu) to balance the higher charge of the C site. The phenocrysts of the transsolvus granite have high proportions of F^-, and low proportions of O^{2-} and OH^- occupying the W-site (see Fig. 5h, Fig. 10). This implies a highly F-enriched melt from the outset (phenocryst cores).

Elevated Mn-concentrations in the amphibole of the northern hypersolvus granite compared to those of amphibole in the fine-grained samples of the southern unit (see Fig. 5e) point to a progressive increase in Mn^{2+} concentration with hypersolvus granite evolution. The relatively incompatible behavior of Mn^{2+} compared to Fe^{2+} was likely caused by the larger ionic radius of $^C Mn^{2+}$ (r=0.83Å) over Fe^{2+} (r=0.78Å) (Hawthorne et al., 2001; Shannon, 1976). Amphibole Zn^{2+} concentrations decrease with hypersolvus granite differentiation (see Fig. 5g), due either to the co-crystallization of another Zn-bearing phase or the progressive replacement of the relatively compatible Zn^{2+} ion by more incompatible cations, such as Fe^{3+}. The amphibole phenocrysts of the transsolvus granite generally have low but highly variable Mn^{2+}- and Zn^{2+}-concentrations, from 0 to 0.12 apfu, and 0.02 to 0.14 apfu, respectively. The latter is due to the much higher Mn and Zn concentrations of the phenocryst rims compared to the cores (see Table 4), which reflects increasing evolution of the magma. A progressive build-up in both Mn and Zn in the Strange Lake amphiboles with evolution was reported by Hawthorne et al. (2001), whereas we observe this trend separately for each granite unit.
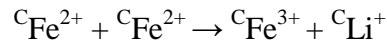
6.3.3 The role of lithium

Lithium is a significant component of the Strange Lake amphiboles and has been reported to be an important constituent in alkali amphiboles of highly evolved alkaline rocks elsewhere (e.g., Hawthorne et al., 1993; Hawthorne et al., 1996; Marks et al., 2004). Owing to the incompatibility

539   of lithium in common rock-forming minerals, its concentration reflects the degree of melt

540   differentiation. The amphiboles of the Strange Lake pluton have an average Li concentration of

541   0.3 apfu, but concentrations reach > 1.0 apfu in some transsolvus granite samples. Lithium

542   concentrations of >0.5 apfu classify a sodic amphibole as ferro-ferri-(fluoro)-leakeite, which is

543   the case for most of the amphibole in the more evolved units. Hawthorne et al. (2001), who

544   reported Li concentrations of up to 0.4 apfu for amphibole in the most evolved members of the

545   Strange Lake pluton, concluded that the elevated Li concentration was due to its high content in

546   the magma rather than the structure of the mineral. The generally low content of Li in amphibole

547   of both the southern and northern hypersolvus granite (avg. 0.16 and 0.31 wt. %, respectively)

548   compared to the transsolvus granite (avg. 0.58 wt. %) (see Table 4), despite the fact that

549   amphibole in the hypersolvus granite was a late crystallizing phase, suggests that the hypersolvus

550   granite magma was relatively poor in Li. In contrast, the occurrence of ferro-ferri-(fluoro)-

551   leakeite as phenocrysts in the transsolvus granite suggests that the corresponding magma was

552   more evolved. Of significance in this regard is the large range in Li-concentrations of the

553   amphibole phenocrysts (0.1 to 1.2 apfu) (Fig. 11), which suggests that they record a large part of

554   the evolution of the magma, a conclusion that is supported by the elevated Li concentrations of

555   crystal rims relative to their cores (see Fig. 6d).

556   As noted earlier, the Li^+ concentration of the amphiboles correlates positively with the C-site

557   occupancy ($R^2 \sim 0.8$), and hence knowledge of the concentration of this ion is essential to reliably

558   evaluate the amphibole formula. In particular, the calculation of the Fe^{3+} concentration, which is

559   highly dependent on Li^+ for charge balance, can only be performed accurately if the Li^+

560   concentration is known (Hawthorne et al., 1993). The lithium concentration in the amphiboles

561   correlates strongly with the Fe^{3+} concentration ($R^2=0.92$ for the transsolvus granite, $R^2=0.83$ for

562   the hypersolvus granite) (Fig. 11), and, with increasing degree of evolution, can be expressed by

563   the coupled substitution reaction

564 $^C Fe^{2+} + {}^C Fe^{2+} \rightarrow {}^C Fe^{3+} + {}^C Li^+$

565   The progressive increase in Li^+ and Fe^{3+} with evolution is consistent with the increase in fO_2 in

566   the hypersolvus granite, and also with the increase in melt F^- and OH^- in the transsolvus granite,

567   both of which were discussed earlier.

568   **6.4 Distribution of the REE and other trace elements**

569   The trace element composition of amphibole-group minerals is a function of the magma

570   composition and the structure of the mineral (i.e., the preference of its sites for ions of a

571   particular size and charge). In the Strange Lake granites, for example, the negative Ba, Pb, Sr,

572   and Eu anomalies in both the amphibole and bulk rock are likely due to voluminous plagioclase

573   fractionation early in the crystallization history. This process is interpreted to have produced the

574   large Mesoproterozoic anorthosite complexes of the Nain Plutonic Suite (Emslie et al., 1994;

575   McLelland et al., 2010). Consistently low Rb concentrations, and negative U and Y anomalies in

576   the amphibole, but not in bulk rock, on the other hand, are interpreted to have been caused by

577   within-pluton-fractionation of K-feldspar (substitution of Rb for K) and of Y- and U-rich

578   minerals, such as gagarinite-(Y), the fluorite-fluocerite solid solution and small amounts of U-

579   bearing thorite.

580   The behavior of the REE in amphibole-group minerals is governed by a combination of crystal

581   chemical constraints and magmatic processes. Several studies have concluded that the trace

582   element composition of amphibole is dependent on the major element distribution, and, to a

583   lesser extent, on the P, T and fO_2 conditions (Bottazzi et al., 1999; Dalpé and Baker, 2000). In

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584   the Gardar Province (Ilímaussaq, Puklen and Grønnedal-Ika intrusions), for example, Ca-rich

585   amphibole- group minerals are strongly enriched in the LREE (order of magnitude), compared to

586   the Na-rich members of the same mineral group (Marks et al., 2004). Consistent with this

587   observation, the Ca-rich ferro-ferri-katophorite at Strange Lake is enriched in the REE by 10^2 to

588   10^3 times the chondrite values, whereas the Na-rich fluor-arfvedsonite and ferro-ferri-(fluoro)-

589   leakeite have much lower total REE concentrations, and show a stronger relative enrichment in

590   the HREE (see Fig. 8).

591   The Ca-rich amphiboles are members of the earlier, less evolved hypersolvus granite, in which

592   they crystallized as a late, interstitial phase from a small proportion of residual liquid. The

593   residual liquid of this overall less evolved unit was relatively enriched in incompatible elements

594   such as the REE, whereas the amphibole phenocrysts of the more evolved transsolvus granite

595   crystallized from a relatively 'dilute' magma with low incompatible element concentrations. In

596   contrast, the amphiboles of the Gardar Province all are late, near solidus phases in all rock types

597   that have been investigated, e.g., augite-syenites, alkali granites, agpaites and nepheline syenites

598   (Markl et al., 2001; Marks et al., 2004). Thus, the fact that the LREE are tied to Ca-rich

599   amphiboles implies that another factor, in addition to the magma composition, may have been

600   important in accommodating the REE in the crystal structure. Rare earth element concentrations

601   in the Strange Lake amphiboles correlate positively with Al^{3+} (R^2=0.59) and Ca^{2+} ($R^2 = 0.61$)

602   concentrations, and negatively with Na^+ (R^2= 0.57), F^- ($R^2 = 0.51$) (Fig. 12) and Si^{4+}

603   concentrations. This suggests that overall the REE become less compatible in the amphibole

604   structure with increasing degree of magma evolution, or alternatively, that the nature of the

605   major elements in the mineral structure control the accommodation of the REE.

606 Interestingly, the amphiboles of the oikocrystic and pegmatitic samples of the southern

607 hypersolvus granite have much lower REE concentrations (avg. ~0.04 wt. %) than their host

608 (avg. 0.16 wt. %), but similar to those of amphiboles in the northern hypersolvus granite (avg.

609 ~0.07 wt. %) (see Table 3). In the latter amphiboles, however, the Al and Ca contents are

610 significantly lower (0.5 vs 1.0 wt. % Al_2O_3 and 0.5 vs. 1.1 wt. % CaO). This is consistent with

611 the interpretation that the oikocrystic and pegmatitic granites crystallized from volatile-rich melt

612 pockets that evolved in-situ, and is further evidence that the northern hypersolvus granite

613 evolved from the southern hypersolvus granite. The decoupling of REE concentrations from

614 those of Ca and Al observed in these two rock units speaks to a factor other than the degree of

615 magma evolution in controlling the incorporation of the REE in amphibole.

616 **6.5 REE inter-site partitioning**

617 Previous studies have concluded that the REE in the amphibole structure are distributed over the

618 B and C sites and that this distribution depends on the nature of the major elements that reside in

619 these sites (Bottazzi et al., 1999; Tiepolo et al., 2007; Tiepolo et al., 2000). These conclusions

620 were reached from studies of the partitioning of the REE between amphibole and melt, with the

621 D_{REE} showing systematic behavior controlled by the B and C site dimensions (*cf.* Blundy and

622 Wood, 2003). Unfortunately, these data do not extend to the amphibole compositions

623 encountered at Strange Lake. In order to obtain a first-order estimate of the localization of the

624 REE in sodic amphibole, apparent mineral-melt partition coefficients were calculated from the

625 bulk rock and median sodic amphibole compositions of transsolvus granite sample 204720.

626 Amphibole was the first major phase to crystallize in this sample, but inclusions of pyrochlore

627 group minerals and monazite-(Ce) indicate that these minerals had likely already saturated. The

628 median compositions of these minerals at their respective modes were subtracted from the bulk

29

629 composition to obtain an estimate of the melt composition at the time of amphibole

630 crystallization. This assumes that sample 204720 acted as a closed system, that it represents a

631 melt composition, that all pyrochlore group minerals and monazite-(Ce) crystallized prior to

632 amphibole, and that all amphibole formed at the same time. However, deviations from these

633 assumptions mainly impact the absolute D values, whereas their systematics are unaffected.

634 A plot of the partition coefficients against the radii of the REE (6-fold and 8-fold coordinated

635 radii for the C and B-sites, respectively, as given in Shannon 1976) is shown in Fig. 13. The

636 LREE in the sodic amphiboles from Strange Lake are most compatible with the B-site (Fig. 13),

637 as also has been shown for calcic and sodic-calcic amphiboles (Bottazzi et al., 1999). The

638 lightest of the lanthanides, La and Ce, which have ionic radii of 1.16 Å and 1.14 Å (at 8-fold

639 coordination) are closest to the ideal radius of the B-site and are thus preferentially incorporated.

640 For reference, the major elements occupying this site are Na and Ca, which with ionic radii of

641 1.12 Å and 1.18 Å, respectively, are slightly smaller or larger than the ideal radius. The HREE,

642 which have ionic radii between 0.86 to 0.94 Å, on the other hand, are compatible with the 6-fold

643 coordinated C-site, and their compatibility increases exponentially with increasing atomic

644 number (Fig. 13). Thus, the 'heaviest' of the REE, Yb and Lu are preferentially incorporated in

645 the crystal structure ($D^{amph-bulk}_{Yb, Lu} > 1.0$), which, indeed, is what is observed in the chondrite-

646 normalized REE profiles (Fig. 7). The middle REE, e.g., Gd, has the lowest apparent partition

647 coefficient as its radius is furthest from that of the ideal radii of both the B and C sites and hence

648 fits in neither site (in Fig. 13 it is shown at its 6-fold coordinated radius). The apparent D values

649 also suggest that $D_{LREE} < D_{HREE}$, in agreement with Tiepolo et al. (2000), who showed that the

650 LREE are incompatible in amphibole ($D^{amph/l}_{La} = 0.06$ to 0.5), whereas the HREE are relatively

651 compatible ($D^{amph/l}_{Yb}$ = 0.25 to 2.0). The apparent (calculated) $D^{amph-bulk}$ and ionic radii at 6- and

652 8-fold coordination are given in Table 6.

6.6 The role of amphibole in concentrating HREE in the pluton

654 A significant proportion of the bulk REE content of the Strange Lake granites is contained in

655 amphibole. Indeed, the REE content of amphibole in both fine-grained and oikocrystic and

656 pegmatitic samples of the southern hypersolvus granite is similar to or exceeds that of the bulk

657 rock, except for La and Ce; the contents of the heaviest of the REE, Yb and Lu, are four times

658 higher than in the bulk rock.

659 Proportions of the bulk REE hosted by the mineral group were estimated from the proportion of

660 the amphibole in each granite facies and the REE contents of the corresponding amphiboles. The

661 amphibole of the southern hypersolvus granite (fine-grained) (~ 14 wt. %) contains about 10 %

662 of the bulk LREE (avg. 0.1 wt. %) and more than 35 % of the bulk HREE (avg. 0.01 wt. %) (Fig.

663 14). In the case of Yb and Lu, the proportions increase to 55 and 70 wt. %, respectively. In the

664 northern hypersolvus granite, REE concentrations are considerably lower than the bulk rock

665 concentrations, except for Tm, Yb and Lu. On average, 2 % of the bulk LREE (avg. 0.15 wt. %),

666 and 17 % of the bulk HREE (avg. 0.02 wt. %) are hosted by amphibole in this unit (~11 wt. %)

667 (Fig. 14). As the bulk rock LREE concentrations of this unit are relatively high (~10^3 times

668 chondrite values), this points to a major LREE bearing phase, e.g., monazite-(Ce), and/or

669 pyrochlore group minerals having crystallized prior to the amphibole or that there was another

670 sink for the LREE. The latter would be consistent with the findings of Vasyukova and Williams-

671 Jones (2014, 2016) that the hypersolvus granite magma saturated with (exsolved) a fluoride

672 liquid into which the LREE partitioned preferentially.

673 Amphibole proportions in the transsolvus granite are relatively high (~18 wt. %), whereas their

674 REE concentrations are particularly low (> 1 and < 100 times the chondrite value). In this unit,

675 only 0.1% of the bulk LREE (avg. 0.28 wt. %) and 4 % of the HREE (avg. 0.03 wt. %), on

676 average, are hosted by the amphibole (Fig. 14). As the amphiboles occur as phenocrysts in the

677 transsolvus granite, they largely record information about the pre-emplacement composition of

678 the magma. Given the low LREE content of the amphibole, it is possible that an early

679 fractionating phase depleted the melt in the LREE. These phases were monazite-(Ce) and

680 gagarinite-(Ce), which crystallized prior to or contemporaneously with the amphibole.

681 As mentioned earlier, some of the enclaves hosted by the transsolvus granite are interpreted to

682 represent the quenched margin of this intrusion. Accordingly, amphibole phenocrysts in these

683 enclaves and the host intrusion should have similar compositions. Indeed, their major element

684 concentrations match closely those of the transsolvus granite (see Fig. 5). However, the light and

685 middle REE contents of the amphiboles from the enclaves are generally higher than those of

686 amphiboles in their host (see Fig. 7e); the chondrite-normalized profiles of the bulk enclaves are

687 parallel to those of the bulk host granite, but their absolute values are slightly lower. The

688 consistently higher light and middle REE concentrations of amphibole in the enclaves compared

689 to their host could indicate that the amphibole crystallized from a melt relatively enriched in

690 these elements. However, much of the amphibole in the enclaves crystallized after emplacement

691 (quenching), which means that it crystallized from the very first and least evolved transsolvus

692 granite magma (lower bulk REE profile, see Fig. 7e). We therefore suggest that amphibole in the

693 enclaves crystallized slightly later than the phenocrysts in the magma chamber (transsolvus

694 granite), resulting in an amphibole more enriched in the REE.

32

The amphibole in the more altered localities of the transsolvus granite was replaced extensively by aegirine and/or hematite during hydrothermal alteration (Gysi and Williams-Jones, 2013; Gysi et al., 2016; Salvi and Williams-Jones, 1990, 1996; Vasyukova et al., 2016). As the REE content of the aegirine is orders of magnitude lower than that of the amphibole, it is very likely that the replacement of amphibole by aegirine (and hematite) led to the release of the REE, particularly the HREE to the hydrothermal fluid and the development of potentially exploitable zones of HREE mineralization.

7. CONCLUSIONS

We have shown that the major and trace-element compositions of amphiboles of the Strange Lake granite complex reflect the magmatic evolution of the pluton. The differentiation of the magma proceeded from the southern hypersolvus granite to the more evolved northern hypersolvus granite, two separate intrusions which both contain amphibole as a late, interstitial phase (Fig. 15a). The most evolved unit, a transsolvus granite, contains early crystallizing amphibole in the form of phenocrysts (Fig. 15b). Amphibole compositions vary from calcic-sodic (ferro-ferri-katophorite) in the least evolved southern hypersolvus granite to sodic members ((fluoro)-arfvedsonite, ferro-ferri-(fluoro)-leakeite) in the other, more evolved granites. The increasing Fe^{3+} concentration in amphibole with hypersolvus granite evolution was a result of crystal chemical effects (Na/Ca proportion) and increasing fO_2 through degassing. The same trend in the phenocrysts of the transsolvus granite implies a higher compatibility of Fe^{3+} with increasing Na/Ca proportions and an increase in OH^- and F^- concentrations in the evolving melt. Variations in Ti-concentrations indicate the presence of Na-Ti-silicates, such as aenigmatite, astrophyllite and narsarsukite, which replaced the amphibole to varying degrees in each unit. In the transsolvus granite, magma evolution is manifested by increasing Ti, Mn and Zn

718   concentrations from amphibole cores to rims. The phenocrysts of the transsolvus granite also

719   contain significant Li (ferro-ferri-fluoro-leakeite) that correlates positively with Fe^{3+}, indicating

720   that this most evolved melt was already enriched in Li at an early stage.

721   The amphiboles of all units are enriched in Nb, Zr and Hf and the HREE compared to the bulk

722   rock, reflecting a combination of magmatic compositional and crystal chemical effects. In the

723   hypersolvus granite, the late crystallization of amphiboles from a small proportion of residual

724   magma resulted in high incompatible element concentrations, whereas the early crystallization of

725   amphiboles in the transsolvus granite ensured relatively low concentrations of these elements,

726   despite the overall more evolved nature of the magma. The concentrations of the relatively

727   incompatible LREE ($D_{arf-bulk} < 0.01$) are positively coupled to the amphibole Ca concentration,

728   with the LREE preferentially incorporated in the larger B-site. The HREE were preferred by the

729   C-site and increased in compatibility ($D_{arf/bulk} > 0.1$) with increasing atomic number and

730   decreasing ionic radius. Variations in the LREE concentrations of the amphiboles were

731   controlled by the relative timing of crystallization of amphibole and the presence of primary

732   LREE minerals, such as monazite-(Ce), pyrochlore group minerals and gagarinite-(Ce), as well

733   as the exsolution of a LREE-rich fluoride melt. The uptake of the HREE by amphibole was

734   controlled by their relative compatibility in the structure of this mineral due to their smaller radii.

735   A significant proportion of the bulk HREE content of the Strange Lake granites was carried by

736   the amphibole, which during subsequent hydrothermal alteration was released to the fluid and

737   contributed to the development of potentially exploitable HREE mineralization.

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Siegel K, Williams-Jones AE, van Hinsberg VJ (2017) The amphiboles of the REE-rich A-type peralkaline Strange Lake pluton – fingerprints of magma evolution. Lithos 288:156-174.
doi: 10.1016/j.lithos.2017.07.012.

Siegel K, Williams-Jones AE, van Hinsberg VJ (2017) The amphiboles of the REE-rich A-type peralkaline Strange Lake pluton –
fingerprints of magma evolution. Lithos 288:156-174.
doi: 10.1016/j.lithos.2017.07.012.

REFERENCES

Abdel-Rahman, A. F. M., 1994, Alkali Amphibole: A Potential Source of Rare Earth Elements in Felsic Alkaline Rocks: Exploration and Mining Geology, v. 3, no. 2, p. 81-94.

Birkett, T. C., Trzcienski, W. E., and Stirling, J. A. R., 1996, Occurrence and compositions of some Ti-bearing minerals in the Strange Lake intrusive complex, Quebec-Labrador boundary: Canadian Mineralogist, v. 34, p. 779-801.

Blundy, J., and Wood, B., 2003, Partitioning of trace elements between crystals and melts: Earth and Planetary Science Letters, v. 210, no. 3-4, p. 383-397.

Boily, M., and Williams-Jones, A. E., 1994, The role of magmatic and hydrothermal processes in the chemical evolution of the Strange Lake plutonic complex, Quebec-Labrador: Contributions to Mineralogy and Petrology, v. 118, no. 1, p. 33-47.

Bottazzi, P., Tiepolo, M., Vannucci, R., Zanetti, A., Brumm, R., Foley, S. F., and Oberti, R., 1999, Distinct site preferences for heavy and light REE in amphibole and the prediction of D-Amph/L(REE): Contributions to Mineralogy and Petrology, v. 137, no. 1-2, p. 36-45.

Camara, F., Hawthorne, F. C., Ball, N. A., Bekenova, G., Stepanov, A. V., and Kotel'nikov, P. E., 2010, Fluoroleakeite, NaNa2(Mg2Fe23+Li)Si8O22F2, a new mineral of the amphibole group from the Verkhnee Espe deposit, Akjailyautas Mountains, Eastern Kazakhstan District, Kazakhstan: description and crystal structure: Mineralogical Magazine, v. 74, no. 3, p. 521-528.

Czamanske, G. K., and Dillet, B., 1988, Alkali amphibole, tetrasilicic mica, and sodic pyroxene in peralkaline siliceous rocks, Questa Caldera, New Mexico: American Journal of Science, v. 288-A, no. 1988, p. 358-392.

773   Czamanske, G. K., and Wones, D. R., 1973, Oxidation during Magmatic Differentiation,

774   Finnmarka Complex, Oslo Area, Norway .2. Mafic Silicates: Journal of Petrology, v. 14,

775   no. 3, p. 349-380.

776   Dalpé, C., and Baker, D. R., 2000, Experimental investigation of large-ion-lithophile-element-,

777   high-field-strength-element- and rare-earth-element-partitioning between calcic

778   amphibole and basaltic melt: the effects of pressure and oxygen fugacity: Contributions

779   to Mineralogy and Petrology, v. 140, no. 2, p. 233-250.

780   Davidson, A., 1982, Petrochemistry of the Blachford Lake Complex near Yellowknife,

781   Northwest Territories.: Maurice, E. T. (ed.) Uranium in Granites. Geological Survey of

782   Canada, p. 71-79.

783   Emslie, R. F., Hamilton, M. A., and Theriault, R. J., 1994, Petrogenesis of a Midproterozoic

784   anorthosite-mangerite-charnockite-granite (AMCG) complex - isotopic and chemical

785   evidence from the Nain Plutonic Suite: Journal of Geology, v. 102, no. 5, p. 539-558.

786   Emslie, R. F., and Stirling, J. A. R., 1993, Rapakivi and Related Granitoids of the Nain Plutonic

787   Suite - Geochemistry, Mineral Assemblages and Fluid Equilibria: Canadian Mineralogist,

788   v. 31, p. 821-847.

789   Giehl, C., Marks, M., and Nowak, M., 2013, Phase relations and liquid lines of descent of an

790   iron-rich peralkaline phonolitic melt: an experimental study: Contributions to Mineralogy

791   and Petrology, v. 165, no. 2, p. 283-304.

792   Giret, A., Bonin, B., and Leger, J. M., 1980, Amphibole Compositional Trends in Oversaturated

793   and Undersaturated Alkaline Plutonic Ring-Complexes: Canadian Mineralogist, v. 18, p.

794   481-495.

795 Gower, C. F., and Krogh, T. E., 2002, A U-Pb geochronological review of the Proterozoic

796   history of the eastern Grenville Province: Canadian Journal of Earth Sciences, v. 39, no.

797   5, p. 795-829.

798 Gysi, A. P., and Williams-Jones, A. E., 2013, Hydrothermal mobilization of pegmatite-hosted

799   REE and Zr at Strange Lake, Canada: A reaction path model: Geochimica et

800   Cosmochimica Acta, v. 122, no. 2013, p. 324-352.

801 Gysi, A. P., Williams-Jones, A. E., and Collins, P., 2016, Lithogeochemical Vectors for

802   Hydrothermal Processes in the Strange Lake Peralkaline Granitic REE-Zr-Nb-Deposit:

803   Economic Geology and the Bulletin of the Society of Economic Geologists, v. 111, p.

804   1241-1276.

805 Hawthorne, F. C., 1976, The crystal chemistry of amphiboles: V. the structure and chemistry of

806   arfvedsonite: Canadian Mineralogist, v. 14, p. 346-356.

807 Hawthorne, F. C., Oberti, R., Cannillo, E., Ottolini, L., Roelofsen, J. N., and Martin, R. F., 2001,

808   Li-bearing arfvedsonitic amphiboles from the Strange Lake peralkaline granite, Quebec:

809   Canadian Mineralogist, v. 39, p. 1161-1170.

810 Hawthorne, F. C., Oberti, R., Harlow, G. E., Maresch, W. V., Martin, R. F., Schumacher, J. C.,

811   and Welch, M. D., 2012, Nomenclature of the amphibole supergroup: American

812   Mineralogist, v. 97, no. 11-12, p. 2031-2048.

813 Hawthorne, F. C., Oberti, R., Ottolini, L., and Foord, E. E., 1996, Lithium-bearing fluor-

814   arfvedsonite from Hurricane Mountain, New Hampshire: A crystal-chemical study:

815   Canadian Mineralogist, v. 34, p. 1015-1019.

816   Hawthorne, F. C., Ungaretti, L., Oberti, R., Bottazzi, P., and Czamanske, G. K., 1993, Li - an

817   Important Component in Igneous Alkali Amphiboles: American Mineralogist, v. 78, no.

818   7-8, p. 733-745.

819   Herrmann, W., and Berry, R. F., 2002, MINSQ - a least squares spreadsheet method for

820   calculating mineral proportions from whole rock major element analyses: Geochemistry:

821   Exploration, Environment, Analysis, v. 2, no. 4, p. 361-368.

822   James, D. T., and Dunning, G. R., 2000, U-Pb geochronological constraints for paleoproterozoic

823   evolution of the core zone, southeastern Churchill Province, northeastern laurentia:

824   Precambrian Research, v. 103, no. 1-2, p. 31-54.

825   Kerr, A., and Rafuse, H., 2012, Rare-earth element (REE) geochemistry of the Strange Lake

826   deposits: Implications for resource estimation and metallogenic models.: Current

827   Research (2012) Newfoundland and Labrador Department of Natural Resources, v. 1, p.

828   39-60.

829   King, P. L., Hervig, R. L., Holloway, J. R., Vennemann, T. W., and Righter, K., 1999, Oxy-

830   substitution and dehydrogenation in mantle-derived amphibole megacrysts: Geochimica

831   Et Cosmochimica Acta, v. 63, no. 21, p. 3635-3651.

832   Konopleva, N. G., Ivanyuk, G. Y., Pakhomovsky, Y. A., Yakovenchuk, V. N., Men'shikov, Y.

833   P., and Korchak, Y. A., 2008, Amphiboles of the Khibiny alkaline pluton, Kola

834   Peninsula, Russia: Geology of Ore Deposits, v. 50, no. 8, p. 720-731.

835   Kovalenko, V. I., Tsaryeva, G. M., Goreglyad, A. V., Yarmolyuk, V. V., Troitsky, V. A., Hervig,

836   R. L., and Farmer, G. L., 1995, The Peralkaline Granite-Related Khaldzan-Buregtey

837   Rare-Metal (Zr, Nb, Ree) Deposit, Western Mongolia: Economic Geology and the

838   Bulletin of the Society of Economic Geologists, v. 90, no. 3, p. 530-547.

839   Leake, B. E., 1968, A Catalog of Analyzed Calciferous and Subcalciferous Amphiboles Together

840   with Their Nomenclature and Associated Minerals: Geological Society of America,

841   Special Papers 1968, v. 98, p. 1-44.

842   Leake, B. E., Woolley, A. R., Arps, C. E. S., Birch, W. D., Gilbert, M. C., Grice, J. D.,

843   Hawthorne, F. C., Kato, A., Kisch, H. J., Krivovichev, V. G., Linthout, K., Laird, J.,

844   Mandarino, J. A., Maresch, W. V., Nickel, E. H., Rock, N. M. S., Schumacher, J. C.,

845   Smith, D. C., Stephenson, N. C. N., Ungaretti, L., Whittaker, E. J. W., and Guo, Y. Z.,

846   1997, Nomenclature of amphiboles: Report of the subcommittee on amphiboles of the

847   International Mineralogical Association, Commission on New Minerals and Mineral

848   Names: Canadian Mineralogist, v. 35, p. 219-246.

849   Locock, A. J., 2014, An Excel spreadsheet to classify chemical analyses of amphiboles following

850   the IMA 2012 recommendations: Computers & Geosciences, v. 62, p. 1-11.

851   Ltd., Q. R. M., 2012, Quest announces that a revised resource estimate for the Strange Lake B-

852   Zone REE deposit shows a doubling of tonnage, http://questareminerals.com/news.php,

853   Volume 2016: Toronto, Quest Rare Minerals Ltd.

854   Markl, G., Marks, M., Schwinn, G., and Sommer, H., 2001, Phase equilibrium constraints on

855   intensive crystallization parameters of the Ilimaussaq complex, South Greenland: Journal

856   of Petrology, v. 42, no. 12, p. 2231-2258.

857   Marks, M., Halama, R., Wenzel, T., and Markl, G., 2004, Trace element variations in

858   clinopyroxene and amphibole from alkaline to peralkaline syenites and granites:

859   implications for mineral-melt trace-element partitioning: Chemical Geology, v. 211, no.

860   3-4, p. 185-215.

861 Mayer, B., Jung, S., Romer, R. L., Pfander, J. A., Klugel, A., Pack, A., and Groner, E., 2014,

862   Amphibole in alkaline basalts from intraplate settings: implications for the petrogenesis

863   of alkaline lavas from the metasomatised lithospheric mantle: Contributions to

864   Mineralogy and Petrology, v. 167, no. 989.

865 McLelland, J. M., Selleck, B. W., Hamilton, M. A., and Bickford, M. E., 2010, Late- to post-

866   tectonic setting of some major proterozoic anorthosite - mangerite - charnockite - granite

867   (AMCG) suites: Canadian Mineralogist, v. 48, no. 4, p. 729-750.

868 Miller, R. R., 1996, Structural and textural evolution of the Strange Lake peralkaline rare-

869   element (NYF) granitic pegmatite, Quebec-Labrador: Canadian Mineralogist, v. 34, p.

870   349-371.

871 Miller, R. R., Heaman, L. M., and Birkett, T. C., 1997, U-Pb zircon age of the Strange Lake

872   peralkaline complex: Implications for Mesoproterozoic peralkaline magmatism in north-

873   central Labrador: Precambrian Research, v. 81, no. 1-2, p. 67-82.

874 Mungall, J. E., and Martin, R. F., 1996, Extreme differentiation of peralkaline rhyolite, Terceira,

875   Azores: A modern analogue of Strange Lake, Labrador?: Canadian Mineralogist, v. 34, p.

876   769-777.

877 Oberti, R., Cannillo, E., and Toscani, G., 2012, How to name amphiboles after the IMA2012

878   report: rules of thumb and a new PC program for monoclinic amphiboles: Periodico Di

879   Mineralogia, v. 81, no. 2, p. 257-267.

880 Petrella, L., Williams-Jones, A. E., Goutier, J., and Walsh, J., 2014, The Nature and Origin of the

881   Rare Earth Element Mineralization in the Misery Syenitic Intrusion, Northern Quebec,

882   Canada: Economic Geology, v. 109, no. 6, p. 1643-1666.

883 Piilonen, P. C., Mcdonald, A. M., Poirier, G., Rowe, R., and Larsen, A. O., 2013, Mafic Minerals
884   of the Alkaline Pegmatites in the Larvik Plutonic Complex, Oslo Rift, Southern Norway:
885   Canadian Mineralogist, v. 51, no. 5, p. 735-770.

886 Pillet, D., Chenevoy, M., and Belanger, M., 1992, Petrology of Peralkaline Granite from Lake
887   Brisson (Central Labrador, Nouveau-Quebec) .1. Intrusion and Chemical Evolution:
888   Canadian Journal of Earth Sciences, v. 29, no. 2, p. 353-372.

889 -, 1993, Petrology of Peralkaline Granite from Lake Brisson (Quebec-Labrador) .2. Mineralogy
890   and Modes of Crystallization: Canadian Journal of Earth Sciences, v. 30, no. 12, p. 2423-
891   2435.

892 Roelofsen, J. N., 1997, The primary and secondary mafic silicates of two alkaline anorogenic
893   complexes: Strange Lake (Québec-Labrador) and Amba Dongar (Gujarat, India) [Ph.D.:
894   McGill University, 321 p.

895 Salvi, S., and Williams-Jones, A. E., 1990, The Role of Hydrothermal Processes in the Granite-
896   Hosted Zr, Y, Ree Deposit at Strange Lake, Quebec Labrador - Evidence from Fluid
897   Inclusions: Geochimica et Cosmochimica Acta, v. 54, no. 9, p. 2403-2418.

898 Salvi, S., and Williams-Jones, A. E., 1992, Reduced Orthomagmatic C-O-H-N-Nacl Fluids in the
899   Strange Lake Rare-Metal Granitic Complex, Quebec Labrador, Canada: European
900   Journal of Mineralogy, v. 4, no. 5, p. 1155-1174.

901 Salvi, S., and Williams-Jones, A. E., 1996, The role of hydrothermal processes in concentrating
902   high-field strength elements in the Strange Lake peralkaline complex, northeastern
903   Canada: Geochimica et Cosmochimica Acta, v. 60, no. 11, p. 1917-1932.

904 Salvi, S., and Williams-Jones, A. E., 1997, Fischer-Tropsch synthesis of hydrocarbons during

905   sub-solidus alteration of the Strange Lake peralkaline granite, Quebec/Labrador, Canada:

906   Geochimica Et Cosmochimica Acta, v. 61, no. 1, p. 83-99.

907 Salvi, S., and Williams-Jones, A. E., 2006, Alteration, HFSE mineralisation and hydrocarbon

908   formation in peralkaline igneous systems: Insights from the Strange Lake Pluton, Canada:

909   Lithos, v. 91, p. 19-34.

910 Shannon, R. D., 1976, Revised Effective Ionic-Radii and Systematic Studies of Interatomic

911   Distances in Halides and Chalcogenides: Acta Crystallographica Section A, v. 32, no.

912   Sep1, p. 751-767.

913 Sun, S. S., and McDonough, W. F., 1989, Chemical and isotopic systematics of oceanic basalts:

914   implications for mantle composition and processes: Geological Society, London, Special

915   Publications, v. 42, p. 313-345.

916 Tiepolo, M., Oberti, R., Zanetti, A., Vannucci, R., and Foley, S. F., 2007, Trace-element

917   partitioning between amphibole and silicate melt: Amphiboles: Crystal Chemistry,

918   Occurrence, and Health Issues, v. 67, p. 417-451.

919 Tiepolo, M., Vannucci, R., Bottazzi, P., Oberti, R., Zanetti, A., and Foley, S., 2000, Partitioning

920   of rare earth elements, Y, Th, U, and Pb between pargasite, kaersutite, and basanite to

921   trachyte melts: Implications for percolated and veined mantle: Geochemistry Geophysics

922   Geosystems, v. 1.

923 Tuttle, O. F., and Bowen, N. L., 1958, Origin of granite in the light of experimental studies in the

924   system $NaAlSi_3O_8$-$KAlSi_3O_8$-SiO_2-H_2O, Geological Society of America, Memoir 74, 146

925   p.:

926　Vasyukova, O., and Williams-Jones, A. E., 2014, Fluoride–silicate melt immiscibility and its role

927　　　in REE ore formation: Evidence from the Strange Lake rare metal deposit, Que´bec-

928　　　Labrador, Canada: Geochimica et Cosmochimica Acta, v. 139, no. 2014, p. 110-130.

929　-, 2016, The evolution of immiscible silicate and fluoride melts: Implications for REE ore-

930　　　genesis: Geochimica et Cosmochimica Acta, v. 172, p. 205-224.

931　Vasyukova, O. V., Williams-Jones, A. E., and Blamey, N. J. F., 2016, Fluid evolution in the

932　　　Strange Lake granitic pluton, Canada: Implications for HFSE mobilization: Chemical

933　　　Geology, v. 444, p. 83-100.

934

FIGURE CAPTIONS

936 Fig. 1: A geological map of the Strange Lake pluton showing the distribution of the major

937 lithological units. Locations of the samples used in this study are indicated.

938 Fig. 2: Thin section photomicrographs showing a) amphibole in hypersolvus granite (Arf),

939 occupying interstices between alkali-feldspar (perthite) (Afs) and quartz (Qtz) (ppl view), b)

940 amphibole in hypersolvus granite showing swapped margin texture with alkali-feldspar (ppl), c)

941 interstitial amphibole in the northern hypersolvus granite that has been largely replaced by

942 aenigmatite (red) (Aen) and astrophyllite (orange) (Ast) (xpl) and d) a Li-bearing amphibole

943 (Lea) phenocryst in transsolvus granite that has been partly replaced by aegirine (Aeg) along its

944 rim (ppl).

945 Fig. 3: Backscattered electron images of Strange Lake amphibole-group minerals showing a)

946 arfvedsonite with one large and numerous small fluorite (Fl) and fluorite-fluocerite solid solution

947 (Fl-Flc) (brighter) inclusions (hypersolvus granite), b) amphibole interstitial to perthitic alkali

948 feldspar and quartz (hypersolvus granite), replaced by fibrous astrophyllite along the rim, c) an

949 euhedral Li-bearing alkali amphibole (ferro-ferri-fluoro-leakeite) crystal (transsolvus granite)

950 containing numerous microcline (Mc) and albite (Ab) inclusions and, d) small subhedral

951 amphibole crystals among K-feldspar (Ksp) and quartz crystals (enclave).

952 Fig. 4: Ternary diagrams showing a) the A-and B-site occupancy of the sodic-calcic to sodic

953 amphibole-group minerals of the Strange Lake pluton (in apfu) (note that theoretically,

954 endmember arfvedsonite can have any composition along the Na-K tie-line), and b) the C-site

955 occupation of the amphibole-group minerals. The diagram (b) organizes the compositional data

956 according to the valence state of the cations, where $R^+ = {}^{C}Li^+$, $R^{2+} = Fe^{2+}$, Mn^{2+}, Mg^{2+}, Zn^{2+} and

957 $R^{3+} = Fe^{3+}, {}^{C}Al^{3+}$. The endmember compositions of katophorite (sodic-calcic), arfvedsonite and

958 leakeite (sodic) are indicated on the diagrams. In the legend "fgr" (southern hypersolvus granite)

959 refers to the fine-grained rocks of the unit, whereas "peg" stands for the oikiocrystic to

960 pegmatitic textured rocks.

961 Fig. 5: Binary diagrams showing major and minor element concentrations of amphibole in atoms

962 per formula unit (apfu), all as a function of Al concentration (X-axis). The decreasing Al content

963 monitors the differentiation of the magma.

964 Fig. 6: Binary diagrams showing the changing concentration (apfu) of selected elements as a

965 function of Al concentration (dashed arrows) from the cores to rims of amphibole phenocrysts in

966 the transsolvus granite.

967 Fig. 7: Chondrite-normalized REE- and trace element profiles of the Strange Lake amphibole-

968 group minerals displayed with the average bulk rock profiles of the respective units. a) REE- and

969 b) trace element spider diagram for the southern hypersolvus granite; c) REE- and d) trace

970 element spider diagram for the northern hypersolvus granite; and e) REE- and f) trace element

971 spider diagram for the transsolvus granite and enclaves. The chondrite values are from Sun and

972 McDonough, 1989.

973 Fig. 8: Chondrite-normalized REE-spider diagrams showing the average distribution of the

974 elements corresponding to the amphibole species identified in the Strange Lake pluton. The

975 chondrite values are from Sun and McDonough, 1989.

976 Fig. 9: Binary diagram showing the amphibole Fe^{2+}/Fe^{3+} ratio as a function of the Na/Ca ratio in

977 both, hypersolvus and transsolvus granite indicating a (low degree) coupled behavior of the

978 ratios in rocks with the same major phase paragenesis.

979   Fig. 10: Bar diagram showing the (average) relative proportion of the anions occupying the W-

980   site for each granite unit.

981   Fig. 11: Binary diagram illustrating the positive correlation between Fe^{3+} and Li^+ in amphibole

982   from the different granite facies. Linear trend lines and correlation coefficients have been added

983   to distinguish amphibole in the hypersolvus granite from that in the transsolvus granite. Lithium

984   concentrations are consistently lower in the hypersolvus granite than in the transsolvus granite.

985   Fig. 12: Binary diagrams showing the total REE concentration in amphibole of the different

986   granite facies as a function of the concentration of selected major elements. Also shown are the

987   corresponding trend lines and correlation coefficients (R^2).

988   Fig. 13: Diagram showing the ionic radii of the REE either in 6-fold (C-site) or 8-fold (B-site)

989   coordination versus the apparent partition coefficient $D_{arf-bulk}$ (median REE content of amphibole

990   / REE content of the bulk rock, sample 204720), plotted with error bars (median absolute

991   deviation). Also shown is a Lattice-Strain Theory fit through these data (solid line).

992   Fig. 14: Chart comparing the relative proportions of the bulk rock REE concentrations hosted by

993   amphibole (average values) for each granite facies (see text for details). The chart for the

994   southern hypersolvus granite only considers fine-grained samples.

995   Fig. 15: Cartoons showing the evolution of amphibole in the context of the textural development

996   of a) hypersolvus and b) transsolvus granite, from liquidus to solidus stages and the subsolidus

997   Na-alteration that affected the transsolvus granite. Crystallization temperature-, pressure- and

998   oxygen fugacity ranges are given, and were taken from the studies of the Strange Lake pluton by

999   Salvi and Williams-Jones (1992) and Vasyukova et al. (2016). The $f\mathrm{O}_2$ ranges are indicated in

1000   respect to the iron oxide buffers, MH (magnetite-hematite), QFM (quartz-fayalite-magnetite) and

1001   QIF (quartz-iron-fayalite).

Tables

1003 Table 1: Average (median) bulk rock major and trace element compositions of the unaltered

1004 granites from the center of the Strange Lake pluton (*fgr = fine grained samples, [+]oik/peg =

1005 oikocrystic and pegmatitic samples)

Unit	Hypersolvus granite S fgr*		Hypersolvus granite S oik/peg[+]		Hypersolvus granite N		Transsolvus granite		Enclaves	
Samples	*7*		*8*		*12*		*24*		*12*	
		+/-		+/-		+/-		+/-		+/-
SiO_2 *wt. %*	69.04	0.89	70.57	0.56	70.68	0.36	71.28	0.53	69.36	0.60
Al_2O_3	11.88	0.26	10.57	0.17	11.74	0.21	10.27	0.39	11.97	0.25
Fe_2O_3	5.78	0.31	6.72	0.52	4.89	0.08	5.98	0.47	5.05	0.10
MnO	0.10	0.01	0.11	0.01	0.10	0.01	0.12	0.01	0.09	0.02
MgO	0.04	0.01	0.02	0.01	0.05	0.01	0.03	0.01	0.04	0.02
CaO	0.73	0.19	0.37	0.11	0.57	0.03	0.45	0.18	0.83	0.15
Na_2O	4.92	0.17	5.11	0.05	5.09	0.10	5.08	0.35	3.60	0.98
K_2O	4.93	0.21	4.48	0.09	4.74	0.11	4.32	0.31	7.60	1.61
TiO_2	0.28	0.03	0.21	0.03	0.27	0.01	0.21	0.05	0.15	0.04
Nb_2O_5	0.03	0.01	0.05	0.01	0.06	0.005	0.05	0.02	0.02	0.02
P_2O_5	0.02	0.00	0.02	-	0.02	0.01	0.01	0.01	-	-
F	0.44	0.02	0.37	0.09	0.46	0.04	0.51	0.06	0.49	0.07
TREO	0.17	0.03	0.19	0.02	0.24	0.03	0.48	0.06	0.25	0.03
LREO	0.12	0.02	0.13	0.02	0.16	0.02	0.33	0.04	0.16	0.02
HREO+Y	0.05	0.005	0.06	0.01	0.08	0.01	0.11	0.04	0.09	0.01
LOI	0.72		0.47		0.70		0.72		0.83	
Total	98.53		99.19		99.14		99.20		99.68	
Agp index	1.13	0.02	1.23	0.02	1.15	0.03	1.27	0.03	1.17	0.02
Be *(ppm)*	36	8	40	14	53	11	54	22	31	7
Zn	285	40	545	30	465	60	585	90	465	145
Ga	45	3	52	3	44	1	60	3	48	5
Rb	417	23	436	31	522	47	672	99	925	241
Sr	18	5	15	5	21	7	21	8	21	5
Y	266	17	293	36	392	74	616	196	556	48
Zr	2413	667	2504	469	3656	268	4984	1917	1488	1126
Ba	76	13	43	8	85	18	43	15	58	14
La	228	33	221	35	305	51	630	81	286	47
Ce	464	73	485	72	629	79	1235	170	589	88
Pr	56	14	60	7	73	10	149	20	74	10
Nd	191	42	207	27	240	35	527	52	282	23
Sm	39	10	51	6	49	6	115	16	68	5
Eu	2	0.4	3	0.4	3	0.4	6	1	4	0.2
Gd	33	5	44	7	45	7	100	18	66	7
Tb	6	1	8	1	10	1	17	4	12	1
Dy	44	7	53	8	69	12	103	29	72	10
Ho	10	2	11	2	15	2	21	7	14	3
Er	33	6	36	7	50	6	64	24	37	10
Tm	5	1	6	1	8	1	9	4	5	2
Yb	36	3	42	9	57	4	58	29	25	10
Lu	6	0.4	7	1	9	1	8	4	4	1

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doi: 10.1016/j.lithos.2017.07.012.

Hf	69	12	67	12	97	15	136	47	42	31
Ta	14	1	20	4	28	4	25	13	7	5
Pb	94	17	169	53	137	38	187	73	38	21
Th	54	9	69	20	88	15	84	40	23	17
U	10	3	14	3	19	2	17	8	4	3

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1007 <mark>Table 2:</mark> Average calculated formulae and cation assignments (in apfu) of amphibole group

1008 minerals, based on 24 oxygens. Ideal site occupation is noted in brackets. The rock units are: HS

1009 S fgr (hypersolvus granite south, fine grained), HS N (hypersolvus granite north), EN (enclaves),

1010 TS (transsolvus granite).

Species	Arfved sonite	Fluor-arfveds onite	Ferro-ferri-leakeite	Ferro-ferri-fluoro-leakeite	Ferro-ferri-kato-phorite
Unit	HS S	all units	HS N	HS N, TS	HS S fgr
Analyses	*n=12*	*n=56*	*n=5*	*n=70*	*n=6*
Formula Assignments					
Si	7.64	7.83	7.64	7.74	7.53
Al	0.23	0.10	0.11	0.07	0.36
Ti	0.09	0.09	0.11	0.09	0.11
Fe^{3+}	0.10	0.03	0.15	0.12	-
T (8)	8.00	8.00	8.00	8.00	8.00
Ti	0.09	0.06	-	0.03	0.10
Zr	0.01	0.01	0.02	0.01	-
Al	0.10	0.05	-	-	-
REE	0.02	0.01	0.01	-	0.03
Fe^{3+}	1.66	1.70	1.99	2.01	1.36
Zn	0.08	0.04	0.11	0.05	0.06
Mn^{2+}	0.09	0.10	0.09	0.08	0.10
Fe^{2+}	2.62	2.49	1.96	2.00	3.02
Mg	0.06	0.04	0.05	0.02	0.09
Li	0.29	0.31	0.71	0.74	0.15
C (5)	4.87	4.75	4.94	4.92	4.91
Li	-	-	0.07	0.08	-
Ca	0.23	0.10	0.09	0.03	0.57
Na	1.77	1.90	1.87	1.95	1.43
B (2)	2.00	2.00	2.00	2.00	2.00
Na	0.79	0.89	0.87	0.86	0.69
K	0.28	0.31	0.31	0.33	0.26
A (0-1)	1.07	1.20	1.18	1.19	0.95
OH	1.05	0.70	0.93	0.61	1.14
F	0.72	1.07	0.85	1.20	0.44
Cl	0.01	-	-	-	0.01
O	0.23	0.22	0.21	0.19	0.41
W (2)	2.00	2.00	2.00	2.00	2.00

1011

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1012   Table 3: List of amphibole and titanium bearing minerals identified in the unaltered Strange Lake

1013   granites with their endmember structural formulae

Mineral name	Formula
Amphibole-group minerals	
(Fluoro)-arfvedsonite	$NaNa_2(Fe^{2+}_4Fe^{3+})Si_8O_{22}(OH,F)_2$
Ferro-ferri-(fluoro)-katophorite	$Na(NaCa)(Fe^{2+}_4Fe^{3+})Si_7AlO_{22}(OH,F)_2$
Ferro-ferri-(fluoro)-leakeite	$NaNa_2(Fe^{2+})_2(Fe^{3+})_2LiSi_8O_{22}(OH,F)_2$
Clinopyroxenes	
Aegirine	$NaFe^{3+}Si_2O_6$
Titano-silicates and Ti-oxide mineral	
Aenigmatite	$Na_2Fe^{2+}_5TiSi_6O_{20}$
Astrophyllite	$(K,Na)_3(Fe^{2+})_7Ti_2Si_8O_{26}(OH)_4$
Narsarsukite	$Na_2(Ti,Fe^{3+})Si_4(O,F)_{11}$
Titanite	$CaTiSiO_5$
Ilmenite	$Fe^{3+}TiO_3$

1014

Unit	Hypersolvus granite S fgr*		Hypersolvus granite S oik/peg[+]		Hypersolvus granite N		Enclaves		Transsolvus granite	
Analyses	n=13		n=19		n=39		n=9		n=72	
		+/-		+/-		+/-		+/-		+/-
SiO_2 *wt. %*	48.29	0.51	49.97	0.80	50.71	0.19	50.71	0.93	51.02	0.52
Al_2O_3	1.47	0.30	0.99	0.15	0.50	0.08	0.36	0.01	0.34	0.05
TiO_2	1.45	0.30	0.84	0.12	1.09	0.14	0.92	0.08	0.71	0.09
FeO	33.67	0.42	33.80	0.41	32.06	0.27	31.78	0.22	32.47	0.38
MgO	0.72	0.05	0.64	0.05	0.85	0.03	0.71	0.08	0.56	0.04
MnO	0.34	0.07	0.10	0.08	0.22	0.03	0.09	0.03	0.08	0.03
ZnO	0.62	0.16	0.24	0.05	0.45	0.04	0.60	0.11	0.30	0.05
ZrO_2	0.04	0.02	0.06	0.03	0.17	0.04	0.13	0.03	0.11	0.03
Nb_2O_5	0.07	0.02	0.02	0.01	0.02	0.02	0.02	0.01	0.01	0.004
Na_2O	7.25	0.54	9.18	0.20	9.36	0.09	9.34	0.19	9.57	0.13
K_2O	1.27	0.15	1.28	0.12	1.59	0.11	1.73	0.09	1.65	0.09
CaO	2.79	0.69	1.11	0.50	0.47	0.08	0.13	0.05	0.13	0.03
F	1.29	0.31	1.97	0.27	2.08	0.12	2.05	0.18	2.56	0.15
Cl	0.03	0.01	0.02	0.01	0.01	0.01	-	-	0.01	0.005
Total	99.18		100.5		99.87		98.84		99.93	
Li *(ppm)*	1613	772	1450	615	3099	549	4802	931	5775	1260
Rb	58.8	17.8	20.9	6.3	61.8	9.4	88.7	15.5	84.3	18.6
Sr	23.3	6.8	8.5	3.0	11.7	3.7	4.0	1.4	1.4	0.5
Y	471	145	70.9	26.0	107	27	92.0	32.0	27.7	5.5
Zr	1208	653	647	124	2648	450	2073	234	1356	339
Sn	160	80.3	21.3	8.9	156	49	90.1	36.2	137	41
La	96.0	11.2	31.9	9.5	32.4	5.9	24.1	8.5	2.8	1.2
Ce	282	24	91.6	14.7	85.9	22.6	45.3	9.7	6.6	2.8
Pr	44.4	4.9	13.5	2.8	13.7	4.3	6.9	1.6	1.0	0.4
Nd	218	25	60.1	15.7	62.3	20.5	32.5	8.0	4.7	2.2
Sm	59.7	7.3	13.8	2.7	11.6	4.5	6.2	1.3	0.91	0.47
Eu	4.0	0.3	0.85	0.22	0.68	0.30	0.37	0.17	0.05	0.02
Gd	50.0	5.8	9.6	2.0	7.6	3.1	9.3	3.9	0.67	0.33
Tb	10.6	1.5	1.7	0.5	1.6	0.6	1.7	0.7	0.21	0.08
Dy	71.7	13.8	12.4	2.3	18.3	5.7	11.4	3.0	2.6	0.6
Ho	17.1	3.7	3.1	0.5	7.7	1.8	3.2	0.9	1.2	0.3
Er	69.7	21.2	15.1	2.9	48.5	12.3	14.9	1.2	8.1	1.4
Tm	14.2	4.4	4.3	1.0	17.5	4.8	4.6	0.8	2.7	0.5
Yb	144	52	53.1	11.8	215	53	52.4	5.7	35.9	6.3
Lu	29.5	11.6	11.7	2.6	50.1	11.5	12.8	3.1	8.6	1.9
Hf	60.3	35.8	27.5	7.0	130	25	85.0	20.6	63.6	17.6
Ta	9.0	1.7	2.2	0.4	2.9	0.8	1.9	0.6	1.1	0.3
Pb	77.9	8.0	8.9	5.1	34.5	10.5	10.7	4.6	5.8	1.7
Nb	468	116	124	51	214	34	109	20	92.4	13.8
Ba	10.5	6.3	3.4	2.5	6.0	2.4	1.9	0.9	0.43	0.26
Th	1.7	1.4	0.75	0.66	0.51	0.47	2.9	2.5	0.02	0.02
U	0.13	0.10	0.13	0.11	0.03	0.03	0.16	0.15	0.01	0.01

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| TREE+Y | 1634 | 297 | 395 | 91 | 708 | 174 | 389 | 117 | 110 | 19 |

1018

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1019   Table 5: Average (median) core and rim compositions (in apfu) with median absolute deviation

1020   (+/-) of selected phenocrysts from the transsolvus granite

Location	Core		Rim	
Analyses	*n=24*		*n=7*	
		+/-		+/-
^{T}Si *(apfu)*	7.906	0.102	7.716	0.039
^{T}Al	0.059	0.006	0.059	0.003
^{T}Ti	0.072	0.010	0.083	0.008
^{T}Fe^{3+}	0.143	0.030	0.135	0.025
^{C}Ti	0.084	0.016	0.001	-
^{C}Zr	0.008	0.003	0.008	0.002
^{C}Al	0.052	0.019	-	-
^{C}REE	0.002	0.001	0.002	-
^{C}Fe^{3+}	1.763	0.215	2.022	0.007
^{C}Zn	0.034	0.006	0.072	0.015
^{C}Mn^{2+}	0.072	0.004	0.081	0.007
^{C}Fe^{2+}	2.441	0.321	1.952	0.058
^{C}Mg	0.026	0.006	0.014	0.001
^{C}Li	0.407	0.232	0.825	0.044
^{B}Li	0.051	0.024	0.066	0.024
^{B}Ca	0.024	0.006	0.019	0.005
^{B}Na	1.973	0.009	1.964	0.017
^{A}Na	0.867	0.042	0.838	0.037
^{A}K	0.317	0.011	0.347	0.050
^{W}F	1.205	0.057	1.027	0.122
total Ti	0.156	0.026	0.083	0.008
total Al	0.111	0.025	0.059	0.003
total Fe^{3+}	0.074	0.011	2.164	0.046
total Na	1.906	0.245	2.769	0.040
total Li	8.034	0.006	0.860	0.071
total Fe	0.156	0.020	0.825	0.044
Fe^{2+}/Fe^{3+}	2.449	0.324	2.134	0.040

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Siegel K, Williams-Jones AE, van Hinsberg VJ (2017) The amphiboles of the REE-rich A-type peralkaline Strange Lake pluton –
fingerprints of magma evolution. Lithos 288:156-174.
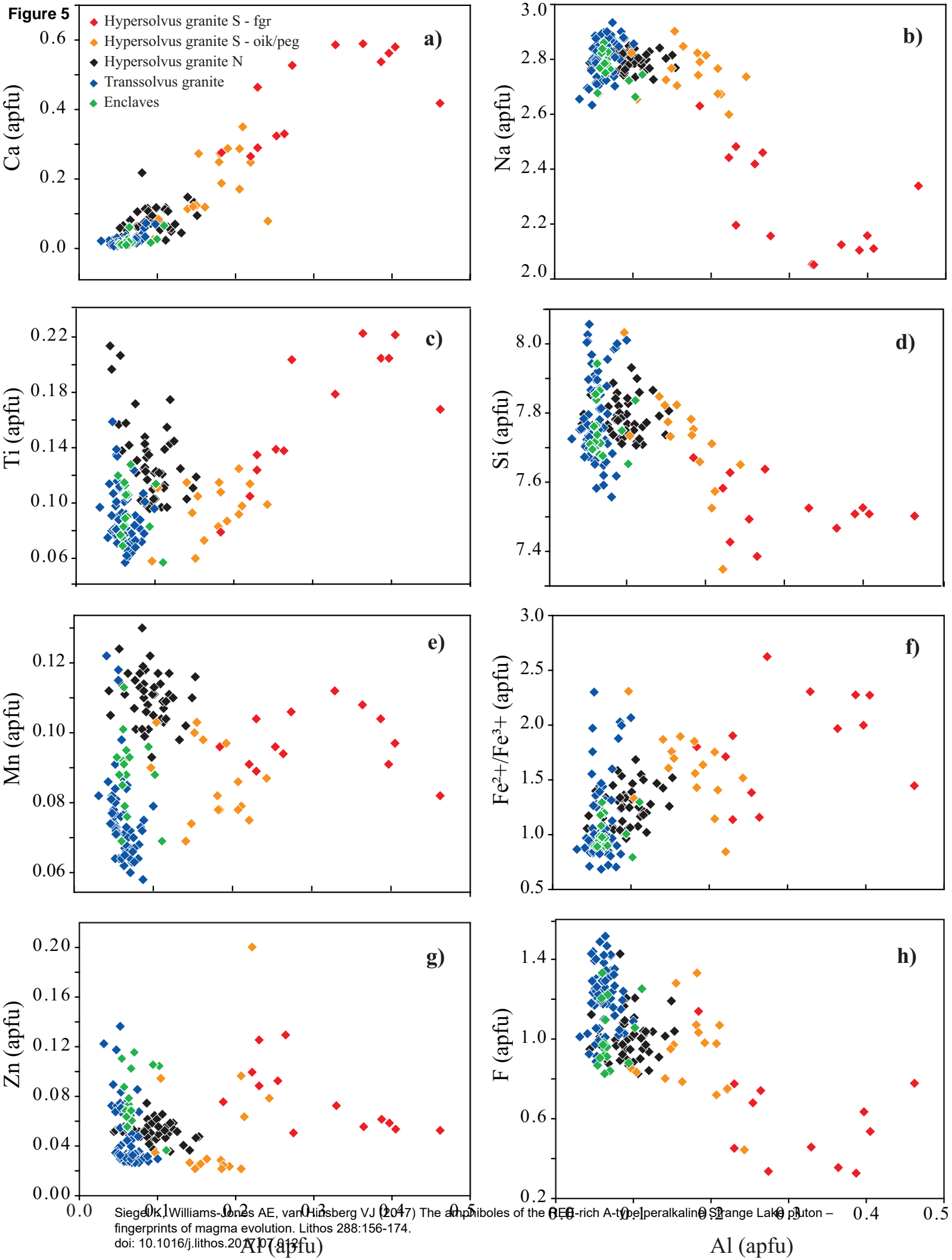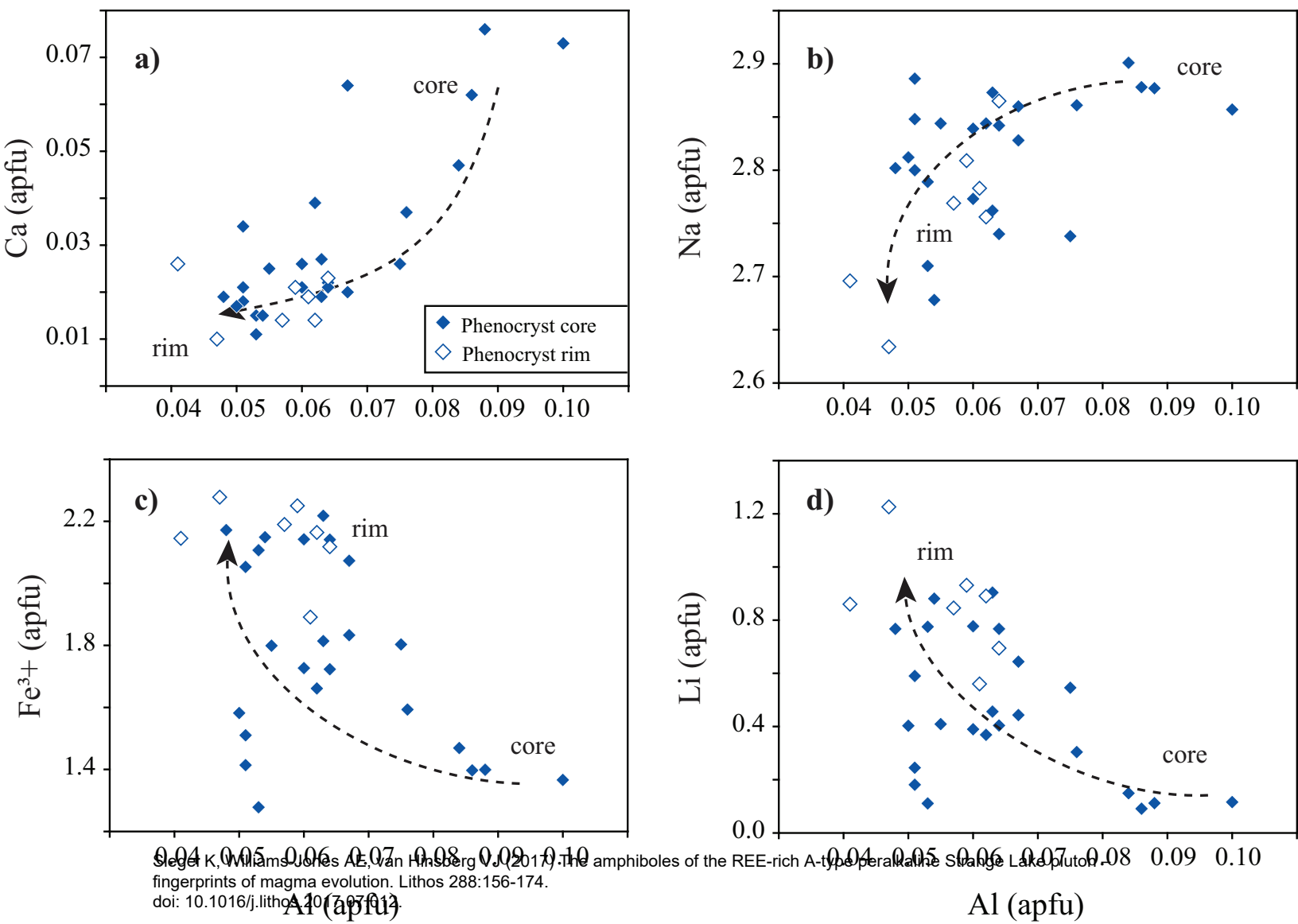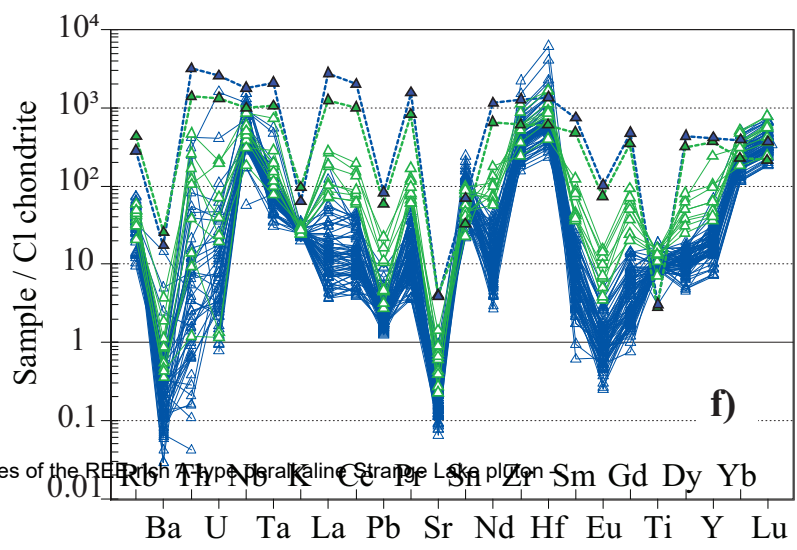doi: 10.1016/j.lithos.2017.07.012.

1022   Table 6: Apparent melt-arfvedsonite partition coefficients ($D_{arf-bulk}$), ionic radius 'r' in 6- and 8-

1023   fold coordination, ideal radius (r) for each element and median absolute deviation (MAD)

	$D_{arf-bulk}$	r_{6-fold}	r_{8-fold}	r	MAD[*]
La	0.006	1.03	1.16	1.2	0.005
Ce	0.005	1.01	1.14	1.1	0.003
Pr	0.005	0.99	1.13	1.1	0.003
Nd	0.008	0.98	1.11	1.1	0.004
Sm	0.006	0.96	1.08	1.1	0.002
Eu	0.006	0.95	1.07	1.1	0.004
Gd	0.006	0.94	1.05	0.9	0.003
Tb	0.014	0.92	1.04	0.9	0.002
Dy	0.027	0.91	1.03	0.9	0.005
Ho	0.075	0.90	1.02	0.9	0.011
Er	0.201	0.89	1.00	0.9	0.016
Tm	0.657	0.88	0.99	0.9	0.053
Yb	1.664	0.87	0.99	0.9	0.165
Lu	3.261	0.86	0.98	0.9	0.321
Y	0.043	0.90	1.02	0.9	0.006

1024

1025   [*]The Median Absolute Deviation (MAD) is reported (plotted as error bars in Fig. 14) instead of the standard deviation, as the
1026   median amphibole concentration was used instead of the mean concentration.

1027

1028   Appendix A: Standards, counting time and detection limits used for electron microprobe

1029   analyses (EMPA) of the amphibole group minerals

Element	Standard	Counting time (s)	Detection limit (ppm)
Na	Albite	20	267
Fe	Hematite	20	264
Mn	Spessartine	20	413
Ti	Rutile	20	370
Zr	Zircon	20	653
Si	Diopside	20	363
Ca	Diopside	20	243
Mg	Diopside	20	266
Al	Orthoclase	20	216
K	Orthoclase	20	205
Cl	Vanadinite	20	218
F	Fluorite	100	1501
Zn	Willemite	20	427

1030

1031   Detection limits and standard deviations (2 σ) represent average detection limits calculated from repeated analyses of standards
1032   during the analytical runs.

Figure 1
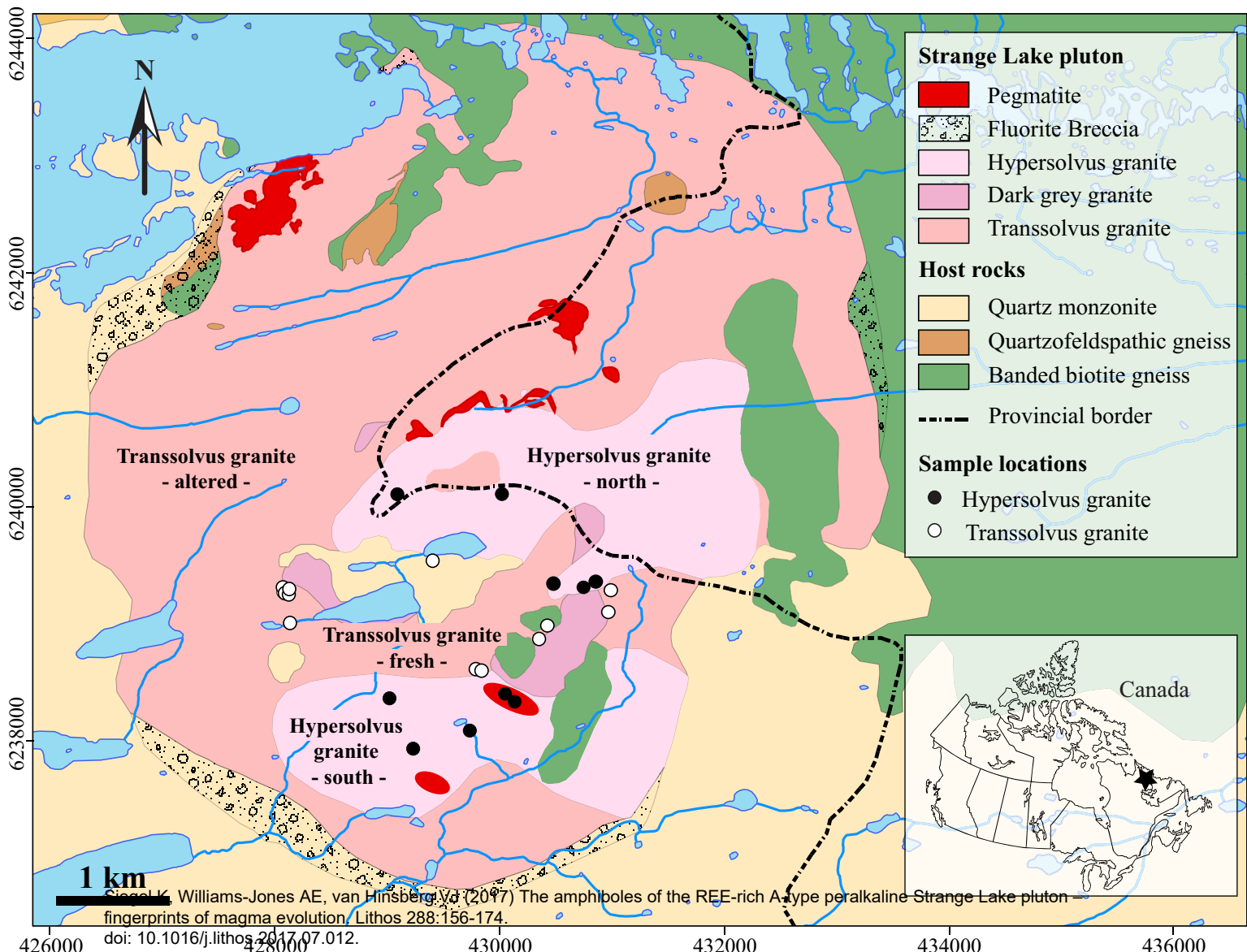
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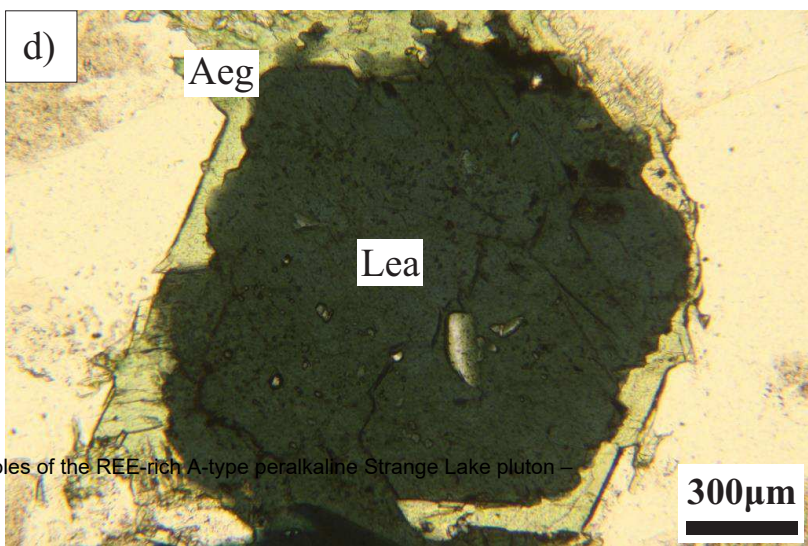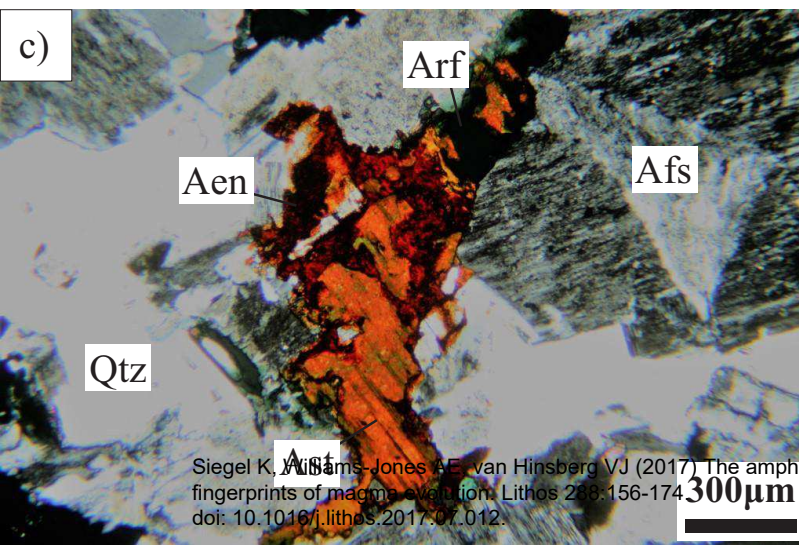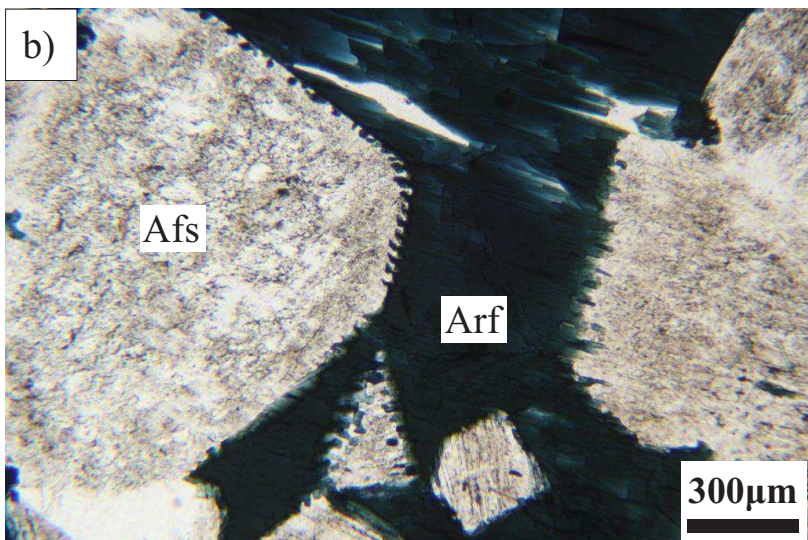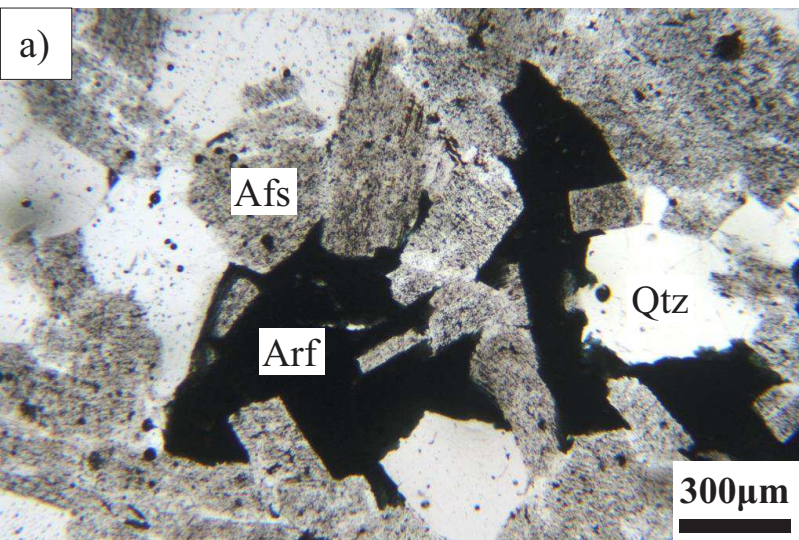
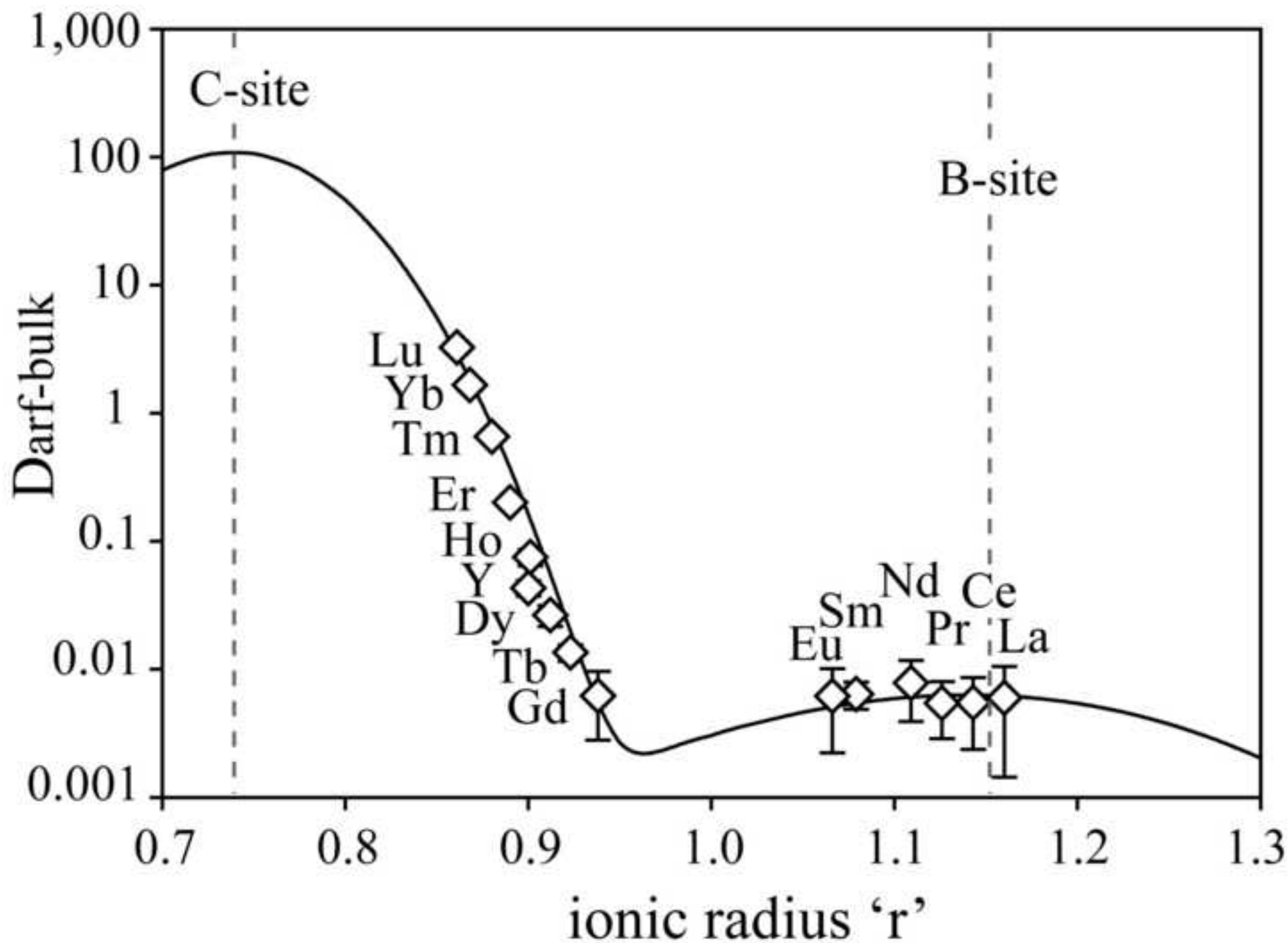**Figure 3**
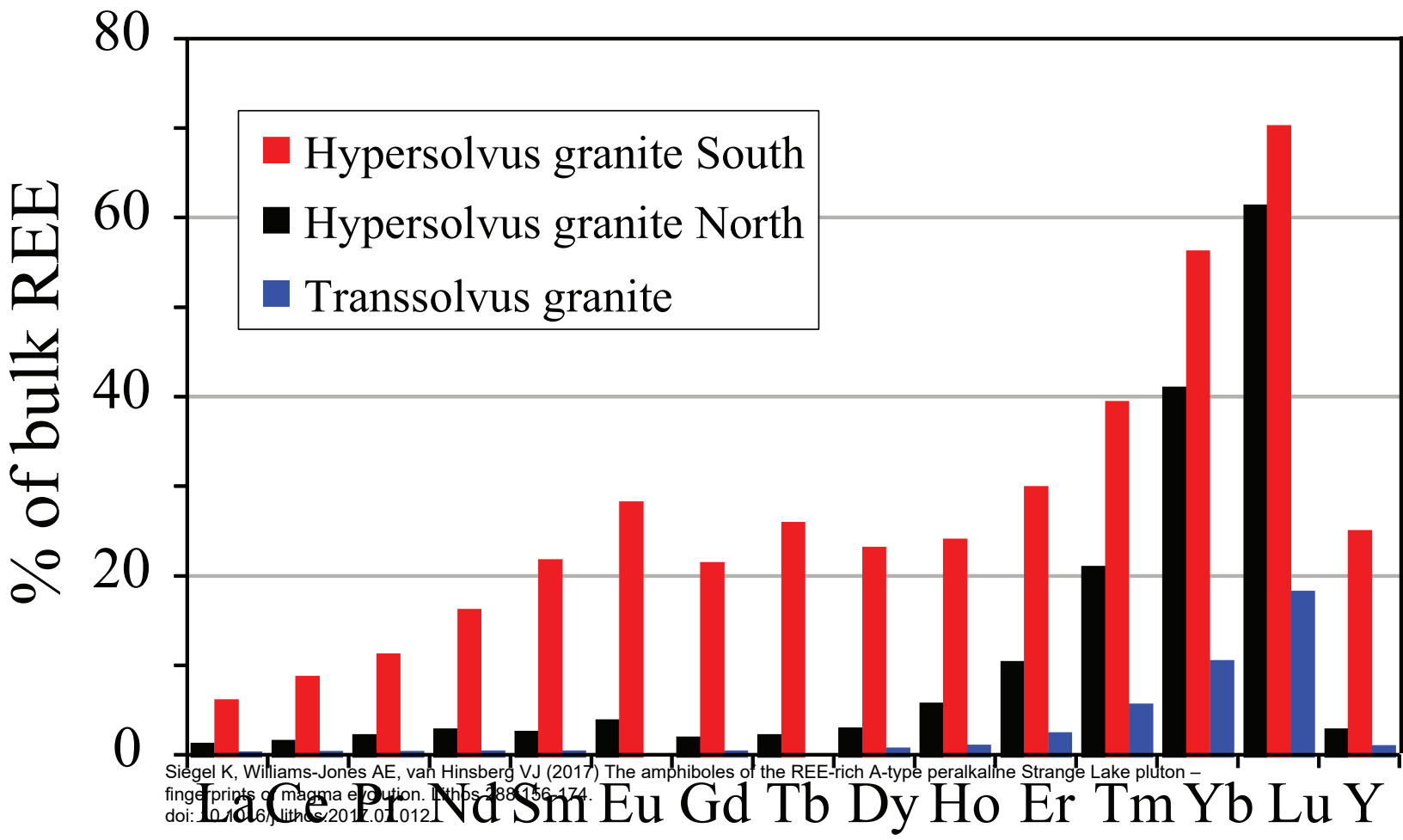[Click here to download high resolution image](#)

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doi: 10.1016/j.lithos.2017.07.012.

Figure 4

a)

10K

Arfvedsonite

Na

20Ca

Katophorite

Hypersolvus granite S - fgr
Hypersolvus granite S - oik/peg
Hypersolvus granite N
Transsolvus granite
Enclaves

b)

10R$^+$

Leakeite

Arfvedsonite

R^{2+}

R^{3+}

Figure 5

Legend:
- Hypersolvus granite S - fgr (red)
- Hypersolvus granite S - oik/peg (orange)
- Hypersolvus granite N (black)
- Transsolvus granite (blue)
- Enclaves (green)

Figure 6

Siegel K, Williams-Jones AE, van Hinsberg VJ (2017) The amphiboles of the REE-rich A-type peralkaline Strange Lake pluton - fingerprints of magma evolution. Lithos 288:156-174.
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Figure 7

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Figure 8
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doi: 10.1016/j.lithos.2017.07.012.

Figure 9

Figure 10

	OH	F+Cl	O
Hypersolvus granite South	1.05 (apfu)	0.62	0.33
Hypersolvus granite North	0.73	1.01	0.26
Transsolvus granite	0.60	1.23	0.17

W-site (apfu)

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Figure 11

Figure 12

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Figure 14

Figure 15

a) **Hypersolvus granite**
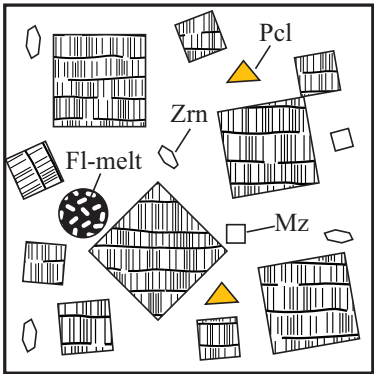
Liquidus (magma chamber)
T ≥ 700 °C
P > 2 kbar
fO$_2$ low (QIF - QFM)

Solidus (after emplacement)
T ~ 700 - 660 °C
P ~ 1-2 kbar
fO$_2$ intermediate (< QFM)

Legend:
Perthitic alkali feldspar
Arfvedsonite - inclusion bearing
Arfvedsonite - late stage
Ti-Na-silicate replacement
Ferro-ferri-leakeite - phenocryst
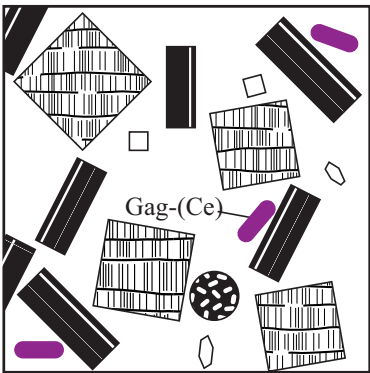Quartz
Microcline   Albite
Na-alteration:
Albitization   Aegirinization

b) **Transsolvus granite**

Liquidus (magma chamber)
T < 700°C
P > 2 kbar
fO$_2$ low (QIF - QFM)

Solidus (after emplacement)
T < 700 - 550 °C
P ~ 1-2 kbar
fO$_2$ intermediate (< QFM)

Subsolidus (Na-alteration)
T ~ 450 - 350 °C
P ~ 1-2 kbar
fO$_2$ high (QFM - MH)

Background dataset for online publication only