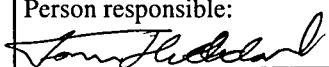NGU Report 99.126

Distribution of Al, Li and Na in granite
pegmatite quartz, South Norway

REPORT

Report no.: 1999.126	ISSN 0800-3416	Grading: Open

Title:
Distribution of Al, Li and Na in granite pegmatite quartz from Evje-Iveland and Froland

Authors: Larsen Rune B.	Client: North Cape Minerals

County: Aust Agder	Commune:

Map-sheet name (M=1:250.000) Arendal, Mandal	Map-sheet no. and -name (M=1:50.000)

Deposit name and grid-reference:	Number of pages: *16* Price (NOK): kr. 100,- Map enclosures:

Fieldwork carried out:	Date of report: 06.12.1999	Project no.: 2728.00	Person responsible:

Summary:
Distribution of Al, Li and Na in granite pegmatite quartz, South-Norway was estimated by LA-HR-ICP-MS (Laser Ablation Inductively Coupled Plasama Mass Spectrometry) analysis of quartz at Monash University, Australia. The results are preliminary and remain to be confirmed at NGU with the analytical method that currently is under development.

Therefore, the present conclusions are subject to the results obtained at NGU and accordingly should be evaluated conservatively.

The average concentration of Al in quartz from 15 localities in the Evje Iveland area varies from <19 to 164 ppm whereas the concentration of Li varies from <4.6 to 28 ppm. In the Froland area the concentration of Al and Li at the four pegmatite localities included from this area is <19 and <4.6 ppm respectively. The maximum concentration of structural bound Na may be approached from the empirical expression: [Al] = [Li] + [Na] in mol%. Accordingly, the concentration of Na in Froland is 1 ppm or less whereas Evje-Iveland features values between 0 and 46 ppm.

Although only four pegmatites from Froland are incorporated in the present study, it is clear that all the pegmatites yielded low concentrations of impurities hence the quality of quartz from pegmatites in this area by far exceed the average quality obtained from Evje-Iveland. Only 2 out of 15 localities in Evje-Iveland (#94 and 95), yielded comparable low concentrations of Al, Li and Na.

Granite pegmatites in Froland are also relatively large, compared to Evje-Iveland and are situated closer to the sea. Therefore, as a cautious preliminary conclusion, depending on the results from the NGU-lab, it is suggested to implement a detailed sampling program of selected Froland pegmatites comprising the desired tonnages.

Keywords: Quartz	Granite Pegmatite	Chemistry

CONTENTS

FIGURES

Figure 1 Geological overview and location of sample sites

Figure 2a-c Distribution of Al, Li and Na in Evje-Iveland pegmatite field

Figure 3 Regional distribution of Al

Figure 4 Regional distribution of Li

Figure 5a-c Field appearance of pegmatite from Froland with low Al, Li and Na contents

TABLES

Table 1 Distribution of Al, Li and Na in granite pegmatite quartz from SE-Norway

1. INTRODUCTION

Granite pegmatite quartz was sampled from 15 localities in Evje-Iveland, 4 localities in Froland and 2 other localities (Fig. 1). These samples were analysed with the LA-HR-ICP-MS (Laser-Ablation High-Resolution Inductively-Coupled-Plasma Mass-Spectrometry) method at Monash University, Australia, however, due to the preliminary nature of this novel analytical method (see section on methodology), a good deal of development remains before a complete analytical package may be launched. Currently, only the distribution of Al, Li and Na may be reported with some confidence although 18 other elements were included in the analysis at Monash. By late November, NGU completed the development of an analytical method comprising most industrially interesting elements in terms of quartz analysis for high purity quartz applications. After completion of an extensive testing program including natural quartz samples and custom made standards, a formal analytical package including Al, B, Ba, Be, Ca, Cr, Cu, Fe, Ge, K, Li, Mg, Mn, Pb, Rb, Sr, Ti, U is ready for routine analysis.

2. ANALYTICAL RATIONALE

The LA-HR-ICP-MS method is a cutting edge analytical technique that in its present form was introduced only three years ago and currently is trialed on geological samples all over the Earth science community. This technique aim at estimating the trace element distribution in solid material (e.g. rocksamples) with detection limits down towards 1 ppb and for certain elements, even much lower. The novel concept is to use a laser beam operating at the ultra violet (UV) wavelength (266 nm) to release microscopic samples from a rock surface. Because of the high energy of UV-light, the part of the sample that is bombarded by the laser-beam is partially melted and detached (i.e. ablated) from the sample surface in an explosive process that throw melt and dust in to an argon-gass current sweeping through the sample chamber. Susequently the ablated sample, which is suspended in the argon gass, is transported towards a magnetic mass spectrometer where the chemical composition is estimated. On the way to the mass spectrometer the sample passes through a torch system that generates an argon plasma, i.e. a very high temperature medium maintaining a tempertaure of ca. 10 000 °C. By passing this temperature regime the sample partially or fully decomposes to form positively charged ions (e.g. Ti^{4+}, Si^{4+} K^+). In continuing inside the mass spectrometer, the ions will enter a strong magnetic field that bend the individual ions according to their energy, mass and charge hence diferent ions continue along distinctive trajectories throughout the magnetic field. After having passed through the magnetic field, a narrow slit is adjusted so that only one specific trajectory, equivalent to the path followed by the desired ion (e.g. Ti^{4+}), will line up with the slit. The ions that are allowed through the slit will subsequently collide with a detector system that measure the number of collisions per time unit, i.e. counts/second. One of the novel features with the mass spectrometer at NGU is its ability to rapidly sweep over large parts of the periodic table (Li^7 to U^{238}) and rapidly to change between Low-, Medium- and High Resolution (respectively LR, MR and HR). In LR, the width (i.e. atomic mass range) over which a particular isotope is measured is quite wide which facilitate very low detection limits (down to the ppt level for some isotopes) and high precision. However, certain compunds having near equal masses may interfere with the measurements and distort the final result. Distortion of the result may be avoided by narrowing

the mass range over which the measurement is performed and depending on the size and proximity of the interfering compund, the measurement may be done in MR of HR mode. These options, although drastically reducing the sensitivity of the measurement, facilitates estimation of difficulat isotopes such as for example K, Ca, S and As that rarely can be quantified with conventional mass spectrometric techniques.

The laser system which is used for the ablation of the samples operates with a typical beam diameter of 10-100 μm a pulse energy of <30 mJ, and with a frequency of max 10 Hz (i.e. 10 shots/second) with a shot-duration of <10 ns. Either, laser sampling is performed in a single spot or in an area (raster) where the laser beam moves along a predefined grid and the final result reflects the average composition over the area.

Absorbtion of UV-laser light varies greatly from one sample to the next hence the volume of material which is ablated can not be predicted. Therefore, Quatification of an element in the sample requires that the concentration of one element is known already. This element is called the internal standard and is typically a major element in the mineral that either is known stoichiometrically as for examples in quartz or is estimated by another analytical method. The concentration of an unknown element in the sampled is then compared to the intensity of the same element in a standard in which the concentration off course is known. Given these information the unknown concentration may be quantified according to a wellknown eqution. Quantification of Ti in quartz, forexample, where Si is used as an internal standard is expressed in the following way

$$C_{Ti_{sample}} = [C_{Ti_{standard}} / (I_{Ti_{standard}} / I_{Si_{standard}})] * [I_{Ti_{sample}} / I_{Si_{sample}}] * [C_{Si_{sample}} / C_{Si_{standard}}]$$

Where C is concentration in ppm and I is intensity in counts/second.

3. METHODOLOGY FOLLOWED AT MONASH UNIVERSITY

During the analysis of quartz at Monash university, both raster (ca. 800 x 400 μm) and single spot analysis were performed on doubly polished quartz wafers with a nominal thickness of 250 μm. Single spot and raster analysis were conducted with a repetition rate of 4 HZ, a laser energy of 0.1 mJ and with a beam diameter of 80 μm. Analysis were conducted at both Low and Medium Resolution although mass-drift in MR and, consequently, in HR modes appeared to be so serious that analysis at MR and HR conditions were discontinued. Mass drift during MR and HR LA-analysis is a common problem encountered at many laboratories and, so far, no laboratories have reported successful LA-analysis at these mass spectrometer settings. However, the LA-HR-ICP-MS facility at NGU is currently testing a method that apparently solve the problems with LA-analysis at MR and HR settings (Flem et al., *in prep*). Si[29] was used as the internal standard and NIST612 was used for external standardisation.

During both raster and single spot analysis the mass spectrometer performed 50 scans over the included isotopes. During the first 10 scans the background levels of each isotope was measured with the laser switched off. At the tenth scan the laser was switched on and the signal-intensity of each isotope was determined during the remaining 40 scans. Al and Si were detected in analogue mode because the high concentration of these isotopes in sample and/or external standard would oversaturate the detector if counting mode was switched on. Li was detected in counting mode. The mass window was set to 22 %, sample time was 0.01 s and samples/peak was set to 15 (Table 1).

After acquisition, the raw data were transferred to a separate PC for data processing. Initial data processing was performed with the custom made software package known as *Schonbein* that currently is only used by Monash University. The primary application of *Schonbein* is to rapidly select the desired parts of the spectrum for each isotope (background as well as analyte signal) and to rinse the signal for spikes derived from fluid and solid inclusions, micro-fractures, or other erratic fluctuations. Manipulation of the data in *Schonbein* is done in graphic interfaces so that the results of spike removal and data selection can be verified simultaneously. Subsequent statistical data management and calculation of LOD's (Limit Of Detection), analyte concentrations are performed by macros in excel spreadsheets.

More information on the LA-HR-ICP-MS method applied to quartz analysis may be found in Larsen and Lahaye (1999).

4. RESULTS

The concentration of Li and Al were measured with good counting statistics in most samples but the absence of well-constrained standards prevents calculation of standard deviations hence uncertainties of the analysis. The concentration of Na can not be determined with the LA-HR-ICP-MS method because Na-contaminations from the atmosphere invalidates quantification of this element. However, the maximum concentration of structural bound Na can be calculated because Na^+, after Li^+, is the most important charge compensator for Al^{3+} in the atomic lattice structure composing quartz (e.g. Larsen et al. 1999). Accordingly the molecular maximum concentration of Na may be calculated from the equation (Dennen, 1966)

$$[Al] = [Li] + [Na] \quad (\text{ all concentrations in mol\%})$$

Concentrations in Table 1 presents a compilation of 3-6 single spot analysis and one raster analysis in each quartz sample.

The chemical analysis (Table 1) of granite pegmatite quartz show that quartz from Evje-Iveland on the average carry 18 ppm Li and 70 ppm Al with a total range in the Li concentration from <4.6 to 28 ppm and in the Al concentration from <19 to 164 ppm (Figure 2a, b). In most quartz. Al is entirely charge balanced by Li hence the concentration of structural bound Na is close to zero. Where present, the maximum Na concentration vary from 6 to 46 ppm (Table 1). Locality 94 and 95 in the northern part of the studied area comprises the best qualities, both with <19 ppm Al and 15 and 17.8 ppm Li, respectively (Figure 2a, b).

Only 4 pegmatite localities in Froland pegmatite field are included in the present analysis (more localities are included in final report coming later). When compared to the Evje-Iveland pegmatite field, they yield consistently lower concentrations of Li, Al, and Na. One locality (100) yield 12.4 ppm Li and <19 ppm Al whereas the remaining 3 localities (103, 108, 109) yields <4.6 ppm Li and <19 ppm Al (Figure 3 and 4). Maximum concentrations of Na are 1 ppm or less.

Table 1 Li, Al and Na concentrations in granite pegmatite quartz

Sample	Area	Locality	UTM-East	UTM-North	Li, ppm	Al, ppm	Na, ppm
97023	Evje-Iveland	81	434300	6475200	16	75	10
97026	Evje-Iveland	82	434475	6475500	17	36	0
97030	Evje-Iveland	83	434650	6476725	11	70	23
97032	Evje-Iveland	84	436150	6477500	28	164	46
97036	Evje-Iveland	85	435750	6478050	19	61	0
97041	Evje-Iveland	86	435675	6478700	21	75	0
97045	Evje-Iveland	87	435400	6481750	17	85	17
97052	Evje-Iveland	88	433350	6483750	19	58	0
97059	Evje-Iveland	90	435350	6485500	18	43	0
97066	Evje-Iveland	91	436575	6486150	19	86	6
97070	Evje-Iveland	92	437175	6488600	22	110	21
97084	Evje-Iveland	94	432950	6491350	18	19	0
97088	Evje-Iveland	95	436100	6494175	15	19	0
97093	Evje-Iveland	96	437900	6495750	22	97	9
97097	Evje-Iveland	97	437850	6497075	4.6	59	35
97101	Steinsvann	98	450650	6470600	4.6	74	48
97104	Begervann	99	461350	6479125	5.6	175	131
97109	Froland	100	466900	6487500	12	19	0
97120	Froland	103	467325	6494850	4.6	19	1
97130	Froland	108	469350	6495125	4.6	19	1
97130	Froland	108	469350	6495125	4.6	19	0
97132	Froland	109	469375	6495250	4.6	19	1

5. CONCLUDING REMARKS

Although Al, Li and Na probably are the most common structural impurities in quartz it is premature to forward any firm conclusions before more comprehensive analysis of quartz are completed. At least the concentration of Ti, Fe, K, Ca and B must be known before the general quality of granite pegmatite quartz from Evje-Iveland and Froland may be approached.

At this point it is implied that granite pegmatites in Froland comprises the best high purity quartz potential because all the pegmatites from this field produced very low values for the concentration of Al, Li and Na,- in fact lower than the limit of detection for all but one analysis (Table 1).

Also talking in favour of the Froland pegmatites is the general impression, from the 1997 fieldwork, that pegmatites in this area on the average are larger when compared to pegmatites in Evje-Iveland. Most of the pegmatites comprises dykes or sills and many of them, as for example locality 103 (Figure 5a-c), could be followed for more than 100 meters before disappearing under the overburden.

Therefore, if the results from the analysis presented here are confirmed at NGU and are supported by low concentrations of Ti, Fe, B, K and Ca, additional sampling and analysis of the largest pegmatites in Froland is recommended.

6. REFERENCES

Dennen W.H. 1966: Stoichiometric substitution in natural quartz. *Geochimica Cocmochimica Acta 30*, 1235-1241.

Larsen R.B., Mireille P. & Juve G. 1999: Composition of granite pegmatite quartz form South Norway: genetic and industrial implications. *Bulletin NGU.* in press

Larsen R.B. & Lahaye Y. 1999: Analytical strategies for LA-HR-ICP-MS analysis of quartz: results from collaboration between Monash University and NGU. *Report Geological Survey of Norway.* in review

7. FIGURE CAPTIONS

Figure 1 General geology of Southeast Norway and demarcation of pegmatite fields and sample localities including in present report. One square is 5x5 kilometres
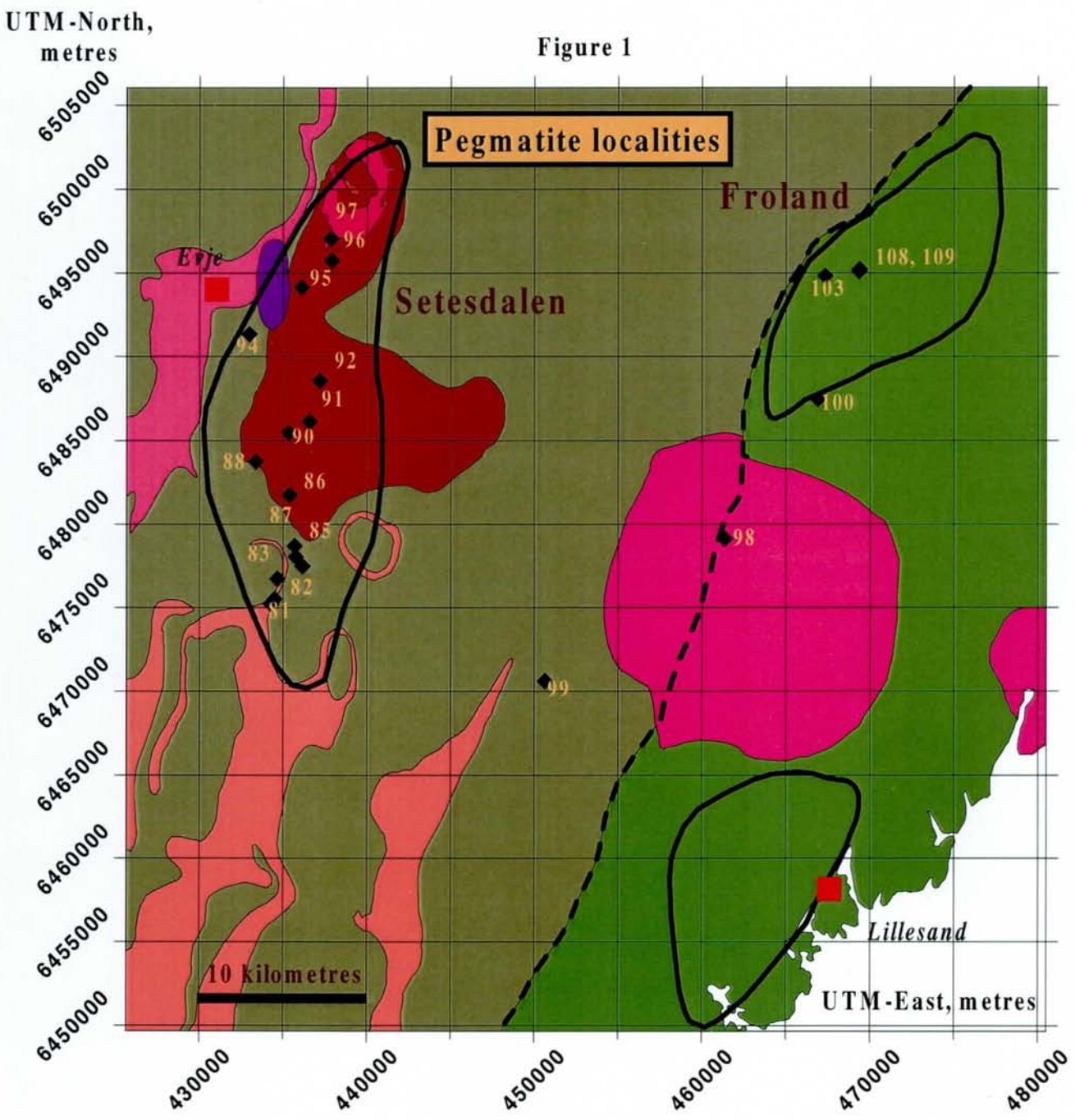
Figure 2a-c Distribution of Al, Li and Na in the Evje-Iveland pegmatite field. Size of triangles is proportional to the concentration of the featured element (see upper right in figures). Yellow crosses marks the exact location of pegmatites and yellow lettering state concentrations in ppm.

Figure 3 Regional comparison of the Al distribution in Evje-Iveland and Froland pegmatite fields, respectively. Same symbols and lettering as in Figure 2.

Figure 4 Regional comparison of the Li distribution in Evje-Iveland and Froland pegmatite fields, respectively. Same symbols and lettering as in Figure 2.

Figure 5a-c Example of one of the pegmatite dykes in Froland (locality 103) that yields low concentrations of Al, Li and Na. a) overview showing the walls and general strike of the vertical pegmatite dyke at locality 103 (Figure 1). Note the patchy greyish core-zone featuring in the upper part of the wall. Grey zones are composed of quartz. b) close up of quartz zone shown in (a). Quartz is grey whereas k-feldspar has a yellowish white appearance on the photo. c) another quartz rich core-zone appearing at the bottom of the wall shown in (a). Note rafts of white feldspar floating in matrix of dark grey quartz. Core zones shown on (b) and (c) are not connected but rather are dispersed as isolated enclaves in the central plane of the pegmatite dyke. Analysed sample is from core-zone displayed on (c).

UTM-North,
metres

Figure 1

6505000

6500000

6495000

Pegmatite localities

Froland

97

96

Evje

95

94

Setesdalen

103

108, 109

92

91

100

90

88

86

87

85

98

83

82

81

99

Lillesand

UTM-East, metres

6490000

6485000

6480000

6475000

6470000

6465000

6460000

6455000

6450000

10 Kilometres

430000 440000 450000 460000 470000 480000

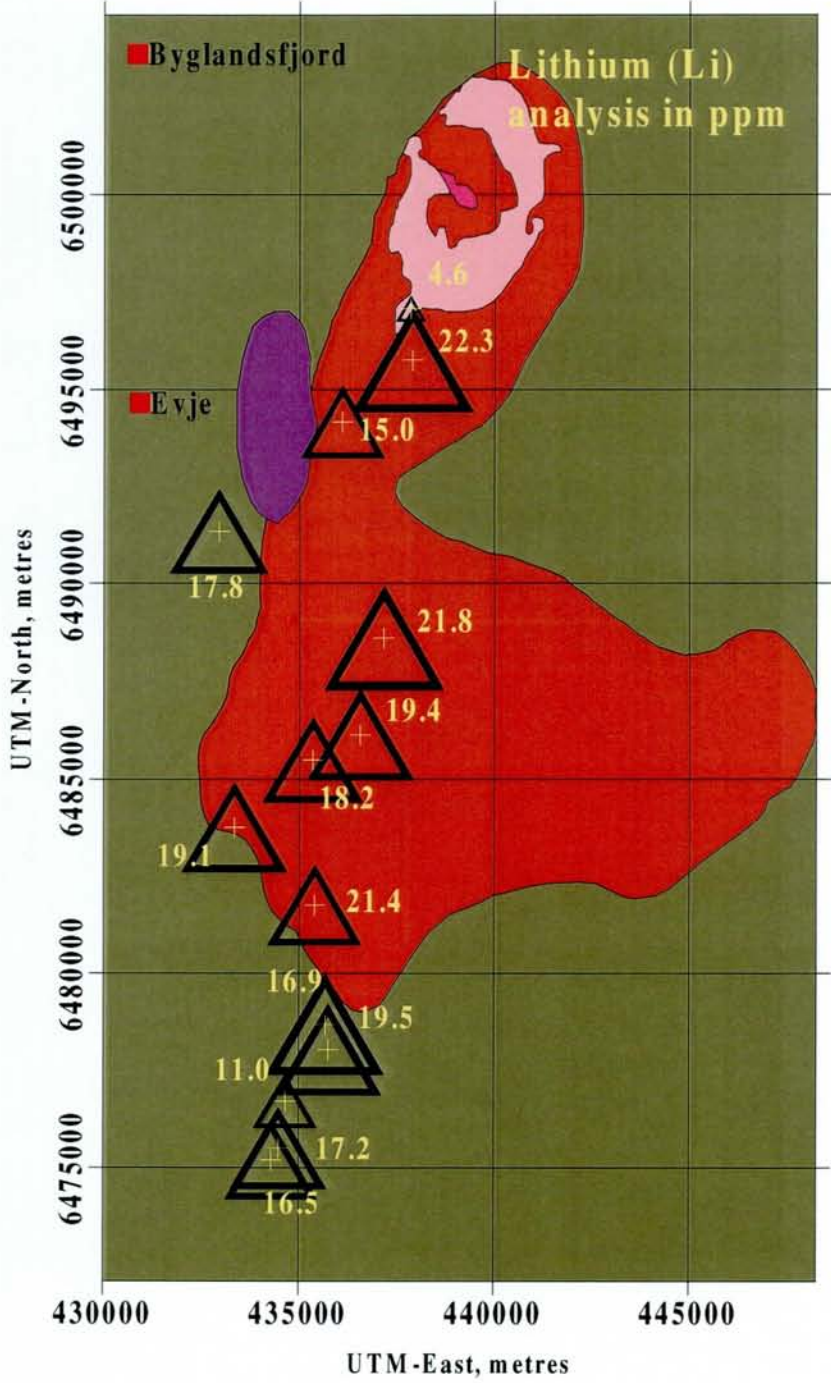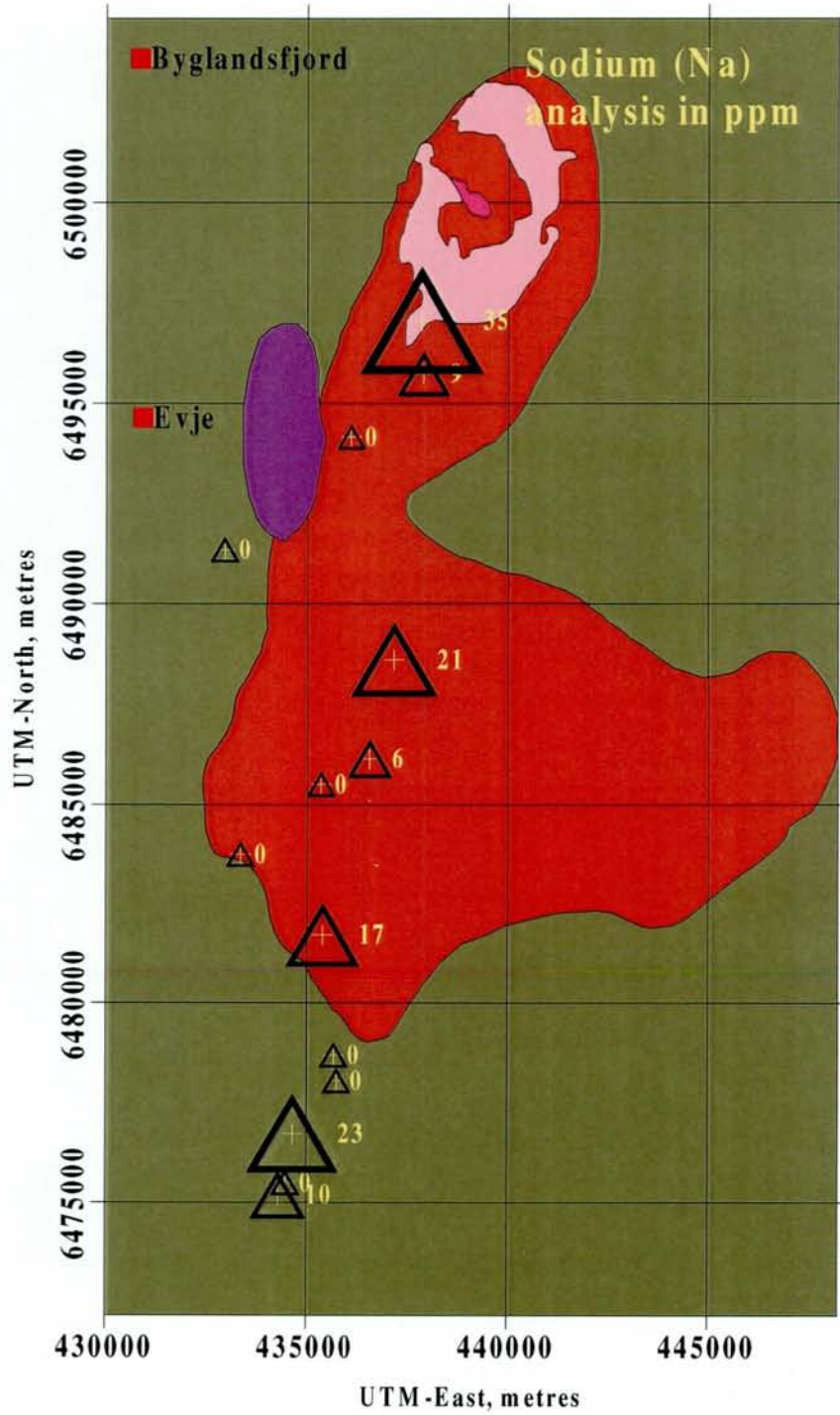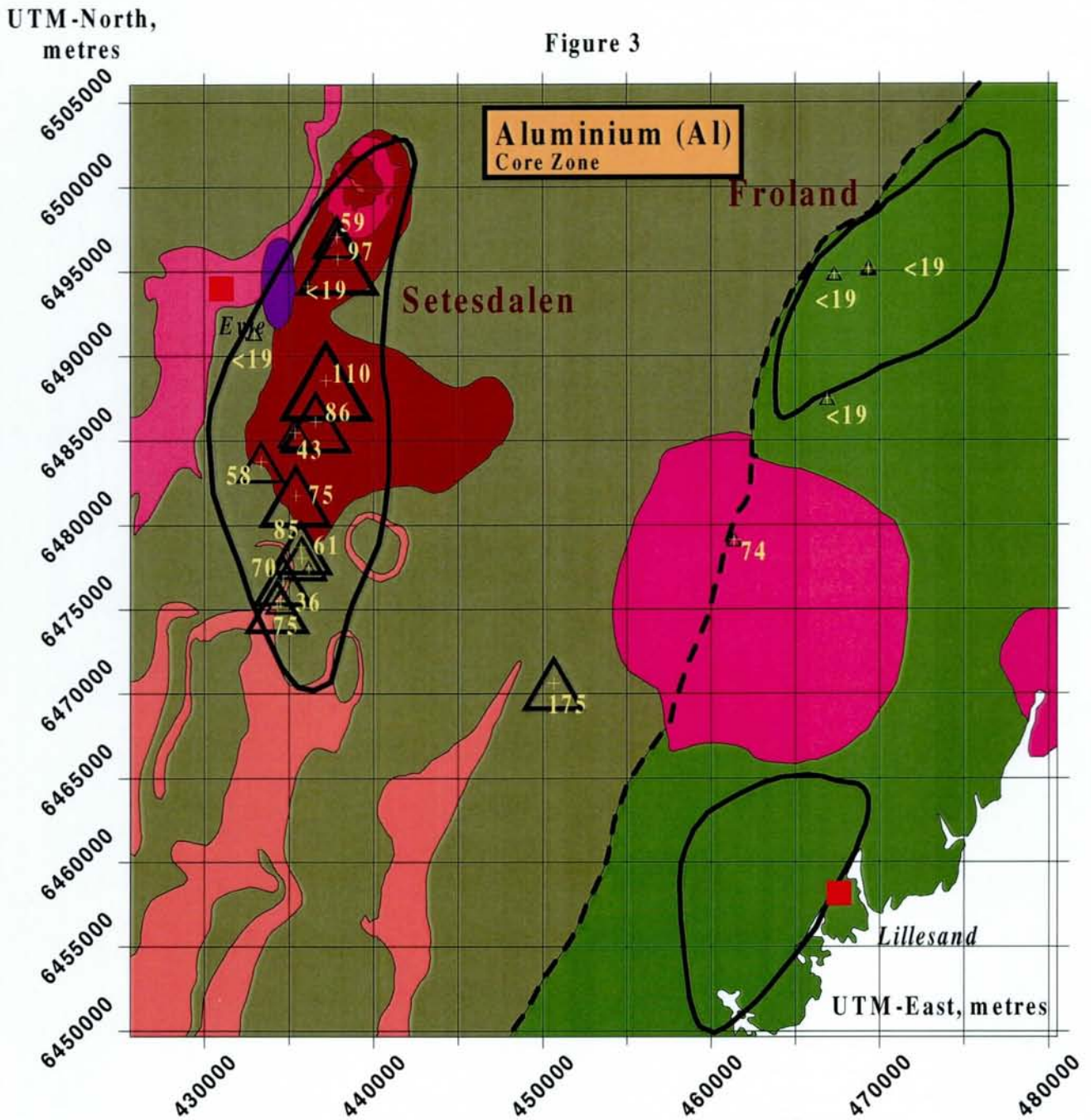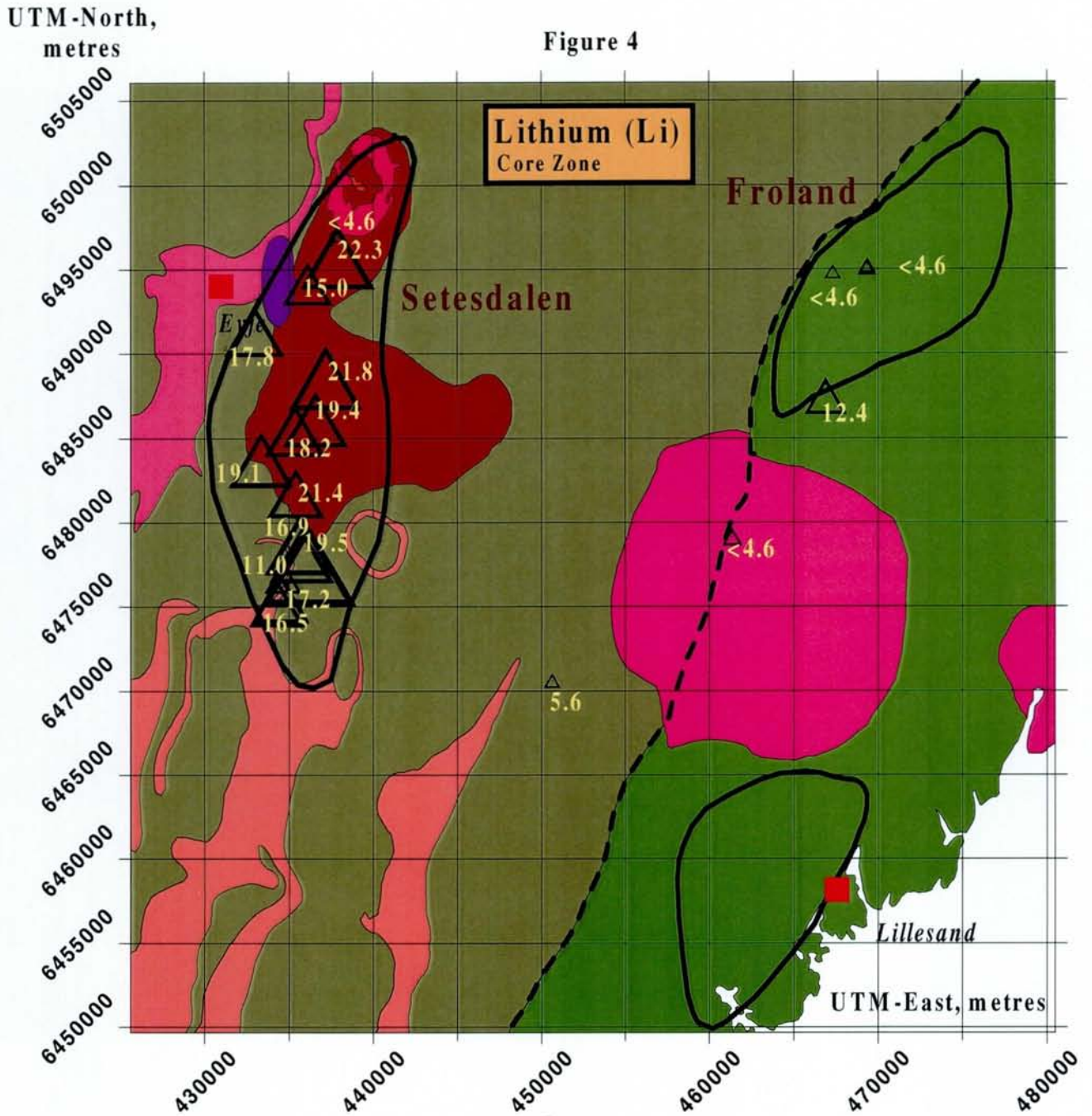|				
Monzonite		Diorite		Gjerstad suite Augen gneiss
Bio. granite		Coarse Granite Herefoss, Grimstad		Agder base-ment complex
Iveland-Gautestad Norite		Fennefos augen gneiss		Bamble base-ment complex

Figure 2a

Figure 2b

Figure 2c

Byglandsfjord

Evje

Sodium (Na) analysis in ppm

UTM-North, metres

UTM-East, metres

Figure 3

UTM-North, metres

Figure 4

Lithium (Li)
Core Zone

Froland

Setesdalen

Eye

<4.6
22.3
15.0
17.8
21.8
19.4
18.2
19.1
21.4
16.9 19.5
11.0
17.2
16.5

<4.6
<4.6
12.4

<4.6

5.6

Lillesand

UTM-East, metres

6505000
6500000
6495000
6490000
6485000
6480000
6475000
6470000
6465000
6460000
6455000
6450000

430000
440000
450000
460000
470000
480000

	Monzonite		Diorite		Gjerstad suite Augen gneiss
	Bio. granite		Coarse Granite Herefoss, Grimstad		Agder basement complex
	Iveland-Gautestad Norite		Fennefos augen gneiss		Bamble basement complex

Figure 5

(a)   (b)

(c)