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Chemistry of quartz from the Knaben locality

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REPORT

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Title:
Chemistry of quartz from the Knaben locality

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Summary:

Trace element concentrations of quartz in the fine- to medium-grained granitic/granodioritic gneiss from the Knaben locality were determined by laser ablation ICP-MS in order to determine the quartz raw material quality. Two quartz generations can be distinguished texturally and chemically within the provided sample: fine-grained quartz of the fine-grained gneiss host and quartz schlieren of the layered mineralised part of the sample. Both quartz types contain sub-microscopic inclusions of rutile needles which will make the quartz processing (separation) difficult. Concentrations are in the range of 80 ppm for Al, 58 for Ti, 15 for Li, 4 for P, 7 for K and 2 for Fe in the schlieren quartz and 19 ppm for Al, 43 for Ti, 4 for Li and 4 for P in the fine-grained quartz. Ti is very high in both quartz generations which indicate crystallisation temperatures >550ºC.

Keywords: fagrapport	LA-ICP-MS	Knaben
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1. Introduction

NGU was contacted by Andreas Sigersvold in September 2006 in order to determine the chemical quality of quartz from the Knaben locality. Andreas Sigersvold send a 1-kg sample to NGU from which two special polished thin sections (500 µm in thickness) were prepared for laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) analysis; one at NTNU and one at the NGU laboratory. 6 analyses were carried out on two different quartz types.

2. Sample description

The 1-kg sample comprises a fine-grained granitic/granodioritic gneiss consisting mainly of quartz, feldspar, biotite and minor garnet (Fig 1). Two textural varieties can be distinguished within the sample: first, a fine-grained gneiss with foliation and, second, a medium-grained layered gneiss containing quartz schlieren and the mineralisation.

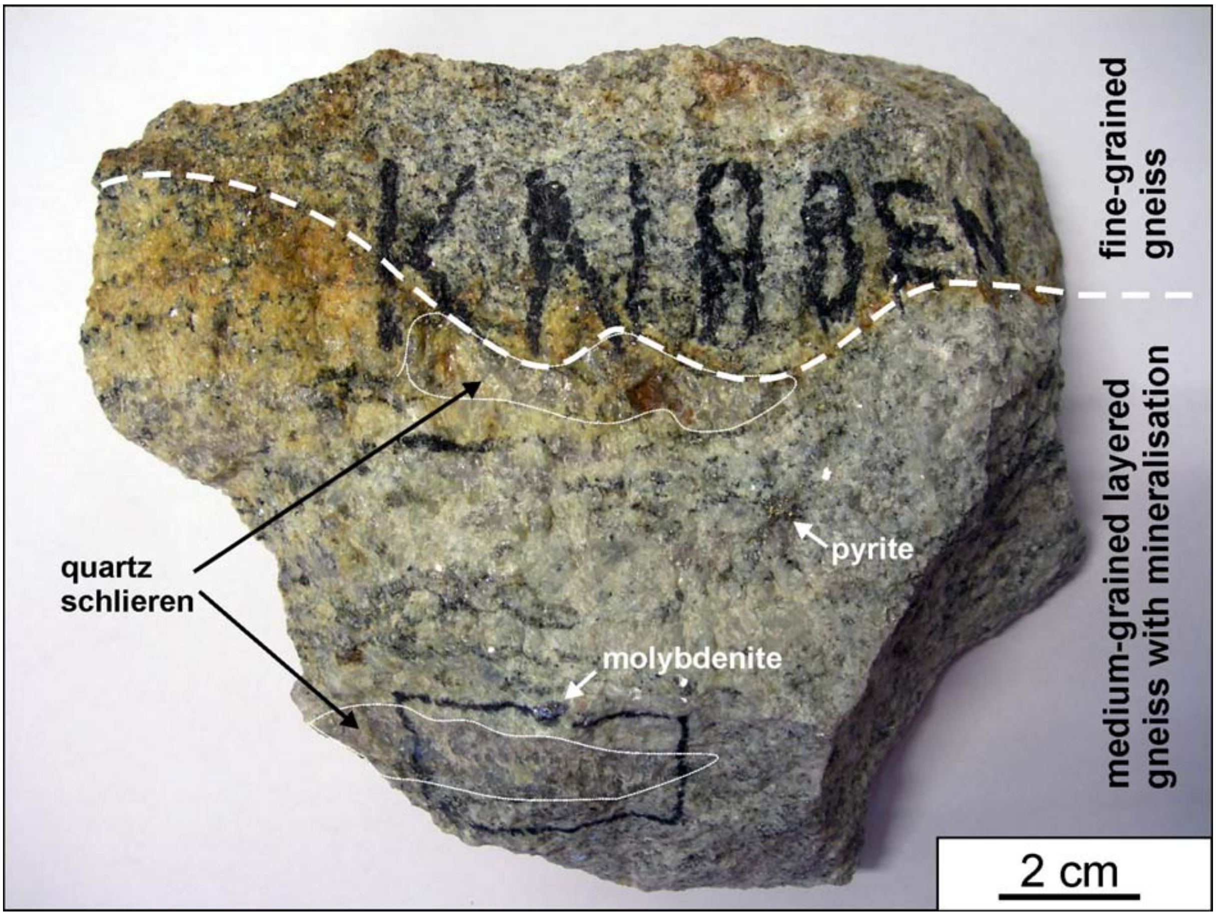

Fig. 1. Fine- to medium-grained granitic/granodioritic gneiss from the Knaben locality with molybdenite mineralisation.

The two prepared polished thin sections represent the two textural types, section "KNAB2" type 1 and section "KNABEN" type 2, in order to determine the trace element concentrations in fine-grained quartz of the gneiss and quartz schlieren of the layered mineralised gneiss. Both quartz types contain sub-microscopic rutile needles (Fig. 2). Such rutile needles can be hardly removed during quartz processing.

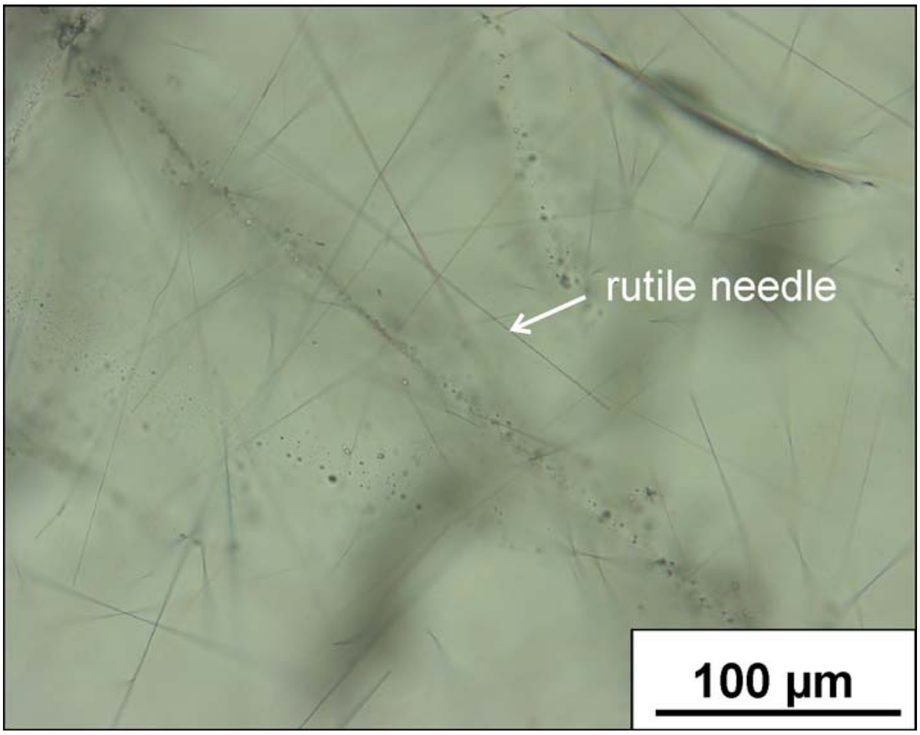

Fig. 2. Sub-microscopic inclusions of rutile needles in schlieren quartz.

3. Laser ablation inductively coupled mass spectrometry (LA-ICP-MS)

Laser ablation inductively coupled plasma mass spectrometry, LA-ICP-MS, was used for the *in situ* determination of Li, Be, B, Ge, Na, Al, P, K, Ca, Ti, Mn and Fe in quartz from the Knaben locality. The ICP-MS used in this study is a double focusing sector field instrument (model-ELEMENT-1, Finnigan MAT, Bremen, Germany). A Finnigan MAT, UV laser probe operating at 266 nm with a Gaussian beam profile was used for ablation. A repetition rate of 20 Hz, and pulse energy of 1.5-1.6 mJ with continuous ablation on an area of approximately 140 times 200 µm was used. The laser is not equipped with an aperture, but the laser beam was adjusted to give a spot size of approximately 20 µm. Helium was used as a carrier gas to enhance transport efficiency of ablated material. The helium carrier was mixed with argon as a make-up gas before entering the ICP-MS in order to maintain stable and optimum excitation conditions. With this laser there could be difficulties in controlling ablation diameter and ablation depth. The ablation parameters therefore had to be carefully selected. Ideally a shorter wavelength UV laser should be used e.g. an eximer laser or Nd:YAG laser operating at 193 nm and with an aperture for the precise control of spot size and with a flat beam profile yielding flat craters.

The existence of spectroscopic interferences required the use of variable mass resolutions. Li, Be, B, Ge, and Al were analysed at low mass resolution ($m/\Delta m \approx 300$), while Mn, K, Na, Ca, P, Ti and Fe required medium mass resolution ($m/\Delta m = 3500$) and K high mass resolution ($m/\Delta m > 8000$). The isotope ^{29}Si, was used as internal standard at low mass resolution, and ^{30}Si at medium and high mass resolution. In addition the argide $^{40}Ar^{40}Ar^+$ was measured in medium and high mass resolution between each analytical measurement and used as lock masses to compensate for time-dependant instrumental mass drift.

External calibration was done using four silicate glass reference materials produced by the National Institute of Standards and Technology (NIST SRM 610, NIST SRM 612, NIST SRM 614, NIST SRM 616). In addition, the standard reference material NIST 1830, soda-lime float glass (0.1 wt.% Al_2O_3) from NIST, the high purity silica BCS 313/1 reference sample from the Bureau of Analysed Samples, UK, the certified reference material "pure substance No. 1" silicon dioxide SiO_2 from the Federal Institute for Material Research and Testing, Berlin, Germany and the Qz-Tu synthetic pure quartz monocrystal provided by Andreas Kronz from the Geowissenschaftliches Zentrum Göttingen (GZG), Germany, were used. Certified, recommended and proposed values for the reference materials are taken from their respective certificates of analysis when available, and if not from Govindaraju (1994), Pearce et al.(1997), Horn et al. (1997), Gao et al.(2002) and Flem and Bedard (2002). Each measurement consists of 15 scans of each isotope, with a measurement time varying from 0.15 s per scan of K in high resolution to 0.024 s per scan of, e.g. Mn in low resolution. An Ar-blank was run before each standard and sample measurement. The background signal was subtracted from the instrumental response of the standard before normalisation against the internal standard. This was done to avoid memory effects between samples. A weighted linear regression model including several measurements of the different standard was used for calculation of the calibration curve for each element.

10 successive measurements on the Qz-Tu were used to estimate the limits of detections (LOD; Table 1). LOD are based on 3 times standard deviation (3σ) of the 10 measurements divided by the sensitivity S. Flem et al. (2002) gave a more detailed description of the measurement procedure.

4. Quartz chemistry

Chemical quality of quartz depends mainly on the structural bound trace elements in quartz lattice but also from the fluid and mineral inclusion inventory. Quartz is designated high purity when it contains less than 50 ppm of structural bound trace elements (B, Li, Al, Ge, Ti, Fe, Mn, Ca, K, Na, P; Harben 2002). However, the average abundance of trace elements in natural quartz is different for each element. Al is the most frequent trace element in quartz followed by Ti, Li, K, Na, H, P, Ge, and B. Therefore it is necessary to assign an upper concentration limit for each element. The upper concentration limits of impurities in high purity quartz are suggested here as follows: Al <25 ppm, Ti <10 ppm, Li <5 ppm, K <5 ppm, Na <5 ppm, P <5 ppm, Ge <2 ppm and B <2 ppm.

Concentrations of Li, Be, B, Ge, Na, Al, P, K, Ca, Ti, Mn and Fe in quartz has been determined by LA-ICP-MS. These are the most common trace elements in quartz which define the quartz quality. The concentrations for the two textural quartz types, fine-grained and schlieren quartz, are listed in Table 1.

The schlieren quartz and the fine-grained quartz have different trace element signatures, which define them as two different quartz generations. The schlieren quartz has higher Al (~80 ppm), Ti (~58 ppm), Li (~15 ppm), K and Fe than the fine-grained quartz which is 19 ppm for Al, 43 for Ti and 4 for Li. The schlieren quartz is presumably related to the mineralisation event. The concentration of Ti is very high in both quartz types and typical for quartz which was formed at temperatures >550ºC. Due to the general high trace element concentrations, in particular Ti, both quartz types of the Knaben locality have low economic quality (Fig. 3).

Table 1. Trace element concentrations in schlieren quartz (KNABEN a-c) and fine-grained gneiss quartz (KNAB2 A-C) in ppm (parts per million) determined by LA-ICP-MS. LOD – Limits of detection.

element	LOD	KNABEN-A	KNABEN-B	KNABEN-C	KNAB2-A	KNAB2-B	KNAB2-C
Li	0.8	15.2	14.1	15.9	3.6	4.6	5.2
Be	0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
B	1.3	2.8	1.8	1.7	2.6	1.9	1.5
Al	7	77.9	84.7	78.5	16.5	18.9	21.9
Mn	0.2	<0.2	0.3	<0.2	<0.2	<0.2	<0.2
Ge	0.1	0.78	0.93	0.85	0.63	0.57	0.67
Na	14	<14	<14	<14	<14	<14	<14
P	3	4.6	3.3	<3	4.1	4.2	4.5
K	1.5	7.9	3.2	8.7	<1.5	<1.5	<1.5
Ca	28	<28	<28	<28	<28	<28	<28
Ti	0.9	59.4	61.3	52.0	34.2	43.5	50.7
Mn	0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2
Fe	0.4	1.6	4.3	1.4	<0.4	<0.4	<0.4
sum (Li+B+Al+Ge+P+K+Ti+Fe)		170	174	159	62	74	84

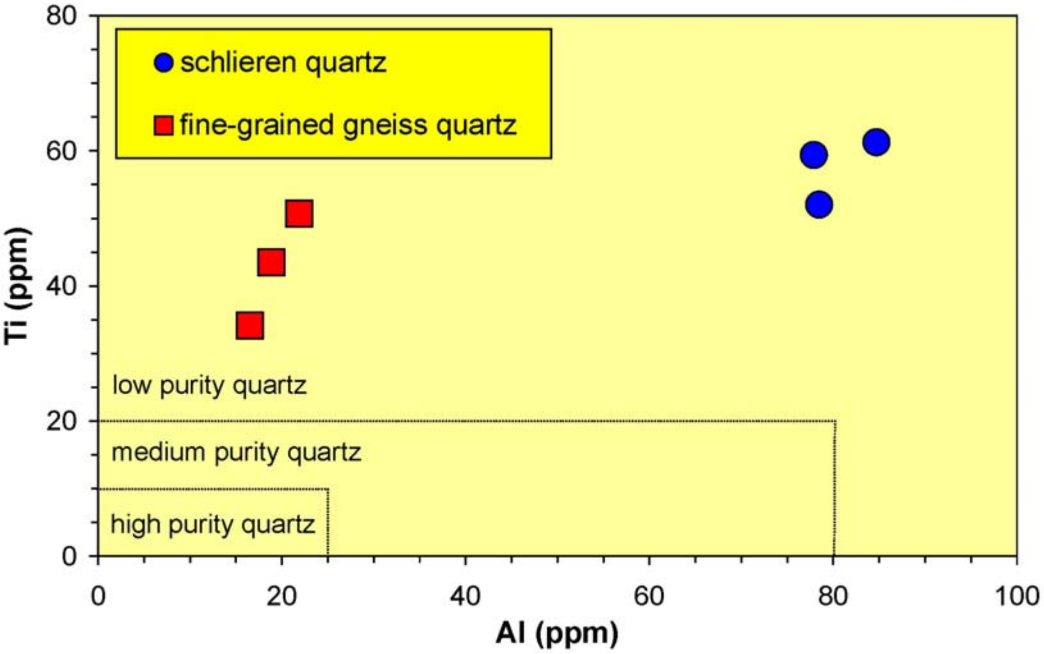

Fig. 3. Plot of Al versus Ti concentration in quartz from the Knaben locality. The high Al and the very high Ti concentration in the fine-grained gneiss quartz and schlieren quartz as well define the quartz as low quality raw material.

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