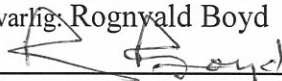


# GEOLOGI FOR SAMFUNNET

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Tittel: Assessment of quartz qualities IV				
Forfatter: Axel Müller		Oppdragsgiver: Koolgarra Mining Limited, Australia		
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Abstract:				
<p>The chemistry of quartz from three potential deposits in eastern Australia was determined by laser ablation inductively coupled mass spectrometry (LA-ICP-MS) by order of Philip Andre Delacretaz, who is consultant for Koolgarra Mining Limited, Australia. The quartz were characterised petrologically to identify non-quartz impurities. LA-ICP-MS was applied to determine the concentrations of the structurally incorporated trace elements Al, Ti, Li, P, B, Fe, K, Na, Ca, Ge, Mn, and Be in quartz. The structurally bound ions cannot be easily removed by processing and, thus, their concentration reflects the qualitative potential of the quartz raw material. Ten LA-ICP-MS analyses were carried out.</p>				
<p>The quartz from the three localities has high purity quality according the classifications by Harben (2002) and Müller et al. (2007). However, to achieve the high purity quality in the final product, fluid inclusions and non-quartz mineral inclusions and coatings have to be removed by advanced processing. The higher concentrations of Na, K, and Ca of the quartz product compared to the crystal chemistry are presumably caused by fluid inclusions and the high Al and Fe by impurity coatings at the grain surfaces, such as iron oxides. Very critical impurities are iron oxide/hydroxide micro inclusions (&lt;1 mm) in the Cont-1 quartz and the kaolinite coating of the WK-1 quartz pebbles.</p>				
<p>The investigated quartz is suitable for a wide range of high tech applications if a high quality can be achieved by advanced processing. B is critical for the use of the quartz for solar grade silicon: the B concentration is relatively high, and should be about 1 µgg<sup>-1</sup> or less. However, some B maybe originate from fluid inclusions and, thus, it can be lowered by processing. P is reasonably low for use of the quartz for production of solar-grade silicon.</p>				
Emneord:	quartz	LA-ICP-MS		
Australia	high purity quartz			

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## 1. Introduction

The Geological Survey of Norway (NGU) was contacted by the consultant Philip Andre Delacretaz by order of Koolgarra Mining Limited (Level 1 58 Lorimer St., Docklands, Victoria, 3008, Australia) in April 2008 in order to characterise the chemical quality of quartz from three potential deposits in eastern Australia.

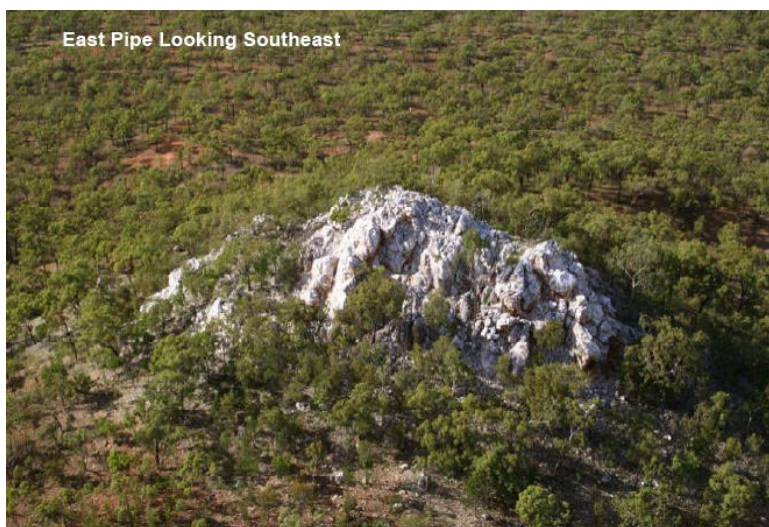
Five polished petrological thin sections were prepared from the quartz samples which were sent to NGU by Philip Andre Delacretaz. The thin sections were used for (1) microscopic characterisation of the quartz and (2) trace element analysis by laser ablation inductively coupled mass spectrometry (LA-ICP-MS). LA-ICP-MS was applied to determine the concentrations of structural incorporated trace elements (Al, Ti, Li, P, B, Fe, K, Na, Ca, Ge, Mn, Be) in quartz. The concentrations of these structurally bound elements controls the chemical quality of quartz and cannot be easily removed by processing. Quartz is designated high purity when it contains less than  $50 \mu\text{g g}^{-1}$  of structurally bound trace elements in quartz concentrates (Harben 2002). The upper concentration limits for the individual trace elements in high purity quartz are suggested as follows: Al  $<25 \mu\text{g g}^{-1}$ , Ti  $<10 \mu\text{g g}^{-1}$ , Li  $<5 \mu\text{g g}^{-1}$ , K  $<5 \mu\text{g g}^{-1}$ , Na  $<5 \mu\text{g g}^{-1}$ , P  $<5 \mu\text{g g}^{-1}$ , Fe  $<3 \mu\text{g g}^{-1}$ , Ge  $<2 \mu\text{g g}^{-1}$  and B  $<2 \mu\text{g g}^{-1}$  (Müller et al. 2007). Quartz of intermediate quality contains 50 to  $300 \mu\text{g g}^{-1}$  and low purity quartz more than  $300 \mu\text{g g}^{-1}$  structural impurities (Harben 2002). The investigations were carried out at NGU in Trondheim, Norway.

## 2. Sample origin and description

The quartz samples come from three different sites in eastern Australia. The geographic location of the localities was not provided and is not of importance for this study.

### 2.1 Locality Lighthouse

The Lighthouse locality comprises two hydrothermal quartz lenses (Figure 1). The quartz lenses have about  $\frac{1}{2}$  million cubic meters of estimated resource in each of them (Koolgarra Mining Limited, personal communication). About 1 kg of white, milky, coarse-grained quartz lumps, 3 to 6 cm in size, was provided (Figure 2). The macroscopic features of the sample are given in Table 1.



*Figure 1. Aerial photograph of the eastern quartz lens of the Lighthouse locality.*

**Figure 2.** Quartz lumps from the Lighthouse locality.



## 2.2 Locality Cont-1

The sample is from a 10 m wide and 300 m long hydrothermal vein deposit which was dug for gold but found to be barren (Koolgarra Mining Limited, personal communication). The 600-gram coarse-grained quartz sample (Cont-1) is milky with a local iron oxide coating giving the sample surface a rusty shade (Figure 3; Table 1).



**Figure 3.** Milky quartz sample Cont-1, 16 cm in length.

## 2.3 Locality WK-1

Quartz pebbles comes from a heap at Balmullock which was a part of the waste during 1850 gold mining operations (Koolgarra Mining Limited, personal communication; Figure 4). The pebbles are embedded in kaolin together with other rock pebbles and gold nuggets. Two milky grey, coarse-grained quartz pebbles, 4 and 8 cm in diameter, were sent (Figure 5). Remnants of kaolinite are found on the pebble surfaces.



**Figure 4.** Heaps at Balmullock left from gold mining operations during 1850.



**Figure 5.** Grey quartz pebbles from the Balmullock heaps (samples WK-1 and WK-2).

**Table 1.** Macroscopic features of quartz samples.

sample	colour	transparency	crystal size	macroscopic impurities
Lighthouse	snow white	milky, almost opaque	>5 cm	minor iron oxide coating at grain surfaces
Cont-1	snow white	milky, almost opaque	2 - >5 cm	minor iron oxide coating at grain surfaces, iron oxide inclusions (<1 mm) in quartz crystals
WK-1	grey	milky, almost opaque	1 - 4 cm	kaolin coating at pebble surface

### **3. Microscopic description of samples**

The five thin sections prepared from the quartz samples at NGU were examined with a petrological microscope. The 500- $\mu\text{m}$  thick polished quartz slabs are mounted on glass slides, 2.4 x 4.8 mm in size. The thin sections were scanned to visualise the transparency and crack systems (fluid inclusion trails) transecting the quartz crystals.

#### **3.1 Lighthouse quartz**

Quartz from the Lighthouse locality shows a very dense network of healed micro-cracks (Figures 6 and 7). The micro-cracks comprise different generations, each of which reflects an event of fluid passage related to regional deformation. Fluid inclusions, 2 to 20  $\mu\text{m}$  in size, are aligned along the healed micro-cracks giving them the dark appearance. The very high number of fluid inclusions causes the almost non-transparency of the quartz. A fluid-inclusion-free quartz crystal would appear clear in the thin section scan. The fluid inclusions are predominantly filled with NaCl-bearing (1-10 weight %) water and occasionally with a  $\text{CO}_2$ -bubble (Figure 7c).

#### **3.2 Cont-1 quartz**

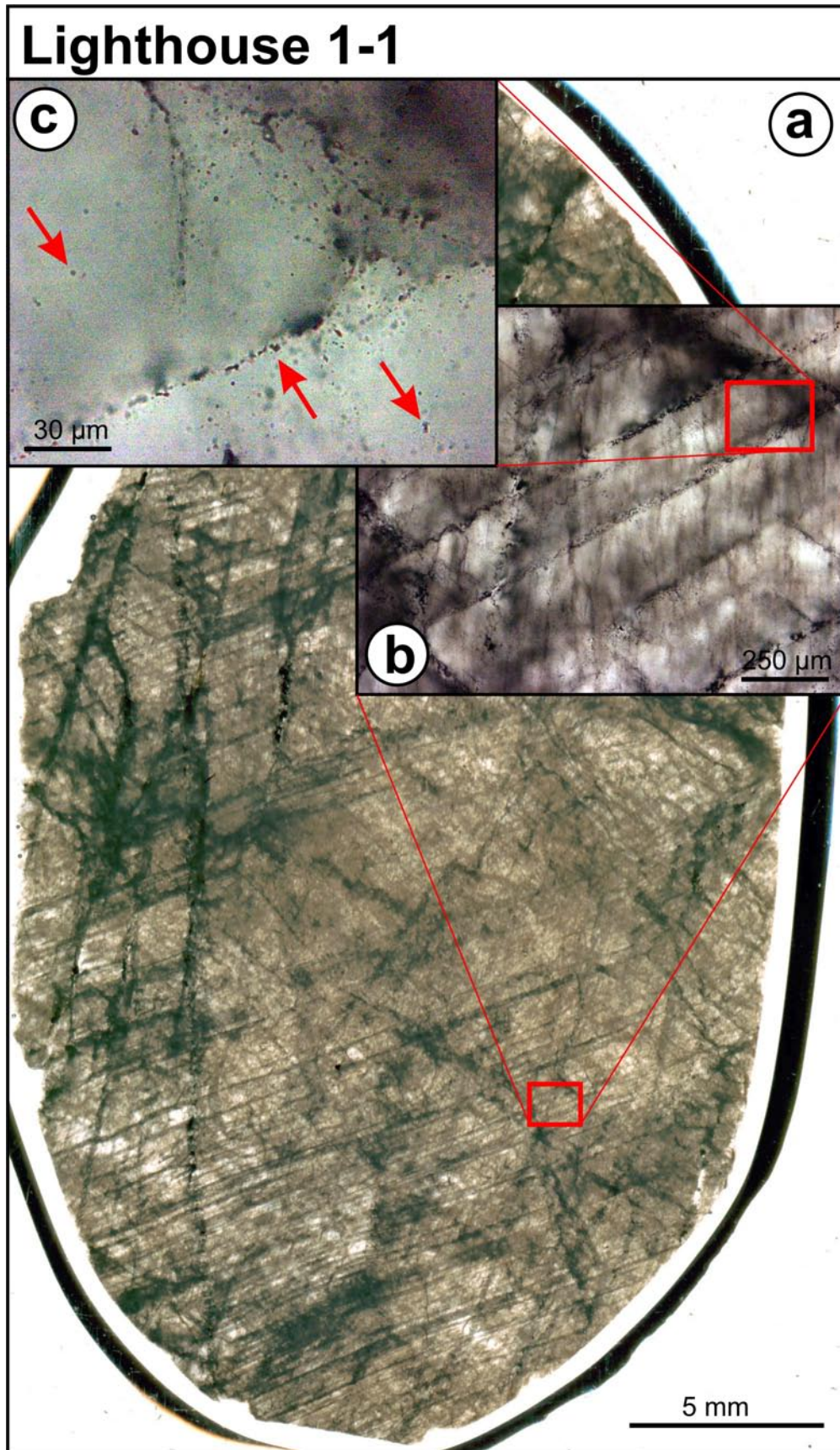
Also quartz from the Cont-1 locality shows a very dense network of healed micro-cracks (Figure 8). The healed cracks are more irregular compared to the Lighthouse quartz. The quartz contains very many large, irregular fluid inclusions, up to 100  $\mu\text{m}$  in size (Figure 8c). Micro cavities, up to 1 mm in size, are aligned along the youngest generation of healed cracks (Figure 8d). These micro cavities are commonly filled with a brown iron oxide/hydroxide mineral, probably goethite.

#### **3.3 WK-1 quartz**

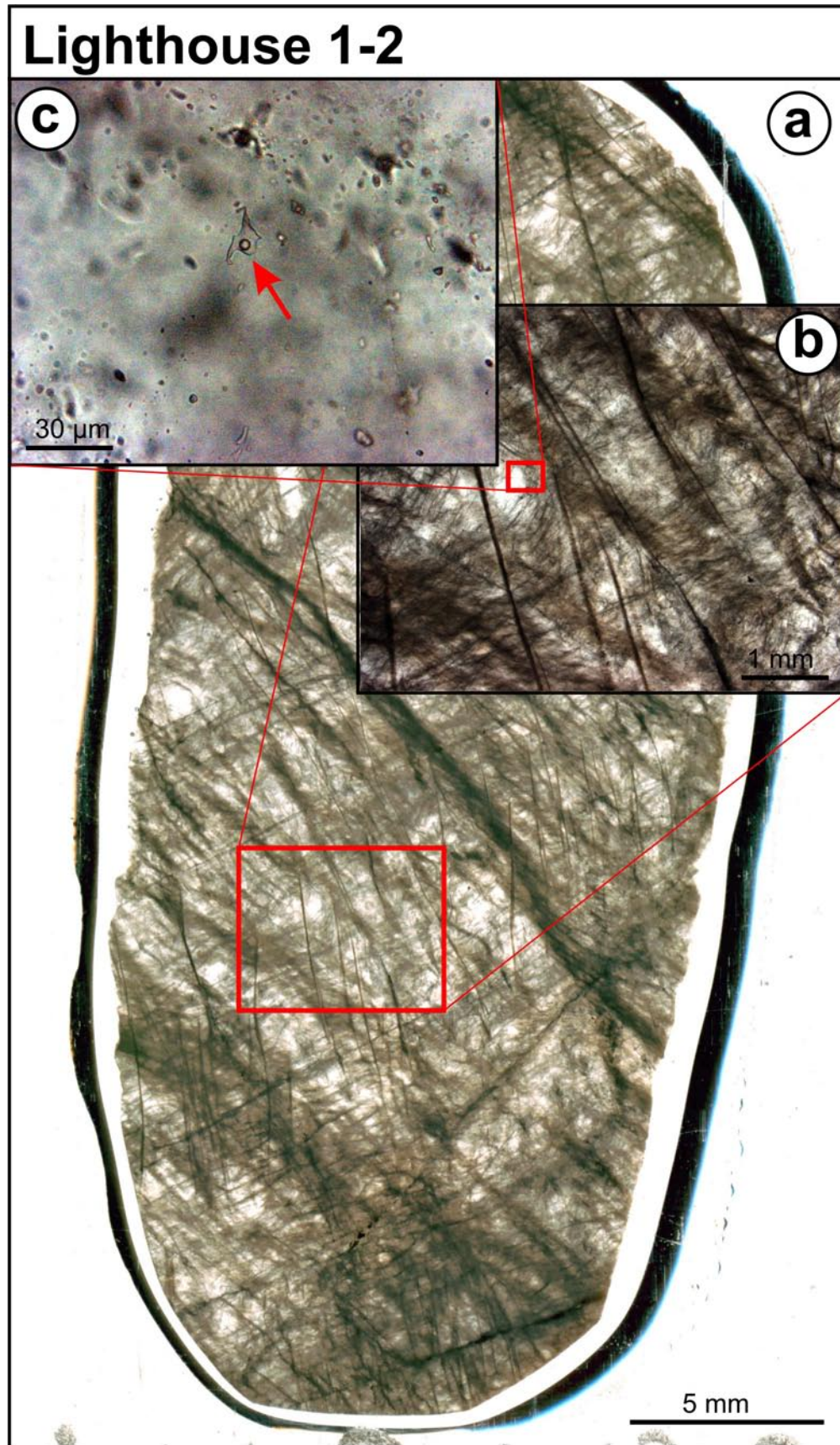
Quartz from the WK-1 locality also shows a very dense network of healed micro-cracks (Figures 9 and 10). The high number of fluid inclusions, 2 to 40  $\mu\text{m}$  in size, causes the almost non-transparency of the quartz. A number of fluid inclusions contain halite (NaCl) crystals indicating an oversaturation of NaCl. Thus, the NaCl content in the water of the fluid inclusions is >12-14 weight % (Figure 10c).

In summary, all the samples contain a very high number of fluid inclusions causing the almost non-transparency of the quartz. The fluid inclusions commonly contain NaCl and presumably traces of KCl. The fluids of these micro inclusions contaminated the LA-ICP-MS analyses, which is discussed below.

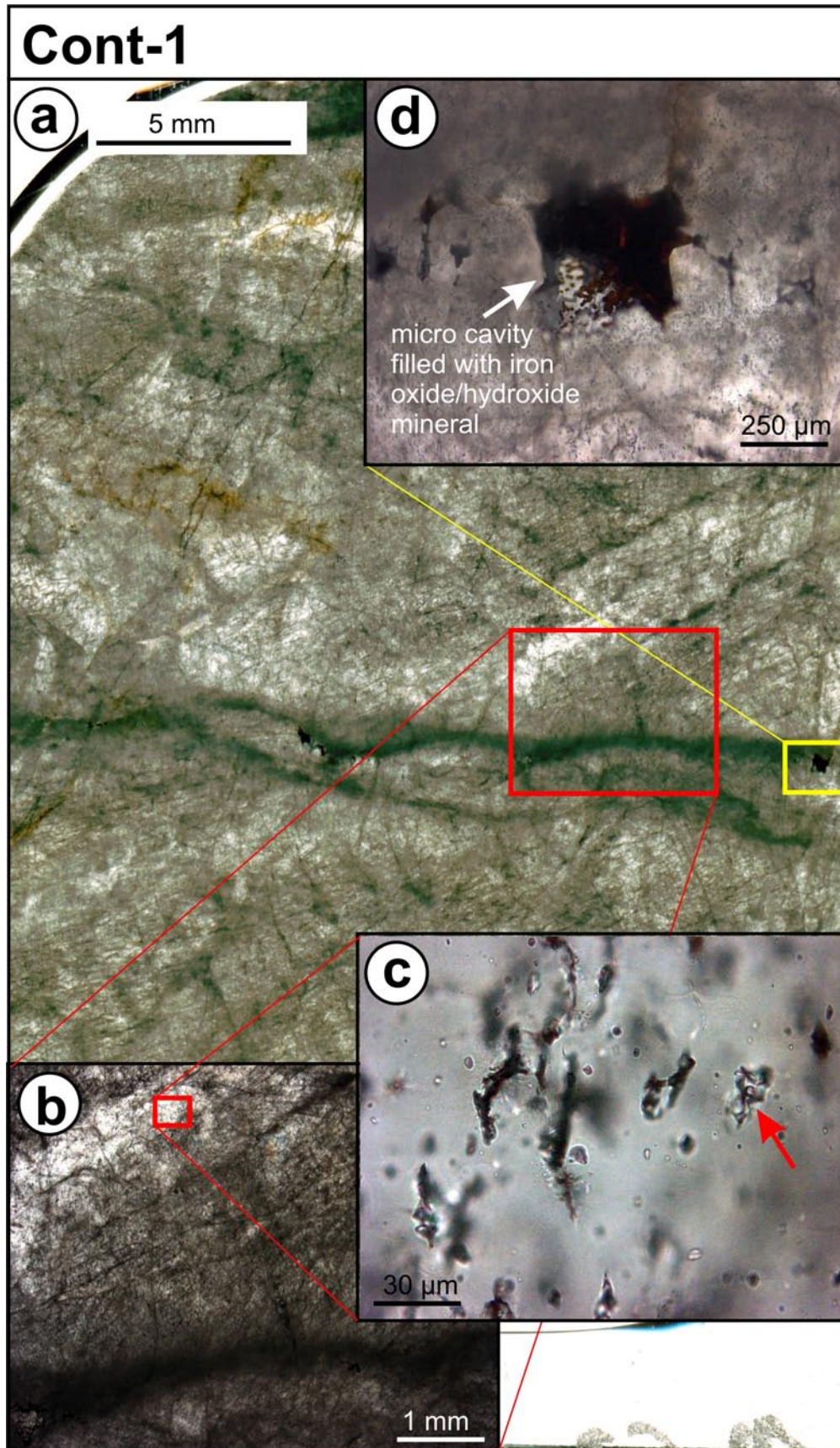




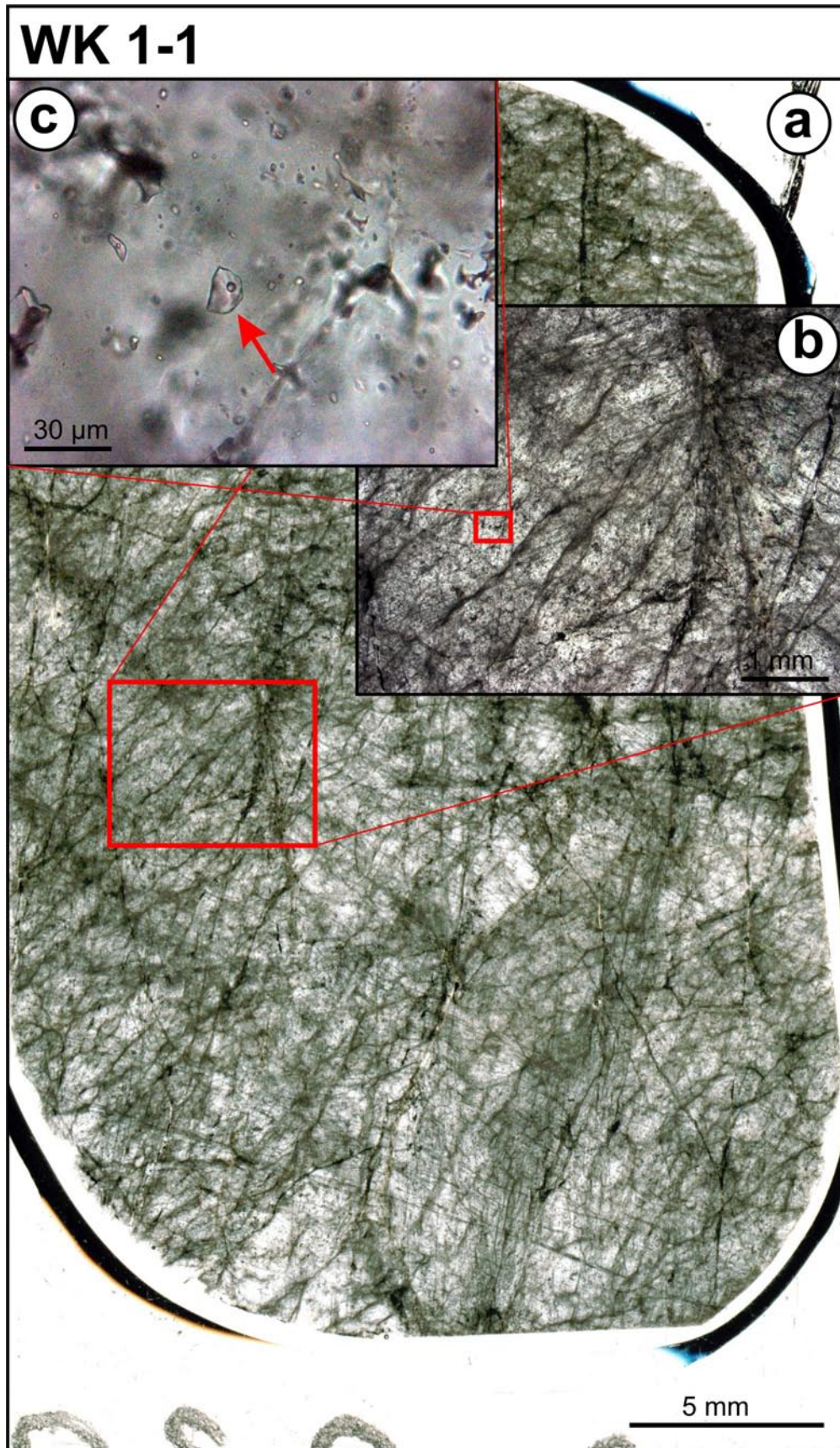
**Figure 6.** *a - Scan of the thin section, b – Zoom into the thin section, c - Fluid inclusions of the Lighthouse-1-1 sample are small (1-3 μm) and appear as black dots when applying 1000x resolution. Examples of fluid inclusions are indicated by red arrows.*



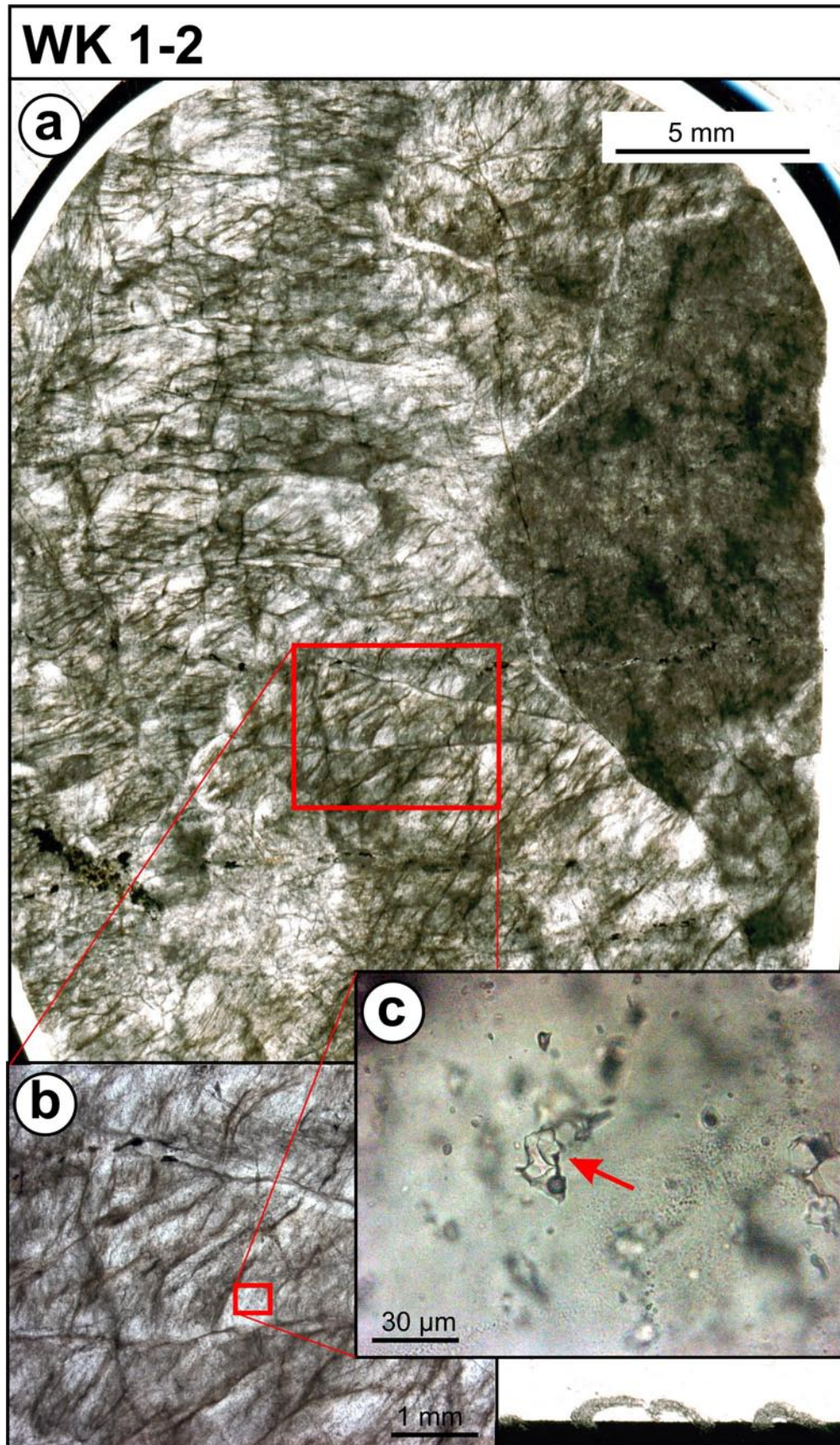
**Figure 7.** *a - Scan of the thin section, b – Zoom into the thin section, c - Fluid inclusions of the Lighthouse-1-2 sample are up to 20 μm in size (red arrow). The fluid inclusion contains NaCl-bearing water and a CO<sub>2</sub>-bubble.*



**Figure 8.** *a - Scan of the thin section, b – Zoom into the thin section, c – Large irregular fluid inclusions containing NaCl-bearing water and a CO<sub>2</sub>-bubble (red arrow). d – Micro cavity filled with a brown iron oxide/hydroxide mineral.*



**Figure 9.** *a - Scan of the thin section, b – Zoom into the thin section, c – Fluid inclusions containing NaCl-bearing water and a small CO<sub>2</sub>-bubble (red arrow).*



**Figure 10.** *a* - Scan of the thin section, *b* - Zoom into the thin section, *c* - Fluid inclusion containing NaCl-bearing water, a CO<sub>2</sub>-bubble, and a greenish halite (NaCl) crystal (red arrow).

#### 4. Laser ablation ICP mass spectrometry method

Laser ablation inductively coupled plasma mass spectrometry, LA-ICP-MS, was applied for the *in situ* determination of Al, Ti, Li, P, B, Fe, K, Na, Ca, Ge, Mn, and Be in the atomic structure of quartz. These elements are the most common structurally bound ions in the quartz crystal lattice. The ICP-MS used in this study is a double focusing sector field instrument (ELEMENT-1, Finnigan MAT) at NGU in Trondheim, Norway. The quartz materials to be analysed were ablated by an UV laser beam with a focused spot size of approximately 30  $\mu\text{m}$  at the sample surface. Samples were ablated over an area of 200 x 200  $\mu\text{m}$  using raster techniques. The ablation depth varies between 150 and 250  $\mu\text{m}$ . The approximate sampling volume (200 x 200 x 200  $\mu\text{m}$ ) involves the risk that micro inclusions of fluids and minerals occurring in this volume contaminate the analyses. The number of fluid inclusions in the analysed quartz samples is so high that a volume of 200 x 200 x 200  $\mu\text{m}$  without fluid inclusions could not be found. Therefore, the determined concentration of Na comprises the structurally bound Na and the Na of the fluid inclusions occurring in the sampling volume. Limits of detection ( $3\sigma$  of background) for the different elements are listed in Table 2. More information about the analytical procedure can be found in Flem et al. (2002). Each thin section was analysed two times at two different places.

#### 5. Quartz chemistry

##### 5.1 Lighthouse quartz

Quartz from the Lighthouse locality has low average Ti (2  $\mu\text{g g}^{-1}$ ) and Fe (<1  $\mu\text{g g}^{-1}$ ) and reasonably low average Al (22  $\mu\text{g g}^{-1}$ ) and Li (2  $\mu\text{g g}^{-1}$ ; Table 2). The concentrations of B, Li and K are moderately high, 2.5, 2 and 4  $\mu\text{g g}^{-1}$ , respectively. The high K may be caused by fluid inclusions which presumably contain traces of K. The very high content of Na is certainly caused by Na in fluid inclusions superimposed on the concentration of structurally incorporated Na. The latter is certainly <5  $\mu\text{g g}^{-1}$ . Concentrations of P are below the limit of detection, <5  $\mu\text{g g}^{-1}$ . Generally, the Lighthouse quartz has a high purity quality according the classifications by Harben (2002) and Müller et al. (2007). However, two of four quartz analysis have Al >25  $\mu\text{g g}^{-1}$ , which corresponds to medium quality (Müller et al. 2007).

##### 5.2 Cont-1 quartz

Quartz from the Cont-1 locality has very low average Al (13  $\mu\text{g g}^{-1}$ ), Ti (<1  $\mu\text{g g}^{-1}$ ), and Fe (1  $\mu\text{g g}^{-1}$ ; Table 2). The content of Li (2  $\mu\text{g g}^{-1}$ ) is moderately high and that of B and K is high, 4 and 4  $\mu\text{g g}^{-1}$ , respectively. The high K may be caused by fluid inclusions which presumably contain traces of K. Concentrations of P are below the limit of detection, <5  $\mu\text{g g}^{-1}$ . The slightly higher Fe content compared to the Lighthouse and WK-1 quartz confirms the macroscopic observation of iron oxide inclusions. The very high content of Na is caused by fluid inclusions which come in addition to the concentration of structurally incorporated Na. The Na content is even higher than in the other quartz samples due to the occurrence of halite (NaCl) crystals in fluid inclusions as well as the dissolved NaCl. The Cont-1 quartz has high purity quality according to the classifications by Harben (2002) and Müller et al. (2007).

##### 5.3 WK-1 quartz

Quartz from the WK-1 locality has very low average Al (10  $\mu\text{g g}^{-1}$ ), Ti (1  $\mu\text{g g}^{-1}$ ) and Fe (<1  $\mu\text{g g}^{-1}$ ; Table 2). The contents of Li (2  $\mu\text{g g}^{-1}$ ), B (2  $\mu\text{g g}^{-1}$ ), and K (3  $\mu\text{g g}^{-1}$ ) are moderately high. The concentration spike of P of 8  $\mu\text{g g}^{-1}$  (analysis WK-1-2-A) is maybe caused by an apatite ( $\text{Ca}_5(\text{PO}_4)_3(\text{OH},\text{F},\text{Cl})$ ) micro inclusion. The very high content of Na is caused by fluid inclusions which are added to the concentration of structurally incorporated Na. The WK-1

quartz has high purity quality according the classifications by Harben (2002) and Müller et al. (2007).

## 6. Discussion and outlook

The quartz of the three investigated localities has high purity quality according to the classifications by Harben (2002) and Müller et al. (2007). The determined trace element concentrations correspond to the contents of ions which are structurally bound in the quartz crystal lattice with the exception of Na. The high Na concentrations of all investigated samples are caused by NaCl-bearing fluid micro inclusions (2-50  $\mu\text{m}$ ) which superimpose additional Na onto the concentration of structurally incorporated Na. The structurally bound ions cannot be easily removed by processing and, thus, their concentration reflects the qualitative potential of the quartz raw material.

In Table 3 trace elements concentrations of seven high-purity quartz products produced by Unimin (USA), Norwegian Crystallites AS (Norway), and JD Quartz & Jewel Co (China) are listed for comparison. All quartz are processed to some degree to achieve high quality. Concentrations of the investigated Australian quartz fall within the range of these products. However, to achieve high-purity quality in the final product, most of the fluid inclusions and non-quartz mineral inclusions and coatings have to be removed by advanced processing including crushing, flotation, and magnetic and electrostatic separation (e.g., Haus 2005). Advice for quartz processing might be given by the Dorfner Analysezentrum und Anlagenplanungsgesellschaft mbH (Anzapla; [www.anzaplan.com](http://www.anzaplan.com)) in Germany (see also Haus 2005). In Table 4 X-ray fluorescence (XRF) analyses of the Lighthouse quartz product provided by Koolgarra Mining Limited are shown. The higher concentrations of Na, K, and Ca of the quartz product compared to the crystal chemistry are presumably caused by fluid inclusions and the high Al and Fe by impurity coatings at grain surfaces, such as iron oxides. The high number of fluid inclusions present in all samples significantly contaminates the quartz product. Most of the fluid inclusions can be removed by crushing and thermal treatment (e.g., Haus 2005). Very critical impurities are: iron oxide/hydroxide micro inclusions (<1 mm) in the Cont-1 quartz and the kaolinite coating of the WK-1 quartz pebbles.

The investigated quartz is suitable for a wide range of high tech applications if high quality can be achieved by processing. B is a limiting factor to the usage of the Australian quartz for solar grade silicon due to the relatively high concentration of B, which should be about  $1 \mu\text{g g}^{-1}$  or less. However, some B maybe originate from fluid inclusions and, thus, it can be lowered by processing. P is at a reasonable level for use of the quartz for the production of solar-grade silicon (Table 4).

**Table 2.** Trace element concentrations (in  $\mu\text{g g}^{-1}$ ) of the Australian quartz samples and their classification of quartz quality according the concentration limits of structurally bound trace elements in quartz by Harben (2002) and Müller et al. (2007). Concentrations marked in intense orange are responsible for the “medium” quality. Concentrations of Na are set in brackets because the concentrations are superimposed on Na from fluid inclusions.

	Al	Ti	Li	P	B	Fe	K	Na	Ca	Ge	Mn	Be	Chemical quality of quartz*
<b>Limit of detection</b>	<b>6.9</b>	<b>1</b>	<b>0.5</b>	<b>5</b>	<b>0.4</b>	<b>1.1</b>	<b>2.8</b>	<b>5</b>	<b>16</b>	<b>0.25</b>	<b>0.18</b>	<b>0.07</b>	
Lighthouse-1-A	22.1	1.03	1.4	<5	2.6	<1.1	5.9	<5	<16	0.46	<0.18	<0.07	Medium
Lighthouse-1-B	14.1	1.89	1.2	<5	2.8	<1.1	5.8	(22.7)	<16	0.63	0.24	<0.07	Medium
Lighthouse-2-A	28.7	2.34	3.0	<5	2.6	<1.1	<2.8	(9.3)	<16	0.50	<0.18	<0.07	Medium
Lighthouse-2-B	26.0	2.28	2.6	<5	2.0	<1.1	<2.8	<5	<16	0.52	<0.18	<0.07	Medium
<b>Average Lighthouse</b>	<b>22.7</b>	<b>1.9</b>	<b>2.0</b>	<b>&lt;5</b>	<b>2.5</b>	<b>&lt;1.1</b>	<b>4.3</b>	<b>(10.5)</b>	<b>&lt;16</b>	<b>0.5</b>	<b>0.2</b>	<b>&lt;0.07</b>	<b>High</b>
Cont-1-A	14.4	<1	2.4	<5	4.9	1.1	4.9	(35.1)	<16	1.27	<0.18	<0.07	High
Cont-1-B	11.5	<1	1.9	<5	3.5	1.7	3.4	(99.1)	<16	1.16	<0.18	<0.07	High
<b>Average Cont-1</b>	<b>12.9</b>	<b>&lt;1</b>	<b>2.2</b>	<b>&lt;5</b>	<b>4.2</b>	<b>1.4</b>	<b>4.2</b>	<b>(67.1)</b>	<b>&lt;16</b>	<b>1.2</b>	<b>&lt;0.18</b>	<b>&lt;0.07</b>	<b>High</b>
WK-1-1-A	<6.9	<1	3.7	<5	1.9	<1.1	2.9	(30.6)	<16	0.99	<0.18	<0.07	High
WK-1-1-B	15.5	1.47	1.5	<5	1.8	<1.1	<2.8	(12.4)	<16	1.02	<0.18	<0.07	High
WK-1-2-A	<6.9	<1	4.2	8.0	2.1	<1.1	<2.8	(7.1)	<16	0.81	<0.18	<0.07	Medium
WK-1-2-B	12.0	<1	2.2	<5	3.4	<1.1	2.8	(28.0)	<16	0.94	<0.18	<0.07	High
<b>Average WK-1</b>	<b>10.3</b>	<b>1.1</b>	<b>2.9</b>	<b>(5.8)</b>	<b>2.3</b>	<b>&lt;1.1</b>	<b>2.9</b>	<b>(19.5)</b>	<b>&lt;16</b>	<b>0.9</b>	<b>&lt;0.18</b>	<b>&lt;0.07</b>	<b>High</b>



**Table 3.** Examples of trace element concentrations (in  $\mu\text{g g}^{-1}$ ) of processed and refined high purity quartz products available on the world market. n.p. – not provided.

	Al	Ti	Li	P	B	Fe	K	Na	Ca	Ge	Mn	Be
lota STD <sup>a</sup>	16.2	1.3	0.9	0.1	0.08	0.2	0.6	0.9	0.5	n.p.	<0.05	n.p.
lota 8 <sup>a</sup>	7.0	1.2	<0.02	0.05	<0.04	<0.03	<0.04	0.03	0.5	n.p.	<0.02	n.p.
NC1CG <sup>b</sup>	25	3	4	n.p.	n.p.	0.8	1.6	3.8	0.7	n.p.	0.01	n.p.
NC2A <sup>b</sup>	8	7	0.8	n.p.	n.p.	0.2	0.3	1.0	0.2	n.p.	<0.01	n.p.
NC3X	9.4	0.6	0.8	n.p.	n.p.	0.2	0.3	0.03	1.0	n.p.	<0.01	n.p.
B1 <sup>c</sup>	15	2	1.2	n.p.	0.2	2	5	0	2	n.p.	0	n.p.
B2 <sup>c</sup>	15	5	1.2	n.p.	0.5	2	5	0	2	n.p.	0	n.p.

<sup>a</sup> data from Moore (2005)

<sup>b</sup> data from Norwegian Crystallites AS (2008)

<sup>c</sup> data from JD Quartz & Jewel Co. (2008)

**Table 4.** X-ray fluorescence (XRF) analysis of the Lighthouse quartz product provided by Koolgarra Mining Limited. Concentrations (in  $\mu\text{g g}^{-1}$ ) were recalculated from oxide concentrations to element concentrations

	Al	Ti	P	Fe	K	Na	Ca
West Pipe	36.5	1.9	0.7	5.6	6.0	21.2	6.6
East Pipe	38.6	3.7	1.0	3.5	4.6	10.5	8.0

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Norges geologiske undersøkelse  
Postboks 6315, Sluppen  
7491 Trondheim, Norge

Besøksadresse  
Leiv Eirikssons vei 39, 7040 Trondheim

Telefon 73 90 40 00  
Telefax 73 92 16 20  
E-post [ngu@ngu.no](mailto:ngu@ngu.no)  
Nettside [www.ngu.no](http://www.ngu.no)

*Geological Survey of Norway  
PO Box 6315, Sluppen  
7491 Trondheim, Norway*

*Visitor address  
Leiv Eirikssons vei 39, 7040 Trondheim*

*Tel (+ 47) 73 90 40 00  
Fax (+ 47) 73 92 16 20  
E-mail [ngu@ngu.no](mailto:ngu@ngu.no)  
Web [www.ngu.no/en-gb/](http://www.ngu.no/en-gb/)*