

## Stress conditions in quartzite and their quantification by Raman spectroscopy

Klaus-Juergen Huenger <sup>(1)</sup>, Matti Danneberg <sup>(2)</sup>, Steven Herold <sup>(3)</sup>, Joerg Acker <sup>(4)</sup>

(1) Brandenburg University of Technology Cottbus-Senftenberg, Cottbus, Germany, email: [huenger@b-tu.de](mailto:huenger@b-tu.de)

(2) Brandenburg University of Technology Cottbus-Senftenberg, Cottbus, Germany, email: [matti.danneberg@b-tu.de](mailto:matti.danneberg@b-tu.de)

(3) Brandenburg University of Technology Cottbus-Senftenberg, Senftenberg, Germany, email: [herolste@b-tu.de](mailto:herolste@b-tu.de)

(4) Brandenburg University of Technology Cottbus-Senftenberg, Senftenberg, Germany, email: [joerg.acker@b-tu.de](mailto:joerg.acker@b-tu.de)

### Abstract

*The silica solubility of aggregates is one of the most important components of the alkali-silica reaction. It is a surface-controlled process that always still requires more detailed studies to better understand the reaction mechanism.*

*Since strained quartz releases more SiO<sub>2</sub> into the pore solution, the properties of grains, crystals and their structure can should be directly quantified.*

*In other work, various possibilities were tested for this purpose in order to obtain analyses of the surface and to correlate these with the mortar bar tests, for example. However, a quantifiable direct measurement of quartz crystal states with satisfactory results has not yet been performed.*

*In this thesis polarization and reflected light microscopy in combination with Raman and confocal microscopy is used to obtain quantifiable data by direct measurement of the strained crystals.*

*First measurements show new surprising signals besides the Raman main peak of the quartz. Such signals cannot be found on the whole sample, but only at places where strains are expected, e.g. at contact zones between different quartz crystals or cracks and sometimes inside of quartz grains too. Thus, a method may have been found to quantify the strained state of different quartz crystals in natural quartzite rocks.*

**Keywords:** ASR; quartzite; Raman microscopy; surface analysis

## 1. INTRODUCTION

The global problems of a deleterious ASR are well known, but extensive research is still needed today to fully understand the reaction mechanisms behind a deleterious ASR.

The dissolution of silica from natural aggregates is one of the most important components of this reaction [1], which leads to a swelling alkali-silica gel in the presence of water. However, this surface-controlled process can only be better understood by taking a deeper look at the surface itself. Various minerals can be found in natural aggregates, but most important for the ASR are those with a high content of soluble SiO<sub>2</sub>. Quartzite, a metamorphic rock, is one of these materials with high SiO<sub>2</sub> content. The surface of a quartzite grain, which is used as a model substance in this work, consists of about 98% SiO<sub>2</sub>. It is known that unstressed, well crystallized quartz dissolves very slowly far from the solubility equilibrium [2]. With increasing stress, the dissolution rate increases until the state of amorphous silica can be reached. There are many transitions between well crystallized and highly stressed states. For this reason, there is a need for methods to quantify the strained regions of quartz in natural aggregates.

Attempts have been made to solve this problem using various techniques. With polarization light microscopy it is possible to visualize the strained areas of the quartz using thin section images and to estimate e.g. the distribution and intensity of the undulose extinction. However, a quantitative evaluation is not possible. Freyburg et.al [in 6] tried to differentiate the range of strained states into five categories. This subjective estimate can only be compared with other methods, e.g. with the expansion values of the mortar bar test [3-4]. However, this does not always provide satisfactory results. Attempts have also

been made to correlate the undulose extinction and other crystal properties with the amount of dissolved silica [5], but again this is only a subjective estimate and not an exact measurement. A direct correlation between polarization light microscopy and other methods therefore obviously does not exist.

Instead, a combination of XRD and polarization light microscopy was used to obtain information about the crystallinity of quartz-containing aggregates [6]. For these experiments the samples had to be ground, which leads to further deformations. In addition, reactive surfaces are released, so that dissolution experiments could not be performed with an undamaged sample. Another problem is that XRD can only measure average values of the crystallinity index, but no single quartz crystal can be analyzed. There is no explanation which part of the total sample is reactive and leads to a high solubility. Furthermore, there are arguments against a direct correlation of the crystallinity and the ASR potential, as there is no general definition of crystallinity or the often used crystallinity index [7-8].

Instead of using powder, it would be much preferable to get information directly from the surface of an intact crystal or natural rock. A very surface sensitive method for this is electron backscatter diffraction (EBSD). Similar to normal X-ray diffraction (XRD), this method allows to be studied the crystal structure directly. In the case of EBSD, however, the penetration depth is only a few nanometers, which makes it possible to compare the results directly with the alkaline solubility of the crystals.

Differences in solubility between well crystallized quartz and quartzite grains in a strongly alkaline solution (0.1 M KOH, 80 °C, grain sizes 4-8 mm) can be clearly measured, as shown in Figure 1.1.

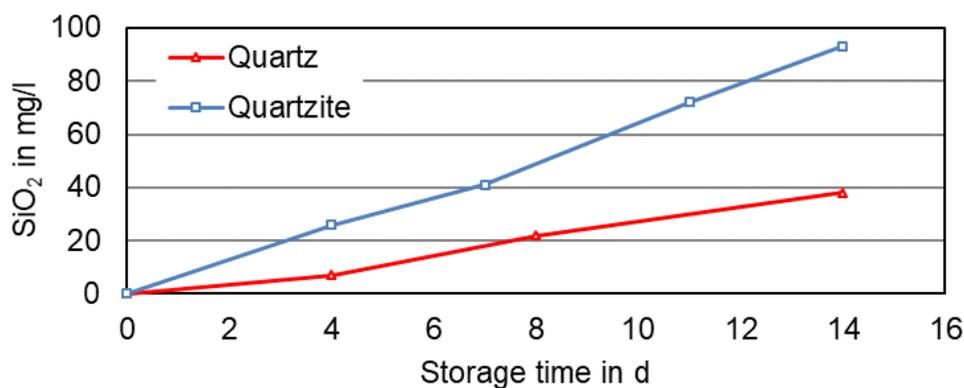


Figure 1.1: SiO<sub>2</sub> solubilities of quartz (red) and quartzite (blue)

The increase in the solubility of quartzite can only be explained by special areas in the grains that show a higher dissolution behavior. Compared to a well crystallized quartz, such areas can be strained zones, which are created by the formation process of this metamorphic rock. A targeted measurement of such conditions by mapping strained areas of natural rocks would generate measurement values that could then be quantitatively correlated with the solubility behavior of quartzite.

As shown by Rößler et al. [9] with EBSD it is possible to obtain a mapping of the rock sample used and to analyze the crystal structure and grain boundaries. This information was compared with mortar bar tests, but also with direct dissolution tests. Depending on the existing grain boundaries, a different dissolution behavior was found which could be directly related to the expansion behavior of the mortar tests. It was therefore clearly shown that the solubility is strongly dependent on the existing structures. However, the EBSD technique requires very well prepared specimens which need a high degree of further preparation especially to the preparation of surface grinding. Furthermore, no information on the chemical composition of the sample can be obtained by EBSD.

Possibly also the Raman microscopy can be a new tool to study crystal surfaces and to measure existing deformations, which can be coupled with measurements of the chemical composition. Changes in the strain states of silica manifest themselves by a shift in the Raman signals of quartz [10] depending on whether the stresses are tensile or compressive. Various experiments were carried out to analyze strain states in quartz samples. High pressure experiments show that a deformation in the quartz matrix can lead to a shift of the main signal, but these experiments can only be performed by using small samples specially prepared for the experiments for example in a diamond anvil cell [11-13]. There is also the problem that if a compressed sample is also heated, not only strain effects occur, but also the formation of different SiO<sub>2</sub> polymorphs, e.g. the conversion of  $\alpha$ -quartz to coesite [14]. A further problem in earlier work is the use of point measurements, with which no evaluation of the strain distribution can be made. Reinosa et

al. [15] have shown that a Raman analysis can be used in combination with an atomic force microscope to obtain a quantifiable mapping of the stressed areas of a ceramic with quartz particles by evaluating the slight peak shift of the main quartz peak.

In this work, in addition to the Raman main peak of the quartz at  $\sim 466\text{ cm}^{-1}$ , two new signals are discovered at  $\sim 1340\text{ cm}^{-1}$  and  $\sim 1600\text{ cm}^{-1}$  [16] on a thin section of a natural quartzite grain. These new signals can only be measured in areas where strain states are expected. Examples are contact zones of different crystals, cracks or areas where the crystal breaks into pieces to achieve relaxation of the strained parts. However, such signals can also be measured sometimes there, where polarized light indicates a strained state inside of a normal unstressed quartz grain. In this paper a characterization of the sample surface is performed which combines reflected light and polarized light microscopy with Raman microscopy.

## 2. EXPERIMENTAL

### 2.1 Sample preparation

The specimen used is a thin section of a quartzite grain. The sample was cut in two halves and embedded in an epoxy resin. Both the plastic sample carrier and the embedded sample were roughened with a silicon carbide slurry. It was then glued together with the same epoxy resin that was used previously. Most of the sample was cut off with a diamond saw and then the surface is ground with another silicon carbide slurry with a smaller particle size. The final polishing was done with an alumina slurry. All slurries used are based on water without additives or oils to prevent contamination of the sample.

### 2.2 Sample analysis

To get an overview of the quartzite grain, in a first step the surface was mapped with polarization and reflected light microscopy using a Zeiss LSM 700 and in a second step different crystallites, cracks and contact zones of the crystals were analyzed with a Thermo Fisher Scientific DXR-Raman microscope using a 532 nm laser.

## 3. RESULTS

### 3.1 Point measurements

During the first series of investigations, different Raman spectra of quartz were measured on the quartzite grain (see Figure 3.1). The black curve shows a spectrum of an area that is probably not strained. The strongest peak measured is the main quartz signal at  $466\text{ cm}^{-1}$ .

However, in areas with expected strain conditions, the red curve can be observed with two completely new broad signals with a higher intensity, visible at  $1600$  and  $1340\text{ cm}^{-1}$ . It is also remarkable that the main peak of the quartz loses more than half of its intensity. The high intensities of the broad new signals are a little surprising. However, this is not an isolated case. In areas where polarization and reflected light microscopy reveals stressed zones, Raman spectroscopy has been able to measure such broad signals.

Other detected smaller peaks belong to the specimen slide used (blue curve) at  $600$ ,  $810$  and  $1450\text{ cm}^{-1}$  and to the epoxy resin (yellow curve) at  $1110$  and  $1610\text{ cm}^{-1}$ .

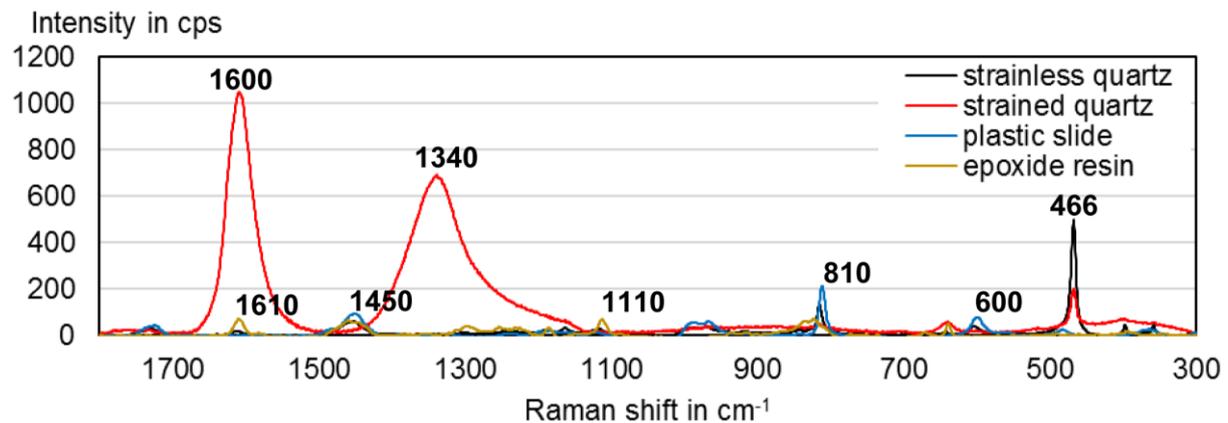


Figure 3.1: Raman spectra of unstrained (black) and strained (red) quartz, also the plastic slide (blue) and the used epoxide resin (yellow)

### 3.2 Line-scan measurements

The correlation between the increase in the broad signals and the decrease in the main crystal peak can be better seen in the line scan shown in Figure 3.2. On the right hand side, the scanning process is shown. The scan runs from point 1 to 13 from a larger quartz grain (position 1) into a damaged zone point 13 to 16 (position 2) and further into another but smaller grain from point 16 to 33 (position 3).

The red curve on the right side of Figure 3.2 shows the distribution of the main quartz signal at 466 cm<sup>-1</sup>. The black curve is the intensity distribution of the stronger signal at 1600 cm<sup>-1</sup>. It can be seen that at the boundaries of the grains at position 1 and 2 the signal that should belong to strained states increases from point 11 to 14 over a range of 6 μm and from point 16 to 22 over a range of 12 μm. In contrast, the intensity of the main quartz peak decreases in these areas. Between these two grains, an increase in the quartz peak can be observed from point 13 to 16, so it is possible that this is a kind of relaxation zone. The fractured zones in the quartz crystal relax the strain in order to reach a better energetic state.

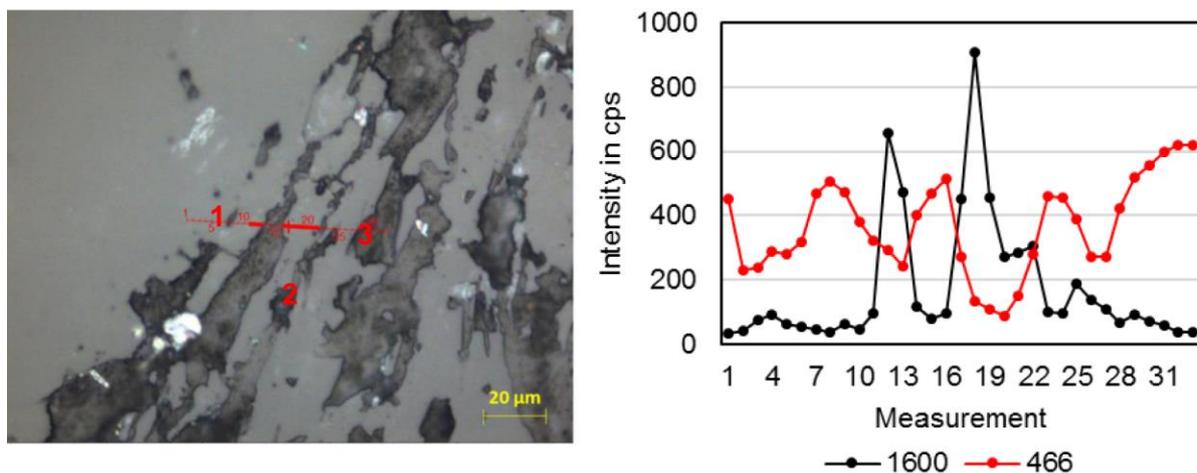


Figure 3.2: Line scan on a quartzite grain through a fracture zone. Left picture: Micrograph of the measured region with the measured points (red curve, distance between the points 2 μm) Diagram on the right side: Comparison of the main quartz peak at 466 cm<sup>-1</sup> and the stronger peak of the stressed regions at 1600 cm<sup>-1</sup>

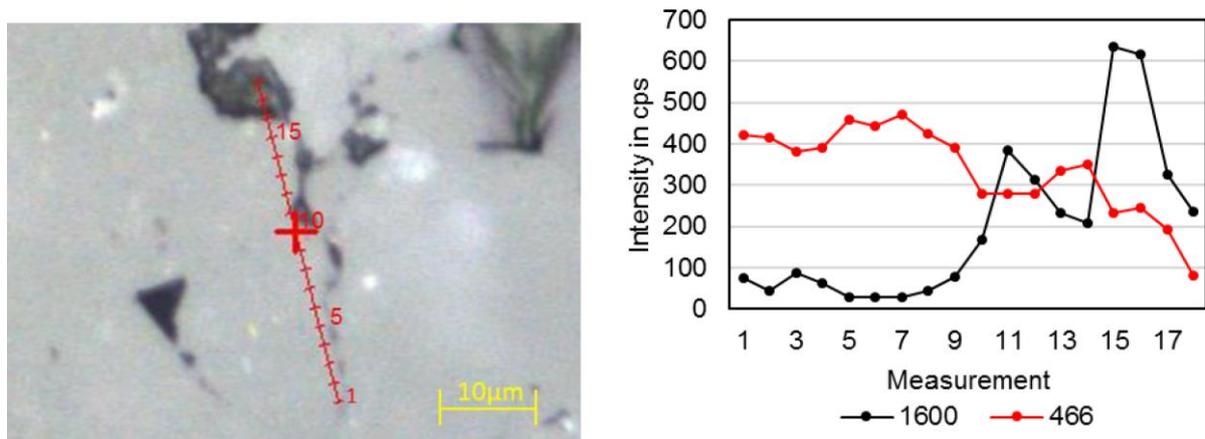


Figure 3.3: Line scan on a grain of quartzite near a crack and a fracture zone. Left picture: Micrograph of the measured area with the measured points (red curve, distance between the points 2 μm) Diagram on the right side: Comparison of the main quartz peak at 466 cm<sup>-1</sup> and the stronger peak of the stressed regions at 1600 cm<sup>-1</sup>

The second line scan shown in Figure 3.3 was performed near a crack. The left side of figure 3.3 shows the course of the crack through the quartz matrix. The crack develops and the small fracture zone near measuring points 7 and 8 is formed. At point 10, when the crack begins to expand, an increase in the intensity of the signal at 1600 cm<sup>-1</sup> and a decrease in the intensity of the main quartz peak at 466 cm<sup>-1</sup> can be measured. The increase continues until the larger fracture zone around measuring point 18 is reached. A possible relaxation again leads to a decrease of the strain signal. A greater distance from the crack leads to lower intensities at the measuring points 12 to 14.

### 3.3 2D Mappings

In further investigations the quartzite thin section shall be stored in a highly alkaline solution to determine the solubility behavior. A detailed characterization of the initial state is required to can be made a comparison between the sample surface before and after the reaction.

It starts with a mapping of the entire quartzite grain using reflected light and polarized light microscopy to find various interesting locations where Raman measurements can be made.

Figure 3.4 shows an image as part of the overall mapping. Due to the duration of the Raman measurements, a selection of spots must be chosen. A problem here is that some signs of stressed areas can only be seen in reflected light microscopy and for others polarized light microscopy must be used.

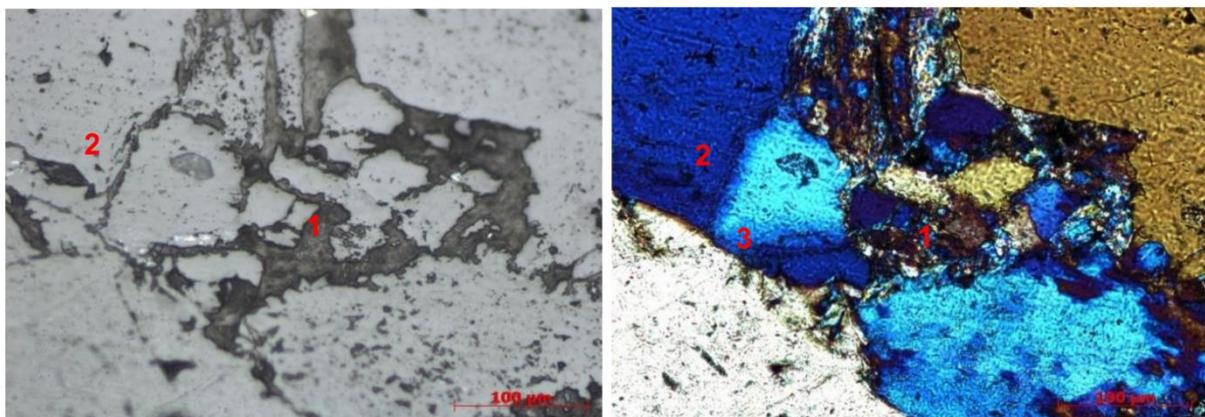


Figure 3.4: Part of the quartzite grain used under reflecting light (left) and polarized light (right) under the microscope. Position 1: Quartz crystal embedded in a fracture area Position 2: Contact zone of two larger crystals Position 3: Transition zone in which different crystal orientations could develop

Interesting points in reflected light microscopy are e.g. quartz crystals surrounded by fracture zones like position 1, contact zones (position 2) or real cracks in the material (see figure 3.3 left). Polarized light microscopy (Figure 3.4 right) is able to show further interesting positions such as transition zones (position 3) where different crystal orientations can be seen. The crystals are deformed by pressure and heat during the formation of quartzite, which leads to different orientations, which can merge into each other or even lie on top of each other.

The selected quartz crystal from Figure 3.4, position 1 is shown in more detail in Figure 3.5. The Raman mapping documents a wide distribution of the  $1600\text{ cm}^{-1}$  signal found. The highest intensities are found in the contact zone with the larger crystal at position 1 in the upper left corner and at the border to a cracked zone on the right side (position 2 in Figure 3.5). At position 2 different crystal orientations seem to merge into each other, as can be seen in the micrograph with polarized light in the middle of Figure 3.5. The small crystal at the bottom of the figure also shows high intensities (position 3).

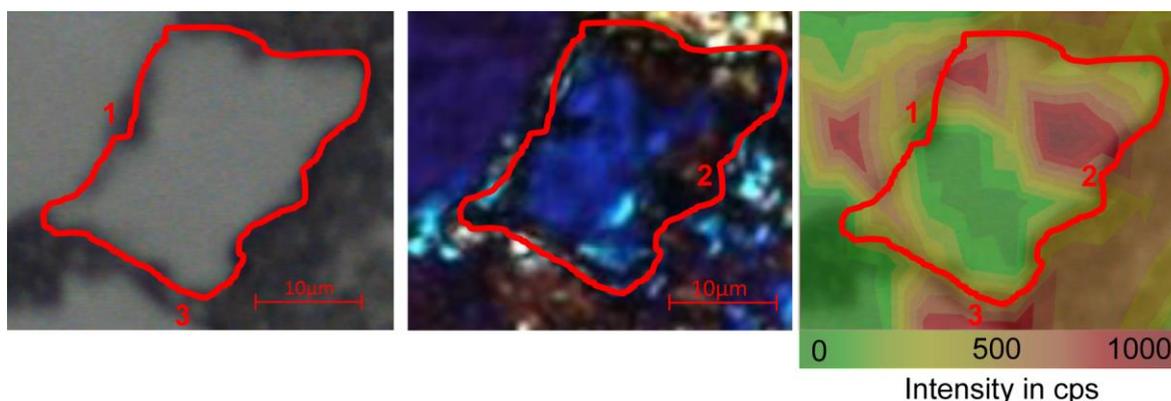


Figure 3.5: Analysed quartz crystal. Reflected light micrograph on the left, polarised light micrograph in the middle, Raman 2D mapping with the intensity of the  $1600\text{ cm}^{-1}$  signal on the right

## 4. DISCUSSION

When comparing the Raman spectra of various other forms of  $\text{SiO}_2$  in Figure 4.1, it is noticeable that the different  $\text{SiO}_2$  modifications show clearly recognizable specific signals but no spectrum, which shows the signals found at  $1600$  and  $1340\text{ cm}^{-1}$ . These signals are also not found in the literature in connection with  $\text{SiO}_2$  or quartz measurements. For this reason, there is currently no physical explanation for what these broad and intense signals stand for.

Mostly, however, these are point measurements on a sample containing  $\text{SiO}_2$ , and in many cases they are made using single crystals, powders or other synthetic materials. The sample used for this study is a natural aggregate consisting not only of one quartz crystal but of hundreds of quartz crystals. During the formation of quartzite, it is possible that each crystal or crystallite got slightly different forces. The deformation of the crystal lattice can therefore be quite different. Therefore, it cannot be assumed that point measurements can be used to characterize the whole crystal, as is the case in this work. The solution can be an intense mapping with a high density of measurement points.

The two new signals normally would be interpreted as carbon G and carbon D bands, but the problem here is that there is no evidence that pure carbon has anything to do with these peaks in this quartzite sample. The measured broad signals are found in compact quartz crystals without visual impurities. Only polarized light microscopy shows different areas with different extinctions, but mostly these should be different orientations of the quartz. Measurements of the plastic sample carrier used and the epoxy resin show spectra without any of these signals, so they cannot be the sources. As mentioned above, the slurries used for sample preparation contain silicon carbide. Also the spectrum of silicon carbide does not contain the measured signals. During the grinding process, the slurries are distributed in a thin film over the entire sample. If there would be a correlation between the components of the slurries and the measured signals, they should be detectable everywhere on the sample, but not only in specific areas.

An indirect proof that the measured broad signal can have nothing to do with pure carbon deposits is shown in Figure 4.2.

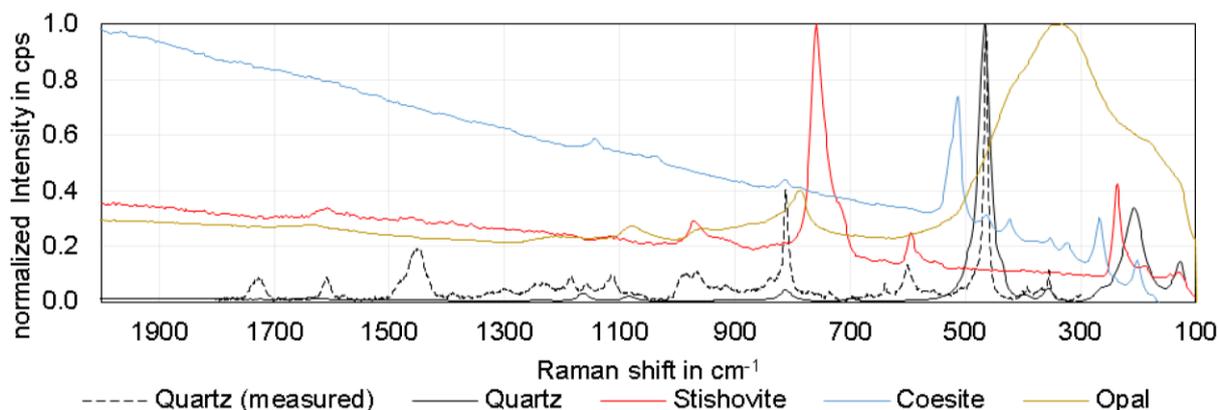


Figure 4.1: Raman shifts with normalized intensities of different forms of SiO<sub>2</sub> containing minerals. Quartz (RRUFF ID R040031), Stishovite (RRUFF ID R080042), Coesite (RRUFF ID R070565), Opal (RRUFF ID X080018) [17]

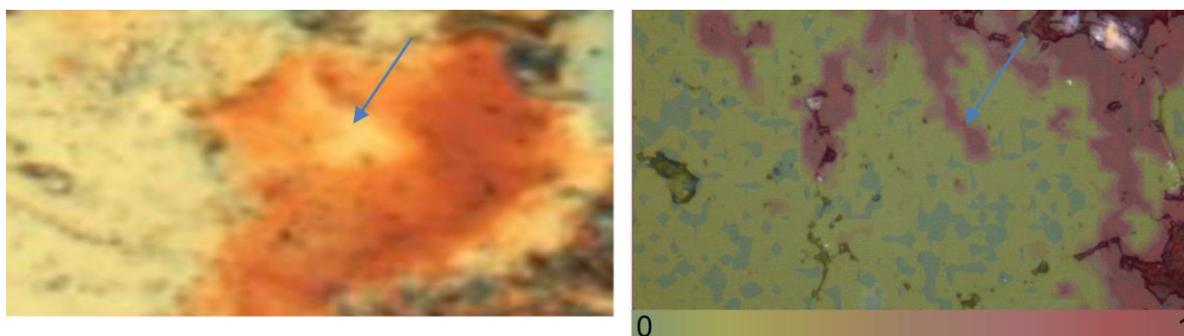


Figure 4.2: Top left: Micrograph with polarized light of a special area within a quartz crystallite; top right: Mapping based on the normalized intensity of the 1600 cm<sup>-1</sup> signal, possible strained zone marked by blue arrow

Both pictures show the same area. As can be seen in the micrograph with polarized light (left), there is an altered (deformed) zone inside the quartz crystallite (see the light yellow area, deformed zone marked by the blue arrow). Further altered or deformed zones can be observed on the right edge of the grain and also on the left side. The broad signals at 1600 cm<sup>-1</sup> with increased intensities can be measured accurately in these areas. There is no plausible explanation that pure carbon can cause this signal there.

However, the signals can be observed in contact areas of different quartz crystallites. Here it is possible that the pressure that forms the rock deforms the crystal structure and leads to strained states.

The chemical potential and also the potential energy of such a defect site is different to a well crystallized quartz [18]. Therefore on the one hand, parts of the structures break down and form cracks and fracture zones in which the fragments remain as relaxed or partially relaxed material. On the other hand also the solubility within an alkaline solution can be increased. Exactly these are the places where there is an increase in the broad Raman peaks. The different states can be quantified by determining the ratio between the intensities of the broad signal at 1600 cm<sup>-1</sup> and the main quartz peak at 466 cm<sup>-1</sup>. This value maybe allows a better characterization of the surface of quartzite and other grains. It is possible that the strain or stress state is not measured directly, but a crystal defect, which may deform the structure and create strain and stress.

Therefore, a combination of reflected and polarized light microscopy to identify these zones and Raman microscopy to evaluate them may possibly be used to quantify stressed areas on natural aggregates. The main goal is after this evaluation, that the samples should be stored in alkaline solutions to measure the strength of the dissolution. The same procedure as used to characterize the initial state is be repeated with the stored samples to obtain more detailed information about the etched areas.

## 5. REFERENCES

- [1] Alaejos P, Lanza V (2012) Influence of equivalent reactive quartz content on expansion due to alkali silica reaction. *Cement and Concrete Research* 42(1): 99-104. <https://doi.org/10.1016/j.cemconres.2011.08.006>
- [2] Rimstidt DJ (1997) Quartz solubility at low temperatures. *Geochimica et Cosmochimica Acta* 61:2553-2558 [https://doi.org/10.1016/S0016-7037\(97\)00103-8](https://doi.org/10.1016/S0016-7037(97)00103-8)
- [3] Gogt BS (1973) An evaluation of some common Indian rocks with special reference to alkali-aggregate Reactions. *Engineering Geology* 7: 138-153. [https://doi.org/10.1016/0013-7952\(73\)90042-2](https://doi.org/10.1016/0013-7952(73)90042-2)
- [4] Tiecher F, Florindo RN, Vieira GL, Gomes MEB, Dal Molin DCC, Lermen RT (2018) Influence of the quartz deformation structures for the occurrence of the alkali-silica reaction. *Materials* 11: <https://doi.org/10.3390/ma11091692>
- [5] Locati F, Marfil S, Baldo E (2010) Effect of ductile deformation of quartz-bearing rocks on the alkali-silica reaction. *Engineering Geology* 116: 117-128. <https://doi.org/10.1016/j.enggeo.2010.08.001>
- [6] Stark J, Berninger AM, Freyburg E (2005) ASR sensitive slow-late aggregates; macrodamage and microstructure. *Proceedings ICF 11 Torino (IT)*
- [7] Guggenheim S, Bain DC, Bergaya F, Brigatti F, Drits VA, Eberl DD, Formoso MLL, Galán E, Merriman RJ, Peacor DR, Stanjek H, Watanabe T (2002) Report of the Association Internationale pour l'Etude des Argiles (AIPEA) Nomenclature Committee for 2001: Order, disorder and crystallinity in phyllosilicates and the use of the 'Crystallinity Index'. *Clay minerals* 37: 389-393. <https://doi.org/10.1180/0009855023720043>
- [8] Marinoni N, Broekmans MATM (2013) Microstructure of selected aggregate quartz by XRD, and a critical review of the crystallinity index. *Cement and Concrete Research* 54: 215-225. <http://dx.doi.org/10.1016/j.cemconres.2013.08.007>
- [9] Rößler C, Möser B, Giebson C, Ludwig HM (2017) Application of Electron Backscatter Diffraction to evaluate the ASR risk of concrete aggregates. *Cement and Concrete Research* 95: 47-55 <http://dx.doi.org/10.1016/j.cemconres.2017.02.015>
- [10] De Wolf I (1995) Micro-Raman spectroscopy to study local mechanical stress in silicon integrated circuits. *Semicond. Sci. Technol.* 11: 139-154.
- [11] Harker YD, She CY, Edwards, DF (1970) Raman Spectra of  $\alpha$ -Quartz Under Uniaxial Stress. *Journal of applied physics.* 41: 5274-5278 <https://doi.org/10.1063/1.1670064>
- [12] Hemley RJ (1987) Pressure dependence of Raman spectra of SiO<sub>2</sub> Polymorphs:  $\alpha$ -quartz, coesite and stishovite. *High-pressure in mineral physics:* 347-359
- [13] McMillan PF, Wolf GH, Lambert P (1992) A Raman spectroscopic study of shocked single crystalline quartz. *Physics and Chemistry of Minerals* 19: 71-79 <https://doi.org/10.1007/BF00198604>
- [14] Su WH, Liu SE, Xu DP, Wang WR, Yao B, Liu XM, Liu ZG, Zhong Z (2006) Effects of local mechanical collision with shear stress on the phase transformation from  $\alpha$ -quartz to coesite induced by high static pressure. *Physical Review B* 73: 144110-1-7 <https://doi.org/10.1103/PhysRevB.73.144110>
- [15] Reinoso JJ, delCampo A, Fernández JF (2015) Indirect measurement of stress distribution in quartz particles embedded in a glass matrix by using confocal Raman microscopy. *Ceramics International* 41: 13598-13606
- [16] Huenger K-J, Danneberg M (2019) Quantification of stress states in quartzite surfaces by using RAMAN spectroscopy. *Zeitschrift Kristallographie* 39: 122
- [17] Lafuente B, Downs R T, Yang H, Stone N (2015) The power of databases: the RRUFF project. In: *Highlights in Mineralogical Crystallography*, T Armbruster and R M Danisi, eds. Berlin, Germany, W. De Gruyter, pp 1-30
- [18] Kolbesen BO, Mähliß J, Possner D (2010) Defect delineation by chemical etching techniques in silicon and engineered silicon substrates: Novel chemistries and basic aspects. *Physica Status Solidi A* 208: 584-587 <https://doi.org/10.1002/pssa.201000240>