

SPECIAL COLLECTION: NANOMINERALS AND MINERAL NANOPARTICLES

Structural characterization of marine nano-quartz in chalk and flint from North Sea Tertiary chalk reservoirs for oil and gas

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ABSTRACT

A new type of quartz, a nano-quartz consisting of spherical particles, is assumed to have formed by crystallization in the sea during sedimentation of the chalk in the North Sea and to have remained largely intact during burial diagenesis. The presence and nature of this nano-quartz have not been identified until recently, despite the fact that this quartz is the type present in the Upper Cretaceous-Danian chalk reservoir for oil and gas in the North Sea, both in the flint and as dispersed particles. In the present work detailed structural analysis of the nano-quartz has been carried out by X-ray diffraction, solid-state ²⁹Si and ²⁷Al MAS NMR, thermal analysis including water release, IR-absorption spectroscopy, and elemental analysis supplemented with analysis of oxygen isotope composition. It is found that ^{IV}Al substitutes for Si and that ^{VI}Al probably is bonded to hydroxyls on the particle surface of the nano-quartz structures. The charge compensation of tetrahedral Al³⁺, in addition to its conventional way of compensation by formation of the local structural arrangement [AlO₄/M⁺]^o defects (M⁺ = H⁺, Na, K, Li), can occur at the expense of the OH⁻ group coordinating one of the four tetrahedral Si⁴⁺ nearest to the Al³⁺ tetrahedron. The most significant feature of the North Sea nano-quartz deduced in the present investigation is the presence of [4H]_{Si} defects, also known as hydrogarnet defects. This defect is present in up to 5% of the tetrahedral sites, whereas Al³⁺ occupies less than 1% of the tetrahedral sites. Two types of distribution of the [4H]_{Si} defects were determined. In one of them the [4H]_{Si} defects aggregates parallel to the (0001) plane to form platelets as cracks with hydroxylated surfaces on both sides. The second type of [4H]_{Si} defect occurs in the form of isolated tetrahedral vacant sites. The formation of the aggregated [4H]_{Si} platelets lying in the (0001) plane mostly increases the *c* parameters of the structure, whereas the isolated [4H]_{Si} defects and K+Na impurities contribute to increasing the *a* parameters.

The remarkable correlation of the positional distribution of the samples revealed from the relationships between *a* and *c* parameters and between amount of OH⁻ groups responsible for formation of [4H]_{Si} defects and *a* and *c* parameters can be considered as evidence for the validity of the structural formulas and, in general, of the main structural features of the studied samples. The unusually high content of [4H]_{Si} defects in the nano-quartz samples may be related to their formation by precipitation in waters of the Danish North Sea.

Keywords: Nano-quartz structure, nano-quartz formation, hydrogarnet defects, X-ray diffraction, ²⁷Al and ²⁹Si MAS NMR, IR spectroscopy, thermal water release, δ¹⁸O isotope chemistry, elemental analysis

INTRODUCTION

Quartz is the most abundant mineral on the Earth's surface and it is composed of nearly pure SiO₂ that gives a strong X-ray diffraction (XRD) powder pattern with sharp *hkl* reflections. Quartz is usually crystallized during magmatism, metamorphism, hydrothermal reactions, or during diagenesis at moderate to high temperatures. Despite the fact that sea water may be supersaturated with respect to quartz crystallization (Millot

1970), this type of crystallization is usually assumed to be too slow at ambient temperature to take place at a significant degree. However, an experimental study has demonstrated that quartz may form at Earth-surface conditions in sea water (Mackenzie and Gees 1971). Quartz is present as an accessory mineral in most carbonate rocks, often together with other silica minerals such as opal-CT and opal-A. Usually quartz is assumed to have the well-established standard α-quartz structure, i.e., trigonal crystal system with space group *P*3₂21 or *P*3₁21. We have in detail investigated silica minerals from Danian chalk in six oil wells in the Danish part of the Central Graben in the North Sea, where the only silica mineral present is a new form of quartz

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composed of nano-size α -quartz spheres. The nano-quartz spheres are dispersed in the chalk matrix, however, the flint in bands and nodules contains the same nano-quartz spheres (Jakobsen et al. 2000; Lindgreen et al. 2010, 2011). In some wells, the dispersed nano-quartz may constitute up to 70% of the chalk (Lindgreen et al. 2010). Quartz-rich layers are generally of low permeability and may act as internal seals for oil in chalk reservoirs (Lindgreen et al. 2010). Current theories assume that flint has formed through syndepositional and post-depositional dissolution of Si-containing organisms in the chalk followed by migration and precipitation in hollows formed by dissolution of the chalk (Holmes 1965, p. 133–134; Bromley and Ekdale 1986; Clayton 1986; Zijlstra 1987; Madsen and Stemmerik 2010). However, the identical structure of the nano-quartz dispersed in the chalk and of the nano-quartz in the flint has, together with observations of structures in the sediments, formed the basis of a new model for formation of flint in North Sea chalk (Lindgreen et al. 2011): the nano-quartz in the flint, like the nano-quartz in the chalk matrix, has crystallized as nano-size particles in the marine Chalk Sea environment. The colloidal quartz particles have then flocculated and have been deposited on the sea floor mixed with calcitic bioclastic material. The pure flint probably formed during periods when decreased pH in the water column dissolved the calcite coccoliths during sedimentation and the silica was probably remolded after sedimentation (Lindgreen et al. 2011).

The unit-cell parameters, as determined by X-ray diffraction, for natural quartz may show a variation of up to 0.03%, and there is a trend of increasing cell size with decreasing metamorphic grade (Hurst and Storch 1981). In the North Sea nano-quartz, the unit-cell parameters, sizes of coherent scattering domains (CSDs) and strain values deviate from those of normal α -quartz, the a and c cell parameters being larger by as much as 0.10% (Lindgreen et al. 2011). Substitution, such as Al^{3+} for Si^{4+} , has been deduced for quartz (Dennen 1966; Dennen and Blackburn 1970), however, the substitution was deduced from elemental analysis and cell parameters. Application of high-resolution Electron Paramagnetic Resonance (EPR) spectroscopy to the study of paramagnetic defects in a large collection of crystalline quartz samples has shown the following centers originating mostly from impurity ions: H, Al, Cu, Ag, Ge, P, Ti, and Fe (Weil 1984). According to the EPR data all Al-associated paramagnetic centers in quartz have shown that Al^{3+} occurs exclusively at the tetrahedral sites (Weil 1984, 2000; Botis and Pan 2009). Using ab initio calculations at the density functional theory level, Botis and Pan (2009) investigated the nature of the $[\text{AlO}_4/\text{M}^+]^\circ$ defects ($\text{M}^+ = \text{H}, \text{Li}, \text{Na}, \text{and K}$) and showed them to be stable in the α -quartz structure. The $[\text{4H}]_{\text{Si}}$ defect, the so-called hydrogarnet defect, where vacant tetrahedral sites have four adjacent OH^- groups, is a common defect in quartz, especially synthetic quartz (McLaren et al. 1983; Shinoda and Aikawa 1993; Cordier et al. 1994; Lin et al. 1994; McConnell et al. 1995; McConnell 1996; Rosa et al. 2005; Stalder and Neuser 2013). The $[\text{4H}]_{\text{Si}}$ defect can cause development of planar defects in quartz in the vacuum and temperature of the electron microscope (McConnell et al. 1995). Rosa et al. (2005) calculated that the $(\text{OH})_4$ group is the thermodynamically most stable water-related defect and suggested that the $(\text{OH})_4$ defects are likely to form platelets lying

in the (0001) plane. The objective of the present investigation is a detailed analysis of the nano-quartz by X-ray diffraction, solid-state MAS NMR, IR-absorption spectroscopy, thermal analysis including analysis of water release, and elemental analysis by atomic absorption spectrometry (AAS) to reveal the particular structural and crystal-chemical features of flint and dispersed particles of nano-quartz.

MATERIALS

The chalk matrix and flint from the Tertiary Danian chalk in Danish North Sea were investigated. Cores from the wells Sif-1 and Nana-1 in the Halfdan Field, from well E-5 in the Tyra Field and from well M-10 in the Dan Field have been sampled. Samples taken from two cores in Sif-1, comprising both flint and chalk, are shown in Figure 1.

The flint samples were crushed to <0.25 mm in a mortar before investigation, whereas the chalk samples were crushed to <2 μm before removal of calcite. Preliminary studies of the samples allowed a choice of only impurity-free samples for the future investigations. One flint sample 5 (Sif-1, 2057.63)

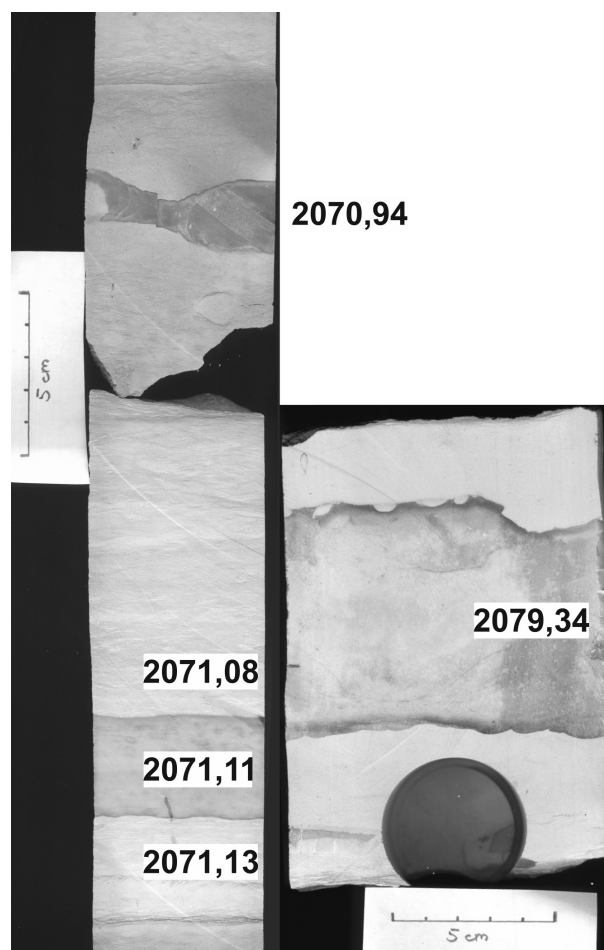


FIGURE 1. Photos of cores from well Sif-1. Positions of chalk samples 11 (Sif-1, 2071.11), 12 (Sif-1, 2071.13), and 10 (Sif-1, 2071.08), and flint samples 9 (Sif-1, 2070.94) and 13 (Sif-1, 2079.34).

(Table 1) was heated to 605 °C for two hours and then investigated at room temperature by XRD and NMR to observe the structural effects of the heating.

EXPERIMENTAL METHODS

Removal of calcite

The large amounts of calcite in chalk have been removed by dissolution prior to the mineralogical investigations of the non-calcite minerals. The chalk samples were crushed to pass a 4 mm sieve. The samples were then added to 200 mL of distilled water, and the calcium carbonate was removed by adding acetic acid while keeping the solution buffered at pH 4.5 to 5. The supernatant was removed by centrifugation and the residues were washed with distilled water to remove excess ions, and air dried. This buffered dissolution of calcite was applied to avoid corrosion or dissolution of the fine-grained non-calcite minerals, such as the clay minerals and nano-quartz. Clay minerals and other mineral impurities were not detected by XRD and carbonates were not present according to DTA-EGA (the CO₂ evolution curve).

Atomic force microscopy

Atomic force microscopy (AFM) was carried out using a Rastroscope 3000 instrument. Intact rock specimens were small pieces of chalk or flint glued onto gold-coated sample holders. In samples with small amounts of non-calcite minerals these could only be identified and imaged in residues. For such samples, the residues were dispersed ultrasonically in distilled water and the specimens prepared by leaving a drop of the suspension to dry under ambient conditions on a block of highly oriented pyrolytic graphite. AFM was carried out at ambient conditions with the tip running in non-contact mode, a force of 0.175 nN and a scanning speed of 500 nm/s.

X-ray diffraction

The flint samples were crushed by hand in a mortar to pass a 250 µm sieve whereas the residual samples were processed after removal of calcite. XRD patterns were obtained using CoKα radiation with a Philips PW3040 diffractometer having a vertical goniometer PW3050 with a curved graphite monochromator and a fine-focus tube. Randomly oriented specimens were analyzed using 1° fixed divergence and anti-scatter slits and intensities were measured for 40 s per 0.02° 2θ step in the range 23–91° 2θ. An internal standard of 5% Si was used.

Determination of the unit-cell parameters. This procedure included the following steps: (1) calibration of *hkl* peak positions using those of Si as an internal standard; (2) removal of the contribution of *Kα₂* from each *hkl* peak mathematically, assuming that profiles of both *Kα₁* and *Kα₂* maxima are described by the same Pearson function that provided a fit with *R_{wp}* < (2–4)%; (3) the profile of each individual *hkl* peak corresponding to *Kα₁* was used to determine its position (2θ) and *d* value. The Jade computer program was used for the determination of the unit-cell parameters by the least-squares method.

Determination of the mean size of coherent scattering domains, CSDs, and microstrains. The effective breadth of each *hkl* reflection corresponding to *Kα₁* is determined as a ratio of its area to amplitude. These values were determined for

hkl reflections of a sample and for those of a flat perfectly crystalline Si standard. To a fair approximation the breadth, *B*, of an experimental reflection is described by the equation (Moore and Reynolds 1997):

$$B^2 = \beta^2 + \beta_{st}^2 \quad (1)$$

where β is the pure, undistorted breadth in degree 2θ (in radians) and β_{st} is the same quantity for a peak from the crystalline Si standard. A reflection breadth, β , is determined by the influence of two main parameters, having different dependences on θ . One of them β_L is related to the mean size of coherent scattering domains, *L*, according to the Scherrer equation:

$$L = k\lambda / \beta_L \cos \theta \quad (2)$$

where θ and λ are the angular position of the studied *hkl* reflection and the wavelength, respectively.

The second factor, β_{str} , is controlled by microstrains determined by a relative variation of *d*-spacing $|\Delta d/d|$ at each given θ and depends on θ as:

$$\beta_{str} = \left| \Delta d / d \right| \tan \theta. \quad (3)$$

A mutual influence of both factors determines the breadth, β , of the experimental reflection that to a good approximation is related to β_L and β_{str} as:

$$\beta^2 = \beta_L^2 + \beta_{str}^2. \quad (4)$$

Thus, to determine both a mean size of CSDs and microstrains along a normal to the (*hkl*) plane requires the use of the β values for at least two reflections having two orders of *hkl* indices, for example 100 and 200. Solution of two Equations 4 for β_{100} and β_{200} allows calculation of the values of interest.

Solid-state NMR spectroscopy

Solid-state ²⁷Al and ²⁹Si experiments were performed on Varian Direct-Drive VNMR-600 (14.09 T) and Varian INOVA-400 (9.39 T) spectrometers, respectively. The ²⁷Al MAS NMR spectra were acquired with a home-built CP/MAS probe for 4 mm o.d. zirconia (PSZ) rotors, using a pulse width of 0.5 µs and a rf field strength of $\gamma B_1/2\pi = 50$ kHz (i.e., a flip angle < $\pi/6$ for ²⁷Al, $I = 5/2$, in a solid) to ensure quantitative reliability of the intensities, observed for the ²⁷Al central transition for sites experiencing different quadrupole couplings. Moreover, ¹H decoupling ($\gamma B_2/2\pi = 50$ kHz), a spinning speed of $\nu_R = 13.0$ kHz, and a relaxation delay of 2–4 s were employed. The ²⁷Al MAS spectrum of the probe itself with an empty spinning ($\nu_R = 13.0$ kHz) PSZ rotor showed a broad resonance of very low intensity. This spectrum was subtracted from the ²⁷Al MAS spectra of the quartz samples prior to the quantitative evaluation of the observed intensities. The ²⁹Si MAS and ²⁹Si{¹H} CP/MAS NMR experiments (9.39 T) used a home-built CP/MAS probe for 7 mm o.d. rotors and spinning speeds of $\nu_R = 6000$ Hz and $\nu_R = 4000$ Hz, respectively, and rf field strengths of $\gamma B_1/2\pi = \gamma B_2/2\pi = 49$ kHz for ²⁹Si and ¹H. The single-pulse experiments employed a 45° excitation pulse, whereas the CP/MAS experiments used a standard CP rf-pulse sequence with ¹H TPPM

TABLE 1. XRD parameters for the unit cells

No.	Sample		Depth	<i>a</i> (Å)	<i>c</i> (Å)	<i>c/a</i>	<i>V</i> = <i>a</i> · <i>a</i> · <i>c</i>	<i>L</i> (nm) h00	mks h00	<i>L</i> (nm) h0h	mks h0h	
1	Quartz	Merck <63 nm	Standard 2012		4.9144	5.4055	1.0999	113.056	122(10)	0.0005	127(10)	0.0006
2	Rigs-1	White Quartz	R91675	2794.3	4.9164	5.407	1.0998	113.179	57(5)	0.001	92(5)	0.0017
3	Rigs-1	Flint	R9274 f1	2826.84	4.9169	5.4047	1.0992	113.158	50(5)	0.0016	73(5)	0.0019
4	Sif-1	Chalk (7%quartz)	6729r	2051.17	4.9182	5.4089	1.0998	113.303	72(5)	0.0009	84(5)	0.0011
5	Sif-1	Flint	6750f +23pt2	2057.63	4.9176	5.4076	1.0996	113.244	58(5)	0.0011	75(5)	0.0016
6	Sif-1	Chalk (40%quartz)	6750k	2057.65	4.918	5.4082	1.0997	113.278	63(5)	0.0011	75(5)	0.0013
7	Sif-1	Flint Lauer	Sif6774 stk9	2065.0	4.9171	5.4071	1.0997	113.214	53(5)	0.0015	81(5)	0.002
8	Sif-1	Flint Lauer	Sif67792	2066.3	4.9171	5.4058	1.0994	120.980	53(5)	0.0018	73(5)	0.0019
9	Sif-1	Flint	6793'2"x3	2070.94	4.9177	5.4074	1.0996	113.263	58(5)	0.0015	81(5)	0.0017
10	Sif-1	Chalk (29%quartz)	Sif 6793 stk1	2071.08	4.9195	5.4097	1.0997	113.377	56(5)	0.0015	68(5)	0.0017
11	Sif-1	Chalk (66%quartz)	Sif 6793 stk2	2071.11	4.9166	5.4072	1.0998	113.193	59(5)	0.0011	74(5)	0.0012
12	Sif-1	Chalk (24%quartz)	Sif 6793 stk3	2071.13	4.9186	5.4096	1.0998	113.335	56(5)	0.0014	67(5)	0.0015
13	Sif-1	Flint	6820'4"+53	2079.34	4.917	5.4063	1.0995	113.190	60(5)	0.0012	84(5)	0.0017
14	Sif-1	Flint	Sif 6851 a	2088.3	4.9172	5.4068	1.0996	113.212	70(5)	0.0011	88(5)	0.0012
15	Nana-1	Flint	6974'10"	2125.93	4.917	5.4067	1.0996	113.200	64(5)	0.0012	82(5)	0.0015
16	Nana-1	Flint	6990_	2130.55	4.9171	5.4066	1.0996	113.204	57(5)	0.0014	80(5)	0.0018
17	Nana-1	Flint	7007'6"	2135.8	4.9171	5.4068	1.0996	113.207	47(5)	0.0016	56(5)	0.0016
18	M-10	Flint	6442 k4d4	1963.52	4.9164	5.4059	1.0996	113.154	57(5)	0.0014	80(5)	0.0018
19	E-5	Flint	6820 stkalR	2078.74	4.9174	5.4069	1.1000	113.221	59(5)	0.0012	83(5)	0.0018

Notes: Errors for *a* and *c* are 0.0004 Å; mks, 0.0003 Å.

decoupling during acquisition. ^{29}Si chemical shifts are referenced to an external sample of tetramethylsilane (TMS), while ^{27}Al chemical shifts are referenced to an external sample of a 1.0 M aqueous solution of $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$.

Elemental composition by atomic absorption spectrometry (AAS)

EDAX analysis of dispersed nano-quartz showed that Si is dominant and only minor amounts of Al, Na, and K are present in the nano-quartz. Other major elements were not detected in significant amounts except for traces of Ca in the residues because Ca in these samples was present as adsorbed cations residual from the removal of calcite. Because of the small contents of cations other than Si, total chemical analyses were made using $\text{HF-H}_2\text{BO}_3$ dissolution in polytetrafluoroethylene vessels (Bernas 1968) followed by AAS determination of dissolved Al, Na, and K. The AAS determination, using a Perkin Elmer Analyst 400 spectrometer, is more accurate than the XRF method especially for the light elements, Na and Al, and in general when the content of cations is low. The amounts of Al_2O_3 , K_2O , and Na_2O were determined by AAS using nitrous oxide-acetylene flame for Al and air-acetylene flame for Na and K. The absorption standard curve was linear in the ranges 0.5–1.0 ppm found in the solutions for the three elements. The dissolution method of Bernas (1968) results in solutions having a very low ionic strength that is very important for accurate AAS determinations at low concentrations, the matrix effect being minimal. The possible errors in estimation of the weight amounts of Al_2O_3 , Na_2O , and K_2O varied from 5 to 15%. The large amounts of Si did not allow an accurate determination of Si better than $\pm 1\%$. The flint samples were raw samples and probably had Na^+ from pore water adsorbed, whereas the chalk residue samples were Ca^{2+} -saturated, because the buffered dissolution of the calcite left the solution with Ca^{2+} as the dominant cation. Al was divided into ^{19}Al and ^{10}Al based on the ^{27}Al NMR analyses.

Infrared spectroscopy

Mid-infrared absorption spectra were obtained at room temperature in transmission mode using a Bruker Vertex 80v FTIR spectrometer, coupled with a Hyperion 1000 microscope using a liquid nitrogen cooled MCT detector and a KBr beamsplitter. 600 scans in a range of $3700\text{--}3200\text{ cm}^{-1}$ were recorded with a spectral resolution of 2 cm^{-1} . Flint specimens were prepared as both side polished plates with $50\text{ }\mu\text{m}$ thickness, whereas residual specimens were recorded from thin layers of powder where the thickness was not controlled.

Each spectrum was analyzed using the OPUS 7.1 software. Baseline correction was performed automatically by the "Concave Rubberband" OPUS function (number of iterations = 15, number of baseline points = 64). Smoothing was also carried out automatically (number of smoothing points = 13). The position of bands was determined by the second derivative and decomposition of the partially overlapping bands. For each studied sample 4–6 spectra were obtained from different parts of the specimen because samples had a certain degree of heterogeneity of density.

Thermal analysis (DTA-EGA)

Thermal analysis was carried out using a Stanton-Redcroft DTA 673-674 instrument with gas outlet to non-dispersive infrared H_2O and CO_2 detectors (Morgan 1977). The sensitivity using infrared detection is very high and makes it possible to quantify carbonates and water release separately (Morgan 1977). The gas (in the present case analytical-grade N_2) flowed through an oven with a specially designed outlet at the top and then through first the IR detector for H_2O and then the IR detector for CO_2 . Both detectors were measuring the gases at a 1000 ppm scale. Furthermore, flow controllers stabilized the flow at 400 mL/min. A run with $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ was used for calibrating the H_2O release. A flow of analytical grade N_2 was used before each sample run until the baselines for the gases were horizontal, the heating was then initiated at $10^\circ\text{C}/\text{min}$ until 1000°C . Peak areas were determined by integration. The overall accuracy of the determinations was about 10%. Both H_2O and CO_2 were determined, which is an advantage compared to thermogravimetric analysis where overlap may occur. The analyses showed that carbonates were not present in the flint samples or in the residue samples after dissolution treatment.

Isotope geochemistry

$\delta^{18}\text{O}$ of silica samples was determined by the Macaulay et al. (2000) modification of the laser fluorination procedure of Sharp (1990). The precision and accuracy of the measurement of the oxygen isotopic composition of the CO_2 are $\pm 0.2\text{‰}$ (1σ) and NBS 28 gives 9.6‰ ; data are reported as δ values in ‰ relative to V-SMOW. The samples were vacuum degassed overnight at room temperature to remove labile adsorbed species; higher temperature was not employed to avoid possible loss of structural water and hydroxyl, which may have differentially affected the samples.

RESULTS

Atomic force microscopy

Atomic force microscope images of the two studied samples, a residue from chalk sample 12 (Sif-1, 2071.13) and from a flint sample 13 (Sif-1, 2079.34), are shown in Figures 2a and 2b. Note the similarity in structure: both are composed of nano-size spherical or rounded particles. These features are seen especially well in Figure 2a.

X-ray diffraction

Nineteen samples were studied using the X-ray diffraction, the list of which is given in Table 1. X-ray diffraction for the region $20\text{--}90^\circ 2\theta$ for a residue sample 12 (Sif-1, 2071.13 m), a flint sample 13 (Sif-1, 2079.34 m) and the standard quartz are shown

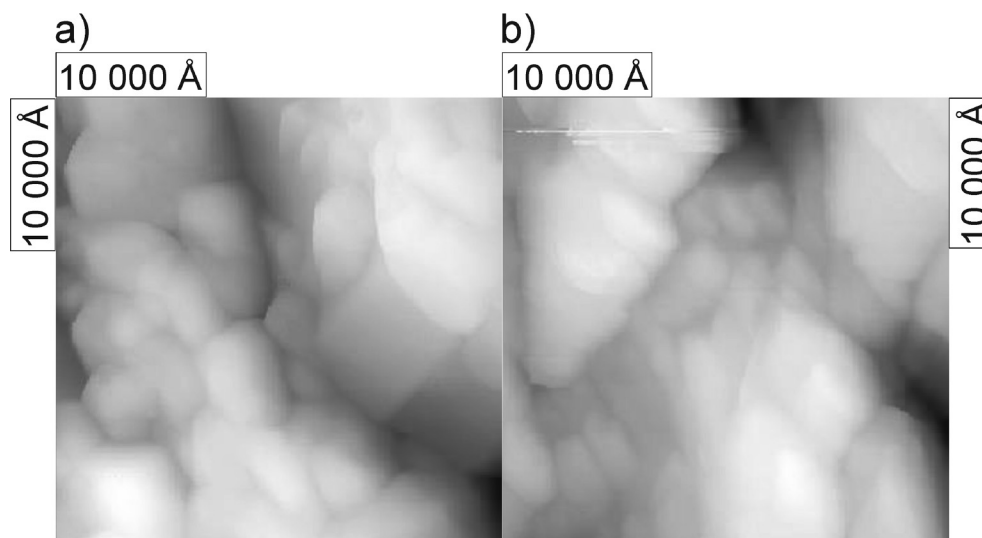


FIGURE 2. Atomic force microscopy images of: (a) sample 12 (Sif-1, 2071.13), residue from chalk sample, deposited on highly oriented pyrolytic graphite (HOPG); (b) sample 13 (Sif-1, 2079.34), flint, raw sample. Samples have been imaged at room conditions in non-contact mode.

in Figures 3a, 3b, and 3c, respectively. The peak height is considerably larger for the standard quartz compared to the two nano-quartz samples, when the standard Si added is used as a reference. The largest discrepancy between the two nano-quartz samples and the standard quartz is observed in the high-angle region $80\text{--}82^\circ 2\theta$, where the sharp 212, 203, and 301 peaks of the standard quartz are strongly different from the broad and poorly resolved peaks of the two nano-quartz samples (Fig. 3d). However, the high-angle patterns for the residue nano-quartz and for the flint nano-quartz are very similar. The observed significant broadening of the reflections results from microstrains having high values (Table 1).

The quartz from the chalk and flint samples has a three-dimensional periodicity of the lattices and is characterized by having significantly larger a and c parameters as compared to those of normal quartz (Table 1). The range of the parameter variation is from 4.9164 to 4.9195 Å for the a parameter, and from 5.4047 to 5.4097 Å for the c parameter, whereas the standard Merck quartz has an a parameter of 4.9144 Å and a c parameter of 5.4055 Å (Table 1). Another distinguishing feature is that the quartz in the studied samples consists of much smaller CSDs compared to those of normal quartz (Table 1). The values of L_{100} of the studied quartz vary from 56 to 72 nm for the chalk and from 47 to 70 nm for the flint samples (Table 1). The L_{101} values of the quartz also vary within similar intervals: 67–84 nm for the chalk and 56–88 nm for the flint samples (Table 1). Note that microstrains have similar values along both studied crystallographic directions (Table 1).

The XRD pattern of the sample 5 (Sif-1, 2057.63), which had been heated to 605°C for two hours, was identical to the pattern of the natural sample.

MAS NMR

Fourteen samples were studied using ^{27}Al MAS NMR, the list of which is given in Table 2. The ^{27}Al MAS NMR spectra of three nano-quartz samples are shown in Figure 4. The spectra of samples 7 (Sif-1, 2065.0, flint), 10 (Sif-1, 2071.08, chalk) and 17 (Nana-1, 2135.8, flint) are dominated by a resonance with a center of gravity at 56 ppm, originating from Al in tetrahedral coordination. The peak falls in the chemical shift range for framework $\text{Al}(\text{--O--Si})_4$ sites and thus it is assigned to Al^{3+} substituting for Si^{4+} in the tetrahedral sites of the quartz structure, following an earlier ^{27}Al NMR study of the incorporation of Al^{3+} guest ions in calcium silicate phases (Skibsted et al. 1994). A minor peak at 4–5 ppm is also observed for all samples, whereas the ^{27}Al MAS NMR spectrum of the flint sample 7 (Sif-1, 2065.0) in addition includes a small resonance at 14 ppm. The 4–5 ppm peak has almost the same chemical shift and line shape as observed for octahedral aluminate species in ^{27}Al MAS NMR spectra of calcium-silicate-hydrate (C-S-H) phases resulting from Portland cement hydration (Andersen et al. 2006) and for dioctahedral Al-rich 2:1 clay minerals (Sanz and Serratos 1984; Sanz 1990; Takahashi et al. 2008). In the work of Andersen et al. (2006) the origin of the octahedral Al resonance at 5 ppm was investigated

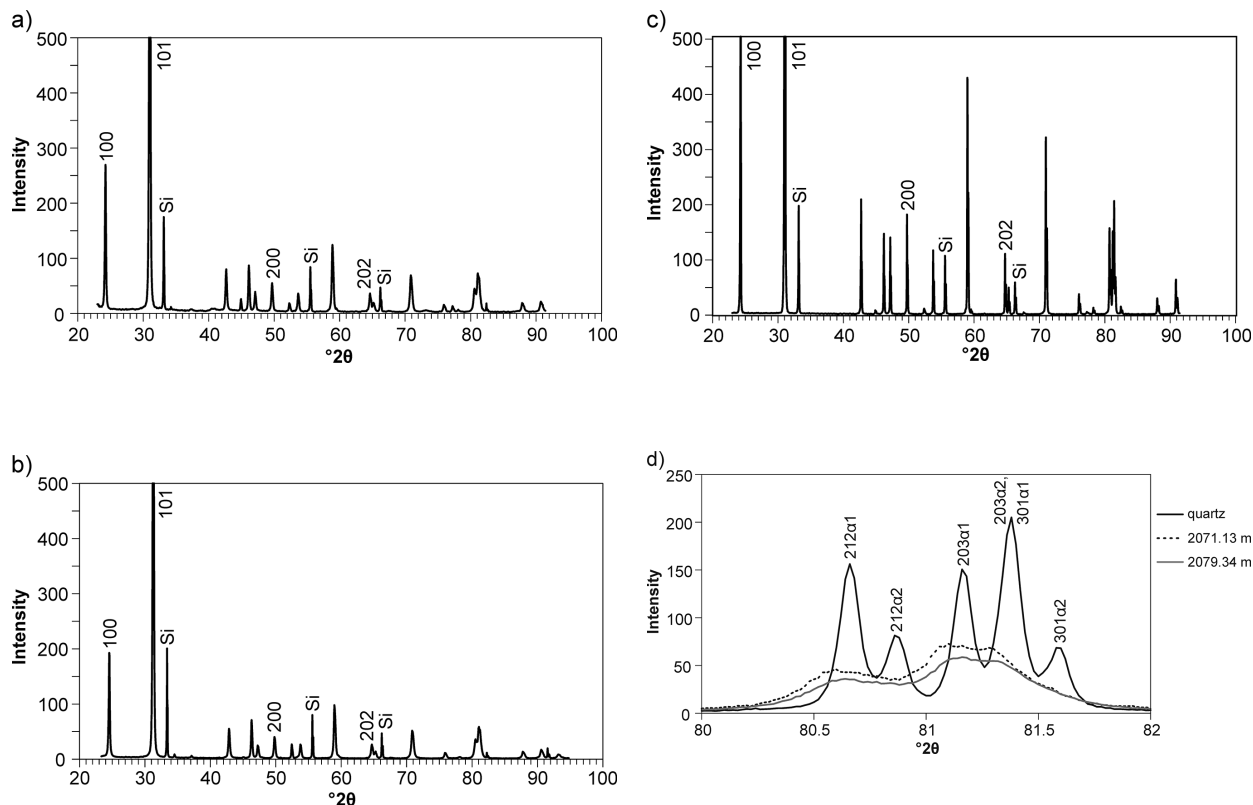
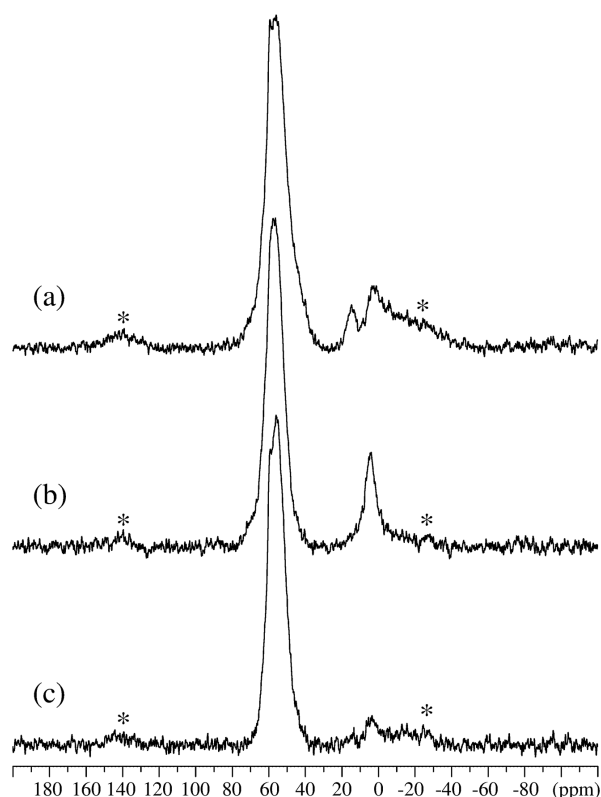


FIGURE 3. X-ray diffraction patterns, using 5% Si as an internal standard and $\text{CoK}\alpha$ -radiation; (a) sample 12 (Sif-1, 2071.13) residue from chalk sample, region $20\text{--}90^\circ 2\theta$; (b) sample 13 (Sif-1, 2079.34), flint; region $20\text{--}90^\circ 2\theta$; (c) quartz standard, Merck, region $20\text{--}90^\circ 2\theta$; (d) region of samples 12 (Sif-1, 2071.13) residue from chalk sample, 13 (Sif-1, 2079.34), flint and quartz standard, Merck recorded in $80\text{--}82^\circ 2\theta$ interval.

TABLE 2. Fractions of Al, K, and Na determined by atomic absorption spectrometry (AAS), and relative ^{29}Si and ^{27}Al distribution determined by ^{27}Al MAS NMR

Well	Sample no.	Depth (m)	Depth (feet)	Sample	AAS % Al_2O_3	AAS % K_2O	AAS % Na_2O	NMR ^{29}Si % Al_2O_3	NMR ^{27}Al % Al_2O_3
Rigs-1	2	2794.3	9167.5	Quartz layer	0.15(0.01)	0.013(0.002)	0.054 (0.008)	0.12	0.03
Rigs-1	3	2826.84	9274.41	flint	0.18(0.01)	0	0.043 (0.006)	0.16	0.02
Sif-1	5	2057.63	6750+23pt2	flint	0.14(0.01)	0.150 (0.023)	0.130 (0.013)	0.13	0.01
Sif-1	7	2065.0	6774'6"stk9	flint	0.27(0.01)	0.083(0.002)	0.075 (0.008)	0.22	0.05
Sif-1	8	2066.3	6779'4"	flint	0.19(0.01)	0.098(0.010)	0.076 (0.008)	0.15	0.04
Sif-1	9	2070.94	6793'2"x3	flint	0.33(0.02)	0.038(0.006)	0.094 (0.009)	0.29	0.04
Sif-1	10	2071.08	6793'2"stk1	residue, chalk	0.73(0.04)	0.220 (0.022)	0.600 (0.060)	0.61	0.12
Sif-1	11	2071.11	6793'2"stk2	residue, chalk	0.21(0.01)	0.005(0.001)	0.053 (0.008)	0.18	0.03
Sif-1	12	2071.13	6793'2"stk3	residue, chalk	0.39(0.02)	0.085(0.009)	0.066 (0.007)	0.24	0.15
Sif-1	13	2079.34	6820'4"+53	flint	0.34(0.02)	0.058(0.006)	0.142 (0.014)	0.28	0.06
Sif-1	14	2088.3	6851'6"	flint	0.21(0.01)	0.013(0.002)	0.050 (0.008)	0.15	0.06
Nana-1	17	2135.8	7007'6"	flint	0.11(0.01)	0.033(0.005)	0.086 (0.009)	0.09	0.02
M-10	18	1963.52	6442'k3b4	flint	0.32(0.02)	0	0.113 (0.011)	0.27	0.05
E-5	19	2078.74	6820'1"stkaIR	flint(IR)	0.38(0.02)	0	0.016 (0.002)	0.31	0.07

**FIGURE 4.** ^{27}Al MAS NMR spectra (14.1 T) of: (a) sample 7 (Sif-1, 2065.0), flint; (b) sample 10 (Sif-1, 2071.08), residue; (c) sample 17 (Nana-1, 2135.8), flint. The spectra used a spinning speed of $\nu_R = 13.0$ kHz, a short excitation pulse (0.5 μs), and a relaxation delay of 2 s. The asterisks indicate spinning sidebands.

in detail for several different samples, using different NMR techniques, and it was finally assigned to nanostructured aluminate species, including $\text{Al}(\text{OH})_6^{3-}$ or $\text{O}_x\text{Al}(\text{OH})_{6-x}$ sites, formed on the surface of the C-S-H phase. Following this assignment, and the strong similarity in ^{27}Al chemical shift and linewidth, the observed ^{27}Al resonance at 4–5 ppm (Fig. 4) will be ascribed to octahedral $\text{Al}(\text{OH})_3$ sites formed at the surface of the quartz crystals. The ^{27}Al MAS NMR spectra allow determination of the relative fractions of aluminum atoms in the different coordination environments as summarized for the samples in Table 2.

The ^{29}Si MAS NMR spectra of the four studied samples—two flint samples 7 (Sif-1, 2065.0) and 17 (Nana-1, 2135.8), the chalk quartz sample 10 (Sif-1, 2071.08), and the commercial quartz (Fig. 5)—all contain a narrow resonance at -107.4 ± 0.2 ppm, in accordance with the well-known chemical shift for α -quartz (Lippmaa et al. 1980; Spearing and Stebbins 1989) with its crystal structure containing fully condensed SiO_4 tetrahedra [i.e., $\text{Q}^4(4\text{Si})$ sites]. The line width of the resonance varies around $\text{FWHM} = 0.60$ ppm (sample 10, Sif-1, 2071.08, chalk) for the studied nano-quartz samples, whereas it is significantly smaller for the commercial quartz ($\text{FWHM} = 0.22$ ppm). Impurity ions in the quartz lattice may distort the nearest SiO_4 tetrahedra and thereby result in an increased linewidth. Moreover, Si sites near the surface of the crystallites will exhibit some distortion/tension that will contribute to the line width as well. Thus, the significantly smaller line width for the commercial quartz reflects that the crystallites in this sample are much larger than those of the core samples, combined with a smaller fraction of impurity ions in the commercial quartz sample. The crystallites of the nano-quartz samples are similar in size, and therefore the variations in line width primarily reflect variations in impurity ions in the crystal lattices. These results are in agreement with small sizes of CSD values and high values of microstrains that provided a significant broadening of the hkl reflections in the XRD patterns of the studied samples.

Improved information about the surfaces in the nano-quartz samples is obtained from $^{29}\text{Si}\{^1\text{H}\}$ CP/MAS NMR spectra (Fig. 6) acquired using three different CP contact times ($\tau_{\text{CP}} = 2.0, 4.0$, and 8.0 ms). These spectra only include resonances from Si sites with hydroxyl groups or bound water molecules in the near vicinity. The resonance at -107.4 ppm is observed for all nano-quartz samples and with increasing intensity on going from a contact time of 2.0–8.0 ms. The observation of this resonance may reflect that the surface is hydrated or hydroxylated since the resonance originates from $\text{Q}^4(4\text{Si})$ sites with structural environments in which Si cations interact directly with hydroxyls or water molecules. Therefore, this resonance most likely originates from hydroxylated surfaces formed by aggregation of empty tetrahedral sites that have four adjacent OH^- groups bonded to Si in adjacent tetrahedral sites, the $[\text{4H}]_{\text{Si}}$ hydrogarnet defect (Fig. 7) (McLaren et al. 1983; Shinoda and Aikawa 1993; Cordier et al. 1994; Lin et al. 1994; McConnell 1996; de Leeuw et al. 1999; Rosa et al. 2005). The $^{29}\text{Si}\{^1\text{H}\}$ CP/MAS NMR spectra of the nano-quartz samples also include a peak at higher frequency that seems to originate from two overlapping resonances, corresponding to

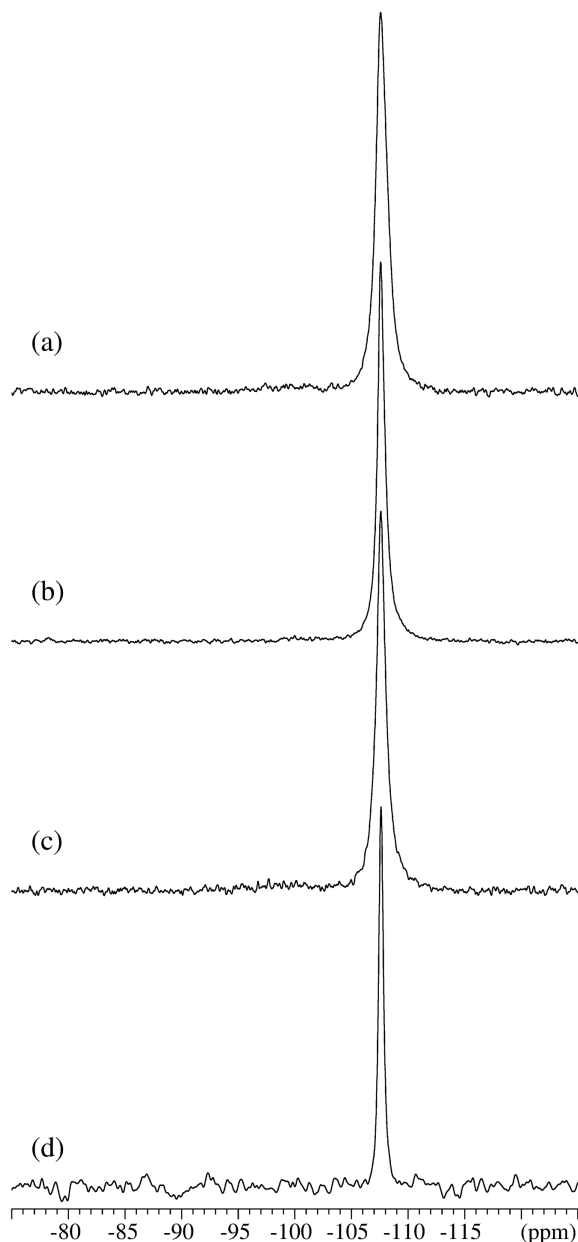


FIGURE 5. ^{29}Si MAS NMR spectra of the three nano-quartz samples (a–c) and commercial quartz (d) acquired at 9.4 T employing a spinning speed of $\nu_R = 6.0$ kHz, a 45° excitation pulse, and a relaxation delay of 300 s. (a) Sample 7 (Sif-1, 2065.0), flint; (b) sample 10 (Sif-1, 2071.08), chalk; and (c) sample 17 (Nana-1, 2135.8), flint.

a high-frequency shoulder at -97.6 to -98.0 ppm and the most intense component in the range -99.6 to -99.8 ppm, for the three nano-quartz samples. Following earlier studies of silica gels and highly siliceous zeolitic framework structures, these resonances reflect the hydroxylated surface and empty tetrahedral sites with OH^- bonded to Si^{4+} . Therefore, the resonances at -99.6 to -99.8 and at -97.6 to -98.0 ppm can be assigned to the overlapping peaks from $(\text{Si}-\text{O})_3\text{-Si}^*\text{-OH}$ sites, which contain the $[4\text{H}]_{\text{Si}}$ hydrogarnet defects distributed in the form of aggregates (Fig. 7) and isolated defects (Fig. 8a), respectively. The $^{29}\text{Si}\{^1\text{H}\}$ CP/MAS

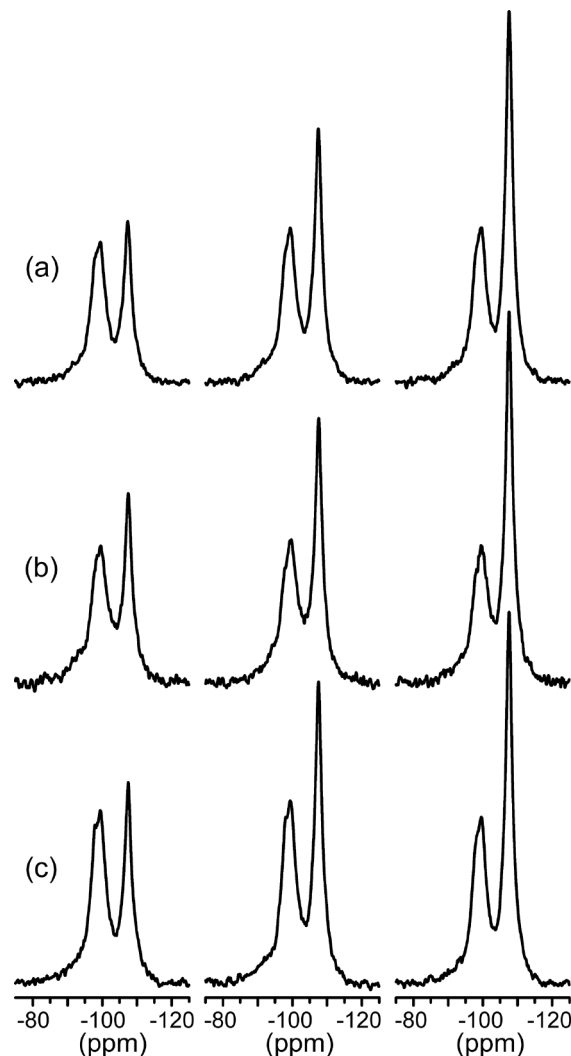


FIGURE 6. $^{29}\text{Si}\{^1\text{H}\}$ CP/MAS NMR spectra (9.4 T) of the three samples (a–c) obtained with a spinning frequency of $\nu_R = 4.0$ kHz, a 4 s relaxation delay and CP contact times of $\tau_{\text{CP}} = 2.0$ ms (left), 4.0 ms (middle), and 8.0 ms (right). (a) Sample 7 (Sif-1, 2065.0), flint; (b) sample 10 (Sif-1, 2071.08), chalk; and (c) sample 17 (Nana-1, 2135.8), flint.

NMR spectra of the studied samples contain also two overlapping peaks located at -94.0 and -91.7 ppm both having very low intensity. The highest intensity for the overlapping -91.7 and -94.0 ppm resonances is observed for the shortest contact time ($\tau_{\text{CP}} = 2.0$ ms), indicating that they originate from Si sites in the very near vicinity of H atoms. Following the information derived from the ^{27}Al MAS NMR spectra of the samples (vide infra), these peaks are ascribed to surface sites of the type $(\text{Si}-\text{O})_2\text{-Si}^*\text{-(OH)}_2$ and $(\text{Si}-\text{O})_2\text{-Si}^*\text{-OH-OAl}$, where the latter represents a $\text{Q}^3(\text{Al})$ site where Si is next nearest neighbor to a hydroxylated Al^{3+} having tetrahedral coordination. The presence of such Al–H defect sites in the studied samples is determined by IR (see below).

Infrared spectroscopy

Eleven samples (nos. 2, 3, 5, 7, 8, 9, 12, 14, 17, 18, and 10) were studied by infrared spectroscopy. The characteristic

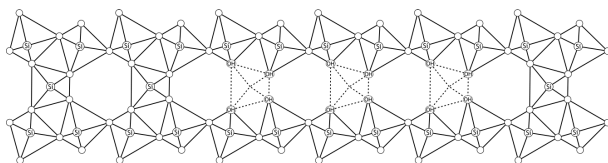


FIGURE 7. Platelets of the aggregated $[4H]_{Si}$ defects parallel to the $(0\bar{1}010)$ plane (modified from Lin et al. 1994).

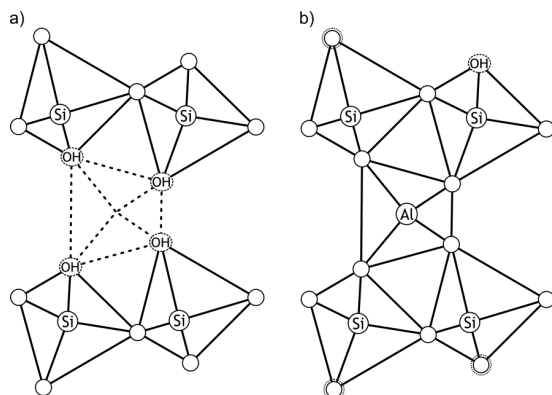


FIGURE 8. Idealized structural fragments of a quartz structure in which (a) a SiO_4 tetrahedron is replaced by a vacant tetrahedron coordinated by 4OH groups; and (b) tetrahedral Si^{4+} is replaced by Al^{3+} and excess of negative charge is compensated by a OH^- group coordinated to one of the four Si^{4+} tetrahedra nearest to the Al^{3+} tetrahedron. Three potentially possible positions for OH^- are shown by double circles.

feature of the IR spectra of the studied nano-quartz samples that strongly distinguish them from spectra of natural quartz of different origins is the presence of two most intense and closely located OH absorption bands at 3588 and 3613 cm^{-1} (Fig. 9). Individual positions and intensities of these partially overlapping bands were determined by second derivatives with a subsequent decomposition procedure (Fig. 9). The ratio of intensities for these bands at 3588 and 3613 cm^{-1} corresponding to the spectra having different integrated intensities of the partially overlapping bands is close to 2:1 (Fig. 10) showing that the origins of these bands are somehow interrelated. Other diagnostic regions of the IR spectra may also be divided into two groups. One of them contains two wide and weak OH absorption bands at 3378–3381 and 3436–3446 cm^{-1} , whereas the second group in addition contains the third band at 3473–3474 cm^{-1} (Fig. 9). Unfortunately, it was not possible to obtain a homogeneous and uniform thickness of the specimens of the different samples for the acquisition of the IR spectra. Moreover, intensities of the absorption bands were varied in the IR spectra obtained from different specimens of the same sample. For example, in different spectra of sample 14 (Sif-1, 2088.3) the maximal and minimal intensities of the bands at 3588 cm^{-1} differ from each other by almost five times. However, after normalization of these spectra to that having the highest intensity of the bands at 3588 and 3613 cm^{-1} , intensities and profiles of the other bands having lower frequencies are almost identical or very similar. It was concluded that the main factor responsible for the observed intensities variation in the spectra from different parts of the same sample is related to

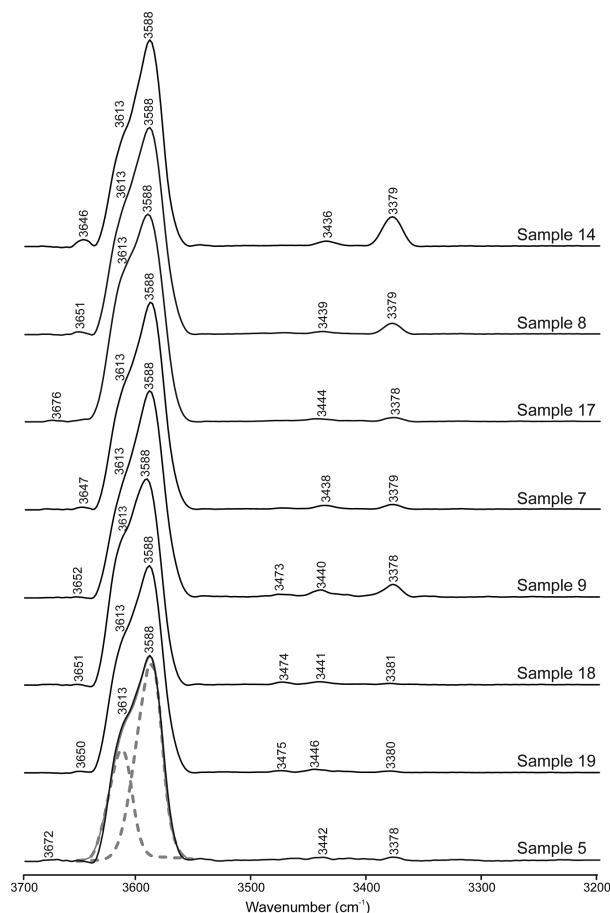


FIGURE 9. Infrared spectra of single pieces of specimens. Random orientation.

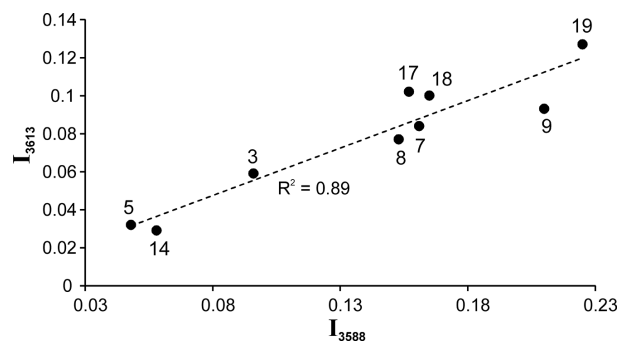


FIGURE 10. Relationship between the maxima of the absorption bands at 3588 and 3613 cm^{-1} .

different thicknesses of these parts. Therefore, intensities of the bands in each spectrum were normalized to that of the band at 3588 cm^{-1} , which was the same in all spectra and equal to 100% in arbitrary units.

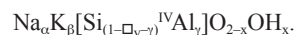
Thermal analysis (DTA-EGA)

Fourteen samples were studied using the thermal analysis, the list of which is given in Tables 3 and 4. The curves for

evolved water (EWA) for all samples have a peak at $\sim 570^\circ\text{C}$ (Fig. 11) and some have an additional peak at $\sim 360^\circ\text{C}$ (Table 3). Two flint samples, 8 (Sif-1, 2066.3) and 9 (Sif-1, 2070.94), have practically identical EWA curves. The H_2O evolution curve for the residue sample 12 (Sif-1, 2071.13) has a double peak at 570 and 650°C (Fig. 11). The amount of water released above 300°C during heating varies from 0.30 to 2.1% (Table 3). Usually, DTA curves for quartz have an exothermic peak at 573°C due to the $\alpha \rightarrow \beta$ transition at this temperature. This peak was not detected in the DTA curves of the nano-quartz samples, despite the fact that this peak usually is very sharp for quartz. This lack of a sharp peak at the $\alpha \rightarrow \beta$ transition temperature probably reflects that the first-order character of the transition is strongly reduced in natural nano-size quartz because of the clamping imposed on each grain by the surrounding nano-crystallites (Rios et al. 2001). In addition, one has to take into account that the hydrogarnet defect incorporation in quartz is an endothermic reaction (Rosa et al. 2005) and thus, the hydrogarnet dehydroxylation also should have the same nature. Surface-adsorbed H_2O is released at low temperature, up to 200°C . The release of the H_2O at $\sim 550^\circ\text{C}$ seen in EWA for the North Sea quartz (Fig. 11; Table 3) corresponds to the release of OH^- from the $[\text{4H}]_{\text{Si}}$ defect at 550°C observed by McLaren et al. (1983), but includes also the release of OH^- from $\text{Al}(\text{OH})_3$ at the particle surfaces. OH^- groups at the surfaces of silica minerals are released continuously as the temperature increases (Segnit et al. 1965).

Structural formulas

The samples contain 0.11–0.73% Al_2O_3 , 0.016–0.60% Na_2O , and 0–0.22% K_2O (Table 2, these values were estimated with relative errors 5–15%). According to the ^{27}Al MAS NMR spectra, each sample contains tetrahedral and octahedral Al sites (Table 2). The results of thermal analysis showed that the weight content of H_2O released from the samples heated from 300 to 560 – 600°C varies from 0.30 to 2.10% with relative errors of 10% or lower (Table 3). According to the ^{27}Al MAS NMR data, each sample can be considered as a physical mixture of two phases: bulk nano-quartz incorporating tetrahedral Al sites and an $\text{Al}(\text{OH})_3$ phase with octahedrally coordinated Al formed at the surface of nano-crystals of quartz. In the general form, the structural formula may be presented as:



The total molar amount of Al was calculated using the ratio of corresponding weight amount of Al_2O_3 to its molar weight, whereas the amount of $^{\text{IV}}\text{Al}$ and $^{\text{VI}}\text{Al}$ were determined using the total molecular amount of Al and the $^{\text{IV}}\text{Al}/^{\text{VI}}\text{Al}$ molar ratio from the ^{27}Al MAS NMR spectrum of the sample. Na_α and K_β are molar amounts of Na and K in the sample, OH_x is equal to the difference between the total molar amount of OH groups in the sample and that related to the molar amount of $^{\text{VI}}\text{Al}$ corresponding to $\text{Al}(\text{OH})_3$. The value of OH_x consists of two parts, one of which compensates the extra positive charge of Na, K, $^{\text{IV}}\text{Al}$ that is equal

TABLE 3. Differential thermal and evolved water analysis (DTA-EWA), 200–800 $^\circ\text{C}$

Well	No.	Depth (m)	Depth (feet)	Sample	Peak T ($^\circ\text{C}$)	% H_2O	Peak T ($^\circ\text{C}$)	% H_2O
Rigs-1	2	2794.3	9167.5	Quartz layer			618	1.2
Rigs-1	3	2826.84	9274.41	flint	379	0.13	603	0.17
Sif-1	5	2057.63	6750+23pt2	flint			560	1.1
Sif-1	7	2065.0	6774'6"stk9	flint			572	1.04
Sif-1	8	2066.3	6779'4"	flint			565, 627	0.77
Sif-1	9	2070.94	6793'2"x3	flint			565	0.73
Sif-1	10	2071.08	6793'2"stk1	residue, chalk			599, 697	1.9
Sif-1	11	2071.11	6793'2"stk2	residue, chalk			605, 710	1.05
Sif-1	12	2071.13	6793'2"stk3	residue, chalk			569, 650	2.1
Sif-1	13	2079.34	6820'4"+53	flint			556 (715) ^a	0.81
Sif-1	14	2088.3	6851'6"	flint			591	1.3
Nana-1	17	2135.8	7007'6"	flint	355	0.2	533	1.7
M-10	18	1963.52	6442'k3b4	flint			597 (760) ^a	0.87
E-5	19	2078.74	6820'1"stk1R	flint(IR)			592	0.87

^a Small shoulder; errors: % H_2O – 10%.

TABLE 4. Chemical formulas for the quartz samples from ^{27}Al NMR, atomic absorption spectrometry, and thermal analysis (EGA)

Well	Sample	Depth (m)	Mol K	Mol Na	Mol $^{\text{IV}}\text{Al}$	Mol $^{\text{VI}}\text{Al}$	Mol Al	Mol Si	Vacancy tetrahedral	Mol O	Mol OH_y	Mol OH_m	Mol OH ($^{\text{VI}}\text{Al}$) ^a
Rigs-1	2 quartz	2794.3	0.0001	0.0009	0.0012	0.0003	0.0015	0.982	0.0164	1.934	0.0656	0.0002	0.0009
Rigs-1	3 flint	2826.84	0.0000	0.0007	0.0016	0.0002	0.0018	0.995	0.0038	1.985	0.0152	0.0009	0.0006
Sif-1	5 flint	2057.63	0.0016	0.0021	0.0013	0.0001	0.0014	0.984	0.0146	1.942	0.0584	0.0024	0.0003
Sif-1	7 flint	2065.0	0.0009	0.0012	0.0022	0.0005	0.0026	0.984	0.0140	1.944	0.0562	0.0001	0.0015
Sif-1	8 flint	2066.3	0.0010	0.0012	0.0015	0.0004	0.0019	0.988	0.0102	1.959	0.0408	0.0008	0.0012
Sif-1	9 flint	2070.94	0.0004	0.0015	0.0028	0.0004	0.0032	0.988	0.0096	1.962	0.0384	0.0009	0.0012
Sif-1	10 residue	2071.08	0.0023	0.0097	0.0060	0.0012	0.0072	0.969	0.0240	1.904	0.0959	0.0060	0.0035
Sif-1	11 residue	2071.11	0.0001	0.0009	0.0018	0.0003	0.0021	0.984	0.0141	1.943	0.0565	0.0009	0.0009
Sif-1	12 residue	2071.13	0.0009	0.0011	0.0024	0.0015	0.0038	0.970	0.0279	1.888	0.1118	0.0004	0.0044
Sif-1	13 flint	2079.34	0.0006	0.0023	0.0027	0.0006	0.0033	0.986	0.0108	1.957	0.0430	0.0002	0.0018
Sif-1	14 flint	2088.3	0.0001	0.0008	0.0015	0.0006	0.0021	0.981	0.0175	1.930	0.0699	0.0005	0.0018
Nana-1	17 flint	2135.8	0.0004	0.0014	0.0009	0.0002	0.0011	0.973	0.0260	1.896	0.1040	0.0009	0.0006
M-10	18 flint	1963.52	0.0000	0.0018	0.0026	0.0005	0.0031	0.986	0.0115	1.954	0.0460	0.0008	0.0015
E-5	19 flint	2078.74	0.0000	0.0003	0.0030	0.0007	0.0037	0.987	0.0109	1.957	0.0435	0.0028	0.0021

^a OH assumed to be bonded to $^{\text{VI}}\text{Al}$.

to $|(Na_{\alpha} + K_{\beta}) - {}^{IV}Al_i| = |m|$, and the other part that is equal to $OH_y = OH_x - |m|$. The number of vacant tetrahedra is $\square_y = OH_y/4$. In the formula the total negative charge ($4-3\times$) is equal to that of the positive charge if the amount of Si is $(1 - \square_y - \gamma)$.

Oxygen isotopic composition

The oxygen isotopic composition of 14 studied samples (Table 5) shows $\delta^{18}O$ values of 24.9 to 29.4‰. While the $\delta^{18}O$ value for sample 18 at the most shallow depth (1963.52 m in Well M-10) is the highest reported (29.4‰), and the two lowest measured $\delta^{18}O$ values (identical at 24.9‰) are at the greatest depths (respectively 2794.3 and 2826.84 m in Rigs-1), see Figure 12, we do not argue that there is convincing evidence for either a systematic, or indeed stepwise, trend with depth: 10 $\delta^{18}O$ values within a narrow depth range of 2057.63 to 2135.8 m have an analytically significant $\delta^{18}O$ variation of 2.5‰ (26.4–28.9). While the details of the $\delta^{18}O$ variations (e.g., with age and syn-depositional characteristics such as temperature, water $\delta^{18}O$, etc.; and/or with post-depositional effects) will likely prove informative, such consideration is beyond the remit of this paper, and so we focus instead on first-order interpretation.

The overall mean of the 13 measured $\delta^{18}O$ values is $27.5 \pm 2.6\text{‰}$ (1σ), and excluding the three extreme values (see Fig. 12) the 10 remaining average to $27.8 \pm 0.9\text{‰}$. These values are similar to those for primary marine silica (26.6–27.7‰ for purified material) precipitated in the South Oman Salt Basin at the Precambrian/Cambrian boundary (Ramseyer et al. 2013).

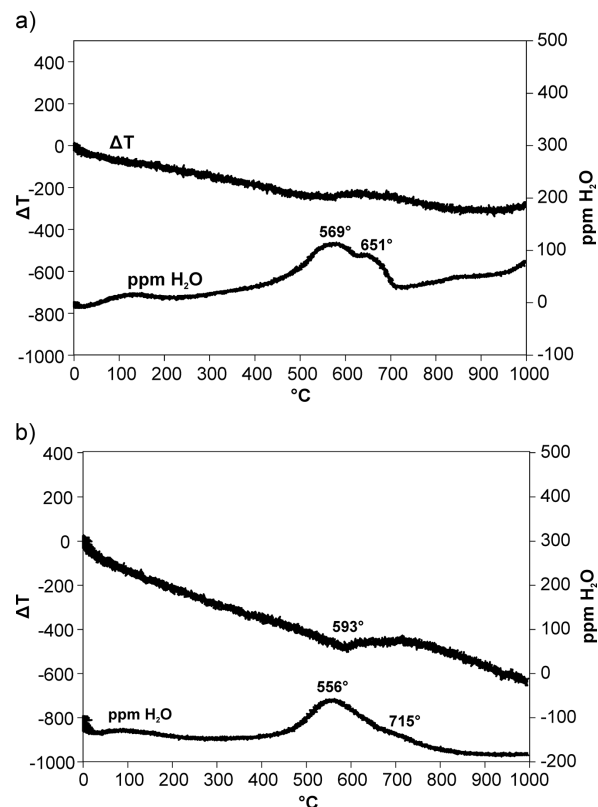


FIGURE 11. Differential thermal analysis (ΔT) with infrared determination of evolved H_2O ; (a) sample 12 (Sif-1, 2071.13) residue from chalk sample; (b) sample 13 (Sif-1, 2079.34), flint.

Using the quartz-water oxygen isotope fractionation calibration suggested by Matsuhisa et al. (1979), the argument is not significantly affected if the amorphous silica calibration of Kita et al. (1985) is substituted, and using an estimated seawater $\delta^{18}O$ of -1.2‰ on a deglaciated Earth (see Jaffres et al. 2007 for a detailed review of seawater $\delta^{18}O$), then the temperature estimated from $27.8 \pm 0.9\text{‰}$ is $48.5 \pm 4^\circ C$. The $\pm 4^\circ C$ estimate of precision arises solely from propagation of the $\pm 0.9\text{‰}$ 1σ spread on measured silica $\delta^{18}O$. On the question of accuracy, we note that a 1‰ decrease in the assumed seawater $\delta^{18}O$ would result in a temperature decrease of $4.8^\circ C$ and that there is also an unquantified error arising from the assumed oxygen isotope equilibrium calibration. There are also issues on whether the measured silica $\delta^{18}O$ was established at the time of precipitation or during a subsequent oxygen isotope exchange process. Notwithstanding all of these concerns, the best estimate of several tens of degrees Celsius (as opposed to estimates different by an order of magnitude, say) does not seem unreasonable at all for the Tertiary sea.

DISCUSSION

Identification of the weak hydrogen absorption bands in the IR spectra

Defects related to $[4H]_{Si}$ hydrogarnet defects. The absorption bands at 3585 cm^{-1} were observed in the IR spectra of synthetic and natural quartz, amethyst (Kats 1962; Chakraborty and Lehmann 1976; Paterson 1982; Stalder and Konzett 2012;

TABLE 5. Oxygen isotope data

No.	Sample	Depth (m)	$\delta^{18}O$ (‰V-SMOV)
2	Rigs-1, 9167.5'	2794.3	24.9
3	Rigs-1, 9274.41'	2826.84	24.9
5	Sif-1, 6750 pr.2	2057.63	28.5
7	Sif-1, 6774' stk9	2065	28.3
8	Sif-1, 6779'4"	2066.3	28.4
10	Sif-1, 6793' stk1	2071.08	26.4
11	Sif-1, 6793' stk2	2071.11	26.8
12	Sif-1, 6793' stk3	2071.13	27.6
13	Sif-1, 6820	2079.34	27.9
14	Sif-1, 6851'a	2088.3	26.5
17	Nana-1, 7007'	2135.8	28.9
18	M-10, 6442	1963.52	29.4
19	E-5, 6820	2078.74	28.8

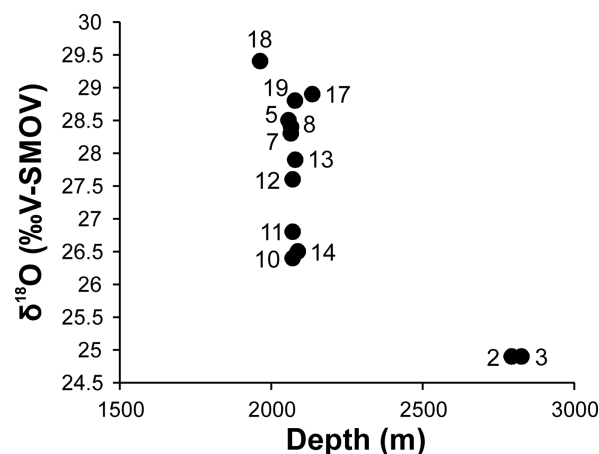


FIGURE 12. Oxygen isotope composition vs. depth of sample.

Stalder and Neuser 2013), and chalcedony (Fron del 1982). This band is assigned to the hydrous defect generated by substitution of Si^{4+} by 4H^+ and is referred to as the $[\text{4H}]_{\text{Si}}$ or hydrogarnet defect. The highest intensity band is observed at 3588 cm^{-1} for all studied samples (Fig. 9) showing that this defect plays the decisive role among all hydrogen defects in their structures. Application of first-principle calculations to investigate the atomic geometries and thermodynamic properties of water-related defects in α -quartz showed that the $[\text{4H}]_{\text{Si}}$ defect is thermodynamically most stable and aggregates to form platelets in the form of micro-cracks with hydroxylated surfaces on both their sides (Lin et al. 1994; McConnell et al. 1995; McConnell 1996; de Leeuw et al. 1999; Rosa et al. 2005). The origin of the other strong absorption band at 3613 cm^{-1} in the IR spectra is not assigned in the literature although a weak band at 3615 cm^{-1} together with a strong band at 3585 cm^{-1} was observed in the spectra of amethyst (Kats 1962) and chalcedony (Fron del 1982). One possible origin of the band at 3613 cm^{-1} is that the nano-quartz structure along with aggregation of $[\text{4H}]_{\text{Si}}$ defects forming a hydroxylated surface contains isolated $[\text{4H}]_{\text{Si}}$ defects (Fig. 8a). According to calculations of Rosa et al. (2005) the formation of planar defects under thermodynamic equilibrium conditions is energetically more favorable than that of isolated $[\text{4H}]_{\text{Si}}$ defects. However, the formation of nano-quartz probably occurred under non-equilibrium conditions that may be favorable for the formation of isolated defects. Thus, the bands at 3588 and 3613 cm^{-1} may correspond to the platelet and isolated $[\text{4H}]_{\text{Si}}$ defects, respectively. In this case, one has to assume that for isolated defects hydrogen bond lengths between H and O atoms should on average be longer as compared with those in the platelet defects providing the higher frequency for the isolated defects. The linear relationship between intensities of the absorption bands at 3588 and 3613 cm^{-1} observed for samples having different thicknesses can be considered as indirect evidence of their similar origin (Fig. 10).

In general, these results are in agreement with the interpretation of the structural imperfections in nano-quartz samples obtained from the $^{29}\text{Si}\{^1\text{H}\}$ CP/MAS NMR spectra (Fig. 6). Indeed, the clear observation of the resonance at -107.4 ppm at different CP contact times is in accordance with the presence of $[\text{4H}]_{\text{Si}}$ defect sites, whereas the appearance of the resonance at -97.67 to -98.0 ppm shows that Si cations interact directly with the hydroxyls on the surface formed by hydrogarnet defects. The presence of two intense bands in the IR spectra is in agreement with two resonance peaks at -97.6 to -98.0 and at -99.6 to -99.8 ppm , observed in the $^{29}\text{Si}\{^1\text{H}\}$ CP/MAS NMR spectra of the nano-quartz samples. Both resonances originate from sites of the type $(\text{Si}-\text{O})_3-\text{Si}^*-\text{OH}$ and are ascribed to Si neighboring the $[\text{4H}]_{\text{Si}}$ defects. The resonance at -97.6 to -98.0 ppm is clearly broader than the -99.6 to -99.8 ppm peak and it is tentatively assigned to the aggregated $[\text{4H}]_{\text{Si}}$ defects as a result of its larger linewidth and its shift toward higher frequency, the latter being expected for the more open structure around the aggregated defects as compared to the isolated defects. Thus, the narrow peak at lowest frequency (-99.6 to -99.8 ppm) is ascribed to isolated $[\text{4H}]_{\text{Si}}$ defects. As will be shown below, these results are in accordance with those following from the relationships between the a and c unit-cell parameters as well as between the OH_y content and the

unit-cell parameters. However, the assignment of the overlapping $(\text{Si}-\text{O})_3-\text{Si}^*-\text{OH}$ peaks is not unambiguous and will require further $^{29}\text{Si}\{^1\text{H}\}$ CP/MAS NMR experiments, e.g., on quartz samples where there is a clear distinction between aggregated and isolated $[\text{4H}]_{\text{Si}}$ defect sites.

The IR region related with Al–H defects. The characteristic feature of the IR spectra of natural quartz is the presence of a strong absorption triplet at 3310 , 3374 , and 3440 cm^{-1} (Kats 1962; Bambauer 1963; Brown and Kahan 1975; Aines and Rossman 1984), which were assigned to coupled substitutions Si^{4+} for $\text{Al}^{3+}+\text{H}^+$ forming so-called Al–H defects. Based on the orientation of the O–H vectors coordinated to tetrahedral Al^{3+} cations, Kats (1962) concluded that there are two types of Al–H defects where one is related to the 3310 cm^{-1} band and the other to the pair of 3374 and 3440 cm^{-1} bands. The first type of Al–H defects results from H^+ bound between the two non-equivalent oxygen atoms in the Al^{3+} tetrahedron and the 3374 and 3440 cm^{-1} pair arises from OH^- group in the Al^{3+} tetrahedron with O–H vectors pointing into the c axis “channel” forming an angle 75° with the c axis. Stalder and Konzett (2012) and Stalder and Neuser (2013) investigated OH defects in detrital quartz grains and identified also the absorption triplet at 3310 , 3378 , and 3430 cm^{-1} . In the IR spectra of the studied samples, the absorption band at 3378 cm^{-1} corresponding to an Al–H defect is partially overlapped with an absorption band at 3384 cm^{-1} of Na related to an OH defect (Aines and Rossman 1984). Positions of the sharp bands, at 3440 and 3330 cm^{-1} , are clearly distinguishable and according to Chakraborty and Lehmann (1976) the 3440 cm^{-1} band should correspond to H^+ bonded directly to Si^{4+} , whereas the band at 3430 cm^{-1} corresponds to an Al–H defect. In different IR spectra of the studied samples two wide bands at 3430 and 3440 cm^{-1} appear with different occurrence probability and the resulting position of the overlapping bands varied from 3436 to 3444 cm^{-1} (Fig. 9). Finally, according to Müller and Koch-Müller (2009) and Baron et al. (2015) the Li-specific OH absorption band is located at 3480 and 3483 cm^{-1} , respectively. Therefore, the origin of the very weak band at 3473 – 3474 cm^{-1} occasionally observed in the studied spectra probably has the same origin.

The relationship between the nature and location of the charge-compensation ions and the features of the IR spectra. Aluminum is the most common trace element in natural and synthetic quartz samples and other impurity elements (e.g., H, Na, Li, K) are incorporated in quartz structures to compensate the negative charge originating from substitution of Si^{4+} by Al^{3+} in the tetrahedral sites of the quartz framework. The charge compensation usually takes place by formation of local structural arrangements, $[\text{AlO}_4/\text{M}^+]^\circ$ defects ($\text{M}^+ = \text{H}^+, \text{Na}^+, \text{Li}^+, \text{and K}^+$), which according to Botis and Pan (2009) are stable in the quartz structure. Therefore, in natural quartz tetrahedral Al stands generally in an approximately stoichiometric relation to the content of (OH) and trace alkalis (Botis and Pan 2009).

The analysis of the IR spectra of the studied samples shows some unusual relationships between IR particular features and location of the cation compensators. To demonstrate this, let us consider at first the relationship between the amount of tetrahedral Al^{3+} cations, C_{Al} , and the total content of Na^+ and K^+ , $C_{(\text{Na}+\text{K})}$, in the structural formulas (Fig. 13; Table 4). All samples can be divided into three groups: in one of them $C_{\text{Al}} > C_{(\text{Na}+\text{K})}$, in the

other $C_{\text{Al}} < C_{(\text{Na}+\text{K})}$, and in the last one $C_{\text{Al}} = C_{(\text{Na}+\text{K})}$ (Fig. 13). In sample 19 (E-5, 2078.74) of the first group the content of $C_{(\text{Na}+\text{K})}$ is negligible (0.0003) in comparison to that of C_{Al} (0.0030). One could expect that the IR spectrum of the sample would contain strong absorption bands corresponding to Al–H defects. In contrast, the intensity modulations observed in the diagnostic region (3200–3500 cm^{-1}) of the spectrum can hardly be distinguished from the background. To explain the observed inconsistency, one has to take into account that some of the studied samples contain local structural fragments in which a negative charge generated by substitution of Si^{4+} for Al^{3+} is compensated by hydration of Si^{4+} placed in the second coordination sphere of $^{\text{IV}}\text{Al}$ (Fig. 8b). Therefore, the IR spectrum of sample 19 (E-5, 2078.74) does not contain absorption bands related to Al–H defects. This way of local charge compensation assists the interpretation of particular features in the IR spectra of samples 9 (Sif-1, 2070.94) and 18 (M-10, 1963.52), both of which have almost the same amounts of (Na+K) and $^{\text{IV}}\text{Al}$, respectively, equal to 0.0019 and 0.0028 for the first and 0.0018 and 0.0026 for the second sample (Table 4). In contrast, the IR spectra of the samples differ from each other by the distribution of intensities of the absorption bands in their diagnostic regions. The IR spectrum of sample 18 (M-10, 1963.52) is quite similar to that of sample 19 (E-5, 2078.74) because the intensities of the bands in the diagnostic region are negligibly small. In contrast, the characteristic absorption bands at 3378 and 3440 cm^{-1} are clearly distinguishable in the spectrum of sample 9 (Sif-1, 2070.94) (Fig. 9). To explain these observations, one has to take into account, that according to Botis and Pan (2009) the structure of both samples contains local $[\text{AlO}_4/(\text{Na}+\text{K})]^\circ$ defects and that the amount of these should be equal to the content of (Na+K) in each sample. In the compared samples the tetrahedral Al^{3+} cations, whose amount is equal to $C_{\text{Al}} - C_{(\text{Na}+\text{K})}$, may have different local positions. In sample 18 (M-10, 1963.52) the charge compensation most probably took

place according to the local environment shown in Figure 8 where an OH^- group coordinated one of the four tetrahedral Si^{4+} closely located to the Al^{3+} tetrahedron. Therefore, the diagnostic region of the IR spectrum of sample 18 (M-10, 1963.52) is similar to that of sample 19 (E-5, 2078.74) (Fig. 8). In contrast, in samples 9 (Sif-1, 2070.94) and 14 (Sif-1, 2088.3) the negative charge originating from the tetrahedral Al^{3+} cations remaining after formation of electroneutral structural arrangements $[\text{AlO}_4/\text{Na}^+]^\circ$ were compensated by formation of Al–H defects. As a result, in the IR spectra of both samples the absorption bands corresponding to Al–H defects are observed (Fig. 9).

Interpretation of the IR spectra of the flint samples is not always unambiguous. As mentioned earlier, for determination of the chemical composition of these samples, raw material was used and probably some amount of Na was adsorbed from the pore water. Because of this uncertainty, the influence on IR effects of a high concentration of $\text{NaOH}+\text{KOH}$ in some of the studied samples was not unequivocally solved within the frame of this study.

Unit-cell parameters of nano-quartz samples as indicators of their main structural imperfections

Comparison of the unit-cell parameters of nano-quartz and well-crystallized quartz. The main feature of the nano-quartz is that tetrahedral vacancies constitute up to 0.03 per 2 anions, whereas Al^{3+} occupies less than 0.006 per 2 anions of the tetrahedral sites (Table 4) and OH^- amounts to up to 0.112 per 2 anions. The tetrahedral vacancies with 4OH^- anions adjacent are therefore for the nano-quartz the most significant deviation from the ideal formula for α -quartz and the main contributors to the deviation of the unit-cell parameters from those of well-crystallized natural quartz. The cell dimensions of the nano-quartz from the chalk and the flint are significantly larger (4.9164–4.9195 Å for the a parameter and from 5.4047–5.4097 Å for the c parameter, Table 1) than the dimensions of natural and synthetic quartz being 4.9121–4.9149 Å for the a cell parameter and from 5.4038–5.4054 Å for the c cell parameter (Table 6) (Cohen and Sumner 1958; Afanas'eva et al. 1960; Hurst and Storch 1981). The presence of tetrahedral vacancies and Al^{3+} ions replacing Si^{4+} should result in distinct $(\text{Si}-\text{O})_3-\text{Si}^*-\text{OH}$ and $(\text{Si}-\text{O})_3-\text{Si}^*-\text{O}-\text{Al}$ resonances in the single-pulse ^{29}Si MAS NMR spectra (Fig. 5). ^{29}Si spin-lattice relaxation times of $T_1 = 3000\text{--}4000$ s have been reported for α -quartz at ambient temperature (Spearing et al. 1992), implying the single-pulse ^{29}Si MAS NMR spectra in Figure 5 only detects a very small fraction of the total intensity (15–19%), considering the actual experimental conditions (45° excitation pulse, 300 s relaxation delay). Thus, the absence of clear resonances from ^{29}Si neighboring the defects in nano-quartz is tentatively ascribed to very long relaxation times for these sites. However, the resonances from the $[\text{4H}]_{\text{Si}}$ defects, $(\text{Si}-\text{O})_3-\text{Si}^*-\text{OH}$ sites, are clearly seen at -97.6 to -99.8 ppm in the $^{29}\text{Si}\{^1\text{H}\}$ CP/MAS NMR spectra, reflecting the fact that the intensity in these experiments depends on the ^1H spin-lattice relaxation, which is generally orders of magnitude faster than the ^{29}Si spin-lattice relaxation for silicate minerals (Skibsted et al. 1995).

Space orientation of platelets formed by aggregated $[\text{4H}]_{\text{Si}}$ defects. As was mentioned, McLaren et al. (1983) suggested that

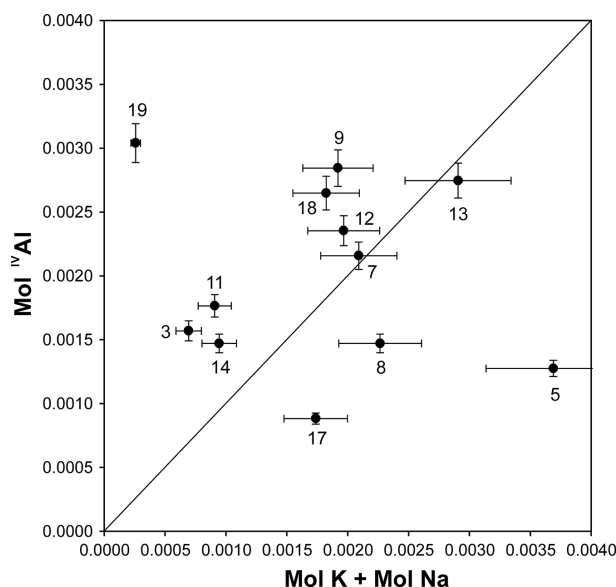


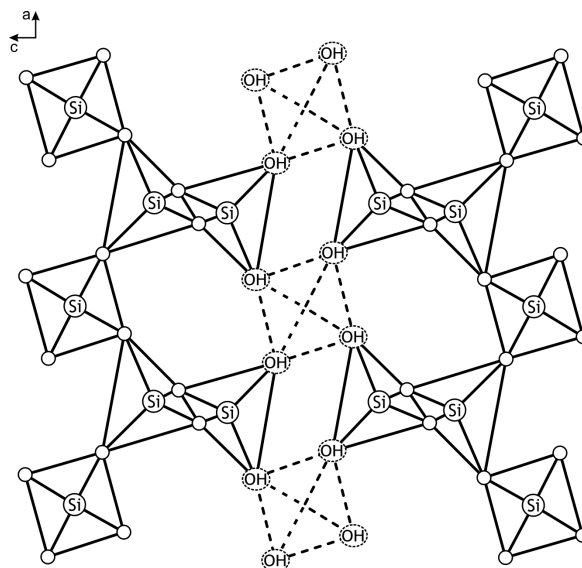
FIGURE 13. Relationship between the contents of mol $^{\text{IV}}\text{Al}$ and mol (K+Na).

TABLE 6. Ranges for the a and c unit-cell parameters compared with literature data

	Natural samples		Synthetic samples	
	a unit-cell parameter	c unit-cell parameter	a unit-cell parameter	c unit-cell parameter
Present investigation	4.9164–4.9195 Å	5.4047–5.4097 Å		
Anafas'eva et al. (1960)	4.9121–4.9137 Å	5.4038–5.4051 Å		
Cohen and Sumner (1958)	4.9131–4.9138 Å	5.4047–5.4052 Å	4.9132–4.9139 Å	5.4049–5.4052 Å
Hurst and Storch (1981)	4.9133–4.9140 Å	5.4044–5.4054 Å		
Brice (1980)	4.9126–4.9149 Å		4.9133–4.9145 Å	

hydrogen is incorporated in the wet quartz structure as $[4H]_{Si}$ defects. On heating these defects migrated toward each other to form clusters. According to the TEM experiments of McLaren et al. (1983), the increase in temperature transformed the aggregated $[4H]_{Si}$ defects into bubbles of high-pressure water fluid lying on dislocation loops with Burgers vector $\mathbf{b} = \mathbf{a}/3 \langle 11\bar{2}0 \rangle$ parallel to the $(0\bar{1}10)$ or $(10\bar{1}0)$ planes. This model was partly reconsidered by Lin et al. (1994), McConnell et al. (1995), and McConnell (1996) who supposed that at a high $[4H]_{Si}$ concentration in wet quartz these defects segregate to form planar precipitate rafts or platelets lying in the $(0\bar{1}10)$ plane (Fig. 7). In contrast, the simulation results of de Leeuw et al. (1999) showed that aggregation of $[4H]_{Si}$ defects forming the (0001) OH surface is more stable than those forming the $(10\bar{1}0)$, $(10\bar{1}1)$, and $(10\bar{1}\bar{1})$ OH surfaces. Rosa et al. (2005) also analyzed thermodynamic properties of a quartz containing platelets of $[4H]_{Si}$ defects lying in the $(0\bar{1}10)$ plane and found that platelets lying in this plane are less stable than the platelets in the (0001) plane (Fig. 14). Moreover, Rosa et al. (2005) considered the influence of dilation of the lattice parameters a and c on the structural and energetic properties of the platelet defects. It was found that for the atomic configuration in which the platelets lie in the (0001) plane, relaxation of the a parameter has negligible effect on the formation energies and the geometry. In contrast, the final most stable atomic geometry was accompanied by increasing the c parameter. At the same time, these authors emphasized that their calculations were carried out assuming thermodynamic equilibrium. Therefore, they do not discard the possibility that the $(0\bar{1}10)$ platelets may be kinetically stabilized. It seems plausible that the studied nano-quartz samples were formed in thermodynamically non-equilibrium conditions. The results obtained by MAS NMR and IR spectroscopic methods in this work are in agreement with the presence of hydroxylated surfaces formed by the aggregated $[4H]_{Si}$ defects but their space orientation in nano-quartz remains uncertain. To solve this problem one has to take into account that the size of the $[4H]_{Si}$ structural unit is larger than the SiO_4 unit. Therefore, it is likely that the replacement of Si by 4H in the same oxygen framework should provide preferential expansion of the lattice along the normal to the platelets formed by aggregated $[4H]_{Si}$ defects, that is either to the (0001) or $(0\bar{1}10)$ planes.

Relationships between a and c parameters. The a and c parameters of most samples follow a linear interdependence, but the positions of some of the samples deviate significantly from the linear regression (Fig. 15). However, the positional distribution of these samples has some particularly interesting features. The most remarkable one is that the positions for about 50% of the samples (all of which are flints) are located along the gray line almost parallel to the c axis (i.e., the abscissa) from sample 3 (Rigs-1, 2826.84) having lower c value to sample 7 (Sif-1, 2065.0) having higher c value (Fig. 15). These samples have practically the same a

**FIGURE 14.** The idealized configuration of the hydrogarnet defects forming an OH surface parallel to the (0001) plane of the quartz structure. O atoms are white circles, positions of Si atoms and OH hydroxyls are marked in the figure.

values, from 4.9169 Å (sample 3) to 4.9171 Å (sample 7) (Table 1; Fig. 15). In contrast, the c values for this set of samples increase from 5.4047 to 5.4071 Å, that is by up to 0.0024 Å. Similarly, samples 18 (M-10, 1963.52) and 11 (Sif-1, 2071.11) have almost the same a value (4.9164 and 4.9166 Å), whereas the c value of the parameter of sample 11 (5.4072 Å) is higher than that of sample 18 (5.4059 Å) by 0.0013 Å (Table 1; Fig. 15). Among the samples deviating strongly from the linear regression is sample 10 (Sif-1, 2071.08) that is also unusual with respect to its cation composition. According to the chemical formula of sample 10, the content of (Na+K) (0.0145) is 3 to 10 times higher than those in other samples (Table 4). The high content of (Na+K) cations, which are located into channels of the quartz structure, strongly increases the a parameter value of the sample (Afanas'eva et al. 1960). For this reason the position of sample 10 falls far from those of the other samples (Fig. 15).

For idealized equilibrium conditions the formation of platelets lying parallel to the (0001) plane should increase only the c parameter. The tendency of increasing a parameter observed in Figure 15 may be due to the following: first, possible isolated $[4H]_{Si}$ defects should increase the cell volume homogeneously in different crystallographic directions. On the other hand, different contents and distributions of structural defects related to tetrahedral Al^{3+} , H^+ , Na^+ , and K^+ impurities have different influence on the unit-cell parameters. Nevertheless, the regularities in the

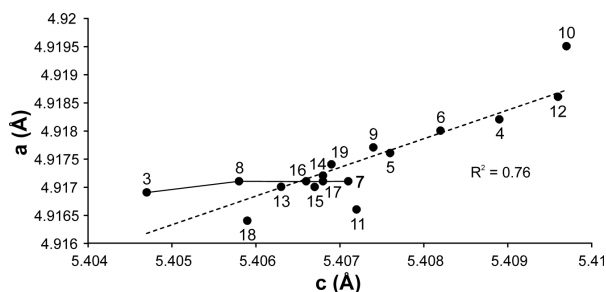


FIGURE 15. Relationship between the a and c unit-cell parameters of the studied samples. The almost horizontal thin line joins positions of the samples having identical or very similar values of the a parameter.

relationships between the a and c parameters, observed in Figure 15, can be considered as independent evidence that the planar defects of hydrogen atoms in the nano-quartz are parallel to the (0001) plane. Knowledge of the space orientation of the aggregated $[4H]_{Si}$ defects, the presence of two strong absorption bands at 3588 and 3613 cm^{-1} and the relationship between their intensities (2:1) allows us to assume that these two bands correspond to two different types of $[4H]_{Si}$ defects in a nano-quartz structure. In one type, aggregated $[4H]_{Si}$ defects form OH surfaces parallel to (0001) plane (Fig. 14), whereas in the second type the $[4H]_{Si}$ defects is probably represented by individual hydrogarnet defects (Fig. 8a).

Direct evidence of decisive and selective influence of $[4H]_{Si}$ defects on the unit-cell parameters of nano-quartz. The origin of the main regularities between the a and c parameters of the unit cells of the studied samples becomes more clear from the analysis of the relationships between the unit-cell parameters and amounts of OH^- groups, designated OH_y , forming $[4H]_{Si}$ defects (Tables 1 and 4). At first let us consider some features observed between the a parameters and the OH_y values. As can be seen in Figure 16a for the majority of the samples, the a parameter values are almost independent of the OH_y . Indeed, the a parameter of a subset of samples 3, 8, 13, 7, and 14 varies in the very narrow interval from 4.9169 to 4.9172 Å, whereas the OH_y values increase from 0.0152 to 0.0699 (Tables 1 and 4, Fig. 16a). In contrast, as can be seen in Figure 16b for the same set of samples, values of the c parameter increase significantly from 5.4047 to 5.4071 Å. This means, first, that the higher the OH_y value the higher value of the c parameter and, second, that most probably the majority of $[4H]_{Si}$ defects were formed as aggregated platelets parallel to the (0001) plane. These conclusions are in agreement with the relationship between the a and c parameters for the samples according to which the increase of the c parameter may occur at the same time as values of the a parameter are within error (Fig. 15). Similarly, the mutual relationship between the unit-cell parameters and the OH_y values is observed for the pair of the samples 18 and 11 whose a parameters are almost the same (4.9164 and 4.9166 Å), whereas the content of OH_y in sample 11 (0.0565) is higher than that (0.0460) in sample 18 (Fig. 16a). In agreement with the regularity mentioned above, the c parameter of sample 18 (5.4059 Å) is lower than that of sample 11 (5.4072 Å) (Fig. 16b).

The amount of OH_y may also control the c parameter for the nano-quartz samples having different values of the a parameter. For example, samples 18 and 8 have different a parameters (4.9164 and 4.9171 Å), close amounts of OH_y (0.0460 and 0.0408) and

identical c values (5.4059 and 5.4058 Å) (Fig. 15). The difference between the a parameters in these samples is due to a high amount of K^+ (0.0010) in the total amount of alkaline cations (0.0022) in sample 8 relative to the content of the Na^+ cations in sample 18 (0.0018). Moreover, in sample 8, $C_{(K+Na)} > C_{Al}$, whereas $C_{Al} > C_{(Na+K)}$ in sample 18 (Table 4). Therefore, the high amount of KOH and NaOH structural units located in the structural channels causes the higher value of the a parameter in sample 8 in comparison with that of sample 18. However, similar values for OH_y in these samples result in almost the same values of their c parameters (Fig. 16b). The results described are in agreement with the interrelations between the a and c parameters of samples 8 and 18 (Fig. 15).

An even more remarkable selective influence of $[4H]_{Si}$ defects on the a and c unit-cell parameters for nano-quartz is seen from the comparison of the unit-cell parameters and chemical composition of samples 12 and 10. As mentioned previously these samples differ from each other by the amounts of alkaline cations [$C_{(K+Na)} = 0.0020$ and 0.0120] and tetrahedral Al^{3+} cations (0.0024 and 0.0060). As a result, the a parameter of sample 10 (4.9195 Å) is higher than that of sample 12 (4.9186 Å) (Fig. 16a). However, a similar content of OH_y (0.1118 and 0.0959) and, thus, vacant tetrahedral sites in samples 12 and 10 (0.0279 and 0.0240) results in similar values of their c parameters (Fig. 16b).

To summarize the observed correlations between the unit-cell parameters, the amount of OH_y groups, and the theoretical predictions concerning the orientation of the aggregated platelets can be considered as direct evidence that the amount of water released during heating of the studied samples does correlate with the amount of OH_y groups in the calculated formulas of the samples. This conclusion is not in conflict with the structural features of samples 19 and 18, which do not follow the relationships between the unit-cell parameters and the amount of $[4H]_{Si}$ defects found for

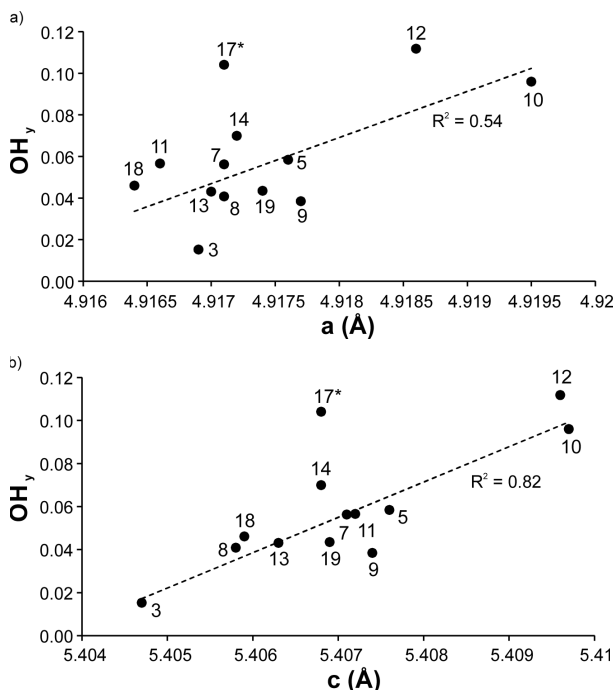


FIGURE 16. Relationships between the amounts of OH_y and the unit-cell a (a) and c (b) parameters.

the other samples. Indeed, these samples contain similar amounts of OH_y (0.0435 and 0.0460) but have different *c* parameters (5.4069 and 5.4059 Å). One plausible explanation of the observed deviation may be related to the high content of tetrahedral Al³⁺ (0.0030) and the negligible amount of alkaline cations in sample 19 (Table 4). Moreover, the IR spectrum of this sample does not contain absorption bands responsible for Al–H defects (Fig. 9). This means that the tetrahedral Al³⁺ cations in sample 19 are coordinated by only oxygen atoms and excess negative charge is compensated by OH hydroxyls each of which coordinates one of the four Si cations nearest to the AlO₄ tetrahedron (Fig. 8b). Because the volume of the AlO₄ structural unit is larger than that of a SiO₄ unit and because the amount of tetrahedral Al³⁺ cations in the structure is significant (0.0030), not only the *a* (4.9174 Å) but also the *c* (5.4069 Å) parameter of sample 19 are higher than those of sample 18 (4.9164 and 5.4059 Å).

Sample 17 is the only example whose crystal-chemical composition does not correlate with the *c* parameter value. According to the formula, the content of OH_y in sample 17 (0.1040) is similar to those in samples 12 (0.1118) and 10 (0.0959) (Fig. 15). Therefore, one may expect that the *c* parameters of samples 17, 12, and 10 should have similar values. In contrast, this expectation is met only for samples 12 and 10 (*c* = 5.4096 and 5.4097 Å), whereas the *c* value for sample 17 is much lower and equal to 5.4068 Å. One possible reason for the observed discrepancy is that the particles in sample 17 along with the [4H]_{Si} defects contain some amount of water molecules located in small bubbles, released from the sample at relatively high temperature.

A general remark concerning the formation of nano-quartz

The fact that quartz is almost pure SiO₂ makes an accurate determination of elements other than Si difficult. The amount of structural impurities has previously been estimated based on interpretation rather than on determination, and the correlation between local structural imperfections and unit-cell parameters has consequently been beset with uncertainties (Hurst and Storch 1981).

In the present investigation of the nano-quartz the application of XRD, IR, and ²⁹Si and ²⁷Al MAS NMR together with thermal analysis of released H₂O and elemental analysis by AAS makes it possible to characterize the nano-quartz structure much more accurately. The main feature of the structure is that tetrahedral vacancies constitute up to 5% of the tetrahedral sites or up to 0.03 per 2 anions, whereas Al³⁺ occupies less than 1% of the tetrahedral sites or up to 0.006 per 2 anions (Table 4). OH[−] amounts up to 0.0112 per 2 anions. The tetrahedral vacancies with 4 OH[−] anions adjacent are therefore, for the nano-quartz, the most significant deviation from the ideal formula for α-quartz.

Laboratory experiments have shown that quartz can be synthesized from sea water at room temperature (Mackenzie and Gees 1971). The new model for the formation of nano-quartz in flint and as nano-quartz particles dispersed in the chalk during sedimentation (Lindgreen et al. 2011; Lindgreen and Jakobsen 2012) is in agreement with a low temperature of formation, as inferred from the isotopic data. The quartz dispersed in the chalk and the quartz in the flint have almost identical unit-cell parameters, strain values and sizes of CSDs and this demonstrates that the quartz in the chalk and in the flint have formed by the same mechanism (Lindgreen et al. 2011).

The formation by crystallization in the sea, the spherical nano-particles and the larger cell dimensions make the North Sea nano-quartz a type of quartz totally different from the well-crystalline quartz of hydrothermal, magmatic or metamorphic origin. This is in agreement with the absence of a sharp α → β transition exothermic peak in DTA, which is due to the nano-size of the quartz crystals (Rios et al. 2001), whereas normal quartz has been characterized by having a sharp α → β peak at 573 °C (Dawson and Wilburn 1970).

IMPLICATIONS

Quartz is the most abundant mineral on the Earth's surface and is usually characterized and identified from its particle shape, the low-angle part of the XRD pattern and an elemental composition as SiO₂. As an example, the quartz in the chalk reservoirs of the oil fields of the North Sea has so far been identified and quantified from XRD patterns in the 10–40° 2θ range. Our application of different methods, allowing us to reveal the finest features at the nano-structural level, has demonstrated that the quartz structure is much more variable than hitherto assumed and that the application of nano-structural methods can discover totally new structures and lead to the understanding of new mechanisms for the formation of quartz at low temperature from biogenic silica, and perhaps eventually reveal specific geochemical conditions in the marine environment resulting in the sedimentary formation of flint.

The new form of quartz, the nano-size spherical α-quartz, is the only silica mineral observed in the Danian chalk in the oil well cores investigated. It has previously been concluded that the quartz formed by crystallization in the water column from dissolved radiolarian organisms. The fact that the nano-quartz has significantly larger dimensions compared to normal quartz and that the elemental structure is special in having a significant proportion of ¹⁹Al substituting for Si and of [4H]_{Si} hydrogarnet defects means that the conditions for formation of this quartz had a strong impact on its structure. The size of the quartz particles makes them effective in packing between coccolithic chalk particles and may cause decreased porosity and permeability in the oil reservoirs, for example contributing to the tight character of the lower part of the Danian Ekofisk Formation. The porous structure of the flint consisting of sedimented quartz spheres makes saturation of the flint with oil during reservoir filling possible and thus reflects the timing of oil migration in the reservoirs (Jakobsen et al. 2014). Investigations should detect this special form of quartz by recording XRD patterns in the high-angle region where the character of this quartz mineral is revealed.

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