Zonar Distribution of ^{18}O in Synthetic Quartz Crystals

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The ^{18}O-content in the mantle-zones of a commercial synthetic quartz was found to increase from the seed towards the surface by 7 ‰. Since the growth took place in a closed container, calculations for the evolution towards the steady state of the ^{18}O-transport could be performed. In the steady state the concentrations of ^{18}O and impurities in the growing quartz are uniform.

Introduction

In earlier work on natural crystals of amethyst [1] and smoky quartz [2] it was found that during the growth of these crystals different faces have incorporated different relative amounts of the isotope ^{18}O. This induced us to perform an analogous study on an industrial synthetic quartz crystal. We had no information about the circumstances of its growth, but the general method of producing such crystals is excellently described in a review article of J. C. Brice [3]: Essentially, the method involves dissovling a nutrient of natural quartz chips at a high temperature. The saturated solution so produced moves by convection to a cooler region where it is supersaturated. To relieve this supersaturation, the solution deposits quartz onto seed crystals. High temperatures (> 300 °C) are necessary to ensure adequate solubility even when mineralizers are added to increase the solubility.

For the growth of synthetic quartz, the necessary conditions are produced in a steel autoclave. See Figure 1. Small (5- to 6-mm) chips of quartz are placed in a basket filling the lower 40% of the autoclave, and suitably oriented seed crystals are held in clips in the upper portion. The autoclave is filled with water so that roughly 80% of the volume is filled, and the system is sealed. Power is supplied to the heaters so that the lower portion of the vessel reaches about 400 °C and the upper portion about 350 °C. A baffle with 5 - 10% opening helps to maintain the temperature difference.

As the temperature is raised, the liquid expands to fill the autoclave at some temperature below the critical point (375 °C for pure water). At the temperatures mentioned previously, the pressure often exceeds 1000 bars.

Table 1. The measured $\delta^{18}O_{SMOW}$-values of the samples 1 - 16. Samples 5 and 14 were not measured.

Probe	$\delta^{18}O_{SMOW}$	σ
Q643–1	+0.74	0.05
Q643–2	+0.62	0.04
Q643–3	+0.77	0.07
Q643–4	+1.07	0.07
Q643–6	–3.60	0.1
Q643–7	–1.90	0.1
Q643–8	–0.60	0.05
Q643–9	+1.86	0.05
Q643–10	+1.74	0.15
Q643–11	–0.20	0.05
Q643–12	–1.90	0.05
Q643–13	–3.70	0.1
Q643–15	+0.60	0.1
Q643–16	+0.69	0.1

Experimental and Results

The synthetic crystal, procured and cut into pieces in Bochum, is shown in Figure 2. Figure 3 shows a cross-section through the oblong crystal with the position of the samples. Dotted lines indicate the seed-plate and dashed lines the growth sectors. The mass-spectrometric analysis of the samples, performed in Bonn as described in [1], gave the results shown in Table 1. A histogram of the $\delta^{18}O_{SMOW}$-values of the

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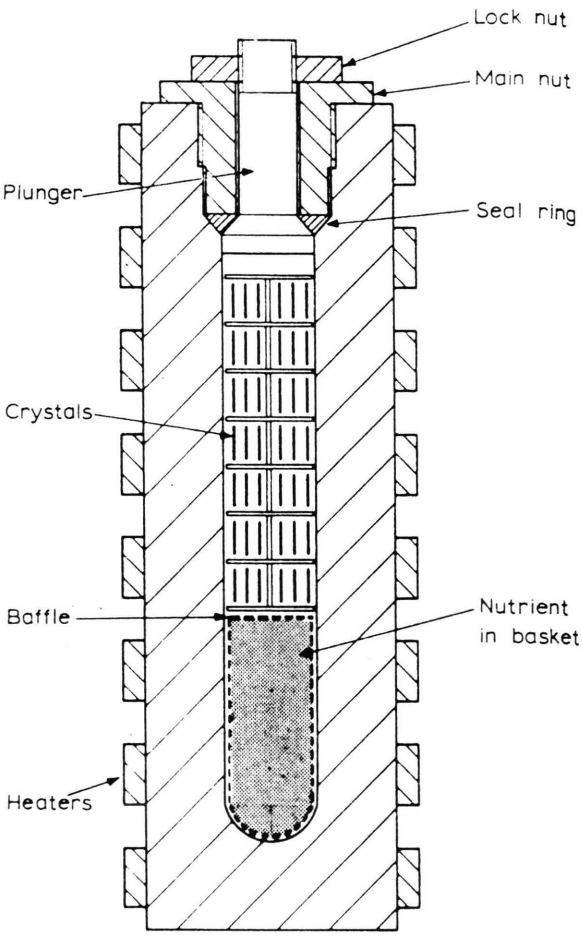

Fig. 1. A schematic drawing of an autoclave for the hydrothermal growth of quartz. Note that different vertical and horizontal scales have been used: typically the height of a system is 18 times its internal diameter. In the most recent autoclaves heights can be up to 8 m. Taken from [3].

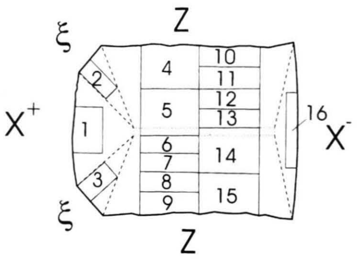

Fig. 3. A cross section trough the synthetic crystal (parallel to the crystallographic *a* and *c* axis or cartesian *X* and *Z* axis), showing crystal faces of the forms Z $\{0001\}$, X$^+\{\bar{2}110\}$, X$^-\{2\bar{1}\bar{1}0\}$, and $\xi\{\bar{2}111\}$, and the position of the samples. Dashed lines indicate the growth-sector boundarys.

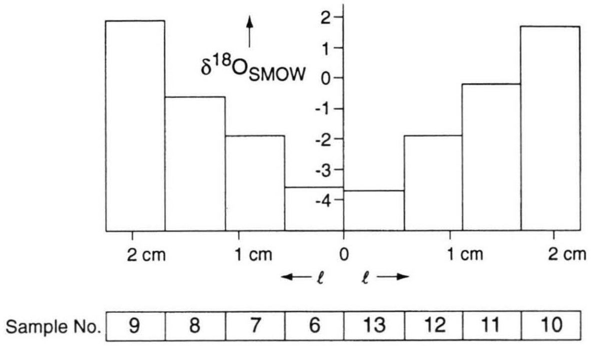

Fig. 4. Histogram of the $\delta^{18}O_{SMOW}$-values of the samples No. 6 - 13 versus the distance *l* of the samples from the surface of the seed-crystal.

samples No. 6 - 13 versus the distance *l* from the surface of the seed-plate is shown in Figure 4. It is seen that the ^{18}O-content of the samples increases linearly with their distance from the seed plate.

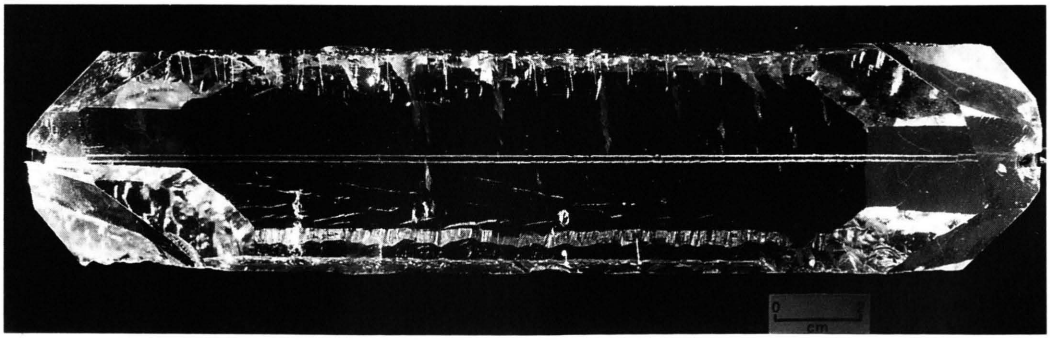

Fig. 2. The synthetic crystal analysed in this work. Length ≈ 24 cm, height ≈ 5 cm, depth ≈ 7 cm view along a crystallographic *a* axis or a cartesian *X* axis. The narrow seed-crystal is seen in the middle.

Discussion

The concentration of ^{18}O in our synthetic crystal was not uniform (see Fig. 4). This shows that the transport of material from the nutrient to the surface of the growing crystal had not reached the steady state. In the steady state, the concentration of ^{18}O deposited on the surface of the growing crystal is uniform because the concentration of ^{18}O in the nutrient is uniform.

The following calculations deal with the evolution towards the steady state.

We consider the growth at a face F of a synthetic crystal whose area A_F does not change during the growth, while growth at other faces of the crystal is prevented. The distance l of the face of the growing crystal from the face of the seed plate increases during the growth, while the volume V_S of the supersaturated growth-solution per crystal, and the concentrations c_S and c_F of oxygen in the growth solution and the face of the growing crystal, respectively, do not change. We introduce the constant

$$l_\mathrm{o} = c_\mathrm{S} V_\mathrm{S} / c_\mathrm{F} A_\mathrm{F} \tag{1}$$

and the variable

$$\lambda = l / l_\mathrm{o}. \tag{2}$$

We further introduce the relative ^{18}O contents x_N, x_S, and x_F of the oxygen in the nutrient, the growth-solution and the face of the growing crystal, respectively, x_N being supposed to be constant. A small, constant quantity ε is to describe the isotope effect occuring during the crystallization at the surface of the growing crystal. Then the change of x_S, with λ is given by

$$\mathrm{d}x_\mathrm{S}/\mathrm{d}\lambda = x_\mathrm{N} - (1+\varepsilon) x_\mathrm{S}. \tag{3}$$

Integration of this differential equation yields

$$x_\mathrm{S}/x_\mathrm{N} = 1 - [\varepsilon/(1+\varepsilon)] \left\{ 1 \pm e^{-(1+\varepsilon)(\lambda+\lambda_\mathrm{N})} \right\}, \tag{4}$$

and thus

$$\mathrm{d}(x_\mathrm{S}/x_\mathrm{N})/\mathrm{d}\lambda = \varepsilon \left\{ \pm e^{-(1+\varepsilon)(\lambda+\lambda_\mathrm{N})} \right\}. \tag{5}$$

The relation between x_F and x_S is given by

$$x_\mathrm{F} = (1+\varepsilon) x_\mathrm{S}. \tag{6}$$

Since in our case $\mathrm{d}x_\mathrm{F}/\mathrm{d}\lambda$ was positive, in (4) and (5) the sign before the exponential must be chosen to be positive if ε is positive, and negative if ε is negative. In Fig. 5 $x_\mathrm{S}/x_\mathrm{N}$ and $x_\mathrm{F}/x_\mathrm{N}$ are shown for the cases $\varepsilon = 0.016$ and $\varepsilon = -0.016$.

The inset of Fig. 5 shows our experimental result if ε is set to be ± 0.016 and λ_N is set to be zero. Of course our experimental result can also be accommodated with the theory if other values of ε and λ_N are chosen. The value of ε can be determined from the dependence of $\delta^{18}\mathrm{O}_\mathrm{SMOW}$ on l (cf. Fig. 4) if $x_\mathrm{S}/x_\mathrm{N}$ at the beginning of the growth and l_o are kown, whereby the question arizes if c_S and x_S imply the oxygen of the water and the mineralizers.

For broadcasting and professional telecommunication systems, quartz resonators are required with maximum frequency deviations of $< 10^{-6}$. For some measurement systems, accuracies of even $< 10^{-10}$ are needed. Therefore defects of synthetic quartz, caused by twin-formation, dislocations, inclusions and impurities have widely been studied [3]. It seems, however, that nothing has yet been published about isotope fractionation in synthetic quartz.

Since the frequency of a quartz resonator is proportional to the reciprocal of its density, the required accuracies of its frequencies are also required for the accuracies of its densitities.

Natural oxygen consists of 99.76% ^{16}O, 0.4 ‰ ^{17}O and 2 ‰ ^{18}O. If two samples of $\mathrm{SiO_2}$ differ by $\Delta\delta^{18}\mathrm{O}_\mathrm{SMOW} = 1$, i. e. if they differ by 10^{-3} in relative ^{18}O content, the relative densities of the samples differ roughly by $\frac{1}{2} \cdot (2 \cdot 10^{-3}) \cdot \frac{1}{8} \cdot 10^{-3} \approx 10^{-7}$, since only $\frac{1}{2}$ of the mass of $\mathrm{SiO_2}$ is mass of oxygen, only $(2 \cdot 10^{-3})$ of the oxygen-nuclei are ^{18}O nuclei and $\frac{1}{8}$ is the realtive difference of the mass-numbers of ^{18}O and ^{16}O. The value $\approx 10^{-7}$ is of the order $< 10^{-6}$ mentioned above for the required accuracy of broadcasting and telecommunication systems and much too large for some measurement systems. We have shown that synthetic quartz crystals with uniform ^{18}O content can be produced in the conventional way if one starts with a growth solution whose ^{18}O content differs by a factor $(1 - \varepsilon)$ from that of the nutrient. In general, for each composition of the nutrient there exists an "aged" growth solution whose composition provides that, when it is applied in combination with the nutrient, the grown synthetic crystals show a homogeneous distribution of ^{18}O and impurities.

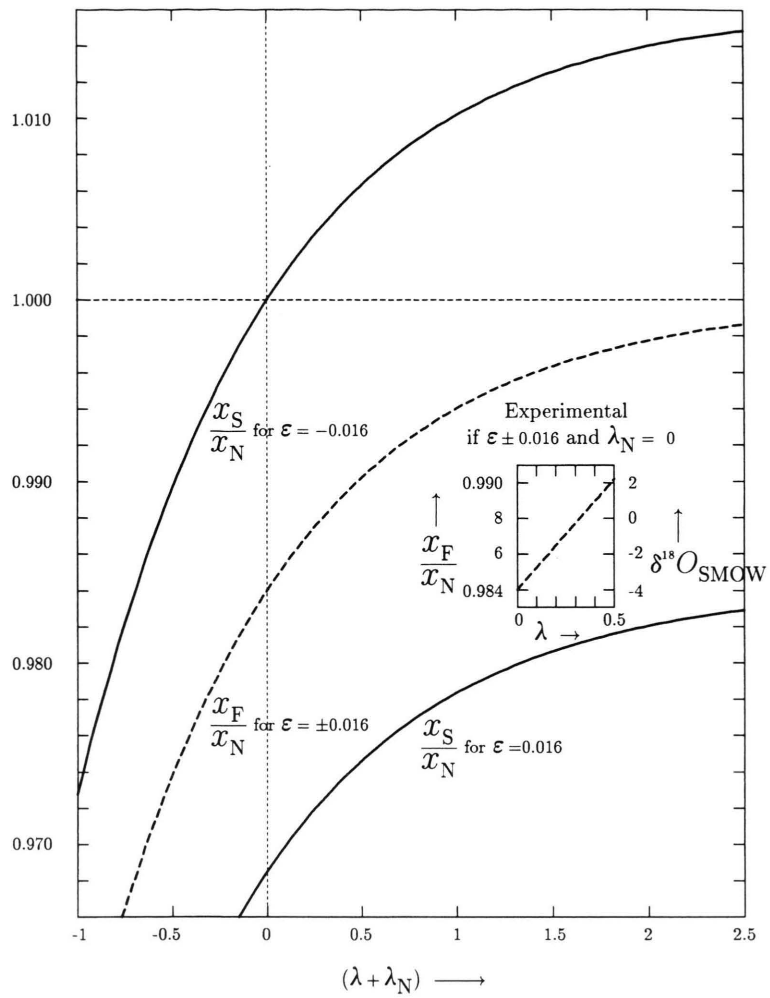

Fig. 5. Illustration of (4) and (6) for $\varepsilon = \pm 0.016$. x_N, x_S, and x_F are the relative ^{18}O contents of oxygen in the nutrient, the growth-solution and the face of the growing crystal, respectively. λ is proportional to the depth l of the grown crystal. The inset shows the experimental result according to Fig. 4, if ε is set to be ± 0.016 and λ_N is set to be zero. The experimental value of $dx_E/d\lambda$ can be reproduced by the theory with any value of ε if using corresponding values of x_N and λ_N.

[1] A. Klemm, A. Banerjee, and S. Hoernes, Z. Naturforsch. **45a**, 1374 (1990); A. Klemm, Nature London **357**, 120 (1992).

[2] A. Klemm, A. Banerjee, and S. Hoernes, Z. Naturforsch. **46a**, 1133 (1991); **47a**, 1232 (1992).

[3] J. C. Brice, Rev. Mod. Physics **57**, 105 (1985).