

Fractionation of Oxygen Isotopes at the Faces of Smoky Quartz

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The $^{18}\text{O}/^{16}\text{O}$ ratio under the m- and r-faces of smoky quartz has been measured; the ratio of the growth velocities was $v_m/v_r=1/3$. The obtained separation factor 1.00020 is compared with that obtained previously for amethyst (1.00043), where the ratio v_m/v_r was unity.

Recently we reported on a new isotope effect [1]: During the growth of natural amethyst, SiO_2 with different ^{18}O content is incorporated at crystallographically different faces of the crystal, the $^{18}\text{O}/^{16}\text{O}$ ratio increasing in the order z-face, r-face, m-face. Meanwhile a similar effect in natural calcite was reported by J. A. D. Dickson [2].

Care must be taken if one wants to single out such an effect because during the hydrothermal growth of the crystal the isotope composition of the mother liquid may have varied, this leading to a corresponding isotopic layering ("mantle zoning") inside the crystal, which is superimposed on the sought for isotopic "sector zoning".

In a polished plane-parallel slice of quartz, which is cut out from the crystal parallel to the c -axis and perpendicular to an m-face, one sees the boundary between the r- and m-sectors if during the growth impurities, which cause colouring, have been incorporated preferentially at one of the two faces. This was the reason why for our first study we had chosen amethyst and in the present one we deal with smoky quartz. The colours of both smoky quartz and amethyst are due to aluminium and iron impurities. If the aluminium impurity Al^{3+} substituting silicon ex-

ceeds the interstitial Fe^{3+} impurity by a large amount, radioactivity will turn the colourless quartz to a smoky quartz. On the other hand, if the amount of interstitial Fe^{3+} exceeds the Al^{3+} impurity, the amethystine colour will appear after irradiation [3].

If one chooses two points on such a visible boundary between r- and m-sectors and cuts through these points parallel to the corresponding r- and m-faces, the material between these cuts in the r- and m-sectors has grown within the same time span. In order to secure that the proportion of the amounts of material

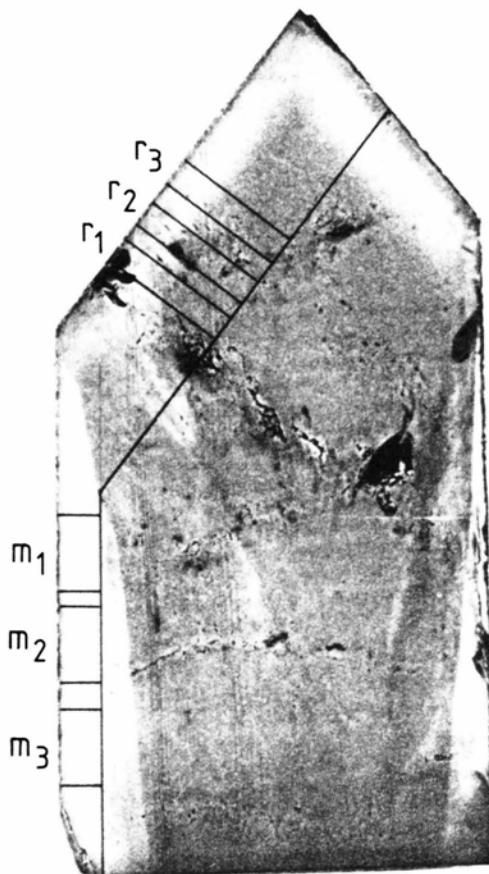


Fig. 1. The position of the samples in a slice of smoky quartz, cut parallel to the c -axis and perpendicular to the m-face. Height 6 cm, thickness 3 mm. In this case, where the average ratio of the growth velocities v_r and v_m was 3, sampling by scraping material from the surfaces, as was done in [2], would have given results where the isotopic mantle zoning is fully involved. Near the surface the sectorial boundary changes its direction. It would therefore have been better to exclude the corresponding layers from the samples.

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grown at the two faces was constant in time, one must choose these two points such that the sectorial boundary between them is straight. If that proportion, i.e. the ratio of the growth velocities, was not constant, the sectorial boundary is curved. One of the above mentioned points can be at the edge of the crystal if the involved parts of the surfaces are intact. Then one needs only the cuts through the other point.

We have found that smoky quartz is even better suited for such an investigation than amethyst because the boundary between the r- and m-sectors is very well visible, the colouring of the m-sector being faint or absent while the r-sector is dark.

Figure 1 shows where the samples from our smoky quartz were taken. The samples were then mass-analyzed in Bonn as described in [1]. The results:

Sample	$\delta^{18}\text{O}$	Sample	$\delta^{18}\text{O}$
r_1	17.40 ± 0.05	m_1	17.6 ± 0.1
r_2	17.40 ± 0.05	m_2	17.60 ± 0.05
r_3	17.4 ± 0.1	m_3	17.60 ± 0.05

This gives a fractionation factor $\alpha_{m-r} = 1.00020$. The ratio of the growth rates was obtained from the depths of the samples to be $v_m/v_r = 1/3$. For the amethyst crystal [1] $\alpha_{m-r} = 1.00043$ and $v_m/v_r = 1$ was found*.

In the discussion of the results of [1] it was suggested there is a kinetic control of the face-controlled fractionation because the r-face with its higher attachment energy and faster growth-rate ($v_r > v_m$) was found to have the lower ability to concentrate ^{18}O than the m-face. These arguments, however, are perhaps not conclusive because (i) the information how the attachment energies have been calculated is lacking and (ii), though generally $v_r > v_m$, for the crystal under consideration in [1] v_r equaled v_m .

The present results together with those of [1] rather suggest that the fractionation is equilibrium controlled because generally equilibrium isotope effects increase with decreasing temperature, and indeed amethyst with its larger isotope effect grows at lower temperatures (70–285 °C) [4] than smoky quartz (above 300 °C) [5]. The equilibrium would be that of isotope exchange between the mother liquid and the growing monomolecular layer at the surface of the crystal.

In most cases, crystals grown under the same temperature conditions show various values of v_r/v_m . This may occur with one and the same crystal for its three r-faces, or for the r-faces of different crystals grown in the same neighbourhood, i.e. under the same temperature conditions. By studying such crystals one could find out if the isotope fractionation depends on v_r/v_m .

- [1] A. Klemm, A. Banerjee, and S. Hoernes, *Z. Naturforsch.* **45a**, 1374 (1990).
 [2] J. A. D. Dickson, *Nature* **353**, 842 (1991); cf. also R. J. Reeder, *ibid.* page 797.
 [3] A. J. Cohen, *Mineralogical Record* **20**, 365 (1989).

- [4] W. H. Dennen and A. M. Puchett, *Can. Mineralogist* **11**, 448 (1972).
 [5] C. Frondel, *DANA – The Systems of Mineralogy*, Vol. 3: Silica Minerals, John Wiley & Sons, New York 1962.

* *Note added in proof*: R. Rykart, author of the book "Quarz Monographie" (Ott Verlag, Thun 1989), told us that our crystal was a twin of the Dauphiné type and that our r-face contained a minority of regions with z-face structure. Our result, considering [1], is therefore $\alpha_{m-z} > 1.00020 > \alpha_{m-r} > 1$ for that crystal.