Further Study of Intersectorial Isotope Fractionation in Quartz

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It is shown that the intersectorial boundary in crystals must be straight if the intersectorial isotope effect is to be measured in the presence of isotopical mantle zoning.

During the growth of crystals, different amounts of isotopes are incorporated at the crystallographically differing crystal faces [1–5]. If the temperature and the isotopic composition of the mother solution are constant in time (as could and should be achieved in artificial crystal growth), this interfacial isotope effect and its dependence on temperature can easily be measured. During natural growth, however, the temperature and isotopic composition of the mother solution may vary with time. This causes isotopic mantle zoning in the crystal, which interferes with the interfacial isotope effect. The depth of a mantle zone is different under the different faces because of the different growth rates of the faces, the depth being proportional to the growth rate of the corresponding crystal face.

The regions in a crystal that have grown from its different faces are called sector zones. If two neighbouring sector zones have grown with a constant ratio of their growth velocities, the two-dimensional boundary between the two sector zones is plane; if not, it is curved.

In our paper on the $^{18}O/^{16}O$ ratio in smoky quartz [4] we had mentioned that the sectorial boundary through the mantle zone from which the samples for the isotope analysis are taken should be plane. In this paper we present a calculation for the case where, due to a sudden change in the ratio of the growth velocities, this boundary is not plane.

We also report on isotope analyses performed on the same smoky quartz crystal as used in [4] but with samples taken from a mantle zone crossed by a *plane* intersectorial boundary.

Figure 1 shows part of a section through a quartz crystal. The section stays parallel to the *c*-axis and perpendicular to an *m*- and neighbouring *r*-face. In the outer mantle zones the boundary between the *m*- and *r*-sector-zones consists of two straight parts meeting at a kink. We consider the two samples shown in Fig. 1 which both comprise the mantle-zones *a* and *b*. The numbers of oxygen atoms in these samples are $n_{ma} + n_{mb}$ and $n_{ra} + n_{rb}$. The isotope analysis of the samples yields the quantity

$$(\alpha_{mr})_{a+b} = \frac{(n_{1ma} + n_{1mb})(n_{2ra} + n_{2rb})}{(n_{2ma} + n_{2mb})(n_{1ra} + n_{1rb})}, \tag{1}$$

where the indices 1 and 2 indicate the isotopes ^{18}O and ^{16}O, respectively. The numbers of oxygen atoms n_{ma}, n_{mb}, n_{ra}, and n_{rb} are proportional to the thicknesses l_{ma}, l_{mb}, l_{ra}, and l_{rb} of the corresponding sectorial parts of the mantle-zones:

$$\frac{l_{ma}}{l_{mb}} = \frac{n_{ma}}{n_{mb}} = q_m^{ab}, \quad \frac{l_{ra}}{l_{rb}} = \frac{n_{ra}}{n_{rb}} = q_r^{ab}. \tag{2a, b}$$

Here and in the following we use symbols q for quotients of particle numbers. The first and second superscript of q indicates the nominator and denominator of the quotient, respectively, while the subscript of q is common for the nominator and denominator.

Let us now assume that during the growth of the mantle-zones *a* and *b* the isotopic composition of the mother solution was constant in time but different for *a* and *b*, and that the growth occurred under equilibrium conditions at a constant temperature. Then one

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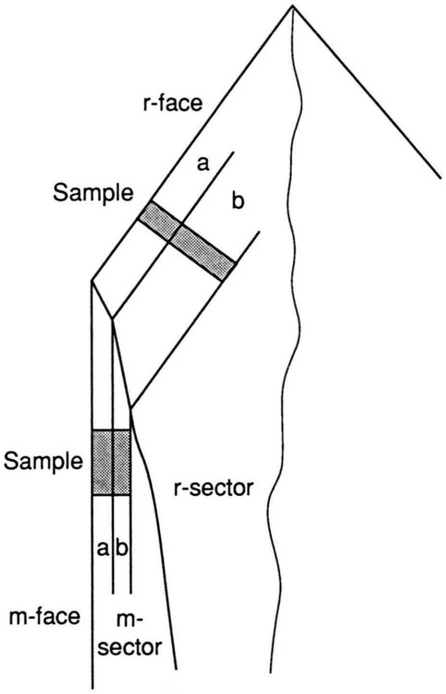

Fig. 1. Drawing of a cross-section through a quartz crystal showing part of the sector-zones *m* and *r* and the mantle-zones *a* and *b*.

can introduce the constants C_{ab} and K_{mr} by

$$C_{ab} = q^{12}_{ma}/q^{12}_{mb} = q^{12}_{ra}/q^{12}_{rb}\,, \tag{3 a, b}$$

$$K_{mr} = q^{12}_{ma}/q^{12}_{ra} = q^{12}_{mb}/q^{12}_{rb}\,. \tag{4 a, b}$$

C_{ab} reflects the change in the isotopic composition of the mother solution during the growth of the mantle zones *a* and *b*. C_{ab} is unity if there was no change. K_{mr} is the isotope exchange constant for equilibrium between the faces *m* and *r*. Equation (3 b) follows from (3 a) and (4 a, b).

We want to calculate the relation between the measured quantity $(\alpha_{mr})_{a+b}$ and the equilibrium constant K_{mr}. For that purpose we express the particle numbers *n* in (1) by their quotients *q*, using the evident relations

$$x = \frac{(x/y)}{1+(x/y)}(x+y), \quad y = \frac{1}{1+(x/y)}(x+y)\,. \tag{5 a, b}$$

One finds

$$(\alpha_{mr})_{a+b} = \frac{\left(\dfrac{q^{12}_{ma}}{1+q^{12}_{ma}}\,q^{ab}_m + \dfrac{q^{12}_{mb}}{1+q^{12}_{mb}}\right)\left(\dfrac{1}{1+q^{12}_{ra}}\,q^{ab}_r + \dfrac{1}{1+q^{12}_{rb}}\right)}{\left(\dfrac{1}{1+q^{12}_{ma}}\,q^{ab}_m + \dfrac{1}{1+q^{12}_{mb}}\right)\left(\dfrac{q^{12}_{ra}}{1+q^{12}_{ra}}\,q^{ab}_r + \dfrac{q^{12}_{rb}}{1+q^{12}_{rb}}\right)}\,. \tag{5}$$

The presence of ^{17}O, its abundance being about 10 times smaller than that of ^{18}O, has been neglected.

According to (3) and (4), the numerators q^{12}_{ma}, q^{12}_{mb}, and q^{12}_{ra} in (5) can be replaced by $K_{mr} C_{ab} q^{12}_{rb}$, $K_{mr} q^{12}_{rb}$ and $C_{ab} q^{12}_{rb}$, respectively. This yields the relation

$$(\alpha_{mr})_{a+b} = K_{mr} \frac{\left(\dfrac{C_{ab}}{1+q^{12}_{ma}}\,q^{ab}_m + \dfrac{1}{1+q^{12}_{mb}}\right)\left(\dfrac{1}{1+q^{12}_{ra}}\,q^{ab}_r + \dfrac{1}{1+q^{12}_{rb}}\right)}{\left(\dfrac{1}{1+q^{12}_{ma}}\,q^{ab}_m + \dfrac{1}{1+q^{12}_{mb}}\right)\left(\dfrac{C_{ab}}{1+q^{12}_{ra}}\,q^{ab}_r + \dfrac{1}{1+q^{12}_{rb}}\right)}\,. \tag{6}$$

In our case of ^{18}O and ^{16}O in natural abundances, the values of q^{12}_{ma}, q^{12}_{mb}, q^{12}_{ra}, and q^{12}_{rb} are of order 2‰ and differ by 1‰ or less, $C_{ab}-1$ is of order 1% or less and the error of $(\alpha_{mr})_{a+b}$ amounts to 0.05‰ or more. This means that (6) can be approximated by

$$(\alpha_{mr})_{a+b} = K_{mr} \frac{(C_{ab}\,q^{ab}_m + 1)(q^{ab}_r + 1)}{(q^{ab}_m + 1)(C_{ab}\,q^{ab}_r + 1)}\,. \tag{7}$$

If the boundary between the *m*- and *r*-sector-zones has no kink, one has $q^{ab}_m = q^{ab}_r$ (cf. (2 a, b)), and (7) reduces to

$$(\alpha_{mr})_{a+b} = K_{mr} \tag{8}$$

even though $C_{ab} \neq 1$, i.e. even though the ^{18}O concentration of the mother solution differed during the growth of the mantle-zones *a* and *b*.

Equation (7) tells us that in any range of a curved boundary between the sector-zones *m* and *r* it is not possible to take samples which yield reliable K_{mr}-values because the isotopic composition of the mother solution may have changed during the growth of the corresponding mantle-zone.

If, however, one finds in a crystal an extended range of a *plane* intersectorial boundary, one could divide the corresponding mantle zone into various subzones and look for the K_{mr}-values in these subzones. If the dependence of K_{mr} on temperature is known from studies on artificially grown crystals, one could find out how the temperature did vary during the growth of the naturally grown crystal, without disturbance by an eventual change of the isotopic composition of the mother solution during the growth.

As can be seen in Fig. 1 of [4], the boundary between the *m*- and *r*-sectors was not plane in the mantle zone which served to take the samples from that crystal. It was, however, plane in the inner part of that mantle zone. We therefore decided to analyse samples taken from that inner part, which corresponds to the mantle zone *b* in the present Figure 1.

Fortunately, the top of our crystal was not pointed but had the form of a straight ridge perpendicular to the slice. This enabled us to cut a second slice from the crystal which looked identical to the slice shown in [4]. The samples were then cut out from that slice with a wafer saw (Disco, type DAD-2H/6T), which produced a cut-width of only 0.28 mm.

The results of the mass-analyses, given like in [4] with respect to Standard Mean Ocean Water, are as follows.

Samples from the mantle zone b ($l_{mb} = 1.35$ mm):

	Sample	$\delta^{18}O$	Sample	$\delta^{18}O$
	m_1	17.08	r_1	16.99
	m_2	17.20	r_2	17.00
	m_3	17.07	r_3	17.00
	m_4	17.16	r_4	16.87
Average:	m	17.13	r	16.96

This gives a fractionation factor $(\alpha_{mr})_b = 1.00017$, which we suppose is the equilibrium constant K_{mr}. In [4] the fractionation factor for samples comprising the mantle zones a and b was found to be $(\alpha_{mr})_{a+b} = 1.00020$.

Under the assumption that the fractionation was an equilibrium process at constant temperature and that the intersectorial boundary was plane for the mantle zone a too, one can calculate from these data the difference in the isotopic composition of the mother liquid during the growth of the mantle zones a and b, using (7) written in the form

$$C_{ab} = \frac{(q_r^{ab} + 1)\, K_{mr} - (q_m^{ab} + 1)(\alpha_{mr})_{a+b}}{(q_m^{ab} + 1)(\alpha_{mr})_{a+b} - (q_r^{ab} + 1)\, K_{mr}} . \qquad (9)$$

Putting $K_{mr} = 1.00017$, $(\alpha_{mr})_{a+b} = 1.00020$, $q_m^{ab} \approx 1$, $q_r^{ab} \approx 2/3$, the latter two values resulting from the breadths of the mantle zones a and b under the faces r and m (cf. (2a, b)), one finds $C_{ab} \approx 1.00030$, i.e. the ^{18}O concentration of the mother solution during the growth of the mantle zone a was by about 0.3‰ higher than that during the growth of the mantle zone b.

These deliberations are of course only justified if the temperature during the growth of the mantle zones a and b was the same.

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