The Dependence of the Oxygen Isotope Fractionation in the Hydration Water of CuSO₄·5H₂O on the Crystallization Temperature

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(Z. Naturforsch. 30 a, 1667–1674 [1975]; received October 10, 1975)

The fractionation of the oxygen isotopes in the water collected by stepwise dehydration of CuSO₄·5H₂O has been measured for the crystallization temperatures 25, 40 and 50 °C. From X-ray and neutron diffraction studies it is known that three different kinds of water, differing in their binding in the crystal, exist in CuSO₄·5H₂O. On the basis of the results reported here it is concluded that isotopic equilibrium exists between the different kinds of water in the crystal and the mother liquor during the crystallization process. In addition it is shown that on stepwise dehydration the water molecules from the different types of sites can be separated. Consequently, the measurements provide the possibility to determine crystallization temperatures from intracrystalline oxygen isotope fractionation alone. Possible applications in isotope geothermometry are discussed.

I. Introduction

The structure of CuSO₄·5H₂O is known from X-ray diffraction studies by Beevers and Lipson and from neutron diffraction studies by Bacon and Curry. The elementary cell contains two copper ions. Three kinds of water (K₁, K₂, and L in the ratio 2:2:1), differing in their binding in the crystal, can be distinguished. Layers consisting of copper ions and K₁-water alternate with layers consisting of copper ions, K₂-water and L-water. They are linked by layers of sulphate ions.

The following bonds keep the three kinds of water molecules and the copper and sulphate ions in their respective positions:

K₁: One Cu-O bond, the bisector of the two lone electron pairs of the water molecule being directed towards the copper ion, and two hydrogen bonds to oxygens of two sulphate ions.

K₂: One Cu-O bond, one lone electron pair of the water molecule being directed towards the copper ion, and two hydrogen bonds, one to an oxygen of a sulphate ion and one to the oxygen of an L-water molecule.

L: Four hydrogen bonds, two to oxygens of two sulphate ions and two to hydrogens of two K₂-water molecules.

Cu: Six Cu-O bonds, two to oxygens of two sulphate ions and four to the oxygens of four K₁-water molecules or four K₂-water molecules.

Measurements of the hydrogen and oxygen isotope ratios in the water liberated by stepwise dehydration of CuSO₄·5H₂O have previously been reported for crystals grown at room temperature. In this work the dependence of these oxygen isotope ratios on the crystallization temperature has been determined. It is shown that a fractionation of the oxygen isotopes between the different kinds of water in the crystal occurs in isotopic equilibrium during crystallization and changes with crystallization temperature. The use of these intracrystalline isotope effects for isotope geothermometry in determining the crystallization temperature of hydrated minerals by means of the described method is suggested.

II. Experimental Procedure

The CuSO₄·5H₂O crystals were grown without stirring from a supersaturated aqueous solution of CuSO₄ at crystallization temperatures of 25, 40 and 50 °C. The degree of supersaturation was dimensioned in such a way that the salt was completely dissolved at temperatures 30 °C above the crystallization temperature. In order to avoid isotope effects caused by the evaporation of water the crystallization proceeded under closed conditions as described in a previous paper. The supersaturated solution was
cooled in a thermostat to the respective crystallization temperature which was kept constant within ±0.1 °C. As the formation of the crystals could not be recognized for several hours after the solution had attained the temperature of the thermostat, isothermal conditions during crystallization were guaranteed.

Ground samples of copper sulphate pentahydrate were dehydrated either all at once or in three fractions under argon atmosphere. The same dehydra-tion procedure and dehydration temperature was applied for all samples. In order to avoid isotope exchange in the crystal the dehydration temperature was chosen to be 30 °C for the first four moles of water per mole of CuSO₄·5H₂O, resulting in a dehydration time of several days. The removal of the fifth mole of hydration water was performed at temperatures of 200 °C in order to avoid unreasonably long dehydration times. Only a few hours were necessary at this temperature. This high temperature, however, caused an isotope exchange between water oxygen and sulphate oxygen. The determination of the oxygen isotope ratio in the sulphate which is necessary for the correction of the ¹⁸O/¹⁶O — ratio in the hydration water is described in a previous publication.

The used experimental arrangement which is shown in Fig. 1 is similar to that of Maiwald and Heinzinger. It has been improved by installing a thermobalance (Netzsch vacuum thermobalance 429) in order to control the loss of water during the dehydration process. The evacuated apparatus was filled to a pressure of about one atmosphere with argon which was forced to circulate by means of a membrane pump. After warming in a furnace the dry argon gas passed the sample holder of the thermobalance. The ground copper sulphate pentahydrate was warmed by the argon gas and the water vapour carried away with the argon stream and collected in a condensor which was cooled with methanol to −70 °C. The dehydration temperature was controlled by means of a thermocouple measuring the temperature near the sample holder.

The water used as solvent had natural isotope abundance. The oxygen isotope ratio of the water fractions has been determined by means of the CO₂-equilibration technique with an Atlas M 86 mass spectrometer.

### III. Results

The results of the measurements are given either as fractionation factors \( a_{A-B} \) defined by

\[
a_{A-B} = \frac{\text{O}^{18}}{\text{O}^{16}}_A / \frac{\text{O}^{18}}{\text{O}^{16}}_B
\]

or as isotope effects \( \delta_{A-B} \) defined by

\[
\delta_{A-B} = (a_{A-B} - 1) \cdot 10^3.
\]

The fractionation of the oxygen isotopes between various amounts of water obtained by partial dehydration of CuSO₄·5H₂O (P) and the saturated solution (M) has been determined. The integral frac-

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Fig. 1. Experimental arrangement for the dehydration of CuSO₄·5H₂O in an argon stream.
The fractionation factor $a_{\text{P-M}}$ is given in Fig. 2 as a function of $m/m_0$, the relative amount of water withdrawn, for the three crystallization temperatures. In most of the experiments the water was collected in three fractions leading to three points in Fig. 2 by employing a mass balance equation. The points at $m/m_0 = 1$ are average values of several dehydration experiments. Figure 2 also shows the experimental points from the work of Maiwald and Heinzinger. They fit well with the points obtained with our new experimental arrangement.

![Fig. 2. The integral oxygen isotope fractionation factor $a_{\text{P-M}}$ between water collected on partial dehydration (P) and water of the mother solution (M) as a function of the relative amount of water withdrawn for three different crystallization temperatures. $m$ and $m_0$ are the masses of the collected and the total crystal water respectively. The crosses are taken from the paper by Maiwald and Heinzinger.](image)

No reproducible results could be obtained for a crystallization temperature of 10°C, although very small degrees of supersaturation were tried at this temperature. The results also became irreproducible for the range $0 < m/m_0 < 0.8$ if the dehydration temperature was 60°C.

### IV. Discussion

We shall first consider the experimental results for the crystallization temperature 25°C.

The plot of the experimental $a_{\text{P-M}}$-values versus $m/m_0$ (Fig. 2) indicates that there are drastic changes in the dependence of $a_{\text{P-M}}$ on $m/m_0$ near the $m/m_0$-values 0.4 and 0.8. Since these $m/m_0$-values correspond to the amounts of water in the three binding stages of CuSO$_4·5$H$_2$O and in the three hydration stages of CuSO$_4$ it is to be concluded that the breaks in the $a_{\text{P-M}}$-curve occur exactly at the $m/m_0$-values 0.4 and 0.8.

The trend in the experimental $a_{\text{P-M}}$-values further suggests that within each of the three $m/m_0$-ranges, henceforth designated with I, II and III, the vapour leaving the crystals (V) has a constant isotopic composition and therefore a constant fractionation factor $a_{\text{V-M}}$ with respect to the mother solution (M).

Due to the low concentration of $^{18}$O, the relation between $a_{\text{P-M}}$ and $a_{\text{V-M}}$ is given with sufficient accuracy by

$$a_{\text{P-M}} = x^{-1} \int_{0}^{x} a_{\text{V-M}} \, dx' ,$$

where $x = m/m_0$. Putting $a_{\text{V-M}} = a_{\text{I-M}}$, $a_{\text{II-M}}$ and $a_{\text{III-M}}$ (each constant) for the $x$-ranges I, II and III respectively, the evaluation of the integral leads to the relations

- $0 < x < 0.4$:
  $$a_{\text{P-M}} = a_{\text{I-M}} ,$$
- $0.4 < x < 0.8$:
  $$a_{\text{P-M}} = a_{\text{II-M}} + (0.4 a_{\text{I-M}} - 0.4 a_{\text{II-M}}) x^{-1} ,$$
- $0.8 < x < 1$:
  $$a_{\text{P-M}} = a_{\text{III-M}} + (0.4 a_{\text{I-M}} + 0.4 a_{\text{II-M}} - 0.8 a_{\text{III-M}}) x^{-1} ,$$

which allow the evaluation of the fractionation factors $a_{\text{V-M}}$ by a least squares fit to the experimental points.

As the dehydration procedure was the same for all samples the experimental points for the crystallization temperatures 40°C and 50°C, though less copious than those for 25°C, can be treated in the same way. The $\delta_{\text{V-M}}$-values thus obtained together with the isotope effects $\delta_{\text{G-M}}$ of the total hydration water (G) with respect to M are listed in Table 1 and the corresponding curves are plotted in Figure 2. The errors in Table 1 are mean square deviations.

The error for the $x$-range III is larger because of the corrections for the isotope exchange between the fifth mole of hydration water and the sulphate ions. A correction necessary for the loss of hydration

<table>
<thead>
<tr>
<th>Temp. (°C)</th>
<th>$\delta_{\text{I-M}}$</th>
<th>$\delta_{\text{II-M}}$</th>
<th>$\delta_{\text{III-M}}$</th>
<th>$\delta_{\text{G-M}}$</th>
<th>$\delta_{\text{I-II}}$</th>
<th>$\delta_{\text{II-III}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>4.2</td>
<td>-1.3</td>
<td>42.9</td>
<td>9.7</td>
<td>5.5</td>
<td>-42.4</td>
</tr>
<tr>
<td>40</td>
<td>-0.7</td>
<td>-2.4</td>
<td>54.2</td>
<td>9.6</td>
<td>1.7</td>
<td>-53.7</td>
</tr>
<tr>
<td>50</td>
<td>-2.4</td>
<td>-2.2</td>
<td>56.2</td>
<td>9.4</td>
<td>-0.2</td>
<td>-55.3</td>
</tr>
<tr>
<td>Error</td>
<td>±0.3</td>
<td>±0.3</td>
<td>±1.7</td>
<td>±0.6</td>
<td>±0.4</td>
<td>±1.7</td>
</tr>
</tbody>
</table>
water during the evacuation at the beginning of each experiment is included.

Because of the scatter of the experimental points in Fig. 2 it is not possible to exclude a certain dependence of \( \delta_{V-M} \) on \( x \) within each of the three \( x \)-ranges due to, e.g. a tendency of the light isotope to leave the crystals more readily than the heavy one. Rather than stressing the constancy of \( \delta_{V-M} \) within the \( x \)-ranges, the \( \delta_{V-M} \)-values given in Table 1 should be considered as mean values for the respective \( x \)-ranges, that is the separation factor of the total water recovered in an \( x \)-range with respect to the mother solution. These total waters are henceforth named water I, II and III respectively.

Having thus condensed our experimental results, we first ask if the isotopic compositions of the waters I, II and III are related to the isotopic compositions of the waters \( K_1, K_2 \) and \( L \) in \( CuSO_4 \cdot 5 H_2O \), or if they are merely a consequence of the fact that \( CuSO_4 \) passes through its three hydration stages when dehydrated from the pentahydrate to the anhydrate.

To clarify this let us first look at the dehydration of the trihydrate. Zahrobsky and Baur\(^8\) have shown by a structure determination of the trihydrate Bonattite, grown at 105 °C from an aqueous solution of \( CuSO_4 \), that in this trihydrate the three water molecules of a unit cell are in very similar positions. Therefore, on dehydration of Bonattite obtained by dehydration of the pentahydrate an isotope effect \( \delta_{II-III} \) could not depend significantly on the formation temperature of the pentahydrate. Since we have found such a temperature dependence (cf. Table 1), it is to be concluded that the trihydrate forming on dehydration of the pentahydrate at 30 °C is different from Bonattite in having two or three substantially different binding positions of its water molecules. Indeed Kohlschütter and Nitschmann\(^9\) have shown by X-ray diffraction that \( CuSO_4 \cdot 3 H_2O \) formed by dehydration of \( CuSO_4 \cdot 5 H_2O \) at room temperature has a structure which is different from Bonattite. Evidently in the trihydrate obtained by gentle dehydration of the pentahydrate the amounts of \( ^{18}O \) in the different binding positions are related to the amounts of \( ^{18}O \) in the binding positions \( K_1, K_2 \) and \( L \) of the pentahydrate, which themselves depend on the formation temperature of the pentahydrate. Only in this way can the observed dependence of \( \delta_{II-III} \) on the formation temperature be understood.

The crystals grown at elevated temperatures have sometimes been left for weeks at room temperature before being dehydrated. A dependence of the mass spectrometric results on such time spans has not been observed, indicating that the distribution of the oxygen isotopes did not adjust itself to the lower temperature during these times. If the diffusion coefficient of the water oxygen in \( CuSO_4 \cdot 5 H_2O \) should have the same order of magnitude as that found in ice \(^{9a}\) and \( KAl(SO_4)_2 \cdot 12 H_2O \) \(^{9b}\), i.e. \( 10^{-12} - 10^{-10} \text{ cm}^2/\text{s} \), the slowness of the water oxygen isotope exchange in \( CuSO_4 \cdot 5 H_2O \) found in our experiments would need a special explanation.

As the crystallization of the pentahydrate proceeded very slowly and the \( \alpha_{V-M} \)-values did not depend on the speed of crystallization, it has to be assumed that the crystallization occurred in thermodynamic equilibrium with a temperature dependent isotope fractionation between the binding positions \( (K_1, K_2 \text{ and } L) \) in the crystal and the mother liquor (M). Dehydration of the pentahydrate thus offers a means of determining the temperature of its formation, a method which could be of interest for geologists when applied to more common minerals.

We may now go into the question of how the waters \( K_1, K_2 \) and \( L \) contribute to the waters I, II and III recovered on dehydration of the pentahydrate. For that purpose we shall discuss four hypotheses specified by the following equations:

1 a) \( \delta_I = \frac{1}{3} (\delta_L + \delta_{K_2} - \delta_2) \)

1 b) \( \delta_I = \frac{1}{3} (\delta_L + \delta_{K_1} - \delta_2) \)

2) \( \delta_I = \delta_{K_1} \)

3) \( \delta_I = \delta_{K_1} \)

In these equations the isotope effects \( \delta_1, \delta_{II}, \delta_{III}, \delta_{K_1}, \delta_{K_2} \) and \( \delta_1 \) are taken with respect to the mother liquor. The index M has been dropped for simplicity. In hypotheses 1 a and 1 b the L-water is contained in water I, in hypothesis 2 it is contained in water II, and in hypothesis 3 it is identical with water III. In the pentahydrate the L-water is bound to \( K_2 \)-water and not to \( K_1 \)-water. Therefore it has been assumed in the hypotheses 1 a, 1 b and 2 that the L-water is joined by \( K_2 \)-water in the waters I and II, respectively. On splitting the \( K_2 \)-water for that purpose, an internal isotope effect might occur.
This has been taken account of by the introduction of $\delta_2$ in the equations. In hypothesis 1b $K_1$-water also splits, giving rise to a second internal isotope effect $\delta_1$, $\delta_1$ and $\delta_2$ are of course independent of the crystallization temperature.

Introducing the experimental oxygen isotope effects $\delta_1$, $\delta_1''$ and $\delta_1'''$ for the crystallization temperatures 25 and 50 °C as given in Table 1, one obtains the $\delta$-values of the waters $K_1$, $K_2$ and L and their temperature dependences as listed in Table 2. The temperature effects $\Delta\delta/\Delta T$ are of course independent of the unknown internal isotope effects $\delta_1$, $\delta_2$ and can be discussed without assumptions about the values of $\delta_1$ and $\delta_2$. It is seen that according to the hypotheses 1a, 1b and 2 the temperature dependences of $\delta_{K_1}$ and $\delta_{K_2}$ would be very dissimilar. This is not to be expected, since the positions $K_1$ and $K_2$ in the crystal are much alike. The observed temperature dependences therefore suggest that the dehydration proceeds according to hypothesis 3.

For the discussion of the oxygen isotope effects at 25 °C the corresponding hydrogen isotope effects

$$\delta'_{A-B} = \left(\frac{(D/H)_A}{(D/H)_B} - 1\right) \times 10^3$$

shall be included. For this purpose the experimental $\delta'_1$, $\delta'_1''$, and $\delta'_1'''$-values reported in 5 have been introduced into the above equations for the four hypotheses. The resulting $\delta'_{K_1}$, $\delta'_{K_2}$ and $\delta'_L$-values are listed in Table 3.

The difference in the Cu – O bond of $K_1$- and $K_2$-water is expected to lead to a small oxygen isotope fractionation between $K_1$- and $K_2$-water while, the rest being hydrogen bonds, no appreciable fractionation of the hydrogen isotopes between $K_1$- and $K_2$-water is to be expected. These expectations are plainly verified when adopting hypothesis 3, while adapting hypotheses 1a, 1b or 2 to these expectations would involve ad hoc assumptions of large and well-fitting $\delta_1$, $\delta_1''$, $\delta_1'''$ and $\delta_2$-values, respectively, which are quite improbable. Thus, the isotope effects found for a single crystallization temperature also support hypothesis 3.

Consequently, from the association of the different isotope ratios measured by stepwise dehydration with the different binding of the water molecules in the crystal and, as shown above, from the temperature dependence of these ratios the following dehydration sequence results: First the copper ion which is surrounded by $K_1$-water loses its four water molecules, then the second one loses its four $K_2$-water molecules, and the L-type water becomes quantitatively the water of the monohydrate.

This dehydration sequence has already been proposed by Taylor and Klug 10 and the authors of

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Table 2. The oxygen isotope effects $\delta$ of the waters $K_1$, $K_2$ and L and their temperature dependences for the four hypotheses of the dehydration sequence. $\delta_1$ and $\delta_2$ are constant values.

<table>
<thead>
<tr>
<th>Hypothesis</th>
<th>Temp. (°C)</th>
<th>$\delta$</th>
<th>$\Delta\delta/\Delta T$ (K$^{-1}$)</th>
<th>$\delta$</th>
<th>$\Delta\delta/\Delta T$ (K$^{-1}$)</th>
<th>$\delta$</th>
<th>$\Delta\delta/\Delta T$ (K$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 a</td>
<td>25</td>
<td>-1.3</td>
<td>-0.04</td>
<td>42.9 - $\delta_2$</td>
<td>0.53</td>
<td>-34.5 + 2 $\delta_2$</td>
<td>-1.06</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>-2.2</td>
<td></td>
<td>56.2 - $\delta_2$</td>
<td></td>
<td>-61.0 + 2 $\delta_2$</td>
<td></td>
</tr>
<tr>
<td>1 b</td>
<td>25</td>
<td>42.9 - $\delta_1$</td>
<td>0.53</td>
<td>-45.5 + 2 $\delta_1$ - $\delta_2$</td>
<td>-0.60</td>
<td>53.9 + 2 ($\delta_2$ - $\delta_1$)</td>
<td>0.08</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>56.2 - $\delta_1$</td>
<td></td>
<td>-60.6 + 2 $\delta_1$ - $\delta_2$</td>
<td></td>
<td>55.8 + 2 ($\delta_2$ - $\delta_1$)</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>25</td>
<td>4.2</td>
<td>-0.26</td>
<td>42.9 - $\delta_2$</td>
<td>0.53</td>
<td>-45.5 + 2 $\delta_2$</td>
<td>-0.60</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>4.2</td>
<td>-0.26</td>
<td>56.2 - $\delta_2$</td>
<td></td>
<td>-60.6 + 2 $\delta_2$</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>25</td>
<td>4.2</td>
<td>-0.26</td>
<td>-1.3</td>
<td></td>
<td>42.9</td>
<td>0.53</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>-2.4</td>
<td>-0.04</td>
<td>-2.2</td>
<td></td>
<td>56.2</td>
<td></td>
</tr>
</tbody>
</table>

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Table 3. The hydrogen isotope effects $\delta'$ of the waters $K_1$, $K_2$ and L for the four hypotheses of the dehydration sequence. $\delta'_1$ and $\delta'_2$ are constant values.

<table>
<thead>
<tr>
<th>Hypothesis</th>
<th>$\delta'_{K_1}$</th>
<th>$\delta'_{K_2}$</th>
<th>$\delta'_{L}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 a</td>
<td>-33.0</td>
<td>22.0 - $\delta'_1$</td>
<td>-88.0 + 2 $\delta'_1$</td>
</tr>
<tr>
<td>1 b</td>
<td>22.0 - $\delta'_1$</td>
<td>-88.0 + 2 $\delta'_1$ - $\delta'_2$</td>
<td>22.0 + 2 ($\delta'_2$ - $\delta'_1$)</td>
</tr>
<tr>
<td>2</td>
<td>-33.0</td>
<td>22.0 - $\delta'_2$</td>
<td>-88.0 + 2 $\delta'_2$</td>
</tr>
<tr>
<td>3</td>
<td>-33.0</td>
<td>-33.0</td>
<td>22.0</td>
</tr>
</tbody>
</table>
earlier works from this laboratory, Beevers and Lipson had suggested the sequence $K_2$, $K_1$, L.

It seems difficult to visualize how the L-water could stay longer in the crystal than the K-waters and could be enriched in $^{18}O$, the binding energies of the K-waters according to a rough estimation being more than five times larger than that of the L-water. The following explanation of this conceptional difficulty offers itself: Dehydration proceeds along the crystal layers mentioned in the introduction. One water molecule after the other leaves its position in its layer and migrates towards the surface of the crystallites. The L-water molecules take energetically more favourable positions when neighbouring $K_1$- or $K_2$-water molecules leave their positions and thus remain longest in the crystal. Sterical hindrance in the original pentahydrate is the reason for the enrichment of $^{18}O$ in the L-water.

It has been reported above that for crystallization temperatures of 10 °C no reproducible curves could be measured and that by increasing the dehydration temperature from 30 to 60 °C again each measurement led to a different dependence of $\alpha_{P-M}$ on $m/m_0$ in the range $m/m_0 < 0.8$. Both effects can be explained in the frame of the proposed mechanism. The crystallization temperature of 10 °C is too low to establish isotopic equilibrium during the crystallization process even if the supersaturation is very small. By increasing the dehydration temperature to 60 °C, water from both octahedra mixes during the dehydration but no mixing occurs with L-water resulting in reproducible $\alpha_{P-M}$-values within the limits of error for $m/m_0 = 0.8$. From the hydrogen isotope effect measurements it can be concluded that at dehydration temperatures of 100 °C K- and L-water are also mixed during the dehydration process.

Tanaka and Negita concluded from the depletion of tritium in the crystal water relative to the mother liquor that kinetic isotope effects are responsible for this isotope fractionation. As discussed in detail previously this wrong conclusion resulted from the fact that the authors investigated only the isotope effects between total crystal water and mother liquor.

The fractionation factors between the different kinds of water molecules in the crystal as derived from Table 1 are given in Table 4. The errors are mean square deviations.

According to Bigeleisen and Van Hook the formula

$$\ln \alpha = \frac{A}{T^2} - \frac{B}{T},$$

derived for the temperature dependence in a restricted temperature range of the isotope fractionation in a system that includes gaseous and liquid phases, may also be applied to a system including liquid and solid phases. The parameters $A$ and $B$ for the four fractionation factors given in Table 4 have been determined by means of a least squares fit. The results are given in Table 5; the errors $\sigma(\ln \alpha)$ are mean square deviations. Because of its small deviations the fractionation factor $\alpha_{K_1-K_1}$ is expected to lead to the most accurate crystallization temperatures determined from intracrystalline oxygen isotope fractionation in the crystal water of CuSO$_4$·5H$_2$O. This fractionation factor is plotted in Fig. 3 as a function of the reciprocal crystallization temperature.

### Table 4. Oxygen isotope separation factors between the different kinds of water in CuSO$_4$·5H$_2$O dependent on the crystallization temperature.

<table>
<thead>
<tr>
<th>Temp. (°C)</th>
<th>$\alpha_{K_1-K_2}$</th>
<th>$\alpha_{L-K_1}$</th>
<th>$\alpha_{L-K_2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>1.0055</td>
<td>1.0385</td>
<td>1.0443</td>
</tr>
<tr>
<td>40</td>
<td>1.0017</td>
<td>1.0549</td>
<td>1.0567</td>
</tr>
<tr>
<td>50</td>
<td>0.9998</td>
<td>1.0587</td>
<td>1.0585</td>
</tr>
<tr>
<td>Error</td>
<td>±0.0004</td>
<td>±0.0017</td>
<td>±0.0017</td>
</tr>
</tbody>
</table>

### Table 5. The constants $A$ and $B$ in the equation $\ln \alpha = A/T^2 - B/T$ as determined from the measured fractionation factors.

<table>
<thead>
<tr>
<th>$\ln \alpha_{K_1-K_2}$</th>
<th>$\ln \alpha_{L-K_1}$</th>
<th>$\ln \alpha_{L-K_2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A$ [K$^2$]</td>
<td>$B$ [K]</td>
<td>$\sigma(\ln \alpha)$</td>
</tr>
<tr>
<td>6.60·10$^3$</td>
<td>20.5</td>
<td>±0.0001</td>
</tr>
<tr>
<td>-2.84·10$^4$</td>
<td>-96.9</td>
<td>±0.0013</td>
</tr>
<tr>
<td>-2.17·10$^4$</td>
<td>-86.0</td>
<td>±0.0012</td>
</tr>
</tbody>
</table>

![Fig. 3. The oxygen isotope fractionation factor between $K_1$- and $K_2$-water in CuSO$_4$·5H$_2$O as a function of the reciprocal crystallization temperature.](image)
As a consequence of the existence of isotopic equilibrium during crystallization these intracrystalline isotope effects offer themselves for use in isotope geothermometry. Recently Matsuo, Friedman and Smith\textsuperscript{15} proposed to determine the crystallization temperature of hydrated minerals with the help of the hydrogen isotope fractionation between hydrated crystals and the solution from which they

Fig. 4. X-ray goniometer curves of the samples (a)—(d) as specified in the Appendix.
were crystallized. This method has a decisional dis-
advantage because in general the saturated solution
from which the minerals were crystallized is no
longer available and so the standard to which the
isotope ratio of the hydrated crystal could be related
is lacking. The advantage of the method described
for \( \text{CuSO}_4 \cdot 5 \text{H}_2\text{O} \) as an example is that all required
information for the determination of the crystalliza-
tion temperature is deducible from the hydrated
crystal alone by means of intracrystalline isotope
effects. No information about the mother liquor is
necessary. Although \( \text{CuSO}_4 \cdot 5 \text{H}_2\text{O} \) is not of interest
in geochemistry, it has been investigated as a typical
example of a hydrated crystal and the results found
here should be helpful for the investigation of other
geochemically more interesting minerals, such as
\( \text{MgSO}_4 \cdot 7 \text{H}_2\text{O} \).

Those minerals to which the described method
could be applied have to fulfil the following condi-
tions:

1) The water molecules in the hydrated crystal must
be at least in two different binding positions
leading to a temperature dependent isotope ef-
fect between them.

2) The hydrated crystal must have been grown in
isotopic equilibrium with the mother liquor at
a constant temperature.

3) There has been no isotope exchange in the crys-
tal water after crystallization.

4) This equilibrium isotope effect is reproducibly
reflected in the water collected by stepwise de-
hydration.

It is to be supposed from present crystallographic
data that a number of hydrated crystals of minera-
logical and geological interest will fulfil condi-
tion 1.

The help of G. Josten during the measurements
is greatly acknowledged.

Appendix

In order to check the results of Kohlschütter and
Nitschmann we have taken X-ray goniometer cur-
ves of

(a) \( \text{CuSO}_4 \cdot 5 \text{H}_2\text{O} \),

(b) \( \text{CuSO}_4 \cdot 3 \text{H}_2\text{O} \) as obtained in our usual way by
dehydration of the pentahydrate at 30 °C,

(c) Sample (b) annealed at 100 °C for 3 hours in
a closed tube,

(d) Bonattite (\( \text{CuSO}_4 \cdot 3 \text{H}_2\text{O} \)) prepared by cool-
ing down a solution containing 8 wt.%
\( \text{CuSO}_4 \cdot 5 \text{H}_2\text{O} \), 55 wt.% \( \text{H}_2\text{SO}_4 \) and 37 wt.%
\( \text{H}_2\text{O} \).

The curves are shown in Figure 4. The curved
background is caused by the plastic foil used to
protect the samples from moisture during the in-
radiation. The numbers given at the top and bottom
of Fig. 4 are lattice spacings taken from the curves
(a) and (d), respectively.

Sample (b) shows all the lines of the penta-
hydrate given numerically in the figure (with the
exception of the line at 4.29 Å) and none of the
lines of Bonattite, while sample (c) shows lines both
of the pentahydrate and Bonattite. The result of
Kohlschütter and Nitschmann, that the trihydrate
formed by gentle dehydration of the pentahydrate
is a transient product which changes into Bonattite
on annealing, is thus confirmed.

The invaluable assistance of Dipl. Min. Astrid
Schäfer from the Institute of Mineralogy of the
Johannes Gutenberg-University in Mainz in taking
the goniometer curves for us is gratefully acknowl-
dged.

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