A New Route of Oxygen Isotope Exchange in the Solid Phase: Demonstration in CuSO$_4$·5H$_2$O

Albert Danon, Avraham Saig, Yacov Finkelstein, and Jacob E. Koresh*

Chemistry Division, Nuclear Research Center of the Negev (NRCN), Beer-Sheva 84190, Israel

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Temperature-programmed desorption mass spectrometry (TPD-MS) measurements on [^{18}O]water-enriched copper sulfate pentahydrate (CuSO$_4$·5H$_2^{18}$O) reveal an unambiguous occurrence of efficient oxygen isotope exchange between the water of crystallization and the sulfate in its CuSO$_4$ *solid* phase. To the best of our knowledge, the occurrence of such an exchange was never observed in a solid phase. The exchange process was observed during the stepwise dehydration (50−300 °C) of the compound. Specifically, the exchange promptly occurs somewhere between 160 and 250 °C; however, the exact temperature could not be resolved conclusively. It is shown that only the fifth, sulfate-associated, anionic H$_2$O molecule participates in the exchange process and that the exchange seems to occur in a preferable fashion with, at the most, one oxygen atom in SO$_4$. Such an exchange, occurring below 250 °C, questions the common conviction of unfeasible oxygen exchange under geothermic conditions. This new oxygen exchange phenomenon is not exclusive to copper sulfate but is unambiguously observed also in other sulfate- and nitrate-containing minerals.

Introduction

Oxygen isotope analysis plays a fundamental role in isotope geology and the geochemistry of water, the atmosphere, rocks, and minerals. These applications rely on the fractionation of the heavy and light oxygen isotopes (^{18}O and ^{16}O) between coexisting phases (solids, fluids, and gases). Isotopic fractionation occurs in the course of several different kinds of chemical reactions and physical processes: (i) isotopic exchange reactions in which isotopes of an element redistribute among different molecules containing that element, (ii) chemical reactions whose rates depend on the isotopic composition of the reactants and products, and (iii) physical processes such as evaporation, crystallization, adsorption, and diffusion.

Isotopic exchange reactions commonly occur between systems incorporating gas, liquid, gas−liquid, gas−solid, or liquid−solid phases. In this work we demonstrate the occurrence of a new isotopic exchange pathway for oxygen. The exchange occurs in the *solid* state, inside the crystal, between differently distributed oxygen atoms in the unit cell. This oxygen exchange pathway is demonstrated on copper sulfate pentahydrate (CuSO$_4$·5H$_2$O) crystals, showing that the exchange occurs between *one* oxygen atom occurring in *one* specific water of crystallization molecule and, at the most, *one* of the oxygen atoms in the sulfate.

CuSO$_4$·5H$_2$O is a crystalline compound containing five water of crystallization molecules per each CuSO$_4$. Four of these molecules are coordinating water molecules which are associated with the Cu^{2+} cation, whereas the fifth one is ionic and is associated with the sulfate anion.[1,2] On heating, this inorganic salt splits off its water molecules via a well-established thermal decomposition route, composed of three sequential key reaction steps that occur along two principal temperature ranges.[3−5] Depending on the heating rate, four of the coordinating water molecules are released along the 100−150 °C temperature range, whereas the remaining SO$_4^{2-}$ associated one, and the most strongly bonded, is released at about 250 °C. Upon further heating, between 600 and 900 °C, the dehydrated copper sulfate decomposes, releasing gaseous SO$_2$ and O$_2$ products. Such clear and full resolution between several desorption steps of water molecules together with the later thermal decomposition of copper sulfate makes the hydrated compound CuSO$_4$·5H$_2$O an ideal complex for gas evolution studies throughout its thermal decomposition period. As hereby reported, carefully planned, detailed measurements of the products desorbed during the thermal decomposition of CuSO$_4$·5H$_2$O revealed the unambiguous occurrence of oxygen isotopic exchange between water of crystallization and the sulfate in the *solid state*.

Experimental Section

CuSO$_4$·5H$_2$O crystals, precrystallized using enriched H$_2^{18}$O, were utilized for the temperature-programmed desorption study of oxygen isotope exchange. ^{18}O-enriched water (Hyox18 LTD) was purchased from Rotem Industries, Israel. The oxygen isotopic abundance of the enriched raw liquid water was redetermined by electrolyzing it, collecting the released gaseous O$_2$ products, and measuring their isotopic composition with a quadropole mass spectrometer (QMS). Initially, as-purchased natural hydrated CuSO$_4$·5H$_2^{16}$O crystals (Merck Ltd.) were fully dehydrated by prolonged evacuation at 400 °C, after which the dehydrated crystals were left to cool to room temperature (rt) under dynamic vacuum. The dried crystals were promptly dissolved in the highly ^{18}O-enriched water. The dissolution was performed at either elevated (∼90 °C) or ambient (rt) temperature. In either case, recrystallization was then carried out, at rt, by slow evaporation of excess enriched water in a desiccator containing silica gel. The thus prepared enriched hydrated crystals were then heated at a controllable rate inside a temperature-programmed desorption (TPD) apparatus to release their water of crystallization molecules and decompose. The oxygen isotopic compositions of the thermally desorbed water molecules and SO$_2$ and O$_2$ decomposition products were measured using a QMS (Balzers QMS 422) at the outlet of the TPD apparatus.

A detailed description of the TPD mass spectrometry (TPD-MS) experimental setup may be found elsewhere.[4,5] Here we

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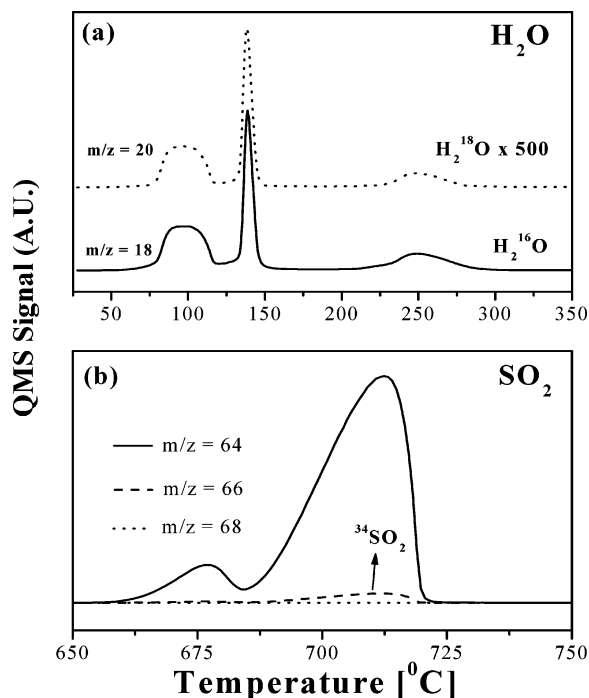
Figure 1. TPD curves of 0.5 mg of $CuSO_4 \cdot 5H_2O$ between 25 and 750 °C (heating rate 15/min). Only water and SO_2 products with isotopic distribution are presented.
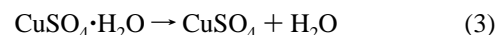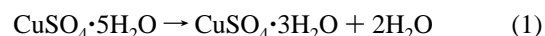
only mention principle key features that enabled the performance of the present study. The apparatus setup incorporates an *atmospheric* pressure TPD reactor provided with a supersonic molecular beam (SMB) inlet. Basically, the TPD-MS instrument with an SMB inlet involves the coupling of two nozzle-via-capillary-connected, differentially pumped vacuum compartments. On the basis of such a configuration, it is practically possible to link between the high vacuum required for the normal operation of the mass spectrometer and the atmospheric pressure existing at the sample-containing TPD reactor. Carriage of the thermally desorbed species from the sample inside the TPD reactor to the MS chamber is achieved by expanding an inert ultra-high-purity (99.999%) dry He carrier gas between the two differentially pumped compartments at a flow rate of 50 sccm. To avoid possible adsorption/desorption reactions of the desorbed water molecules along its trajectory throughout the inlet system, the inlet system is constantly heated to 120 °C. A resulting supersonic molecular beam, containing the desorbed products and the carrier gas, enters axially to the mass spectrometer ion source and flies through, free of any collisions with the walls. TPD data were acquired during linear ramping of the sample temperature between rt and 900 °C, utilizing various predetermined heating rates between 2 and 30 °C/min. The isotopic abundance of the oxygen isotopes in each dissociation reaction were determined by integrating the area occupied by the TPD curve along the characteristic temperature desorption range of interest. These integrals were then used to calculate the depletion/enrichment percentages quoted in the Results and Discussion. Accounting for both the signal to background ratios and the reproducibility of the TPD scans, these estimates have *relative* uncertainties of 2% (2 standard deviations).

Results and Discussion

Figure 1 depicts typical TPD scans of an as-received $CuSO_4 \cdot 5H_2^{16}O$ crystal, 0.5 mg in mass, acquired during sample heating (15 °C/min) between rt and 750 °C. A simultaneous acquisition

of several m/z values was carried out: masses 18 and 20, representing $H_2^{16}O$ and $H_2^{18}O$, respectively (Figure 1a), and 64, 66, and 68, representing the $S^{16}O_2$, $S^{18}O^{16}O + {}^{34}S^{16}O_2$, and $S^{18}O_2 + {}^{34}S^{16}O^{18}O$ species, respectively (Figure 1b). The mass at $m/z = 70$ (${}^{34}S^{18}O_2$) was also measured; however, it resulted in minor intensities that negligibly affected the deduced values relevant to the present study. Hence, its contribution was not accounted for throughout all the calculations.

The three TPD water peaks (Figure 1a) that occur along the temperature range from rt to 350 °C represent the well-established stepwise dehydration of copper sulfate pentahydrate and correspond to the following three reactions:

$$CuSO_4 \cdot 5H_2O \rightarrow CuSO_4 \cdot 3H_2O + 2H_2O \qquad (1)$$

$$CuSO_4 \cdot 3H_2O \rightarrow CuSO_4 \cdot H_2O + 2H_2O \qquad (2)$$

$$CuSO_4 \cdot H_2O \rightarrow CuSO_4 + H_2O \qquad (3)$$

The calculated ratio between the integrated areas under the three background-subtracted peaks in Figure 1a is approximately 2:2:1, resembling the stoichiometry of the above reaction steps (eqs 1–3). Moreover, the relative intensities of the TPD profiles of masses 18 and 20 are in excellent qualitative accordance with the natural abundance of ^{18}O, which is expected to amount to ~0.2 atom %. For an exact quantitative check, one should account for the differences in the sensitivities of the QMS to the different masses, the effect of mass discrimination in the molecular beam, and the fragmentation contribution of the enriched water molecules at $m/z = 18$. These corrections however are minor, and the above apparent relative intensities may be considered to be in fairly good agreement with the natural isotopic abundances expected for oxygen. Following the third and last dehydration step (eq 3 and Figure 1a), further heating above 350 °C shows no major desorption activity for the entire m/z range up to about 650 °C. Somewhat above 650 °C, thermal decomposition of dehydrated copper sulfate is initiated, resulting in characteristic TPD peaks of gaseous SO_2 isotopes as shown in Figure 1b. It may be seen that $CuSO_4$ decomposes in a stepwise doublet fashion, reaching full steep completion at about 725 °C. As in the case of desorbed water molecules, the relative intensities of the desorbed SO_2 isotopes are also found to be in accordance with those expected from the natural abundance of oxygen isotopes. An exact quantitative evaluation in that case is more complicated due to the contribution of ~4.2% naturally abundant ^{34}S to the measured intensities. The calculated abundance of mass 66 from the integral beneath the corresponding TPD curve in Figure 1b was 4.8% instead of 4.6% as expected from the contributions of ^{34}S and ^{18}O isotopes ($^{32}S^{18}O^{16}O + {}^{34}S^{16}O_2$). Once more, this minor dissimilarity may be understood as occurring due to differences in the response function (sensitivity) of the apparatus to the various isotopes. In addition to SO_2, the decomposition reaction of $CuSO_4$ also produces gaseous O_2. However, the calculation of the isotopic abundance of the oxygen gas is a quite complicated task because the ion currents at masses 32–36 also include contributions from fragmentation of SO_2 in the ion source of the mass spectrometer. The last remaining product, CuO, can undergo further decomposition at 900 °C to give oxygen gas and solid Cu_2O. The oxygen isotopic composition of this reaction was also measured (not shown), calculated, and found to match the natural oxygen abundance.

In all, it is clear from the above full resolution between the several dehydration steps and the copper sulfate decomposition that $CuSO_4 \cdot 5H_2O$ is an ideal compound for testing the possibility

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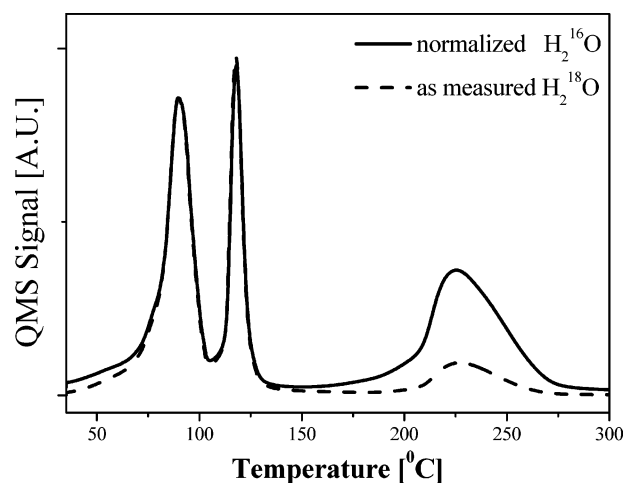
Figure 2. Oxygen isotopic distribution of water from temperature-programmed decomposition of $CuSO_4 \cdot 5H_2O$ crystals grown in ^{18}O-enriched water. The $m/z = 18$ curve was normalized by the ratio of water enrichment.

Figure 3. Oxygen isotopic distribution of SO_2 from temperature-programmed decomposition of $CuSO_4 \cdot 5H_2O$ crystals grown in water with 82% ^{18}O (spectrum no. 1) and after six cycles of dehydration–recrystallization in fresh enriched water (spectrum no. 6).

of oxygen isotope exchange between water of crystallization and sulfate in the solid state during the dehydration and decomposition processes.

In Figure 2 we show the intensities of the TPD profiles of natural ($H_2^{16}O$, $m/z = 18$) and enriched ($H_2^{18}O$, $m/z = 20$) water from an enriched crystal, initially dehydrated at 400 °C, then dissolved in highly ^{18}O-enriched hot water (90 °C), and recrystallized by slow evaporation. It should be mentioned that dissolution in ambient enriched water practically provided the same result.

On dealing with a crystal that was grown using enriched water, one may expect the two curves to be equal following intensity normalization by the ratio of water enrichment. As may be seen in Figure 2 this is indeed the case for the first two TPD water peaks. Surprisingly, however, as depicted by the third TPD water peak, while the normalized curves yielded precise reconstructions of the intensities of the first four desorbed water molecules (eqs 1 and 2), the relative normalized intensities of the fifth desorbed water molecule (eq 3) reveal a clear misfit that unambiguously indicates an ^{18}O deficit in the water of crystallization in the enriched crystal. In other words, the ^{18}O enrichment of the fifth desorbed water molecule is lower than that of the first four water molecules. The calculated isotopic abundance of the first four water molecules, relying on the integrated areas of the relevant TPD profiles up to 150 °C, were 81.0 ± 1.6% ^{18}O and 19.0 ± 0.4% ^{16}O, in agreement with the isotopic composition of the raw liquid water used for the crystal growth (81% ^{18}O). The isotopic composition of the fifth water molecule in the TPD spectra of Figure 2 is however highly suppressed, with an ^{18}O abundance of only 44 ± 0.9%. As will be discussed later, it is interesting to note that this value is slightly higher than half of the ^{18}O enrichment of the raw water used for growing the crystal. One may fairly expect that the overall isotopic composition of all five thermally desorbed water molecules will remain intact with respect to that of the enriched water utilized for the crystallization. Nonetheless, the occurrence of a deficit in the relative amount of desorbed enriched water from such an enriched crystal is clearly evident, inevitably leading to the consideration of a possible isotopic exchange. In that case, accounting for conservation laws, the above deficit is expected, in turn, to manifest itself somewhere else among the desorbed products. The origin for this surprising deficit was indeed traced out by noting the behavior of the TPD curves of the $CuSO_4$ decomposition products, SO_2 and O_2. The SO_2
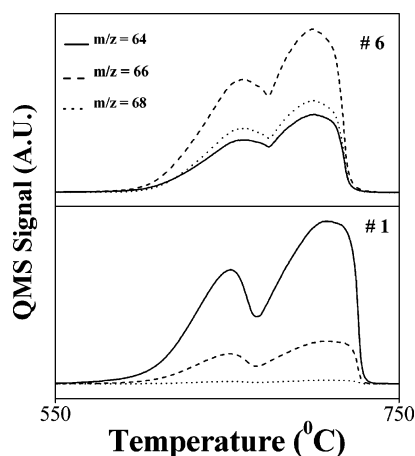
isotopic distribution in the enriched crystals is shown in the lower frame (no. 1) of Figure 3.

The measured abundances of masses 66 and 68 of the enriched crystal increased from 4.70 ± 0.09% and practically 0% to 20.37 ± 0.41% and 1.60 ± 0.03%, respectively. By accounting for the 4.2% natural abundance of ^{34}S, these values indicate an overall ^{18}O enrichment of 9.7 ± 0.2% in the SO_2 product. In view of the extremely slow rate known for the oxygen isotope exchange reaction between dissolved sulfate ion and water molecules in the aqueous phase,[6–10] one may conclude from the above SO_2 isotopic enrichment that the ^{18}O deficit noted for the fifth desorbed water molecule could be attributed to the incorporation of ^{18}O atoms *into the sulfate groups*. Combining the data of desorbed water and SO_2 products provides straightforward qualitative solid evidence of isotopic oxygen exchange between the fifth water molecule of crystallization and the sulfate. Moreover, the isotopic enrichment of the sulfate is further expressed in the decomposition of the CuO product at 900 °C to Cu_2O and gaseous oxygen. The measured abundances of masses 34 ($^{16}O^{18}O$) and 36 ($^{18}O_2$) are 19 ± 0.4% and 1.0 ± 0.5%, respectively, the latter containing a large uncertainty due to the occurrence of a noisy background at this mass. This gives a total of 10.5 ± 0.6% ^{18}O enrichment of the oxygen gas, fairly close to the value of 9.7 ± 0.2% measured for the desorbed SO_2 gas. Practically all the relevant data are now available to calculate approximately the average ^{18}O abundance of the enriched $CuSO_4 \cdot 5H_2O$ crystal. Such a calculation initially relies on the assumption that, during the recrystallization process with enriched water, all five water of crystallization molecules are equally enriched to 82%, the ^{18}O measured abundance of the raw enriched liquid water. Also, intactness of the sulfate group is assumed in the sense that its oxygen atoms remain naturally abundant (0.2% ^{18}O). Then, the average ^{18}O abundance of the as-grown enriched crystal should be 45.6% {(5 × 82% + 4 × 0.2%)/9}. Following thermal decomposition of this crystal, the ^{18}O abundance of the first four water molecules that desorb was found to be 81.0 ± 1.6%, that of the fifth desorbed water molecule was 44.0 ± 0.9%, and the enrichment in the SO_2 and oxygen decomposition products averaged to 10.5 ± 0.6%. The weighted average of these values is ca. 46%, in excellent agreement with 45.6%, the value calculated above for the "as-grown" enriched crystal prior to its thermal decomposition. The significance of the above agreement is that the isotope exchange reaction occurs between the water of crystallization and the sulfate inside the crystal

whereas the oxygen isotopic exchange between the sulfate and the water in the aqueous solution can be, as expected,[6−10] considered negligible.

To explore the mechanism of the isotopic exchange reaction, knowledge of the exchange steps as well as the rate-determining processes is essential. Accounting for the present workflow of the experiment, one may think of two possible oxygen exchange routes: during the initial crystallization process or during heating of the crystal in the TPD reactor, following the dehydration of the first four coordinating water molecules. To test these possibilities, the enrichment of the crystals was studied versus several predetermined crystallization routes, differing in the dissolution and recrystallization steps as follows.

(a) Initial dehydration by evacuation at 400 °C of an as-received natural crystal → dissolution of the dehydrated crystal in enriched water at room temperature → crystallization by slow evaporation. The product was then dehydrated at 400 °C, dissolved in a *new* stock of raw enriched water (enriched to the same degree as in the first dissolution), and recrystallized again via slow evaporation at rt. Six recrystallization cycles were performed. After each cycle a few probe crystals were sampled for TPD measurements.

(b) Initial dehydration by evacuation at 400 °C of an as-received natural crystal → dissolution in enriched water at 90 °C → crystallization by cooling the water to room temperature in a closed vessel, and then dissolution and recrystallization with the *same* water by heating and cooling it, 20 repetitions in total.

The TPD spectra of SO_2, one of the $CuSO_4$ decomposition products, following the first (no. 1) and sixth (no. 6) exchange cycles performed via route a are shown in Figure 3. After six exchange cycles the ^{18}O enrichment of the SO_2 is much more pronounced than that after a single exchange cycle. It is nicely seen in Figure 3 that the intensities of ^{18}O-enriched SO_2 isotopes (masses 66 and 68) following six exchange cycles *both* exceed that of the natural molecule (mass 64). After six exchange cycles the calculated ^{18}O abundance in the sulfate was almost 42%. The ^{18}O abundance in the sulfate increases in a progressive fashion with the exchange cycle. The ^{18}O abundance in the fifth desorbed water molecule (not shown) also increases with the recrystallization cycle via process a. In that case, however, the oxygen isotopic composition of the first four water molecules remains practically constant irrespective of the recrystallization cycle. This important evidence means that the exchange process occurs in a preferable fashion *only* between the fifth anionic water molecule and the sulfate ion and that the first four coordinating water molecules do not participate in the exchange process.

In contrast to the results of process a, in the exchange reaction via route b, after 20 successive crystallization/dehydration cycles, the oxygen isotopic compositions of the fifth water molecule and of the sulfate ion were found to be similar to those after only one exchange cycle via route a. It is thus established that the exchange process does not take place during the crystallization process in the liquid solution but during the last dehydration step upon the release of the fifth water of crystallization molecule from $CuSO_4$ in its solid form (in the present case during heating of the sample inside the TPD reactor). In other words, as long as the sample, after giving up the first four *copper-associated* water molecules, is not further heated to release the fifth *sulfate-associated* water molecule, the exchange most probably will not occur. This is why the sulfates of the crystals obtained either after one cycle via process a or after many cycles via process b are equally enriched with ^{18}O.
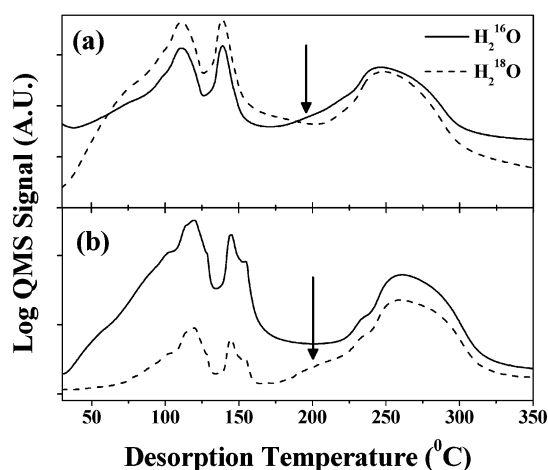
Figure 4. TPD spectra of (a) $CuS^{16}O_4 \cdot 5H_2{}^{18}O$ and (b) $CuS^{18}O_4 \cdot 5H_2{}^{16}O$. Intensities are presented on a logarithmic scale.

Our results strongly suggest that the oxygen isotope exchange occurs during the dehydration reaction, after desorption of the first four water molecules. In the remaining $CuSO_4 \cdot H_2O$ solid, a redistribution of oxygen atoms occurs between the fifth anionic H_2O molecule and the four oxygen atoms of the sulfate ion along the 160−200 °C temperature range. One can assume that the oxygen atoms will redistribute equally, resulting in identical ^{18}O abundances in the fifth water molecule and in the sulfate ion, both expected to amount to one-fifth of the ^{18}O abundance of the enriched water used for crystallization. Nonetheless, as aforesaid, the measured ^{18}O abundance of the fifth water molecule was found to be higher than that in the sulfate, and it was shown that this occurs already after a single exchange cycle and that quantitatively this abundance is slightly higher than half of the ^{18}O abundance in the raw liquid water. Such behavior could be understood if the exchange occurs preferably between the oxygen of the fifth water molecule and, at the most, one specific oxygen atom in the sulfate. Testing the extent of exchange versus the heating rate inside the TPD reactor was inconclusive. We found possible indications that the amount of exchange is larger for heating rates as low as 2° C/min; however, the measured relative enrichment differences are within the measurement reproducibility boundaries. Obviously, the exact temperature and the kinetic properties of the exchange are critical interesting parameters. However, the destructive nature of the TPD technique, in the sense of requiring heating of the samples to temperatures exceeding that of exchange, makes it inadequate for that specific purpose. We intend to reexamine this issue by in situ spectroscopic techniques such as IR and Raman.

A close inspection of the TPD spectra of the enriched crystals along the dehydration temperature range reveals an interesting phenomenon. Shown in Figure 4 are TPD spectra of water isotopes ($H_2{}^{18}O$ and $H_2{}^{16}O$) desorbed from natural copper sulfate hydrated with enriched water, $CuS^{16}O_4 \cdot 5H_2{}^{18}O$ (Figure 4a), and from enriched copper sulfate hydrated with naturally abundant water, $CuS^{18}O_4 \cdot 5H_2{}^{16}O$ (Figure 4b). For the clarity of the discussion, the TPD curves in Figure 4 are given in a logarithmic representation. The initial oxygen enrichment of the water in spectrum a is 97 ± 1.9%, and that of the sulfate in spectrum b is 10.0 ± 0.2%.

A marked structural difference between the $H_2{}^{16}O$ and $H_2{}^{18}O$ TPD profiles is clearly noticed along the 160−250 °C temperature range between the water-enriched and sulfate-enriched crystals. While the desorption rate of $H_2{}^{18}O$ from the water-enriched crystal continues its moderate decrement from about

150 to ∼210 °C (Figure 4a), that of $H_2^{16}O$ starts to increase at about 160 °C. Also, above 175 °C the desorption rate of $m/z = 18$ is higher than that of $m/z = 20$. In addition, a very small shift in the maximum desorption rate of the fifth water molecule at ∼250 °C may also be noted between the two water isotopes. The occurrence of such a phenomenon due to a mass difference effect was checked by testing the desorption spectrum of $CuSO_4$ initially hydrated with heavy water, D_2O, for which no similar differences in the desorption rates among the three isotopes H_2O, HDO, and D_2O ($m/z = 18$, 20, and 22, respectively) were observed. Figure 4b depicts the desorption spectrum of water from a sulfate-enriched crystal. Such specific enrichment of the sulfate ion was achieved via two steps. Initially, an [^{18}O]water-enriched crystal was dehydrated, by which oxygen exchange took place between desorbed water and the sulfate. Then it was rehydrated using *natural* water. In that case, all five H_2O molecules are naturally abundant, whereas only the sulfate group is partially enriched with ^{18}O. In contrast to Figure 4a, a clear reversed effect is indicated in Figure 4b where it is now the $H_2^{18}O$ curve that is inversing its desorption rate at lower temperature with respect to that of $H_2^{16}O$. This effect can be explained by noting the existence of a small water shoulder at 175−220 °C (indicated in Figure 4 by arrows). In Figure 4a this shoulder occurs only in the $H_2^{16}O$ TPD curve, while in Figure 4b it exists mainly in the TPD profile of the $H_2^{18}O$ isotope. If the oxygen atoms of this small $H_2^{18}O$ shoulder originate from oxygen bound to the sulfate, then the intensity of the $H_2^{18}O$ in Figure 4a should have come out negligible, as is indeed the case. In contrast, in Figure 4b where the ^{18}O isotopes are bound only to the sulfate, the observed $H_2^{18}O$ shoulder seems to be a result of partial sulfate decomposition. Hence, since the oxygen exchange process must involve both decomposition and formation of sulfur−oxygen bonds, we believe that the oxygen isotope exchange takes place already between 160 and 250 °C. Traces of some sulfur oxide evolution at 250 °C was observed in earlier works[12] and is also detected by the present TPD study. At high magnifications, an additional SO_2 peak was clearly observed between 250 and 400 °C. These products (H_2O and SO_2) indicate some dissociation of the sulfate at low temperature. However, the SO_2 signal at this temperature range is lower by a factor of 500 compared to the signal at the major dissociation temperature. In Figure 4b it is clearly seen that the $H_2^{18}O$ intensity of the fifth water molecule is higher than the sum of the intensities of the first four water molecules. This is because the origin of the ^{18}O isotope of the fifth water is from the enriched *sulfate* which exchanges its oxygen with that of the fifth water molecule.

Finally, we mention that this new exchange phenomenon is not specific to copper sulfate but was also observed in the present study for other molecules such as $KAl(SO_4)_2 \cdot 12H_2O$ and $FeSO_4 \cdot 7H_2O$.

Conclusions

A new isotopic oxygen exchange route was demonstrated between water of crystallization and a sulfate ion in the solid state. The exchange occurs between the fifth anionic water molecule and the hydrogen-bonded oxygen atoms of the sulfate ion. The exchange was shown to take place below 250 °C within a very short time, in contrast to the common conviction of unfeasible oxygen exchange in sulfates in the aqueous phase under geothermic conditions. Accounting for the fact that dissolved sulfate ion (SO_4^{2-}) plays a key role in geothermal research by serving as a standard oxygen isotope geo-thermometer,[9−11] the new exchange route observed here may have fundamental implications in the field of isotope geology. In this field the effect of fractionation, which is a function of the temperature, is utilized to evaluate the temperatures of equilibration (inside a rock or between a rock and a fluid). To interpret the data, all likely isotope exchange pathways must be accounted for and determined. The existence of a major oxygen exchange mechanism such as that observed in the present work may significantly affect the interpretation of oxygen isotopic ratio results and possibly lead to important consequences over geological time scales. For instance, descent of geothermal fluid can initiate oxygen isotope exchange of hot hydrous minerals by dehydration. Then, after ascent of the geothermal fluid, the isotopic abundance of the dissolved ions can be very different from that if the fluid height had remained constant.

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