Stable Isotope Geochemistry: A Tribute to Samuel Epstein
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Oxygen isotope studies of zeolites: Stilbite, analcime, heulandite, and clinoptilolite—I. Analytical technique*

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Abstract—An analytical technique for measuring $\delta^{18}O$ values of the zeolites stilbite, analcime, heulandite, and clinoptilolite has been developed and tested. The framework oxygen of these minerals can be isotopically analyzed with a good precision using a standard dehydration procedure developed in this study. The analytical accuracy, however, is impaired by isotopic exchange between the framework oxygen and channel water, which is unavoidable during the process of dehydration. The errors thus introduced into the isotopic analyses can be corrected empirically using a calibration curve generated by controlled experiments.

INTRODUCTION

THE OXYGEN ISOTOPIC composition of a mineral is a function of both the $^{18}O/^{16}O$ ratio of the ambient fluid and the temperature of the environment in which it formed. If the mineral is not in equilibrium with its environment, its isotopic composition is also affected by the extent to which it exchanged with the environment prior to the time it was collected. Therefore, the isotopic composition of a mineral may carry some information both about the environment in which it formed and about its subsequent history. These concepts have been the basis for numerous studies of paleoenvironment and of diagenesis and other low temperature processes.

In isotopic studies of diagenesis, $\delta^{18}O$ values of quartz, feldspars, carbonates, and clays are commonly measured (ESLINGER and SAVIN, 1973; YEH and SAVIN, 1977; LAND, 1984; DUTTON and LAND, 1985; LONGSTAFFE, 1986; LAND and FISHER, 1987; AYALON and LONGSTAFFE, 1988; LEE *et al.,* 1989; GIRARD *et al.,* 1989; and many others). Zeolite minerals are common products of low-grade metamorphism and diagenesis, particularly in volcanogenic sediments. Knowledge of the conditions of their formation is important not only to an understanding of problems directly related to the characteristics (*e.g.,* porosity and permeability) of reservoirs in clastic rocks, but also to an understanding of high-grade diagenetic and low-grade metamorphic processes. However, stable isotope methods have only rarely been applied to the study of zeolites.

There are two main reasons for the paucity of isotopic analyses of zeolites. The first is the difficulty of performing isotopic analyses of zeolites. The $\delta^{18}O$ value of the framework (*i.e.,* aluminosilicate) oxygen of a zeolite can be measured only after the removal of channel water. Second, the occurrence of labile channel water within the open framework structure of zeolites raised suspicions that the framework oxygen of these minerals might be susceptible to post-formational isotopic exchange. If so, their isotopic compositions would be of limited usefulness in studies of diagenesis and metamorphism. This paper is a report of the development and testing of a technique for precise, accurate measurement of $\delta^{18}O$ values of zeolites. The preservation of isotopic records in naturally occurring zeolites will be discussed in another paper (FENG and SAVIN, in prep.).

PREVIOUS WORK

SAVIN and EPSTEIN (1970) analyzed three authigenic phillipsite samples, separated from ocean floor sediments. Samples were treated by drying at room temperature in a dry box for between 24 and 72 hours prior to loading in the Ni reaction vessels. The results of drying aliquots of the same sample for differing lengths of time pointed out the complexity of the dehydration behavior of phillipsite and the difficulty of measuring its $^{18}O/^{16}O$ ratio accurately. SAVIN and EPSTEIN (1970) estimated a value of 1.034 for $\alpha_{\text{phillipsite-water}}$ at 0°C.

FENG (1985) analyzed phillipsite that had been handpicked from within a manganese nodule collected in the central North Pacific Ocean. This analysis also indicated a fractionation factor of about 1.034 at ocean bottom temperature. BOHLKE *et al.* (1984) reported $\delta^{18}O$ values of a phillipsite from Deep Sea Drilling Project (DSDP) Hole 396B and of a number of bulk rock samples containing zeolite minerals from the same core and from DSDP Holes 417A and 417D. They studied alteration of deep-sea basalts by correlating the $\delta^{18}O$ values of minerals and bulk rocks in those cores with the H_2O^+ contents. HAY *et al.* (1991) studied clay mineral diagenesis in core KM-3 from Searles Lake, California. They used $\delta^{18}O$ values of a number of minerals, including phillipsite, as the basis for conclusions about the water chemistry of the lake dur-

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ing diagenesis. Both BOHLKE *et al.* (1984) and KITA and HONDA (1987) used $\delta^{18}O$ values of mordenite and clinoptilolite, as well as quartz, cristobalite, kaolinite, and other minerals to distinguish hydrothermally altered rocks from those of diagenetic origin.

In all of the studies mentioned above except that of SAVIN and EPSTEIN (1970), zeolites were dehydrated in the Ni reaction vessels of the fluorination line prior to reaction with BrF_5 according to the technique of CLAYTON and MAYEDA (1963). Because the reaction vessels become lined with hygroscopic fluorine compounds, the water liberated from the zeolites may be absorbed on the sides of the vessels. If this occurs, the oxygen of the absorbed water will be liberated during fluorination of the minerals, resulting in erroneous measurements.

STALLARD and BOLES (1989) reported $\delta^{18}O$ values of laumontite, stilbite, and heulandite from zeolite-facies metavolcanic rocks of the Hokonui Hills, New Zealand. They pointed out that incompleteness of dehydration of the zeolites significantly affects the reproducibility of the isotopic analysis, and showed large isotopic effects of dehydrating at different temperatures and for different lengths of time. In their geological interpretations, they used the data obtained using those dehydration conditions that gave the best precision.

Recently, KARLSSON and CLAYTON (1990) reported $\delta^{18}O$ values of both framework oxygen and channel water of analcime, chabazite, clinoptilolite, laumontite, mordenite, and natrolite. They dehydrated their samples outside of the fluorination line by heating under high vacuum to 450°C prior to analysis of framework oxygen. They qualitatively examined the possibility of isotope exchange between framework oxygen and channel water during dehydration by varying the conditions of dehydration and by exchanging the channel water with a water of different isotopic composition. They concluded that the $\delta^{18}O$ values of dehydrated analcime and mordenite are not affected significantly by changing the procedures of dehydration, and argued that this indicated that the measurements were accurate. However, their treatments affected the $\delta^{18}O$ values of chabazite and laumontite by as much as 2 per mil, leading KARLSSON and CLAYTON (1990) to conclude that the $^{18}O/^{16}O$ ratios of those minerals should be interpreted with caution.

In this paper we show that the dehydration conditions used by STALLARD and BOLES (1989) may not have been appropriate to yield $\delta^{18}O$ values representative of the framework oxygen of stilbite. In addition, we show that dehydration conditions which yield high precision do not necessarily yield accurate $\delta^{18}O$ values.

EXPERIMENTAL

Sample selection and preparation

Stilbite, analcime, heulandite, and clinoptilolite were used in our experimental studies. Purity was the main consideration in the selection of large clean crystals of stilbite (Lonavla, India), analcime (Mont St. Hilaire, Quebec, Canada) and heulandite (Nasik, India). The crystals were crushed, ground, and sieved into two size fractions, 100–200 mesh (74–149 μm) and <200 mesh (<74 μm). Most isotope analyses were made with the 100–200 size fraction. Dehydration experiments and X-ray diffraction analyses (XRD) were mainly done with the finer than 200 mesh fraction. Clinoptilolite, which has a framework structure similar to that of heulandite, but which does not undergo a phase transformation during dehydration, was selected later in the study for comparison with heulandite. Two clinoptilolite samples were used. One (denoted as Clinoptilolite-1) was donated by Giday WoldeGabriel of Los Alamos National Laboratory. He separated the mineral from a bulk rock sample (Yucca Mountain Nuclear Waste Repository Site, bore hole G1) by particle size separation. The 1 to 3 μm fraction used in this study was more than 90% pure clinoptilolite. A second clinoptilolite (Castle Creek, Owyhee Co, Idaho) was obtained from Miriam Kastner of Scripps Institution of Oceanography. XRD and TGA analyses indicated that this sample was greater than 95% clinoptilolite. This clinoptilolite sample will be referred to as Clinoptilolite-2.

Thermogravimetric analysis (TGA)

Thermogravimetric analyses or dehydration studies of the zeolites were undertaken using two methods. In the first method, a Tem-Pres Research TG-716 Thermogravimetric Analyzer was used to obtain curves of weight loss *vs.* temperature while the temperature was raised at a controlled rate. With this instrument the sample can be heated either in the atmosphere or under vacuum ($\approx 10^{-3}$ torr). Weight can be measured with a relative error of less than 5%, and temperature with a relative error of 2%.

In the second method, a McBain-Bakr balance was used to measure the weight loss of the sample during dehydration. The McBain-Bakr balance (Fig. 1) consists of a quartz spring with a hook at either end. The spring is suspended from one hook and a sample cup hangs from a wire about 20 cm long attached to the other. The spring stretches or contracts in proportion to the change in weight of the material in the sample cup. The sample and the balance were enclosed in a 25 mm O.D. quartz tube, sealed at the bottom and connected to a vacuum system at the top. A furnace operated by a temperature controller was placed around the quartz tube. The length of the spring (and hence the sample weight) is measured with a cathetometer. The precision of the cathetometer is 0.005 cm, corresponding to a weight change of 0.05 mg. The amount of sample used for each dehydration experiment was greater than 100 mg, and thus the relative error introduced by the cathetometer reading is smaller then 0.1%.

The apparatus was designed to permit collection of the water liberated upon dehydration. In some experiments, water vapor was introduced into the system by evaporation from a water reservoir held at a constant temperature. The reservoir temperature was always kept lower than room temperature in order to prevent water from condensing on the inner surfaces of the system. The vapor pressure inside the system is determined solely by the temperature of the reservoir.

Oxygen isotope analysis

In preparation for oxygen isotopic analysis, zeolites were partially or completely dehydrated outside of the fluorination line, using the methods described below. To prevent rehydration, samples were exposed only to vacuum or to dry air after dehydration. Oxygen was extracted from the partially or completely dehydrated material using the BrF_5 method of CLAYTON and MAYEDA (1963). Oxygen was converted to CO_2 by a reaction with a hot carbon rod, and then analyzed on a mass spectrometer.

Oxygen was liberated from water samples extracted from

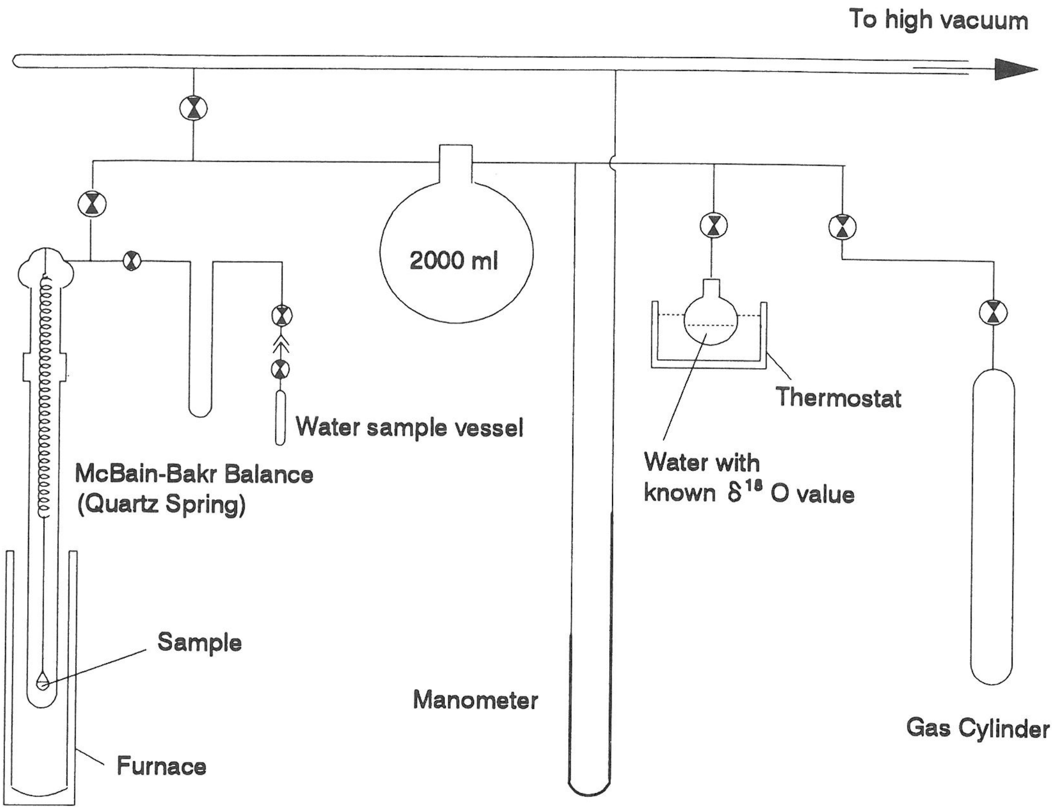

FIG. 1. McBain-Bakr balance used for thermogravimetric studies of zeolites at controlled temperature and P_{H_2O}, studies of gas absorption by zeolites, and extraction of channel water from zeolites.

zeolites by reaction with BrF_5 at 300°C using the method of O'NEIL and EPSTEIN (1966).

Oxygen isotope ratios are expressed in δ notation as deviation in per mil from SMOW (Standard Mean Ocean Water). The $\delta^{18}O$ values of water samples were directly calculated using the $\delta^{18}O$ value of V-SMOW (Vienna SMOW provided by the International Atomic Energy Agency) relative to the mass spectrometer reference gas. The calculated $\delta^{18}O$ values were then normalized using a scale in which the $\delta^{18}O$ value of SLAP (Standard Light Antarctic Precipitation) is defined as -55.5 relative to V-SMOW (COPLEN *et al.,* 1983). The $\delta^{18}O$ value of NBS-28, the isotopic reference material for silicates, was also determined in this fashion. The $\delta^{18}O$ value of NBS-28 was $+9.66$ with respect to V-SMOW after normalization, and this value was used in the calculations of $\delta^{18}O$ of the framework oxygen of the zeolites.

DEHYDRATION BEHAVIOR OF ZEOLITES

Zeolites contain oxygen in at least two distinct structural positions, the oxygen of the aluminosilicate framework and the oxygen of the channel water. The channel water of most zeolites exchanges with the environment very rapidly (KARLSSON, 1988), and, consequently, it does not preserve geological information about the formation of the mineral. In isotopic analysis of the framework oxygen of zeolites, therefore, two things are important: (1) that the channel water be completely eliminated from the zeolite structure and (2) that the dehydration be done in such a way that isotopic exchange between the framework oxygen and the zeolitic water is minimized.

The dehydration behavior of zeolites has been well documented by GOTTARDI and GALLI (1985). Data are mostly in the form of thermogravimetric analysis (TGA) and differential thermal analysis (DTA). Most published data were collected while the zeolite minerals were heated in air at a constant heating rate (typically, 20°C/min). These data are not sufficient for our needs. In order to determine the optimal dehydration condition for isotope analysis of a zeolite it is necessary to investigate carefully its dehydration behavior as a function of temperature, time, and P_{H_2O}. The results of our investigations of the dehydration of analcime, stilbite, clinoptilolite, and heulandite are summarized below. Details can be found in FENG (1991).

1) The dehydration state of each of the four minerals studied is a function of temperature, P_{H_2O}, and, until equilibrium with the surroundings is established, the time the sample is held at a particular temperature and P_{H_2O}.

2) Clinoptilolite, heulandite, and stilbite lose approximately half of their total channel water during evacuation overnight at room temperature. Analcime, on the other hand, does not lose any measurable weight, *in vacuo,* at room temperature.

3) At every temperature, the dehydration of the zeolites is rapid at first and decreases with increasing time.

4) Stilbite undergoes a phase transformation to metastilbite between 100 and 150°C. If the maximum temperature to which the stilbite was heated is less than 250°C, the mineral returns to its original structure when cooled to room temperature and returns to its original hydration state if water vapor is present at room temperature. Heulandite is irreversibly transformed to metaheulandite (heulandite B) when heated to 250 to 300°C. When heated to temperatures lower than 250°C it undergoes no phase transformation, and when cooled to room temperature it regains its original water content.

5) Clinoptilolite, heulandite, and stilbite all undergo structural collapse when completely dehydrated. Collapse of heulandite and stilbite occurs at about 450 to 500°C. Collapse of clinoptilolite occurs between 700 and 800°C. The crystal structure of analcime is not altered at temperatures at least as high as 800°C.

6) Reversible or nearly reversible rehydration is possible for all the zeolites except zeolite analcime if they are not heated above a critical temperature (250°C for the heulandite and stilbite and 450°C for clinoptilolite).

ISOTOPIC ANALYSIS OF ZEOLITES

Dehydration procedure

The dehydration behavior of the zeolites studied suggests that the optimal dehydration procedure preceding the isotopic analysis of the framework oxygen ought to consist of evacuation at room temperature followed by stepwise thermal dehydration. This procedure is based on the assumption that if isotope exchange between framework oxygen and channel water occurs during dehydration it would occur to the greatest extent at higher temperatures. The procedure was therefore designed to remove as much channel water as possible at low temperatures.

Heulandite, stilbite, and clinoptilolite samples are held under vacuum for exactly 14 hours. This time is sufficient to remove 50% of the channel water from the structure of those zeolites. Because analcime does not lose weight at room temperature (FENG, 1991), it may be evacuated for a shorter interval.

Stepwise thermal dehydration *in vacuo* is done using a 50°C interval between steps. Below 300°C, the system is held at each temperature for 1.5 hours. Since constant weight is approached much more rapidly at higher temperatures, the time of evacuation often can be reduced to one hour or even less at temperatures of 300°C and above. In the following context, we shall call this two-stage, stepwise dehydration procedure the *Standard Procedure.*

Analytical precision

Aliquots of each of our samples were dehydrated using the standard procedure. These were all treated identically except for the ultimate dehydration temperature, which varied from room temperature to 700°C.

The results of these experiments are contained in Table 1. Figures 2 to 5 show the relationships between $\delta^{18}O$ and the ultimate dehydration temperature for each zeolite.

When the ultimate dehydration temperature is below 150°C, the $\delta^{18}O$ values of dehydration residues of stilbite are low and increase with increasing temperature (Fig. 2). Above 150°C the curve levels off. The shape of the curve through the data points is very similar to the curve of weight loss of stilbite as a function of temperature (FENG, 1991). The low $\delta^{18}O$ values obtained in experiments with ultimate dehydration temperatures lower than 150°C probably reflects the analysis of mixtures of framework oxygen and residual ^{18}O-depleted channel water. At temperatures between 150 and 650°C, the total range of variation of $\delta^{18}O$ values is only 0.56 per mil. The average $\delta^{18}O$ value is 24.18 ± 0.16 (one standard deviation). This standard deviation is similar to those we typically obtain in our laboratory for oxygen isotope analyses of quartz.

Similar results were obtained for analcime (Fig. 3). The $\delta^{18}O$ values increase slightly with temperature up to 250°C. They then increase sharply with temperature between 250 and 400°C, the interval in which the greatest loss of channel water occurs (FENG, 1991). The curve levels off above 400°C. The average of the seven $\delta^{18}O$ analyses with ultimate dehydration temperatures of 400°C and above is 13.36 ± 0.12.

The data obtained for heulandite do not indicate any plateau temperature above which the measured $\delta^{18}O$ values of the framework oxygen remain es-

Table 1. Oxygen isotope analyses of stilbite, analcime, heulandite, and clinoptilolite: Effect of dehydration on $\delta^{18}O$ value and analytical precision.

Mineral	Ultimate dehydration temperature (°C)*	$\delta^{18}O$ (per mil)	Statistics
Stilbite	28	22.20	For ten samples dehydrated up to 150°C and higher temperatures: Mean: 24.18 Standard Deviation: 0.16 *n*: 10
	50	22.71	
	100	23.36	
	150	24.29	
	230	24.09	
	250	24.11	
	300	24.29	
	320	23.95	
	340	23.87	
	400	24.22	
	521	24.43	
	600	24.20	
	653	24.32	
Analcime	24	9.11	For seven samples dehydrated up to 400°C or higher temperatures: Mean: 13.36 Standard Deviation: 0.12 *n*: 7
	100	9.33	
	150	9.35	
	200	9.51	
	250	9.79	
	300	10.28	
	350	11.76	
	400	13.16	
	450	13.31	
	500	13.28	
	550	13.38	
	600	13.59	
	650	13.38	
	700	13.39	
Heulandite	24	20.74	For eight samples dehydrated up to 350°C or higher temperatures: Mean: 25.45 Standard Deviation: 0.27 *n*: 8
	50	21.54	
	100	22.38	
	150	23.59	
	200	24.02	
	250	23.94	
	300	24.34	
	350	25.16	
	400	25.10	
	450	25.26	
	500	25.34	
	550	25.44	
	600	25.72	
	650	25.87	
	700	25.72	
Clinoptilolite-1	24	18.15	For seven samples dehydrated up to 150°C or higher temperatures: Mean: 17.03 Standard Deviation: 0.10 *n*: 7
	50	17.69	
	100	17.54	
	150	17.09	
	200	17.24	
	250	17.01	
	300	16.94	
	350	17.08	
	400	16.92	
	450	16.95	

* Ultimate dehydratation temperature: Samples were dehydrated stepwise to these temperatures using the Standard Procedure as defined in the text.

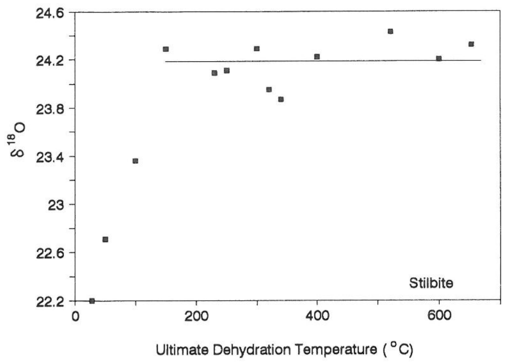

FIG. 2. Measured $\delta^{18}O$ value of stilbite following stepwise dehydration according to the standard procedure at a range of ultimate dehydration temperatures. Each point represents a different aliquot of stilbite. The horizontal line shows the average $\delta^{18}O$ value, 24.18 ± .16 (one standard deviation), of the aliquots dehydrated to ultimate dehydration temperatures between 150 and 650°C.

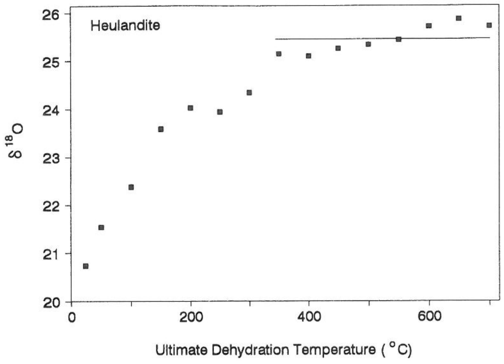

FIG. 4. Measured $\delta^{18}O$ value of heulandite following stepwise dehydration according to the standard procedure at a range of ultimate dehydration temperatures. Each point represents a different aliquot of the heulandite. The horizontal line shows the average $\delta^{18}O$ value, 25.45 ± .27, of aliquots dehydrated to ultimate dehydration temperatures between 350 and 700°C.

sentially constant (Fig. 4). Weight loss measurements done under the same dehydration conditions (FENG, 1991) show that heulandite continues to lose weight up to at least 850°C, with no obvious sign of becoming completely dehydrated. The eight analyses with ultimate dehydration temperatures between 350 and 700°C give a range of $\delta^{18}O$ values between 25.10 and 25.87, with an average of 25.45 ± 0.27. The standard deviation (which includes variation other than random errors) is slightly greater than those obtained for stilbite and analcime.

Unlike the other three minerals, the $\delta^{18}O$ value of clinoptilolite decreases with increasing temperature at temperatures below 150°C (Fig. 5). Consistent analyses were obtained for those aliquots that were heated to 150°C or higher (mean $\delta^{18}O = 17.03 \pm 0.10$). The residual channel water in aliquots with ultimate dehydration temperatures less than 150°C must have been enriched in ^{18}O relative to the framework oxygen in order to yield the results shown in Fig. 5. In a later section we show that when the channel water of a zeolite is removed from the mineral structure, there is an isotopic fractionation between the evolved and the residual channel water, in which the water removed is preferentially enriched in $H_2{}^{16}O$. The clinoptilolite data can be

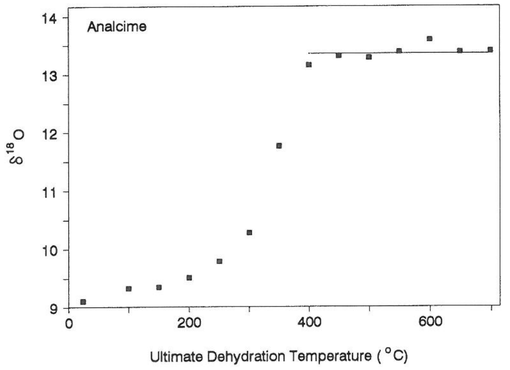

FIG. 3. Measured $\delta^{18}O$ value of analcime following stepwise dehydration according to the standard procedure at a range of ultimate dehydration temperatures. Each point represents a different aliquot of analcime. The horizontal line shows the average $\delta^{18}O$ value, 13.36 ± .12, of aliquots dehydrated to ultimate dehydration temperatures between 400 and 700°C.

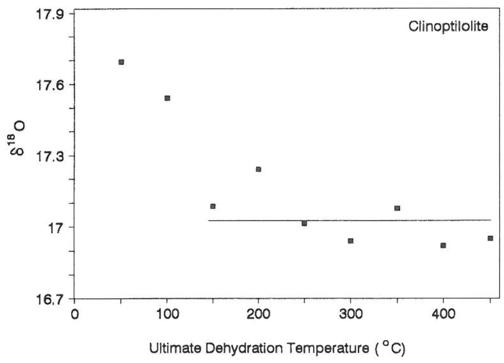

FIG. 5. Measured $\delta^{18}O$ value of clinoptilolite following stepwise dehydration according to the standard procedure at a range of ultimate dehydration temperatures. Each point represents a different aliquot of the clinoptilolite. The horizontal line shows the average $\delta^{18}O$ value, 17.03 ± .10, of aliquots dehydrated to ultimate dehydration temperatures between 150 and 450°C.

interpreted as resulting from an isotopic fractionation between the evolved and the residual channel water so large that the $\delta^{18}O$ value of the residual channel water at room temperature became higher than that of the framework oxygen.

In summary, consistent $\delta^{18}O$ values can be obtained when analcime, clinoptilolite, stilbite, and possibly heulandite are analyzed using the standard stepwise dehydration procedure.

Oxygen isotope exchange between zeolite framework and channel water during dehydration

The good precision obtained in the isotopic analysis of the four zeolite minerals suggests two alternative interpretations: (1) there is no isotopic exchange between the framework oxygen and channel water during dehydration, so that the mean of the $\delta^{18}O$ values (obtained at ultimate dehydration temperatures in the plateau temperature range) represents the true isotopic composition of the framework oxygen; (2) alternatively, isotopic exchange between the framework oxygen and channel water does occur, but the amount of exchange is equal for those aliquots that give the same $\delta^{18}O$ values. If the latter possibility is true the measured $\delta^{18}O$ values may be inaccurate. To test whether isotopic exchange between channel water and framework oxygen occurs during dehydration, a set of experiments was conducted using the procedure described below.

Aliquots of stilbite, heulandite, and clinoptilolite were partially dehydrated, following the standard procedure, up to a desired ultimate temperature, 230°C for stilbite and 250°C for heulandite and clinoptilolite. (This partial dehydration procedure will be referred to as *Dehydration Procedure-I.*) Samples were then isolated from the vacuum pump and allowed to cool to room temperature. Water vapor (evaporated, *in vacuo,* at a constant temperature, usually 23.5°C, from a water reservoir with a $\delta^{18}O$ of $+102.3$) was then introduced into the system. The temperature determines both the $\delta^{18}O$ value of the vapor ($\approx +93$) and the P_{H_2O} (about 21 torr). The zeolites were exposed to the vapor for no less than 30 min in order to become largely rehydrated. Following rehydration the samples were disconnected from the water reservoir and dehydrated for a second time, following the standard procedure to various ultimate dehydration temperatures. (This step will be called *Dehydration Procedure-II.*) The $\delta^{18}O$ values of the dehydration residues were measured, and the analytical results are listed in Table 2.

A plot of the $\delta^{18}O$ value of stilbite *vs.* ultimate heating temperature of Dehydration Procedure-II is shown in Fig. 6. The original $\delta^{18}O$ value of the material before rehydration with ^{18}O-enriched water vapor is also shown.

The $\delta^{18}O$ values decrease sharply with increasing ultimate dehydration temperature up to approximately 200°C. Most of this decrease in $\delta^{18}O$ must reflect progressive loss of the ^{18}O-enriched channel water that was introduced into the mineral. While measurements of oxygen yields obtained from these partially hydrated residues are not particularly accurate, the samples with dramatically high $^{18}O/^{16}O$ ratios definitely yield more oxygen upon fluorination than the stoichiometric amount of framework oxygen. As the ultimate dehydration temperature increases above 250°C, the $\delta^{18}O$ value, as expected, approaches a constant value (28.16 ± 0.35 and a total range of values of 0.84). This value is about 4 per mil higher than the $\delta^{18}O$ value obtained by analysis of the original stilbite (24.14 ± 0.16). This clearly indicates that the aluminosilicate structure of the stilbite was isotopically altered during the treatments following Dehydration Procedure-I (*i.e.,* during rehydration at room temperature and/or during Dehydration Procedure-II). Isotopic exchange between framework oxygen and channel water at room temperature is slow (FENG, 1991), suggesting that most of the observed isotopic exchange occurs during Dehydration Procedure-II. It is possible that some additional exchange may also occur during rehydration (FENG, 1991). Although analytical precision was poorer by about 0.2 per mil following Dehydration Procedure-II, this would nevertheless be satisfactory for many geological applications. It is clear from the results, however, that the precision of the analyses is in no way an indicator of their accuracy.

The results for heulandite and clinoptilolite are illustrated in Figs. 7 and 8. Although quantitatively different, these two curves are similar in shape to the one for stilbite (Fig. 6). Below an ultimate dehydration temperature of 150°C, $\delta^{18}O$ values and oxygen yields both decrease progressively with increasing temperature. This indicates that the dehydration residues contain ^{18}O-rich remnant channel water. At higher ultimate dehydration temperatures the $\delta^{18}O$ value of each mineral approaches a constant value, which is significantly higher than the $\delta^{18}O$ values measured for the original framework oxygen (6 per mil higher for heulandite and 1.5 per mil higher for clinoptilolite). For each of those minerals the standard deviation of the measurements is comparable to that obtained before rehydration and is much smaller than the shift in $\delta^{18}O$ values. This indicates that, as with stilbite, isotope

Table 2. Oxygen isotope analyses of zeolites after dehydration and rehydration with ^{18}O-enriched water.

Sample	Ultimate dehydration temperature (°C)	Oxygen yield (percent)	δ^{18}O (per mil)	Statistics
Stilbite	25	115	44.64	Temperature Range: 250–600°C
	60	109.5	42.24	Mean: 28.16
	90	102.3	40.22	Standard Deviation: 0.35
	125	90.2	36.04	*n*: 5
	175	96.3	34.02	
	230	75.6	29.86	
	250	94.1	28.55	
	300	93.6	27.88	
	400	94.3	27.78	
	500	95.8	28.62	
	600	93	27.99	
Heulandite	24	118.4	36.35	Temperature Range: 150–700°C
	100	114.1	33.94	Mean: 31.45
	150	106	31.53	Standard Deviation: 0.34
	200	106	31.49	*n*: 7
	300	103.9	30.94	
	400	101.3	31.25	
	500	96.8	31.84	
	600	96.8	31.95	
	700	90.6	31.15	
Clinoptilolite-1	24	106.8	22.36	Temperature Range: 150–450°C
	50	103.3	21.59	Mean: 18.56
	100	98	19.43	Standard Deviation: 0.18
	150	96.9	18.63	*n*: 7
	200	95.3	18.46	
	250	91.2	18.31	
	300	91.3	18.38	
	350	92.1	18.59	
	400	92.4	18.87	
	450	87	18.68	

* Ultimate dehydration temperature: samples were dehydrated using Dehydration Procedure-I (see text), then cooled to room temperature. Water vapor with δ^{18}O value of about +93 was introduced. After the zeolites were completely rehydrated, they were again dehydrated, using Dehydration Procedure-II and heating to the indicated temperature.

exchange takes place between the channel water and the framework oxygen during Dehydration Procedure-II.

Additional evidence that isotope exchange between channel water and framework oxygen occurs during dehydration comes from the isotopic analyses of the fractions of channel water extracted during dehydration (Table 3). In Fig. 9a the δ^{18}O value of each fraction of channel water is plotted against the temperature at which it was extracted. The lower curve is drawn through the data points obtained by stepwise dehydration of the original stilbite, and the upper curve is drawn through the data points obtained from the stilbite rehydrated with ^{18}O-enriched water. In each case, at low temperatures the δ^{18}O values of the water fractions increase sharply with extraction temperature. This indicates that during evolution of channel water from the zeolite structure $H_2{}^{16}O$ molecules are lost preferentially to $H_2{}^{18}O$, leaving the residual channel water increasingly enriched in ^{18}O. This progressive isotopic enrichment of the residual water terminates at around 200°C and the trend then reverses; in the latter part of the dehydration process channel water becomes progressively enriched in ^{16}O as the ultimate dehydration temperature increases. This reversal is especially striking in the dehydration of stilbite rehydrated with ^{18}O-rich water. It is also clear, and is shown in Fig. 9b, that the difference between the δ^{18}O values of the water fractions in the two sets of experiments decreases sharply with temperature at temperatures above 100°C.

Because the liberated water was immediately removed from the system and P_{H_2O} was very low, back exchange between water vapor and channel water was limited. If the only mechanism affecting

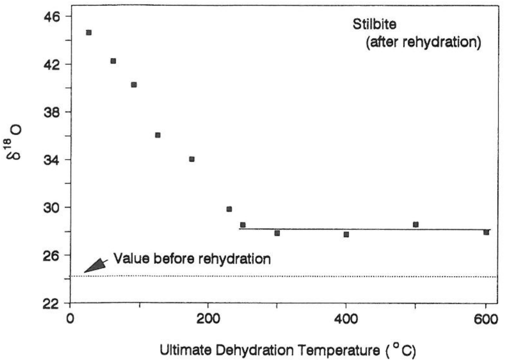

FIG. 6. Measured $\delta^{18}O$ values of the framework oxygen of stilbite analyzed after partial dehydration using the Dehydration Procedure-I and rehydration at room temperature with ^{18}O-enriched water vapor ($\delta^{18}O_{vapor} \approx +93$). The second dehydration was done using Dehydration Procedure-II. The dashed line shows the average $\delta^{18}O$ value before the water vapor was introduced (from Fig. 2). The solid line is the average $\delta^{18}O$ value ($28.16 \pm .35$) obtained from the aliquots which were heated to ultimate temperatures between 250 and 600°C during Dehydration Procedure-II.

the isotopic compositions of the water fractions in the two experiments was the fractionation which occurs during the evolution of channel water, the two curves of Fig. 9a would be almost parallel and the difference between them (Fig. 9b) would be almost constant. Thus, an additional mechanism must be affecting the isotopic composition of the channel water. As suggested by the analysis of the zeolite residues following Dehydration Procedure-II and confirmed here, this mechanism is isotopic exchange between channel water and the framework oxygen of stilbite. Both mechanisms, isotope fractionation during evolution of channel water and isotopic exchange between framework oxygen and channel water, must occur throughout the entire process of dehydration. At low temperatures, at which the rate of exchange is low and the amount of channel water is large, the $\delta^{18}O$ value of the evolved water is largely controlled by the fractionation that accompanies its evolution. As the temperature is raised and the ratio of channel water to framework oxygen decreases, isotope exchange between the channel water and the framework oxygen becomes progressively more important. In the case of stilbite, this exchange is measurable at temperatures as low as 100°C. In the extreme, at high temperatures the isotopic composition of the evolved water is controlled almost completely by exchange between the channel water and the framework oxygen, as witnessed by the convergence of the two curves in Fig. 9a.

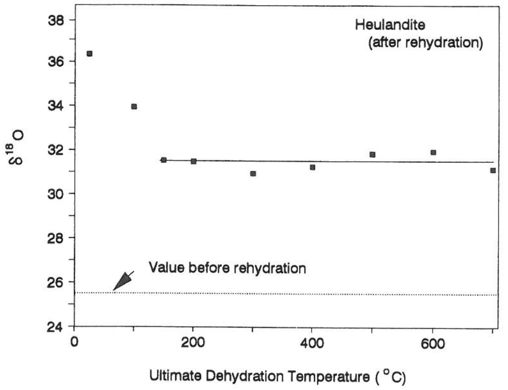

FIG. 7. Measured $\delta^{18}O$ values of the framework oxygen of heulandite analyzed after partial dehydration using the Dehydration Procedure-I and rehydration at room temperatures with ^{18}O-enriched water vapor ($\delta^{18}O_{vapor} \approx +93$). Details are described in caption to Fig. 6. The solid line is the average $\delta^{18}O$ value ($31.45 \pm .34$) obtained from the aliquots which were heated to ultimate temperatures between 150 and 700°C during Dehydration Procedure-II.

The isotopic exchange of the framework oxygen of stilbite, heulandite, and clinoptilolite with channel water during dehydration clearly impairs the accuracy of analysis of these zeolites. In the following section we discuss an approach for determining the effect on the measured $\delta^{18}O$ value of this isotopic exchange and present a method for correcting the analytical data to obtain $\delta^{18}O$ values that are accurate as well as precise.

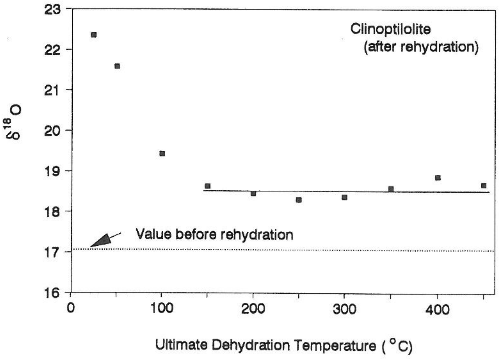

FIG. 8. Measured $\delta^{18}O$ values of the framework oxygen of clinoptilolite analyzed after partial dehydration using the Dehydration Procedure-I and rehydration at room temperature with ^{18}O-enriched water vapor ($\delta^{18}O_{vapor} \approx +93$). Details are described in caption to Fig. 6. The solid line is the average $\delta^{18}O$ value ($18.56 \pm .18$) obtained from the aliquots which were heated to ultimate temperatures between 150 and 450°C during Dehydration Procedure-II.

Table 3. Oxygen isotope ratios of channel water fractions extracted during dehydration of stilbite.

Channel water	Extraction temperature (°C)	Water amount (μl)	Oxygen yield (percent)	$\delta^{18}O$ (per mil)
Original*	23	0.95	98.5	−27.47
	23	3.45	99.2	−44.89
	23	3.00	93	−46.2
	23	2.55	88.3	−39.43
	60	1.87	80.9	−28.69
	90	2.97	94.5	−18.55
	125	1.37	94.5	7.23
	175	2.76	90	27.62
	230	2.10	87.4	29.12
	330	1.50	78	11.94
	500	0.76	66.3	1.54
^{18}O rich**	25	1.90	108	66.06
	25	3.25	97	54.88
	25	3.16	99.7	56.22
	25	1.99	103	57.48
	60	1.76	102.4	68.58
	90	2.10	97.6	79.48
	125	2.49	102.6	94.21
	175	1.61	91.7	102.88
	175	1.37	92	94.24
	230	2.21	88	94.31
	330	1.25	93.6	47.25
	500	0.78	87.6	7.95

* Original channel water is the water which existed in the stilbite channels prior to any treatment in our laboratory. Fractions of water were collected at the indicated extraction temperatures.

** ^{18}O rich water was extracted from stilbite that had been dehydrated and then rehydrated with water vapor that had a $\delta^{18}O \approx +93$.

Analytical accuracy

The results of stepwise dehydration experiments such as those shown for stilbite in Fig. 2 and for heulandite in Fig. 4 suggest an empirical approach to determine the $\delta^{18}O$ value of a zeolite. For each zeolite studied there is an ultimate dehydration temperature (*e.g.*, 150°C in the case of stilbite) above which (1) the measured $\delta^{18}O$ value is approximately constant and (2) it is possible to rehydrate the partially dehydrated mineral almost completely. It is thus possible to create in the laboratory a zeolite with framework oxygen of known $\delta^{18}O$ value. This dehydrated zeolite can be rehydrated in a water vapor atmosphere of known $\delta^{18}O$. The measured $\delta^{18}O$ value of this rehydrated zeolite is, in general, different from that of the before rehydration. The magnitude of the shift in the measured $\delta^{18}O$ value can be determined as a function of the $^{18}O/^{16}O$ ratio of the introduced water vapor. The relationship obtained can be used as a calibration curve to correct the measured $\delta^{18}O$ value of the framework oxygen.

In practice, the calibration curve is generated as follows: Several aliquots of a zeolite are treated according to Dehydration Procedure-I. One aliquot is analyzed directly and the others are subject to rehydration in water vapor atmospheres of different isotopic compositions. This is followed by Dehydration Procedure-II and, then, isotopic analysis of each residue.

The ultimate heating temperature of Dehydration Procedure-II was uniformly 600°C for each aliquot of stilbite and heulandite. Several duplicates were run to improve statistical significance. The results of these experiments are included in Table 4 and are plotted in Figs. 10 and 11. In these figures and in the discussion below,

$$\Delta_{ff\text{-}wv} = 10^3 \ln \alpha_{ff\text{-}wv}, \quad \text{and}$$

$$\Delta_{ff\text{-}of} = 10^3 \ln \alpha_{ff\text{-}of}$$

where *ff* designates the final framework oxygen after

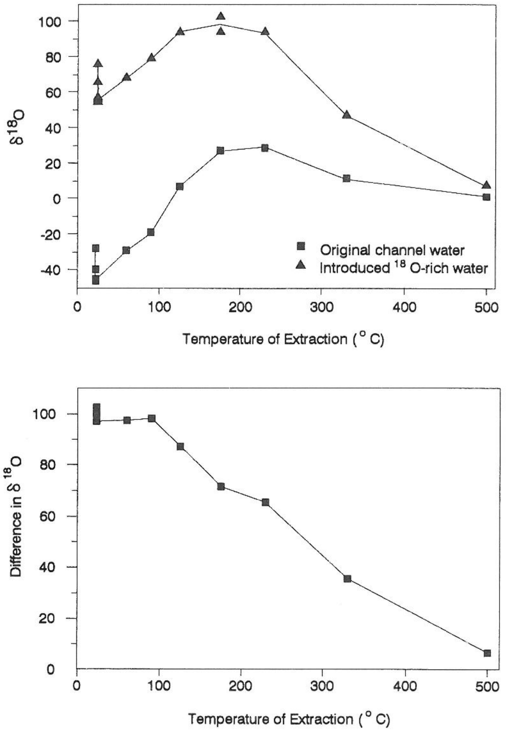

FIG. 9. (a) Isotopic evolution of fractions of channel water extracted from the original stilbite (squares) and stilbite rehydrated with ^{18}O-rich water vapor (triangles). (b) Arithmetic difference between $\delta^{18}O$ values of fractions of channel water fractions extracted, under the same experimental conditions, from the original stilbite and the stilbite rehydrated with ^{18}O rich water vapor.

Table 4. Effect of $\delta^{18}O$ value of channel water on the measured $\delta^{18}O$ value of framework oxygen of stilbite and heulandite.

Mineral	$\delta^{18}O_{of}$*	$\delta^{18}O_{wv}$*	$\delta^{18}O_{ff}$*	$\Delta_{ff\text{-}wv}$†	$\Delta_{ff\text{-}of}$‡
Stilbite	24.18	−32.31	24.22	56.77	0.05
	24.18	−32.31	24.04	56.60	−0.12
	24.18	−8.52	24.73	32.98	0.54
	24.18	−8.52	24.51	32.77	0.33
	24.18	16.79	24.93	7.98	0.74
	24.18	16.79	25.49	8.52	1.29
	24.18	46.23	26.27	−19.26	2.05
	24.18	91.92	27.99	−60.34	3.72
Heulandite	25.45	−32.31	26.66	59.15	1.17
	25.45	−32.31	26.91	59.40	1.43
	25.45	−8.52	28.84	36.99	3.30
	25.45	−8.52	28.87	37.02	3.33
	25.45	16.79	29.70	12.61	4.13
	25.45	16.79	29.99	12.90	4.42
	25.45	46.23	30.53	−15.12	4.94
	25.45	46.23	30.79	−14.87	5.20
	25.45	91.92	31.95	−56.49	6.32
	25.45	91.92	31.15	−57.27	5.54

* $\delta^{18}O_{of}$ (*of* denotes original framework oxygen) is the $\delta^{18}O$ value of the mineral prior to rehydration (*i.e.*, the true $\delta^{18}O$ value of the framework oxygen at the start of the experiment). $\delta^{18}O_{wv}$ (*wv* denotes the water vapor) is the $\delta^{18}O$ value of the vapor used to rehydrate the mineral after Dehydration Procedure-I. $\delta^{18}O_{ff}$ (*ff* denotes the final framework oxygen) is the measured $\delta^{18}O$ of the framework oxygen following rehydration with isotopically labeled vapor and dehydration according to Dehydration Procedure-II.

† $\Delta_{ff\text{-}wv} = 10^3 \ln \alpha_{ff\text{-}wv}$, where *ff* denotes the final framework oxygen and *wv* denotes the water vapor.

‡ $\Delta_{ff\text{-}of} = 10^3 \ln \alpha_{ff\text{-}of}$, where *of* denotes original framework oxygen.

Dehydration Procedure-II, *of* designates the original framework oxygen after Dehydration Procedure-I, and *wv* designates water vapor (note that $\delta^{18}O_{of}$ for all of the runs using Dehydration Procedure-II is equivalent to $\delta^{18}O_{true}$ for those runs). In the experiment design used, $\delta^{18}O_{wv}$ may be taken to be constant for the duration of any single rehydration experiment.

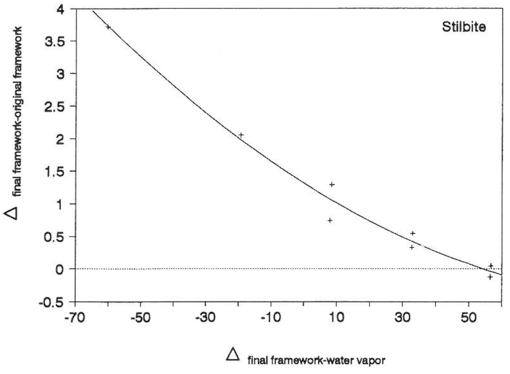

FIG. 10. Calibration curve for correction of isotopic analyses of stilbite. The curve is the quadratic fit to the experimental data and is given by the equation

$$\Delta^{stilbite}_{ff\text{-}of} = 1.312 - 0.0317\Delta^{stilbite}_{ff\text{-}wv} + 1.4 \times 10^{-4}(\Delta^{stilbite}_{ff\text{-}wv})^2.$$

When used for the purpose of correction of analyses, the final framework oxygen is equivalent to the measured framework oxygen and the original framework oxygen corresponds to the true framework oxygen of the natural stilbite.

Figure 10 is a plot of $\Delta_{ff\text{-}of}$ *vs.* $\Delta_{ff\text{-}wv}$ for stilbite, and Fig. 11 is a similar plot for heulandite. Polynomial regressions through the data points are also plotted on the figures. A quadratic fit of the stilbite data gives the following equation:

$$\Delta^{stilbite}_{ff\text{-}of} = 1.312 - 0.0317\Delta^{stilbite}_{ff\text{-}wv} + 1.4 \times 10^{-4}(\Delta^{stilbite}_{ff\text{-}wv})^2. \quad (1)$$

The regression is statistically significant and the standard error of $\Delta^{stilbite}_{ff\text{-}of}$ estimate is 0.20 per mil. This error is comparable to the analytical precision.

Both quadratic and a cubic fits through the heulandite data are statistically significant, but a smaller standard error (0.28) comparable to the analytical precision is obtained with the cubic fit, which has the equation (where *heul* denotes heulandite)

$$\Delta^{heul}_{ff\text{-}of} = 4.732 - 0.0232\Delta^{heul}_{ff\text{-}wv} - 3.02 \times 10^{-4}(\Delta^{heul}_{ff\text{-}wv})^2 - 4.647 \times 10^{-6}(\Delta^{heul}_{ff\text{-}wv})^3. \quad (2)$$

If several assumptions and conditions are satisfied

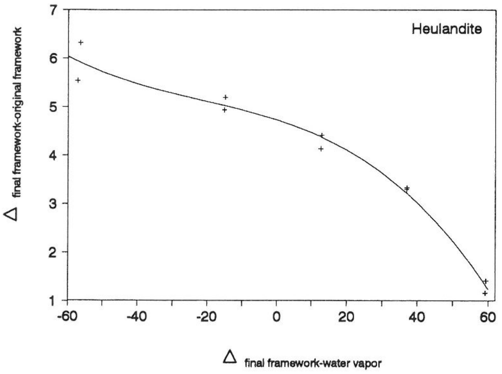

FIG. 11. Calibration curve for correction of isotopic analyses of heulandite. The curve is the quadratic fit to the experimental data and is given by the equation

$$\Delta^{\mathrm{heul}}_{\mathrm{ff\text{-}of}} = 4.732 - 0.0232\Delta^{\mathrm{heul}}_{\mathrm{ff\text{-}wv}} - 3.02 \times 10^{-4}(\Delta^{\mathrm{heul}}_{\mathrm{ff\text{-}wv}})^2 - 4.647 \times 10^{-6}(\Delta^{\mathrm{heul}}_{\mathrm{ff\text{-}wv}})^3.$$

When used for the purpose of correction of analyses, the final framework oxygen is equivalent to the measured framework oxygen and the original framework oxygen corresponds to the true framework oxygen of the natural heulandite.

we may use Figs. 10 and 11 to estimate $\delta^{18}O_{\mathrm{true}}$ for stilbite and heulandite.

1) *The $\delta^{18}O$ value of water vapor in the environment of the zeolite prior to analysis must be known or estimated.* In the analysis of an unknown sample, this condition may be met if the $\delta^{18}O$ value of the water vapor in the natural environment is known or if the channel water in the sample has been completely exchanged with water vapor in the laboratory.
2) *The channel water of the stilbite or heulandite must be in isotopic equilibrium with this water vapor.* This condition is nearly valid for the samples and conditions used to generate the calibration curve in Fig. 10 (FENG, 1991). It is much harder to verify for natural zeolites. Because of the mobility of channel water and the relatively large size of the internal channels in stilbite and heulandite, we suspect that the channel water exchanges with the atmospheric water vapor fairly rapidly on the laboratory shelf. However, the details of the kinetics of this exchange require further study.
3) *Oxygen isotope exchange between the channel water and the framework oxygen of the stilbite or heulandite must occur in the same way and in the same rate in the unknown sample as in the stilbite and heulandite used in this study.* The calibration curves in Figs. 10 and 11 were generated using one stilbite sample and one heulandite sample, each of uniform grain size. Further study is required to determine whether these curves are sensitive to grain size or to chemical or crystallographic variability of the zeolites.

The calibration curves for stilbite and heulandite may be used to estimate $\delta^{18}O_{\mathrm{true}}$ of those minerals. In that application, $\delta^{18}O_{\mathrm{ff}}$ is the measured $\delta^{18}O$ value of the mineral, $\delta^{18}O_{\mathrm{measured}}$, and as in the calibration experiments, $\delta^{18}O_{\mathrm{of}}$ is equivalent to $\delta^{18}O_{\mathrm{true}}$. Use the calibration curve for stilbite as an example. Imagine that the channel water in a hypothetical stilbite has equilibrated, either in nature or in the laboratory, with a water vapor atmosphere with $\delta^{18}O$ of, say, -10 per mil, and that $\delta^{18}O_{\mathrm{measured}}$ is $+30$ per mil. $\Delta_{\mathrm{measured\text{-}wv}}$ is $10^3\ln[(1000 + 30)/(1000 - 10)]$, or 39.61. This corresponds to a value of 0.28 for $\Delta_{\mathrm{measured\text{-}true}}$ using the curve in Fig. 10 or regression Eqn. (1). Thus, $\delta^{18}O_{\mathrm{true}}$ is 29.72 per mil $(30 - 0.28)$.

It is clear that precise but inaccurate results may be obtained if no correction is made for isotopic exchange between the framework oxygen and the channel water of at least some zeolites. Using extremes of natural ranges of variation of waters and silicates as a guide, one might expect errors as large as 1 or 2 per mil in the analysis of stilbite and 4 or 5 per mil in the analysis of heulandite, although in most cases the errors would be smaller. A few preliminary experiments suggest that the errors in the analysis of clinoptilolite would be smaller than those of stilbite, but those results require confirmation.

CONCLUSIONS

The rather complex series of experiments described in this article were necessary for the development of analytical techniques for measuring $\delta^{18}O$ values of the framework oxygen of zeolites, and for the assessment of both the precision and accuracy of those techniques. A dehydration procedure (Standard Dehydration Procedure) was developed that yields $\delta^{18}O$ values that are precise. However, it quickly became clear that isotopic exchange occurs between the channel water and framework oxygen of stilbite, heulandite, and clinoptilolite during dehydration. This exchange causes some degree of analytical inaccuracy. A direct test of isotopic exchange between channel water and framework oxygen of analcime was not conducted because analcime does not rehydrate easily after partial dehydration. FENG (1991) analyzed two sets of analcime aliquots dehydrated with slightly different procedures and found a difference of more than 0.5 per mil between the mean $\delta^{18}O$ values of the two sets. This suggests that exchange between framework oxygen and channel water may also have occurred during a the dehydration of analcime at temperatures above 250–300°C (temperatures which must be achieved if analcime is to be completely dehydrated). This will be discussed further in a separate paper (FENG and SAVIN, in prep.).

The magnitude of the errors produced by isotopic exchange between channel water and framework oxygen can be estimated and the analytical results can be adjusted through an empirical calibration. However, further testing is required to determine the general applicability of the calibration curves generated from the single stilbite and heulandite samples used in this work to the isotopic analyses of other stilbite and heulandite samples with different chemical compositions, physical characteristics, and crystallographic properties.

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