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The nature of water in hydrous silica[1]

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Abstract

The nature of water in hydrous silica has been investigated by measuring the hydrogen isotopic composition of successive increments of water evolved under vacuum during heating of the silica to 1000°C. Water increments evolved from Monterey diatomite are progressively enriched in deuterium up to 87°C, behaving isotopically like free, structurally nonessential water subjected to distillation. Between 87° and 218°C successive water increments have constant δD values, suggesting a bound water component. Above 218°C water with relatively lower δD values is outgassed, and this water is interpreted as hydroxyl.

Isotope exchange experiments at 25°C and 100°C in which the silica is exposed to D-enriched water and analyzed as above suggest at least 5 types of water in Monterey diatomite. (1) At least 2 wt.% water occurs as adsorbed or mechanically trapped H_2O which cannot be completely pumped away at 25°C and exchanges readily with D-enriched water. (2) Approximately 3.6 wt.% occurs as H_2O in sites protected from interaction with external water at 23°C, but exchanges isotopically at 100°C. (3) Approximately 0.2 wt.% occurs as surface hydroxyls which exchange at 23°C. (4) Approximately 1.3 wt.% occurs as nonsurface hydroxyls which exchange at 100°C. (5) Approximately 0.9 wt.% water exists as nonsurface hydroxyls which exchange slowly, if at all, with waters external to the silica.

The nonessential and easily exchangeable water fraction of diatomite cannot be readily separated from other water in the silica. However, water evolved above 700°C may be derived from hydroxyl groups which have preserved a geologically useful isotopic record.

Applications of this analytical procedure to other hydrous minerals may help to refine the stoichiometry of various water components in these minerals.

Introduction

The nature of water in minerals is often determined by assuming that water liberated above 110°C is "structural" water while that liberated below 110°C is labile and nonessential. As part of an investigation of hydrogen and oxygen isotope ratio variations in authigenic silica and the relationship of those variations to past climatic temperature changes (Knauth and Epstein, 1976) it became necessary to develop a method to obtain refined information about the amount and type of water in the various forms of hydrous silica. In this communication we describe this method and the results obtained for water-rich biogenic silica. The results have significance for the question of whether or not D/H ratio measurements of Opal-A have geological implications. The method, however, could be applied to any hydrous phase.

Although it is known that biogenic and authigenic silica are hydrous phases which may contain structural hydroxyl groups (Keller *et al.*, 1952; Keller and Pickett, 1949; Sun, 1962; Micheelson, 1966), little is known concerning (1) the amount of water

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present, (2) its state or how much of it is adsorbed, mechanically trapped, or chemically bound as H_2O or as OH, and (3) the extent to which the isotopic compositions of these different waters is resistant to exchange. The nature of the water and its resistance to isotopic exchange undoubtedly depends upon whether the silica in which it resides is Opal-A, Opal-C, Opal-CT, granular microcrystalline quartz (the most common constituent of ancient cherts), one of several varieties of fibrous quartz, or well-crystallized α-quartz. This investigation was restricted to determining the isotopic exchangeability of hydrogen found in Opal-A.

An experimental technique, called Differential Isotopic Analysis (referred to hereafter as DIA) has been developed. This technique allows the determination of the hydrogen isotopic composition of water in different sites in hydrous silica. Basically, this method involves the sampling of successive increments of water driven off during heating of the silica and the measurement of δD for these water samples. The isotopic pattern established for the δD-values of successively driven-off water samples varies markedly depending upon the hydration state of the silica. In addition, if the silica samples are exposed to deuterium enriched waters at various temperatures, the isotopic pattern of successively driven-off samples depends upon the degree to which the water in the silica has been exchanged. The fraction of the water or hydroxyl groups that is most resistant to exchange and most difficult to drive off is that water or hydroxyl group most likely to contain the original hydrogen which was incorporated in the silica when it formed.

Experimental procedure

DIA technique

The DIA technique to decipher the nature of water in hydrous silica was first used on a sample of Miocene diatomite from the Monterey Formation at the Palos Verdes Hills, California. The diatomite contains a few sponge spicules and a small amount of organic matter is probably also present. The silica is isotropic under crossed nicols. A pure, white sample of diatomite collected from a quarry face was selected for the experiments.

The diatomaceous earth was subjected to a stepwise heating during which the water liberated was measured volumetrically and analyzed for its δD. The technique determines the manner in which water is isotopically fractionated as it is removed from the sample. Since differential thermal analyses of hydrous minerals such as clays reveal that water in different structural sites is given off at different temperatures, it is desirable to see if this is also the case for silica. It is possible that the isotopic fractionation pattern during dehydration differs for the different sites. This method combines Differential Thermogravimetric Analysis with isotopic analysis of the water as it is extracted and is thus called Differential Isotopic Analysis (DIA).

In the actual procedure for the DIA experiments, about .5 gm of hydrous silica is placed in a nichrome bucket which is suspended from a quartz spring by a nichrome wire as shown in Figure 1. The water liberated from the heated sample in the furnace under vacuum is condensed in one of two sample tubes cooled with liquid nitrogen. The loss of weight of the silica during heating is recorded by the quartz spring balance. The sensitivity of the quartz spring balance is such that a 0.2 mg weight loss can be readily detected. Thus, a water loss as small as 10 μmoles from the sample could be measured with this technique.

After the desired amount of water is liberated and collected, the two-way stopcock is turned, diverting the flow to the other sample tube. The sample tube containing the collected sample is replaced with a new tube. The amount of water liberated can be controlled by the temperature to which the sample is heated by the furnace. The result of the procedure is a set of water samples of about equal

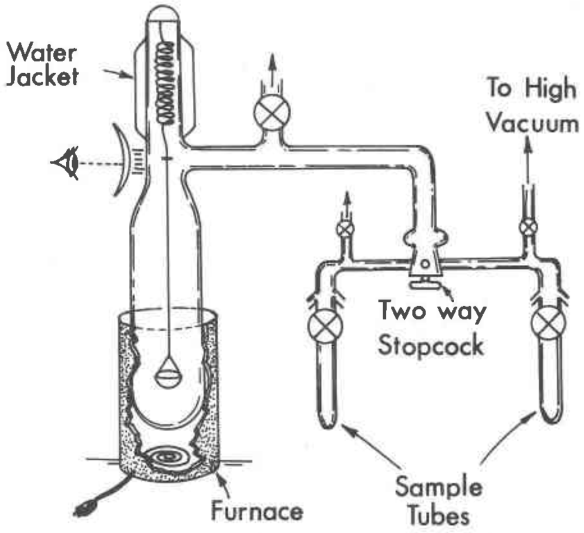

Fig. 1. Apparatus for Differential Isotopic Analysis (DIA) using quartz spring balance.

volumes obtained at progressively higher temperatures. The water is passed over hot (750°C) uranium metal to produce H_2 gas, which is analyzed in the mass spectrometer. The variation in the D/H ratio is reported in the usual δD notation. Further experimental details for this and subsequent experiments are given by Knauth (1973).

The data for the DIA for Monterey diatomite are given in Table 1 and Figure 2. In Table 1 are listed the fraction number of collection, temperature interval at which sample is collected, the heating time necessary to extract the sample, the amount of water given off at each interval in μm/mg and, finally, the δD value relative to SMOW for each fraction of water collected. The graph shows the hydrogen-isotope pattern for the extracted water samples plotted sequentially from left to right. The total water content of opaline silica at room temperature is largely dependent on the relative humidity to which a sample is exposed before dehydration. In this and most subsequent experiments, the samples were allowed to air dry and were placed in the vacuum line and evacuated. For the experiment illustrated in Figure 2, collection of the first water sample started after a vacuum of about 10^{-2} mm was reached. This starting point varied from experiment to experiment, and because it is desirable to compare the DIA pattern from experiment to experiment, it was found convenient to plot the numerical values of the abscissa from right to left. The abscissa thus expresses the amount of water left in the sample, and does not depend on the total water content prior to the start of dehydration.

Table 1. Water yields and δD-values for successive fractions of water given off in the stepwise heating of Monterey diatomite

Fraction	Temperature Interval (°C)	Heating Time Interval	Yield µm/mg	δD ‰
1	21	0^h10^m	.253	- 75.1
2	21	11^m	.317	- 47.9
3	21-55	1^h04^m	.298	- 17.2
4	55-87	1^h10^m	.344	- 6.8
5	87-97	59^m	.293	- 37.1
6	97-102	1^h34^m	.363	- 41.6
7	102-130	58^m	.288	- 43.9
8	130-158	31^m	.312	- 40.1
9	158-169	28^m	.350	- 42.7
10	169-176	38^m	.261	- 46.6
11	176-218	57^m	.229	- 45.7
12	218-294	33^m	.183	- 56.1
13	294-360	1^h17^m	.177	- 80.4
14	360-404	19^m	.075	- 92.0
15	404-514	22^m	.199	- 99.8
16	514-735	23^m	.379	-104.2
17	735	40^m	.086	-109.8
18	735-846	36^m	.065	-101.8
19	846-982	3^h01^m	.022	- 75.4

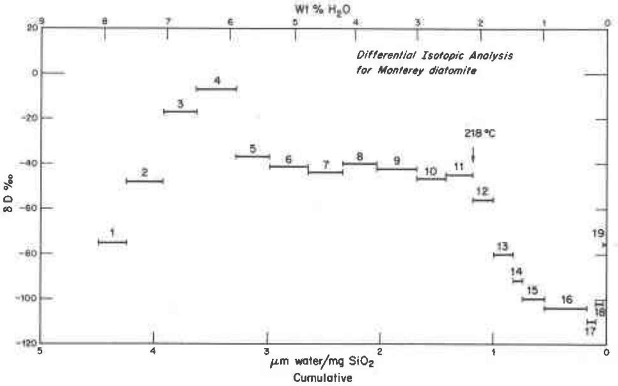

Fig. 2. Differential isotopic analysis for Monterey diatomite. Yields and δD-values are for successive fractions of water given off in the stepwise heating of Monterey diatomite. Fraction numbers are those given in Table 1.

The first four fractions in Figure 2 show a continuous enrichment in deuterium as the sample is dehydrated. The next seven fractions, from 87° to 218°C are relatively uniform isotopically with $\delta D \cong -43‰$. The next six fractions, from 218° to 735°C, decrease in δD; and the last two fractions between 735° and 982°C, show a large increase in δD. These last fractions, however, are very small.

The range in δD for water fractions extracted in this manner is 105‰, a very large range. Any single δD-value for the water in a diatomite will depend critically upon the drying of the sample and upon the initial and final temperatures of dehydration.

The DIA data suggest that water occurs in diatomite in at least three different types of sites or hydration states. Water I can be extracted below 87°C and can be interpreted as loosely bound or mechanically trapped H_2O. This water behaves isotopically like free, structurally nonessential water which was subjected to distillation; the residual liquid water becomes progressively enriched in the heavier isotope (D). Consequently, δD in fractions of the vapor successively sampled becomes more positive as observed for the pattern for the first four fractions in this experiment.

Water II is liberated between 87° and 218°C (fractions 5–11) and appears to have relatively constant δD of about −43‰. Above 218°C there is suggestion of a third type of water, beginning to be outgassed, water III, which has a very low δD-value of ∼−100‰. The isotopic enrichment pattern for fractions 12–15 is suggestive of a mixing curve between water II and water III, in which water III becomes a more appreciable component as temperatures are increased above 218°C.

The deuterium enrichment in the final fraction may be an experimental artifact resulting from the very small amount of water analyzed (11 μm), and will not be considered further.

Low temperature hydrogen isotope exchange experiments on Monterey diatomite

The DIA pattern of a sample of Monterey diatomite indicates that the sample contains at least three types of waters. Water in silica which exchanges at room temperature is geologically of little interest since D/H measurements of this water merely reflect the D/H ratio of the laboratory air, treatment solutions, or the last rainfall on the outcrop. The following experiment was undertaken to decide which of the water fractions in Figure 2 are readily exchangeable with liquid water at room temperature.

Procedure. Approximately .5 gm of sample was exposed for about 12 hours to 5 cc of water of δD = +1715 ‰. The exchanged sample was vacuum dried rather than air dried for 8 hours to avoid back-exchange with low-D atmospheric water vapor. After drying, the sample was quickly transferred to the extraction apparatus. A DIA was then done. It was unnecesary to monitor the quartz spring balance for this and for further DIA experiments because the rate of dehydration of diatomite had been ascertained from the initial DIA.

Results. The results of the DIA are given in Table 2 and shown in Figure 3. For purposes of comparison Figure 3 includes the DIA of Figure 2.

A comparison of the DIA patterns for the exchanged and unexchanged diatomite shows that waters released from the silica at the lower temperatures have the highest D/H ratio and consequently have suffered the most exchange, but water extracted from the diatomite over the whole temperature range has been exchanged to some extent. The D/H change of consecutive samples in the stepwise dehydration are here vastly larger than those of the natural sample and, thus, cannot be due to isotopic fractionation. The heavy δD for a given fraction must represent a mixture of silica water derived from sites which have and have not exchanged.

Table 2. Differential isotopic analysis for diatomite exchanged at room temperature with deuterium-enriched water (δD = +1715‰)

Fraction	Temperature Interval (°C)	Time Interval	Yield μm/mg	δD ‰
1	26	1^h40^m	.099	1808
2	26-66	22^h50^m	.915	1299
3	66-114	1^h15^m	.599	520
4	114-154	1^h55^m	1.212	98.8
5	154-218	50^m	.273	34.1
6	218-311	1^h40^m	.300	40.4
7	311-574	3^h15^m	.717	32.5
8	574-1000	3^h50^m	.261	0.9

The relative amount of exchanged and unexchanged water for a given fraction can be calculated from a material balance equation when the δD values of the exchanging H_2O is taken as +1715‰ and the δD value of the water in the original sample is taken from the data in Table 1. The following equation is valid for obtaining the combined δ-value of any two waters or gases of known isotopic composition which are mixed together.

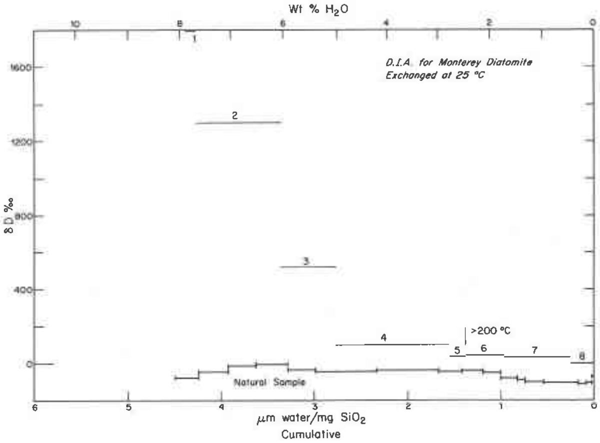

Fig. 3. Differential isotopic analysis of Monterey diatomite exchanged overnight at 25°C with deuterium-enriched water (δD = +1715‰). The DIA pattern for untreated diatomite is shown by the lower curve. The numbered fractions are for the exchanged diatomite.

$$\delta_t = X_1\delta_1 + (1 - X_1)\delta_2 \qquad (1)$$

where δ_1 = δ-value of water #1
δ_2 = δ-value of water #2
δ_t = combined δ-value
X_1 = mole fraction of water #1

The difference in exchangeability of waters may result because they are in different hydration states (OH or bonded H_2O), or exchange at different rates due to their structural positions. The numerical values used and the results of this calculation performed for all the fractions are given in Table 3. The cumulative curves for the exchangeable and non-exchangeable water are plotted in Figure 4. The first derivatives of the cumulative curve in Figure 4 obtained by constructing tangents at 50°C intervals are shown in Figure 5.

The maxima and minima of Figure 5 undoubtedly shift to higher and lower temperatures depending upon the rate of heating during the dehydration. Nevertheless, the qualitative relationship between

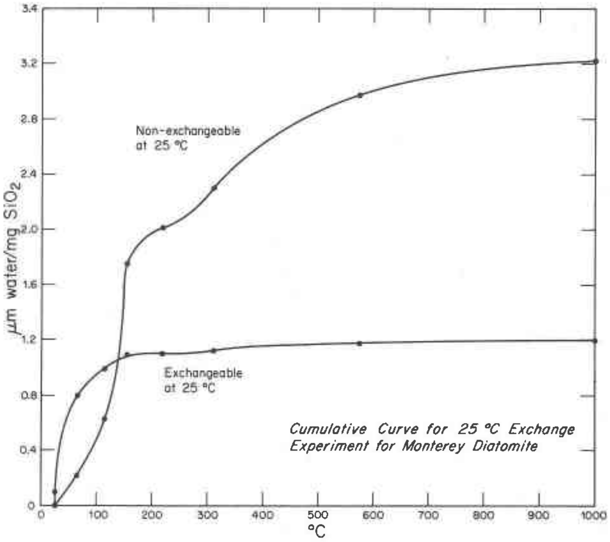

Fig. 4. Cumulative curves for µm/mg of exchangeable and non-exchangeable water released at successively higher temperatures for Monterey diatomite exchanged overnight with D-enriched water at 25°C.

Table 3. Values used for calculations of actual amount of exchanged and nonexchanged water for each fraction in DIA of table 2, and results of the calculation

Fraction	Temperature (°C)	δ_t ‰	δ_1 ‰	δ_2 ‰	X_1	$X_1(\frac{\mu m}{mg})$	$(1-X_1)$	$(1-X_1)\frac{\mu m}{mg}$
1	26	1808	--	--	1.0	.099	--	0
2	26-66	1299	1715	- 20	.76	.70	.24	.22
3	66-114	520	1715	- 30	.32	.19	.68	.41
4	114-154	99	1715	- 40	.08	.10	.92	1.12
5	154-218	34	1715	- 45	.04	.01	.96	.26
6	218-311	40	1715	- 50	.05	.02	.95	.29
7	311-574	33	1715	- 85	.07	.05	.93	.67
8	574-1000	0	1715	-105	.06	.02	.94	.25

δ_t = measured δ-value for water extracted over the indicated temperature range
δ_1 = δ-value of water with which the samples is exchanging
δ_2 = δ-value of water extracted from the unexchanged sample over the indicated temperature range
X_1 = mole fraction of water extracted over the indicated temperature range which exchanged completely with D-enriched water.
$X_1(\frac{\mu m}{mg})$ = Product of X_1 and the actual amount of water extracted over the indicated temperature range. This is the actual amount of water which exchanged completely with the D-enriched water.
$(1-X_1)$ = Mole fraction of water extracted over the indicated temperature range which did not exchange with D-enriched water.
$(1-X_1)\frac{\mu m}{mg}$ = Actual amount of water extracted over the indicated temperature range which did not exchange with the D-enriched water.

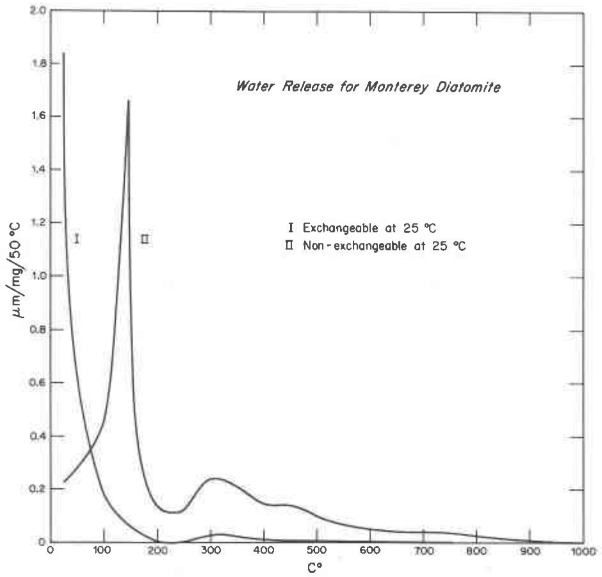

Fig. 5. Water release for Monterey diatomite. Area under curve equals amount of water released between 25°C and 1000°C.

temperature and dehydration pattern is clear, and suggests that the room-temperature exchangeable fraction is almost entirely removed in vacuum below 200°C. The small rise in curve I appearing at around 300°C is probably due to exchange at the increased temperature of the more tightly bound H_2O or OH with the D-rich water not yet removed from the silica. The two peaks of curve II, the non-exchangeable fraction, suggest a loosely-bound H_2O component which can be removed below 200°C and a more tightly bound water component removable at higher temperatures, possibly in the form of hydroxyl.

The results of the experiment described above suggest that it would be most difficult to physically separate the exchangeable H_2O fraction from the non-exchangeable H_2O fraction by stepwise heating. However, extensive pumping under vacuum or heating to about 75°C removes most of the easily exchangeable water. The combined δ-value of the remaining water may be geologically meaningful. Its δD-value is largely independent of any water exposed to the sample during collection, storage, or analysis.

100°C hydrogen isotope exchange experiments on Monterey diatomite

The low temperature hydrogen exchange experiments on the diatomite indicated that a large fraction of the water in this silica does not exchange isotopically at 25°C with liquid water if exchange is limited to a relatively short period of time. More geologically meaningful exchange experiments were made by testing the exchangeability of the silica hydrous water at 100°C and for longer periods of time.

Procedure. .5 to 1.5 gm of diatomite was placed in evacuated glass bulbs with 8 to 13 ml of D-rich water ($\delta D = +1715‰$). The bulbs were sealed and placed in a boiling water bath. At the desired time interval, the contents of the bulb were removed and the sample dried in various ways as described below. A DIA was then performed on the differently dried samples.

Results. Data for the DIA for each experiment are given in Tables 4–7 and are plotted in Figure 6. The DIA pattern represented by curve B in Figure 6 is for diatomite exchanged for 4,252 hours. The exchanged sample was transferred directly to the vacuum line and dried by vacuum pumping at room temperature. It was found that this procedure allows a high vapor pressure of water to build up in the line initially and causes contamination of the glass walls and vacuum grease with D-rich water which subsequently exchanges with the "unexchanged" water outgassed from the diatomite at higher temperatures. In other words, an isotopic "memory effect" is introduced by this drying procedure, which causes the subsequent fractions of the DIA to be more enriched in deuterium than the actual water outgassed from the sample. The result is that the data shown for each fraction of curve B are probably somewhat heavier than the true δ-values. Curve B, therefore, represents maximum isotopic exchange under the conditions described.

Table 4. Differential isotopic analysis for diatomite exchanged 4,252 hours at 100°C (curve B in Figure 6)

Fraction	Temperature (°C)	Time Interval	Yield μm/mg	δD ‰
1	24	28^h25^m	.34	1714.9
2	24-119	7^h20^m	1.92	1731.9
3	119	112^h35^m	.61	1671
4	119-181	22^h50^m	.13	1624
5	181-248	51^h35^m	.20	—
6	248-314	17^h15^m	.15	1013
7	314-536	18^h0^m	.67	999.9
8	536-742	17^h15^m	.21	933.9
9	742-1000	3^h0^m	.03	584.6

Table 5. Differential isotopic analysis for diatomite exchanged 700 hours at 100°C, air dried (curve C in Figure 6)

Fraction	Temperature (°C)	Time Interval	Yield μm/mg	δD ‰
1	25-95	37^m	1.88	474.6
2	95-211	1^h30^m	2.32	1516.7
3	211-316	43^m	.33	1517.2
4	316-445	50^m	.36	738.1
5	445-643	1^h20^m	.49	810.9
6	643-776	2^h01^m	.17	875.5
7	776-1022	2^h49^m	.06	700.0

The true DIA pattern probably falls below curve B by a small amount. It is apparent that waters outgassed at temperatures above 200°C have not completely exchanged with the heavy water, even after 4,252 hours at 100°C.

The relative amount of exchanged and unexchanged water for a given fraction was calculated using equation (1), assuming that the δ-value of a given water fraction results from a mixture of deuterium enriched water ($\delta D = +1715‰$) and unexchanged water with a δD-value given by curve A, the DIA for the unexchanged sample. The results of this calculation performed for all the fractions are given in Table 8 and the results plotted as cumulative curves in Figure 7. The water-release pattern obtained from the first derivative of the cumulative curve is shown in Figure 8. The figure shows that nearly all of the more "loosely bound" water released below 200°C is exchangeable at 100°C. About 40% of the water released above 200°C is unexchanged. Comparison of these data with the exchange experiment at 25°C (Figure 5) shows that approximately 16% less water was released above 200°C for the sample exchanged at 100°C. This result suggests that heating for 6 months in boiling water reduces the amount of water located in the more strongly bonded sites. This reduction in water may be related to partial crystallization or ordering of the silica in response to higher temperatures.

Table 6. Differential isotopic analysis for diatomite exchanged 328.5 hours at 100°C, air dried 240 hours (curve D in Figure 6)

Fraction	Temperature (°C)	Time Interval	Yield μm/mg	δD ‰
1	22-63	1^h23^m	1.01	218.3
2	63-127	2^h26^m	1.35	569.1
3	127-135	20^m	.16	—
4	135-143	38^m	.56	1234.4
5	143-163	34^m	.31	1408.1
6	163-178	26^m	.22	1418.8
7	178-192	54^m	.15	—
8	192-223	45^m	.16	1168.2
9	223-322	41^m	.29	940.9
10	322-492	1^h48^m	.48	631.7
11	492-678	3^h55^m	.39	683.5
12	678-777	1^h08^m	.09	717.6
13	777-902	1^h57^m	.04	592.2
14	902-981	3^h0^m	.02	592.9

The results of the exchange experiments at 25°C and 100°C can be combined to further characterize the different types of water in the Monterey diatomite. The integral of curve II of Figure 5 which represents the amount of nonexchangeable water at 25°C, is the sum of the amount of water which will exchange at 100°C and the amount of water which will not exchange at 100°C. The water which does not exchange at 100°C is known from curve II of Figure 8, and can be subtracted from curve II of Figure 5 to yield the release pattern of water which will exchange at 100°C but not at 25°C. The result of this subtraction is shown in Figure 9. This figure shows the water release with temperature of the water in the diatomite which (a) has exchanged at 25°C (curve I), (b) has exchanged at 100°C but not at 25°C (curve II), and (c) has not exchanged at 100°C (curve III). In general, water released from a hydrous mineral at or below 100–200°C can be considered to be primarily loosely bound H_2O while water released at higher temperatures is probably derived

Table 7. Differential isotopic analysis for diatomite exchange 333 hours at 100°C, air dried in oven at 100°C (curve E in Figure 6)

Fraction	Temperature (°C)	Time Interval	Yield μm/mg	δD ‰
1	23-102	16^h0^m	.658	95.9
2	102-159	4^h0^m	.242	926.2
3	159-198	3^h50^m	.197	1073.7
4	198-283	3^h33^m	.197	794.9
5	283-418	1^h42^m	.337	448.3
6	418-496	12^h0^m	.378	450.4
7	496-790	4^h20^m	.356	530.5
8	790-1060	3^h32^m	.041	488.0

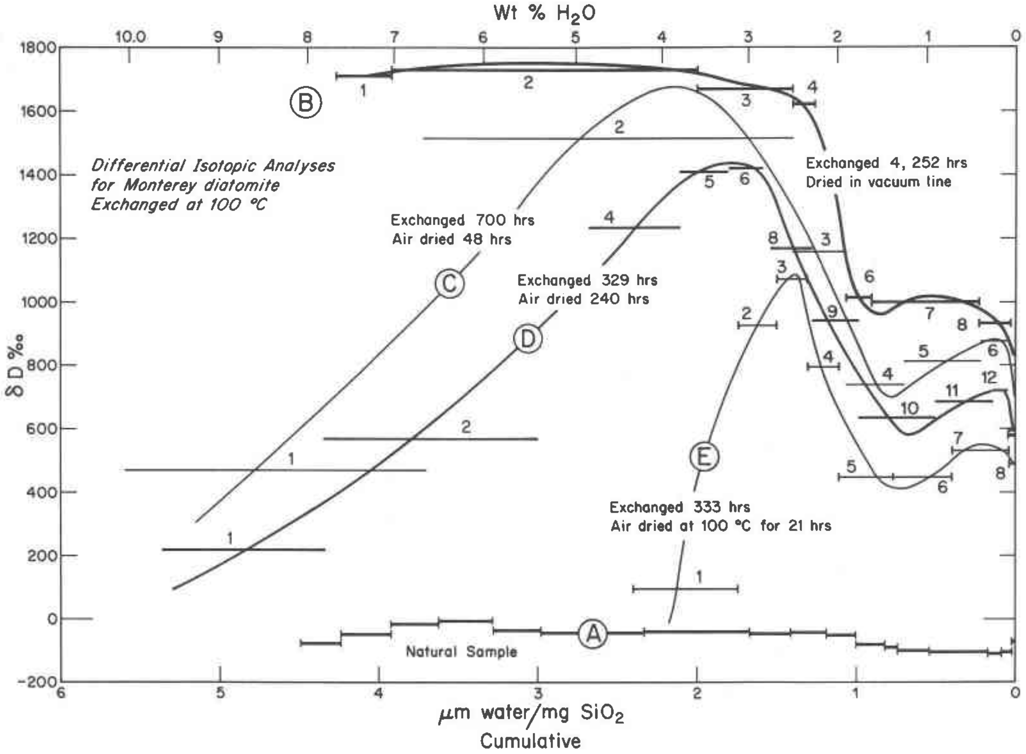

Fig. 6. Differential isotopic analyses for Monterey diatomite exchanged at 100°C. The exchange time, the drying interval, and the manner of drying are indicated for each curve. Curve A from Figure 2.

from more strongly bound hydroxyl groups. Assuming that this is also the case for hydrous silica then the integrals of the water release curves shown in Figure 9 can be interpreted in the following way.

(1) At least 2 wt.% water in diatomite occurs as adsorbed H_2O which cannot be completely pumped away at 25°C and exchanges readily with deuterium-enriched water. This amount was obtained by integrating curve I, Figure 9, between 25°C and 200°C. Natural samples exposed to air contain variable amounts of this type of water depending on the humidity.

(2) Approximately 3.6 wt.% water in diatomite occurs as H_2O groups within the silica or in sites otherwise protected from interaction with any external water at room temperature. This amount was obtained by integrating curve II from 25°–200°C. At temperatures of 100°C these H_2O groups exchange with external water.

(3) In terms of resistance to isotopic exchange at least 3 different hydroxyl groups occur in diatomite. Approximately .2 wt.% water exists as hydroxyls which exchange readily at room temperature. These hydroxyls are probably surface hydroxyls, either initially present or formed while heating the sample during the DIA. This figure is derived by integrating the high temperature (>200°C) portion of curve I in Figure 9. Approximately 1.3 wt.% water probably occurs as non-surface hydroxyls. These hydroxyls exchange with external water at 100°C within 6 months. Approximately .88 wt.% water (the integral of curve III, Figure 9) exists as nonsurface hydroxyls in sites highly protected from water external to the silica. These hydroxyls had not exchanged at 100.C after at least 6 months of interaction with deuterium-rich water. The relative amounts of the different types of water in Monterey diatomite as characterized by their temperatures of dehydration and isotopic exchange characteristics are shown graphically in Figure 10.

Additional exchange experiments were undertaken at 100°C for different lengths of time in order to examine the validity of the water release curves shown in Figure 9. The results of these additional experiments are shown as curves C, D, and E in Figure 6. Curve C is for diatomite exchanged for

Table 8. Values used for calculation of actual amount of exchanged and nonexchanged water for each fraction in the DIA of Table 4, and results of the calculation. Table 3 gives explanation of column headings.

Fraction	Temperature (°C)	δ_t ‰	δ_1 ‰	δ_2 ‰	X_1	$X_1(\frac{\mu m}{mg})$	$(1-X_1)$	$(1-X_1)\frac{\mu m}{mg}$
1	24	1715	---	---	---	.34	---	---
2	24-119	1715	---	---	---	1.92	---	---
3	119	1671	1715	- 40	.97	.59	.03	.02
4	119-181	1624	1715	- 45	.95	.12	.05	.01
5	181-248	missing, estimate		from figure 5-12		.06	---	(.03)
6	248-314	1013	1715	- 60	.60	.09	.40	.06
7	314-536	1000	1715	-100	.61	.41	.39	.26
8	536-742	934	1715	-100	.57	.12	.43	.09
9	742-1000	585	1715	-100	.38	.01	.62	.02

700 hours and then dried in air for 48 hours at room temperature. Curve D is for diatomite exchanged for 329 hours and then dried in air for 240 hours. Curve E is for diatomite exchanged for the same length of time as the sample giving curve D, but was dried for 21 hours in a 100°C drying oven exposed to laboratory air. This method of drying allowed the sample to back-exchange at 100°C with water vapor in the laboratory air.

For water released above 200°C it is apparent that the samples which were exchanged for the longest period of time suffered the most deuterium enrichments. Water extracted above 200°C for diatomite exchanged 329 hours (curve D) has a δ D value of approximately +700‰, representing 39% exchange with the heavy water. After 700 hours, this δD-value is approximately +800‰, representing 44% exchange; and after 4,252 hours it is +1000‰, or

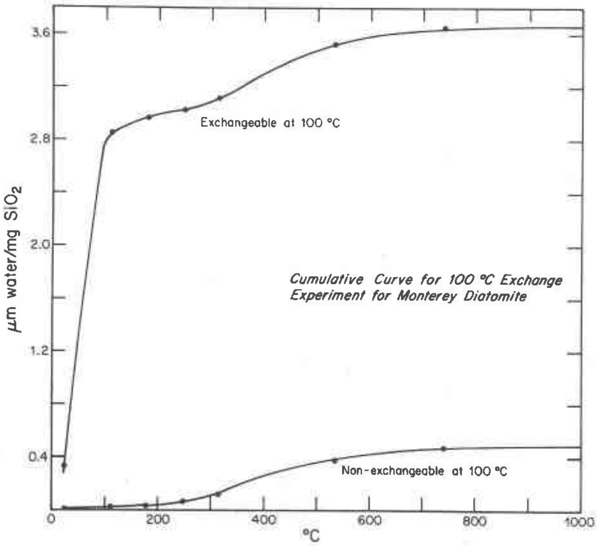

Fig. 7. Cumulative curves for μm/mg of exchangeable and non-exchangeable water released at successively higher temperatures for Monterey diatomite exchanged 4,252 hours with D-enriched water at 100°C.

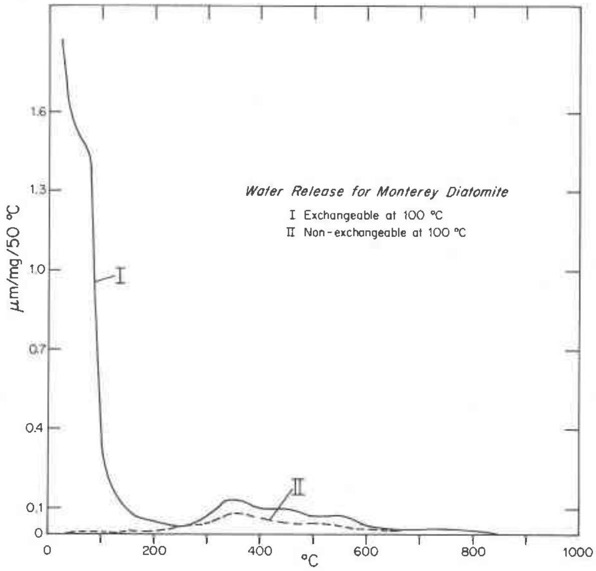

Fig. 8. Water release for Monterey diatomite for exchangeable and nonexchangeable water at 100°C. Area under each curve equals the amount of water released between 25°C and 1000°C.

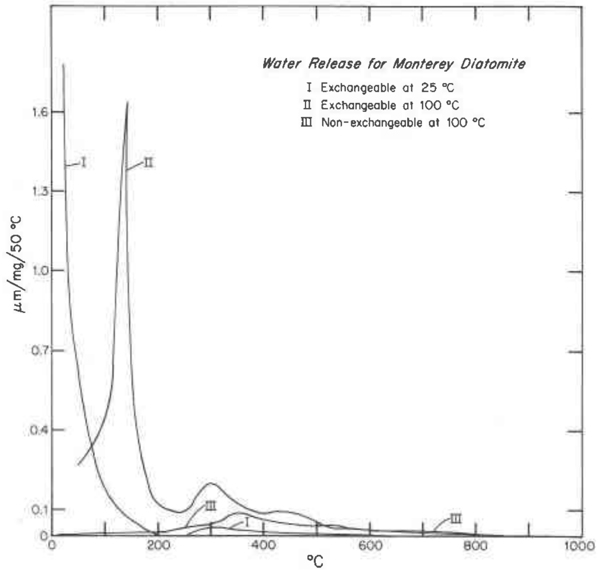

Fig. 9. Combined water release patterns for Monterey diatomite. Area under each curve equals the amount of water released between 25°C and 1000°C with the designated exchange characteristics. Curve II derived by subtracting curve II of Figure 8 from curve II of Figure 5.

55% exchange. Since curve E represents the DIA pattern for silica initially exchanged for about the same length of time as for that represented by curve D, water released above 200° was probably initially exchanged to δD = +700‰ but began to exchange back during 100°C drying toward a value near that of water vapor in the laboratory air δD(≈−100‰). 21 hours of such exchange apparently lowered the δD-value by about 200‰, representing an exchange of 11%. The rates of exchange of the high temperature fraction (assumed to be predominately hydroxyl) are shown graphically in Figure 11.

Below 200°C the DIA patterns clearly show the effects of exchange which occurred during drying in the presence of water vapor in air. Curve D, the DIA pattern for diatomite dried in air for 240 hours, shows this effect more strongly than curve C, which is for diatomite exposed to air for only 48 hours. The corresponding section of curve E has also been extensively "back-exchanged" with water vapor in the drying oven, although most of this low-temperature, easily exchangeable water has been removed in the drying oven.

The behavior described above can be understood in terms of the water release patterns shown in Figure 9. Curve D can be explained by assuming that the absorbed and trapped water represented by curve 1, Figure 9, was exchanged to δD = +1715, but re-equilibrated with atmospheric water vapor during the drying period. The initial fraction of the DIA contained water largely composed of this re-equilibrated water yielding a δD-value of +278‰. As the temperature was increased and further fractions collected, more water was released from the "site" represented by curve II, Figure 9. Water in these "sites" should have exchanged at 100°C to the heavy value, but should not have back-exchanged with laboratory water vapor during drying. Therefore, the progressive enrichment in deuterium shown in curve D for fractions approaching 200°C is satisfactorily explained by the water release patterns of Figure 9.

Above 200°C curve D shows δD-values indicating that about half the water in the diatomite has exchanged with the heavy water. This result can be understood from the water release patterns in Figure 9 which shows that above 200°C about half the water should exchange at 100°C and half should not. Curve D as well as all those in Figure 6 shows an isotopic minimum between 300° and 400°C, indicating that the greatest proportion of unexchanged hydroxyl groups is outgassed over this temperature range.

Curve C is qualitatively similar to curve D. It can be explained exactly as curve D was explained if it is assumed that the shorter drying time did not allow complete exchange of the adsorbed and trapped water with the atmospheric water vapor.

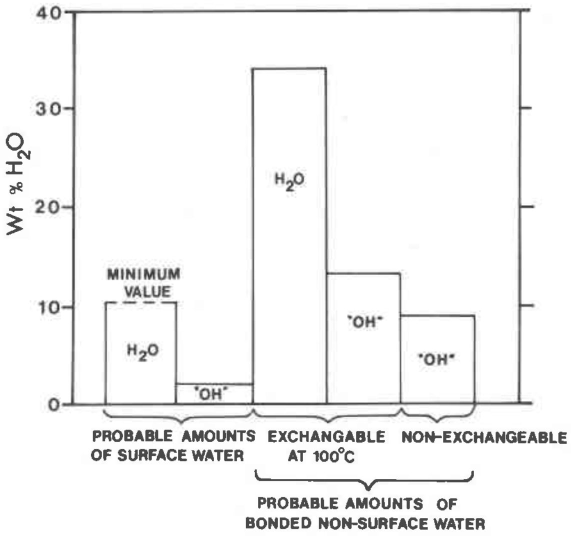

Fig. 10. Relative amounts of water in Monterey diatomite as deduced from the isotope exchange experiments. "OH" is here defined as water released above 200°C.

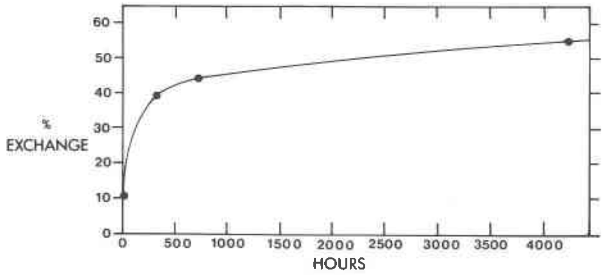

Fig. 11. Rate of hydrogen isotope exchange of all "hydroxyl" in Monterey diatomite at 100°C.

It was hoped that the non-essential and easily exchangeable water fraction of this diatomite could be removed at low temperatures allowing the more geologically meaningful water fraction to be collected separately. However, as shown by the water release patterns in Figure 9, water from the various sites is outgassed simultaneously as the temperature is raised. Heating to 50°C will remove a large fraction of the trapped and adsorbed H_2O without significantly dehydrating the other sites. Above this temperature the more essential water components begin to outgas along with further dehydration of the labile components.

It is clear from the above results that if natural samples of biogenic silica have been exposed to ground waters at 100°C, then the bulk of the water extracted from them has been profoundly exchanged. The fact that significant exchange occurs rapidly at 100°C leaves open the strong possibility that exposure of the material to low temperature ground waters over geologic time could also result in significant exchange.

Summary of the experimental results on diatomite

(1) Water in Monterey diatomite occurs in at least 5 different forms with regard to hydration state and isotopic exchange properties. This is shown graphically in Figure 10.

(2) Experimental water release patterns as a function of temperature for those sites with similar exchange properties are best represented in the case of naturally occurring diatomite as shown in Figure 9. The precise shape of these curves is a function of the rate of dehydration, but their general form probably is not.

(3) Adsorbed and mechanically trapped water can be largely removed by vacuum pumping overnight at room temperature.

(4) Natural samples which have been heated to 100°C in the presence of ground waters have probably lost their original δD values.

Applicability of the DIA method to other minerals

For most geological purposes the usual method of determining stoichiometric amounts of water in minerals by measuring weight loss above and below 110°C has proven satisfactory. Differential isotopic analysis combined with isotope exchange experiments provides a means to explore in greater detail the nature of water in solids. In the case of biogenic silica we have attempted to determine how many different types of hydration states of water are present, the amounts of these types, and some understanding of whether or not any of this water would have D/H ratios preserved from the time of precipitation. Application of this method to other hydrous minerals could possibly refine the stoichiometry of the hydroxyl component, and provide useful information relevant to mineral dehydration characteristics.

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