Deuterium Incorporation into the Polar Regolith of Mars by Sublimation Fractionation

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ABSTRACT

Using a cryostat, the behavior of particulate rich ice as an analogue for the ice-rich polar regolith of Mars is investigated. In particular, we examine the isotopic enrichment of this ice in deuterium and its role as a sink for the heavier isotope. We have chosen an appropriate concentration and size (1.6 microns in radius) for these particles based on the assumption that martian ices are emplaced by precipitation from the atmosphere under near-current conditions. A 25wt% mixture of this size of TiO$_2$ dust in a 5vol% Deuterium D$_2$O/H$_2$O solution was used as a regolith stimulant and was found to undergo significant deuterium fractionation. Unlike previous crystalline samples, the fractionation did not end rapidly – typical of solid samples with limited molecule mobility within the bulk. Instead, the hydrogen content of the sublimed gas continued to increase with time possibly as a result of preferential movement of deuterium away from the surface towards the colder part of the sample. Using a petrographic microscope ice grain sizes were confirmed to be similar in diameter to snows seen by Viking Lander 2 in 1979.

1 INTRODUCTION

Any physical process which depends on the atomic mass of a substance is capable of separating and fractionating isotopes of different masses. One of the most familiar examples of this is Jeans escape at the top of a planetary atmosphere which preferentially removes the lighter isotopes from the planet. Fractionation is also known to occur in liquid systems, such as the enhancement of H$_2$O, the lighter isotopic form of water, over D$_2$O and HDO$^\ast$ compared to Standard Mean Ocean (SMOW) values as observed in rainwater or snow on Earth. More recent work has also shown that this type of fractionation may be important in solid sublimation under certain conditions. Unlike a liquid or a gas, we cannot assume that a solid is well mixed and therefore it is much harder for molecules to move in the lattice and thus maintain the bulk isotopic concentrations of the sample at the surface. As a result, we would expect the surface to become enriched in the heavier isotope as the lighter isotope is preferentially removed by sublimation since the energy to remove it from the surface is lower. As the surface becomes enriched with the heavier isotope, the concentration of the heavier isotope in the sublimated gas increases until it reaches the same concentration as that of the bulk sample. At this point, equilibrium has been reached and fractionation stops. Thus to have effective fractionation it is important to have a mechanism for removing the heavier isotope from the surface.

2 DEUTERIUM DIFFUSION

2.1 METHODS OF DIFFUSION

Classically, two mechanisms have been proposed for moving molecules through a sample. First, there is standard diffusion whereby different molecules within the crystal lattice swap places and are able to move...
within the solid. There is also vacancy-assisted diffusion in which the lattice is filled with many defects and voids at the molecular level allowing molecules to jump about more freely. This latter process plays a role in crystalline samples. In fact, greater fractionation has been seen in samples where the diffusivity is higher\(^1\) (for instance as a result of dissolved air which easily escapes when the temperature is raised leaving voids behind).

However, neither of these methods explains why the rate of crystallization has been the dominant effect observed in experiments to date\(^1\). To understand what is happening, we need to examine the crystallization of liquids. If a liquid is cooled rapidly, then crystals have very little time to grow. Therefore, the grain size of the particles in the sample is small. If, instead, the liquid is cooled slowly then there is time for larger crystals to form. This suggests that the main mechanism of deuterium transport within the bulk sample may be due to diffusion along grain boundaries.

There is good reason to believe that diffusion along grain boundaries may play an important role. For instance, cold working on small grains in the interstellar medium has long been known in meteoritics as an effective way to obtain significant fractionation of hydrogen and deuterium\(^2\) in the gas phase. The reason for this is that the heavier molecules stick more readily to the surface of the grains where they remain adsorbed while the lighter elements are able to escape the surface. The smaller the grains are the more surface area is available relative to their volume and the more effective this method will be. Thus, this provides us with another mechanism for preferentially trapping deuterated water within a cold solid sample.

Lastly, diffusion in the vapor state is also applicable in samples with significant void space. This is a Bergeron-Findeisen-like process except here the gas is sublimed instead of evaporated from liquid and molecules are adsorbed onto grain surfaces instead of being directly incorporated into the crystal structure. Once in the vapor phase, the sublimed water permeates the sample and is condensed in the deeper, colder parts of the sample. Since heavier molecules stick more readily to grain surfaces at lower temperatures, this provides a means for fractionation. Of course, more grain boundaries provide more adsorption sites and more avenues along which the vapor can travel. Therefore this effect should be more important in a sample in which the grain size is small.

### 2.2 OTHER CONSIDERATIONS

The microstructure of the sample is not the only important factor – external forcing also plays a role. In any of these fractionation processes, the highest effectiveness is achieved when the input energy is close to the activation energy. For instance, while evaporation from ocean water is an effective means of fractionation, boiling water is not because so much energy is being supplied that all isotopic species have similar evaporation rates.

In terms of a solid sample the situation may be complicated by gradients, such as solar forcing only from the top. This may create a cold trap at the bottom in which adsorbed molecules have less energy and thus have a more difficulty escaping from grain boundaries. Thus these areas will tend to accumulate the heavier isotope.

### 3 THE MARTIAN REGOLITH

One situation in which this is significant is sublimation of water ice at typical high-latitude martian temperatures (170K-230K) and pressures\(^3\) (6-9 mBar). This environment also has the potential to incur significant fractionation. The reason for this lies with precipitation deposition in which we continue to deposit isotopically fresh layers on top of more mature layers. If the deposition occurs quickly enough, the difficulties with transporting the heavier isotope within the solid sample may be reduced. This would allow more thorough fractionation to occur on each separate layer and subsequently a great deal more deuterium could be “folded” into the regolith then if the entire deposit was laid down at once.
In fact by examining the deuterium to hydrogen (D/H) ratio as we pass through an ice layer it may be possible to determine the age of the layers and how quickly the layers were deposited based upon the extent of fractionation. It may also be possible to determine exactly how much deuterium is stored in the Polar Regions. However, it is first important to get a good picture of what is occurring at the polar caps and in the regolith on Mars.

The method of water-ice deposition in the Polar Regions of Mars is unknown. Examination from orbit tells us only that the age of the current surface of the polar caps appears to be about 100,000 years. However, given that ice caps are very prone to retreat and advance both in areal and vertical extent, the true age of the ice cap may be far older and not correspond to current conditions at all. Still, there is reason to believe that precipitation may have played a significant role: even recently, Viking Lander 2 observed snow at 47.97°N in Utopia Planitia.

However, this snow was far different from its terrestrial water-ice precipitation analogue. For instance, the snow likely did not fall from a distinct cloud but appears to have coalesced around martian atmospheric dust. Given that the distribution of dust is rather tight around 1.6 microns in size and the very low abundance of precipitable water in the martian atmosphere (between 0 and 100 precipitable microns in the northern polar region where abundances are highest) these grains, visible at the Viking landing site, are heavily enriched in dust and are probably less than 1 mil (25 microns) thick.

This conclusion is supported by evidence of high dust content in the polar caps which may be as high as 50% by weight. First, the pole is surrounded by vast fields of material which appear to be eroding directly from the polar cap as the polar troughs march around.
Secondly we can see successive light and dark (interpreted to be representative of dust content) layers, such as those shown in Figure 2, which may indicate a cyclical dust deposition process or changes in received insolation which drive off some of the water on the surface and leave a darker dust-rich slag which is then covered by a new deposition of more water-rich ice. More importantly, studies have shown that dust entrainment can severely restrict the size of grains within an ice sheet at concentrations as low as 0.05% by weight\textsuperscript{10}.

As such, since it is a reasonable assumption that the polar caps are made up of compacted martian snow, it is important for the procedure to replicate the assumed grain size\textsuperscript{8} (<25 microns) with a significant amount of entrained dust. Exactly how much dust is required was verified by petrographic microscopy.

4 EQUIPMENT

The central piece of equipment used in this experiment was the Lunar and Planetary Lab Cryostat, designed and built by Professor Robert Brown. This capable device is schematically composed of a vertical chamber capable of cooling a sample from below using a Liquid Helium cold finger and heating it from above using a xenon lamp [see fig. 4]. This allows the temperature gradient in the sample to be controlled over a wide range of temperatures which can be verified by the three temperature sensors mounted at different heights along the exterior of the chamber. Connected to the chamber are two pressure taps with different scales and a linkage to a mass spectrometer which reads the partial pressure of different mass species present at the cold cathode. The readings from these instruments are collected and logged by a Data Acquisition card hooked up to a PC.

For the purposes of this experiment, the mass spectrometer was set to monitor masses 2 (atomic D and H\textsubscript{2}), 3 (DH\textsubscript{2}), 4(D\textsubscript{2}), 14(atomic N\textsubscript{14}), 17(O\textsubscript{17}), 18(O\textsubscript{18} and H\textsubscript{2}O\textsubscript{16}), 19(HDO and H\textsubscript{2}O\textsubscript{17}), 20(D\textsubscript{2}O, HDO\textsubscript{17} and H\textsubscript{2}O\textsubscript{18}), 21(HDO\textsubscript{18} and D\textsubscript{2}O\textsubscript{17}), 22(D\textsubscript{2}O\textsubscript{18}), 28(N\textsubscript{2}), 32(O\textsubscript{2} and H\textsubscript{2}S) and 40(Ar). As a result the instrument was able to sample the entire spectrum at a rate of one reading approximately every 90 seconds. The pressure taps and the temperature sensors were sampled at a much higher rate (~1Hz) and averaged over 60 second intervals with this value being logged.

A calibrated spreadsheet was used to collect the data and appropriate fractionation factors (which account for typical abundances of different isotopes of Oxygen and the destruction of molecules by the Mass Spectrometer) were calculated in software. This allowed us to back out the overall Deuterium to Hydrogen ratio in the gas coming off of the sublimating sample.

The other major piece of equipment used for analysis was a petrographic microscope using cross-polarized lenses. This was used in conjunction with several modified petrie dishes which were altered to function at cryogenic temperatures using epoxy and machined Styrofoam. These were able to maintain a bath of LN\textsubscript{2} over a sample while simultaneously insulating the sides of the dishes (to prevent structural failure of the petrie dishes) and the microscope itself from the extreme cold. This also allowed the dishes to be easily manipulated by the operator.
5 EXPERIMENTAL METHOD

The objective of this experiment was to produce and sublime a martian ice stimulant. In order to accomplish this it was first necessary to determine the required dust loading to produce appropriate grain sizes based on the Viking Lander 2 observations. Thus the first exercise was the selection of an appropriate dust simulant. Following this, we attempted to simulate the microstructure of a disaggregated dust-rich snow deposit. Lastly the structure created was verified using petrographic microscopy.

5.1 SIMULATING THE DUST

Based on data from the Pathfinder mission we know that the suspended martian dust has a high iron content and is heavily weathered. As such, we attempted to find a dust with a similar density to common mafic minerals. The second criterion was insolubility in water since in actual nucleation of ice onto dust there is no time for dissolution to occur. Lastly we considered cost and availability of ~1.6micron sized particles, a size consistent with the scattering properties of martian dust.

Titanium dioxide, a common white pigment used in toothpaste, paint and many sunscreens proved to be the best candidate. It has a bulk density of 4.23g/cc similar to the density of fayalite (4.39g/cc) and it is essentially insoluble in water. This product was also available for US$35 for 250g of 1-2 micron particles from Alfa Aesar as Titanium (IV) Oxide Rutile 99.5% metals basis APS powder.

5.2 SIMULATING THE GRAINS

Next we needed to combine these grains with the Deuterium-salted water (salted at 5vol% D$_2$O on the advice of Robert Brown) in such a way as to approximate the grains as they would appear in an ice deposit.

Time and cost constraints made it impossible to design and build a device to nucleate the water directly onto the dust grains. Thus, it was decided to mix the dust directly with the water and to flash freeze the mixture by pipetting an aquilot directly into a bath of Liquid Nitrogen (LN2), located in the cryostat chamber, in order to send all of the water directly to the amorphous state without allowing it to exclude the entrained dust. This had the additional benefit of excluding the atmosphere from the sample chamber during LN2 boil-off which prevented condensation on the sample. As well, the violent boiling of the LN2 as the dust-rich water was pipetted in lead to a macroscopically disaggregated sample as desired. This was further enhanced by grinding the surface of the sample using metal tools.

Note that particles of this size are a severe silicosis hazard and precautions including the use of a fume hood and protective equipment were necessary during the mixing phase (Carroll O’Quest of the Phoenix Mission Research group provided essential advice on working with this material)
Following this, the temperature in the cryostat was elevated to just over 150K and the Xenon lamp was illuminated to heat the sample from above. This was done in an attempt to move the ice above the amorphous-crystalline transition slowly in the hopes that crystalline ice grains would nucleate around the entrained dust particles, thus allowing the dust content to influence the preferred grain size. This microstructure was then verified by petrographic microscopy on similar samples before setting the sample in the cryostat sublimating.

Note that we did not impose a temperature on the top of the sample, but simply increased the heating from the Xenon Lamp until the pressure in the chamber was sufficiently high for the mass spectrometer to read with as little non-linearity and as high a signal to noise ratio as possible. This range is $10^{-7}$ to $10^{-5}$ torr in the cold cathode chamber directly preceding the Mass Spectrometer and was achieved using ~6 Watts of input power on the lamp. Based on a vapor-ice equilibrium curve, the temperature of the ice at the start of the experiment was 202.88K.

### 5.3 PETROGRAPHIC MICROSCOPY

Based on the paper of Clifford et al. it was decided to try 5wt%, 25wt% and 45wt% dust in ice to see which of these would form grains of the appropriate size. Note that even though the dust content was high, all three formed opaque heterogeneous mixtures which could be pipetted. Stock solutions of all three prospective simulants were mixed with pure water and 0.2ml were placed in the modified petrie dishes.

After a great deal of experimentation it was discovered that the easiest way of producing a thin layer for analysis was to flatten the drop with a circular glass slide and to flash freeze the entire mixture by pouring in a bath of LN2. Next, the thin layers were observed by prying away the glass and exposing the TiO$_2$-rich ice underneath. Typical examples of each of the frozen ices are provided below for each of the three dust concentrations. Note that these images have been stretched in contrast to bring out details.

![5wt% TiO$_2$ dust in water - the grains appear to be excluding the dust from the matrix during the amorphous to crystalline transition. Typical grain size ~25 to 50 microns (this image). This size increases rapidly up to ~100 microns as the sample heats up.](image1)

![25wt% TiO$_2$ in water – the grains seem to be regularly formed and flash in from the glassy state. Typical Grain Size ~ 10 to 20 microns](image2)

Using a geometric model composed of spherical dust particles ($R_{DUST}$) surrounded by spherical ice grains ($R_{WATER}$) and the density of the particles ($\rho_{DUST}$) and surrounding water ($\rho_{WATER}$), we can determine what the grain sizes should be for the various dust weight concentrations ($\chi_{DUST}$) assuming perfect nucleation. This is given by:
Using our values for the densities of particles and water and assuming a 1.6 micron dust we expect a grain diameter of 6.93 microns for the 5wt% mixture, 3.83 microns for the 25wt% mixture and 2.93 microns for the 45wt% mixture.

$$R_{\text{WATER}} = R_{\text{DUST}} \left[ \frac{\rho_{\text{DUST}}}{\rho_{\text{WATER}}} \left( \frac{1}{\chi_{\text{DUST}}} - 1 \right) + 1 \right]^{1/3}$$  [1]

From the photographs it seems evident that the dust concentration is having some control over the sizes of grains. However, they are not producing a simple spherical pattern and do not appear to be producing the expected sizes of particles. In particular, for the 5% sample, we have exclusion of the TiO2 to the grain boundaries and grains of different sizes. The 25wt% sample is more representative and was able to create grains of the same size and appearance in a reproducible manner. This typical size was 10-20microns across. More importantly, these grains would pop in to view fully formed suggesting that the whole grain made the transition from a glassy (amorphous) state to a clear crystalline one at once.

The only visible grain-like structure in the 45wt% sample was very small, on the order of a few pixels which was inconclusive at the highest useful magnification of the microscope. It was very difficult to view samples at this concentration due to the darkening and this resulted in low contrast except in regions where the film was very thin.

It also is important to mention how long range order was affected by these three cases. The 5wt% case did not appear to act in any strange manner and appeared quite similar to pure water in most respects. While 25wt% did form very distinct grains, long range order was still apparent and the grains were arranged into hexagonal patterns in places.

The most important piece of information to extract is that the 25wt% sample produces grains which are of the correct size for simulating martian ice and therefore this is the concentration used in the cryostat for the main sublimation experiment.
6 RESULTS

As of this writing, the 25wt% TiO₂ sample has been sublimating in the cryostat chamber for almost 11 days. The trends in D/H ratio, calculated escape rates, pressure in the sample chamber and recorded temperature near the top of the sample are displayed on the following pages for the period under consideration. The Mass 19/18 ratio (HDO/H₂O abundance) is also shown. Note that the D/H ratio takes into account the appropriate fractionation factors for this Mass Spectrometer and the escape rate is a calculated value based upon the counts (and resulting output partial pressure) as output by the Mass Spectrometer. Furthermore, the calculated initial D/H ratio of the sample was 0.053 and contained 40ml of liquid water.

7 DISCUSSION

The most obvious feature of the D/H plot is a steady downward trend which lasts until day nine and is broken only by a plateau from day three until day four and several more minor events. This is very surprising and not at all what was expected based either upon classical diffusion or upon the previous crystalline work. In a liquid or gaseous sample the implication of a well-mixed substance is that at first we preferentially remove the lighter isotope resulting in a D/H ratio of the output gas which begins below the initial D/H ratio of the sample and becomes isotopically heavier (i.e. increasing in Deuterium content) with time.

This has also been observed to occur in crystalline samples. In fact, this trend is much more pronounced and occurs much more rapidly since the mobility of surface molecules is severely restricted and the sample can no longer be considered well-mixed. As such the surface typically becomes isotopically heavy more quickly then in a liquid or gaseous sample and this shows up as the familiar increasing trend in the D/H ratio of the output gas.
Therefore we must invoke some mechanism which is able to remove molecules from the actively sublimating surface and hide them deeper in the sample. Given the mechanisms discussed in section 2 only one mechanism makes logical sense considering the required speed: vapor diffusion through the sample by means of pores and grain boundaries.

The major difference between this sample and previous crystalline samples is the assumed increase in porosity and the known decrease in the grain size. Therefore we may explain the decreasing trend in the following way:

First, the Xenon lamp heats the surface and the upper layers of the sample. This releases gas which is isotopically light since deuterated molecules require more energy to escape the surface. Some of this released gas escapes and is measured by the mass spectrometer; however, some of the gas travels down through the sample to the cold trap at the bottom. Here there are many cold grain surfaces available for adsorption upon which the deuterated molecules, being heavier, will be preferentially adsorbed.

Thus after passing through the sample the output gas becomes more and more depleted in deuterated molecules. The longer this continues, the greater the fractionation in the recirculating gas and the more deuterated molecules are moved from near the surface of the sample to deeper within the sample.

A second effect is the decrease in the total pressure by almost 2 orders of magnitude which is a much higher drop then what has been seen with similar crystalline samples. This suggests that a lag deposit is being produced in which the grains on the surface have been completely sublimed away leaving

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a residual layer of TiO2. This lag likely restricts heating to the subsurface (though no effect was observed on the temperature right below the surface) and blocks escaping gas causing more and more of the sublimate to cycle through the sample where it becomes isotopically lighter. In this way the creation of a lag may also help explain the decrease in the D/H ratio with time.

Lastly we observe several rapid sublimation events known as “cascades.” These are the spikes in the total pressure seen just before day four and right after day seven, to name two events. These must be sudden increases in sublimation rate since the temperature suddenly drops indicating a loss of heat from the sample which can only come from the latent heat of sublimation of more mass.

Interestingly, these cascades are visible in the D/H ratio and the Mass 19 to 18 ratio indicating that the material being sublimated at these times is isotopically different then what is typically being sublimated. There are several possible explanations. First, we could be witnessing a sudden increase in surface area. Since the sample is porous this could represent breaking through to a pore in which the D/H ratio of the internal surfaces is different then the typical sublimate at that time. Another explanation suggested by Robert Brown is the creation of tenuous microstructures which favour one isotope over the other. Eventually these intertwined structures become so tenuously bound that they all release from the surface and sublimate at once.

Two other features bear mention out of puzzlement. First there is a plateau in the
D/H ratio from day three to day four. Interestingly, this plateau appears to have been preceded by a cascade and then ended by a cascade as if we suddenly entered a region of different isotopic character which became the main sublimate until it was used up. This could be suggestive of some kind of microstructure. Also, between days four and seven the Mass 19/Mass 18 ratio is flat again suggesting the sublimation of a surprisingly homogenous layer.

Of course, due to the disaggregated nature of the sample it is very difficult to determine exactly what is occurring structurally. There was no effort made to observe the sample – in fact direct observation was impossible without disturbing the Xenon lamp and as such the changes in material being sublimated could correspond to structural changes in the sample such as a collapse of the sample, or the jetting of TiO2 slag away from a surface or out from a pore.

8 FUTURE WORK

This experiment attempted to replicate martian regolith assuming a precipitation origin to the polar ices. As such, only one concentration of TiO2 was tried. However, it would first and foremost be beneficial to complete the experimental matrix and try different concentrations of the particulate since Mars is unlikely to have had precisely the same ratio of ice to dust over geological time even if the icy deposits are the results of precipitation.

More importantly, active nucleation of the particles should be employed to construct a sample as similar to martian snow as possible. The experiment conducted here was only able to simulate the grain size without the spherical symmetry we expect from fully formed precipitation.

Furthermore, martian analogue materials, for instance palagonites, should be used both as nucleation sites and as a covering slag layer of regolith. Currently no palagonites are available in the sizes required from any major chemical supply house and only particles down to 50 microns were available from the Phoenix Mission research group.

This same experiment could also be tried with carbon dioxide ice or H2O-CO2 clathrates, both of which have been shown to be stable under current martian conditions at particular times of the year. It is conceivable that a large part of the residual polar caps may be made up of this material. In fact, the presence of CO2 ice surrounding martian precipitation has been invoked in the past to explain the rapidity with which the frost layer precipitated by suggesting that it increases the weight of the particles. Still, there are challenges to working with clathritic materials. Not only are the conditions required to form a clathrate difficult to simulate, but confirmation of a clathritic microstructure as opposed to some other combination of the constituents requires X-ray Crystallography.

A more readily applicable idea would be to use a low power laser (~ a few watts) to bore down through the sample once it has been set sublimating for awhile. This would allow us to quickly determine how the deuterium concentration is varying with depth in a mature sample without disturbing it and is something that the current setup is designed to do since we would be giving off gas for analysis. As well, the laser could be used in a ranging mode to determine the depth to which we are cutting. The only modification would be precautionary – a filter would need to be installed on the sample chamber side of the cold cathode to prevent micron sized dust from clogging the mass spectrometer.

The fractionation that occurs between the atmosphere and the snow during nucleation also bears some investigation. The nucleation sites will primarily accrete the heavier isotope for the same reason that the cold trap does, i.e. the deuterated molecules can be adsorbed much more easily onto grain boundaries. This is seen on earth where ice clouds can be isotopically lighter then their precipitation. As such, in considering snow, we may be starting with a source that is more highly enriched in deuterium then the atmospheric water vapor.
Lastly, this problem of icy dust can easily be extended to other situations. The original sublimation experiments conducted by Robert Brown were intended to study comets undergoing active sublimation. Since comets are not actually purely crystalline samples but are mixtures of ice and dust a more thorough exploration of the behavior of icy dust may shed some light on the problem. In this context it would be useful to videotape the sample to watch for jets or other visible signs of sublimation cascades.

9 CONCLUSIONS

Using the Lunar and Planetary Lab Cryostat we were able to monitor the sublimation of a disaggregated, dust rich martian ice simulant. Over the 11 days of the experiment the sublimate gas coming from the sample was seen to become progressively isotopically lighter with time in direct contradiction to what is typically observed in a sublimation experiment. The reason for this is likely transport of the sublimate gas through the porous sample and down to the cold trap where deuterium-rich molecules are preferentially adsorbed onto grain surfaces. This may have been helped by the creation of a dust lag on the surface which could have prevented sublimate gas from escaping the surface and explained the large decrease in pressure.

Thus this sample, with the simple additions of dust and porosity to control the grain size behaved very differently then a typical crystalline sample. Even so there were similarities to the crystalline experiments. Most notably, the sublimation cascades also were found to occur in the dust-rich small grained, disaggregated sample.

Still there remain many open issues for future investigation. Overall this experiment has shown that a process as simple as sublimation in an icy regolith may yet hold some surprises. In fact, our results suggest that the polar regolith of mars may be a much larger store and effective means of fractionation of deuterium then is currently thought.

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