# A Technique for the Determination of $^{18}O/^{16}O$ and $^{17}O/^{16}O$ Isotopic Ratios in Water from Small Liquid and Solid Samples

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**We have developed a new technique in which a solid reagent, cobalt(III) fluoride, is used to prepare oxygen gas for isotope ratio measurement from water derived either from direct injection or from the pyrolysis of solid samples. The technique uses continuous flow, isotope ratio monitoring, gas chromatography/mass spectrometry (irmGC/MS) to measure the $\delta^{18}O$ and $\delta^{17}O$ of the oxygen gas. Water from appropriate samples is evolved by a procedure of stepped pyrolysis (0−1000 °C, typically in 50 °C increments) under a flowing stream of helium carrier gas. The method has considerable advantages over others used for water analysis in that it is quick; requires only small samples, typically 1−50 mg of whole rock samples (corresponding to ~0.2 μmol of $H_2O$); and the reagent is easy and safe to handle. Reproducibility in isotope ratio measurement obtained from pyrolysis of samples of a terrestrial solid standard are $\delta^{18}O \pm 0.54$, $\delta^{17}O \pm 0.33$, and $\Delta^{17}O \pm 0.10$‰, $1\sigma$ in all cases. The technique was developed primarily for the analysis of meteorites, and the efficiency of the method is illustrated herein by results from water standards, solid reference materials, and a sample of the Murchison CM2 meteorite.**

Oxygen isotope studies of silicate minerals from igneous, metamorphic, and sedimentary rocks go back to the 1950s.[1] Early analyses were completed, not only because of the potential to study alteration effects and low-temperature processes,[2] but also to probe long-term secular changes in the lithosphere-hydrosphere system.

In the history of analysis of oxygen isotopes in meteorites,[3] little work has been directed toward studying that contained in the water of hydrated minerals. This is despite the fact that water has clearly played an important role in the evolution of meteorite parent bodies, such as the carbonaceous chondrites derived from primitive asteroids[4−7] or the SNC meteorites from Mars.[8,9] Of those few studies of meteoritic water that have been completed, only one[10] has analyzed oxygen, others[12,13] having concentrated on hydrogen isotopes.

A significant problem for the study of O−H in meteorites is obtaining sufficient water vapor to allow meaningful isotopic measurements of the resulting oxygen. The quantities of water contained in meteorite samples are small compared to the amount of oxygen present as part of silicates. For example, a typical stony meteorite is ~40 wt % oxygen, mainly in the form of silicates, and even meteorites possessing large proportions of hydrated minerals, for example, CI and CM carbonaceous chondrites, may contain only 2−15 wt % water (equivalent to 1.8−14 wt % oxygen). The altered igneous martian meteorites typically have water contents of ~0.04−0.4 wt %,[10] equivalent to 0.036−0.36 wt % oxygen. Previous studies of martian samples were forced to overcome the comparative lack of water by using samples in excess of 1 g of this priceless resource for each analysis.[10,13]

Unlike terrestrial geochemical processes in which, within limits, it is possible to assume that the $^{17}O/^{16}O$ ratio of a sample is related to $^{18}O/^{16}O$ by processes of mass fractionation (and as such does not need to be measured separately), the case is not true for meteorites. This is a consequence of the incomplete homogenization of oxygen isotopic reservoirs in the early Solar System, with the preservation of primitive isotope anomalies retaining evidence of either presolar nucleosynthetic components or mass-independent processes in the early Solar System. Meteorites also contain other low-temperature minerals such as carbonates,[14,15] and the study of these together with the hydrated components can help elucidate episodes of hydrothermal activity or aqueous alteration.

There is, in fact, a need for a generally applicable analytical technique that is capable of addressing all kinds of sample types, with the express purpose of determining the oxygen isotope composition of water. In the study of meteorites, such a technique would have to satisfy constraints including (1) discrimination between adsorbed, terrestrial surface contaminating water and

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(1) Silverman, S. R. *Geochim. Cosmochim. Acta* **1951**, *2*, 26−42.

(2) Taylor, H. P. *Geochemistry of Hydrothermal Ore Deposits*; Holt, Reinhart and Winston: New York, 1967.

(3) Clayton, R. N. *Annu. Rev. Earth Planet. Sci.* **1993**, *21*, 115−149.

(4) Kerridge, J. F.; Bunch, T. E. *Asteroids*; University of Arizona Press: Tucson, AZ, 1979, 745.

(5) Bunch, T. E.; Chang, S. *Geochim. Cosmochim. Acta* **1980**, *44*, 1543−1577.

(6) Clayton, R. N.; Mayeda, T. K. *Earth Planet. Sci. Lett.* **1984**, *67*, 151−161.

(7) Endress, M.; Zinner, E.; Bischoff, A. *Nature* **1996**, *379*, 701−703.

(8) Watson, L. L.; Hutcheon, I. D.; Epstein, S.; Stolper, E. M. *Science* **1994**, *265*, 86−89.

(9) Farquhar, J.; Thiemens, M. H.; Jackson, T. *Science* **1998**, *280*, 1580−1582.

(10) Karlsson, H. R.; Clayton, R. N.; Gibson, E. K.; Mayeda, T. K. *Science* **1992**, *255*, 1409−1411.

(11) Zolensky, M.; McSween, H. Y., Jr. In *Meteorites and the Early Solar System*; University of Arizona Press: Tucson, AZ, 1988; p 114.

(12) Robert, F.; Epstein, S. *Geochim. Cosmochim. Acta* **1982**, *46*, 81.

(13) Leshin, L. A.; Epstein, S.; Stolper, M. *Geochim. Cosmochim. Acta* **1996**, *60*, 14. 2635−2560.

(14) Warren, P. H. *Icarus* **1987**, *70*, 153−161.

(15) Burgess, R.; Wright, I. P.; Pillinger, C. T. *Meteoritics* **1991**, *26*, 55−64.

indigenous water; (2) the ability to analyze small quantities of water, (3) measurement of all three stable isotopes of oxygen.

Use of a multi-stage fluorination procedure at varying temperatures[16] with the lowest temperatures giving $\delta^{18}O$ of the OH groups and increasing temperature giving the $\delta^{18}O$ of the mineral structure was the first technique that went some way to addressing the problem. The fluorinating agent used was fluorine gas. The success of this technique was explored further[17] using stepwise fluorination (in this case, at constant temperature but with varying pressure of the fluorinating agent) to remove water, hydroxyl, organic matter, and other impurities from hydrous silica samples. However, both of these techniques converted the oxygen to $CO_2$ for mass spectrometer analysis and as such were only able to analyze the $\delta^{18}O$ of the resulting oxygen. They also required samples of up to 200 mg.

Only one previous attempt to quantify all three oxygen isotopes in water from meteorites has been successfully completed.[10] Analyses were made of five different SNC meteorites and involved vacuum pyrolysis of gaseous products at selected temperatures up to 1000 °C. Samples were heated for 1 h at each temperature, and the resulting gas was condensed at liquid nitrogen temperatures to facilitate cryogenic separation from other evolved volatiles. Conversion to oxygen was by the use of $BrF_5$,[18] and mass spectrometric analysis was completed directly with oxygen gas. The method proved to be viable in that the results of four out of the five samples analyzed seemed to possess water with an extraterrestrial signature. However, each experiment required a sample of between 2.0 and 3.4 g, and because dual inlet mass spectrometry was used, this still provided sufficient water for only four separate temperatures steps. In addition, errors, which are not given, appear to be large and variable.

The technique described herein addresses all the major issues outlined above and is directly applicable to terrestrial samples, both solid and liquid, without modification, but is described with the application to meteorites as its primary goal. Selective sampling of components within samples is achieved by heating a sample in a stepwise manner with the result that water vapor from different source regions is extracted at different temperatures, beginning with adsorbed water, then interlayer water, and finishing with water from O−H groups bound within the structure of the minerals.

One of the major problems with isotopic analysis of water is its propensity to adhere to the walls of system components and to undergo isotopic exchange. This can lead to marked memory effects whereby the measurement of any sample is influenced partially by the isotopic composition of the preceding sample. To measure both the $^{17}O/^{16}O$ and the $^{18}O/^{16}O$ ratios, $O_2$ must be used as the analyte, and therefore, to minimize memory effects, $H_2O$ is converted to $O_2$ rapidly, utilizing the minimum path length between source and conversion in a He flow system. Use of a continuous flow mass spectrometer for analysis of the resulting oxygen offers exceptional sensitivity while maintaining suitable levels of analytical precision.

## EXPERIMENTAL SYSTEM

Figure 1 is a schematic representation of the system up to and including the gas chromatograph. It can be seen that water for chemical processing and analysis can be either from injections of liquid water directly into the helium carrier gas supply or, alternatively, in the case of solids, samples are heated in a pyrolysis tube by an in-line furnace, which causes water and other volatiles to be added to the helium stream directly. From either source, water is then swept through a solid fluorinating reagent, facilitating conversion of water to oxygen gas. The main byproduct HF is subsequently removed by a chemical trap, with a cryogenic trap as backup and to remove other condensable species. The $O_2$ gas is then carried to a GC column for further purification, following which it is admitted to a continuous flow isotope ratio mass spectrometer via an open split assembly to reduce the pressure to an atmospheric value. A detailed breakdown of the individual subcomponents follows.

**Helium Supply.** The technique relies on a continuous flow of 99.996% pure helium gas (BOC, Guildford, U.K.) to transport the extraction products and analyte. To further improve the purity of the helium carrier gas, particularly with regard to oxygen-bearing species, the gas passes through an array of carrier gas purifiers (Alltech, Carnforth, U.K.) comprising a hydrocarbon trap, a moisture trap, and two oxygen traps, one of which indicates when its capacity for absorbance has been exhausted. After purification, the helium divides into a number of separate flows servicing different parts of the processing and analysis system. The main flow to the pyrolysis tube, where volatile extraction takes place, is further purified by passage through an 80-cm length of Ultimetal PLOT column containing a 5-Å molecular sieve, Catalog no. 6937 (Chrompack, London, U.K.), which is immersed in liquid nitrogen (−196 °C) during system operation. This final step removes not only any residual water and oxygen but also nitrogen and argon from the flow. After this final purification step, the helium passes through a single-stage, stainless steel pressure regulator valve, Porter no. 8286, 0−60 psi (Thames Restek, Windsor, U.K.) and, finally, to a mass flow controller GFC17 (Aalborg, Orangeburg, New York).

**Pyrolysis Furnace for Solid Sample Analysis.** The stepped heating extraction is carried out using a small (100-mm length), horizontally mounted resistance wire furnace capable of reaching temperatures of 1200 °C and controlled by a digital temperature controller, model 91e (Eurotherm, Worthing, U.K.). Positioned inside this furnace is a length of quartz tube (220-mm length of 6-mm o.d.) into which the sample, held in a platinum bucket, is admitted. The platinum bucket (∼2 mm in diameter and 15 mm in length) is spot-welded via a 40-mm platinum arm to an iron weight. The design of the assembly (total length about 80 mm) means that once loaded and sealed in, the sample tube can be pushed into and out of the furnace using an externally held magnet. The ability to introduce and withdraw the sample from the furnace enables heating steps to be completed at specific temperatures and for precise durations.

**Injection System for Liquid Water Analysis.** A separate system format is used for analysis of liquid water samples. To facilitate the introduction of liquid water by syringe, the pyrolysis furnace is replaced by a stainless steel injection head containing a noncoring, high-temperature septum, chromsep red (Chrompak, London, U.K.) (Figure 1, inset). The remainder of the system is

(16) Hamza, M. S.; Epstein, S. *Geochim. Cosmochim. Acta* **1980**, *44*, 173−182.

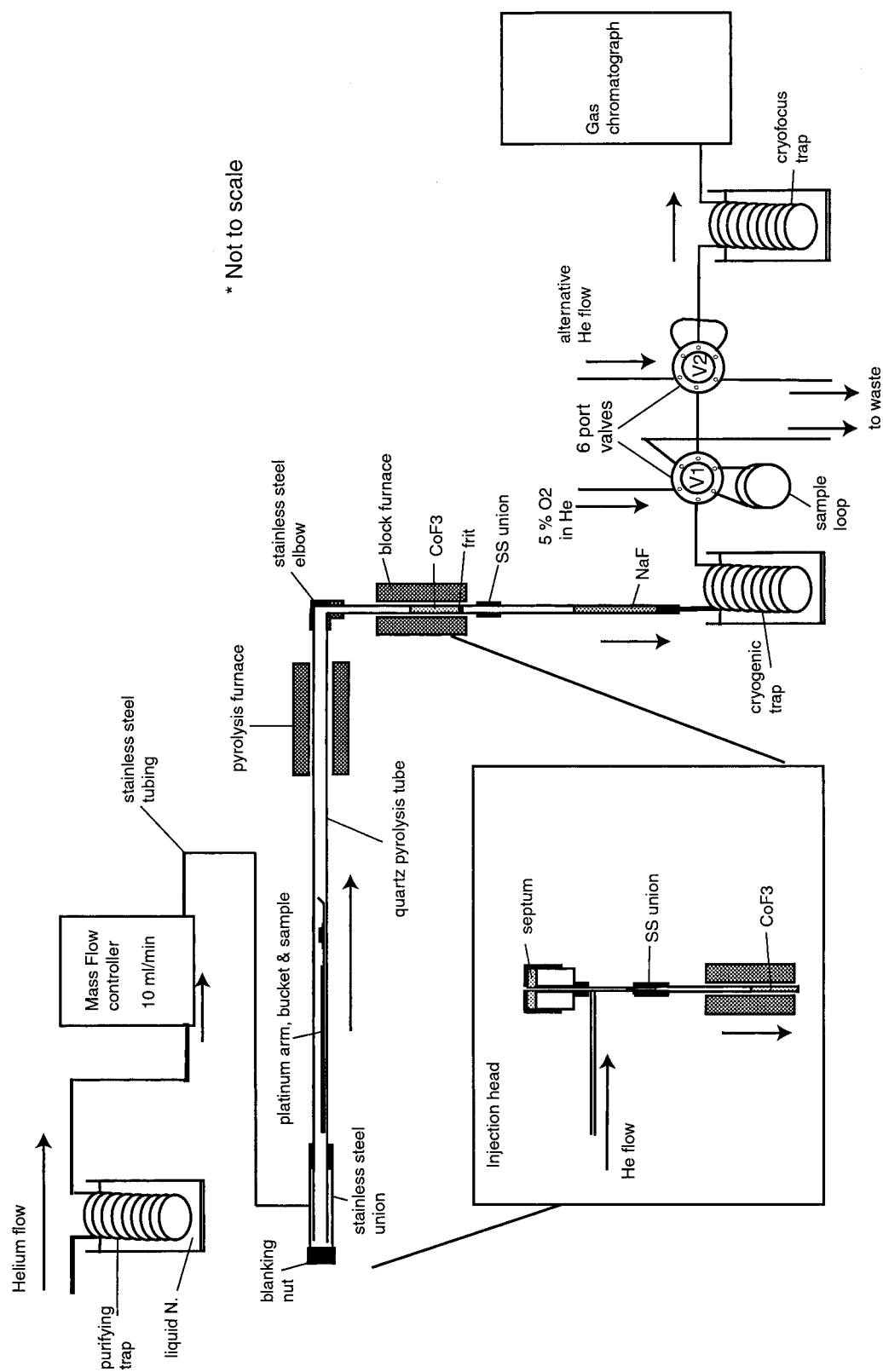(17) Haimson, A. G.; Knauth, L. P. *Geochim. Cosmochim. Acta* **1983**, *47*, 1589−1595.

**Figure 1.** Simplified schematic representation of the system apparatus. A supply of helium carrier gas is used to sweep pyrolysis products from solid samples heated in the extraction furnace through a bed of fluorinating reagent, which converts the $H_2O$ to $O_2$. This oxygen then passes through traps before a GC column and a continuous flow stable isotope ratio mass spectrometer. The insert shows the injection head used for analysis of water samples introduced by syringe.

unchanged. Injections of 0.02 $\mu$L are made immediately above the CoF$_3$ reactor, using a 0.5-$\mu$L syringe. Since water from such injections enters the reaction tube as a discrete pulse, the resulting oxygen does not display the tailing effect observed during pyrolysis of solids; therefore, there is no need for cryofocusing. Consequently, data from multiple injections can be acquired during a single experiment with a gap of only 2 min between successive injections.

**Fluorination.** Conversion of the evolved water vapor to molecular oxygen during each step is accomplished by flushing the pyrolysis products in the helium stream through cobalt(III) fluoride (CoF$_3$) powder (99.5% purity, Sigma-Aldrich, Gillingham, U.K.), maintained at a temperature of 370 °C. Water is converted via the reaction

$$2H_2O + 4CoF_3 \rightarrow 4CoF_2 + 4HF + O_2 \qquad (1)$$
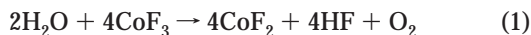
All volatiles released during sample pyrolysis are swept immediately by the helium flow, via a stainless steel elbow, directly onto the CoF$_3$ fluorinating agent. The distance that evolved water has to travel is kept to the absolute minimum, ~70 mm, and all surfaces with which it comes into contact are maintained at a minimum temperature of 150 °C to prevent adherence to system components and minimize the possibility of isotopic exchange.

Approximately 180 mg of the reagent is held in a nickel tube, 120 mm length × 1/8 in. o.d. × 0.083 in. i.d. (Catalog No. 30803, Alltech, Carnforth, U.K.), forming a column of reagent about 40 mm in length resting directly on a stainless steel frit, 20-$\mu$m pore size (Alltech) that is inserted ~10 mm inside the base of the reaction tube. Loading of the reagent is carried out in a fume cupboard to prevent the spread of the fine powder. Providing care is taken to exclude sources of liquid water during the loading procedure, any HF produced as a byproduct of CoF$_3$ reacting with atmospheric water (see eq 1, above) would be extremely small. Even during use, the amount of water passing through the reagent would not exceed 0.02 $\mu$L, such that the total amount of HF produced is essentially negligible and readily dealt with by the NaF trap (see below). The reaction tube is connected to the extraction system using stainless steel fittings, Catalog no. SS-200-6 (Swagelok, Solon, OH), and a furnace fashioned in two halves, from a block of aluminum (~100 × 40 × 40 mm in size) containing two cartridge heaters, Catalog No. 837-600 (RS components, Corby, U.K.), fits closely around, ensuring that the entire reaction tube is maintained at an even temperature. Conditioning of the CoF$_3$ is achieved by heating it to 400 °C for 3 days to ensure removal of adsorbed water and to allow reaction between the reagent and any remaining contaminants, after which the furnace temperature is reduced to its operating temperature of 370 °C. Exhausted reaction tubes are discarded as chemical waste as per local regulations without removing the spent reagent.

**HF Removal.** Byproduct HF is routinely removed to prevent long-term deleterious effects on system components and the formation of species that might interfere with measurements of oxygen isotopes by traps immediately downstream of the reaction furnace. The first, a chemical trap, comprises NaF, 99% purity (Aldrich), in a length of Hi-EFF stainless steel tubing, 200 mm × 0.125 in. o.d. × 0.083 in. i.d. (Catalog No. 30106, Alltech) supported by a stainless steel frit, 20-$\mu$m pore size (details as above). This

is operated at room temperature, removing HF as follows.

$$NaF + HF \rightarrow NaHF_2 \qquad (2)$$

Immediately following the sodium fluoride is a cryogenic trap comprising a length of coiled stainless steel tubing, 600 mm × 1/16 in. o.d. × 0.040 i.d. (Catalog No. 3003, Alltech), immersed in liquid nitrogen (−196 °C). This second trap removes all condensable volatiles, including any trace amounts of HF that may pass through the NaF. After use of the system, the contents of this trap are vented to safety.

**Air Actuated Sample Loop Valve.** Valve V1, type 4C6UWEPH (Valco, Europe) (Figure 1), fitted with a 50-$\mu$L sample loop, facilitates automated injection of oxygen aliquots. The inlet to the loop is supplied with a specialist gas mix of 5% oxygen in helium (Air Products, Crewe, U.K.).

**Cryo-Focusing of O$_2$.** Oxygen evolved from the fluorination procedure is collected by cryofocusing the gas on a coiled, 50-cm length of Ultimetal 5-Å molsieve PLOT column immersed in liquid nitrogen (−196 °C). This concentration loop is mounted just prior to the GC column outside the oven. After allowing sufficient time for collection of all oxygen evolved following an individual heating step, rapid warming of the trap allows a narrow pulse of gas to enter the GC column. This not only aids efficient chromatographic separation of any interfering species, but also provides the opportunity to optimize the He flow rate for isotope analysis by the mass spectrometer. Gas flow to the GC column, GC interface and mass spectrometer is via fused-silica capillaries (0.32-mm i.d.) and is controlled by a helium-purged switching valve, V2, type 3-c6wez-m4-ph-cert (Valco, Europe) (see Figure 1). At the helium flow rate of 10 mL/min employed during sample pyrolysis, the majority of gases travel from the extraction furnace to the concentration loop in about 20 s. However, even with the precautions taken to reduce the effect of water adsorbing to system components, some tailing of the O$_2$ release dictates that cryogenic trapping is continued for an additional 2 min after the sample has been removed from the furnace to ensure quantitative collection of the O$_2$. After this time, valve V2 is switched to provide an alternative helium flow of 2 mL/min, and after waiting for an additional minute to allow resumption of smooth flow through the GC column, the gas retained in the cryogenic trap is released for subsequent analysis by warming the trap in water at ~40 °C.

**Gas Chromatography.** The GC consists of a 10-m length of Ultimetal PLOT column with a coating of 5-Å molecular sieve, Catalog No. 6937 (Chrompack, London, U.K.), maintained at a temperature between −15 and −20 °C. At this temperature, coupled with the 2 mL/min flow rate of helium, the retention time of oxygen is about 5 min, and effective separation from all other species is achieved (in particular, argon elutes 8−10 s ahead of oxygen and nitrogen, 6 min later). Although separation of small amounts of argon would not normally be required for oxygen isotope analysis, in this case, it was found to be crucial, because the presence of this gas caused an interference in the mass spectrometer. A reflection of the [40]Ar beam impinged upon the $m/z$ 34 collector (with no effect on $m/z$ 32 or 33), resulting in a negative signal. This produced highly erroneous baseline measurements, resulting in errors in $\delta^{18}$O of the order of several tens of per mil.

**Table 1. Examples of Minerals Found in Meteorites Capable of Releasing Water under Stepped Pyrolysis[a]**

| group name | elemental composition | mineral name |
| --- | --- | --- |
| fluid inclusions | $H_2O$ | water |
| hydroxides | $Mg(OH)_2$ | brucite |
| | $a\text{-}FeO\cdot OH$ | goethite |
| sulfates | $MgSO_4\cdot 7H_2O$ | epsomite |
| | $CaSO_4\cdot 2H_2O$ | gypsum |
| carbonate | $Mg_5(CO_3)_4(OH)_2\cdot 4H_2O$ | hydromagnesite |
| phyllosilicates | $K(Mg,Fe)_3(Si_3Al)O_{10}(OH,F)_2$ | biotite mica |
| | $(K,Na,Ca)(Al,Mg,Fe)_{2-3}(Si,Al,Fe)_4O_{10}(OH,F)_2$ | muscovite mica |
| | $Mg_3Si_2O_5(OH)_4$ | serpentine (e.g., antigorite) |
| | $(Na,Ca)_{0.3}(Al,Mg)_2Si_4O_{10}(OH)_2\cdot nH_2O$ | sectite (e.g., montmorillonite) |
| hydroxysulfides | $2[(Fe,Mg,Cu,Ni)S]\cdot 1.57-1.85[(Mg,Fe,Ni,Al,Ca)(OH)_2]$ | tochilinite |
| phosphates | $Ca_5(PO_4)_3(F,OH,Cl)$ | apatite |
| | $Ca_5(PO_4)_3OH$ | hydroxy-apatite |
| oxalate | $Ca_2C_2O_4\cdot H_2O$ | whewellite |

[a] The list is not exhaustive, and carbonaceous chondrites ,in particular, are known to contain a wide range of additional "water"-bearing minerals.[11]

**GC/MS Interface.** Prior to the admission of gases to the mass spectrometer, effluent from the GC column passes to the base of an open split assembly, part of a standard GC/MS interface. The interface allows automated control of gases entering the mass spectrometer source, either from the open split or the reference gas inlet. Although the inlet configuration does not permit variable aliquoting of sample gas into the mass spectrometer, the percentage of total sample admitted could be reduced by installing narrower capillaries (0.05- and 0.075-mm i.d.) than the 0.11-mm i.d. recommended by the manufacturer, Finnigan Mat. By using different capillaries, the sensitivity of the system could be altered to suit the yields of water from different samples. This was particularly important with regard to injections of water, for which even the smallest reproducible volume (0.02 $\mu$L) would have saturated the mass spectrometer using the factory-installed capillary. No detrimental effect to measured isotope ratios was observed as a result of using capillaries with internal diameters less than that recommended.

**Mass Spectrometer.** Measurement of the isotopic composition of the sample oxygen gas is carried out using a continuous flow isotope ratio mass spectrometer Delta C (Finnigan Mat, Bremen, Germany) equipped with three collectors for simultaneous measurement of the ion beams at $m/z$ 32 ($^{16}O^{16}O^+$), 33 ($^{17}O^{16}O^+$) and 34 ($^{18}O^{16}O^+$). This instrument comprises a 9-cm-radius flight tube, 90° magnetic sector (electromagnetic) fitted with a standard electron impact ionization source utilizing a tungsten filament. Control of the instrument is via a PC running Isodat software, version 5.2. Vacuum in the analyzer and source is provided by a Balzers TMV260 turbomolecular pump backed up by an Edwards E2M5 rotary pump.

Satisfactory function of the mass spectrometer is assessed by zero-enrichment analyses using pulses of reference gas oxygen. This reference gas was independently calibrated against NBS-28 quartz ($\delta^{18}O$) following laser fluorination,[19] thus allowing direct comparison with the sample gas calibrated against V-SMOW (see below). Precision of the mass spectrometer as determined using the reference gas alone was typically $\pm$ 0.07‰ for $\delta^{18}O$ and $\pm$ 0.10‰ for $\delta^{17}O$. During the measurement of samples, a routine

method was adopted such that each data acquisition experiment comprised a series of four reference peaks prior to analyses of sample oxygen, followed by two further reference peaks for comparison and validation. The resulting data were recorded with reference to an internal standard and were subsequently recalculated and displayed relative to Vienna Standard Mean Ocean Water (V-SMOW), the normal reference material for oxygen isotope investigations.

## SYSTEM EVALUATION

**Sample Loop Oxygen Injections.** Injections of aliquots of 5% $O_2$ in He from the sample loop were used for both regular evaluation of the trapping and analysis parts of the system and for quantification of oxygen yields from samples. Calculation of the oxygen yield from a sample pyrolysis is accomplished by comparison of the peak area resulting from the major mass-32 ion beam with that of the known volume within the sample loop.

**Liquid Water Standards.** Three water standards (National Institute of Standards and Technology, Gaithersburg, MD), V-SMOW, SLAP (Standard Light Antarctic Precipitation), and GISP (Greenland Ice Sheet Precipitation) have been used to evaluate the ability of the $CoF_3$ to quantitatively convert $H_2O$ to $O_2$ without isotopic fractionation. $\delta^{18}O$ results from the analysis of 41 consecutive water injections (0.02 $\mu$L) using all three water standards are shown in Table 2 and illustrated graphically in Figure 2. These injections were carried out without cryofocusing at a relatively fast flow rate to facilitate multiple injections in a short space of time. As a result, peak widths are too small for accurate measurement of the less abundant $^{17}O$ isotope, and although these values have been included in Table 2, the resulting $\Delta^{17}O$ values would be meaningless and have been omitted. Of these injections, the first 14 are of SLAP, the next 14 are of GISP, and the last 13 of V-SMOW. A measure of the potential memory effect in the analytical system is gained by looking at those $\delta^{18}O$ values recorded immediately after switching from one standard to another (i.e., injection numbers 15 and 29, Figure 2). On the basis of the isotopic measurements, it is concluded that a memory effect of about 10% is evident. The value of 10% was only achieved after exhaustive tests with various specifications of system components. Among the many parameters tested were reagent temperature, pyrolysis and reaction tube lengths, and carrier gas

(18) Clayton, R. N.; Mayeda, T. K. *Geochim. Cosmochim. Acta* **1963**, *27*, 43−52.
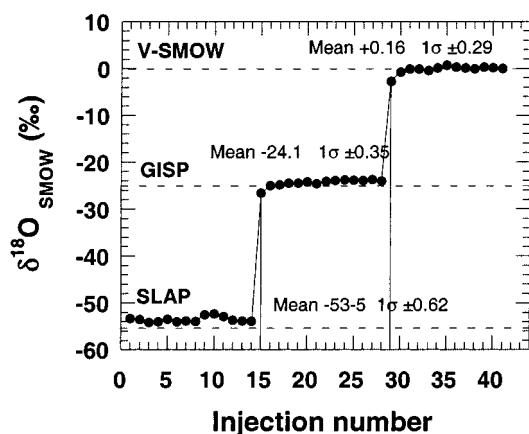(19) Miller, M. F.; Franchi, I. A.; Pillinger, C. T. *Ninth Ann. V. M. Goldschmidt Conf.* **1999**, 200.

**Figure 2.** Plot showing $\delta^{18}O$ isotopes from 41 consecutive injections of standard waters SLAP, GISP, and SMOW. Each filled circle represents one injection. Broken lines show accepted values for each water used. Vertical lines at injection numbers 15 and 29 highlight the change from SLAP to GISP and GISP to SMOW, respectively.

flow rates. Clearly, when multiple injections of the same water are carried out, the memory problem is effectively removed by the second injection. It is considered that there must be within the analytical system a reservoir of isotopically exchangeable oxygen such that during each individual fluorination, this reservoir exchanges with either sample water or product oxygen gas. Because the effect appears in only one subsequent injection, the exchange must be essentially complete before the following analysis. Since the absolute differences in $\delta^{18}O$ between subsequent temperature increments of stepped pyrolyses of unknown samples are likely to be relatively small, it is considered that memory effects of this magnitude can be largely discounted. Notwithstanding issues of memory, it can be seen from Table 2 that the $\delta^{18}O$ values measured herein agree well with accepted values. In particular, the value for V-SMOW of +0.16 ± 0.29 is in excellent agreement with the expected value following the calibration of the reference gas against NBS-28 quartz. The $\delta^{18}O$ values shown in Table 2 also illustrate the reproducibility and precision of the method. Note that the 1σ standard deviations

calculated for each water standard ignore data from the first two injections in each case (affected by the large difference in isotopic composition between water standards, ~20−30‰). $\delta^{18}O$ measurements of SMOW, isotopically closest to the values found in solid samples, display a precision of ±0.29‰. Although it is clear from Figure 2 that memory effects are small, it can also be seen that measurements of the $\delta^{18}O$ of SLAP (even for freshly prepared aliquots) are ~1−2‰ away from the accepted value (Table 2). This is considered to be largely the result of scale compression within the mass spectrometer, an effect that is only noticeable when samples of extreme isotopic composition are measured. In addition, small but variable amounts of atmospheric oxygen entering during the act of injection tend to moderate extreme isotopic compositions. Because SLAP is so depleted in $\delta^{18}O$ (−55.5‰), even an atmospheric blank of 1% (~+23.5‰) could modify the isotopic composition of the resulting sample peak, producing a small enrichment of the heavy isotopes. The trend of increasing uncertainty with increasingly extreme isotopic composition strongly suggests some role for such a variable blank contribution. Neither of these effects represents a problem for the major application of the technique (solid sample analysis), since the act of injection would not be part of such analyses, and $\delta^{18}O$ values as extreme as those in SLAP are considered to be unlikely in the samples of interest.

During normal operation, water injections were used only rarely. Instead, regular evaluation of system performance was accomplished by pyrolysis of aliquots of calcium oxalate monohydrate.

**Solid Standards.** Unfortunately, no international standards exist in which the oxygen isotopic composition of any water of hydration are known. To evaluate the practicality and reproducibility of the system, two materials were used: a laboratory standard, calcium oxalate monohydrate; and an international standard, NBS-30 biotite.

**Calcium Oxalate Monohydrate.** Calibration of the overall pyrolysis and fluorination system was achieved using powdered samples of calcium oxalate monohydrate (98% purity, Sigma-

**Table 3. Oxygen Isotopic Measurements of an Internal Terrestrial Standard, Calcium Oxalate Monohydrate[a]**

| sample | $\delta^{17}O$ (‰) | $\delta^{18}O$ (‰) | $\Delta^{17}O$ (‰) |
|--------|------|------|------|
| 1 | −0.29 | −0.47 | −0.05 |
| 2 | −0.38 | −0.63 | −0.05 |
| 3 | −0.72 | −1.35 | −0.02 |
| 4 | −0.65 | −1.38 | +0.07 |
| 5 | −0.68 | −1.15 | −0.08 |
| 6 | −1.08 | −2.01 | −0.03 |
| 7 | −0.90 | −1.65 | −0.04 |
| 8 | −0.81 | −1.49 | −0.04 |
| 9 | −0.47 | −1.22 | +0.16 |
| 10 | −1.38 | −2.21 | −0.23 |
| mean ± 1σ | −0.74 ± 0.33‰ | −1.36 ± 0.54‰ | −0.03 ± 0.10‰ |

[a] Individual samples.

Aldridge, Gillingham, U.K.). Small quantities (0.05−0.5 mg) taken from an airtight container were loaded into the extraction system, pyrolyzed, and cryofocused in the same way as unknown solid samples. Calcium oxalate was used because (a) it has a high water content (~12 wt %) and (b) it quantitatively loses all of its water of hydration at a well-defined temperature (~110 °C).

The main benefit from the use of calcium oxalate was checking the ability of the system to measure $\Delta^{17}O$ values from solid samples, in which $\Delta^{17}O$ represents a measurement of the deviation of sample oxygen from that expected as a result of mass fractionation processes. The $\Delta^{17}O$ value is calculated using the equation $\Delta^{17}O = \delta^{17}O - (0.52\delta^{18}O)$. A $\Delta^{17}O$ of 0‰ implies that the sample lies on the same mass fractionation line (same starting reservoir) as V-SMOW (i.e., bulk Earth), a negative value implies a deficiency of $^{17}O$, and a positive value means an excess of $^{17}O$. The simple formulation given above is merely an approximation for a more accurate power law dependence of variation in $\delta^{17}O$ and $\delta^{18}O$,[19] but with the analytical precision herein and with limited ranges in $\delta^{18}O$ (~20‰), such a linear approximation is valid. Deviations from 0‰ have recently been detected in terrestrial samples involving respiration[20] and materials formed by energetic particles in the upper atmosphere,[21] together with other photochemical processes.[22] These subtleties may prove to be of tremendous importance for terrestrial geochemistry, but for extraterrestrial studies, the magnitude of $\Delta^{17}O$ variations are so large that the simple relationship given above ($\Delta^{17}O = \delta^{17}O - 0.52\delta^{18}O$) still largely holds true. The $\Delta^{17}O$ value is an important parameter in studies of oxygen isotopes from extraterrestrial materials following on from the observation[6] that samples from different parts of the Solar System can be distinguished by different $\Delta^{17}O$ values. Results from >50 analyses of water extracted from calcium oxalate by pyrolysis at 300 °C over a period of more than 18 months produced a standard deviation for $\Delta^{17}O$ of ~±0.14‰. A series of analyses completed with calcium oxalate over a two-month period produced a $\Delta^{17}O$ value of −0.03 ± 0.10‰ (Table 3), more than adequate for most applications in this field. However, the $\delta^{18}O$ values from these analyses exhibit a 1σ deviation of ± 0.54‰ which is considerably poorer than that

(20) Lane, G.; Dole, M. *Science* **1956**, *123*, 574−576.
(21) Thiemens, M. H.; Jackson, T. L.; Brenninkmeijer, C. A. M. *Geophys. Res. Lett.* **1995**, *22*, 3, 255−257.
(22) Bao, H.; Thiemens, M. H.; Farquhar, J.; Campbell, D. A.; Lee, C. C. W.; Heine, K.; Loope, D. B. *Nature* **2000**, *406*, 176−178.
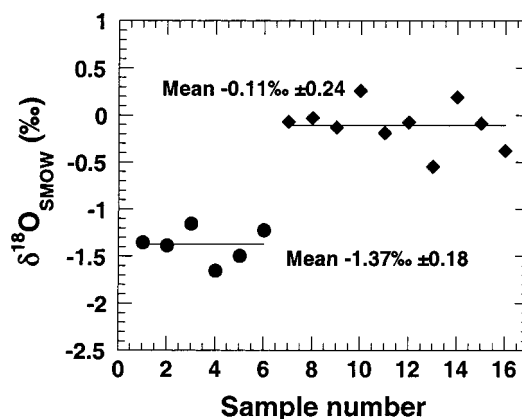
**Figure 3.** $\delta^{18}O$ ratios derived from individual calcium oxalate samples. Filled circles represent pyrolysis of solid samples, and diamonds represent injections of distillate.

**Table 4. $\delta^{18}O$ Ratios from Pyrolyzed Samples of Calcium Oxalate Monohydrate and Aliquots of Injected Distillate**

| | solid pyrolysis | | | liquid injection | | |
|--------|------|------|------|------|------|------|
| sample | $\delta^{17}O$ (‰) | $\delta^{18}O$ (‰) | $\Delta^{17}O$ (‰) | $\delta^{17}O$ (‰) | $\delta^{18}O$ (‰) | $\Delta^{17}O$ (‰) |
| 1 | −0.72 | −1.35 | −0.02 | | | |
| 2 | −0.64 | −1.38 | +0.07 | | | |
| 3 | −0.67 | −1.15 | −0.08 | | | |
| 4 | −0.90 | −1.65 | −0.04 | | | |
| 5 | −0.82 | −1.49 | −0.04 | | | |
| 6 | −0.47 | −1.22 | +0.16 | | | |
| 7 | | | | −0.20 | −0.07 | −0.16 |
| 8 | | | | +0.20 | −0.03 | +0.22 |
| 9 | | | | −0.06 | −0.13 | +0.01 |
| 10 | | | | +0.24 | +0.26 | +0.11 |
| 11 | | | | −0.51 | −0.19 | −0.41 |
| 12 | | | | −0.02 | −0.08 | +0.02 |
| 13 | | | | −0.09 | −0.55 | +0.19 |
| 14 | | | | −0.06 | +0.19 | −0.16 |
| 15 | | | | −0.04 | −0.09 | +0.01 |
| 16 | | | | −0.34 | −0.38 | −0.14 |
| mean (‰) | −0.70 | −1.37 | +0.01 | −0.09 | −0.11 | −0.03 |
| ± 1σ | 0.15 | 0.18 | 0.09 | 0.22 | 0.24 | 0.19 |

obtained for the standard waters (see above). The variability in $\delta^{18}O$ results from the readily exchangeable water of hydration in calcium oxalate, which makes its isotopic value sensitive to its duration of exposure to atmospheric water vapor.

Figure 3 and Table 4 illustrate this effect further. In an attempt to show the compatibility of the two system formats (liquid injection and solid pyrolysis) a small quantity of water was distilled from a large volume of fresh calcium oxalate. Syringe injections of this water produced $\delta^{18}O$ values ~1.2‰ heavier than those derived from the pyrolysis of solid samples that had been subject to greater atmospheric exposure. Atmospheric water vapor was measured and found to have a $\delta^{18}O$ of ~−15‰ (consistent with previous work[23]).

**Linearity.** Ideally, the linearity of the fluorination of water by $CoF_3$ would have been tested using injections of standard waters. However, as already discussed, the minimum repeatable injection by syringe of about 0.02 $\mu$L is too large for analysis with this system using either the standard 0.11- or 0.075-mm-i.d. sample

(23) Hoefs, J. *Stable Isotope Geochemistry*; Springer-Verlag: Berlin, 1987.

**Table 5. Water Yield and Oxygen Isotopic Data from a Stepped Heating Experiment with Biotite NBS-30**

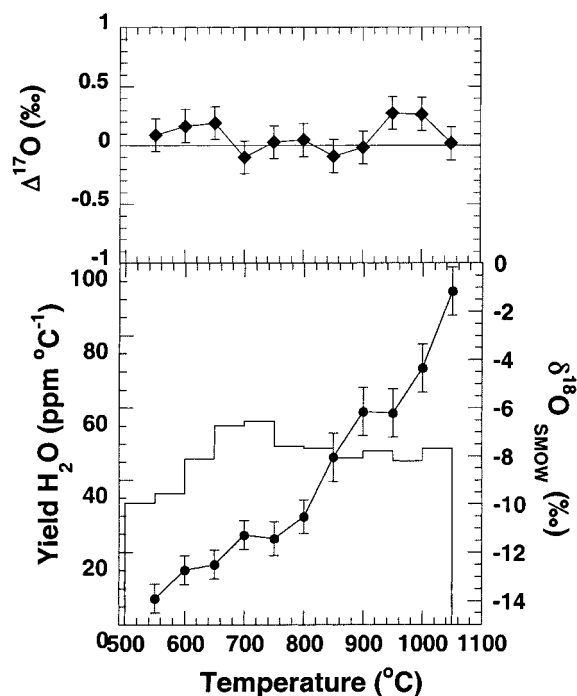| temp step (°C) | $\delta^{17}O$ (‰) | $\delta^{18}O$ (‰) | $\Delta^{17}O$ (‰) |
|---|---|---|---|
| 550 | −6.84 | −13.91 | +0.09 |
| 600 | −6.15 | −12.73 | +0.17 |
| 650 | −6.01 | −12.51 | +0.19 |
| 700 | −5.66 | −11.28 | −0.10 |
| 750 | −5.61 | −11.43 | +0.03 |
| 800 | −5.12 | −10.52 | +0.05 |
| 850 | −3.97 | −8.05 | −0.09 |
| 900 | −2.91 | −6.15 | −0.02 |
| 950 | −2.65 | −6.21 | +0.28 |
| 1000 | −1.69 | −4.35 | +0.27 |
| 1050 | −0.28 | −1.16 | +0.02 |
| wtd mean | | −8.79‰ | |
| mean | | | +0.08 ± 0.13‰ |
| yield. 2.57 wt % | | | |



**Figure 4.** Plot showing water release profile and oxygen isotopic composition of water derived from a stepped heating experiment with biotite NBS-30. The $1\sigma$ error bars shown are derived from analyses of standards and take into consideration the likely extent of isotopic exchange and errors introduced by the data reduction software. Errors introduced by system memory effects between temperature steps vary according to the isotopic difference between those steps.

capillaries. Illustration of the linearity can instead be provided by analysis of samples of calcium oxalate. Aliquots of calcium oxalate were used regularly with both versions of the system, that is, with the 0.05- and 0.075-mm-i.d. sample capillaries. Halving the inside diameter of a capillary reduces flow to the fourth power, thereby greatly reducing the amount of sample-derived gas entering the mass spectrometer source. As a result, very different sample sizes were used to obtain optimum peaks by the mass spectrometer with the different system formats. The data in Table 3 were acquired using the system with a 0.05-mm-i.d. sample capillary, but those in Table 4 were acquired using a 0.075-mm-i.d. capillary. The samples of calcium oxalate required varied between 0.02 mg for the larger bore sample capillary to ∼1 mg when less sample gas was used by the mass spectrometer. Despite this, the results are essentially identical. However, with the smaller sample sizes, it was increasingly important to keep loading time to the absolute minimum to reduce air incursion. Any delay allowed more atmospheric water into the system and to the $CoF_3$, thus resulting in an atmospheric memory effect.

**NBS-30.** A additional standard, used in the same way as samples, was a crushed biotite, NBS-30 (National Institute of Standards). This standard was useful, because it released its water (about 2.6 wt %) at higher temperatures than the calcium oxalate, starting above 500 °C. As such its behavior was more like that expected from higher-temperature components in unknown meteorite samples. Yield and isotopic results from a full-stepped heating experiment with a 4.49-mg sample of NBS-30 are shown in Table 5. Figure 4 is a stepwise plot of the analyses showing yields and isotopic values. The lower half displays $\delta^{18}O$ values superimposed upon a histogram of the yield, and $\Delta^{17}O$ values are displayed on a separate vertical axis. The simple trend of increasing $\delta^{18}O$ values suggests a kinetic fractionation process may be present during dehydration, but it does not fit a simple Rayleigh fractionation curve, possibly because of the presence of more than one source of water. The possibility of a kinetic fractionation process will be investigated further in later work. Nevertheless, the most important parameter in the study of extraterrestrial materials is the $\Delta^{17}O$ values, which from Figure 4 and Table 5 can be seen to lie close to the terrestrial fractionation line with a mean $\Delta^{17}O$ of +0.08 ± 0.13‰.

## PROCEDURES

**Sample Preparation.** To assist with the release of volatiles during pyrolysis, all solid samples were first ground in a clean pestle and mortar. The sample size required for the pyrolysis technique depended upon the anticipated water content. Each temperature increment of the stepped heating procedure needed to provide at least 0.1 $\mu$mol of $O_2$ gas to allow accurate isotopic measurement by the mass spectrometer. For those samples containing a relatively large proportion of water, for example, CI and CM carbonaceous chondrites (typically, ∼5−15 wt % water), ∼1 mg was sufficient to allow 10−15 individual analyses (i.e., 10−15 steps). In contrast, meteorites with low water contents, for example, monomict eucrites, (∼0.02 wt % water) required 100-mg-sized samples, giving 6−8 viable steps.

Before each sample was loaded, the empty platinum bucket (accessed by removal of the blanking nut, BN in Figure 1), was removed and rinsed with acetone, grade GPR (Fisher, Loughborough, U.K.). Residual acetone was removed from the bucket with a hot air gun (∼200 °C) before the bucket was replaced and, after allowing time for helium to flush air from the system, the furnace and bucket were then heated to 1000 °C for 10−15 min. After cooling, the bucket was again removed, and the weighed sample was transferred before both bucket and sample were returned to the pyrolysis tube. To minimize air incursion during the loading procedure, the open end was continually purged by a 10 mL/min flow of helium.

Once sealed into the pyrolysis tube, samples were left overnight in the helium flow at room temperature to allow any atmospheric gases in either the system or the sample to be flushed out.

**System Blank.** Before commencing a stepped heating experiment, the system blank was first assessed. This was accomplished by leaving the helium gas flowing with the sample removed from the furnace and cryofocusing any gases liberated during an equivalent length of time to that which would be used during sample analysis (usually 8−12 min, depending upon sample size). All other system parameters were kept the same during the blank run. Typical blank yields were ~0.002−0.005 $\mu$mol of $O_2$ at the lowest temperature steps and decreased to even lower values at higher steps as adsorbed water was lost.

**Sample Pyrolysis.** Stepped heating experiments usually commenced at a temperature of 50 °C. The heating duration and subsequent increase in temperature between steps were dependent upon sample size and water content. Typically, however, the majority of gas would evolve inside 6−8 min, and only the largest samples were heated for longer periods. In general, increments of ~50 °C were sufficient to produce the volume of gas necessary for analysis by continuous flow isotope ratio monitoring mass spectrometry, which has a limited dynamic range. For particularly large or small yields, temperature increments were adjusted accordingly. Runs were concluded between 700 and 1050 °C.

Sample pyrolysis was completed with valve V2 positioned to allow flow of the sample gas to the concentration loop. Once a sample had been heated for its allotted time at a particular temperature, it was withdrawn from the pyrolysis furnace and allowed to cool to room temperature. After cryofocusing was complete, valve V2 was switched to allow a second flow of He gas at 2 mL/min through the analysis part of the system, providing optimum conditions for gas chromatography and mass spectrometry. At the same time, the temperature of the furnace was increased to the next step and allowed to stabilize for about 10 min. The procedure of removing the sample between temperature steps prevented continued pyrolysis while other gas manipulation activities were carried out. It also allowed close control of the temperature at which volatiles were extracted and prevented any possibility of isotopic reequilibration of water remaining in the sample with the large reservoir of oxygen represented by the silicates.

Once measurement of all reference peaks and the sample peak by the mass spectrometer was complete, valve V2 was again switched, and flow from the extraction and processing system resumed in preparation for the next pyrolysis step.

**Analysis of Unknown Samples.** Oxygen isotope data acquired using the technique herein from a sample of the Murchison carbonaceous chondrite are shown in Table 6 and Figure 5. The step heating process allows discrimination of different water reservoirs evolving at different temperatures from the sample. These can be discerned by both the yield and the isotopic data. The yield of water from Murchison reveals two main releases, the first up to about 250 °C and a second between 300 and 600 °C. The distinction is illustrated further by the $\Delta^{17}O$ data, which shows two clear groups, one at ~0‰ and the other at ~−0.7‰. These releases of isotopically distinct water represent separate reservoirs within the meteorite.

Although the distinction between the $\Delta^{17}O$ values of oxygen in water evolved at low and high temperatures from the meteorite is very clear, Murchison is a complicated meteorite. Water extracted from Murchison during pyrolysis will have been from

**Table 6. Water Yield and Oxygen Isotopic Data from a Stepped Heating Experiment Using a Sample of Murchison, a CM2 Carbonaceous Chondrite**

| temp step (°C) | yield $H_2O$ (wt %) | $\delta^{17}O$ (‰) | $\delta^{18}O$ (‰) | $\Delta^{17}O$ (‰) |
|---|---|---|---|---|
| 100 | 0.57 | 0.00 | 0.18 | −0.10 |
| 150 | 0.51 | 0.30 | 0.60 | −0.02 |
| 200 | 0.43 | 1.58 | 2.93 | +0.05 |
| 250 | 0.43 | 2.05 | 4.31 | −0.20 |
| 300 | 0.37 | 1.93 | 5.35 | −0.86 |
| 350 | 0.78 | 2.45 | 6.26 | −0.81 |
| 400 | 1.39 | 3.81 | 8.33 | −0.53 |
| 450 | 0.73 | 4.13 | 9.36 | −0.74 |
| 500 | 0.93 | 5.06 | 10.70 | −0.51 |
| 600 | 1.26 | 4.84 | 11.09 | −0.93 |
| 800 | 0.20 | 5.40 | 11.35 | −0.51 |

Summary Data

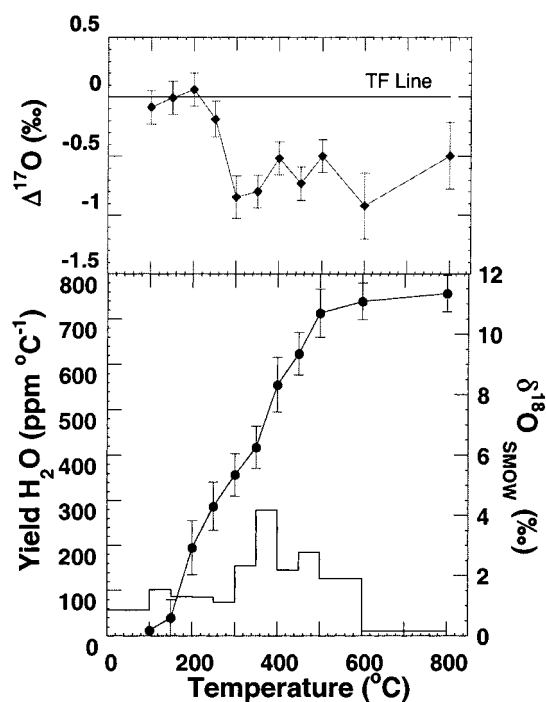| | |
|---|---|
| sample weight, 1.31 mg | wtd mean $\delta^{18}O$, + 7.2‰ |
| water content, 7.6 wt % | wtd mean $\Delta^{17}O$, − 0.53‰ |



**Figure 5.** Plot showing water release profile and oxygen isotopic composition of water derived from step heating a sample of the Murchison CM2 carbonaceous chondrite using the technique described herein. Error bars shown are 1$\sigma$, derived from analysis of standards as for Figure 4.

numerous sources, some held as true water either adsorbed or between layers in hydrated silicates and some from OH groups making up the structure of many hydrated phases. Gaining a full understanding of the sources of water measured from this meteorite is beyond the scope of this paper, but it will be discussed in greater detail as part of a more comprehensive investigation of carbonaceous chondrite samples.