Determination of the hydrogen isotopic compositions of organic materials and hydrous minerals using thermal combustion – OA-ICOS laser spectroscopy

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Abstract

Hydrogen isotopic compositions of hydrous minerals and organic materials were measured by combustion of the organics to water, followed by optical isotopic analysis of the water vapour by Off-Axis Integrated Cavity Output Spectroscopy. Hydrogen and oxygen isotopic compositions were calculated by numerical integration of the individual isotopologue concentrations measured by the optical spectrometer. Rapid oxygen isotope exchange occurs within the combustion reactor between water vapour and molecular oxygen so that only hydrogen isotope compositions may be determined. Over a wide range in sample sizes, precisions were ± 3 – 4 per mil. This is comparable but worse than CF-IRMS methods owing to memory effects inherent in water vapour transfer. Nevertheless, the simplicity and reduced cost of this analysis compared to classical IRMS or CF-IRMS methods make this an attractive option to determine the hydrogen isotopic composition of organic materials where the utmost precisions or small sample sizes are not needed.

Key words: hydrogen, stable isotope, organics, laser spectroscopy

Introduction

The hydrogen stable isotopic composition of organic materials are instrumental to the study of animal migration and show promise for archeological and forensic applications (Hobson and Wassenaar, 1996; Ehleringer et al., 2008). Typically, these analyses are accomplished by pyrolysis of hydrogen in the organic material to \( \text{H}_2 \) by reaction with carbon at high temperature, followed by continuous flow isotope ratio mass spectroscopy (CF-IRMS) (Wassenaar and Hobson, 2003, for example). Another approach is to combust the organic material in sealed tubes (Buchanan and Corcoran, 1959), followed by reduction of the water to \( \text{H}_2 \) by reaction with zinc (Coleman et al., 1982), chromium (Morrison et al., 2001; Gehre et al., 1996), or manganese (Tanweer and Han, 1996). The resulting \( \text{H}_2 \) is then inlet and measured with an isotope ratio mass spectrometer.

With the increasing commercial availability of tunable laser-based infrared molecular spectrometers able to measure the isotopic composition of water vapour, it seemed feasible that we could use one of these instruments to measure the hydrogen isotopic composition of combusted water vapour from organic material directly, without any conversion to \( \text{H}_2 \) and subsequent mass spectrometric analysis. By extension, the isotopic composition of mineral, fluid inclusion, or other waters that may be released at high temperature could also be measured isotopically as water vapour. This approach has several distinct advantages over traditional isotope ratio mass spectrometry: IRMS instruments and associated peripherals are costly, non-portable, and typically require compressed tanks of helium and other gasses and stable laboratory environments. By contrast, the laser spectrometers are of simple design, low power, relatively inexpensive, and require nothing more than dry air as a carrier. They can be purchased directly from different manufacturers and are based on off-axis integrated cavity output spectroscopy (OA-ICOS) or wavelength scanning cavity ring-down spectroscopy (WS-CRDS)(see Kerstel, 2004, for review).

Experimental

Our experimental apparatus setup is illustrated in Figure 1. We used a Los Gatos Research model 908-004 water vapour analyzer connected through a reference water vapour source to a variable temperature sample combustion furnace. A CaSO\(_4\) or molecular sieve air dryer was connected to the input of the furnace to eliminate atmospheric water vapour. The reference water vapour source was a Los Gatos Research model 908-004-001 WV1SS water vapour generator. This reference source uses a spray nebulizer and a heated cavity to generate water vapour of known isotopic composition at variable vapour-air mixing ratios, and was used to calibrate the measured hydrogen and oxygen isotopic compositions of the vapour stream.
The furnace was a Eurovector HT-PyroOH, equipped with a Costech zero-blank carousel-type autosampler. To minimize leakage of atmospheric water vapour into the dry air stream, the stream was kept at a slightly positive pressure of about 5 psi over ambient using pressurized house air connected to the input of the air dryer.

The furnace reactor packing is also illustrated in Figure 1. We used as simple packing as possible. The bottom of the ceramic reactor was filled with quartz chips to the hot zone of the furnace and a thin layer (5 mm) of Cr$_2$O$_3$ added on top to assist with combustion of the sample. We used a ceramic tube for the reactor rather than quartz because we wanted to experiment with temperatures higher than 1000 °C. In the end, however, temperatures of combustion between 850 and 1000 °C were satisfactory for complete combustion of the samples. Therefore, the ceramic tube reactor and high temperature furnace are not necessary and may be replaced by a simple quartz tube and resistance furnace. A small snarl of silver wool was added at the bottom of the reactor to support the quartz chips and remove acid gases (i.e. HCl) from the vapour stream. Combusting samples consisted of dropping samples into the hot zone of the furnace. No extra oxygen source was required other than the 20 percent by volume in the dry air or included in the Cr$_2$O$_3$. The components were connected with 1/4 inch Teflon tubing with compression-style stainless steel connectors.

A typical combustion analysis is shown in Figure 2. The reference vapour generator produces a reference pulse of water vapour of known isotopic composition at the beginning of the analysis. Samples of organic material are then sequentially dropped into the hot reactor with the sampling carousel. Each sample peak in Fig. 2 represents the combustion of a single tin boat containing an aliquot of the analyte. Sample drops were spaced at 8 minute intervals. We used two organic materials. The first was a ground polyethylene powder with a δD value of about -60 per mil and one of our in-house keratin reference materials that are used for conventional CF-IRMS in our laboratory. Sample amounts are typically 1-2 mg, and the samples were encapsulated in tin boats.

Unlike most applications where a continuous stream of water vapour is measured by the laser spectrometer, a sample combustion results in a single pulse of water vapour entrained in a dry air stream. Thus, it is analogous to conventional CF-IRMS methods where the stable isotopic composition small sample peak must be measured. In CF-IRMS, ion currents on each of the collectors are measured as the analyte passes through the ion source. These currents are then integrated to give the raw mass ratios. Instantaneous mass ratios cannot be used because isotope chromatography occurs within the preparatory inlet and gas chromatograph. The analyte peaks detected on each collector are therefore separated slightly in time and must be independently integrated to arrive at the correct mass ratios (see Sessions, 2006, for review). Because of the relatively small numbers of ions that constitute each sample pulse, such isotopic measurements are close to the statistical limit (Merritt and Hayes, 1994).

**Data Analysis**

Measurement of water pulses moving through the laser spectrometer can be mathematically treated exactly the same way as CF-IRMS analyses (Sessions, 2006). The concentrations of each of the DOH, H$_2$O, and H$_2$O isotopologues of water can be integrated across the peak to yield the bulk stable isotopic compositions of the water pulse. A typical water peak is
shown in Figure 3. As with CF-IRMS, the instantaneously measured D/H ratio of the analyte changes continuously throughout the peak. This behaviour is attributable to two effects, isotope chromatography and a non linear amount effect. Even though there was no chromatographic column in the combustion stream, there was nevertheless a small amount of isotopic chromatography whereby DOH and H$_{2}^{18}$O were preferentially delayed during transport to the laser spectrometer. It is likely that this is a property of the water vapour during flow through the Teflon transfer tubing. Secondly, isotope ratio laser spectrometers are known to have an amount dependent effect whereby the calculated isotope ratios are slightly dependent on the amount of vapour in the cavity (Lis et al., 2008; Gupta et al., 2009; Koehler and Wassenaar, 2011). Because, In this experimental design, the concentration of water vapour in the measurement cavity changes continuously as the pulse of water moves through the system, so the effect of concentration on measured D/H ratio must be removed by post-processing of the transient output signals.

Both of these issues were addressed by software, which was written in-house. Isotope chromatography is treated as it is in traditional CF-IRMS. The DOH, H$_{2}^{18}$O, and H$_{2}$O data streams are independently processed to remove the time delay. Peaks were identified from the digital data by an amplitude threshold trigger and numerically integrated. Although the threshold trigger is adjustable, the signal noise becomes too great for accurate analysis below about 3000 ppmV H$_{2}$O (Los Gatos Research; pers. comm.). Not surprisingly, a peak threshold and baseline setting of 3000 ppmv H$_{2}$O typically gives the best results. The non-linear amount effect was quantified by calibration with the reference vapour source (Fig 4). A vapour stream of constant isotopic composition from 5000 to 25000 ppmV was sequentially injected into the laser spectrometer and the bias in measured D and $^{18}$O were calculated for any amount of H$_{2}$O vapour in the optical cavity. Calibration of our instrument revealed a non-linear relationship (Fig 4.) which was modelled by a least squares fit. This fit is used by the post analyses software to correct the DOH and H$_{2}^{18}$O data stream prior to integration. Measurement precisions decreased from $\pm 2$ permil $1 \sigma$ at 25000 ppmV water vapour concentration to $\pm 7$ per mil $1 \sigma$ at 5000 ppmV.

### Results and Discussion

The results of a number of different materials measured by this technique are shown in Table 1. A good estimate of the best practical precisions can be found by measuring reference peaks produced by the vapour generator. For 100 second water pulses, our $\delta$D measurement precisions were $\pm 0.7$ per mil, similar to those obtained by most CF-IRMS methods. For vapour pulses of 30 second duration, the measurement precision drops to $\pm 3$ per mil. The 30 second vapour pulses are approximately the same size as those generated by combustion of a typical 0.5 mg organic sample, and precisions are close to the statistical limit. As a further test, we also sampled water vapour in equilibrium with liquid water in a sealed ziploc bag by using a stainless steel canula attached to a man-

![Figure 3: Typical water vapour peak. HDO is the top trace and is not to scale](image)

![Figure 4: Bias in measured concentrations of HDO on amount of water vapour in the optical cavity, and the modelled fit (line). An HDO bias of 0.1 is equivalent to about 5 per mil $\delta$D.](image)

<table>
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<tr>
<th>Material</th>
<th>amount</th>
<th>mean</th>
<th>$1\sigma$</th>
<th>n</th>
<th>known value</th>
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<td>0.7</td>
<td>9</td>
<td>-136</td>
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<td>16</td>
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<td>10</td>
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<td>3</td>
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<td>-</td>
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Table 1: Hydrogen isotopic compositions of selected materials determined by combustion or high temperature release of water vapour followed by OA-ICOS laser spectrometry.
We measured this material at -65°C during cooling and -60°C during heating of sealed silver capillaries containing water vapour for precise analyses and over about 10 mg analytical peak shapes become variable, suggesting condensation may occur in the transfer lines. Sample sizes of about 2 mg gave good results. Because keratins contain exchangeable hydrogen, their hydrogen isotopic compositions are variable, depending on the amount and isotopic composition of atmospheric water vapour. As a first test, we avoided this problem by combusting polyethylene powder, which contains no exchangeable hydrogen. The hydrogen isotopic composition of this material was previously measured at -65 ± 5 per mil by high temperature conversion followed by CF-IRMS, calibrated against sealed silver capillaries containing water of known isotopic composition (Qi et al., 2010). We measured this material at -65 ± 5 per mil, which agreed within experimental error. In a similar way, we could measure two commercially available organic materials which are similar to typical tissue or feather materials (PRC gelatin, a porcine gelatin from Sigma Life Sciences, and SPK Keratin, a keratin sold by Spectrum Laboratory Products) with precisions of ±3 and 4 per mil respectively (Table 1). A known in-house reference keratin, CHS Keratin, was measured at -193 ± 2 per mil. This value compares well to -194 per mil measured by high temperature conversion followed by CF-IRMS in our laboratory.

One problem that became evident during analyses was that water vapour has a large memory effect (Fig. 5). Memory effects of 1–4 % are reported for both pyrolysis of organic materials and reduction of liquid water followed by IRMS analysis (Wang and Sessions, 2008; Olsen et al., 2006). A similar, but larger, memory effect of 5 % of the difference between the δD values of sequential samples, assuming equal amounts can be calculated from the data of Lis et al. (2008) for a typical liquid-injection inlet for optical spectrometers. In our combustion inlet, however, the memory effect was much larger at about 16 %. The large memory effect compared to conventional hydrogen analyses is probably because the analyte is water vapour rather than hydrogen gas, as is the case for conventional IRMS analyses. It is most likely that memory effects are attributable to vapour-surface interactions in the transfer tubing and is dependent on the material used (Schmidt et al., 2010). Moreover, the larger memory effect in this apparatus compared to liquid injection followed by optical analysis suggests that part of the memory effect may be attributable to the large surface area in the ceramic reactor. In a typical analysis, the vapour generator produces a square topped pulse of known isotopic composition (Fig. 2). This is generally done at the beginning of a sample run, and the raw isotopic compositions of the following water vapour pulses are calculated using the reference pulse. Therefore, the first aliquot or two immediately following the reference pulse must be discarded and any measurement sequence will have to include multiple aliquots of the same material so that the memory error can be minimized. Although we did not try stainless steel tubing, we heated the Teflon tubing to 50 °C, with little improvement.

As a final test, we used the same experimental setup to measure water vapour released at high temperature without chemical conversion. In this way, the hydrogen isotopic compositions of fluid inclusions, encapsulated water or hydration water in minerals may be measured. Strictly, this differs from the combustion of organic materials in that the water is simply released by pyrolysis of organic matter in that the water is simply released without chemical conversion. In this way, the hydrogen isotopic compositions of fluid inclusions, encapsulated water or hydration water in minerals may be measured. Strictly, this differs from the combustion of organic materials in that the water is simply released at high temperature as is accomplished conventionally by off line heating methods (Sofer, 1978). As a starting point, we measured a small amount of water of known isotopic composition sealed in a silver capillary (Qi et al., 2010), followed by 2 mg of ground gypsum encapsulated in tin capsules. Measured δD values were -185 and -94 per mil, respectively. Standard deviations (n=5) were about 3 per mil (Table 1). The measured hydrogen isotopic compositions of water in silver capillaries agree well with known values (Table 1).

With combustions, it was not possible to determine
the oxygen isotopic compositions of organic materials by this method. The laser spectrometer is capable of these measurements, and the reference and headspace vapour tests described previously demonstrated that we could accurately measure the oxygen isotopic compositions of the headspace vapour with precisions of about 0.3 per mil. Oxygen in the water vapour from combustions is a mixture of oxygen in the organic material and atmospheric oxygen used for combustion of the sample. Even so, a small covariance with $\delta^D$ values is expected, because atmospheric $O_2$ has a relatively constant $\delta^{18}O$ value of +23.5 (Bender et al., 1994), and the $\delta^{18}O$ values of natural organics are expected to covary with their $\delta^D$ values (Ehleringer et al., 2008, eg.). This was not observed. Figure 6a illustrates a typical isotopic compositions of water vapour from keratin combustions. While the $\delta^D$ values matched expected values, $\delta^{18}O$ values were generally lower than expected and ranged between +10 to +20 per mil for each material, with no covariance with $\delta^D$ values. Moreover, a similar effect was seen with the silver capillary waters and the gypsum hydration waters, except $\delta^{18}O$ values were much higher than expected and were similar to those from keratin combustions (Fig 6b). There is no combustion with these materials and therefore no contribution of atmospheric oxygen. Perhaps as a result, small covariance was observed between hydrogen and oxygen isotopic compositions.

The most likely explanation for these observations is that oxygen isotopes in the water vapour very rapidly exchanges with another oxygen reservoir in the combustion reactor at high temperature. Sources of oxygen include the ceramic reactor, quartz chips, $Cr_2O_3$, or atmospheric $O_2$. Although oxygen isotope exchange between molecular oxygen and water is not predicted to occur without a catalyst (Lerman and Clauer, 2010), oxygen isotope exchange between quartz and water vapour is predicted at high temperature (Cole and Ohmoto, 1986). Unexpectedly, it appears at first glance that the oxygen isotope exchange is nearly complete. Although we did not measure the oxygen isotopic composition of the quartz chips or the ceramic reactor, most granitic rocks have a limited range in $\delta^{18}O$ values, from 6 – 10 per mil (Hoefs, 2009). At high temperature, the fractionation factor for oxygen isotopes between water vapour and quartz is small or even slightly negative (Clayton et al., 1972). Therefore, the observed values of ca. 10–14 per mil are not unreasonable for water vapour in equilibrium with quartz at 1000 °C. If this is indeed the process, the rapidity of oxygen isotope exchange at high temperature between water vapour and oxygen in the ceramic reactor or the quartz is astonishing.

To further test this hypothesis, we devised a simple experiment whereby the air-dryer was removed and atmospheric water vapour was drawn through the reactor at various temperatures up to 1000 °C using the same flow rate as the combustions. Three different reactors arrangements were used: a ceramic reactor packed with quartz chips, a SiC reactor packed with quartz chips, and a SiC reactor packed with SiC chips. The results are shown on Figure 7. In all three reactors, the $\delta^{18}O$ values of water vapour increase with...
increasing temperature up to 1000 °C. This is another surprising result. Because there is no oxygen available for exchange in the SiC reactor packed with SiC chips, the only explanation is that oxygen isotope exchange occurs not only between water vapour and quartz and ceramic, but also between water vapour and atmospheric molecular oxygen at high temperatures. The fractionation factor between water vapour and oxygen gas can be calculated from the partition functions of Richet et al. (1977), and is close to unity at 1000 °C. If variable isotope exchange occurs, therefore, the observed oxygen isotopic composition of water vapour should approach that of atmospheric oxygen, which has a relatively constant $\delta^{18}O$ value of 23.5 per mil (Bender et al., 1994). If equilibrium isotope exchange occurs, the temperature dependence of the oxygen isotopic composition of water vapour should be similar what is predicted from theoretical considerations. Clearly, it does not (Fig. 7), suggesting rapid temperature dependent non-equilibrium oxygen isotope exchange occurs between water vapour and molecular oxygen at temperatures between 500 and 1000 °C. Below 500 °C, $\delta^{18}O$ values are ca. -30 per mil, typical of atmospheric water vapour in Saskatchewan, suggesting that oxygen isotope exchange only occurs above this temperature. The presence of quartz or ceramic seems result in slightly lower $\delta^{18}O$ values of water vapour (Fig. 7) indicating that isotopic exchange with quartz or the ceramic reactor may also occur, but it is very difficult to quantify this further without additional experimentation.

To circumvent these effects during dehydration of hydrous minerals, it may be possible get satisfactory oxygen isotope measurements below 500 °C, where oxygen isotope exchange does not occur, or to eliminate the molecular oxygen completely by using a dry nitrogen carrier gas.

Conclusions

The hydrogen isotopic composition of organic materials was determined by combustion followed by measurement of the resultant water vapour by optical methods. Precisions were ± 3 –4 per mil, acceptable for a range of ecological applications where the utmost precision is not necessary. Advantages to the laser combustion method were ease of use and lower cost compared to IRMS as well as greater flexibility in sample mass ranges (1-5 mg) that are convenient for fast sample preparation and does not require the cost and precision of an analytical microbalance. The disadvantages clearly stem from intersample memory effects, thereby requiring at least 4-5 replicate analyses of the same sample. This has the added drawback of additional sample weighing and preparation and thus results in a practical analysis time of 15-20 minutes per sample compared to 3 minutes by IRMS. Similar results were found for hydrogen isotope measurements of vapour by dehydration of gypsum and water encapsulated in silver capillaries.

Measurement of oxygen isotopic compositions of water released at high temperature was complicated by rapid, non-equilibrium oxygen isotope exchange between water vapour and atmospheric oxygen. Measurement of both hydrogen and oxygen isotopic compositions of hydrous minerals or other encapsulated waters may be possible using temperatures lower than 500 °C or using a pure nitrogen carrier so that oxygen isotope exchange does not occur.

Acknowledgments

This research was funded by Environment Canada. We thank Manish Gupta and Doug Baer at Los Gatos Research for many technical discussions that greatly improved this manuscript. This work benefitted from the reviews to two anonymous reviewers. We would like to further thank one of the reviewers for suggesting the last experiment which explored the high temperature oxygen isotope exchange.

References


