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$^2\text{H}/^1\text{H}$ measurements of amphiboles and nominally anhydrous minerals

(clinopyroxene, garnet and diamond) using high-temperature CF-EA-PY-IRMS

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Abstract

RATIONALE: We have used a high-precision, high efficiency method for the measurement of the $^2\text{H}/^1\text{H}$ ratios of hydrous silicates (amphiboles) and nominally anhydrous minerals (NAM) such as clinopyroxene, garnet and diamond, which are usually extremely resistant to pyrolysis. This opens up new fields of investigation to better understand the conditions of formation for deep-Earth minerals.

METHOD: The technique described here involves Isotopic Ratio Mass Spectrometry (IRMS) online in continuous flow mode with an Elemental Analyzer (EA) using “purge and trap” technology rather than conventional packed column-GC gas separation. The system is equipped with a special high temperature furnace reaching 1500°C , with a longer hot zone and improved temperature stability. Emphasis is put on the efficiency of the system to reliably pyrolyse refractory minerals difficult to analyse with other conventional systems.

RESULTS: While conventional systems usually fail to generate hydrogen suitable for isotopic analyses, with the technique presented here we were able to measure $^2\text{H}/^1\text{H}$ ratios from 4 diamond samples ($\delta^2\text{H} = -60, -77, -84$ and -79‰ V-SMOW; average SD = 4.5‰ ; $n=2$), 3 garnet samples ($\delta^2\text{H}$ from -70 to -63‰), and 9 clinopyroxenes ($\delta^2\text{H}$ from -92 to -58‰) associated with 7 amphiboles ($\delta^2\text{H}$ from -76 to -27‰) from single mantle rock.

CONCLUSIONS: The possibility of using such a system to reliably measure $^2\text{H}/^1\text{H}$ ratios from refractory minerals, which are usually extremely difficult to analyse, offers a new tool of investigation for giving us unrivaled clues to study the Earth’s deep interiors.

Keywords: hydrogen, isotope, pyrolysis, elemental-analyser, diamond

Introduction

Hydrogen is the simplest chemical element of the Periodic Table of Elements but its physical and chemical properties have been used in various fields to resolve complex scientific questions. Hydrogen isotopic fractionation between mineral and fluid phases in particular has been used since the early days of isotopic studies in geochemistry. Recently, Gehre et al.¹ have summarised the various steps of hydrogen isotopic analyses. In the early days these analyses used off-line preparation systems based on complex vacuum lines, usually equipped with hazardous mercury-based Toepler pumping devices to prepare hydrogen samples for analysis with isotopic ratio mass spectrometers in dual inlet mode. The first hydrogen isotopic analyses were devoted to water analyses but, with the evolution of mass spectrometry techniques, application to organic matter analyses were adopted. Different techniques were used through time, such as reduction with uranium, chromium and vanadium. More recently, along with the development of continuous flow techniques applied to hydrogen analyses, online elemental pyrolysis was developed mainly for $^{18}\text{O}/^{16}\text{O}$ analyses^{2,3,4} but it has also been used for hydrogen isotopic determinations^{5,6}. There has been some debate about appropriate conversion temperatures of elemental analyser ovens for better measurement quality in pyrolysis mode depending on the sample matrix^{2,3,4,7,8,9,10,11}. Particularly for refractory mineral samples such as diamonds¹², pyroxenes or garnets, the yield of the pyrolysis conversion is of paramount importance, especially at low (less than 100 ppm) hydrogen content in these samples. The Elemental Analyser in Pyrolysis mode connected online in Continuous Flow mode to a mass spectrometer performing Isotopic Ratio Mass Spectrometry (CF-EA-Py-IRMS) has been optimised to enhance pyrolysis yields, and this system has been previously tested for alkaline basalt-hosted clinopyroxenes and amphibole pyroxenites. An explanation for the origin of pyroxenes and amphiboles, with the exception of the Tobaj locality, is given in Kovács et al.¹³ Tobaj is located in the Styrian Basin where

Plio-Pleistocene volcanic activity brought a great variety of xenoliths and phenocrysts to the surface. The studied amphiboles originate from euhedral grains from basaltic tuffs in the vicinity of Tobaj described in Bojar et al.¹⁴ We also performed $^2\text{H}/^1\text{H}$ measurements on four diamond samples: three of them are gem diamonds of which one (V913) is a diamondite from the Venetia kimberlite pipe in South Africa described in Jacob et al.¹⁵, as well as two garnet crystals (G1 split into 2 samples, the rim (G1B \approx 5 g) and the core (G1C \approx 1.5 g), and G2RT with a bulk weight \approx 5 g). Those garnets have been separated from one eclogite from the Les Essarts Unit, South Armorican Massif, France. These world famous eclogites (studied sample shown in Figure 1) have been known for a long time near St-Philbert-de-Grand-Lieu, Vendée^{16,17,18}. The eclogitic paragenesis comprises omphacite, pyrope-rich pink centimetric garnet, kyanite, magnesio-hornblende and zoisite; garnet and kyanite are retrogressed into kelpite (amphibole) and white micas, respectively¹⁹. The eclogites are derived from an oceanic tholeiitic gabbro of troctolitic affinity²⁰ emplaced during Ordovician times ($487 \pm 12 \text{ Ma}$ ²¹). The pressure and temperature (PT) conditions of eclogitic metamorphism associated with subduction were estimated at $700 \pm 100^\circ\text{C}$ and 15-20 kbar²⁰. The age of metamorphism in the St-Philbert-de-Grand-Lieu eclogites is poorly constrained but is probably between 360 and 380 Ma, by comparison with ages obtained on the neighbouring high pressure (HP) units in the Armorican Massif²¹.

The main challenges in the analysis of nominally anhydrous minerals are not restricted to their refractory character and very low hydrogen concentration, but also encompass the amount of sample, which can be very limited in the case of precious minerals such as diamonds and thus restrict the number of tests that can be performed before analysis. In this study, we propose a technique to obtain reliable $^2\text{H}/^1\text{H}$ measurements of nominally anhydrous minerals. Those isotopic compositions can be very helpful in tracking the origin and evolution of the tiny amounts of aqueous fluids in the Earth's deep interiors.

Analytical techniques

The system used is an elemental analyser (EA) called the Pyrocube, developed by Elementar GmbH (Elementar Analysensysteme GmbH, Hanau, Germany) and recently made available to connect online in continuous flow mode with IRMS instruments. This system had already been widely investigated in pyrolysis mode for the elemental and $^{18}\text{O}/^{16}\text{O}$ isotopic analysis of organic and inorganic compounds^{4,22}, but it has not yet been fully investigated for hydrogen isotopic analyses, especially applied to H-poor refractory minerals. The critical parameters here for the analyses of H-poor matrices are the temperature stability of the furnace and the length of the furnace hot zone which is significantly longer than for equivalent systems.

The general setup of the Pyrocube system is illustrated in Figure 2. The pyrolysis reaction tube is a glassy carbon tube packed with glassy carbon chips from the bottom to the hot zone of the furnace. The conversion temperature was set at 1450°C. A graphitic ash remover system is placed in the upper part of the reaction tube. The bottom part of the ash remover is blocked while the side walls of the ash remover are drilled with submillimeter holes allowing the helium carrier gas to flow through. This ash removing system is extremely useful for analyses where high amounts of ash are generated, in order to limit the downtime of the instrument. The glassy carbon tube is placed inside a ceramic tube with a significantly higher internal diameter, allowing a 150 mL/min backflush of helium between the two tubes. The rest of the system is similar to what was described in Fourel et al.⁴ After various attempts, we decided to configure our Pyrocube in the HD/CO solid pyrolysis mode so that we could monitor, trap and eliminate the CO peak generated during the pyrolysis step, although we were not interested in the $^{18}\text{O}/^{16}\text{O}$ measurements. With this purge and trap setup the hydrogen peak is not trapped and goes straight to the Thermal Conductivity Detector (TCD) of the Pyrocube system where gas concentrations can be measured. Different helium

flow rates were investigated to check the influence of flow rate on the pyrolysis efficiency. Considering the conversion yields from known material we finally used the standard 250mL/min flow rate for all our experiments. The sample sizes were usually more than 10 mg, with some ranging up to 40-50 mg. The samples were weighed in 5x9 mm silver capsules, placed in specially designed aluminum trays and heated in an oven at 60°C for at least an hour prior to being placed in the carousel of the Pyrocube heated at 65°C⁴. The capsules were admitted into the pyrolysis furnace through a ball valve system constantly purged with helium during sample introduction.

Our Pyrocube system was connected online and in continuous flow mode to an IsoPrime isotope ratio mass spectrometer (Elementar UK Ltd, Cheadle Hulme, UK) equipped with a Dual Inlet and electrostatic filter, to filter low energy helium ions potentially disturbing the mass 3 measurements. Although the measurements were carried out in continuous flow mode we used the dual inlet system to introduce the hydrogen calibration gas. Usually with this setup, in order to account for any potential drift of the H_3^+ factor, users introduce the same hydrogen gas on both sides of the dual inlet with different intensities and thus generate an H_3^+ factor with each sample. This so-called H_3^+ correction was calculated using the algorithm developed by Elementar and implemented in the IonVantage software used to control our system²³. Here, as we worked with rather short batches of samples and measured extremely stable H_3^+ factors below 5ppm/nA, we decided that this feature was not necessary. A complete analytical run lasted 700 seconds, including desorption of the trapped CO. The reference material that we used on a daily basis to calibrate our D/H measurements is IAEA-CH7^{24,25,26} with a δ^2H_{SMOW} value of -100.3‰ (SD=2‰). We also used the NBS30 biotite reference material²⁷ (δ^2H_{SMOW} = -65.7‰; SD=0.3‰) to validate the method. As the samples contain very low amounts of hydrogen, knowledge of the blank is crucial. Accordingly, during each batch of sample analysis, empty positions on the sample tray were run as

“empty” samples to measure the blank signal as well as to check for potential memory effects due to incomplete pyrolysis. The blank samples did not generate any detectable hydrogen signal. Several silver capsule blanks were analysed with each analytical batch and also did not show any detectable hydrogen peaks. To further check for potential blank interactions we enabled the IsoPrime IonVantage software blank subtraction subroutine that we have thoroughly tested for $^{15}\text{N}/^{14}\text{N}$ and $^{34}\text{S}/^{32}\text{S}$ analyses²⁸. The original algorithm, unlike most isotopic blank subtraction methods, does not rely on the measurements of isotopic ratios from very small peak areas that are associated with large uncertainties. It is instead based on the subtraction of measured blank/peak areas from sample peak areas prior to calculating the area ratios, meaning that only large areas are used to calculate isotopic ratios. We have applied this arithmetic blank subtraction to our diamond hydrogen isotope data and did not see any significant difference between corrected and uncorrected data, confirming very low blank levels. Lastly, we loaded pure silica grains from Aldrich (Sigma-Aldrich Chemie S.a.r.l., Saint-Quentin Fallavier, France), previously annealed at 1000 °C, of similar size (≈ 1 mm) and weight (close to 50 mg) to the analysed natural samples. The blank mass 2 signal measured for Aldrich quartz was less than 0.015 nA (below the detection limit for $^2\text{H}/^1\text{H}$ ratio measurements). Garnet and diamond natural samples were measured with maximum mass 2 beam sizes between 1 nA and 3 nA, which represent minimum sample/quartz blank major peak area ratios above 100. As the blank contribution is being investigated from different aspects, we can investigate low H-content samples for $^2\text{H}/^1\text{H}$ analyses. Hydrogen contents from minerals can be variable which results in variable hydrogen intensities measured with the analytical system. Linearity tests for the whole analytical setup were then performed with IAEA-CH7 calibrated material; 28 aliquots of IAEA-CH7 were run for sample weights ranging from 70 μg to 500 μg , generating maximum mass 2 beam intensities between 1 nA and 15 nA. The total standard deviation of those 28

measurements was 1.8%. Although, due to the nature of the sample, this systematic linearity test was more difficult to accomplish with NBS 30, we also tried to run different aliquot sizes for this reference material. We analysed two sets of 7 aliquots; each measured between 1.5 nA and 5.5 nA and we again obtained a SD=2.2% when taking into account all the data. Considering those results, no linearity correction was applied to the measurements other than the H_3^+ factor. Full results of the linearity tests are included in the supplementary information. Although the results from Qi et al.²⁹ were based on a different analytical setup, taking into account what was found by these authors, we used IAEA-CH7 as a reference material for the day-to-day calibrations.

Results and Discussion

Using the optimized setup described above we first analysed some aliquots of the reference material. The mass 2 and mass 3 chromatograms from an aliquot of IAEA CH7 are shown in Figure 3. Although hydrogen gas is not trapped and released in the same way as CO, the resulting high quality of the chromatography for such analyses must be emphasized here. The peaks are narrow and symmetrical, having thus a direct impact on the quality of the isotopic ratios measured from those peaks. Table 1 shows the reproducibility for $^2H/^1H$ measurements for IAEA-CH7. The sample weight is 200 μ g on average, generating maximum mass 2 beam sizes close to 5 nA. The data are corrected for H_3^+ contribution as well as drift. Each day before starting an analytical batch, aliquots of IAEA-CH7 were used to calibrate the $^2H/^1H$ value of the calibration gas. This value was used throughout the day to calculate sample $^2H/^1H$ ratios. The standard deviation for these measurements is between 1.5 and 2% on average, which defines a range expected from such an analytical device^{1,5,6}.

In a second set of experiments we measured the $^2H/^1H$ ratios of hydroxylated

(amphibole) and nominally anhydrous silicates (clinopyroxene and garnet). Data for clinopyroxenes were published in Kovacs et al.¹³ The hydrogen concentrations in clinopyroxenes are of the order of hundreds of ppm. Consequently, the sample weights were in the range of 40-50 mg although the size limitation was not the capacity of the reactor but the geometry of the carousel. Indeed, larger samples would have resulted in pressed capsules too large to be properly introduced into the ash remover with the risk of blocking the ball valve system. Examples of the reproducibility obtained for the studied silicates are reported in Table 2. The average aliquot sizes for amphiboles and clinopyroxenes are close to 3 mg and 45 mg, respectively, generating maximum mass 2 beam sizes between 1 and 3 nA. The amphibole samples were measured on two different days, both batches being calibrated with IAEA-CH7. The average $\delta^2\text{H}$ values range from -77‰ to -27‰ (V-SMOW) and are presented in Table 2. The clinopyroxene $\delta^2\text{H}$ values, ranging from -92 to 58‰ (V-SMOW), come from the same analytical batch and are also calibrated with IAEA-CH7. Low amounts of hydroxyl ions are also known to be present in garnets, from a few tens to a few hundreds of ppm^{30,31}. For sample aliquots close to 20 mg, the bulk garnet crystal G2RT has a $\delta^2\text{H}$ value of -66‰ while the core and rim of a second garnet crystal have $\delta^2\text{H}$ values of -70 and -63‰ , respectively, that bracket the bulk composition of sample G2RT. These results are reported in Table 3 along with the analysis of the NBS30 reference, providing a $\delta^2\text{H}$ value of $-65.7 \pm 1.9\text{‰}$. The sample weight for garnet aliquots was kept at 20 mg on average, generating maximum mass 2 beam sizes close to 1 nA. Such results can be compared with those obtained by Gong et al.³² who determined $\delta^2\text{H}$ values of eclogitic garnets of close to -90‰ by using TC/EA-MS analysis.

Based on the capacities of this pyrolysis setup we then tried to tackle a more difficult challenge - the $^2\text{H}/^1\text{H}$ measurement of four diamond samples. Due to the scarcity of diamonds, it was not possible to analyse several samples to adjust the pyrolysis conditions and the

system had to be optimized for each sample. The mass 2 and mass 3 chromatograms for a diamond sample are shown in Figure 4. The sample aliquot sizes vary between 45 and 70 mg, generating maximum mass 2 beam sizes between 1nA and 12nA. For the samples with lower hydrogen concentration we were able to obtain an analytical hydrogen peak and the mass 2 intensity reached beyond 1nA, a signal large enough to safely measure accurate $^2\text{H}/^1\text{H}$ ratios. Two aliquots of the same diamond powder were made available for each of the four diamond samples (Table 4). The average $\delta^2\text{H}$ values vary from $-59.5 \pm 5.1\text{‰}$ (V-SMOW) to $-83.6 \pm 2.4\text{‰}$ (V-SMOW) with an average standard deviation of 4.5‰ (N=2).

It is thus noteworthy that our measured $^2\text{H}/^1\text{H}$ ratios of mantle-derived minerals, including clinopyroxenes, match the range of compositions already documented for mantle (xenoliths) or mantle-derived rocks such as the Mid-Ocean Ridge Basalts^{33,34,35,36}.

Conclusions

The results that we are presenting here demonstrate the capacities of the Pyrocube system in hydrogen pyrolysis configuration to generate reliable $^2\text{H}/^1\text{H}$ isotopic ratios from refractory nominally anhydrous minerals, including diamond. There is a triple challenge to face in achieving those measurements. First, those samples are extremely difficult to pyrolyse without suffering any isotopic fractionation. Second, the hydrogen concentration is very low, not exceeding a few tens of ppm. Third, the rarity and cost of diamonds do not allow the measurements of several aliquots in order to test the analytical conditions. This is why the analytical protocol presented here was achieved step by step, first validating our technique with the $^2\text{H}/^1\text{H}$ measurements of amphiboles, clinopyroxenes and garnets prior to measuring the diamond samples. The $^2\text{H}/^1\text{H}$ measurement of small aliquots (a few tens of mg) of nominally

anhydrous minerals containing low amounts of hydrogen (a few tens to a few hundreds of ppm) appears promising for unravelling the origin and history of aqueous fluids circulating in the Earth's deep interiors.

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Table 1: $\delta^2\text{H}_{\text{VSMOW}}$ measurements of various aliquots of certified material IAEA-CH7. Weight (mg) is the sample aliquot weight in milligrams. M2 Area(A_s) is the area of the mass 2 peak measured by IRMS in A.s. $\delta^2\text{H}_{\text{VSMOW}}$ is the $^2\text{H}/^1\text{H}$ isotopic composition reported to VSMOW. $\delta^2\text{H}_{\text{ave}}$ is the average for the $\delta^2\text{H}_{\text{VSMOW}}$ measurements. SD is the standard deviation for the $\delta^2\text{H}_{\text{VSMOW}}$ measurements.

SAMPLE	Weight (mg)	M2 Area(A_s)	$\delta^2\text{H}_{\text{SMOW}}$	$\delta^2\text{H}_{\text{ave}}$	SD
DAY1					
IAEA_CH7-1	0.11	6.3E-08	-101.7		
IAEA_CH7-2	0.09	5.1E-08	-100.7		
IAEA_CH7-3	0.11	6.4E-08	-99.1		
IAEA_CH7-4	0.11	6.5E-08	-100.0		
IAEA_CH7-5	0.13	8.4E-08	-100.0		
IAEA_CH7-6	0.12	8.0E-08	-100.6		
IAEA_CH7-7	0.10	6.6E-08	-97.9		
IAEA_CH7-8	0.11	7.8E-08	-99.9		
IAEA_CH7-9	0.11	7.2E-08	-102.7	-100.2	1.5
DAY2					
IAEA_CH7-1	0.09	5.3E-08	-98.5		
IAEA_CH7-2	0.13	9.0E-08	-100.2		
IAEA_CH7-3	0.12	9.2E-08	-102.5		
IAEA_CH7-4	0.14	1.0E-07	-97.4		
IAEA_CH7-5	0.12	9.0E-08	-102.4		
IAEA_CH7-6	0.13	9.6E-08	-98.6		
IAEA_CH7-7	0.12	8.7E-08	-102.6	-100.6	2.2

DAY3

IAEA_CH7-1	0.15	1.2E-07	-99.3		
IAEA_CH7-2	0.15	1.2E-07	-101.9		
IAEA_CH7-3	0.14	1.2E-07	-100.5		
IAEA_CH7-4	0.15	1.3E-07	-99.4		
IAEA_CH7-6	0.12	8.7E-08	-101.2		
IAEA_CH7-7	0.08	5.9E-08	-98.4		
IAEA_CH7-8	0.10	7.2E-08	-101.5	-100.6	1.5

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Table 2: $\delta^2\text{H}_{\text{VSMOW}}$ measurements of various aliquots of amphibole (Amph.) and clinopyroxene (Pyrox.) samples. $\delta^2\text{H}_{\text{VSMOW}}$ is the $^2\text{H}/^1\text{H}$ isotopic composition reported to VSMOW. Amphibole data were generated from batches analysed on two different days $\delta^2\text{H}_{\text{VSMOW}1}$ to $\delta^2\text{H}_{\text{VSMOW}5}$. Pyroxene data were generated from one batch $\delta^2\text{H}_{\text{VSMOW}1}$ to $\delta^2\text{H}_{\text{VSMOW}3}$. $\delta^2\text{H}_{\text{ave}}$ is the average for the $\delta^2\text{H}_{\text{VSMOW}}$ measurements. SD is the standard deviation for the $\delta^2\text{H}_{\text{VSMOW}}$ measurements. N is the number of measurements. Weight (mg) is the average of the sample aliquot weights in milligrams. $\text{SD}_{\text{weight}}$ is the standard deviation of the sample weights in mg. M2 Area (As) is the area of the mass 2 peak measured by IRMS in A.s. $\text{SD}_{\text{M2Area}}$ is the standard deviation of the area of the mass 2 peak measured by IRMS in A.s.

Name	$\delta^2\text{H}_{\text{VSMOW}1}$	$\delta^2\text{H}_{\text{VSMOW}2}$	$\delta^2\text{H}_{\text{VSMOW}3}$	$\delta^2\text{H}_{\text{VSMOW}4}$	$\delta^2\text{H}_{\text{VSMOW}5}$	$\delta^2\text{H}_{\text{AVE}}$	$\text{SD}_{\delta^2\text{H}}$	N	Weight (mg)	$\text{SD}_{\text{weight}}$	M2 Area (As)	$\text{SD}_{\text{M2Area}}$
Szigliget amph2	-70.0	-51.8	-61.9	-68.79	-72.95	-65.1	8.5	5	2.7	0.6	1.1E-08	1.9E-09
Tobaj amph1/1	-29.0	-24.6	-36.3	-20.99	-31.95	-28.6	6.0	5	2.6	0.5	1.5E-08	2.6E-09
Tobaj amph1/2	-78.6	-69.6	-71.9	-83.14	-77.13	-76.1	5.4	5	2.7	0.7	1.0E-08	2.2E-09
Tobaj amph1/3	-25.8	-18.5	-32.5	-36.01	-31.84	-28.9	6.9	5	2.7	1.0	1.4E-08	1.6E-09
Tobaj amph2	-17.8	-28.2	-30.8	-36.58	-23.56	-27.4	7.1	5	3.3	0.2	2.0E-08	2.1E-09
AMPH_TRS16	-31.8	-26.4	-39.1	-32.24	-15.75	-29.1	8.7	5	3.1	0.0	1.3E-08	1.7E-09

AMPH_TRS22	-33.7	-38.7	-32.4	-32.06	-41.49	-35.7	4.2	5	3.5	0.3	2.1E-08	3.5E-09
TRS22	-84.6	-79.6	-83.4			-82.5	2.6	3	49.3	2.9	4.3E-08	4.0E-09
Kapolcs px2/2	-74.9	-93.1	-77.4			-81.8	9.9	3	39.1	6.9	6.8E-09	1.4E-09
RK4-Px	-54.1	-62.4	-58.2			-58.2	4.1	3	43.6	2.4	4.1E-09	4.7E-10
RK2-Px	-60.8	-70.2	-56.3			-62.4	7.1	3	41.6	2.2	1.0E-08	5.8E-10
Kapolcs px1	-92.2	-90.3	-93.4			-92.0	1.5	3	47.7	5.5	2.5E-08	4.3E-09
Szb-1/0	-76.6	-74.3	-73.1			-74.7	1.8	3	46.7	2.4	4.4E-08	2.3E-09
RK-3-Px	-88.2	-94.7	-87.4			-90.1	4.0	3	44.9	0.8	1.6E-08	2.8E-10
RK-5Px	-81.8	-86.0	-90.5			-86.1	4.3	3	39.6	9.7	1.9E-08	5.7E-09
Szb-108	-87.5	-85.4	-93.8			-88.9	4.4	3	49.3	0.6	1.5E-08	7.6E-09

Table 3: $\delta^2\text{H}_{\text{VSMOW}}$ measurements of various aliquots of three garnet samples with reference material NBS30 biotite. Weight(mg) is the sample weight in milligrams. $\text{SD}_{\text{weight}}$ is the standard deviation of the sample weights in milligrams. M2 Area(As) is the area of the mass 2 peak measured by IRMS in A.s. $\text{SD}_{\text{M2Area}}$ is the standard deviation of the area of the mass 2 peak measured by IRMS in A.s. $\delta^2\text{H}_{\text{ave}}$ is the average for the $\delta^2\text{H}_{\text{VSMOW}}$ measurements. SD is the standard deviation for the $\delta^2\text{H}_{\text{VSMOW}}$ measurements. N is the number of analysed aliquots. %H is the hydrogen concentration calculated from the mass 2 isotopic trace. SD_{H} is the standard deviation for the %H measurement.

SAMPLE	Weight (mg)	$\text{SD}_{\text{weight}}$	M2 Area(As)	$\text{SD}_{\text{M2Area}}$	$\delta^2\text{H}_{\text{SMOW}}$	SD	N	%H	SD_{H}
Biotite NBS30	5.1	0.3	7.2E-08	4.4E-09	-65.7	1.9	4	0.368	0.006
GARNET_GIB	20.4	0.9	1.5E-08	4.8E-09	-62.8	1.7	4	0.018	0.005
GARNET_GIC	19.5	1.0	2.1E-08	3.8E-09	-69.6	2.6	4	0.028	0.005
GARNET_G2RT	21.4	10.6	1.4E-08	1.4E-09	-66.2	1.5	4	0.016	0.002

Table 4: $\delta^2\text{H}_{\text{VSMOW}}$ measurements of 4 diamond samples. Weight(mg) is the sample weight in milligrams. M2 Area(As) is the area of the mass 2 peak measured on the IRMS in A.s. $\delta^2\text{H}_{\text{VSMOW}}$ is the D/H isotopic composition reported to VSMOW. $\delta^2\text{H}_{\text{ave}}$ is the average for the $\delta^2\text{H}_{\text{VSMOW}}$ measurements. SD is the standard deviation for the $\delta^2\text{H}_{\text{VSMOW}}$ measurements. %H is the hydrogen concentration calculated from the mass 2 isotopic trace. SD_H is the standard deviation for the %H measurement.

SAMPLE	Weight (mg)	M2 Area(As)	$\delta^2\text{H}_{\text{SMOW}}$	$\delta^2\text{H}_{\text{ave}}$	SD	H (ppm)	SD_H
FRAM_913-1	69.1	1.1E-08	-55.9				
FRAM_913-2	55.0	1.1E-08	-63.1	-59.5	5.1	38	5
SOY2_7-1	49.2	9.9E-08	-83.9				
SOY2_7-2	48.1	6.5E-08	-70.2	-77.1	9.7	302	83
SOY2_6-1	69.1	2.2E-07	-85.3				
SOY2_6-2	46.1	1.3E-07	-81.9	-83.6	2.4	527	49
SOY1_1B-1	46.1	1.8E-07	-79.8				
SOY1_1B-2	45.1	1.7E-07	-77.5	-78.6	1.7	684	35

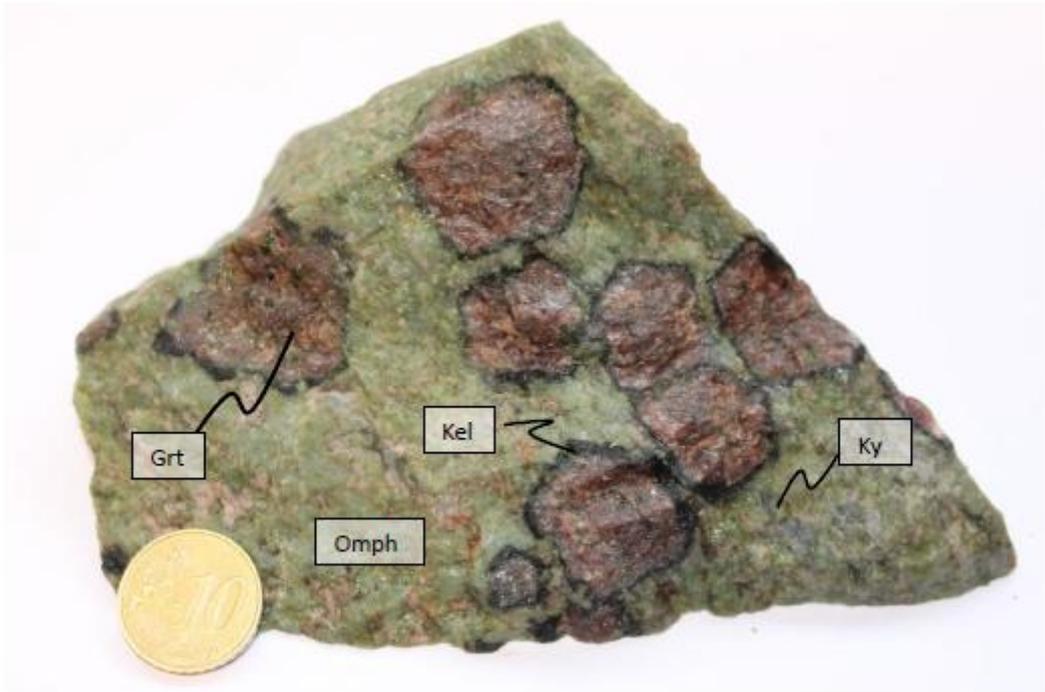


Figure 1: Hand specimen of eclogite from St-Philbert-de-Grand-Lieu (Vendée, France). Grt : Garnet; Omph: omphacite; Kel: keliphite (amphibole); Ky: kyanite.

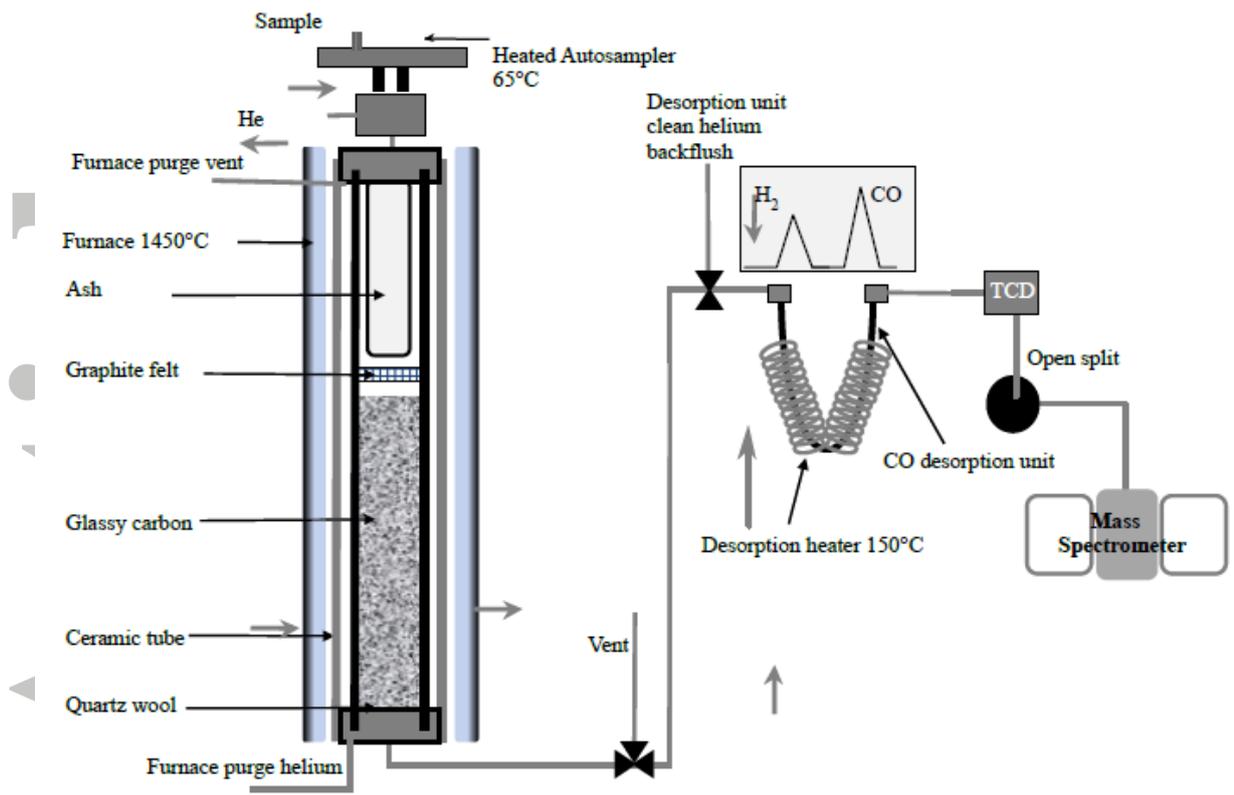


Figure 2: Hydrogen pyrolysis setup used with the Pyrocube elemental analyser system.

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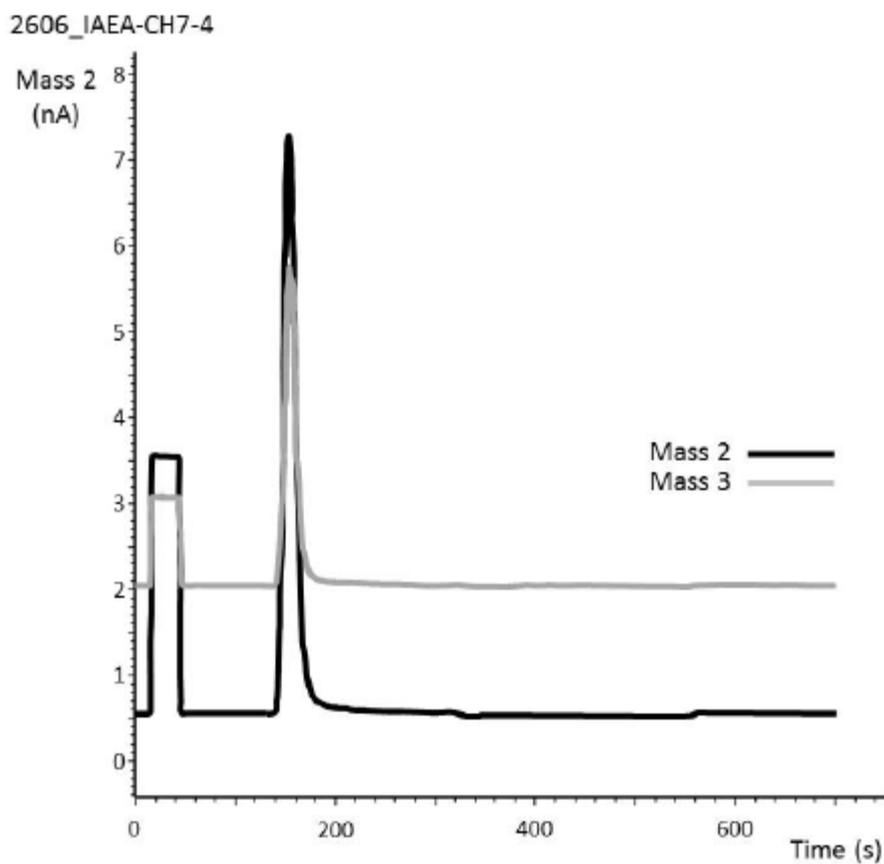


Figure 3: Mass 2 and Mass 3 isotopic traces generated from an aliquot of the certified material IAEA-CH7 with the optimized hydrogen pyrolysis setup.

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Mass 2
(nA)

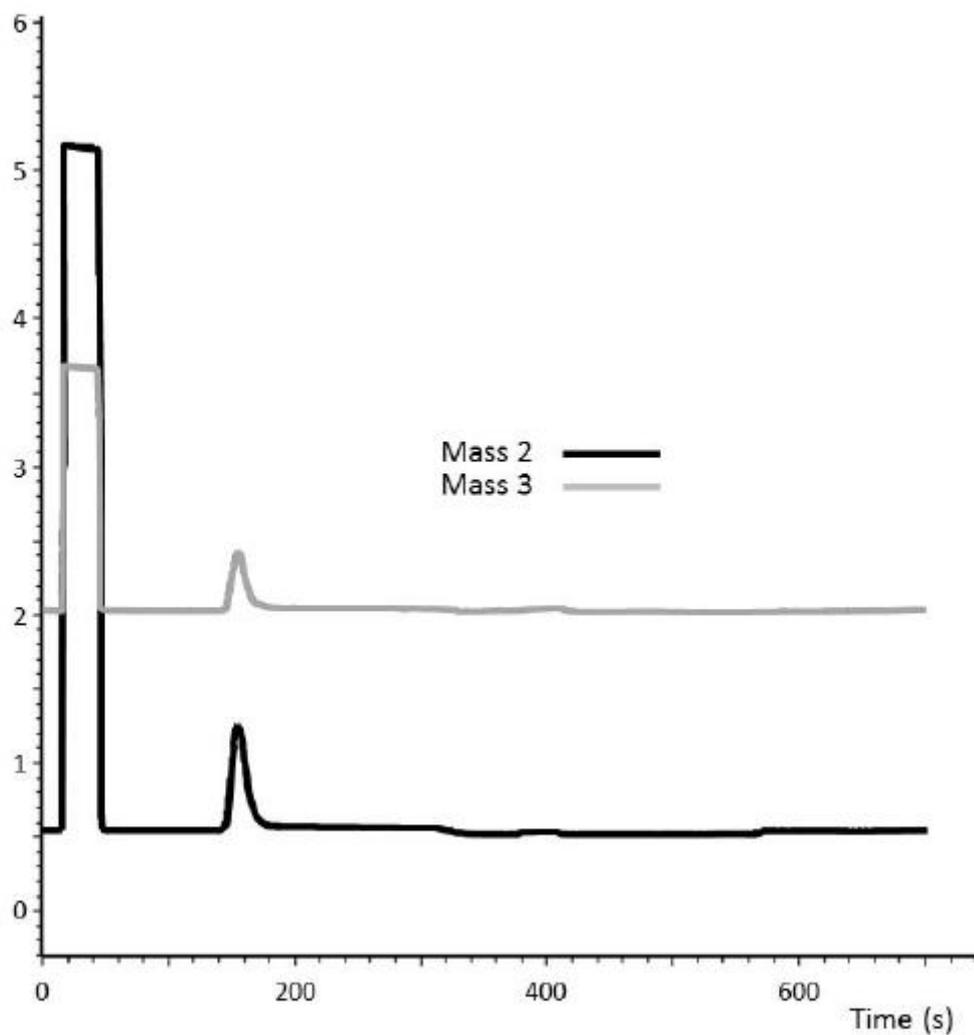


Figure 4: Mass 2 and Mass 3 isotopic traces generated from an aliquot of diamond sample with the optimized hydrogen pyrolysis setup.

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