ELSEVIER

Chemical Geology 144 (1998) 195–203

CHEMICAL GEOLOGY
INCLUDING
ISOTOPE GEOSCIENCE

The rapid heating, defocused beam technique: a CO_2-laser-based method for highly precise and accurate determination of $\delta^{18}O$ values of quartz

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Received 13 February 1997; accepted 23 September 1997

Abstract

We describe a laser fluorination technique specifically for quartz that allows both high-accuracy and high-precision determination of oxygen isotope ratios, regardless of grain size. The rapid heating, defocused beam technique (RHD) utilizes a defocused 32 W CO_2 laser at full power which delivers 17 W ($\sim$ 20 W/mm^2) to the sample to quickly react quartz. In contrast, other recent laser fluorination studies use a tightly focused laser beam and slow heating (i.e. Sharp and Kirschner, 1995; Fouillac and Girard, 1996; Kirschner and Sharp, 1997), and find laser analysis of fine-grained quartz to be inaccurate. Three quartz standards, NBS-28, QZ-BRA, and QZ-CWRU were analyzed using the RHD technique at the University of Wisconsin to test for grain size effects. RHD analyses show no correlation between grain size and $\delta^{18}O$ values and are in excellent agreement with $\delta^{18}O$ values obtained using conventional fluorination techniques. Additional analyses of the same quartz standards performed at University of Wisconsin using slow heating and a focused beam yield $\delta^{18}O$ values that are both less precise and significantly (up to 0.8‰) lower than the accepted values. Attempts to use the RHD technique with a 20 W CO_2 laser which delivers 8 W ($\sim$ 10 W/mm^2) to the sample at BRGM were unsuccessful, probably due to insufficient power density of the defocused beam. We conclude that the RHD technique yields excellent accuracy and precision, but that power densities of $>$ 15–20 W/mm^2 may be necessary across a large part of the sample surface. We recommend the use of lasers with at least 30 W of power. © 1998 Elsevier Science B.V.

Keywords: geochemistry; oxygen isotopes; silicates; laser fluorination; quartz

1. Introduction

Laser-heated fluorination techniques utilizing infra-red lasers (CO_2 and Nd-YAG) provide a high-precision method for the determination of oxygen isotope ratios for many silicates and oxides (e.g., Sharp, 1992; Kohn et al., 1993; Mattey and Macpherson, 1993; Young and Rumble, 1993; Valley et al., 1995). Prior to the advent of the laser-based systems, fluorination techniques utilizing externally heated nickel reaction vessels (Clayton and Mayeda, 1963) were used exclusively for the determination of $\delta^{18}O$ values of silicates and oxides, and therefore

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PII S0009-2541(97)00131-9

analyses from Ni reaction vessels form the basis on which the accuracy and precision of laser analyses are judged (see Valley et al., 1995 for a comparison of the two techniques).

The principal advantages of laser-based systems over the conventional fluorination techniques which follow Clayton and Mayeda (1963) are that: (1) smaller sample sizes (as low as 0.3–0.6 mg) can be analyzed (Sharp, 1992; Kohn et al., 1993; Mattey and Macpherson, 1993); (2) higher temperatures achieved using lasers allow analysis of refractory minerals (e.g., garnet, olivine, zircon, Al_2SiO_5, corundum) (e.g. Chamberlain and Conrad, 1991, 1993; Sharp, 1992, 1995; Kohn et al., 1993; Mattey and Macpherson, 1993; Young and Rumble, 1993; Valley et al., 1994, 1995; Eiler et al., 1996; U.W., unpubl. data); (3) samples can be analyzed more rapidly (< 15 min per analysis, Valley et al., 1995); (4) extremely high precision can be achieved (e.g. see Kohn et al., 1993; Mattey and Macpherson, 1993; Valley et al., 1995); and (5) the entire extraction process can be standardized each day (Valley et al., 1995).

The accuracy and precision of stable isotope analyses should be independently established by all analysts. This need is especially great for recently developed techniques such as laser-heating fluorination. While precision is relatively easy to assess, establishing accuracy is more difficult and typically involves comparison of laser analyses with conventional analyses of a well characterized standard. Because there are only two international silicate standards for oxygen isotope ratios (NBS-28 quartz, NBS-30 biotite), potential mineral-specific 'fractionations' are difficult to discern. While an analytical yield approaching 100% is generally accepted as necessary for accuracy, good yields are not sufficient to guarantee accuracy.

Historically, the accuracy of $\delta^{18}O$ values for silicate and oxide analyses using the conventional fluorination techniques (Clayton and Mayeda, 1963) are assessed by analyzing either NBS-28 (quartz sand, Friedman and Gleason, 1973; Hut, 1986), or an internal laboratory silicate standard calibrated against NBS-28. (A biotite standard, NBS-30 (Hut, 1986), is available from NIST but is not widely reported in oxygen isotope studies.) This tie to NBS-28 allows interlaboratory comparisons.

Sharp and Kirschner (1995) and Fouillac and Girard (1996) report a discrepancy in the $\delta^{18}O$ values obtained by laser analysis of coarse (> 250 μm) and fine (< 250 μm) splits of quartz (and other minerals). For coarse splits of quartz, the agreement between the $\delta^{18}O$ values of conventional analyses and laser analyses is good. The finer splits, however, yield $\delta^{18}O$ values up to 0.8‰ lower than the accepted values.

2. Laser analysis of quartz

Analyses of NBS-28 using CO_2 laser ($\lambda = 10.6$ μm, IR) systems are reported in only a few studies (Sharp, 1990; Elsenheimer and Valley, 1993; Kohn et al., 1993; Valley et al., 1994, 1995; Fouillac and Girard, 1996). For Nd-YAG laser ($\lambda = 1.064$ μm, near IR) systems, difficulties arise in analyzing quartz (e.g. Elsenheimer and Valley, 1992; Mattey and Macpherson, 1993; Akagi et al., 1993, 1995), primarily because of the high transparency of quartz to the 1.064 μm wavelength. In contrast, CO_2 laser radiation is readily absorbed by oxygen-bearing minerals and NBS-28 quartz should be well suited for analysis.

Unfortunately, the response of quartz grains to laser radiation is often unpredictable, and many workers have recommended careful, slow heating of quartz to reduce the tendency of grains to jump out of the sample holder (e.g. Sharp, 1990; Conrad and Chamberlain, 1992; Elsenheimer and Valley, 1993; Sharp and Kirschner, 1995; Fouillac and Girard, 1996). In contrast, Valley et al. (1995) proved that short reaction times and a defocused laser beam could result in both good precision and accuracy for NBS-28.

Fouillac and Girard (1996) reported good agreement between the $\delta^{18}O$ values of laser-based analysis of coarse (> 250 μm) fractions of three different quartz standards and corresponding conventional fluorination analyses. For progressive splits (from < 70 μm up to 500 μm) of two different quartz samples (QZ-BRA and QZ-CWRU) that were ground and sieved, they reported $\delta^{18}O$ values close to conventional values for coarse splits, but showed a systematic lowering of $\delta^{18}O$ values for finer splits of up to 0.8‰. In addition, all analyses of NBS-28 (120–250

μm) and powdered NBS-28 were lower than the accepted value of 9.59‰ (Hut, 1986), averaging 8.8‰.

Kirschner and Sharp (1997) used LiF as a binder to facilitate the lasing of fine-grained quartz. They achieved good agreement with accepted $\delta^{18}O$ values when analyzing the mixture, but low $\delta^{18}O$ values and poor precision for pure quartz powders.

We describe a method for analysis of quartz that has been employed at the University of Wisconsin since 1992 (Valley et al., 1995) and present new data for three different quartz standards. Our results show that high-precision and high-accuracy analysis of quartz can be produced by rapid heating with a defocused beam (RHD technique) using the UW laser extraction system. We report $\delta^{18}O$ values of NBS-28 quartz heated slowly with a focused beam (the method described by Fouillac and Girard, 1996) that are both less precise and have a significantly lower $\delta^{18}O$ value than the accepted value, corroborating the findings of Fouillac and Girard (1996). Finally we show that the grain size dependency of $\delta^{18}O$ values for quartz analyses can be readily avoided.

2.1. Equipment and sample preparation

The University of Wisconsin laser extraction system employs a 32 W Synrad laser which delivers at least 17 W to the sample chamber after all turning mirrors and focusing lenses. The samples are loaded into the chamber in a nickel sample holder (3.2 cm diameter, 1.2 cm thick) into which 73 pits are drilled. The 2 mm wide pits have vertical sides 1 mm deep, with a conical bottom (standard drill bit taper). The rest of the UW extraction system is analogous to conventional extractions systems (Clayton and Mayeda, 1963) with the addition of an in-line Hg diffusion pump which acts as a fluorine getter (see Sharp, 1990, 1992; Elsenheimer and Valley, 1992, 1993).

The nickel sample holder is prepared for samples by cleaning with 5 *M* HCl, rinsing in 95% ethanol, and drying in an oven at 105°C. Samples are loaded into the sample holder. A brass (non-magnetic) disc equipped with a funnel-shaped hole aids loading and reduces the possibility of cross-contamination. A 2 mm diameter Teflon rod is used to tamp powders. The loaded sample holder is kept in a drying oven prior to introduction into the sample chamber.

The sample holder is loaded into the sample chamber and the system is pumped to a vacuum of 10^{-4} to 10^{-5} Torr. An aliquot of BrF_5 (~400 μmoles) is inlet for 1 min (to react adsorbed water) and then pumped away. A second aliquot of BrF_5 is inlet for 5 min and the system is returned to vacuum. Failure to make these short pre-fluorinations can result in the production of significant amounts of HF which frosts the BaF_2 window and may react with some minerals. Samples which do not react appreciably with BrF_5 at room temperature are expected to yield low blanks and good yields (e.g. we have achieved good results with various ortho- and ring-silicates, pyroxenes, amphiboles, oxides, coarsely crystalline micas and chlorite, quartz, wollastonite and coarsely crystalline unaltered feldspars). For these samples a third aliquot of BrF_5 is inlet and left in the chamber overnight to assure complete reaction of adsorbed water and reduce other contaminants which readily react at room temperature.

Each day at the beginning of analysis, the entire extraction line is evacuated to 10^{-4} to 10^{-5} Torr. A blank is run by introducing BrF_5 (1000–1300 μmoles) into the chamber for 20–30 min. If the blank is sufficiently small (depending on the sample size, generally less than 0.2 μmoles O_2) the laboratory garnet standard, UWG-2 (Valley et al., 1995), is analyzed (generally 4–5 times) to assess the precision and accuracy of the extraction system. If the amount of oxygen in the blank is considered too high, successive 10–20 min blanks are run until it is reduced to acceptable levels.

2.2. Rapid heating, defocused beam (RHD) technique for lasing of quartz

Accurate and precise data for quartz are achieved using a CO_2-laser beam defocused to approximately 1 mm diameter with BrF_5 pressure of 70–100 Torr (1000–1300 μmoles). The absolute reagent pressure is not considered to be a critical factor. Each laboratory must independently determine the minimum reagent pressure required for its system. Our experiments (unpublished data) indicate that analyses are unaffected by increased reagent pressures up to 3–4 times the minimum pressure, but that lowered reagent

pressures cause incomplete yields and spuriously low $\delta^{18}O$ values.

Both granular quartz and quartz powder are heated by first centering the CO_2 laser in the pit to be analyzed using a coaxial He–Ne aiming laser. The laser is turned on at full power (> 17 W delivered to sample chamber) in continuous mode and the sample is quickly moved beneath the laser so as to fuse the upper surface. Some ejecta of unreacted material can occur during the initial surficial melting, but this procedure greatly reduces the chance for subsequent ejecta. The heated quartz quickly melts and forms a spherical bead which reacts rapidly without significant spattering (in contrast to most other minerals which require slower heating). Throughout the laser heating, the sample is positioned so as to maximize the intensity of the incandescence until the melt bead is completely reacted. Typically the reaction time for 0.5–3.0 mg of quartz is less than one minute. Rarely, a few grains are not included in the reacting glass bead and remain in the pit; however, we have found no evidence that this affects the $\delta^{18}O$ value of the analysis.

Quartz grains large enough to analyze individually can be heated at low power until a noticeable change in transparency and luster occurs. Then the laser is rapidly increased to full power, a glass bead forms, and the procedure becomes similar to the lasing of grains or powders. Ejecta from and unreacted material in the pit are uncommon. Analytical yields are typically 90–100% for 1–2 mg samples.

3. Tests for grain size effects at the University of Wisconsin

We analyzed three quartz standards reported in Fouillac and Girard (1996) (NBS-28, QZ-BRA, and QZ-CWRU) using the RHD technique to test for a grain size dependency and determine the overall accuracy and precision at the University of Wisconsin. A split of NBS-28 was ground with an Al_2O_3 mortar and pestle and sieved. The QZ-BRA (three grain size splits) and QZ-CWRU (four grain size splits) reported here are from the same sieved samples analyzed by Fouillac and Girard (1996).

All reported $\delta^{18}O$ values for quartz using the RHD technique have been corrected based on an accepted value for UWG-2 of 5.80‰ (Valley et al., 1995). However, conclusions are not dependent on the corrections.

3.1. NBS-28 quartz

Fig. 1 shows analyses of three size splits of NBS-28 using two different heating methods (Table 1). The grain size of NBS-28 as supplied by NIST is 120–250 μm (Friedman and Gleason, 1973). An aliquot of NBS-28 was ground and sieved. The 50–100 μm fraction and the < 50 μm fraction were analyzed. All fractions were heated using both the RHD technique and also by a slow heating, highly focused (150 μm beam diameter) 'SHF' technique similar to that of Fouillac and Girard (1996). At the beginning of the day, UWG-2 (Valley et al., 1995) averaged 5.81‰ ($n = 4$, 1 sd = ±0.08‰).

Analyses of the 120–250 μm size split of NBS-28 performed using the RHD technique average 9.53‰ ($n = 6$, 1 sd = ±0.04‰) (Table 1). The 50–100 μm split yields an average of 9.62‰ ($n = 3$, 1 sd = ±0.02‰). The < 50 μm split averages 9.68‰ ($n = 3$, 1 sd = ±0.02‰). All splits combined yield a

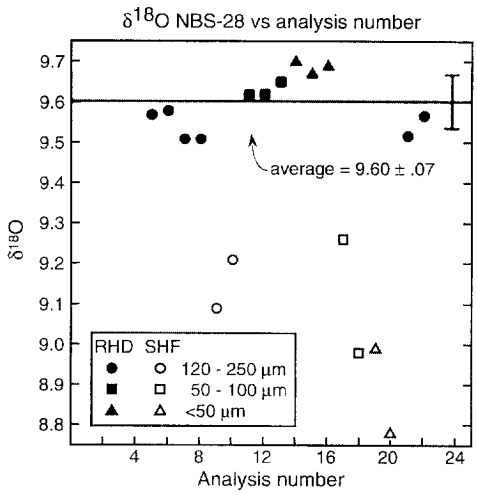

Fig. 1. Comparison of raw $\delta^{18}O$ values of NBS-28 versus analysis number on September 26, 1996. *RHD* refers to the rapid heating, defocused beam technique. *SHF* refers to a slow heating, focused beam technique. Shaded band is 9.60±0.07‰ (1 sd) for all analyses performed using the RHD technique. The first four analyses for this day were of a garnet standard. UWG-2 (5.81±0.08‰).

Table 1
NBS-28 quartz analyses performed at the University of Wisconsin on Sept. 26, 1996

Anal. Nr.	Method	Grain size (μm)	wt. (mg)	Yield %	$\delta^{18}O$ raw (‰)	$\delta^{18}O$ cr'd (‰)	Comments
5	RHD	120–250	2.12	99	9.57	9.56	
6	RHD	120–250	2.40	99	9.58	9.57	$n = 6$ (anal. # 5–8, 21–22)
7	RHD	120–250	1.29	94	9.51	9.50	$x = 9.53 + 0.03$ (1 sd)
8	RHD	120–250	1.18	97	9.51	9.50	reaction time < 1 min
9	SHF	120–250	1.16	88	9.09	9.08	
10	SHF	120–250	2.72	74	9.21	9.20	5 min reaction
11	RHD	50–100	1.86	82	9.62	9.61	$n = 3$
12	RHD	50–100	1.94	78	9.62	9.61	$x = 9.62$, ±0.02 (1 sd)
13	RHD	50–100	2.03	80	9.65	9.64	reaction time < 45 s
14	RHD	< 50	1.42	73	9.70	9.69	$n = 3$
15	RHD	< 50	1.44	87	9.67	9.66	$x = 9.68$, ±0.02 (1 sd)
16	RHD	< 50	1.82	78	9.69	9.68	reaction time < 45 s
17	SHF	50–100	1.54	72	9.26	9.25	
18	SHF	50–100	1.94	70	8.98	8.97	3 min reaction time
19	SHF	< 50	1.79	56	8.99	8.98	
20	SHF	< 50	1.13	61	8.78	8.77	3 min reaction time
21	RHD	120–250	3.19	80	9.52	9.51	
22	RHD	120–250	1.17	90	9.57	9.56	reaction time < 1 min

Analyses 1–4 were of UWG-2 (5.81 ± 0.09).
RHD method: rapid heating, defocused laser technique. SHF method: slow heating, focused laser technique.
Yields are calculated based on 16.65 μmoles of CO_2/mg for quartz.
n = number of analyses; x = mean. Corrected $\delta^{18}O$ values based on accepted value of 5.80‰ for UWG-2 (Valley et al., 1995). All RHD analyses ($n = 12$) yield an average of 9.59‰ ± 0.07 (1 sd)

corrected average of 9.59‰ ($n = 12$, 1 sd = ±0.07‰).

The slight apparent correlation between grain size and $\delta^{18}O$ value is very small (Fig. 1, Table 1), but if the standard deviations accurately describe the small data populations, then the difference is statistically significant (< 50 μm is 0.15‰ higher than the 120–250 μm size split). The correlation of grain size with $\delta^{18}O$ value is opposite to the larger trends of Fouillac and Girard (1996). In general yields correlate inversely with grain size (yields for the analyses of five of the six 120–250 μm split are 90–99% while five of the six analyses of finer splits (three 50–100 μm and three < 50 μm size splits) range from 73 to 82%).

The low yields for finer-grained size could be explained by increased spattering during lasing (though this was not observed) or increased partial reaction during pretreatment (due to higher surface area). The correlation between grain size and $\delta^{18}O$ value may reflect fractionation relating to the observed low yields or possibly to the grinding/sieving process. We acknowledge that the measured compositional differences are small, but the precision of the data presented here is excellent and suggests that the potential for fractionation related to partial reaction of powder during pretreatment should be further investigated.

Analyses of the different size splits of NBS-28 using the SHF technique (slow heating, focused beam) resulted in significantly lower $\delta^{18}O$ values. The average for all analyses of NBS-28 is 9.04‰ ($n = 6$, 1 sd = ±0.17‰). These values are similar to those of Fouillac and Girard (1996), supporting their conclusion that slow heating with a focused laser can result in low $\delta^{18}O$ values.

3.2. QZ-BRA and QZ-CWRU quartz

Analyses of QZ-BRA and QZ-CWRU splits (Table 2) were performed using only the RHD technique on October 5, 1996. On this day, the average value

Table 2
Oxygen isotope analyses of quartz standards performed at the University of Wisconsin using the rapid heating, defocused beam (RHD) technique on October 6, 1996

Anal. Nr.	Quartz standard	Grain size (μm)	Wt. (mg)	Yield (%)	δ^{18}O raw (‰)	δ^{18}O cert'd (‰)
5	NBS-28	120–250	2.17	91	9.44	**9.48**
6	NBS-28	120–250	2.17	103	9.45	**9.49**
7	NBS-28	120–250	1.73	97	9.46	**9.50**
						$n = 3$, ave = 9.49 ± 0.01
8	QZ-BRA	140–250	2.07	94	9.45	**9.49**
9	QZ-BRA	140–250	1.67	97	9.45	**9.49**
10	QZ-BRA	100–125	1.66	85	9.50	**9.54**
11	QZ-BRA	250–500	1.31	104	9.54	**9.58**
12	QZ-BRA	100–125	1.32	91	9.51	**9.55**
						$n = 5$, ave = 9.53 ± 0.04
13	QZ-CWRU	250–500	1.80	99	24.61	**24.65**
14	QZ-CWRU	100–250	2.00	98	24.64	**24.68**
15	QZ-CWRU	75–100	2.03	99	24.75	**24.79**
16	QZ-CWRU	< 75	2.87	80	24.82	**24.86**
17	QZ-CWRU	< 75	2.67	90	24.78	**24.81**
						$n = 5$, ave = 24.76 ± 0.09

Analyses # 1–4 are of UWG-2 (5.76‰ ± 0.05). Accepted values for standards reported in Fouillac and Girard (1996) are: NBS-28, 9.59‰; QZ-BRA, 9.6‰; QZ-CWRU, 24.6‰.
n = number of analyses. Corrected δ^{18}O values based on accepted value of 5.80 for UWG-2 (Valley et al., 1995).

of NBS-28 analyzed was 9.49‰ ($n = 3$, ±0.01‰) UWG-2 averaged 5.76‰, $n = 3$, 1 sd = ±0.04‰ and an upward correction of the δ^{18}O value by 0.04‰ was made (see Valley et al., 1995).

The δ^{18}O value of QZ-BRA determined using conventional fluorination techniques is 9.60‰ (Fouillac and Girard, 1996). The combined average δ^{18}O value for 100–125, 140–250, and 250–500 μm size splits of QZ-BRA using the RHD technique is 9.53‰ ($n = 5$, 1 sd = ±0.04‰) (Table 2).

Conventional fluorination analysis of QZ-CWRU yields a value of 24.6‰ (Fouillac and Girard, 1996). Using the RHD technique, the analyses of the < 70, 70–100, 100–250, and 250–500 μm grain size splits taken together yield an average of 24.76‰ ($n = 5$, 1 sd = ±0.09‰) (Table 2).

Table 3
Comparison of six quartz standards analyzed at the University of Wisconsin using the RHD technique

Quartz standard	Grain size (reported)	δ^{18}O‰ UW-RHD	δ^{18}O‰ Conventional	$\Delta_{(UW-conv)}$
NBS-28	120–250 μm	9.51 (n = 9)	9.59 [a]	−0.08
NCS	100 mesh	11.60 (n = 6)	11.66 [b]	−0.06
GBW04409	120–180 mesh	11.05 (n = 3)	11.11 [c]	−0.06
GBW04410	120–180 mesh	−2.03 (n = 4)	−1.75 [c]	−0.28
QZ-BRA	see Table 2	9.53 (n = 5)	9.6 [d]	−0.07
QZ-CWRU	see Table 2	24.76 (n = 5)	24.6 [c]	+0.16
				Average = −0.06 ± 0.14

UW-RHD values are averages of at least three analyses (1 sd < 0.10) and have been corrected based on UWG-2 garnet standard values (Valley et al., 1995).
Conventional δ^{18}O values from:
[a] Hut (1986).
[b] William Showers, unpubl. data.
[c] Yichang Inst. of Geology and Mineral Resources, Z. Zichao, pers. commun., 1995.
[d] Fouillac and Girard (1996).

Values obtained for all grain size splits of QZ-BRA and QZ-CWRU are in good agreement with the conventional values. As in the case of NBS-28, there were no large differences between the measured $\delta^{18}O$ values of different grain size splits for these quartz standards using the RHD technique (Table 2).

3.3. Other quartz standards

We have analyzed a total of six quartz standards from various sources with grain sizes that range from < 50 to 500 μm (Table 3). The average agreement is -0.06 ± 0.14‰. This comparison of $\delta^{18}O$ values from the RHD technique and conventional nickel reaction vessels suggests that data from the two techniques are statistically indistinguishable, regardless of grain size.

4. Test of the RHD technique at BRGM

Tests were conducted at BRGM (Orleans, France) to investigate whether the RHD technique can be used with a lower-power laser. A detailed description of the BRGM laser fluorination system and analytical procedures can be found in Fouillac and Girard (1996). The extraction system is similar to that of the University of Wisconsin but utilizes a lower-power CO_2 laser (20 W, Melles-Griot). Maximum power measured at the sample chamber after focusing lenses was only 8 W (vs. 17 W at UW). For these experiments, the sample holder, preparation, and pretreatment are similar to those used at UW. Prior to sample analysis, the precision and accuracy of the system was assessed by analyzing aliquots of a laboratory standard (aegirine AEG-GRE, $\delta^{18}O = 6.5$). On these days (Sept. 23–24, 1996) the UWG-2 standard was also run, and yielded an average $\delta^{18}O$ value of 5.77‰ ($n = 5$, 1 sd = ±0.16).

At BRGM, a defocused beam was used to rapidly heat fine-grained splits of QZ-BRA (100–125 μm) and QZ-CWRU (< 75 μm), as well as NBS-28 (120–250 μm). Results are shown in Table 4. Unmoderated application of full laser power to the

Table 4
Analyses of NBS-28 and fine-grained splits of QZ-BRA and QZ-CWRU performed at BRGM using a 20 W laser on Sept. 23–24, 1996

Anal. Nr.	Quartz standard	Grain size (μm)	Wt. (mg)	Yield (%)	$\delta^{18}O$ (‰)
Low-power RHD[a] *procedure*					
L822	NBS-28	120–250	1.3	56	8.88
L823	NBS-28	120–250	0.8	81	9.05
					ave. = 8.97
L824	QZ-BRA	100–125	0.9	73	9.15
L825	QZ-BRA	100–125	1.1	60	9.05
L806	QZ-BRA	100–125	1.2	95	9.09
L827	QZ-BRA	100–125	1.0	94	9.11
					ave. = 9.10 ± 0.04
L826	QZ-CWRU	< 75	0.9	45	22.16
L827	QZ-CWRU	< 75	0.8	54	22.72
					ave. = 22.44
RHF[b] *procedure*					
L831	NBS-28	120–250	0.8	63	9.15
L832	NBS-28	120–250	1.6	75	9.36
L835	NBS-28	120–250	1.1	nd.	9.37
					ave. = 9.29 ± 0.12
L833	QZ-BRA	100–125	1.1	93	9.54
L836	QZ-BRA	100–125	1.1	88	9.56
					ave. = 9.55
L837	QZ-CWRU	< 75	1.4	69	23.47
L834	QZ-CWRU	< 75	1.0	50	22.91
					ave. = 22.69

[a] Low-power RHD refers to a rapid heating, defocused beam technique using a 20 W CO_2 laser at BRGM.
[b] RHF refers to a rapid heating, focused beam technique using a 20 W CO_2 laser at BRGM.

quartz grains with a defocused beam often resulted in very significant ejecta. It also failed to melt the uppermost grains rapidly or develop a reacting glass bead (as is observed at UW). In addition, even after prolonged heating (> 3 min), some unreacted and/or partially reacted material remained in the bottom of the pit. These factors caused very low yields (Table 4). $\delta^{18}O$ values averaged 9.0‰ for NBS-28, 9.1‰ for QZ-BRA, and 22.4‰ for QZ-CWRU (Table 4). These values are significantly lower than the accepted values obtained using conventional fluorination techniques and the RHD technique at UW. Clearly, the power density was insufficient to take advantage of the RHD technique.

Because of the difficulty of obtaining complete reaction using a defocused laser beam at BRGM, a second set of analyses was performed using a focused beam (250–300 μm dia.). This technique (rapid heating, focused beam), referred to as RHF in Table 4, initiated melting faster (presumably due to higher power density) and produced less ejecta, resulting in improved oxygen yields (Table 4). An average $\delta^{18}O$ value of 9.3‰ was obtained for NBS-28, 9.6‰ for QZ-BRA, and 23.2‰ for QZ-CWRU (Table 4). The $\delta^{18}O$ values for NBS-28, and, for QZ-BRA in particular, are in much better agreement with the conventionally determined values. In contrast, the $\delta^{18}O$ value for QZ-CWRU is still 1.4‰ lower than the accepted value.

5. Discussion and conclusions

The cause of inaccuracy of SHF analyses of quartz samples heated with a focused laser remains unclear. Extensive experience and visual examination of rapidly reacted quartz samples during analysis by the RHD technique lead to the following observations and conclusions.

(1) The RHD technique for lasing of quartz yields accurate and precise determination of $\delta^{18}O$ values, independent of grain size when using a laser of sufficient power.

(2) The initial melting of the surface layer of the sample effectively traps most, if not all, of the quartz as the highly viscous silica-rich melt reduces the potential for grains to exit the pits in a partially reacted state.

(3) Initial ejecta are either unreacted, unfractionated, or of insufficient mass to affect the resultant $\delta^{18}O$ value of the analysis.

(4) For the RHD technique, the beam should be defocused to cover as much of the sample as possible, while maintaining sufficient power density to initiate rapid melting of the uppermost grains.

(5) Low reagent pressures should be avoided while excess reagent appears to have little effect on the $\delta^{18}O$ value.

(6) While incandescence during heating is extremely high (greatly reducing the ability to observe the reaction), moderation of the reaction in order to eliminate ejecta and/or spattering is unnecessary for the RHD technique.

(7) Sufficient laser power and the ability to defocus the beam may be crucial to reproducing the RHD technique.

(8) For laser systems with insufficient power to fully reproduce the RHD technique, better results might be attainable by using the largest beam diameter that can still initiate rapid melting of quartz.

(9) Grain size effects on the $\delta^{18}O$ values of quartz can occur with lower-power lasers or other techniques.

(10) Grain size effects on accuracy and precision should be evaluated by each laboratory making stable isotope analyses utilizing laser fluorination methods.

Acknowledgements

We would like to thank Brian Beard for helpful discussions and insightful comments on several versions of this paper. Jochen Hoefs and an anonymous reviewer reviewed this paper. This work was supported by grants from NSF (EAR9304372, 9316349, and 9628260) and DOE (93ER14389) to JWV.

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