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SCIENTIFIC COMMENT

UWG-2, a garnet standard for oxygen isotope ratios: Strategies for high precision and accuracy with laser heatingJOHN W. VALLEY, * NAMI KITCHEN, MATTHEW J. KOHN, CHRISTOPHER R. NIENDORF, and MICHAEL J. SPICUZZA
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Abstract—UWG-2 is a new garnet standard for oxygen isotope analysis prepared from a single large porphyroblast that was homogeneous ($\pm 0.21\%$) at the millimeter-scale before grinding. The $\delta^{18}\text{O}$ value of UWG-2 has been determined in seven laboratories using either a laser probe system or externally heated Ni reaction vessels. The raw laser probe value is 5.74% at the University of Wisconsin. If all data are normalized to NBS-28 = 9.59% , then the UW value (5.89%) is in good agreement with the average of all labs (5.78%). There is no significant difference between garnet analyses made with the two techniques, nor among labs using different wavelengths of IR laser. UWG-2 is available for interlaboratory comparison, and for assessing the performance of microanalytical techniques including laser probes and ion microprobes with a recommended value of $\delta^{18}\text{O} = 5.8\%$ SMOW.

Multiple, daily analyses of UWG-2 at the University of Wisconsin provide an accurate evaluation of all components in our laser-probe, mass-spectrometer system, and allow analytical problems to be rapidly identified. With this standardization, the accuracy of a single laser probe analysis is better than $\pm 0.10\%$. Over 1000 analyses of UWG-2 have been made. The average of all uncorrected $\delta^{18}\text{O}$ values is $5.74 \pm 0.15\%$ (1 sd). The precision on a single day averages $\pm 0.07\%$ and is frequently better than 0.05% . The uncertainty in the mean for all analyses is $\pm 0.005\%$ (1σ). A small drift of the daily average over time results from inevitable changes in the vacuum line which require careful attention and maintenance.

1. INTRODUCTION

The analysis of oxygen isotope ratios in silicates and oxides has always been one of the most difficult of stable isotope techniques. Conventionally, this has been done by reaction with fluorine compounds at $600\text{--}700^\circ\text{C}$ in externally heated Ni reaction vessels (Clayton and Mayeda, 1963). More recently, focussed IR laser beams have been employed for heating samples for oxygen (Sharp, 1990) or for sulfur (Crowe et al., 1990; Kelley and Fallick, 1990) isotope analysis.

Both conventional and laser techniques of oxygen isotope analysis by fluorination can encounter analytical problems that may be difficult to diagnose. In the vacuum line where the O_2 from each sample is cryogenically purified and converted to CO_2 , potential problems include leaks, out-gassing or memory from the graphite rod, contaminant gases, or contamination in cryogenic traps. Routine analysis of standards permits tests of the operation of this portion of an extraction line to guard against unsuspected errors. However, for conventional analysis, additional difficulties can arise in the individual Ni reaction vessels such as leaks, humidity, or memory or contamination from unreacted debris from previous samples. If uncorrected, these problems will be specific to a single reaction vessel. Thus, not all aspects of the conventional extraction line are evaluated by analysis of a standard. While much of the vacuum line in a laser system is merely a miniaturization of the conventional technique, significant dif-

ferences arise in the reaction chamber where samples are fluorinated to release O_2 . Rather than employing a separate reaction vessel for each sample, a single chamber is used and all samples are loaded in separate, open holes in a sample mount. One major advantage of using a single sample chamber is that standards can be run before, after, or interspersed with samples. Thus, every standard and sample gas is exposed to the same vacuum system, and by careful standardization it is possible to assess the performance of the entire extraction line and to guard against undetected problems in analytical technique.

The use of a single sample chamber presents a potential problem for some materials such as clays or finely ground feldspars which may react with BrF_3 at room temperature contributing oxygen to that derived from another sample. We routinely evaluate the magnitude of such "cross-talk" by measuring a blank at the beginning of each day; reagent is introduced into the chamber, but the laser is not turned on. We pretreat refractory minerals with reagent overnight and blanks are negligible, below $0.1 \mu\text{mol}$ of CO_2 . Most igneous and metamorphic minerals do not react appreciably at room temperature. We fuse anhydrous whole-rock powders in vacuo to form glass spheres in order to reduce surface area and to reduce blanks to an acceptable level. Thus, the effects of cross-talk can be evaluated in all samples and, with care, are not significant for most samples.

Recent progress in laser heated analysis has been made in reducing sample size, improving precision, and reducing the time required for analysis. Our laser system permits up to

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seventy-three samples to be loaded at one time and on-line operation permits up to four analyses/hour. The short analytical time makes it practical to analyze several standards per day and to routinely duplicate sample analyses. Daily precision of $< \pm 0.1\%$ (1 sd) is typical for samples as small as 0.5 mg. Smaller samples (see Mathey and Macpherson, 1993) or better precision are sometimes possible. For example, since December 12, 1994, the average daily precision for UWG-2 was $\pm 0.07\%$ (Fig. 1). Commercial mass-spectrometers are capable of analyzing CO_2 samples 100 times smaller than those produced from 0.5 mg of mineral with precision of ± 0.01 (1 sd), and procedures exist to analyze far smaller samples (Merritt and Hayes, 1994). It is clear that the development of accurate laser techniques for analysis of smaller samples, in situ or as chips, depends on development of better ways to produce and purify oxygen-bearing gas from solid samples. This is an active area of research and one of the fundamental requirements is for isotopically homogeneous standard materials.

In this paper, we report the preparation and characterization of UWG-2, a new garnet standard, and we use it to document the accuracy and long-term precision of our IR laser probe system for analysis of chips or powder. This standard is also appropriate for evaluating the performance of in situ analysis by UV laser (Wiechert and Hoefs, 1995; Rumble and Christensen, 1995) or by ion microprobe (Valley and Graham, 1991; Hervig et al., 1992; Riciputi and Paterson, 1994; Graham et al., 1996).

2. PREPARATION OF GARNET STANDARDS

Two garnet standards have been prepared and analyzed at the University of Wisconsin for oxygen isotope ratio analysis. Both standards are from individual garnet porphyroblasts in granulite facies mafic amphibolite from the Gore Mountain mine, Adirondack Mountains, NY, USA.

Large, > 10 cm diameter, garnets are common and comprise 10–20% of the hornblende-rich garnet-ore at Gore Mountain (Luther, 1976). This rock is mafic to ultramafic in composition and averages 17% garnet. Variable amounts of plagioclase, hornblende, and garnet are the major minerals; orthopyroxene, biotite, clinopyroxene, ilmenite, rutile, and iron sulfide are common minor constituents of the rock, and occasional inclusions in the garnets. Large garnets are also found at Gore Mountain in felsic to intermediate composition gneiss. The total range in $\delta^{18}\text{O}$ of these garnets is from 3.5 to 6.5‰ (M. J. Kohn and J. W. Valley, unpubl. data). While garnets from the mafic amphibolite show a more restricted range of about 1‰, care must be taken not to compare analyses of different garnets from Gore Mountain.

UWG-2, UW-Gore Mountain Garnet #2, was prepared in 1994 from a 2 kg block of garnet from the center of a single crystal. Its use supersedes UWG-1, UW-Gore Mountain Garnet #1, previously called simply Gore Mt. Garnet, which has been analyzed over 1000 times, and is now in short supply (Kohn et al., 1993; Valley et al., 1994). The chemical composition of glass prepared from UWG-2 is identical to the average composition of other garnets from the mafic amphibolite at Gore Mountain, $\text{Gr}_{13}\text{Alm}_{47}\text{Py}_{30}\text{Sp}_1$ (Luther, 1976), indicating an analytical yield of 13.25 $\mu\text{mol CO}_2$ per mg of UWG-2. Small amounts of cation zoning are observed in garnets from Gore Mountain, including increases in X_{Alm} within 100 μm of biotite that result from diffusional exchange during postmetamorphic cooling. A total of sixteen analyses of 1–2 mg chips from different parts of the UWG-2 crystal were made by laser to test homogeneity before crushing, yielding $\delta^{18}\text{O} = 5.73 \pm 0.21\%$ (1 sd). The sample was crushed, sieved and washed to 75–105 and 105–177 μm diameter fractions. The 105–177 μm fraction was purified of inclusions by Frantz magnetic separator; small amounts of ilmenite, pyroxene, hornblende,

biotite, plagioclase, rutile, apatite, and iron sulfide were removed. Seventy-two grams of the separated garnet were then split into 1 g samples and bottled. UWG-2 analyses are listed in the Appendix.

3. ION MICROPROBE ANALYSIS OF UWG-2

The homogeneity of oxygen isotope ratio within and among individual grains of Gore Mountain garnets has been evaluated in a preliminary manner by repeated ion microprobe analysis in two laboratories. Both labs used Cameca ims-4f ion probes, the high energy offset technique of Hervig et al. (1992), and spot sizes of 20–30 μm . At the University of Edinburgh, analyses of twenty-four spots showed a chip of Gore Mountain garnet similar to UWG-1 and UWG-2 to be homogeneous within analytical error ($\pm 0.9\%$, 1 sd) (J. Craven, unpubl. data, 1995; see Graham et al., 1996). At Oak Ridge National Laboratory, three or four spots were analyzed on multiple grains of UWG-2 on each of five different days with daily standard deviations ranging from 0.1 to 1.6‰ (L. Riciputi, unpubl. data, 1995; see Riciputi and Paterson 1994). The Oak Ridge data may indicate that real heterogeneity exists in some microdomains of UWG-2, but alternatively the days with poorer precision may reflect statistics of small sample sets or the effect of Fe/Mg gradients within 100 μm of grain boundaries with biotite which, if undetected, would create errors in the ion probe correction procedure of 1.6‰ for less than 5 mol% variations in X_{Alm} (Riciputi and Paterson, 1995). Analysis of 1 cm chips of the UWG-2 crystal are in progress to further evaluate homogeneity at the μm -scale.

4. HIGH PRECISION GARNET ANALYSIS BY LASER

The use of a high energy laser for sample heating and reaction with BrF_3 or other F compounds permits rapid analysis of refractory minerals with smaller sample sizes than are routinely used with externally heated Ni reaction vessels (Sharp, 1990; Kohn et al., 1993; Mathey and Macpherson, 1993; Valley et al., 1994; Eiler et al., 1995). While analyses of garnets have been made by reacting spots in situ in a block or wafer of garnet, the use of infrared (IR, 1.064 or 10.6 μm) lasers results in spots that are surrounded by thin haloes of partially reacted and fractionated sample resulting in poor precision of ± 0.3 to 0.5‰ (1 sd) (Elsenheimer and Valley, 1992; Sharp, 1992; Chamberlain and Conrad, 1991, 1993; Young and Rumble, 1993). Such "edge effects" around the laser pit were first described for in situ sulfur isotope analysis, but precision is better than $\pm 0.15\%$ and corrections are possible for sulfides (Crowe et al., 1990). Shorter wavelength ultraviolet (UV, 0.24 μm) lasers have recently been shown to avoid measurable edge effects and precision of ± 0.1 to 0.2‰ has been obtained from 0.5 to 1 mg sized in situ pits (Wiechert and Hoefs, 1995; Rumble and Christensen, 1995). Similar precision has been obtained with smaller samples, 0.1–0.5 mg, but an additional correction is required based on sample size (Wiechert and Hoefs, 1995). Thus far, the best accuracy and precision in oxygen isotope ratios has been obtained through quantitative reaction of powder or chips with a 10.6 μm IR laser. The use of a thin diamond saw blade (100 μm thick) to cut ~ 500 μm cubes of garnet (~ 0.5 mg) from a microscope slide has permitted accurate sample location and contouring of oxygen isotope ratio with a sampling density of

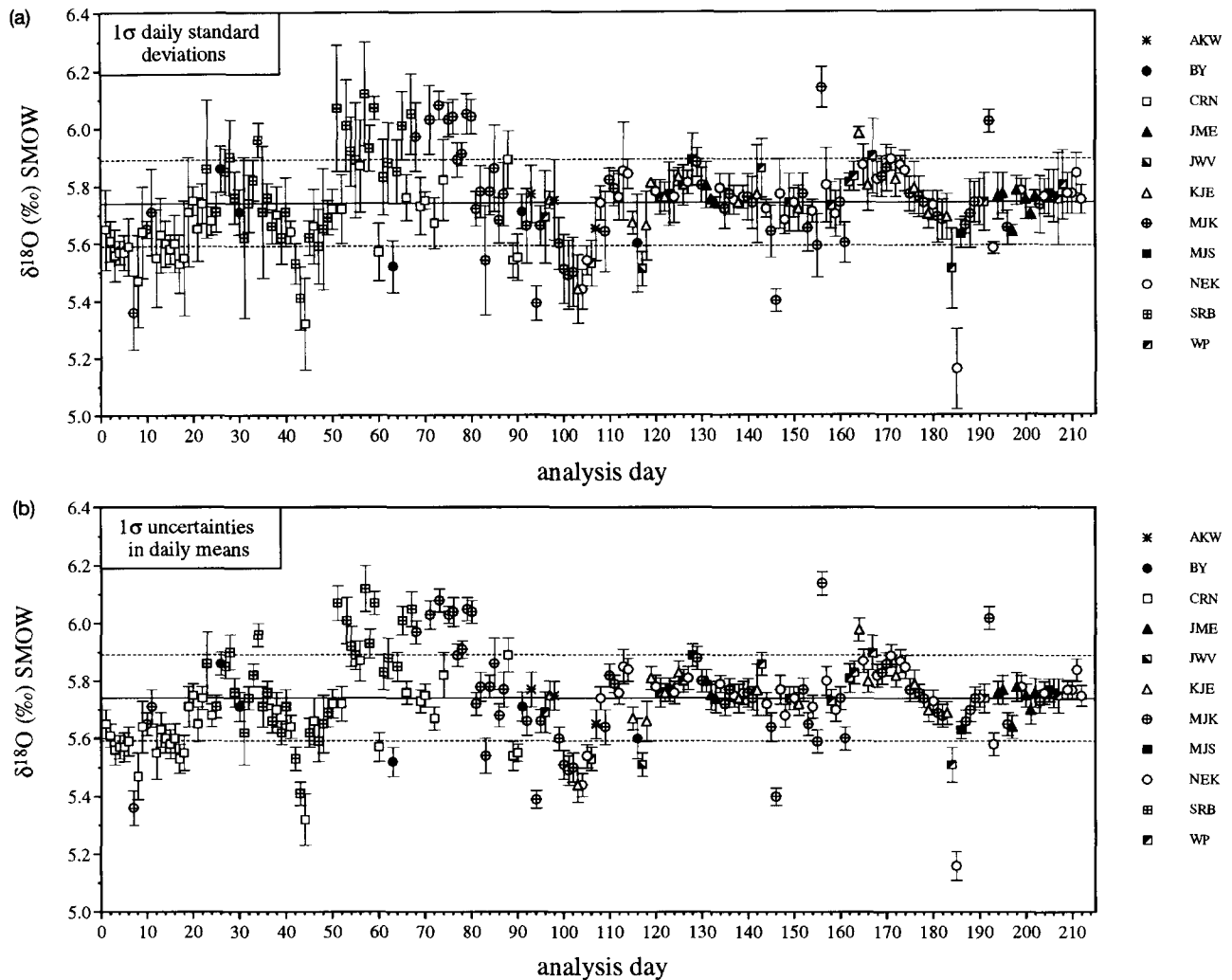


FIG. 1. Uncorrected values of $\delta^{18}\text{O}$ for 1081 analyses of UWG-2 standard on 212 days at the University of Wisconsin. Data are coded according to analyst. The average value for all data is $5.74 \pm 0.15\text{‰}$ (1 standard deviation about the mean, see Table 2) with an uncertainty in the mean of $\pm 0.005\text{‰}$. Small amounts of systematic drift about the long term average are seen with the precision on most days better than $\pm 0.1\text{‰}$. Daily averages, standard deviations and # of analyses are included in Appendix A. (a) Data with uncertainties about the daily mean. (b) Data with uncertainties in the daily mean. Figure 1b shows that drift was significantly larger than uncertainty and that the cause is not related to different analysts. In at least some instances, drift was caused by wear of the laser system and, once identified by these standard analyses, was easily remedied.

over 120 analyses/cm² and a precision of $\pm 0.05\text{‰}$ (Kohn et al., 1993).

In this paper, we report the results of 1081 analyses of UWG-2 standard employing a 10.6 μm CO₂ laser with BrF₅. Details of our procedures are published elsewhere (Elsenhimer and Valley, 1993; Kohn et al., 1993; Valley et al., 1994). Since 1992, each day of oxygen isotope analysis by laser at UW has started with at least three to five analyses of UWG-2 or UWG-1. The first standard analyses of a day sometimes deviate from the daily mean for later standards by more than three standard deviations and are discarded, but no data are culled once the system is stable. Poorer precision for the first analyses is most common after periods of inactivity or venting of the line for maintenance. Figure 1a shows the average and 1 standard deviation for 1081 analyses of UWG-2 made on

212 days from March 15, 1994 to June 4, 1995. No corrections have been made to these data other than the conventional procedures for a triple-collecting Finnigan/MAT 251 mass-spectrometer. Standard analyses have constituted 20–25% of all analyses made during this period. We justify this effort because we are still refining technique and careful standardization permits enhanced accuracy and precision.

Figure 1a and b shows that standard analyses vary with time in a systematic manner that affects all users. The long term average for UWG-2 is 5.74‰ with a one standard deviation = $\pm 0.15\text{‰}$ (Fig. 1a). The average on any single day is much more precise, $\pm 0.09\text{‰}$ on average and frequently better than $\pm 0.05\text{‰}$. Figure 1b shows the uncertainties in daily means, conservatively calculated by dividing the daily standard deviation or 0.09‰ (whichever is larger) by $n^{0.5}$. This figure

UWG-2 vs. NBS-28

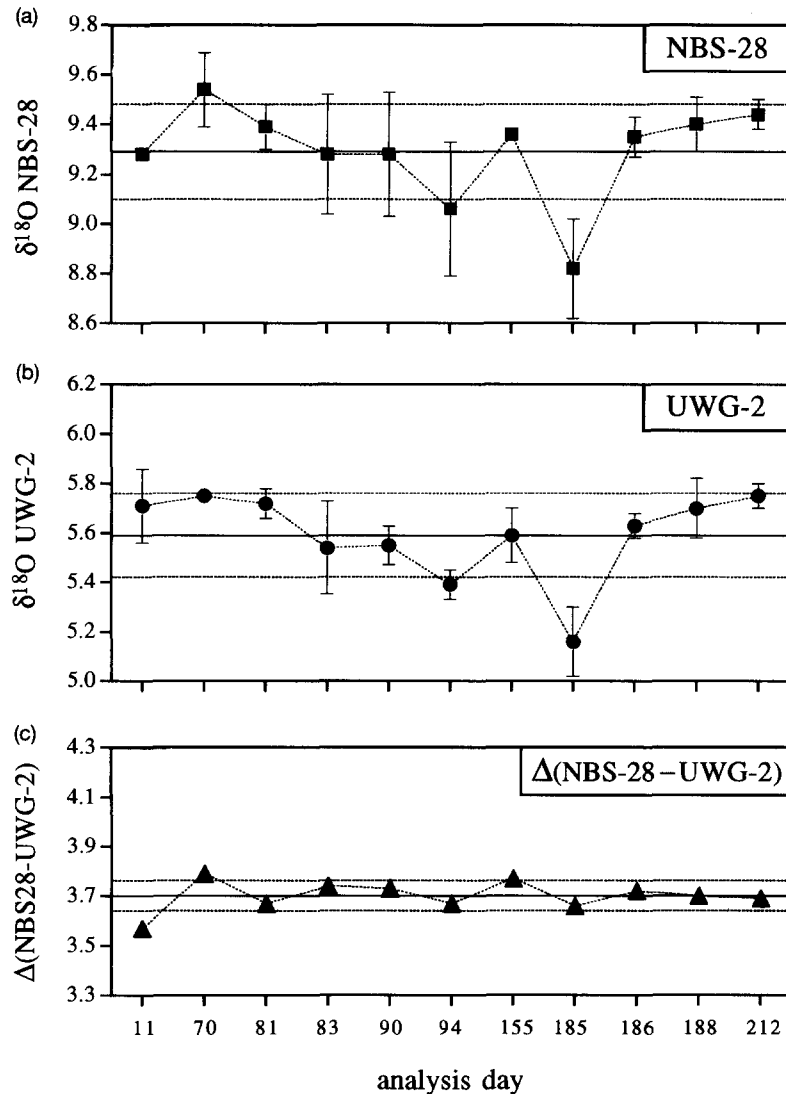


FIG. 2. A total of 82 UWG-2 and 65 NBS-28 analyses have been made together on 11 days (see Table 1). (a) Data for NBS-28, African Glass Sand. (b) Data for UWG-2, UW-Gore Mountain Garnet #2. Figure 2c shows that analyses of the two standards track each other with an average difference of $3.70 \pm 0.06\text{‰}$.

shows that the day to day variations are statistically significant. Larger shifts in the daily mean for analyses of UWG-1 were seen before September 1992, when the conditions of the laser system were less consistent (Elsenhimer and Valley, 1993; Kohn et al., 1993). The variations in Fig. 1 reflect a variety of factors including leaking valve tips, buildup of contamination in the sample chamber, cold traps and/or Hg diffusion pump/F₂ scrubber, outgassing of the graphite rod, and new aliquots of reagent. Sometimes these events took time to diagnose such as days 50 to 80 when the valve on the sample chamber leaked slightly making analyses erroneously heavy; one user who consistently reacts samples and moves the sample gas more quickly was apparently less affected than others who are more deliberate. More commonly, however, all users are similarly affected.

An additional source of variation in Fig. 1 might result if daily differences exist in calibration of the mass-spectrometer working standard. This is done each day by extracting a fresh aliquot of CO₂ from a large glass reservoir mounted on the mass-spectrometer. The same working standard was used until the end of day 143 (Fig. 1) when the glass reservoir was refilled and recalibrated against NBS-19 (calcite) and break-seals of known CO₂. Every day, before lasing of the first garnet standard, the mass-spectrometer calibration is further checked by analysis of a CO₂ sample that was analyzed on previous days. This procedure ensures that the calibration of the mass-spectrometer is constant within 0.01 to 0.03‰. The fact that highs and lows in Fig. 1 significantly exceed 0.03‰ and are marked by more than one day proves that mass-spectrometer calibration is not the cause of the trends seen.

Figure 1 shows analyses by eleven different users of the laser system, and with the exception mentioned above, there is no significant correlation with user. Since 1994, there were three other users who mostly worked on samples that have undergone hydrothermal alteration. These samples tend to be hydrous and to react with BrF_5 at room temperature in the sample chamber, creating cross-talk among the samples which share a sample plug, creating a measurable blank, and yielding poorer standard precision. Including data for these users would imperceptibly change the long-term average to $5.72 \pm 0.17\text{‰}$; however, for consistency, all analyses by these users are omitted from the standardization.

The precision seen in Fig. 1 suggests that accuracy can be improved at the 0.1 to 0.2‰ level by correction based on the daily average for UWG-2.

5. ACCURACY OF GARNET ANALYSIS BY LASER

Accuracy for oxygen isotope analysis is typically defined in terms of the difference in permil of the isotope ratio compared to that in SMOW (standard mean ocean water) which has been determined to have an absolute $^{18}\text{O}/^{16}\text{O}$ ratio of 2.00520×10^{-3} (Baertschi, 1976; see O'Neil 1986). In practice, the comparison of a silicate mineral to a water standard involves several steps, including equilibration of the water with CO_2 . However, values of $\alpha(\text{CO}_2\text{-H}_2\text{O})$ used by different labs vary by up to 0.4‰ (see Friedman and O'Neil, 1977). In order to avoid this uncertainty, we compare UWG-2 to the NBS-28 standard, African Glass Sand. NBS-28 is fine-grained quartz of uncertain isotopic homogeneity and with small amounts of other mineral impurities. We use it because it is the international standard closest to garnet in its analysis properties and it is the most widely reported interlaboratory silicate standard.

In order to compare with UWG-2, NBS-28 has been analyzed a total of sixty-five times on eleven of the days reported in Fig. 1. Figure 2a and b shows the analyses of NBS-28 and UWG-2. It is significant that the analyses track each other. The average difference between the two standards is $3.70 \pm 0.06\text{‰}$ (Fig. 2c). The exact $\delta^{18}\text{O}$ value of NBS-28 is not agreed upon. In 1986, a compilation of five labs yielded an average value of $9.59 \pm 0.12\text{‰}$ SMOW (Hut, 1986). If NBS-28 is assigned this value, then the data in Fig. 2 indicate UWG-2 to be 5.89‰. Alternatively, if the measured value of UWG-2 is taken to be correct, then $\delta^{18}\text{O}$ (NBS-28) = 9.44‰, within the range reported by Hut (1986).

The accuracy of the value reported for UWG-2 depends critically on the precision of the analyses reported in Fig. 2, on the accuracy of the accepted value for NBS-28, and on the assumption that analyses of quartz and garnet are either unfractionated by the process of laser analysis or that they are fractionated by equal amounts. This last assumption is implicit whenever a mineral different from the standard is analyzed, and this assumption could be questioned if sample size is consistently different for the two materials or differences occur in the laser-heated reaction between sample and BrF_5 .

The effect of variable sample size has been evaluated for garnet in Fig. 3 where the analyses of UWG-1 are plotted as a function of weight. Note that the value of UWG-1 is 0.3–0.4‰ higher than UWG-2. For best routine standard analysis,

2 mg of garnet are used, but the data show no significant difference with sample size down to 0.5 mg. On some occasions, we have measured small memory effects when samples of contrasting isotope ratio are analyzed consecutively. This may correlate with buildup of contaminants in the liquid nitrogen cold-traps, the Hg diffusion pump, or on the graphite rod. Many of the 0.1 to 0.2‰ excursions in Figs. 1 and 2 correlate with routine maintenance which is necessary in order to prevent memory effects. If the memory effect is not evaluated and becomes significant, then small samples will be more affected than larger samples. A better understanding of these effects may ultimately permit accurate analysis of samples far smaller than 0.5 mg (see Matthey and Macpherson, 1993).

Each mineral behaves differently during the reaction with BrF_5 . We find that visual observation of the reaction is important. The main differences from mineral to mineral relate to the fluorides that are produced which vary with the composition of the mineral, and to the amount of sputtering upon reaction. Some fluorides, principally SiF_4 , are volatile. At the other extreme, CaF_2 forms a relatively immobile melt which may shield oxygen-bearing material from reaction with BrF_5 . For this reason, Ca-rich minerals like clinopyroxene can be difficult to analyze. Sputtering can also influence an analysis if partially reacted and fractionated material is ejected from the site of analysis. We have found that for the high temperatures and short time spans of laser reaction, fractionation is generally small. Even when samples of quartz or garnet are intentionally reacted to extract only 50% of the oxygen, the results are within 0.5‰ of the correct value. Thus, the effect of large amounts of sputtering may be detected at the 0.1‰ level. Careful visual observation usually allows one to prevent more than a few percent sputtering and the effect should not be measurable. A potential disadvantage of our sample chamber is that material ejected by sputtering can contaminate other unanalyzed samples. Visual observation allows the analyst to avoid analyzing contaminated samples. For the minerals reported here, garnet is the easiest and most reliable to react. Slow heating typically produces no sputtering and

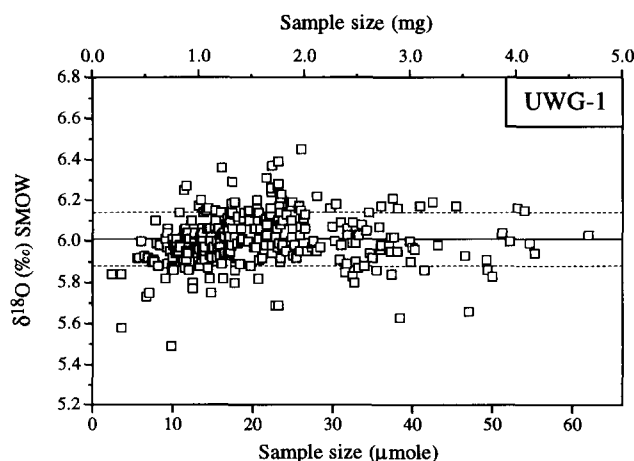


FIG. 3. Uncorrected analyses of UWG-1 as a function of sample size. There is no difference with sample size from 0.5 mg to over 4 mg.

leaves a small solid fluoride residue. Measured yields are within uncertainty of 100%. Quartz is more problematic, slow heating may produce low $\delta^{18}\text{O}$ values and a dependence on grain size (Fouillac and Girard, 1995; Sharp and Kirschner, 1995). We routinely react fine or coarse quartz with a partly defocused laser beam at high power. A minimum of sputtering occurs, no residue remains at the site of reaction, yields are good, no dependence on grain size has been observed, and precision is excellent (Table 1).

Ultimately, the acceptance of oxygen isotope analyses by laser will depend on comparisons to analyses made by externally heated Ni reaction vessels (Clayton and Mayeda, 1963). This technique accounts for the majority of analyses that have been made of silicates and oxides over the past 40 years. Unfortunately, such comparisons are difficult for refractory minerals that do not react well at the lower temperatures attained by external heating of Ni-vessels. Garnet, as well as olivine, zircon, spinels, corundum, sphene, and Al_2SiO_5 , fall into this category (see Sharp, 1992; Kohn et al., 1993; Valley et al., 1994; Matthey et al., 1994; Eiler et al., 1995). Garnets have been reacted in Ni vessels through use of fine grinding, higher temperatures, long reaction times, or prior fusion in vacuo to form glass of the same isotopic composition.

UWG-2 has been analyzed by externally heated Ni reaction vessels or by laser in seven labs. These data are reported in Table 2 as raw data and after small corrections to normalize NBS-28 analyses to $\delta^{18}\text{O} = 9.59\text{‰}$. The corrections account for differences lab to lab: in the calibration of mass-spectrometers, in the calibration of NBS-28, and in the analysis. All corrected values are in excellent agreement, $\pm 0.09\text{‰}$, indicating that no significant fractionation exists for these laser analyses relative to conventional analyses.

6. STANDARDIZATION OF LASER DATA

Our data show that the accuracy and day-to-day precision of laser probe analyses can be improved by routine analysis of a standard such as UWG-2 and by making a small $\leq 0.2\text{‰}$ correction based on the average of each day's standard analyses. The UWG-2 values vary systematically as shown in Fig. 1 and we attribute this variation largely to factors in the handling of gas, after the laser fluorination step. Thus, any difference that occurs in a garnet analysis will systematically occur in analyses of other minerals. Figure 2 shows that this

Table 1. Comparison of oxygen isotope analysis of NBS-28 Quartz and UWG-2 Garnet on the same day at the University of Wisconsin.

Date	analysis day #	ave. $\delta^{18}\text{O}$		n	ave. $\delta^{18}\text{O}$		n	$\Delta^{18}\text{O}$ (NBS28-UWG2)
		NBS-28	$\pm 1\text{sd}$		UWG-2	$\pm 1\text{sd}$		
4/18/94	11	9.28	0.01	2	5.71	0.15	6	3.57
9/1/94	70	9.54	0.15	8	5.75	0.03	6	3.79
10/6/94	81	9.39	0.09	2	5.72	0.06	6	3.67
10/10/94	83	9.28	0.24	7	5.54	0.19	9	3.74
10/31/94	90	9.28	0.25	11	5.55	0.08	9	3.73
11/10/94	94	9.06	0.27	14	5.39	0.06	9	3.67
2/27/95	155	9.36	0.03	5	5.59	0.11	6	3.77
4/24/95	185	8.82	0.20	5	5.16	0.14	7	3.66
4/25/95	186	9.35	0.08	4	5.63	0.05	9	3.72
4/27/95	188	9.40	0.11	4	5.70	0.12	9	3.70
6/4/95	212	9.44	0.06	3	5.75	0.05	6	3.69

Average = 3.70 ± 0.06

Table 2. Summary of analyses of UWG-2, UW-Gore Mountain Garnet #2, by laser probe and externally heated Ni reaction vessels.

Lab/analyst ^A	Average $\delta^{18}\text{O}$ ^B		#days	n	1sd ^C	1 σ ^D	Sample size
	Raw	Normalized					
LASER PROBE							
1. Wisconsin	5.74	5.89	212	1081	0.15	0.005	0.5-5.0mg
2. Michigan	5.58	5.67	3	4	0.11	0.06	
3. So. California	5.68	5.77	7	23	0.18	0.04	0.5-2.7mg
4. Royal Holloway	5.82	5.77		11	0.11	0.03	1.0-1.5mg
EXTERNALLY HEATED Ni REACTION VESSELS							
5. Chicago	5.32	5.72	2	9	0.16	0.05	4-6mg
6. Jerusalem	5.64	5.83	3	5	0.17	0.08	8-12mg
7. Monash	5.78	5.83	3	12	0.17	0.05	7-9mg

FOOTNOTES:

- A. Lab/Analyst: 1. University of Wisconsin, 11 analysts from 3/94 to 6/95, see fig. 1, CO₂ laser; 2. University of Michigan, J.R. O'Neil, T.W. Vennemann, CO₂ laser; 3. University of Southern California, Keane and Morrison (1995), CO₂ laser; 4. Royal Holloway University, D. Matthey, Nd/YAG laser; 5. University of Chicago, R.N. Clayton, T. Mayeda; 6. Hebrew University of Jerusalem, A. Matthews; 7. Monash University, I. Cartwright.
B. Analyses are reported as raw value and as normalized to NBS-28, $\delta^{18}\text{O}=9.59\text{‰SMOW}$.
C. 1sd=standard deviation about the mean for raw data= $((n\Sigma\delta^2)-(\Sigma\delta)^2)/n(n-1))^{0.5}$.
D. 1 σ =uncertainty in the mean= $1\text{sd}/n^{0.5}$.

is clearly the case for quartz and garnet and we have similar experience with many minerals.

While UWG-2 has not yet been analyzed by as many labs as NBS-28, it is superior in several important ways. First, the isotopic homogeneity of UWG-2 was demonstrated by laser probe analyses before it was ground. Quartz grains from a sandstone, like NBS-28, have been shown to differ by up to 25‰ in $\delta^{18}\text{O}$ (e.g., Graham et al., 1996). While this may have little effect on analyses of large samples of ground material, variability of analyses may result for small samples, and in situ analysis is impossible. Second, for laser systems, garnet reacts well for all wavelengths while optically transparent quartz is difficult to react at 0.24 and 1.064 μm , and can sputter at 10.6 μm . Third, pieces of unground UWG-2 are available to evaluate in situ techniques.

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APPENDIX A Daily UWG-2 analyses
at the University of Wisconsin.

analysis					analysis						
Date	day	Ave.	± 1 SD	n	User	Date	day	Ave.	± 1 SD	n	User
3/15/94	1	5.65	0.14	8	CRN	9/7/94	72	5.67	0.09	4	CRN
3/22/94	2	5.61	0.07	4	CRN	9/8/94	73	6.08	0.05	4	MJK
3/25/94	3	5.56	0.09	3	CRN	9/9/94	74	5.82	0.14	3	CRN
3/29/94	4	5.57	0.04	4	CRN	9/12/94	75	6.03	0.06	7	MJK
4/1/94	5	5.57	0.06	3	CRN	9/14/94	76	6.04	0.06	3	MJK
4/5/94	6	5.59	0.10	4	CRN	9/15/94	77	5.89	0.06	6	MJK
4/6/94	7	5.36	0.13	5	MJK	9/16/94	78	5.91	0.04	9	MJK
4/7/94	8	5.47	0.16	4	CRN	9/20/94	79	6.05	0.07	6	MJK
4/13/94	9	5.64	0.16	3	CRN	9/21/94	80	6.04	0.06	4	MJK
4/14/94	10	5.65	0.03	4	MJK	10/6/94	81	5.72	0.06	6	MJK
4/18/94	11	5.71	0.15	6	MJK	10/9/94	82	5.78	0.09	4	MJK
4/19/94	12	5.55	0.17	4	CRN	10/10/94	83	5.54	0.19	9	MJK
4/29/94	13	5.63	0.13	5	CRN	10/11/94	84	5.78	0.08	5	MJK
5/3/94	14	5.60	0.08	3	CRN	10/13/94	85	5.86	0.15	3	MJK
5/6/94	15	5.58	0.05	3	CRN	10/16/94	86	5.68	0.08	6	MJK
5/16/94	16	5.60	0.10	5	CRN	10/20/94	87	5.77	0.11	4	MJK
5/18/94	17	5.53	0.10	4	CRN	10/24/94	88	5.89	0.10	3	CRN
5/31/94	18	5.55	0.20	12	CRN	10/27/94	89	5.54	0.06	3	CRN
6/2/94	19	5.71	0.19	7	CRN	10/31/94	90	5.55	0.08	9	CRN
6/10/94	20	5.75	0.05	4	CRN	11/3/94	91	5.71	0.06	3	BY
6/15/94	21	5.65	0.11	4	CRN	11/6/94	92	5.66	0.13	6	MJK
6/17/94	22	5.74	0.07	4	CRN	11/7/94	93	5.77	0.10	3	AKW
6/18/94	23	5.86	0.24	5	SRB	11/10/94	94	5.39	0.06	9	MJK
6/20/94	24	5.68	0.05	6	CRN	11/14/94	95	5.66	0.07	6	MJK
6/22/94	25	5.71	0.07	5	SRB	11/15/94	96	5.69	0.16	6	WP
6/23/94	26	5.86	0.08	5	BY	11/17/94	97	5.75	0.03	3	KJE
6/24/94	27	5.85	0.08	4	SRB	11/18/94	98	5.75	0.14	8	AKW
6/27/94	28	5.90	0.13	5	SRB	11/22/94	99	5.60	0.09	6	MJK
6/29/94	29	5.76	0.09	4	SRB	11/27/94	100	5.51	0.12	5	MJK
6/30/94	30	5.71	0.08	3	BY	11/28/94	101	5.49	0.12	6	MJK
7/1/94	31	5.62	0.28	6	SRB	11/29/94	102	5.50	0.12	6	MJK
7/4/94	32	5.74	0.10	5	SRB	12/1/94	103	5.44	0.12	4	KJE
7/6/94	33	5.82	0.07	6	SRB	12/2/94	104	5.44	0.07	5	NEK
7/7/94	34	5.96	0.06	4	SRB	12/4/94	105	5.54	0.05	5	NEK
7/9/94	35	5.71	0.23	11	SRB	12/6/94	106	5.53	0.08	4	WP
7/10/94	36	5.76	0.05	4	SRB	12/8/94	107	5.65	0.11	5	AKW
7/13/94	37	5.66	0.06	5	SRB	12/9/94	108	5.74	0.06	6	NEK
7/15/94	38	5.70	0.10	3	CRN	12/11/94	109	5.64	0.14	5	MJK
7/16/94	39	5.62	0.09	4	SRB	12/12/94	110	5.82	0.04	6	MJK
7/17/94	40	5.71	0.12	4	SRB	12/13/94	111	5.79	0.06	8	MJK
7/19/94	41	5.64	0.04	4	CRN	12/15/94	112	5.76	0.08	5	NEK
7/23/94	42	5.53	0.07	5	SRB	12/19/94	113	5.85	0.17	7	NEK
7/24/94	43	5.41	0.11	6	SRB	12/20/94	114	5.84	0.05	4	NEK
7/27/94	44	5.32	0.16	3	CRN	12/21/94	115	5.67	0.04	5	KJE
7/28/94	45	5.62	0.06	3	SRB	12/22/94	116	5.60	0.17	6	BY
7/29/94	46	5.66	0.13	3	CRN	12/29/94	117	5.51	0.06	4	JWV
7/30/94	47	5.59	0.13	4	SRB	1/5/95	118	5.66	0.12	3	KJE
7/31/94	48	5.65	0.21	4	SRB	1/9/95	119	5.81	0.01	4	KJE
8/2/94	49	5.69	0.06	3	SRB	1/10/95	120	5.78	0.04	5	NEK
8/3/94	50	5.72	0.07	3	CRN	1/11/95	121	5.76	0.06	3	WP
8/4/94	51	6.07	0.22	12	SRB	1/14/95	122	5.76	0.05	9	KJE
8/5/94	52	5.72	0.12	4	CRN	1/16/95	123	5.77	0.11	8	WP
8/7/94	53	6.01	0.16	4	SRB	1/17/95	124	5.76	0.09	5	NEK
8/9/94	54	5.92	0.12	3	SRB	1/18/95	125	5.83	0.03	5	KJE
8/10/94	55	5.89	0.20	19	SRB	1/20/95	126	5.80	0.07	5	WP
8/11/94	56	5.87	0.16	5	CRN	1/21/95	127	5.81	0.04	6	NEK
8/12/94	57	6.12	0.18	5	SRB	1/22/95	128	5.89	0.09	5	WP
8/13/94	58	5.93	0.08	3	SRB	1/25/95	129	5.88	0.05	5	MJK
8/15/94	59	6.07	0.04	4	SRB	1/26/95	130	5.80	0.06	6	MJK
8/17/94	60	5.57	0.10	4	CRN	1/27/95	131	5.80	0.08	4	JME
8/20/94	61	5.83	0.13	4	SRB	1/28/95	132	5.75	0.01	3	JME
8/21/94	62	5.88	0.14	4	SRB	1/29/95	133	5.74	0.02	3	JME
8/22/94	63	5.52	0.09	4	BY	1/30/95	134	5.79	0.05	7	NEK
8/23/94	64	5.85	0.11	4	SRB	1/31/95	135	5.72	0.07	4	MJK
8/24/94	65	6.01	0.12	6	SRB	2/1/95	136	5.77	0.07	5	MJK
8/25/94	66	5.76	0.08	4	CRN	2/3/95	137	5.75	0.05	5	NEK
8/26/94	67	6.05	0.14	5	SRB	2/4/95	138	5.74	0.01	3	KJE
8/29/94	68	5.97	0.12	7	MJK	2/7/95	139	5.76	0.04	5	NEK
8/31/94	69	5.73	0.10	5	CRN	2/8/95	140	5.76	0.08	3	MJK
9/1/94	70	5.75	0.03	6	CRN	2/9/95	141	5.74	0.09	6	MJK
9/3/94	71	6.03	0.12	5	MJK	2/11/95	142	5.77	0.17	4	KJE

APPENDIX A (Continued)

analysis						analysis					
Date	day	Ave.	± 1 SD	n	User	Date	day	Ave.	± 1 SD	n	User
2/12/95	143	5.86	0.10	7	WP	4/6/95	178	5.74	0.04	7	MJK
2/14/95	144	5.72	0.03	5	NEK	4/8/95	179	5.70	0.05	4	KJE
2/15/95	145	5.64	0.09	4	MJK	4/11/95	180	5.73	0.05	6	NEK
2/16/95	146	5.40	0.04	7	MJK	4/12/95	181	5.69	0.09	6	MJK
2/17/95	147	5.77	0.12	7	NEK	4/13/95	182	5.68	0.07	6	MJK
2/18/95	148	5.68	0.05	6	NEK	4/22/95	183	5.69	0.08	5	KJE
2/19/95	149	5.74	0.10	5	WP	4/23/95	184	5.51	0.14	6	WP
2/20/95	150	5.74	0.05	5	NEK	4/24/95	185	5.16	0.14	7	NEK
2/21/95	151	5.72	0.08	5	KJE	4/25/95	186	5.63	0.05	9	MJS
2/22/95	152	5.77	0.07	4	MJK	4/26/95	187	5.66	0.03	4	MJK
2/23/95	153	5.65	0.08	6	MJK	4/27/95	188	5.70	0.12	9	MJK
2/24/95	154	5.71	0.04	5	NEK	4/28/95	189	5.74	0.07	4	MJK
2/27/95	155	5.59	0.11	6	MJK	4/29/95	190	5.74	0.08	7	NEK
3/1/95	156	6.14	0.07	5	MJK	4/30/95	191	5.74	0.10	4	WP
3/2/95	157	5.80	0.13	7	NEK	5/1/95	192	6.02	0.04	4	MJK
3/5/95	158	5.73	0.08	4	WP	5/2/95	193	5.58	0.02	5	NEK
3/7/95	159	5.70	0.08	6	NEK	5/4/95	194	5.76	0.08	4	JME
3/8/95	160	5.74	0.08	6	MJK	5/5/95	195	5.77	0.07	3	JME
3/9/95	161	5.60	0.07	6	MJK	5/6/95	196	5.65	0.06	5	MJK
3/11/95	162	5.81	0.03	3	WP	5/7/95	197	5.64	0.02	5	JME
3/12/95	163	5.83	0.05	4	WP	5/8/95	198	5.78	0.05	3	JME
3/13/95	164	5.98	0.02	4	KJE	5/10/95	199	5.78	0.04	5	NEK
3/15/95	165	5.87	0.07	5	NEK	5/12/95	200	5.75	0.07	4	JME
3/17/95	166	5.80	0.09	5	KJE	5/13/95	201	5.70	0.02	3	JME
3/19/95	167	5.90	0.13	5	WP	5/14/95	202	5.76	0.02	3	JME
3/21/95	168	5.82	0.06	5	NEK	5/16/95	203	5.73	0.10	6	MJK
3/22/95	169	5.83	0.07	4	MJK	5/17/95	204	5.76	0.06	5	NEK
3/23/95	170	5.86	0.08	6	MJK	5/18/95	205	5.77	0.08	4	WP
3/24/95	171	5.89	0.04	4	NEK	5/19/95	206	5.76	0.09	4	WP
3/26/95	172	5.82	0.06	4	KJE	5/22/95	207	5.75	0.16	8	WP
3/27/95	173	5.87	0.03	5	NEK	5/24/95	208	5.80	0.12	5	WP
3/29/95	174	5.85	0.07	5	NEK	5/25/95	209	5.77	0.07	7	NEK
3/30/95	175	5.77	0.06	5	MJK	5/31/95	210	5.77	0.07	7	NEK
4/1/95	176	5.79	0.09	4	KJE	6/3/95	211	5.84	0.07	5	NEK
4/5/95	177	5.76	0.07	10	MJK	6/4/95	212	5.75	0.05	6	NEK

Average = 5.73 \pm 0.15

n = 212

Total # of analyses = 1081