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In situ oxygen isotope analysis with an excimer laser using F₂ and BrF₅ reagents and O₂ gas as analyte

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Abstract—In situ oxygen isotope analysis of silicate minerals has been validated by interlaboratory calibration using an excimer laser (KrF fill gas, 248 nm), F₂ gas fluorinating reagent, and O₂ gas as mass spectrometer analyte. A value of $\delta^{18}\text{O}_{\text{SMOW}} = 5.82\text{‰} (\pm 0.03, 4 \text{ analyses})$ was obtained for almandine UWG-2 compared to a recommended value of 5.8‰ (Valley et al., 1995). The interhalogen BrF₅ was tested by comparing in situ analyses made alternatively with either BrF₅ or F₂ gas on crystals of almandine, epidote, forsterite, tourmaline, and zircon. Results for different pressures of BrF₅ (20 to 40 torr) in the reaction chamber show that $\delta^{18}\text{O}$ values decrease by 1 permil for an increase of 10 torr in BrF₅ pressure. In strong contrast, $\delta^{18}\text{O}$ values measured with purified F₂ gas are precise and accurate over a range of from 15 to 150 torr F₂ gas pressure. Use of F₂ gives higher yields of O₂ than with BrF₅. Values of $\delta^{17}\text{O}$ and $\delta^{18}\text{O}$ measured in situ on a variety of silicates all plot on the terrestrial mass fractionation line, provided that NF₃ contamination is eliminated from the O₂ gas analyte. Copyright © 1997 Elsevier Science Ltd

1. INTRODUCTION

It has been shown that in situ analysis of oxygen isotopes in silicate minerals may be performed successfully with a KrF excimer laser, F₂ reagent, and CO₂ gas analyte. Wiechert and Hoefs (1995) demonstrated precision and accuracy of 0.1 to 0.3 per mil $\delta^{18}\text{O}$ in analyses of enstatite, diopside, olivine, and spinel. The spatial resolution of their in situ analyses was sub-millimeter; ablation craters were several hundred microns in diameter. A lower limit on minimum crater size was imposed not by the laser but by the requirement to obtain sufficient amounts of analyte gas for the mass spectrometer. Approximately 1 micromole of CO₂ was required to maintain inlet pressure high enough to avoid the transition from non-fractionating to fractionating flow in the conventional dual capillary inlet system (McKinney et al., 1950) used in their experiments. Difficulties with isotope fractionation were encountered by Wiechert and Hoefs (1995) in converting small amounts of O₂ to CO₂ for mass spectrometer analysis. Successful analyses were achieved using F₂ gas as fluorinating agent but results with ClF₃ were unsatisfactory (Wiechert and Hoefs, 1993). The pioneering work of Wiechert and Hoefs (1995) establishes the validity of in situ analyses of oxygen isotopes with excimer lasers and merits respect.

We have designed, built, and tested a KrF excimer laser system for in situ analysis of oxygen isotopes that alleviates the difficulties encountered by Wiechert and Hoefs (1995) in converting O₂ to CO₂. In the new system, oxygen gas is analyzed directly in the mass spectrometer, thus avoiding possible isotope fractionation during the conversion of O₂ to CO₂. The use of BrF₅ as fluorinating reagent has been tested by direct comparison with F₂ gas.

The primary goal of the present study is the validation of

in situ analysis of oxygen isotopes with a KrF excimer laser and O₂ gas analyte. Towards this end, a conventional mass spectrometer inlet was used: e.g., adjustable volume reservoir and microvolume with molecular sieve 5A to cryofocus O₂ gas. Gas samples were sufficiently large so that the effects of blank and adsorption were minimized. At the beginning of the study, oxygen yields were in the range of 20 to 30 micromoles. Large samples were required because the UV laser system was not connected on-line to the mass spectrometer. The O₂ was transferred to the mass spectrometer frozen on molecular sieve 5A in sample tubes and expanded into a variable volume reservoir. Since February, 1996, however, the UV laser system has been connected directly to the changeover valve block of the mass spectrometer (Fig. 1), and samples are cryofocused in a microvolume with molecular sieve 5A. With the new inlet, oxygen yields required for accurate analysis have been reduced to 3 micromoles. In most cases, however, gas samples of 6 to 8 micromoles have been analyzed. The data presented in Table 1 give a continuous chain of analytical validation starting with milligram quantities and ending with ablation craters equivalent to mineral weights of tenths of a milligram.

2. INSTRUMENTATION

The laser used in the experiments is a Lambda-Physik, Inc. COMPex model 110 (Fig. 1). The laser is filled with a Kr-F₂-Ne gas mixture that lases at 248 nanometers (nm), providing a maximum of 30 watts average power, up to 400 millijoules of single pulse energy, and a maximum repetition rate of 100 shots per second. The light beam emerging from the output coupler is rectangular in cross-section, measuring 1 × 2 cm. The optical system for delivering the laser beam to the sample surface consists of turning mirrors coated for

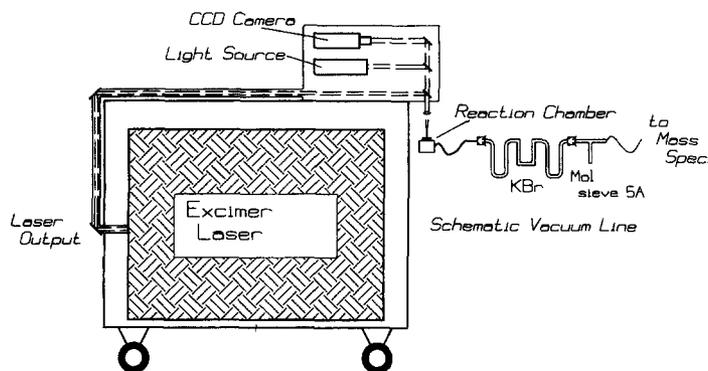


Fig. 1. Diagram of Excimer Laser Oxygen Isotope Microprobe.

maximum reflectivity at 248 nm, a dielectric mirror that reflects 98% of the ultra violet (UV) light at 248 nm but transmits visible light, and a choice of turret-mounted 50 mm or 100 mm UV-grade quartz plano-convex lenses to focus energy on the sample. A video microscope images the sample through the dielectric mirror; illumination is provided by a fiber optic light source, condenser lens, and beam splitter. Pulse energies are measured by a photo-diode mounted behind the dielectric mirror. The photo-diode was calibrated with a Molelectron J-43MAX pyroelectric detector temporarily mounted in place of the reaction chamber. Laser spot size is controlled by substituting aluminum metal apertures of different diameter in a slotted holder mounted coaxial with the beam and near the output coupler. Spot size can be changed from 800 by 600 microns (no aperture) to 50 by 30 microns (1mm aperture).

3. VACUUM EXTRACTION LINE

The reaction chamber is in the shape of a cylinder, 4 cm high and 6.5 cm in diameter, open on its top side and cut from a single block of 316 alloy stainless steel. The chamber is topped with a polished MgF_2 window, transparent to both

laser and visible light, and vacuum sealed with a Kalrez O-ring. The reaction chamber is connected to the vacuum extraction line by a 321 alloy stainless steel flexible metal bellows with VCR alloy 316 stainless steel fittings. The reaction chamber is mounted on motorized X-Y stages supported by a precision lab jack. Aiming and focusing the laser on the sample is accomplished by moving the reaction chamber under computer control. Stage movement and laser firing are both computer controlled, making it possible to ablate preselected single points, line traverses, circles, rectangles, and arbitrary convex polygons. The extraction line is built from 0.25 inch nickel metal tubing, Swagelok stainless steel fittings, and Nupro stainless steel bellows-sealed high vacuum valves. The vacuum line consists of two liquid nitrogen cold traps guarding a U-trap filled with broken chips of IR-grade KBr and a cold finger with granules of molecular sieve 5A. The vacuum pumping system is an Edwards all-steel diffusion pump (aluminum jet stack replaced by stainless steel parts) backed by an Alcatel corrosion resistant rotary vane pump, both charged with appropriate grades of Fomblin. The extraction line is connected directly to the changeover block of a Finnigan-MAT 252 mass spectrometer by a 1 m crimped stainless steel capillary. The mass

Table 1. $\delta^{18}\text{O}_{\text{SMOW}}$.

| | Geophysical laboratory | | | | Other laboratories | Yields ³ | | |
|---------------------------|-----------------------------|-----------------|-------------------------------------|----------------|----------------------------|-----------------------|-------------------------|----------------|
| | Excimer laser (in situ) | | CO ₂ laser (whole grain) | | | $\delta^{18}\text{O}$ | Excimer laser (in situ) | |
| | BrF ₅ | F ₂ | BrF ₅ | F ₂ | | | BrF ₅ | F ₂ |
| Almandine UWG-2 | 6.11 (0.12, 6) ⁴ | 5.82 (0.03, 4) | | | 5.8 ¹ | 1.4 (0.1, 3) | 1.7 (0.2, 4) | |
| Almandine USNM 107144 | 6.40 (0.06, 7) | 6.02 (0.14, 15) | 5.80 (0.23, 6) | 5.94 (0.17, 5) | | 1.4 (0.1, 6) | 1.9 (0.2, 7) | |
| Zircon USNM R12984 | 6.23 (0.3, 14) | 5.33 (0.18, 3) | 5.34 (0.22, 4) | | 5.04 and 5.31 ² | | | |
| Epidote USNM 126360 | 6.49 (0.36, 7) | 5.87 (0.11, 3) | 5.88 (0.24, 4) | | | 1.6 (0.2, 5) | 2.7 (0.3, 3) | |
| Forsterite USNM 136718 | 5.74 (0.13, 7) | 5.23 (0.15, 11) | 4.99 (± 0.18 , 7) | | | 1.6 (0.1, 4) | 2.6 (0.1, 4) | |
| Forsterite Harvard 131265 | 5.63 (0.11, 8) | 5.19 (0.08, 4) | 5.14 (± 0.2 , 4) | | | 1.6 (0.1, 6) | 2.7 (0.1, 4) | |
| Tourmaline USNM R11871-1 | 9.66 (0.16, 5) | 9.16 (0.07, 9) | | 9.08 (0.01, 3) | | 1.9 (0.1, 5) | | |

¹ Valley et al. (1995).

² J. W. Valley, pers. commun.; see Valley et al. (1994).

³ Yield units are nanomoles (10^{-9} mol) of O₂ per laser shot. Data are reported for crater sizes of 600×800 microns in plan and fluence of 12 to 15 Joules/cm².

⁴ First number in parenthesis is standard deviation, second number is number of measurements.

spectrometer is equipped with three collectors for simultaneous measurement of the ion beams at m/e 32 ($^{16}\text{O} \cdot ^{16}\text{O}$), 33 ($^{17}\text{O} \cdot ^{16}\text{O}$), and 34 ($^{18}\text{O} \cdot ^{16}\text{O}$).

4. REAGENTS

Fluorine is the reagent of choice for UV laser fluorination (Wiechert and Hoefs, 1995). It is the most transparent of commonly used fluorinating reagents in the UV region (Fig. 2). Renowned chemical aggressiveness assures rapid and complete liberation of oxygen. Fluorine is, however, a hazardous permanent gas. An additional disadvantage of F_2 is that the commercial product is contaminated with 1 to 2% of O_2 and N_2 . Commercial F_2 may be purified satisfactorily (Asprey, 1976), but the procedure is time consuming. For these reasons, it was decided to test BrF_5 as an alternative to F_2 .

Bromine pentafluoride is widely used for fluorinating refractory minerals in externally heated reaction vessels (Clayton and Mayeda, 1963). It has also been used in laser fluorination studies with a CO_2 laser (Sharp, 1990). The reagent is somewhat less hazardous than F_2 in the sense that it has lower vapor pressure, but it is almost equally aggressive chemically. Reference to Fig. 2 shows that BrF_5 is more strongly absorbing than F_2 at 248 nm by a factor of nearly 10.

5. PROCEDURE

Samples are prepared for in situ analysis by cutting and polishing chips of rock or mineral as thin as possible and 1 by 2 cm in size. No epoxy or other insoluble glues should be used, nor should oil-lubricated sawing or polishing equipment. The chips are heated and evacuated in a vacuum oven for hours or days to remove moisture. Once cleaned, samples should not be touched as finger oils contribute CF_4 and NF_3 . Reaction chambers are cleaned by ultrasonication in deionized distilled water. Samples are loaded in the chamber and the complete assembly is vacuum heated overnight before

attaching to the vacuum extraction line. After loading, pre-fluorination treatments are repeated until blank levels are acceptably low. For an analysis, F_2 gas is added at a pressure of 30 torr. Laser operating conditions are adjusted to deliver a fluence of 12 to 15 joules per cm^2 at the sample surface. An ablation crater measuring 800 by 600 microns requires pulse energies at the sample surface of 60 millijoules. Note that because of the high power of an excimer laser, large craters may be cut without moving either the sample or the laser beam. The laser is fired 2,500 to 5,000 shots at 20 shots per second to accumulate enough oxygen (3×10^{-6} mol) for analysis in the cold finger, crimped capillary inlet. Product O_2 gas is separated cryogenically from BrF_5 and BrF_3 with liquid nitrogen cold traps; excess F_2 is eliminated by reaction with KBr heated to 100°C . The cold traps are isolated, heated, and refrozen during each transfer into the cold finger in order to free trapped O_2 . Use of granules of molecular sieve 5A in the cold finger not only makes it possible to quantitatively transfer O_2 into the mass spectrometer inlet but also helps to eliminate traces of NF_3 that interfere with the $^{17}\text{O} \cdot ^{16}\text{O}$ ion beam at m/e 33. A typical analysis is completed in 30 min. The general principles of vacuum line design, construction, and operation used in the present study are similar to those described by Taylor and Epstein (1962) and Clayton and Mayeda (1963).

6. RESULTS

6.1. Interlaboratory Calibration and Intralaboratory Comparisons

Intralaboratory calibration for almandine garnet and zircon validates the accuracy of in situ analyses with an excimer laser, F_2 gas reagent, and O_2 gas analyte (Table 1). A value of $\delta^{18}\text{O}_{\text{SMOW}} = 5.82\text{‰}$ (± 0.03 , 4 analyses) was obtained for garnet UWG-2, compared to 5.8‰ recommended by Valley et al. (1995). In situ analysis of zircon gives 5.33‰ (± 0.18 , 3 analyses), compared to values of 5.04 and 5.31‰ measured on whole grains by J. W. Valley with a CO_2 laser and BrF_5 reagent (J. W. Valley pers. commun., 1997; cf. Valley et al., 1994).

Intralaboratory comparisons between an excimer and a CO_2 laser and between different reagents provide additional confirmation of in situ analyses. (Table 1). For almandine (USNM 107144) and tourmaline there is agreement within 0.2‰ for whole grain and in situ analyses conducted with CO_2 and excimer lasers, respectively, and using F_2 gas reagent. Results for zircon and epidote using BrF_5 and a CO_2 laser for whole grain and F_2 for in situ analyses agree within 0.1‰. A similar comparison of two samples of San Carlos forsterite agrees within 0.05 and 0.24‰, respectively (Table 1, columns 2 and 3).

6.2. Sources of Analytical Error

The minerals investigated in this study were subjected to analysis by different operators. Arbitrary choices of analytical conditions led to discrepancies of up to several permil in values of $\delta^{18}\text{O}$ obtained by different investigators on aliquots of the same sample. The disparate analyses have been

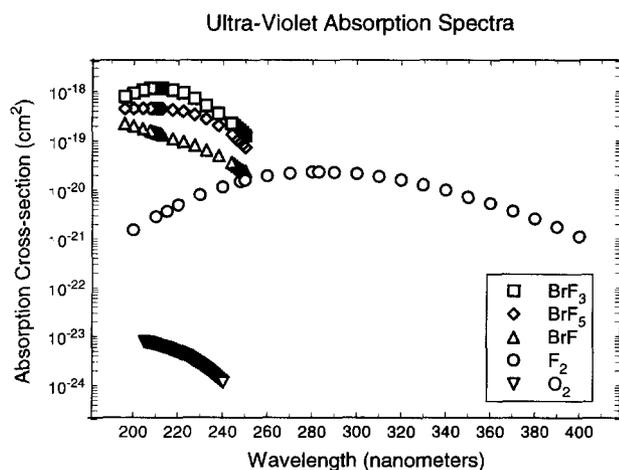


Fig. 2. Absorption spectra of oxygen gas and fluorinating reagents (Buben and Chaikin, 1980; Holland and Lyman, 1987; Yoshino et al., 1992).

used to identify sources of error. Three sources of error are discussed below: crater rim fractionation; use of O₂ gas as analyte; and choice of BrF₅ or F₂ as fluorinating reagent. As discussed below, use of BrF₅ led to the largest errors. Interlaboratory calibrations and intralaboratory comparisons were indispensable in objectively evaluating errors. Once sources of error were identified, steps were taken to develop optimal analytical methods in order to minimize potential errors. The values reported in Table 1 were measured under conditions favoring the highest accuracy and precision.

6.2.1. Crater rim fractionation

Fractionation of oxygen isotopes in crater rims during laser fluorination with infrared lasers has been reported by Sharp (1990, 1992) Elsenheimer and Valley (1992; see their Fig. 5), Chamberlain and Conrad (1993; see their Fig. 3), and Rumble and Hoering (1994; see their Fig. 3). These investigators found chemically and isotopically altered non-stoichiometric annular regions extending up to several hundred microns radially beyond crater rims. The Ultra Violet laser craters of this study, however, show no chemical alteration or oxygen isotope fractionation in crater rims. The chemical analysis profile of Fig. 3 shows that almandine garnet retains its stoichiometry to within a few microns of the crater wall. Semiquantitative chemical composition maps made from gridded electron microprobe data reveal no variations in mineral stoichiometry at the 1 to 100 micron scale either circumferentially or radially to UV laser craters in almandine, andalusite, apatite, forsterite, ilmenite, orthopyroxene, rutile, spessartine, or tourmaline. There is no chemically altered host for fractionated oxygen. It is concluded that crater rim fractionation is not a significant source of error for in situ analysis with a UV laser.

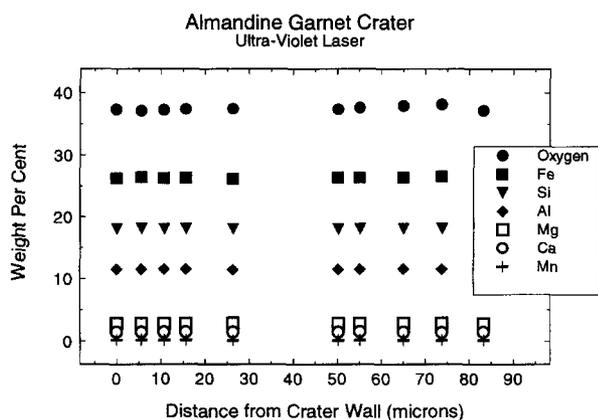


Fig. 3. Chemical composition profile across rim of UV laser crater in almandine garnet. Single crystal of garnet was cut in 3 mm thick slices approximately 1 cm square, then polished with SiC and Al₂O₃ water slurry on polishing lap. Sample was loaded in sample chamber, evacuated, pre-fluorinated, then lased at 248 nm under 30 torr of F₂. Sample surface was prepared for chemical analysis on JEOL-8900 electron microprobe analyzer by polishing away fluoride reaction products.

6.2.2. Tests of O₂ gas analyte

A number of writers have reported on the difficulty of converting small amounts of O₂ to CO₂ for mass spectrometric analysis without fractionation of oxygen isotopes (Mattey and Macpherson, 1993; Wiechert and Hoefs, 1995). Accordingly, we set out to test the use of O₂ gas as analyte in order to avoid the potential for isotope fractionation in converting O₂ to CO₂. The use of O₂ gas analyte in conjunction with Infrared laser fluorination of whole mineral grains was described previously (Rumble and Hoering, 1994). At that time, δ¹⁷O measurements were made by peak-hopping between *m/e* 32 and 33. In the present work, a multi-collector assembly with separate collectors for *m/e* 32, 33, and 34 was used.

Below, we address two potential problems in performing in situ analysis for oxygen isotopes with O₂ gas analyte: (1) Thiemens and Jackson (1987) demonstrated that UV photodissociation of O₂ to produce O₃ induces mass independent fractionation of ¹⁶O/¹⁷O/¹⁸O between O₂ and O₃. Ozone was isolated from O₂ in a liquid nitrogen cold trap as soon as it formed in their experiments. Analysis of separated O₃ and residual O₂ showed that their δ¹⁷O and δ¹⁸O values defined a straight line with slope of 1.0. The specific conditions of the Thiemens-Jackson experiment, i.e., prompt isolation of O₃, are not known to be present in the apparatus described herein. Nevertheless, if ozone were produced, and if it became involved in an irreversible reaction with residual sample, product fluorides, or sample chamber walls, non-mass dependent fractionation might ensue. Thus, it is prudent to evaluate the δ¹⁷O vs. δ¹⁸O data for evidence of mass independent fractionation. (2) Clayton and Mayeda (1983) found the analysis of O₂ for ¹⁷O/¹⁶O ratios to be critically intolerant of even the smallest traces of NF₃ contamination. The compound NF₃ is a common product of fluorination reactions as it is virtually impossible to eliminate atmospheric N₂ or organic nitrogen quantitatively from rock samples. Molecules of NF₃ dissociate under electron bombardment in the ion source of a mass spectrometer yielding NF⁺ ions. The ¹⁴N¹⁹F⁺ ions interfere with measurement of ¹⁷O·¹⁶O⁺ ions at *m/e* 33.

The two potential problems are interrelated in the sense that mass dependent vs. mass independent fractionation cannot be evaluated without scrupulous elimination of NF₃ contamination. Figure 4 gives an immediate sense of the interrelationship. Most of the data points lie along the terrestrial mass fractionation line. A significant number, however, lie above the line, indicating NF₃ contamination. Note that the data do not define a slope of 1.0, as was observed by Thiemens and Jackson (1987).

Clayton and Mayeda (1983) recommended purifying oxygen by trapping NF₃ on molecular sieve 13X, frozen in a pentane-liquid nitrogen slush. It has been found, however, that exposure of analyte gas to molecular sieve 5A heated to 80°C slowly eliminates NF₃ contamination. The efficacy of the purification is shown in Fig. 5, where it may be seen that raw δ¹⁷O achieves stationary values after 30 min. exposure to mol sieve 5A. A correlation between δ¹⁷O_{S.M.O.W.} and NF₃ abundance is shown in Fig. 6. Detailed examination of

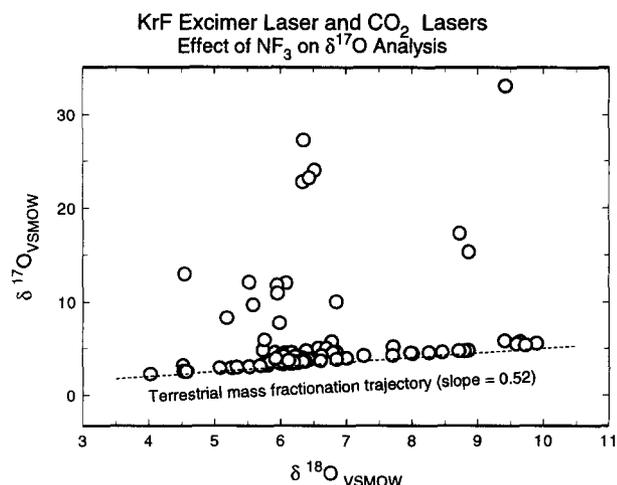


Fig. 4. Plot of $\delta^{18}\text{O}$ vs. $\delta^{17}\text{O}$ analyses for a variety of silicate minerals. Data points lying above dashed line show effects of NF_3 contamination on $\delta^{17}\text{O}$ analyses.

the outgassing of molecular sieve 5A shows that, upon thawing from liquid nitrogen temperature, NF_3 is initially driven off the sieve by escaping O_2 and CF_4 but subsequently re-sorbs.

It is concluded that use of an excimer laser at 248 nm to ablate a sample immersed in 30 torr of F_2 does not lead to mass independent fractionation of oxygen isotopes.

An additional source of error is that the isotopic composition of O_2 released from the sieve is dependent on outgassing temperature. An increase of 0.1‰ $\delta^{18}\text{O}$ has been observed for an increase of 25°C. The results reported in Table 1 were obtained at an outgassing temperature of 80°C.

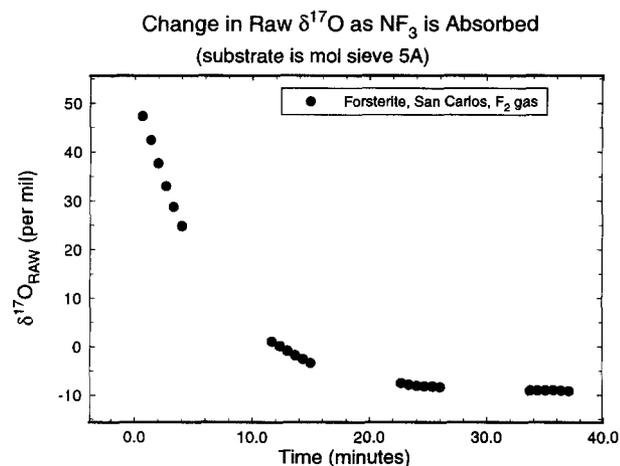


Fig. 5. Measured change in $\delta^{17}\text{O}$ (raw) with time as NF_3 is absorbed on molecular sieve 5A heated to 80°C. Plotted data obtained by repeated analysis of same gas sample. Each data point gives a single comparison (e.g., standard-sample-standard) between standard and sample gas. Values of $\delta^{17}\text{O}$ (raw) reported in relation to standard gas, not VSMOW.

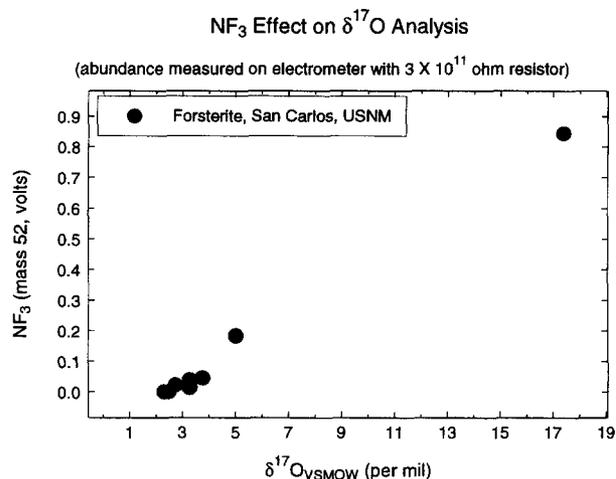


Fig. 6. Effect of increasing NF_3 abundance on $\delta^{17}\text{O}_{\text{VSMOW}}$ value. Abundance of NF_3 measured as voltage of NF_2^+ (m/e 52) on electrometer with 3×10^{11} ohm resistor.

6.2.3. Fluorinating Reagents: F_2 versus BrF_5

Comparison of the first two columns of Table 1 shows that in situ analyses with a UV laser using BrF_5 are less precise and higher by 0.3 to 1.0‰ than measurements with F_2 . Inasmuch as the F_2 results are validated by interlaboratory comparisons, it is concluded that F_2 is the preferred reagent for in situ analysis. Analysis of the BrF_5 data shows that $\delta^{18}\text{O}$ values are dependent on BrF_5 pressure with $\delta^{18}\text{O}$ decreasing 1‰ for an increase in pressure of 10 torr. The pressure that yields the most accurate results in our system is 30 torr of BrF_5 . In the case of F_2 , however, no pressure effect on $\delta^{18}\text{O}$ values has been seen in the range 15 to 150 torr F_2 .

An additional disadvantage of using BrF_5 rather than F_2 gas is illustrated in the last two columns of Table 1. Yields of O_2 gas are systematically lower when using BrF_5 rather than F_2 as fluorinating reagent for in situ laser fluorination at 248 nm. Reference to the absorption cross-sections presented in Fig. 1 and application of the Beer-Lambert law explains the discrepancy in yields, at least in part. The intensity ratio of 248 nm light transmitted through F_2 vs. BrF_5 increases from 1.16 at 20 torr to 1.24 at 30 torr to 2.0 at 100 torr reagent pressure (3 cm path length). Thus, laser fluence at the sample surface is 20% greater when F_2 is used at the pressures typical of these measurements.

7. CONCLUSION

The routine use of UV lasers for in situ oxygen isotope analysis of silicate minerals at a spatial resolution of 0.8 mm is now established. Note, however, that minerals such as quartz, transparent to 248 nm light, cannot be analyzed with a KrF laser. The ArF laser (193 nm) must be used instead (U. Wiechert, pers. commun., 1997). Crater rim fractionation is not a significant source of error. The UV light from the laser does not introduce mass independent fractionation effects in the analysis of $^{17}\text{O}/^{16}\text{O}$ and $^{18}\text{O}/^{16}\text{O}$. It is strongly recom-

mended that F₂ gas be chosen as fluorinating reagent (cf. Wiechert and Hoefs, 1993). Efforts to reduce sample size are continuing with the goal of achieving crater sizes of 50 microns with an accuracy and precision of 0.2%.

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