

Initial results with a UV laser based microanalytical preparation technique for *in-situ* determination of oxygen isotope ratios of silicates and oxides

U. Wiechert
J. Hoefs

Geochemisches Institut der Universität Göttingen,
Goldschmidtstr. 1, 37077 Göttingen, Germany.

Introduction

The new laser ablation technique for oxygen isotope analyses (e.g. Sharp, 1990) has two major advantages relative to the conventional technique: it allows the analyses of Mg-rich minerals being resistant in the conventional technique and maybe even more important it opens the possibility to measure isotope profiles in single minerals. One of the main disadvantages of laser techniques is the generation of large melt zones during *in-situ* ablation. These zones may cause large isotope fractionations (Crowe *et al.*, 1990) limiting the spatial resolution to a few hundred microns. Due to the high absorption rate of most minerals for UV radiation our UV laser based system allows much smaller ablation structure down to few microns.

Principles and sample preparation

Polished sample slaps or thick sections were used for laser preparation. Ablation is performed with a LEXTRA 200 excimer laser (Fa. Lambda Physik) operating alternatively with KrF, ArF or fluorine. Most experiments were done at 248 nm (KrF) and energy densities above 5 J/cm². Ablation structures were formed by depicting a mask on the

sample surface through the MgF₂ window of the sample chamber. During ablation the sample can be observed remotely on a video monitor. Our lens system allows ablation of sharply formed pits with diameters down to 10µm, but minimum sample size is given by the detection limit of our dynamic mass spectrometer (~1µmol CO₂). Positioning of the laser spot will be performed by flying optics. The latter allows a very close connection of the sample chamber and gas preparation line.

Sample preparation takes place in a 137 cm³ large stainless steel chamber filled with 10 mbar pure fluorine. The principle of the UV laser based silicate and oxide analysis is similar to the fluorination technique described by Baertschi and Silverman (1951). Metal atoms or ions generated by laser vaporisation react during plasma condensation with fluorine. Structurally bound oxygen is released as molecular oxygen. Beside oxygen the gas mixture contains mainly fluorine and small amounts of SiF₄. Fluorine and SiF₄ must be removed and oxygen is converted to CO₂ for measurement in the mass spectrometer (MAT 251). SiF₄ can easily frozen out in a N₂-trap, whereas fluorine must be completely reacted with KCl at 150°C. The latter reaction produces chlorine, which is frozen out into another N₂-trap. The residual gas is pure oxygen, which must be converted with carbon to CO₂ for oxygen isotope analysis.

Isotope fractionation effects associated with oxygen conversion

Conversion of oxygen is the most sensitive part of the gas handling system. Conventionally oxygen is reacted on a hot graphite rod, but this is problematical for small sample sizes (Mattey and Macpherson, 1993). Fig. 1 shows oxygen isotope data for a single obsidian sample from Iceland. The first analysis is more than 6‰ heavier than the conventionally prepared sample (assumed to represent the correct value), but later prepared samples shift continuously until the conventional determined value is reached.

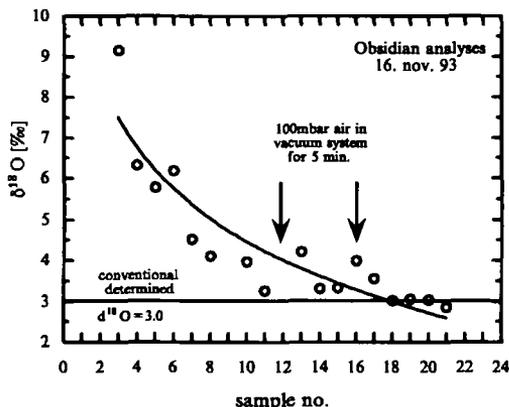


FIG. 1. Obsidian analyses prepared with graphite.

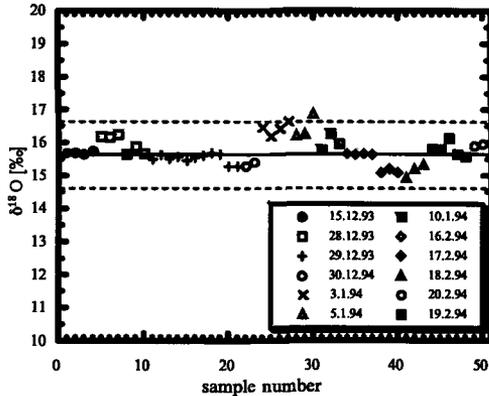


FIG. 2. $\delta^{18}\text{O}$ values of oxygen gas used as standard for accuracy correction of sample analyses. All oxygen samples were converted to CO_2 with diamonds. Conventional determined $\delta^{18}\text{O} = 15.7$; sample sizes 1–3 μmol CO_2 .

Similar shifts have been found for a standard oxygen gas being introduced into the sample chamber. We presume that deviations from expected values are caused by a memory effect of the graphite rod, which might have been produced by oxygen bound at the graphite surface. The formation of CO during combustion as argued by Matthey and Macpherson (1993) seems to be only of minor importance in our system. To reduce the memory effect we experimented with diamonds for oxygen conversion to CO_2 , because diamonds have much smaller surfaces than graphite. As can be seen from fig. 2 most of the oxygen samples plot close to the conventional determined value. Only one analysis out of 50 deviates more than 1‰ from the expected value. The largest negative deviations result from extremely high preparation temperatures, whereas large positive deviations result from a small leak, or are connected with long preparation times, reflecting high blanks.

For constant preparation conditions the precision of oxygen conversion to CO_2 is better than ± 0.2 for oxygen amounts between 1 to 3 μmol . Accuracy is much lower and must be corrected for sample analyses with a standard oxygen gas. For most analyses the accuracy should be better than ± 0.5 ‰ $\delta^{18}\text{O}$.

Results for minerals

To check the precision of our UV laser line one of

TABLE 1. Laser oxygen isotope $\delta^{18}\text{O}$ values of 'homogeneous' minerals

	n	average (‰)	std ($\pm 1\sigma$)	CO_2 (μmol)	ref. value (‰)
eclogite:					
Gt	7	6.07	± 0.46	≈ 1.5	5.9
Omph	4	6.87	± 0.12	≈ 1.5	7.1
Omph/Gt	4	6.66	± 0.27	≈ 1.5	mixture
peridotite:					
Cpx	6	5.87	± 0.15	≈ 1.0	5.8
Ol	4	5.18	± 0.07	≈ 1.0	5.2 ?
Ol/Cpx	3	5.41	± 0.04	≈ 1.0	mixture

the biggest problems is to find minerals homogeneous in composition. We started with mantle rocks assuming that their minerals are homogeneous in oxygen isotope composition. So far, two samples have fulfilled this conditions: one eclogite from Oberkotzau, Bavaria and one spinel peridotite from Balmuccia, Northern Italy (Table 1). Especially pyroxenes and olivines show standard errors comparable with the precision determined for the gas handling system indicating that UV laser vaporisation does not fractionate the original oxygen isotope composition. The higher error for garnet is caused by analyses of the garnet rims, which are systematically heavier than the cores. Thus the UV laser is a valuable tool for oxygen isotope microanalysis, but we have done only few analyses on homogeneous minerals. To constrain the possibilities of a UV laser based microprobe for isotope analysis much more work on homogeneous material and a mass spectrometer with a detection limit in the subnanomole range is necessary.

References

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