

IN SITU MICROANALYSIS OF OXYGEN ISOTOPES USING ONLINE UV LASER FLUORINATION.

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Oxygen isotopic analysis of terrestrial samples yields information on paleothermometry, water rock interaction and sample provenance. Similar information has been gleaned about meteoritic parent bodies from the analysis of extraterrestrial materials. Moreover interactions between the solids, liquids and gases in the nebula left their isotopic imprint upon the oxygen isotopic compositions of meteorites and their constituent parts. To better understand some of these effects requires high precision, high spatial resolution analysis.

Infrared lasers have been widely used for the analysis of mineral separates [4] or small samples [5] but the precision of *in situ* measurements are compromised by partial reaction due to a thermal aureole around the laser pit.

The use of a UV laser avoids the differential heating problem as the UV light interacts with the Si-O bond causing cleavage rather than heating. This produces a plasma which reacts with fluorine gas to produce fluorides and O₂.

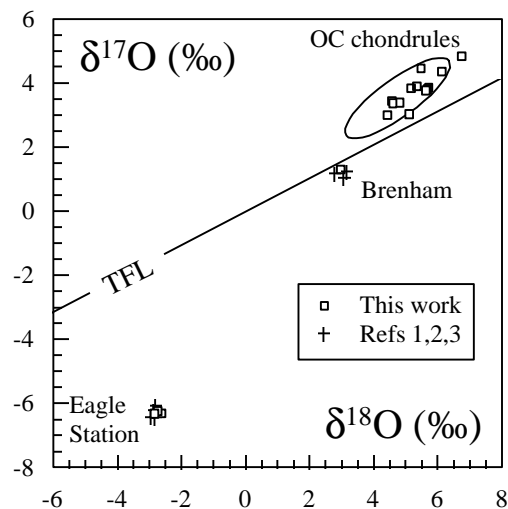
We have used a KrF excimer laser which gives light at 248nm at a fluence of 10-30mJ cm⁻² *per* pulse. The diameter of the incident beam is regulated by the insertion of stops into the beam path.

Fluorine gas is used as the preferred reagent as Br-F compounds absorb at UV wavelengths leading to low yields and isotopic fractionation.

Once reaction is complete (typically 1000-3000 laser shots) the gas is cleaned in the conventional fashion (*i.e.* excess fluorine is removed by reaction with KBr, with the resultant bromine separated from O₂ cryogenically). The purified O₂ is then transferred cryogenically onto a 5A molecular sieve in the mass spectrometer inlet. Heating of the molecular sieve then enables the oxygen into the mass spectrometer. Mass scans for the presence of hydrocarbons and NF₃ (which breaks down to NF, at mass 33, thereby interfering with ¹⁷O¹⁶O).

This apparatus has been used for the analysis of terrestrial samples [6], and we are now applying this method to extraterrestrial samples. The figure shows results of four *in situ* olivine

analyses of Eagle Station and two Brenham olivine separates. The precision and accuracy of the technique is better than 0.15‰ for both δ¹⁷O and δ¹⁸O (see also Ash *et al.*, this volume).



This technique offers several advantages over other methods of oxygen isotope analysis. UV laser fluorination allows the *in situ* analysis of oxygen isotopes to a precision an order of magnitude better than that of the ion microprobe, although the latter offers advantages in spatial resolution. The laser probe can also analyse polyminerallic samples as, unlike the ion probe, matrix effects have not been observed.

At present the minimum sample size is determined by the gas pressure required to maintain capillary flow into the mass spectrometer. This is approximately 1μmol which equates to a sample spot of *ca.* 200μm.

We envisage continued development of this instrument to enable the *in situ*, high precision analysis of oxygen isotopes at the nmol level, corresponding to a laser spot size of *ca.* 50μm.

References: [1] Clayton & Mayeda (1978) *EPSL* **40** 168. [2] Clayton *et al.* (1991) *GCA* **55**, 2317. [3] Clayton *et al.*, (1996) *GCA* **60** 1999. [4] Sharp (1992) *Chem Geol.* **101**, 3. [5] Bridges *et al.* (1997) *L.P.S.C.* **XXVIII** 155. [6] Rumble *et al.* *GCA* submitted.