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Application note 011

$\delta^{18}O$ analysis of diatom silica via laser ablation -IRMS and associated methods for removing exchangeable oxygen

Oxygen in silica that forms the skeletons of oceanic organisms takes a value of $\delta^{18}O$ that depends on the ocean temperature. When an organism dies and its skeleton is buried in the ocean floor, it preserves the value for later analysis. Hence the $\delta^{18}O$ in diatom silica found in deep-sea cores is a surrogate for past ocean temperature. A method for accurately determining $\delta^{18}O$ via laser-fluorination IRMS is reported

Method

Before the oxygen from the silica can be measured, unwanted OH and H_2O inclusions in the silica were removed (dehydration). This OH and H_2O is loosely bound, and their $\delta^{18}O$ is not related to temperature of formation. Two alternative removal processes were studied, vacuum bead melting and helium flow dehydration. The latter was found to be superior following an analysis of efficiency versus temperature and time of dehydration. In this method, a set of samples on a Ni plate is heated under helium flow to 1100°C, in an oven, for a total of 7 hr. Tests identified the minimum temperature and time for dehydration. Eventual $\delta^{18}O$ results for one sample were within 0.1‰ of those from a standards laboratory

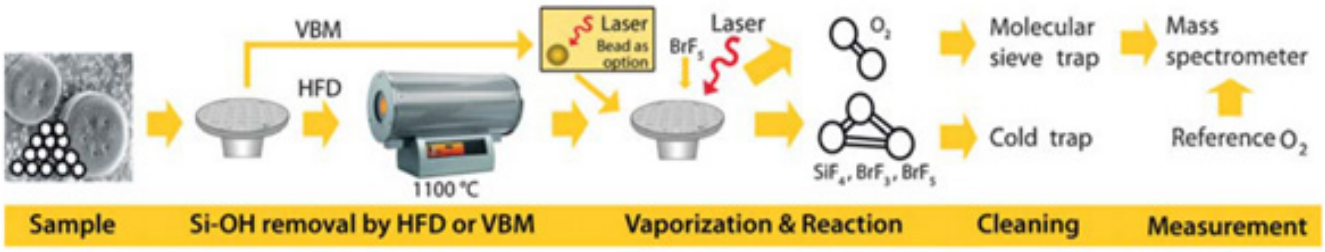

Figure 1: The removal of exchangeable oxygen - two methods were tested (Helium Flow Dehydration = HFD; Vacuum Bead Melting = VBM)

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Following the removal of exchangeable oxygen, the O from the SiO_2 was liberated via laser fluorination, trapped, and sent to a Sercon isotope ratio mass spectrometer. To avoid isotope fractionation of the O_2 captured on the molecular sieve, all the samples were degassed before analysis. As shown in figure 2, during the laser fluorination reaction, the reaction chamber, BrF_5 supplies, cold traps to remove SiF_4 from the O_2 formed by reaction, most valves, main pump and cleaning pump were in a separate room with its own fume hood, with no personnel during a sample run. Personnel were in the control room, together with the molecular sieve to trap the O_2 formed by the reaction, the mass spectrometer, and control of the reaction room's pneumatic valves. In this way, it was ensured that the procedure was as safe as possible. Waste BrF_5 and BrF_3 were trapped by soda-lime and the system cleaned at the end of a working day. The method was also modified to reduce the detection limit, and it was shown that a correction for small sample size could be reliably made.

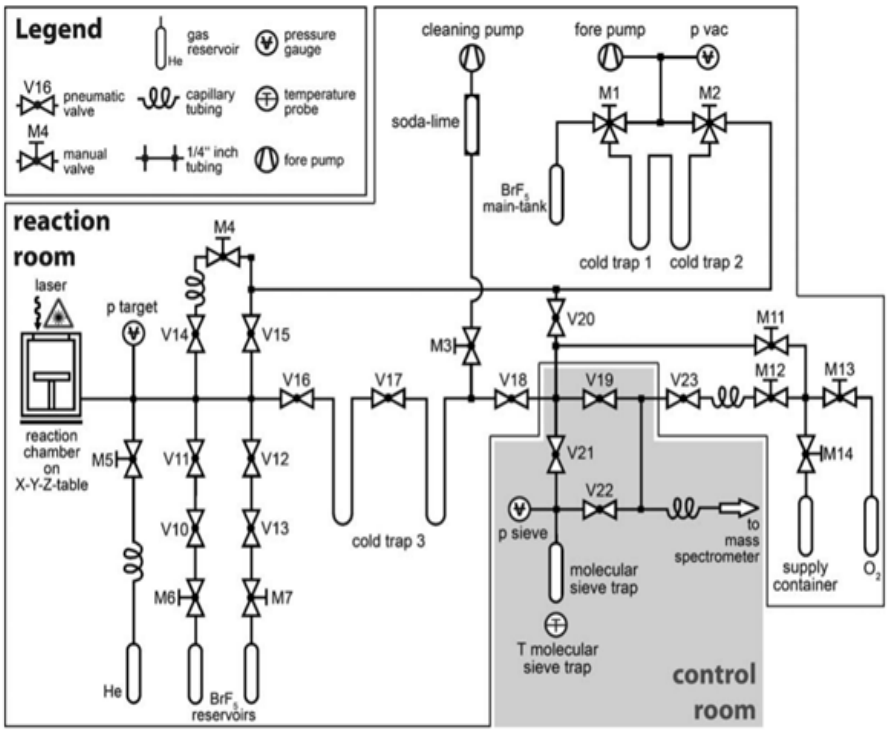

Figure 2: Valve chart of the instrumentation, set up in two different rooms

Results

Tests showed that a sample of size down to 1 mg could be analysed with standard deviation of 0.25‰, and that a correction curve could be found and applied that allowed samples down to 0.3 mg to be analysed to the same standard deviation. 21 samples can be analysed within an 11-hour day.

Sercon are grateful to Bernardt Chapligin for assistance in writing this applications note. More information on the study can be found in Chapligin et al "A high-performance, safer and semi-automated approach for the $\delta^{18}O$ analysis of diatom silica and new methods for removing exchangeable oxygen" Rapid Commun. Mass Spectrom. 24, 2655–2664 (2010).