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A new protocol for oxygen isotope analysis of authigenic and biogenic fine silica grains using laser-extraction technique

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Abstract

We report here a 30 W CO_2 laser heating protocol for analyzing oxygen isotope composition ($\delta^{18}O$ in ‰ vs. V-SMOW) of quartz and amorphous silica grains lower than 50 and 2 μm with a good external precision ($1\sigma < 0.15$‰). This technique is used to investigate $\delta^{18}O$ composition of macro-, micro- and crypto-crystalline quartz cements of quartzite levels occurring in a sand sequence from the South of France (Apt Series), after a physical separation of the quartz cements. $\delta^{18}O$ data obtained from this technique are compared with $\delta^{18}O$ data obtained from in situ ion microprobe analyses. This study also presents promising results on $\delta^{18}O$ analysis of phytoliths obtained with the laser heating protocol ($1\sigma < 0.1$‰).

Keywords: Oxygen isotope analysis; Silica grain; Laser-extraction technique

1. Introduction

Infra-red laser-heated fluorination techniques are now commonly used for analyzing oxygen isotope composition ($\delta^{18}O$) of grains of silicate and oxide minerals (e.g. Sharp et al., 2002) in order to investigate mineral genesis and related paleo-environments (temperature and water source). However, loss of ejecta or necessity to use a binder have prevented the spread of laser-heated fluorination investigations on grain size fraction lower than 30–50 μm (Fouillac and Girard, 1996; Kirschner and Sharp, 1997). This size fraction, enclosing most of authigenic and biogenic silica particles, is still analyzed using the conventional fluorination method, which is more time consuming and involves higher amount of material than laser-heated fluorination techniques.

We report here a 30 W CO_2 laser heating protocol that leads to good external precision of $\delta^{18}O$ analyses of quartz and opal size fractions lower than 50 and 2 μm.

This technique is used to investigate $\delta^{18}O$ composition of macro-, micro- (with a structure made of crystals large enough to be distinguished under the optical microscope) and crypto-crystalline quartz (with a structure made of crystals too small to be distinguished under optical microscope). These quartz are physically separated (Alexandre et al., 2004) from cements of quartzite levels occurring in a sand sequence from the South of France (Apt Series) (Basile-Doelsch et al., 2005). $\delta^{18}O$ data obtained from this technique are compared with $\delta^{18}O$ data obtained from in situ ion microprobe analyses (SIMS, CRPG, Nancy, France; external reproductibility of ±0.3‰).

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Investigating $\delta^{18}O$ of biogenic silica particles from soils, buried soils and continental sediments also give indications on terrestrial water cycle and temperature. Laser heating of biogenic silica particles has never been reported up to now. This study also presents first results on laser heating and $\delta^{18}O$ analysis of phytoliths, which contain exchangeable oxygen that makes necessary an equilibration procedure with water of known isotopic composition (Labeyrie and Juillet, 1982), prior to oxygen extraction. $\delta^{18}O$ is expressed in ‰ vs. V-SMOW.

2. Results

A new laser heating protocol for analyzing $\delta^{18}O$ of silica powders <50 and <2 μm is presented below. Molecular O_2 is extracted from quartz using a laser extraction technique close to the one described by Sharp (1990) and bulk oxygen isotope ratio is measured from O_2 gas using a ThermoQuest Finnigan Delta Plus mass spectrometer at CEREGE (Aix en Provence, France). A Merchanteck 30 W CO_2 IR laser is used. Thirty-three samples of 1.5 mg are loaded in a nickel sample holder, dried at 105 °C for 1 h and prefluorinated in a vacuum line for 1 h. In an atmosphere of hundred millibars of BrF_5, samples are preheated with a 0.1 W laser beam of 2000 μm of diameter for 20 s. The power of the 2000 μm of diameter laser beam is then increased up to 12–13 W and samples are heated starting at the center and slowly moving the laser beam following concentric circles until a bowl of liquid silica forms. The laser beam is then focused to 1000 μm and then to 200 μm of diameter. Laser emission is stopped when all particles have disappeared. This protocol prevents ejectas. Replicate analyses of the international standard NBS 28 (120–250 μm) give an average of 9.6 ± 0.15‰ vs. V-SMOW. Replicate analyses of a laboratory quartz standard ("Boulangé") of 200/100, 100/50, 50/2 and <2 μm yield an average value of 16.46‰ vs. V-SMOW and an external precision of 0.15‰ ($\pm 1\sigma$; 76 analyses over 12 weeks), without any decreasing or increasing trend of $\delta^{18}O$ averages with decreasing grain size (Fig. 1).

$\delta^{18}O$ data obtained from cements of the quartzite levels from the South of France (Apt Series) using the ion microprobe show two groups of values: 1) Cements from samples S11, S4c and S14b have a similar $\delta^{18}O$ composition averaging 26.45 ± 0.71‰, whatever is the mineralogical phase. They form in upper quartzitic layers. This value is typical of authigenic quartz. 2) Crypto-quartz cements from samples S5b and S13 have similar $\delta^{18}O$ values averaging 31‰. They form in lower quartzitic layers. This value is typical of shallow sea cherts (Sharp et al., 2002).

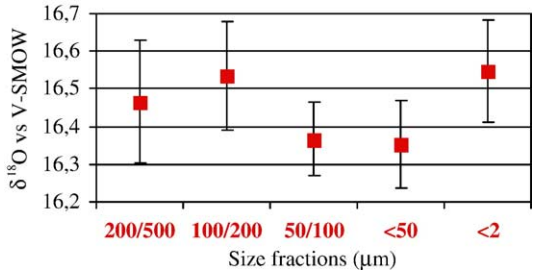

Fig. 1. Average $\delta^{18}O$ values of several size fractions of the quartz lab standard "Boulangé" analyzed using Infra-red laser-heated fluorination technique. Average value: 16.46‰ vs. V-SMOW; Error bars give external precision calculated from replicate analyses: ± 0.15‰ ($\pm 1\sigma$); 76 analyses performed over 12 weeks. No $\delta^{18}O$ trend with size is displayed which makes our laser heating protocol a success.

The comparison of $\delta^{18}O$ data obtained by physical separation associated with the laser-heated fluorination technique, and by in situ ion microprobe analyses of the quartzite is presented in Table 1: 1) $\delta^{18}O$ values measured on the 5–10 μm, 2–5 μm and <2 μm fractions of macro- or crypto-crystalline quartz by laser-fluorination are far lower than $\delta^{18}O$ values measured in situ with the ion microprobe. 2) However, $\delta^{18}O$ values measured on the <2 and <1 μm fraction of micro-crystalline quartz by laser-fluorination are similar to $\delta^{18}O$ values measured in situ with the ion microprobe.

$\delta^{18}O$ analysis of a phytolith lab standard with the laser-heated fluorination technique is presented, for the first time. The lab phytolith standard is extracted from a soil layer made of 95% of grass phytoliths that occurs in volcanic soils of La Reunion (France) (Meunier et al., 1999). External precision (1σ) of the $\delta^{18}O$ measurements including equilibration procedure, laser-heated fluorination and IRMS analysis of O_2 average ± 0.1‰ (30 analyses).

3. Discussion and conclusions

3.1. Reliability of laser extraction for analyzing $\delta^{18}O$ of microscopic fine silica grains

The laser protocol reported here allows the analyses of the $\delta^{18}O$ composition of silica grain fractions lower than 30, 20, 10, 5 and 2 μm with a reproducibility better than 0.15‰, without any decreasing or increasing trend of $\delta^{18}O$ averages with decreasing grain size. Thirty-three analyses of 1.5 mg of fine powder are made over 4 days. Up to now, these size fractions were still processed using conventional analysis which is a lot more time consuming and requires a much higher amount of