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 CO₂ laser heating protocol for analyzing oxygen isotope composition (δ¹⁸O in ‰ vs. V-SMOW) of quartz and amorphous silica grains lower than 50 and 2 μm with a good external precision (1σ<0.15‰). This technique is used to investigate δ¹⁸O 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. δ¹⁸O data obtained from this technique are compared with δ¹⁸O data obtained from in situ ion microprobe analyses. This study also presents promising results on δ¹⁸O analysis of phytoliths obtained with the laser heating protocol (1σ<0.1‰).

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1. Introduction

Infra-red laser-heated fluorination techniques are now commonly used for analyzing oxygen isotope composition (δ¹⁸O) 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 CO₂ laser heating protocol that leads to good external precision of δ¹⁸O analyses of quartz and opal size fractions lower than 50 and 2 μm.

This technique is used to investigate δ¹⁸O 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). δ¹⁸O data obtained from this technique are compared with δ¹⁸O data obtained from in situ ion microprobe analyses (SIMS, CRPG, Nancy, France; external reproducibility of ±0.3‰).
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 $\%e$ vs. V-SMOW.

2. Results

A new laser heating protocol for analyzing $\delta^{18}$O of silica powders <50 and <2 $\mu$m 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 Merchantek 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 $\mu$m of diameter for 20 s. The power of the 2000 $\mu$m 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 $\mu$m and then to 200 $\mu$m of diameter. Laser emission is stopped when all particles have disappeared. This protocol prevents ejections. Replicate analyses of the international standard NBS 28 (120–250 $\mu$m) give an average of 9.6 ± 0.15‰ vs. V-SMOW. Replicate analyses of a laboratory quartz standard (“Boulange”) of 200/100, 100/50, 50/2 and <2 $\mu$m yield an average value of 16.46‰ ± 0.15‰ 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).

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 $\mu$m, 2–5 $\mu$m and <2 $\mu$m 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 $\mu$m 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 (1$\sigma$) 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 $\mu$m 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...
material (10 mg). To overcome these methodological problems brings a significant improvement to the analysis of δ¹⁸O value of microscopic fine silica grains common in chert, quartzite, silicrete, weathering profiles and among biogenic silica particles.

3.2. Efficiency of physical concentration of macro-, micro- and crypto-crystalline quartz size fractions

Comparison of δ¹⁸O data obtained by size fraction separation associated with laser fluorination technique and from in situ microprobe analyses show that:

1) Fractions higher than 2 and 1 μm give under-estimated δ¹⁸O values. This under-estimation indicates a mixture between detrital quartz (δ¹⁸O values ranging from 6.4‰ to 20‰, Garlick and Epstein, 1967; Savin and Epstein, 1970; Clayton et al., 1972; Eslinger et al., 1973; Blatt, 1986; Graham et al., 1996) and authigenic quartz (δ¹⁸O values ranging from 20‰ to 32‰, Savin and Epstein, 1970; Graham et al., 1996; Kolodny and Epstein, 1976; Bird et al., 1992; Abdel-Wahab et al., 1998; Webb and Golding, 1998; Alexandre et al., 2004).

2) When the cement sample contains crypto-quartz only, δ¹⁸O values of the <2 μm fraction is also underestimated. Thus the separation method improperly concentrates crypto-crystalline quartz.

3) When cement samples include micro-crystalline quartz only, δ¹⁸O values of the <2 and 1 μm fractions are similar to δ¹⁸O values obtained for the cement. Thus micro-crystalline quartz appear to be efficiently concentrated in the <2 μm fraction. Finally, the separation technique must be improved or applied to cement made of micro-crystalline quartz only, unless a δ¹⁸O plateau is displayed when analyzing decreasing size fractions.

Implications of the δ¹⁸O results presented above in term of cement genesis and paleo-environmental reconstruction were discussed previously (Alexandre et al., 2005).

3.3. Reliability of laser extraction for investigating δ¹⁸O composition of phytoliths

External precision using the laser-extraction technique for analyzing phytoliths (1σ < 0.1‰) is better than external precision published up to now for diatom and phytolith analyses using the conventional method (e.g. Shahack-Gross et al., 1996; Schmidt et al., 2001; Webb and Longstaffe, 2000: 1σ ± 0.2‰ or 0.3‰). This technique also allows small amounts of material to be analyzed faster than with the conventional method. Thus, the laser-heated fluorination technique is very promising for investigating δ¹⁸O compositions of modern and fos-
sil biogenic siliceous particles such as phytoliths, diatoms or sponge spicules, in a paleo-climatic reconstruction perspective.

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