Oxygen isotope analyses of fine-grained minerals and rocks using the laser-extraction technique

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Abstract

The $\delta^{18}O$ values of fine-grained materials made with the laser-extraction technique are often lower than those obtained conventionally. We propose a simple method to overcome this problem that involves the mixing of samples with a LiF binder and pressing the powder into pellets prior to evacuation and analysis. The presence of the LiF allows for rapid fluorination of all minerals or whole-rock samples to be made, thus eliminating potential problems related to loss of partially reacted ejecta, slow laser heating, and incidental fluorination. Accurate isotope determinations of fine-grained materials can be made with this method.

Keywords: Oxygen isotopes; Stable isotopes; Quartz; Mica; Feldspar; Laser

1. Introduction

Medium- to coarse-grained mineral separates can be easily and accurately analyzed for their oxygen isotope values with laser-extraction systems (e.g., Sharp, 1990). This is not always the case for the analysis of very fine-grained material, where the $\delta^{18}O$ values and oxygen yields obtained with laser-extraction systems are frequently lower than those obtained conventionally (Fouillac and Girard, 1995; Sharp and Kirschner, 1995). Fouillac and Girard (1995) report a systematic, reproducible lowering of
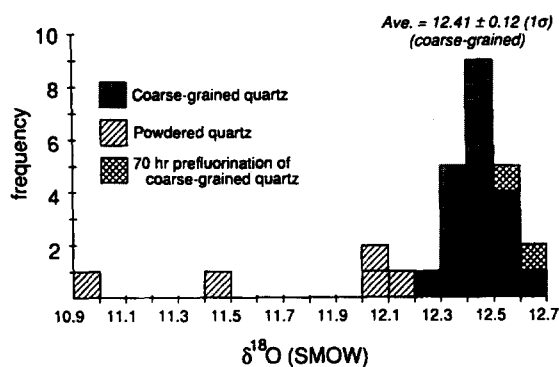

Fig. 1. $\delta^{18}O$ values of coarse-grained and powdered quartz. The $\delta^{18}O$ value of the fine-grained material is up to 1.6‰ lower than its coarse-grained equivalent. Also shown are the $\delta^{18}O$ values of coarse-grained quartz that was prefluorinated (at 0.1 bar BrF_5) for 70 hr, which overlap the normal values. Experiments on K-feldspar gave similar results.

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δ^{18}O values for quartz from +24.5‰ for 250–500-μm-grained size fraction (accepted value +24.6‰), to +24.0‰ for 100–250-μm-size fraction, to +23.6‰ for < 75-μm-size fraction. We have obtained similar results for the analyses of fine-grained quartz samples with the laser-extraction system at the Université de Lausanne (Fig. 1; Table 1). The problem exists for other phases, but is most severe for quartz. We have developed a LiF binder technique that allows for rapid laser heating of fine-

Table 1
δ^{18}O values obtained with the laser-extraction system

Number	Mineral [a]	Grain size [b]	Mixing compound	Comments	Relative yield [c]	δ^{18}O (‰ vs. V-SMOW)
Results of coarse-grained samples:						
S269-2	Quartz 1	granular	none	prefluorinated 10 hr		+12.45
S273-2	Quartz 1	granular	none			+12.58
S273-3	Quartz 1	granular	none			+12.56
S274-2	Quartz 1	granular	none			+12.05
S274-3	Quartz 1	granular	none			+12.24
S278-1	Quartz 1	granular	none			+12.45
S278-2	Quartz 1	granular	none			+12.20
S278-3	Quartz 1	granular	none			+12.45
S279-2	Quartz 1	granular	none			+12.35
S279-4	Quartz 1	granular	none			+12.27
S281-2	Quartz 1	granular	none	no prefluorination		+12.55
S283-2	Quartz 1	granular	none			+12.14
S283-3	Quartz 1	granular	none			+12.46
S288-2	Quartz 1	granular	none			+12.42
S288-3	Quartz 1	granular	none			+12.42
S290-2	Quartz 1	granular	none			+12.52
S290-4	Quartz 1	granular	none			+12.56
S279-11	K-feldspar	granular	none			+12.13
S279-12	K-feldspar	granular	none			+12.14
S288-5	K-feldspar	granular	none			+11.90
S288-6	K-feldspar	granular	none			+12.01
S281-4	Biotite	granular	none	no prefluorination		+5.09
S330-17	Biotite	granular	none			+4.89
Results of clay size powders:						
S278-15	Quartz 1	powdered	none	prefluorinated 20 min	0.77	+12.02
S278-16	Quartz 1	powdered	none	prefluorinated 20 min	0.63	+10.98
S331-12	Quartz 1	powdered	none	prefluorinated 40 min	0.83	+11.40
S331-13	Quartz 1	powdered	none	prefluorinated 60 min	0.90	+12.02
S331-14	Quartz 1	powdered	none	prefluorinated 60 min	0.68	+12.19
S279-13	K-feldspar	powdered	none	prefluorinated 20 min	0.96	+12.35
S279-14	K-feldspar	powdered	none	prefluorinated 20 min	0.93	+12.34
S331-8	K-feldspar	powdered	none	prefluorinated 40 min	0.89	+11.94
S331-9	K-feldspar	powdered	none	prefluorinated 60 min	0.85	+11.91
S331-10	K-feldspar	powdered	none	prefluorinated 60 min	0.91	+12.18
S281-5	Biotite	powdered	none	no prefluorination	0.74	+4.71
S330-18	Biotite	powdered	none	prefluorinated 20 min	0.84	+4.46
S331-4	Biotite	powdered	none	prefluorinated 40 min	0.93	+4.19
S331-5	Biotite	powdered	none	prefluorinated 60 min	0.89	+5.10
S331-6	Biotite	powdered	none	prefluorinated 60 min	0.94	+5.03
S331-7	Biotite	powdered	none	prefluorinated 60 min	0.87	+4.84

Table 1 (continued)

Number	Mineral [a]	Grain size [b]	Mixing compound	Comments	Relative yield [c]	$\delta^{18}O$ (‰ vs. V-SMOW)
Effect of extremely long prefluorination:						
S291-2	Quartz 1	granular	none	prefluorinated 70 hr	0.82	+ 12.69
S291-3	Quartz 1	granular	none	prefluorinated 70 hr	0.95	+ 12.53
S291-5	K-feldspar	granular	none	prefluorinated 70 hr	0.86	+ 12.10
S291-6	K-feldspar	granular	none	prefluorinated 70 hr	0.79	+ 12.09
S291-7	K-feldspar	granular	none	prefluorinated 70 hr	0.92	+ 12.25
S291-9	Biotite	granular	none	prefluorinated 70 hr	0.98	+ 5.11
S291-10	Biotite	granular	none	prefluorinated 70 hr	0.97	+ 4.97
Variations in $\delta^{18}O$ due to reaction time:						
S289-2	Quartz 1	granular	none	reacted 3 min	0.93	+ 12.23
S289-3	Quartz 1	granular	none	reacted 3 (+7) min	0.91	+ 12.45
S289-4	Quartz 1	granular	none	reacted 11 min	1.01	+ 11.78
S289-5	Quartz 1	granular	none	reacted 21 min	0.97	+ 11.73
S289-6	Quartz 1	granular	none	reacted 32 min	1.04	+ 11.40
S289-7	Quartz 1	granular	none	reacted 2 (+27) min	0.98	+ 12.45
Results from LiF:						
S294-2	Quartz 1	powdered	LiF (1:1)		0.95	+ 12.45
S294-3	Quartz 1	powdered	LiF (1:1)		0.81	+ 12.38
S294-4	Quartz 1	powdered	LiF (1:1)		0.90	+ 12.58
S294-6	Quartz 1	powdered	LiF (1:1)		0.87	+ 12.37
S295-2	Quartz 1	powdered	LiF (1:1)		0.80	+ 12.17
S295-3	Quartz 1	powdered	LiF (1:1)		0.88	+ 12.27
S295-4	Quartz 1	powdered	LiF (1:1)		0.89	+ 12.29
S295-5	Quartz 1	powdered	LiF (1:1)		1.00	+ 12.57
S296-2	Quartz 1	powdered	LiF (1:1)		0.98	+ 12.38
S296-3	Quartz 1	powdered	LiF (1:1)		0.98	+ 12.45
S296-4	Quartz 1	powdered	LiF (1:1)		0.87	+ 12.41
S330-5	Quartz 1	powdered	LiF (2:1)		0.91	+ 12.31
S330-6	Quartz 1	powdered	LiF (2:1)		1.04	+ 12.17
S330-7	Quartz 1	powdered	LiF (4:1)		0.89	+ 11.80
S333-2	Quartz-QZ2	powdered	LiF (1:1)		0.90	+ 24.49
S333-6	Quartz-QZ2	powdered	LiF (1:1)		1.04	+ 24.52
S333-8	Quartz-QZ2	powdered	LiF (1:1)		1.07	+ 24.48
S288-11	K-feldspar	powdered	LiF (0.5:1)		0.76	+ 11.91
S288-7	K-feldspar	powdered	LiF (1:1)			+ 11.60
S288-8	K-feldspar	powdered	LiF (1:1)		0.94	+ 11.75

grained materials — with this method accurate $\delta^{18}O$ values are obtained.

2. Mechanisms causing the isotopic shift

There are several potential explanations for the decrease in $\delta^{18}O$ values of fine-grained samples. First, the fine-grained material may partially react in the presence of fluorine at room temperature. Clays, particularly, suffer from partial fluorination (J.R. O'Neil and Z.D. Sharp, unpublished data). If multiple samples of "reactive" minerals are loaded in the same sample chamber, passive fluorination of the unreacted samples may occur, especially as the sample block is heated by the laser. Second, partial reaction of fine-grained material due to particles jumping out of the sample cup during heating might

Table 1 (continued)

Number	Mineral [a]	Grain size [b]	Mixing compound	Comments	Relative yield [c]	$\delta^{18}O$ (‰ vs. V-SMOW)
Results from LiF:						
S288-9	K-feldspar	powdered	LiF (1:1)		0.82	+11.90
S288-10	K-feldspar	powdered	LiF (1:1)		0.85	+11.95
S283-7	K-feldspar	powdered	LiF (2:1)			+11.68
S283-9	K-feldspar	powdered	LiF (2:1)			+11.57
S283-10	K-feldspar	powdered	LiF (4:1)			+11.31
S330-9	K-feldspar	powdered	LiF (4:1)		0.75	+11.63
S330-10	K-feldspar	powdered	LiF (4:1)		0.96	+11.65
S330-11	Biotite	powdered	LiF (1:1)		0.70	+3.91
S330-12	Biotite	powdered	LiF (1:1)		0.99	+4.91
S330-13	Biotite	powdered	LiF (2:1)		0.86	+4.94
S330-14	Biotite	powdered	LiF (2:1)		0.96	+5.03
S330-15	Biotite	powdered	LiF (4:1)		0.92	+4.99
S330-16	Biotite	powdered	LiF (4:1)		0.86	+4.83
S277-1	Whole rock 1	powdered	LiF (1:1)			+8.9
S277-5	Whole rock 1	powdered	LiF (1:1)			+9.2
S275-2	Whole rock 2	powdered	LiF (1:1)			+5.3
S275-6	Whole rock 2	powdered	LiF (1:1)			+5.4
Results with CaF₂:						
S269-3	Quartz 1	granular	CaF$_2$ (1:1)	prefluorinated 10 hr	0.90	+12.46
S269-5	Quartz 1	granular	CaF$_2$ (2:1)	prefluorinated 10 hr	1.01	+12.87
S269-6	Quartz 1	granular	CaF$_2$ (2:1)	prefluorinated 10 hr	1.00	+12.87
S269-7	Quartz 1	granular	CaF$_2$ (4:1)	prefluorinated 10 hr	1.00	+12.51
S269-8	Quartz 1	granular	CaF$_2$ (4:1)	prefluorinated 10 hr	1.03	+12.48
S268-3	Quartz 1	granular	CaF$_2$ (4:1)		0.94	+12.46
S268-4	Quartz 1	granular	CaF$_2$ (10:1)		1.58	+9.62
S268-5	Quartz 1	granular	CaF$_2$ (10:1)		1.09	+11.03
S269-9	Quartz 2	granular	CaF$_2$ (1:1)	prefluorinated 10 hr	1.22	+11.47
S269-10	Quartz 2	granular	CaF$_2$ (1:1)	prefluorinated 10 hr	0.99	+10.22
S269-11	Quartz 2	granular	CaF$_2$ (2:1)	prefluorinated 10 hr	0.92	+10.03
S269-12	Quartz 2	granular	CaF$_2$ (2:1)	prefluorinated 10 hr	0.91	+9.82
S269-13	Quartz 2	granular	CaF$_2$ (4:1)	prefluorinated 10 hr	0.94	+9.93
S269-14	Quartz 2	granular	CaF$_2$ (4:1)	prefluorinated 10 hr	0.97	+9.71
S268-13	Quartz 2	granular	CaF$_2$ (10:1)	prefluorinated 10 hr	1.45	+8.07

[a] Accepted $\delta^{18}O$ values of Quartz 1 = +12.45‰, Quartz 2 (NBS-28) = +9.60‰, QZ2 Quartz = +24.56‰ from Fouillac and Girard (1995), K-spar = +11.9‰, Biotite NBS-30 = +5.1‰, Whole rock 1 — granitoid = +8.9‰, Whole rock 2 — cordierite–sillimanite gneiss ≈ +5.5‰.
[b] Coarse-grained samples > 300 μm, powdered samples < 30 μm.
[c] Reported yields are relative to the average yield of coarse-grained samples.

result in isotopic fractionation in the lost ejecta. Third, slow reaction of the powder samples, which helps to reduce ejecta, might result in simple vaporization of the mineral (or oxide components) in place of fluorination. Vaporization would be manifest as low $\delta^{18}O$ values, as the heavier cation–^{18}O bonds are more difficult to break.

In order to evaluate which of the above effects causes the isotopic shift, we have analyzed coarse-grained and powdered samples of quartz, biotite, K-feldspar, and whole rocks. The powdered samples were prepared from the coarse-grained material by grinding in a mortar and pestle under acetone. The quartz is a clear, gem quality crystal used as an

in-house standard in the Lausanne laboratory. The biotite is NBS-30, and the K-feldspar was originally analyzed at the Geophysical Laboratory by D. Rumble III.

2.1. Prefluorination / passive fluorination

The $\delta^{18}O$ values of coarse-grained quartz, biotite, and K-feldspar that had been prefluorinated for 70 hr in a BrF_5 atmosphere at room temperature are essentially the same as equivalent samples that had only the normal 5–15-min prefluorination (Fig. 1; Table 1). Similarly, the $\delta^{18}O$ values of fine-grained powders that were prefluorinated for 40–60 min did not systematically differ from those prefluorinated for < 20 min (Table 1). Short prefluorinations (e.g., generally < 15 min in the Lausanne laboratory) can be discarded as a potential cause of the isotopic shift associated with fine-grained material, at least for the phases quartz, biotite, and K-feldspar. (We have, however, observed passive prefluorination in very fine-grained synthetic hydrous phases.)

2.2. Reaction time

The effect of reaction time was evaluated by heating coarse-grained samples with the laser in a BrF_5 environment (0.1 bar) at very low power for different durations. The $\delta^{18}O$ values of quartz sys-

Fig. 2. The effect of reaction rate was determined by heating coarse-grained quartz with the laser at low power in the presence of BrF_5 for an extended time period. The $\delta^{18}O$ values of coarse-grained quartz decreased systematically by up to 1‰ with increasing reaction time. Samples that were reacted quickly (~ 3–5 min) and then maintained in an BrF_5 environment for an additional 10–30 min with the laser on yielded the accepted (unfractionated) value of ~ + 12.4‰, thus demonstrating that the slow laser heating causes the systematic decrease.

tematically decreased with increasing time of reaction — the sample heated for 30 min had a $\delta^{18}O$ value 1‰ lower than the expected value (Fig. 2; Table 1). In order to isolate the effect of reaction time on $\delta^{18}O$ values and negate any effects of passive fluorination, samples of the coarse-grained equivalent were reacted quickly (~ 2 min), after which the laser was left on with BrF_5 present for an additional 27 min. The $\delta^{18}O$ value of the coarse-grained material was unchanged from its accepted value.

One possible explanation for the correlation between reaction rate and $\delta^{18}O$ value might be related to vaporization (sputtering?) of the quartz during the slow heating. If a sample is heated slowly, SiO_2 molecules could vaporize without undergoing fluorination. As $Si-^{16}O$ bonds are more easily broken than the $Si-^{18}O$ bonds, ^{16}O should preferentially react with the fluorine. As a result, the oxygen obtained with slowly reacted (and partially vaporized) samples should have a low $\delta^{18}O$ value. In rapid, high-temperature laser fluorination experiments, essentially all of the oxygen is liberated as O_2, and there is no isotope fractionation.

3. Method for analysis of fine-grained materials

We propose that the problems associated with laser fluorination of fine-grained materials can be minimized or eliminated if the loss of ejecta can be prevented and laser heating rates can be increased. Our method for accomplishing this is to mix the sample with a binder. Several different techniques and compounds were tried during the course of this study. The binder has to meet several criteria: (1) it must not contain oxygen; (2) it must not be hygroscopic; (3) it should be relatively non-toxic; and (4) it should have a low melting point. Of numerous chlorides, bromides and fluorides considered and tested, we settled on LiF as an optimal binder (although BiF_3 and CuF — not yet tested — may be equally suitable or preferable). Our initial tests were made with CaF_2, an acceptable, though less attractive alternative, due to its higher melting point.

Various sample preparation methods were attempted. In all cases, the sample is mechanically mixed with the LiF in an agate mortar. The samples are then loaded either as loose powders into the
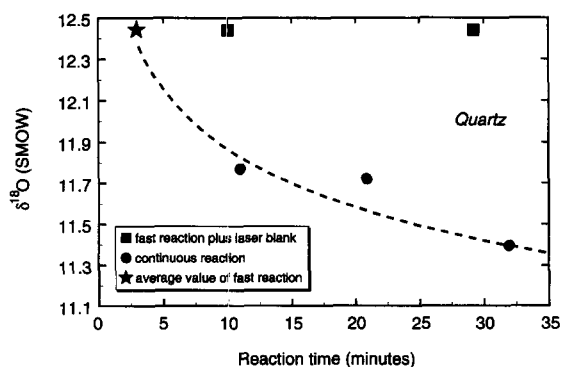
sample block or as pressed pellets, 2 mm in diameter. The pressed pellets can be fluorinated more easily and rapidly. The samples are loaded into a sample block, and heated to 200°C. They are placed in the sample chamber which is evacuated while the sample block is still hot. Degassing continues overnight and is followed by two to three brief (1–3-min duration) prefluorinations in order to liberate any water and the most easily stripped oxygen on the mineral surfaces and sample chamber walls. Analyses then proceed as normal (Sharp, 1990).

4. Results

Results for both LiF and CaF_2 experiments are presented in Fig. 3 and Table 1. The $\delta^{18}O$ values generally agree well with those obtained conventionally. For example, we obtained a correct $\delta^{18}O$ value of +24.5‰ (accepted value +24.6‰) for the same fine-grained quartz sample QZ2 analyzed in the study of Fouillac and Girard (1995; their results are described in Section 1). At high LiF/sample and especially CaF_2/sample ratios, the $\delta^{18}O$ values are lower than expected. We attribute this effect to slight contamination from water and to partial retention of dissolved oxygen in the viscous fluoride melt. As

oxygen is removed from the melt, the absorbance of the infrared radiation from the CO_2 laser decreases. Temperature of the fluoride–sample melt drops and the last remnants of oxygen may remain in the residue, causing an isotope fractionation. The effect is less important with the LiF binder, as opposed to the CaF_2, because the melting point of LiF is far lower than CaF_2 (844°C vs. 1395°C), consequently resulting in a lower viscosity of the melt. The lower viscosity apparently results in faster diffusion of fluorine into the melt and liberation of oxygen out of the melt. Oxygen is retained in the fused bead only when the ratio of LiF (and CaF_2) relative to mineral is 4:1 or greater. The calculated oxygen yields for these experiments (Table 1) are only approximations due to variable loss of sample powder during pellet formation.

The one disadvantage that we have found with this method is that the sample chamber and adjacent line become coated with a white (LiF?) residue after several days of analyses, which necessitates periodic cleaning of the sample chamber and adjacent line. Apart from this one drawback, this LiF binder technique, either as mixed powders or as pellets, is effective in obtaining reproducible and accurate $\delta^{18}O$ analyses of fine-grained material with the laser-extraction system. Two whole-rock powder samples

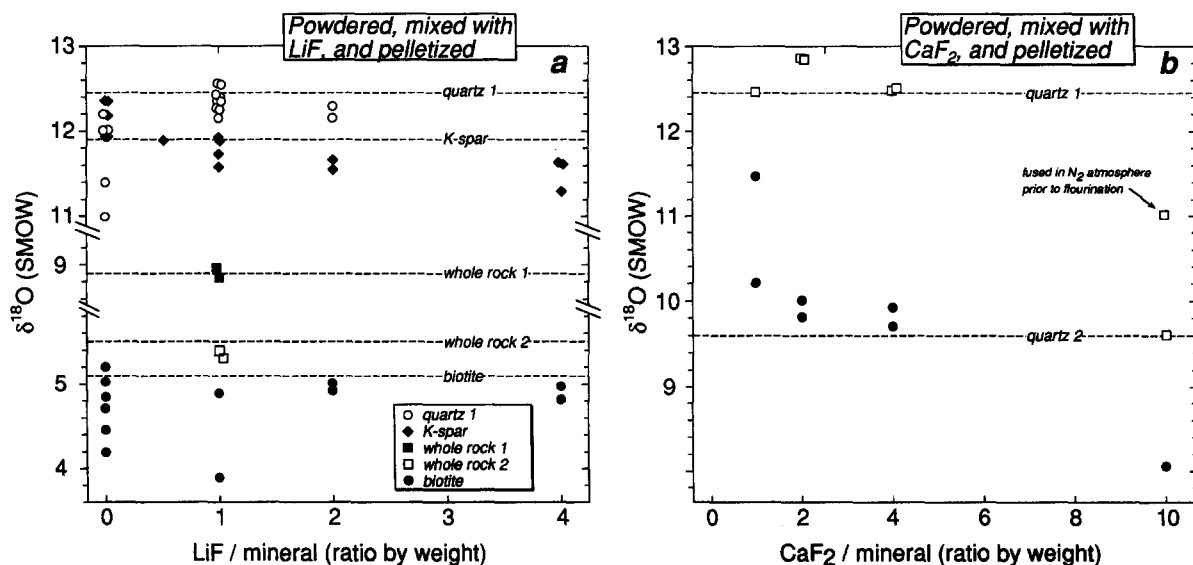
Fig. 3. (a) The $\delta^{18}O$ values of quartz, K-feldspar, whole rock, and biotite powders that had been mixed with LiF and pressed into pellets. The *dashed lines* are the accepted values for the coarse-grained equivalents. (b) Equivalent figure for CaF_2 (Quartz 2 is NBS-28).

have been successfully analyzed with this technique (Table 1) and there is no reason to believe that most minerals and whole-rock powders cannot be analyzed with this method.

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