Geochimica et Cosmochimica Acta, Vol. 69, No. 6, pp. 1473–1478, 2005

0016-7037/05 $30.00 + .00

doi:10.1016/j.gca.2004.09.010

Use of in situ–produced ^{10}Be in carbonate-rich environments: A first attempt

R. Braucher,[1,*] L. Benedetti,[1] D. L. Bourlès,[1] E. T. Brown,[2] and D. Chardon[1]
[1]CEREGE—CNRS—Université Aix-Marseille III, Plateau de l'Arbois, BP80, 13545 Aix en Provence, France
[2]Large Lakes Observatory, University of Minnesota, Duluth, MN 55812, USA

(*Received July* 9, 2004; *accepted in revised form September* 10, 2004)

Abstract—We have determined the production rate of in situ–produced ^{10}Be in calcite through measurements of ^{10}Be and ^{36}Cl concentrations in the same calcite samples and of ^{10}Be concentrations in depth profiles of flint from the same erosional surface. This yields a ^{10}Be production rate in calcite of 37.9 ± 6.0 at/g/yr at sea level and high latitude, approximately sixfold higher than production in the coexisting flint. We propose that this higher rate of production may be due to high production cross sections for C spallation by cosmic rays with energies below 50 MeV. These results also open the possibility of dating burial events in carbonate-rich environments by differential radioactive decay of ^{10}Be and ^{36}Cl. *Copyright © 2005 Elsevier Ltd*

1. INTRODUCTION

Accumulation of in situ–produced cosmogenic nuclides can be used to date geological events that exhume material from depth, such as glaciation, mass wasting, volcanic and tectonic activity, and meteor impact (Gosse and Phillips, 2001). Such applications of ^{10}Be ($T_{1/2}$: 1.5 My) are generally restricted to silicate rich environments, whereas ^{36}Cl ($T_{1/2}$: 0.31 My) has been applied primarily in carbonates. Because they have significantly different half-lives, measurement of this pair of nuclides in a single mineral phase would permit evaluation of a wider range of surface processes (Phillips et al., 1997). In addition, as the time span that can be evaluated using a given cosmogenic nuclide increases with its half-life, constraining the in situ ^{10}Be production rate within carbonates can extend the range of cosmic ray exposure ages that can be determined in carbonate rich environments. Here we present the first measurements of in situ ^{10}Be produced in calcite, together with a new cleaning method for removing meteoric ^{10}Be contamination.

2. SAMPLING AND METHODOLOGY

2.1. Sampling Locations

We collected calcite samples for developing our cleaning procedure from Oligocene carbonates sampled at Limans, France (43°58′N; 5°43′E; alt: 671 m). In addition, we sampled coexisting depth profiles of calcite and flint from the vertical southern limb of the Trevaresse anticline (43°37′N; 5°25′E; alt 375 m; Tortonian lacustrine series (Chardon and Bellier, 2003), Fig. 1). The calcite and flint samples were collected along separate vertical profiles less than 1 m apart within a single trench.

2.2. Sample Preparation

X-ray diffraction indicates that all the carbonate samples are pure calcite. Calcium and Cl contents are summarized in Table 1. Bulk densities for flint (2.57) and carbonate (2.61) were determined for all the samples.

2.2.1. Development of the ^{10}Be Cleaning Procedure

Because the average atmospheric ^{10}Be flux to the Earth surface is orders of magnitude higher than the integrated total rate of in situ ^{10}Be produced in a 1 cm^2 column of surficial rock, measurement of the accumulated in situ–produced ^{10}Be concentration requires elimination of the meteoric ^{10}Be contamination. A cleaning procedure to remove meteoric ^{10}Be contamination was developed using the Limans samples (Lim 02, 04, 08, 09). To test different cleaning procedures, each sample was crushed, sieved (250–500 μm) and divided into five subsamples. The first group was stirred for 24 hours in ultra pure water (18 MΩ-cm), dried, and weighed. This cleaned material was prepared for ^{10}Be measurement by complete dissolution in 15 M HNO_3 followed by addition of 300 μg ^{9}Be carrier (Merck 1000 mg/L Be standard) and subsequent purification by solvent extractions and alkaline precipitations (Bourlès, 1988). The second group, after being subjected to the same deionized water treatment, was partially dissolved by gradual addition of sufficient 1.5 M HNO_3 to dissolve ~10% of the calcite. The pH was monitored and maintained below 5 throughout this step. The cleaned calcite was then dried, weighed, and prepared for ^{10}Be measurement as described above. The other three groups were treated similarly, but were subjected to two, three and four repetitions of the partial dissolution treatment in 1.5 M HNO_3.

2.2.2. ^{10}Be in Samples from Depth Profiles

Calcite samples from the Trevaresse profile were cleaned by deionized water treatment, followed by four repetitions of the partial dissolution before total dissolution of the cleaned material. To evaluate the efficacy of the cleaning method, we also measured ^{10}Be in samples that had not been subjected to prior cleaning. The flint samples were processed using sequential HF dissolutions (Brown et al., 1991).

All ^{10}Be measurements were performed by accelerator mass spectrometry at the Tandétron AMS facility, Gif-sur-Yvette. Measured ^{10}Be/^{9}Be ratios were calibrated directly against the National Institute of Standards and Technology (NIST) standard reference material SRM 4325 using its certified ^{10}Be/^{9}Be ratio of $(26.8 \pm 1.4) \times 10^{-12}$. It has been noted that the ratio

---

[*] Author to whom correspondence should be addressed (braucher@cerege.fr).

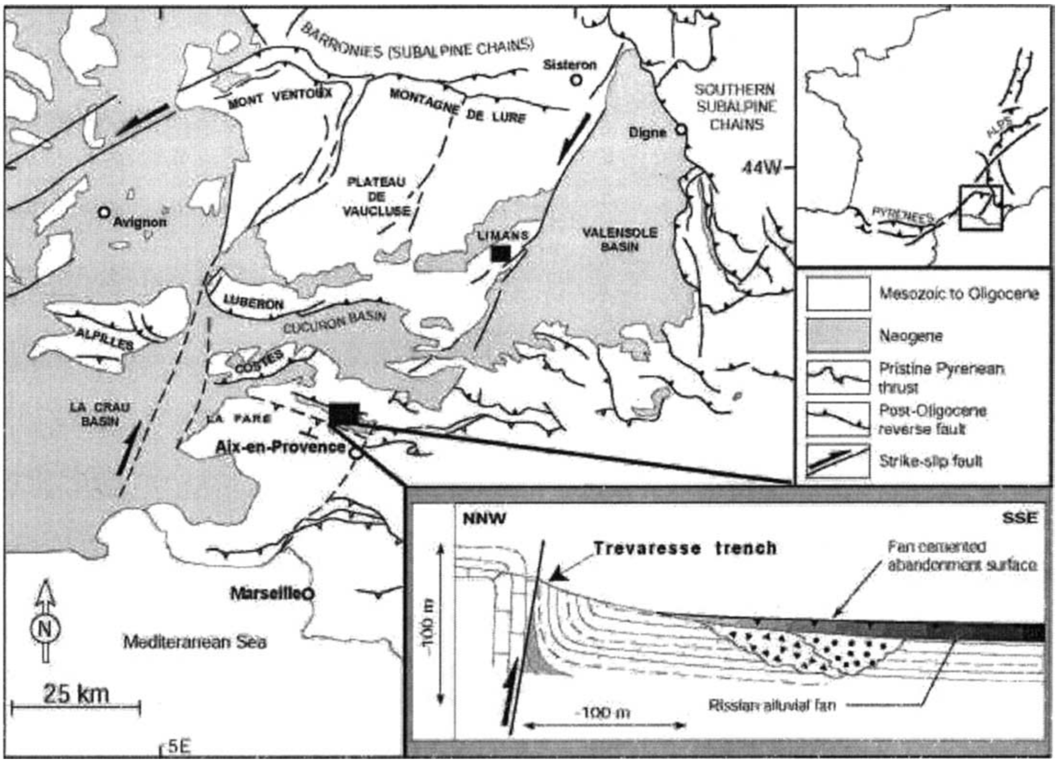

Fig. 1. Site map (modified after Chardon and Bellier, 2003).

reported by NIST is incompatible with the ICN standards used at the University of Pennsylvania and at the University of California (Middleton et al., 1993). We have thus normalized our ^{10}Be concentrations by a factor of 0.875 ± 0.030 to make them directly comparable to those based on ICN standards. ^{10}Be uncertainties (1σ) include a 3% contribution conservatively estimated from observed standard variations during the runs, a 1σ statistical error in the number of ^{10}Be events counted, uncertainty on the blank correction (associated ^{10}Be/^{9}Be blank ratio was $(2.4 \pm 1.2) \times 10^{-15}$), and a 15% uncertainty on in situ ^{10}Be production rate within quartz (Lal, 1987, 1991b; Gosse et al., 1996).

2.2.3. *^{36}Cl in Samples from Depth Profile*

After grinding, leaching and chemical separation of chlorine by precipitation of silver chloride, the ^{36}Cl and chloride concentration in the carbonate were determined for all samples by isotope dilution accelerator mass spectrometry at the Lawrence Livermore National Laboratory CAMS facility. Blanks were two orders of magnitude lower than the samples. Uncertainties on ^{36}Cl concentration include measurements statistical uncertainties and the blank correction.

^{36}Cl production rates from calcium of Stone et al. (Stone et al., 1998) were used. Those production rates were calculated for our site latitude and altitude using Lal coefficients (Lal, 1991a).

3. RESULTS AND DISCUSSION

3.1. Cleaning Procedure on Carbonate Samples

The constant ^{10}Be concentration of the stepwise dissolutions, even after the first water washing step, indicates that meteoric

Table 1. In situ–produced ^{10}Be and ^{36}Cl concentrations in the Trevaresse calcite samples (density: 2.61).

Samples	Depth (cm)	Dissolved material (g)	^{10}Be[a] ($\times 10^6$ at/g)	^{10}Be error ($\times 10^6$ at/g)	Cl (ppm) (error <3%)	Ca (%) (error <3%)	^{36}Cl ($\times 10^6$ at/g)	^{36}Cl error ($\times 10^6$ at/g)
TR03-06	40	25.13	1.90	0.08	7.60	40.09	1.15	0.02
TR03-07	54	24.17	1.73	0.08	7.20	39.48	1.04	0.02
TR03-08	70	14.33	1.53	0.07	8.65	37.66	0.93	0.04
TR03-09	90	13.05	1.27	0.06	10.46	38.16	0.87	0.03
TR03-06 Bulk[b]	40	15.60	3.15	0.37	7.60	40.09		
TR03-07 Bulk	54	13.68	1.95	0.27	7.20	39.48		Not measured
TR03-08 Bulk	70	15.45	1.95	0.23	8.65	37.66		
TR03-09 Bulk	90	13.17	1.97	0.25	10.46	38.16		

[a] ^{10}Be concentrations have been normalized to ICN standard.

[b] Bulk refers to untreated samples (samples were crushed then totally dissolved).