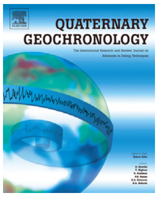
Quaternary Geochronology 26 (2015) 11–19

Contents lists available at ScienceDirect

Quaternary Geochronology

journal homepage: www.elsevier.com/locate/quageo



Research paper

An inter-laboratory comparison of cosmogenic ^{3}He and radiogenic ^{4}He in the CRONUS-P pyroxene standard

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ARTICLE INFO

Article history:
Received 1 February 2014
Received in revised form
27 August 2014
Accepted 28 August 2014
Available online 7 September 2014

Keywords:
Cosmogenic
^{3}He
Radiogenic
^{4}He
CRONUS-P
Standard
Calibration

ABSTRACT

This study reports an inter-laboratory comparison of the ^{3}He and ^{4}He concentrations measured in the pyroxene material CRONUS-P. This forms part of the CRONUS-Earth and CRONUS-EU programs, which also produced a series of natural reference materials for in situ produced ^{26}Al, ^{10}Be, ^{14}C, ^{21}Ne and ^{36}Cl.

Six laboratories (GFZ Potsdam, Caltech Pasadena, CRPG Nancy, SUERC Glasgow, BGC Berkeley, Lamont New York) participated in this intercomparison experiment, analyzing between 5 and 22 aliquots each. Intra-laboratory results yield ^{3}He concentrations that are consistent with the reported analytical uncertainties, which suggests that ^{3}He is homogeneous within CRONUS-P. The inter-laboratory dataset (66 determinations from the 6 different labs) is characterized by a global weighted mean of $(5.02 \pm 0.12) \times 10^{9}$ at g^{-1} with an overdispersion of 5.6% (2σ). ^{4}He is characterized by a larger variability than ^{3}He, and by an inter-lab global weighted mean of $(3.60 \pm 0.18) \times 10^{13}$ at g^{-1} (2σ) with an overdispersion of 10.4% (2σ).

There are, however, some systematic differences between the six laboratories. More precisely, 2 laboratories obtained mean ^{3}He concentrations that are about 6% higher than the clustered other 4 laboratories. This systematic bias is larger than the analytical uncertainty and not related to the CRONUS-P material (see Schaefer et al., 2015). Reasons for these inter-laboratory offsets are difficult to identify but are discussed below. To improve the precision of cosmogenic ^{3}He dating, we suggest that future studies presenting cosmogenic ^{3}He results also report the ^{3}He concentration measured in the CRONUS-P material in the lab(s) used in a given study.

1. Introduction

Cosmogenic ^{3}He is a powerful dating tool that can be used in a large range of geological applications. First, it is the best-suited cosmogenic nuclide for mafic minerals such as olivine or pyroxene (e.g. Ackert et al., 2003; Bruno et al., 1997), minerals in which ^{10}Be cannot be used in a straightforward way (Blard et al., 2008; Ivy-Ochs et al., 1998). Second, it is not affected by radioactive decay, a property that theoretically permits dating very old landscapes or geological events (e.g. Margerison et al., 2005; Schaefer et al., 1999). Third, ^{3}He can also be combined with another cosmogenic nuclide in the same sample, such as ^{36}Cl or ^{10}Be. Such a multi-isotope study allows determination of complex exposure histories and dating of burial events. Fourth, ^{3}He is the cosmogenic nuclide having one of the lowest *detection limit/production rate* ratios (together with ^{10}Be), which also allows measurement of

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http://dx.doi.org/10.1016/j.quageo.2014.08.004

exposure ages as small as few hundreds of years using small amounts of minerals (<1 g) (e.g. Blard et al., 2006). Fifth, helium isotopes can be measured with commercial noble gas mass spectrometers, such as VG-5400, MAP or Helix-SFT instruments, and do not require complicated chemical pre-treatments. Sixth, the knowledge of its production rate has recently improved, thanks to the discovery of well-constrained calibration sites (Blard et al., 2013; Fenton et al., 2013; Goehring et al., 2010).

However, despite the recent report of well-constrained calibration sites, a non negligible variability of the worldwide production rates remains, after scaling to sea level and high latitude (Blard et al., 2013; Fenton et al., 2013; Goehring et al., 2010). Although both geological scatter and scaling model inaccuracies may explain a part of this dispersion, analytical variability may also be involved. To make progress on these issues and improve the accuracy and precision of the cosmogenic ^{3}He dating tool, it is important to inter-calibrate the laboratories analyzing cosmogenic ^{3}He. We report here the results of an inter-laboratory comparison, an experiment that was part of the NSF funded CRONUS-Earth and the EU-Commission funded CRONUS-EU project. Similar studies have already been performed for ^{10}Be, ^{14}C and ^{26}Al (Jull et al., 2015; Merchel et al., 2012) and ^{21}Ne (Vermeesch et al., 2015). The main goals of this study are (i) to test the inter-laboratory ^{3}He calibration and examine the source of systematic differences, and, (ii) if possible, to propose a ^{3}He value for a reference pyroxene material (CRONUS-P) that can be used by the cosmogenic noble gas community.

2. Description of the CRONUS-P pyroxene standard

The CRONUS-P standard is composed of pure pyroxenes in the 125–250 μm grain-size fraction, which have been isolated from a dolerite boulder collected on Mount Feather, Dry Valleys, Antarctica (160.4°E, 77.9°S, 2555 m above sea level). This sample has already been studied and described by Schaefer et al. (1999) where it is labeled NXP 93 × 52. More characteristics of CRONUS-P material, notably its chemical composition, are provided in a companion article (Schaefer et al., 2015). The total ^{3}He concentration in CRONUS-P pyroxene is assumed to be cosmogenic, since both magmatic and nucleogenic ^{3}He components are negligible in this sample (Niedermann et al., 2007; Schaefer et al., 1999; Schaefer et al., 2015). The eruption age of this dolerite is about 180 Ma (Fleming et al., 1997), implying that the majority of its ^{4}He inventory is of radiogenic origin (Schaefer et al., 2015). In the ETH Zurich noble gas laboratory, Schaefer et al. (1999) measured a cosmogenic ^{3}He concentration of $5.21 \pm 0.08 \times 10^{9}$ at g^{-1} for NXP 93 × 52 pyroxenes, which corresponds to a minimal exposure age of 4 Ma, using the most recent synthesis of sea-level-high-latitude ^{3}He production rates (Blard et al., 2013) and the atmospheric pressure field measured over Antarctica (Stone, 2000). A later re-analysis at GFZ Potsdam yielded a consistent ^{3}He concentration of $5.11 \pm 0.26 \times 10^{9}$ at g^{-1} (Niedermann et al., 2007).

Details about the method used to isolate the CRONUS-P pyroxenes, and their chemical composition, are available in a companion article (Schaefer et al., 2015).

3. Analytical methods

The 6 laboratories (GFZ Potsdam, Caltech Pasadena, CRPG Nancy, SUERC Glasgow, BGC Berkeley, Lamont New York) used different analytical procedures and noble gas mass spectrometers. All labs applied their own routines, regarding the gas standard, the amount of time and temperature used during extraction, purification and measurement on their mass spectrometers. As such, this inter-calibration experiment fully captured the different methods used for cosmogenic ^{3}He analysis.

Table 1 lists the main procedures and the standards used in each lab and Table 2 lists all extraction temperatures, heating times and masses of aliquots.

3.1. Caltech, Pasadena, CA, USA

Samples were wrapped in tin foil and placed in vacuo in a loading arm located above the extraction furnace. The line was not baked during overnight pumping. Noble gases were extracted in a single step, at 1500 °C during 15 min in a resistance-heated double vacuum furnace. Complete extraction was checked by measuring a hot blank after each sample. The extracted gas was purified, cryofocused at 8 K and separated from neon at 35 K, before being inlet in a MAP 215-50 mass spectrometer. ^{3}He and ^{4}He were measured by peak-jumping according to the standard procedure used at Caltech (Patterson and Farley, 1998). The absolute sensitivity was determined measuring two gas standards of known composition and pressure: one standard is an artificial mixture of ^{3}He and ^{4}He, with a ratio of 2.05 Ra ($\text{Ra} = 1.39 \times 10^{-6}$), and the second one is the “Murdering Mudspots” (MM) gas standard, made from volcanic gas of Yellowstone National Park (Craig et al., 1978; Welhan et al., 1988), with a certified ^{3}He/^{4}He value of 16.52 Ra ($\text{Ra} = 1.39 \times 10^{-6}$). He abundances in the standards tanks were initially determined using a capacitance manometer. Tank depletion was regularly checked against a reference tank experiencing little depletion. For each analysis, the size of the standard was adjusted so that the ^{4}He pressure in the mass spectrometer is similar for samples and standards (Burnard and Farley, 2000). Sensitivities were $\sim 1.7 \times 10^{-5}$ cps at^{-1} and $\sim 3 \times 10^{-7}$ mV at^{-1} for ^{3}He and ^{4}He, respectively. Blanks were $(1.6 \pm 1.2) \times 10^{9}$ and $(5.2 \pm 5.2) \times 10^{3}$ at, representing less than 1‰ of the analyzed samples. Total analytical uncertainties attached to the measured ^{3}He and ^{4}He concentrations ranged between 2 and 3% (given as 1σ).

Caltech analyzed 9 aliquots ranging in weight from 8.8 to 83.5 mg.

3.2. GFZ, Potsdam, Germany

Samples were wrapped in aluminum foil and placed in vacuo in a carrousel above the extraction furnace, where they were baked at 100 °C for about one week. Noble gases were extracted in two heating steps (20 min extraction time at final temperature) of 900 and 1750 °C in a resistance-heated double vacuum furnace equipped with a tantalum crucible and molybdenum liner. Gas

Table 1
Summary of the analytical procedures used in the 6 laboratories.

Laboratory	^{3}He/^{4}He absolute ratio of the STD (10^{-6})	STD material reference	Check MS linearity (pressure effect)	Check STD tank depletion
Caltech Pasadena	2.85 and 22.96	(Craig et al., 1978; Welhan et al., 1988)	Yes, by STD dilution and spiking	Yes, using a gas standard
GFZ Potsdam	21.66 ± 0.24	Internal standard	Occasionally by STD dilution	Yes, using a rock standard
CRPG Nancy	28.55	(Matsuda et al., 2002)	Yes, by STD dilution	Yes, using a rock standard
SUERC Glasgow	28.68	(Matsuda et al., 2002)	Yes, by STD dilution	Yes, using a rock standard
BGC Berkeley	611.6	Internal standard	Yes, by spiking	Yes, using a gas standard
Lamont NY	22.77	(Craig et al., 1978; Welhan et al., 1988)	Yes, by STD dilution	Yes, using a rock standard