



Research paper

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

P.-H. Blard ^{a, *}, G. Balco ^b, P.G. Burnard ^a, K.A. Farley ^c, C.R. Fenton ^d, R. Friedrich ^{e, f}, A.J.T. Jull ^g, S. Niedermann ^d, R. Pik ^a, J.M. Schaefer ^{e, f}, E.M. Scott ^h, D.L. Shuster ^{b, i}, F.M. Stuart ^j, M. Stute ^e, B. Tibari ^a, G. Winckler ^{e, f}, L. Zimmermann ^a

^a CRPG, Université de Lorraine, UMR 7358, CNRS, Vandoeuvre-lès-Nancy, France

^b Berkeley Geochronology Center, 2455 Ridge Road, Berkeley, CA, USA

^c Division of Geological and Planetary Sciences, California Institute of Technology, Pasadena, CA, USA

^d Deutsches GeoForschungsZentrum GFZ, Potsdam, Germany

^e Lamont-Doherty Earth Observatory, Geochemistry, Palisades, NY, USA

^f Department of Earth and Environmental Sciences, Columbia University, New York, NY, USA

^g Department of Geosciences, NSF Arizona AMS Laboratory, Tucson, AZ, USA

^h School of Mathematics and Statistics, University of Glasgow, Glasgow, Scotland, UK

ⁱ Department Earth and Planetary Science, University of California, Berkeley, CA, USA

^j Scottish Universities Environmental Research Centre, Glasgow, UK

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

^3He

Radiogenic

^4He

CRONUS-P

Standard

Calibration

ABSTRACT

This study reports an inter-laboratory comparison of the ^3He and ^4He 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 ^3He concentrations that are consistent with the reported analytical uncertainties, which suggests that ^3He 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). ^4He is characterized by a larger variability than ^3He , 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 ^3He 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 ^3He dating, we suggest that future studies presenting cosmogenic ^3He results also report the ^3He concentration measured in the CRONUS-P material in the lab(s) used in a given study.

© 2014 Elsevier B.V. All rights reserved.

1. Introduction

Cosmogenic ^3He 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, ^3He 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, ^3He is the cosmogenic nuclide having one of the lowest detection limit/production rate ratios (together with ^{10}Be), which also allows measurement of

* Corresponding author.

E-mail address: blard@crpg.cnrs-nancy.fr (P.-H. Blard).

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 ^3He dating tool, it is important to inter-calibrate the laboratories analyzing cosmogenic ^3He . 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 ^3He calibration and examine the source of systematic differences, and, (ii) if possible, to propose a ^3He 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 \times 52. More characteristics of CRONUS-P material, notably its chemical composition, are provided in a companion article (Schaefer et al., 2015). The total ^3He concentration in CRONUS-P pyroxene is assumed to be cosmogenic, since both magmatic and nucleogenic ^3He 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 ^4He inventory is of radiogenic origin (Schaefer et al., 2015). In the ETH Zurich noble gas laboratory, Schaefer et al. (1999) measured a cosmogenic ^3He concentration of $5.21 \pm 0.08 \times 10^9$ at g^{-1} for NXP 93 \times 52 pyroxenes, which corresponds to a minimal exposure age of 4 Ma, using the most recent synthesis of sea-level-high-latitude ^3He 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 ^3He 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 ^3He 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. ^3He and ^4He 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 ^3He and ^4He , with a ratio of 2.05 Ra (Ra = 1.39×10^{-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 $^3\text{He}/^4\text{He}$ value of 16.52 Ra (Ra = 1.39×10^{-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 ^4He 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 ^3He and ^4He , 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 ^3He and ^4He 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 carousel 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	$^3\text{He}/^4\text{He}$ 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

Table 2³He and ⁴He concentrations measured in the CRONUS-P pyroxene material by six different laboratories.

Lab	Mass (mg)	Temperature (°C)	Heating time (min)	⁴ He (10 ¹³ at g ⁻¹)	1σ	³ He (10 ⁹ at g ⁻¹)	1σ	³ He/ ⁴ He (Ra) ^a	1σ
Caltech Pasadena	33.1	1600	15	3.29	0.10	4.64	0.10	102	4
Caltech Pasadena	83.5	1600	15	10.86	0.33	5.09	0.14	34	1
Caltech Pasadena	36.2	1600	15	12.69	0.02	5.03	0.14	29	1
Caltech Pasadena	26.8	1600	15	3.41	0.01	4.83	0.13	102	3
Caltech Pasadena	29.5	1600	15	3.66	0.01	4.79	0.13	95	3
Caltech Pasadena	10.6	1600	15	3.40	0.01	4.89	0.13	104	3
Caltech Pasadena	8.8	1600	15	3.32	0.01	4.79	0.13	104	3
Caltech Pasadena	14.6	1600	15	3.70	0.08	4.98	0.17	97	4
Caltech Pasadena	17.7	1600	15	3.62	0.08	4.82	0.16	96	4
			Means^{b,c}	3.48	0.14	4.86	0.07	101	2
GFZ Potsdam		900	20	3.51	0.09	4.92	0.13	101	1
GFZ Potsdam		1750	20	0.04	0.01	0.05	0.01	98	4
GFZ Potsdam	99.4	Total		3.55	0.09	4.97	0.13	101	1
GFZ Potsdam		900	20	2.90	0.07	3.25	0.09	81	1
GFZ Potsdam		1750	20	0.51	0.01	1.47	0.04	208	3
GFZ Potsdam	51.7	Total		3.41	0.07	4.72	0.10	100	1
GFZ Potsdam		900	20	3.51	0.09	4.86	0.13	100	1
GFZ Potsdam		1750	20	0.05	0.01	0.07	0.01	106	4
GFZ Potsdam	49.6	Total		3.56	0.09	4.93	0.13	100	1
GFZ Potsdam		900	20	3.53	0.09	4.93	0.14	101	1
GFZ Potsdam		1750	20	0.04	0.01	0.06	0.01	97	6
GFZ Potsdam	50.1	Total		3.57	0.09	4.99	0.14	101	1
GFZ Potsdam		900	20	3.40	0.09	5.04	0.14	107	2
GFZ Potsdam		1750	20	0.03	0.01	0.05	0.01	118	6
GFZ Potsdam	50.7	Total		3.43	0.09	5.09	0.14	107	2
GFZ Potsdam		900	20	3.43	0.09	4.81	0.13	101	1
GFZ Potsdam		1750	20	0.04	0.01	0.05	0.01	109	5
GFZ Potsdam	50.8	Total		3.46	0.09	4.86	0.13	102	1
GFZ Potsdam		900	20	3.47	0.09	4.89	0.13	102	1
GFZ Potsdam		1750	20	0.03	0.01	0.03	0.01	96	4
GFZ Potsdam	21.0	Total		3.50	0.09	4.92	0.13	102	1
			Means^b	3.49	0.03	4.91	0.05	102	2
CRPG Nancy	54.5	1400	15	3.68	0.04	4.93	0.09	97	2
CRPG Nancy	12.2	1400	15	4.19	0.04	4.87	0.09	84	2
CRPG Nancy	10.4	1400	15	3.43	0.03	4.94	0.09	104	2
CRPG Nancy	27.9	1400	15	3.69	0.04	4.91	0.09	96	2
CRPG Nancy	42.0	1400	15	3.63	0.04	4.93	0.09	98	2
CRPG Nancy	23.0	1400	15	3.56	0.04	5.05	0.10	103	2
CRPG Nancy	23.6	1400	15	3.64	0.04	4.97	0.09	99	2
CRPG Nancy	11.0	1400	15	4.01	0.04	4.97	0.10	89	2
CRPG Nancy	27.4	1400	15	3.32	0.06	4.86	0.10	106	3
CRPG Nancy	14.4	1400	15	3.33	0.06	4.87	0.10	106	3
			Means^b	3.64	0.25	4.93	0.03	98	7
SUERC Glasgow	26.8	>1400	5	3.46	0.11	5.11	0.16	107	5
SUERC Glasgow	4.1	>1400	5	2.97	0.10	4.95	0.16	120	6
SUERC Glasgow	3.9	>1400	5	3.12	0.11	4.91	0.16	114	5
SUERC Glasgow	2.4	>1400	5	3.27	0.12	5.36	0.18	118	6
SUERC Glasgow	7.5	>1400	5	3.25	0.11	4.97	0.16	110	5
SUERC Glasgow	9.9	>1400	5	3.38	0.11	5.11	0.16	109	5
SUERC Glasgow	14.2	>1400	5	3.71	0.12	5.23	0.17	102	5
SUERC Glasgow	10.6	>1400	5	3.26	0.11	5.10	0.16	113	5
SUERC Glasgow	12.5	>1400	5	3.20	0.10	5.22	0.17	118	5
SUERC Glasgow	10.0	>1400	5	3.12	0.10	5.09	0.16	118	5
SUERC Glasgow	23.4	>1400	5	3.19	0.10	5.02	0.16	114	5
SUERC Glasgow	7.3	>1400	5	2.85	0.09	4.75	0.15	120	6
SUERC Glasgow	4.5	>1400	5	3.22	0.11	4.61	0.15	103	5
SUERC Glasgow	16.9	>1400	5	3.41	0.11	5.12	0.16	108	5
SUERC Glasgow	10.0	>1400	5	3.27	0.10	4.81	0.15	106	5
SUERC Glasgow	1.9	>1400	5	2.88	0.10	4.90	0.17	123	6
SUERC Glasgow	3.6	>1400	5	3.06	0.11	4.75	0.16	112	6
SUERC Glasgow	5.4	>1400	5	3.17	0.11	4.80	0.16	109	5
SUERC Glasgow	10.5	>1400	5	3.14	0.10	4.73	0.15	109	5
SUERC Glasgow	15.5	>1400	5	3.40	0.11	4.96	0.16	105	5
SUERC Glasgow	12.9	>1400	5	3.26	0.10	4.85	0.15	108	5
SUERC Glasgow	21.8	>1400	5	3.43	0.11	5.15	0.16	109	5

(continued on next page)

Table 2 (continued)

Lab	Mass (mg)	Temperature (°C)	Heating time (min)	⁴ He (10 ¹³ at g ⁻¹)	1σ	³ He (10 ⁹ at g ⁻¹)	1σ	³ He/ ⁴ He (Ra) ^a	1σ
			Means^b	3.22	0.16	4.98	0.09	111	2
BGC Berkeley	16.6	1200	15	3.78	0.10	5.20	0.16	99	4
BGC Berkeley	33.9	1200	15	4.15	0.11	5.24	0.16	91	4
BGC Berkeley	51.7	1200	15	3.77	0.09	5.08	0.15	97	4
BGC Berkeley	26.5	1200	15	3.97	0.10	5.31	0.17	97	4
BGC Berkeley	19.9	1200	15	3.90	0.09	5.16	0.15	96	3
			Means^b	3.91	0.09	5.20	0.07	96	2
Lamont NY	16.29	1350	15	3.78	0.08	5.30	0.13	101	3
Lamont NY	17.05	1350	15	3.66	0.07	5.27	0.13	104	3
Lamont NY	16.26	1350	15	3.87	0.02	5.44	0.11	102	2
Lamont NY	17.29	1350	15	3.78	0.02	5.39	0.09	103	2
Lamont NY	14.33	1350	15	3.92	0.02	5.34	0.09	98	2
Lamont NY	14.65	1350	15	3.88	0.02	5.26	0.08	98	2
Lamont NY	18.35	1350	15	3.67	0.02	5.25	0.09	103	2
Lamont NY	12.42	1350	15	3.87	0.05	5.21	0.11	97	2
Lamont NY	16.43	1350	15	3.82	0.03	5.32	0.08	101	2
Lamont NY	15.67	1350	15	3.55	0.04	5.04	0.09	102	2
Lamont NY	17.34	1350	15	3.86	0.01	5.20	0.06	97	1
Lamont NY	15.17	1350	15	3.77	0.01	5.20	0.07	100	1
Lamont NY	15.08	1350	15	3.69	0.01	5.19	0.05	102	1
			Means^b	3.78	0.10	5.25	0.03	100	2

^a Ra = 1.384 × 10⁻⁶.

^b Means are weighted averages and reported uncertainties are the intra-lab overdispersion (at 1σ).

^c Two outliers were removed before calculating the ⁴He mean of the Caltech dataset.

purification involved a dry ice trap, two titanium sponge or foil getters, and two SAES (Zr–Al) getters. The noble gases were trapped at 11 K on activated charcoal in a cryogenic adsorber and sequentially released for He (at 35 K), Ne (at 80 K), and Ar–Kr–Xe analysis (at 340 K) in a VG5400 noble gas mass spectrometer. Absolute noble gas concentrations were calculated by peak height comparison against a 0.1 cm³ pipette of our calibration gas, an artificial mixture of the five noble gases in nitrogen (20% He, 8% Ne, 8% Ar, 0.05% Kr, 0.1% Xe, 64% N₂) with an elevated ³He/⁴He ratio of (21.66 ± 0.24) × 10⁻⁶. This ³He/⁴He ratio was calibrated both against atmosphere (assuming the absolute ³He/⁴He ratio of air is 1.39 × 10⁻⁶) and against the HESJ Japanese standard (Matsuda et al., 2002). The absolute noble gas concentrations of our standard are judged accurate to ~3% at 95% confidence level. Original total pressure was calculated based on expansion of standard gas at air pressure from the Dörflinger pipette (V = 0.1030 cm³) to the tank (V = 6.3 l). The helium partial pressure was calculated from the total pressure and the He abundance of this standard (20%). It was also cross-calibrated against glass ampoule He standards provided by Otto Eugster (University of Bern; see Niedermann et al., 1997). The depletion factor per pipette is 0.999984, so after a few hundred pipettes the pressure is still expected to be >99% of the original. To make sure that we would notice problems with the calibration gas concentrations (shifts or sudden losses), we include one of three rock standards (a MORB glass, CREU-1 quartz, CRONUS-P pyroxene) in each measurements series.

Total analytical ⁴He blanks amounted to (1–2) × 10⁸ atoms at 900 °C and (4–20) × 10⁸ atoms at 1750 °C, corresponding to ³He blanks of a few hundred to a few thousand atoms. Further details about the analytical procedures and data reduction methods can be found in (Niedermann et al., 1997).

GFZ analyzed 7 aliquots ranging in weight from 21.02 to 99.36 mg.

3.3. CRPG, Nancy, France

Samples were wrapped in tin foil and placed in vacuo in a carousel above the extraction furnace. The carousel was baked at 100 °C for about 12 h. Noble gases were extracted in one single heating step of 15 min at 1350 °C in a single vacuum resistance furnace (Zimmermann et al., 2012). Complete extraction was

checked by measuring a hot blank after each sample. The extracted gases were then purified using several hot (400 °C) and cold (20 °C) titanium sponges and charcoals cooled in liquid nitrogen. Although this CRPG extraction line is now equipped with a cryo-trap, helium was not separated from neon during the analytical sessions of this CRONUS-P standard. ³He and ⁴He were measured using a bicollecion Split Flight Tube mass spectrometer (based on a GV Instruments Helix SFT). The absolute sensitivity was determined measuring variable amounts of the pure helium HESJ standard, using a certified ³He/⁴He ratio of 20.63 Ra (Ra = 1.384 × 10⁻⁶) (Matsuda et al., 2002). He abundance in the standard tank was initially determined using a capacitance manometer. Tank depletion was regularly checked using an internal rock standard of known helium abundance. For each analysis, the size of the standard was adjusted so that the ⁴He pressure in the mass spectrometer was similar for samples and standards (Burnard and Farley, 2000; Sano et al., 2008). Sensitivities were ~1.5 × 10⁻⁵ cps at⁻¹ and ~3 × 10⁻⁷ mV at⁻¹ for ³He and ⁴He, respectively. Hot furnace blanks were (2.4 ± 1.1) × 10⁹ and (7.6 ± 3.5) × 10³ at, for ⁴He and ³He, respectively. This represented less than 1% and 1‰ of the ⁴He and ³He concentrations in the analyzed aliquots. Total analytical uncertainties attached to the measured ³He and ⁴He concentrations were ~2% (1σ).

CRPG analyzed 10 aliquots ranging in weight from 10.4 to 54.5 mg.

3.4. SUERC, Glasgow, Scotland, UK

Samples were weighed into 10 mm diameter recesses in a Cu pan. The pan is loaded into a laser cell and pumped to <10⁻⁷ torr prior to baking at ~100 °C for more than 24 h. Samples were melted by heating for 5 min using a 808 nm diode laser (Foeken et al., 2006). Gas purification takes place in an all-metal line by sequentially exposing gases to two hot SAES G50 (Zr–Al) getters then liquid N₂-cooled charcoal. Helium isotope analysis is performed using a MAP 215-50 noble gas mass spectrometer in peak jumping mode. Absolute He concentrations are calculated by peak height comparison against a 0.1 cm³ pipette of the HESJ calibration gas (Matsuda et al., 2002). Absolute concentrations are accurate to ±3% (1σ). The helium blank of the analytical procedure is determined by melting pyroxenes from a young lava flow from Merapi that have previously been degassed in the ultra-high vacuum line. Blanks

were typically $1\text{--}2 \times 10^8$ atoms ^4He and $3\text{--}6 \times 10^4$ atoms ^3He . A more detailed explanation of the analytical procedures can be found in (Williams et al., 2005).

SUERC analyzed 22 aliquots ranging in weight from 1.9 to 26.8 mg.

3.5. BGC, Berkeley, CA, USA

BGC uses a laser “microfurnace” system in which each sample was encapsulated in a Ta packet, and the packet was heated under vacuum by a 150 W, 810 nm diode laser. The temperature of the packet was controlled by a feedback loop involving the laser and an optically coaxial pyrometer. The emissivity of the Ta packet was calibrated separately by placing a thermocouple in an identical apparatus. He extraction involved a single heating step of 15 min at 1200 °C. Subsequent heating steps at 1200° for all aliquots and higher temperatures for some aliquots yielded He signals indistinguishable from blank, so all He was assumed to be extracted in the initial step. The extracted gas was purified by reaction with a SAES getter followed by freezing on activated charcoal at 11.5 K and release of He into the mass spectrometer at 33 K. All sample heating, gas processing, and measurement operations were automatically controlled. The ^4He signal was measured on a Faraday cup, and the ^3He signal on a continuous dynode electron multiplier operated in pulse-counting mode of a MAP-215 mass spectrometer. He abundances were quantified by peak height comparison with aliquots of a custom-mixed standard having an absolute $^3\text{He}/^4\text{He}$ ratio of 6.116×10^{-4} . Standard reservoir and pipette volumes were measured by differential pressure measurements, using a Baratron capacitance manometer, against two separate glass reference volumes whose absolute volumes were determined by filling with Hg and weighing. The absolute fill pressure of the standard reservoir was determined using a MKS Baratron. As the He standard on this system is optimized for low-level ^4He analyses required by single-grain apatite $^4\text{He}/^3\text{He}$ thermochronometry, the (much larger) ^4He signal encountered in analyzing CRONUS-P was outside the range of our calibration. Thus, we assessed and corrected for nonlinearity between samples and standards by introducing a pure ^3He spike (of similar magnitude to ^3He in samples and standards, that is, negligible in size compared to the ^4He pressure) into the mass spectrometer during each analysis after several measurement cycles had been completed, and observing the size of the increase in the ^3He signal upon spike inlet. The standard tank depletion was regularly checked against a reference tank experiencing little depletion.

Reported uncertainties on He abundances were intended to represent the reproducibility of multiple analyses of the same sample on the BGC system, so include i) the internal measurement precision (i.e., the uncertainty in regression to time zero) of each analysis ($\sim 1\%$ for these samples); ii) uncertainty associated with the nonlinearity correction described above ($\sim 1\%$); iii) uncertainty in blank subtraction (negligible for these samples) and iv) reproducibility of analyses of the He standard during the period of these measurements ($\sim 2\%$); but do not include any estimate of the absolute uncertainty on the He abundance in the standard.

BGC analyzed 5 aliquots ranging in weight from 16.6 to 51.7 mg.

3.6. Lamont, Palisades, NY, USA

Samples were wrapped in aluminum foil cups and placed in a carousel above the furnace, which is held under vacuum. Subsequently, the system was pumped over night without baking. Noble gases were extracted in two heating steps (5 min at ~ 900 °C and 15 min at 1350 °C extraction time) in a resistance-heated double vacuum furnace equipped with a molybdenum crucible (no liner).

Gas purification involved a liquid nitrogen-cooled charcoal trap and SAES getter. The extracted noble gases were trapped at 14 K on activated charcoal in a cryogenic trap and the helium fraction was separated from neon at 45 K, before being analyzed in a MAP 215–50 mass spectrometer. ^3He and ^4He were measured by peak-jumping. The absolute sensitivity was determined by measuring gas standards of known composition and pressure. The “Murdering Mudspots (MM)” gas standard originates from volcanic gas captured in Yellowstone National Park (Craig et al., 1978; Welhan et al., 1988). The certified $^3\text{He}/^4\text{He}$ value is 16.45 Ra ($\text{Ra} = 1.384 \times 10^{-6}$). In addition, gas standards of various sizes were analyzed in order to account for non-linearity effects. Typical hot furnace ^4He blanks were 2×10^9 atoms and several thousand atoms of ^3He , representing less than 0.5% of the ^4He and ^3He concentrations in the analyzed aliquots. The standard tank depletion was not checked against a reference gas, but using an internal reference rock standard. More analytical details are available in (Winckler et al., 2005).

Lamont analyzed 13 aliquots ranging in weight from 12.42 to 18.35 mg.

4. Results

All ^3He and ^4He concentrations data are provided in Table 2. Figs. 1 and 2 provide a summary plot of these ^3He and ^4He concentrations, while Fig. 3 shows the $^3\text{He}/^4\text{He}$ ratios. For each dataset reported by the labs, we calculated the MSWD value (Figs. 1–3). MSWD is the Mean Square of the Weighted Deviates, i.e. the “reduced chi-squared”, $\text{MSWD} = \chi^2/n$, where n is the degree of freedom ($n = N - 1$, N being the number of measurements) (McIntyre et al., 1966). The MSWD provides information about the dispersion of each analytical dataset. If the MSWD is larger than 1, data are over-dispersed regarding the analytical uncertainties, which can indicate either heterogeneous material or an underestimate of uncertainties. If the MSWD is close to 1, the data dispersion reflects the analytical uncertainties. And finally, if the MSWD is

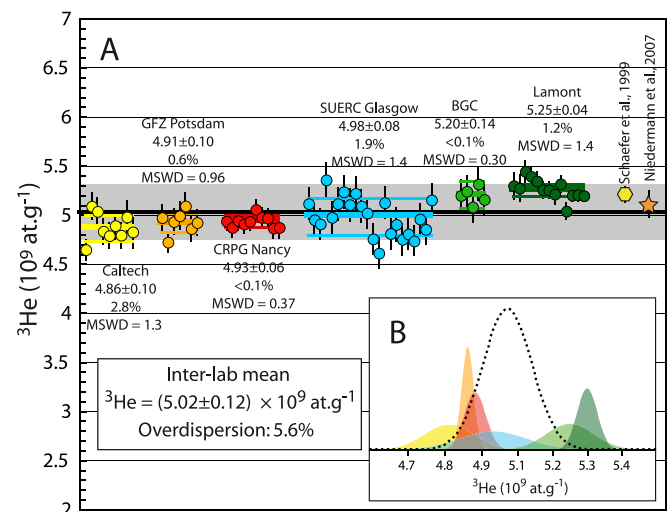


Fig. 1. A) Inter-laboratory comparison of the measured ^3He concentrations in CRONUS-P pyroxenes. Plotted individual analytical uncertainties are at 1σ . For each lab are also given the weighted mean (2σ), the standard error of the mean (2σ), the intra-lab overdispersion and MSWD. The standard error of the global weighted mean and the inter-lab overdispersion are given at 2σ . B) Probability density plots. The 6 weighted means and intra-lab overdispersions are represented by 6 Gaussian density curves (in color), while the global mean and inter-lab overdispersion are represented by the black dotted curve (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.).

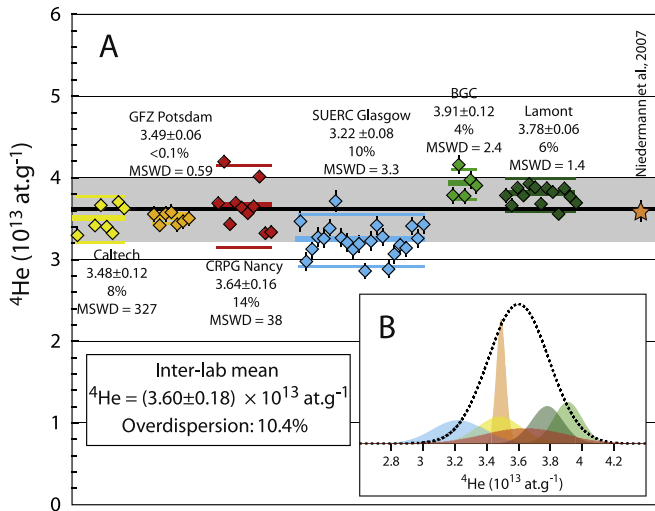


Fig. 2. A) Inter-laboratory comparison of the measured ^4He concentrations in CRONUS-P pyroxenes. Plotted individual analytical uncertainties are at 1σ . For each lab are also given the weighted mean (2σ), the standard error of the mean (2σ), the intra-lab overdispersion and MSWD. The standard error of the global weighted mean and the inter-lab overdispersion are given at 2σ . B) Probability density plots. The 6 weighted means and intra-lab overdispersions are represented by 6 Gaussian density curves (in color), while the global mean and inter-lab overdispersion are represented by the black dotted curve (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

lower than 1, it is an indication that analytical uncertainties are probably overestimated.

The six labs produced ^3He concentrations with internal MSWDs ranging between 0.3 and 1.4 (Fig. 1). Such values are reasonably close enough to unity to suggest both that: i) analytical error bars are correctly estimated and ii) the analyzed aliquots have homogeneous ^3He concentrations. According to Chauvenet's criterion, no outliers were identified for any laboratory. The six weighted means are: Caltech 4.86 ± 0.10 , GFZ 4.91 ± 0.10 , CRPG 4.93 ± 0.06 , SUERC 4.98 ± 0.08 , BGC 5.20 ± 0.14 and Lamont 5.25 ± 0.04 ($\times 10^9$ at g^{-1})

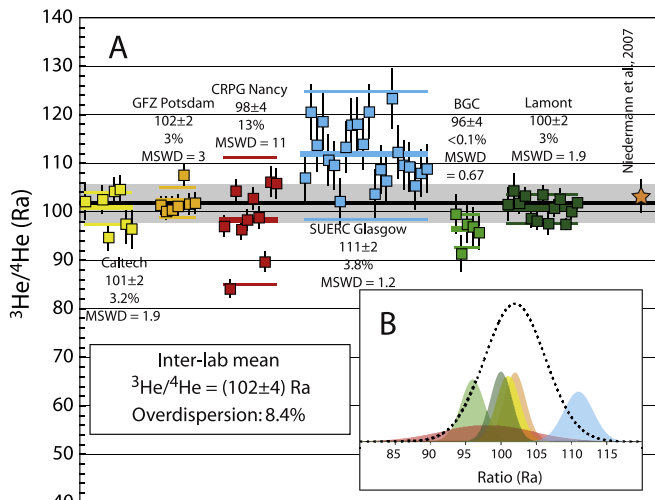


Fig. 3. A) Inter-laboratory comparison of the measured $^3\text{He}/^4\text{He}$ ratios in CRONUS-P pyroxenes. Plotted individual analytical uncertainties are at 1σ . For each lab are also given the weighted mean (2σ), the standard error of the mean (2σ), the intra-lab overdispersion and MSWD. The standard error of the global weighted mean and the inter-lab overdispersion are given at 2σ . $R_a = 1.384 \times 10^{-6}$. B) Probability density plots. The 6 weighted means and intra-lab overdispersions are represented by 6 Gaussian density curves (in color), while the global mean and inter-lab overdispersion are represented by the black dotted curve (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

(Tables 2 and 3; Fig. 1). The uncertainties are the standard errors of the means at 2σ , i.e. the square roots of the variance of the weighted mean, which do not include the intra-laboratory overdispersion (see Equation (1) below). Intra-lab overdispersions are given in Table 3.

The measured ^4He concentrations are characterized by a somewhat larger variability than ^3He : the calculated MSWD range from 0.59 to 327 and five of the six labs have MSWD greater than 2.4 (Fig. 2). As it is doubtful that error bars are underestimated, such scatter clearly indicates that the analyzed aliquots are characterized by heterogeneous ^4He concentrations. According to Chauvenet's criterion, two outliers were identified in the Caltech dataset and removed before calculating a mean for this lab. For all labs, the scatter of the measured ^4He concentrations is larger than the analytical uncertainties. This is probably due to the CRONUS-P material itself, not to an underestimate of uncertainties (Schaefer et al., 2015). Hence, the following weighted averages are reported with uncertainties corresponding to the 2σ intra-lab overdispersion: Caltech 3.48 ± 0.28 , GFZ 3.49 ± 0.06 , CRPG 3.64 ± 0.50 , SUERC 3.22 ± 0.32 , BGC 3.91 ± 0.18 and Lamont 3.78 ± 0.20 ($\times 10^{13}$ at g^{-1}) (Tables 2 and 3; Fig. 2).

The $^3\text{He}/^4\text{He}$ measured ratios are: Caltech 101 ± 2 , GFZ 102 ± 2 , CRPG 98 ± 4 , SUERC 111 ± 2 , BGC 96 ± 4 and Lamont 100 ± 2 (in Ra, where $R_a = 1.384 \times 10^{-6}$; Clarke et al., 1976) (Tables 2 and 3; Fig. 3). These values are weighted means with the standard errors of the mean at 2σ .

In order to interpret the statistical distribution of these results we can assume that any measurement follows a Laplace-Gauss normal distribution with two sources of variance (Vermeesch et al., 2015):

$$x_i \approx N\left(\mu, \sigma_i^2 + \xi^2\right) \quad (1)$$

x_i being a measurement (i.e. ^3He , ^4He or $^3\text{He}/^4\text{He}$), μ the global mean, σ_i^2 the analytical uncertainty of the lab i , and ξ^2 the variance that cannot be explained by the analytical uncertainty alone. ξ^2 is also called *overdispersion*, and represents the best estimate of the inter-laboratory dispersion (Vermeesch et al., 2015). Hence, ξ^2 is the most accurate estimate of the uncertainties attached to these experimental determinations of the CRONUS-P ^3He and ^4He concentrations.

Following this approach, the global inter-laboratory CRONUS-P means are $(5.02 \pm 0.12) \times 10^9$ at g^{-1} for ^3He (2σ overdispersion is 5.6%), $(3.60 \pm 0.18) \times 10^{13}$ at g^{-1} for ^4He (2σ overdispersion is 10.4%), and 102 ± 2 Ra for the $^3\text{He}/^4\text{He}$ ratio (2σ overdispersion is 8.4%). We also calculated z-scores following the approach of Jull et al. (2015) (Table 3).

5. Discussion

5.1. ^3He and ^4He standard homogeneity

All labs reporting ^3He datasets have MSWD close to unity, an observation that strongly suggests that the CRONUS-P pyroxenes is a homogeneous material, at least regarding its ^3He concentrations (Schaefer et al., 2015). The intra-laboratory variances of each individual lab are indeed close to the analytical uncertainties, i.e. typically about 2% at 2σ , while the intra-lab overdispersions are limited ($<1\%$) (Fig. 1; Tables 2 and 3). Regarding ^3He exposure dating, such reproducibility is very good, indicating that the CRONUS-P pyroxenes can be considered an appropriate ^3He reference material (Schaefer et al., 2015).

On the other hand, the ^4He concentrations of CRONUS-P are characterized by a larger variability than ^3He (Fig. 2; Tables 2 and 3).

Table 3

Summary of the CRONUS-P inter-laboratory results.

Laboratory	Number of aliquots	^3He (10^9 at g^{-1})	1σ overdispersion	z-score	^4He (10^{13} at g^{-1})	1σ overdispersion	z-score	$^3\text{He}/^4\text{He}$ (Ra)	1σ overdispersion	z-score
Caltech Pasadena	9	4.86 ± 0.05	1.4%	-1.2	3.48 ± 0.06	4%	-0.7	101 ± 1	1.6%	-0.3
GFZ Potsdam	7	4.91 ± 0.05	0.3%	-0.8	3.49 ± 0.03	<0.1%	-0.6	102 ± 1	1.5%	0.0
CRPG Nancy	10	4.93 ± 0.03	<0.1%	-0.6	3.64 ± 0.08	7%	0.2	98 ± 2	6.7%	-0.9
SUERC Glasgow	22	4.98 ± 0.04	1.9%	-0.3	3.22 ± 0.04	5%	-2.0	111 ± 1	1.9%	2.3
BGC Berkeley	5	5.20 ± 0.07	<0.1%	1.2	3.91 ± 0.06	2%	1.6	96 ± 2	0.0%	-1.3
Lamont New York	13	5.25 ± 0.02	0.6%	1.6	3.78 ± 0.03	3%	1.0	100 ± 1	1.5%	-0.3
Global mean		5.02 ± 0.06	2.8%		3.60 ± 0.09	5.2%		102 ± 2	4.2%	

For each laboratory, the reported uncertainty is the 1σ standard error of the mean. Overdispersion represents the variance that cannot be explained by the analytical uncertainty (cf. Equation (1)).

The intra-laboratory overdispersions are indeed larger than the analytical uncertainties, and may reach up to 14% at 2σ (Table 3). Although there may be multiple causes for this dispersion, it is likely that U and Th heterogeneities caused “nugget-effects” of radiogenic ^4He variations in this 180 Ma old dolerite (Schaefer et al., 2015).

5.2. Global ^3He and ^4He means and inter-laboratory variability

Using the weighted means reported from each lab, it is possible to calculate an overall inter-laboratory weighted mean of $(5.02 \pm 0.12) \times 10^9$ at g^{-1} (2σ) for the ^3He concentration of CRONUS-P (Table 3). The associated MSWD of this mean however reaches 19, which strongly suggests that there are some systematic differences between laboratories (Fig. 1). The inter-laboratory overdispersion is indeed 5.2% at 2σ (Table 3). This value is larger than the analytical errors reported by each laboratory (Fig. 1; Table 3). However, it is worth noting that the 6 lab results are characterized by a bimodal distribution: 4 labs yield ^3He mean concentrations clustering at $\sim 4.9 \times 10^9$ at g^{-1} , while 2 other labs have ^3He mean clustering at $\sim 5.2 \times 10^9$ at g^{-1} , i.e. 6% above the four other labs (Fig. 1B). The arithmetic mean of the 6 labs is 5.01×10^9 at g^{-1} , with a standard deviation of 3% (Fig. 1).

Although the CRONUS-P material is characterized by some ^4He heterogeneities, it is also possible to estimate the inter-lab variance for ^4He . The calculated inter-laboratory overdispersion is 10.4% at 2σ , a value that is quite high, indicating that some inter-laboratory systematic differences also exist for ^4He (Fig. 2; Tables 2 and 3).

5.3. Potential sources of inter-lab variability

Several sources of inaccuracy may contribute to the ^3He and ^4He differences observed between the 6 labs. The measurement of noble gas isotope ratios may indeed be subject to several potential biases, and there are still a larger number of potential inaccuracies attached to the determination of helium abundances. We assume that uncertainties associated with weighing CRONUS-P are negligible compared with those determining ^3He amounts. Unrecognized systematic errors can thus originate from:

- *Estimate of the initial pressure in the standard tanks.* This determination must avoid any source of inaccuracy. Potential sources are non-linear behavior of capacitance manometers, or use of poorly calibrated volumes during dilution of the calibration gas into the reservoir.
- *Tank depletion after several standard iterations.* Many labs use a large bottle of gas standard from which a small aliquot is extracted regularly (daily or more frequently) to establish the sensitivity of the mass spectrometer. It is essential to know both the volume of this aliquot and that of the standard bottle. This permits a correct calculation of the amount of standard gas

remaining in the bottle with time. However, as most systems have very small aliquot/standard reservoir ratios (typically 10^4), this source of systematic error is likely only significant after several thousand aliquots. Nevertheless, modern automated extraction systems can easily use $>10^3$ standard aliquots per year.

- *Volume calibration of the extraction and purification line.* Given the relatively high pressure in a high temperature furnace ($>10^{-5}$ mbar), it is often necessary to split the extracted gas to remove the gas fraction being in the “dirty” part of the line. This implies different dilution procedures between sample and gas standard, which requires a precise and accurate knowledge of the volumes involved. Volumes are generally determined using vacuum gauges (usually capacitance manometers), at pressure levels ranging between a few mbar to 1 bar. However, adsorption on the internal volume surfaces may induce apparent non-linear response of the gauge, leading to erroneous volume determinations.
- *Pressure effects on the linearity of the mass spectrometer sensitivity.* Several studies have shown that the amount of helium present in the mass-spectrometer may change the respective sensitivities of ^3He and ^4He , and, hence, the measured $^3\text{He}/^4\text{He}$ ratio (Burnard and Farley, 2000; Mabry et al., 2012, 2013; Sano et al., 2008). This effect may be higher than 5%, between ^4He beams of a few mV and larger beams of several V (Sano et al., 2008). The mechanisms producing this pressure dependence are still difficult to understand. It has been hypothesized that such instrumental fractionation may occur in a Nier-type source due to a space-charge effect on the ionization efficiency (Burnard and Farley, 2000; Sano et al., 2008). Alternative explanations involve the flight tube or the detectors of the mass-spectrometers (Sano et al., 2008). Moreover, this pressure effect seems to vary significantly from one mass-spectrometer to another (Sano et al., 2008) and is also sensitive to the source settings (Burnard and Farley, 2000; Mabry et al., 2013). For these reasons, it is important to ensure that similar amounts of gas standard and samples are introduced in the mass-spectrometer, and that there is no difference in the purity of the He between standards and samples in order to reduce such pressure effects. However, this procedure often requires the use of gas standards splits, and its accuracy can thus be affected by volume calibration bias.
- *Variations of the absolute $^3\text{He}/^4\text{He}$ atmospheric ratio.* Many labs prepare and use internal standards that are generally enriched in ^3He compared to atmospheric helium. It is necessary to cross-calibrate these standards against a gas of known composition to establish their absolute contents of helium and their $^3\text{He}/^4\text{He}$ ratio. For simplicity, this cross-calibration is often performed using aliquots of atmospheric helium. However, only three studies have tried to establish the absolute $^3\text{He}/^4\text{He}$ ratio in air, and two of these estimates are separated by more than 4%.

Analyzing the atmosphere of Saint Petersburg (Russia), Mamyrin et al. (1970) established a value of 1.399×10^{-6} , while Sano et al. (1988) later reported a ratio of 1.34×10^{-6} using air collected in the center of Tokyo (Japan). The value that has been the most extensively quoted and used as a reference is 1.384×10^{-6} , determined by Clarke et al. (1976) from an atmosphere sample collected in Ontario (Canada). But we cannot rule out the possibility that routinely used helium standards were initially calibrated using different values of the absolute atmospheric $^3\text{He}/^4\text{He}$ ratio. The bias induced by this effect may reach 4%. Additionally, temporal and spatial variations of the $^3\text{He}/^4\text{He}$ air ratio are also proposed by several authors, but these effects are probably smaller than 2% in the Northern Hemisphere, over the past 40 years (Sano et al., 2010).

In the worst case, all these potential sources of systematic uncertainties may accumulate, leading to under or over-estimates, and to inter-laboratory discrepancies larger than 5%. Such amplitude is comparable with the 7% difference between the lowest and the highest determinations of the ^3He concentrations of CRONUS-P (Table 2; Fig. 2).

6. Recommendations and conclusion

This article has not been written under the pretense of deciding which lab produces the more accurate ^3He and ^4He measurements, but rather it aims to quantify, report and openly discuss the sources of inter-laboratory variability in these determinations. Despite the variability, it is possible to calculate a weighted mean of the ^3He concentration in CRONUS-P from the six labs involved, yielding $(5.02 \pm 0.12) \times 10^9$ (2σ) at g^{-1} and an inter-lab overdispersion of 5.6% (2σ). This value may change in the future, due to progress in resolving potential sources of systematic errors. ^4He measured in CRONUS-P is characterized by a larger variability than ^3He , and by an inter-lab global mean of $(3.60 \pm 0.18) \times 10^{13}$ at g^{-1} (2σ) and an inter-lab overdispersion of 10.4% (at 2σ).

The corresponding $^3\text{He}/^4\text{He}$ ratios measured in this CRONUS-P material yield a global mean of 102 ± 4 Ra (2σ) ($\text{Ra} = 1.384 \times 10^{-6}$), with an overdispersion of 8.4% (2σ). This suggests that this material could also be used as a rock standard for helium isotopic studies.

We recommend that laboratories reporting measurement of cosmogenic ^3He concentrations, for dating or production rate calibrations, should also analyze and report their own measurement of ^3He in CRONUS-P: this procedure will effectively eliminate inter-laboratory calibration errors thereby allowing external precision of cosmogenic ^3He determination to be of the order 1–2%. This will also be extremely useful for future studies seeking to homogenize existing data and to improve the accuracy and the precision of the cosmogenic ^3He dating tool. However, it can lead to erroneous conclusions if the CRONUS-P results presented in this article are used to recalculate all the previously published ^3He data by the 6 participating labs. Indeed, the absolute calibration of one given laboratory may have evolved over time. This consideration reinforces the necessity that future studies provide CRONUS-P results with each batch of newly released ^3He data.

Acknowledgements

This work was funded as part of the CRONUS-Earth program by the US National Science Foundation, grant EAR0345150. Pieter Vermeesch and an anonymous reviewer are thanked for their constructive comments that improved the submitted manuscript. This is CRPG contribution 2327.

Editorial handling by: Fred Phillips

References

- Ackert, R.P., Singer, B.S., Guillou, H., Kaplan, M.R., Kurz, M.D., 2003. Long-term cosmogenic ^3He production rates from $^{40}\text{Ar}/^{39}\text{Ar}$ and K–Ar dated Patagonian lava flows at 47°S. *Earth Planet. Sci. Lett.* 210, 119–136.
- Blard, P.-H., Bourlès, D., Lavé, J., Pik, R., 2008. In situ cosmogenic ^{10}Be in olivines and pyroxenes. *Quat. Geochronol.* 3, 196–205.
- Blard, P.-H., Lavé, J., Sylvestre, F., Placzek, C., Claude, C., Galy, V., Condom, T., Tibari, B., 2013. Cosmogenic ^3He production rate in the high tropical Andes (3800 m, 20°S): implications for the local last glacial maximum. *Earth Planet. Sci. Lett.* 377–378, 260–275.
- Blard, P.-H., Pik, R., Lavé, J., Bourlès, D., Burnard, P.G., Yokochi, R., Marty, B., Trusdell, F., 2006. Cosmogenic ^3He production rates revisited from evidences of grain size dependent release of matrix sited helium. *Earth Planet. Sci. Lett.* 247, 222–234.
- Bruno, L.A., Baur, H., Graf, T., Schlüchter, C., Signer, P., Wieler, R., 1997. Dating of Sirius Group tillites in the Antarctic Dry Valleys with cosmogenic ^3He and ^{21}Ne . *Earth Planet. Sci. Lett.* 147, 37–54.
- Burnard, P.G., Farley, K.A., 2000. Calibration of pressure dependent sensitivity and discrimination in Nier-type noble gas ion sources. *Geochem. Geophys. Geosyst.* 1 <http://dx.doi.org/10.1029/2000GC000038>.
- Clarke, W.B., Jenkins, W.J., Top, Z., 1976. Determination of tritium by mass-spectrometric measurement of ^3He . *Int. J. Appl. Radiat. Isot.* 27, 515–522.
- Craig, H., Lupton, J.E., Welhan, J.A., Poreda, R., 1978. Helium isotope ratios in Yellowstone and Lassen Park volcanic gases. *Geophys. Res. Lett.* 5, 897–900.
- Fenton, C.R., Mark, D.F., Barford, D.N., Niedermann, S., Goethals, M.M., Stuart, F.M., 2013. $^{40}\text{Ar}/^{39}\text{Ar}$ dating of the SP and Bar Ten lava flows AZ, USA: laying the foundation for the SPICE cosmogenic nuclide production-rate calibration project. *Quat. Geochronol.* 18, 158–172.
- Fleming, T.H., Heimann, A., Foland, K.A., Elliot, D.H., 1997. $^{40}\text{Ar}/^{39}\text{Ar}$ geochronology of Ferrar Dolerite sills from the Transantarctic Mountains, Antarctica: implications for the age and origin of the Ferrar magmatic province. *Geol. Soc. Am. Bull.* 109, 533–546.
- Foeken, J.P.T., Stuart, F.M., Dobson, K.J., Persano, C., Vilbert, D., 2006. A diode laser system for heating minerals for (U–Th)/He chronometry. *Geochem. Geophys. Geosyst.* 7 <http://dx.doi.org/10.1029/2005GC001190>.
- Goehring, B.M., Kurz, M.D., Balco, G., Schaefer, J.M., Licciardi, J., Lifton, N.A., 2010. A reevaluation of in situ cosmogenic ^3He production rates. *Quat. Geochronol.* 5, 410–418.
- Ivy-Ochs, S., Kubik, P.W., Masarik, J., Wieler, R., Bruno, L., Schlüchter, C., 1998. Preliminary results on the use of pyroxene for ^{10}Be surface exposure dating. *Schweiz. Mineral. Petrogr. Mittl.* 78, 375–382.
- Jull, A.J.T., Scott, E.M., Bierman, P., 2015. The CRONUS-Earth inter-comparison for cosmogenic isotope analysis. *Quat. Geochronol.* 26, 3–10.
- Mabry, J., Burnard, P.G., Blard, P.H., Zimmermann, L., 2012. Mapping changes in helium sensitivity and peak shape for varying parameters of a Nier-type noble gas ion source. *J. Anal. At. Spectrom.* 27, 1012–1017.
- Mabry, J., Lan, T., Burnard, P.G., Marty, B., 2013. High-precision helium isotope measurements in air. *J. Anal. At. Spectrom.* 28, 1903.
- Mamyrin, B.A., Anufriyev, G.S., Kamenskiy, I.L., Tolstikhin, I.N., 1970. Determination of the isotopic composition of atmospheric helium. *Geochem. Int. USSR* 7, 498–505.
- Margerison, H.R., Phillips, W.M., Stuart, F.M., Sugden, D.E., 2005. Cosmogenic ^3He concentrations in ancient flood deposits from the Coombs Hills, northern Dry Valleys, East Antarctica: interpreting exposure ages and erosion rates. *Earth Planet. Sci. Lett.* 230, 163–175.
- Matsuda, J., Matsumoto, T., Sumino, H., Nagao, K., Yamamoto, J., Miura, Y., Kaneoka, I., Takahata, N., Sano, Y., 2002. The $^3\text{He}/^4\text{He}$ ratio of the new internal He Standard of Japan (HESJ). *Geochem. J.* 36, 191–195.
- McIntyre, G.A., Brooks, C., Compston, W., Turek, A., 1966. Statistical assessment of Rb–Sr isochrons. *J. Geophys. Res.* 71, 5459.
- Merchel, S., Bremser, W., Akhmadaliev, S., Arnold, M., Aumaitre, G., Bourlès, D.L., Braucher, R., Caffee, M., Christl, M., Fifield, L.K., Finkel, R.C., Freeman, S.P.H.T., Ruiz-Gómez, A., Kubik, P.W., Martschini, M., Rood, D.H., Tims, S.G., Wallner, A., Wilcken, K.M., Xu, S., 2012. Quality assurance in accelerator mass spectrometry: results from an international round-robin exercise for ^{10}Be . *Nucl. Instrum. Methods Phys. Res. B* 289, 68–73.
- Niedermann, S., Bach, W., Erzinger, J., 1997. Noble gas evidence for a lower mantle component in MORBs from the southern East Pacific Rise: decoupling of helium and neon isotope systematics. *Geochim. Cosmochim. Acta* 61, 2697–2715.
- Niedermann, S., Schaefer, J.M., Wieler, R., Naumann, R., 2007. The production rate of cosmogenic ^{38}Ar from calcium in terrestrial pyroxene. *Earth Planet. Sci. Lett.* 257, 596–608.
- Patterson, D.B., Farley, K.A., 1998. Extraterrestrial ^3He in seafloor sediments: Evidence for correlated 100 kyr periodicity in the accretion rate of interplanetary dust, orbital parameters, and Quaternary climate. *Geochim. Cosmochim. Acta* 62, 3669–3682.
- Sano, Y., Furukawa, Y., Takahata, N., 2010. Atmospheric helium isotope ratio: possible temporal and spatial variations. *Geochim. Cosmochim. Acta* 74, 4893–4901.
- Sano, Y., Tokutake, T., Takahata, N., 2008. Accurate measurement of atmospheric helium isotopes. *Anal. Sci.* 24, 521–525.
- Sano, Y., Wakita, H., Xu, S., 1988. Atmospheric helium isotope ratio. *Geochem. J.* 22, 177–181.

- Schaefer, J.M., Ivy-Ochs, S., Wieler, R., Leya, J., Baur, H., Denton, G.H., Schluchter, C., 1999. Cosmogenic noble gas studies in the oldest landscape on earth: surface exposure ages of the Dry Valleys, Antarctica. *Earth Planet. Sci. Lett.* 167, 215–226.
- Schaefer, J.M., Winckler, G., Blard, P.-H., Balco, G., Shuster, D.L., Friedrich, R., Schluechter, C., 2015. Performance of CRONUS-P – a pyroxene reference material for helium isotope analysis. *Quat. Geochronol.* (in press).
- Stone, J.O., 2000. Air pressure and cosmogenic isotope production. *J. Geophys. Res. Solid Earth* 105, 23753–23759.
- Vermeesch, P., Balco, G., Blard, P.-H., Dunai, T.J., Kober, F., Niedermann, S., Shuster, D.L., Strasky, S., Stuart, F.M., Weiler, R., Zimmermann, L., 2015. Inter-laboratory comparison of cosmogenic ^{21}Ne in quartz. *Quat. Geochronol.* 26, 20–28.
- Welhan, J.A., Poredai, R.J., Rison, W., Craig, H., 1988. Helium isotopes in geothermal and volcanic gases of the western United States, I. Regional variability and magmatic origin. *J. Volcanol. Geotherm. Res.* 34, 185–199.
- Williams, A.J., Stuart, F.M., Day, S.J., Phillips, W.M., 2005. Using pyroxene microphenocrysts to determine cosmogenic ^3He concentrations in old volcanic rocks: an example of landscape development in central Gran Canaria. *Quat. Sci. Rev.* 24, 211–222.
- Winckler, G., Anderson, R.F., Schlosser, P., 2005. Equatorial Pacific productivity and dust flux during the mid-Pleistocene climate transition. *Paleoceanography* 20, PA4025.
- Zimmermann, L., Blard, P.H., Burnard, P.G., Medynski, S., Pik, R., Puchol, N., 2012. A new single vacuum furnace design for cosmogenic ^3He dating. *Geostand. Geoanalytical Res.* <http://dx.doi.org/10.1111/j.1751-908X.2011.00145.x>.