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Performance of CRONUS-P – A pyroxene reference material for helium isotope analysis

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ABSTRACT

Helium isotope analyses are central to modern earth science and measured by many noble gas laboratories around the globe (Burnard, 2013; Wieler et al., 2002), spanning a wide spectrum of fundamental research – from identifying primordial reservoirs in the Earth mantle to paleoclimate reconstructions. The CRONUS-Earth initiative included the manufacturing, distribution and analysis of a pyroxene reference material (CRONUS-P) that was designed to be useful for internal reliability control of ^{3}He measurements within a few percent and potentially for ^{4}He on a higher level of uncertainty.

This short paper describes the CRONUS-P material and its performance as ^{3}He and ^{4}He reference sample for noble gas laboratories. The companion paper by Blard et al. 2015 describes in depth the inter-laboratory helium isotope experiment within CRONUS-Earth.

We show normalized helium isotope data of CRONUS-P measured at three different noble gas laboratories. Data from all three laboratories show no relation between helium isotope concentrations and sample mass, implying that the material is homogeneous. The data show that CRONUS-P is useful as an internal standard for ^{3}He within better 2% (1σ) and for ^{4}He within better 10%.

1. Introduction

Helium isotopes are widely used as fundamental tracers in Earth Science (Burnard, 2013; Wieler et al., 2002). Here we present a new mineral reference material that could improve the inter-laboratory consistency of helium isotope measurements. CRONUS-P is a high-purity pyroxene separate from a Ferrar dolerite boulder sampled at the summit of Mt Feather (160.4°E/77.9°S/2555 m), Dry Valleys, Antarctica. First helium (and neon) isotope measurements from pyroxenes separated from this rock were done at the noble gas laboratory at ETH Zuerich and published in (Schäfer et al., 1999), under the sample name NXP 93*52. During the preparation it became apparent that the pyroxenes were of exceptional purity and very easy to separate compared to all other pyroxenes separated from Ferrar Dolerite by (Schäfer, 2000; Schäfer et al., 1999). The initial measurement showed very high cosmogenic helium (and neon) concentrations (minimum helium and neon exposure ages of 4.5 Ma at 2550 m altitude), and exceptionally low non-cosmogenic helium and neon backgrounds, resulting in some of the highest ^{3}He/^{4}He (~100 R_a, with R_a the atmospheric ^{3}He/^{4}He ratio of 1.384×10^{-6} (Clarke et al., 1976) and ^{21}Ne/^{20}Ne (0.5) ratios reported from surface rocks. Pyroxene samples from this boulder were again measured for helium isotopes at the noble gas laboratory at the GFZ Potsdam, Germany (Niedermann et al., 2007) and at the noble gas laboratory at the Lamont-Doherty Earth Observatory (Schaefer et al., 2006). All these analyses relied on indpendently prepared pyroxene separates from the same rock, and show overall consistent helium isotope concentrations.

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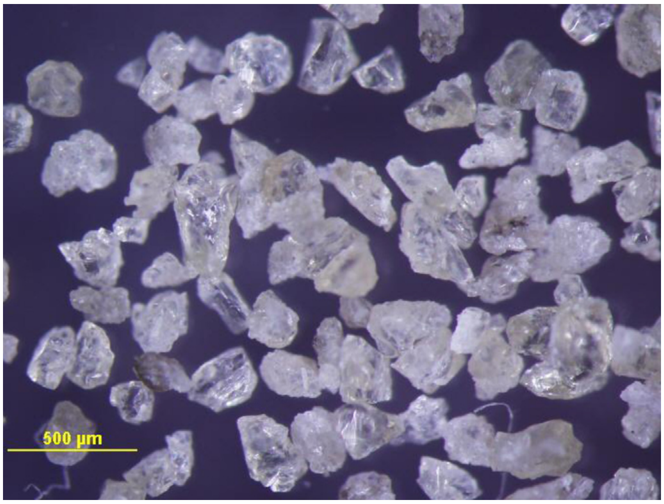

Fig. 1. Pyroxenes of the CRONUS-P reference material produced from the NXP 93*52 sample. Minerals appear clean, without accessory mineral inclusions.

2. Methods

To manufacture the CRONUS-P material for the CRONUS-Earth initiative, we used the top 1 cm of the entire surface of boulder NXP 93*52 to separate ~100 g of ultra-clean, homogenized pyroxenes. To separate the large amount of pyroxene, we followed the protocol given by Schäfer et al. (1999), which includes crushing the whole rock to 125–310 µm, leaching in diluted hydrochloric acid to remove iron stain of the pyroxene grains, heavy liquid separation at 3.2 g/cm^3 to remove the lighter minerals such as feldspars, and magnetic separation (FRANTZ magnetic separator, 20° forwards tilt, 15° sideward tilt) using the mineral fraction that is non-magnetic at 0.1 A, but magnetic at 0.4 A FRANTZ field strength. Careful inspection of the pyroxene separate under the binocular indicated high purity (Fig. 1). However small accessory mineral inclusions on the µm level could not be excluded (and are present in pyroxene separates from most Ferrar Dolerite samples). We subsequently used a 4-way mineral splitter iteratively to produce ~20 CRONUS-P fractions at 5 g pyroxene each. The major element composition was determined by ICP-MS (see Table 1), and the CRONUS-P pyroxene reference material samples were sent to interested laboratories.

The eruption age of Ferrar Dolerite is determined to about 177 Ma ago (Fleming et al., 1997). Combined with the Li concentration measured in the CRONUS-P pyroxenes, we estimate the amount of nucleogenic ^{3}He produced by the radiogenic thermal neutron capture on ^{6}Li (n,α) ^{3}He: this yields less than 10^5 at g^{-1}, an amount which is negligible compared to the cosmogenic ^{3}He content of this material (~5×10^9 at g^{-1}; Blard et al., 2015).

3. Results and discussion

For the purpose of evaluating the performance of the CRONUS-P material as reference sample, we give ^{3}He, ^{4}He and ^{3}He/^{4}He data measured at the noble–gas laboratories at the Lamont-

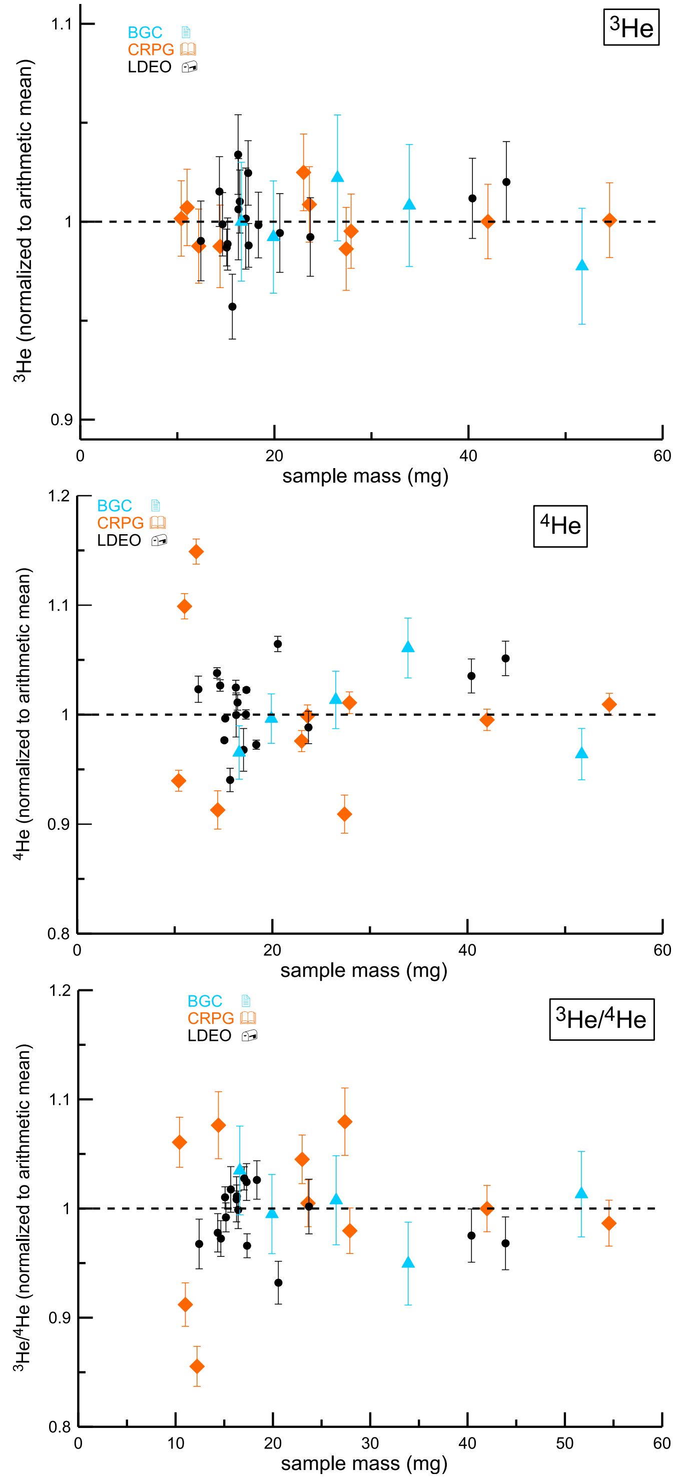

Fig. 2. CRONUS-P helium Isotope data with 1σ errors (normalized per laboratory to the respective arithmetic mean) as a function of sample mass. See Blard et al. 2015 for full data details of an inter-laboratory data comparison.

Table 1
Major Element Composition of the CRONUS-P pyroxene material.

Conc. in pyroxene	Mn ppm	Fe ppm	Mg ppm	Si ppm	Al ppm	Ca ppm	Ti ppm	Na ppm	K ppm	U ppb	Li ppb	Th ppb
CRONUS-P	1900	82,400	158,000	228,000	16,040	43,700	890	1600	320	30	4100	260

Please note that the concentrations are given in ppm except for U, Li and Th concentrations which are given in ppb.

Doherty Earth Observatory (LDEO; (Winckler et al., 2005)), the Centre de Recherches Pétrographiques et Géochimiques (CRPG, Nancy, France) and the Berkeley Geochronology Center (BGC), normalized to their respective arithmetic means. The accompanying paper by Blard et al. 2015 discusses in detail the helium isotope inter-laboratory comparison based on the CRONUS-P data.

Fig. 2 shows the normalized helium isotope data for a range of sample masses (10–55 mg). The ^{3}He data of all three laboratories show a high level of internal consistency, with a standard error of the mean smaller than 2% for all three laboratories. The scatter among the CRONUS-P ^{4}He analyses is slightly higher, with the standard error of the mean smaller than 10% for all three laboratories. Small mineral inclusions or accessory minerals attached to the pyroxenes such as zircons or monazite, that are common in Ferrar Dolerite and known to contain a lot radiogenic ^{4}He, may increase the radiogenic ^{4}He, and we expected that these inclusions and accessory minerals introduce considerable scatter in the ^{4}He concentrations. However, the reproducibility observed in each of the three data sets implies that the impurities and accessory minerals in the CRONUS-P pyroxenes only slightly increase the ^{4}He concentration variability and that CRONUS-P might be useful also as a ^{4}He reference material. Finally, we do not see any trend in the ^{3}He concentration measurements towards smaller (or larger) sample sizes, although we included samples as small as 10 mg. There might be a slight trend towards higher scatter in the ^{4}He concentration measurements of very small CRONUS-P samples (<15 mg) in the 10–15% range.

4. Conclusions

Taken together, we conclude that the CRONUS-P material documents high purity and can be considered homogeneous, and thus useful for ^{3}He replicate measurements within a few % for sample sizes of 10 mg and potentially even smaller. The internal consistency of the CRONUS-P ^{4}He measurements is slightly worse, and we would recommend to use sample of 15 mg or more. The CRONUS-P reference material should be useful for noble gas laboratories as internal long-term consistency monitor of helium isotope measurements and for the wider helium community as tool to execute inter-laboratory experiments such as presented in the companion paper by Blard et al. 2015.

CRONUS-P material is held at Lamont (contact J. Schaefer). This is an outcome of the CRONUS-Earth project. The value of the archive depends on the quality of the test materials and on the willingness of labs to participate, and report their results.

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