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Inter-comparison of cosmogenic in-situ $^3$He, $^21$Ne and $^{36}$Cl at low latitude along an altitude transect on the SE slope of Kilimanjaro volcano (3°S, Tanzania)

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Abstract

Because the intensity and energy spectrum of the cosmic ray flux are affected by atmospheric depth and geomagnetic-field strength, cosmogenic nuclide production rates increase considerably with altitude and to a lesser degree with latitude. The scaling methods used to account for spatial variability in production rates assume that all cosmogenic nuclides have the same altitude dependence. In this study we evaluate whether the production rates of cosmogenic $^{36}$Cl, $^3$He and $^{21}$Ne change differently with altitude, which is plausible due to the different threshold energies of their production reactions. If so, nuclide-specific scaling factors would be required.

Concentrations of the three cosmogenic nuclides were determined in mafic phenocrysts over an altitude transect between 1000 and 4300 m at Kilimanjaro volcano ($3°$ S). Altitude-dependence of relative production rates was assessed in two ways: by determination of concentration ratios and by calculation of apparent exposure age ratios for all nuclide pairs. The latter accounts for characteristics of $^{36}$Cl that the stable nuclides $^3$He and $^{21}$Ne do not possess (radioactive decay, high sensitivity to mineral composition and significant contributions from production reactions other than spallation). All ratios overlap within error over the entire transect, and altitudinal variation in relative production rates is not therefore evident. This suggests that nuclide-specific scaling factors are not required for the studied nuclides at this low latitude location. However, because previous studies have documented anomalous altitude-dependent variations in $^3$He production at mid-latitude sites, the effect of latitude on cross-calibrations should be further evaluated.

We determined cosmogenic $^{21}$Ne/$^3$He concentration ratios of $0.1864 \pm 0.0085$ in pyroxenes and $0.377 \pm 0.018$ in olivines, agreeing with those reported in previous studies.
Despite the absence of independently determined ages for the studied lava surfaces, the consistency in the data set should enable progress to be made in the determination of the production rates of all three nuclides as soon as the production rate of one of the nuclides has been accurately defined.

To our knowledge this is the first time that $^{36}\text{Cl}$ has been measured in pyroxene. The Cl extraction method was validated by measuring $^{36}\text{Cl}$ in co-existing plagioclase phenocrysts in one of the samples.

Key words: Cosmogenic nuclides; Chlorine-36, Helium-3, Neon-21; Cross-calibration; Pyroxene; Olivine; Kilimanjaro; Altitude dependent scaling
1. Introduction

Accurate application of the surface-exposure dating technique, using terrestrial cosmogenic nuclides (TCN) such as $^3$Cl, $^3$He, $^21$Ne, $^10$Be or $^{26}$Al, requires precise and accurate knowledge of the production rate of the nuclide of interest (the number of atoms produced per gram of target material per year) and the variation of this production rate in space and time (scaling).

Reference production rates have been determined to allow application of the TCN method anywhere on Earth (see review in Gosse and Phillips, 2001). These are extrapolated to a particular location using scaling factors calculated according to one of the published scaling models (e.g. Stone, 2000, Dunai, 2001a, Desilets and Zreda, 2003, Lifton et al., 2005). Experimental calibrations of reference production rates are made by (1) measuring the concentration of the nuclide of interest in a geological sample from an independently dated surface at a specific geographic location, and (2) scaling the calculated time-integrated local production rate to the traditional reference position at sea-level and high latitude (SLHL) and to the present (Gosse and Phillips, 2001).

It is clearly imperative that scaling methods accurately quantify the spatial and temporal variability of TCN production on Earth. Recently however, some authors have cast doubt on our understanding of this variability, suggesting it could be one of the main causes for inconsistencies between calibrated SLHL production rates, thereby constituting a major source of uncertainty in TCN exposure ages (Balco et al., 2008, 2009, Schimmelpfennig et al., 2011).

Published scaling methods generally assume that the scaling factor for a particular type of nuclear-reaction (neutron- or muon-induced) is valid for all TCN and independent of the target element on which the reaction occurs. For example, at any given location production of $^7$Be by spallation of Si and O is scaled using the same factor as production of $^3$Cl by spallation
of Ca. However, this approach is controversial and the need for nuclide specific scaling factors, as first discussed by Dunai (2001b), is currently being debated. The argument is based on two aspects of TCN production. First, excitation functions for the various TCN production reactions are known to be different (e.g. Desilets et al., 2006, Amidon et al., 2008 and references therein). This means that the threshold energies (minimum energies of secondary nucleons required for the reactions) and cross sections (probabilities of the occurrence of the reaction at a certain nucleon energy) differ between the various production reactions. Second, it has been hypothesized that the energy spectrum of the secondary nucleons shifts towards lower energies with increasing atmospheric depth (Desilets and Zreda, 2003). For example, the threshold energy for the production of $^{36}$Cl from spallation of K (about 5 MeV) is lower than that from spallation of Ca (about 20 MeV; see excitation functions in Fig. 2 in Desilets et al., 2006). It might therefore be expected that the ratio of $^{36}$Cl production from K to that from Ca will increase with increasing atmospheric depth (i.e. decreasing altitude). If so, nuclide- and even target-element-specific scaling factors would be needed.

One way of assessing TCN production and the global consistency in scaling is to determine relative production rates of different TCN in geomorphic surfaces. These cross-calibrations do not necessarily require that surfaces be independently dated nor perfectly preserved. Measurements of multiple TCN in the same or in different mineral phases from a single sample can be used to refine poorly known SLHL production rates using TCN with well-constrained production rates (e.g. Amidon et al., 2009, Balco and Shuster, 2009, Goethals et al., 2009). In addition, performing cross-calibrations over a range of altitudes, latitudes or exposure times enables assessment of any spatial and/or temporal dependence in the production of the different TCN. For example, Gayer et al. (2004) measured $^3$He/$^10$Be in Himalayan garnets over an altitude transect between 3000 and 4600 m and determined production ratios higher than previously documented (Cerling and Craig, 1994). The apparent
He overproduction, which seemed to be prevalent at high altitude, was tentatively attributed to a significant difference in the threshold energies for the production of the two nuclides. More recently, Dunai et al. (2007) considered a second cosmogenic 3He production mechanism, via low-energy neutron capture on 6Li, to explain the higher 3He production reported in Gayer et al. (2004). Some later studies were unable to identify an altitude-dependence unique to 3He production (Blard et al., 2006, Vermeesch et al., 2009). In others, higher than expected apparent He production rates were also inferred: at high altitudes in the Himalayas (Amidon et al., 2008) and on the Puna plateau in Argentina (Niedermann et al., 2009), and even at lower altitudes in the Coso Volcanic field and the Bishop Tuff (both in California, USA; Amidon et al., 2009, Niedermann et al., 2009).

In this study, we evaluate whether relative production rates of TCN change with altitude at a low-latitude site (3°S) and if overproduction of 3He at high altitudes occurs. We cross-calibrate production of 3He, 21Ne and 36Cl in lava-flow and glacial surfaces outcropping over an altitude profile between 1000 and 4300 m, on the slopes of Mt. Kilimanjaro, Tanzania. All three nuclides can be measured in clinopyroxene phenocrysts and this mineral phase provides the most complete data set in this study. In addition, 3He was measured in olivine phenocrysts in all samples except one, and 21Ne was measured in olivines at two different altitudes. To our knowledge, this is the first time that 36Cl has been measured in a mafic mineral phase. To validate the method, 36Cl was measured in plagioclase phenocrysts coexisting with pyroxenes in one of the samples.
2. Geological setting and sampling

Based on an initial project objective of calibrating absolute and relative production rates of TCN at a low-latitude site and over a large altitude transect, sampling was undertaken in 2005 at Mount Kilimanjaro, Tanzania (3°S) (Fig. 1). This large shield volcano, Africa's highest mountain (5892 m), is located at the eastern end of the Ngorongoro-Kilimanjaro Volcanic Belt, which forms one arm of the triple rift-system that characterizes the eastern branch of the East African Rift System. Kilimanjaro consists of three NW-SE aligned volcanic peaks, Shira (3962 m), Kibo (5892 m) and Mawenzi (5149 m), constructed in multiple phases. The first phase took place between 2.5 Ma and 1.9 Ma at the Shira vent (Nonnotte et al., 2008). A large sector collapse signalled the end of this phase, after which volcanic activity shifted eastwards to the Kibo and Mawenzi peaks, at around 1 Ma. Activity at Mawenzi ceased around 500 ka, but continued at Kibo with two major periods of volcanic activity occurring between 460 ka and 340 ka. The final stages of volcanism at Kilimanjaro consisted of the eruption of basaltic flows and scoria from small parasitic cones located on the volcano flanks, between around 200 ka and 150 ka (Nonnotte et al., 2008).

For this study, we principally targeted cones and lava flows from this last volcanic period in a region known as the Rombo Zone, located on the south-eastern flank, south of Mawenzi Peak (Downie and Wilkinson, 1972). This zone comprises olivine- and pyroxene-rich basanitic and ankaramitic flows erupted from parasitic cones distributed over a large elevation range, from < 1500 to > 4500 m. Suitable exposure of lava-flow surfaces is limited however between 1700 and 2500 m due to the presence of a dense tropical rainforest (Fig. 1). Flow-top preservation is also compromised above ~ 3700 m as a result of significant glacial activity during the Quaternary (Shanahan and Zreda, 2000).
While an effort was made to sample pristine flow-top features for absolute calibration of TCN production rates, at many sites this was not possible. Between 2700 and 3200 m, well-preserved ropy tops of lava-flows (Fig. A1 in Appendix) out-crop at the bases of parasitic cones. However, accessing the inner, degassed parts of the flow in order to extract rock suitable for precise Ar/Ar or K/Ar dating was difficult, and most flows were also too small and thin to have well developed massive interiors. As such, our efforts to obtain independent ages and absolute production rates for these flows were unsuccessful. For the parasitic cones erupted in the Rombo Zone, the only precise published eruption ages are K/Ar ages of 165 ± 5 ka and 195 ± 5 ka for two basaltic flows (Nonnotte et al., 2008), but their surfaces were not appropriate for exposure dating. For the investigation of relative TCN production rates, however, it is possible to use surfaces, such as glacially-polished surfaces, for which the eruption age of the lava-flow is not necessarily equal to the apparent exposure age.

Eight surface samples were collected at six different altitudes between 1000 and 4300 m (Table 1 and Fig. 1). Half of the samples were taken from well-preserved surfaces of two lava-flows (TZ10, TZ12, TZ13 and TZ14), two from eroding surfaces (TZ09, TZ17) and two from glacially polished surfaces (TZ15, TZ19). Based on field observations, the maximum rock thickness removed from the lava-flow at the lowest sample site at 1013 m altitude (TZ09) is estimated to be 30 cm. The surface of sample TZ17 also appeared to be slightly degraded in the field and the outcrop was surrounded by scoria and gravel deposits. Sample TZ15 was taken from a glacially polished doleritic dyke bearing large plagioclase laths in addition to pyroxene and minor olivine. A formation age of 527 ± 3 ka was determined for the dyke by 39Ar/40Ar dating (see Appendix). The exposure age of the surface can be expected to be significantly younger. The highest sample (TZ19) also exhibits slight glacial polishing. More detailed descriptions and photographs of sample sites are given in the Appendix.
3. Methods

3.1 Physical sample preparation

Prior to sample preparation, pieces of whole rock from each surface were set-aside for thin-section preparation and bulk-rock composition analyses. For TCN analyses, the top 5 to 10 cm of each whole rock sample was sawn off, then crushed and wet-sieved to remove dust particles and the finest grain sizes (< 125 µm). A hand-magnet was passed over all fractions to remove magnetic groundmass. Using a binocular microscope, olivine and pyroxene phenocrysts were hand-picked to obtain pure mineral separates, with care taken to ensure complete removal of altered crystals and crystals with adhering groundmass. For 36Cl analyses, approximately 5 to 10 g of pure pyroxene phenocrysts were handpicked from the coarsest fractions. For sample TZ15, a Frantz magnetic separator was used to separate several grams of 0.5-mm sized plagioclase phenocrysts from the more magnetic mafic minerals. Plagioclases were handpicked in order to maximize sample purity. For noble gas extractions, approximately 2 g of the coarsest pure fractions were cleaned in acetone and set aside for in vacuo crushing and determination of magmatic helium isotope ratios. For the melt extractions, up to 3 g of phenocrysts from the 0.5 to 0.7 mm size fraction were cleaned in acetone, hand-crushed and sieved to 0.1 - 0.3 mm and then re-picked and cleaned once more in acetone, to ensure the highest degree of sample purity.
3.2 Chemical $^{36}\text{Cl}$ extraction and measurement

Chemical extraction of $^{36}\text{Cl}$ was conducted at CEREGE (Aix en Provence, France). The procedure is detailed in the Appendix. Several procedural blanks were performed in order to assess cleanliness during chemical extraction and to correct sample measurements for laboratory $^{36}\text{Cl}$ and stable Cl sources.

Concentrations of $^{36}\text{Cl}$ and Cl were determined using the Lawrence Livermore National Laboratory FN accelerator mass spectrometer (LLNL-CAMS, USA). Isotope dilution (addition of a $^{35}\text{Cl}$-enriched carrier) allows simultaneous determination of $^{36}\text{Cl}$ and Cl concentrations. $^{36}\text{Cl}/^{35}\text{Cl}$ ratios were determined by normalizing to a $^{36}\text{Cl}$ standard prepared by K. Nishiizumi (Sharma et al., 1990). The stable ratio $^{36}\text{Cl}/^{37}\text{Cl}$ was also normalized to this standard, assuming a natural ratio of 3.127. Measured ratios and their uncertainties are presented in Table A1 in the Appendix. The precision of the $^{36}\text{Cl}/^{37}\text{Cl}$ ratios accounts for 2% or less (standard deviation of repeat measurements). The precision of the $^{36}\text{Cl}/^{35}\text{Cl}$ ratios ranges from 2 to 7%.

Blank $^{36}\text{Cl}/^{35}\text{Cl}$ ratios range between $7 \times 10^{-15}$ and $9 \times 10^{-15}$, and are one to two orders of magnitude lower than the sample $^{36}\text{Cl}/^{35}\text{Cl}$ ratios (Table A1). The resulting blank-corrected $^{36}\text{Cl}$ and Cl concentrations range from $(0.63$ to $5.25) \times 10^6$ atoms $^{36}\text{Cl}$ g$^{-1}$ and from 1 to 10 ppm Cl, respectively (Table A1). The $^{36}\text{Cl}$ concentrations are also given in Table 3.

3.3 Noble gas measurements

Helium measurements were carried out using the Helix Split Flight Tube and Helix Multi-collector mass spectrometers (GV instruments) at CRPG (Nancy, France) and a VG-5400 mass spectrometer at GFZ (Potsdam, Germany) (Table A3 in the Appendix shows where each measurement was made). Neon measurements were performed with the VG-5400 mass spectrometer at GFZ. While samples were degassed in a single step at CRPG, a two-step
heating procedure (900°C and 1750°C) was used at GFZ in order to separate a possible high atmospheric Ne component from the major cosmogenic fraction. Mass spectrometers were cross-calibrated by way of internal standard replication and measurement of CRONUS-EU mineral standards. Further details of these inter-comparisons and of the noble gas extraction and measurement procedures in the two laboratories can be found in the Appendix.

Determination of cosmogenic ³He concentrations

Concentrations of cosmogenic ³He in pyroxene and olivine are traditionally calculated from melt and crush measurements using an equation that corrects for the trapped (magmatic) He component (Kurz, 1986):

\[
³He_{cos} = ³He_{m} - ³He_{c} \times (³He/⁴He)_{mag}
\]

Eq. 1

where ³He_{c} is the cosmogenic ³He concentration, ³He_{m} and ³He_{c} are the concentrations of ³He and ³He measured from melt extractions and (³He/⁴He)_{mag} is the magmatic ³He/⁴He value, normally determined from phenocryst crush extractions. Because of insufficient sample material and low He yields, not all (³He/⁴He)_{mag} values in this study were determined by crushing. Isochron intercepts according to the method by Blard and Pik (2008) were used for samples TZ17 and TZ19 (Fig. A2 in Appendix). For samples TZ09 and TZ15 the value for (³He/⁴He)_{mag} was estimated. A description of the magmatic ³He/⁴He determinations is given in the Appendix.

A critical step in the determination of cosmogenic ³He is the correction for the implanted or ingrown radiogenic ³He (³He*), which may be significant even in very young rocks (e.g. Dunai and Wijbrans, 2000, Blard and Farley, 2008, Blard and Pik, 2008). In this study, for partially eroded volcanic surfaces (TZ09 and TZ17) and glacially polished surfaces (TZ15 and TZ19),
He* was estimated from whole-rock and phenocryst U and Th concentrations following Farley et al. (2006). The calculated He* was subtracted from the He, abundance prior to using Eq. 1. For TZ09, TZ17 and TZ19, the magnitude of He* correction ranged between 4% and 25% of total He,; for pyroxene and olivine replicates of TZ15 it was calculated to be 53% to 68% based on the rock formation age of ~525 ka (see discussion in section 4.2). For the non-eroded volcanic surfaces (TZ10, 12, 13, 14) we applied the R-factor correction of Blard and Pik (2008). The R-factor is a function of the production rate ratio between He* and He., which is constant over time for non-eroded volcanic surfaces, and (He/He). The R-factor values for all four samples are > 0.98 (see Table A3 in the Appendix), which corresponds to a He* correction of < 2%.

Helium data were systematically obtained for pyroxenes and olivines, except for sample TZ09 where only pyroxenes were available in sufficient quantity. Full raw data and calculated cosmogenic He concentrations are presented in Table A3. Concentrations of He, range from (9.6 to 99.8) × 10^-6 at g^-1 in pyroxenes and from (13.1 to 97.9) × 10^-6 at g^-1 in olivines. Relative He, production in the two minerals is compared in Fig. 2. As observed in previous studies (e.g. Blard et al., 2005, Fenton et al., 2009), for most samples, cosmogenic He concentrations in cogenetic olivines and pyroxenes are identical within analytical uncertainty. The exceptions are samples TZ13 and TZ10, where the concentrations in olivine are ~8% lower than in pyroxene, and sample TZ15, where a difference of ~17% is observed. The latter might be explained by an inaccurate magmatic He correction due to the high He* correction estimated for this sample.

For those sites where two samples were taken from a single flow (TZ10 and TZ12 at 2740m; TZ13 and TZ14 at 3050m) the He, concentrations in pyroxenes differ by 10% (TZ10 and TZ12) and 7% (TZ13 and TZ14) and in the olivines of TZ13 and TZ14 by 12%. The concentrations in the olivines of TZ10 and TZ12 agree within analytical uncertainties (1σ).
Determination of cosmogenic $^{21}\text{Ne}$ concentrations

In young (< 500 ka) basalts concentrations of cosmogenic $^{21}\text{Ne}$ are calculated using:

$$^{21}\text{Ne}_{\text{cos}} = \left(\frac{^{21}\text{Ne}}{^{20}\text{Ne}}\right)_{\text{m}} - \left(\frac{^{21}\text{Ne}}{^{20}\text{Ne}}\right)_{\text{tr}} \times ^{20}\text{Ne}_{\text{m}}$$  
Eq. 2

(Niedermann, 2002), where $^{21}\text{Ne}_{\text{cos}}$ is the cosmogenic $^{21}\text{Ne}$ concentration, $(^{21}\text{Ne}/^{20}\text{Ne})_{\text{m}}$ and $(^{21}\text{Ne}/^{20}\text{Ne})_{\text{tr}}$ are the measured Ne isotope ratio and concentration from melt extractions, and $(^{21}\text{Ne}/^{20}\text{Ne})_{\text{m}}$ is the trapped $^{21}\text{Ne}/^{20}\text{Ne}$ value. Most subaerially erupted basalts have a trapped Ne isotopic composition similar to that of atmospheric Ne (e.g., Dunai and Porcelli, 2002, Althaus et al., 2003), with isotope ratios of $(^{21}\text{Ne}/^{20}\text{Ne}) = 0.00296$ and $(^{21}\text{Ne}/^{20}\text{Ne}) = 0.1020$ (Eberhardt et al., 1965). It is assumed in this calculation that the nucleogenic $^{21}\text{Ne}$ component is insignificant.

Neon isotope data are presented in Table A4 and in Fig. 3. All isotope data have been corrected for isobaric interferences, mass discrimination effects and analytical blanks (see Appendix). Examination of neon measurements on a three-isotope plot enables assessment of the neon inventory in a sample. In Fig. 3, olivine and pyroxene data are defined by a linear regression line $y = 1.0539x + 0.0994$, which is the same, within error, as the spallation line for pyroxenes $(1.069 \pm 0.035)x + 0.099$ reported by Schäfer et al. (1999). The regression line passes through the air component and no nucleogenic or mantle component is identified in the heating steps. This supports our assumption that the trapped component has an atmospheric composition.

Concentrations of $^{21}\text{Ne}_{\text{cos}}$ range from $(2.79 \text{ to } 19.0) \times 10^6$ at g$^{-1}$ in pyroxenes and from $(24.8 \text{ to } 34.9) \times 10^6$ at g$^{-1}$ in olivines (Table 3). In the four samples containing cogenetic olivine and
pyroxene, \(^{21}\text{Ne}_{\text{ol}}/^{21}\text{Ne}_{\text{px}}\) range from 0.50 to 0.54. These are indistinguishable from the values predicted by modelling \(^{21}\text{Ne}_{\text{cos}}\) production rates for the olivines (Fo\(_{81}\)) and pyroxenes (En\(_{41-44}\)) in this study (\(^{21}\text{Ne}_{\text{ol}}/^{21}\text{Ne}_{\text{px}}\) = 0.50 to 0.53) using major element compositions determined by microprobe and the elemental production rates of Masarik (2002) (see Table 2c). Our values are also the same within analytical error as (i) a measured ratio of 0.49 ± 0.07, deduced from the \(^{21}\text{Ne}\) concentrations in cogenetic olivines (Fo\(_{82}\)) and pyroxenes (En\(_{44}\)) of sample 250406-16 in Fenton et al. (2009), and (ii) a calculated ratio of 0.56 ± 0.18, determined from experimentally calibrated \(^{21}\text{Ne}\) production rate values for olivines and pyroxenes (\(P^{21}\text{Ne}_{\text{cos}}(\text{Fo}_{81}) = 45 \pm 4 \text{ atoms g}^{-1} \text{ a}^{-1}\), Poreda and Cerling, 1992; \(P^{21}\text{Ne}_{\text{cos}}(\text{En}_{43-44}) = 25 \pm 8 \text{ atoms g}^{-1} \text{ a}^{-1}\), Fenton et al., 2009). The large uncertainty associated with the experimental production rate ratio is mainly a function of the 32% uncertainty in the independent lava-flow age determined in the study of Fenton et al. (2009). Despite the differences in pyroxene composition among the samples and experimental production rates, our mean value of 0.52 ± 0.02 thus seems a reasonable estimate of the relative production ratio of \(^{21}\text{Ne}\) in olivines (Fo\(_{81-82}\)) and pyroxenes (En\(_{41-44}\)).

Both olivine \(^{21}\text{Ne}_{\text{ol}}\) concentrations and pyroxene \(^{21}\text{Ne}_{\text{px}}\) concentrations of samples TZ10 and TZ12 (flow at 2740 m) agree within analytical error (1σ). Also, for the samples taken from the flow at 3050 m (TZ13 and TZ14), the olivine \(^{21}\text{Ne}_{\text{ol}}\) concentrations in the two samples are identical within uncertainties, but the concentration of \(^{21}\text{Ne}_{\text{px}}\) in the pyroxenes is 12% higher in TZ14 than in TZ13.
3.4 Major and trace elements

For the calculations of cosmogenic $^{36}$Cl, chemical compositions of the mineral aliquots and of bulk-rock were analyzed at the Service d'Analyse des Roches et des Minéraux du CNRS (CRPG, Nancy, France). Major elements were determined by ICP-OES and trace elements by ICP-MS, except Li (atomic absorption), B (colorimetry), H$_2$O (Karl Fischer titration) and Cl (spectrophotometry). Bulk-rock concentrations of the major elements and of H, Li, B, Sm, Gd, U, Th and Cl are given in Table A2. These are required for calculating low-energy neutron distributions at the land/atmosphere interface. Aliquots of the etched mineral grains, taken before their complete dissolution, represent the part of sample dissolved for $^{36}$Cl extraction and served for the analysis of the corresponding target element concentrations (Ca, K, Ti and Fe). These concentrations (Table 2a) and the Cl concentrations, determined by isotope dilution during AMS measurements (Table A1), were used to calculate $^{36}$Cl production from all production mechanisms in the dissolved samples.

U and Th concentrations in groundmass and phenocryst separates, required for calculation of $^4$He* (as described in the previous section), were measured by ICP-MS at CRPG using the procedure optimized for low abundances in (U-Th)/He dating (Carignan et al., 2001; Kraml et al., 2006). Measured U and Th concentrations are listed in Table 2b (minerals) and Table A2 (groundmass). Li concentrations in the phenocrysts are required to estimate the cosmogenic $^3$He production from thermal and epithermal neutron capture on $^6$Li. The concentrations were measured at CRPG and are listed in Table 2b.

The compositions of chemically untreated olivine and pyroxene phenocrysts were determined by electron microprobe at l’Université Henri Poincaré, Nancy (Table 2c) and served to assess dependence of $^9$Ne production on mineral composition (see previous section). Elemental production rates estimated for $^9$Ne by Masarik (2002) are also given in Table 2c.
4. Approaches to TCN cross-calibrations

A common approach for comparing different TCN production rates in the same sample is to calculate ratios of cosmogenic nuclide concentrations. This approach has previously been adopted for cross-calibration of $^3$He and/or $^{21}$Ne production rates with $^{10}$Be (Gayer et al., 2004, Kober et al., 2005, Farley et al., 2006, Amidon et al., 2008, Amidon et al., 2009), and for evaluation of relative $^3$He and $^{21}$Ne production rates (Fenton et al., 2009). When cross-calibrating TCN in several samples along an altitude transect, an increasing or decreasing trend versus altitude would indicate that the nuclides have different altitude dependences (Gayer et al., 2004, Amidon et al., 2008).

In these studies, the compared nuclides are primarily produced by spallation reactions. In the case of the noble gases $^3$He and $^{21}$Ne, trapped nucleogenic and radiogenic contributions were subtracted prior to cross-calibration, so that only cosmogenic components were taken into account. Predominantly spallation-produced nuclides such as $^3$He, $^{21}$Ne and $^{10}$Be should accumulate in a given sample with a constant ratio. However, despite the fact that these nuclides are predominantly spallogenic in origin, there are nevertheless variations in production rate related to the chemical composition of the mineral involved.

1) Cosmogenic production of $^3$He by thermal neutron capture on $^6$Li has been shown to be potentially significant in Li-rich minerals and rocks (Dunai et al., 2007) and may require a correction. This approach has not been done in the pioneer paper of Gayer et al. (2004) but has since been addressed (e.g. Amidon et al., 2009). However, Li concentrations in mafic
minerals such as olivine and pyroxenes are generally low (< 10 ppm). In this study Li concentrations range between 2 and 7 ppm (Table 2b) and thus contribute less than 1% to the \(^3\)He budget.

2) Even though \(^3\)He and \(^21\)Ne are commonly calibrated for a given mineral phase, their production rates also depend on the mineral chemical composition (e.g. Masarik and Reedy, 1996). \(^3\)He is mainly produced from O and Si, as well as from Mg, Fe, Al and Ca, with relatively uniform elemental production rates. In contrast, \(^21\)Ne is not produced from O, but from Na, Mg, Al, Si, Ca and Fe with significant variations between elemental production rates (e.g. Masarik and Reedy, 1996, Masarik, 2002, see Table 2c). The production rate of \(^21\)Ne is therefore more sensitive than that of \(^3\)He to variations in mineral composition. As a consequence, if the composition of a mineral phase varies significantly within the sample set, \(^3\)He/\(^21\)Ne ratios may also vary significantly.

While relative \(^3\)He, \(^21\)Ne and \(^10\)Be production rates are only slightly dependent on mineral chemistry, the situation is significantly more complex for \(^36\)Cl. In order to compare spallogenic nuclides with \(^36\)Cl, three issues have to be considered.

i) Mineral composition is more important when comparing cosmogenic noble gas concentrations to those of \(^36\)Cl. \(^36\)Cl is produced from fewer target elements than \(^3\)He and \(^21\)Ne, dominantly from Ca, K and \(^35\)Cl (review in Schimmelpfennig et al., 2009), making its production rate extremely sensitive to the mineral composition.

ii) The noble gases \(^3\)He and \(^21\)Ne are stable TCN, while \(^10\)Be and \(^36\)Cl are radioactive. Concentration ratios of a stable and a radioactive nuclide will not remain constant over long exposure durations due to decay of the radionuclide. In the case of \(^10\)Be, which has a half-life of 1.39 Ma (Chmeleff et al., 2010, Korschinek et al., 2010), this becomes significant for exposure ages longer than 100 ka, while in the case of the shorter-lived \(^36\)Cl (half-life 301 ka),
the effect is significant for even shorter exposure durations. In addition, the effect depends on erosion (Goethals et al., 2009), whereas the stable nuclides (3He, 21Ne) accumulate with a constant ratio, irrespective of erosion rate. For example, the concentration ratio of 36Cl/He or 36Cl/21Ne is approximately 12% smaller than their production ratio for a 100 ka old surface eroding at <1 m/Ma; at lower ages or higher erosion rates the difference becomes smaller (according to Goethals et al., 2009; the muogenic 36Cl contribution is neglected here). Therefore, radioactive decay should be taken into account when comparing TCN concentrations, especially if the samples have a range of exposure ages as they do in this study.

iii) Cosmogenic 36Cl is not only produced by spallation. A significant 36Cl contribution is also derived from slow negative-muon capture by Ca, and to a lesser degree by K (review in Schimmelpfennig et al., 2009). Because the altitude-dependence of the muon flux is weaker than that of the fast neutrons (e.g. Stone, 2000), with increasing altitude the production of 36Cl by spallation increases at a higher rate than 36Cl production by muon-capture. Hence, over a given altitude transect, total 36Cl production will not be proportional to the production of TCN derived almost purely from spallation. 36Cl is also produced by thermal and epithermal neutron capture on the trace element 35Cl, and a significant proportion of 36Cl can result from a high level of Cl (>50 ppm) in a sample (Schimmelpfennig et al., 2009). However, as for 3He production due to 6Li, when Cl concentrations in a sample are low (a few ppm) this mechanism contributes generally insignificantly to the 36Cl production. Variations in 36Cl concentrations in samples of the same lithology might therefore be a consequence of varying Cl concentrations.
4.1 Comparing cosmogenic $^{36}\text{Cl}$, $^3\text{He}$ and $^{21}\text{Ne}$ concentrations

Because of the favourable chemical composition of the pyroxene phenocrysts in our samples (notably low Cl, low K concentrations and similar Ca concentrations) we first directly compare the ratios of the cosmogenic $^{36}\text{Cl}$, $^3\text{He}$ and $^{21}\text{Ne}$ concentrations (Fig. 4), ignoring the effects of radioactive decay, erosion and muogenic $^{36}\text{Cl}$ contribution. The $^{36}\text{Cl}$ contribution from Ca spallation is maximized by extraction from the Cl-poor, Ca-rich pyroxenes (max. 10 ppm Cl, see Table A1). Hence, spallation of Ca contributes between 86% and 90% of $^{36}\text{Cl}$ in these samples, while the contribution from spallation of K is < 1% and that from spallation of Ti and Fe together is about 3% (calculated using the $^{36}\text{Cl}$ calculation spreadsheet published in Schimmelpfennig et al., 2009). The contributions from thermal and epithermal neutron capture on $^6\text{Li}$ and $^{36}\text{Cl}$, respectively, are < 1% for $^3\text{He}$ and 3.7% or less for $^{36}\text{Cl}$. The Li-derived $^3\text{He}$ contribution is based on Li concentrations measured in the minerals, Table 2b, and calculated using a version of CHLOE (Phillips and Plummer, 1996) modified for $^3\text{He}$ production (R. Pik and P. Burnard, unpublished). The $^{36}\text{Cl}$ contributions due to slow negative-muon capture are 10% at 1000 m altitude and decrease to 5% at 4300 m. As a consequence we might expect a slight overestimate of the $^{36}\text{Cl}$ to noble gas nuclide ratios at low altitudes relative to high altitudes due to the muogenic $^{36}\text{Cl}$ contribution.

Since, to our knowledge, $^{36}\text{Cl}$ has never been measured in pyroxene before, we validate this method by measuring $^{36}\text{Cl}$ in co-genetic plagioclases in sample TZ15. Feldspar is an accepted $^{36}\text{Cl}$ target mineral (Stone et al., 1996, Evans et al. 1997, Schimmelpfennig et al. 2009). The $^{36}\text{Cl}$ concentrations in both mineral phases of TZ15 are given in Table A1 in the Appendix. Since the Ca concentrations are higher in the pyroxene by almost a factor of two and also the K and Cl concentrations differ between both mineral phases, $^{36}\text{Cl}$ concentrations cannot be directly compared. We therefore calculated the apparent exposure ages from these two minerals using the $^{36}\text{Cl}$ calculation spreadsheet (Schimmelpfennig et al., 2009) and the SLHL
production rate for spallation of Ca by Stone et al. (1996), which yields 14.4 ± 1.1 ka for pyroxene and 14.3 ± 1.1 ka for plagioclase, confirming that pyroxene is a suitable mineral for 36Cl surface exposure age determinations.

Fig. 4 shows the ratios of the cosmogenic nuclide concentrations versus altitude. In pyroxene, the mean values of the ratios and their standard deviations are 0.0582 ± 0.0061 (n=8) for 36Cl/He, 0.1864 ± 0.0085 (n=6) for 21Ne/He and 0.301 ± 0.020 (n=6) for 36Cl/21Ne. For each of the three TCN ratios, all individual measurements, except the 36Cl/He ratio of TZ15, lie within the standard deviation of the respective mean values and therefore do not show any altitudinal dependence. It should be noted that TCN concentration ratios are composition-dependent, particularly when 36Cl and 21Ne are involved, and they should not be expected to be the same in different mineral phases or in pyroxenes with significantly different compositions. In this study, the compositions of the pyroxene minerals are very similar, only TZ09 (En45) and TZ15 (En44) diverge slightly from the other samples (En41-43). Significant differences are observed in the Ca, Fe and Al concentrations (Table 2), each of them being an important target element for at least one of the TCN in this study. Theoretical calculations of mineral production rates, based on these compositions and on the elemental production rates by Masarik (2002), predict that the 36Cl/He and 36Cl/21Ne ratios of these two samples should be about 10% to 15% lower than those of the other samples.

21Ne/He was also determined in olivine from four of the samples: TZ10 and TZ12 from the 2740 m sample site and TZ13 and TZ14 from the 3000 m site (Table 3b, Fig. 4b). At higher altitudes, only 3He could be determined in olivines. 36Cl could not be measured in olivine since this mineral contains no abundant target element for production of this nuclide. A mean 21Ne/He value of 0.377 ± 0.018 was determined and all four measurements lie within the standard deviation of the mean value. No variation is observed between the two sample locations.
4.2 Comparing apparent $^{36}$Cl, He and $^{21}$Ne exposure ages

If erosion is negligible, samples collected from a single lava-flow or glacially created surface should yield the same exposure age irrespective of TCN or mineral phase. All composition-, production pathway- and decay-related differences between the nuclides should be accounted for in the exposure age calculation. Errors in scaling factors for spallation reactions will cancel out provided the same scaling method is applicable for all reactions. A separate scaling factor is required for production of $^{36}$Cl from muons. However, errors in the muon scaling factor are expected to have only a minor influence on calculated exposure age ratios, because $^{36}$Cl contributions from muons are not higher than 5-10%. We choose the scaling method of Stone (2000), because all the SLHL production rates considered below were originally scaled according to either Stone (2000) or to Lal (1991); these two methods are equivalent to each other. The applied scaling factors are listed in Table 1.

The selection of SLHL production rates poses a more serious challenge, because for each nuclide several experimentally calibrated and modelled production rates exist, covering a quite large range of values. We will limit our study to select a single SLHL production rate for each nuclide. If the SLHL production rates of all nuclides were perfectly known and all nuclides were equally altitude-dependent, the exposure age ratios should be equal to 1 (cf. Fig. 5). Systematic discrepancies would indicate that one or both SLHL production rates are inaccurate. Without an independent age control it is, however, not possible to determine which production rate is correct.

For $^{36}$Cl, production rates are not mineral- but target-element-specific. Spallation of Ca is the most important production mechanism in our pyroxenes. We use the production rate for
spallation of Ca with a value of 48.8 ± 1.7 atoms (g Ca))⁻¹· a⁻¹ (Stone et al., 1996). For ³⁷Ar, we use the production rate of 128 ± 5 atoms (g mineral)⁻¹· a⁻¹ (Blard et al., 2006). This production rate is assumed to be valid for pyroxene as well as olivine because cosmogenic ³⁷Ar concentrations are identical within analytical uncertainty in the cogenetic olivines and pyroxenes of our study (Fig. 2). For ²¹Ne, both modelled elemental production rates and experimentally calibrated mineral-specific production rates are available. Here, we use the calibrated SLHL production rate of 25 ± 8 atoms (g pyroxene)⁻¹· a⁻¹ of Fenton et al. (2009). The compositions of pyroxenes in Fenton et al. (2009) (En₄₃-₄₄) fall within the range of those in our study (En₄₁-₄₅).

The resulting apparent exposure ages range between 14 ka and 170 ka (Table 4). For each nuclide pair, the exposure age ratios are then calculated. These are plotted as a function of altitude in Fig. 5. This graph shows a similar pattern to the concentration plot, indicating that the radioactive decay of ³⁶Cl (as can be expected for relatively young exposure ages), differences in mineral composition and the ³⁶Cl production by slow muon capture have only a minor impact on the altitudinal trend of these data.

Despite this overall similarity, exposure age ratios appear to exhibit a slight dependence on altitude. Notably ³⁶Cl/³⁷Ar decreases with altitude; this trend is essentially defined by samples TZ09 (1000 m) and TZ15 (4100 m), with 30% difference between these two samples without overlap of the estimated uncertainties. However, the TZ15 ³⁶Cl/²¹Ne age ratio is indistinguishable from those at lower altitudes. An error in the calculation of the ³⁷Ar age of TZ15 is therefore possible. Since TZ15 was taken from a polished glacial surface of an old dyke (see section 2, formation age >> exposure age), it is subject to an uncertain correction for radiogenic ³⁷Ar*, which affects the cosmogenic ³⁷Ar concentration estimation (section 3.3). The black circles at the altitude of TZ15 in Fig. 5a and b represent the age ratios when assuming the highest correction for radiogenic ³⁷Ar* based on measured U and Th.
concentrations, the $^{39}\text{Ar}/^{40}\text{Ar}$ age and the minimum grain size of the phenocrysts (2 mm). The open circles mark the ratios if no such correction is done, thus indicating the trend towards higher ratios if the radiogenic $^{4}\text{He}$ correction was overestimated. Furthermore, the surface of the TZ09 flow was clearly eroded. Erosion can have an effect on ratios involving $^{36}\text{Cl}$, because it has a shorter half-life than the other nuclides and because the $^{36}\text{Cl}$ contribution from slow negative-muon capture is less dependent on erosion than the $^{36}\text{Cl}$ contribution from spallation due to the longer attenuation length of the muons. Consequently, if erosion is not taken into account then the calculated apparent $^{36}\text{Cl}$ exposure age is higher relative to the calculated apparent He exposure age. The ratio of the apparent exposure ages of TZ09 is displayed in Fig. 5a by the black circle, while the open diamond represents the ratio if erosion is taken into account. For this calculation we assumed an eroded rock layer of 30 cm, which corresponds to the estimated maximum erosion based on field evidence. When these considerations are taken into account all exposure age ratios overlap within their uncertainties over the examined altitude range. No clear altitudinal variation in nuclide production can be demonstrated without ambiguity, regardless of the production rate or nuclide pair examined. Also, no correlation of the ratios with the different exposure durations of the surfaces can be observed.

At present, accurate independent age constraints are not available for the sampled lava flows, preventing us from evaluating SLHL production rates. The production rates chosen here result in exposure ages that mostly agree between all three nuclides (Table 4), i.e. the exposure age ratios presented in Fig. 5 are generally equal to 1. But it is important to stress that this would also have been the case if for all three nuclides accordingly lower or higher SLHL production rates had been chosen and that this does not affect the evaluation of the altitude dependence of the relative nuclide production rates.
5. Comparison with other cross-calibrations

A significant altitudinal variation of the relative production rates of \(^3\)He compared to other nuclides, as was proposed by Gayer et al. (2004) and Amidon et al. (2008), is not documented by the Kilimanjaro data set. Even though the altitude range of samples TZ10 to TZ19 is similar to that of the Himalayan samples (3000 - 4600 m in Gayer et al., 2004, and 3200 - 4800 m in Amidon et al., 2008) and Amidon et al. (2008) documented an increase in the \(^3\)He/\(^{10}\)Be concentration ratio of up to 40% for their transect, all exposure age ratios in our study agree at the 1\(\sigma\) level for the corresponding altitude range (2700 - 4300 m) (Fig. 5). Regarding only the nominal values of the \(^{36}\)Cl/He exposure age ratios over the whole altitude range in our study (1000 – 4300 m), i.e. ignoring the overlapping uncertainties, results in a 17% increase. However, this variation is much less than that documented for the Himalayan transects (Fig. 6). Possible explanations could be that i) no significant differences in relative production rates exist and the anomaly in the nuclide ratios of the Himalayan samples is due to factors other than changes in the nucleon energy spectrum; ii) the altitude dependences of \(^{36}\)Cl, \(^{21}\)Ne and \(^3\)He production are more similar than for \(^{10}\)Be and \(^3\)He; or iii) a latitude effect must be considered, since the Himalaya sites are at higher latitudes (27-28°N) than Mt. Kilimanjaro (3°S). Due to the decreasing shielding effect of the geomagnetic field with increasing latitude, the cosmic ray flux becomes stronger. As a consequence, the flux at 4000 m altitude and a latitude of 30° is about 35% higher than at the same altitude and a latitude of 3° (according to the scaling method by Stone, 2000). Also, at high latitudes the energy spectrum of the flux
becomes on average less energetic (Gosse and Phillips, 2001). This could explain different
altitude dependences of the relative production rates, even though the altitudes are very
similar for all studies considered here. However, the possibility of such a latitude effect has to
be further investigated.

The mean values of the \(^{21}\text{Ne}/\text{He}\) concentration ratios in pyroxene (0.1864 ± 0.0085) and
olivine (0.377 ± 0.018) are slightly lower but in agreement within 1σ with those of a number
of studies undertaken at mid latitudes and altitudes between 1000 and 2000 m, e.g. Fenton et
al. (2009) (0.204 ± 0.014 in pyroxene and 0.400 ± 0.029 in olivine), Poreda and Cerling
(1992) (0.41 ± 0.05 in olivine) and Kounov et al. (2007) (0.225 ± 0.027 in pyroxene),
suggesting that the production rates of \(^{3}\text{He}\) and \(^{21}\text{Ne}\) in these minerals have the same altitude
and latitude dependences. However, two studies from Antarctica reported significantly higher
\(^{21}\text{Ne}/\text{He}\) ratios in pyroxene from altitudes around 1000 – 2000 m (0.22-0.26 in Bruno et al.,
1997; 0.21 - 0.26 in Schäfer et al., 1999). The compositions of their pyroxenes are
significantly different from those in our study, but theoretical calculations based on these
compositions and the elemental production rates of Masarik (2002) predict \(^{21}\text{Ne}/\text{He}\) ratios
lower than those in our study. The compositional differences cannot therefore explain the
discrepancy in the ratios. Other possible explanations are (i) the latitude effect proposed
before, suggesting that the production rate of \(^{21}\text{Ne}\) increases at a higher rate than that of \(^{3}\text{He}\)
with increasing latitude, or (ii) significant fractions of plagioclase and quartz in the Antarctic
pyroxene separates, as suggested by Niedermann et al. (2007). The presence of plagioclase
and quartz would lower the \(^{3}\text{He}\) concentration, because these minerals are less retentive for
Helium than pyroxene. Several studies (Margerison et al., 2005, Niedermann et al., 2007,
Oberholzer et al., 2008) reported difficulties in obtaining pure pyroxene separates from the
sampled Antarctic dolerite, and \(^{21}\text{Ne}/\text{He}\) ratios of four pure pyroxene separates re-measured
from the sample suite of Schäfer et al. (1999) are indeed lower (0.181-0.217, Niedermann et al., 2007) than in the earlier study.

Staudacher and Allègre (1993) measured significantly lower $^{21}\text{Ne}/\text{He}$ ratios in olivine (0.23 - 0.30) at latitude 21°S and altitudes around 2300 m. Neither the mineral compositions, which are very similar in their and our study, nor the hypothesized latitude effect seem likely to explain this discrepancy. Assumedly, the calculations of their cosmogenic noble gas concentrations were subject to inaccurate correction for non-cosmogenic components.

To our knowledge, Licciardi et al. (2008) is the only study in which $^{36}\text{Cl}$ has been co-calibrated with another nuclide, $^{3}\text{He}$. $^{36}\text{Cl}$ was measured in basaltic whole rock, while $^{3}\text{He}$ was determined in olivine phenocrysts of the same samples (Licciardi et al., 2006). However, a comparison between the relative production rates of $^{36}\text{Cl}$ and $^{3}\text{He}$ in their study and ours cannot be performed for several reasons. $^{36}\text{Cl}$ concentrations are not given in Licciardi et al. (2008). Also, the basalts have varying Cl concentrations (up to 61 ppm), which result in $^{36}\text{Cl}$ contributions from capture of low-energy neutrons on $^{35}\text{Cl}$ of up to 26%, so that $^{36}\text{Cl}/\text{He}$ concentration ratios could not be expected to be constant from sample to sample. Finally, all samples come from a narrow range of altitudes (20-460 m) excluding altitude dependent comparisons.

6. Conclusions

This is the first study that deals with the cross-calibration of three cosmogenic nuclides ($^{36}\text{Cl}$, $^{3}\text{He}$ and $^{21}\text{Ne}$) in minerals over a large altitudinal profile (1000 - 4300 m) at low latitude (3° S). All three nuclides have been measured in pyroxene phenocrysts, and $^{3}\text{He}$ and $^{21}\text{Ne}$ have additionally been measured in olivine at two elevations. $^{36}\text{Cl}$ has also been determined in
plagioclase co-existing with pyroxene in one of the samples. Calculated exposure ages from both minerals yield the same result confirming the reliability of $^{36}$Cl measurements in pyroxene.

Cosmogenic $^{21}$Ne/$^3$He concentration ratios in pyroxene are $0.1864 \pm 0.0085$ and those in olivine are $0.377 \pm 0.018$, agreeing with previously determined ratios of these nuclides (Poreda and Cerling, 1992, Kounov et al., 2007, Fenton et al., 2009). In our samples, the $^{36}$Cl/$^3$He and $^{36}$Cl/$^{21}$Ne concentration ratios are $0.0582 \pm 0.0061$ and $0.301 \pm 0.020$, respectively. These concentration ratios can be very different between samples, since the $^{36}$Cl production rate in a mineral depends strongly on the target element concentrations.

No significant altitude dependence of the relative production of any of the nuclides can be observed, in contrast to altitude-dependent variations documented in previous studies (Gayer et al., 2004, Amidon et al., 2008). Our observation is based on nuclide concentration ratios and calculated apparent exposure age ratios plotted versus the elevations of the sample sites. This suggests that production rates of the investigated nuclides are proportional to each other between mid and high altitudes at low latitude, implying that no nuclide-specific scaling factors are needed at this site. However, the latitude effect for cross-calibrations has to be further evaluated.

Although independently determined ages for the studied lava surfaces are not available at present, the consistency in the data-set should enable progress to be made in the determination of the production rates of all three nuclides as soon as the production rate of one of the nuclides has been accurately defined.
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Table captions:

Table 1: Sample details. Geographic sample locations, scaling factors for neutron induced and slow negative muon induced reactions calculated according to Stone (2000), sample thickness and thickness correction factors for spallation reactions.

Table 2: Element concentrations in minerals. a) Concentrations of target elements for $^{36}$Cl production in pretreated pyroxene separates (px) and one plagioclase separate (plg) before $^{36}$Cl extraction, determined by ICP-OES at the SARM (CRPG, France). "$<\text{D.L."} = "below detection limit". b) Concentrations of U, Th and Li in chemically untreated pyroxene (px) and olivine (ol) separates, determined by ICP-MS (U, Th) and atomic absorption (Li) at SARM. c) Concentrations of target elements for $^{21}$Ne production in chemically untreated pyroxene and olivine separates determined by electron microprobe at the Université Henri Poincaré on 6-8 grains (mean values and their standard deviations). Calculated elemental production rates for $^{21}$Ne according to Masarik (2002) are also shown.

Table 3: Cosmogenic components of the measured $^{36}$Cl, $^3$He and $^{21}$Ne concentrations and their ratios, with mean values and standard deviations, in a) pyroxene and b) olivine separates. Note that the $^{36}$Cl concentrations of samples TZ10 and TZ12 are mean values of the two replicates of each (Table A1) with the corresponding standard deviations.

Table 4: Apparent exposure ages calculated using the cosmogenic $^{36}$Cl, $^3$He and $^{21}$Ne concentrations in pyroxene (Table 3) and the SLHL production rates detailed in the footnotes. $^{36}$Cl exposure ages were calculated with the $^{36}$Cl calculation spreadsheet (Schimmelpfennig et al., 2009). Note that the $^{36}$Cl exposure ages for samples TZ10 and TZ12 are mean values of the exposure ages of the two replicates of each with the corresponding standard deviations. The uncertainties (1σ) of the exposure ages do not include the uncertainties in the SLHL production rates, but those in the cosmogenic nuclide concentrations and for $^{36}$Cl those in the contributions of the production reactions other than spallation.
Fig. 1: Sample location. a) Google Maps satellite image of Mt. Kilimanjaro, Tanzania. b) Side face (NW-SE) of Mt. Kilimanjaro (Image PIA03355, Courtesy NASA/JPL-Caltech), showing its peaks Shira, Kibo and Mawenzi as well as the sample locations and altitudes. Topography is vertically exaggerated two times.

Fig. 2: Cosmogenic He concentrations in olivine and pyroxene phenocrysts. The red lines represent the mean values of the concentrations in pyroxene. For sample TZ09 He was only measured in pyroxene.

Fig. 3: Neon three-isotope diagram showing data from olivines and pyroxenes at two temperature steps. The regression line defines a spallation line, which passes through the air component and is indistinguishable from the air-spallation mixing line of Schäfer et al. (1999).

Fig. 4: TCN ratios, calculated from the total cosmogenic He, Ne and Cl concentrations, as a function of altitude. Black circles correspond to the ratios in pyroxene, gray circles to those in olivine. The continuous and dashed lines indicate the means of the ratios and their standard deviations, respectively, with values given to the left.

Fig. 5: Exposure age ratios calculated from cosmogenic Cl, He and Ne concentrations in pyroxene. Production rates used are: 48.8 atoms (g Ca)\(^{-1}\) a\(^{-1}\) for Cl (Stone et al., 1996), 128 atoms (g mineral)\(^{-1}\) a\(^{-1}\) for He (Blard et al., 2006) and 25 atoms (g mineral)\(^{-1}\) a\(^{-1}\) for Ne (Fenton et al., 2009). Standard deviations of these production rates are not propagated in the ratio uncertainties (see Table 4). The black circles at the altitude of sample TZ15 in panels a) and b) represent the age ratios when assuming the highest possible correction for radiogenic He\(^*\), while the open circles mark the ratios if no such correction is done (see text for details). The black circle at the altitude of TZ09 in panel a) represents the age ratio ignoring erosion, while the open diamond represents the ratio if erosion is taken into account (see text for details).

Fig. 6: Cl/He exposure age ratios as in Fig. 5a with apparent altitudinal trend. TZ15 is not considered due to uncertain cosmogenic He concentrations, and the TZ09 composition has been corrected for erosion (section 4.2). The 40% increase of the He/Be trend in Himalayan zircons between 3200 and 4800 m
(Amidon et al., 2008) is indicated in gray. Note that here $^{10}$Be/$^3$He concentration ratios are compared to $^{36}$Cl/$^3$He exposure age ratios.
Figure 1
Figure 3

Regression line: Ol + Px
\[ y = 1.0539x + 0.0994 \]

Pyroxene air-spallation mixing line
(Schäfer et al., 1999)

Air-Nucleogenic
Air-mantle
Figure 4

- a) $^{36}\text{Cl}/^{3}\text{He}$
  - Pyroxene: $0.0582 \pm 0.0061$
  - Olivine: $0.377 \pm 0.018$

- b) $^{21}\text{Ne}/^{3}\text{He}$
  - Pyroxene: $0.1864 \pm 0.0085$
  - Olivine: $0.377 \pm 0.018$

- c) $^{36}\text{Cl}/^{21}\text{Ne}$
  - Pyroxene: $0.301 \pm 0.0020$
Figure 5

- a) $^{36}\text{Cl}/^{3}\text{He}$
- b) $^{21}\text{Ne}/^{3}\text{He}$
- c) $^{36}\text{Cl}/^{21}\text{Ne}$
Figure 6

The graph shows the relationship between altitude (m) and $^{36}\text{Cl}/^{3}\text{He}$ exposure age ratios. The data points represent samples labeled TZ10, TZ12, TZ13, TZ14, TZ17, and TZ19. The graph is labeled as "Himalayan high altitude equivalent."
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<th>Sample</th>
<th>latitude South</th>
<th>longitude East</th>
<th>altitude [m]</th>
<th>scaling neutrons</th>
<th>scaling muons</th>
<th>thickness [cm]</th>
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<td>3.16</td>
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<td>37° 25’.240</td>
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<td>K [%]</td>
<td>Ti [%]</td>
<td>Fe [%]</td>
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</tr>
<tr>
<td>TZ09-px</td>
<td>13.87±0.28</td>
<td>&lt; D.L.</td>
<td>0.88±0.04</td>
<td>5.71±0.11</td>
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<tr>
<td>TZ10A-px</td>
<td>15.71±0.31</td>
<td>&lt; D.L.</td>
<td>1.37±0.07</td>
<td>4.66±0.09</td>
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<td>TZ10B-px</td>
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<tr>
<td>TZ12A-px</td>
<td>15.56±0.31</td>
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<td>1.37±0.07</td>
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<td>TZ12B-px</td>
<td>15.48±0.31</td>
<td>&lt; D.L.</td>
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<td>4.77±0.10</td>
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<td>TZ13-px</td>
<td>15.19±0.30</td>
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<td>1.16±0.06</td>
<td>4.64±0.09</td>
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<tr>
<td>TZ14-px</td>
<td>15.14±0.30</td>
<td>&lt; D.L.</td>
<td>1.11±0.05</td>
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<td>TZ17-px</td>
<td>15.22±0.31</td>
<td>0.04±0.01</td>
<td>1.16±0.06</td>
<td>4.57±0.09</td>
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<tr>
<td>TZ15-px</td>
<td>13.06±0.26</td>
<td>&lt; D.L.</td>
<td>0.98±0.05</td>
<td>7.61±0.15</td>
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<tr>
<td>TZ19-px</td>
<td>15.44±0.31</td>
<td>&lt; D.L.</td>
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<td>5.32±0.10</td>
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<tr>
<td>TZ15-plg</td>
<td>7.46±0.15</td>
<td>0.50±0.02</td>
<td>0.10±0.01</td>
<td>0.45±0.01</td>
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<table>
<thead>
<tr>
<th>Sample</th>
<th>U [ppm]</th>
<th>Th [ppm]</th>
<th>Li [ppm]</th>
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<tbody>
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<td>TZ09-px</td>
<td>0.039</td>
<td>0.156</td>
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<td>TZ12-px</td>
<td>0.079</td>
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<td>TZ14-px</td>
<td>0.113</td>
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<td>0.100</td>
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<td>TZ15-px</td>
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<tr>
<th>Sample</th>
<th>Mg [%]</th>
<th>Al [%]</th>
<th>Si [%]</th>
<th>Ca [%]</th>
<th>Fe [%]</th>
<th>Na [%]</th>
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</thead>
<tbody>
<tr>
<td>TZ10/12-px</td>
<td>8.06±0.43</td>
<td>3.70±0.30</td>
<td>22.24±0.52</td>
<td>16.23±0.22</td>
<td>4.60±0.40</td>
<td>0.55±0.04</td>
</tr>
<tr>
<td>TZ13/14-px</td>
<td>8.85±0.58</td>
<td>3.03±0.50</td>
<td>23.23±0.62</td>
<td>15.73±0.34</td>
<td>4.20±0.48</td>
<td>0.56±0.02</td>
</tr>
<tr>
<td>TZ17-px</td>
<td>10.04±0.24</td>
<td>1.97±0.26</td>
<td>24.32±0.25</td>
<td>15.34±0.21</td>
<td>3.33±0.13</td>
<td>0.51±0.03</td>
</tr>
<tr>
<td>TZ15-px</td>
<td>9.17±0.68</td>
<td>1.65±0.24</td>
<td>23.92±0.46</td>
<td>14.45±0.54</td>
<td>7.03±1.47</td>
<td>0.35±0.03</td>
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<tr>
<td>TZ10/12-ol</td>
<td>26.13±0.64</td>
<td>0.01±0.03</td>
<td>18.76±0.24</td>
<td>0.39±0.30</td>
<td>12.96±1.03</td>
<td>0.02±0.03</td>
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<tr>
<td>TZ13/14-ol</td>
<td>25.79±0.73</td>
<td>0.01±0.03</td>
<td>18.64±0.17</td>
<td>0.26±0.14</td>
<td>13.46±1.06</td>
<td>0.02±0.02</td>
</tr>
</tbody>
</table>

| Elemental prod. rates<sup>a</sup> | 175.1 | 62.4 | 41.7 | 1.8 | 0.2 | 102.0 |

<sup>a</sup> [atoms $^{21}$Ne (g element)$^{-1}$ a$^{-1}$]
Table 3  

a) Pyroxene

<table>
<thead>
<tr>
<th>Sample</th>
<th>$[^{36}\text{Cl}] (\text{px})$ [10$^6$ atoms g$^{-1}$]</th>
<th>$[^{3}\text{He}]_{\text{cos}} (\text{px})$ [10$^6$ atoms g$^{-1}$]</th>
<th>$[^{21}\text{Ne}]_{\text{cos}} (\text{px})$ [10$^6$ atoms g$^{-1}$]</th>
<th>$[^{36}\text{Cl}]/[^{3}\text{He}] (\text{px})$</th>
<th>$[^{21}\text{Ne}]/[^{3}\text{He}] (\text{px})$</th>
<th>$[^{36}\text{Cl}]/[^{21}\text{Ne}] (\text{px})$</th>
</tr>
</thead>
<tbody>
<tr>
<td>TZ09</td>
<td>0.631±0.017</td>
<td>9.60±0.29</td>
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<td>0.0658±0.0027</td>
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</tr>
<tr>
<td>TZ10</td>
<td>4.246±0.065</td>
<td>73.8±1.1</td>
<td>13.52±0.44</td>
<td>0.0576±0.0012</td>
<td>0.1834±0.0066</td>
<td>0.314±0.011</td>
</tr>
<tr>
<td>TZ12</td>
<td>4.029±0.074</td>
<td>66.2±2.1</td>
<td>12.91±0.60</td>
<td>0.0608±0.0022</td>
<td>0.195±0.011</td>
<td>0.312±0.016</td>
</tr>
<tr>
<td>TZ13</td>
<td>4.94±0.12</td>
<td>93.5±2.7</td>
<td>16.62±0.67</td>
<td>0.0529±0.0020</td>
<td>0.1780±0.0089</td>
<td>0.297±0.014</td>
</tr>
<tr>
<td>TZ14</td>
<td>5.25±0.10</td>
<td>99.8±2.3</td>
<td>18.96±0.69</td>
<td>0.0526±0.0016</td>
<td>0.1899±0.0082</td>
<td>0.277±0.011</td>
</tr>
<tr>
<td>TZ17</td>
<td>2.059±0.059</td>
<td>32.1±2.2$^a$</td>
<td>6.30±0.53</td>
<td>0.0642±0.0048</td>
<td>0.196±0.021</td>
<td>0.327±0.029</td>
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<tr>
<td>TZ15</td>
<td>0.781±0.021</td>
<td>15.84±0.78</td>
<td>2.79±0.14</td>
<td>0.0493±0.0028</td>
<td>0.176±0.012</td>
<td>0.279±0.016</td>
</tr>
<tr>
<td>TZ19</td>
<td>1.47±0.10</td>
<td>23.5±1.1$^a$</td>
<td></td>
<td>0.0626±0.0052</td>
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<tr>
<td>mean ± st.dev</td>
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<td></td>
<td></td>
<td>0.0582±0.0061</td>
<td>0.1864±0.0085</td>
<td>0.301±0.020</td>
</tr>
</tbody>
</table>

b) Olivine

<table>
<thead>
<tr>
<th>Sample</th>
<th>$[^{3}\text{He}]_{\text{cos}} (\text{ol})$ [10$^6$ atoms g$^{-1}$]</th>
<th>$[^{21}\text{Ne}]_{\text{cos}} (\text{ol})$ [10$^6$ atoms g$^{-1}$]</th>
<th>$[^{21}\text{Ne}]/[^{3}\text{He}] (\text{ol})$</th>
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</thead>
<tbody>
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<tr>
<td>TZ12</td>
<td>66.9±1.4</td>
<td>24.8±1.2</td>
<td>0.371±0.019</td>
</tr>
<tr>
<td>TZ13</td>
<td>85.7±1.4</td>
<td>32.8±1.4</td>
<td>0.383±0.017</td>
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<tr>
<td>TZ14</td>
<td>97.9±7.7</td>
<td>34.9±2.2</td>
<td>0.357±0.061</td>
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<tr>
<td>TZ17</td>
<td>34.8±0.54</td>
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<tr>
<td>TZ15</td>
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<tr>
<td>TZ19</td>
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<td>mean ± st.dev</td>
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<td>0.377 ± 0.018</td>
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</table>

$^a$ Magmatic $^3\text{He}/^4\text{He}$ values were determined applying the isochron method by Blard and Pik (2008)
Table 4

<table>
<thead>
<tr>
<th>Sample</th>
<th>$^{36}$Cl (px) $^a$ [ka]</th>
<th>$^3$He (px) $^b$ [ka]</th>
<th>$^{21}$Ne (px) $^c$ [ka]</th>
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<tbody>
<tr>
<td>TZ09</td>
<td>71.7±5.4</td>
<td>61.7±1.9</td>
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</tr>
<tr>
<td>TZ10</td>
<td>156.1±9.1</td>
<td>154±2.3</td>
<td>144.3±4.7</td>
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<tr>
<td>TZ12</td>
<td>148.7±8.7</td>
<td>137.9±4.4</td>
<td>137.6±6.4</td>
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<tr>
<td>TZ13</td>
<td>157±13</td>
<td>161.9±4.7</td>
<td>147.5±5.9</td>
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<td>TZ14</td>
<td>171±14</td>
<td>173.7±4.0</td>
<td>168.9±6.1</td>
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<tr>
<td>TZ17</td>
<td>40.9±3.0</td>
<td>40.4±2.8</td>
<td>40.6±3.4</td>
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<td>TZ15</td>
<td>14.4±1.0</td>
<td>15.98±0.78</td>
<td>14.43±0.72</td>
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<td>TZ19</td>
<td>21.1±2.0</td>
<td>21.90±1.0</td>
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</table>

$^a$ $^{36}$Cl SLHL production for spallation of Ca 48.8±1.7 atoms $^{36}$Cl (g Ca)$^{-1}$ a$^{-1}$ according to Stone et al. (1996)

$^b$ $^3$He SLHL production for pyroxene 128±5 atoms $^3$He (g px)$^{-1}$ a$^{-1}$ according to Blard et al. (2006)

$^c$ $^{21}$Ne SLHL production for pyroxene 25±8 atoms $^{21}$Ne (g px)$^{-1}$ a$^{-1}$ according to Fenton et al. (2009)
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