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This technical note is a non-peer reviewed preprint submitted to EarthArXiv

The CREp ³⁶Cl exposure age calculator: development version “dev”

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Abstract

Chlorine-36 (^{36}Cl) is currently the only *in situ* cosmogenic nuclide applicable in carbonates, Ca- and K-rich feldspars and aphyric silicate rocks. Because the production reactions of ^{36}Cl are more numerous and complex than those of other cosmogenic nuclides (e.g. ^{10}Be , ^3He), comprehensive and user-friendly calculators are essential for routine application of ^{36}Cl to Earth surface research questions. However, the existing, commonly used calculators are affected by several drawbacks, such as oversimplification of the muon production model, or the absence of choice regarding production rate parameters. Here, we present the novel ^{36}Cl exposure age calculation tool in development, “CREp ^{36}Cl dev”, which we have implemented as a new functionality in the existing cosmic-ray-exposure program CREp for ^{10}Be and ^3He exposure ages. Taking advantage of the most recently developed scaling, muon and low-energy neutron models, “CREp ^{36}Cl dev” allows calculating surface exposure ages, providing several choices between scaling and muon models and production parameters. “CREp ^{36}Cl dev” can be accessed at <https://crep-dev.otelo.univ-lorraine.fr/#/>.

1. Introduction

The so far existing CREp online calculator for *in situ* cosmogenic ^{10}Be and ^3He exposure age calculations (Martin et al., 2017; <https://crep.otelo.univ-lorraine.fr/>) is a versatile tool with advantageous characteristics. It has a user-friendly web interface combined with a high computation speed and a permanent link to the ICE-D production rate database, permitting to account for the most recent production rate calibrations (<http://calibration.ice-d.org/>). It also allows the choice between global, regional or local production rates, several scaling schemes, atmospheric pressure models, and Virtual Dipole Moment database.

Chlorine-36 (^{36}Cl) is currently the only *in situ* cosmogenic nuclide applicable in carbonate environments, and it is now quasi-routinely analyzed in Ca- and K-rich silicate rocks and minerals. However, given the complexity of the ^{36}Cl production systematics, computation of ^{36}Cl exposure ages consists in intricate and dense procedures. Unlike most of the other nuclides, multiple production pathways and target elements have to be considered, with their relative contributions depending on the chemical composition of the sample: spallation of the target elements K, Ca, Ti and Fe; muon capture by Ca and K; capture of low-energy neutrons (derived both from cosmic ray particles and from nucleogenic, i.e. non-cosmogenic reactions in the rock) by target element ^{35}Cl . The flux of these low-energy neutrons within the rock sensitively depends on the concentration of elements with certain neutron-absorption and moderation characteristics, and the nucleogenic ^{36}Cl production pathway is in addition controlled by the concentrations of U and Th in the rock. Also, the fraction of stopped negative muons that are captured by Ca and K to produce ^{36}Cl is dependent on the bulk composition (Fabryka-Martin, 1988). Therefore, accurate ^{36}Cl age calculations require input not only of the ^{36}Cl concentrations deduced from accelerator mass spectrometry (AMS) measurements and site- and sample-specific data collected during sampling, but also of detailed chemical compositions of the bulk rock and of the analyzed material.

Two comprehensive and user-friendly ^{36}Cl calculators have been published and routinely used over the past years, the excel® spreadsheet for ^{36}Cl exposure ages and profiles by Schimmelpfennig et al. (2009) and the CRONUS-Earth online calculator (Marrero et al., 2016). They account for all the complex reaction mechanisms, mainly based on the calculations presented in Phillips et al. (2001) and Gosse and Phillips (2001). These calculators have

considerably facilitated the application of ^{36}Cl , leading to a growing number of studies in the fields of geomorphology, paleoseismology and paleoclimatology that are based on the use of this cosmogenic nuclide. However, these existing calculators are affected by several drawbacks, such as the need to calculate scaling factors apart and oversimplification of the muon production model, potentially leading to inaccurate calculations at depth (Schimmelpfennig et al., 2009), and the absence of choice regarding production rate parameters by imposition of a global default production rate (Marrero et al., 2016).

To overcome these weaknesses, we are developing the new CREp ^{36}Cl exposure age calculator, based on the Excel® spreadsheet of Schimmelpfennig et al. (2009), (see Appendix A and B in Schimmelpfennig et al., 2009 for equations adapted from Gosse and Phillips, 2001, and Phillips et al., 2001), and we included the following improvements.

- The site-specific, time-dependent scaling is automatically calculated. Users have the same choices as for ^{10}Be and ^3He calculations, i.e. they can select between the two scaling methods Lm (Lal, 1990; Stone et al., 2000; Balco et al., 2008) and LSD (Lifton et al., 2014) combined with the choices between two atmospheric pressure models (US standard atmosphere; NOAA, 1976; and ERA-40, Uppala et al., 2005) and several Virtual Dipole Moment databases. The scaling method LSD is nuclide-specific and – in the case of ^{36}Cl – target element-specific, and was implemented following the model integrated in the CRONUS-Earth online calculator (Marrero et al., 2016). Note that the original study that first conceptualized the LSD model (Lifton et al., 2014) did not account for the scaling of ^{36}Cl .
- Muogenic ^{36}Cl production is not anymore approximated by an exponential function (Gosse and Phillips, 2001), but computed after integration of the muon flux and stopping rates as a function of depth (Heisinger et al., 2002a, b), following the implementation of Balco et al. (2008) for the Lm scaling model and that of Lifton et al. (2014) for the LSD scaling model.

In the current development version of the calculator, sea level/high latitude (SLHL) production rates for spallation of Ca, K, Ti and Fe and the parameter for cosmogenic ^{36}Cl production from low-energy neutrons $Pf(0)$ can either be selected from published values in dropdown menus, or users can manually type in their own values. Note that some of the proposed published production rates were not calibrated with neither of the two scaling methods available in CREp and are therefore not always coherent with the user's choice of scaling. This incoherence is planned to be tackled in a future version of CREp. Note that the systematic errors arising from this currently employed simplification are generally within the uncertainties of the calibrated spallation production rates.

2. Instructions for use and necessary inputs

The use of "CREp ^{36}Cl dev" follows a very similar principle to the current CREp online calculator for ^{10}Be and ^3He exposure age calculations. Users need to go through four tabs to choose scaling-related parameters, load their data and choose productions rates, before obtaining the exposure age results.

Tab 1 Parameters (Fig. 1): After ticking the nuclide of interest, users can choose between:

- two scaling models: (1) the empirical Lal-Stone time-dependent model (Balco et al., 2008; Lal, 1991; Stone, 2000) with the muon implementation of Balco et al. (2008), and (2) the Lifton-

Sato-Dunai (LSD) theoretical model (Lifton et al., 2014) and the associated muon implementation.

- two atmosphere models: (1) the one based on the ERA-40 data-base (Uppala et al., 2005), and (2) the standard atmosphere (N.O.A.A, 1976).
- three geomagnetic databases according to (1) Muscheler et al. (2005), (2) Lifton et al. (2014), (3) Lifton (2016), or import their own geomagnetic database for paleomagnetic corrections.

The screenshot shows the 'Parameters' tab of the CREp ³⁶Cl dev interface. It is divided into four sections: 1-Nuclide, 2-Scaling scheme, 3-Atmosphere model, and 4-Geomagnetic Database. In the 1-Nuclide section, ³⁶Cl is selected. In the 2-Scaling scheme section, 'Lal-Stone time corrected (Lm)' is selected. In the 3-Atmosphere model section, 'ERA40 (Uppala et al., 2005)' is selected. In the 4-Geomagnetic Database section, 'Atmospheric ¹⁰Be-based VDM' is selected. A line graph displays VDM (10²² A.m²) on the y-axis (0 to 15) against Age (ka BP) on the x-axis (0 to 100). The graph shows a fluctuating blue line representing the VDM over time. Below the graph are 'Reset' and 'Next' buttons.

Fig. 1: Screen shoot of the Parameter tab of “CREp ³⁶Cl dev”.

Tab 2 Samples (Fig. 2): By clicking on “Download template”, users download an excel file that has to be filled with all sample-specific information before loading it on the CREp web page. All sample input is then displayed for verification. Note that there are 51 columns for data input per sample (see Appendix), which can be verified on the display by scrolling to the right.

The screenshot shows the 'Samples' tab of the CREp ³⁶Cl dev interface. It features a table for sample data and a 'Next' button. The table has the following columns: CREp Fields, Sample name, Latitude (deg), Longitude (deg), Altitude (masl), Shielding, Density (g/cm³), Ztop (cm), Zbottom (cm), Erosion (cm/a), ± Erosion (cm/a), 36Cl conc (at/g), ± 36Cl conc (at/g), and Formation age (a). A sample named 'test_PLG_Etna' is listed with the following values: Latitude 37.7095, Longitude 15.0258, Altitude 2070, Shielding 1, Density 2.37, Ztop 0, Zbottom 10, Erosion 0, ± Erosion 0, 36Cl conc 246767.96474132466, ± 36Cl conc 11324.744226399796, and Formation age 1000.

CREp Fields:	Latitude	Longitude	Altitude	Shielding	Density	Ztop	Zbottom	Erosion	± Erosion	36Cl conc (at/g)	± 36Cl conc (at/g)	Formation age (a)
Sample name	(deg)	(deg)	(masl)		(g/cm ³)	(cm)	(cm)	(cm/a)	(cm/a)			
test_PLG_Etna	37.7095	15.0258	2070	1	2.37	0	10	0	0	246767.96474132466	11324.744226399796	1000

Fig. 2: Screen shoot of the Samples tab of “CREp ³⁶Cl dev”.

Tab 3 Production Rates (Fig. 3): In this “CREp ³⁶Cl dev” calculator, the production rates for spallation of Ca, K, Fe and Ti and the production parameter for the low-energy neutron capture pathway (Pf(0)) can either be selected from dropdown menus with published values or users may type manually their own values. Note that the proposed published production rates are sometimes not scaled with the same parameters as the ones chosen in "1 Parameters".

Elemental Production Rate choice for ³⁶Cl (Caution: in this present version, SLHL PR only from literature, not specifically scaled)

Element	Production rate spallation (atoms ³⁶ Cl/ g element/yr)	Chosen PR value	Reference	Comment
Ca	42.2 +/- 4.8 ✓ Schimmelpfennig et al. (2011): 42.2 ± 4.8 Stone et al (1996): 48.8 ± 1.7 Marrero et al. (2016): 51.7 ± 4.9 Licciardi et al. (2008): 57.3 ± 5.2 My values: ±	42.2 ± 4.8	Schimmelpfennig et al. (2011)	St
K		145.5 +/- 7.7	Schimmelpfennig et al. (2014)	St
Fe	1.628 +/- 0.04 Moore et al. (2019): 1.628 ± 0.04	1.628 +/- 0.04	Moore et al. (2019)	Lm
Ti	3.8 +/- 0.4 Marrero et al. (2016)/ Masarik (2002)/ Stone et al. (2005): 3.8 ± 0.4	3.8 +/- 0.4	Marrero et al. (2016)/ Masarik (2002)/ Stone et al. (2005)	/
Element	Production rate Pf(0) (neutrons/g air/yr)	Chosen PR value	Reference	Comment
Cl	691 +/- 186 Marrero et al. (2016): 691 ± 186	691 +/- 186	Marrero et al. (2016)	Lm

Reset

Chosen Parameters
 Nuclide : ³⁶Cl
 Scaling Scheme : Lal Stone
 Atmosphere Model : ERA40
 Geomagnetic Database :
 Muscheler et al., 2005

Previous Calculate

CREP
 COSMIC RAY EXPOSURE PROGRAM

Fig. 3: Screen shot of the Production Rate tab of “CREp ³⁶Cl dev”.

Tab 4 Results (Fig. 4): The calculated exposure ages are given with full uncertainties, i.e. including the production rate errors as well as analytical errors, and with their analytical errors only (without PR error). The scaling factors for each production reaction is displayed (sp: spallation; th: thermal neutron capture; epi: epithermal neutron capture; mu: muon capture), and a summary of the associated chosen parameters is shown. Ticking “PDF (graphic)” produces a graph with gaussian distributions of all ages. Clicking on “PDF (tab) download” provides an excel file with these results including the probability values of all ages, and the references of the chosen parameters.

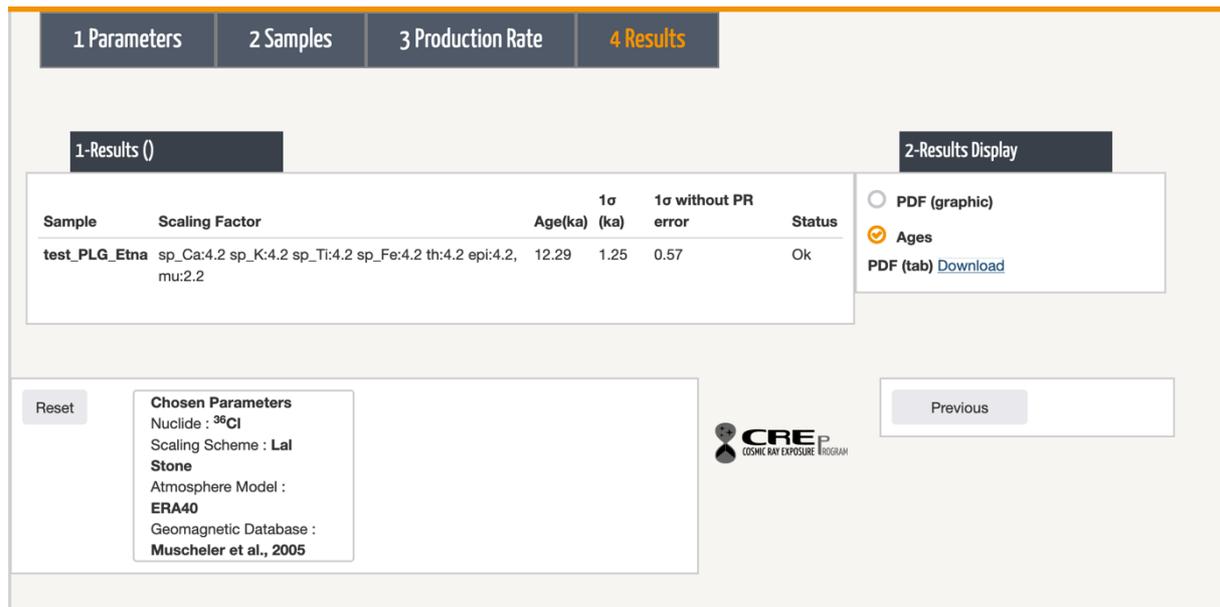


Fig. 4: Screen shot of the Results Rate tab of "CREP ^{36}Cl dev".

3. Work in progress

The existing ^{36}Cl production rate calibration data is currently being implemented in the ICE-D calibration data base with the objective to connect it to CREP ^{36}Cl , similar to the current functioning of ^{10}Be and ^3He calculations. This will allow for 1) regularly updates on global elemental production rates, whenever new calibration data will be added, and 2) potentially for the choice of local production rates. However, it must be noted that ^{36}Cl production rate calibrations are still much scarcer than those of the other nuclides, in particular with regard to mono-elemental production rate material.

Further work in progress concerns the implementation of an updated muon production models that are relevant for ^{10}Be and ^3He calculations at depth (<20 cm) and the addition of a new Virtual Dipole Moment database, which will be applicable to all nuclides in CREP.

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APPENDIX

Instructions for ^{36}Cl data input in the sample file:

Fill numbers in all cells. If you do not know a sample-specific value, either use a standard value or zero if applicable.

All yellow columns refer to the composition of the "target" material, i.e. the sample material that was totally dissolved for ^{36}Cl extraction. Usually this is either an etched mineral separate or rigorously etched whole rock grains.

All green columns refer to the major element concentrations in the "bulk" material, i.e. the chemically untreated and homogenized bulk sample, the composition of which can be significantly different from the target material. If it can be assumed that target and bulk material of the same sample have similar compositions (e.g. most limestones or aphyric volcanics that have only been leached with HNO_3), the same sample concentrations can probably be used for both the target and bulk materials.

All blue columns refer to the trace element concentrations in the "bulk" material, i.e. the chemically untreated and homogenized bulk sample, the composition of which can be significantly different from the target material. If it can be assumed that target and bulk material of the same sample have similar compositions (e.g. most limestones or aphyric volcanics that have only been leached with HNO_3), the same sample concentrations can probably be used for both the target and bulk materials.

"Ztop" refers to the depth of upper side of the sample

"Zbottom" refers to the depth of the lower side of the sample (the sample thickness results from the "Ztop" and "Zbottom" and does not have to be provided separately)

"formation age" is the age when the rock was formed (in years), e.g. eruption age for volcanic rocks. This is necessary for the estimation of the nucleogenic ^{36}Cl contribution.

Table A1: List of all input data to be filled into the sample file with units and comments for clarification.

Column	Characteristic	Unit	Comment
A	sample name		
B	latitude	decimal degrees	Negative values for Southern Hemisphere

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C	longitude	decimal degrees	Negative values for Western Hemisphere
D	altitude	m.a.s.l.	
E	shielding	dimensionless	Value <1
F	density	g/cm ³	Bulk rock density
G	Z top	cm	Upper depth of sample (i.e. 0 if surface sample)
H	Z bottom	cm	Lower depth of sample (i.e. corresponds to sample thickness if surface sample)
I	erosion	cm/a	Assumed constant surface erosion rate
J	± erosion	cm/a	Uncertainty on the assumed constant surface erosion rate (put 0 if no information is available)
K	³⁶ Cl conc	atoms/g	Measured ³⁶ Cl concentrations
L	± ³⁶ Cl conc	atoms/g	Uncertainty on measured ³⁶ Cl concentrations
M	formation age	years	Age when the rock was formed
N	Cl target	ppm	Cl concentration in the target fraction (³⁵ Cl is a target element for ³⁶ Cl production by cosmogenic and nucleogenic low-energy neutron capture)
O	± Cl target	ppm	Uncertainty on Cl concentration in the target fraction
P	SiO ₂ target	%	SiO ₂ concentration in target fraction
Q	Al ₂ O ₃ target	%	Al ₂ O ₃ concentration in target fraction
R	Fe ₂ O ₃ target	%	Fe ₂ O ₃ concentration in target fraction (Fe is a target element for spallogenic ³⁶ Cl production)
S	± Fe ₂ O ₃ target	%	Uncertainty on Fe ₂ O ₃ concentration in target fraction
T	MnO target	%	MnO concentration in target fraction
U	MgO target	%	MgO concentration in target fraction
V	CaO target	%	CaO concentration in target fraction (Ca is a target element for spallogenic and muogenic ³⁶ Cl production)
W	± CaO target	%	Uncertainty on CaO concentration in target fraction
X	Na ₂ O target	%	Na ₂ O concentration in target fraction
Y	K ₂ O target	%	K ₂ O concentration in target fraction (K is a target element for spallogenic and muogenic ³⁶ Cl production)
Z	± K ₂ O target	%	Uncertainty on K ₂ O concentration in target fraction
AA	TiO ₂ target	%	TiO ₂ concentration in target fraction (Ti is a target element for spallogenic ³⁶ Cl production)
AB	± TiO ₂ target	%	Uncertainty on TiO ₂ concentration in target fraction

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AC	P2O5 target	%	P2O5 concentration in target fraction
AD	H2O target	%	H2O concentration in target fraction
AE	CO2 target	%	CO2 concentration in target fraction
AF	SiO2 bulk	%	SiO2 concentration in bulk
AG	Al2O3 bulk	%	Al2O3 concentration in bulk
AH	Fe2O3 bulk	%	Fe2O3 concentration in bulk
AI	MnO bulk	%	MnO concentration in bulk
AJ	MgO bulk	%	MgO concentration in bulk
AK	CaO bulk	%	CaO concentration in bulk
AL	Na2O bulk	%	Na2O concentration in bulk
AM	K2O bulk	%	K2O concentration in bulk
AN	TiO2 bulk	%	TiO2 concentration in bulk
AO	P2O5 bulk	%	P2O5 concentration in bulk
AP	H2O bulk	%	H2O concentration in bulk
AQ	CO2 bulk	%	CO2 concentration in bulk
AR	S bulk	%	S concentration in bulk
AS	Li bulk	ppm	Li concentration in bulk
AT	B bulk	ppm	B concentration in bulk
AU	Cl bulk	ppm	Cl concentration in bulk
AV	Sm bulk	ppm	Sm concentration in bulk
AW	Gd bulk	ppm	Gd concentration in bulk
AX	Th bulk	ppm	Th concentration in bulk
AY	U bulk	ppm	U concentration in bulk