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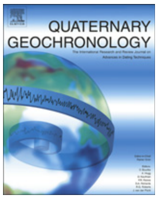

Research Paper

Sources of in-situ ^{36}Cl in basaltic rocks. Implications for calibration of production rates

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ABSTRACT

In-situ cosmogenic ^{36}Cl production rates from spallation of Ca and K determined in several previously published calibration studies differ by up to 50%. In this study we compare whole rock ^{36}Cl exposure ages with ^{36}Cl exposure ages evaluated in Ca-rich plagioclase in the same 10 ± 3 ka lava sample taken from Mt. Etna (Sicily, 38° N). The exposure age of the sample was determined by K–Ar and corroborated by cosmogenic ^{3}He measurements on cogenetic pyroxene phenocrysts. Sequential dissolution experiments showed that high Cl concentrations in plagioclase grains could be reduced from 450 ppm to less than 3 ppm after 16% dissolution. ^{36}Cl exposure ages calculated from the successive dissolution steps of this leached plagioclase sample are in good agreement with K–Ar and ^{3}He age. Stepwise dissolution of whole rock grains, on the other hand, is not as effective in reducing high Cl concentrations as it is for the plagioclase. 330 ppm Cl still remains after 85% dissolution. The ^{36}Cl exposure ages derived are systematically about 30% higher than the ages calculated from the plagioclase. We could exclude contamination by atmospheric ^{36}Cl as an explanation for this overestimate. Magmatic ^{36}Cl was estimated by measuring a totally shielded sample, but was found to account for only an insignificant amount of ^{36}Cl in the case of the 10 ka whole rock sample. We suspect that the overestimate of the whole rock exposure age is due to the difficulty in accurately assessing all the factors which control production of ^{36}Cl by low-energy neutron capture on ^{35}Cl, particularly variable water content and variable snow cover. We conclude that some of the published ^{36}Cl spallation production rates might be overestimated due to high Cl concentrations in the calibration samples. The use of rigorously pretreated mineral separates reduces Cl concentrations, allowing better estimates of the spallation production rates.

In the Appendix of this paper we document in detail the equations used. These equations are also incorporated into a ^{36}Cl calculation spreadsheet made available in the supplementary data.

1. Introduction

In-situ cosmogenic chlorine-36 is widely used to quantify surface processes in geosciences (e.g. Zreda and Phillips, 1994; Benedetti et al., 2003; Shabanian et al., 2009). Clearly, accurate results require that the production rates be well constrained. However, since the first evaluation of ^{36}Cl production rates (Zreda et al., 1991), their determination has been controversial. Different studies have proposed values that vary by up to 50% (Table 1). Possible explanations for these discrepancies were discussed in Swanson and Caffee (2001) and Licciardi et al. (2008). These include the effects of inheritance or erosion on the calibration samples, poorly constrained absolute ages, uncertainties in altitude–latitude scaling effects, temporal magnetic field variability, and neglecting to consider minor production mechanisms.

Cosmogenic ^{36}Cl is produced by various reaction mechanisms in rocks: spallation of K, Ca, Ti and Fe; slow negative muon capture by K and Ca; and low-energy (thermal and epithermal) neutron capture by ^{35}Cl. The ^{36}Cl contributions from each production mechanism depend mainly on the target element concentrations in the rock material from which ^{36}Cl is extracted. The most important target elements are Ca, K and ^{35}Cl. Since ^{35}Cl accounts for 75% of total chlorine in nature, low-energy neutron induced ^{36}Cl production is strongly dependent on the Cl content. The complex behavior of the low-energy neutron flux at the land/atmosphere boundary and its high sensitivity to water content, snow cover, surface geometry, and

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Table 1

^{36}Cl production rate calibration studies. Production rates are scaled to sea level and high geographic latitude (>60°). The scaling methods used are given in the referenced papers. Total production rates from Ca and K comprise spallation and slow negative muon capture and are, thus, not directly comparable to spallation production rates (in bold) or muon capture production rates.

Study	Production pathway	SLHL production rate from			Rock material	Cl content in rock material [ppm] (determined by)	^{36}Cl extraction method	Pretreatment	Comment
		Ca[a]	K[a]	Low-energy neutrons					
Zreda et al. (1991)	Spallation of Ca	**76 ± 5**			Basaltic whole rock	94–111 (ion-selective electrode)	Air stripping method, closed system, no carrier	24 h leaching in MQ water (+2 h leaching in 10% HNO_3 in the case of basaltic whole rock)	Stone et al. (1996) recalculated total prod. rate from Ca to 54.8 ± 5.0 and spall. prod. rate from K to 190
	Spallation of K		**106 ± 8**		Bulk rock and K-microcline	Bulk rock: 130–160, microcline: 140, Qtz: 100–135 (ion-selective electrode)			
	low-energy neutron capture on ^{35}Cl			307 ± 24[c]	Bulk rock and quartz				
Stone et al. (1996)	Total production from Ca	53.6 ± 3.6			Ca-feldspar from basalt	2–5 (ion chromatography)	Method "Stone et al. (1996)", with and without carrier	Leaching in deionised water + 2x in 2% HNO_3 (approx. 15% leached)	Sequential dissolution experiment on limestone: no atmospheric ^{36}Cl found
	Spallation of Ca	**48.8 ± 3.4**							
	Muon capture on Ca	4.8 ± 1.2							
Evans et al. (1997)	Total production from K		170 ± 25		K-feldspar	0–315 (ion chromatography)	Method "Stone et al. (1996)", with carrier	Leaching in hot 10% HNO_3 in ultrasonic bath	Sequential dissolution experiment: no atmospheric ^{36}Cl found
Stone et al. (1998)	Muon capture on Ca	5.3 ± 1.0			Calcite from marble	25–190 (ion chromatography)	Method "Stone et al. (1996)"	like " Stone et al. (1996)"	
Phillips et al. (2001)	Spallation of Ca	**66.8 ± 4.4**			Divers whole silicate rocks	6–350 (not specified)	not specified	not specified	Recalibration of production rates of Phillips et al. (1996)
	Spallation of K		**137 ± 9**						
	low-energy neutron capture on ^{35}Cl			626 ± 46[b]					
Swanson and Caffee (2001)	Total production rate from Ca	91 ± 5			Whole silicate rocks	42–290 (ion-selective electrode)	Modified from Zreda et al. (1991), no carrier	not specified	Discussion of validity of ^{14}C dating used (Easterbrook, 2003; Swanson, 2005)
	Total production rate from K		228 ± 18						
	low-energy neutron capture on ^{35}Cl			762 ± 28[b]					
Licciardi et al. (2008)	Spallation of Ca	**57 ± 5**			Basaltic whole rock	29–61 (isotope dilution)	Modified from Stone et al. (1996), with carrier	Sonication in distilled water and 2% HNO_3	Higher production rate relative to Stone et al. (1996) interpreted as due to atmospheric pressure anomalies in Iceland

[a] [atoms ^{36}Cl (g target element)$^{-1}$ a^{-1}].
[b] [neutrons (g air)$^{-1}$ a^{-1}].
[c] [neutrons (g rock)$^{-1}$ a^{-1}].