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Determination of cosmogenic ^{36}Cl in rocks by isotope dilution: innovations, validation and error propagation

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Abstract

Measurements of cosmogenic ^{36}Cl in terrestrial rocks provide quantitative information about exposure ages of landforms and surface features. The isotope dilution method for preparing ^{36}Cl samples is now widely used because it allows ^{36}Cl and Cl to be measured simultaneously on a single accelerator mass spectrometry target, increases the accuracy and precision of Cl determinations, and reduces rock sample size and laboratory work. In this paper we describe a new implementation of isotope dilution to ^{36}Cl dating, report experimental data verifying the accuracy of this approach, and show how errors in the measured stable isotope ratio propagate to errors in exposure ages.

Successful application of isotope dilution to ^{36}Cl dating requires that Cl be retained during digestion. We performed extractions in a sealed acid-digestion bomb to prevent Cl losses and to reduce digestion times by more than 90%. Isotope dilution gives ^{36}Cl/Cl values within 1σ of conventional (unspiked) values for 8 paired silicate samples, and gives Cl concentrations that are consistent with the ion specific electrode method for 14 of 17 silicate samples. Results from three spiked replicates of a carbonate sample are also consistent with the unspiked ^{36}Cl/Cl, but we found that isotope dilution gives a more accurate estimate of native Cl concentration than the ion specific electrode method. We also prepared five limestone samples in open vessels in the presence of excess Ag^+ to prevent volatilization of Cl. This method would permit processing of larger samples (the bomb's capacity is 5 g), and would be useful for samples with low concentration of Cl or low ^{36}Cl/Cl when insoluble fluorides do not precipitate in the digestion vessel. Results from paired samples digested in both open and closed vessels suggest that open-vessel digestion is a reliable way of preparing spiked carbonate samples.

Keywords: ^{36}Cl; Isotope dilution; Cosmogenic nuclides; Exposure dating; Accelerator mass spectrometry

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1. Introduction

Cosmogenic ^{36}Cl is widely used for surface exposure dating because it is produced at measurable levels from three elements common in most rocks: Ca, K and Cl. Production of ^{36}Cl in surface rocks is dominated by interactions of energetic cosmic-ray neutrons with ^{40}Ca and ^{39}K targets and by thermal neutron activation of ^{35}Cl (Phillips et al., 2001). Because the production rates for

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these three mechanisms are known from calibrations on independently dated landforms, exposure ages can be calculated from measurements of the near-surface inventory of ^{36}Cl in mineral grains.

Accelerator mass spectrometry (AMS) is the standard method for measuring ^{36}Cl at the very low levels (part-per-trillion) of terrestrial samples (Elmore and Phillips, 1987). Because AMS measures only the atomic ratio of ^{36}Cl to Cl, determination of the ^{36}Cl inventory in a sample requires an independent measurement of Cl concentration. In the past, a sample split was retained for total Cl determination and elemental analysis while a substantially larger split was digested in a loosely capped bottle, from which AgCl was extracted for AMS analysis (e.g. Zreda et al., 1991).

Independent measurements of chlorine concentration in unspiked samples are usually made by the ion-selective electrode method following digestion of samples in diffusion cells (Aruscavage and Campbell, 1983; Elsheimer, 1987). Precise Cl determinations require at least three ion-selective electrode measurements on separate aliquots. For samples with <40 ppm Cl, several more measurements may be needed both because the method is less precise and because ^{36}Cl ages are more sensitive to Cl concentration in low Cl rocks when isotope dilution is not used. This higher sensitivity is a result of how errors in Cl concentration are propagated to the ^{36}Cl inventory. For example, with a high Cl rock (where neutron activation is the dominant production mechanism) an erroneously high Cl determination will lead to an erroneously high calculation of the ^{36}Cl inventory, but this will be compensated by a proportionately higher estimated abundance of ^{35}Cl targets, and therefore the age does not change much. In low Cl rocks, where production from Ca and K targets usually dominate, this compensating effect is small, and erroneously high (low) Cl contents from the ion-selective electrode will lead to ages that are too young (too old). For samples < 10 ppm Cl, the ion-selective electrode method becomes impractical because of poor precision and poor reproducibility. Moreover, for carbonate samples, we found that the ion-selective electrode overestimates Cl concentration by as much as a factor of two.

An alternative method for measuring Cl concentration is to spike AMS samples with a known amount of isotopically-enriched stable chloride carrier during chemical preparation (Elmore et al., 1997; Sharma et al., 2000). Total Cl concentration is then calculated from the ^{35}Cl/^{37}Cl ratio which is measured on Faraday cups in the AMS ion injector before acceleration (Elmore et al., 1997). The composite ^{35}Cl/^{37}Cl ratio is the result of simple binary mixing between carrier Cl, of known ^{35}Cl/^{37}Cl ratio and concentration, and sample Cl of unknown concentration and known (natural) ^{35}Cl/^{37}Cl. Isotope dilution is now widely used in ^{36}Cl dating because it has five advantages:

(1) Both ^{36}Cl/Cl and total Cl are determined simultaneously on the same AMS target prepared from the same aliquot of the rock sample.
(2) Total Cl measurements by isotope dilution mass spectrometry are more precise than by ion-selective electrode, particularly at low Cl concentrations.
(3) Sample size is reduced; in our experience approximately by a factor of ten over samples without Cl carrier.
(4) Total Cl can be measured accurately in carbonates, for which the ion-selective electrode method overestimates values.
(5) Calculated ages are less sensitive to contamination by Cl from reagents and other sources.

Successful application of the isotope dilution method requires that the ratio of spike-derived Cl to rock-derived Cl is maintained throughout the chemical extraction and purification processes. Once sample Cl has been liberated from mineral grains and has equilibrated with Cl carrier, losses of Cl do not affect ^{36}Cl/Cl or ^{35}Cl/^{37}Cl. But if losses occur prior to isotopic equilibration, ages calculated from diluted samples would be inaccurate. The most critical factor is the timing of the carrier addition in relation to the slow release of Cl from the dissolving mineral grains. If added prior to digestion, carrier could be preferentially lost before rock Cl is released, resulting in erroneously old ages; if carrier is added after digestion, Cl might be preferentially lost, leading to erroneously young ages. Preferential losses of chlorine would also affect samples diluted with natural carrier, potentially making ages too high or too low depending on the timing of carrier and silver nitrate additions.

Our work was partially motivated by the possibility that Cl losses could occur during open-vessel digestions before attainment of isotopic equilibrium between sample Cl and carrier. One possible mechanism for chlorine loss is the volatilization and escape of Cl from the low-pH and (for silicates) high-temperature (90 °C) digestion environment. The volatility of Cl in the form of neutral HCl molecules is well-known (Simonson and Palmer, 1993) and is the basis of at least one early air-stripping method for extracting Cl from silicate rocks (Zreda et al., 1991; Zreda and Phillips, 1994). Prevention of significant Cl losses prior to isotopic equilibration is critical if either isotopically enriched carrier or natural carrier are added to samples.

A potential complication in performing isotope dilution mass spectrometry in the AMS system is that there is a small memory in the ion source and injector magnet from contamination by previous samples. For isotopically enriched samples, a substantial fraction of the low beam current for the less abundant isotope may consist partly of cross contamination from samples that contain a natural ratio of ^{35}Cl/^{37}Cl (e.g. ^{36}Cl standard). Although in principle the background can be measured in blanks and subtracted from samples, measurements at the Purdue Rare Isotope Measurement Laboratory (PRIME Lab) show that the cross-contamination can be variable (different by as much as a factor of two between spike blanks loaded on an 8-sample wheel) and therefore adds additional uncertainty to the final ^{35}Cl/^{37}Cl (a new ion source at the PRIME Lab produces beam currents that are 5–10 times more intense than most AMS ion sources and should greatly reduce the problem at that facility (Jackson et al., 2004)). We show in Section 4 that although large errors in ^{35}Cl/^{37}Cl propagate to proportionately large errors in both Cl concentration and ^{36}Cl/Cl, exposure ages of low Cl samples are insensitive to stable isotope errors because of canceling effects.

Isotope dilution is now widely used in ^{36}Cl dating (Barrows et al., 2002; Benedetti et al., 2003; Phillips, 2003), but there are few published experimental data to validate the technique. To test the accuracy of this method, we compared measurements on spiked samples digested in a high-pressure acid-digestion bomb with those from unspiked samples digested in loosely-capped PTFE (poly-tetra-fluoro-ethylene) bottles. Advantages of the pressure bomb are that Cl loss is minimized or eliminated and that samples can be digested at a high temperature (up to 150 °C) and pressure (up to 13 MPa), reducing the digestion time for silicates tenfold. A disadvantage is that a maximum of 5 g of rock can be digested at a time, thus requiring multiple digestions (usually no more than 3) for larger samples.

In this paper we discuss experimental results from paired samples that were digested in open vessels without adding spike and in the bomb with ^{35}Cl spike added prior to digestion. We also discuss paired open-vessel and closed vessel digestions of two spiked carbonates, and give equations for propagating analytical uncertainties in measurements of ^{35}Cl/^{37}Cl to uncertainties in Cl concentration, ^{36}Cl/Cl and landform age.

2. Theory

Two conditions must be met when diluting samples with stable Cl. First, ^{36}Cl/Cl in the sample must remain above the detection limit for AMS analysis. Currently, ^{36}Cl/Cl can be measured by AMS with 5% precision at ratios as low as 30×10^{-15}, with better precision being obtained at higher ratios. Second, the composite ^{35}Cl/^{37}Cl ratio must be different enough from the native rock ratio so that Cl concentration can be accurately determined. Our experiments show that accurate Cl determinations can be made on samples with ^{35}Cl/^{37}Cl as low as 4 when ^{35}Cl enriched carrier is used; however, because Cl concentration is not well-known in most samples before analysis, we recommend aiming for ^{35}Cl/^{37}Cl > 10 in order to give a safe margin for samples with unexpectedly high Cl. As shown quantitatively in Section 4, the sensitivity of Cl content (and therefore of landform age) increases rapidly at ratios smaller than 10. The equations for calculating the ^{36}Cl/Cl ratio and Cl content from AMS measurements on spiked samples are given below.

The measured stable Cl ratio, $(^{35}\mathrm{Cl}/^{37}\mathrm{Cl})_{\mathrm{meas}}$, is the ratio of the sum of Cl from rock, $\mathrm{Cl}_{\mathrm{rck}}$, carrier, Cl_{c}, and background, Cl_{b}:

$$\left(\frac{^{35}\mathrm{Cl}}{^{37}\mathrm{Cl}}\right)^{*}_{\mathrm{meas}}=\frac{[^{35}\mathrm{Cl}^{*}]}{[^{37}\mathrm{Cl}^{*}]}=\frac{[^{35}\mathrm{Cl}_{\mathrm{rck}}]+[^{35}\mathrm{Cl}_{\mathrm{c}}]+[^{35}\mathrm{Cl}_{\mathrm{b}}]}{[^{37}\mathrm{Cl}_{\mathrm{rck}}]+[^{37}\mathrm{Cl}_{\mathrm{c}}]+[^{37}\mathrm{Cl}_{\mathrm{b}}]} \tag{1}$$

where the star indicates that the measured quantity includes cross contamination. The contaminated isotope ratio can be corrected by subtracting the background component:

$$\left(\frac{^{35}\mathrm{Cl}}{^{37}\mathrm{Cl}}\right)_{\mathrm{meas}}=\frac{[^{35}\mathrm{Cl}^{*}]-[^{35}\mathrm{Cl}_{\mathrm{b}}]}{[^{37}\mathrm{Cl}^{*}]-[^{37}\mathrm{Cl}_{\mathrm{b}}]} \tag{2}$$

The total atoms of rock Cl, $[\mathrm{Cl}_{\mathrm{rck}}]$, in a spiked sample can be obtained from measurements of ^{35}Cl/^{37}Cl using the relation:

$$[\mathrm{Cl}_{\mathrm{rck}}]=\left[\frac{\left(\frac{^{35}\mathrm{Cl}}{^{37}\mathrm{Cl}}\right)_{\mathrm{meas}}[^{37}\mathrm{Cl}_{\mathrm{c}}]-[^{35}\mathrm{Cl}_{\mathrm{c}}]}{\left(\frac{^{35}\mathrm{Cl}}{^{37}\mathrm{Cl}}\right)_{\mathrm{rck}}-\left(\frac{^{35}\mathrm{Cl}}{^{37}\mathrm{Cl}}\right)_{\mathrm{meas}}}\right]\left[1+\left(\frac{^{35}\mathrm{Cl}}{^{37}\mathrm{Cl}}\right)_{\mathrm{rck}}\right] \tag{3}$$

where $[^{37}\mathrm{Cl}_{\mathrm{c}}]$ and $[^{35}\mathrm{Cl}_{\mathrm{c}}]$ represent the amounts of ^{35}Cl and ^{37}Cl carrier in atoms, $(^{35}\mathrm{Cl}/^{37}\mathrm{Cl})_{\mathrm{meas}}$ is the measured composite stable isotope ratio, and $(^{35}\mathrm{Cl}/^{37}\mathrm{Cl})_{\mathrm{rck}}$ is the natural ratio of 3.127.

The ^{36}Cl/Cl ratio determined from AMS measurements on a spiked target is represented by:

$$\left(\frac{^{35}\mathrm{Cl}}{\mathrm{Cl}}\right)_{\mathrm{meas}}=\frac{[^{36}\mathrm{Cl}_{\mathrm{rck}}]}{[^{37}\mathrm{Cl}_{\mathrm{rck}}]+[^{37}\mathrm{Cl}_{\mathrm{c}}]+[^{35}\mathrm{Cl}_{\mathrm{rck}}]+[^{35}\mathrm{Cl}_{\mathrm{rck}}]} \tag{4}$$

At the PRIME Lab, where our samples were measured, ^{36}Cl/^{37}Cl is directly measured and ^{36}Cl/Cl is calculated from ^{35}Cl/^{37}Cl measured before the

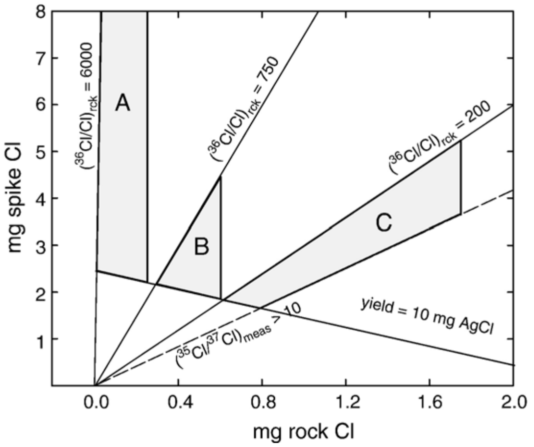

Fig. 1. Applications of the spike optimization problem. The solid lines labeled $(^{36}\mathrm{Cl/Cl})_{\mathrm{rck}}$ (units of 10^{-15}) define the maximum amount of spike that can be added to a sample while satisfying the constraint $(^{36}\mathrm{Cl/Cl})_{\mathrm{meas}} > 100 \times 10^{-15}$ for the given value of $(^{36}\mathrm{Cl/Cl})_{\mathrm{rck}}$. The dashed line defines the minimum spike needed to obtain $(^{35}\mathrm{Cl}/^{37}\mathrm{Cl})_{\mathrm{meas}} > 10$ for carriers having $^{35}\mathrm{Cl}/^{37}\mathrm{Cl}$ from 50 to 300. Spike-sample combinations plotting above the negatively-sloping line give theoretical yields of at least 10 mg of AgCl. These constraints define a domain (shaded) of optimal AMS results for a given $(^{36}\mathrm{Cl/Cl})_{\mathrm{rck}}$, rock amount (maximum of 5 g per digestion) and spike isotopic composition. Optimal domain *A* corresponds to a sample with $(^{36}\mathrm{Cl/Cl})_{\mathrm{rck}} = 6000 \times 10^{-15}$ and 50 ppm Cl. Because of low Cl content and high $(^{36}\mathrm{Cl/Cl})_{\mathrm{rck}}$, a large amount of spike can be added to achieve increased yield. Optimal domain *B* corresponds to a sample with $(^{36}\mathrm{Cl/Cl})_{\mathrm{rck}} = 750 \times 10^{-15}$ and 120 ppm Cl. The constraint on $(^{36}\mathrm{Cl/Cl})_{\mathrm{meas}}$ tightly controls the amount of spike that can be safely added. Optimal domain *C* corresponds to of 350 ppm Cl rock with $(^{36}\mathrm{Cl/Cl})_{\mathrm{rck}} = 200 \times 10^{-15}$. Here, the constraints on $(^{35}\mathrm{Cl}/^{37}\mathrm{Cl})_{\mathrm{meas}}$ and $(^{36}\mathrm{Cl/Cl})_{\mathrm{rck}}$ narrowly define the minimum and maximum amounts of spike that can be added.

accelerator. In the past, both ^{35}Cl and ^{37}Cl currents were measured before and after the accelerator to correct for mass fractionation. Because this correction has been shown to be both small and uncertain at the PRIME Lab, the ratios reported in this work were not corrected for mass fractionation in the accelerator.

The ^{36}Cl/Cl ratio in the rock, $(^{36}\mathrm{Cl/Cl})_{\mathrm{rck}}$, can be calculated from measured ratio $(^{36}\mathrm{Cl/Cl})_{\mathrm{meas}}$ according to:

$$\left(\frac{^{36}\mathrm{Cl}}{\mathrm{Cl}}\right)_{\mathrm{rck}} = \left(\frac{^{36}\mathrm{Cl}}{\mathrm{Cl}}\right)_{\mathrm{meas}} \cdot \left[1 + \frac{[\mathrm{Cl_c}]}{[\mathrm{Cl_{rck}}]}\right] \qquad (5)$$

where $[\mathrm{Cl_{rck}}]$ is from Eq. (3) and $[\mathrm{Cl_c}]$ is the total atoms of spike added to a sample.

The optimal carrier amount is determined from initial estimates of $(^{36}\mathrm{Cl/Cl})_{\mathrm{rck}}$ and $[\mathrm{Cl_{rck}}]$. A single ion-selective electrode measurement should give an adequate initial estimate of Cl concentration. The ^{36}Cl/Cl of a sample can be estimated from the Cl concentration, the ^{36}Cl production rate at the sample site, and an initial guess of the minimum exposure age.

Three examples illustrating spike optimization are shown in Fig. 1. Sample *A* has high ^{36}Cl/Cl (6000×10^{-15}), but low Cl concentration and therefore requires a large addition of carrier to achieve adequate AgCl yield. This is typical of samples that have a combination of the following: long exposure times (hence high ^{36}Cl content), low Cl concentrations (hence high ^{36}Cl/Cl), and high production rates (high concentration of Ca and/or K, and/or located at high altitudes). Sample *B* has a lower ^{36}Cl/Cl (750×10^{-15}) and a higher Cl concentration (120 ppm). The main challenge is to achieve adequate yield by adding spike while keeping $(^{36}\mathrm{Cl/Cl})_{\mathrm{meas}} > 100 \times 10^{-15}$. The optimization results in a small area (*B*) that can be expanded only by digesting a larger sample. Sample *C* has the lowest ^{36}Cl/Cl and highest Cl concentration (350 ppm). It is typical of samples that are young, or have high Cl concentration and/or have low production rates (low altitude and/or low concentration of target elements Ca and K). This problem is similar to *B* except that the lower constraint on $(^{35}\mathrm{Cl}/^{37}\mathrm{Cl})_{\mathrm{meas}}$ must also be considered. In this type of sample, high yields are possible but the optimal spike amount is narrowly restricted. If too little spike is used, $(^{35}\mathrm{Cl}/^{37}\mathrm{Cl})_{\mathrm{meas}}$ will drop below 10, if too much is used, $(^{36}\mathrm{Cl/Cl})_{\mathrm{meas}}$ will drop below 100×10^{-15}.

3. Isotope dilution experiments

3.1. Procedure for closed vessel digestions

3.1.1. Silicate rocks

A closed-system was maintained during Cl extractions by digesting samples in a large-capacity acid-digestion bomb (Almasi, 2001). We used Parr Instrument Company

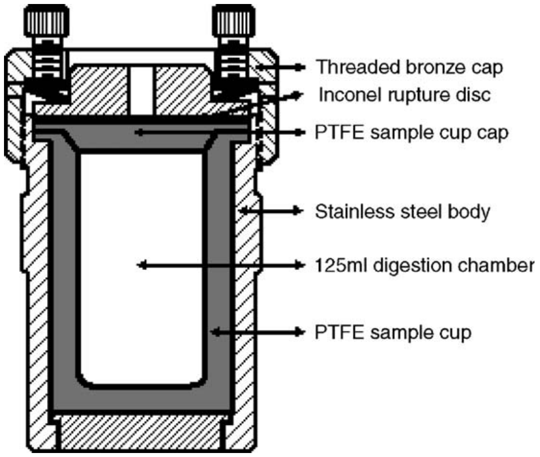

Fig. 2. High-pressure acid-digestion vessel (Parr Instrument Co. Model 4748).

Model 4748 with removable 125 ml PTFE cup designed to digest up to 5 g of crushed rock (Fig. 2). The stainless-steel case and threaded bronze cap withstand pressures up to 13.1 MPa, allowing digestion temperatures to reach 150 °C. The high temperature and pressure in the bomb substantially reduces the digestion time compared with conventional open-vessel digestion. For example, complete digestion of 2 g of silicate rock can be achieved in 2 h at 130 °C, compared with 72 h at 90 °C in an open vessel.

All silicate samples were first crushed, sieved (0.25–1.00 mm fraction) and then leached for 24 h in dilute HNO_3. Dried samples were then loaded into the PTFE cup and weighed. A known mass of 250 ppm NaCl spike (99.66% ^{35}Cl, from Sigma-Aldrich, Inc) solution was pipetted to the cup, followed by the addition of ~40 g of 45% HF and ~5 g of 70% HNO_3. At room temperature the digestion of silicates is sufficiently slow that the bomb can be assembled and sealed before significant vapor losses occur. The sealed bomb was heated to 130 °C in an oven for 2–8 h. Before dismantling, the bomb was air cooled for 30 min. Approximately 5 ml of 0.1 M $AgNO_3$ were then added to the sample to precipitate the mixed spike and sample Cl as AgCl. The resulting AgCl was purified of the interfering ^{36}S isobar by barium sulfate extractions followed by rinses in deionized water (Zreda et al., 1991).

3.1.2. Carbonate rocks

Carbonate samples were prepared similarly to silicates, but were digested in HNO_3 at room temperature for 30 min. Because acids react violently with carbonates, it was necessary to isolate samples from the HNO_3 until the bomb could be sealed. This was accomplished by encasing the sample in ice made of 18 MΩ Milli-Q water before inserting the sample into the acid-containing PTFE cup (Almasi, 2001). This allowed ~ 30 s to assemble the bomb cover and tighten the screw cap before the acid would begin dissolving the rock sample.

3.2. Results for closed vessel digestions

3.2.1. Silicate rocks

Closed-vessel isotope dilution results mostly agree with results from the conventional (without carrier) open-vessel method (Table 1, Fig. 3). For 14 of 17 samples, Cl concentrations calculated from isotope dilution agree with ion-selective electrode determinations. The three exceptions are HAW00-5, HAW00-8 and HAW00-26, for which the ion-specific electrode gives higher Cl concentrations. Chlorine loss during digestion can be ruled out as a possible explanation because losses could only have occurred either preferentially from the carrier during digestion before the

Table 1
$^{36}Cl/Cl$ (10^{-15}) and Cl concentration in silicate rocks determined from isotope dilution compared to values measured in unspiked samples

Spiked							Unspiked	
Sample ID	Sample (g)	^{35}Cl spike (mg)	Measured (spike+rock Cl)		Calculated (rock Cl)		Cl (ppm)	$(^{36}Cl/Cl)_{rck}$
			$(^{35}Cl/^{37}Cl)_{meas}$	$(^{36}Cl/Cl)_{meas}$	Cl (ppm)	$(^{36}Cl/Cl)_{rck}$		
Granite								
CH96-6-A2F	2.00	0.915	11.40±0.60	1230±60	367±28	3811±268	374±7	4030±90
CH96-6-A2F	2.01	1.862	19.05±0.30	781±31	376±6	4021±122		
CH96-6-A2F	1.00	1.826	29.60±0.80	436±21	428±13	3563±196		
					Mean:	3882±229		
Hawaiites and basalts								
HAW00-1-L1	11.99	0.379	3.77±0.15	620±60	314±76	719±75	335±13	724±35
HAW00-2-L1	6.51	0.268	4.11±0.03	690±30	284±8	859±38	296±22	845±38
HAW00-3-L1	12.01	0.358	4.09±0.04	775±21	210±9	961±28	211±20	923±38
HAW00-4-L1	8.00	0.403	6.13±0.11	711±50	113±4	1243±94	106±7	–
HAW00-5-L1	6.00	0.092	3.84±0.09	750±50	146±18	883±62	292±28	842±32
HAW00-6-L1	14.05	0.358	3.95±0.14	710±50	210±35	855±67	192±16	–
HAW00-7-L1	16.53	0.501	3.74±0.15	480±40	335±80	553±50	305±20	382±16
HAW00-8-L1	9.00	0.269	4.37±0.07	349±28	163±9	457±37	224±9	503±13
HAW00-9-L1	12.02	0.537	5.65±0.04	357±27	120±2	581±44	117±6	–
HAW00-10-L1	9.00	0.511	13.95±0.25	500±160	35±0.8	1885±615	27±16	–
HAW00-11-L1	18.06	0.817	10.74±0.06	1000±40	40±0.3	2926±125	46±6	–
HAW00-12-L1	12.02	0.740	7.6±0.40	810±50	93±8	1717±202	61±30	–
HAW00-13-L1	9.01	0.208	3.68±0.15	550±30	281±74	626±41	290±30	–
HAW00-14-L1	6.00	0.141	3.69±0.15	480±30	283±73	547±40	256±30	–
HAW00-15-L1	17.99	0.816	7.31±0.29	620±40	73±5	1269±123	74±1	–
HAW00-26-L1	13.33	0.228	4.72±0.17	770±40	73±8	1075±72	200±20	1031±30

Reported $(^{36}Cl/Cl)_{meas}$ and $(^{35}Cl/^{37}Cl)_{meas}$ ratios are from multiple runs on the same AMS target.

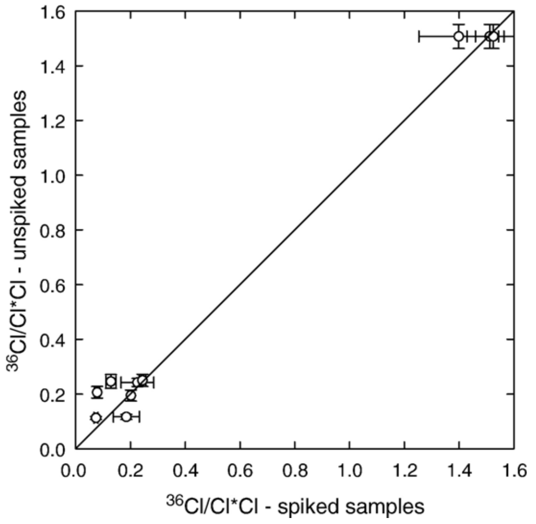

Fig. 3. Comparison of ^{36}Cl inventories for spiked samples and unspiked samples.

sample had completely dissolved or while spike Cl and sample Cl were in equilibrium. The first scenario would give erroneously high Cl concentrations, in contrast to the observed lower Cl concentrations, and the second scenario would not change the Cl concentration. Moreover, significant preferential losses from either carrier or sample would produce large errors in calculated $(^{36}Cl/Cl)_{rck}$ from spiked samples, which are not observed (Table 1). Laboratory mistakes resulting in erroneous total Cl would likewise produce erroneous $(^{36}Cl/Cl)_{rck}$. Because the dilution replicates yield ages that are in better agreement with other samples from the same landform, we conclude that Cl concentrations determined by isotope dilution are more accurate in these cases.

Most of the HAW00 samples have $(^{35}Cl/^{37}Cl)_{meas}$ well below our target ratio of 10. These samples tend to be high in Cl (150–300 ppm) and therefore require large additions of spike in order to achieve high stable isotope ratios. However, because the exposure age was poorly constrained beforehand the amount of spike that could be safely added to these samples while maintaining $^{36}Cl/Cl > 100$ was limited.

3.2.2. Carbonate rocks

The ion-selective electrode method consistently gives higher Cl concentrations for carbonates than the isotope dilution method (Table 2). At the relatively low concentrations measured here (<20 ppm), ion-selective electrode values are on average higher by 45%. Given that our ^{36}Cl/Cl ratios from the spiked bomb digestions agree with the ratios from the open-vessel, unspiked digestions, we believe that the isotope dilution Cl concentrations are correct, and that there is a systematic error in applying the ion-selective electrode method to carbonate rocks with low Cl.

Our results show that within analytical uncertainties spiked samples give ^{36}Cl/Cl values identical to unspiked samples, confirming the accuracy and precision of the bomb method for preparing samples.

3.3. Open-vessel digestion of carbonates

Two disadvantages of closed-vessel digestions are the expense and smaller capacity (5 g) of digestion bombs compare to PTFE bottles (100 g). We therefore investigated the feasibility of performing isotope dilution in samples extracted from open PTFE bottles. A major concern with open-vessel digestions is the possibility of Cl volatilization in the acidic (and for silicates, hot) digestion environment. Stone et al. (1996) reported that volatilization of Cl can occur in the presence of concentrated HNO_3 but indicated that losses could be avoided if samples are exposed to strengths less than 2 M for silicates and less than 0.5 M for carbonates. If Cl losses are significant, it would be difficult to ensure that preferential losses of carrier or rock Cl do not occur before isotopic equilibrium is attained, and calculated ages could be inaccurate. In our open-vessel procedure we ensure retention of both rock and carrier Cl by adding $AgNO_3$ before dissolving the sample so that Cl is

Table 2
^{36}Cl/Cl (10^{-15}) and Cl concentration in carbonate rocks determined from isotope dilution compared to values measured in unspiked samples

Spiked							Unspiked	
Sample ID	Sample (g)	^{35}Cl spike (mg)	Measured (spike+rock Cl)		Calculated (rock Cl)		Cl (ppm)	$(^{36}Cl/Cl)_{rck}$
			$(^{35}Cl/^{37}Cl)_{meas}$	$(^{36}Cl/Cl)_{meas}$	Cl (ppm)	$(^{36}Cl/Cl)_{rck}$		
HL96-34	15.00	0.550	20.03 ± 0.30	1433 ± 52	14.1 ± 0.2	7700 ± 352	20.0 ± 0.4	7550 ± 150
HL96-34	10.00	0.728	33.94 ± 0.50	831 ± 38	14.6 ± 0.3	7814 ± 378		
HL96-34	5.00	0.727	62.00 ± 0.80	376 ± 18	13.4 ± 0.2	7214 ± 297		
				Mean:	14.0 ± 0.6	7522 ± 199	20.0 ± 0.4	7550 ± 150

Reported $(^{36}Cl/Cl)_{meas}$ and $(^{35}Cl/^{37}Cl)_{meas}$ ratios are calculated from multiple runs on the same AMS target.

immediately precipitated and remains in the vessel. This procedure has only been validated for carbonate rocks, where insoluble fluoride residues that could possibly sequester Cl are not produced during digestion.

3.3.1. Validation of open-vessel procedure for spiked limestone samples

To test the accuracy of our open-vessel isotope dilution procedure, we performed paired open-vessel ("O" at the end of sample name) and closed-vessel ("C" at the end of sample name) digestions of five spiked limestone samples. In the closed-vessel digestions we followed the procedure in Section 3.1. Open-vessel digestions were performed in 500 ml PTFE beakers by adding 1 g of $AgNO_3$ to the spiked samples followed by 10 ml of deionized water and 20 ml of 30% HNO_3. After allowing samples to dissolve for 10 min, the resulting AgCl precipitate was purified according to standard methods (Zreda et al., 1991).

Our results (Table 3) validate the open-vessel method for preparing spiked carbonate samples. Calculated values for $[Cl_{rck}]$, $(^{36}Cl/Cl)_{rck}$ and exposure age are consistent to well within 1σ for four of five paired replicates. The exposure ages of these samples are insensitive to large errors in spike amount or to analytical errors in $(^{35}Cl/^{37}Cl)_{meas}$ because ^{36}Cl production is dominated by spallation of ^{40}Ca. In spallation-dominated rocks, an error in $(^{36}Cl/Cl)_{rck}$ propagated from $(^{35}Cl/^{37}Cl)_{meas}$ is compensated by an error of equal magnitude but opposite direction in $[Cl_{rck}]$. For example, the uncertainty in the landform age would increase by less than 2% on the PV03–30 samples if the uncertainty in $(^{35}Cl/^{37}Cl)_{meas}$ were increased by an order of magnitude, even though the uncertainties in Cl concentration and $^{36}Cl/Cl$ would be an order of magnitude greater. The reason for this insensitivity is explored analytically in the following section which deals with propagating AMS errors to landform age.

4. Error analysis

4.1. Sensitivity of exposure ages to measured stable isotope ratio and spike composition

We asssume that the general error propagation formula:

$$\sigma_z^2 = \left[\sigma_x \frac{\partial z}{\partial x}\right]^2 + \left[\sigma_y \frac{\partial z}{\partial y}\right]^2 + 2r\sigma_x\sigma_y \frac{\partial z}{\partial x}\frac{\partial z}{\partial y} \tag{6}$$

for a function $z(x,y)$ with Gaussian errors and correlation coefficient r is valid for propagating analytical errors in AMS measurements to calculations of $[Cl_{rck}]$, $(^{36}Cl/Cl)_{rck}$ and exposure age. Eq. (6) is valid only when σ_z^2 is not very large compared with $z(x,y)$, a condition that is met in most error propagation problems related to isotope dilution calculations.

AMS measurements of $^{35}Cl/^{37}Cl$ can sometimes include a systematic error related to cross contamination between samples. The contaminated isotope ratio can be corrected by subtracting the background. The uncertainty in the corrected ratio, $\sigma(^{35}Cl/^{37}Cl)_{meas}$, is then given by:

$$\begin{aligned}\left[\sigma\left(\frac{^{35}Cl}{^{37}Cl}\right)_{meas}\right]^2 = {} & \frac{(\sigma[^{35}Cl_b])^2}{([^{37}Cl_c]-[^{37}Cl_b])^2} \\ & +(\sigma[^{37}Cl_b])^2\left[\frac{([^{35}Cl_c]-[^{35}Cl_b])}{([^{37}Cl_c]-[^{37}Cl_b])^2}\right]^2 \\ & +\left[\sigma\left(\frac{^{35}Cl}{^{37}Cl}\right)^{*}_{meas}\right]^2\end{aligned} \tag{7}$$

Table 3

Comparison of results from open-vessel and closed-vessel digestions of limestone samples

Sample ID	Amount added			Measured		Calculated		
	Sample g	^{35}Cl spike mg	Cl natural mg	$(^{36}Cl/Cl)_{meas}$	$(^{35}Cl/^{37}Cl)_{meas}$	$(^{36}Cl/Cl)_{rck}$	Cl (ppm)	Age (yrs)
PV03–80-C	10.02	0.901	0.497	1020±32	8.2±0.05	7624±3923	21.6±0.7	42,732±1350
PV03–80-O	10.00	0.901	0.494	950±35	8.3±0.05	7391±3439	20.6±0.7	39,585±1465
PV03–60-C	19.90	1.283	0.991	728±24	7.9±0.07	18,835±3236	4.6±0.8	22,974±769
PV03–60-O	10.05	0.606	0.496	782±35	7.8±0.06	33,150±8369	2.7±0.7	23,378±1003
PV03–42-C	15.02	1.835	0.362	457±7	19.0±0.03	12,344±234	5.6±0.1	18,437±288
PV03–42-O	20.30	3.755	0.483	295±9	28.56±0.025	18,535±587	3.4±0.0	16,669±521
PV03–39-C	15.12	1.896	0.375	390±15	19.43±0.047	12,407±526	4.9±0.1	16,078±629
PV03–39-O	21.03	3.669	0.808	276±10	18.96±0.0058	14,295±521	4.2±0.0	15,939±589
PV03–30-C	15.11	1.826	0.369	320±9	20.27±0.053	17,488±747	2.7±0.1	12,664±361
PV03–30-O	20.14	2.672	0.483	289±9	22.62±0.08	22,617±1435	2.0±0.1	12,306±389

Reported $(^{36}Cl/Cl)_{meas}$ (units of 10^{-15}) and $(^{35}Cl/^{37}Cl)_{meas}$ ratios are calculated from multiple runs on the same AMS target.

where the first two terms account for the error in removing an uncertain background contamination $\sigma[\mathrm{Cl_b}]$ from the ratio and the last term accounts for the uncertainty in the measured stable isotope ratio.

The uncertainty in $[\mathrm{Cl_{rck}}]$ due only to $\sigma(^{35}\mathrm{Cl}/^{37}\mathrm{Cl})_{\mathrm{meas}}$ is given by:

$$(\sigma[\mathrm{Cl_{rck}}])^2 = \left[\sigma\left(\frac{^{35}\mathrm{Cl}}{^{37}\mathrm{Cl}}\right)_{\mathrm{meas}}\right]^2 \left[\left[\frac{\left(\frac{^{35}\mathrm{Cl}}{^{37}\mathrm{Cl}}\right)_{\mathrm{meas}}[^{37}\mathrm{Cl_c}]-[^{35}\mathrm{Cl_c}]}{\left[\left(\frac{^{35}\mathrm{Cl}}{^{37}\mathrm{Cl}}\right)_{\mathrm{rck}}-\left(\frac{^{35}\mathrm{Cl}}{^{37}\mathrm{Cl}}\right)_{\mathrm{meas}}\right]^2}\right]\left[1+\left(\frac{^{35}\mathrm{Cl}}{^{37}\mathrm{Cl}}\right)_{\mathrm{rck}}\right]+\left[\frac{[^{37}\mathrm{Cl_c}]\left[1+\left(\frac{^{35}\mathrm{Cl}}{^{37}\mathrm{Cl}}\right)_{\mathrm{rck}}\right]}{\left[\left(\frac{^{35}\mathrm{Cl}}{^{37}\mathrm{Cl}}\right)_{\mathrm{rck}}-\left(\frac{^{35}\mathrm{Cl}}{^{37}\mathrm{Cl}}\right)_{\mathrm{meas}}\right]}\right]\right]^2 \tag{8}$$

The uncertainties in $[\mathrm{Cl_{rck}}]$ and $(^{36}\mathrm{Cl}/\mathrm{Cl})_{\mathrm{meas}}$ propagate to $(^{36}\mathrm{Cl}/\mathrm{Cl})_{\mathrm{rck}}$ through the relation:

$$\left[\sigma\left(\frac{^{36}\mathrm{Cl}}{\mathrm{Cl}}\right)_{\mathrm{rck}}\right]^2 = \left[\left[\sigma\left(\frac{^{36}\mathrm{Cl}}{\mathrm{Cl}}\right)_{\mathrm{meas}}\right]\left[1+\frac{[\mathrm{Cl_c}]}{[\mathrm{Cl_{rck}}]}\right]\right]^2 + \left[\sigma[\mathrm{Cl_{rck}}]\left[1-\frac{[\mathrm{Cl_c}]\cdot\left(\frac{^{36}\mathrm{Cl}}{\mathrm{Cl}}\right)_{\mathrm{meas}}}{[\mathrm{Cl_{rck}}]^2}\right]\right]^2 \tag{9}$$

which assumes that there is no correlation between analytical errors in $(^{35}\mathrm{Cl}/^{37}\mathrm{Cl})_{\mathrm{meas}}$ and $(^{36}\mathrm{Cl}/\mathrm{Cl})_{\mathrm{meas}}$. The first term accounts for uncertainty in $(^{36}\mathrm{Cl}/\mathrm{Cl})_{\mathrm{meas}}$ and the second term accounts for uncertainty in $[\mathrm{Cl_{rck}}]$.

Propagation of uncertainty in $(^{35}\mathrm{Cl}/^{37}\mathrm{Cl})_{\mathrm{meas}}$ to exposure age requires consideration of the relative importance of $^{36}\mathrm{Cl}$ production mechanisms, the relation between $(^{36}\mathrm{Cl}/\mathrm{Cl})_{\mathrm{calc}}$ and $[\mathrm{Cl_{rck}}]$ and the exposure age. These relations are given in the buildup equation for the inventory (N) of $^{36}\mathrm{Cl}$ (Zreda and Phillips, 1994):

$$\frac{\mathrm{d}N}{\mathrm{d}t} = -\lambda N + [n_{\mathrm{sp}}]P_{\mathrm{sp}} + \frac{[\mathrm{Cl_{rck}}]}{M_{\mathrm{rck}}}P_{\mathrm{th}} \tag{10}$$

where

N	inventory of $^{36}\mathrm{Cl}$ [atoms/g]
t	time [yrs]
M_{rck}	mass of rock [g]
P_{sp}	spallogenic production rate [(atoms $^{36}\mathrm{Cl}$) (atoms of target)$^{-1}$ yr^{-1}]
P_{th}	production rate from thermal neutron reactions [(atoms $^{36}\mathrm{Cl}$) (atoms of Cl)$^{-1}$ yr^{-1}]
$[n_{\mathrm{sp}}]$	content of spallation targets [atoms g^{-1}]
$[\mathrm{Cl_{rck}}]$	chlorine content in rock [atoms Cl]
λ	decay constant [yr^{-1}]

The solution to Eq. (10) is (Zreda and Phillips, 1994):

$$t = -\frac{1}{\lambda}\ln\left[1-\frac{\lambda\cdot\frac{[\mathrm{Cl_{rck}}]}{M_{\mathrm{rck}}}\cdot\left(\frac{^{36}\mathrm{Cl}}{\mathrm{Cl}}\right)_{\mathrm{rck}}}{[n_{\mathrm{sp}}]P_{\mathrm{sp}}+\frac{[\mathrm{Cl_{rck}}]}{M_{\mathrm{rck}}}P_{\mathrm{th}}}\right] \tag{11}$$

where t is the exposure age. The uncertainty in t is given by:

$$\sigma_t^2 = \left[\sigma\left(\frac{^{36}\mathrm{Cl}}{\mathrm{Cl}}\right)_{\mathrm{meas}}\frac{\partial t}{\partial\left(\frac{^{36}\mathrm{Cl}}{\mathrm{Cl}}\right)_{\mathrm{meas}}}\right]^2 + \left[\sigma[\mathrm{Cl_{rck}}]\frac{\partial t}{\partial[\mathrm{Cl_{rck}}]}\right]^2 \tag{12}$$

where the first term accounts for the uncertainty in the AMS measurement of $^{36}\mathrm{Cl}/\mathrm{Cl}$, the second term accounts for the uncertainty in the measurement of $^{35}\mathrm{Cl}/^{37}\mathrm{Cl}$, and correlation between the two measurements is assumed to be zero. The partial derivatives in Eq. (12) are given by:

$$\frac{\partial t}{\partial\left(\frac{^{36}\mathrm{Cl}}{\mathrm{Cl}}\right)_{\mathrm{meas}}} = \frac{[\mathrm{Cl_{rck}}]}{M_{\mathrm{rck}}}\left[\left[\frac{[\mathrm{Cl_{rck}}]}{M_{\mathrm{rck}}}P_{\mathrm{th}}+[n_{\mathrm{sp}}]P_{\mathrm{sp}}\right]\left[1-\frac{\lambda\frac{[\mathrm{Cl_{rck}}]}{M_{\mathrm{rck}}}\left(\frac{^{36}\mathrm{Cl}}{\mathrm{Cl}}\right)_{\mathrm{meas}}}{\frac{[\mathrm{Cl_{rck}}]}{M_{\mathrm{rck}}}P_{\mathrm{th}}+[n_{\mathrm{sp}}]P_{\mathrm{sp}}}\right]\right]^{-1} \tag{13}$$

$$\frac{\partial t}{\partial[\mathrm{Cl_{rck}}]} = \left[-\frac{\left(\frac{^{36}\mathrm{Cl}}{\mathrm{Cl}}\right)_{\mathrm{meas}}}{M_{rck}\left(\frac{[\mathrm{Cl_{rck}}]}{M_{\mathrm{rck}}}P_{\mathrm{th}}+[n_{\mathrm{sp}}]P_{\mathrm{sp}}\right)}\left[-\left(\frac{[\mathrm{Cl_c}]}{[\mathrm{Cl_{rck}}]}+1\right)+\frac{[\mathrm{Cl_c}]}{[\mathrm{Cl_{rck}}]}+\frac{[\mathrm{Cl_{rck}}]P_{\mathrm{th}}\left(\frac{[\mathrm{Cl_c}]}{[\mathrm{Cl_{rck}}]}+1\right)}{M_{\mathrm{rck}}\left(\frac{[\mathrm{Cl_{rck}}]}{M_{\mathrm{rck}}}P_{\mathrm{th}}+[n_{\mathrm{sp}}]P_{\mathrm{sp}}\right)}\right]\right]\left[1-\frac{\lambda[\mathrm{Cl_{rck}}]\left(\frac{^{36}\mathrm{Cl}}{\mathrm{Cl}}\right)_{\mathrm{meas}}\left(\frac{[\mathrm{Cl_c}]}{[\mathrm{Cl_{rck}}]}+1\right)}{M_{\mathrm{rck}}\left(\frac{[\mathrm{Cl_{rck}}]}{M_{\mathrm{rck}}}P_{\mathrm{th}}+[n_{\mathrm{sp}}]P_{\mathrm{sp}}\right)}\right]^{-1} \tag{14}$$

The propagation of uncertainty in $(^{35}Cl/^{37}Cl)_{meas}$ to exposure age is controlled mostly by the abundance of Ca and K target elements, Cl concentration and spike amount. The largest uncertainties in exposure age propagated from $\sigma(^{35}Cl/^{37}Cl)_{meas}$ are for samples with low abundances of Ca and K and high Cl concentrations. For samples with high Ca and/or K and low Cl concentration, exposure ages are insensitive to errors in $(^{35}Cl/^{37}Cl)_{meas}$ because $(^{36}Cl/Cl)_{rck}$ and $[Cl_{rck}]$ are affected in opposite directions, and these errors cancel if ^{36}Cl production from $^{35}Cl(n,\gamma)^{36}Cl$ reactions is small. Similarly, trace Cl contamination in reagents should have little effect on ages calculated from contaminated samples when isotope dilution is used, although contamination would erroneously increase calculated Cl concentrations and decreases ^{36}Cl/Cl.

Fig. 4 shows the sensitivity of calculated ages to errors in the $(^{35}Cl/^{37}Cl)_{meas}$ ratio for three samples from Tables 1 and 3. Sample PV03–60 has the lowest thermal neutron activation component and the least sensitivity to errors in the $(^{35}Cl/^{37}Cl)_{meas}$ ratio, but all samples become insensitive at large ratios. Because of high rock Cl concentrations, many of the $(^{35}Cl/^{37}Cl)_{meas}$ ratios that we actually measured (Table 1) are lower than our recommended ratio of 10, making those samples more sensitive to the stable isotope ratio. However, because uncertainties on the $^{35}Cl/^{37}Cl$ measurements are fairly small (<5%) and because errors in $^{35}Cl/^{37}Cl$ propagate to proportionately smaller errors in landform age, the precision of the stable isotope measurements has only a small effect on the precision of age determinations for those samples. On average 85% or more of the analytical uncertainty in the landform age for samples in Table 1 is from the ^{36}Cl/Cl measurement.

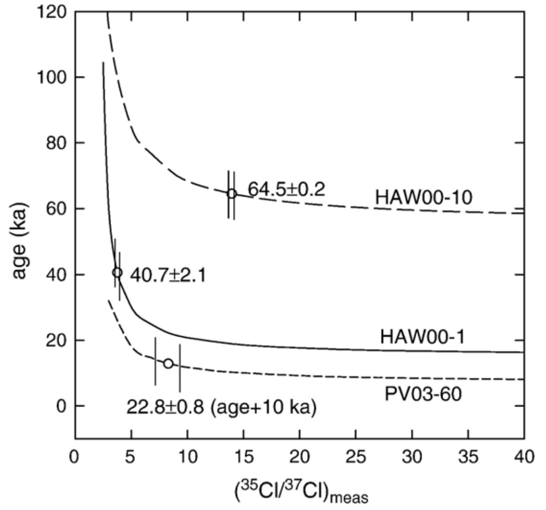

Fig. 4. Sensitivity of calculated ages to uncertainty in $(^{35}Cl/^{37}Cl)_{meas}$ for three rock compositions. To keep lines from overlapping, the line labeled PV03–60 is offset by −10 ka from the true age. The circles represent the measured $(^{35}Cl/^{37}Cl)_{meas}$, and the bars give the corresponding 1σ uncertainty. Sample HAW00-1 is a hawaiite with 40% spallation and 60% neutron activation, HAW00-10 is a hawaiite with 84% spallation and 16% neutron activation, and PV03–60 is a limestone with 90% spallation and 10% neutron activation.

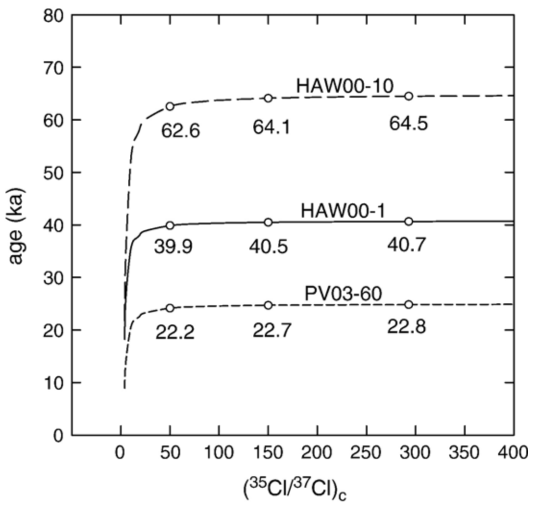

Fig. 5. Sensitivity of calculated age to uncertainties in carrier composition for samples HAW00-1, HAW00-10 and PV03–60. The assumed spike composition is $(^{35}Cl/^{37}Cl)_c = 293$ based on information provided by Sigma-Aldrich, Inc.

Fig. 5 shows that calculated ages are insensitive to uncertainty in the carrier isotopic composition over a wide range of $(^{35}Cl/^{37}Cl)_c$ ratios. If the assumed $(^{35}Cl/^{37}Cl)_c$ ratio is lower than the true ratio, the calculated $(^{36}Cl/Cl)_{rck}$ ratio will be too high and the calculated $[Cl_{rck}]$ will be too low. Because the errors in $(^{36}Cl/Cl)_{rck}$ and $[Cl_{rck}]$ are inversely correlated, they largely cancel out when calculating exposure ages.

4.2. Choice of spike isotope — ^{35}Cl or ^{37}Cl?

Rock samples can be diluted with either ^{35}Cl or ^{37}Cl. But is one spike isotope analytically more advantageous? In conventional isotope dilution mass spectrometry it is customary to dilute the less abundant isotope, which theoretically reduces errors in determining elemental concentration (Smith, 2000). This advantage is related to the fact that isotopic ratios in conventional mass spectrometry are determined from ion or charge counting (Patterson et al., 1994), and errors in the measured isotopic ratio will always be less because of the way in which Poissonian counting errors in the numerator and denominator propagate to the ratio. However, in the case of Cl analysis, both stable isotopes are fairly abundant (75.8% ^{35}Cl, 24.2% ^{37}Cl) in the natural material, and this advantage is much less than for other elements. More importantly, because stable isotopes in the AMS injector are measured as currents on Faraday cups rather than by ion or charge counting, the error on the stable isotope ratio is not determined by counting statistics and therefore the error propagation for conventional mass spectrometry is not valid for measurements in the AMS system, where systematic uncertainties dominate. The ^{37}Cl enriched spike may offer the advantage of better precision on the stable isotope ratio when the ratio of spike Cl to sample Cl is high (because the ^{35}Cl beam current with ^{37}Cl spiked samples will be higher than the ^{37}Cl beams with ^{35}Cl spiked samples), but this happens to be the case in which landform ages are least sensitive to the stable isotope ratio because the samples are usually dominated by spallogenic ^{36}Cl.

Given that (1) we get reproducible results for a wide range of stable isotope ratios using the ^{35}Cl spike; (2) errors in Cl concentration generally propagate to small errors in landform age; (3) errors due to cross contamination are generally small and do not depend on the choice of isotopic spike; and (4) the precision with which stable isotope ratios can be measured also appears to be mostly unrelated to the choice of spike, it remains to be shown that ^{37}Cl can give better precision on ^{35}Cl/^{37}Cl ratios measured in the AMS injector. However, because of technical challenges in changing the AMS system between the two spikes, there would be a pragmatic advantage to the AMS community in users adopting a standard isotopic spike. We suggest that ^{35}Cl enriched carrier be adopted as the standard isotopic spike because it is less expensive for the same enrichment and is already more frequently used.

5. Summary

(1) ^{36}Cl/Cl values calculated from closed-vessel isotope dilutions agree with values from the conventional (no carrier) method.

(2) Our experiments confirm that closed-vessel and open-vessel methods of isotope dilution give consistent Cl concentrations and ^{36}Cl/Cl for carbonate rocks. However, to prevent inaccurate ages due to Cl loss, $AgNO_3$ should be added to the sample prior to digestion. This method may not work for silicate rocks.

(3) For silicate rocks, Cl concentrations calculated from isotope dilution experiments agree with results from the ion-selective electrode in most cases. The cause for disagreements in a few remaining cases could be inaccuracies in the ion-selective electrode measurements.

(4) The ion-selective electrode method overestimates Cl concentrations of carbonate rocks, particularly at low Cl concentrations.

(5) Ages for samples with low Cl and high K+Ca concentrations are insensitive to analytical uncertainty in $(^{35}\mathrm{Cl}/^{37}\mathrm{Cl})_{\mathrm{meas}}$ or to trace natural Cl contamination, although calculations of $[\mathrm{Cl}_{\mathrm{rck}}]$ and $(^{36}\mathrm{Cl}/\mathrm{Cl})_{\mathrm{rck}}$ are sensitive to both. The reason is that errors in $(^{35}\mathrm{Cl}/^{37}\mathrm{Cl})_{\mathrm{meas}}$ are canceled out when propagated to age.

(6) We suggest that ^{35}Cl enriched carrier be adopted as the standard isotopic spike for ^{36}Cl measurements because it is less expensive for the same enrichment, offers age precision comparable to ^{37}Cl spike and is already more frequently used.

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