

## **Chlorine-36 Primary and Secondary Calibration Data Sets**

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### ***General Calibration Site Requirements***

In general, a good chlorine-36 calibration dataset needs to be internally consistent with no outliers and it needs to represent a variety of compositions as well as a variety of latitudes and elevations. There should be little uncertainty in the parameters (such as erosion rate, location, independent age constraints, etc.). The sites that fit this set of criteria have been categorized as primary calibration sites. In order to test the calibrated production rate parameters, a second dataset was created. The secondary dataset contains additional sites with independent age constraints, but which not used during the calibration of production rate parameters. These samples are also important because they can be used in conjunction with the primary dataset to aid in calculating realistic uncertainties in the dating technique.

### ***Particular Challenges of $^{36}\text{Cl}$ Calibration***

The  $^{36}\text{Cl}$  calibration faces particular challenges due to the large number of production reactions and of target nuclides. A reasonably complete listing of target elements would include the following: Cl (spallogenic thermal and epithermal neutrons), Cl (mugenic neutrons), K (neutron spallation), K (mugenic reactions), Ca (neutron spallation), Ca (mugenic reactions), Ti (neutron spallation), Ti (mugenic reactions), Fe (neutron spallation), Fe (mugenic reactions). Many of the reactions are quite minor and if only targets that are important for ordinary surface-exposure dating are included, we still must constraint the following: Cl (spallogenic thermal and epithermal neutrons), K (neutron spallation), K (mugenic reactions), Ca (neutron spallation), Ca (mugenic reactions).

In contrast to  $^{36}\text{Cl}$ , nuclides such as  $^{10}\text{Be}$  and  $^{26}\text{Al}$  require only two types of reactions to be constrained: a spallation reaction and muon reactions. The CRONUS-Earth Project has only marginally been able to measure samples from enough true 'primary quality' calibration sites to reliably calibrate these two nuclides. Using the same set of calibration sites clearly leaves the  $^{36}\text{Cl}$  calibration, with three more production-rate calibration parameters, severely underconstrained. We are therefore considering importing some data from 'legacy' studies in order to provide sufficient constraints to obtain a practically useful calibration.

Fortunately, the CRONUS-Earth official primary sites provided samples adequate to constrain the principal production reactions by spallation of K and Ca.

K-feldspar separates from Scotland and Huancáne and Ca-feldspar separates from Tabernacle Hill yielded consistent and precise analytical results. However, none of these sites contained high-Cl phases that could be separated. Whole-rock analyses were attempted, but yielded erratic analytical results, and in any case Cl concentrations were not high enough to definitively constrain low-energy neutron production off of Cl. In order to provide a Cl constraint, after exploring numerous alternatives, we have opted to use a mixture of CRONUS and legacy samples from latest-Pleistocene glacial features in the Sierra Nevada. This sample set has very good independent  $^{14}\text{C}$  age constraints and has associated  $^{10}\text{Be}$  and  $^{26}\text{Al}$  analyses that corroborate the independent age assignments. Additionally, the sample compositions span a range from almost purely spallogenic to a high proportion of low-energy Cl production, thus forcing the  $\text{Pf}(0)$  parameter governing low-energy neutron production to be assessed in the context of the spallation parameters for which we have a higher degree of confidence.

Assessment of mugenic production systematics requires a suite of samples of appropriate chemical composition and from considerable depth. Under the CRONUS-Earth Project the drilling of a deep core hole into the Ferrar Dolerite in a low-erosion setting in Antarctica was attempted, but was not successful due to technical problems and the rigorous environmental protections that had to be respected in that research area. We have therefore turned to the alternative of legacy studies conducted by John Stone in deep quarries in Australia. These are not as definitive as the Antarctic core would have been, due to factors associated with higher erosion rates and uncertainties deriving from human disturbance at the sample sites, but should provide sufficiently accurate parameters for surface-exposure dating purposes.

In taking the approach described above, we have followed a philosophy similar to that used in selecting the  $^{10}\text{Be}$  and  $^{26}\text{Al}$  primary calibration suite: that it is preferable to base the primary calibration data set on a small number of very secure sites than to found it on a larger data base including possibly questionable samples, in order to maximize the accuracy of the estimation. Although we cannot afford to be as rigorous as is possible with  $^{10}\text{Be}$  and  $^{26}\text{Al}$  calibration, due to the much larger number of parameters that must be fitted, we have restricted the primary data set to sites having very secure independent chronology and that show very good internal reproducibility. The principal objective of this approach is to obtain the most accurate estimates of the production parameters. However, the unfortunate corollary of this approach is that the data base is not large enough to permit rigorous evaluation of the uncertainties associated with the parameter estimates. Our strategy for addressing this deficiency is to use the secondary data set not only for confirmation of the general accuracy of the parameters but also to help quantify the parameter uncertainties. This places additional emphasis on acquiring a large secondary data set that spans a wide

range of geographical locations, elevations, and target-element concentrations.

### ***Descriptions of <sup>36</sup>Cl Primary Calibration Sites***

#### Lake Bonneville, Utah

The Lake Bonneville, Utah, site contains two distinct sampling sites, Promontory Point and Tabernacle Hill. For chlorine-36, only samples from Tabernacle Hill (39° N and 1450 m elevation) are being used in the calibration. This basalt flow erupted into the Provo-level Pleistocene lake. This eruption is well constrained by the maximum limiting age of the Bonneville flood and the minimum limiting age of tufas collected from the edges of the basalt flow. The limiting ages constrain the eruption of the basalt to 18,200±300 years before 2010. Calcium feldspar mineral separates were prepared by John Stone at the University of Washington. Whole rock samples were prepared at New Mexico Tech by Shasta Marrero and at LDEO by John Gosse. Due to scatter in the whole rock samples, the calibration results are reported both with and without this subset of samples. Any whole rock samples more than three standard deviations away from the mean of the other samples were removed from the analysis entirely.

#### Huancáne, Peru

The Huancáne, Peru, site is located in the central Peruvian Andes at approximately 13° S and very high elevation (4850 m). The Quelccaya ice cap created several sets of moraines, with these samples taken from the middle set. These moraines are known as the Huancáne II moraines. The moraines have a well-constrained age based on radiocarbon found in peats and lake cores. The maximum and minimum bracketing ages yield a site age of 12,320 ± 110 years before 2010. Potassium feldspar mineral separates were prepared by Shasta Marrero at New Mexico Tech and John Stone at the University of Washington. The mineral separates by Stone had significantly lower chlorine and less scatter than those from NMT, so the NMT mineral separates were moved into the "other primary" dataset. Whole rock samples were also prepared at New Mexico Tech by Shasta Marrero. These whole rock samples are entirely inconsistent with any other samples in the dataset, yielding estimates of <sup>36</sup>Cl production from low-energy neutrons that were lower than independent estimates by a factor of >10. These samples also show significant scatter in the results so the Huancáne whole rock samples were not used in the final calibration for chlorine-36.

#### Isle of Skye, Far Western Highlands of Scotland

The Isle of Skye, Scotland site is located in the Inner Hebrides along the northwest coast of Scotland at approximately 57° N with sample elevations ranging from 300-450 m. The most reliable samples were collected from very

large rockfall boulders carried either sub- or supra-glacially and exposed at the end of the Loch Lomond readvance. The age assigned to these samples is  $17,700 \pm 300$  years based on varve counting, radiocarbon, pollen analysis, and correlation with the Greenland ice Core. The independent age control is not local, but is well-constrained for deglaciation of the larger region. These boulders are considered most reliable because, given that they were deposited by massive rockfalls at the end of the Loch Lomond, their age is well defined and the likelihood of inheritance is minimized. Inheritance is a particular concern because the Loch Lomond readvance was a relatively minor and brief reformation of cirque glaciers after the prolonged Late Devensian maximum glaciation, and thus glacial erosion was limited in extent due to previous quarrying down to bedrock. A set of four potassium feldspar mineral separate samples from Coire Fearchair were analyzed by John Stone at the University of Washington. These yielded consistent results (9% maximum spread) and were employed in the calibration. On the other hand, 12 Ca-rich separates from bedrock and moraine boulders (not clearly from large-scale rockfall) from Coire a Ghrunnda in the Black Cuillins gave results that were quite discordant with those from Tabernacle Hill (consistently higher by about 20%). We believe that this discrepancy is due to inheritance between the Late Devensian retreat and the Loch Lomond readvance that was not removed due to the limited erosivity of the Loch Lomond corrie glacier. These samples were not used in the primary calibration, but they will be described in the paper on the Scotland sites and will be discussed in the  $^{36}\text{Cl}$  calibration paper.

## Sierra Nevada

The Sierra Nevada, California, site is located in western California at approximately  $37^\circ$  N and an elevation range of 2400-3600 m. The chronology of the deglaciation of the Sierra Nevada has been well established by radiocarbon dating of lake sediments inside and outside of the glacial limits and is corroborated by pollen chronologies and more distant lake cores as well (summarized in Phillips et al., 2012, which also gives detailed site descriptions). The radiocarbon data constrain the Recess Peak terminal position to  $13301 \pm 250$  years, the Tioga IV final deglaciation to  $15810 \pm 500$  years, and the Tioga IV terminal position to  $1606 \pm 500$  years. The core of this data set is three boulders on the Recess Peak-age moraine that surrounds the Baboon Lakes. These were collected and analyzed as part of the CRONUS-Earth Project and have given good-quality data for K-feldspar and biotite separates. The biotite separates are the only CRONUS-Earth samples that yield strong constraints on the  $\text{Pf}(0)$  parameter. We suggest that these 6 samples be supplemented by legacy samples from the same site and close by. The advantage of including the legacy samples is that they provide a spectrum of production-rate mechanisms ranging from nearly pure spallation through to mostly production by muon absorption by  $\text{Cl}$ . They are entirely consistent with the results from the mineral separates. The

subset used here was chosen from the larger dataset presented in [Phillips 2009] due to the internal consistency, composition, clear independent age context, and small snow cover corrections. Three sets of samples from the Humphreys Basin, the Middle Fork of Bishop Creek, and the Bishop Creek drainage are suggested as primary calibration samples. The chlorine samples have a wide range of compositions (from K to Ca), but contain higher chlorine concentrations (16-120 ppm) as well. The whole rock samples were processed at the New Mexico Tech laboratory.