

# On the reliability of target element data for cosmogenic nuclide exposure dating

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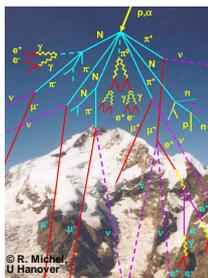
## Cosmogenic nuclide exposure dating

Radioactive or stable cosmogenic nuclides are products of nuclear reactions induced by cosmic rays. The development of the interdisciplinary field of the quantification of cosmogenic nuclides has been increased dramatically in the last decades. Especially, the progress in the field of accelerator mass spectrometry (AMS) improved detection limits and accuracy and allows nowadays the determination of radionuclide concentrations as low as of  $10^4$ - $10^5$  atoms/(g rock).

In particular, in-situ produced cosmogenic nuclides - so-called terrestrial cosmogenic nuclides (TCN) - have proved to be valuable tools for quantifying Earth's surface processes [1]. Here, the work-horses are  $^{10}\text{Be}$  and  $^{26}\text{Al}$  in quartz, and  $^{36}\text{Cl}$  in Ca- or K-rich minerals.



Possible dating "objects": volcano eruptions, rock avalanches, glacier movements.



Particle cascade in the atmosphere and terrestrial environment induced by cosmic rays.

In siliceous environments both radionuclides,  $^{10}\text{Be}$  and  $^{26}\text{Al}$ , are pure high-energy spallation products, thus, the influence on the secondary neutron field by changing trace element concentrations in the original bulk matrix is negligible. Another advantage: Usually, quartz can be easily cleaned from other mineral phases making the normalization to  $(\text{g SiO}_2)^{-1}$ , i.e. only two target elements, very straightforward. There is usually no need for a full chemical analysis. Solely intrinsic aluminium has to be determined for conversion of measured  $^{26}\text{Al}/^{27}\text{Al}$  to  $^{26}\text{Al}$  in atoms/g.

In contrast,  $^{36}\text{Cl}$  can be produced by several different nuclear reactions: Spallation on different target elements, mainly Ca and K (to a lesser extent Ti and Fe), induced by high-energy neutrons and muons. Thus, every sample that will be analysed for  $^{36}\text{Cl}$  has to be chemically analyzed for the main target elements, too. Additionally, as  $^{36}\text{Cl}$  can be produced by thermal neutron-capture on  $^{35}\text{Cl}$ , trace elements influencing the thermal neutron field have to be unavoidably also measured. This includes U and Th as "background"-neutron emitter, all elements with high neutron absorption cross sections like B, Gd, and Sm, and all light elements, which take part in  $(\alpha, n)$ -reactions. Thus, a complete bulk rock analysis (for the neutron field) and measurements of the main target elements in the dissolved fraction are absolutely necessary. As  $^{36}\text{Cl}$  concentrations will be normalized to  $(\text{g Ca})^{-1}$ ,  $(\text{g K})^{-1}$  etc., the overall result cannot be more precise than the corresponding target element data.

2 analyses needed per " $^{36}\text{Cl}$ -TCN-sample":

- representative bulk (for neutron field)
- individual solution aliquot (for main target elements – if sample produces residue during dissolution)



Typical AMS machine (5 MV ASTER [2]) for measurements of TCN.

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## Proficiency testing methods: ICP-OES, INAA, and PGAA

We have selected typical samples with different fractions of silicate- and calcite-rich phases to have them analyzed by the method of choice of most TCN-user: inductively coupled plasma optical emission spectrometry (ICP-OES). Unfortunately, the two French CNRS laboratories involved, CEREGE [3] and SARM [4], did not produce concordant results for all elements of interest. Thus, we have tested the capability of two non-destructive activation analysis methods: We performed Instrumental Neutron Activation Analysis (INAA) [5] ourselves at Vienna and we sent solid aliquots for Prompt Gamma Activation Analysis (PGAA) to Budapest [6].

### INAA details

INAA has been performed in two irradiation and measurement runs

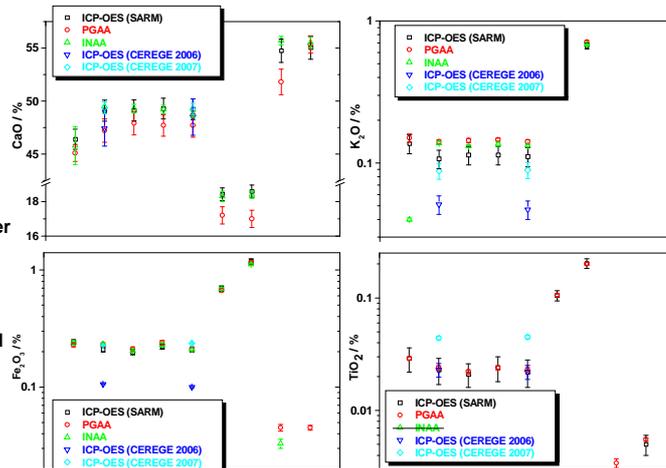
sample size: 200-300 mg  
 irradiation times: 1 min, 1 h  
 neutron flux (thermal):  $3 \times 10^{12}$ ,  $1 \times 10^{13} \text{ cm}^{-2} \text{ s}^{-1}$   
 cooling time: 4 min, >48 h  
 measuring time: 300 s, >7200 s  
 detector: HPGe, Canberra GC4518, 48% rel. eff.  
 signal processing: Canberra 2060, LFC 599  
 standard reference materials: CANMET SO1;  $\text{CaF}_2$ ,  $\text{CaCO}_3$  (p.a.)

nuclides &  $\gamma$ -energies

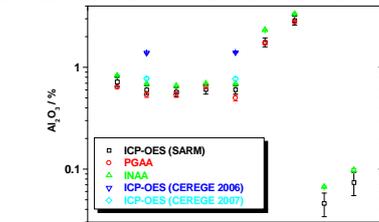
$^{24}\text{Na}$	2754 keV
$^{26}\text{Al}$	1778 keV
$^{42}\text{K}$	1525 keV
$^{49}\text{Ca}$	3084 keV
$^{56}\text{Mn}$	1811 keV
$^{59}\text{Fe}$	1099 keV
$^{239}\text{Np(U)}$	277 keV
$^{233}\text{Pa(Th)}$	312 keV

## Results of proficiency testing

- 4 laboratories performed differently depending on the analyte >>> there is no "best for all elements" lab or method!
- all methods produce Ca-data with high uncertainties (0.6-3.9%)
- PGAA seems to underestimate the "true" Ca-value of some samples
- $\text{K}_2\text{O}$ -data (@ 0.1-0.7%) by ICP-OES has higher uncertainties and is constantly lower as corresponding INAA- and PGAA-data
- non-destructive nuclear methods have lower detection limits for Fe
- INAA could not provide any Ti-data, but PGAA has lowest detection limit for Ti (and highest for Al)
- ICP-OES from CEREGE seems to improve ('06 to '07) for nearly all elements (except Ti)
- some labs might underestimate their accuracy for certain elements, as they do not produce concordant results



Bulk concentrations of  $^{36}\text{Cl}$ -target elements measured by ICP-OES, INAA, and PGAA.



Bulk concentrations of Al, which are needed for  $^{26}\text{Al}$ -data calculation, measured by ICP-OES, INAA, and PGAA.

For trace elements influencing the neutron field the impact on TCN-data-quality is very variable. Thus, only one example: For a  $100 \mu\text{g/g}$   $^{36}\text{Cl}$ -sample, differences in measured B-concentrations ( $27 \pm 2 \mu\text{g/g}$  by SARM by colorimetric determination as B-carmine &  $43.0 \pm 0.6 \mu\text{g/g}$  by PGAA) can change a surface exposure age up to more than 2% using a sophisticated calculator [7].

It seems advisable to use more than a single analytical method and/or validate that the lab is providing accurate results, if overall accuracy is important for TCN applications.

>>> TCN-data cannot be any better than the underlying analytical data!

## Impact for TCN-applications

For main target elements of  $^{36}\text{Cl}$ , i.e. Ca, K, Ti, and Fe (for most common rocks), the results have to be most accurate in higher concentrations as their uncertainty is directly taken into account for the production, thus for a calculated time or rate. I.e. if the main target element is accurate to 2%, all deduced data cannot be better than 2%. The lower the concentration, the less important is accuracy. For pure  $\text{CaCO}_3$  with 40% Ca, some  $\mu\text{g/g}$  of other target elements do not need to be determined at all.

CRONUS networks [8,9] try to minimize uncertainties in TCN-applications e.g. by new production rate determinations and improved scaling models. This approach is in the right direction for the goal of an overall uncertainty of less than 5%. However, it might be impossible to reach, if analytical laboratories cannot improve with respect to more precision and accuracy. Because these uncertainties are taken into account twice: 1.) for the production rate calculation and 2.) for the individual sample.

## References

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