

## Neutron-induced $^{37}\text{Ar}$ recoil ejection in Ca-rich minerals and implications for $^{40}\text{Ar}/^{39}\text{Ar}$ dating

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The  $^{40}\text{Ar}/^{39}\text{Ar}$  dating technique requires the transformation of  $^{39}\text{K}$  in  $^{39}\text{Ar}$  by neutron activation. Neutron activation has undesirable secondary effects such as interfering isotope production and recoil of  $^{39}\text{Ar}$  and  $^{37}\text{Ar}$  atoms from their (dominant) targets of K and Ca. In most cases, the grains are large enough (>50  $\mu\text{m}$ ) that the amount of target atoms ejected from the grains is minimum and has negligible effect on the ages obtained. However, increasing needs to date fine-grained rocks requires constraining, and in some case correcting for, the effect of nuclear recoil. Previous quantitative studies about recoil loss focus mostly on  $^{39}\text{Ar}$  [1, 2]. However,  $^{37}\text{Ar}$  loss can affect the age of Ca-rich minerals via interference corrections on  $^{36}\text{Ar}$  (and to a lesser extent  $^{39}\text{Ar}$ ), yielding lower  $^{40}\text{Ar}^*/^{39}\text{Ar}_K$  and thus, an age spuriously too young [2]. New results focused on  $^{37}\text{Ar}$  recoil by measuring the apparent age of multi-grain populations of plagioclase and hornblende with discrete sizes ranging from 210  $\mu\text{m}$  to <5  $\mu\text{m}$ . We use our previous result on sanidine grains [2] to correct for the  $^{39}\text{Ar}$  recoil loss. For plagioclase, the loss of  $^{39}\text{Ar}$  seems to have the predominant effect on apparent age down to 25  $\mu\text{m}$ . Below this threshold, the loss of  $^{37}\text{Ar}$  has an increasingly competing effect with  $^{39}\text{Ar}$  loss. This results in ages indistinguishable from the nominal age of the mineral (instead of an age few % older if only  $^{39}\text{Ar}$  loss was occurring). Loss of  $^{37}\text{Ar}$  is predominant below 5  $\mu\text{m}$  with ages ~37% younger than the age of the mineral and where most of the  $^{37}\text{Ar}$  seems to have been ejected from the grain. We calculate a  $d_0$ -value of  $1.27 \pm 0.53 \mu\text{m}$  ( $2\sigma$ ), significantly higher than suggested by current models. The hornblende results suggest that the loss of  $^{37}\text{Ar}$  start to have a noticeable effect on the calculated age below ~50  $\mu\text{m}$ . As observed for plagioclase, the effect of  $^{37}\text{Ar}$  loss becomes predominant only below 5  $\mu\text{m}$  where the measured age is ~15% younger. The mean  $d_0$ -value calculated from these results is  $1.78 \pm 0.72 \mu\text{m}$ , similar the  $d_0$ -value obtained for plagioclase.

[1] Paine *et al.* *GCA* **70**, 1507-1517. 2006. [2] Jourdan *et al.* *GCA* **71**, 2791-2808. 2007.

## Zn isotopic fractionation: Why organic matters

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Zinc isotopic fractionation during adsorption onto a purified humic acid (PHA), an analogue of organic matter (OM), has been investigated experimentally as function of pH. The Donnan Membrane (DM) device [1] is used to separate Zn bound to the PHA from free  $\text{Zn}^{2+}$  ions in solution and successfully adapted for isotopic measurements, allowing the measurement of isotopic ratios of free  $\text{Zn}^{2+}$ . Below pH 6, adsorption of Zn on the PHA results in no measurable isotopic fractionation, while at higher pH, a significant enrichment of heavy isotopes for Zn bound to PHA ( $\Delta^{66}\text{Zn}_{\text{PHA-FreeZn}} = +0.24 \text{‰} \pm 0.06 \text{‰}$ ) is observed.

The isotopic variations are associated to changes in Zn speciation with pH, with higher complexation constants and shorter bond lengths for Zn-PHA complex compared to the aqueous free Zn. Complexation of Zn with PHA occurs mostly through binding with high affinity sites (HAS) and low affinity sites (LAS). Fractionation factors determined by mass balance calculations are equal to 1.0004 for HAS and 1.0000 for LAS.  $\Delta^{66}\text{Zn}_{\text{OM-FreeZn}}$  varies then according to the heterogeneous nature of the OM, because of the variable relative proportion of these two types of site.

The NICA-Donnan model, along with these fractionation factors and the  $\delta^{66}\text{Zn}_{\text{TotalDissolved}}$  (Chen *et al.* [2]), is used to simulate the corresponding isotopic composition of free Zn in the Seine river, France. The  $\Delta^{66}\text{Zn}_{\text{TotalDissolved-freeZn}^{2+}}$  values obtained vary from +0.02 ‰ to +0.18 ‰, depending on the amount of HAS and LAS assumed for the OM. This study allows a better understanding of Zn isotope fractionation mechanisms associated with organic matter binding and emphasizes the need for further investigations on the link between isotopic fractionation and speciation for metals in natural systems.

[1] Temminghoff E. J. M., *et al.* (2000) *Anal. Chim. Acta* **417**, 149-157. [2] Chen J., *et al.* (2008) *Environ. Sci. Technol.* **42**, 6494-6501.