

Considerations in dating impact craters using the $^{40}\text{Ar}/^{39}\text{Ar}$ method: The problem of inherited $^{40}\text{Ar}^*$

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A large number of impact structures on Earth remain to be dated accurately and precisely (e.g. <http://www.unb.ca/passc/ImpactDatabase/index.html>) and [1]. A very versatile and powerful chronometer is the $^{40}\text{Ar}/^{39}\text{Ar}$ method, because of its sensitivity to thermal input, the availability of internal reliability criteria such as age plateaux and/or isochrons, and the possibility to obtain compositional parameters (i.e., Ca/K, K/Cl and $^{40}\text{Ar}^*$). Apart from alteration and/or metamorphic processes that can strongly bias the measurement of the age of a sample, accurate $^{40}\text{Ar}/^{39}\text{Ar}$ age determinations are often challenged by the presence of inherited $^{40}\text{Ar}^*$ (i.e., Ar not completely degassed from the target rock during the impact) in the sample.

Here, through the study of 2 impact structures (Tswaing, South Africa and Jänisjärvi, Russia) and comparison with results from 4 other structures, we study the cause and consequence of the presence of inherited $^{40}\text{Ar}^*$. For example, in the case of Tswaing impact glass particles, no ages approximating the previously accepted impact age of 250 ± 104 ka [2] could be obtained, whereas the Jänisjärvi impact melt rock yielded a statistically robust global isochron age of 682 ± 4 Ma.

The main characteristic controlling the apparent age bias (for a given proportion of inherited $^{40}\text{Ar}^*$) is the age difference between the impact and the target rocks. The buffer effect for a given crater structure can be predicted knowing the age of the impacted basement and having a rough estimation of the age of the crater structure itself. The occurrence of $^{40}\text{Ar}^*$ inherited is likely influenced by (1) the degree of polymerization (i.e., silicate structure complexity) of the target rock and presumably related to the diffusivity of Ar in the melt/glass, (2) the Ar partial pressure at grain boundaries, (3) the quantity of energy involved in the impact, and (4) the porosity of the target rocks. In addition, the degree of polymerization will control the degree of homogenization of the melt and the rate of $^{40}\text{Ar}^*$ diffusion in the melt. Homogenization of the inherited $^{40}\text{Ar}^*$ ratio at the grain scale (i.e. 150-250 μm) facilitates accurate age determination through isochron analysis, although in completely melted rocks a homogenization of atomic scale environments for inherited and radiogenic Ar eliminates the possibility to resolve the two components thermally, i.e., by step-heating.

References

[1] Renne *et al.*, *This volume*

[2] Storzer *et al.*, *Spec. pub. Geol. Survey S. Africa*, 64-71.

Zn isotopic fractionation during complexation with organic matter

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Organic matter (OM) is of great importance for the speciation, mobility and bioavailability of metals in the environment. The knowledge of zinc isotopic fractionation during complexation with OM is therefore crucial to understand zinc isotopic signatures in the environment.

Zinc isotopic fractionation during adsorption onto humic acid, an analogue of OM, has been investigated experimentally as a function of pH. Two different techniques were used to isolate free zinc in solution from zinc bound to OM.

Experiments were made with an insolubilized humic acid [1] that allows us to separate OM and the solution by centrifugation. Results show no fractionation at acidic pH (below pH 6) and a significant fractionation at higher pH (above 6) with an enrichment of heavy isotopes in the OM ($\Delta^{66}\text{Zn}_{\text{OM-Solution}} = 0.52\text{‰} \pm 0.08$ for $0.1 \text{ mol.L}^{-1} \text{ KNO}_3$). This result can be interpreted as a change of zinc complexation with pH, zinc being preferentially complexed by “carboxylic type groups” at low pH and by “phenolic type groups” above pH 6.

The insolubilization process may however alter partly the binding properties of the humic acid. We have decided to use another complementary approach with a Purified Peat Humic Acid (PPHA). The Donnan Membrane Technique (DMT) developed by Temminghoff *et al* [2] is used as a more efficient way to separate zinc complexed by untreated PPHA from free zinc in solution.

First tests in absence of PPHA have been done to check the eventual fractionation due to the complexation of zinc onto the membrane. Although less important than the fractionation observed in the previous experiments, it is not negligible ($\Delta^{66}\text{Zn}_{\text{Membrane-Solution}} = 0.15\text{‰} \pm 0.03$). Despite this fractionation on the membrane, once fully validated for isotopic measurements this technique will be a powerful tool to measure zinc fractionation during its complexation with different kind of ligands like humic substances or organic chelating acids (i.e. siderophores). It can also be used for other elements as well as in situ measurements.

References

[1] Seki, H., Suzuki, A., (1995) *Journal of Colloid and Interface Science*, **171**, 490-494.

[2] Temminghoff, E. J. M.; Plette, A. C. C.; Van Eck, R.; Van Riemsdijk, W. H. (2000) *Anal. Chim. Acta*, **417**, 149-157.