Ar primary measurement standards for the calibration of argon isotopes

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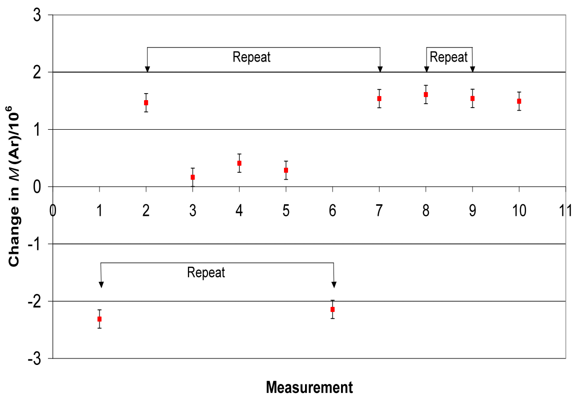
In this work a procedure is described to prepare SI-traceable argon isotope amount ratios in high purity argon, following a gravimetric approach. These synthetic mixtures serve as reference gases to calibrate ion current ratio measurements in argon with a total relative combined uncertainty of 0.9×10^{-6}.

Recently a JRP-iMERA programme was started to measure the Boltzmann constant *k* fully independently. The new measurement of *k* will be used in a redefinition of the *kelvin*, which leads to an improved International System of Units (SI).

Using argon, has many experimental advantages, but requires a determination of the isotopic mass of the actual gas used in the experiment. For atotal uncertainty below $1{\times}10^{-6}$ on*k*, molar mass with total combined uncertainties of $3{\times}10^{-7}$ are required.

Variability of the Ar molar mass (10 samples), with a reproducibility of the measurements is better than 1 part in 10^6.



[1] Fellmuth, Gaiser & Fischer (2006) 'Determination of the Boltzmann constant - status & prospects.' *Meas. Sci. Technol.* **17**, 145–159.

Magmatic zircons: Evolution of δ18O through time – Revisited *in situ*

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Analysis of igneous zircons provides unique capability to correlate the oxygen isotope ratios of magmas to age, which provides a sensitive monitor of melt interaction with the crust. A compilation of $\delta^{18}O$ from dated igneous zircons in 1200 rocks of all ages showed unsuspected trends in evolution of the crust [1]. Zircons from 4.4-2.5Ga are relatively constant ($\delta^{18}O$=5.0-7.5‰), while higher values (7.5-11‰) are increasingly common after 2.5Ga; values <5‰ appear in specific occurrences. This trend indicates increased availability of high $\delta^{18}O$ sediment in the Proterozoic, esp. clay-rich mudstones, possibly combined with more efficient recycling of crust into magmas. Low $\delta^{18}O$ magmas (now rocks) are selectively preserved in younger terranes. The vast majority of $\delta^{18}O$ (Zrc) data in 2005 had been measured in bulk (~2mg) samples comprised of many crystals and the importance of inheritance or zoning was not evaluated. Now, 1000's of new *in situ* analyses of $\delta^{18}O$ by ion microprobe are correlated to age, documenting inter- and intra-grain variability. The two data sets are complimentary; fluorination data confirm accuracy of the ion microprobe $\delta^{18}O$ analyses (±0.3‰), but *in situ* data document important details that previously were missed. Archean zircons are fairly homogeneous in $\delta^{18}O$; more variability is found in zircons younger than 2.5 Ga. Some zircons have rims with subtle differences in $\delta^{18}O$ reflecting evolving magma chemistry. Low $\delta^{18}O$ igneous zircons often are zoned, commonly with inherited more-normal cores. Metamorphic or anatectic zircons in metasediments are typically high in $\delta^{18}O$, reflecting protolith, and igneous cores with metamorphic overgrowths preserve $\delta^{18}O$ gradients from time of crystallization with possible exceptions in UHT (>950°C) metamorphism (Page *et al*. 2007 Am Min). Hydrothermal zircons are distinctive, texturally and in $\delta^{18}O$ [2]. Some hydrothermal overgrowths may be deuteric [3]. To date, few zircon studies are of minerals in matrix. The ability to make accurate and precise *in situ* measurements of $\delta^{18}O$ with spots of 1 to 10 μm diameter [4] opens many exciting opportunites for studies combining petrography, imaging, and other trace element and isotope systems (e.g. Hf, Li, REEs, and Ti) and in comparison to minerals with slow (e.g. garnet) or faster oxygen diffusion (e.g. titanite), that may preserve P-T-t-f (H_2O) history.

[1] Valley *et al*. (2005) *CMP*. [2] Fu *et al*. (2010) *CMP*. [3] Grimes *et al*. (2010) *CMP*. [4] Valley & Kita (2009) *MAC* **41**.