

Heavy noble gases from the Southwest Indian Ridge: Insights into upper mantle heterogeneity

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Basalts from the ultra-slow spreading Southwest Indian Ridge (SWIR) exhibit remarkable variability in helium isotopic composition: SWIR $^4\text{He}/^3\text{He}$ varies from 51,000 to 120,000 ($^3\text{He}/^4\text{He}$ of 14.1 to 6 R_A ; [1]), spanning half the range observed in mantle-derived basalts. $^4\text{He}/^3\text{He}$ values both higher and lower than the canonical mid-ocean ridge basalt range ($^4\text{He}/^3\text{He}$ of 80,000 to 100,000; $^3\text{He}/^4\text{He}$ of 9 to 7 R_A) are erupted in close proximity. Low $^4\text{He}/^3\text{He}$ ratios reflect a mantle source that is less degassed than the mid-ocean ridge basalt (MORB) source, while high $^4\text{He}/^3\text{He}$ ratios are commonly attributed to the presence of recycled crust in the source region. Therefore, the SWIR provides a unique window into the nature and distribution of heterogeneities in the upper mantle.

We have measured Ne, Ar and Xe abundances and isotopic compositions, along with He and CO_2 abundances, in glasses from the SWIR. There is good correlation between Ne and He: $^4\text{He}/^3\text{He}$ ratios less radiogenic than N. Atlantic popping rock [2] are associated with Ne less nucleogenic than popping rock, MORB-like He is paired with Ne indistinguishable from popping rock, and more-radiogenic He is associated with more-nucleogenic Ne. This observation stands in contrast to Ne less nucleogenic than popping rock measured in HIMU ocean island basalts that have radiogenic He [3]. SWIR source $^{40}\text{Ar}/^{36}\text{Ar}$, corrected for air contamination, is low relative to N. Atlantic $^{40}\text{Ar}/^{36}\text{Ar}$ of $\sim 28,000$, but consistent with values of $\sim 15,000$ in the southernmost Atlantic [4]. $^{129}\text{Xe}/^{130}\text{Xe}$ excesses up to 7.3 in a sample with radiogenic He (i. e., volatile-depleted source) indicate that substantial atmospheric Xe is not recycled into the SWIR source relative to the N. Atlantic source. Further, Xe systematics indicate that within the uncertainties, SWIR source (Pu+U)/I is similar to that of other mantle sources.

SWIR noble gas systematics reflect the influence of reservoirs more and less degassed than normal MORB source. If the degassed component is recycled crust, then SWIR and Cook-Austral Ne [3] demonstrate a dual fate for recycled crust in the mantle: a fraction circulates in the upper mantle, while the rest is injected into the lower mantle.

[1] Georgen *et al.*, *EPSL* 2003; [2] Moreira *et al.*, *Science* 1998; [3] Parai *et al.*, *EPSL* 2009; [4] Sarda *et al.*, *JGR* 2000.

Disposable sensors for $[\text{Zn}^{2+}]$, $[\text{Cd}^{2+}]$ and $[\text{Pb}^{2+}]$ determination in natural samples

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The knowledge of the free ion concentrations of metals like Zn, Cd or Pb is key to predict the biouptake of trace elements. Electrochemical techniques, such as ion selective electrode (ISE), are of particular relevance for metal studies, but commercial ISE's sometimes lack the required sensitivity. The analytical challenge is to develop a technique able to determine free metal ion concentrations at trace levels.

Absence of Gradient and Nerstian Equilibrium Stripping method (AGNES) is an emerging electroanalytical technique typically implemented with the hanging mercury drop electrode (HMDE) [1]. In AGNES conditions, the stripping step leads to a measured charge just proportional to the free metal ion concentration in the solution.

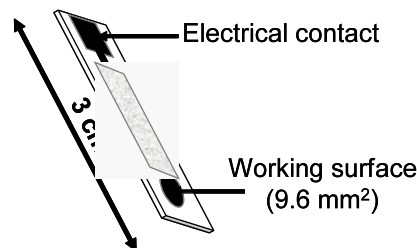


Figure 1: A screen-printed electrode

We have undertaken the application of AGNES with screen-printed electrodes (Figure 1), which can be deployed *in situ* and, thus, avoid problems of contamination [2]. These disposable sensors can also be easily modified to enhance selectivity and/or sensitivity.

First, the area of the working surface of the disposable sensor and the thickness of the mercury film have been optimized, as well as the parameters of AGNES technique. Then, calibration curves were performed in synthetic solutions for Cd (II), Zn (II) and Pb (II). In addition, the free ion metal concentrations were determined in synthetic solutions containing a complexing ligand and compared with results obtained with conventional HMDE.

This study shows that sensitivity and repeatability were strongly related to the volume of the mercury film. Lower limits of detection were reached with SPE, due to the possibility of using higher preconcentration factors than with HMDE. Speciation results were consistent with speciation codes.

[1] Galceran *et al* (2004) *J. Electroanal. Chem.* **566**, 95-109.

[2] Parat *et al* (2007) *Electroanalysis* **19**, 403-406.