Measurement of $^{232}Th/^{230}Th$ in volcanic rocks by PIMMS, using the ThermoFinnigan Neptune

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A technique is presented for the determination of $^{232}Th/^{230}Th$ in volcanic rocks by plasma ionization multicollector mass spectrometry (PIMMS) utilizing the ThermoFinnigan Neptune. These analyses were made statically, measuring ^{232}Th on a Faraday cup and ^{230}Th on the RPQ channel using the SEM. Because of the large dynamic range in the $^{232}Th/^{230}Th$ of volcanic rocks (> 10^5), accurate and precise measurement of $^{232}Th/^{230}Th$ using PIMMS requires: 1) high abundance sensitivity to minimize tailing of ^{232}Th onto ^{230}Th, and 2) explicit knowledge of the instrumental mass bias and the gain calibration of the two detectors used for the measurement. Using the RPQ on the Finnigan Neptune, the abundance sensitivity at 95% transmission was ~25ppb over 2 amu, resulting in a tail correction of ^{232}Th on ^{230}Th of 0.7% for a ratios of $3x10^5$ and 0.3% for ratios of $1.5x10^5$. To correct for both instrumental mass fractionation between masses 230 and 232 and the relative difference in the efficiency of the Faraday and SEM detectors, Th isotopic measurements were corrected based upon a linear interpolation of the $^{238}U/^{236}U$ measured in the NBS U010 interspersed between each sample, and normalized to its certified value (14,535 +/149). Over three days of analyses (ca. 10 hrs each), the reproducibility in the measured $^{238}U/^{236}U$ of the NBS U010 (n= 40) was 0.6% (2σ). Replicate measurements of $^{232}Th/^{230}Th$ in synthetic and rock Th isotopic standards provide an overall reproducibility on the $^{232}Th/^{230}Th$ of 0.1-0.5% (2σ) and show excellent agreement with their "known" values established by other techniques, supporting the reliability and accuracy of this method. This level of precision indicates that the Th isotopic measurements on the Neptune are being limited by counting statistics on ^{230}Th rather than system stability. This PIMMS technique has considerable advantages over existing TIMS and SIMS techniques in terms of ionization efficiency and total sample consumption (and hence sample size requirement), as well as the rapidity of analysis.

The mantle zero paradox noble gas concentration

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We show that the three most important noble gas constraints on the geochemically layered mantle are entirely dependent on the low ^3He concentration of the mantle beneath mid ocean ridges estimated from the present day ^3He flux. A factor of 3.5 increase in this mantle noble gas concentration removes all requirements for: i) a ^3He flux into the upper mantle from a deeper high ^3He source; ii) a boundary in the mantle capable of separating heat from helium; and iii) a substantial deep mantle reservoir to contain a hidden ^{40}Ar rich reservoir. We call this reference value the 'mantle zero paradox noble gas concentration' (Ballentine et al., 2002).

The ^3He concentration of the mantle sourcing mid-ocean ridges is derived from the observed ^3He flux into the oceans and the average ocean crust generation rate. The time-integrated flux of ^3He into the oceans is a robust observation, but only representative of the ocean floor activity over the last 1000 years. The ocean floor generation rate is derived from averaging a process that occurs over tens of millions of years. We argue that combining these two observations to obtain the ^3He concentration of the mantle beneath mid-ocean ridges is unsound. Other indicators of mantle ^3He concentration, such as the 'popping rock' and independent estimates of mantle carbon concentrations suggest that the real value may be significantly higher.

As the Zero Paradox concentration is approached the noble gas requirement for mantle layering at 670km is removed. While noble gas isotopic differences (e.g. $^3He/^4He$) between ocean island and mid-ocean ridge settings demand the presence of at least two long lived geochemical reservoirs, noble gases alone do not at present constrain the size or location of these reservoirs.

Reference

Ballentine C. J., van Keken P. E., Porcelli D., and Hauri E. H. (2002) *Phil. Trans. Royal Soc. London* **in-press**