Mantle helium in sulphides deposited in a Palaeozoic arc setting

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Present views of the internal chemical structure of the mantle owe much to interpretation of noble gas isotopes trapped in rocks and minerals originating in the upper mantle and in deep ocean water which has passed through and reacted with the newly formed crust. Some ocean water with its complement of dissolved noble gases is trapped in inclusions within black smoker deposits and can be used to determine ^{3}He/^{4}He ratios and helium/heat ratios which are in substantial agreement with measurements in the emerging water column[1]. The present work is part of an attempt to extend measurements on these trapped fluids back in time. The so-called steady state model of upper mantle noble gas compositions is based on the dilution of an in-situ radiogenic component (^{4}He, ^{40}Ar and ^{21}Ne) with a primordial component introduced by plumes and characterised by high ^{3}He/^{4}He ratios. The term steady state is justified by estimates that mixing times in the upper mantle, ~10^8 yrs, are much shorter than residence times, ~10^9 yrs. Since there is no obvious physical requirement that the plume input and the ocean ridge output should be in balance the model does not preclude secular changes on timescales of a few times 10^8 yrs. With this in mind we have analysed noble gases trapped in arc related Silurian and Devonian sulphide deposits in the Southern Urals. Some of these contain well-preserved fossils of fauna comparable to those around present day black smokers. It is unlikely that they have experienced temperatures in excess of 120°C since deposition. ^{3}He/^{4}He ratios range from 0.02 to 2.15 Ra, and ^{40}Ar/^{36}Ar from 299 to 372. On a 3D plot of ^{3}He/^{40}Ar vs. ^{4}Ar/^{40}Ar vs. ^{36}Ar/^{40}Ar the data points are coplanar indicating that the gases are a mixture of air, radiogenic ^{4}He, and mantle derived He and Ar. The intersection of the plane with ^{36}Ar/^{40}Ar=0 passes close to the ^{4}He/^{40}Ar production ratio of ~5 at a ^{3}He/^{4}He ratio of 11.3 ± 2.5 Ra, close to present day MORB (8 Ra). Several analyses from a single deposit, Alexandrinka, are collinear suggesting the mantle helium and the radiogenic ^{4}He component were well mixed before trapping occurred. We infer that the radiogenic component was acquired by the passage of hydrothermal fluids through sea floor sediments at temperatures below the release temperature for argon. The maximum ^{3}He/^{40}Ar ratio can be used to estimate helium/heat ratios for the hydrothermal fluids based on an assumed fluid temperature[1]. A value of ^{4}He/heat = $1.5.10^{-7}$cc/J is estimated, a factor of ~ 4 greater than the production ratio and a factor of ~ 40 greater than the present estimated global value. The high value can be understood in terms of decoupling of fluid flow and heat flow in the sediments or upper crust.

[1] Turner G and Stuart F *Nature* **357** 581-583,1992.

Advances in High Precision Isotope Ratio Measurements of Calcium using TIMS

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Since the pioneering work of Russell et al. (1978), many geochemists have applied calcium isotope measurements to earth science problems. Calcium isotope measurements have proven useful in geochronologic studies (Marshall and DePaolo, 1982), especially when comparing the behavior of argon and calcium (Marshall et al., 1986). Variation in initial radiogenic calcium-40 can reveal the fractionation of potassium from calcium during igneous processes yielding useful information regarding the origin of ultrapotassic rocks and granites (Marshall and DePaolo, 1989).

More recently, the isotopic fractionation of calcium in the oceans has suggested application to paleoceanography. In these studies, the precision of the calcium isotope ratios made by thermal ionization mass spectrometry (TIMS) are on the order of 100 ppm (2σ); in most cases this limits the widespread application of calcium isotopes in geochemistry. Calcium isotopes may also be measured on MC-ICP-MS (e.g. Halicz et al, 1999), but this technique is likely to be less accurate than TIMS due to spectral interferences.

In our recent study high precision calcium analyses were performed on the new **Thermo**Finnigan TRITON in thermal ionization mode (TIMS).

Due to its increased dynamic range to 50 Volts @ 10^{11} Ω, excellent amplifier performance and innovative new features, like the *Virtual Amplifier* and the *Dynamic Zoom,* the TRITON ensures precise and accurate analyses of Neodymium and Strontium with guaranteed internal and external precisions better than 5ppm (1RSD).

Our studies on calcium especially benefit from these features and demonstrate improved internal and external precisions on ^{40}Ca/^{42}Ca of better than 25ppm (1RSD), approaching theoretical limits.

References:

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