Steady-state $^{226}Ra/^{230}Th$ disequilibrium in hydrous mantle minerals

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The short half-life of ^{226}Ra (~1.6 ka) makes it an ideal isotope for studying magmatic processes. However, observed excesses of ^{226}Ra are often larger than expected based on other U series nuclides and difficult to explain. The ^{226}Ra excesses in primitive IAB ($^{226}Ra/^{230}Th \leq 7$) are particularly large in comparison to MORB ($^{226}Ra/^{230}Th \leq 3$) and OIB ($^{226}Ra/^{230}Th \leq 1.5$) (Turner et al., 2001). The IAB super-excesses of ^{226}Ra may be a consequence of strong Ra/Th fractionation by the hydrous mantle minerals amphibole and phlogopite, coupled with a high diffusivity of Ra at mantle temperatures (calculated using the model of Van Orman et al., 2001). Partition coefficients (calculated and/or experimentally determined) suggest that equilibrium Ra/Th ratios in phlogopite (amphibole) are ca. 10000 (100) times higher than in clinopyroxene. Radium diffusion is predicted to be several orders of magnitude faster than Th in cpx. Consequently, as ^{230}Th decays to ^{226}Ra, the latter can diffuse out of cpx and into neighboring phlogopite or amphibole. The efficiency of the diffusional fractionation effect is related to the ratio of the cpx grain radius to $(D_{Ra}/\lambda\_)^{1/2}$. At temperatures >1000°C, the effect is significant for radii up to 1cm. Hydrous minerals present in low modal abundance can maintain large steady state $^{226}Ra/^{230}Th$ excesses (>10x equilibrium). Clinopyroxene will have complementary steady state depletions. Incipient melts may inherit the strong Ra excesses in the hydrous minerals by preferential incorporation of these early-melting phases, and hence could have Ra excesses larger than would be predicted by the ratio of Ra and Th distribution coefficients in major mantle minerals. The degree of ^{226}Ra excess in derived melts increases with ambient mantle temperature, and decreases with clinopyroxene grain size, degree of partial melting, and the time required for melt extraction. Further Ra enrichment during melt transport could contribute to the large observed ^{226}Ra excesses and hence relax the requirements for super-fast magma transport.

References

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On-line separation of PGE

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The increase in applications for the Re-Os and Pt-Os isotope systems raised the interest of determining the other platinum group elements (PGE). In the past few years, various analytical procedures have been developed to meet the demand on analyzing platinum group elements at the sub 10 ng/g level. The well known nugget effect tends to mislead the analytical geochemist making him believe that irreproducible results are caused or dominated by this effect. The complexity of separating uncertainties due to sample inhomogeneity from deficiencies of the methods (e.g. digestion, measurements) especially close to the limit of quantification make it difficult to validate the procedure. Validations of procedures with reference materials (RM) are currently not possible since these are not adequately certified. But being able to analyze RM accurately not necessarily allows to infer that every determination of unknown samples will be correct.

Preconcentration techniques are essential for PGE determinations. Thus not only complete digestions but also an effective analyte-matrix separation is required. The use of ICP-MS is very demanding, since problems of molecular interference are often uncontrolled. Separations via ion-chromatography with anion or cation exchange resins rely on the reproducible behavior of PGE (mostly as chloro-complexes) and the interfering species on the column.

Here complete liberation of the PGEs is achieved with a high pressure asher (HPA-S). But only through the on-line coupling of a cation-exchange column to an ICP-MS it is possible to monitor molecular interferences and the completeness of the species separation. Through this procedure (HPA-S and online separation) were are now able to gain confidence on the “trueness” of analytical results of every sample analyzed. As a consequence we can now identify uncertainties due to true sample heterogeneity since reproducibilities (1s) are 2-3%rel. for Pd, Pt and Re, 6-7%rel. for Ru, Os and Ir in UB-N, a peridotite RM. The differences between the two PGE subgroups is explained by the different affinities to mineral phases e.g. homogeneous distributed interstitial base metal sulfides and PGM nuggets e.g. laurites ($Ru(Os,Ir)S_2$).