Protactinium determination in manganese crust VA13/2 by thermal ionization mass spectrometry (TIMS)

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Here we present the first high precision $^{231}\text{Pa}$ measurements in a manganese crust applying thermal ionization mass spectrometry (TIMS) using the double filament technique. The detection limit using TIMS is at least one order of magnitude lower, the statistical uncertainty 6 to 8 times better than for conventional $\alpha$-spectrometry.

The developed method combines an easy chemical sample preparation (yields of 92 ± 7%) with the possibility to measure down to ten fg of protactinium. The detection is limited to approx. 2 or 3 fg of $^{231}\text{Pa}$ due to instrumental background. Another limiting factor is the total procedural blank. From regularly measured blank samples an amount of 4.9 ± 0.5 fg $^{231}\text{Pa}$ was estimated for the whole procedure of sampling and chemical separation.

While handling extreme low ion beam intensities (down to 1 cps) effects of counting statistics had to be considered.

With the new determination limit of approx. 10 fg older sections of manganese crust VA13/2 from the Northern Equatorial Pacific could be measured precisely for their $^{231}\text{Pa}$ concentration. Significant variations of the $^{231}\text{Pa}_{\text{ss}}$ activity during the past 150 ka are corroborated by existing $\alpha$-spectrometric data. A constant growth rate between 0—450 ka indicates a variable protactinium flux from the water column into manganese encrustations. Thus, $^{231}\text{Pa}_{\text{ss}}$ is not suitable for dating marine Mn/Fe deposits.

This method should be well applicable for the protactinium determination in smallest geological samples and has widespread applications e.g. Pa/U dating of continental and marine carbonates.