In situ measurement of Hf isotopes in rutile by LA-MC-ICPMS

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The measurement of hafnium (Hf) isotopes in accessory minerals such as zircon is now a well-established geochemical tool for tracing input from different crustal and mantle reservoirs. Recent studies have pioneered the *in situ* measurement of Hf isotopes in rutile, and demonstrated an intriguingly large range in $^{176}Hf/^{177}Hf$ values for rutile from MARID and eclogitic xenoliths [1, 2]. However, with one to two orders of magnitude less Hf than zircon, rutile presents a number of technical challenges for *in situ* measurement of Hf isotopes. We present the first rigorous assessment of the accuracy and precision with which Hf isotopes can be measured *in situ* for rutile, along with a revised LA-MC-ICPMS protocol adapted to suit this low-Hf mineral.

In order to maximse accuracy and precision, well-determined baselines are critical, and can be achieved by a combination of long baseline measurement times and averaging across an analytical session. Another key factor is the regular analysis of a synthetic rutile doped with c.5000ppm Hf to monitor, and if necessary externally correct for, mass bias. It can be demonstrated that although mass bias does change perfectly linearly with time, the low precision with which mass bias coefficients can be determined for rutile induces a much greater degree of scatter in apparent mass bias than the real variation, in some cases negating the advantages of internally correcting for mass bias.

Accuracy of the technique is confirmed by results for two rutiles for which the $^{176}Hf/^{177}Hf$ is known by independent means. Analyses of synthetic rutiles doped with Hf do not show a systematic offset in measured $^{176}Hf/^{177}Hf$ with varying Ti/Hf, as previously proposed for solution MC-ICPMS [3]. Although precision is lower than for zircon by a factor of 5 to 10, it is sufficient to distinguish between rutile from different samples. Zircon and rutile from a single metamorphic sample have also been shown to record different $^{176}Hf/^{177}Hf$ signatures, demonstrating that Hf isotopes in rutile provide an important complementary tool for deciphering metamorphic histories.

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Small scale mining and heavy metals pollution of agricultural soils: The case of Ishiagu mining district, South Eastern Nigeria

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Methods

This research assesses the distribution pattern of Pb, Zn, Cu, Cd, Co and Ni in agricultural soils in the Mining District of Ishiagu. The pollution level of the soils was also evaluated, based on existing guidelines. 26 samples of surface soil picked at the interval of about 1000m was digested by use of aqua regia and analyzed by use of AAS for Pb, Zn, Cu, Cd, Co and Ni. Detailed description of the methods is discussed in the paper.

Results

The contour maps, each showing the distribution of individual metals were generated. After evaluation, pollution map for the individual polluting metal were also made.

The case of pollution of soils in parts of Ishiagu by Pb, Zn and Cd was established. This is attributable to releases from mine dumps, concealed Pb-Zn lodes and the bedrock which get exposed during mining activities. The bedrock which comprises basic intrusive and dark coloured shales contains high concentrations of these metals [1]. Fertiliser application in soils is minimal and thus contributes very little metal to soils. Their accumulation in soils results from the clayey and the ferraltic nature of the soils [1, 2], and the presence of carbonate materials [3–5].

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