A silicon isotopic record of long term changes in continental weathering

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High precision MC-ICP-MS analyses of a suite of globally sourced clastic sediments suggest that the Si isotope system behaves more conservatively than other stable isotope tracers (i.e. Li, Mg, O) during continental weathering. This is contrary to expectation, as previous studies have shown that Si isotopes can be significantly fractionated toward lighter compositions during formation of secondary phases [1]. Nevertheless, Si isotopes in shales do not correlate with canonical proxies for weathering. Instead, good negative correlations between δ^{30}Si values and insoluble element concentrations (Nb, Hf, TiO_2) indicate that intensive chemical weathering is required before resolvable negative Si isotopic fractionation occurs in such lithologies.

On this basis, Si isotope variations in the long-term clastic sedimentary record could be used to provide a reliable proxy for investigating long term changes in the degree of reworking of continental crust and/or the intensity of continental weathering. When there is extensive formation and exposure of continental material (the Si in which has not undergone prior weathering), erosion should produce sediment with Si isotopic compositions similar to igneous continental crust [2]. If the availability of new crustal material is reduced, then the sedimentary record will become increasingly dominated by reworking of pre-existing lithologies, which will drive the Si isotope compositions to lighter values over time.

Such a hypothesis has been tested here using the post-Archaean Australian shale (PAAS) suite [3]. These samples are ideal, as they were all sourced from the same continental mass (Australia and, before, Gondwanaland) and have a wide range of depositional ages, from 1500Ma to 200Ma. The data display an enrichment in isotopically light Si with time, which appears to relate to increasing Nd crustal residence age [4]. As such, sediment derived from sources dominated by recycling of older crustal lithologies display the lightest isotopic compositions, as predicted. There is also evidence, however, that incorporation of authigenic marine lithologies can complicate this simple relationship.

Extremely negative Si isotopic compositions in Archaean shales (also sourced from Gondwanaland) cannot be explained by long-term continental weathering, as they were deposited when new continental crust dominated the budget. This could, therefore, reflect more intense weathering, due to more aggressive climatic conditions, early in Earth history.

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[4] Allègre and Rousseau, (1984) *EPSL*, **67**, pp 19-34

Improved calibration technique for magnetite analysis by LA-ICP-MS

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Oxide minerals such as magnetite and chromite are becoming popular in the field of geochemical exploration because the wide variety of trace elements present could potentially be used in provenance studies [1]. The method of analysis used is commonly LA-ICP-MS because it provides limits of detections down to ng/g levels when the analytical parameters can be optimized. No matrix-matched reference materials (RM) are available at the moment for *in-situ* calibration. Artificial glasses could be used to calibrate but only Fe can be used as an internal standard because of the inhomogeneous distribution of most of the other elements in magnetite. [2] proposed using NIST-610 to calibrate. However, the Fe content in NIST-610 is low at c.a. 0.05% while Fe in magnetite is c.a. 72%, thus limiting the use of NIST-610 to a beam >25µm, with a maximum precision of $R^2<0.85$ when results are compared to EMPA analysis of natural magnetite. [3] proposed the combination of 5 iron-rich RM to cover the elements of interest. Based on the elements for which EMPA results are available this calibration is satisfactory. However, this technique is time consuming and reduces the space available in the ablation cell.

We have found that USGS glasses GSE-1g and GSD-1g provide an accurate calibration for a beam size down to 4µm. The glasses are produced from natural basaltic material, containing c.a. 10% Fe, doped with a wide variety of trace elements. Figure 1 shows a good correlation between working values and those obtained at LabMaTer (UQAC) using a 193nm Resonetics M-50 laser and Aglilent 7700X ICP-MS. GSE-1g was used to calibrate while GSD-1g was used to monitor the precision and accuracy of the calibration. A natural magnetite from the Bushveld, BC-28 [4], was used as a quality control RM. Based on EMPA data, the calibration technique is also suitable for chromites, ilmenites and other Fe-rich oxides.

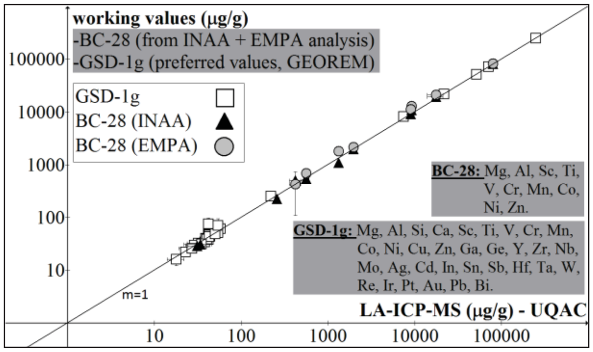

Figure (1): Accurate LA-ICP-MS calibration for magnetite analysis using GSE-1g as calibrant, GSD-1g and BC-28 as quality controls, and ^{57}Fe as internal standard.

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