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Analysis of light lithophile (Li, Be, B) and Alkali (Rb, Cs) elements by laser ablation sector field ICP-MS

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Light lithophile (B, Be, Li) and alkali elements (Rb, Cs) provide many constraints on the origin and evolution of magmatic rocks. However these elements can also be analytically challenging and present at low abundances, particularly in primitive magmas. B, Cs and Rb are also prone to mobilization during alteration and weathering and to contamination during preparation of bulk samples for dissolution and analysis using conventional techniques. We have developed a technique for rapid, in-situ, analysis of B, Be, Li, Rb and Cs abundances in glasses, glass inclusions and minerals using laser ablation microsampling and analysis by high sensitivity magnetic sector ICP-MS. By coupling the high sensitivity, dynamic range and low backgrounds of the sector ICP-MS with the spatial resolution, speed and minimal sample preparation requirements of laser ablation, we can analyze these elements with detection limits that rival many solution-based techniques. Analyses take ~60 s and use << 200 ng of material. Our technique also allows measurement of the B/Be and Rb/Cs ratios independently from calibration of elemental concentrations.

Analyses were conducted using a NewWave DUV 193 nm ArF Excimer laser system, with He as a carrier gas. Samples were ablated at energies of 10-12 mJ/cm^2 and ablated material was analyzed with a VG Axiom single collector ICP-MS. Although all peaks were checked at high mass resolving power for isobaric interferences, analyses were conducted at low resolving power (~400) to maximize transmission. Using high laser pulse rates (10-15 hz) our detection limits were 1-2 ppb (Cs, Be), 2-4 ppb (Li) and 10-15 ppb (B, Rb) for laser spots sizes between 50-100 µm. A pre-ablation step using a larger spot centred on the analysis location was found to be highly effective at removing surficial B, Cs and Rb. Analysis of standard glasses showed excellent agreement with accepted values and repeat analysis of standards and a suite of submarine back-arc glasses from the Lau Basin show external errors are typically < 5-10%.

Lau Basin glasses show strong enrichments in B, Rb and Cs that correlate with a slab-fluid signature. B, Be, Rb and Cs contents are low in MORB-like samples from the north end of the basin, but are enriched in more evolved lavas from propagating ridge tips.

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Diet of Creteceous crocodile; revealed from carbon isotopic analysis of teeth using UV laser system

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A technique is described whereby in situ carbon isotope analyses of carbonates and organic phosphates can be made with the use of a UV laser. The measurement technique involves laser ablation-combustion in the presence of CuO at 700°C-GC separation of CO_2-isotope ratio mass spectrometric analyses with a reproducibility of 0.1 ‰. Our experiment was intended to document minor/major variation in diet of crocodile by examining preserved growth rings of tooth enamel in *Crocodylus* sp, collected from Maastrichtian inter-trappean beds of Naska [1]. Palaeoecological inferences are drawn based on the carbon isotope composition of fossil enamel directly compared with the teeth and dietary habit of a living crocodile and otoliths from fish. XRD analysis reveal well preserved bio-apatite and no signature of alteration. Previous studies have shown that bio-apatite in the teeth of carnivores show isotopic enrichment of ^{13}C with respect to their diet by 9.0 ‰ [2]. Our results show variation in $\delta^{13}C$ from -17.1‰ in the early cortex region to -18.7‰ in the exterior rim of a tooth specimen. In addition, cyclic patterns were observed corresponding to a signal of 1‰ in a tooth specimen. Such patterns probably resemble metabolic cycles and reflect changes in the diet of the crocodile. Examination of teeth samples of crocodile collected from zoos confirmed their dietary habits. In general, crocodile prefer fish and ground meats [3]. Otoliths, the 'ear-bones' of fish, partly preserve information about the diet of the fish [4]. Remains of fish otoliths from the same sediments offer the opportunity to check this possibility for Cretaceous reptiles. Otoliths samples analysed show $\delta^{13}C$ values varying between -12‰ to -13.7‰ suggesting C_3 type (average -25‰) diet for these fish. Cyclic patterns in the teeth of crocodile suggest warm periods promoting consumption of fish and therefore depletion in $\delta^{13}C$ values, followed by enrichment in $\delta^{13}C$ values indicating cold winters with a scarcity of food, hibernation and survival of animal from stored animal tissue.

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