Accuracy of in-situ Sr isotope analysis of biogenic phosphates by LA-MC-ICPMS – a problem reassessed

WOLFGANG MÜLLER[1, *)], ROBERT ANCZKIEWICZ[2]

[1]Dept. of Earth Sciences, Royal Holloway University of London, Egham, UK, w.muller@es.rhul.ac.uk

[2]Inst. of Geological Sciences, Polish Academy of Sciences, Krakow, Poland, ndanczki@cyf-kr.edu.pl

In-situ Sr isotope analysis by LA-MC-ICPMS has been available for more than fifteen years [1]. While precise and accurate data can be obtained in this way for (high-Sr) carbonates and other materials, for phosphates accuracy (and precision) of in-situ analyzed Sr isotope data have proven difficult to obtain [2, 3]. Specific to Ca-phosphates, CaPO, a molecular interference on mass 87 ($^{40}Ca^{31}P^{16}O$), as well as doubly-charged Yb & Er in case of REE-rich inorganic apatite have been invoked as analytical obstacles, besides $^{84,86}Kr$, ^{87}Rb, Ca-Argides. Moreover, all is exacerbated by the relatively low Sr concentrations of biogenic phosphates (<100 to few 100 ppm Sr).

In view of the importance of Sr-isotopes in biogenic phosphate as mobility proxy in vertebrates - in teeth potentially providing sub-seasonal resolution when analyzed in-situ by LA-MC-ICPMS - we have evaluated in-situ Sr-isotope analysis for a range of biogenic phosphates. Using a RESOlution M-50 193 nm excimer laser-ablation system, featuring a Laurin two-volume cell, coupled to a Neptune MC-ICPMS, we evaluate spectral interferences on ^{87}Sr by focussing on: 1) Routine 'robust' plasma conditions ($ThO^+/Th^+ < 0.1$ %), which because of the highest oxide bond strength for ThO [4] imply that all other oxides will be present in lower abundances. 2) Accurate naturally invariant $^{84}Sr/^{86}Sr$ ratio (0.0565 after mass bias correction) as monitor of appropriate interference corrections (Kr, CaAr, REE^{2+}). 3) Careful mass scans at medium mass resolution ($M/\Delta M = 4000$) because CaPO and ^{87}Sr are resolvable above $M/\Delta M = 3900$. 4) Focus on the accuracy of the ^{87}Rb-correction on mass 87 since mammalian bioapatite can have relatively high $^{85}Rb/^{86}Sr$ of up to ~0.01 and sometimes even higher.

For the analytical (plasma) conditions utilized, we find no evidence for any molecular interference (CaPO) at mass 87 using medium resolution mass scans. Furthermore we obtain accurate $^{84}Sr/^{86}Sr$ ratios (0.0565) for both shark teeth (high-Sr) as well as mammalian enamel (few 100 ppm Sr maximum). $^{87}Sr/^{86}Sr$ ratios for modern shark teeth of 0.70917 ± 3 (2 SD) are indistinguishable from modern seawater (0.70917). Comparing TIMS and LA-MC-ICPMS Sr isotope data of the same tooth enamel characterized by variable Sr-isotope ratios inevitably highlights the problem of scale because mg-sized fragments are utilized for TIMS vs. ~100 µm spot sizes for LA-ICPMS. Nevertheless we find very good agreement in $^{87}Sr/^{86}Sr$ for corresponding enamel sections using both methodologies, but the ultimate accuracy depends on the magnitude of the necessary ^{87}Rb correction; corresponding results will be presented.

[1] Christensen *et al* (1995) *Earth Planet. Sci. Lett.* **136**, 79-85. [2] Simonetti *et al* (2008) *Archaeometry* **50,** 371-385. [3] Horstwood *et al* (2008) *Geochim. Cosmochim. Acta* **72,** 5659-5674. [4] Kent & Ungerer (2005) *J. Anal. Atom. Spectrom.* **20,** 1256-1262.

Evaluation of contaminated sediment remediation techniques

CATHERINE N. MULLIGAN [1*]

[1*]Concordia University, Montreal, Canada, mulligan@civil.concordia.ca

Introduction

An evaluation of the management options must be made for contaminated sites. In particular, the various techniques must be considered for the remediation of sediments when the sediment leads to the accumulation of contaminants in aquatic life or when the release of hazardous materials from sediments becomes a serious problem. The options can include capping, dredging, or physical, biological, and/or chemical treatments. Sustainable management options for contaminated sediments are required and will be evaluated. In situ remediation could be beneficial over dredging due to a reduction in costs and lack of solid disposal requirements.

Approach

Selection of the most appropriate remediation technology must coincide with the environmental characteristics of the site and the ongoing sediment fate and transport processes. To be sustainable, the risk at the site must be reduced, and the risk should not be transferred to another site. The treatment must reduce the risk to human health and the environment. Cost-effectiveness and permanent solutions are significant factors in determining the treatment. Sites vary substantially, and there can be substantial uncertainty involved in the evaluation process. However, decisions must be made based on the information available.

Both in situ and ex situ treatment approaches are examined. For example, environmental dredging requires evaluation of the risk of dredging, determination of disposal methods and/or potential beneficial use. Innovative integrated decontamination technologies must be utilized.

Results and Conclusions

To work towards sustainability, indicators must be identified and quantified, including waste must be minimized, natural resources must be conserved, landfill deposition should be minimized and benthic habitats and wetlands must not be lost and must be protected. Innovative integrated decontamination technologies must be utilized. The fate and transport of contaminants must be understood more thoroughly to develop appropriate strategies. A long term vision is needed. Otherwise, natural resources will continue to be depleted, landfills will continue to be filled with contaminated sediments, and biodiversity in the aquatic geoenvironment will be diminished. Integrated innovative management practices need to be developed and applied such as in situ techniques that reduce waste management requirements.