

## Stable isotope microanalysis – A SIMS perspective

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Modern micro-sampling methods invariably reveal greater isotope heterogeneity than bulk sampling methods, a general rule being that the smaller the scale of observation, the more variation is seen. The challenge to most in situ methods is to measure accurate isotope composition variations at the highest possible precision and, preferably, with minimum sample consumption in order to preserve material for other methods. This presentation will review the state-of-the-art in secondary ion mass spectrometer (SIMS) measurement of both traditional and non-traditional stable isotopes, with particular emphasis on what can be achieved with the current generation of multicollector-equipped, high mass resolution instruments (e.g. Cameca IMS1270/80).

A key element in driving down analytical precision to a commonly achievable level of ca. 0.1-0.2 ‰ (RSD) is the ability to measure large (preferably  $>2 \times 10^6$  cps) secondary ion signals simultaneously using low noise Faraday detectors and amplifiers. Such large signals are readily obtained for the most abundant isotopes of major elements in specific targets and permit most analyses to be performed in only a few minutes, thus limiting sample consumption. Studies of S isotope variations in sulphides by SIMS now achieve  $<0.2$  ‰ precision on both  $\delta^{34}\text{S}$  and  $\Delta^{33}\text{S}$ , the latter revealing non mass-dependent variations that, for example, have been successfully used to investigate ancient atmosphere evolution. Measurement of  $\delta^{18}\text{O}$  in zircon is now a major element of many crustal evolution studies and an essential complement to in situ U-Pb geochronological and trace element studies, while  $\delta^{18}\text{O}$  measurements in other silicates (e.g. garnet) are critical for evaluating metamorphic fluid evolution. The minor isotope of oxygen,  $^{17}\text{O}$ , while of little interest for terrestrial studies is important in cosmochemistry. At the typical signal level obtained for  $\delta^{18}\text{O}$  studies using Faraday detectors,  $^{17}\text{O}$  is too small to measure with reasonable precision but may still be measured simultaneously using an electron multiplier, although introduction of EM's into such measurement will be accompanied by gain drift which must be monitored and corrected, and requires substantially longer count times to achieve reasonable precision.

Recent development of in situ Fe isotope measurement by SIMS, using multiple Faraday detectors, highlights the potential of the method for such non-traditional stable isotopes, for example revealing hitherto unknown small scale heterogeneity of Fe isotopes in magnetite from banded iron formations. As with all SIMS stable isotope measurements, appropriate matrix matching of standards is critically important for accuracy and highlights the continuing need for collaboration between SIMS analysts and practitioners of other analytical techniques.

## Novel functions of siderophores in *Azotobacter vinelandii*

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The symbiotic  $\text{N}_2$ -fixing soil bacterium *Azotobacter vinelandii* requires the metals Mo and Fe for diazotrophic growth. It acquires Fe by excreting small organic ligands (siderophores) that bind iron and increase its availability. But recent evidence suggests that the catechol siderophores of *A. vinelandii* also affect the bioavailability of other metals, and particularly of the oxoanions molybdate, vanadate, and tungstate. Here, we investigate the various functions of these catechols using a combined approach of short-term uptake-experiments and HPLC analytics.

### Results

High (toxic) concentrations of tungstate induce the release of large amounts of tris(catechol) siderophore protochelin in the growth medium. The excretion of protochelin is modulated in such a way that there is just enough protochelin to bind all the  $\text{WO}_4^{2-}$  in the medium. Further, we show that the formation of W-protochelin suppresses W uptake by the cells, demonstrating that protochelin is used for W detoxification in *A. vinelandii*. A similar study shows that protochelin (and possibly the bis(catechol) azotochelin) are also used for vanadate detoxification.

At very low (limiting) Mo concentrations, protochelin is also present in the growth medium, and it is released preferentially to other catechol compounds. In this case, using short term uptake experiments with  $^{98}\text{Mo}$ , we show that Mo-protochelin (unlike W-protochelin) is available to the bacteria, indicating that protochelin is a metallophore used not only for Fe but also for Mo acquisition in these bacteria.

### Conclusion

The catechol compounds excreted by *A. vinelandii*, previously believed to be dedicated to iron acquisition, are multiple functional tools used for the acquisition and/or detoxification of various metals (Fe, Mo, V, W).

From a broader perspective, the elucidation of the mechanisms used by  $\text{N}_2$  fixers to acquire and detoxify metals may lead to a better understanding of the nitrogen cycle, as metals, and particularly Mo, now appear as potential controls on nitrogen fixation in terrestrial ecosystems.

### References

- Belleger, J.-P. *et al.* (2007), *J. Biol. Inorg. Chem.* **12**. 367-376.  
Cornish, A. S. and Page W.J., (2000), *Appl. Environ. Microbiol.* **66**. 1580-1586.