

What can we learn on Sulfur and Selenium from geochemical reference materials?

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Studies on the geochemistry of sulfur, selenium and S/Se ratio are important for mineral deposits modeling, petrogenetic interpretations, and environmental studies. In mineral deposits, the main approach relies on Se behaving similarly to S in reducing conditions and substituting for S in base metal sulfides. When conditions are oxidizing their behavior is decoupling where S is mobile and Se is not. In order to be able to study S and Se properly, analyte determinations have to be accurate. Until reference materials (RM) with values that fit the purpose are available, such interpretations are questionable. There are very few RM with certified values and when values are available uncertainties are often in the range of 50 relative %. Obviously if numerator and denominator have large uncertainties the S/Se ratio will have huge uncertainties. As an example the S/Se ratio of RM BX-N using published values vary between 650 to 2 000; S ranges from 115-160 µg/g and Se 0.08-0.18 µg/g. Values for some reservoirs can be erroneous by a factor two.

To improve accuracy of values for different rock types, S and Se were determined in a variety of RM using fit for purpose protocols with "state of the art" instruments. Ultramafic to mafic rocks contain 0.02-0.2 µg/g Se, intermediate to felsic rocks <0.02 µg/g Se, sediments vary from 0.04-2 µg/g Se and sulfide ores up to 100 µg/g. Basalt BE-N and anorthosite AN-G show a mantle S/Se ratio of 4340 and 3370 respectively. Felsic rocks (RGM-1, SY-2 and SY-3) have a S/Se ratio larger than 4000. The widest range in S/Se ratio is present in sediments (BSK-1, SBC-1, SCo-1, SDO-1, SGR-1b and SSAR-1) varying from 600 to 36 000 associated to the variation in weathering processes. Sulfide ores associated with mafic to ultramafic rocks (UMT-1 and WMS-1) show a S/Se compatible with a mantle origin (700-3000).

Although S is a common minor element, its determination has been neglected as can be inferred by large uncertainties in RM and small number of reported results in proficiency testing. Se on the other hand is a difficult analyte to determine with very low abundance. Until more determinations are done and published on RM, a fit for purpose accuracy is unlikely for S, Se and S/Se ratio.

Toward the *in situ* quantification of organic molecules in solid samples: Development of sample handling and processing hardware

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One theme of Martian exploration revolves around understanding the potential for Mars to have supported life at any point in its history. Laboratory investigations of organic material present in meteorites, rocks and soil samples collected from terrestrial environments inevitably include some form of solvent extraction (cf. [1]). Developing and demonstrating a wet chemistry preparation system that allows operation at Martian pressures and temperatures, will make possible a complete wet chemistry laboratory as part of future missions. Future complex landed missions such as ExoMars, Deep Drill and AFL all assume some kind of wet chemistry instrument as the heart of the analytical payload [1, 2].

We have developed two solvent based techniques for solid phase extraction of target molecules from rocks using high temperature water based and super critical CO₂ extractions. Each of these methods offers different advantages with respect to target molecules and extraction efficiencies while possessing different engineering challenges.

In most analytical investigations, there is a need to purify complex field samples to minimize interferences for the unique detection of analytes. It is especially true for techniques such as ESI/MS, CE, and MALDI where unique identification requires at least some de-salting of mixtures. In order to perform detail *in situ* analysis using these instruments, we have designed, constructed and are currently testing an ion exchange column that would enable a small light weight, low power *in situ* analytical system.

- [1] Liu, D., L.W. Beeple & I. Kanik (2008) *Astrobiology* 8(2) 1-12. [2] Beeple, L. W., M. G. Wilson, F. Abilleira, J. F. Jordan & G. R. Wilson (2007) *Astrobiology* 7(4) 545-577. [3] Miller, S. L., J. C. Essmiller & D. W. Beaty (2004) Space 2004 Conference and Exhibit, San Diego, California, AIAA.