

'Hidden' metals and minerals: How to detect nanocompounds

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Mining waste dumps provide materials suitable to investigate the fate of some metals and minerals during processing/alteration by meteoric waters. Such materials contain commonly all the minerals of the primary ores. It has been proven that, in addition, some minerals or compounds at nanometric scale can form within the waste dumps. Such minerals we can call 'hidden', as they escape the routine investigation by mineralogical methods. Their identification relies on structural techniques such as TEM/SAED, NGR (Mössbauer), XRD etc.

A waste dump in the Leaota Mts., South Carpathians, Romania, has been selected for detailed investigations. The material was produced by exploration of several types of ores, i.e. a combination of pentametallic ores (Ag-Co-Ni-Bi-U) and gold + Cu-Pb-Zn ores. Note that the waste dump is about 50-60 years old.

Attempts were made for the uptake of metals by using *Zea mays* and *Trifolium repens* planted on waste dump materials and neutral soils artificially enriched in metals (Au, U, Cu, As). Good results were obtained in both experiments. Significant enrichment factors of metals (plants vs. starting substratum) were obtained in both cases and both plants, plus surprisingly by analysing also *Alnus incana*, a spontaneously grown tree on the waste dump [2].

The 'hidden' compounds of nanometric size were identified in all the samples analysed: Au, Au-Ag alloys, Ag₂CO₃ (probably the first occurrence under natural conditions), maghemite, wüstite, pseudobrookite, lavendulan, and an amorphous phase, on which the silver carbonate develops. Such nanocompounds are likely to facilitate the metals uptake by plants as the nano-sized compounds show a greater bioavailability as compared to the crystalline (larger size) equivalents [1, 3].

The search for nanocompounds in plants and a deeper investigation of the amorphous phase are in progress.

- [1] Hochella (2008) *Elements* **4**, 373–379. [2] Udubasa *et al.* (2010) *Rev. Roum. Geol./Rom. J. Geology*, **53–54** (in press). [3] Waychunas & Zhang (2008) *Elements* **4**, 381–387.

Ultraviolet Spectra of ^{32/33/34/36}SO₂; implications for the Archaean atmosphere

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Photodissociation of SO₂ is known to yield mass independent fractionation of sulfur isotopes (S-MIF). The MIF recorded in the Archaean sedimentary rocks can be an important tracer for the atmospheric chemistry at that time, though wavelength dependency of the MIF by SO₂ photolysis is still poorly understood. We newly determined the ultraviolet absorption cross sections of not only ³²SO₂, ³³SO₂ and ³⁴SO₂ but also ³⁶SO₂ from 190 to 220 nm with a resolution of 4 cm⁻¹. The spectra of the ³²S, ³³S and ³⁴S samples are in agreement with our previously published spectra [1]. The cross sections of the isotopically enriched species (>98% for all the four isotopologues) were corrected based on the isotopic composition of the samples used for the measurements. The absorption spectra show rich vibrational structure and the positions and widths of the peaks change with isotopic substitution in a complex fashion.

The results show that the mass independent fractionation observed during broadband photolysis is product of the change in the amount of red shifting of the heavier isotopologues as suggested by our previous analyses [1, 2].

We will discuss the implications for the chemical composition of the Archaean atmosphere and its evolution based on our calculated wavelength dependency of mass independent fractionation factors for ³³S and ³⁶S.

- [1] Danielache *et al.* (2008) *J Geophys Res* **113**, D17314.

- [2] Ueno *et al.* (2009) *PNAS* **106**, 14784–14789.