Investigation of weathering rinds on Earth and Mars by depth selective Mössbauer spectroscopy

I. FLEISCHER[1], G. KLINGELHÖFER[1], D. RODIONOV[1,2], AND C. SCHRÖDER [1]

[1]Institut für Anorganische und Analytische Chemie, Universität Mainz (fleischi@uni-mainz.de)
[2]Space Research Institute IKI, Moscow, Russia

The two Mars Exploration Rovers, "Spirit" and "Opportunity", each carry a miniaturised Mössbauer spectrometer (MIMOS II) [1]. MIMOS II operates in backscattering geometry and can obtain 14.4 keV gamma ray spectra and 6.4 keV X-ray spectra simultaneously. Comparing 14.4 keV and 6.4 keV spectra yields depth selective information about a sample: 14.4 keV gamma rays have a larger escape depth from a sample than 6.4 keV X-rays because of their higher energy. As a consequence, a 6.4 keV spectrum contains more information about the near-surface part of a sample than a 14.4 keV spectrum. This allows for the detection and characterization of coatings such as weathering rinds without abrading the surface of the sample.

At the landing site of the Spirit rover in Gusev crater, a dark coating was detected on the rock "Mazatzal" [2]. 14.4 keV spectra and 6.4 keV spectra obtained on the brushed surface of Mazatzal show significant differences in the relative intensity of "nanophase oxide", a "poorly crystalline product of oxidative weathering that contains nanometer-sized particles of Fe^{3+}-bearing material" [3].

To investigate the depth selectivity in Mössbauer spectra experimentally, measurements were done on samples composed of thin sections of one mineral or iron foil, respectively, on another mineral. The influence of coatings of varying thickness and composition on Mössbauer spectra can be studied in a simulation. A Monte Carlo simulation compiled for this work allows the modelling of a sample composed of two homogeneous layers, each containing up to ten different minerals. The thickness of a coating can be determined by comparing measured and the according simulated spectra. In the case of Mazatzal, modelling the coating with a thickness of 10 micrometers leads to best agreement between measured and simulated spectra. [4]

References:

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[3] Morris *et al.*, (2006) *J. Geophys. Res.* **111** doi:10.1029/2006JE002791.
[4] Fleischer *et al.*, (2007) *Lunar Planet. Sci.* **38** Abstract # 1701.

Integrated air quality assessment – Pine needle $\delta^{13}C$, $\delta^{15}N$ as proxy for atmospheric CO_2 and NO_x loads

U. FLENKER[1], F. HUELSEMANN[1] , E. LEHNDORFF[2] AND L. SCHWARK[2]

[1]German Sport University Cologne, Carl-Diem-Weg 6, 50933 Cologne, [2]Department for Geology and Mineralogy, University of Cologne, Germany; (uli@biochem.dshs-koeln.de; lorenz.schwark@uni-koeln.de)

In a multidisciplinary approach atmospheric quality in the Greater Cologne Area (GCA) was studied using pine needles as pollutant bioreceptors. Here we discuss the potential of the $\delta^{15}N$ and $\delta^{13}C$ isotopic composition of pine needle biomass to record the atmospheric loading with CO_2 and NO_x released from anthropogenic combustion processes. The gaseous pollutant load estimated by isotope proxies is compared and interpreted in concert with persistent organic pollutant as well as major and trace element concentration data.

The GCA comprises a variety of CO_2 and NO_x emission sources, including lignite fueled power plants, regions of high traffic density, domestic heating, intensive agriculture and large industrial complexes along the Rhine Valley. A substantial part of atmospheric CO_2 in large conurbations will derive from fossil fuel combustion. Two reaction modes for increased CO_2 in atmosphere are known. A fertilizing effect by which the addition of isotopically light CO_2 will lead to a decline in foliage $\delta^{13}C$ values. Conversely, high concentration of CO_2 will cause stress and trigger closure of stomata, resulting in heavier foliage isotopes. For 5 needle age classes taken separately in summer and winter a systematic trend to $\delta^{13}C$ values heavier by about 2.5 permil with age was noted, attributed to declining photosynthetic activity. Differences between locations were larger than within location. Although influenced by a variety of environmental conditions the significantly lighter $\delta^{13}C$ of pine needles in urban Cologne reflects traffic emissions. The area affected by lignite combustion revealed no deviation in foliage $\delta^{13}C$ due to more intensive air mixing in these regions.

The $\delta^{15}N$ values of vegetation have been shown react to NO_x in surrounding air via direct stomatal uptake or via precipitation and root uptake. Hereby pollution stress induces heavier $\delta^{15}N$ values. Most often foliage and soil $\delta^{15}N$ are decoupled emphasizing the importance of atmospheric NO_x uptake and remineralization for foliage N-isotopes.

Investigation of 5 needle cohorts shows a systematic trends towards slightly lighter $\delta^{15}N$ values with age. Intra-site variability was low but inter-site variation high, allowing for excellent spatial discrimination. The $\delta^{15}N$ of pine needles showed a trend to heavier values in farming and forested areas but lighter values in urbanized regions and in areas affected by lignite mining. A trend inversion occured in inner city areas, where changes from high to low $\delta^{15}N$ were noted. Heavier N-isotopes of foliage caused by NO_x-stress are in compliance with previous observation but seem to be restricted to areas most affected by traffic emissions.