Arsenic in spring waters and soils in southern Switzerland : evidence of complex weathering and redeposition processes

EMILE TEMGOUA & HANS-RUDOLF PFEIFER

Centre d'Analyse Minérale, Université de Lausanne, BFSH2, 1015 Lausanne, Switzerland, Email: Emile.Temgoua@cam.unil.ch Email: Hans-Rudolf.Pfeifer@cam.unil.ch

In southern Switzerland, several areas, all lying in the Sottoceneri area, exhibit elevated As-values in their surface and ground waters. The Vedeggio/Oggio watershed in Val Isone studied here is characterized by gneisses and minor amphibolites without specially high As-contents. When surveying the whole watershed, a zone of 200 x 500 m with elevated As-concentrations was detected, situated above the village of Camignolo. Spring waters contain 20 to 60µg/l and soils 150 to 400 mg/kg As. In order to better understand this As-anomaly, a toposequence, 1200 m in length, of seven soil profiles has been studied in detail. Trace element content correlation with arsenic and organic matter have been investigated. The trace metals show values typical for soils resulting from silicate weathering (Zn: 95-200, Pb: 14-78, Cu: 9-35, Ni & Co:15-80, Cr: 60-200, Ba:500-600, all ppm), while arsenic is usually higher than the proposed limiting value of most European countries of 20 ppm, i.e. it varies between < 3 to 400 mg/kg. Iron-selective extraction methods where used to analyse arsenic in dithionite-, oxalate- and EDTA-Na₄extracts. The main factors responsible for the observed variation in the arsenic contents are the soil-mineralogy (upper part of the toposequence) and the organic carbon content (middle and lower part). The Brunisols (French soil nomenclature) developed on the upper part of the sequence, show the highest As concentration (170 - 260 mg/kg) in the weathering horizon (C, pH 4.5 or 5) and the lowest one in the topsoil (< 3 mg/kg As, pH 4 to 4.5). In the profiles situated further down-slope, As is enriched in all horizons with values between 250- 400 mg/kg. In the lower part of the studied sequence, corresponding to a more gently dipping part of the slope, an Organosol developed, consisting of a deep organic matter horizon (100cm), with a pH of 5 to 6. The Fe-extracts indicate that most of the As is contained in the amorphous organic fraction. Going down the slope, As-values of spring and superficial slope water decrease from 60 to 20 µg/L, supporting the idea that the soil behaves as a filter for arsenic. From this we conclude, that the studied weathering process first mobilises the arsenic contained in the local rock (mainly in allanite) and then emerges dissolved in the spring water, which flows over the local soil. There it is, depending on the local situation, several times adsorbed (its exact form is not known yet) or re-mobilised under reducing conditions by the slope water and finally flows almost exempt of As to the local river.

Controls of Undersaturation on Etch Pit Formation

H. HENRY TENG

Dept. of Earth & Environmental Sciences, The George Washington University, Washington, DC 20052 (hteng@gwu.edu)

Mineral dissolution is a vital component of natural weathering processes and controls various geochemical processes at both local and global scales. It is one of the intensively studied topics in the broad area of mineral-fluid interfacial geochemistry. To date it is widely recognized that overall dissolution at the Earth surface or near-surface conditions may be a surface reaction controlled process for many minerals. This conclusion arrives from a plethora of observations. Among them, the nearly ubiquitous occurrence of etch pits on dissolved surfaces stands the most noticeable.

Viewing surface etching in a bigger picture, however, the dislocation theories predict a saturation-dependent nature for pit formation. Observations on crystal faces of simple salt compounds, metals, and even laboratory dissolved and field weathered quartz grains corroborate the prediction. Yet, the controls of undersaturation on pit formation have not been literally incorporated into our knowledge base for mineral dissolution, for conventional approaches either treat dissolution as independent of undersaturation or attempt to extrapolate dissolution rate to near equilibrium conditions based upon the linear dependence of kinetics on chemical affinity. Thus, it is apparent that what we understand so far may only represent certain extreme cases at high undersaturation conditions, or a possible over-estimation of the actual dissolution kinetics since little dissolution can occur on flat surfaces when pits do not nucleate.

This study attempts to look into the controls of solution undersaturation on etch pit formation using calcite as a model system. Experiments were conducted on $\{10\overline{1}4\}$ cleavage faces at various undersaturations to study the behaviour of surfaces and the responses of defects exposed at the surfaces. Observations were made using in situ fluid cell Atomic Force Microscope. The goal is to determine the undersaturation ranges where pit-induced and step-induced dissolution dominate. Three dissolution modes were observed: above 79% of equilibrium activity $(0.79a_e)$, no pits form and dissolution occurs at existing steps; in between $0.79a_{\rm e}$ and $0.11a_{\rm e}$, pits form in a controlled fashion while dissolution continues at steps; finally at below $0.04a_{\circ}$, rapid nucleation of etch pits becomes dominant. These observations are explained as two-dimensional surface nucleation controlled dissolution for below $0.04a_{e}$, defect- and step-induced dissolution in between $0.79a_e$ and $0.11a_e$, and step-induced dissolution for above $0.79a_e$. From the undersaturation needed to open up two-dimensional pit nucleus, a critical radius of the pit is estimated to be 2.94 nm. This corresponds to a free energy maximum of 3.63×10⁻¹⁸ J to be overcome before twodimensional pitting becomes the dominant dissolution mechanism. These findings may have implications toward establishing new guidelines for developing geochemical rate laws and explaining the discrepancy between field and laboratory measured dissolution rates.