

Microscale geochemical data as a proxy of weathering of mineralized sedimentary rocks

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INTRODUCTION

Rock weathering transforms competent bedrock into unconsolidated and altered saprolite, initiating soil formation, and releasing elements into groundwater. Weathering proceeds through rock fracturing and a sequence of chemical reactions between rock minerals and water, solutes and atmospheric and subsurface gases. These reactions play an important role in elemental cycles controlling not only element mobility between bedrock and ground or surface water, but also consuming atmospheric CO₂ (Dessert et al., 2003). The presence of sulfide minerals has a major influence on weathering and watersheds because the oxidative dissolution of sulfide minerals generates acidity that can accelerate mineral dissolution and mobilize metals into freshwater (Nordstrom, 2011). Decadal trends in increasing sulfate concentrations in stream and lake waters at upper mountain basins, simultaneously to a temperature increasing, reflect climate sensitivity of the weathering of sulfidic rock in this area (Manning et al., 2013), which may increase the release of contaminants such as selenium.

Weathering overprints the host rock with records of mineral reactions, especially reactions involving redox-sensitive phases as sulphate. These records are generally characterized at the meter scale in homogeneous lithologies and can be interpreted to generate models for weathering pathways and element export (Brantley & Lebedeva, 2011). In mineralized sedimentary rocks, however, weathering patterns can be challenging to identify from bulk observations due to sharp variations in mineralogy and rock chemistry imposed by rock history. However, weathering fundamentally involves rock-fluid interactions at the surfaces of fractures that are open to groundwater flow. At this scale, the bedrock composition is more uniform and hence millimeter-to-centimeter-scale weathering records may provide clearer depictions of the weathering. Here we apply micron-scale X-ray imaging to reveal the sequence of mineralogical transformations and infer the controls on element mobilization within a weathered fracture surface.

MATERIALS AND METHODS

Core samples were collected from the first 10 meters of sandstone core in a hydrothermally altered sandstone from the Redwell Basin (CO, USA), where weathering could be identified around fractures on the rock by changes in color or texture. The weathering profiles were revealed by cuts perpendicular to the fracture surfaces and were made into thin sections for Microscale X-ray fluorescence (μ XRF) imaging, performed on beamline 10.3.2 at the Advanced Light Source (USA) for tender-X-ray analysis (S, P, Si, Al) and on beamline 2-3 at the Stanford Synchrotron Radiation Light Source (USA) for hard-X-ray analysis (Fe, Mn, Se, Zn). X-ray absorption near-edge structure (μ -XANES) spectroscopy were also performed at the Fe and S k-edge.

RESULTS AND DISCUSSION

The mineral composition of the sandstone was quartz, white mica (e.g., illite and/or muscovite), chlorite, feldspar and a minor proportion of sulfide (e.g., pyrite and sphalerite) and carbonates (e.g., calcite and siderite) minerals. Distribution maps and integrated profiles of major and trace elements and the oxidation states of iron (Fig. 1) reveal a weathering profile with two distinct weathering fronts (~3 and ~7 mm from the fracture surface, blue and green triangle, respectively) that divide the profile into three zones (A, B and C). Zone A is characterized as the shallowest and most affected by weathering reactions where there is a loss of chlorite, sulfide and carbonate minerals. The weathering front between Zone A and B is defined by a sharp calcium profile, where Ca peaks disappear in a

homogeneous background, mirrored by a transition in Fe oxidation state from Fe(II), mostly contained in chlorite, to Fe(III) (Fig. 1). Fe and S XANESs from different locations in the weathered region are consistent with goethite and jarosite. Zone B is a partially weathered area where there is a loss of sulfide minerals. In addition, Fe XANES match reference spectra for chlorite indicating that this mineral is not affected by weathering in this zone. The second weathering front, is defined by the oxidative weathering of sulfide minerals and marks the division between weathered rock (Zone A and B) with pristine rock (Zone C). The sulfide mineral was confirmed to be sphalerite by S K-edge XANES on S- and Zn-rich spots as seen in the μ XRF map. Fe K-edge spectra in Zone C were reasonably best matched by a linear combination of pristine chlorite and siderite. The co-location of Se with Zn and S indicates that, in this sample, Se is dominantly hosted by sphalerite in the unweathered rock.

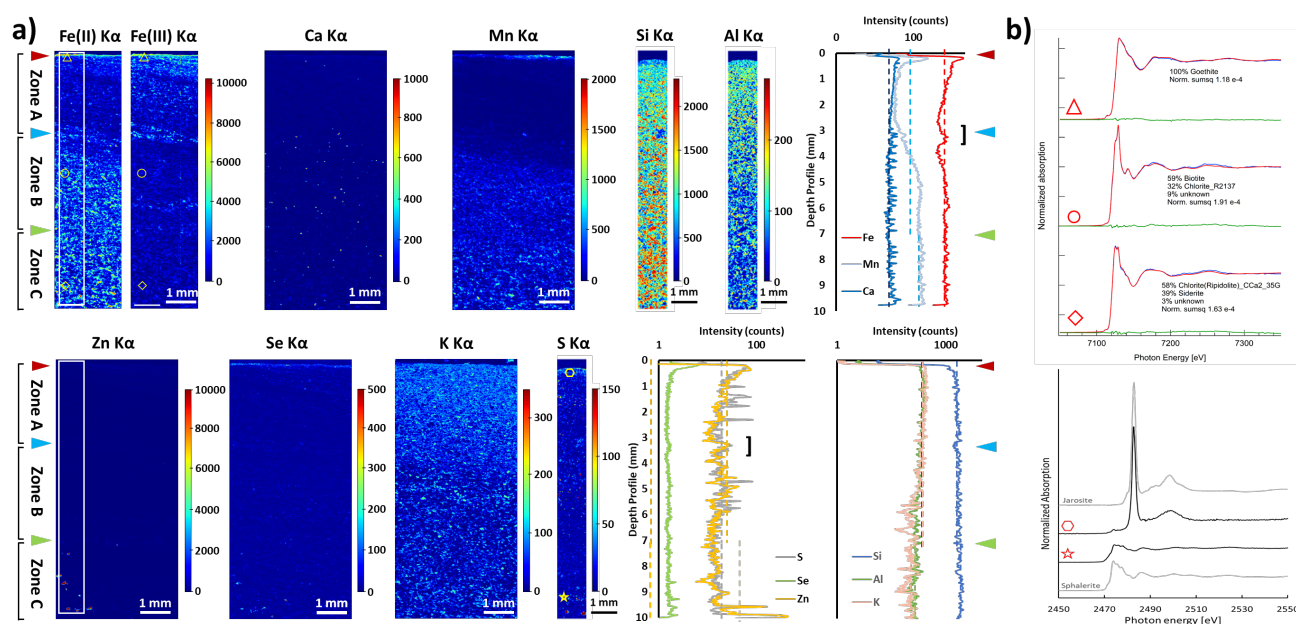


Fig. 1. Chemical maps in weathered sample with its integrated profiles (a) and XANES results for Fe and S k-edge fitted with lineal combination (b).

The microscale analysis of fracture surface weathering allows a geochemical model to be developed describing the principal mineral and elemental transformations and mobility. Iron is mostly released by the weathering of chlorite and sulfite minerals. The pore water is likely to be acid, with pH 2-3, due to the presence of jarosite. The acidity should be released by sulfide mineral oxidation (e.g. pyrite), which is not neutralized due to the low content in carbonates, allowing a high mobility of both Fe(III) and Fe(II) and silicate mineral alteration (e.g. chlorite and feldspar). The increasing iron content towards the fracture and the coating of nanophase goethite along the fracture are consistent with the mixing of circumneutral groundwater exchanging and neutralizing acidic pore water, rich in Fe from the weathering profile. For that reason, the mass valance through the weathering profile indicates that most of the Fe is retained *in situ* by Fe-oxide precipitation, retaining other elements (e.g., Se and Zn). However, Ca, Mn and S display a clear depletion from the weathering zone, indicating releasing into de groundwater. This study concludes that fracture-controlled weathering at this location makes little contribution to the export of acidity and metals, but the expected changes in climatic factors could accelerate the weathering, increasing metal releasing.

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