Determining solute sources and water flowpaths in catchments using the Ca-Sr-Ba multi-tracer

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Determining solute sources and water flowpaths in catchments is essential for understanding how catchments function. For example, stream water chemistry is determined by multiple factors including delivery of water from different portions of the catchment and from different depths along hillslopes and processes such as mineral weathering, ion exchange and biological cycling. As part of a larger study aimed at understanding the inter-relationships of these factors, we are using a hydropedologic approach to interpret concentration and isotope ratios of the alkaline earth elements Ca, Sr and Ba in stream water, groundwater, the soil exchange pool and plants from a catchment at the Hubbard Brook Experimental Forest, New Hampshire, USA. This 41 hectare forested headwater catchment supports a beech-birch-maple-spruce forest growing on vertically- and laterally-developed Spodosols and Inceptisols formed on granitoid glacial till that mantles Paleozoic metamorphic bedrock. Across the watershed in terms of the soil exchange pool, the forest floor has high Sr/Ba and Ca/Sr ratios, weathered mineral soil has intermediate Sr/Ba and low Ca/Sr ratios, and relatively unweathered till has low Sr/Ba and high Ca/Sr ratios. Waters moving through these various soil compartments obtain Sr/Ba and Ca/Sr ratios reflecting these characteristics, and thus variations of Sr/Ba and Ca/Sr ratios of streamwater provide evidence of the depth of water flowpaths feeding the streams. ^{87}Sr/^{86}Sr of soil exchangeable Sr spans a broad range from 0.715 to 0.725, with highest values along the mid- to upper flanks of the catchment and lowest values in a broad zone along the central axis of the catchment associated with groundwater seeps. Thus, variations of ^{87}Sr/^{86}Sr in streamwater provide evidence of the spatial distribution of water flowpaths feeding the streams. In addition, we are using Ca, Sr and Ba stable isotope ratios (^{44}Ca/^{40}Ca, ^{88}Sr/^{86}Sr, ^{138}Ba/^{134}Ba) as novel tracers of Ca, Sr and Ba sources and transport pathways in catchments. Initial results indicate that: 1) Sr and Ba stable isotopes are fractionated by plants similarly to patterns observed globally for Ca stable isotopes; 2) organic soils have the lightest values and weathered mineral soils have the heaviest values of exchangeable Ca, Sr and Ba, with particularly heavy Sr and Ba associated with accumulation of humic materials (i.e., in Bh horizons); and 3) the total range of isotope ratios observed for the exchange pool on a mass percent basis increases unexpectedly in the order Ca<Sr<Ba, suggesting an important role for Ca-oxalate that contains lighter Ca than that sampled in the exchange pool. We hypothesize that while biologically-cycled Ca is efficiently retained in the organic soil-plant system (e.g. as Ca-oxalate), biologically-cycled Sr and especially Ba will be more easily leached by soil waters and delivered to the streams and thus their stable isotope ratios may provide an additional means to distinguish between shallow and deep water flowpaths.

XRF archaeometry for lithic characterization and provenance.

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The use of XRF over the last forty years to determine whole-rock geochemistry and establish an internationally approved chemical nomenclature for igneous rocks [1] has proven to be vital for the geological community. Its use as an archeometric tool specifically for lithic materials has been limited and historically overshadowed by INAA. This is in part due to the lower amount of material required to perform the latter, which is more in line with archaeological conservation guidelines.

If one considers the silicate nature of lithic materials used in the fabrication of sharp-edged tools one is immediately confronted by the inability of INAA to determine the major component of such materials: silica. This precludes the use of rock type based chemical classifications which for aphanitic materials have proven to be crucial, and unbiased, when compared to macroscopic ones (mineralogy based). A complete set of major element oxide determinations, compatible with data found in geological publications, is essential to determine the rock type and in turn narrow possible geological sources . Most importantly, for igneous types, it permits the use of an internationally approved and established chemical rock nomenclature (basalt, andesite, rhyolite, etc.) [1].

Non-destructive methods were developed [2, 3] in order to comply fully with archaeological conservation rules, and in order to profit from the many advantages of XRF when characterizing archaeological lithic materials, such as relative cost, throughput, and the immediate reuse of samples (non-radioactive) for other specific archaeological and geochemical assays.

Concentration data for major and trace elements produced with a specific non-destructive method using long counting times, calibrations using certified rock reference materials, and a geochemical data treatment approach [4] – notwithstanding the caveats imposed by unprocessed samples (slabs versus fused beads and powder pellets) such as surface irregularities, inhomogeneities and varying thicknesses – will be shown here to be quite useful for 1) the correction of macroscopic misclassifications in archaeological collections, 2) the assessment of chemical variations among chert types (nodular, bedded, chemically precipitated, etc.), 3) the determination of specific chemical markers, 4) the evaluation of the geochemical effects of weathering, and finally 5) the determination of provenance.

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