LETTER

Reduced As components in highly oxidized environments:
Evidence from full spectral XANES imaging using the Maia massively parallel detector

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Abstract

Synchrotron X-ray fluorescence (SXRF) and X-ray absorption spectroscopy (XAS) have become standard tools to measure element concentration, distribution at micrometer- to nanometer-scale, and speciation (e.g., nature of host phase; oxidation state) in inhomogeneous geomoerials. The new Maia X-ray detector system provides a quantum leap for the method in terms of data acquisition rate. It is now possible to rapidly collect fully quantitative maps of the distribution of major and trace elements at micrometer spatial resolution over areas as large as 1 × 5 cm². Fast data acquisition rates also open the way to X-ray absorption near-edge structure (XANES) imaging, in which spectroscopic information is available at each pixel in the map. These capabilities are critical for studying inhomogeneous Earth materials. Using a 96-element prototype Maia detector, we imaged thin sections of an oxidized pisolithic regolith (2 × 4.5 mm² at 2.5 × 2.5 μm² pixel size) and a metamorphosed, sedimentary exhalative Mn-Fe ore (3.3 × 4 mm² at 1.25 × 5 μm²). In both cases, As K-edge XANES imaging reveals localized occurrence of reduced As in parts of these oxidized samples, which would have been difficult to recognize using traditional approaches.

Keywords: Arsenic, oxidation state, XANES, element distribution, imaging, X-ray fluorescence

Introduction

Much of geochemistry relies on measurements of the distribution and speciation (e.g., oxidation state; bonding and crystallographic arrangement) of elements in soils, rocks, and associated fluids. Synchrotron-based μ-spectroscopy has become a standard method in geochemistry, thanks to its ability to quantify the concentrations of trace and major elements at high spatial resolution (<100 nm) using X-ray fluorescence (SXRF) combined with the ability to measure concurrently elemental speciation using X-ray absorption near-edge structure (XANES) spectroscopy (e.g., Brugger et al. 2010; Sutton et al. 2002). However, the slow readout and limited count rate (usually ≤3 × 10³ counts/s) of conventional energy dispersive X-ray detectors mean that SXRF maps seldom exceed ~40 kpixels; at 1 μm resolution, this corresponds to a 200 × 200 μm² mapping area for typical collection times of 6–12 h. This introduces severe sampling bias when mapping heterogeneous samples such as those typically encountered in geological and environmental studies.

To address these limitations, the Maia detector was developed jointly by CSIRO (Australia) and BNL (U.S.A.). The design combines several innovations: a massively parallel architecture (96-element prototype, 384-element to be commissioned in early 2010; Kirkham et al. 2009) insures a large dynamic range for the count rates (3 × 10⁹ counts/s for the 96-element prototype), while integration with sample stage controls enables high-speed scanning of large (cm) areas while minimizing dwell-time. Consequently, trace as well as major elements can be mapped over whole thin sections (e.g., Ryan et al. 2009).

The “holy grail” of SXRF is the capacity to combine micrometer-scale imaging with speciation analysis using μ-XANES spectroscopy. Current workflows for the study of heterogeneous materials typically involve selecting areas of interest of a few mm² using non-synchrotron techniques, then mapping parts of these areas using μ-SXRF (several hours per map). Based on the SXRF maps, particular spots are selected and XANES spectra are obtained at those points. Brugger et al. (2008) illustrated this traditional workflow and its limitation: understanding the origin of the variation of the XANES signal would be much easier if it was possible to image speciation.

Rau et al. (2003) demonstrated the concept of building XANES images from a stack of SXRF images collected at different monochromator energies. The applications of the method reported so far are severely limited due to slow collection times: the individual maps do not exceed 10⁴ pixels and typically use...