Bioturbating animals control the mobility of redox-sensitive trace elements in organic-rich mudstone

Dario Harazim1*, Duncan McIlroy1, Nicholas P. Edwards2,3, Roy A. Wogelius2,3, Philip L. Manning2,4, Kristin M. Poduska5, Graham D. Layne1, Dimosthenis Sokaras6, Roberto Alonso-Mori6, and Uwe Bergmann6
1Department of Earth Sciences, Memorial University of Newfoundland, St. John’s, Newfoundland A1B 3X5, Canada
2School of Earth, Atmospheric, and Environmental Sciences, University of Manchester, Manchester M13 9PL, UK
3Williamson Research Centre for Molecular and Environmental Science, University of Manchester, Manchester M13 9PL, UK
4Department of Geology and Environmental Geosciences, College of Charleston, 66 George Street, Charleston, South Carolina 29424, USA
5Department of Physics and Physical Oceanography, Memorial University of Newfoundland, St. John’s, Newfoundland A1B 3X7, Canada
6SLAC National Accelerator Laboratory, Menlo Park, California 94025, USA

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ABSTRACT

Bioturbating animals modify the original mineralogy, porosity, organic content, and fabric of mud, thus affecting the burial diagenetic pathways of potential hydrocarbon source, seal, and reservoir rocks. High-sensitivity, synchrotron rapid scanning X-ray fluorescence elemental mapping reveals that producers of phycosiphoniform burrows systematically partition redox-sensitive trace elements (i.e., Fe, V, Cr, Mn, Co, Ni, Cu, and As) in fine-grained siliciclastic rocks. Systematic differences in organic carbon content (total organic carbon >1.5 wt%) and quality (Δ13Corg ~−0.6‰) are measured between the burrow core and host sediment. The relative enrichment of redox-sensitive elements in the burrow core does not correlate with significant neo-formation of early diagenetic pyrite (via trace metal pyritization), but is best explained by physical concentration of clay- and silt-sized components. A measured mass loss (~15%) of the large-ionic-radius elements Sr and Ba from both burrow halo and core is most likely associated with the release of Sr and Ba to pore waters during biological (in vivo) weathering of silt- to clay-sized lithic components and feldspar. This newly documented effect has significant potential to inform the interpretation of geochemical proxy and rock property data, particularly from shales, where elemental analyses are commonly employed to predict reservoir quality and support paleoenvironmental analysis.

INTRODUCTION

Bulk-rock geochemical interpretation of organic-rich mudstones is fundamental to geological models of both hydrocarbon systems (Ratcliffe et al., 2012) and oceanic anoxic events (Jenkyns, 2010). This study documents for the first time the effects of deposit-feeding organisms on the spatial (centimeter to decimeter scale) patterns and characteristics of redox-sensitive trace elements in bioturbated siliciclastic mudstone. Bioturbation has hitherto been modeled as a predominantly physical phenomenon that facilitates oxidation of buried organic matter and metal sulfides, thereby driving trace elements into solution (Aller and Rude, 1988). The incomplete understanding of the effects of bioturbation on sediment biogeochemistry is a significant shortcoming of such models, especially because most whole-rock geochemical and compositional data sets use destructive sampling that mixes sedimentary components of dissimilar origin (e.g., Hesselbo et al., 2007). Quantifying the spatial chemical heterogeneity of fine-grained sedimentary rocks on a centimeter scale (Zhu et al., 2006) is critical if we are to place constraints on mass transfer between sediment fabrics and thereby contribute to the understanding about the origin of directional shale anisotropy at a range of scales (cf. Hart et al., 2013). Conventional scanning electron microscope (SEM)–based energy dispersive X-ray spectroscopy techniques for surface compositional mapping are very slow (~12 h/cm2), limiting the area that can be analyzed during one continuous sample run (cf. Edwards et al., 2014). Non-destructive synchrotron rapid scanning X-ray fluorescence (SRS-XRF) elemental mapping images the spatial distribution of both mineralized and amorphous inorganic products of organic matter remineralization (i.e., carbonates, silicates, phosphates, and metal sulfides) at a range of scales (Wogelius et al., 2011). SRS-XRF maps are integrated with conventional organic and inorganic geochemistry to elucidate the effect of grain-selective deposit feeding on elemental distribution, sediment mineralogy, and both the composition and abundance of organic matter.

METHODS

Geological Background and Sampling Strategy

Phycosiphoniform burrows (Fig. 1) are the earliest component of the studied ichnofabric from the Cretaceous turbidites of the Rosario Formation (Baja California, Mexico) (Callow et al., 2013, their figure 5A). Large (5 kg) samples with phycosiphoniform trace fossils were collected from fresh sandstone and mudstone outcrops in channel overbank deposits (Callow et al., 2013; Fig. 2B) and slabbed to remove any effects of surface weathering. The large phycosiphoniform burrows enabled sufficient

Figure 1. A: Location map of sampling area near Rosario (Baja California, Mexico). B: Three-dimensional reconstruction of burrow halo and core by an unknown vermiform organism (after Bednarz and McIlroy, 2009).
material for analysis to be collected from the different burrow components using a handheld rotary drill. The sample powder was analyzed via X-ray diffraction (XRD) and Fourier transform infrared analysis (FTIR) (see Poduska et al., 2011) to determine composition and to exclude chemical diagenesis as a potential source of uncertainty. Host sediment, halo, and core were analyzed for weight percentage (wt%) of total organic carbon (TOC) using a Carlo Erba elemental analyzer. All compositional analyses (except solution inductively coupled plasma-mass spectrometry [ICP-MS] analyses) were carried out on the same aliquot. Additional powder samples were obtained from fresh surfaces using a stationary high-precision micro mill. These powders were geochemically analyzed via ICP-MS (see Jenner et al., 1990).

Chemical Imaging via SRS-XRF

Non-destructive SRS-XRF imaging (Fig. 3) was performed at wiggler beam line 6-2 at the Stanford Synchrotron Radiation Lightsource (Menlo Park, California, USA). Spatial elemental maps were acquired with incident X-ray beam energies of 12 and 3.15 keV to image elements of high (Ca to As K-emission) and low (Al to K K-emission) atomic weight, respectively, using a 100 μm tantalum pinhole that generated a similar beam spot size. Flux was calculated to be between 1010 and 1011 photons s−1 at high Z (high atomic weight elements), and ~109 photons s−1 at low Z. High-Z experiments were carried out under ambient conditions. Low-Z experiments were carried out with specimens enclosed within a helium atmosphere in order to avoid X-ray absorption and the scattering effects of air at low incident beam energy (see Edwards et al., 2014).

RESULTS

Visual estimates of porosity using transmitted light microscopy reveal a post-compaction porosity of up to 30% in the burrow halo (Fig. 2A). Grain-selective deposit feeding by the trace maker accounts for the redistribution of the silt- and clay-sized fraction (<40 μm in grain diameter) and relative enrichment of organic material (Figs. 2B and 2C). The average TOC values for the burrow core (1.8 wt%) were determined to be 1.0 wt% higher than for unbioturbated host sediment (0.7 wt%) and 1.1 wt% higher than for the burrow halo (0.6 wt%). Average δ13C organ values were found to be ~24.4‰, with systematic variations of organic carbon quality between halo (~23.8‰) and burrow core (~24.4‰, δ13C org ~0.6‰). Combined SRS-XRF (Fig. 3) and ICP-MS analyses (Fig. 4) reveal that within the burrow halo, redox-sensitive trace elements (including Rb and Zr) are depleted by 10%–20%, whereas the same elements appear to be enriched by 40%–80% in the burrow core. Conversely, Sr and Ba are depleted in both the halo and burrow core (Fig. 4A).

Using FTIR spectroscopy the fecal core was determined to be enriched in illite and/or smectite relative to host sediment and burrow halo (Fig. 4B). The 3620 cm−1 absorption band represents the OH stretch for hydroxyl bonded to a double Al-Al (Besson and Drits, 1997). Within the fecal burrow core, the peak broadening and attenuated intensities of XRD peaks characteristic of feldspar (25.6° and 28.5° 2θ) indicate alteration of clay- to silt-sized Ca-rich feldspar (Fig. 4C). Despite the presence of significant amounts of organic matter (TOC ~1.8 wt%) within the burrow core, both XRD and FTIR spectroscopy demonstrate the absence of the early diagenetic reaction products of organic carbon remineralization (e.g., pyrite, mackinawite, and greigite) in both the burrow halo and fecal core (Figs. 4B and 4C).

DISCUSSION

Food web experiments demonstrate that the isotopic composition of residual organic matter deviates from values expected from kinetic isotope fractionation effects alone (Landrum and Montoya, 2009; contra Hayes, 1993), yielding compounds with δ13C organ values that are persistently lighter by ~0.5‰ to ~2‰ compared to the original ingested food. Future research will demonstrate whether the early authigenic reaction products are formed or reduced in beds exhibiting a higher bioturbation intensity (cf. Harazim and McIlroy, 2015).

The rare pyrite in the burrow core is directly correlated with localized enrichment of Co, Ni, Cu, and Zn. These elements are preferentially incorporated into the pyrite lattice via trace metal pyritization (Huerta-Diaz and Morse, 1992).
Some pyrite grains could have been ingested from the host sediment (see Izumi, 2014), though we consider the likelihood of such grains surviving the acidic portions of the gut unlikely. The abundant iron in the burrow cores (Fig. 3B) is mainly associated with smectite (Fig. 4B) or, potentially, with some lesser iron-rich dioctahedral mica. Because these ferrous iron–bearing silicate minerals are known to have low reactivity with H$_2$S (e.g., Canfield et al., 1992), they are unlikely to be an important source of iron for pyrite precipitation in the burrow core. The rarity of pyrite, together with the persistence of organic carbon in the fecal core, suggests that the carbon was most likely too refractory to fuel the formation of pyrite by bacterial sulfate reduction during early diagenesis (cf. Widerlund and Davison, 2007).

The near absence of pyrite in the burrow core suggests that the observed enrichment of transition metals within the fine-grained fecal burrow core is a result of an animal-sediment interaction. The partitioning of some elements in the phycosiphoniform burrows occurs without any bulk enrichment relative to the host sediment, inferring simple mechanical redistribution by the trace maker. Zirconium and Rb are significantly enriched in the fecal burrow core relative to the halo (by ~30%; Fig. 4A). Zirconium is concentrated in the heavy accessory mineral zircon, and Rb is most likely present as a trace element substituting for K within micas and feldspars. Neither element has any known biological importance, and as such, the relationship is likely to be simply due to grain-selective deposit feeding. Likewise, V and Cr are also most likely to be associated with phyllosilicates (Brigatti et al., 2003), consistent with the observed relative enrichment of dioctahedral mica in the burrow core relative to the burrow halo (Fig. 4C). In comparison, phosphorus is the only imaged element that does not co-occur with the spatial distribution of organic carbon (Fig. 3C). Phosphates and nitrates are important microbial nutrients, controlling microbial productivity in sediments (e.g., del Giorgio and Cole, 1998). Zones enriched in phosphorus surrounding Planolites isp. burrows (Fig. 3C) may reflect enhanced microbial productivity in the near-burrow environment caused by bioirrigation (cf. Herringshaw and McIlroy, 2013). In contrast, there is no enrichment in phosphorous associated with phycosiphoniform burrows (Fig. 3C), probably due to the deposit-feeding activity of the trace-making organism and absence of bioirrigation in its near-burrow environment.

While absolute element concentrations are controlled by the initial starting composition of the host sediment, they can also vary as a function of post-compaction mobility of certain elements during burial diagenesis. The measured concentrations of Sr and Ba indicate a significant depletion from both the burrow halo and fecal core. This trend cannot be explained by spatial mechanical redistribution of existing mineral phases (Fig. 2C). Because Ba and Sr are common components of biominerals such as teeth and shells, their depletion in the burrow relative to the host sediment might be explained by biomineralization (e.g., Lowenstam, 1981). Alternatively, feeding activity of macroorganisms is capable of degrading unstable minerals (e.g., biotite and chlorite) and feldspars (McIlroy et al., 2003).

A combination of techniques (XRD, FTIR, SEM) demonstrates that there is some preferential weathering of grains in the fecal core of the burrows (Figs. 2 and 4), and authigenic clay minerals absent in the host sediment are found there (Fig. 2D). The fecal core of the burrow also contains altered silt-sized lithic fragments and feldspars. Peak broadening in the XRD traces of plagioclase and albite (Fig. 4C) indicates weathering and may explain the mass balance deficit of Sr and Ba within the burrow fecal core. When weathered, feldspars and other detrital minerals rich in Sr and Ba release high-ionic-radius elements from their crystal lattices as they alter to illite and/or smectite (Drake

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GSA Data Repository item 2015338, isotope ratios and elemental concentrations of total organic carbon, and trace element concentrations of host sediment, burrow halo, and core, is available online at www.geosociety.org/pubs/ft2015.htm, or on request from editing@geosociety.org or Documents Secretary, GSA, P.O. Box 9140, Boulder, CO 80301, USA.
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