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The relative mobility of trace elements from short-term weathering of a black shale

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ABSTRACT

Black shales contain high concentrations of trace elements, which may be liberated to the environment as a result of natural weathering and, potentially, during shale gas development and future mining of black shales for extraction of shale oil. The Sunbury Shale is one of the youngest units making up the thick Devonian and Mississippian black shale sequence in the Appalachian Basin. This study compares the trace element geochemistry of samples collected from two exposures of Sunbury Shale located <8 km apart in northeastern Kentucky, one a fresh excavation, the second, a roadcut exposed for 50 years, wherein the shale was visibly weathered. Core samples obtained from sites ~40 km NE and ~60 km SW of the exposures were also analyzed. The 50-year period of surface weathering resulted in significant loss of some trace elements, particularly Mn and elements associated with sulfides (e.g., Cd, Cu, Ni, and Zn). It is expected that Mn would be maintained in its soluble reduced form in the presence of sulfides and our results suggest Mn is a particularly sensitive indicator of weathering in carbonate-poor black shales. The relative immobility of As, Sb, and Se, also found in sulfides, reflects preferential sorption of oxyanions under the locally acidic conditions resulting from sulfide oxidation. Leaching experiments show waters in contact with the shale may, nonetheless, acquire concentrations of As and Se well in excess of water quality standards. No significant differences were found in the concentrations of Cr, Mo, or V that are associated with refractory phases.

1. Introduction

Black shales are known to contain high concentrations of trace elements in addition to their high organic carbon contents (Vine and Tourtelot, 1970). Natural weathering of black shales liberate trace elements at varying rates, including many that could pose threats to human and environmental health. The increased use of hydrofracturing for shale gas development as well as potential future mining of oil shale could potentially facilitate the release of trace elements to process, surface, and ground waters. In addition, while some black shales host important ore deposits (e.g., VMS, SEDEX), many more could potentially be exploited in the future as nonconventional mineral resources. Thus, understanding the relative stability/mobility of trace elements from black shales is important from environmental and commercial perspectives.

Black shales of Devonian and Mississippian age are present throughout much of the Appalachian Basin, from New York southwestward through Pennsylvania, Maryland, Ohio, West Virginia, and Kentucky, into Tennessee and Alabama (Roen and Kepferle, 1993). Important black shale units include the Devonian Marcellus Shale, the Geneseo Shale, the Rhinestreet Shale Member of the West Falls Formation, the Pipe Creek Shale Member of the Java Formation, the Huron and Cleveland members of the Ohio Shale, the Devonian–Mississippian Chattanooga Shale in southern Kentucky, Tennessee and Alabama and the Mississippian Sunbury Shale in Ohio, Kentucky, Pennsylvania and West Virginia (de Witt et al., 1993; Ryder, 1995). Of the seven major black-shale units that occur in the Catskill Delta and adjacent parts of western Pennsylvania and Ohio (Marcellus, Geneseo, Middlesex, Rhinestreet, Huron, Cleveland and Sunbury), only the youngest three units were displaced to the western edge of the Appalachian Basin and onto the Cincinnati Arch by prograding clastic wedges (Ettensohn and Barron, 1981). As a result, and despite their widespread occurrence, these units only outcrop in a limited area, chiefly along the eastern edge of the Cincinnati Arch in eastern Kentucky and Ohio and south into central Tennessee (Dyni, 2006).

This study compares the trace element geochemistry of the Sunbury Shale from locations spanning a distance of 100 km along the eastern margin of the Cincinnati Arch in eastern Kentucky. The Sunbury Shale, the youngest of the major Devonian–Mississippian

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black shale units in the Appalachian Basin, extends from western Virginia into Ohio and Kentucky. Equivalent units, defined by their conodont assemblages and high gamma-ray emissions, occur in West Virginia and Tennessee. Two sets of samples were collected at the central location from two outcrops of Sunbury Shale located <8 km apart (Fig. 1). The first of these outcrops (Site 1) was a freshly excavated roadcut in which the shale was relatively unweathered and the other (Site 2) a roadcut exposed for ~50 years, wherein the shale was clearly, visibly weathered. The Sunbury Shale has, on average, higher levels of trace elements than the much thicker Ohio Shale that also outcrops in the study area (Perkins et al., 2008) and its 5-m thickness readily allowed for comparative sampling of the entire unit from each of the outcrops.

The results of this study will be of value in documenting the trace element geochemistry of this important unit and in assessing threats to human and environmental health posed by the release of toxic trace elements from this and similar marine black shales resulting from natural weathering and, potentially, during shale gas and oil development. Further, the relative stabilities of elements reported here should be of interest in mineral exploration and to geochemists using trace elements to determine paleo-environmental conditions.

1.1. Study sites and field sampling

A highway project north of Morehead, Kentucky removed 2–5 m of hillside, providing a fresh exposure of the entire thickness (5.3 m) of the Sunbury Shale and the uppermost part of the underlying Bedford Shale (Fig. 2). The freshly exposed shale at this location (Fig. 1, Site 1) was relatively unweathered, as evidenced by its dark black color, relative competence, predominantly thin to medium bedding, abundant sulfides, including massive nodules with little to no sign of surface oxidation, and the very prominent cone-in-cone features in the top of the underlying Bedford Shale, which tend to become relatively obscure with weathering. The section was measured and samples collected approximately every 0.5-m within a month of the excavation. Although some degree of weathering cannot be ruled out, we will, for the purposes of this paper, refer to these samples as "unweathered outcrop" samples.

Samples from the entire thickness of the Sunbury Shale were also obtained from another road cut, located <8 km SSW of the first (Fig. 1, Site 2). This cut, along Farmers Airport Road, which was completed circa 1960, is incised nearly vertically through overlying layers of sandstone and gray shale comprising, respectively, the Farmers Member and Henley Bed of the Mississippian Borden Formation (Fig. 2). At the time this fieldwork was completed, the roadcut had not been re-widened, so the rocks were exposed to surface weathering for the intervening period of 45–50 years. The Sunbury Shale at this location is 5.2 m thick. The appearance of the Sunbury Shale at this location is markedly different from the freshly exposed Site 1 section. Specifically, the unit exhibited oxidized bedding surfaces and "paper" fissility, characteristic of weathered black shale units in the area (Fig. 3).

Additional samples were obtained from the core libraries of the Kentucky Geological Survey and the Kentucky Transportation Cabinet. The cores were collected from sites 100 km apart along the eastern margin of the Cincinnati Arch and ~40 km northeast and ~60 km southwest of the surface exposure sites (Fig. 1). Core records and physical examination of the core indicate that the thickness of the Sunbury Shale at the south-westerly Site 5 in Estill County (~1.1 m) is significantly condensed relative to the measured outcrop thickness in the central site (5.2–5.3 m; Fig. 2), as is the thickness of the underlying Bedford Shale which separates the Sunbury Shale from the Ohio Shale. The logged thickness of the core obtained from the north-eastern Sites 3 and 4 in Lewis County is 4.1 m; however, the top of the unit in the "full section" appears truncated by erosion and is overlain by ~3.7 m of overburden. To eliminate the possibility of analyzing samples impacted by weathering near this erosion horizon, two core sections were used. Samples representing the upper 1.6 m of Sunbury Shale were collected from a deeper borehole in which the top of the Sunbury was encountered at 13.6 m. As this borehole did not penetrate the full thickness of the unit, samples representing the lower and middle portions (from the base to 2.7 m above) were collected from a shallower borehole in which the contact with the underlying Bedford Shale was evident. Thus, while we know samples from the uppermost Sunbury were collected in the deeper borehole, we cannot be certain of their actual position relative to the base of the unit. The positions listed in Table 1S (Supporting Information) are estimated based on the total thickness recorded in the shallower borehole; it may well be that the "B1" samples are actually from higher above the base (i.e., 4.1–5 m). All samples were taken from depths greater than 5 m and are considered non-weathered to minimally weathered as is evidenced by lack of oxidized surfaces

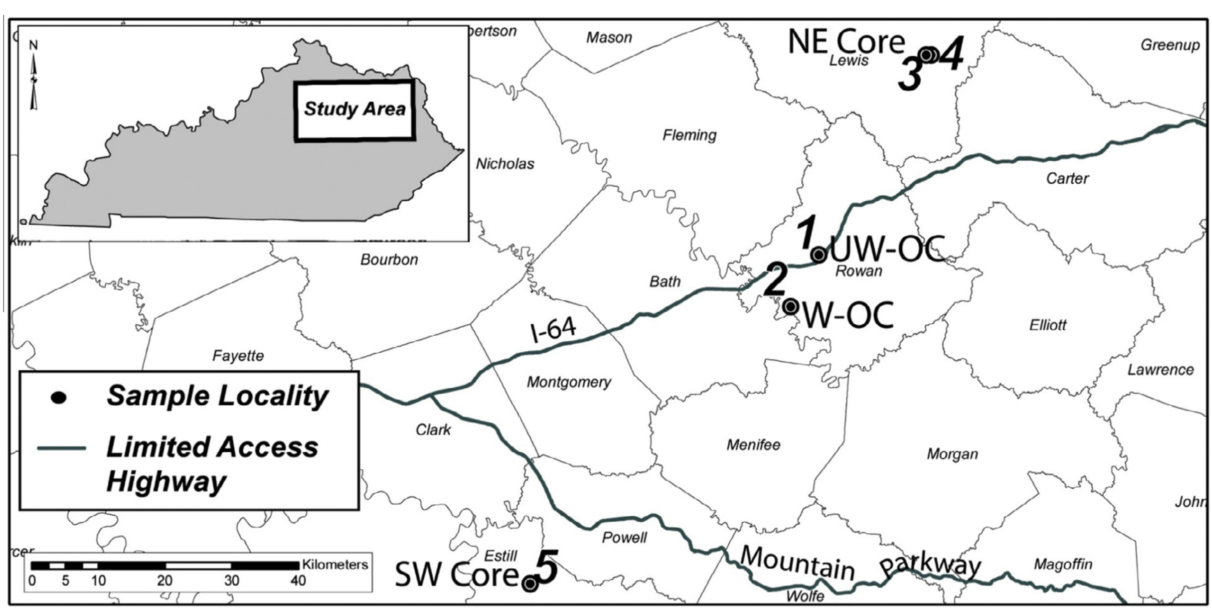

Fig. 1. Location of sampling sites (black dots). Numbers refer to sites in Table 1S (Supporting Information).