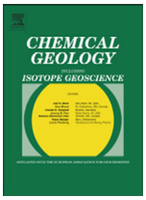
Chemical Geology 356 (2013) 50–63

Contents lists available at ScienceDirect

Chemical Geology

journal homepage: www.elsevier.com/locate/chemgeo



Evolution of porosity and geochemistry in Marcellus Formation black shale during weathering

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ARTICLE INFO

Article history:
Received 9 November 2012
Received in revised form 15 July 2013
Accepted 16 July 2013
Available online 27 July 2013

Editor: J. Fein

Keywords:
Pyrite dissolution
Organic matter
Shale gas
Trace metals
Neutron scattering
Computed tomography

ABSTRACT

Soils developed on the Oatka Creek member of the Marcellus Formation in Huntingdon, Pennsylvania were analyzed to understand the evolution of black shale matrix porosity and the associated changes in elemental and mineralogical composition during infiltration of water into organic-rich shale. Making the reasonable assumption that soil erosion rates are the same as those measured in a nearby location on a less organic-rich shale, we suggest that soil production rates have on average been faster for this black shale compared to the gray shale in similar climate settings. This difference is attributed to differences in composition: both shales are dominantly quartz, illite, and chlorite, but the Oatka Creek member at this location has more organic matter (1.25 wt.% organic carbon in rock fragments recovered from the bottom of the auger cores and nearby outcrops) and accessory pyrite. During weathering, the extremely low-porosity bedrock slowly disaggregates into shale chips with intergranular pores and fractures. Some of these pores are either filled with organic matter or air-filled but remain unconnected, and thus inaccessible to water. Based on weathering bedrock/soil profiles, disintegration is initiated with oxidation of pyrite and organic matter, which increases the overall porosity and most importantly allows water penetration. Water infiltration exposes fresh surface area and thus promotes dissolution of plagioclase and clays. As these dissolution reactions proceed, the porosity in the deepest shale chips recovered from the soil decrease from 9 to 7% while kaolinite and Fe oxyhydroxides precipitate. Eventually, near the land surface, mineral precipitation is outcompeted by dissolution or particle loss of illite and chlorite and porosity in shale chips increases to 20%. As imaged by computed tomographic analysis, weathering causes i) greater porosity, ii) greater average length of connected pores, and iii) a more branched pore network compared to the unweathered sample.

This work highlights the impact of shale–water–O_2 interactions in near-surface environments: (1) black shale weathering is important for global carbon cycles as previously buried organic matter is quickly oxidized; and (2) black shales weather more quickly than less organic- and sulfide-rich shales, leading to high porosity and mineral surface areas exposed for clay weathering. The fast rates of shale gas exploitation that are ongoing in Pennsylvania, Texas and other regions in the United States may furthermore lead to release of metals to the environment if reactions between water and black shale are accelerated by gas development activities in the subsurface just as they are by low-temperature processes in our field study.

1. Introduction

Black shales cover only a small percentage of continental land area but are economically and environmentally important (e.g., Tourtelot, 1979; Falk et al., 2006; Shpirt et al., 2007; Piper and Calvert, 2009; Pollack et al., 2009). Specifically, these shales often host significant amounts of methane that can be exploited profitably. For example, the Devonian black shales of the northeastern U.S.A. are being developed for natural gas by increasing shale porosity using hydraulic fracturing (Engelder et al., 2009). Here, we explore the major mineral–water–gas reactions at Earth surface that lead to black shale alteration and porosity changes.

Analysis of shale weathering is also of importance for geologically long-term C and O balances. Specifically, mineral weathering reactions,

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0009-2541/$ – see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.chemgeo.2013.07.012

release of volcanic gases, burial of organic matter, and weathering-driven re-oxidation of organic matter over geologic time frames all contribute to the global balance of atmospheric CO_2 and O_2 (Petsch et al., 2005). Furthermore, black shales are not only rich in organic material, but also in metals (Vine and Tourtelot, 1970; Shpirt et al., 2007). When they are exposed at earth's surface or by drilling, they can release significant amounts of metals to solution (Jaffe et al., 2002; Tuttle and Breit, 2009; Tuttle et al., 2009). Indeed, black shale weathering worldwide is a major contributor to the global cycles of Mo, Os, carbon, and other elements and shales are a source of metal contaminants in surface waters (Jaffe et al., 2002; Huh et al., 2004; Wilde et al., 2004; Petsch et al., 2005; Pollack et al., 2009; Tuttle and Breit, 2009; Tuttle et al., 2009; Miller et al., 2011). Finally, the opening of fractures in shales by hydraulic fracturing stimulates the return to the surface of a variety of organic and inorganic constituents in flowback water that are also of significant environmental concern (Kargbo et al., 2010; Gregory et al., 2011).

The target of this study is the black shale of the Middle Devonian Marcellus Formation within the Hamilton group. This formation underlies much of Pennsylvania, extending into Ohio, West Virginia, and New York (Obermajer et al., 1997; Faill, 1998; Harper, 2008). Deposited during a period of rapid transgression in anoxic waters less than 100 m deep, the Marcellus Shale is characterized by its black color, high pyritic content, organic-rich nature, enrichment of trace metals, and lack of fossils (Potter et. al., 1980; Roen, 1983; Obermajer et al., 1997; Shultz, 1999; Sageman et al., 2003). In Pennsylvania, natural gas is currently exploited in the northeastern, north central, and southwestern regions using horizontal drilling followed by hydraulic fracturing to stimulate production (Harper, 2008; Soeder and Kappel, 2009). The opening of fractures stimulates the methane sorbed to organic or mineral matter or contained in pores to be released into the fracture network. The underlying hypothesis of our work is that mineral–water reactions studied in the soil zone can contribute to our understanding of deep shale–water interactions and the potential for contamination during shale gas exploration and recovery. Fractures formed during hydraulic fracturing and the porosity network created during weathering are very different but both expose fresh mineral surface area to reactive fluids and a better understanding of the low-temperature processes can help provide fundamental understanding for the prediction of water–rock reactions during shale–gas development.

We investigate weathering of the Marcellus shale where it is exposed in Huntingdon, Pennsylvania, using combined neutron scattering, computed tomography, elemental analysis, and X-ray diffraction. This location is one of satellite sites for the Susquehanna Shale Hills critical zone observatory, SSHO. The goals of this work are to: (1) identify the important mineralogical reactions during weathering; (2) determine the primary porosity of the Marcellus shale and how the pores open or close in the rock as weathering proceeds; and (3) compare and contrast reaction rates with a similar study on organic-poor gray shale (Rose Hill shale in SSHO) located within 20 miles (Jin et al., 2010). This study complements our previous study on Cu mobility and transport during shale weathering at the same location presented by Mathur et al. (2012).

2. Methods

2.1. Rock and soil sampling

We investigated mineral weathering and elemental mobility on mid-Devonian Marcellus black shale on a forested northwest-facing planar hillslope located in Jackson Corner, Huntingdon County, Pennsylvania (Fig. 1). Our focus is an exposed section of the Oakta Creek unit that forms the basal portion of the Hamilton Group (Obermajer et al., 1997; Faill, 1998; Soeder, 2010). This unit is currently being explored intensively for shale gas in other parts of Pennsylvania where the unit remains buried and still contains gas. The Huntingdon area was logged 2–3 times in the past 200 years like most of central Pennsylvania, and is currently under private ownership. The current vegetation is a mature maple–pine forest.

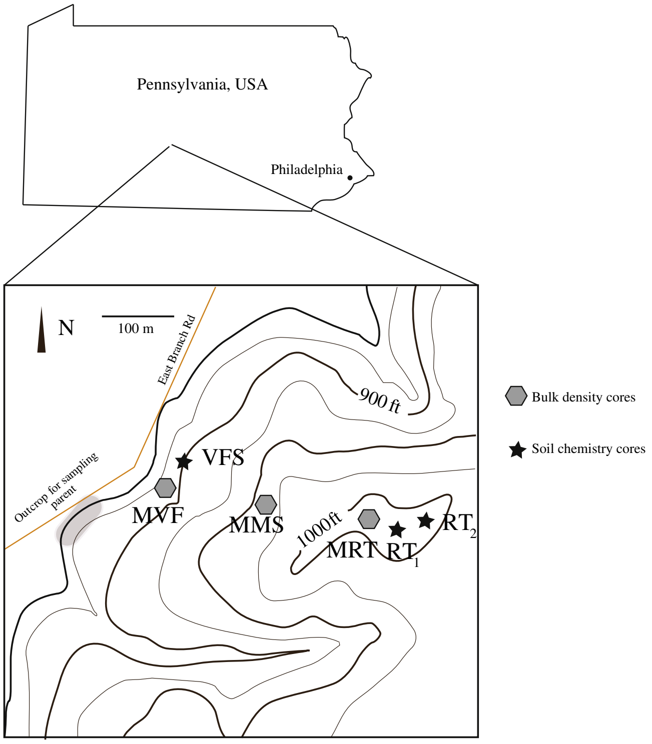

Fig. 1. Study sites on Marcellus shale in central Pennsylvania (modified from Mathur et al., 2012). Soils were collected from the ridge top (RT_1, RT_2) and valley floor (VFS) sites; bulk density cores were collected at the ridge top (MRT), mid-slope (MMS) and valley floor (MVF). All sites are situated along a hillslope which is roughly planar. Rock fragments were sampled at an outcrop at the base of the planar hillslope and also from the bottom of soil profiles and were used to approximate parent Marcellus shale.

The field sites, previously described in Mathur et al. (2012), are briefly summarized here. The location is a convex-upward hillslope along a zeroth-order catchment (i.e. water flows only ephemerally in the low area). A total of three soil profiles were sampled: two along the ridgetop within 10 m of one another (RT_1, RT_2), and one at the base of the hillslope (VFS). The elevation drop from RT to VFS is approximately 30 m. At these sites, soils were hand-augered until it was impossible to auger further (refusal). The three cores varied in total depth, described here as soil thickness, ranging from 84 cm at the base of the hill to 134 cm at the ridgetop. Soil samples were collected every 5 to 15 cm, with depth 0 defined as the organic soil mineral soil interface (O–A interface).

A total of 8 “parent rock” samples from the Oakta Creek member were also collected and analyzed. Parent rock hypothetically represents the initial composition of the bedrock but as discussed later, these samples have been slightly altered. Four of these putative parent samples were rock fragments collected from the bottom of the three augered cores. In addition, four hand samples were collected from a road outcrop at the base of the zeroth-order watershed within 5 m of the augered core VFS (Fig. 1). Visual inspection of the outcrop reveals that bedding in the unit is subhorizontal. Sub-perpendicular jointing was also observed that is typical of Alleghanian fracture patterns throughout the region.

Porosity and permeability are known to vary within the Marcellus Formation due to variations in texture, chemistry, mineralogy, organic content, thermal maturity, fracture spacing, veining, and stratigraphic relationships (Soeder, 1988; Arthur et al., 2008). The most organic-rich member of the Marcellus Formation that is currently targeted for shale gas is the Union Springs member. To place our study of mineral–