



# Mineralogy and trace element geochemistry of gas shales in the United States: Environmental implications



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## ABSTRACT

This paper presents a compilation of published mineralogic and trace element data from nine gas shales in the United States. Formations analyzed include the Antrim, Bakken, Barnett, Eagle Ford, Haynesville, Marcellus, New Albany, Utica and Woodford. These mineralogic and trace element data can be used to assess the potential for environmental impacts during hydraulic fracturing. Impacts addressed in this study include: 1) the potential for acid rock drainage generation during gas shale weathering, 2) the distribution of trace elements in gas shales and comparison with regulatory guidelines, and 3) the implications for environmental management of well cuttings. The use of the mineralogic data to assess the fracability of the gas shales is also considered. Compilations of the mineralogy and geochemistry of gas shales can be a valuable resource for managing real and perceived environmental problems associated with their exploitation. Comprehensive environmental assessment to fully address these issues, in addition to other potential environmental impacts, will require collection and collation of additional data on the mineralogy and trace element geochemistry of gas and other hydrocarbon producing shales.

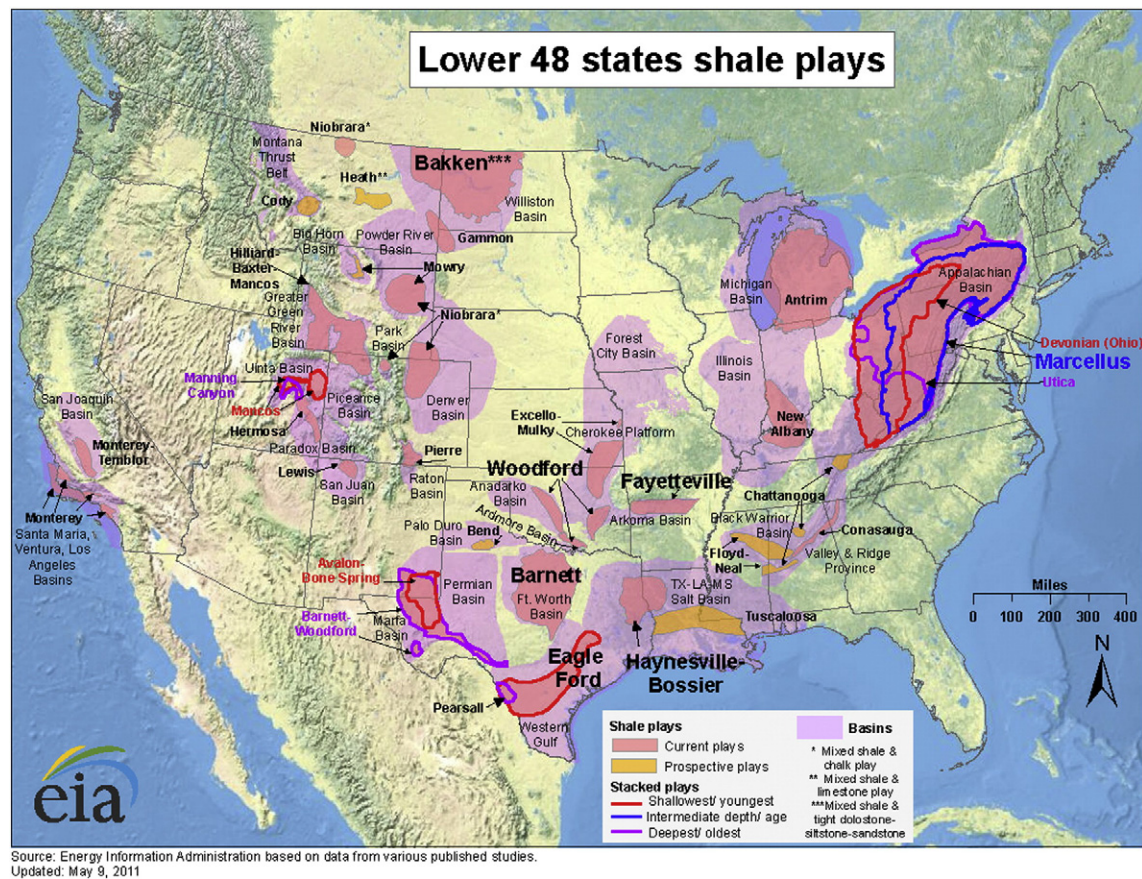
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## 1. Introduction

As the U.S. evaluates the possibility of energy independence and increased hydrocarbon production, an important aspect in this pursuit is the recovery of gases and liquid petroleum from source rock materials through hydraulic fracturing. Source rocks are those which accumulated organic matter during deposition and experienced limited migration of the resulting hydrocarbons during the burial process and these black shales are generally classified as having a total organic carbon, TOC >2% (Hosterman and Whitlow, 1980). These source rocks are often called gas shales or more accurately tight rock formations as analysis of the mineralogic and textural characteristics of these source rocks reveal that they consist of shales and siltstones, as well as carbonates. Shale is defined as a fine grained, clastic rock that exhibits fissility and a more general classification of mudstone (Aplin and Macquaker, 2011; Boggs, 2001; Day-Stirrat et al., 2010). Although shales are the original source of the organic matter, other low permeability rocks can act as both source and cap material. This paper will use the term gas shales for the materials currently or potentially yielding the gas, wet gas, and/or liquid petroleum recoverable by hydraulic fracturing although it should be noted that these deposits are also often called tight rock, tight formations, tight oil resources, mudstones, or black shales in the literature (e.g., Howarth et al., 2011). United States gas-shale formations used in this analysis are shown on Fig. 1 and include the Antrim, Bakken, Barnett, Eagle Ford, Haynesville, Marcellus, New Albany, Utica and Woodford.

Hydraulic fracturing methods are being used to extract fossil fuels in many regions in the United States and are also being considered

internationally (Badics and Veto, 2012; Bernard et al., 2012; Chalmers et al., 2012; Sachsenhofer and Koltun, 2012; Selley, 2012). These methods have the potential to impact water, air, land, biota, and people, so that industry, government agencies, researchers and the public are asking scientific and regulatory questions about extraction management, impact analysis and environmental protection. The potential environmental impacts during exploration, construction, operations, and closure during resource recovery activities in the United States and internationally have been well documented (Haluszczak et al., 2013; Lutz et al., 2013; Vidic et al., 2013). An example of impact evaluation and mitigation can be found in the Supplemental Generic Environmental Impact Statement (SGEIS) on the Oil, Gas and Solution Mining Regulatory Program conducted by the by the State of New York in 2009 (NYSDEC, 2009). The report compared traditional oil and gas extraction to hydraulic fracturing and concluded that there are three additional impacts from hydraulic fracturing that are not a concern for traditional extraction methods. These additional factors are: 1) hydraulic fracturing requires larger water volumes, 2) hydraulic fracturing was being conducted in “sensitive” watersheds, and 3) hydraulic fracturing requires longer disturbance times due to the multi-well nature of this activity. The U.S. Environmental Protection Agency (USEPA) is currently conducting a study to better evaluate any potential impacts of hydraulic fracturing on drinking and ground water and this study is due to be released for public comment and peer review in the future (estimated as 2014). To address potential impacts and mitigation approaches, information about the source rock, including mineralogy and trace element geochemistry, is critical as discussed below.



**Fig. 1.**—Map showing locations of United States shale plays (EIA, 2011). Mineralogy and/or trace element data used include Antrim, Bakken, Barnett, Eagle Ford, Haynesville, Marcellus, New Albany, Utica and Woodford.

### 1.1. Shale mineralogy

Shales primarily consist of mixtures of fine grained quartz and clay minerals and can contain other minerals including feldspars, carbonate minerals, sulfide minerals, and oxide minerals (O'Brien and Slatt, 1990; Slatt and Rodriguez, 2012; Vine and Tourtelot, 1970; Yaalon, 1962). Depending on depositional environment, shales may contain sufficient quantities of organic matter to be classified as black shales (Arthur and Sageman, 1994; Tourtelot, 1979; Trabucho-Alexandre et al., 2011). Ternary plots of clay minerals, quartz and feldspars, and carbonate minerals have been used to aid in determining depositional environment and tectonic setting (Boggs, 2001; Lev et al., 2008). The dominant clay minerals in shales include illite, mixed layer illite/smectite, smectite, kaolinite, and chlorite (Aplin and Macquaker, 2011; Boles and Franks, 1979). Burial diagenesis occurs when the originally deposited shale and associated clay minerals undergo increasing temperatures, pressures and associated changes in fluid chemistry (Fig. 1 in Chermak and Rimstidt, 1990; McDonald and Surdam, 1984).

### 1.2. Trace elements in shales

Trace elements are generally defined as elements which have concentrations less than 0.1% in the earth's crust. Black shales are commonly enriched in trace elements relative to average shales (Leventhal, 1998), and some, such as the metal rich black shales, can host economically relevant metal ores (see Leventhal, 1998). Several papers provide "average" concentrations of trace elements in shales (Gromet et al., 1984; Ketris and Yudovich, 2009; Turekian and Wedepohl, 1961; Vine and Tourtelot, 1970) (Table 1).

Trace element concentrations in shales have been utilized for interpretation of paleoenvironmental conditions during shale deposition; see Tribouillard et al. (2006) for a comprehensive review of the use of trace elements for paleoredox characterization, focusing on Co, Cr, Mo, U, and V. The use of trace elements as paleoredox indicators stems from the geochemical behavior that different oxidation states of these and other trace elements exhibit under oxic, suboxic and anoxic conditions. For example, U and Cr are more soluble under oxidizing conditions, while Fe and Mn are more soluble under anoxic conditions. Other trace elements, such as Ni, Cu, Zn, Cd, Cr, U, and V can complex with organic matter. As the organic matter is oxidized, coupled with sulfate reduction, these trace elements can become incorporated into sulfide minerals. Algeo and Rowe (2012) used Mo and total organic carbon (TOC) to constrain degree of restriction, and residence time and chemical evolution of deep water in marine basins. Other elements, like V and Ni, form metallo-organic complexes (metalloporphyrins) in the high molecular weight fraction of crude oils, shales and coals (Filby and Van Berkel, 1987; Lewan et al., 2002; Ocampo et al., 1987; Quirke, 1987; Warty and Goldhaber, 1992). Results of this comprehensive literature clearly demonstrate that trace element data in combination with measurements of Fe and Mn, TOC, sulfur species, mineralogy, and isotopes provide a rich dataset that can be used for a variety of interpretations of shale paragenesis.

Although trace elements in shales have been studied for many applications, including the examples described above, there are no previously published studies on trace element distributions in gas-producing shales for the purpose of examining how trace elements, especially those that may have toxic effects to humans and/or organisms, and are regulated in soils, sediment and water (e.g. As, Se, Mo, Cd, Th, and

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