The global energy landscape has changed significantly in the last few years as a result of technological advances in the recovery of unconventional hydrocarbon resources such as tight oil and shale gas. Studies have been initiated to assess the impacts of extraction and production of unconventional hydrocarbons on surface water, groundwater, and local air quality. There is additional concern over how their extraction and utilization on a global scale may contribute to atmospheric chemistry and global climate change. This article provides an overview of opportunities and challenges offered by the abundance of unconventional hydrocarbons, the driving forces that encourage our rush to employ them, and the need for Earth scientists to engage in studies of their properties and impacts on the environment. A fundamental understanding of geological, mineralogical, and geochemical processes is integral to how we responsibly extract and utilize these resources.

**Keywords:** gas shale, hydraulic fracturing, NORM, flowback, emissions

## INTRODUCTION

For nearly 100 years, we have relied on oil and gas resources extracted from large sedimentary reservoirs (conventional oil). As these reserves dwindle in parallel with increasing energy requirements, unconventional natural gas and oil resources have grown in importance. Developing these resources requires a paradigm shift in exploration and production compared to conventional hydrocarbons (Johnson and Dore 2010). The physical and chemical properties of unconventional reservoirs differ significantly from those of conventional reservoirs. Unconventional reservoirs require stimulation methods to improve economic recovery rates; these reservoirs typically include tight-gas sandstones, gas hydrates, oil shale formations, heavy-oil sandstones, and shale gas.

The hydrocarbon resource triangle (Fig. 1a) provides perspective into the differences between conventional and unconventional hydrocarbons. Conventional hydrocarbon accumulations tend to exhibit some flow immediately upon drilling. Unconventional formations are typically fine-grained, organic carbon–rich strata that are both the source of and the reservoir for oil and natural gas. They may be pervasive throughout a large area, and these have been termed “continuous-type deposits” or “tight formations.” Although unconventional reservoirs may be as porous as some conventional reservoir rocks, their extremely small pore sizes and lack of permeability make them resistant to hydrocarbon flow. As a result, hydrocarbons typically remain in the source rock unless natural or induced fractures occur (Ratner and Tiemann 2013).

Oil shale occurs where a thermally immature source rock has generated but not expelled hydrocarbons. Oil or “tar” sands occur where near-surface conventional crude oil has become degraded by evaporation, biodegradation, and water washing to produce a viscous heavy-oil residue. In contrast to conventional gas reservoirs, unconventional natural gas can also be found in more-difficult-to-extract rock formations (such as coal beds or shale), in low-quality (tight) reservoirs, or as gas hydrates.

Because of improved technology, the global energy landscape has changed significantly in the last decade. According to the U.S. Energy Information Administration (US EIA 2013a), natural gas could become the world’s second most important energy source after oil, with global demand predicted to rise over 50% between 2010 and 2035. For example, the fast and large-scale development of unconventional natural gas in North America (Fig. 1b) has created a new geopolitical and economic paradigm on the world stage (Bocora 2012). The discovery of large deposits of shale gas in the United States has led to the birth of new local markets and provided a benchmark for other countries to emulate. Unconventional gas (and oil) in other parts of the world will give rise to opportunities for many countries to lower their dependence on imported gas and oil and strengthen their energy security.

This issue of *Elements* focuses on key examples of unconventional resources, their global impact, and the potential environmental implications of their exploitation. Blumsack (2014) explores market forces driving the “dash for gas” that are likely to lead to further development of domestic gas markets in North America and liquefied natural gas (LNG) exports. Bryndzia and Braunsdorf (2014) offer an overview of the mineralogical and geochemical properties of unconventional shale reservoirs and describe the importance of those properties to the chemistry of recovered water. They conclude that water availability, treatment, and disposal represent a risk—one of several “above-ground”
issues unrelated to drilling that could impact the economic viability of some unconventional source rock resource plays (a “play” is a relatively large hydrocarbon accumulation that occurs over a broad geological area). Rostron and Arkadakskiy (2014) demonstrate the utility of geochemical techniques in forensic studies of the origin of “excess” water recovered with shale oil and show how geochemistry can help to improve well design for unconventional plays. Tar or oil sands represent significant potential unconventional oil resources. Larter and Head (2014) show that “oil sands” are a global resource of trillions of barrels of heavily biodegraded oil that are increasingly being tapped to meet global oil demand. Water-use and water-quality impacts loom large for oil sand development, but there are possibilities for using biological processes for cleaner energy recovery. Etiope and Schoell (2014) argue that abiotic gaseous hydrocarbons can be generated by chemical reactions, without organic matter involvement, and occur in association with volcanic activity and serpentinization of ultramafic rocks. Although not commonly considered a resource, these gases may contribute to accumulations in some reservoirs.

**Unconventional Hydrocarbons Today with a Shale Gas/Oil Focus**

Contrary to conventional natural gas, where 75% of known reserves are concentrated in a number of key regions, such as the Middle East, Russia, China, and the Commonwealth of Independent States (CIS), unconventional gas occurs worldwide (US EIA 2013b). In the United States and Canada, declines in the production of conventional hydrocarbon reserves are being countered by increasing exploitation of unconventional hydrocarbon deposits within shale resource plays (Fig. 1a).

Exploitation of unconventional forms of gas and oil and the rapid shift from the dominance of traditional producers to plentiful domestic resources in many countries represent the dawn of a new era in global energy. On the positive side, there is the potential for job creation, business revitalization, the creation of markets for new by-products, greater energy independence, and newfound wealth for landowners, municipalities, and governments that hold subsurface mineral rights. On the negative side, stresses on communities, housing availability and cost, and potential health effects are legitimate issues that can impede progress and thwart development.

Environmental impacts may be the most challenging issues when considering prospects for unconventional gas development. Potential impacts include problems with water availability and usage, induced seismicity from fracking and disposal, potential groundwater contamination, surface spills, air-quality problems, road infrastructure and maintenance issues, the treatment and disposal of flowback waters, and fluxes of greenhouse gases to the atmosphere. Best-practice protocols do exist, and better governmental regulation, informed by further studies, will provide a framework to which all operators can conform (Richardson et al. 2013).

**CHARACTERISTICS OF SHALE RESERVOIRS**

**Geologic Setting and Origin of Continuous Hydrocarbon Accumulations**

Most currently producing gas shale reservoirs are mature to overmature organic-rich source rocks (Fig. 2). Sediments occur as organic carbon (OC)–rich muds deposited in deeper marine environments, in lakes, or in associated swamps and mires along lakes or seas. Shales (i.e. laminated mudstones) are not stratigraphically or spatially homogeneous, nor do they form solely in low-energy, deep-marine environments as traditionally thought. Deep-marine depositional settings leading to significant accumulations of OC-rich sediments
Mineralogy and Pore Features

As with other sedimentary rocks, the mineral compositions of mudrocks containing OM range from mostly silicates to mostly carbonates, with varying amounts of clay minerals (Fig. 3a). The main inorganic, primary phases transported and deposited in muddy sediments include clay minerals (e.g., smectite, illite, chlorite), quartz (detrital), feldspar, calcite, and apatite (and amorphous phosphate), although not all of these minerals are found in any one shale.

The original mineralogy of sediments can be altered through diagenesis, resulting in clay transformations (smectite to illite), pyritization, cementation, and/or dissolution. The X-ray mineral map in Figure 3a–c illustrates the diverse mineralogy of these rocks and the fine-grained nature of the phases. Gas shale plays that contain more than 50% quartz or carbonate tend to be more brittle and respond well to hydraulic fracturing (see Bryndzia and Braunsdorf 2014). Smectite-rich shales are water sensitive and must be treated with different hydraulic fracturing fluids.

Significant secondary porosity can also be hosted by kerogen, pyrobitumen, and char. Scanning electron microscope (SEM) images of ion-beam-milled samples reveal the development of a separate nanoporosity system contained within organic material, in some cases composing greater than 50% of the total porosity (Fig. 3d, i). These pores tend to sorb and retain hydrocarbon gas species, at least during most of the thermal maturation process, and likely host most of the free gas formed at high thermal maturity.

Naturally Occurring Radioactive Materials and Trace Metals

The oil and gas industry is continually challenged to maintain high standards of safety and control over occupational exposures to radiation and chemical hazards, as well as to protect the public and environment through proper management of wastes (Smith 2011). This is complicated by the mobilization of naturally occurring radioactive materials (NORMs) in reservoirs, drill cuttings, and flowback waters produced during hydraulic fracturing. Black shale formations, such as the Marcellus Shale, often contain trace levels of $^{238}$U, $^{235}$U, $^{40}$K, and $^{232}$Th in higher concentrations than those found in less OC-rich grey shales, sandstone, and limestone. U and Th are not generally mobilized from reservoir rocks that contain oil, gas, and formation water.

In addition to the enrichment of U and Th observed in organic-rich shales, other key minor and trace elements, such as Mo, V, Cr, Ti, and Mn, can also exhibit elevated concentrations. A number of these, such as Cr and V, may constitute health threats if inadvertently released into potable groundwater supplies. Redox behavior is an important parameter that influences the preservation of organic matter, which in turn controls the differences in trace-metal accumulation rates between oxic (>2.0 ml O$_2$ L$^{-1}$), suboxic (2.0–0 ml O$_2$ L$^{-1}$), and anoxic facies (Sageman et al. 2003).

Subsurface Brines and the Issue of Flowback Water

Deep saline brines are well documented within the stratigraphic sections of many large sedimentary basins that contain gas shales, such as the Appalachian, Michigan, and Western Canadian basins of North America (Kharaka and Hanor 2005; Rostron and Arkadaksky 2014). In general, brine salinity tends to increase with depth. Salt concentrations in excess of 300 g L$^{-1}$ have been observed at depths below about 3 km in formations dominated by sandstone and limestone.
Proposed mechanisms for the enrichment of brines to salt concentrations many times that of seawater include (1) the evaporation of seawater and (2) the diffusive transport and dispersive mixing of halite-saturated waters with either indigenous formation waters or near-surface meteoric waters with low total dissolved solids (TDS). In the Appalachian Basin, the former of these two mechanisms is thought to control the chemistry of oil and gas field brines (Haluszczak et al. 2012).

The introduction of freshwater into these formations during hydraulic fracturing (abbreviated to fracking) leads to imbibition (the displacement of one fluid by another immiscible fluid), followed by the diffusion of salts probably in response to osmotic processes or mixing with what indigenous formation water is present. For example, large quantities of highly saline brine flow from gas wells in the Marcellus Formation after fracking; the volume of this brine is usually less than 20% of the volume of water pumped down the well during hydraulic fracturing (Rossenfoss 2011). The concentrations of most inorganic components in flowback water (Cl, Br, Na, K, Ca, Mg, Sr, Ba, Ra, Fe, Mn, total dissolved solids, and others) increase with time after hydraulic stimulation (Haluszczak et al. 2012). In the case of the Marcellus Formation, the flowback waters from hydraulic fracturing resemble brines produced from conventional gas wells that tap into other Paleozoic formations in the region. Clearly the treatment and disposal of flowback waters from gas shale production are critical environmental issues that must be addressed (Gaudlip et al. 2008).

**IMPACTS ON SURFACE WATER AND GROUNDWATER RESOURCES**

**Impacts on Water Availability**

Shale energy development is a water-intensive activity. The reported volumes of water required for a slick-water frack of a single shale gas well are usually in the millions of gallons. In the United States, industry practices for water utilization, transportation, and treatment (or disposal) are rapidly evolving, although practices vary widely by region. Consumptive water use is of concern in producing areas that are drought-prone or may become drought-prone in the future.

The amount of water used during hydraulic fracturing depends on the length of the “lateral” or horizontal well section and the number of stages fracked. As an example, the total estimated water use for Marcellus Shale operations is a very small proportion of the total consumption for the state of Pennsylvania (FIG. 4) and is not a serious concern there except during drought periods. However, water-limited regions such as California (Monterey Formation shale oil play) may need to consider alternative fracking fluids (see below). Life cycle considerations for natural gas indicate that water demand is lower than for most other fuels (e.g. coal, biofuels) (Carter 2010; Mielke et al. 2010).

**Water Contamination Issues**

Water quality, including methane contamination of drinking water, is potentially affected by (1) accidental spills of chemicals used in hydraulic fracturing; (2) spillage or leakage of brines from “flowback” water; (3) improper disposal of wastewater; (4) leaking valves and casing on wells, and uncontrolled “blowouts”; (5) leakage and migration of gas up the annulus of wells resulting from lack of cement or poor cementing; and (6) migration from poorly protected (uncased or unplugged) orphaned/abandoned legacy oil or gas wells. In a recent analysis of unconventional oil and gas wells drilled in Pennsylvania, Vidic et al. (2013) found that the rate of citation for regulatory offenses was less than 3% and that these varied widely in significance. Most of the more serious problems were related to poor casing or cement integrity, and all were remedied according to the records.
Abandoned ("orphaned") oil and gas wells are a significant concern in some areas of active shale energy exploration. Their location and status is commonly unknown and they may not have been properly plugged above and within producing zones and across freshwater aquifers. Proper plugging by cement ensures that fluid or gas cannot migrate or create reservoir problems through downward drainage. Pennsylvania, for example, may have as many as 180,000 such wells, only some 12,140 of which have known locations. Other states have fewer orphaned wells, but New York has an estimated 40,000 abandoned wells that remain unplugged or whose locations are unknown. Significant efforts are needed to locate and properly plug such wells, but funding to do so is an issue. All oil- and gas-producing states now regulate well plugging, most have standards for cement quality, and most require advance notice so that regulatory personnel can witness operations.

In addition to orphaned wells, there are other possible sources of natural gas in shallow aquifers. Groundwater contamination has frequently been attributed to "drilling" or "fracking" and has largely consisted of methane in drinking water. Although such contamination is unacceptable and can be an explosion hazard, it can be easily remedied compared to contaminants such as arsenic, barium, and NORM. Methane in groundwater is, in some regions, a well-known issue.

There are many possible natural sources of methane in groundwater, and "fracking" is the least likely cause (Molofsky et al. 2011; Vidiani et al. 2013). For example, consider the individual water wells in the Marcellus Shale. Osborn et al. (2011) suggested that methane concentration in individual water wells was related to proximity to shale gas wells, with the implication that this may indicate a relationship to fracking. However, other researchers (e.g. Molofsky et al. 2011) argue that the methane already exists in the relatively shallow subsurface and has naturally migrated into shallow freshwater aquifers or, at worst, has resulted from leakage of poorly constructed gas wells (e.g. poor cementing or casing failures). A major issue is the lack of predrilling baseline studies. More recently, Beyer et al. (2012) documented preexisting methane contamination in 40% of private water wells sampled and no significant difference in methane concentrations between pre- and postdrilling samples.
Recycling and reuse of flowback liquids have decreased freshwater consumption and greatly reduced the need for treatment and disposal. Additionally, there is now, in Pennsylvania, an initiative to use abandoned mine drainage (AMD) as a source of frac water. This could be a win-win effort, improving stream quality in regions impaired by the prior cycle of coal mining while providing a large volume of water for fracking. Research is needed to test whether the chemistry of AMD, particularly the high sulfate concentrations, will affect fracking efficiency.

**The Need for Effective Regulation and Enforcement**

In the United States, a comparison of oil and gas regulations as of 2012 (Richardson et al. 2013) indicates significant differences from state to state with respect to reporting of water withdrawals and use, among other issues. Oil and gas regulation has been enhanced as the result of the shale energy boom, but the most significant concerns are (1) proper casing and cementing of wells, with checks such as cement bond logs to prevent aquifer contamination; (2) disclosure of hydraulic fracturing chemicals; (3) proper management of wastewater; (4) adequate regulations for disposal of wastes containing NORMs; and (5) effective hiring and training of regulatory personnel.

**ATMOSPHERIC IMPACTS OF HYDROCARBON EXTRACTION AND UTILIZATION**

Although the benefits of the abundant unconventional hydrocarbon energy source are obvious if continuing dependence on oil and gas resources is desirable, there are additional considerations—particularly greenhouse gas (GHG) emissions. Here we briefly examine the benefits and issues accompanying utilization of vast resources of shale gas and oil. Larter and Head (2014) offer perspectives on the potential impacts of oil sand resources.

**Natural Gas versus Coal**

Natural gas utilization has the potential to reduce emissions of GHGs and other pollutants to the atmosphere per unit of energy produced compared to the use of coal in generating electric power. Coal-fired power plants had emitted to the atmosphere 50% of the mercury, 60% of the SO\(_2\), and 62% of the arsenic from all sources in the United States as of 2011 (US EPA 2013). Natural gas combustion does not emit these compounds. Natural gas is more efficient in combustion than coal by an average factor of 1.32 per kilowatt-hour of energy production. Over the past decade, the proportion of power plants utilizing natural gas has increased substantially (US EIA 2012). Stack gases from power plants using natural gas with combined-cycle technology emit CO\(_2\) at about 44% of the rate of coal-fired plants (De Gouw et al. 2014). In 2012, power plants in the United States emitted 23% less CO\(_2\) than they would have if coal produced electricity at the same percentage as it had in 1997. Combined-cycle natural gas–fired plants also emitted >40% fewer NO\(_x\) and SO\(_2\) pollutants compared to coal-fired plants (De Gouw et al. 2014). Natural gas combustion by vehicles also emits 20–45% fewer smog-producing pollutants and 5–9% lower GHG on a per gallon–equivalent basis compared to gasoline or diesel.

**Fugitive Methane Emissions from Extraction**

An important consideration in comparing energy resources is a life cycle assessment of emissions, from extraction to utilization. Generally, if the rate of leakage of methane through production and transportation is less than about 2.7% of natural gas production (e.g. Howarth et al. 2011), natural gas is considered advantageous over coal in electric-power production from a GHG-emissions standpoint (equivalent radiative forcing).

Life cycle considerations favor natural gas over coal in terms of total GHG emissions (Fulton et al. 2011). The major disagreement among various studies is in the estimates of leakage from wells during completions and from transportation infrastructure (pipelines, compressor stations, storage, and distribution networks within cities with natural gas services). Howarth et al. (2011) suggested that the total life cycle GHG emissions, taking methane into account, exceed those of coal extraction and combustion. This analysis is flawed because much of the methane is “flared”—that is, combusted and converted to carbon dioxide (for example, Allen et al. 2013 estimate that flaring is 98% efficient in converting methane to carbon dioxide).

In an analysis of about 4000 unconventional natural gas wells completed in 2010, O’Sullivan and Paltser (2012) concluded that hydraulic fracturing–related fugitive methane emissions were, on average, 0.4–0.6% of the estimated ultimate gas recovery from those wells. Allen et al. (2013) came to the same conclusion from extensive monitoring of fugitive methane emissions (0.53% of gross production). These studies were performed on United States wells, for which regulation is more stringent and industry innovation more rapid compared to many other countries.

As of January 1, 2015, a U.S. Environmental Protection Agency ruling will require that all wells completely capture natural gas and condensate in order to reduce smog-producing volatile organic compound (VOC) emissions. These “green completions” will substantially reduce fugitive methane emissions during well completions in conjunction with closed-loop systems that allow capture of all effluents.

**Present and Future Greenhouse Gas Emissions and Radiative Forcing**

Atmospheric concentrations (so-called mixing ratios) of all GHGs have increased over the past two decades, with the exception of methane. Of interest is the 1994–2007 period during which atmospheric methane concentrations were relatively constant (Fig. 5A), indicating an overall decrease in methane emissions. Simpson et al. (2012) suggested that this period of constancy could have resulted from decreased fugitive emissions from natural gas production, which could account for 30–70% of the calculated decrease in methane flux, on the basis of a coincident decrease in ethane fluxes (Kirschke et al. 2013). Since 2007, atmospheric methane concentrations have increased (Fig. 5A). This increase could be the result of larger wetland and permafrost emissions due to high-latitude warming (Kirschke et al. 2013). It has also been suggested (Ohara et al. 2007) that the onset of the shale gas and oil “boom” and/or greater rates of coal extraction to fuel the economies of India and China are the cause of higher methane concentrations.

Perhaps the best way to view these increases in GHG concentrations is in terms of their relative radiative forcing—the effect of an individual GHG on global heat retention. From 2007 to 2012, the calculated radiative forcing of CO\(_2\), whose concentration increased from 380 to 394 ppmv, rose by 0.136 W/m\(^2\), or nearly 8%. Methane, which increased from 1.796 to 1.836 ppmv (Fig. 5A), rose by 0.009 W/m\(^2\), or about 0.136 W/m\(^2\), or nearly 8%. Methane, which increased from 1.796 to 1.836 ppmv (Fig. 5A), rose by 0.009 W/m\(^2\), or about 0.136 W/m\(^2\), or nearly 8%.
not including the huge potential reserves of the Middle East and Caspian Sea regions. In addition, there are an estimated 16,000 Tcf of conventional natural gas resources (US EIA 2011). At the global yearly rate of consumption in 2010 (113 Tcf; US EIA 2013b), natural gas resources would last in excess of 200 years, whereas for estimated utilization rates in 2040 (186 Tcf; US EIA 2013b), perhaps 125 years!

**FIGURE 5A** illustrates carbon dioxide emission rates (US EIA 2013a) on the basis of global resource availability, population growth, and rising economic prosperity, particularly in developing countries. Energy demand, as compared to 2010, is predicted to rise by a factor of 1.3 by 2040, and the US EIA predicts that 80% of this increase will be from fossil fuels. Much of the consumption increase over the next three decades will be in developing countries (US EIA 2013b). Thus from 2010 to 2040, global natural gas production (and consumption) is predicted to increase by about 76 Tcf/y, and carbon dioxide emissions from energy production will increase by a factor of 1.46 (31.2 to 45.5 Gt CO2/y) during the same period.

**FIGURE 5B** Worldwide carbon dioxide emissions (10^9 metric tons/y) related to the production of energy, by fuel type (US EIA 2013a). Total emissions were 31.2 × 10^9 metric tons/y in 2010 and are predicted to reach 45.5 × 10^9 metric tons/y in 2040.

**PROSPECTUS**

Water resources, in terms of amounts of freshwater and water quality, may also be impacted should extraction of shale gas and oil and increased dependence on oil sands hydrocarbons occur. However, economic incentives to conserve water and future research will provide cost-effective methods to deal with shale-energy wastewater through treatment and disposal (Bryndzia and Braunsdorf 2014). Moreover, new, biologically based, efficient means of extracting oil from oil sands will significantly reduce resulting water use and contamination (Larter and Head 2014).

Concerns regarding possible global warming as the result of rising atmospheric GHG concentrations have led to much debate regarding the advisability of continuing dependence on hydrocarbon fuels. Natural gas is often referred to as a “bridge fuel,” implying that it will be used only as long as necessary until technological improvements bring forth economical non-GHG-producing alternatives, such as wind and solar power. However, as long as natural gas is relatively inexpensive and abundant, it will be difficult to resist (e.g. Blumsack 2014).

Although the United States has led in developing unconventional hydrocarbon resources, there are substantial global reserves. Larter and Head (2014) cite global bitumen and heavy-oil resources of around 5.6 trillion barrels. This huge resource will be attractive as oil reserves dwindle and prices rise in the future. Leakage from abiogenic gas sources must also be considered, but it is not clear that this background source will make an important contribution on a short timescale (Etiope and Schoell 2014). Thus, it is likely that GHG emissions from hydrocarbon combustion will increase over the next several decades, leading to further global warming (US EIA 2013a). Because coal is not replaced by natural gas in the US EIA (2013a) future scenario, we estimate that the total CO2 emissions from fossil fuels used in energy production will contribute to higher atmospheric CO2 levels, which could produce a warmer world and further ocean acidification (Doney 2010).

Carbon capture and storage measures will be necessary to reduce the global environmental impacts of fossil fuel burning. Elliot and Celia (2012) have drawn attention to the possibility that potential subsurface sequestration sites in the United States largely (80%) underlie necessary “seals” for carbon dioxide sequestration—shale and tight gas strata that are now being hydraulically fractured. On the other hand, there is also significant potential for carbon dioxide storage in depleted shale gas horizons if atmospheric carbon capture can be accomplished economically.

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