Fingerprinting "Stray" Formation Fluids Associated with Hydrocarbon Exploration and Production

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Pumpjack on a producing well of the Bakken Formation, southeastern Saskatchewan

Formation water or hydrocarbons occurring at surface and subsurface locations away from their point of origin are often referred to as "stray fluids." Efforts to identify the sources of these fluids have provided important insights for optimizing hydrocarbon exploration and production. With the rapid growth in hydraulic fracturing operations, the source of associated fluids is becoming the focus of scientists and environmental regulators. Many geochemical techniques are available for fingerprinting stray fluids, but the information from traditional approaches can be difficult to interpret in some oil and natural gas settings. New isotopic techniques, using signatures of ^{18}O, ^2H, ^{13}C, $^{87/86}Sr$, and others, are now placing better constraints on the interpretation of stray-fluid origins. These new isotopic fingerprinting methods are being used by the hydrocarbon industry to solve problems and safeguard public health.

KEYWORDS: hydrochemistry, stable isotopes, formation water, natural gas, hydraulic fracturing

INTRODUCTION

Hydrocarbon exploration and production (E&P) activities that use multistage hydraulic fracture treatments to exploit unconventional reservoirs have increased. The public is becoming increasingly aware of these activities, and E&P operations are more closely scrutinized than before. In particular, environmental and public health concerns have arisen regarding the potential for unwanted migration of stray fluids associated with these activities (e.g. Osborn et al. 2011; Chapman et al. 2012; Warner et al. 2012; Baldassare et al. 2014, and references therein). Following Baldassare et al. (2014), we define stray fluids as the formation water or hydrocarbons found at locations (surface or subsurface) away from their point of origin.

The public, governments, and scientists are concerned about possible migration of natural gas and/or saline brine from deep hydrocarbon reservoirs and the disposal of flowback waters from hydraulic fracturing operations. However, stray-fluid migration is much more widespread than just these two examples and impacts many aspects of the entire hydrocarbon E&P process. Migration can occur (1) prior to drilling in the initial exploration process, (2) during well drilling and well evaluation, (3) post drilling during wellbore production-enhancement operations (e.g. chemical-stimulation treatments or hydraulic fracturing), (4) routinely as water coproduced with hydrocarbons (FIG. 1A), (5) potentially as out-of-zone water production by wells (FIG. 1B), (6) during secondary oil-recovery operations (such as waterflooding or pressure maintenance schemes), or (7) as surface spills of produced fluids.

The potential for stray-fluid migration into wellbores has increased over time, with the expanded use of horizontal wells that may consist of multiple wellbores, each of which can be stimulated by one or more stages of hydraulic fracturing. FIGURE 2 illustrates possible sources of stray formation waters associated with a hydraulically fractured horizontal well. In both conventional and unconventional wells, stray ("abnormal" or "out-of-zone") water production can occur (e.g. FIGS. 1B, 2) if water-bearing zones are present above the hydrocarbon reservoir and wellbore integrity issues exist with the well casing(s), and/or wellbore cement (e.g. Harrison 1985). As illustrated in FIGURE 2, multiple sources of formation water can be produced into a single wellbore besides the "in-zone" formation water produced from the target horizon. Stray formation water could invade the producing zone from directly above via natural or induced fractures. It could also enter the wellbore through improper wellbore construction or improper wellbore cementing. Although less common, stray water could also be drawn from below, again invading via natural or induced fractures. Identifying the origins of stray water is critically important to the operation of the well because expensive water handling and/or disposal costs can make the difference between an economically successful operation and premature abandonment.

Fortunately, time-tested geochemical practices, combined with new scientific advances, are successfully being applied to the issue of stray-fluid migration. This paper reviews some of the novel geochemical methods that are used to fingerprint formation fluids. Questions regarding stray-fluid migration, in both conventional and unconventional hydrocarbon E&P environments, are now being answered.

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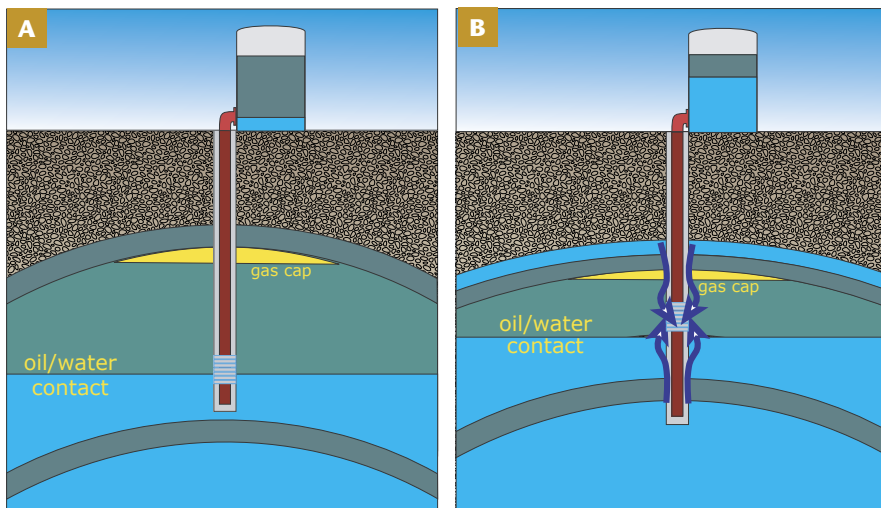
FIGURE 1 Schematic of normal water production from a hydrocarbon well (**A**) compared to abnormal water production from a well due to stray-fluid inflow into the producing reservoir (**B**). In a normally producing well, oil and water enter the wellbore (red) via perforations in the casing and cement surrounding the well. Oil and water are transferred to the surface and collected in tanks for distribution. Normal production includes mostly oil with some formation water. Abnormal water production arises when stray water (blue arrows) from other zones enters the producing wellbore across damaged or improperly sealed casing, either from above or below. The stray water is produced along with the normal oil and water, and this extra production water increases the water/oil ratio of the fluids collected in the tank at surface (not drawn to scale).

FINGERPRINTING STRAY FORMATION WATERS AND GASES

Standard Techniques

"Fingerprinting fluids" refers to the complementary geochemical techniques used to differentiate "true" or "ambient" formation water (or gas) from a "contaminated" or "out-of-zone" or "migrated" formation water/gas. Fingerprinting formation fluids is not a new concept, and many different geochemical approaches have been applied over the last several decades.
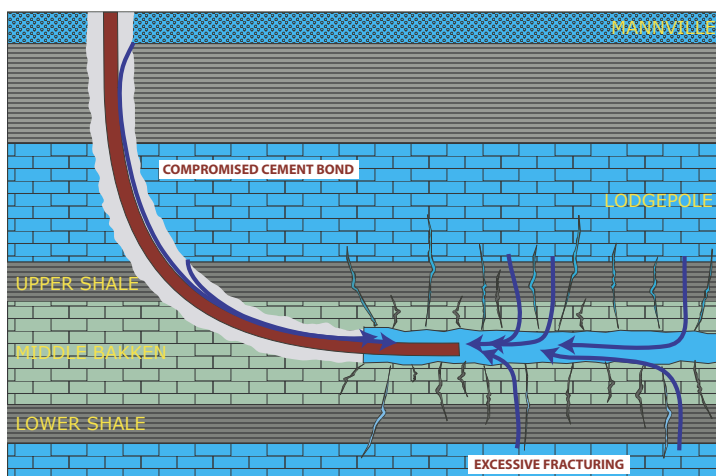
"Standard" fingerprinting techniques for water are historically based upon major-ion chemistry and "type" graphs or visual patterns, such as Stiff diagrams (Stiff 1951), Piper diagrams (Piper 1944), or similar plots. For natural gas, various crossplots of molecular composition(s), gas wetness index (%C_2+), and ratios of (C_1/[C_1+C_2]), C_2/C_3 are used (e.g. Baldassare and Laughrey 1997; Laughrey and Baldassare 1998; Zumberge et al. 2012). Catalogs or collections of "type" water compositions (e.g. CWLS 1987; Johnson and Johnson 1992; Warren and Smalley 1994; Block 2001) and numerous scientific publications containing routine major-ion-chemistry determinations

can be found for many different locations throughout the world (see Kharaka and Hanor 2014 for a recent review). Using a "standard" method involves comparing the attributes of a test sample (e.g. the shape on a Stiff diagram or location in a ternary diagram) to the "type" chemical pattern for that formation in that particular location. If the sample matches the type, then it is most likely an uncontaminated sample (Johnson and Johnson 1992). If the sample doesn't match the type diagram, qualitative or quantitative estimates can be made of the fraction of the contaminating stray fluid by using ratios or mixing models to estimate the different constituents in the sample.

An example of how major and minor element compositions of formation fluids are used to identify multiple stray formation water sources comes from the Bakken Formation in the Williston Basin of eastern Saskatchewan, Canada. In 2010 and 2011, Lightstream Resources (PetroBakken) tested water samples collected from a number of closely spaced horizontal wells completed in the Bakken Formation. These wells had been hydraulically fractured to increase oil-production rates, and some of these exhibited a rapid decline in oil production accompanied by an increased fraction of coproduced water (Molina 2012).

As with other areas throughout the Williston Basin, the suspected source of stray-water influx into hydraulically fractured Bakken wells was the overlying Lodgepole Formation (e.g. FIG. 2). The stratigraphically lower Nisku/Birdbear aquifer was considered of lesser importance since the depth to the top of that zone in the area is estimated at ~50 m beneath the lower Bakken shale (Hasses and Zotskine 2013). Other water-rich zones in the basin (e.g. the Mannville Group) are found over 600 m above the Bakken Formation, rendering them a possible source for casing leaks only.

FIGURE 2 Schematic of a hydraulically fractured horizontal well in the Bakken Formation of the Williston Basin and multiple potential sources of produced water. Sources of water could include normal production from the Middle Bakken or stray fluids from one or more of the following: a compromised cement bond and inflow from the Mannville, Lodgepole, or other shallow formation; or as a result of excessive hydraulic fracturing and inflow from the Lodgepole Formation above or Birdbear/Nisku below (not to scale).

A review of the dissolved element concentrations and chemical ratios of the produced water was undertaken to determine which of the four possible sources of produced water were impacting horizontal wells in the Bakken aquifer (potential sources shown in FIGURE 2). Ratios of dissolved trace element concentrations indicated the presence of significant quantities of external water originating from the underlying Birdbear/Nisku aquifer (aquifer below the Lower Shale; FIG. 2). The presence of Birdbear/Nisku formation water in these samples was rather unusual since, as noted above, that formation is approximately 50 m beneath the lower Bakken shale.

Geophysical data (seismic sections) acquired in the vicinity of the wells identified structural anomalies indicative of salt collapsing in the deeper Paleozoic sediments (Molina 2012). Micro-image logging conducted along the horizontal section of another well nearby confirmed the existence of open fractures intersected by the wellbore (Molina 2012). Hence, the presence of Nisku/Birdbear water in the samples collected from these wells was explained by either (1) the existence of salt collapse related to natural fracture systems or (2) hydraulic fracturing in the immediate vicinity of open fractures apparently connected to the salt dissolution structures. Avoiding salt collapse structures and placing hydraulic fracturing intervals away from open fractures resulted in significantly lower water production in new wells in the area (Molina 2012).

Unfortunately, these standard fingerprinting techniques can have at least three main problems:

1. *Unknown "type" fingerprint.* It is possible that type diagrams don't exist for a particular locale. This is often the case in frontier basins, exploration areas in producing basins, and even untested horizons in well-characterized basins.

2. *Drilling through formations where the drilling fluid is similar to native, low-salinity formation fluid.* For example, drilling Upper Cretaceous–aged strata in the Western Canadian Sedimentary Basin (e.g. Milk River or Belly River formations) typically uses a drilling fluid made of surface water or shallow groundwater. If the hydrocarbon drilling target is in a shallow formation, it is possible that the associated formation water is relatively fresh. Thus there would be little chemical difference between the (fresh surface water) drilling fluid and the pure formation fluid.

3. *Drilling through formations where the drilling fluid is similar to high-salinity formation fluid.* For example, in Paleozoic strata of the Williston Basin in Canada (e.g. Mississippian strata or deeper), many deep oil and gas wells drilled thousands of meters into the subsurface encounter saline brine commonly associated with the presence of evaporites (e.g. gypsum, anhydrite, halite). In these zones the drilling fluids are artificially saturated with additives (e.g. halite, barite, gypsum) to prevent washouts or borehole collapse. Thus, artificially saturated drilling-fluid chemistry will commonly resemble the natural saline formation water.

In each of these cases, standard fingerprinting techniques work poorly, if at all, and other methods to distinguish between stray fluids and formation fluids are needed.

Isotopic Techniques

Stable isotope techniques are used to fingerprint formation waters in hydrocarbon exploration and production operations. Of particular interest are the applications of these techniques to interpreting cases of possible stray-fluid migration associated with unconventional hydrocarbon production (e.g. Rostron et al. 1998; Rostron and Holmden 2000; Frost et al. 2010; Peterman et al. 2010; Chapman et al. 2012; Osborne et al. 2012; Warner et al. 2012). Carbon isotopes have been used for decades in North America for fingerprinting stray gas (e.g. Stahl 1974; Schoell 1980; Whiticar 1999). Important examples include: mud–gas isotope profiles for fingerprinting surface casing vent flows (SCVF) from conventional heavy-oil wells (Rowe and Muehlenbachs 1999; Arkadakskiy 2006; Vlad 2009); unconventional gas production from the Barnett and Fayettville formations in the Fort Worth and Arkoma basins (Zumberge et al. 2012) and the Marcellus Formation in the Appalachians (e.g. Baldassare et al. 2014); and novel applications of noble gas isotopes to fingerprint natural gases in the northern Appalachian Basin (Hunt et al. 2012).

Stable isotope techniques are also able to fingerprint the origin of stray formation fluids when standard molecular composition–based methods cannot. Selected applications are provided below.

EXAMPLES OF FINGERPRINTING USING STABLE ISOTOPES

### Drill Stem Testing a Conventional Well Using a Well-Defined Isotope Fingerprint

In the late 1990s, numerous oil and gas discoveries in the Midale area of southeast Saskatchewan, Canada, led to the development of a vertical isotopic profile (δ^{18}O, δD, ^{87}Sr/^{86}Sr) from deep aquifers (Rostron et al. 1998; Rostron and Holmden 2000). An expanded version of that profile is presented in FIGURE 3. For comparison purposes, the total dissolved solids (TDS) of the water chemistry is also shown. In this case, the TDS was used as a proxy for the bulk water chemistry of each aquifer because each aquifer contains sodium chloride–type formation waters. The most notable insight from FIGURE 3 is that each aquifer possesses a unique isotopic fingerprint, in contrast to the relatively uniform water-chemistry values (e.g. TDS is approximately 300 g/L) below the Bakken Formation. Fingerprinting individual aquifers below the Bakken Formation using major-ion compositions was not possible because of the near homogeneous major-ion composition of formation waters in the section. The presence of unique isotopic signature(s) for each aquifer enabled the use of stable isotopes for fingerprinting formation waters in the Midale area.

An example from the Yeoman Formation shows the success of stable isotope fingerprinting methods. A newly drilled well (02/7-15-6-11W2) in the Midale area was tested for production using a drill stem test (DST). The DST was considered successful with no evidence of mechanical failure, and a comparatively large amount of fluid was produced (approximately 4.8 m^3), with a "typical" salinity for this depth in the basin (i.e. approx. 300 g/L). However no oil was found in the recovered fluid, giving rise to the possibility that no hydrocarbons were present in the Yeoman Formation at this location. The δ^{18}O and δD compositions of the DST fluid sample were –12.1‰ and –144‰, respectively, in contrast to the typical isotopic values of –1.1‰ and –60‰ from the Yeoman aquifer in the area (FIG. 3). In this case the isotopic data demonstrated that the DST-recovered fluid comprised a large component of drilling fluid prepared with near-surface groundwaters or surface meteoric waters. This was known because the isotopic composition of the recovered fluid plotted along the Global Meteoric Water Line while the pure formation waters from the Yeoman Formation fell along the Williston Basin isotope trend line (Rostron et al. 1998; Rostron and Holmden 2000). The lack of hydrocarbons recovered from the DST had no bearing on the presence of oil/gas in the formation, because the recovered fluid was not a sample of formation fluid. Stable isotope fingerprinting correctly verified the lack of formation water in this DST sample. This well was subsequently cased and this zone produced over 20,000 m^3 of oil.

Conventional Well Production Application Using a Well-Defined Isotope Fingerprint

A second example of stable isotope fingerprinting is the analysis of coproduced waters, again from the Yeoman Formation. A producing well (6-3-7-11 W2) in the Midale area showed a significant increase in its water-to-oil ratio over time (reaching 94% water) Almost all conventional oil wells eventually demonstrate increased water to oil ratios, as the finite volume of oil in the reservoir is ultimately
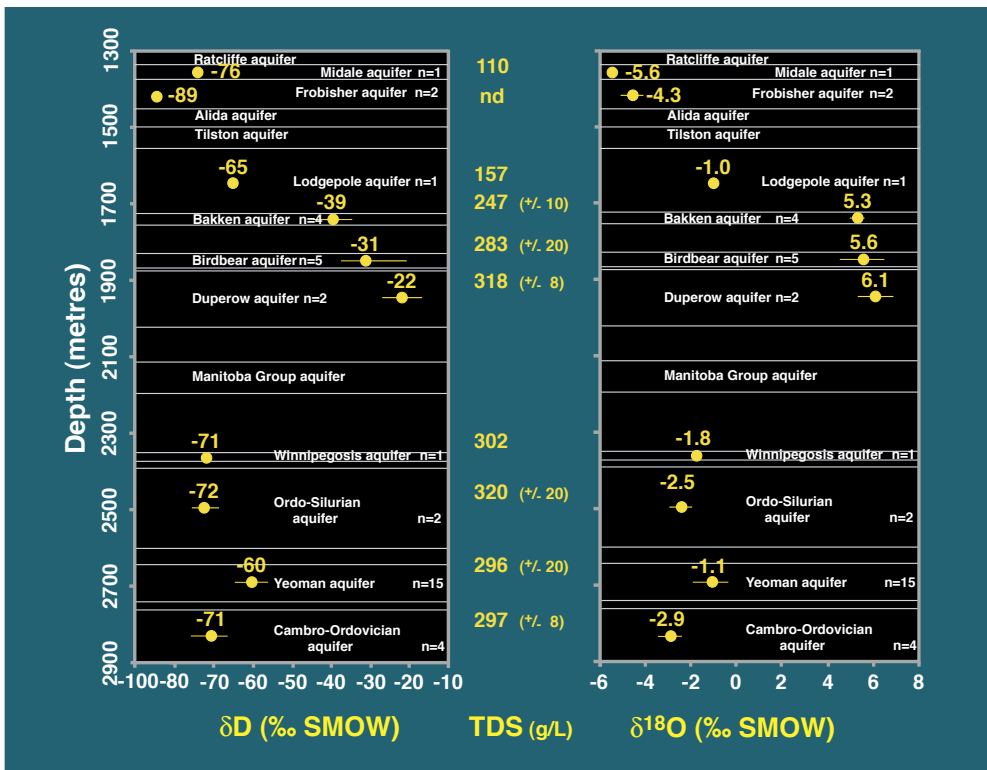
FIGURE 3 Average $\delta^{18}O$ (‰ Standard Mean Ocean Water, or SMOW), δD (‰ SMOW), and TDS (g/L) versus depth (m) for Mississippian to Cambrian aquifers in the Midale area of the Williston Basin (southeast Saskatchewan, Canada). Average isotopic compositions are plotted as yellow dots for each aquifer, with ranges in values illustrated for reference. Analytical uncertainties are smaller than the plotted symbols. TDS = total dissolved solids.

extracted and water is drawn into the wellbore (e.g. FIG. 1A). So the following questions arose: Was this well at the end of its life and therefore should be abandoned (e.g. normal water production illustrated in FIG. 1A)? Or was the increased water production due to stray-water influx into the wellbore? The salinity of the produced water was measured at approximately 255 g/L, which was slightly lower than expected but not unusual for brines from the Yeoman Formation. The $\delta^{18}O$ and δD of the produced water from this well were measured to be –10.1‰ and –108‰, respectively. Comparison with "typical" isotopic values from the Yeoman aquifer (FIG. 3) showed that the coproduced brine from the well was not formation water from the target horizon. Since there was no water injection in the oilfield at the time of sampling, the produced water in the well was from an unknown horizon, at least shallower than the Bakken aquifer. Isotopic compositions of formation water from the Mannville Formation, approximately 1 km above the Yeoman Formation, matched the produced-water values. Therefore, the source of the produced water was attributed to a leak in the well casing at the Mannville level. Subsequent remedial action (patching) on the casing of this well reduced the volume of coproduced water, lowered the water-to-oil ratio, and extended the life of the well.

Tracking Produced Fluids after Hydraulic Fracturing Treatments

Stable isotope fingerprinting of formation waters is also very effective for tracing the origin of waters produced from conventional and unconventional wells that have been stimulated by hydraulic fracturing. Oxygen and hydrogen stable isotope compositions of water produced from 36 wells drilled in the Bakken Formation are shown in FIGURE 4. These wells are from one field that covers an area of approximately 16 km[2] in the eastern portion of the Canadian Williston Basin and all were hydraulically fractured due to the relatively thin and low-permeability nature of the Bakken Formation.

Artificially induced fractures increase the pathways for oil and water to flow into the producing wellbores, and generally the larger the hydraulic fracture treatment, the greater the increase in productivity. However, excessive fracturing can lead to fractures that migrate out (up or down) of the producing zone (FIG. 2), creating pathways for unwanted formation water influx into producing wells. These out-of-zone inflows do not contain hydrocarbons and thus reduce the economic viability of a well. Identification of the source and amounts of out-of-zone fluids is critical for optimal development of this field and others like it.
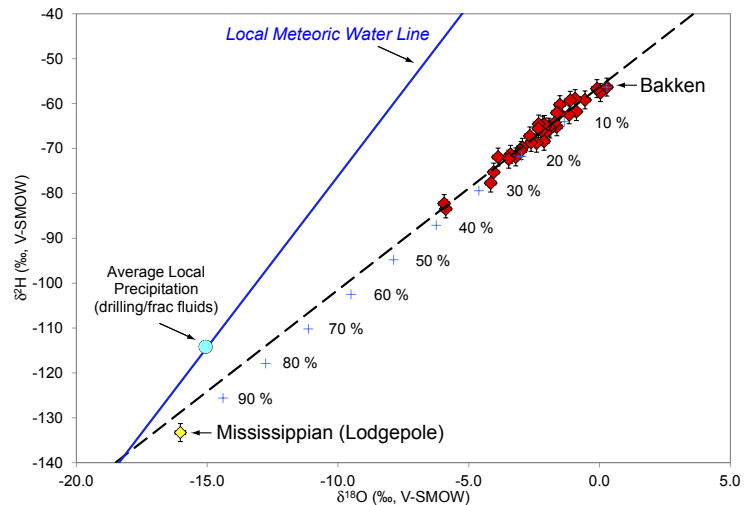
FIGURE 4 $\delta^{18}O$ versus δ^2H for 36 producing wells (red diamonds) from the Bakken Formation (Saskatchewan, Canada), eastern margin of the Williston Basin. Reference data from unfractured Lodgepole Formation (yellow) and Bakken Formation (purple) define the end-points of a mixing line. Values shown (blue + symbols) are percentage of Lodgepole Formation water in produced fluids from the Bakken Formation. A surface-water or drilling/fracture fluid source of the stray fluids can be ruled out because the produced-fluid samples neither plot along the Local Meteoric Water Line nor form a linear mixing line with the drilling/fracture fluid (blue circle).

The stable isotope composition of water samples obtained from unfractured wells in the Bakken producing zone and overlying Lodgepole aquifer provided reference finger-prints for the two zones of interest (Fig. 4). Stable isotope data from the 36 wells showed a well-defined mixing line between the Bakken and Lodgepole formations, indicating a Lodgepole aquifer water source for the stray fluid. Simple binary mixing models were used to calculate the relative contribution of the overlying Lodgepole formation water to the produced fluids: amounts ranged from approximately 6 to 40%, with an average of 15% (Fig. 4). Knowledge of the source and the amount of the unwanted fluids can be applied to the design of the hydraulic fracture treatment to reduce the inflow from overlying aquifers in future wells.

Tracking Flowback Water from Unconventional Gas Wells

In northeast British Columbia, Canada, a horizontal well was drilled into a thick, prolific, gas-producing Devonian shale horizon, then completed and hydraulically fractured. Flowback water from the well was sampled daily for one month. Dissolved element and $\delta^{18}O$ and δ^2H compositions were measured. Over time, a significant increase of the $\delta^{18}O$ and δ^2H compositions and the total dissolved solute content (TDS) of the flowback-water samples was observed (Fig. 5). Although not shown, most of the individual element concentrations also increased with time, with Ca, Mg, and Sr concentrations exhibiting greater total increases than those of dissolved HCO_3^- and monovalent ions such as Na, Li, Cl, and Br. The systematic temporal variability of the stable isotope and most major and trace dissolved-element concentrations suggested that the flowback samples consisted of formation fluid diluted with variable (decreasing) amounts of low-TDS fluid (i.e. surface water–derived fracturing fluid).

To determine the amount of stray fracturing fluid present in a produced-water sample, the $\delta^{18}O$ and δ^2H compositions of both the fracturing fluid and formation water must be known. As shown in Figure 4, once the stable isotope compositions of the two end-members are known, the proportion of stray fluid can be calculated with simple binary mixing equations. For this example, a sample of the surface water–derived fracturing fluid was not available, but the $\delta^{18}O$ and δ^2H values were inferred to be –10‰ and –100‰, respectively, by linear regression of the TDS versus $\delta^{18}O$ (or δ^2H) composition of the flowback samples. These isotopic compositions closely matched the isotopic compositions of evaporated local precipitation values estimated from the GNIP database (IAEA/WMO 2014). The other end-member was determined by analysis of coproduced-water samples collected from older nearby wells producing local Upper Devonian formation water (Fig. 5). These nearby values were similar to the $\delta^{18}O$ and δ^2H values of the samples collected in the last four days of sampling from the well under investigation, implying that after approximately 25 days of production, it returned to producing formation water from the hydraulically fractured zone.

Calculations using the $\delta^{18}O$ and δ^2H compositions of the two end-members showed that the proportion of formation water in all samples for the sampling period varied from approximately 60% by volume in the beginning of the sampling period to 100% in the last four days of the sampling period. This case demonstrated that the presence and/or fraction of stray hydraulic fracturing water in flowback samples could be estimated relatively accurately, without the need for artificial tracers, by using the $\delta^{18}O$ and δ^2H compositions of the flowback samples, even if the compositions of the local fracturing fluid were unknown.
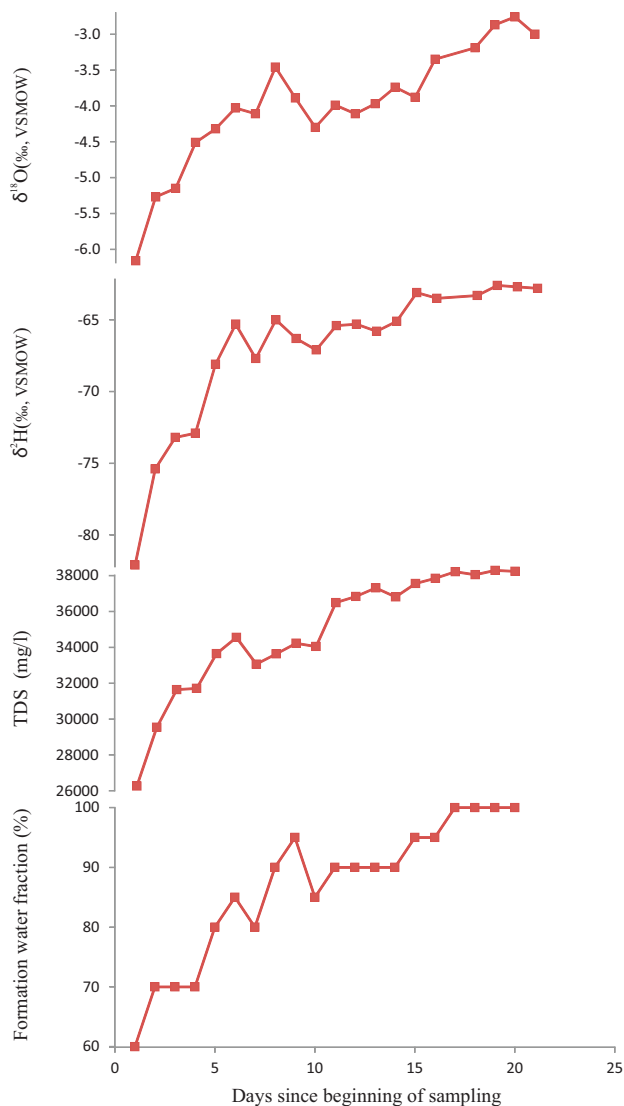
Figure 5 $\delta^{18}O$, δ^2H, and total dissolved solids (TDS) compositions of flowback samples versus time (days after sampling). The fraction of formation water (%) in the flowback samples is calculated from linear mixing of the estimated end-members. See the text for details.

CONCLUSIONS

Stray fluids are defined as formation water or hydrocarbons that are found at a location (surface or subsurface) away from their point of origin. Stray-fluid migration can be widespread and significant. Particular concerns are the possible migration of natural gas and/or saline brine from deep hydrocarbon reservoirs and the disposal of flowback waters from hydraulic fracturing operations. Owing to the potential for adverse health and environmental effects, these fluids are receiving considerable scrutiny from scientists, the public, and governmental groups. Thanks to the long history of work in deciphering the origins of stray fluids for exploration and production operations, an extensive body of science-based geochemical techniques exists that can be applied successfully to fingerprint the source of stray formation fluids.

Geochemical fingerprinting techniques were initially based on the use of the molecular compositions of water, oil, and natural gas. These techniques required knowing the geochemical signature of the ambient formation fluid(s),

and subsequently comparing suspect fluid samples to the ambient geochemical fingerprint. Although successful, these methods can be of limited use in certain situations.

Isotopic fingerprinting methods, used alone or in conjunction with molecular compositions, have proven superior for fingerprinting water, oil, and natural gas. The isotopes of ^{18}O, ^2H, ^{13}C, and other elements, as well as $^{87/86}Sr$, are particularly important for many different conventional and unconventional hydrocarbon E&P settings. Useful settings include: (1) during well testing and swabbing operations, (2) production monitoring for tracking water generated during the hydraulic fracturing of both conven-

tional and unconventional horizontal wells, (3) remediation of surface casing vent flows from oil and gas wells, and (4) environmental applications such as identifying the source of produced-water spills at surface. The use of stable isotope fingerprinting methods has improved our understanding of the sources of produced water, oil, and natural gas. This holds great promise for reducing public heath risks, increasing safety, and improving the economics of hydrocarbon wells. As new techniques and applications are developed, our ability to identify the origins of stray fluids will continue to increase. ▪

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