A Study Yielding The First Demonstration That Rare-Earth Elements Could Be A Useful Geochemical Tracer In Formation Hydraulic Fracturing Schemes For Enhanced Gas And Oil Production

ABSTRACT
A reliable geochemical tracer has yet to be developed which can be beneficial to hydraulic fracturing schemes for enhanced production of gas and oil from organic-rich shale beds. Our preliminary study on rare-earth elements in various fluids collected from hydraulic fracturing of Woodford Shale at a location (Sec. 21, T.1N., R.10E.) in Coal County, Oklahoma shows that relative rare-earth element distribution patterns of temporally different flow-back fluids, normalized to the pre-frac fluid used, could prove to be a useful geochemical tracer, giving additional insights into the geometry of the induced-fracture system. The tracer can be particularly useful to determine whether or not induced fractures from a hydro-fracturing event might have been extended to adjacent stratigraphic units beyond the production formation. The preliminary results of this study open a promising window for more extensive studies to be conducted in conjunction with engineering plans and microseismic controls in many different areas where hydraulic fracturing of organic-rich shale beds are intended for enhanced production of gas and oil.

INTRODUCTION
Hydraulic fracturing (or hydro-fracturing) is now widely used as a development strategy to aid increased recovery of gas and oil from geological formations that have low permeability, especially from many shale reservoirs in North America and elsewhere in the world. Partial success of this technique has been documented by a number of efforts in exploitation of oil and gas from well-known organic-rich black shale formations in North America, such as the Barnett Shale in Texas, Marcellus Shale in Pennsylvania, Woodford Shale in Oklahoma, Bakken Shale in the Williston Basin, New Albany Shale in the Michigan Basin, and a few others. Recently, Waters et al. (2009) presented a paper on hydraulic fracturing of adjacent horizontal wells. The report was based on the employment of simultaneous hydraulic-fracturing strategy for the company’s Woodford Shale acreage in the Arkoma Basin of eastern Oklahoma. Microseismic technology employed in the hydro-fracturing process has been used to gain insights into the propagation direction of induced fractures. Based on their exploratory study which showed increased production rates in two out of three projects, operational benefits were explored for developing acreage with simultaneous hydraulic fracturing performed in closely spaced horizontal wells that were parallel to each other. Waters et al. (2009) also recognized that an initial gain in the production rate was soon followed by a drop in the gas production and suggested that the drop could be due to fluid invading the producing fracture systems. Fluid that could have been assimilated into a lower pressured reservoir may also impact the production. Geologic structure undoubtedly also impacts the geometry of the hydro-frac-
induced fracture systems. Failure to gain any significant increase in the production rate for one of the simultaneous multiple horizontal-fracturing projects and a quick drop in the initial production rate suggest that studies are needed to describe fully the spatial configuration of induced fractures achieved through hydro-fracturing.

Hydraulic fracturing essentially involves the high-pressure injection of a fluid into the formation. The injection fluid is typically a mixture of water, quartz sand, a variety of organic and inorganic chemical compounds which may include such materials as guar powder (which comes from the leguminous guar plant and may be used as binder, thickener and/or emulsifier), some alkali salts, an enzymatic compound (which influences time-triggered change in the viscosity of the fluid), a low level of an acidifying agent (commonly hydrochloric acid), and several others. This high-pressure fluid-injection process widens and lengthens existing fractures and creates additional new fractures within the targeted formation. As a result, gas and oil find more open passages to travel within the formation. Knowledge of the spatial extent and architectural pattern of fractures developed within the formation becomes important for determining the effectiveness of a given hydraulic-fracturing scheme. Situations may arise where there are quick drops in production rates. This could happen from the development of cross-formation fractures induced by hydraulic fracturing of the production formation, whereupon gas and oil from the targeted formation may be lost to a relatively low-pressure underlying or overlying formation. The development of significant cross-formation fracturing could entail a large economic loss.

The employment of a managed fracturing scheme becomes especially important for production from formations that are not very thick. The benefits of knowing the induced-fracture distribution pattern go beyond maximum hydrocarbon recovery. Some environmental concerns exist as to the safeguards of useable ground water in formations adjacent to the hydro-fractured formations, especially those at relatively shallow depths. Cross-fracture formation development through hydro-fracturing of shallow low-permeability oil- and gas-bearing formations could result in widespread contamination of useable ground water in adjacent formations. Any knowledge that can advance the assurance of hydro-fracturing without cross-fracture formation development will be highly beneficial to both enhanced production from low-permeability formations and for the prevention of contamination of useable ground water in adjacent formations.

Physical and chemical tracers may be used to identify any cross-fracture formation development as a consequence of hydraulic fracturing of low-permeability oil- and gas-producing formations. Oil and gas industries involved in enhanced production of hydrocarbons from low-permeability formations by means of hydro-fracturing have essentially depended until now on a micro-seismic technology to depict the directions of induced-fracture propagation and the geometric patterns of the developed fractures. Industry has not yet recognized the benefits of the study of a chemical signal or of a collection of chemical signals that may be captured from the analyses of flow-back fluids. This study describes a technique for proving insights into the spatial configurations of fracture development, especially any development of fractures that extended into overlying or underlying formations following a hydro-fracturing event.

Progress remains slow towards finding a chemical tracer that can indicate cross-fracture formation development. It could be that any previous effort made to gather chemical evidence toward an increased understanding of spatial configuration of induced fractures essentially relied on analyses of the common major chemical components (primarily common alkali and alkaline earth elements, chlorides, sulfates, and carbonates) of the flow-back fluids. A reliance on the major chemistry alone is inherently problematic. The make-up of the injection fluid for hydro-fracturing is such that no discernible major chemical trend among the flow-back fluids may be clearly established, therefore making cross-fracture formation development impossible to delineate. A different chemical approach is necessary in order to provide useful information about fracture development from a hydro-fracturing scheme.

Our plan for a new approach to the study of the flow-back fluids examines a group of chemically very closely related elements known as the rare-earth elements (REEs). The distribution trends of the REEs can be used as a chemical tracer for an analysis of potential cross-fracture formation development and for additional insights into the configuration of induced-fracture development. The REEs are a group of chemically very similar elements known to form complexes with various natural inorganic and organic ligands. It is also well known that the stability of the complexes involving the REEs and many of these natural ligands changes progressively across the REE series. REEs are ideally suited to put forward our hypothesis which states that the relative distribution of REEs in flow-back fluids from a hydro-fracturing event could provide significant insights into spatial configurations of induced fractures.

To test our hypothesis, we have made a preliminary study of the REEs in flow-back fluids collected over a span of several days. The collections began one day after a well located in the western Arkoma Basin in Coal County, Oklahoma that was drilled into the Devonian Woodford Shale was hydro-fractured. We analyzed the prefrac liquid (essentially the water from a local pond) used for the hydro-fracturing as the reference sample to construct the patterns of relative distribution of the REEs in the collected flow-back liquids. The objectives of this paper are the following: to report some preliminary test data on the relative distributions of the REEs in these
flow-back fluids, to provide an account of inheritance of the REEs distribution patterns by these back-flow fluids, and to make an assessment of the potential use of these geochemical data to gain an additional understanding of the spatial configurations of induced fractures, including the development of any cross-fracture fluids, from a hydro-fracturing event. We should not lose sight of the fact that this is a preliminary study and the results of it at this stage appear promising. In the future, more extensive studies will be needed in concert with information from engineering plans and microseismic results from many different targeted areas to establish this geochemical approach as a reliable tool to provide valuable information regarding the spatial development of fractures produced in organic-rich shale beds from hydraulic-fracturing.

**SOME FUNDAMENTALS OF RARE-EARTH ELEMENT GEOCHEMISTRY**

Because the analyses of REEs remain at the core of this study, and some in the industries involved in hydro-fracturing low-permeability rocks may not be fully familiar with the application of REEs in studies of natural systems, it is necessary to give here a brief outline of the basic principles of the chemistry of the REEs in natural materials.

The lanthanides (Ln) are a group of 15 elements including: lanthanum (La) (atomic number 57), cerium (Ce) (58), praseodymium (Pr) (59), neodymium (Nd) (60), promethium (Pm) (61), samarium (Sm) (62), europium (Eu) (63), gadolinium (Gd) (64), terbium (Tb) (65), dysprosium (Dy) (66), holmium (Ho) (67), erbium (Er) (68), thulium (Tm) (69), ytterbium (Yb) (70), and lutetium (Lu) (71). Because of the absence of Pm in terrestrial materials, the Ln group actually includes 14 elements. All Ln atoms have completely filled 5s², 4d¹⁰, 5p⁶, and 6s² orbitals. The atoms differ from each other in their electronic configurations based on electron filling at the next higher energy orbitals beyond 6s², namely, either at 4f orbitals or a higher-energy 5d orbital. The electron structure of La, the first element within the Ln group, consists of completely filled 5s, 4d, 5f, and 6s orbitals plus a single electron in a higher-energy 5d orbital rather than the comparatively lower-energy 4f orbital. Following the La filling with 1 electron in a 5d orbital, the electron filling for successively higher atomic number elements from Ce to Eu occurs at the expected lower-energy 4f orbitals, keeping at the same time 5d orbitals completely empty. For the next Ln element, Gd, the additional electron, following the filling of Eu with seven electrons in 4f orbitals, goes to the relatively higher energy 5d orbital and not to the lower-energy 4f orbital. Following the electron orbital filling of Gd, the next electron filling for atoms of the elements with successively higher atomic numbers, from Tb to Yb, takes place in the 4f orbitals, keeping the 5d orbital completely empty. With the electron filling necessary in Yb, the 4f orbitals become completely filled (4f¹⁴). The only remaining Ln atom is Lu, and its electron structure consists of completely filled 5s, 4d, 5p, 6s, and 4f orbitals and a sole electron in a 5d orbital.

In most common terrestrial environments, Ln typically occur as trivalent ions (Ln³⁺), with the exceptions of Eu, which can occur as a divalent (Eu²⁺ or Eu II) or a trivalent (Eu³⁺ or Eu III) ion and Ce, which can occur as a tetravalent (Ce⁴⁺ or Ce IV) or a trivalent (Ce³⁺) ion. The loss of the single 5d electron plus the two 6s electrons from La, Gd, and Lu atoms results in the formation of their trivalent ionic forms, whereas the loss of one 4f electron plus the two 6s electrons from Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, and Lu atoms results in the formation of their trivalent ionic forms. Hence the valence electrons for the trivalent Ln are: 6s² and 5d¹ electrons for La, Gd, and Lu, whereas 6s² and 4f¹ electrons for the remaining Ln.

Because Ln vary primarily in the number of 4f electrons, these elements are very similar in chemical properties and are always found occurring together in natural materials. However, their occurrence together in natural materials does not imply that they respond equally to chemical changes of natural systems. In fact, the Ln ions separate to some degree when optimum atomic radii for accommodation in mineral structures are available or when they are in solution and become involved in complex ligands having different stabilities, especially in the formation of chelates (the same ligand offering two donor atoms to form bonds with the REEs). In some mineral structures, such as those in amphiboles and garnets, Ln with smaller ionic radii (or the heavier Ln) are accommodated, whereas in some other mineral structures, such as in the feldspars, Ln
with larger ionic radii are favored. In solutions, some degree of separation among Ln occurs because the stability constants of many different Ln-ligand complexes are typically varied in a gradual or steady fashion, but not necessarily in a smooth pattern, across the Ln series. The variations that have been observed in natural materials have led studies on Ln to subdivide the elements into three groups: the light Ln group (from La to Eu), the middle Ln group (from Sm to Ho), and the heavy Ln group (from Gd to Lu). The middle Ln group includes the two end-members (Sm and Eu) of the light Ln group and the first four members (Gd, Tb, Dy, and Ho) of the heavy Ln group (Topp, 1965).

In Pearson’s (1963) terminology, the Ln\(^{3+}\) ions are classified as “hard” ions, which causes them to bond preferentially with “hard” base ligands such as H\(_2\)O, OH\(^-\), CO\(_3\)\(^-\), NO\(_3\)\(^-\), SO\(_4\)\(^2-\), PO\(_4\)\(^3-\), F\(^-\), Cl\(^-\), R-NH\(_2\), NH\(_2\), NH\(_3\), R-CN\(^-\), R-OH (alcohols). Ln, like many other “hard” acid ions, have strong preference for O donor atoms. Bonding to Cl\(^-\) ion has been known, but it is relatively weak compared to bonding to O and F ions. Complexes solely with NH\(_3\), R-NH\(_2\), (amines), HS\(^-\) and CN\(^-\) are extremely weak (Evans, 1990; Wood, 1990). Ln coordination with N alone is weak and such a complex is easily hydrolyzed by water. But in a polydentate complex formation or chelation, N can serve as an effective donor when Ln\(^{3+}\) is also coordinated to at least one O donor atom. In general, the Ln ion preference for donor atoms is O > N > S (Thompson, 1979).

Water is a very strong ligand for Ln\(^{3+}\) ions. In aqueous environments, other ligands would form strong bonds with Ln\(^{3+}\) ions only if the different ligands become able to dislodge or displace water molecules from the coordination sphere. In aqueous solutions the Ln\(^{3+}\) ions water molecules from attract around them and form a hydration shell by forming Ln\(^{3+}\)-H\(_2\)O complexes. The basic properties of Ln in natural aqueous solutions depend greatly on the degree of removal of the hydration shell by other coordinating compounds that may be present in the aqueous system. Ln ions have generally high coordination numbers (anion ligands surrounding the Ln cations) that commonly range between 7 and 9 in aqueous solutions. Studies of different Ln complexes have established that water molecules associated with Ln complexes are not waters of hydration but they are coordinated (Thompson, 1979). The chemistry of Ln in natural aqueous environments is influenced by the ability of ligands present in the environmental solutions to form as inner sphere complexes that have no intervening water molecules to keep the ligands being separated from the central Ln or outer sphere complexes that have intervening water or solvent molecules.

Wood (1990) gave a comprehensive review of the stability constants of Ln-complexes with many common inorganic anions or ligands. Thompson (1979) and Evans (1990) provided data on stability constants of Ln-complexes with a number of different organic ligands. The sulfate ligands cause very little fractionation between the light Ln\(^{3+}\) ions (LREE) and the heavy Ln\(^{3+}\) ions (HREE). Fluoride complexation can cause fractionation of the Ln ions in dilute fluoride solutions. Similar to that of fluoride complexations, the stability of Ln-CO\(_3\)\(^2-\) complexes also progressively increases with increasing atomic number of the Ln. In general, the stability of chloro complexes decrease with increasing atomic number, a trend that is opposite of the behavior of the fluoro complexes (Wood, 1990). Several studies have noted that precipitation of phosphate minerals from solutions causes the minerals to have a relative enrichment of the middle Ln across the series, displaying a convex relative distribution pattern often marked by the highest enrichment of Sm and the corresponding equilibrium solutions to have a relative depletion for the middle Ln, displaying a concave upward relative distribution pattern with the most depletion of Sm (Byrne et al., 1996; Robyn and Sholkovitz, 2001).
element of a chosen standard or reference material. The observed trends in REE distribution patterns among samples of interest may cast light on similarities or dissimilarities of their chemical evolutionary process or processes. The REE relative distribution patterns of natural materials fall into a small number of broad categories. The distributions are commonly described by one of the following expressions: a light REE (LREE) (from La to Eu) enriched distribution pattern, a heavy REE (HREE) (from Gd to Lu) enriched distribution pattern, and a middle REE (MREE) (from Sm to Ho) enriched distribution pattern, or a combination of the MREE and either the HREE or the LREE enriched pattern (Topp, 1965). Typically, but not always, an apparently smooth distribution pattern within the LREEs may be interrupted at Ce and Eu. These departures, which may be linked to a crystallo-chemical or solution-chemistry effect, or even an enzymatic effect in a living system, are identified as either positively anomalous if the observed relative concentrations of them are in excess of relative concentrations that could be predicted from the relative distribution trend defined by their two immediate respective neighbor REEs, or negatively anomalous if the observed relative distribution values are short of the predicted values determined by the trend line that connects their two respective immediate neighbor REEs. A theoretical or predictable Eu relative distribution value is defined by the mid-point of the Sm and Gd relative distribution values, whereas a theoretical or predictable Ce relative distribution value is defined by the mid-point of the La and Pr relative distribution values. An understanding of the nature of temporal variations in relative distribution patterns of the REEs in flow-back fluids that arrive at different times at the wellbore is important because it may provide some significant insights into the configuration of induced fracture development from a hydro-fracturing event.

The reference sample that may be used to construct the relative distribution patterns of the REEs of the materials under investigation depends largely on the scope of the investigation. In studies of the REE distributions of terrestrial crustal crystalline materials, a chondrite meteorite, with its generally accepted REE values, has served well as a reference sample. In analyzing the depositional and diagenetic history of sedimentary rocks, both the North American Shale (NAS) (a composite of Paleozoic and younger materials) and the Post-Archean Australian Shale (PAAS) have been used as reference samples. Alternatively, it may be convenient to use a defined starting material as the reference sample for constructing relative distribution patterns of REEs in the materials selected for a geochemical investigation.

The amount of REEs in sedimentary rocks varies. Clay minerals typically contain ten to 20 times more REEs than carbonate minerals because REEs are selectively incorporated into silicate minerals. In comparison to clay minerals like smectite, illite, and mixed-layer illite-smectite whose REE contents are often in few tens of parts per million (ppm), feldspar has a much lower REE content – only a few ppm. Because of the variable amount of quartz, which is not a host for REEs, and of calcite, which commonly has low rare-earth content, shale has a wide range of total REE contents from a few 10s to more typically a few 100s ppm. More significant than the total REE content is the relative distribution among the REEs in shale as compared to a reference sample. In general, average shale with its REEs normalized to chondrite meteorite REE abundances has a distribution pattern that can be characterized by an enrichment of the LREEs relative to the HREE elements and a negative Eu anomaly (Taylor and McLennan, 1988). In contrast to a high REE content in shale (typically 200 to 300 ppm) and to a relatively low content of REEs in carbonate rocks (typically only few ppm), the REE contents in river, ground and ocean waters are extremely low, at most a few parts per billion (ppb) and often at few parts per trillion (ppt).

While the sedimentary rocks may be found to be LREE enriched, the associated fluids may show a significant relative enrichment in the HREEs. The fluid REE characteristics are influenced by variation in the stability of the different rare-earth complexes within the solution.

GENERAL STRATIGRAPHY AND LITHOLOGY OF THE DEVONIAN WOODFORD SHALE IN THE ARKOMA BASIN IN SOUTHEASTERN OKLAHOMA

The stratigraphy and lithology of the Devonian Woodford Shale in Oklahoma have been described in recent papers by Andrews (2009) and Waters et al. (2009). In the western Arkoma Basin in Oklahoma, the Devonian Woodford Shale, which is recognized as being among the richest source rocks in the country, unconformably overlies a number of different older formations, including the Sylvan Shale (Ordovician), the Viola Limestone (Ordovician), and the Hunton Group (Ordovician to Lower Devonian). The Woodford is overlain by the Sycamore/Mayes Limestone (Lower Mississippian) which consists of interbedded shale and limestone in the lower part and grades upward into massive carbonates.

Andrews (2009) reported that the organic-carbon-rich units of the Woodford Shale occur in black shale with cherty beds and some phosphatic nodules. The total organic carbon (TOC) content typically is between 3% and 28%. The Woodford Shale in the subsurface in the Arkoma Basin about 7,000 to 10,000 ft deep and about 75 to 200 ft thick. The organic material in the Woodford throughout most of the Arkoma Basin has a vitrinite reflectance value (Rv) between 1 and 2.5, with 3 being near the thermal limit of gas generation. The southern part of the Arkoma Basin in Oklahoma is known for gas production with variable amounts of condensate, suggesting that TOC, kerogen type, and hydrocarbon migration all have important roles. Andrews (2009) divided the Wood-
ford Shale into three informal members based on outcrop characteristics. The lower member consists of interbedded non-calcareous black-gray siliceous shale and thin cherty beds. The middle member consists mostly of siliceous, non-calcareous black-gray fissile shale. The upper member consists largely of black-to-gray siliceous shale with abundant phosphate nodules as large as two inches in diameter and fractured thin (three inches or less) beds of chert with common radiolarian tests and uncommon thin dolomitic beds. The lower and the middle members normally contain few phosphate nodules.

**MATERIALS AND METHODS**

Flow-back fluids in this study came from a single well in which the Woodford Shale was hydraulically fractured. The well is located in Sec. 21, T.1N., R.10E. in Coal County, Oklahoma. Following high-pressure injection of pre-frac fluids, flow-back fluids were collected each day for several days beginning one day after the hydro-fracturing. The collected samples were labeled with a number that indicated which day the collection occurred following the day of the hydro-fracturing. For example, the sample designated as Flow-back 1 was collected one day after the day of the hydro-fracturing; Flow-back 2 was collected two days after the day of the hydro-fracturing, and so on. Each time, about 1,500 to 2,000 ml of fluid was collected. This large amount was needed because from our past experiences in analyzing formation waters we have found that the REE concentrations are often at the levels of several tens of ppt and occasionally at the levels of few ppb.

Because flow-back fluids contain variable amounts of fine colloidal materials, it was necessary to filter each sample prior to its analyses for REEs and other chemical constituents. We filtered each water sample first through coarser than 0.45 micron Millipore filter paper, and then through less than 0.45 micrometer Millipore filter paper, and then finally through less than 0.25 micrometer Millipore filter paper. We analyzed separately the REE contents of the two finest filtered fractions of one sample (Flow-back 9) to determine if the filtering affected the analyses. For this sample we observed no difference between the two as the difference across the series between the two ranged between 3% and 8%, which is within the normal analytical errors encountered in routine analyses for the REEs made in this labo-
A Study Yielding The First Demonstration That Rare-Earth Elements Could Be A Useful Geochemical Tracer In Formation Hydraulic Fracturing Schemes For Enhanced Gas And Oil Production, cont.

Laboratory. Although it appeared to give us an encouraging set of results, this very limited test did not give us the full confidence for using a sample that is filtered only through less than 0.45 micrometer paper. Hence, all reported analytical data in this paper are on samples that were filtered through less than 0.25 micrometer Millipore filter, even though the filtering process was very time consuming for each 1,200- to 1,400-ml-filtered sample.

To have an analytically reliable set of REE data for the pre-frac fluid which could serve as the reference sample for the flow-back fluid, and to have an estimate of the analytical reproducibility of the REE data, we analyzed separately three fractions of the pre-frac fluid. The analytical differences among the three remained within 9%. We concluded, therefore, that any two samples are different in their REE contents when they differ by more than 15%.

As the concentrations of individual REE, other than La and Ce, were expected to be very low, pre-concentrated filtered fluids were used for the rare-earth analyses. The analyses for the REEs were made using an ICP-MS analytical instrument at Ecole et Observatoire des Sciences de la Terre of Université Louis Pasteur in Strasbourg, France. Routine multiple analyses of various materials with periodic checks on the analyses of a standard sample made at this laboratory have shown that the analytical results are accurate to within 10% at a 95% confidence level.

RESULTS AND DISCUSSION

The REE concentrations of pre-frac and flow-back fluids are given in Table 1. The total concentration of REEs (with the exclusion of Lu which is normally very low in concentration as compared to others and which was not measured in this study) ranged from about 6.29 ppb for the pre-frac fluid to about 3.80 to 4.46 ppb for the flow-back fluids. Figure 4 shows the relative differences in REE concentrations among the different fluids. Very commonly investigations of REEs for their use as a tracer in studies of sedimentary systems have sought to examine the distribution patterns of the REEs of individual samples by selecting a comparison either with the PAAS or the NAS. PAAS-normalized or NAS-normalized relative distribution patterns of the fluids have some noticeable features.

Figures 2a and 2b. PAAS-normalized (x10^6) REE distributions of flow-back fluids.
of them have an apparent LREE enrichment and some degree of a negative Ce anomaly, which is reflected by the fact that the measured normalized Ce value is less than the projected or calculated normalized Ce value based on the average value between that of La and of Pr which are the two immediate neighbor elements of Ce. In addition the pre-frac fluid, but not the flow-back fluids, appearance to show a MREE enrichment, an aspect that deserves some notice. One clearly evident feature is seen with one of the back-flow frac-fluids, namely the Flow-back 2 fluid. It was found to have a prominent positive Eu anomaly.

The PAAS-normalized REE distributions cast some light on the interactions between the pre-frac fluid and the targeted formation. The pre-frac fluid, by coming into contact with the fracture-induced surfaces of the targeted formation, apparently lost part of its REE load. This is clearly evident from the REE concentration data. Whereas the pre-frac fluid had a REE concentration of 6.29 ppb, the flow-back fluid samples had REE concentrations between 3.84 and 4.46 ppb.

As previously indicated, REEs have strong affinity for O donors. The Woodford Shale in the studied well contains a number of O donor minerals to which REEs could be bonded. The common minerals in the Woodford Shale, as reported by Andrews (2009), are clay minerals, quartz, carbonate minerals, and phosphate minerals. The concentrations of the REEs in all the flow-back fluids warrant consideration in terms of the influence of these minerals.

The PAAS-normalized relative distribution pattern of the REEs in the pre-frac fluid was found to have a MREE enrichment (Figure 1). The flow-back fluids, by contrast, lacked any such trend. Quartz, although it can absorb REEs on its surface, is not known to cause any fractionation among the REEs. It can be safely concluded that quartz had no role in changing the REE distribution pattern of the pre-frac fluid. Like quartz, clay minerals, by way of surface adsorption reaction, could cause a reduction in the concentration of the REEs but without any significant influence on the relative distribution pattern. But clay minerals are well known for their ion-exchange ability. Because clay minerals are typically a major carrier of REEs, ion-exchange events could have influenced the relative REE-distribution patterns of the flow-back fluids. It is not unusual to find clay minerals with varied Eu and Ce anomalies and varied relative REE distributions. The surfaces of carbonate minerals (calcite and dolomite) have a much lower affinity for REEs than the surfaces of clay minerals. Carbonate minerals do not have any inherent crystalllochemical that would selectively exclude or include either Eu or Ce. But by way of reactions with fluids, the minerals can provide carbonate ligands which can en-
A Study Yielding The First Demonstration That Rare-Earth Elements Could Be A Useful Geochemical Tracer In Formation Hydraulic Fracturing Schemes For Enhanced Gas And Oil Production, cont.

able the fluids to become HREE enriched. Wood (1990) and studies by several others have reported that the stability of the REE complexes increase progressively with increases in the atomic number of the elements. Phosphate minerals, which are known to occur as nodules in the Woodford Shale (Andrews, 2009), can have an impact on the relative distribution of the REEs. Byrne et al. (1996) reported that phosphate ligands form relatively strong complexes with the MREEs.

To obtain a clue as to significance of clay and phosphate minerals on the relative REE distributions in the different fluids, we analyzed aluminum (Al) concentrations in both the pre-frac and the flow-back fluids. No discernible correlation is evident between the Al and total REE concentrations, at least not for the small number of samples analyzed in this study. Nevertheless, it became apparent in the present study that the Al concentration of the pre-frac fluid was significantly much higher (about 864 ppb) than any of the flow-back fluids (130 to 380 ppb). Thus, in one respect, the hydro-fracturing had nearly the same effect on the Al and the total REE concentrations. The flow-back fluids were found to have lower concentrations of these elements than the pre-frac fluid. A process may now be conceived for not only the decrease in concentrations of both Al and REEs, but also the selective removal of the enriched MREEs in the pre-frac liquids. To explain the chemistry of the flow-back fluids compared to the pre-frac fluid, we envision that a reaction occurred between the pre-frac fluid and the Woodford Shale which resulted in the precipitation of Al-bearing phosphate phases.

The REE geochemical signatures of the flow-back fluids collected in this study clearly reveal that the Flow-back 2 has a pronounced positive Eu anomaly, as normalized to the PAAS. We cannot clearly establish with the information at hand how this anomaly occurred, although a positive Eu anomaly can occur in some minerals (especially feldspar) due to a crystallochemical effect in which Eu$^{2+}$ is preferred over Eu$^{3+}$. We suggest that cross-formation fracture development may have been responsible for this distinctive REE distribution feature. To provide additional evidence in support of this claim, we examined the pattern of relative distribution of REEs in all the flow-back liquids relative to the REEs of the pre-frac fluid. The pre-frac normalized relative REE distributions of the flow-back fluids are shown in Figures 2a and 2b. It is clear from these figures that while all flow-back fluids were with a pronounced HREE-enrichment trend, Flow-back 2 was found to be different from the others by having not only a positive Eu anomaly but also a positive Ce anomaly. The other flow-back fluids, while while lacked in any kind of positive or negative Eu anomaly, all had varied degrees of negative Ce anomalies, unlike Flow-back 2 which had a positive Ce anomaly. A likely cause for the Flow-back 2 fluid with positive Ce and Eu anomalies would be that this flow-back fluid encountered a different formation, in comparison to what other flow-back fluids encountered.

A closer look at the HREE-enrichment trends of all the flow-back liquids brings out further distinction between the Flow-back 2 fluid and the rest. The pre-frac normalized Yb/Gd ratio for each flow-back fluid is used as a measure of their relative degree of HREE enrichment. The pre-frac normalized Yb/Gd ratio of the Flow-back 2 fluid was found to be about 3.03, whereas that of the others ranged from 2.17 to 2.67, four of which had very similar values (2.17 to 2.30) and the remainder (the Flow-back 1) with the value of 2.67. The stability constants of complexes of REEs with carbonate ligands and also with carboxyl ligands have been known to increase with increases in the atomic numbers (Wood, 1990). Hence, a higher REE enrichment for the Flow-back 2 fluid would suggest that this fluid likely encountered either a distinctly different carbonate formation (a source for the carbonate ligand) or encountered a distinctly different organic-rich formation (a source of carboxylic ligands) (availability from organic materials) or both, in comparison to what the other flow-back fluids encountered. It may be that the induced fracture
or fractures related to Flow-back 2 fluid likely went out of the producing formation. Whether the cross-formation fracture propagated into the overlying or underlying formation could not be determined from the data gathered from this study. Perhaps Sr-isotope analyses of such fluids may be useful for determining the extent of induced-fractures and whether or not they extend beyond the target formation.

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**References Cited**


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**Biographical Sketch**

S. Chaudhuri, a professor of geochemistry at Kansas State University, has authored two books on isotopes in sedimentary rocks, clay minerals and waters. He has made some important contributions to the understanding of the origin of oil-field brines and of the evolution of clay minerals in weathering and sub-surface diagenetic environments. Some of his recent works are on the biogeochemistry of the rare-earth elements in plant-mineral-microbe interactions. He was an invited professor of CNRS and Louis Pasteur University (now known as the University of Strasbourg) in France and received a special recognition for his scholarship from the French National Academy of Sciences.