Evolution of H–O isotopes from fracturing flowback fluids for shale gas wells: A case study in Chongqing, China

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Abstract. The hydrogen and oxygen isotopes of the fracturing flowback fluids from 3 wells in the Longmaxi Formation in Dazu area of western Chongqing, China provides insights into the source of the flowback fluids. We use the valued of δ²H and δ¹⁸O, combined with concentrations of ions to discuss the changing rule of H and O isotopes throughout the flowback period. The values of δ²H and δ¹⁸O for Z2 and Z5 wells show different changing trends. But he values of δ²H and δ¹⁸O for Z2 and Z5 wells have similar changing trends. There is no obvious correlation between hydrogen and oxygen isotopes for 3 wells. The fracturing fluids, formation brines, meteoric water, and water-rock reaction can change the H and O isotopes for flowback fluids from shale gas wells.

Keywords: hydrogen and oxygen isotopes, flowback fluids, shale gas well

1. Introduction
Shale gas is a new and clean gas energy. The successful development of shale gas in the United States has had an important impact on the global energy pattern. Shale gas exploration and development is at the exploratory and experimental stage, and some achievements have been made in China [1]. Horizontal Wells have gradually formed at home and abroad. "Well factory" type large-scale sliding water or "sliding water + linear glue" stage fracturing, synchronous fracturing mainly, to achieve the purpose of "volume transformation" shale gas fracturing main technology [2]. Large volumes of water are used for fracturing. More than 20, 000 m³ water was used for per well during a year in Marcellus Basin [3]. Likewise, mean water use of is more than 30,000 m³ per well in Weiyuan and Fuling gas field from Sichuan basin in China [4-6]. About 60-80% of the injected fracturing fluid is returned to the surface [7].

Some studies on the isotopes of the flowback fluid have been done, such as follows. Sr isotope ratios
can be used to sensitively differentiate between Marcellus Formation produced water and other potential sources of TDS into ground or surface waters [8]. The late stage flowback contains concentrations of Ra$^{226}$, Ra$^{228}$, far higher than drinking water limits from Marcellus wells [9]. Skalak [10] found accumulations of $^{226}$Ra and Sr in roadside soils resulted from the use of road spreading of brines from oil and gas wells for deicing. In the Appalachian Basin, flowback from the Marcellus Shale has distinctive trace element (B/Cl, Li/Cl) and isotopic ($^{87}$Sr/$^{86}$Sr, $\delta^{11}$B, $\delta^{7}$Li, $^{228}$Ra/$^{226}$Ra) fingerprints that are different from those in produced waters from conventional oil and gas wells [11]. Osselin [12] quantified the extent of flowback of hydraulic fracturing fluids using chemical and isotopic tracer approaches, such as $\delta^{2}$H and $\delta^{18}$O, and demonstrated that the mixing scenario is the only applicable model explaining the increase of salinity in the flowback water. The concentrations of minor and redox-sensitive metals, and $\delta^{2}$H, $\delta^{18}$O, $\delta^{7}$Li, $\delta^{11}$B, and $^{87}$Sr/$^{86}$Sr in produced waters, can be used to evaluate water-rock interactions in a fracturing fluid-rock-in situ brine system [13]. The mixing ratios vary for some wells depending on whether Cl concentration or $\delta^{18}$O and $\delta^{2}$H isotopic values are used to calculate the percentage of formation water [14]. Chongqing is one of the important producing areas of shale gas in China. But there is lack of isotope research on fracturing flowback fluid in shale gas wells from Chongqing. Hydrogen and oxygen are the main elements in the flowback fluid, and their isotope changes are helpful to understand the characteristics of the flowback fluid. The main purpose of this study is to discuss the hydrogen and oxygen isotope characteristics of three shale gas wells in Dazu area of western Chongqing to understand the source of flowback fluid.

2. Samples and Analytical Methods
In this study, time-series fracturing flowback fluids from three shale gas Wells (Z2, Z5, and Z6) was collected over a period of 80, 25, and 62 days, respectively. The Shale gas wells are located in Dazu, city of Chongqing, China. Samples of flowback fluids are collected in brown plastic bottles, each about 2 liters in volume. Z2, Z5, and Z6 were hydraulically fractured from July 7th to August 10th 2017, November 5th to August 10th 2019, and July 17th to August 21th 2019. After the samples were transported back to the laboratory, water and sediment were separated after standing for 2-3 days. A portion of the separated aqueous solution is used for hydrogen and oxygen isotope analysis.

Isotopic compositions of H ($\delta^{2}$H) and O ($\delta^{18}$O) of water were analyzed by MAT-253 Mass spectrometer at the Stable Isotope Lab at East Mineral Development Technology Research Institute, Chenghua District, Chengdu. The accuracy of hydrogen and oxygen isotope analysis are ±2‰ and ± 0.1‰, respectively. All isotope values are reported in per mil (‰) relative to VSMOW (Vienna Standard Mean Ocean Water), as in:

\[
\delta^{2}H \text{ (or } \delta D) = \left[ \frac{(D/H)_{\text{sample}}}{(D/H)_{\text{V-SMOW}}-1} \right] \times 1000 \quad (1)
\]

\[
\delta^{18}O = \left[ \frac{(^{18}O/^{16}O)_{\text{sample}}}{(^{18}O/^{16}O)_{\text{V-SMOW}}-1} \right] \times 1000 \quad (2)
\]

3. Results
The $\delta^{2}$H and $\delta^{18}$O values of produced water from Z2, Z5, and Z6 range from −42.38 to −14.90‰, −34.07 to −32.43‰, and −28.48 to −19.90‰ for $\delta^{2}$H, and −5.77 to +4.98‰, +25.62 to +28.64‰, and −0.85 to +2.19‰ for $\delta^{18}$O, respectively (Fig. 1). The values of produced water are different from the values of organic matters from the Longmaxi Formation ($\delta^{2}$H = -38.64 to -32.38‰, $\delta^{18}$O = +1.66 to 2.60‰; unpublished data).

The hydrogen and oxygen isotopes of the flowback fluids for the three wells have different trends. The values of $\delta^{2}$H for Z2 well showed a stepwise increase over time during the first 40 flowback days, ranging from -42.38‰ to -14.9‰. After 40 days, the $\delta^{2}$H values range from -17.83‰ to -16.75‰. The correlation coefficients between ion concentrations and values of $\delta$D and $\delta$18O are given in Fig. 1. There is obvious correlation between the values of $\delta^{2}$H and Na+, K+, Ca2+, Ba2+, Mg2+, Sr2+, and Cl− concentrations, with the correlation coefficient ranging from 0.86 to 0.94. The values of $\delta^{18}$O for Z2 have a small change in the first 5 flowback days, and begins to decline after reaching the highest value on the 10th day, and changes little after 40 days, ranging from -5.77‰ to -5.53‰. The correlation between the values of $\delta^{18}$O and the concentration of anion and cation is not good, except for HCO3−.
Fe$^{3+}$ (correlation coefficients are 0.62, 0.6, respectively). There is no obvious correlation between the values of $\delta^2$H and $\delta^{18}$O for Z2 (Fig. 2).

Fig. 1 The values of $\delta$D and $\delta^{18}$O versus flowback times for fracturing flowback fluids from three shale gas wells.

The values of $\delta^2$H (ranging from -32.43‰ to -34.07‰) for Z5 well show a decreasing trend in the
first 5 days of flowback, and gradually increased from 5th to 15th day (ranging from -34.07‰ to -33.25‰). Then the values change in a narrow range (from -33.25‰ to -33.34‰) from 15th to 25th days. The values of δ¹⁸O (from 25.62‰ to 28.64‰) for Z5 gradually increased significantly in the first flowback 10 days, but the change (from +27.85‰ to +27.27‰) is small, from 15th to 25th days.

There is no correlation between the values of δ²H and cations, except for SO₄²⁻, with the correlation coefficient 0.94. The correlation coefficients of oxygen isotopes with all cations are less than or equal to 0.8, and the correlation coefficients with Li⁺, Na⁺, K⁺, Ca²⁺,Cl⁻ are 0.74, 0.73, 0.74, 0.70, and 0.69, respectively. There is no obvious correlation between the values of δ²H and δ¹⁸O for Z5 (Fig. 2).

The values of δ²H and δ¹⁸O for Z6 well increased rapidly in the first 10 flowback days, and the values of δ²H and δ¹⁸O increased from -28.48‰ to -22.17‰, from -0.76‰ to +0.92‰, respectively. Both the values increased slowly from 10th to day 36th days, with increasing from -22.17‰ to -19.9‰ for δ²H values, and from +0.92‰ to +2.04‰ for δ¹⁸O values, respectively. From the 41st to the 62nd day, the range of δ²H and δ¹⁸O values was small, ranging from -25.70‰ to -23.98‰, and from 1.61‰ to 1.67‰, respectively.

The correlation coefficients between the values of δ²H and ions concentrations are the same as these of between the values of δ¹⁸O and ions concentrations for the flowback liquids from Z6 well, and all the coefficients do not exceed 0.7. The correlation coefficients between δ²H and δ¹⁸O values and concentrations of Na⁺, K⁺, and Ca²⁺ are 0.56, 0.67, and 0.65, respectively, and the correlation coefficient is 0.58 for Cl⁻. There is no obvious correlation between the values of δ²H and δ¹⁸O for Z6 (Fig. 2).

Fig.2 The values of δD versus δ¹⁸O for fracturing flowback fluids from three shale gas wells. I, II, III, and IV refer to type I, II, III, and IV brines in Sichuan Basin [15].

4. Discussion and Conclusions
In the mixed model of fracturing fluid and formation water, δ²H, δ¹⁸O and Cl⁻ have excellent correlation, with the two correlations are almost the same, plus the significant correlation between δ²H and δ¹⁸O values [14]. For the three wells in this study, δ²H, δ¹⁸O and Cl⁻ do not have the characteristics of a mixed model mentioned above. Therefore, the flowback fluids from the three wells are not formed by the binary mixture of fracturing fluid and formation water. The created fracture network and any natural fractures in the formation increases the area of contact and thus increases mobility of the water [16]. To some extent, the interaction between water and rock is also an exchange reaction process of stable isotopes, such as hydrogen and oxygen [17]. At the temperatures higher than 80°C, the heat absorbed by water is enough to break the polar covalent bonds inside the water molecules, and the isotope exchange speed increases. The hydrogen and oxygen isotope exchange in the water-rock reaction process is called thermodynamic fractionation, which is one of the important reasons for the difference in hydrogen and oxygen isotopes in nature [18].

The gas production layers of the three wells in this study are all below 3000 meters underground. According to the 3°C/100m geothermal gradient, the temperature formed at this depth is about 90°C,
and there are a large amount of minerals containing H and O, such as clay minerals, quartz and a small amount of organic matter and feldspar in the formation. So, obvious hydrogen and oxygen isotope exchange can occur between the water and these minerals at 90°C. Therefore, we speculate that one of the reasons for the changes in the flowback of liquid hydrogen and oxygen isotopes is water-rock reaction.

The values of $\delta^2$H and $\delta^{18}$O of the flowback fluid from Z2 well fall in the fields of type II and III underground brine and meteoric water line, indicating that the H and O isotopic compositions of the flowback fluids are affected by type II and III underground brine and meteoric water (Fig. 2). The values of $\delta^2$H and $\delta^{18}$O of the flowback fluids for Z6 well plot in the fields of type II and III underground brine, indicating that the H and O isotope compositions of the flowback fluids have contributions from type II and III underground brine (Fig. 2). The values of $\delta^2$H and c for Z5 well plot in the fields far away from the fields of Z2 and Z6, the underground brine area, and the atmospheric precipitation line, because of the larger values of $\delta^{18}$O (Fig. 2). We speculate that flowback water for Z5 well has been significantly modified by the $^{18}$O-rich materials, which may be the $^{18}$O-rich groundwater or/and stratum.

The results of this study demonstrate that the flowback fluid is a complex product of fracture fluids, formation brines, meteoric water, and water-rock reaction. The H and O isotopes are important tools that can trace the source of flowback fluids of shale wells. Our study also proves that the flowback fluids can be different even in adjacent wells in the same formation.

Acknowledgment

The authors are grateful to the Natural Science Foundation Project of Chongqing Science and Technology Bureau (GN: cstc2019jcyj-msxmX0069, and GN: cstc 2019 jcyj -zdxmX0024).

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