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Hydrogen-rich gas discovery in continental scientific drilling project of Songliao basin, Northeast China: new insights into deep earth exploration

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Supplying an ever-growing world population with industrial raw materials, energy and clean water, and at the same time addressing the threats posed by global change, these are the two fundamental challenges facing mankind today. Developing alternative energy sources, with a switch from high-carbon to low-carbon and non-carbon is of key importance globally, and China has the goal of developing new energy resources that are carbon neutral. One potentially important clean energy component of the energy mix is hydrogen because it has a calorific value far greater than that of coal, oil, and methane [1]. Presently, the main methods of obtaining hydrogen are industrial, via grey and blue technologies rely on fossil fuel-based feedstocks (with and without carbon capture, utilisation and storage, respectively). These hydrogen production processes come with a high cost and actually emit greenhouse gases, which presents a problem of unsustainability. Utilising naturally occurring molecular hydrogen in the Earth's crust is not part of the above strategies. While hydrogen certainly plays a role in chemical reactions occurring in sedimentary basins, the geological circumstances under which it can be generated, concentrated and preserved have been largely overlooked.

Hydrogen has a strong chemical activity and low density. These special physicochemical properties cause the hydrogen to preferentially be in the form of organic compounds, such as the hydrocarbon components in natural gas [2]. In petroliferous basins, tectonically active zones, geothermal regions and volcanic rock

regions worldwide, the content of hydrogen in natural gas varies widely. Some contain only a trace amount of hydrogen, and some are mainly composed of hydrogen, for example, a well in Mali, West Africa, produced almost pure hydrogen, and it has been commercially exploited for several years [3]. Hydrogen can be generated from both inorganic and organic sources. Inorganic hydrogen occurrence is mainly related to the degassing of the Earth, water-rock reaction and the radiolytic decomposition of water, and organic hydrogen is mainly formed via biological processes and, in the laboratory, the pyrolysis of organic matter [4,5]. Different types of hydrogen-containing natural gas usually contain traces of nitrogen and methane, and carbon dioxide as well as other hydrocarbon gases may also be present, and the proportions of these components vary significantly [6]. The rare gas concentration and isotopic composition characteristics can be used as favorable evidence to identify the source of hydrogen, but hydrogen is prone to isotope exchange, and the isotopic composition of hydrogen is wide. There are multiple explanations for the hydrogen-rich natural gas in different regions [7]. As oil and gas exploration moves toward deep and unconventional areas, studying the geological conditions and distribution of hydrogen sources in sedimentary basins, and discussing the genetic mechanism and prediction models of hydrogen will help to fully understand the potential of deep natural gas resources. Hydrocarbon generation by the thermal evolution of source rock organic matter is a complex reaction process. After conventional primary and secondary cracking has concluded, the generation of hydrogen might significantly affect the production of alkanes in the high thermal evolution stage. The diversity of hydrogen genesis makes it a relevant link between organic and inorganic hydrocarbon generation theory [8]. There are rare studies on geological conditions of hydrogen generation in China, and the hydrogen distribution and formation mechanism in sedimentary basins are not clear. Here we report the highly encouraging discovery of hydrogen-rich gas, thanks to insights afforded by the Continental Scientific Drilling Project, Songliao Basin, Northeast China, and offer some preliminary insights into its possible origins.

The sedimentation time of the Songliao Basin during the Cretaceous period was 86 Ma, and the late Cretaceous sedimentation area exceeded 26×10^4 km^2, making it the

world's largest super-large lake basin with the longest development history [9]. The Songliao Basin has abundant natural gas resources with diverse genetic types. Most of the previous studies focused on the source analysis of alkane gas and carbon dioxide, and analyzed the geochemical evidence of organic and inorganic origins. However, the research understanding of free molecular hydrogen in natural gas has not been studied in any detail to date. The extensive and intensive exploration of new frontiers afforded by drilling deep Earth systems in China and elsewhere presents new opportunities for examining molecular hydrogen formation. Earth's structure and evolution have been investigated via several spectacularly deep boreholes, yielding important new insights into, for example, deep aqueous fluid transport and chemistry. Most recently, the Continental Scientific Drilling Project (SK-1, SK-2 and SK-3), drilled in the Songliao Basin of Northeast China from 2006 to 2021, recovered a continuous high-resolution lacustrine record that has provided the basis for investigations of paleoclimate, evaluations of resource and energy exploration protocols, the conducting of "primary" geological research, as well as enabling deep Earth exploration technologies to be developed [10, 11]. The SK-2 is located in the Songzhan structural belt in the northern part of the Xujiaweizi fault depression. The Shahezi Formation develops multiple intervals of black shale with large cumulative thickness and high organic matter content. Moreover, three high radioactive and uranium anomalous intervals occur in the Nenjiang Formation and Yingcheng Formation. During the drilling of SK-2, obvious hydrogen gas anomalies were detected in the Denglouku, Yingcheng and Basement Formations, and the hydrogen gas occurrences were distributed in various lithologies including shale, sandstone, conglomerate, volcanic and metamorphic rocks (Fig. 1). Intriguingly, molecular hydrogen has also been detected in certain intervals of SK-3.

There are indications of the presence of hydrogen in drilling wells in different areas of the Songliao Basin. The hydrogen content of deep natural gas ranges from 0.07% to 1.99% in the Saertu, Chaoyanggou, Putaohua and Fuyu blocks of the Daqing Oilfield in the Songliao Basin [12]. The hydrogen content of the natural gas ranges from 0.001% to 0.352% affected by biological activities in the shallow intervals of the northern basin area [13]. The hydrogen gas contents are abnormal with wide range of changes in

Xujiaweizi fault depression, such as 0.016% in Xushen-9 well, 0.08% in Weishen-5 well, 1.94% in Shengshengeng-2 well and 10.744% in Fangshen-7 well [14]. For the SK-2, hydrogen gas logging value ranges from 0.0012% to 2.3912% (Fig. 1). Meanwhile, we collected gas samples at different depths during the drilling process, and carried out laboratory tests using Agilent 7890A instruments in accordance with the gas chromatography standard for natural gas composition analysis (GB/T 13610-2014). The laboratory test results of natural gas composition (6460 – 6490 m) show that the hydrogen gas content is relatively high, ranging from 10.38% to 26.89%. The continuous large-thickness hydrogen gas logging anomalies in SK-2 and the exceptionally high content values confirmed by laboratory tests have brought new insights into hydrogen occurrence in the deep reaches of the Songliao Basin.

The relatively stable geochemical parameters of the associated helium are added to the identification of hydrogen origin. From the $H_2/^3He$ vs. R/Ra mapping results, it can be seen that the hydrogen in SK-2 has both crust and mantle sources, which reveals the complexity and diversity of hydrogen origin (Fig. 2). The deep seismic reflection profile result shows that there is an obvious Moho discontinuity in the deep part of Xujiaweizi fault depression (Fig. 1), and there are research reports on mantle derived inorganic natural gas in Refs. [12, 14]. Therefore, from the perspective of structural background, the deep intervals of SK-2 have the geological framework enabling the introduction and mixing of mantle derived hydrogen. According to radioactive logging results, there are two high radioactive anomalous intervals at the depths of 3096.8 – 3102.8 m (the range of GR is 164.27 API to 355.46 API) and 3168.3 – 3170.9 m (the range of GR is 174.29 API to 251.25 API). The existence of this phenomenon indicates that the high gas measurement value of hydrogen at the depth of 2814 – 3125 m in SK-2 may be related to the radiation decomposition of water to generate hydrogen. The source of these relatively high concentrations of H_2 is still an ongoing debate. For instance, the Shahezi shale formation of SK-2 has a high organic matter content, large cumulative thickness and high thermal evolution maturity, and can therefore be conjectured to provide quantitatively significant volumes of organic hydrogen. In addition, the material and energy brought by deep fluid activities may also promote the

water-rock reactions represented by serpentinization of igneous rocks to produce hydrogen [15].

Geological research into the formation and occurrence of hydrogen-rich gas is in its infancy, especially in addressing whether it can form commercial accumulations [8]. The formation and distribution of hydrogen in natural gas need to be studied in depth. There are various genetic types of natural gas in the Songliao Basin, which is an excellent laboratory for studying the formation mechanism of hydrogen, and this geological particularity provides beneficial conditions for in-depth analysis of hydrogen from different origins. The availability of high quality core material from SK wells makes an investigation of putative hydrogen generation possible. Furthermore, the hydrogen-rich gas discovery in Continental Scientific Drilling Project indicates that the Songliao Basin has potentially favorable geological conditions for hydrogen generation and storage. We expect to gain a better understanding of the origin of molecular hydrogen in the Songliao Basin, and in sedimentary basins in general.

Conflict of interest

The authors declare that they have no conflict of interest.

Acknowledgments

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Figure caption

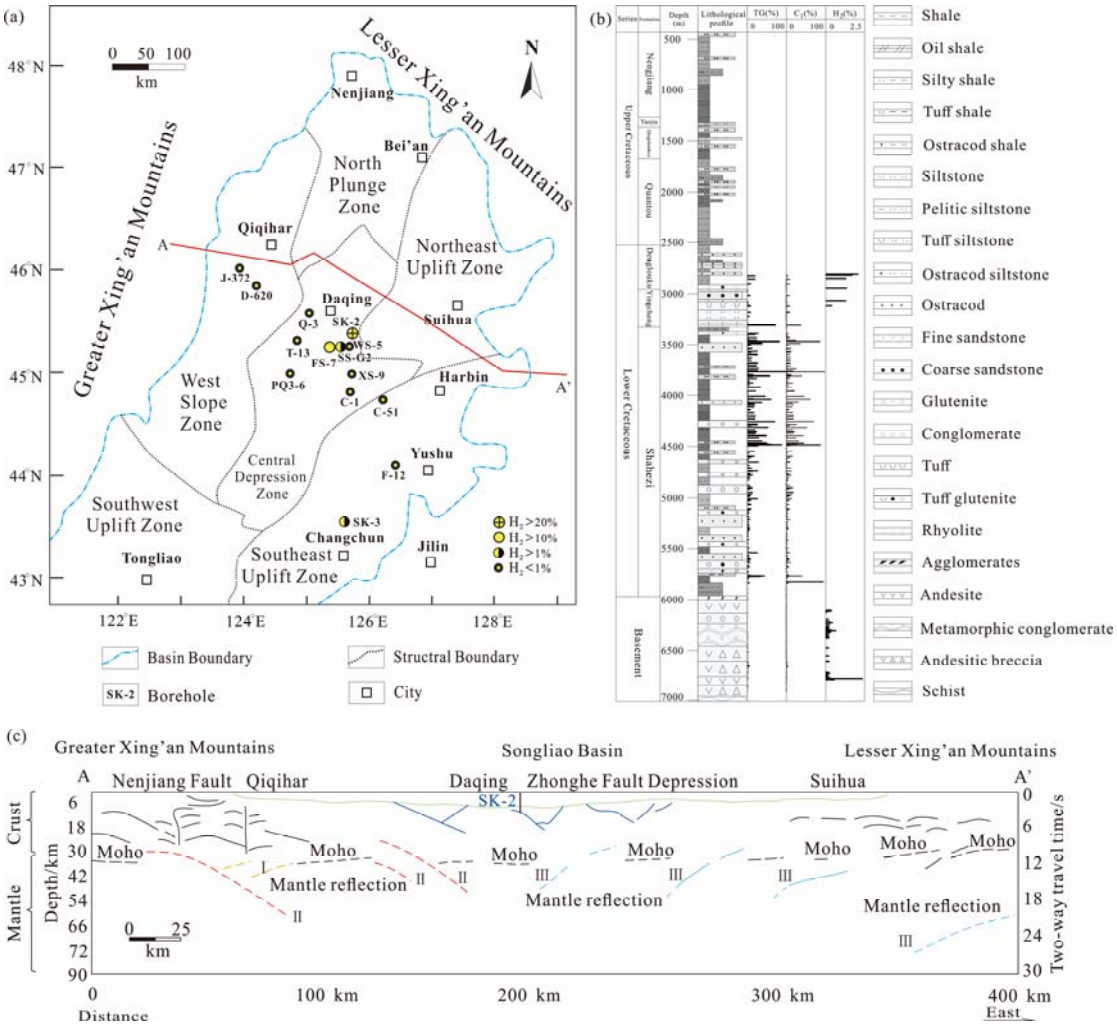

Fig. 1. Hydrogen-rich gas discovery in the Songliao Basin. (a) The hydrogen gas occurrence of different wells. (b) The hydrogen-rich gas logging data of SK-2. (c) Lithospheric section of Songliao Basin in east-west direction modified after Ref. [11].

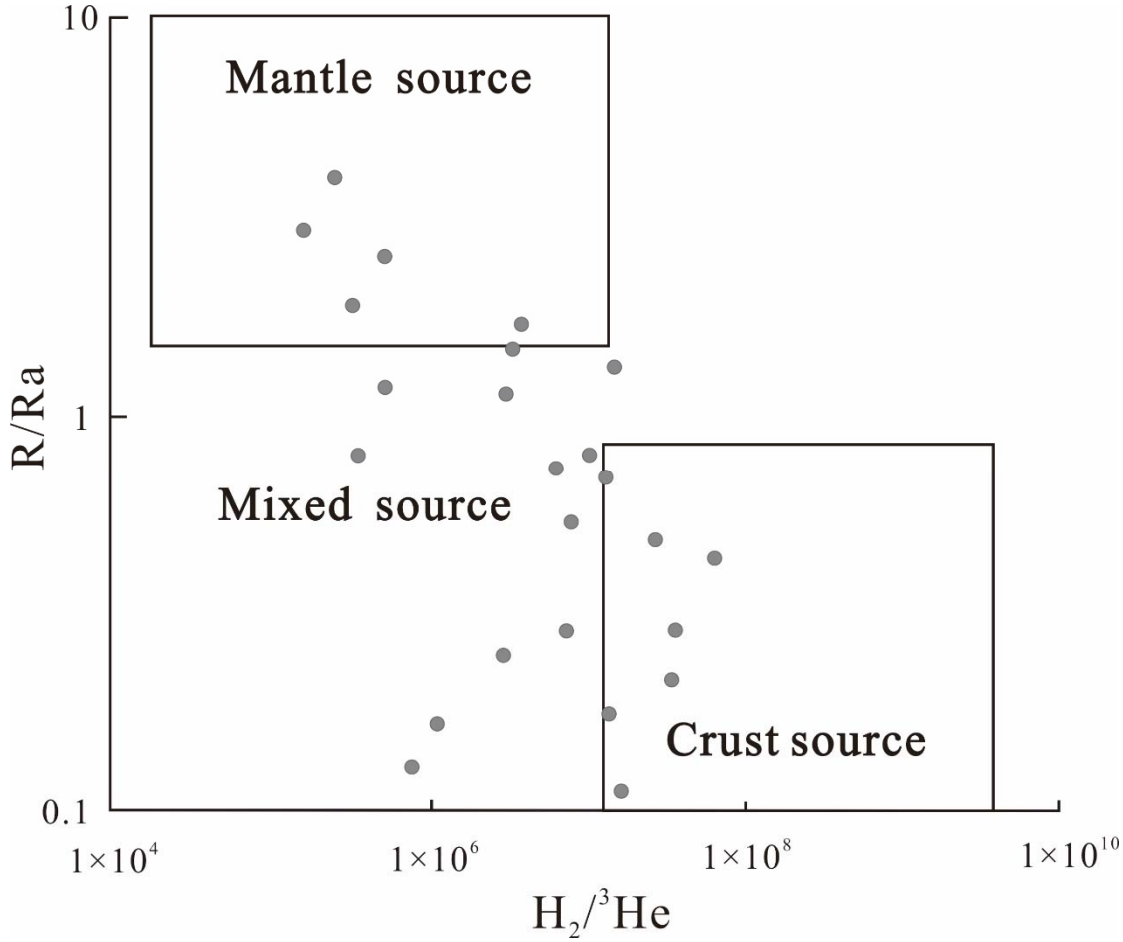

Fig. 2. Geochemical characteristics of hydrogen in natural gas of SK-2 (R: $^{3}He/^{4}He$ of the sample; Ra: $^{3}He/^{4}He$ of the air). Base map modified after Ref. [5]