

Geochemical Characteristics of Mercury in Oil and Gas

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Abstract. As an important element in oil and gas, the process of mercury formation, migration and enrichment, has an important practical significance to determine the nature and preservation status of deep oil-gas reservoirs, which can provide reliable geochemical basis for oil-gas exploration departments. Therefore, basing on the study of mercury formation, migration and enrichment, the geochemical anomaly patterns of mercury are determined, and the geochemical characteristics in oil and gas are discussed. Study shows that the mercury have strong affinity with oil and gas, and it will migrate and accumulate with the maturation of kerogen; Because of the abyssal faults, magmatic activity and deep geological process, in some petroliferous basins, the oil type gas have higher mercury content; On the basis of geochemical anomaly characteristics and morphological combination of mercury in surface, the anomaly patterns in oil and gas geochemical exploration are summarized to guide the anomaly interpretation and evaluation of testing zone, so as to provide the reliable geochemical basis for oil and gas exploration department.

1. Introduction

Because of the high dispersion of mercury in the lithosphere, the natural gas has the low mercury phenomenon. However, due to the secondary enrichment caused by chelation and cation exchange of coal, humus and sulfide to mercury, making the natural gas in many mercury enrichment areas are rich in mercury [1]. Form the migration, transformation and enrichment of mercury in the ore source layer, to a series of physical and chemical reactions of mercury from the ore source layer into the natural gas, they will be controlled by various geological factors, and which will determine the origin, content and distribution of mercury in natural gas [2]. Therefore, based on the origin and associated effect of mercury in petroleum and natural gas, the mercury anomaly pattern and formation mechanism are summarized, so as to provide a reference for oil and gas exploration.

The abnormal enrichment of mercury is a new geochemical prospecting method, which has the advantages of good stability and high abnormal recurrence rate [3]. In the early 80s, the adsorption phase mercury technique was applied to oil and gas geochemical exploration, and proved by practice that it has good oil and gas exploration effect, and is an effective index for oil and gas geochemical exploration. But at present, we lack the systematic understanding of mercury anomaly formation processes, morphological types or patterns, and methods for recognizing anomalies and techniques for evaluating anomalies [4]. Therefore, it is urgent to summarize the abnormal patterns of mercury above oil and gas reservoirs, analysis the formation mechanism, and innovate the effective methods, to guide oil and gas exploration and play the role of oil and gas geochemical exploration.



2. Sources of mercury in oil and gas

More and more evidences prove that the mercury has strong affinity with oil and gas, the mercury in the nature circle migration, circulation and accumulation constantly [5]. For the different mercury in different spheres, their origin and occurrence are also different. So, in the process of migration and transformation, the different geological background and environmental conditions (oxidation and reduction) make the distribution of mercury in coal and oil are different [6].

2.1. Mercury in source rocks

The formation of oil and gas is a process of thermal evolution, and with this process, the mercury in natural gas will be enriched from the source bed to the oil and gas continuously, and the different ability to absorb mercury, will inevitably lead to different mercury content from the different source rocks of parent materials [7]. The mercury is relative rich in terrigenous organic matter, and the content of mercury in oil type gas which is produced by mixed humic organic matter is usually lower than produced by humic type organic matter, so the difference of mercury content can be used as an important index to identify coal formed gas and oil type gas effectively.

In general, the rock and coal are not the main reasons that the mercury enrichment in natural gas, and it is probably produced by the magmatic hydrothermal activity. Coal has strong absorption capacity and can be used as the “middle storage station” of mercury. In the coalification, due to mercury in coal with the lowest of melting point, boiling point and heat of vaporization in the metal, so it is easy to deepen gasification with burial depth, and it will migrate with the gas channel that generated by coalification, into the trap. Therefore, when the gas-forming of coal is formed, the mercury content is high. So in the analysis of mercury content in natural gas, on the one hand from the main source of mercury-hydrothermal activity, on the other hand to study mercury enrichment and preservation conditions, this may be the reason why the mercury in gas reservoir is higher than that in coal field gas. (Table 1).

Table 1. Mercury content in natural gas bearing basins in China

Basins	Natural gas		Coal-formed gas		Oil-type gas	
	Scope (ng/m ³)	Arithmetic mean	Scope (ng/m ³)	Arithmetic mean	Scope (ng/m ³)	Arithmetic mean
Ying Qiong basin	430000–450000	440000	430000–450000	440000	—	—
Liu He basin	14400–1930000	216100	25200–52500	36900	14400–19300	298800
Huang Hua basin	170–7000	1190	—	—	170–7900	1510
Ji Zhong basin	170–256000	64640	610–256000	108600	170–142000	20600
Pu Yang basin	130–140000	12540	1440–140000	48640	130–1100	510
Si Chuan basin	40–125100	7830	250–125000	36400	40–400	690
Ordos basin	40–48100	7780	390–48000	10830	40–230	150
Junnar Basin	200–5450	2010	5450	5450	270–320	290
Traim Basin	170–8780	—	3530–8780	5680	170–2340	890
Qaidam Basin	760–9848	3970	4510–9840	5330	760–1840	1300

2.2. Inorganic mercury

The mercury from the deep earth is meaningful, according to the phenomenon that the mercury in hydrothermal origin mercury and crude oil near San Joaquin Valley oilfield in California, USA, Bailey, etc. proposed that mercury in oil and gas comes from ore-forming fluid in the deep of the earth.

In space, mercury deposits, oil and gas field and deep fracture zone is often three-in-one. For example, the mercury content is generally high in California, USA, while the mercury content of oil are mostly from San Joaquin Valley, which Cymric oilfield produced the highest mercury content of oil, up to $3 \times 10^4 \text{ ng/m}^3$. Cymric San Joaquin Valley oilfield is located in the west, and associated with the mercury deposits of New Almaden, New Idria (Fig.1). The above oil and mercury deposits are

controlled by the San Andreas great fault, which be explained that the oil and gas fields with high mercury content have the same tectonic background, that is, they are distributed in the compound and transfer sites of the giant tectonics, which is related to the great faults and deep faults zone.

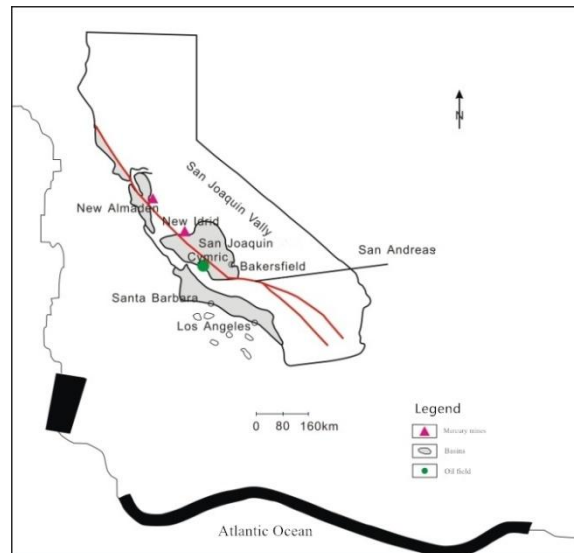


Figure 1. The location of Cymric San Joaquin Valley oilfield

At present, many scholars believe that the mercury is related to the tectonic activity and deep geological action of the basin [8]. Under normal circumstances, the faults are exists in the basin, due to the presence of the earth's deep source of mercury, the mercury content in oil and gas is high. For example, the mercury content is highest in extensional active basin in eastern China, while the middle cratonic stable basin is relatively low, and followed by the Northwest Asia stable Basin (Fig. 2).

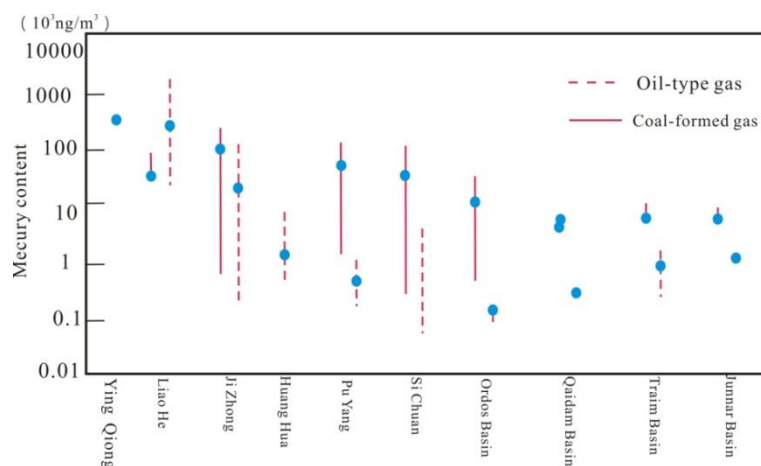


Figure 2. The distribution of mercury in oil-formed gas and coal-formed gas

3. Mercury migration

Due to the large ionization potential of mercury, mercury can be reduced to Hg⁰ in various forms, while Hg⁰ is highly volatile, and the volume is smaller than water, so that when the mercury diffusion and migration, it will has a great ability to penetration [9]. The mercury in oil-gas reservoirs, in order to maintain a certain physical and chemical equilibrium with the outside world, it will through the pores, peripheral faults and fractures, and accompanied with the cyclic action of groundwater, penetrating through thick rock upward diffusion, migration to the surface, and the formation of

mercury anomalies in the surface soil layer.

Mercury can not only migrate in gaseous, but also in the form of complexes with organic matter. In recent years, the geochemical effects of Hg in oil-gas exploration have been paid more and more attention, and the inspiration has been drawn from the similarity of oil and gas fields and mercury deposit formation conditions [10]. The global mercury ore belt distribution along with the convergent plate boundary with compressional properties, in the space, adjacent to the convergent sedimentary basin of huge oil and gas fields in Alaska, California, Indonesia and some parts of the Mediterranean Sea (Fig.3). About 90% of the Hg ore bodies occur at the top of the anticline, about 86.4% of oil and 88.4% of natural gas are distributed in anticline type reservoirs.

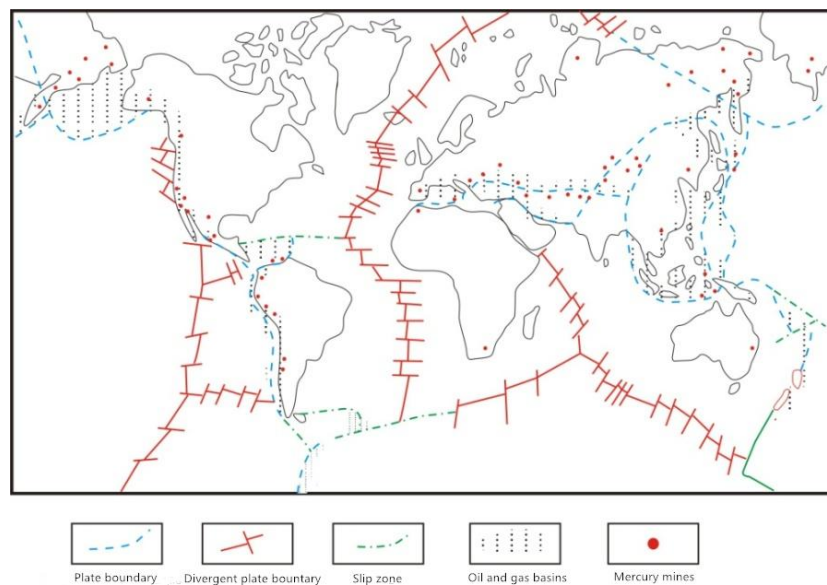


Figure 3. The major mercury mine and oil and gas basin in the world

The high porosity rocks under the weak permeable layer are both favorable positions for Hg and oil and gas reservoir occurrence. 75% of natural gas and 42% of oil are distributed in sandstone; terrigenous rocks (clastic rock) in the occurrence of Hg reserves of 75%, about 20% in carbonate rocks. Both of them have similar formation temperature and pressure conditions. Oil generation is mainly in the 1.5~6 km depth, and the temperature is range from 60 to 150Mpa, while the temperature and pressure conditions of the Hg deposit are from 70 to 170 °C and from 60 to 100Mpa accordingly. Mercury and oil and gas are similar in metallogenic epoch, both of them are mainly formed in Mesozoic Cenozoic Era.

4. Geochemical significance of mercury in oil-gas

The physical, chemical and geochemical properties of mercury are special, creating the complexity of mercury distribution in natural environment and oil and natural gas. Oil and gas contain different amounts of mercury more or less, which is directly related to the migration of mercury. But practice shows that because of different types of reservoirs, the hydrocarbon and associated group structure, characteristics of reservoir and cap rock, the migration loss method of components are different, the corresponding mercury enrichment patterns are also different, showing that mercury anomaly patterns are not the same.

4.1. Diversification characteristics of mercury anomaly

4.1.1. Mercury anomaly in annular. This abnormal index not only showed annular, half annular, embayment distribution in gas reservoir of edge, but also above the gas reservoir is the massive and banded, but its abnormal strength is slightly lower than the abnormal side gas reservoir (Fig.4). But at the specific natural gas reservoir, the abnormal distribution of different indicators of annular may be having a certain displacement or the horizontal zoning law has some differences. However, most of the indicators, especially the natural gas reservoir hydrocarbon anomaly of ring are basically consistence to each other. Such as the Yangxin sag area stores found the heat release mercury anomaly, which the anomaly were distribution of irregular large annular with strong north and weak south, and the anomaly of hydrocarbon forms a high concentration of half annular anomaly in the inner ring of mercury anomaly. It is inferred that the anomaly may be related to oil and gas reservoirs, and probably is the gas reservoirs. After verification by Y-16 well, the $418 \times 104 \text{ m}^3$ of natural gas and nearly 30m thick oil reservoir were obtained under the well depth of 1500m.

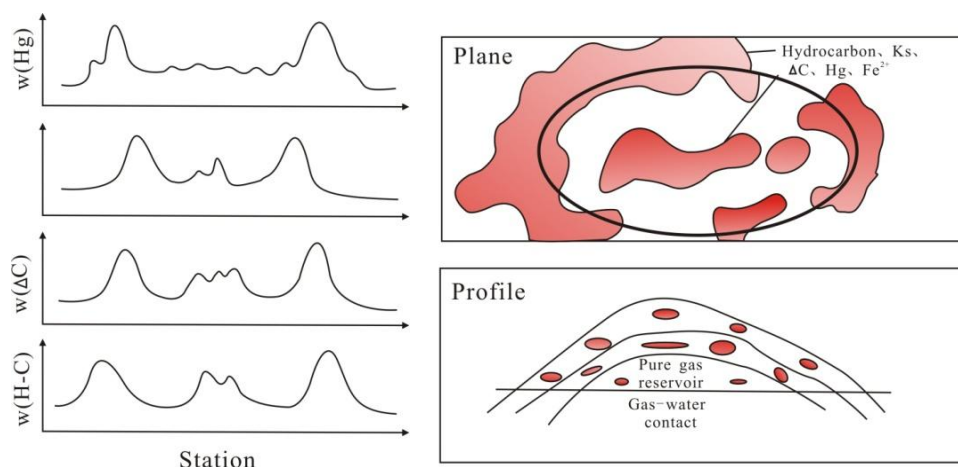


Figure 4. Geochemical anomaly pattern in the upper part of the gas reservoir

4.1.2. Mercury anomaly in massive. The main indicators of the model are regular or irregular planar or massive in shape and distributed in the upper part of the natural gas reservoir, that is often called the "top of the halo". This is mainly due to when the cap layer sealing property is poor, the hydrocarbons and mercury are transported vertically to the surface from the oil-gas reservoirs in various ways, such as percolation, diffusion and micro bubble, and showing a variety of irregular massive mercury anomaly. The mercurimetric survey showing, the southwest of Wan'an Basin found a large mercury anomaly area, including the two anomalies of No. 6 and No. 11 (Fig.5). The No. 6 is the medium anomaly of the sea, the morphology is regular and with a large scale. The anomalies located at the sedimentary center of north and south basin, the world famous Daxiong oil field is in the abnormal range, the area is about 50 km^2 , the recoverable oil is estimated at 7-8 billion barrels ($1.1 \sim 13 \text{ m}^3$), and with a large number of unassociated gas.

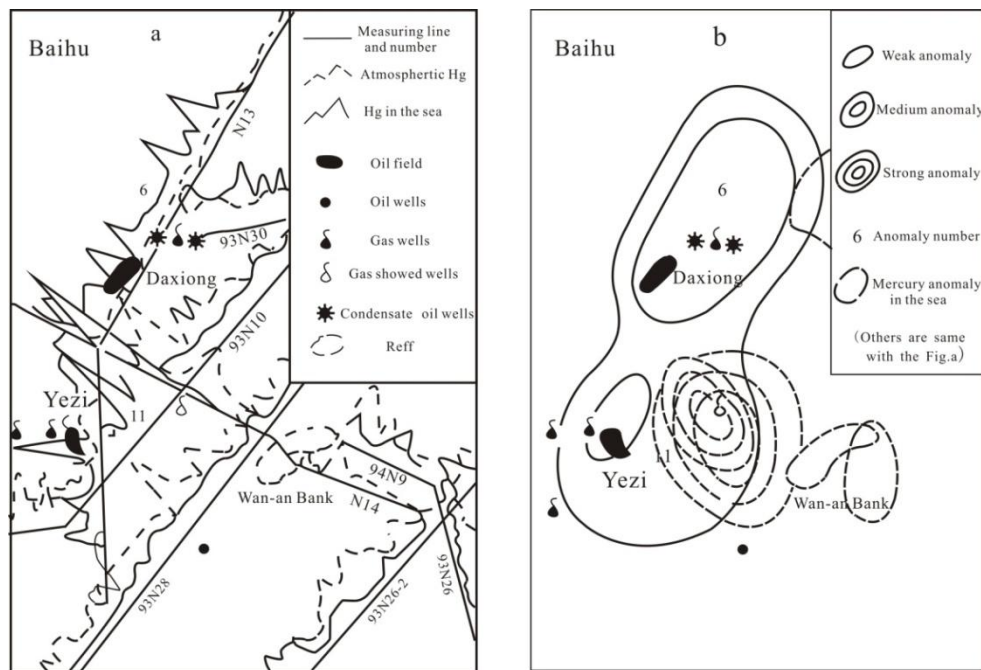


Figure 5. The anomaly distribution and content of mercury in Wan'an Basin

The 11 anomaly is located in the southern slope of the NO.6. It is a complex anomaly which is composed by the atmospheric mercury and mercury in the sea. The anomaly has a large scale and with good continuity, the Yezi oil field and a lot of wells are in the range.

4.2. Duality of mercury sources

The results show that, the anomaly of adsorption phase Hg and adsorption hydrocarbon often showed great differences, which absorbed mercury exhibits good ring halo or ring top halo anomaly, but the adsorption of hydrocarbon anomaly is very weak, scattered or not even. At the same time, the mercury in the adsorbed phase is not a reflection of oil and gas reservoirs, but an empty trap structure in the deep underground. For example, in Southwest Sichuan Z1 gas reservoir, the combination of the adsorbed phase mercury and the adsorbed hydrocarbon anomaly is very different, and the C1 anomaly of the Z1 gas reservoir is characterized by the top halo, and the abnormal body is in the middle of the abnormal prospect area; While the Hg is a "halo feature top" loop, the abnormal C1 abnormal distribution around the outer edge of the subject (Fig.6).

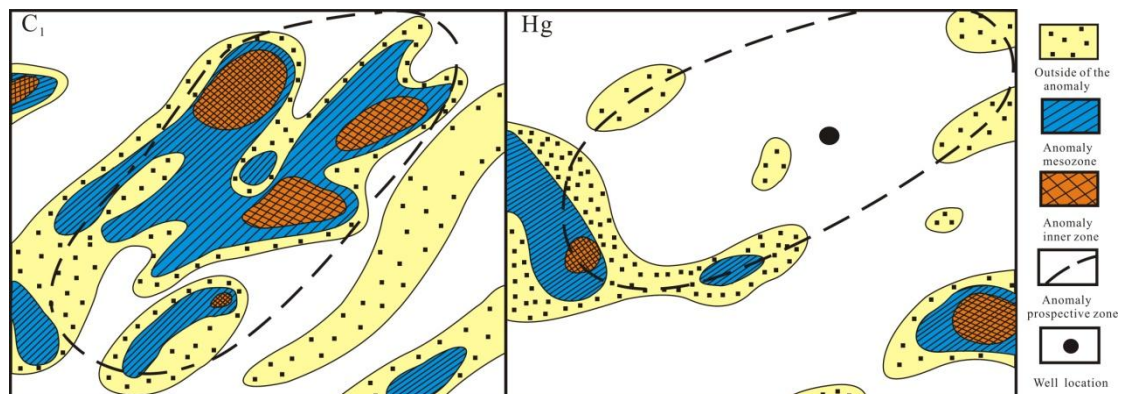


Figure 6. Duality of mercury sources

It can be seen the Hg from the deep underground oil and gas has two kinds of source, one is released in the process of oil and gas generation is released in the oil and gas generation process of Hg; And the other is from the deep of the earth to the oil and gas production layer through the fault channel. Because of the two character of the Hg source, leading to the double indication of the adsorption phase Hg anomaly.

4.3. The mechanism of oil-gas geochemical anomaly model

In the past 40 years, a large amount of dates obtained from the practice of oil and gas geochemical exploration have proved that the formation of geochemical anomaly is not controlled by a single factor[11-12]. The dispersion and migration of oil and gas is complex with each other. In addition, the complex effects of physical, chemical, physical, chemical and biochemical factors will occur in the process of percolation, that is to say, the fugitive migration is a dynamic system, its initial or boundary conditions with the change of geological environment and dynamic change, this is an important point of the main oil-bearing basins of the world. The conceptual model of Figure 7 is mainly based on the main factors of migration mechanism, dynamics, channel, phase, rate, intensity, microbial action and mineral alteration, and the formation mechanism of oil and gas geochemical anomalies were displayed by the system.

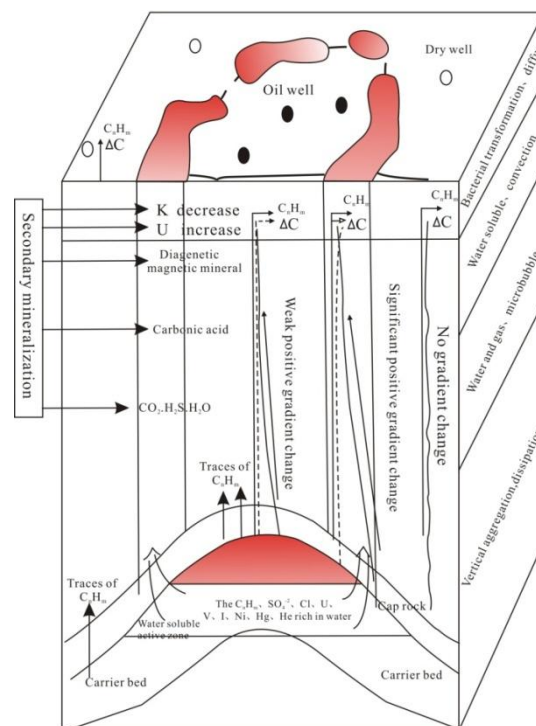


Figure 7. Basic mechanism of oil and gas geochemical exploration

5. Conclusion

1) The formations of mercury in natural gas are organic and inorganic. The organic origin refers to the mercury in natural gas from hydrocarbon source rocks, and the gas content is influenced by different types of parent material source, in general, the mercury content in coal type gas is higher than the oil type gas; The inorganic origin refers to the mercury in natural gas, which is mainly comes from the deep of the earth's ore-forming fluid, and the mercury content in natural gas is higher than that the oil bearing basin that with the basement fault structure and magmatic activity.

2) Both of the oil and gas are contain of the mercury composition, physical and chemical properties of mercury element can not only determine it can migrate as the form of gaseous, forming a certain

abnormal pattern on the surface, but also can be transported in the form of complexes with organic matter.

3) In the geochemical exploration of oil and gas, the characteristics of surface geochemical anomalies and morphology can determine the nature and preservation status of deep oil and gas reservoir. According to the above rules, the geochemical anomaly of oil and gas can be comprehensively interpreted and evaluated, and get the more accurate results, so as to make an objective and scientific prediction for the prospective area of oil and gas exploration and the location of underground oil and gas reservoirs, and provide reliable geochemical exploration for oil and gas exploration departments.

6. References

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