

Article

Not peer-reviewed version

Occurrence Characteristics of Gold in Crude Oil and Its Geological Significance

[Zhiyong Ni](#)^{*}, Wen Zhang, [Jie Liu](#), Shenbao Shi, [Xue Wang](#), Yang Su

Posted Date: 29 December 2023

doi: 10.20944/preprints202312.2290.v1

Keywords: crude oil; gold; affinity; organic acid



Preprints.org is a free multidiscipline platform providing preprint service that is dedicated to making early versions of research outputs permanently available and citable. Preprints posted at Preprints.org appear in Web of Science, Crossref, Google Scholar, Scilit, Europe PMC.

Copyright: This is an open access article distributed under the Creative Commons Attribution License which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

Article

Occurrence Characteristics of Gold in Crude Oil and Its Geological Significance

Zhiyong Ni ^{1,2,*}, Wen Zhang ^{1,2}, Jie Liu ^{1,2}, Shengbao Shi ^{1,2}, Xue Wang ^{1,2} and Yang Su ^{1,2}

¹ National Key Laboratory of Petroleum Resources and Engineering, China University of Petroleum (Beijing), Beijing, China. 102249

² College of Geosciences, China University of Petroleum (Beijing), Beijing, China. 102249

* Correspondence: nizhy@cup.edu.cn.com

Abstract: Gold and petroleum are also strategic resources of great importance to national security. With the increasing demand for energy, multi-energy cooperative exploration has become an inevitable trend of resource development and utilization. Petroleum and hydrothermal gold deposits may form together, with similar evolutionary trends in their formation, migration, and enrichment. Petroleum reservoirs and gold deposits are closely coupled under certain geological conditions. The solubility of gold in crude oil and its forms of occurrence are important in determining the mechanisms of interaction between gold and petroleum and in facilitating the recovery of gold from gold-bearing petroleum. In this study, the occurrence of gold in crude oil from the Linnan Depression in the Bohai Bay Basin, China, was studied using inductively coupled plasma–mass spectrometry and X-ray photoelectron spectroscopy. Concentrations of gold in crude oil from the Linpan and Shanghe oilfields averaged 44.5 ppb, which is well above the minimum concentration required for hydrothermal gold mineralization. Gold has an affinity with carbon, oxygen, and sulfur, and its concentration in crude oil is positively correlated with total acid and sulfur contents. We speculate that gold may exist in crude oil as complexes with organic acids or thiols, with crude oil thus being a transport medium for gold.

Keywords: crude oil; gold; affinity; organic acid

1. Introduction

Petroleum and low-temperature hydrothermal Au deposits may form together and exhibit similar evolutionary trends in their formation, migration, and enrichment. Under certain circumstances, oil reservoirs and low-temperature hydrothermal Au deposits such as Carlin-type deposits exhibit a close coupling relationship on macro to micro scales [1–6] that may manifest in three ways, as follows. (1) Oil and gas reservoirs and Au deposits may have similar spatial distributions. For example, northeastern Nevada, USA, hosts abundant Carlin-type Au deposits and contains numerous oil and gas fields [7,8]; such deposits are also widely developed in the Youjiang Basin, China, together with numerous ancient and residual oil and gas reservoirs [9,10], and many low-temperature hydrothermal Hg, Sb, As, and Au deposits are distributed in the Tongren–Wanshan and Kaili–Majiang–Danzhai paleo-reservoir belts of eastern Guizhou Province, China [11]. (2) Hydrothermal Au deposits provide records of oil and gas activities. Carlin-type deposits are a type of low-temperature hydrothermal deposit containing ore-bearing rocks that are rich in organic matter, with evidence of organic components participating in mineralization [12]. Liquid-hydrocarbon inclusions have been found in Carlin-type Au deposits in Nevada, and temperature analyses have indicated that the capture temperature of oil-containing inclusions is below 150°C and within the oil-generation window (80°C–160°C) [7,13]. In the Shuiyindong Au mine in the Youjiang Basin, the ore is rich in organic matter and bitumen, and CH₄, CO₂, and N₂ inclusions occur in ore-bearing quartz veins. The sources of these inclusions have been linked to decomposition of organic matter [14–18]. (3) Many types of organic matter are enriched in metals. For example, lower Paleozoic dark mudstones of eastern Guizhou, China, are rich in organic C and elements such as Au, V, Ni, and Mo, with metal contents often being positively correlated with total organic C contents. These mudstones are considered “double-source beds” with both mineral and hydrocarbon sources [19,20].

There are also examples of metal-rich bitumen of varying maturity [21]. For example, the Boss deposit in Nevada has a high Au content of 1.3 mg g^{-1} in bitumen within dolomitic limestone. Scanning electron microscopy studies have shown that Au is present in the bitumen in the form of an Hg alloy $[(\text{Pd}_{81}, \text{Au}_{13}, \text{Pt}_{01}) \text{Hg}]$ [22]. It is possible that metals can be transported in crude oil [23–26]. Contents of Au in the Shengli oilfield, China, are close to the industrial grade of 980 ppb [27], which is several orders of magnitude higher than the average abundance of Au in continental crust (5 ppb). However, there are few examples of the industrial recovery of Au from crude oil worldwide, and there have been no reports of the recovery of Au, Ag, and other precious metals in China because of the difficulty in their recovery.

Although many low-temperature hydrothermal Au deposits and oil and gas reservoirs are closely coupled, the mechanisms of ore-formation and oil-accumulation coupling in the interaction between Au and hydrocarbons are poorly understood. Currently many geologists have focused on the role of hydrocarbon fluid in the metallogenic process, ability of mobilization and transportation of metal elements and metallogenic mechanism of hydrocarbon fluid during basin evolution [3,4,26]. Noble metals such as gold are thought to play a catalytic role in the process of hydrocarbon generation to improve the efficiency of hydrocarbon generation [5]. Petroleum are considered to provide reduced sulfur directly or indirectly for sulfide precipitation during mineralization [1]. It remains unclear whether crude oil can directly participate in the formation of low-temperature hydrothermal Au deposits as a migration medium, but there have been relatively few studies of contents and forms of Au in crude oil worldwide. This study focused on the Linnan Sag in the Bohai Bay Basin to determine the Au content of crude oil and its form(s) of occurrence. Our results provide insights into the migration of Au in petroleum and its recovery from crude oil.

2. Geological Setting

The Linnan Sag is located in the southwest of Huimin Depression, Bohai Bay Basin, and contains Linpan oil-field, Shanghe oil-field, Jiangjiadian oil-field and Linan oil-field and so on [28]. The Linnan Sag is controlled by the Linshang and Xiakou Fault in northern and southern edge, respectively (Figure 1).

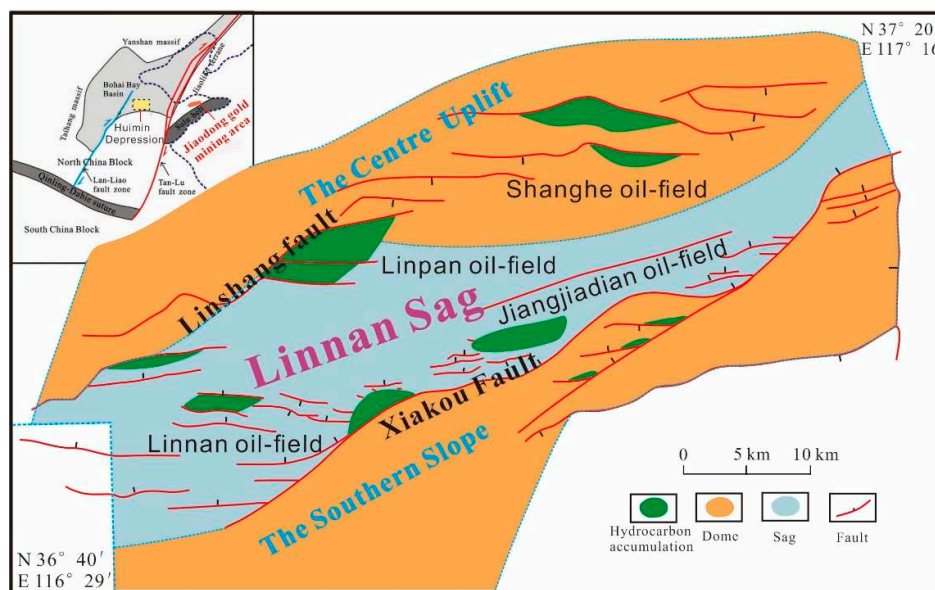


Figure 1. Simplified structural map of the Bohai Bay Basin, sketch map of Linnan Sag and the main oil fields (modified by reference [28]).

The Linnan Sag is the main source kitchen of the Huimin Depression, and the distributions of oil-field are mainly controlled by faults. The Cenozoic tectonic movements of this region include five stages: the initial rifting stage (66.0–46.0 Ma), the intense rifting stage (46.0–38.0 Ma), the shrinking

rifting stage (38.0–24.6 Ma), the uplift stage (24.6–14.0 Ma), and the subsiding stage (14.0–0.0 Ma). There exist the unconformity between the Paleogene and Neogene sequences due to uplift during the Dongying movement (24.6–14.0 Ma). The Cenozoic strata in the Linnan Sag comprise the Paleogene Shahejie Formation (Es) and Dongying Formation (Ed), the Neogene Guantao Formation (Ng) and Minghuazhen Formation (Nm), and the Quaternary Pingyuan Formation (Qp) [29]. The Es formation is divided into four parts, which are labeled, respectively, as Es4, Es3, Es2, and Es1 from the bottom to top (Figure 2).

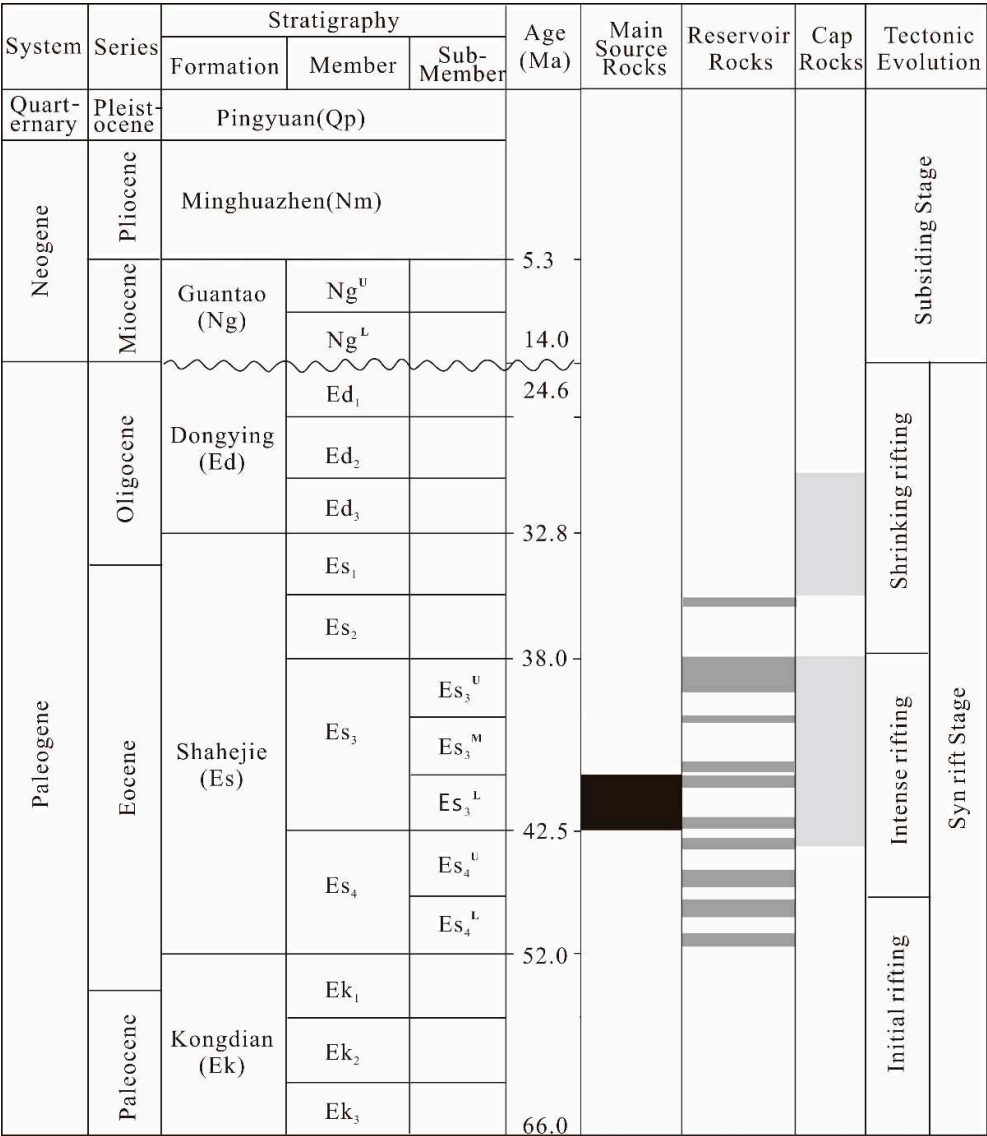


Figure 2. Schematic Cenozoic stratigraphy and tectonic evolution of the Linnan Sag.

The widely distributed lacustrine mudstones and shales in the lower part of Es3 are the dominant source rocks with an average total organic carbon content (TOC) of 1.55%. The conglomerate and sandstone in the Es4, Es3, and Es2 are main reservoirs, and Paleogene mudstones are regional cap rocks [30]. It is worth noting that China's famous Jiaodong gold mining area is distributed in the eastern part of the study area (Figure 1).

3. Materials and Methods

Crude oil samples were collected from formations in the Linpan and Shanghe oilfields of the Linnan Sag. The main production beds of crude oil were the Paleogene Shahejie and Neogene Guantao formations. The samples were black solids or viscous semi-solids at room temperature with densities of $>0.90 \text{ g cm}^3$ (i.e., heavy oil).

3.1. Determination of Au contents

The measurements of elemental analysis were performed at the Analytical Instrumentation Center of Peking University. Microwave digestion and inductively coupled plasma-mass spectrometry (ICP-MS) were employed to determine the Au contents of crude oil. An UltraWAVE ECR (Milestone, Italy) microwave digestion system was used: 50 mg of crude oil or its components was weighed into a dry digestion tank, 2% HNO_3 was added (1.5 mL), and the sample was sealed and heated to 260°C for 20 min for microwave digestion. The sample was then cooled to below 50°C and transferred to a 30 mL volumetric flask for analysis.

A NexION 350X (PerkinElmer, USA) ICP-MS system was used for elemental analysis, with a three-cone interface (sampling, interceptor, over-interceptor cones), a triple four-pole ion deflector, and a universal cell technology with a wide linear range. Working parameters were set by automatic optimization, with a transmission power of 1250 W, carrier-gas flow rate of 0.82 L min^{-1} , peristaltic pump speed of 20.0 rpm, scanning 20 times, and triplicate sample analyses. The standard-addition method was used with internal standards containing Ni, V, and other elements.

3.2. Au-tube thermal simulation

The Au-tube thermal simulation equipment was developed by the State Key Laboratory of Oil and Gas Resources and Exploration, China University of Petroleum (CUP), Beijing, China. Au-tube thermal simulation treatments were undertaken at 420°C and 40 MPa with a reaction time of 72 h. The tube was 60 mm long with an inner diameter of 5.55 mm and wall thickness of 0.25 mm. A mudstone sample (15 mg of low-maturity source rock from the Bohai Bay Basin) and 160 mg deionized water were placed in the tube, which was sealed by welding in an Ar gas flow. The tube was opened after cooling.

3.3. XPS analysis

Residual oil on Au-tube surfaces was analyzed by XPS (ThermoFisher, USA) at the CUP using Al K α radiation, a spectral range of 0–1100 eV, 20 eV resolution, 0.1 eV step size, and a spot diameter of 300 μm . The instrument etched the Au tube inner surfaces with X-rays for periods of 0, 30, and 60 s, and changes in carbon (C), oxygen (O), nitrogen (N), Sulfur (S) and gold (Au) concentrations with etching depth were recorded. ORIGIN software was used for graph plotting.

3.4. Determination of total acid values of crude oil

The total acid values (TAN) of crude oil samples were determined by acid-base titration (GB/T 264, PRC National Standard) at the CUP. Crude oil samples (2 g) were dissolved in 25 mL neutral ethanol in a conical flask, and anhydrous ether (25 mL) was added. A blank sample containing 25 mL ethanol and 25 mL ether was also prepared. Phenolphthalein solution (1 mL) was added to each of the mixtures, titration with 0.1 mol L^{-1} KOH was undertaken until the pink endpoint, and the acid value was calculated by $\text{TAN} = (V1 - V2) \times C \times 56.1$, where V1 is the volume of KOH used in sample titration, V2 is the volume of the KOH solution used in the blank titration, and C is the concentration of the KOH solution.

4. Results

4.1. Crude oil Au, S, and total acid contents

Twenty-five crude oil samples from the Shahejie and Guantao formations were selected for Au and S analysis; the results are shown in Table 1. Au contents ranged from 12.0 to 107.5 ppb with an average of 44.5 ppb. S contents ranged from 0.10 to 0.56 wt.% (average 0.32 wt.%). The TAN values ranged from 0.64 to 1.75 mg g⁻¹ (average 1.17 mg g⁻¹).

Table 1. Contents of Au and S and total acid values of crude oil samples.

Oilfield	Well	Fm.	Depth (m)	Density (g/cm ³)	Viscosity (mpa.s)	S (%)	TAN (mg/g)	Au (ppb)
Linpan	L2-x201	G2	1414.4-1423.6	0.945	377.75	0.51	1.63	13.4
Linpan	L23-11	G3	1642.2-1645.0	0.923	90.90	0.37	0.95	105.3
Linpan	L55	S3	2626.6-2992.8	0.866	11.07	0.12	0.92	90.7
Linpan	L7-x28	S2	1799.2-1823.6	0.909	27.46	0.10	0.64	12.0
Linpan	L75-17	S3	1859.2-1909.0	0.918	138.00	0.35	1.11	24.4
Linpan	L75-x30	S4	2474.0-2512.6	0.895	18.00	0.35	1.09	16.0
Linpan	L76-3	S4	2069.0-2094.0	0.893	41.00	0.10	0.82	32.4
Linpan	P14-6	S4	1588.6-1594.4	0.986	5951.00	0.50	1.39	36.6
Linpan	P18-x3	S3	1597.1-1630.3	0.935	119.00	0.42	1.21	38.1
Linpan	P20-6	S1	1556.0-1599.4	0.936	352.30	0.25	1.36	63.1
Linpan	P2-504	S3	1576.0-1606.4	0.965	921.00	0.56	1.21	23.2
Linpan	P40-12	G	1337.6-1354.0	0.960	384.00	0.41	1.49	47.9
Linpan	P40-17	G	1345.4-1350.4	0.951	324.00	0.38	1.33	31.4
Shanghe	S23-70	S2	1710.0-1734.2	0.897	48.94	0.25	0.9	57.2
Shanghe	S25-11	S4	2044.2-2126.8	0.899	48.84	0.14	1.28	18.9
Shanghe	S25-40	S4	1969.6-2267.8	0.897	58.23	0.44	1.21	107.5
Shanghe	S42-2	S2	1655.2-1675.4	0.932	140.30	0.44	0.7	27.3
Shanghe	S70-x5	S2	2348.5-2374.0	0.863	11.26	0.25	1.22	17.5
Shanghe	S73-13	S2	2275.8-2334.2	0.892	40.10	0.37	1.75	34.3
Shanghe	S8-29	S2	1854.2-1859.4	0.887	21.49	0.36	1.52	29.0
Shanghe	S8-300	S2	1776.0-1833.0	0.900	27.90	0.24	0.74	69.0
Shanghe	S8-33	S1	1653.0-1675.0	0.946	322.10	0.50	1.14	83.9
Shanghe	S84-4	S1	1899.0-1903.6	0.872	24.27	0.25	1.31	-
Shanghe	S847	S1	1884.6-1890.4	0.883	29.89	0.17	1.18	41.1
Shanghe	S8-52	S2	1846.0-1861.0	0.897	37.84	0.11	1.15	26.2

4.2. XPS analyses

After the Au-tube thermal simulation, the tube was cut open to reveal the inner wall covered by generated crude oil. The tube with the most oil was analyzed by XPS, and spectra of Au, C, N, O, and S were recorded for etching times of 0, 30, and 60 s (Figure 3). The double peaks of Au (4f_{5/2} and 4f_{7/2}) were clear, with corresponding binding energies of 82 and 86 eV, respectively. Carbon (1s), N (1s), O (1s), and S (4p_{3/2}) had respective XPS peaks at 283, 398, 530, and 162 eV. Origin software was used to process the data, and the results indicate that peak areas of Au, C, and O increased with etching time, whereas that of N decreased (Figure 3, Table 2).

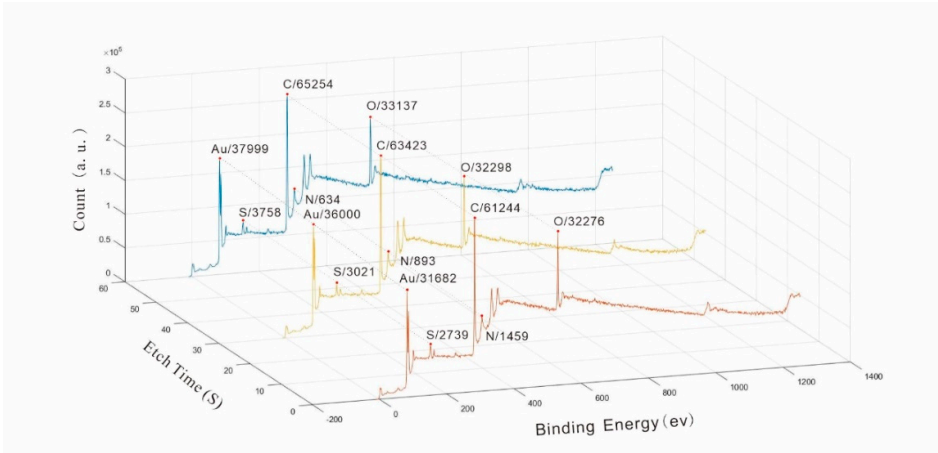


Figure 3. XPS peak areas of Au, C, N, O, and S at etching times of 0, 30, and 60 s.

Table 2. Elemental XPS spectral characteristics.

Eleme nts	Spectral Line	Etch Time (s)	Peak Area	Peak Center (ev)	Eleme nts	Spectral Line	Etch Time (s)	Peak Area	Peak Center (ev)
Au	4f5/2	0	31682	82	N	1s	0	1459	398
Au	4f5/2	30	36000	82	N	1s	30	893	398
Au	4f5/2	60	38000	82	N	1s	60	634	398
Au	4f7/2	0	26368	86	O	1s	0	32276	530
Au	4f7/2	30	30378	86	O	1s	30	32299	530
Au	4f7/2	60	32330	86	O	1s	60	33137	530
C	1s	0	61244	283	S	4p3/2	0	2739	162
C	2s	30	63423	283	S	4p3/2	30	3021	162
C	3s	60	65254	283	S	4p3/2	60	3758	162

5. Discussion

The average Au content of raw oil samples from the Linpan and Shanghe oilfields was 44.5 ppb. The industrial Au grade is typically 0.3–0.5 g tonne⁻¹ (300–400 ppb). Although the average oil Au content is below industrial grade, it may have economic value if an appropriate recovery method is used. The Linpan and Shanghe oilfields are in the Linpan oil-production block, which has an oil-bearing area of 174.6 km² with geological reserves of 283 million tons (Mt) and recoverable reserves of 84 Mt. Based on the average crude oil Au content, the total recoverable Au would be 84 × 10⁶ × 44.5 × 10⁻⁹ = 3.74 tons, which is equivalent to a small Au mine. Soft/hard acid–base theory [31] implies that Au, as a soft acid, would tend to bind to soft bases such as organic acids and reduced S [32–34]. Previous studies have shown that there is strong correlation between contents of N, O, S, and other heteroatoms and metal elements in crude oil [35,36]. XPS peak areas represent relative contents, and our results (Figure 3) indicate that Au and C peak areas are positively correlated with etching time (i.e., depth), implying a close relationship between Au and organic matter in crude oil. The relative content of O also increased with etching depth, indicating a further correlation between Au and oxygen contents. Trends in Au, carbon, and oxygen contents were similar, indicating that Au has a strong affinity for C- and O-containing compounds in crude oil. Most O exists as carboxylic acids in crude oil [9]; therefore, Au contents may be closely related to carboxylic acid contents. The relative abundance of S increases with etching depth, and its binding energy corresponds to the XPS peak of Au–thiolate complexes (162.4 eV; Figure 4) [37,38], implying that at least some Au in crude oil may exist in the form of Au thiolate [39–41]. The relative abundance of N decreased with increasing etching depth (Figure 3), indicating no close relationship between Au and nitrogen compounds.

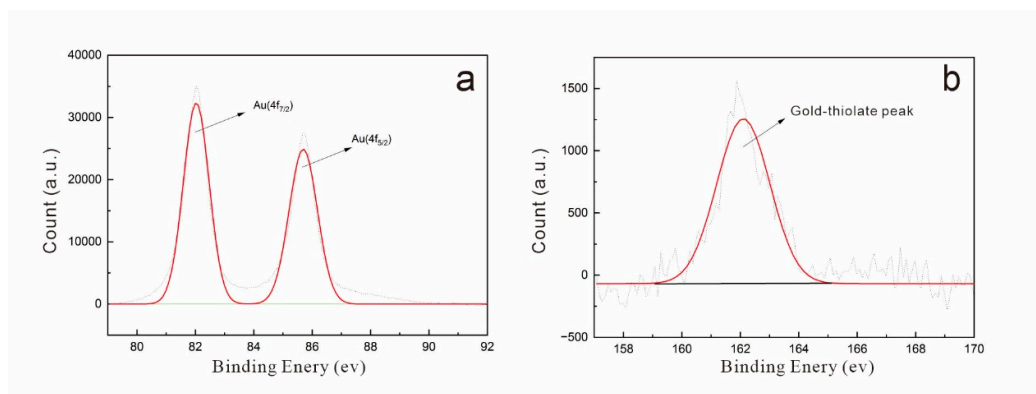


Figure 4. XPS spectra of Au and thiolate.

To further investigate the occurrence of Au in crude oil, a correlation analysis of Au contents, TAN values, and S contents of 25 crude oil samples was undertaken (Figure 5). When the TAN value was below 1.1, there was a positive correlation between Au content and TAN value; with values above 1.1, there was no obvious correlation. When the oil S content was below 0.35 wt.%, Au contents were positively correlated with S contents, but not at higher S contents. The most important determinant of the TAN value of crude oil is the content of organic acids such as carboxylic acid and naphthenic acid [42]. Organic acids are generally formed by biodegradation, as a by-product of bacterial metabolism [43,44]. Contents of N, O, S, and other heteroatoms increase as crude oil undergoes biodegradation [45,46]; therefore, we speculate that crude oil samples with higher TAN values (>1.1) and S contents (>0.35 wt.%) may have been affected by biodegradation, resulting in insignificant correlation between Au contents and TAN values or S contents. The TAN values and S contents would increase through biodegradation, whereas Au contents would not. This may be due to biodegraded crude oil having a stronger ability to complex Au through its high TAN value and S content, but it would fail to bind more Au owing to its low fluidity.

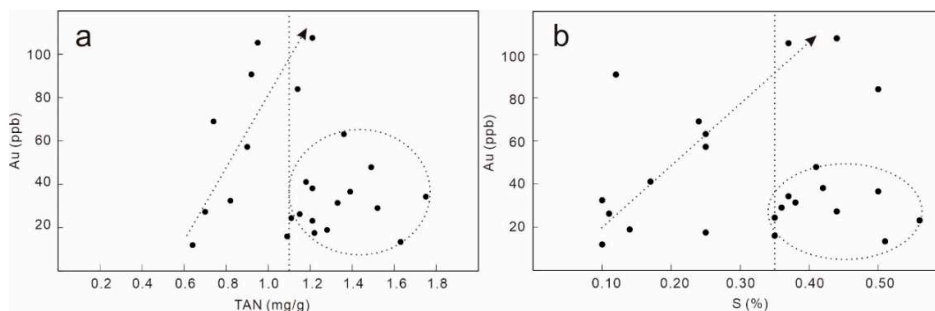


Figure 5. Relationships between crude oil Au contents and (a) total acid (TAN) values and (b) S contents.

6. Conclusions

Crude oil may function as an effective ore-forming fluid for Au deposits, with Au existing as organic acid salts and thiolates. Oilfield brine rich in organic acids and organic S may also act as potential ore-forming fluids. Some black shales are rich in metal elements and although organic-rich shales (e.g., the Shahejie Formation) generate oil, the metal elements may migrate with crude oil to spaces favorable for enrichment, resulting in coupling between oil reservoirs and low-temperature hydrothermal Au deposits.

Author Contributions: Formal data analysis, Ni Z. Y., Zhang W., Liu J. Shi S. B., Wang X. and Su Y.; project administration, Ni Z. Y.; writing original draft, Ni Z. Y. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by National Natural Science Foundation of China (Grant No. 42273069).

Data Availability Statement: The data presented in this study are available on request from the corresponding author. The data are not publicly available due to privacy.

Acknowledgments: The help from Dr. Wu Jia, Fang Peng and Liang Yun of CUP and Dr. Liu Jiahui of Peking University in experiments were acknowledged.

Conflicts of Interest: The authors declare no conflict of interest.

References

- Gu, X. X.; Zhang, Y. M.; Li, B. H.; Xue, C. J.; Dong, S. Y.; Fu, S. H.; Cheng, W. B.; Liu, L.; Wu, C. Y., The coupling relationship between metallization and hydrocarbon accumulation in sedimentary basins. *Earth Science Frontiers* **2010**, 17, (2), 83-105.
- Clark, J. R.; Williams-Jones, A. E., Analogues of epithermal gold-silver deposition in geothermal well scales. *Nature* **1990**, 346, 644-645.
- Williams-Jones, A. E.; Migdisov, A. A., An experimental study of the solubility of gold in crude oil: Implications for ore genesis. *Geochimica et Cosmochimica Acta* **2006**, 70, A703.
- Emsbo, P.; Williams-Jones, A.; Koenig, A. E.; Wilson, S. A., Petroleum as an agent of metal transport: metallogenic and exploration implications. *Proceeding of the tenth Biennial SGA Meeting, Townsville* **2009**, 99-101.
- Hu, S.-Y.; Plet, C., Introduction to a special issue on organic- and microbe-metal interactions in mineral systems. *Ore Geology Reviews* **2022**, 146.
- Gu, X. X.; Zhang, Y. M.; Li, B. H.; Dong, S. Y.; Xue, C. J.; Fu, S. H., Hydrocarbon- and ore-bearing basinal fluids: a possible link between gold mineralization and hydrocarbon accumulation in the Youjiang basin, South China. *Mineralium Deposita* **2012**, 47, (6), 663-682.
- Hulen, J. B.; Collister, J. W.; Stout, B.; Curtiss, D. K.; Dahdah, N. F., The exhumed "Carlin-type" fossil oil reservoir at Yankee Basin. *JOM* **1998**, 50, (12), 30-34.
- Collister, J. W.; Hulen, J. B., The oil-bearing, carlin-type gold deposits of Yankee Basin, Alligator Ridge District, Nevada. *Economic Geology* **1999**, 94, (7), 1029-1049.
- Wang, G. Z.; Hu, R. Z.; Su, W. C.; Zhu, L. M., Fluid and mineralization of Youjiang Basin in the Yunnan-Guizhou-Guangxi area, China. *Science in China (Series D: Earth Science)* **2002**, 46, 99-109.
- Hu, Y.; Liu, W.; Wang, J.; Zhang, G.; Zhou, Z.; Han, R., Basin-scale structure control of Carlin-style gold deposits in central Southwestern Guizhou, China: Insights from seismic reflection profiles and gravity data. *Ore Geology Reviews* **2017**, 91, 444-462.
- Hu, Y. Z.; Han, R. S.; Mao, X. X., Relationship between metal mineralization and accumulation oil and gas in the eastern Guizhou. *Geology and Prospecting* **2007**, 43, (5), 51-56.
- Arehart, G. B., Characteristics and origin of sediment-hosted disseminated gold deposits: A review. *Ore geology reviews* **1996**, 11, (6), 383-403.
- Peters, K. E.; Walters, C. C.; Moldowan, J. M., The biomarker guide: Volume 2, Biomarkers and isotopes in petroleum systems and earth history. Cambridge University Press: 2007.
- Su, W. C., Geochemistry of the Ore-Forming Fluids of the Carlin-Type Gold Deposits in the southwestern Margin of the Yangtze Block [D]. Guiyang: Institute of Geochemistry. Chinese Academy of Sciences. **2002**, 1-120.
- Xia, Y.; Chen, Q. N.; Zhou, W. C., The simulating experiments of gold mineralization in low temperature and open system. *Journal of Nanjing university (Natural sciences)*, **1996**, 32, (4), 634-639.
- Liu, J. Z., Ore characteristics and gold occurrence of the Shuiyindong gold deposit, guizhou. *Guizhou Geology* **2003**, 20, (1), 30-34.
- Liu, J. Z.; Deng, Y. M.; Liu, C. Q.; Zhang, X. C.; Xia, Y., Metallogenic conditions and model of the superlarge Shuiyindong stratabound gold deposit in Zhenfeng County, Guizhou Province. *Geology in China* **2006**, 33, (1), 169-177.
- Liu, J. Z.; Xia, Y.; Zhang, X. C.; Deng, Y. M.; Su, W. C.; Tao, Y., Model of strata Karlin-type gold deposit: the Shuiyindong super-scale gold deposit. *Gold Science and Technology* **2008**, 16, (3), 1-15.
- Tu, G. Z., Gechemistry of strata-bound Deposits in China (Volume III). Science Press, Beijing, 1988.
- Fu, J. M.; Peng, P. A.; Lin, Q.; Liu, D. H.; Jia, R. F.; Shi, J. X.; Lu, J. L., Several problems in the study of organic gechemistry of strata-bound Deposits. *Progress in Earth Science* **1990**, 5, 43-
- Parnell, J., Metal enrichments in solid bitumens: A review. *Mineralium Deposita* **1988**, 23, 191-199.
- Jedwab, J.; Badaut, D.; Beaunier, P., Discovery of a palladium-platinum-gold-mercury bitumen in the Boss Mine, Clark County, Nevada. *Economic Geology* **1999**, 94, (7), 1163-1172.
- Baker, W. E., The role of humic acid in the transport of gold. *Geochimica et Cosmochimica Acta* **1978**, 42, 645-649.

24. Liu, J. Z., Fu, J. M., Lu, J. L., Experimental study on the role of organic matter in the mineralization of Sedimentary-reformed gold deposits. *Science in China (Series B)* **1993**, 9, 993-1000.
25. Zhang, J. R., Lu, J. J., Yang, F., Wu, J. W., Zhu, F. H., An experimental study on gold solubility in amino acid solution and its geological significance. *Geochimica* **1996**, 25, (2), 190-195.
26. Crede, L.-S.; Liu, W.; Evans, K.; Rempel, K.; Testemale, D.; Brugger, J., Crude oils as ore fluids: An experimental in-situ XAS study of gold partitioning between brine and organic fluid from 25 to 250 °C. *Geochimica et Cosmochimica Acta* **2019**, 244, 352-365.
27. Xu, Z. H., Zhan, Y. L., Zhu, J. H., Li, X., The research progress in the utilization of metal resources in crude oils. *Multipurpose Utilization of Mineral Resources* **1998**, 3, 22-26.
28. Wang, D., Wu, Z. P., Yang, L. L., Liu H., Zhang, Y., Growth and linkage of the Xiakou fault in the Linnan Sag, Jiyang Depression, Eastern China: Formation mechanism and sedimentation response. *Marine and Petroleum Geology* **2020**, 116, 104319.
29. Li, C., Zhang, L. K., Luo, X. R., Wang, B., Lei, Y. H., Cheng, M., Luo, H. M., Wang, C. J., Yu, L., Modeling of overpressure generation-evolution of the Paleogene source rock and implications for the Linnan Sag, Eastern China. *Frontiers in Earth Science* **2022**, 10, 829322.
30. Guo, X. L., Xiong, M., Zhou, Q., Tian, H., and Xiao, X. M., Petroleum generation and expulsion kinetics: A case study of the Shahejie Formation source rocks from Linnan Sag of Huimin Depression. *ACTA Sedimentologica SINICA* **2009**, 27, 723-731.
31. Pearson, R. G., Hard and Soft Acids and Bases. *Journal of the American Chemical Society* **1963**, 85, (22), 3533-3539.
32. Seward, T. M., Thio complexes of gold and the transport of gold in hydrothermal ore solutions. *Geochimica et Cosmochimica Acta* **1973**, 37, (3), 379-399.
33. Giordano, T. H., Evaluation of Organic Ligands and Metal-Organic Complexing in Mississippi Valley-Type Ore Solutions. *Economic Geology* **1985**, 80, 96-106.
34. Vlassopoulos, D.; Wood, S. A.; Mucci, A., Gold speciation in natural waters : II . The importance of organic complexing- Experiments with some simple model ligands. *Geochimica et Cosmochimica Acta* **1990**, 54, 1575-1586.
35. Sanz-Robinson, J.; Williams-Jones, A. E., The solubility of Nickel (Ni) in crude oil at 150, 200 and 250°C and its application to ore genesis. *Chemical Geology* **2020**, 533, 119443.
36. Hughey, C. A.; Rodgers, R. P.; Marshall, A. G.; Walters, C. C.; Qian, K.; Mankiewicz, P., Acidic and neutral polar NSO compounds in Smackover oils of different thermal maturity revealed by electrospray high field Fourier transform ion cyclotron resonance mass spectrometry. *Organic Geochemistry* **2004**, 35, (7), 863-880.
37. Castner, D. G.; Hinds, K.; Grainger, D. W., X-ray Photoelectron Spectroscopy Sulfur 2p Study of Organic Thiol and Disulfide Binding Interactions with Gold Surfaces. *Langmuir* **1996**, 12, (21), 5083-5086.
38. Sanz-Robinson, J.; Sugiyama, I.; Williams-Jones, A. E., The solubility of palladium (Pd) in crude oil at 150, 200 and 250°C and its application to ore genesis. *Chemical Geology* **2020**, 531, 119320.
39. Lewan, M. D., Factors controlling the proportionality of vanadium to nickel in crude oils. *Geochimica et Cosmochimica Acta* **1984**, 48, (11), 2231-2238.
40. Giordano, T. H., Metal Transport in Ore Fluids by Organic Ligand Complexation. In *Organic Acids in Geological Processes*, Pittman, E. D.; Lewan, M. D., Eds. Springer Berlin Heidelberg: Berlin, Heidelberg, 1994; pp 319-354.
41. Speight, J. G., *Handbook of Petroleum Analysis*. John Wiley & Sons Inc: 2001.
42. Park, L. K. E.; Liu, J.; Yiacoumi, S.; Borole, A. P.; Tsouris, C., Contribution of acidic components to the total acid number (TAN) of bio-oil. *Fuel* **2017**, 200, 171-181.
43. Kawamurat, K.; Tannenbaum, E. L. I.; Huizinga, B. J.; Kaplan, I. R., Long-chain carboxylic acids in pyrolysates of Green River kerogen. *Advances in Organic Geochemistry* **1986**, 10, 1059-1065.
44. Shock, E. L., Organic acid metastability in sedimentary basins. *Geology* **1988**, 16, 886-890.
45. Head, I. M.; Jones, D. M.; Larter, S. R., Biological activity in the deep subsurface and the origin of heavy oil. *Nature* **2003**, 426, (6964), 344-352.
46. Wenger, L. M.; Davis, C. L.; Isaksen, G. H., Multiple Controls on Petroleum Biodegradation and Impact on Oil Quality. *SPE Reservoir Evaluation & Engineering* **2002**, 5, (05), 375-383.

Disclaimer/Publisher's Note: The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.