DOI: 10.13656/j.cnki.gxkx.1998.04.001
广西科学 Guangxi Sciences 1998, 5 (4): 241～245

Coal-derived Hydrocarbons in Metallic Ore Deposits*
金属矿床中的煤型烃类

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Abstract Gas chromatographic data show that there are several species of hydrocarbons such as methane, ethene, propane, propylene, acetylene, isobutane, normal butane, isopentane, normal pentane and hyxane in primary aqueous inclusions. The dry-wet ratio of light hydrocarbon is very high (0.972～0.998) which is characteristic of coal-type gas. It can be considered that the light hydrocarbon in the fluid inclusions associating with coal inclusions along some healing fractures may derive from coal instead of petroleum during coalification.

Key words hydrocarbon, inclusion, mineralizing fluid, coal, tungsten

摘要 气相色谱分析表明，原生包裹体内存在着数种烃类诸如 CH_4，C_2H_4，C_3H_8，C_3H_6，C_2H_2，iC_4，nC_4，iC_5，nC_5和 C_6。轻烃的干湿比很高 (0.972～0.998)，具有煤型气的特征。流体包裹体常沿着愈合断裂与煤包裹体共生，由此推断成矿流体内的轻烃可能来自于煤而非石油。

关键词 烃类 包裹体 成矿流体 煤 钨
中图法分类号 P 618.205

It is widely documented that concentrations of metal may be associated with diverse organic materials, from living plants and animals through organic-rich sediments to crude oil, solid bitumen/pyrobitumen, and coal. The significance of organic matter in mineralizing processes has been the subject of several special publications[1～5], Henley D. et al.,[6] Burruss R. C.,[7] Rowan E. L. et al.[8] and Hu M. et al.[9] discovered various complex hydrocarbon in fluid inclusions in some metallic ore deposits such as gold, tin and lead-zinc deposits. Kvenvolden Keith A. et al.[10] began to notice the relationship between petroleum and polymetallic sulfide in sediment from Gorda Ridge. Goldberg Iosif S. et al.[11,12] studied the genesis of ore concentration in heavy oil and bitumens as well as the metallogenetic problem of heavy oils, natural bitumens and oil shales. Parnell Jonn et al.[14] determined the hydrocarbon migration into a bitumen-bearing ore deposit during petroleum evolution by means of Pb-Pb dating. According to the fluid inclusion evidence, Burruss R. C.[7] considered that there would be oil-water interaction in the ore deposits. In addition, Lu G. et al.[15] discovered and studied the genetic link between the gold-mercury mineralization and petroleum in the Danzhai mine, Guizhou, China. Based on the organic geochemical data from the bitumens in the metallic deposits, Quirk D. G. et al.[16] and Wilson N. S. F.[17] also considered that the hydrothermal petroleum might be associated with mineralization.

In 1989, Ting F. T. C. et al.[18] noticed that there would be a spatial relationship between coal metamorphism and gold-copper mineralization in the Chinkuashih district, Taiwan. Chen R. et al.[19,20] also discovered and studied in detail the spatial and genetic relationship between hydrothermally metamorphosed coals and endogenetic metallic deposits (Hg, Sb, Pb, Zn, Cu, Au, Ag etc.) in Hunan-Guangxi-Guangdong Provinces, China. Dvornikov

1998-08-10收稿，1998-09-08修回。
* 广西壮族自治区自然科学基金资助项目(桂科回 9615002)。

A. G.[21] investigated some patterns of the distribution of cinnabar in coal measures of the Donbas, Russia. Since 1992, more and more people have been interested in the relationship between coals and metallic ore deposits.[22~24]

Generally, the coals relative to the endogenetic ore deposits may be hydrothermally or magmatically metamorphosed coals, whose metamorphic ranks range from lean coal to superanthracite. It is very possible that derived-coal hydrocarbons would be carried into some hydrothermal systems during coal metamorphism or metallic mineralization. In order to determine organic matter in deposits, we analyzed light hydrocarbon of fluid inclusions in minerals from the Yaogangxian tungsten deposit, Hunan province, China.

1 Geologic Setting

The Yaogangxian area, Yizhang county, Hunan province, China, occurs in the Early Yanshanian granitoid suite, consisting of many exposed or hidden small-scale bodies and dykes. The Early Yanshanian (169–178 Ma, K–Ar dating) granite, as a principal igneous rock type, is regarded as an ore-forming parent rock at the Yaogangxian mine. Mostly, the granitic body is hidden, and the exposed area is only 1.2 km^2. There are several large-scale tungsten, tin, lead-zinc ore deposits within the granitoid suite.

The wall rocks from Sinician to Triassic can be intruded by the above-mentioned granitoid suite. The Caledonian layer (Sinician to Silurian) is distributed in the deep basement and to the east of the area. It is composed mainly of epimetamorphic quartz sandstone, slate and silicalite, locally imbedding limestone and dolomitite. The Indosinian layer (Devonian to Middle Triassic) is majorly distributed to the west of the area, consisting of sandstone, limestone, marl, dolomite, dolomitic limestone, silicalite, locally imbedding coal bed in the Early Carboniferous. Late Triassic occurs along the faulted basin nearby the Yaoganxian deposit, consisting of quartz sandstone and feldspar quartz sandstone, locally imbedding coal bed. In the northeast–southwest-trending wall rocks, locally there are many kinds of hydrothermal alteration such as sericitization, greisenization, chloritization, pyritization etc., being resulted from hydrothermal fluids relative to granitoid evolution.

The Yaoganxian tungsten deposit lies within the top belt of partly hidden granite of Early Yanshanian. It occurs in granites, pegmatites, skarns, as well as sandstones and epimetamorphic rocks intruded by the hidden granite body. The depth of mineralized rocks is from 600 m to 1400 m at above-sea level. Granite-, pegmatite- and greisen-type wolframite deposits, occurring in the upper granite body, are closely related to granite magmatism and autumetamorphism. Skarnoid scheelite deposit, lying out of the contact zone, is resulted from the interaction between Devonian limestone and the hydrothermal fluid relative to granite magma. Stockwork sandstone-type scheelite deposit, found in Devonian sandstone, is ascribed to the metasomasis and filling of hydrothermal fluid. However, quartz-vein-type wolframite deposit, a principal deposit type, occurs in the Cambrian epimetamorphic rocks, Devonian sandstone and Late Triassic sedimentary rocks, including coal bed. Tungsten mineralization is associated with the veins composed predominantly of quartz, fluorite, sericite, muscovite, pyrite and topaz. The veins were formed by the open-space filling of hydrothermal fluid.

A small-scale coal bed of Late Triassic occurs within the deposit, 650 m from the top of hidden granite body. The coal bed strikes northeast-southwest and dips to the northwest at 7°~15°; its average thickness is about 0.5 m. The coal bed can be traced for more than 500 m along strike and downdip. It is estimated that there would be about 80 000 tons of coal reserves.

2 Analytic Method and Results

In order to determine the types of organic matter in fluid inclusions, the authors analyzed the light hydrocarbon of fluid inclusions in quartz, fluorite and wolframite from the hydrothermal veins in the Yaogangxian tungsten deposit by means of gas chromatography. After doing many tests, we have gained the following gas chromatographic conditions which can completely separate the light hydrocarbon.

(1) *Chromatographic column* A quartz glass capillary column, 50 m× 0.53 mm, with an internal covering of Al_2O_3/KCl

(2) *Detector* FID

(3) *Temperature of chromatographic column* When the temperature of chromatographic column increases, it is not good for the separation of C_1–C_3. However, the lower temperature of chromatographic column will influence the stability of gas separation. It is appropriate to select a chromatographic column of 40℃ at a carrier flow rate of 6.4 mL/min until a peak of ethene occuring at a position for 80 seconds or so. And then, the temperarure of chromatographic column will increase at a rate of 30℃/min until 150℃.

(4) *Carrier* Hydrogen (H_2), given by a high-quality hydrogen generator. Its flow rate is 6.4 mL/min, and its ratio of partial flow is 4.5 mL/min.

(5) *Temperature of feeder* 150℃

(6) *Temperature of detector* 250℃

(7) *Flow rate of air* 6.00 mL/min

In addition, we have selected two groups of standard gases to determine the peak positions of separated gases. The content (10^{-6}) of the first group is methane (990), ethane (1000), ethene (1000), propane (1010), propylene (1010) and acetylene (100), and the content (%) of the second group is methane (87.86), ethane (5.20), ethene (0.45), propane (3.70), propylene (0.31), isobutane (0.63), normal butane (1.26), isopentane (0.21), normal pentane (0.26), hyxane (0.18). The first group is used to determine the peak positions of methane, ethane, ethene, propane, propylene and acetylene, and the second group is used to determine the peak positions of isobutane, normal butane, isopentane, normal pentane and hyxane.

As shown in Table 1, many kinds of light hydrocarbon such as methane (CH_4), ethene (C_2H_4), propane (C_3H_8), propylene (C_3H_6), acetylene (C_2H_2), isobutane (iC_4), normal butane (nC_4), isopentane (iC_5), normal pentane (nC_5) and hyxane (C_6) have been detected in vein minerals associated each other including quartz, fluorite and wolframite.

We notice that the content of methane is much higher than other light hydrocarbon in the inclusions of all minerals, and that there are much more methane in vein wolframite and vein quartz occurring in the coal bed. In addition, there are less kinds of hydrocarbons in the fluid inclusions from the vein quartz occurring in the coal bed. The dry-wet ratio ($C_1 / \sum (C_{1-5})$) of the light hydrocarbon is greater than 0.95 (from 0.972 to 0.998). It is characteristic of coal-gas.

Based on the geological fact of coal inclusions associated with primary fluid inclusions along some healing fractures, we consider that the light hydrocarbon in fluid inclusions may derive from Late Triassic coal bed during coal metamorphism. It is very difficult to determine how much light hydrocarbon comes from magmatic thermal-contact metamorphism or from biodegration and burial metamorphism.

3 Discussion

The nature of metal-organic associations is often unclear. Organic matter can mobilize metals by the formation of complex, or immobilize metals by sorption or precipitation and can also affect the oxidation potential and/or pH of ore solutions[25]. Parnell[5] also considered that metals may be taken up or reduced by organic materials from mineralizing fluids in petroleum reservoirs and hydrothermal system. On one hand, the hydrocarbon-bearing fluids may have influenced the deposition of metal and/or sulphides by reduction processes where metal-bearing and hydrocarbon-bearing fluids meet. On the other hand, hydrocarbon may play a role in the transport of metals through the formation of organometallic complexes.

Table 1 Hydrocarbons of fluid inclusions in the Yaogangxian tungsten mine

Number of Samples	Location	Height (m)	Analyzed mineral	CH_4	C_2H_4	C_3H_8	C_3H_6	C_2H_2	iC_4	nC_4	iC_5	nC_5	C_6	$C_1/\sum C_{1-5}$
910802-4(2)	tungsten vein	707	quartz	8.116	0.132	0.015	0.274	0	0.075	0.028	0	0.117	0.084	0.972
910802-1(1)	tungsten vein	905	wolframite	84.654	0	0	0.149	0	0.076	0.014	0.044	0.023	0.01	0.998
910802-3	tungsten vein	905	fluorite	10.926	0.132	0.013	0.269	0	0.092	0.012	0.048	0.127	0.084	0.974
910802-1(3)	tungsten vein	905	quartz	15.472	0	0.011	0.077	0	0.052	0.01	0.047	0.061	0.016	0.988
910802-6	vein in coal	1 300	quartz	61.795	0	0	0.102	0.064	0	0.232	0.073	0	0	0.995

Generally, evidence for direct involvement of organic matter in metallic transport and deposition is difficult to identify. However, the hydrocarbons in fluid inclusions at the Yaogangxian mine suggest a clear genetic connection between the organics and the tungsten mineralization, namely, the derived-coal hydrocarbons may play a role in the transport of tungsten instead of the deposition of tungsten during mineralization. As mentioned above, Late Triassic coal bed occurs within the deposit, 650 m from the top of hidden granite body. Before penetrating into the coal bed, a quartz vein has a high tungsten concentration, consisting of wolframite, fluorite and quartz. However, the same vein extending into the coal bed has no wolframite, only consisting of pure quartz and pyrite. If organic matter in coal would be helpful to the deposition of tungsten, more tungsten-bearing quartz veins should be found in the coal bed. Evidently, coal is not a geochemical barrier although it is an important source of hydrocarbons during tungsten mineralization. Since there is no tungsten concentration in the hydrocarbon source area, it can be considered that hydrocarbon-bearing fluids may only mobilize tungsten during migration.

4 Acknowledgment

The authors wish to thank the Yaogangxian mine, Hunan Province, China, for providing full access to the mine. The coal geologists at China University of Geosciences at Beijing, Yang Qi, Pan Zhigui, Luo Zengqiang, have contributed to many fundamental and helpful discussions, and Xu Yongchang, Shen Ping of Lanzhou Institute of Geology, Sinica Academia, provided thoughtful stimulating comments on our interpretations of organic matter in minerals; these colleagues are gratefully acknowledged for their aid in this study. We also thank Tu Guangchi for his help and encouragement on the project relative to this paper, the relationship between hydrothermally metamorphosed coals and metallic ore deposits. Financial support was provided by the Foundation of Natural Sciences of Guangxi Zhuang Autonomous Region.

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物理学家的惶惑——“终极”理论

当众多科学爱好者静下心来聆听的时候,探索宇宙最深奥秘的物理学家们把希望寄托于一项美丽炫目却又令人困惑的发明。这一发明叫做超弦论。这项理论称,如果把成百上千的亚原子粒子想象成为10维空间中极其纤细的琴弦上所发出的音符,那么,最终将会得到有关自然的最根本的解释。不要在意宇宙看起来只是4维(包括时间)空间的表象。据说其余的6个维随意地“卷起”成为虚无飘渺的小球,为人类的目力和思维所不逮。

M理论

自从60年代初悄然出现以来,这种理论几度沉浮。其中有80年代初的第一次“超弦革命”,以及10多年后的第二次革命。最近几个月里;一大批新发现正在酝酿着一场被某些物理学家兴奋地欢呼为第三次革命的突破,从而使得有那么一天,所有的物理定律将会被置于同一个简洁的理论框架之下。

但是,使物理学家们在最近迸发出热情的这个课题已不再叫做超弦论。如今,这种理论的名字已经改成了M理论,M的含义是指“魔术”(Magic)、“神秘”(Mystery)、“母亲”(Mother)——指该理论是所有理论之母,或者更直接地说,是指“超”(Meta)、“矩阵”(Matrix)或“薄膜”(Membrance)。因为,在颤动的超弦之外,又增加了新的抽象存在。这些新的抽象存在便是薄膜,或称“膜”,其维数最多可达9维。

根据最近的一些思考,宇宙万物可能是由这些几乎无法想象的物体结合而成的:它们是上帝组装的产物。如果这种认识正确的话,那么,物理学可能会比任何时候更接近于能够把难以表述的量子引力理论付诸笔端,这一成就将能把量子力学与广义相对论统一起来,并且以同样的说法来解释自然界所有的作用力。

弦论物理学家的影响正在波及到其他的领域,例如宇宙论领域。哈佛大学物理学家安德鲁°施特罗明格最近利用M理论进行跨越不同学科的研究,解决了一个涉及黑洞的问题。

解释引力

今年夏天的一个傍晚,在加州圣巴巴拉召开的超弦论学术界年度盛会“弦98”上,200多名物理学家和着西班牙热门歌曲《马卡雷纳》的节奏翩翩起舞,庆祝最新的研究进展。确切他说,他们跳的是《马卡雷纳》的一个新版本,叫做“马尔达塞纳”,是用任教于哈佛大学的阿根廷理论物理学家胡安°马尔达塞纳的名字命名的,理论物理界最近的兴奋情绪正是源于他所提出的新理论。

这里的信息可以归结为下面这句话:物理学家拥有一个非常成功的叫作量子场论的理论框架,可以对自然界4种作用力中的3种作出描述。强作用力使原子核聚合在一起,弱作用力支配核辐射过程,而电磁作用则把电和磁的作用结合在一起。这3种作用力都可以描绘成是由量子所发射的场电磁作

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