# The occurrence of gold in pyrite from the Liulincha gold ore belt, western Hunan Province, China

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**Abstract** In this study, an electron microprobe analyzer (EMPA) was used to map the spatial distribution and the occurrence of invisible gold in pyrite from the Liulincha gold ore belt. EPMA data show that gold mainly occurs as submicroscopic-microscopic inclusions. From the contrast of the major guide elements of pyrite from the Liulincha gold ore belt and those from four hydrothermal-type gold deposits in the Jiaodong region, we can see the pyrites were formed in two stages: the pyrite from wall rock is mainly sedimentogenic, with simple structure; and the pyrite from ore body experienced early sedimentary process to late hydrothermal activity, the pyrite is regular in crystal form and exhibits fractured structure.

Key words occurrence of gold; pyrite; invisible gold; Liulincha gold ore belt

## **1** Introduction

The Liulincha gold ore belt is one of the major metallogenic belts in the Xuefeng mountains, western Hunan, China. A number of albite-quartz vein-type gold deposits have been discovered in this metallogenic belt, and the main gold-bearing minerals include quartz, albite and pyrite. Usually, the visible gold exists in albite and quartz, and "invisible gold' exists in pyrite. Gold contained in the structure of the common sulfide minerals and that present as discrete inclusions smaller than 1000 Å are collectively termed "invisible gold", not detectable by optical and scanning electron microscopy (Cook and Chryssoulis, 1990). "Invisible gold" appears to be preferentially concentrated in pyrite and arsenopyrite (Cook and Chryssoulis, 1990; Palenik et al., 2004; Saha and Venkatesh, 2002; Fleet et al., 1993; Sung et al., 1993; Mumin et al., 1994; Majzlan et al., 1994; Yang Sixue et al., 1998; Pals et al., Simon et al., 1999). Basically, there are two viewpoints on the occurrence state of "invisible gold" in sulfides: one is that the gold is present in solid solutions in pyrite and arsenopyrite, and the other is that the gold occurs as submicroscopic inclusions (Simon, 1999; Healy and Petruk, 1990; Hannington, 1995; Larocque and Hodgson, 1995; Wagner et al., 2007; Vikentyev, 2004; Arechart, 1993; Bortnikon, 2003). Palenik (2004) gave two possible forming mechanisms for submicroscopic inclusions: (1) Au exceeded its solubility limit in arsenian pyrite, thus causing it to be deposited as nanoparticles of native gold; and (2) exsolution of native gold from metastable arsenian pyrite was caused by a later event in the history of the deposit (Palenik, 2004). Reich (2005) thought that the As and Au contents of arsenian pyrites plot in a wedge-shaped zone with an upper compositional limit defined by the line  $C_{Au}=0.02^*C_{As}$  $+4\times10^{-5}$ , indicating a maximum Au/As molar ratio of -0.02 (Reich et al., 2005). According to the gold content analysis of pyrite in the Liulincha gold mine belt, the average gold content reached  $114.67 \times 10^{-6}$  in fine-grained pyrite and  $5.67 \times 10^{-6}$  in medium-fine grained (The Headquarter of Chinese Armed Police, 1996), but there has been no direct evidence for the occurrence state of gold in the pyrite.

The study on the occurrence state of gold in pyrite is useful to guide prospecting, mineral deposit evaluation and improvement of gold extracting method. Electron probe microanalysis (EPMA) has become a main approach to study preliminary "invisible gold", because it has high resolution, can give element distribution map, the content of element, etc. Using an electron probe microanalyzer (EPMA), the author has investigated the distribution characteristics and concentrations of invisible gold at different spots in pyrites of various grain sizes, crystal forms, and paragenetic stages. The samples used in this study were collected from the Herenping and Tongshumian gold mines of the Liulincha gold ore belt.

## 2 Geological setting

The Liulincha gold ore belt is located in Wuqiangxi Town, Yuanling Country, Hunan Province. The gold ore belt is about 40 km in length, and contains more than ten gold deposits. Both two selected gold mines are of the auriferous quartz-albite vein type. Of the two, the Herenping gold mine has a long history, which was recorded in the Ming Dynasty. Also it is one of the four main gold mines in Hunan in the late Ming and early Qing dynasties (The Headquarter of Chinese Armed Police, 1996). (Fig. 1, location of the gold deposit).

The strata exposed in this area consist mainly of the Neoproterozoic Banxi Group Madiyi Formation. The lower segment of the Madiyi Formation is not exposed; the middle segment is mainly composed of mauve sericitic slate and mingled with greyish-green banded sericite slates; and the upper segment is composed of greyish-green thin sandy slate. Folds and faults are developed in this zone, and the auriferous albite-quartz vein is mainly restricted within the mauve sericitic slate in the middle Madiyi Formation, and controlled by interlay faults. Magmatic activities are generally weak in western Hunan, and no igneous rocks outcrop within or around the Liulincha gold ore belt.

By appearance, orebodies can be divided into bedded vein, stockwork and joint vein (or veinlet). The metallic minerals include native gold, pyrite, etc.; sphalerite, galena and tetrahedrite are found on the Au-concentrated position. The gangue minerals include quartz, albite, and minor amounts of sericite, calcite and chlorite. Wall-rock alterations are predominated by decolorization, silicification, pyritization, carbonatization and sericitization.

### **3** Samples and methods

Samples for this study were collected from the Herenping and Tongshumian gold mines of the Liulincha gold ore belt. The analysis was finished at the State Key Laboratory of Ore Deposit Geochemistry, Chinese Academy of Sciences. The equipment used in this study was EPMA-1600, which is high in stability and accuracy. Electron microprobe analyses (EDS and WDS) were carried out under the following conditions, accelerating voltage: 25 kV, and sample current, 10 nA.

#### 4 Results and discussion

The pyrites were formed in two stages (Fig. 2).



Fig. 1. Geological sketch map of the Liulincha gold ore belt modified from the reference (Wang Guoqiang, 2009). 1. Cretaceous; 2. the lower series of Cambrian; 3. the upper series of Sinian; 4. the lower series of Sinian; 5. Neoproterozoic Banxi Group Wuqiangxi Formation; 6. Neoproterozoic Banxi Group Madiyi Formation; 7. Neoproterozoic Lengjiaxi Group; 8. stratigraphic unconformity boundary; 9. reverse fault; 10. type-unknown fault; 11. gold deposit.



Fig. 2. BSE images of pyrites from the Liulincha gold ore belt. a. Pyrite from ore body; b. pyrite from wall rock.

The pyrites formed in the early stage of mineralization are euhedral and coarse grained, mostly cubic and porous; the pyrites formed in the late stage are medium-fine grained, anhedral and fractured. The gold concentrations are higher in fine-grained pyrites than in coarse-grained ones.

A lager number of submicroscopic-microscopic gold inclusions were found in this study (Fig. 3). These gold inclusions are distributed mainly on the edges of arsenian pyrite crystals or fractured fissures, of which the biggest one is 15  $\mu$ m in scale and the smallest is less than 1  $\mu$ m.

The contents of S and Fe in sedimentogenic pyrites are close to the theoretical values, or the content of S is slightly higher (Zhao Jiexin and Bao Mingxue, 2007). Under the condition of high temperature, the content of Te is higher in pyrite; and under the low temperature, the content of Se is higher, the content of S shows a little variation. The formation condition of pyrite can be distinguished by the values of w(S)/w(Se) and w(Se)/w(Te). Generally, the ratio of w(S)/w(Se) is more than  $20 \times 10^4$  in sedimentogenic pyrite; the ratio varies between  $1 \times 10^4$  and  $2.67 \times 10^4$  in pyrite of hydrothermal origin. The ratio of w(Se)/ w(Te)lies between 6 and 10 in magmatogenic pyrite; and the ratio is about 0.2 in pyrite of hydrothermal origin (Tong Jinggui et al., 2004). The contents of Co and Ni and the values of w(Co)/w(Ni) can indicate the deposit genesis. Generally, the ratio of w(Co)/w(Ni) is less than 1 in sedimentogenic pyrite; it is more than 1 in pyrite of hydrothermal origin.

Table 1 lists the mineral chemistry of pyrite by EMP.

(1) Pyrite from ore body: it is shown that the contents of S in pyrite from ore bodies are within the range of 51.103%-53.003%, those of Fe are within the range of 43.010%-46.184%, and those of S and Fe are lower than the theoretical values. That is because of the isomorphism of As, Co, Ni, Te, Au, Ag and so on, among which the content of As is highest. As has a

great influence on the major component of pyrite, because As can substitute S easily.

Table 2 shows the contrast of the major guide elements of pyrite from the Liulincha gold ore belt and those from four the hydrothermal-type gold deposits in the Jiaodong region. The proportion of n(S)/n(Fe)>2 of pyrite from the Liulincha gold ore belt is 66%, which has the characteristics of the epithermal- or sedimentary-type gold deposits, and it is similar to that of pyrite in the hydrothermal-type gold deposits in Jiaodong. The average value of w(Co) /w(Ni) is less than 1, which shows a sedimentary-type pyrite. The average value of w(Se)/w(Te) is 0.53, it is similar to the value of the hydrothermal-type pyrite in Jiaodong, which shows that the pyrite is not normally sedimentary, whereas it has a close relationship with the hydrothermal process.

(2) Pyrite from wall rock: the contents of S are within the range of 51.085%-52.855%; and those of Fe, 44.376%-45.906%; both are lower than the theoretical values. The contents of As in pyrite from wall rock are lower than those of As from ore body, so the contents of Au are also relatively low. The value of w(Co)/w(Ni) is less than 1, so the pyrite may be sedimentogenic. From the backscattered electron images we can see that though the crystal form of pyrite from wall rock is good and the core is porous, it is likely that in the early growth period of pyrite silicic impurities are interfused.

Pyrites from the Liulincha gold ore belt generally contain a certain amount of As, which cause the contents of Fe and S to be deviated from the theoretical values. As viewed from backscattered electron images in combination with the spectrum data, it is concluded that the pyrite from wall rock is mainly sedimentogenic with good crystal form and simple structure; the pyrite from ore body experienced early sedimentary process to late hydrothermal activity, the pyrite has a regular crystal form and exhibites fractured structure.



Fig. 3. Gold particles and energy dispersion spectra.

Table 1Mineral chemistry of pyrite (EMP wt.%)

Sample No.	Test point	S	Fe		Co	Ni	Se	Те	Δ11	Δσ	Total
Sample No.	1	52 812	10	1 622	1	\	0.021	10	0.207	0.023	00.276
	2	51 866	44.078	1.003	```	0.043	0.021	0.077	0.087	0.023	08 202
	2	51.006	44.220	1.995	```	0.045	0.02	0.077	0.087	0.007	96.292
	5	52.022	43.442	1.040	```	```	0.03	0.019	0.007	0.007	99.077
Um 2 (and hadre)	4	52.955	43.010	1.094	0.041	0.026	0.075	0.018	0.007	1	97.002
Hrp-3 (ore body)	5	52.252	44.205	1.253	0.041	0.026	0.075	0.185	0.206	0.043	98.286
	6	51.895	45.887	1.125	\	0.037	0.001	\	0.010	1	98.954
	7	51.103	45.302	1.490	\	\	0.040	0.029	0.091	0.026	98.081
	8	51.410	45.561	1.997	0. 181	0.162	\	\	0.002	0.004	99.317
	9	51.381	44.799	1.740	\	0.044	0.015	\	\	0.056	98.035
	10	52.761	45.931	0.991	\	\	\	0.019	0.023	0.005	99.730
	11	53.003	45.942	1.043	/	/	\	0.015	/	0.010	100.093
Tsm-3 (ore body)	12	52.774	46.184	0.629	\	0.009	\	\	0.032	\	99.591
	13	52.882	45.607	0.760	0.029	0.020	\	\	\	\	99.298
	14	52.416	45.653	0.796	\	0.054	\	\	0.016	0.018	98.953
	15	52.716	45.875	0.853	\	0.058	\	\	0.029	0.015	99.547
	16	52.029	45.373	0.658	\	0.058	\	0.002	0.016	0.006	98.142
Tom 1 (well reals)	17	51.376	44.376	0.593	\	0.046	\	0.002	0.018	0.007	96.418
Ism-1 (wall rock)	18	52.855	44.663	0.641	\	\	\	0.026	0.030	0.055	98.269
	19	52.852	45.104	0.581	\	0.024	0.001	0.094	0.050	0.018	98.725
	20	52.235	45.906	0.590	0.001	0.136	/	0.022	0.089	0.015	98.995
	21	52.212	45.273	0.486	\	\	\	\	0.075	0.004	98.050
Hrp-1 (wall rock)	22	51.085	45.222	0.532	١	0.061	0.026	\	0.059	0.022	97.007
	23	52.760	44.570	0.579	١	\	0.086	0.043	0.092	\	98.135
Tsm-2 (wall rock)	24	52.403	44.924	0.611	0.041	0.076	\	0.018	\	0.023	98.095
	25	51.888	45.091	0.740	0.127	0.146	\	0.066	0.032	\	98.090
	26	52.044	45.548	0.591	0.002	0.092	\	\	\	0.008	98.284
	27	52.049	45.338	0.600	0.036	0.098	0.024	\	\	١	98.145
	28	52.481	44.576	0.639	\	0.071	\	0.032	١	0.008	97.809
Hrp-2 (wall rock)	29	52.483	44.972	0.590	0.056	0.135	\	\	0.032	0.015	98.282
	30	52.836	44.417	0.609	0.075	0.095	\	\	0.007	0.027	98.066
	31	51.669	44.539	0.577	0.123	0.111	0.007	N N	0.096	N I	97.122
	32	52.788	44.613	0.572	\	0.020	0.017	\	\	0.017	98.027

Note: Hrp. Herenping gold mine; tsm. T. ong<br/>shumian gold mine;  $\$  no data.

## Table 2The comparison of some chemical typomorphic characteristics between pyrites from the Liulincha<br/>gold ore belt and those from gold deposits in the Jiaodong region

Deposit			W(trace ele	ement) (10 <sup>-6</sup> )		$n(\mathbf{S})/n(\mathbf{E}_{\mathbf{S}})$	$w(C_0)/w(N_i)$	$w(\mathbf{S})/w(\mathbf{S}_{\mathbf{A}})$	w(Se)/w(T
		Co	Co Ni		Se	- "((3)/"((10)	w(CO)/w(INI)	w(3)/w(3e)	e)
Turbidite- hosted	Liulincha					1.974–2.153,			
	gold ore	167.33	302.00	13095.33	121.33		0.55 (average)	$0.43 \times 10^{4}$	0.53
	belt					>2 (66%)			
Hydrother- mal filling type	Jinqing- dinggold mine	131.35	85.86	2576.00	4.89	>2 (64%)	2.83	13.6×10 <sup>4</sup>	0.43
	Xishan gold mine	81.50	54.30	689.00	1.70	most< 2	0.08–9.5 2.41 (average)	49.2×10 <sup>4</sup>	1.34
Hydrother- mal	Sanshan- dao	77.24	23.33	7530.70	<1.00	>2 (60%)	0.33-7.83	52.04×10 <sup>4</sup>	0.17
me- tasomatic type	gold mine					<2 (40%)	2.22 (average)		
	Jiehe gold mine	365.00	277.40	14.99	100.00	2.008 (average)	1.3 (average)	$0.5 \times 10^{4}$	0.10

#### **5** Conclusions

(1) Gold in pyrites from the Liulincha gold ore belt occurs as submicroscopic to microscopic size gold particles that are occasionally present on the gold-bearing arsenian pyrite edges and in fissures.

(2) The pyrite from wall rock is mainly sedimentogenic, with simple structure; and the pyrite from ore body experienced early sedimentary process to late hydrothermal activity, and the pyrite is regular in crystal form and exhibits fractured structure.

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