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江西金山金矿床含金黄铁矿的稀土元素和微量元素特征*

毛光周 华仁民** 高剑峰 赵葵东 龙光明 陆慧娟 姚军明

(南京大学地球科学系,壳幔演化与成矿作用研究国家重点实验室,江苏 南京 210093)

摘 要 金山金矿床位于赣东北矿集区内,是与韧性剪切带有关的超大型金矿床。黄铁矿是该矿床最主要的载金矿物。文章利用含金黄铁矿的稀土元素组成示踪了金山金矿床的成矿物质及成矿流体的来源和性质。研究结果表明,金山金矿床黄铁矿稀土元素总量较高,ΣREE 平均为 171.664×10^{-6},富集轻稀土元素,LREE 平均为 159.556×10^{-6},HREE 平均为 12.108×10^{-6},轻重稀土元素比 ΣLREE/ΣHREE 平均为 12.612,$(La/Yb)_N$ 值平均为 11.765,为轻稀土元素富集型;轻稀土元素有较明显的分馏,而重稀土元素的分馏不明显,$(La/Sm)_N$ 值平均为 3.758,$(Gd/Yb)_N$ 值平均为 1.695;Eu 负异常明显,δEu 值平均为 0.664;基本无 Ce 异常,δCe 值平均为 1.044。黄铁矿的稀土元素特征与该矿床的围岩(蚀变变形的变质岩)、区域地层具有相似的地球化学特点,而与邻近的花岗闪长斑岩稀土元素特征不同,所以金山金矿床的成矿物质来源于变质岩围岩,成矿流体主要为变质水。黄铁矿中的 Co/Ni 比值显示金山金矿床为中低温矿床;成矿经历了沉积成岩、区域变质、韧性剪切带的动力变质作用及表生氧化作用的演化过程。从黄铁矿的 Y/Ho 比值推断金山金矿床含金黄铁矿的成矿流体为变质流体。黄铁矿中微量元素与矿区变质岩也有相似的组成,亏损 HFSE。从黄铁矿的 REE、LREE、HFSE、Hf/Sm、Nb/La、Th/La、Co/Ni、Y/Ho 等特征,可推断金山金矿床的成矿流体是 Cl 多于 F 的变质流体。

关键词 地球化学;稀土元素;微量元素;黄铁矿;成矿流体;金山金矿床

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REE composition and trace element features of gold-bearing pyrite in Jinshan gold deposit, Jiangxi Province

MAO GuangZhou, HUA RenMin, GAO JianFeng, ZHAO KuiDong, LONG GuangMing, LU HuiJuan and YAO JunMing

(State Key Laboratory of Crust-Mantle Evolution and Mineralization, Department of Earth Sciences, Nanjing University, Nanjing 210093, Jiangsu, China)

Abstract

Located in the northeast Jiangxi ore-concentration area, the Jinshan gold deposit is a superlarge gold deposit related to the ductile shear zone. Pyrite is the main gold-bearing mineral. Based on REE composition of Au-bearing pyrite, the present paper traced the sources of ore-forming materials and the sources and characteristics of ore-forming fluids in the Jinshan gold deposit. The ΣREE of gold-bearing pyrite is as high as 171.664×10^{-6} on average, with relatively high LREE (159.556×10^{-6}) and low HREE (12.108×10^{-6}). The ΣLREE/ΣHREE ratio 12.612 and the $(La/Yb)_N$ ratio 11.765 indicate that the gold-bearing pyrite belongs to the

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第一作者简介 毛光周,男,1978 年生,南京大学矿物学岩石学矿床学专业研究生,E-mail:gzmao-nju@yahoo.com.cn。** 通讯联系人:huarenmin@nju.edu.cn。

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LREE-rich type. $(La/Sm)_N$ is 3.758 and $(Gd/Yb)_N$ is 1.695, showing an obvious LREE fractionation. The REE distribution patterns show obvious Eu anomaly with average values of δEu 0.664 and δCe 1.044. REE characteristics are similar to those of wall rocks (altered and deformed metamorphic rocks) and regional strata, but differ from those of the granodiorite porphyry nearby. All this indicates that the ore-forming materials of the Jinshan gold deposit were derived from the wall rocks, and that ore-forming fluids were metamorphic water. The Co/Ni ratio of pyrite suggests that the Jinshan gold deposit is a medium-low temperature deposit. The mineralization of the Jinshan gold deposit has undergone such evolutionary process as sedimentation-diagenesis, regional metamorphism, dynamic metamorphism of the ductile shear belt, and supergene oxidation. It is also shown that the ore-forming fluids of the Jinshan gold deposit were composed mainly of metamorphic water. Other features of trace elements in the pyrite are also similar to those of metamorphic rocks, such as the depletion of HFSE. Such features as REE, LREE, HFSE, Hf/Sm, Nb/La and Th/La, together with Co/Ni and Y/Ho ratios of gold-bearing pyrite, reveal that the ore-forming fluid of the Jinshan gold deposit originated from the Cl-rich deep metamorphic water.

Key words: geochemistry, REE, trace element, pyrite, ore-forming fluid, Jinshan gold deposit

金山金矿床位于江西省东北部,是赣东北金铜矿集区的主要矿床之一,金的远景储量达超大型,有巨大的经济价值。金山金矿床又是中国韧性剪切带型金矿的代表性矿床之一,具有重要的科学研究价值。因此,自上世纪 80 年代以来,国内地质学者对金山金矿床的研究从未间断过,并且在矿床地质地球化学、成矿物质来源、成矿流体性质及来源、成矿物理化学条件等方面取得了大量的成果(朱训等,1983;刘英俊等,1989;肖勇,1990;2001;黄宏立等,1990;曾祥福,1991;朱恺军等,1991a;1991b;范宏瑞等,1992;朱庆祖,1992;季峻峰等,1994a;1994b;梁毓鎏,1995;韦星林,1995;1996;梁湘辉,1997;张文淮等,1998;曾键年等,1998;2001;2002;王可勇等,1999;王秀璋等,1999;张涛,1999;李晓峰等,2001;2002;华仁民等,2002;2003;刘志远等,2005a)。

金山金矿床的主要载金矿物为黄铁矿,作为一种由成矿流体沉淀而形成的矿石矿物,黄铁矿的稀土元素组成反映了成矿流体的稀土元素组成。本文试图通过研究黄铁矿的稀土元素和微量元素特征,来示踪金山金矿床成矿流体的来源与性质。

1　地质概况

金山金矿床地质简图如图 1 所示。该矿床位于江西省德兴市花桥镇北,赋存于赣东北深大断裂带上盘的金山韧性剪带内。区域出露的地层主要是中元古界双桥山群浅变质岩系(王燕等,1993)。矿区出露双桥山群第三岩组,同位素年龄为 1.371 Ga(刘英俊等,1989)。区域内的岩浆活动强烈,多集中在四堡期和燕山期,次为加里东期和印支期(王燕等,1993)。矿区范围内虽无重要的岩体出露,但在双桥山群地层第二、三岩性段中发育一些顺层玄武岩透镜体,它们多为变质作用前沉积-成岩期火山岩浆活动之产物(王可勇等,1999)。金山金矿床矿体形态为似层状、透镜状,主要受控于韧性剪切带内脆性层间裂隙系统和构造滑脱层(曾键年等,2002)。韧性剪切带被稀散发育的北东向、南北向两组正断层错切(韦星林,1996)。

金矿石自然类型有蚀变构造岩型和石英脉型两大类。蚀变构造岩矿石主要包括浸染状硅化、黄铁矿化、铁白云石化超糜棱岩-糜棱岩矿石、千枚岩矿石、碎裂岩-角砾岩矿石,矿体规模大,形态和品位相对较为稳定。含金石英脉多位于蚀变构造岩矿体的上方,呈小扁豆状,品位较富,但变化大(韦星林,1995)。

矿石矿物组成简单,自然金是矿石中唯一的金矿物。自然金富集于具半自形-他形粒状结构、超糜棱、糜棱结构、碎裂结构及浸染状构造和角砾状构造的矿石中。金属矿物除自然金外,主要有黄铁矿,其次是磁铁矿、赤铁矿、金红石、毒砂、闪锌矿、黄铜矿、黝铜矿和方铅矿等。脉石矿物主要是石英,次为绢云母、钠长石、铁白云石和绿泥石等。黄铁矿是最主要的载金矿物。

金山金矿床的主要成矿过程可划分为 2 期 4 阶段,其中,早期即内生热液成矿期包括黄铁矿-石英阶段、石英-金属硫化物-自然金阶段、石英-碳酸盐阶

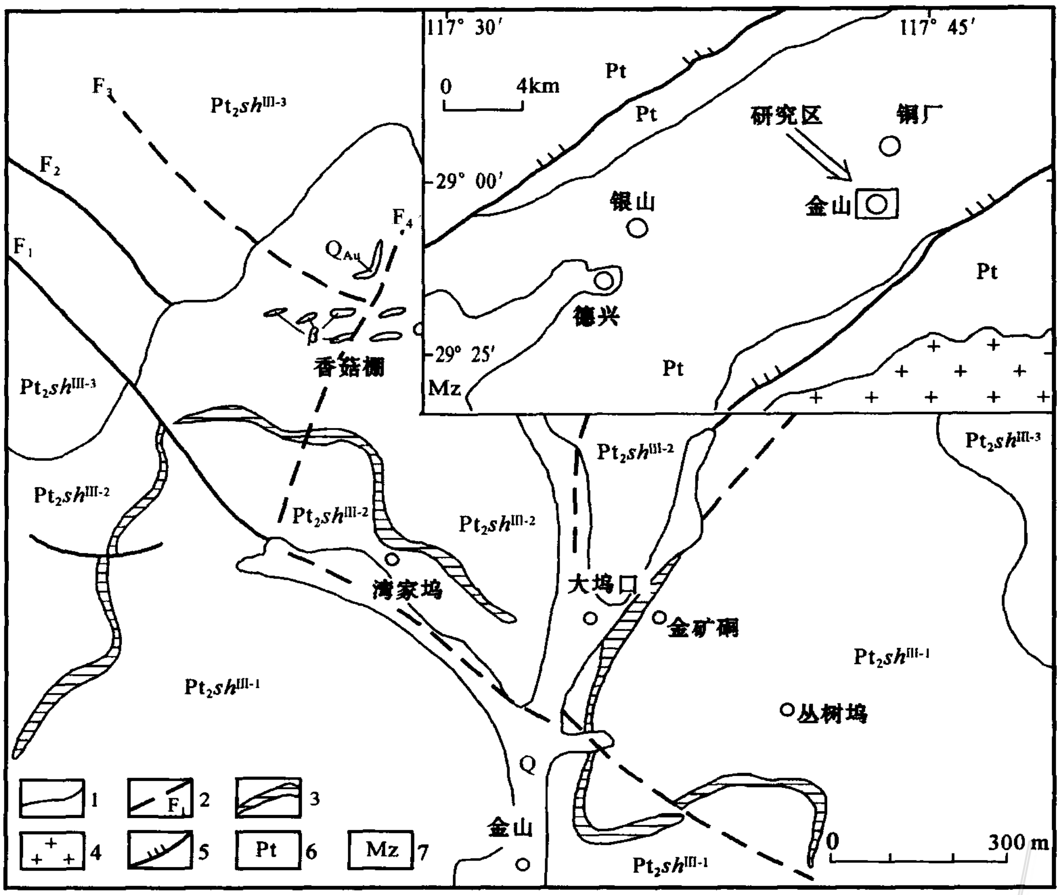

图 1　江西金山金矿床地质简图(据黄宏立等,1990;王可勇等,1999;姚春亮等,2005 修改)

Q—第四系;Pt_2sh^{III-3}—双桥山群第三岩性组第三岩性段;Pt_2sh^{III-2}—双桥山群第三岩性组第二岩性段;Pt_2sh^{III-1}—双桥山群第三岩性组第一岩性段;δ—变余辉石闪长岩;β—变余玄武岩;Q_{Au}—含金石英脉;1—地质界线;2—断裂;3—含金剪切带 4—花岗岩;5—区域断裂带;6—新元古界地质;7—中生代火山盆地

Fig. 1　Geological map of the Jinshan gold deposit (modified after Huang et al, 1990; Wang et al, 1999; Yao et al., 2005.)

Q—Quaternary; Pt_2sh^{III-3}—3rd Lithologic Member of 3rd Lithologic Formation of Shuangqiaoshan Group; Pt_2sh^{III-2}—2nd Lithologic Member of 3rd Lithologic Formation of Shuangqiaoshan Group; Pt_2sh^{III-1}—1st Lithologic Member of 3rd Lithologic Formation of Shuangqiaoshan Group; δ—Meta-gabbro-diorite; β—Meta-basalt; Q_{Au}—Au-bearing quartz veins; 1—Geological boundary; 2—Fault; 3—Au-bearing shear zone; 4—Granite; 5—Major regional fault; 6—Neo-Proterozoic strata; 7—Mesozoic volcanic basin

段;晚期则为表生氧化富集期(王燕等,1993)。韧性剪切带在形成-演变过程中,带内外普遍遭受不同程度的蚀变。蚀变类型有硅化、黄铁矿化、绢云母化、绿泥石化、碳酸盐化(铁白云石化、菱铁矿化、白云石化、方解石化)等,其中硅化、黄铁矿化、铁白云石化与金矿化关系密切。硅化分为早期、中期和晚期,其中中期硅化主要形成深灰色-浅灰色-乳白色的石英脉体,与金矿化的关系尤为密切。黄铁矿化分布广泛,但黄铁矿含量甚微,主要分布于超糜棱岩、糜棱岩带,按其产状可分为 3 个世代:第一世代的黄铁矿呈点状体,形态为立方体,一般粒度小于 0.02 mm,稀疏浸染状分布于早期石英脉中;第二世代的黄铁矿是由五角十二面体与立方体组成的复晶,粒度在 0.02~1 mm 之间,多呈碎裂细粉末状,沿面理、裂隙呈浸染状或细脉状产出,含量约为 2%,伴有铁白云石化、毒砂化等复杂金属硫化物,本世代黄铁矿与黄铜矿、方铅矿、闪锌矿、自然金基本同时生成,代表主要的金矿化阶段;第三世代黄铁矿呈粗粒自形-半自形的立方体,粒度在 0.5~2 mm 之间,浸染状、脉状分布,金矿化弱。

2　样品采集及处理方法

在金山金矿床阳山 - 105 m 中段采集含浸染状细粒黄铁矿的糜棱岩(样号 DX-12，DX-15，DX-16，DXⅡ-11，DXⅡ-12，DXⅡ-13，DXⅡ-19，DXⅡ-20，DXⅡ-21，DXⅡ-22)和矿化玄武岩(DX-14)。其中的黄铁矿为上文所述的第二世代与金成矿关系密切的黄铁矿。该期黄铁矿呈他形-半自形粒状集合体分布，明亮，颜色较深。将样品清洗干净，粉碎到 60～80 目，通过人工重砂法从样品中分离出黄铁矿，再在双目镜下手工挑选与金成矿关系密切的黄铁矿(吴学益等，2000)，挑选出的黄铁矿单矿物经过了详细的镜下检查，纯度高于 99%。在双目镜下挑选黄铁矿的过程中还发现了自然金(DXⅡ-20)，说明所选黄铁矿与金成矿关系密切。

选好的黄铁矿样品用 Milli-Q 超纯水超声清洗，除去吸附在表面的杂质，清洗干净的样品在 40 ℃下烘干，称取约 50 mg，放入干净的 Teflon 溶样罐中，加入 1 ml HNO_3 和 1 ml HCl，置于电热板上，约 120 ℃的条件下溶解 1～2 天，使硫化物完全溶解。样品溶解完全蒸干后，加入 1 ml HF 和 1 ml HNO_3 溶解残渣两天，蒸干溶液后，再加入 HNO_3，反复蒸干。最后蒸干的样品用 30% 的 HNO_3 提取，加入 500 ng 的 Rh 作为内标，将溶液定容到 50 ml。

样品处理及测试中的每一步操作均在南京大学壳幔演化与成矿作用研究国家重点实验室 100 级同位素超净化学台中进行，以避免其他物质的污染。

3　分析结果及讨论

上述定好容的溶液在南京大学壳幔演化与成矿作用研究国家重点实验室的高分辨率电感耦合等离子质谱仪(FINNIGAN MAT ELEMENT2 ICP-MS)上测试其稀土元素和微量元素含量。溶液的后处理、等离子质谱仪工作状态、仪器的检出限和测定限及测试方法均见参考文献(高剑峰等，2003)。

3.1　稀土元素特征

本文所测黄铁矿样品稀土元素数据，以及搜集的前人测定的金山金矿床矿石围岩(变形的变质岩)(朱恺军等，1991a；1991b；韦星林，1996；王可勇等，1999a；华仁民等，2002；李晓峰等，2001；2002；刘志远等，2005d)、区域火成岩(花岗闪长斑岩)(朱训等，1983；钱鹏，2003；钱鹏等，2005)、区域地层(双桥山群)(刘英俊等，1989；刘志远等，2005b；2005c)的稀土元素含量及特征值列于表 1、表 2。据这些数据制作的球粒陨石标准化曲线如图 2 所示。

从表 2、图 2 可以看出，几类样品均为明显的右倾型，轻稀土元素富集，轻稀土元素有较明显的分馏，而重稀土元素的分馏不明显。

黄铁矿的稀土元素特征与金矿围岩(变质岩)是很相近的，而与区域火成岩(花岗闪长斑岩)差别较明显。但黄铁矿和变质岩均具有明显的 δEu 负异常，而区域火成岩(花岗闪长斑岩)的 δEu 负异常则不明显，甚至有些样品的 δEu 为正异常。黄铁矿和变质岩的稀土元素总量相当，平均值分别为 171.66×10^{-6} 和 155.96×10^{-6}，区域花岗闪长岩的稀土元素总量略低，为 92.36×10^{-6}；稀土元素配分模式上，黄铁矿和变质岩的轻稀土元素和重稀土元素分馏差别较大，轻稀土元素较富集，$(La/Sm)_N$ 分别为 3.76 和 3.23，重稀土元素则比较平坦，$(Gd/Yb)_N$ 分别为 1.70 和 1.48；区域花岗闪长岩轻稀土元素和重稀土元素分馏大致相同，$(La/Sm)_N$ 和 $(Gd/Yb)_N$ 分别为 2.16 和 2.18。

黄铁矿和围岩(变质岩)在稀土元素特征方面有如此多的相似性，而与区域火成岩(花岗闪长斑岩)的相似性则较弱。由此可见，金山金矿床变质岩与区域双桥山群的稀土元素含量特征、配分曲线相似，而与区域花岗闪长斑岩有明显区别。金山金矿床中与金矿化关系密切的含金黄铁矿样品虽然其各自的稀土元素含量有差别，但其球粒陨石标准化模式图与变质岩及区域双桥山群相似，而与区域花岗闪长斑岩有较大的差别。

稀土元素属于不活泼元素，在热液体系中，稀土元素地球化学可以十分有效地示踪成矿流体的来源和水-岩相互作用(Henderson，1984)。对现代海底热液系统的研究表明，硫化物具有与热液流体相似的 REE 组成特征(Mills et al.，1995)。由于 REE^{3+} 的离子半径(0.977×10^{-10}～1.16×10^{-10})与 Zn^{2+} 和 Fe^{2+} 的离子半径(分别为 0.74×10^{-10} 和 0.78×10^{-10})相差较远(Shannon，1976)，REE^{3+} 替换闪锌矿或黄铁矿矿物晶格中的阳离子是比较困难的，推测硫化物中的 REE 可能主要赋存在流体包裹体中。因此，硫化物的 REE 组成特点应该可以直接反应成矿流体中的 REE 组成特点(赵葵东，2005)和沉淀时的温度、压力、pH 值及 E_h 值等物理化学条件的影响

表 1 金山金矿床含金黄铁矿中稀土元素含量($w_B/10^{-6}$)及特征值

Table 1 REE composition and feature of gold-bearing pyrite from the Jinshan deposit($w_B/10^{-6}$)

	DX-12	DX-14	DX-15	DX-16-1	DX-16-2	DXII-11	DXII-12	DXII-13	DXII-19	DXII-20	DXII-21	DXII-22-1	DXII-22-2
La	9.356	72.215	14.524	21.765	20.338	32.452	45.377	56.624	47.733	61.105	9.544	40.382	35.163
Ce	21.080	162.795	33.946	48.148	44.435	56.437	99.365	109.348	96.755	131.010	21.003	80.301	76.197
Pr	2.615	14.616	3.405	4.921	4.751	6.231	9.353	11.573	9.401	12.456	2.643	7.902	7.249
Nd	12.433	55.377	15.714	21.299	18.424	21.412	34.553	44.814	33.319	49.211	10.924	30.141	28.955
Sm	2.499	11.710	3.223	3.901	3.725	3.787	7.673	13.060	6.053	7.878	2.232	5.404	5.307
Eu	0.594	1.265	0.719	0.831	0.743	0.817	1.696	2.110	1.074	1.273	0.660	0.903	0.972
Gd	2.499	7.724	2.717	2.878	2.689	3.095	5.719	7.158	3.994	5.351	2.241	3.581	3.556
Tb	0.343	0.763	0.376	0.328	0.313	0.366	0.493	0.614	0.387	0.413	0.316	0.342	0.341
Dy	2.523	4.261	2.339	1.956	1.743	1.682	1.278	2.807	2.051	2.251	2.491	1.908	1.664
Ho	0.529	0.876	0.543	0.409	0.380	0.349	0.326	0.779	0.531	0.447	0.518	0.358	0.341
Er	1.523	2.903	1.677	1.375	1.389	1.462	1.060	3.135	2.034	1.596	1.575	1.636	1.518
Tm	0.258	0.562	0.285	0.258	0.214	0.267	0.211	0.554	0.452	0.350	0.247	0.295	0.265
Yb	1.589	3.696	1.566	1.673	1.503	1.867	1.264	2.848	2.947	2.304	1.470	1.924	1.582
Lu	0.232	0.583	0.246	0.278	0.223	0.348	0.253	0.597	0.564	0.481	0.238	0.348	0.314
ΣREE	58.073	339.347	81.280	110.018	100.870	130.571	208.620	256.019	207.295	276.127	56.103	175.425	163.423
LREE	48.577	317.979	71.530	100.864	92.416	121.135	198.017	237.528	194.335	262.934	47.007	165.033	153.843
HREE	9.496	21.368	9.750	9.154	8.454	9.436	10.603	18.492	12.960	13.193	9.096	10.392	9.580
LREE/HREE*	5.115	14.881	7.337	11.018	10.932	12.837	18.675	12.845	14.995	19.930	5.168	15.881	16.058
δCe*	1.011	1.142	1.124	1.078	1.052	0.897	1.103	0.975	1.037	1.084	0.991	1.019	1.091
δEu*	0.719	0.383	0.724	0.727	0.686	0.709	0.751	0.607	0.629	0.567	0.894	0.591	0.646
$(La/Yb)_N$*	3.969	13.172	6.255	8.769	9.123	11.719	24.200	13.406	10.919	17.880	4.378	14.154	14.987
$(Gd/Yb)_N$*	1.269	1.686	1.401	1.388	1.444	1.338	3.651	2.028	1.093	1.874	1.230	1.502	1.814
$(La/Sm)_N$*	2.355	3.879	2.835	3.510	3.435	5.390	3.720	2.727	4.960	4.879	2.689	4.701	4.168

注：由南京大学壳幔演化与成矿作用研究国家重点实验室 ICP-MS 室高剑峰测试；分析仪器：ELEMENT-2 型 ICP-MS，分析精度(RED)< ±0.01%。其中 DX-16-1，DX-16-2，DXII-22-1，DXII-22-2 为进行的平行样分析。* 单位为 1。

表 2 金山金矿床稀土元素特征值

Table 2 REE composition and feature of the Jinshan deposit

		黄铁矿	变质岩*	区域花岗闪长斑岩**	双桥山群	上亚群	下亚群
ΣREE/10^{-6}	含量区间	56.10 ~ 339.35	91.47 ~ 227.86	55.95 ~ 126.85			
	均值	171.66	155.96	92.36	157.08	141	192
ΣLREE/10^{-6}	含量区间	47.01 ~ 317.98	80.59 ~ 196.78	51.74 ~ 118.80			
	均值	159.56	136.15	85.96			
ΣHREE/10^{-6}	变化区间	8.80 ~ 21.37	10.88 ~ 31.08	4.21 ~ 8.05			
	均值	12.11	19.81	6.4			
ΣL/ΣH	变化区间	5.12 ~ 19.93	5.99 - 7.32	12.29 ~ 14.77			
	均值	12.61	6.94	13.22	7.22		
$(La/Yb)_N$	变化区间	3.97 ~ 24.20	5.59 ~ 8.52	15.08 ~ 23.98			
	均值	11.77	6.77	19.14	8.14		
$(La/Sm)_N$	变化区间	2.36 ~ 5.39	2.65 ~ 3.53	1.26 ~ 3.09			
	均值	3.76	3.23	2.16	3.3		
$(Gd/Yb)_N$	变化区间	1.09 ~ 3.65	1.24 ~ 1.71	1.60 ~ 2.56			
	均值	1.7	1.48	2.18	1.76		
δEu	变化区间	0.38 ~ 0.89	0.53 ~ 0.83	0.92 ~ 1.05			
	均值	0.66	0.7	0.97	0.73	0.74	0.62
δCe	变化区间	0.90 ~ 1.14	0.92 ~ 1.24	0.75 ~ 0.89			
	均值	1.04	1.01	0.83			

注:* 来自朱恺军等,1991a;1991b;韦星林,1996;王可勇等,1999a;李晓峰等,2001;2002;华仁民等,2002;刘志远等,2005d 的平均值;** 来自朱训等,1983;钱鹏,2003;钱鹏等,2005 的平均值;双桥山群数据来自刘志远等,2005b;2005c;上、下亚群数据来自刘英俊等,1989。

(李厚民等,2003)。铕在还原条件下呈 Eu^{2+} 状态与其他 3 价稀土元素分离,而铈在还原条件下呈 Ce^{3+} 状态,只有在氧化条件下才呈 Ce^{4+} 状态与其他稀土元素分离。因此,黄铁矿的稀土元素具明显铕负异常、而铈无明显异常表明金成矿物理化学条件为还原环境,这与矿区黄铁矿为主要载金金属矿物的事实一致,说明金山金矿床成矿流体具弱还原性。

3.2 微量元素特征

金山金矿床含金黄铁矿的微量元素组成列于表 3,相应的上地壳微量元素(Taylor et al., 1985)标准化蛛网图见图 3。由表 3、图 3 可以看出,与大陆上部地壳相比,金山金矿床含金黄铁矿中 Ti、Co、Ni、Cu、Zn、Mo、Cd、W、Pb、Bi 的富集系数均大于 2(富集系数为某元素在黄铁矿中的平均含量与大陆上部地壳平均含量的比值),为强富集元素;V、Zr 的富集系数 1 ~ 2,为中等富集元素;其他富集系数 <1 的元素则为贫化元素。这种贫化现象可能与剪切带中有较大体积的流体通过,造成这些元素淋失有关;而水-岩反应导致的岩石体积增加也使这些元素含量相对减小(华仁民等,2002)。

黄铁矿中富集 Cu、Zn、Cd、Pb、Bi 等亲硫重金属族元素,Ti、Co、Ni、V 等亲硫的第一过渡族元素,以及 Mo、W、Zr 等高温成矿元素族(赵伦山等,1988),显示了微量元素的地球化学亲合性。李厚民等(2004)对胶东焦家金矿中黄铁矿及其包裹体中微量元素的研究表明,黄铁矿中这些微量元素的富集也可能反应了成矿流体富集成矿元素的特征。

表 4 列出了金山金矿床变质岩、含金黄铁矿及区域地层和岩石的微量元素平均含量及元素比值,证明金山金矿床的成矿物质和成矿流体与矿区变质岩及区域地层有密切的成因关系,与前人从其他方面得到的结果是一致的(季峻峰等,1994a;韦星林,1995;1996;王可勇等,1999a;1999b;华仁民等,2000)。

由表 1 和表 3 可以看出,黄铁矿中亏损高场强元素,富集 LREE,Hf/Sm、Nb/La 和 Th/La 值小于 1。以往认为,Cl 优先配合 LREE,而 F 则易与 HREE 结合。近年的研究发现,富 F 的热液亦可迁移大量的 LREE(Flynn et al., 1978;Alderton et al., 1980;Haas et al., 1995)。富 Cl 的热液富集 LREE,Hf/Sm、Nb/La 和 Th/La 值一般小于 1,而富 F 的热液富集 LREE 和 HFSE,Hf/Sm、Nb/La 和 Th/La 值一般大于 1(Oreskes et al., 1990;毕献武等,2004)。所以,金山金矿床中与金成矿关系密切的黄铁矿的特征表明成矿热液应该是 Cl 多于 F 的。

矿物中所含的微量元素在一定程度上反映了矿

表 3 金山金矿床含金黄铁矿床中微量元素含量($w_B/10^{-6}$)及特征值

Table 3 Trace element abundances and features of gold-bearing pyrite from the Jinshan gold deposit($w_B/10^{-6}$)

	DX-12	DX-14	DX-15	DX-16-1	DX-16-2	DXII-11	DXII-12	DXII-13	DXII-19	DXII-20	DXII-21	DXII-22-1	DXII-22-2	上陆壳*
Li	5.347	3.151	6.429	5.617	5.747	8.336	16.536	54.422	1.521	2.489	3.424	4.485	4.827	20.0
Sc	7.244	8.844	6.838	5.454	5.573	4.601	11.974	31.422	6.304	5.681	8.811	3.667	3.302	11.0
Ti	11356.863	4300.142	11159.010	8358.136	8528.690	4158.899	4505.046	5768.235	3266.710	2539.857	11532.244	3033.719	2734.893	3000.0
V	162.351	29.871	189.154	133.807	126.595	38.419	44.228	70.817	39.797	20.033	235.358	26.990	26.711	60.0
Cr	4.565	40.664	6.409	12.745	12.310	47.462	37.640	58.813	50.396	27.309	4.342	27.030	23.193	35.0
Mn	21.483	53.565	39.531	20.528	21.976	50.632	87.918	35.571	9.960	23.769	27.312	163.274	36.039	600.0
Co	304.379	314.314	260.436	254.264	257.231	436.810	321.218	416.359	169.448	285.161	223.266	407.042	382.839	10.0
Ni	123.555	589.549	150.850	318.571	335.379	1394.604	1645.316	3039.880	621.503	555.702	67.570	882.282	935.594	20.0
Cu	184.150	105.000	250.779	323.658	277.237	216.285	618.555	901.170	295.148	181.455	166.518	198.267	190.763	25.0
Zn	336.511	148.575	471.024	489.680	508.020	123.530	1194.596	1738.997	219.727	796.632	263.025	256.656	227.973	71.0
Ga	4.003	3.987	4.446	4.255	4.090	2.062	5.453	10.350	3.483	4.001	4.498	3.031	2.909	17.0
Rb	10.391	2.737	11.624	9.546	10.011	0.862	28.183	64.899	7.577	4.487	9.121	1.102	1.108	112.0
Sr	11.263	22.893	19.165	11.649	12.681	12.434	41.697	57.439	17.290	11.937	11.966	10.946	11.605	350.0
Y	10.891	19.457	11.111	8.526	8.394	9.529	8.451	19.830	12.319	9.105	10.048	8.906	8.104	22.0
Zr	96.229	337.765	92.300	125.258	109.610	256.659	172.208	299.468	370.105	298.139	81.000	206.601	171.728	190.0
Nb	5.803	10.624	7.239	7.149	6.247	8.494	8.214	13.331	8.939	6.662	5.674	6.299	5.670	25.0
Mo	2.623	1.987	1.926	1.597	1.903	26.838	1.820	3.660	1.945	1.572	2.021	221.690	193.410	1.5
Cd	0.907	0.336	1.033	0.838	0.811	0.324	1.859	5.256	0.652	2.583	0.771	1.000	0.997	0.1
Sn	1.382	1.304	1.314	1.222	1.125	0.708	2.201	11.715	1.082	0.468	1.778	0.791	0.585	5.5
Cs	2.526	0.735	2.490	1.843	1.886	0.148	3.373	5.095	1.064	0.469	1.659	0.407	0.351	3.7
Ba	37.700	11.050	47.263	40.615	39.233	7.118	88.075	122.295	21.152	14.666	35.671	7.404	7.508	550.0
Hf	2.098	8.921	2.153	2.955	2.752	5.886	3.202	7.664	8.701	8.321	2.129	5.452	4.642	5.8
Ta	0.414	0.850	0.493	0.504	0.436	0.529	0.596	1.167	0.711	0.561	0.410	0.526	0.460	2.2
W	146.188	84.391	181.588	120.065	140.577	82.979	36.664	78.284	118.759	54.885	159.450	63.190	57.715	2.0
Pb	103.116	281.420	243.876	174.563	175.702	392.394	1051.729	1568.469	1279.451	822.706	80.933	403.934	397.406	20.0
Bi	1.346	12.362	3.060	4.318	4.636	13.538	17.120	35.187	30.684	14.895	1.142	17.347	17.888	0.1
Th	2.511	23.790	3.195	5.774	5.396	6.507	9.277	14.384	11.379	12.588	2.725	8.876	8.550	10.7
U	0.484	3.678	0.565	1.112	1.131	1.884	1.901	3.596	4.640	3.649	0.536	2.452	2.134	2.8
Hf/Sm	0.840	0.762	0.668	0.758	0.739	1.554	0.417	0.587	1.437	1.056	0.954	1.009	0.875	1.289
Nb/La	0.620	0.147	0.498	0.328	0.307	0.262	0.181	0.235	0.187	0.109	0.594	0.156	0.161	0.833
Th/La	0.268	0.329	0.220	0.265	0.265	0.201	0.204	0.254	0.238	0.206	0.286	0.220	0.243	0.357
Y/Ho	20.588	22.221	20.446	20.866	22.106	27.281	25.946	25.449	23.208	20.379	19.408	24.856	23.781	27.500
Nb/Ta	14.021	12.499	14.677	14.192	14.345	16.069	13.792	11.427	12.572	11.885	13.828	11.984	12.322	11.364
Zr/Hf	45.869	37.861	42.876	42.384	39.823	43.606	53.790	39.075	42.534	35.830	38.053	37.897	36.994	32.759
Co/Ni	2.464	0.533	1.726	0.798	0.767	0.313	0.195	0.137	0.273	0.513	3.304	0.461	0.409	0.500

注：由南京大学地球科学系壳幔演化与成矿作用研究国家重点实验室 ICP-MS 室高剑峰测试；分析仪器：ELEMENT-2 型 ICP-MS，分析精度(RED)＜±0.01%。“*”来自 Taylor et al.，1985。比值单位为 1。

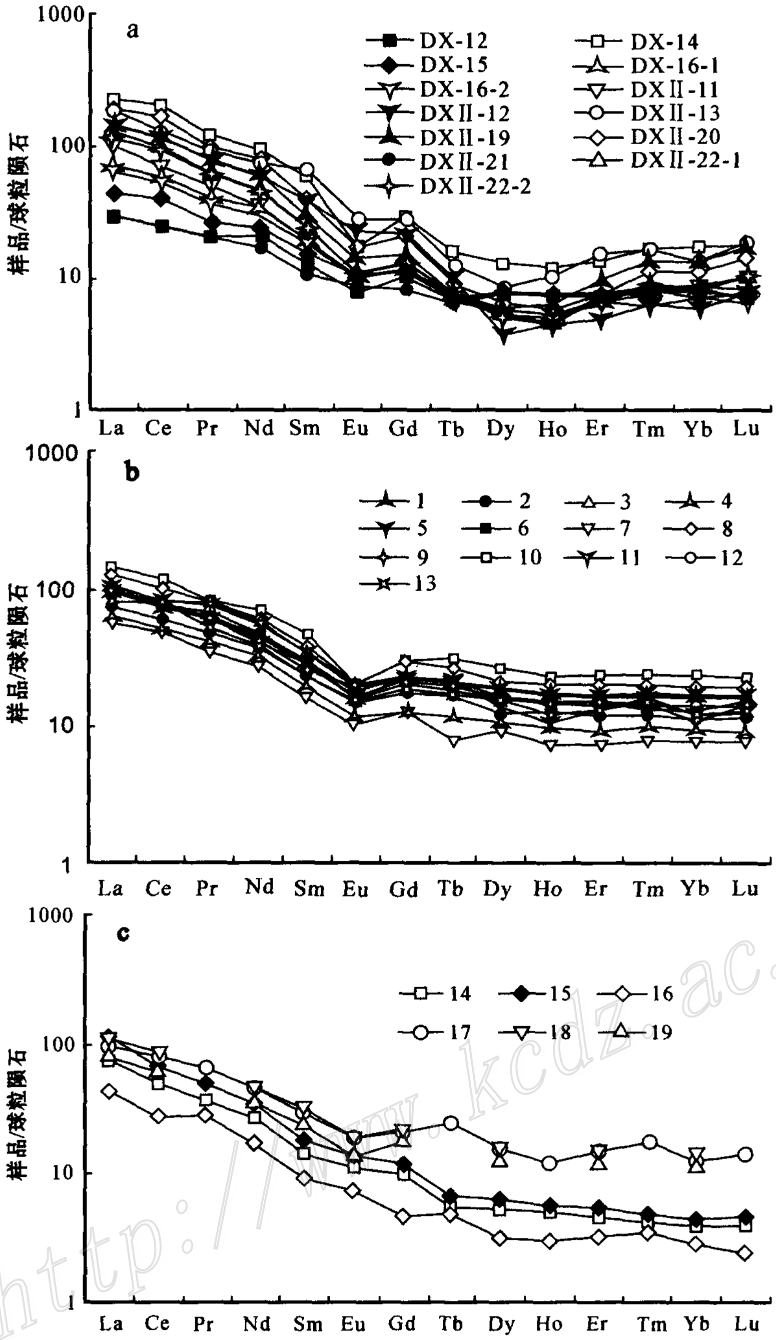

图 2　金山金矿床不同岩石和黄铁矿的稀土元素球粒陨石标准化模式图

(REE 标准化值采用 Boynton , 1984 的 Cl 球粒陨石值)

a . 矿床中黄铁矿 ; b . 金山矿区变质岩 ; c . 区域火成岩(14-16) 及地层(17-19)

Fig . 2　Chondrite-normalized REE patterns of rocks and pyrite in the Jinshan gold deposit

a . Pyrite of the Jinshan gold deposit ; b . Metamorphite of the Jinshan deposit ; c . Regional igneous rocks (14-16) and strata (17-19)

石的形成条件 ,可作为成因的指示剂。黄铁矿中的杂质元素 Co 、Ni 等呈类质同象取代 Fe ,而 Co 在周期表中的位置离 Fe 更近 ,所以 Co 较 Ni 更易进入黄铁矿晶格 ,因此黄铁矿中的 Co/ Ni 比值对成矿条件具有一定的指示意义 。一般来说 , Co/ Ni 比值越大 ,矿物的形成温度越高(盛继福等 ,1999) 。金山金矿床黄铁矿中 Co/ Ni 比值平均为 0. 38 ,说明成矿温度不高 ,矿床为中低温矿床 。

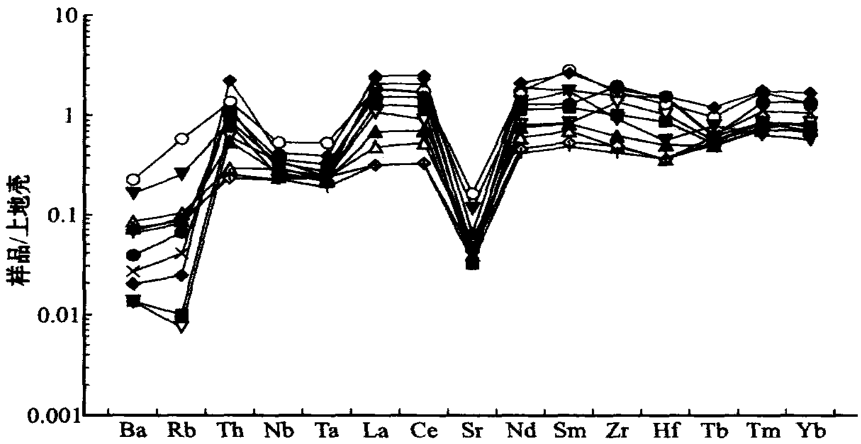

图 3 金山金矿床含金黄铁矿微量元素比值蛛网图

Fig. 3 Spider diagram of trace elements of gold-bearing pyrite in the Jinshan gold deposit

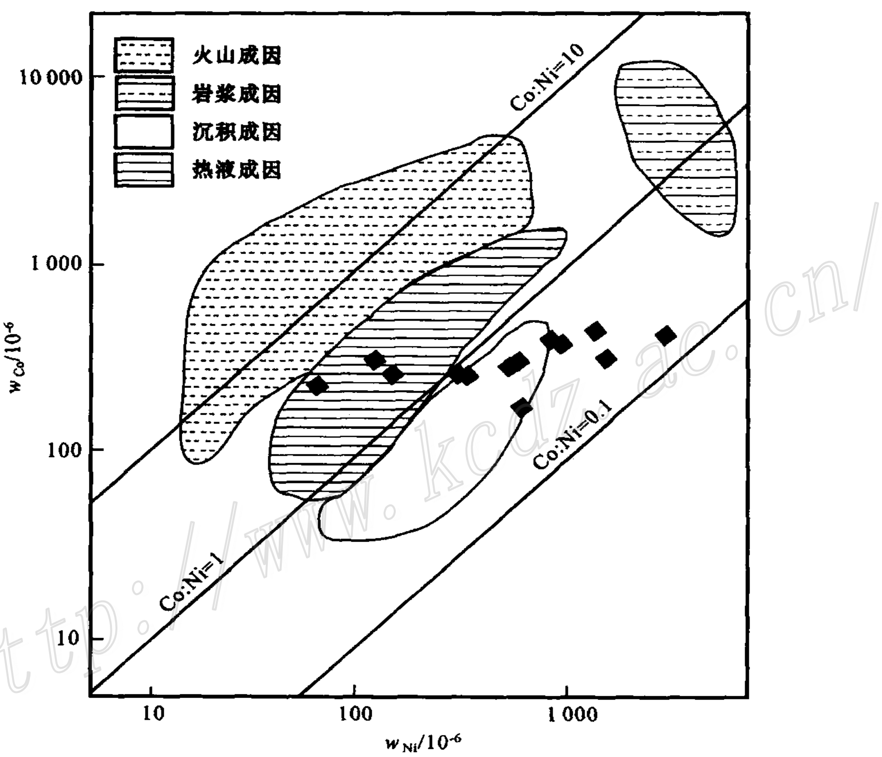

图 4 金山金矿床中黄铁矿的 Co/ Ni 分布图

(不同地质环境边界的定义据 Bajwah et al., 1987; Brill, 1989)

Fig. 4 Co/ Ni distribution diagram of pyrites from the Jinshan gold deposit

(Boundaries of different geological settings are defined after Bajwah et al., 1987; Brill, 1989)

仿照 Xu(1998) 对黄铁矿中的 Co/ Ni 进行了比较。在图 4 中,金山金矿床黄铁矿分别落在热液成因与沉积成因黄铁矿区及 Ni 含量增高的外部。相比较而言,Co 含量变化不大,而 Ni 含量变化较大,穿越了热液成因与沉积成因区,这也符合对金山矿田成矿经历了沉积成岩、区域变质、韧性剪切带的动

表 4　金山金矿床黄铁矿、区域地层和岩石的微量元素含量($w_B/10^{-6}$)及特征值

Table 4　Trace element abundance ($w_B/10^{-6}$) and features of pyrite, regional strata and rocks from the Jinshan gold deposit

	1	2	3	4	5	6	7	8	9
	黄铁矿(13)	千枚岩(5)	糜棱岩(3)	超糜棱岩(4)	双桥山群下亚群(84)	双桥山群上亚群(34)	铜厂花岗闪长斑岩(6)	富家坞花岗闪长斑岩(2)	上地壳
Li	9.41	65.49	83.93	45.85			52.68	49.42	20
Sc	8.44	17.73	10.13	4.35			10.35	9.08	11
Ti	6249.42				4756.00	4175.00	2750.51	2778.04	3000
V	88.01	121.79	75.09	47.51	129.00	117.00	111.10	101.02	60
Cr	27.14				152.00	207.00			35
Mn	45.50				863.00	916.00	273.73	242.77	600
Co	310.21	15.86	9.21	8.31	27.00	25.00	10.02	7.71	10
Ni	820.03	40.01	27.67	28.26	38.00	37.00			20
Cu	300.69	44.74	25.98	25.82	49.00	41.00	4195.21	2132.19	25
Zn	521.15	102.06	50.61	63.85	121.00	111.00			71
Ga	4.35	24.68	18.43	7.74			20.26	21.42	17
Rb	12.43	146.80	135.96	10.96			94.45	63.59	112
Sr	19.46	110.26	97.34	232.28	104.00	16.00	2917.76	578.61	350
Y	11.13						10.00	10.07	22
Zr	201.31	255.84	228.16	116.85			142.72	162.15	190
Nb	7.72	14.09	10.60	5.59			8.80	9.51	25
Mo	35.61								1.5
Cd	1.34								0.098
Sn	1.98						1.27	0.84	5.5
Cs	1.70	15.20	18.52	2.94			27.35	5.89	3.7
Ba	36.90	593.20	565.69	66.55	723.00	471.00	1454.42	1305.02	550
La	35.89	38.09	29.84	73.85	23.72	32.82	23.19	33.52	30
Ce	75.45	81.24	63.24	89.38	48.74	68.44	40.10	54.34	64
Pr	7.47	9.70	7.59	47.12			4.44	5.91	7.1
Nd	28.97	36.17	27.68	36.95	20.18	28.15	16.06	20.58	26
Sm	5.88	7.37	5.54	24.92	4.48	6.06	2.75	3.45	4.5
Eu	1.05	1.55	1.23	15.07	0.97	1.37	0.82	0.99	0.88
Gd	4.09	7.46	6.17	18.17	4.39	5.75	2.50	2.99	3.8
Tb	0.41	1.24	1.05	16.52			0.26	0.31	0.64
Dy	2.23	6.85	5.89	12.53	3.95	4.99	1.71	1.98	3.5
Ho	0.49	1.47	1.32	12.69			0.37	0.41	0.8
Er	1.76	4.13	3.64	11.97	2.45	3.04	0.97	1.11	2.3
Tm	0.32	0.64	0.56	12.08			0.13	0.15	0.33
Yb	2.02	4.01	3.42	11.30	2.39	2.97	0.85	0.94	2.2
Lu	0.36	0.62	0.52	11.84			0.13	0.15	0.32
Hf	4.99	6.62	6.00	3.01			3.62	4.10	5.8
Ta	0.59	0.90	0.64	0.30			0.73	0.82	2.2
W	101.90	40.49	30.46	42.89					2
Pb	536.59	14.20	12.49	8.97	45.00	39.00	14.01	16.20	20
Bi	13.35	0.21	0.19	0.34			0.27	0.09	0.127
Th	8.84	11.96	8.96	4.28			15.76	16.27	10.7
U	2.14	2.64	2.03	1.12			2.24	2.77	2.8
Ag		1.72	1.68	1.09	0.06	0.05			
Au		4.09	3.88	20.35	0.00	0.02			
As					14.00	47.00			
Hg					0.01	0.01			

续表 4-1

Table 4-1 continued

	1	2	3	4	5	6	7	8	9
	黄铁矿 (13)	千枚岩 (5)	糜棱岩 (3)	超糜棱岩 (4)	双桥山群下亚群(84)	双桥山群上亚群(34)	铜厂花岗闪长斑岩(6)	富家坞花岗闪长斑岩(2)	上地壳
Co/ Ni	0.38	0.40	0.33	0.29	0.71	0.68			
Sr/ Ba	0.53	0.19	0.17	3.49	0.14	0.03	2.01	0.44	
U/ Th	0.24	0.22	0.23	0.26			0.14	0.17	
Th/ Sc	1.05	0.67	0.88	0.98			1.52	1.79	
Th/ Co	0.03	0.75	0.97	0.52			1.57	2.11	
Y/ Ho	22.66	33.60*	32.33*	35.02*			27.05	24.66	
Nb/ Ta	13.11	15.66	16.56	18.63			12.03	11.66	
Zr/ Hf	40.34	38.65	38.03	38.82			39.46	39.51	
Sr/ Eu	18.52	71.14	79.14	15.41	107.22	11.68	3576.26	585.61	
Zr/ Nb	26.08	18.16	21.52	20.90			16.23	17.05	
Sm/ Nb	0.76	0.52	0.52	4.46			0.31	0.36	

数据来源:1:本文;2~4:华仁民等(2002)、李晓峰等(2001;2002),其中有*者为刘英俊等(1993);5~6:刘英俊等(1989);7~8:钱鹏(2003)、钱鹏等(2005);9:Taylor et al (1985)。比值的单位为1。括号中数字为样品数。

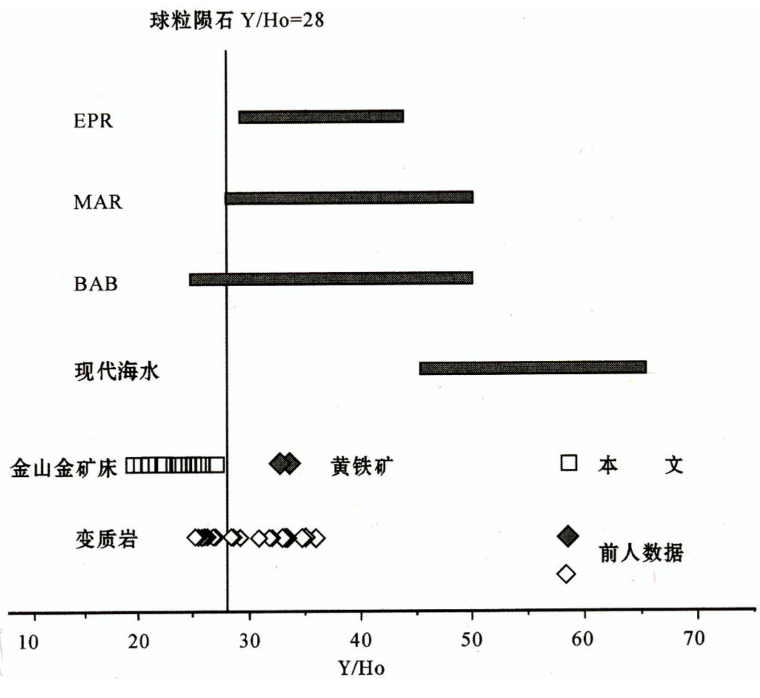

图 5 金山金矿床中黄铁矿、现代海底热液和海水的 Y/ Ho 比值比较

现代海水、BAB(弧后盆地)、MAR(中大西洋洋脊)和 EPR(东太平洋洋脊)

热液流体数据引自 Bau et al., 1997;1999;Douville et al., 1999

Fig. 5 Y/ Ho ratios of pyrite from Jinshan, modern submarine hydrothermal fluids and seawater

Data of hydrothermal fluids and modern seawater, BAB (Back-Arc Basin), MAR (Middle-Atlantic Ridge) and EPR (East Pacific Ridge) from Bau et al., 1997; 1999; Douville et al., 1999

力变质作用及表生氧化作用的演化过程的认识(韦星林,1995)。Co/ Ni 变化于 0.14~3.30 之间,与岩浆热液成因的铜厂金铜矿床中黄铁矿的微量元素比值特征不同。这 2 个矿床代表了 2 种不同的成矿作用,金山金矿床是一种变质热液改造金矿床,成矿物质和热液来自围岩(朱恺军等,1991b)。

前人利用 Y 和 Ho 对成矿流体及现代海底热液进行了研究(Bau et al., 1995;1997;1999;Douville et al., 1999;赵葵东,2005)。Y 和 Ho 具有相同的价态和离子半径,八次配位时,两者的离子半径分别为 1.019×10^{-10} 和 1.015×10^{-10}(Shannon,1976),因此,Y 和 Ho 常常具有相同的地球化学性质,在许多地质过程中,Y/Ho 比值并不发生改变。地球上大多数岩浆岩和碎屑沉积物都保持着球粒陨石的 Y/Ho 比值 28 ±(Bau et al., 1995)。本文也作了黄铁矿 Y/Ho 比值与现代海底热液流体之间的比较(图 5)。从图 5 可以看出,金山金矿床黄铁矿的 Y/Ho 与矿区的变质岩很相似,而与现代海底热液及区域花岗岩的 Y/Ho 比值变化相差较大。因此,黄铁矿的 Y/Ho 比值提供了新的证据,表明与金成矿关系密切的黄铁矿的热液流体来源与变质岩关系密切。

4　结　论

(1) 黄铁矿中的 REE 组成代表了成矿溶液的 REE 组成。江西金山金矿床与金成矿关系密切的黄铁矿的稀土元素组成与矿区变质岩及区域地层的稀土元素组成相似,表明该金矿床的成矿物质来源于变质岩,成矿流体为变质水。

(2) 利用黄铁矿的 Y/Ho 比值推断金山矿床的成矿流体为变质流体。

(3) 利用黄铁矿中的 Co/Ni 比值判断黄铁矿的成因,显示金山金矿床为中低温矿床;成矿经历了沉积成岩、区域变质、韧性剪切带的动力变质作用及表生氧化作用。

(4) 金山金矿床黄铁矿成矿流体中富集 LREE、亏损 HFSE,Hf/Sm、Nb/La 和 Th/La 比值小于 1,推断金山金矿床成矿流体为富 Cl 流体而非富 F 流体。

综合上述,与金成矿关系密切的黄铁矿的稀土元素和微量元素特征,可以推断金山金矿床的成矿热液来源于变质岩,为 Cl > F 的变质流体。

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