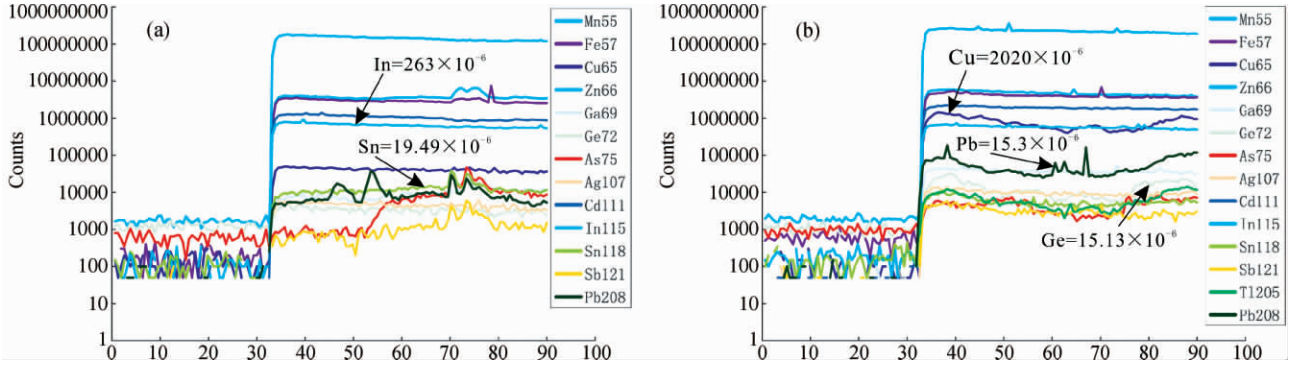

图 5 闪锌矿 LA-ICPMS 时间分辨率剖面图

(a)-样品 Lc-19-1;(b)-样品 Lc-18-3

Fig. 5 Representative time-resolved depth profiles for sphalerite analysed by LA-ICPMS

(a)-sample Lc-19-1; (b)-sample Lc-18-3

表明这些元素以类质同象形式赋存于闪锌矿中，而 Cu、Pb、Sn 和 Bi 等元素则呈现变化幅度较大曲线(图 5)，说明这些元素是以显微包裹体形式赋存于闪锌矿中，这与矿相及 SEM 分析所发现闪锌矿中存大量黄铜矿“病毒”结构及方铅矿及黝锡矿等矿物显微包裹体一致。此外，相关分析结果表明，闪锌矿中 Cu 与 Sn($R=0.73$, $n=38$)、Pb 与 Bi($R=0.85$, $n=38$)、Pb 与 Ag($R=0.87$, $n=38$) 有很好正相关关系，暗示 Sn、Bi、Ag 等元素局部富集可能与闪锌矿中显微包裹体黄铜矿、方铅矿等有关。

4 讨论

4.1 成矿温度

闪锌矿中微量元素有规律的变化是成矿温度由高到低的客观反映，已有的研究表明，高温条件下形成闪锌矿富集 Fe、Mn、In、Se、Te 等元素，并以较高 In/Ga 比值为特征，而低温条件下形成闪锌矿则相对富集 Cd、Ga、Ge 等元素，以较低 In/Ge 比值为特征(刘英俊等，1984；韩照信，1994；蔡劲宏等，1996)。本矿床中的闪锌矿 Fe 含量多大于 10%，相对富集 Cd，且其中 In 含量较高，远高于低温闪锌矿，介于中温与高温闪锌矿之间，尽管个别闪锌矿 Ga 含量较高，但总体上均介于中温闪锌矿范围。表 1 计算结果可知，矿床中闪锌矿 In/Ga(0.88～99.65，平均 17.92，$n=38$) 和 In/Ge(11～1689，平均 176，$n=38$) 比值相对较高，但明显低于高温热液矿床，如芙蓉锡矿田狗头岭矿区产出的闪锌矿(In/Ga 为 149.8～792.7，In/Ge 为 2091～16923，蔡劲宏等，1996)，其 Zn/Cd 比值介于 119～152 之间，平均为 133($n=8$)，与中温条件下形成闪锌矿 Zn/Cd 比值($100<Zn/Cd<500$，刘英俊等，1984) 相似。此外，闪锌矿的微量元素 Ga/Ge 比值可与形成闪锌矿的溶液温度相对比(Peter，1987)，本矿床闪锌矿在 logGaGe-T 关系图(图略) 中投影点分布 196～272℃之间，平均 230℃(±22℃)。可见，本矿床成矿温度应以中温为主，这与前人包裹体测温结果(207～283℃，平均值为 256℃，王增润等，1997) 相似，与喷流沉积成因的块状硫化物矿床的形成温度(250～350℃) 基本吻合。

4.2 成矿物质来源

Y 和 Ho 具有相同的价态和离子半径，八次配位，两者的离子半径分别为 1.019×10^{-10} 和 1.015×10^{-10}，它们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(Shannon，1976)，因此，可以利用 Y 和 Ho 对成矿流体及现代海底热液进行研究(Bau and Dulski，1999；Douville *et al.*，1999；毛光周等，2006)。本矿床闪锌矿 Y/Ho 具有相对较宽变化范围，其比值在 22.60～38.33 之间(表 2、图 6)，平均为 29.74，与现代海底热液系统(BAB-弧后盆地；MAR-中大西洋洋脊；EPR-东太平洋洋脊) Y/Ho 比值较相似，接近地

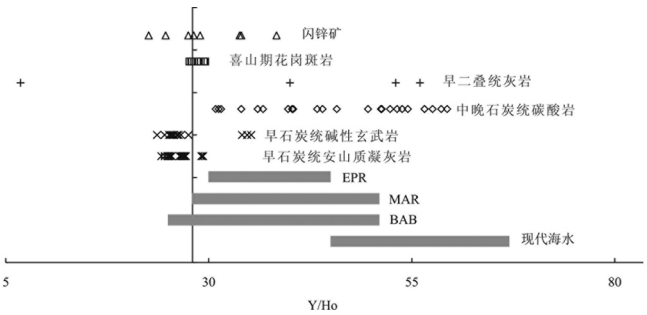

图 6 老厂矿区地层、岩体及硫化物与现代海底热液和海水的 Y/Ho 比值比较

BAB-弧后盆地；MAR-中大西洋洋脊；EPR-东太平洋洋脊(引自 Bau *et al.*，1997；Bau and Dulski，1999；Douville *et al.*，1999)

Fig. 6 Y/Ho ratios of stratum, rock body and sulfides from Laochang ore area, modern submarine hydrothermal fluids and seawater

BAB: back-arc basin; MAR: Middle-Atlantic Ridge; EPR: East Pacific Ridge (after Bau *et al.*, 1997; Bau and Dulski, 1999; Douville *et al.*, 1999)

表 2 老厂矿区地层、岩体及闪锌矿 Y/Ho 比值对比表

Table 2 Contrast table of Y/Ho ratios of stratum, rock body and sulfides from Laochang ore area

	样品数	Mean	Min	Max	S. D	资料来源
C_1^{5+6}安山质凝灰岩(n=15)	15	26.36	24.16	29.28	1.51	本文
C_1^{7} 碱性玄武岩(n=8)	8	25.61	24.56	26.57	0.67	本文
C_{2+3}^{1+2}碳酸盐(n=23)	23	45.72	30.83	59.33	9.48	本文; 龙汉生,2009
早二叠统灰岩(n=4)	4	38.96	6.83	56.00	22.51	龙汉生,2009
喜山期花岗斑岩(n=13)	13	28.46	27.65	29.55	0.73	龙汉生,2009
闪锌矿(n=8)	8	29.74	22.60	38.33	5.26	本文
现代海水			45	67		Bau *et al.*, 1997; Bau and Dulski, 1999; Douville *et al.*, 1999
BAB			25	51		
MAR			28	51		
EPR			30	45		

注: 样品由中国地质科学院国家地质测试中心 ICP-MS 分析

层-早石炭统依柳组火山岩之安山质凝灰岩(24.16~29.28, 平均 26.36)和碱性玄武岩(24.56~26.57, 平均 25.61)变化范围, 相对低于中晚石碳统碳酸岩(30.83~59.33, 平均 45.72)和早二叠统灰岩(6.83~56.00, 平均 38.96), 而与深部隐伏花岗斑岩极其狭窄 Y/Ho 变化范围(27.65~29.55, 平均 28.46)明显不同, 表明本矿床成矿物质(Pb、Zn 等)应主要来源于早石炭世火山岩(玄武岩及凝灰岩), 在火山喷流作用下通过该地层及其基底物质的淋滤作用富集成矿, 而与深部隐伏喜山期隐伏花岗斑岩关系不大。此外, 喜山期隐伏花岗斑岩中 Cu、W、Sn、Mo、Sb、Ga 等元素富集程度较高, 并形成巨厚 Mo(Cu)矿化, 而其 Pb、Zn 含量低于或相当于世界花岗岩平均值(李雷等, 1996), 同样表明其并非为 Pb 和 Zn 潜在矿源层。

4.3 矿床类型

上述研究结果表明该矿床具有以下地质地球化学特征:

(1)本矿床存在大量同生沉积结构构造, 尽管其赋矿围岩类型与黑矿型矿床不同, 但矿床位于拉张构造环境、成矿元素水平及垂向分带(上"黑矿"下"黄矿", 且上部以层状和块状矿石为主, 而深部以网脉状矿化为主)以及中等成矿温度等地质地球化学特征均与黑矿型矿床类似;

(2)近矿围岩蚀变强烈, 类型复杂, 具多期叠加改造特点。矿石中分布大量 Sb-、As-Pb 和 Cu-硫盐矿物(如碲硫砷铅矿-砷硫碲铅矿、车轮矿-硫砷铅铜矿、黝铜矿-砷黝铜矿系列, 砷铜铅矿和细硫砷铅矿等), 常包裹或与方铅矿共生, 这类矿物组合与其结构构造与世界上加里东期 VMS 和 SEDEX 型矿床受改造作用矿床极其相似(如 Sulitjelma, Bleikvassli, Norway; Cook, 1996; Cook *et al.*, 1998)。此外, 闪锌矿中大量黄铜矿"病毒"结构存在, 也表明本矿床可能遭受了晚期富含 Cu 的流体改造。可见, 本矿床后期热液叠加改造作用明显, 闪锌矿中 Cu 与 Sn 极好的正相关关系, 暗示改造流体富集 Cu、Sn、Sb 和 As 等成矿元素, 可能与深部隐伏花岗斑岩的侵入作用有关。

(3)矿床中闪锌矿以富 Fe、Mn、Cd、In、Ga 等元素为特征, 其中 Fe、Mn、Cd 等元素含量相对较稳定, 而 In、Sn、Pb、Cu 和 Bi 等元素含量变化范围较大。其中 Fe 和 Mn 等微量元素组成与一般 VMS 矿床类似, 但 In 和 Cd 的异常富集可能暗示其独特的成矿机制, 该特征明显不同与矽卡岩型矿床(如核桃坪与鲁子园, 其闪锌矿以富 Co、相对富集 Fe 和贫 In、Ga、Sn 为特征, Ye *et al.*, 2011), 而与燕山-喜山期花岗岩叠加改造作用有关的喷流沉积铅锌矿床(如云南白牛厂和广东大宝山)类似, 该类型矿床与老厂矿床矿石具相似的结构构造, 其闪锌矿均以富集 Fe、In、Ga 和 Sn 为主要特征(Ye *et al.*, 2011)。在 Ga+Ge-Se+Te+In-Ag 三角图解(图 7)中, 本矿床闪锌矿投影点分布于 Se+Te+In 端员, 而与长江中下游岩浆热液型矿床中闪锌矿差异明显, 表明铅锌成矿作用应与矿区喜山期花岗斑岩无关。而在 In-Fe、In-Sn、Cu+Ag-In+Sn 和 Cd/Fe-In/Fe 关系图(图 8)及 In-Ge、In-Co、Cu-Sn、Fe-Mn、Fe-Cd、Ga-Ge、Fe-Ge 和 Cd/Fe-Co/Ni 等关系图解(图略)中, 老厂闪锌矿投影点均与受晚期热液叠加改造作用有关的喷硫沉积铅锌矿床(如云南白牛厂和广东大宝山)分布于相同区域, 而明显不同于矽卡岩型矿床(如核桃坪与鲁子园), 更不同于 MVT 型铅锌矿床(牛角塘、会泽和勐兴, 该类型矿床闪锌矿以富 Cd 贫 In 和 Fe 为特征)和金顶铅锌矿床(其闪锌矿微量元素组成与 MVT 型矿床相似, 但 Ge 和 Tl 富集程度相对较高)。可见, 本矿床闪锌矿微量元素组成具喷流沉积成因闪锌矿特征, 同时, 后期叠加改造作用可能使其微量元素组成(如 Sn 等)发生一定程度变化。

此外, 本矿床黄铁矿及方铅矿微量元素组成研究结果表明其成因复杂, 既有火山喷流沉积成因, 也有晚期岩浆热液叠加改造成因(高伟, 2011)。因此, 综合本矿床产出地质特征, 结合闪锌矿等硫化物单矿物微量元素组成特征, 笔者认为老厂铅锌多金属矿床中铅锌矿化作用应与喷流沉积作用有关, 但喜山期花岗斑岩侵入带来了丰富的 Cu 和 Sn 等成矿

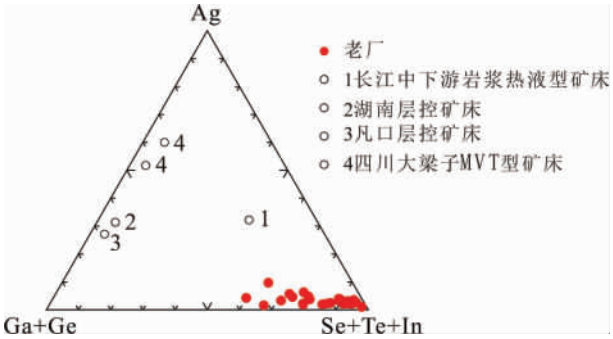

图 7 闪锌矿 Ga + Ge-Se + Te + In-Ag 三角图解(底图据朱赖民等,1995)

Fig. 7 Triangular diagram of Ga + Ge-Se + Te + In-Ag for sphalerite (after Zhu *et al.*, 1995)

物质,并对早期形成的铅锌矿体进行了强烈叠加改造,致使矿体、硫化物及其相关地层不同程度富集 Sn 等元素,这与 Pb、H、O 等同位素研究认为成矿流体具有多期、多阶段、多来源等特征(徐楚明和欧阳成甫,1991; 叶庆同等,1992; 龙汉生,2009)相吻合。

5 结论

综上所述,我们可以得到以下认识:

(1) 硫化物单矿物微量元素分析中,LA-ICPMS 相对于 ICP-MS 分析具有更高精度,不仅可以进行硫化物原位分析,并能即时了解微量元素在硫化物中赋存状态,而且克服了 ICP-MS 分析中单矿物选样不纯等弱点;

(2) 云南澜沧老厂铅锌多金属矿床中闪锌矿属于铁闪锌矿,形成于中温环境,以富 Fe、Mn、Cd 和 In 等元素为特征,其中 Fe、Mn、Cd、In 等元素以类质同象形式赋存于闪锌矿中,而 Sn、Pb、Cu 和 Bi 等元素含量变化范围较大,局部富集,以显微包裹体赋存于闪锌矿中。本矿床闪锌矿中 Fe 和 Mn 等微量元素组成与一般 VMS 矿床类似,但 In 和 Cd 的异常富集可能暗示其独特的成矿机制。总体上闪锌矿中微量元素组成特

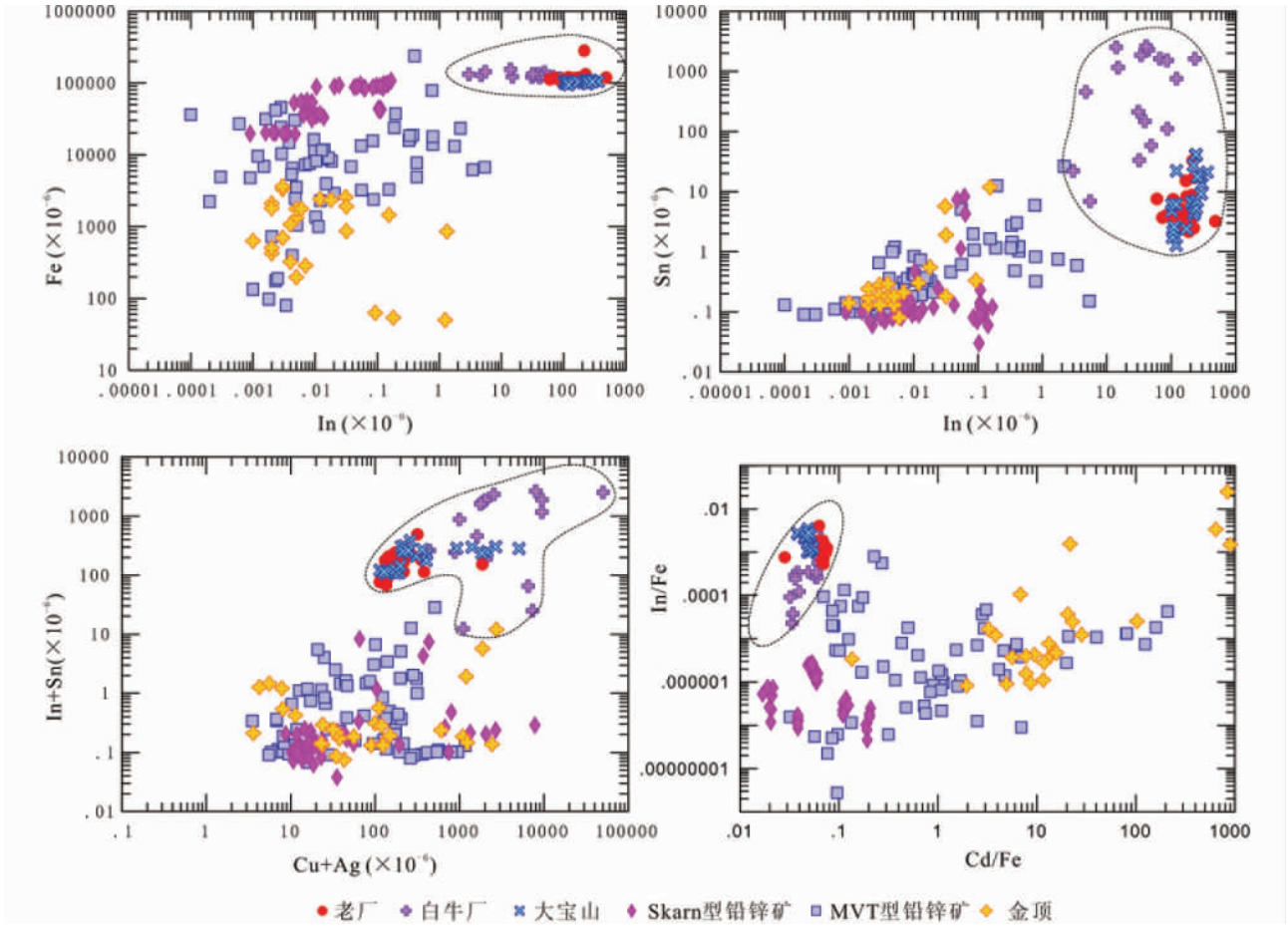

图 8 老厂及国内其它铅锌矿床闪锌矿 In-Fe、In-Sn、(Cu + Ag) -(In + Sn) 和 Cd/Fe-In/Fe 关系图(LA-ICPMS 分析结果,其它铅锌矿床闪锌矿数据源自 Ye *et al.*, 2011)

Fig. 8 Binary plots of In vs. Fe, In vs. Sn, (Cu + Ag) vs. (In + Sn), Cd/Fe vs. In/Fe in sphalerite from Laochang and other Pb-Zn deposits in China (plotted based on LA-ICPMS data, the data of other deposits after Ye *et al.*, 2011)

征和与燕山-喜山期花岗岩叠加改造作用有关的喷流沉积铅锌矿床(如云南白牛厂和广东大宝山)相似,而明显不同与矽卡岩型矿床(如核桃坪与鲁子园),更不同于 MVT 型铅锌矿床(如牛角塘、会泽和勐兴)和金顶铅锌矿床。

可见,云南澜沧老厂铅锌多金属矿区经历了古、中、新特提斯期不同程度的拉张与闭合发展演化,使矿床多期同位叠加成矿特征明显,其闪锌矿微量元素组成具喷流沉积成因特征,深部喜山期花岗斑岩与铅锌成矿作用关系不大,但在其侵入过程中叠加改造作用使闪锌矿等硫化物组合及其微量元素组成发生一定程度变化(如局部富集 Sn 和 Sb 等元素),并形成大量黄铜矿"病毒"结构等。

致谢 分析测试过程中得到澳大利亚 Adelaide 大学 Nigel J. Cook 教授和 Cristiana L. Ciobanu 博士的指导;野外采样过程中得到云南澜沧老厂铅锌矿石增龙总工等地质科研人员的帮助;在此一并致谢!

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