Trace Elements in Fluid Inclusions in the Carlin-Type Gold Deposits, Southwestern Guizhou Province*

SU WENCHAO (苏文超), HU RUIZHONG (胡瑞忠), QI LIANG (漆　亮), AND FANG WEIXUN (方维萱)

(*Open Lab. of Ore Deposit Geochemistry, Institute of Geochemistry, Chinese Academy of Sciences, Guiyang 550002, China*)

Abstract: Fluid inclusions in quartz from the Lannigou and Yata Carlin-type gold deposits in southwestern Guizhou were analyzed by inductively coupled plasma-mass spectrometry for their trace elements (Co, Ni, Cu, Pb, Zn, Pt, etc.). The results show that quartz fluid inclusions entrapped at different ore-forming stages contain higher Co, Ni, Cu, Pb and Zn. It has been found for the first time that the ore-forming fluids responsible for the Carlin-type gold deposits are rich in Pt. From this it can be concluded that basic volcanic rocks seem to be one of the important sources of ore-forming materials for the Carlin-type gold deposits.

Key words: **fluid inclusion; trace element; ICP-MS; Carlin-type gold deposit; southwestern Guizhou**

Introduction

Fluid inclusions refer to the fluid entrapped during the formation of minerals and they are the most direct naturally-occurring samples for the study of ore fluids producing hydrothermal ore deposits. The studies available have indicated that the routine major element (K, Na, Ca, Mg, F, Cl, etc.) analysis of fluid inclusions can no longer satisfy the needs for tracing the ore-forming processes of hydrothermal ore deposits. However, trace elements contained in fluid inclusions can play an important role in tracing the ore-forming processes. But, owing to the extremely fine size of fluid inclusions in minerals, how to analyze the low-level trace elements in fluid inclusions has long been a hard nut to crack. Since the end of the 1980's, with the sophistication of analytical techniques, especially high-precision inductively coupled plasma mass spectrometry (ICP-MS), it has become possible steadily to analyze ultra-micro-level trace elements in fluid inclusions. Unfortunately, little work has been done in this aspect. Ghazi and Branks et al. determined the REE contents of quartz fluid inclusions using cracking-leaching ICP-MS techniques. The present authors have established the high-temperature (>500℃) decrepitating-leaching ICP-MS procedure to determine the REE contents of quartz fluid inclusions (Su Wenchao et al., 1998). In this work the authors used this method to determine the contents of Co, Ni, Cu, Pb, Zn, Pt, etc. in quartz fluid inclusions separated from the Lannigou and Yata Carlin-type gold deposits in southwestern Guizhou Province. On this basis the present paper discusses the possible source region of ore-forming materials.

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Experimental Conditions

Instrument and parameters

The ELEMENT-Type high-resolution inductively coupled plasma-mass spectrometer made by Finnigan MAT Company was employed in this study and the resolution power of the instrument can be adjusted at 300, 3000 and 7500. The designed parameters for the instrument in this experiment are listed in Table 1.

Table 1. Parameters for the instrument (ICP-MS)

Instrument	Parameter	Instrument	Parameter
Forward power	1.20 kW	High vacuum	$(1-9)\times10^{-5}$ Pa
Reflected power	<2 W	Sample time	0.001 s
Nebulizer	0.64 L/min	Resolution power	300
Auxiliary	0.60 L/min	Scanning manner	Peak jumping
Cool (plasma)	14.0 L/min	Mass range	7-250
Sample uptake rate	1.0 mL/min	Number of sweeps	20
Fore vacuum	2.31×10^{-2} Pa	Number of peaks per isotope	10
		Dwell time per point	50 ms

Limit of instrumental determination and blank determination of leach solution

Listed in Table 2 are the limits of instrumental determination of trace elements in this work and the results of blank determination for leach solution. The limits of determination refer to the concentrations corresponding to the standard deviations ×3 obtained from ten times of continuous determination of blank solution in the whole experimental procedure; the blank of leach solution refers to the repeatedly purified 5% HNO_3 solution which was used to extract the components in fluid inclusions. It can be seen that the blank values of leach solution and the limits of instrumental determination are both extremely low.

Table 2. The limits of instrumental determination and the blank (5% HNO_3) values of leach solution ($\times10^{-9}$)

Element	Blank values of leach solution							Limit of instrumental determination
	1	2	3	4	5	6	Average	
Co	0.021	0.040	0.049	0.046	0.014	0.017	0.031	0.02
Ni	0.307	0.374	0.170	0.160	0.095	0.343	0.242	0.16
Cu	0.037	0.022	0.135	0.115	0.097	0.078	0.081	0.37
Pb	0.413	0.254	0.389	0.512	0.350	0.369	0.381	0.07
Zn	0.47	0.376	0.489	0.572	0.632	0.606	0.524	0.66
Pt	0.015	0.010	0.012	0.022	0.023	0.013	0.016	0.05

Experimental Procedure

Sample description

The samples studied were collected from the Lannigou and Yata Carlin-type gold deposits in southwestern Guizhou Province. Samples N9296 and N9278 were colleted from quartz veins formed at the main metallogenetic stage of the Lannigou gold deposit, samples LN9805 and

LN9419 were collected from late quartz veins of the Lannigou gold deposit; sample YT9306 was collected from quartz veins formed at the main metallogenic stage of the Yata gold deposit while sample YT 9301 was collected from late quartz veins of the Yata gold deposit. Microscopic examination of fluid inclusions indicated (Su Wenchao et al., 1998) that fluid inclusions in quartz veins in both the gold deposits are predominated by pure liquid phase and vaper/liquid phase, and most of them are primary inclusions. The homogenization temperatures of quartz fluid inclusions at the main metallogenic stage are 184 – 228 ℃, their salinities are 3.2 – 5.7 wt% NaCl equivalent; the homogenization temperatures of late quartz fluid inclusions are 154 – 166℃ and their salinities are 3.1 – 4.6 wt% NaCl equivalent.

Experimental procedure

(1) *Sample purification* Quartz samples were ground as fine as – 40 mesh and pure quartz monominerals (1 – 2 g, purity 99%) were selected carefully under the microscope. The pure quartz monominerals were boiled with super-pure HNO_3 at 150℃ for 5 – 10 h to dissolve impurities present on the surface or in the fissures of quartz and remove part of the secondary inclusions in quartz. Then the monominerals were washed several times with doubly de-ionized water till the conductivity of the eluate reached that of the doubly de-ionized water, and then baked at low temperature for 12 h.

(2) *Fluid extraction* Fluid inclusions must be opened first before fluid can be extracted from the fluid inclusions in quartz. There are many approaches available to opening fluid inclusions, mainly including crashing, ball grinding, grinding and decrepitation. The former three approaches have the following disadvantages: on one hand, fine fluid inclusions are hard to open completely, and on the other hand, the finer the quartz minerals are ground, the more ions will be adsorbed on the surface of mineral grains and the greater the losses will be. The decrepitation method has its own unique advantages, but it is first and for most to chose the suitable decrepitation temperature. According to Li Huaqin et al. (1993), when quartz was heated to 570℃ or so, the most majority of the fluid inclusions could be opened. So, in this experiment a high decrepitation temperature of 600℃ was chosen in an attempt to open all fluid inclusions in quartz. The procedure is described below. The purified samples were sealed into U-shaped quartz tubes full of argon, and decrepitated at the high temperature of 600℃ for 5 min. Meanwhile, the fluid inclusions were precisely determined on a gas chromatograph for their H_2O contents. After decrepitation, 5 mL super-pure 5% HNO_3 eluate was added in the samples and the fluid was extracted from the fluid inclusions by way of ultra-sonic vibration and centrifugal separation, followed by ICP-MS analysis.

Results and Discussion

As compared with the crashing, ball grinding and grinding methods, the high-temperature decrepitation method has one more advantage, i.e., while decrepitated at high temperature, the fluid inclusions can be accurately determined by gas chromatography for their H_2O contents to avoid the negative influence caused by incomplete opening of fluid inclusions in quartz. The relative deviation is less than 5% in this experiment (Su Wenchao et al., 1998).

Listed in Table 3 are the contents of trace elements in leach solution and their actual concentrations in fluid inclusions. As can be seen from the table, the contents of Co, Ni, Cu, Pb, Zn and Pt in the leach solution are all relatively high, far higher than the limits of instrumental determination and the blank values of leach solution (Table 2), and are of good reputability. All these indicate that the analytical results are highly reliable.

The contents of Co, Ni, Cu, Pb and Zn in quartz fluid inclusions entrapped at different ore-forming stages of the two gold deposits are relatively high (Table 3), similar to the compositions of modern mid-ocean ridge hydrothermal solutions formed as a result of extraction of ocean-floor basalts by fluids (Lu Huanzhang, 1997). REE studies of quartz fluid inclusion population in the Lannigou gold deposit (Su Wenchao et al., 1998) showed that the REE distribution patterns in the ore-forming fluids are similar to those of Late Yanshanian slightly alkaline ultrabasic rocks in the periphery of the mining district and ferrodolomite veins near the rockbodies (Fig.1). The ferrodolomite veins were found containing higher Co, Ni, Cu, Pb and Zn, indicating that basic-ultrabasic volcanic rocks seem to be one of the most important sources of ore-forming materials for the Carlin-type gold deposits in southwestern Guizhou Province. Previous studies showed① that in the Yunnan-Guizhou-Guangxi region are widespread volcanic rocks in the strata ranging in age from Devonian to Middle Triassic. For example, trachybasalt has been recognized in the Devonian strata around Napo, Guangxi; basalts, basaltic tuffs and basaltic pyroclastic rocks in the Late Permian strata around the Funing-Qiubei and Longling-Tianlin areas; basaltic tuffs in the Early-Middle Triassic strata around the Funing-Qiubei areas; slightly alkaline ultrabasic rock swarms in the surroundings of the Lannigou gold deposit; the Carlin-type gold deposits such as the Shijia, Badu and Longhe in Guangxi Autonomous Region, which occur in the endo- and exo-contact zones of diabase bodies and fault broken zones within them (Pan Jiayong et al., 1994). Such distribution characteristics of basic and ultrabasic volcanic rocks may be the best direct evidence for the above deduction.

Table 3. The contents of trace elements in quartz fluid inclusions from the Carlin-type gold deposits

Ore deposit	Lannigou								Yata			
Metallogenic stage	Main stage				Late stage				Main stage		Late stage	
	Concentration in leach solution ($\times 10^{-9}$)											
Element	N9278		N9296		LN9805		N9419		YT9306		YT9301	
	(1)	(2)	(1)	(2)	(1)	(2)	(1)	(2)	(1)	(2)	(1)	(2)
Co	87.285	86.909	2.752	2.891	0.437	0.365	55.763	55.888	64.764	59.592	46.046	48.837
Ni	6.862	6.520	4.585	4.440	2.612	2.321	49.782	49.860	10.680	10.059	3.853	4.368
Cu	31.329	30.356	16.058	17.897	15.309	14.149	58.017	63.755	18.403	16.784	8.540	9.669
Pb	3.340	3.365	3.433	3.516	23.179	25.072	8.701	11.204	4.790	4.225	6.294	6.787
Zn	83.375	88.397	709.20	788.57	44.660	40.693	112.50	112.56	41.139	40.411	26.700	30.275
Pt	0.243*	0.265**	0.764*	0.759**	n.d.	n.d.	n.d.	n.d.	0.246*	0.082**	n.d.	n.d.
H_2O	2736.2		1571.5		1280		1259.3		2209.0		2040.6	
	Concentrations in fluid inclusions ($\times 10^{-6}$)											
	N9278		N9296		LN9805		N9419		YT9306		YT9301	
Co	159.16		4.49		1.57		110.83		70.37		58.12	
Ni	12.23		7.18		9.63		98.91		11.74		5.04	
Cu	56.36		27.01		57.54		120.88		19.91		11.16	
Pb	6.13		5.53		94.24		19.76		5.12		8.01	
Zn	156.94		1191.35		166.71		223.4		46.15		34.90	
Pt	0.46		1.21		n.d.		n.d.		0.37		n.d.	

Note: (1) and (2) stand for the times of repeated determination; the concentrations of trace elements in fluid inclusions are the average concentrations deduced from the concentration values of leach solution determined twice. * indicates the concentrations determined by the isotope dilution method; * * directly determined; H_2O in $\times 10^{-6}$; n.d. not detected.

① Institute of Geochemistry, Chinese Academy of Sciences, etc., 1992, Ore-forming conditions and prognosis of micro-fine disseminated gold deposits in the Yunnan-Guizhou-Guangxi region—A research report.

What is interesting is that high contents of Pt have been detected in quartz fluid inclusions entrapped during the main metallogenic stages of both gold deposits (Table 3, Fig.2). In order to confirm the reliability of these data , the authors tested again the same portion of leach solution using the isotope dilution method and the result showed that, in addition to one sample from the Yata gold deposit, two samples from the Lannigou gold deposits were found containing the same amount of Pt as detected by the direct detection method (Table 3).

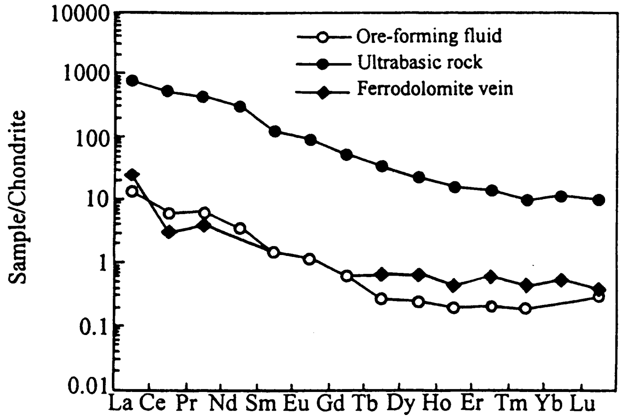

Fig. 1. The REE distribution patterns in quartz fluid inclusions from the Lannigou gold deposit, slightly alkaline ultrabasic rock swarms and near-rockbody ferrodolomite veins.

Do the ore fluids responsible for the Carlin-type gold deposits really contain Pt ? In order to find a definite answer to the question, the authors determined again the blank value of Pt in leach solution (5% HNO_3) and the result showed that the blank value of Pt in leach solution (0.014×10^{-9}) is far lower than the concentrations of Pt in the leach solution after it has interacted with fluid inclusions $(0.243 - 0.764) \times 10^{-9}$. Clearly, the possibility can be ruled out that the blank leach solution has been contaminated.

Pt minerals present in fissures of the quartz samples are another possible source of Pt in the leach solution which has interacted with quartz samples. However, a few Pt-containing minerals found in some Carlin-type gold deposits in the Yunnan-Guizhou-Guangxi region are all Pt-alloy minerals [e.g. Pt-Au mineral found in the Jinya Carlin-type gold deposit (Wang Kuiren et al., 1994)]. Experimental studies showed that the blank leach solution (5% HNO_3) for sample treatment is unable to dissolve the Pt-containing minerals which are present in the form of alloy.

Therefore, Pt can only occur in the form of ions in ore fluids which are similar in chemical composition with the fluid inclusions and its contents are $(0.37 - 1.21) \times 10^{-6}$ (Table 3). This result is in consistence with the report on PGE anomalies observed in recent years in some Carlin-type gold deposits in the Yunnan-Guizhou-Guangxi region (Wang Kuiren et al., 1994; Su Wenchao et al., 1999), and it is also in consistence with the conclusion that there exists a huge Pt, Pd geochemical anomaly province there (Cheng Hangxin et al., 1998). Preliminary studies on the PGE in ferrodolomite veins near the slightly alkaline ultrabasic rockbodies have indicated that these veins contain abnormally high Pt $(4.87 - 6.01) \times 10^{-9}$. It is inferred that the origin of Pt in ore fluids producing the Carlin-type gold deposits seems to be related with the slightly alkaline ultrabasic rocks. The discovery of high Pt contents of ore fluids for the Carlin-type gold deposits is of great significance in further deciphering the mechanism of Pt enrichment in the Carlin-type gold ore fields.

Conclusions

From trace element studies of fluid inclusions from the Lannigou and Yata Carlin-type gold deposits in southwestern Guizhou the present paper presents the following conclusions:

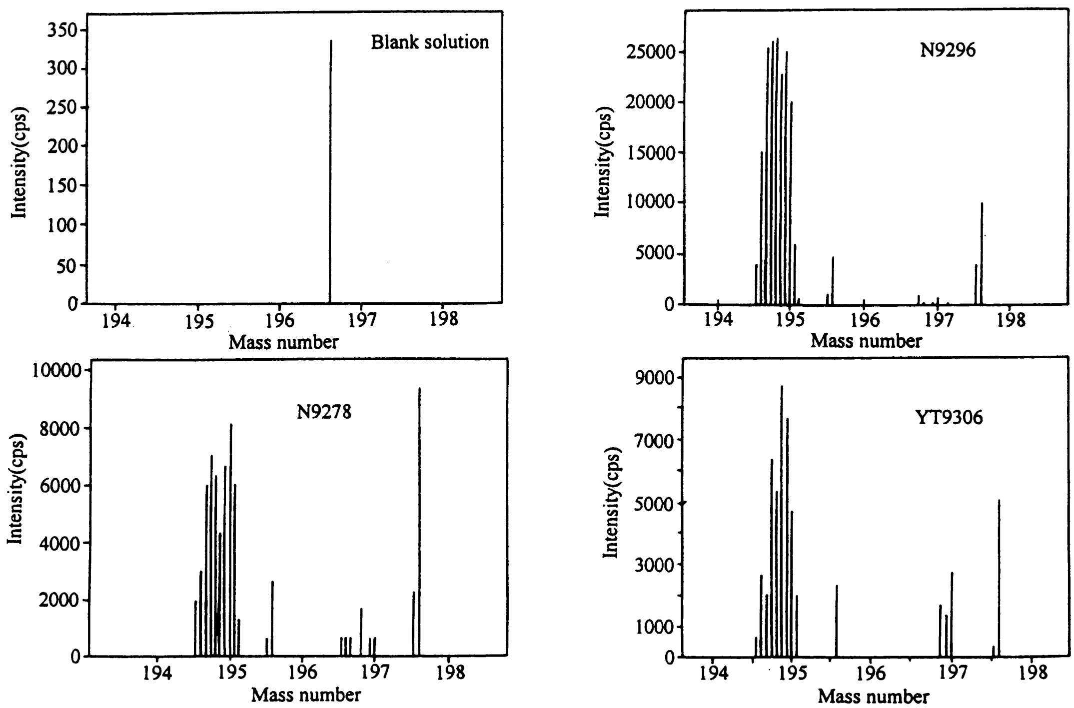

Fig. 2. Mass spectra of the element Pt in leachates of fluid inclusions from the Lannigou and Yata gold deposits.

(1) Ore fluids producing the Carlin-type gold deposits have relatively high contents of Co, Ni, Cu, Pb, and Zn, and basic-ultrabasic volcanic rocks seem to be one of the important sources of ore-forming materials for the Carlin-type gold deposits in southwestern Guizhou.

(2) Ore fluids responsible for the Carlin-type gold deposits are rich in Pt. This discovery is of great significance in deciphering the mechanism of Pt enrichment in the Carlin-type gold ore fields.

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