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Laterization and its control to gold occurrence in Laowanchang gold deposit, Guizhou Province, Southwest of China

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ABSTRACT

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Keywords: Laterization Source of ore-forming substance REE Trace elements Gold occurrence Laowanchang gold deposit, located in Qinglong County, Guizhou Province, Southwest China, is the firstdiscovered laterite type gold deposit in Guizhou Province. Although most scholars are inclined to agree that oreforming substance was closely correlated with "Dachangceng layer", it still remained controversial. Former researchers did not find existences of visible Au grains in limonite, clay minerals or pyrite under SEM observation; therefore, they considered Au occurrence mainly as micro-disseminated form.

In this study, mineral composition, chemical components and chemical index of alteration of laterites indicated that three chemical weathering processes, including argillaceous, bauxitic and ferric process can be observed in Laowanchang laterization. Geochemically, such laterization can be attributed to early laterization stage. Components of K₂O, Na₂O, and CaO were highly leached during weathering indicating a strong chemical alteration.

Concentrations of ore-forming elements (Au, As and Sb) varied greatly along laterite profiles. Concentrations of Au were usually in the range of 40×10^{-9} - 4551×10^{-9} ; As in 0.1–0.9% with the highest value of 1.8%; Sb <0.1%. Concentrations of Au, As and Sb in laterites were obviously higher than in silicalites of Dachanceng layer. During laterization, enrichment of Au and As were obviously related with enrichment of Fe. Au and As enriched in relatively reductive locations, while Sb in the relatively oxidized circumstances.

Rare earth element (REE) contents were higher in laterite profiles with LREE/HREE ratios usually less than 10. REE had very similar distribution patterns in laterites, significantly differing from those of Dachanceng layer. Features of trace element pairs (including large ionic lithophile elements and incompatible elements) and ore-forming element pairs diagramed great differently between laterites and Dachanceng layer. These phenomena supported that laterites would not directly be developed from Dachanceng layer rocks, but mainly be related with Quaternary sediments. Ore-forming substances of Laowanchang gold deposit also connected less with Dachanceng layer.

Au occurrences in laterites varied under TEM-EDX observations. Gold existed either as granular natural gold, or adsorbed by goethite and As-bearing goethite, or by siliceous matter and quartz, sometimes by illites. Reduction of Au^{3+} to Au^{0+} by Fe^{2+} played an important role in enrichment of Au during laterization.

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1. Introduction

Lateritic type gold deposit, was firstly discovered in 1980's, received worldly attentions from then on due to its apparent advantages of large scales (middle-large to ultra-large type ore mines), readily exploitation (with loose mine layers and open pit), easy milling and metallurgy, especially higher extraction ratios (larger than 75%) and great investment incomes.

First large-scale lateritic type gold deposit is Boddington gold mine in Australia with an average Au grade of 1.8 mg kg⁻¹ and a reserve of 96 t, was well studied geochemically (Davy and El Anssary, 1986). They found Au is one of the elements mobilized and reprecipitated within laterite

* Corresponding author. *E-mail address:* yangyuangen@hotmail.com (Yuangen Yang). profiles. In 1985, second large-scale lateritic type gold deposit, Bahia Au mine with an average grade of 5.0 mg kg⁻¹, was discovered in Brazil (Costa, 1993). These led to the successive discovery of laterite gold deposits, such as Nong Dong Au mine in Thailand, Salaikena Au mine in India, Vunaa Au mine in Fiji, etc., their ore-forming mechanisms were well studied.

Vertical zoning of laterites was one interest aspect of previous studies. Six zones, including surface laterite, iron crust, bauxite, clay layer, sapropelite and basal rock, were discriminated down to the vertical profile of laterite (Costa, 1993; Zang and Fyfe, 1993), in which the iron crust zone is the remarkably common feature of such lateritic Au deposits.

Regarding to mineral compositions down to laterite profile, Davy and El Anssary (1986), Costa (1993), and Zang and Fyfe (1993) found that surface laterite and iron crust mainly consisted of iron oxides and hydroxides, bauxite formed speckle zone, and kaolinite dominated in clay layers.

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Gold mineral occurrence was another interest of previous studies on lateritic gold deposit (Mann, 1984; Freyssinet et al., 1989; Colin and Vieillard, 1991). They found that Au mainly exists as dissociative form, and is closely related with Fe oxides and hydroxides; occasionally, Au is formed as visible gold grain or gold nugget.

In China, Laterite type gold deposit was primitively explored from 1986. The first lateritic gold deposit, Shewushan large-scale Au mine, was discovered in 1991 in Hubei Province, Central China. A series of laterite gold deposits were found in succession from end of 1980's to beginning of 1990's, and have became an important type of gold resource in China.

Li and Chen (1994) summarized and confirmed that there exists six vertical zones of laterites in these gold deposits in china, i.e., surface layer, iron crust (occasionally found in certain deposits), red clay layer, black clay layer (occasionally existing in certain deposits), gray clay layer, and sapropelite layer (and basal rock layer). This is similar to the classification result of Costa (1993) and Zang and Fyfe (1993).

Mineral compositions of laterites were studied by Liu (1996), and Rao et al. (2004). They found supergene minerals consist predominatingly of clay minerals such as illite, kaolinite and goethite; however, chlorite, montmorillonite and gibbsite occasionally exist. Quartz is commonly occurring as a residue of basal rocks.

Gold occurrence and Au mineral character were also reported by many studies (Liu, 1996; Rao et al., 2004). They discovered that Au is frequently as natural gold grains as small as to nano scale with the purity over 990, and is commonly adsorbed onto clay minerals such as illite and kaolinite or stuck to the edge of goethite.

Laowanchang gold deposit, located in Qinglong County, Guizhou Province, Southwest China, being the first gold deposit of lateritic type in Guizhou Province, discovered by the Physical and Chemical Exploration Academy of Guizhou Geology and Exploration Bureau in 1992 in a chemical exploration campaign. However, Tu (1999) named it as a red clay type gold deposit due to its significant difference in ore compositions and forming mechanism with the typical laterite type gold deposit — Boddington Au mine, especially due to its lack of iron crust in laterite profile. Previous studies concentrated on the genesis and ore mineral compositions of this ore deposit (Liu, 1999; Wang 1998; Chen, 2000; Yang et al., 2001). Wang et al. (1995) described it as a laterite gold deposit of karst collapse and conglomeration, and emphasized epigenic mineralization of microorganisms (Wang et al., 2000).

However, no evident ore source bed was unveiled around Laowanchang Au mine (Gao and Li, 2002), ore-forming substance remained uncertain. Most scholars inclined to accept an opinion that ore-forming substance was closely related with "Dachangceng layer" that was originated from silicification alteration of Emeishan basalt (Feng, 2000). Wang et al. (2000) did not find natural gold grains larger than 1µm size in limonite, clay minerals and pyrite under SEM observation, and highly valued the importance of disseminated ultramicroscopic gold. However, many unfathomed problems, such as source of ore-forming substances, Au occurrence and its relation to laterization in Laowanchang gold deposit, required further studies. Therefore, aims of this study were to understand the relation of Laterization with migration or enrichment of ore-forming substances

Table 1
Clay mineral constituents in lateritic profiles

Position	Sample ID	Mineral constituents
Surface layer	lwp2-8	Quartz + kaolinite + chlorite + potassium feldspar + anatase + plagioclase
¢	lwp2-7	Quartz + kaolinite + chlorite + feldspar + illite + montmorillonite + gibbsite + anatase + potassium feldspar
	lwp2-5	Qibbsite + kaolinite + quartz + illite + chlorite + montmorillonite + anatase + potassium feldspar + plagioclase
	lwp2-3	Quartz+kaolinite+illite+chlorite+gibbsite+anatase+calcite
Bottom layer	lwp2-1	Kaolinite+quartz+illite+goethite+anatase+gibbsite+calcite

Table 2

Computed weathering parameters in laterite profiles

Sample ID	lwp4-1	lwp4-2	Lwp4-3	lwp4-4	lwp4-5	lwp4-6	lwp4-7
Profile layers	Surface	layer \rightarrow b	ottom lay	er			
$SiO_2 + Al_2O_3 + Fe_2O_3$	85.19	85.28	86.03	86.35	87.26	87.43	85.17
SiO ₂	58.45	61.54	59.49	58.24	60.80	60.70	57.92
Al ₂ O ₃	14.79	13.60	14.79	15.98	14.07	15.50	14.31
FeO	0.15	0.26	0.35	0.17	0.21	0.07	1.56
SiO ₂ /Al ₂ O ₃	6.71	7.68	6.83	6.19	7.34	6.65	6.87
R ₂ O ₃ /SiO ₂	0.23	0.19	0.22	0.24	0.21	0.22	0.23
CIA	89.43	90.42	93.15	92.69	93.83	92.66	85.55

Note: SiO₂, Al₂O₃, FeO, SiO₂+Al₂O₃+Fe₂O₃ are expressed as weight percent (wt.%), others are mole ratios. CIA: chemical index of alteration, CIA=100×Al₂O₃/(K₂O+Na₂O+CaO*+Al₂O₃), where CaO* refers to CaO content in silicate (McLennan, 1993), R₂O₃=Al₂O₃+Fe₂O₃.

and to probe the source of ore-forming substances and Au existing forms.

2. Geological setting of Laowanchang gold deposit

Laowanchang gold deposit is located 40 km southwest of Qinglong County, southwest of Guizhou Province. Au mine is in the south part of Bihenying syncline intersecting with Xiaganhe fault in southwest Guizhou turbine structure. Regionally, dominantly sedimentary strata mainly consist of carbonate rocks of shallow-sea facies of Permian period and Triassic period (including Maokou group, Dachangceng layer, Omeishan basalt and Longtan group), and consist of sediments of Quaternary period. Of the sedimentary rocks, Maokou group carbonates and Quaternary sediments are dominant with coverage of 70% of this region. Magmatic activity in this region was weak, tholeiitic basalt of continental effusion during Permian period was observed overlying disconformity on Maokou group limestone. Dachangceng layer, located between upper part of Maokou group and bottom of Emeishan basalt, is a complex of silicification alteration body. Antimony mine is one of the main deposits in this region, fluorite, troilite, coal and gypsum mines can be occasionally found. Some Carlin type gold ore spots with no commercial value, such as Shaziling and Gulu, can also be found in the region. All these ore mines distributed in the Dachangceng layer.

Laowanchang gold deposit was found in Quaternary cliff debris and collapsed materials overlying on karst erosional surface of Maokou group limestone of early Permian period. Ore-containing layer is Quaternary laterite. Mine ores are commonly a mixture of clays, siliceous rocks and limonite blocks, in which kaolinite, hydromica, montmorillonite, quartz, hydrogoethite, calcite, dolomite, jarosite, gypsum, pyrite and arsenopyrite are main minerals.

3. Experiments and methods

Four vertical lateritic profiles were sampled in this study according to color and composition to discriminate zones in each profile. Samples were then air-dried; subsamples were grounded to less than 100 meshes before chemical analyses.

Trace element (including rare earth element, REE) contents were determined using an ICP-MS machine (Finnigan MAT, ELEMENT, Germany) in Institute of Geochemistry, Chinese Academy Sciences (IGCAS). Simply, after 50 mg of samples was digested in 1 ml HF and 1 ml HNO₃ at about 190 °C for about 12 h, they were extracted using 2 ml HNO₃ and 5 ml deionzied (DI) H₂O and made up to a volume of 50 ml together with 1 ml Rh as an internal standard. International Standard Reference Materials (SRM) NBS-1633A and GXR-2 were used as measurement quality controls with analytical errors <±10% for REEs and <±5% for other trace elements.

Bulk rock chemical compositions (major elements) were measured by application of routine wet chemistry analysis in IGCAS (Rao et al., 2004). For Au content determination, samples were first digested in aqua

Table 3							
Concentrations	of Au, As	and Sb	in	laterites	in	Laowanch	ang

	Laterites	(n=32)	Dacha (n=3)	ngceng l	ayer	
	Au	Sb	As	Au	Sb	As
Minimum	40	51	120	45	82	20
Maximum	4551	8100	18,000	495	100	470
Average	1500	592	5332	277	94	247
Standard deviation	1166	1421	4420	225	10	225
Crust abundance	1.8	0.2	1.0			
Enrichment coefficient	833	2960	5332	154	470	247

Note: calculation units are $\mu g kg^{-1}$ for Au, mg kg^{-1} for Sb and As, respectively. In parenthesis are sample numbers.

regia, Au contents in digestion were then measured on a graphite atomic absorption spectrophotometer (Model PE5100PC, Perkin Elmer, USA) after enrichment on plastic foams. Analytical accuracies were reliable with analytical errors $<\pm 2\%$ for all major elements, and $<\pm 5\%$ for gold.

Clay minerals were discriminated on an X-ray diffraction machine (D/Max-2200, Japan) in IGCAS after samples were totally dispersed in distilled water in a measuring cylinder, let standstill for 5 min, then suspended substances were extracted using a pipette and dried using an infrared lamp. The machine ran at conditions of scanning speed: 6–8°/min; sampling width: 0.02° or 0.04°(2 θ); working electrical current and voltage: 20 mA, 40 kV; scan range: 2–70° (2 θ); scattering slit and emission slit was 1°; and acceptor slit was 0.15 mm. When analysis performing, accuracy of the angle tester was better than 0.02°, resolution of machine was better than 60%, and total stability was better than ±1% (Rao et al., 2004).

For microscope observation of Au morphology, samples with higher Au contents were washed in distilled water to remove very fine particles; the coarse parts were then air-dried, fixed on a copper supporting net, coated with graphite and then ready for observation and identification on a TEM instrument (JEM-2000FX, Japan) equipped with EM-ASID20 imaging system and Oxford Link ISIS energy spectrum in IGCAS.

4. Results and discussion

4.1. Clay minerals in laterite profiles

Goethite was mainly observed at the bottom of laterite profiles, montmorillonite dominated in the middle of profiles. Illite and gibbsite were commonly observed in whole laterite profiles except for surface layer, while kaolinite existed in the whole laterite profiles (Table 1). In the surface layer, no other clay minerals except kaolinite can be found. Apparently, clay minerals evolved from 1:1 type to 2:1 type down laterite profiles (Table 1). According to these clay mineral compositions varying in laterite profiles, three chemical weathering processes, including argillaceous, bauxitic and ferric process, can be inferred in laterization process in the Lanwanchang ore region. Furthermore, according to a classification method of weathering crust type (Guo and Sheng, 1980), laterization in Laowanchang region can be rated as Aland Fe-rich type, or geochemically as early laterization stage, not yet reaching ferric stage of laterization evolution. Existence of calcite at bottom and feldspar minerals at surface of laterite profiles might reflect its close relation to carbonate strata at bottom and with Quaternary diluvial and alluvial substances at surface.

4.2. Bulk rock chemical compositions of laterite profile

Certain geochemical parameters using bulk rock chemical compositions of laterites were calculated according the method of Huang (1996). Apparently, SiO₂, Al₂O₃, Fe₂O₃ dominated in all laterites, totally accounting for 85.17–87.26% with an average of 86.10% (Table 2). This average value is very close to a previous study result of 86.18% (Chen, 1999), which this feature fits in well with that of contemporary lateritic weathering crust (Li and Chen, 1994). Mole ratios of SiO₂/Al₂O₃ varied in the range of 6–7, while R₂O₃/SiO₂ ratios were around 0.2 (Table 2).

According to discrimination standard of Al-enrichment grade of weathering crust by using SiO_2/Al_2O_3 and R_2O_3/SiO_2 ratios (Huang, 1996), Al-enrichment grade of laterite in Laowanchang region could be classified as slightly Al-enrichment grade (Table 2). Chemical alteration



Fig. 1. Concentrations of Au ($\mu g \ kg^{-1}$), Sb (mg kg^{-1}) and As (mg kg^{-1}) in laterite profiles.

Table 4

	Sample ID	REE	LREE	HREE	L/HREE	La/Sm	Gd/Yb	La/Yb	δCe	δEu
		mg kg ⁻¹								
Dachangceng layer	dcc1	5.06	4.61	0.45	10.2	5.26	2.17	14.8	-0.17	-0.30
	dcc2	301	284	17.2	16.5	2.99	1.90	15.0	-0.01	-0.25
	dcc3	145	131	13.4	9.83	2.57	1.76	8.63	-0.01	-0.16
Laterites	Minimum	59.2	52.7	6.48	5.50	2.53	1.58	7.3	-0.49	-0.43
	Maximum	616	547	94.8	9.96	4.06	3.83	14.7	0.07	-0.17
	Average	377	334	41. 9	8.34	3.61	2.10	10.6	-0.06	-0.35
	Standard deviation	159	140	21.8	1.46	0.45	0.55	1.78	0.16	0.06

Calculated REE parameters in Laowanchang gold deposit

index (CIA) is usually used to reflect leaching of base components compared with Al during surface weathering (McLennan, 1993). High CIA can be obtained in laterites (Table 2), indicating a great leaching of K₂O, Na₂O and CaO compared with Al₂O₃. However, no regular decrease of CIA down to laterite profiles was observed in Laowanchang region, which might attribute to the melange or superposition of lateritic matters during karst collapse. This can be supported by Wang et al. (1995) who suggested a four-stage model for karst collapse and conglomeration-induced oreforming process of laterization.

Silicate compositions of sillcalite and Sb-mineralized rocks in Dachangceng layer in Laowanchang Au deposit region are apparently different from those of laterites in Laowanchang region. Higher SiO₂ and FeO contents, with an average of 80.06% for SiO₂ and 1.20% for FeO, respectively, however, lower TiO₂, Al₂O₃, Fe₂O₃ and K₂O contents (<0.3% for TiO₂,<4% for Al₂O₃, <2% for Fe₂O₃, and <0.4% for K₂O) were measured for rocks of Dachangceng layer than laterite samples. It is reasonable to deduce that if laterites in Laowanchang region were originated from rocks of Dachangceng layer through weathering, there would be chemical processes of strong desiliconization, intensive Al- and Fe-enrichment. However, the laterization process in Laowanchang region merely

included slight Al- and Fe-enrichment processes with no iron crust (Tables 1 and 2), therefore, under weathering condition in Laowanchang, it is impossible for Dachangceng layer to form laterites with features of high Al_2O_3 and Fe_2O_3 contents through surface weathering.

4.3. Features of ore-forming elements

Concentrations of Au, As and Sb varied greatly in laterite samples (Table 3). Au varied in 40–4551 μ g kg⁻¹ with a high standard deviation of 1166. One laterite sample had extreme high Sb abundance of 23.4% probably due to the existence of mineral crystal of antimonite. After omitting this odd sample, average Sb concentration in laterites was 592 mg kg⁻¹ with most samples < 1000 mg kg⁻¹ (Table 3). Concentrations of As in laterites varied in 120–18,000 mg kg⁻¹ with an average of 5332 mg kg⁻¹. However, ore-forming element abundances in Dachangceng layer were greatly lower than in laterites (Table 3). Presuming that ore-forming substances originated form Dachangceng layer, enrichment coefficients of Au, Sb and As could be as high as to 5.4, 6.7 and 21, respectively based on their average concentrations. Under weak surficial weathering process in Laowanchang such enrichments were quite difficult to reach.



Fig. 2. REE distribution patterns in Laowanchang gold deposit. dcc1 dcc2 dcc3 refer to Dachangceng layer samples. Laterite profile samples were plotted as in the range from lowest to highest.



Fig. 3. Diagrams of trace element pairs of laterites and Dachangceng layer in Laowanchang gold deposit region. O laterites; • Dachangceng layer; I Carlin type gold ores.

Au, Sb and As were observed greatly varying in vertical profiles of laterites (Fig. 1). Au frequently concentrated in middle and bottom of lateritic profiles, especially in profile 1 and profile 2, even though it fluctuated in whole profiles (Fig. 1). As varied similarly to Au with great fluctuation in laterite profiles. However, Sb was totally different from Au and As lying in less fluctuation in laterite profiles except for one sample due to the existence of mineral crystal of antimonite. In general, Sb tended to enrich in upper and bottom, however, to deplete in middle of laterite profiles (Fig. 1).

4.4. Rare earth elements (REE)

Total REE contents in Dachangceng layer were low, with the lowest value of 5.06 mg kg⁻¹; however, laterites had high REE contents with an average of 377 mg kg⁻¹ (Table 4). LREE were dominant both in Dachangceng layer and laterites, however, Dachangceng layer had larger LREE/HREE ratios (>10) than laterites (<10) (Table 4). Large LREE/HREE ratio is commonly regarded as a remarkable fractionation between LREE and HREE; therefore, REE of Dachangceng layer might experience a strong fractionation.

Except for a few samples with large negative δCe values, most samples had δCe values around zero, indicating no significant Ce abnormities (Table 4). Negative δEu values were frequently observed, especially in laterites (-0.43 to -0.17) (Table 4). Negative δEu abnormity is frequently linked to clay minerals in surficial weathering; higher contents of clay minerals such as kaolinites in laterites can result in more significantly negative δEu values (Huang, 1996). Therefore, differences of

Table 5

Correlations of ore-forming elements with weathering parameters

 δEu in laterites in Laowanchang might reflect the differences in weathering strength.

Distribution patterns of REE of laterites were greatly consistent with a feature of right incline type, which is different from those of Dachangceng layer (Fig. 2). Such differences suggested that parent materials of laterites were not directly originated from sillcalite or silification-altered rocks of Dachangceng layer.

4.5. Trace elements

Generally, concentrations of element Be in most studied samples were below detection limit of ICP-MS, and great variations of other trace elements were observed in samples. However, trace element contents except for Sn and Cs in laterites were much higher than in Dachangceng layer. Contents of Zr, Ni and Co in laterites were nearly one order of magnitude higher than in Dachangceng layer (date not shown).

Trace element pairs can be used to discriminate genesis relationship of laterite due to their very identical geochemical behavior under surficial laterization. As shown in Fig. 3, on large ion lithophile element pair (Rb/Sr–Cs/Ba) diagram and incompatibility element pair (Nb/Ta–Zr/ Hf) diagram, plots of laterites, similar to Carlin type gold ores, were significantly different from plots of Dachangceng layer. On ore-forming element pair (Co/Ni–Cu/Zn) diagram, plots of laterites and Carlin type gold ores concentrated in the side of Co/Ni ratio larger than 0.4, while plots of Dachangceng layer were in the side of Co/Ni ratio less than 0.4 (Fig. 3). On ore-forming element pair (As/Sb–W/Sn) diagram, plots of Dachangceng layer were obviously close to W/Sn axis with much small

	SiO_2/Al_2O_3	R_2O_3/SiO_2	CIA	Al_2O_3/Fe_2O_3	$Fe_2O_3/(Fe_2O_3+FeO)$	Au	Sb	As	δCe	δΕυ
Au	-0.30	0.53*	-0.76**	-0.62**	-0.44*	1.00			-0.16	-0.38
Sb	-0.32	-0.02	0.73**	0.88**	0.80**	-0.01	1.00		0.19	-0.12
As	0.52*	-0.37	-0.83**	-0.39	-0.66**	0.55*	-0.01	1.00	-0.24	0.05

Note: silicate-related ratios are calculated as mole ratios. * and ** represent 95% and 99% significance levels respectively. Statistic samples are 17 for silicate components, 32 for Au, As and Sb, and 22 for REE parameters, respectively.



Fig. 4. Morphology of Natural gold grain in samples (Left) and its gold spectrum (Right). The Cu spectrum was caused by copper supporting net.

As/Sb ratios, while plots of laterites and Carlin type gold ores were scattered with much larger As/Sb ratios (Fig. 3). Such great differences between laterites and Dachangceng layer suggested that laterites were not developed on Dachangceng layer but might be developed or evolved on Quaternary alluvial or diluvial substances in this region. Correspondingly, ore-forming substances were not directly originated from Dachangceng layer, but might be partly related to Carlin type gold ores.

4.6. Relations of ore-forming elements to laterization

Extremely positive correlations (P<0.01) between ore-forming element Au and As can be observed, however, there were no such relationships between Au and Sb or between As and Sb (Table 5). This might suggest that Au and As have similarly geochemical behaviors in

hypergene ore-forming process, which led to coexistence or differentiation of Au, As or Sb in surficial environment.

In laterites, Au was positively correlated with R_2O_3/SiO_2 ratio (P<0.05), while As positively with SiO_2/Al_2O_3 ratio (P<0.05). Furthermore, CIA, Al_2O_3 / Fe₂O₃ and Fe₂O₃/ (Fe₂O₃+FeO) ratios were significantly positively correlated with Sb content, but negatively with Au and As contents (Table 5). These correlations demonstrated that Au and As had different geochemical behaviors from Sb during surface weathering, and enrichment of Au and As were commonly correlated with iron-enrichment process, but not with desiliconization, bauxitic process during laterization.

Strong holding capacity of ferric or ferrous minerals led to enrichment of ore-forming elements Au and As in surficial environment, therefore, negative correlations of $Fe_2O_3/(Fe_2O_3+FeO)$ ratio



Fig. 5. Natural gold grain (Au) adsorbed by illite (IL) (Left) and its X-ray spectrum (Right).



Fig. 6. Natural gold grain (Au) coexisted with As goethite (Goe) (Left) and its X-ray spectrum (Right).

with Au and As can be observed. However, a reverse phenomenon can be observed for Sb (Table 5). Such difference suggested that enrichment of Au and As was related to relatively reductive circumstances, such as below groundwater table or microorganisminduced reduction. For example, Wang et al. (2000) ever isolated microbial strains from lateritic gold ores; Zhang et al. (1999) simulated a re-growth of Au in existence of microorganisms. However, Sb was related to relatively oxidation environment. Au and As tended to enrich below groundwater table with relatively reductive circumstance in laterite profiles, therefore, higher Au and As contents were often observed in deeper horizon of lateritic profiles (Fig. 1).

Furthermore, Au and As were weakly negatively correlated with δ Ce, while Au and Sb were weakly negatively correlated with δ Eu (Table 5). Such correlations further supported that accumulation of Au during laterization was in relatively reductive circumstance; however, it was less correlated with desiliconization.

4.7. Occurrence of Au in ores

For further understanding Au occurrence in Laowanchang gold deposit, TEM-EDX was applied to scan ore samples with high Au contents. Under TEM observation, not only native gold grains but also many accessory minerals were identified. For example, rounded-rutile grains, rounded-zircon grains could be noticed adsorbed on goethite, As-pyrite, illite or Fe-illite, ilmenite, and halloysite in laterites.

Native gold grains were commonly rounded-shaped, differing from placer gold grains that usually formed complicatedly as branch shape, horse-headed shape or irregular shape (Ma and Qi, 1995). Such difference might reflect a chemical precipitation mechanism of Au in laterites. The largest Au grain with a diameter $>0.2 \ \mu m$ in laterites was attached at the edge of goethite grain (Fig. 4). Au also existed as fine grains adsorbed on goethite, As-goethite and on fine granular quartz, or even on illite (Figs. 5 and 6).

Wang et al. (2000) found that Au existed as ultra-microscopic grains adsorbed on clay minerals and ferrohydrite or as ultra-microscopic inclusions enclosed by other minerals by using a scanning electric microscope (SEM) and a proton probe. However, they did not find gold grains $>0.1 \mu$ m. Hong et al. (1999) reported that invisible Au existed in clay minerals and goethite as ultra-microscopic Au grains in Shewushan lateritic gold deposit. Their results are similar to this study; however, native Au grains with diameter $>0.1 \mu$ m were found in this study.

Apparently, Au is closely correlated with epigenic mineral-goethite in Laowanchang laterites, therefore, the following reaction possibly existed in this lateritic gold deposit:

$[AuCl_4]^- + 3Fe^{2+} + 6H_2O \rightarrow Au^0 + 3FeO(OH) + 4Cl^- + 9H^+$

This reaction suggested that a reduction function of Fe²⁺ led to coprecipitation of gold grain with iron hydroxide and then adsorbed by iron hydroxides. Existence of chlorine in gold ores could be a good evidence for this reaction. Wang et al. (2000) found that Au and Fe contents were commonly very low in samples containing Cl, and no Mn was detected in these samples by using a proton probe. But, high Fe, Mn and Au contents could be detected in samples containing no Cl. Their findings indicated that the above reaction would be favorable to right direction when Cl was removed into or migrated with ground water, Therefore, Au and goethite could co-precipitate, and Au was then frequently found captured by Fe and Mn oxides or hydroxides in lateritic gold deposits.

5. Conclusions

Laterization in Laowanchang gold deposit undergoes three chemical weathering processes: argillation, bauxitic-enrichment and Feenrichment, which geochemically fit to the early development stage of laterization. Chemical alteration of laterites is strong, with high CIA values. However, CIA does not decrease down lateritic profiles, indicating miscellaneous overlaying and superposition of laterites due to karst collapse.

Ore-forming element Au and As are frequently enriched in middle and bottom horizons of laterite profiles, while Sb in upper horizon. In laterization, Au and As are enriched with enrichment of Fe, and are related to relatively reductive circumstance; while Sb is enriched in relatively oxidative circumstance. Laterites are not directly developed on Dachangceng layer, however, are correlated with Quaternary alluvial and diluvial substances. Ore-forming substances of Laowanchang gold deposit are not directly originated from Dachangceng layer, however, are more closely related to Carlin type gold deposit.

Various occurrences of Au in laterites can be observed. Au can exist not only as rounded native gold grains, but also as ultramicroscopic gold adsorbed by goethite (As-goethite), fine granular quartz or illite.

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