Vol. 43 No. 1 SCIENCE IN CHINA (Series D) February 2000

The Lanmuchang Tl deposit and its environmental geochemistry

ZHANG Zhong (张 忠), CHEN Guoli (陈国立), ZHANG Baogui (张宝贵), CHEN Yecai (陈业才) & ZHANG Xingmao (张兴茂)

Institute of Geochemistry, Chinese Academy of Sciences, Guiyang 550002, China
Correspondence should be addressed to Zhang Zhong

Received April 13, 1999

Abstract Tl is a dispersed element and it seldom occurs in the form of independent minerals. The world annual production of Tl is about 13 ton, most of which is by-product separated from non-ferrous metal products. Lanmuchang is the only large-size independent Tl deposit in the world. Bio-enrichment and hydrothermal reworking are the two important metallogenic mechanisms of this Tl deposit. Samples of plant and animal organs and villagers' urine as well as hair and nail (toenail) samples from the Tl mining district were analyzed. Analytical results showed that the contents of Tl, Hg and As are high, suggesting that the residents and villagers in the mining district have been affected by Tl-Hg pollution, and on the other hand, they can serve as the guidelines for ore prospecting. The contents of Tl, Hg, and As in human beings and other organic bodies depend largely on the background values of these metals in rock, ore, soil and water.

Keywords: Tl deposit; environmental geochemistry of Hg, Tl and As, metallogenesis by bio-enrichment, metallogenesis by hydrothermal reworking, indicators, Tl, Hg and As pollution.

The Lanmuchang Tl deposit in Xingren County, Guizhou Province, is a rare example in the world as viewed either from its metallogenic mechanisms (bio-enrichment and hydrothermal reworking) or from the composite pollution of Tl, Hg and As and the composite Tl-Hg poisoning. For many years the authors have carried out a systematic research on Tl deposits and the hypergenetic geochemistry of Tl, Hg and As and their ecological environmental effects during the exploitation of Tl deposits. The contents, existing forms, metallogenic mechanisms and ore-search indicators of Tl in low-termperature deposits, as well as the problems of environmental pollution caused by Tl, Hg and As in the process of exploitation of Tl deposits have been discussed[1−5]. On the basis of previous studies this paper further deals with the Lanmuchang Tl deposit from the following three aspects: the metallogenic mechanism of the Lanmuchang independent Tl deposit, the contents of Tl, Hg and As in organic samples from the mining district, and the contents of Tl, Hg and As in the samples of urine, hair and nail of human bodies.

The contents of Tl, As and Hg in rock and ore samples as well as digestive juice of living organisms were analyzed and calculated on a PE-5100 PC atomic absorption spectrometer using the flameless atomic absorption, hydride atomic absorption and cold atomic absorption techniques. The blank measurements were conducted with the same techniques with detection limits being all less than 0.01 (10^{-9}).

1 Metallogenic model of the Lanmuchang independent Tl deposit

1.1 Geological characteristics of the Lanmuchang Tl deposit

The Tl deposit occurs in the depression zone of southwestern Guizhou on the southwestern margin of the Yangtze peneplatform which is adjacent to the northwestern margin of the South China folded zone, belonging to the platform-type sedimentary regions. The orebodies occur largely in the Upper Permian strata of the Longtan and Changxing formations. A large number of micro-paleofossils, especially foramina and zoaria (fig. 1(a)—(d)) are still observable in the ores, showing that they were formed as a result of bio-enrichment during sedimentary diagenesis. Most of the fossils have been replaced by Tl-bearing ore fluid, hence forming Tl minerals with biological pseudomorphs, such as lorandite and christite (fig. 1(e)—(h)). As indicated by an analysis of the time-bound nature of biocoenoses and the metallogenic mechanism of bio-enrichment, the bio-enrichment metallogenesis of the Lanmuchang Tl deposit experienced two stages, i.e. the Late Permian stage and the Hercynian stage. The ore-bearing beds are as many as 14 in number and the main ore-bearing beds are a set of hybrid rocks, a sedimentary complex composed of several different lithologies[6]. The location where hybrid rocks occur is the rock phase transformation zone, i.e., the most favorable locus of Tl metallogenesis. Some individual orebodies in the deposit are generally measured at 60—240 m in length, 40—80 in width, and 2—5 m in thickness. The orebodies are stratoid, banded, pocket-like, breaded and lenticular in forms. The attitudes of orebodies and ore-bearing bodies are consistent with those of the host strata with a dipping angle of about 25°. The main independent Tl minerals of commercial importance include lorandite, christite and raguinite[7].

1.2 The element association of Tl, Hg, As, Au and W

It has been proved that there are more than fifty associated elements in the Tl deposit, of which the most useful ore-forming and mineralization elements are Tl, Hg, As, Au and W, which constitute a characteristic five-element association. Tl and Hg are involved in the mineralization of large-sized deposits, As and Au can be comprehensively utilized, and W mineralization is common. All the five elements are indicator elements for ore prospecting. Some individual samples reach the grade of tungsten ores and contain tungsten minerals. The contents of tungsten in rocks and ores as well as in soils are $n \times 10$ to $n \times 10^2$ times higher than the Clark values of the crust.

1.3 The metallogenic model of the Tl deposit

According to the metallogenic model of Tl deposits, two metallogenic stages can be distinguished, i. e. bio-enrichment and hydrothermal reworking. The former stage is contemporaneous with Late Permian sedimentary diagenesis or later. The average $\delta^{34}S$ value of 14 sulfide minerals

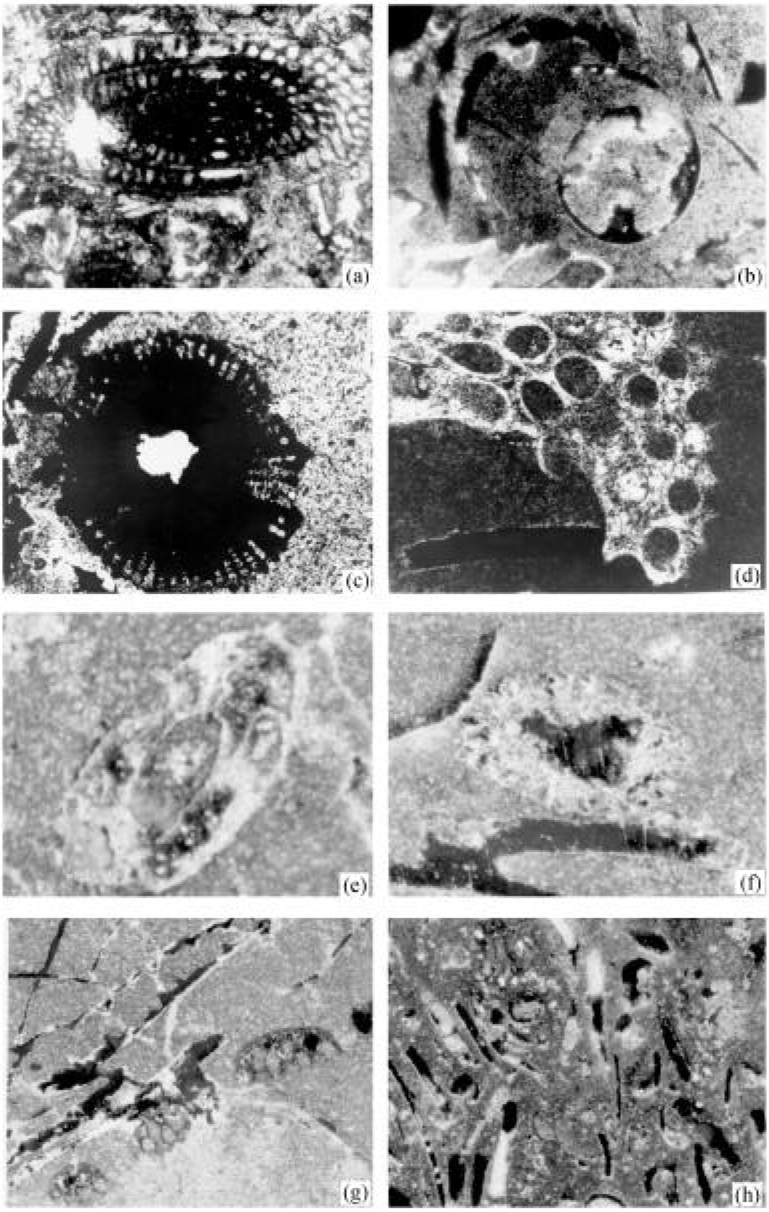

Fig. 1.(a) Paleofusulina, thin section, ×30; (b) geimitzina sp., thin section, ×30. (c) fenestella sp., thin section, ×30. (d) zoaria, thin section, ×30; (e) paleofusulina biopseudomorphous lorandite (red), polished section, ×35; (f) fenestella pseudomorphous lorandite (red), polished section, ×35; (g) zoaria pseudomorphous lorandite (red), polished section, ×35; (h) geimitzina pseudomorphous loranidite (red) and pseudomorphous christite (black), polished section, ×35.

is 7.30‰, equivalent to that of SO^{2-}_4 in Late Permian seawater, indicating that Tl mineralization took place in the Late Hercynian period. The latter stage of mineralization happened during the Middle Triassic, belonging to the Indosinian mineralization. During the metallogenic stage of bio-enrichment the abundant fossils, especially micro-paleofossils in the strata were replaced by

Tl-bearing ore fluids (Tl, As, S, etc.) to form Tl minerals as bio-pseudomorphs. Particularly those Tl minerals present in the form of foraminferal pseudomorphs are indicative of the sedimentary diagenesis and metallogenesis, i.e. the stage of metallogenesis due to Tl bio-enrichment. The Tl minerals crystallized during this stage almost all appear as bio-pseudomorphs. The minerals are fine in grain size (mostly less than 1 mm) and they are distributed as disseminated or colloidal grains in the ore-host horizons. The grade of Tl ores depends on the abundance of micro-paleontological fossils, with a positive correlation between them. Biologically enriched Tl-bearing orebodies have basically preserved the attitudes of the strata and their geological character at the time of sedimentation. The difference lies in the fact that micro-paleontological fossils in the ore-host beds have been completely replaced by Tl minerals. The Tl-bearing orebodies formed at this stage appear to have been destroyed completely by later hydrothermal reworking processes with a little amount of residues.

During the metallogenic stage of hydrothermal reworking the reworked ores, especially the reworked-type high-grade ores, deposited as a result of hydrothermal reworking and superimposition (fig. 2) were almost changed, showing quite a difference from the ores deposited during the metallogenic stage of bio-enrichment. The rocks and ores almost display no difference both in texture and in mode of occurrence from common non-ferrous metallic ore deposits (Hg, Sb, Pb, Zn, etc.). The minerals, especially Tl minerals, formed during this stage are significantly different from those formed at the mtallogenic stage of bio-enrichment. They are larger in grain size, generally greater than 1 mm in size. Some individual crystals are even as large as 5—10 mm. The minerals are diverse in form, including massive, radiating and tabular ores. The Tl orebodies are diverse in shape with stratiforms lenticular and pocket-like. No bio-fossils and Tl minerals in the form of bio-pseudomorphs have been identified in both Tl orebodies and ores, indicating that they have been replaced by typical hydrothermal minerals.

2 Tl, Hg and As in vegetables, plants and chiken organs from the Lanmuchang Tl mining district

2.1 Tl, Hg and As in vegetables

Nine kinds of representative vegetables were sampled from the mining district, and their roots, stems, leaves and seeds (fruit) were analyzed to determine the contents of Tl, Hg and As (table 1). The analytical results show that Hg content is the highest, followed by Tl and As (880.04×10^{-9}, 109.55×10^{-9} and 4.817×10^{-9}, respectively). The enrichment factors (the content of an element: its average content in crust) of Tl, Hg and As are 11.001, 0.255 and 0.003, with a content proportion of Hg：Tl：As being 8：1：0.044. Obvious variations are noticed in contents of the three elements among different vegetables on the one hand and among different organs of the same vegetable on the other hand. With the exception of some individual samples, the three elements Hg, As and Tl tend to be enriched in vegetable roots and leaves, but to decrease remarkably in vegetable stems. The lowest contents of the three elements are observed in fruits and stem tubers. In the roots of wild cabbage and Beta vulgaris var. cicla L. for example, the contents of Hg are so high as up to 5 910.6×10^{-9} and 2 526×10^{-9}, respectively. In lettuce and cabbage the contents of Hg are as high as 3 001×10^{-9} and 2066×10^{-9}. In pumpkin seeds and sweet potatoes the contents of Hg are mostly lower than 60×10^{-9}. Again, in wild cabbage leaves, especially those overgrown leaves, the contents of Tl even reach 1 614.339×10^{-9} against a value of 114.011×10^{-9} for wild cabbage stems, on average 55.005×10^{-9}. In pumpkin seeds, sweet potatoes and potatoes the contents of Tl vary within the range of 8.5×10^{-9}—19.504×10^{-9}. In vegetables the content of As (2×10^{-9}—8×10^{-9}) is generally lower than those of Hg and Tl. The contents of Tl, Hg and As generally follow such a variation trend that their contents in vegetable leaves and roots are higher than in vegetable stems.

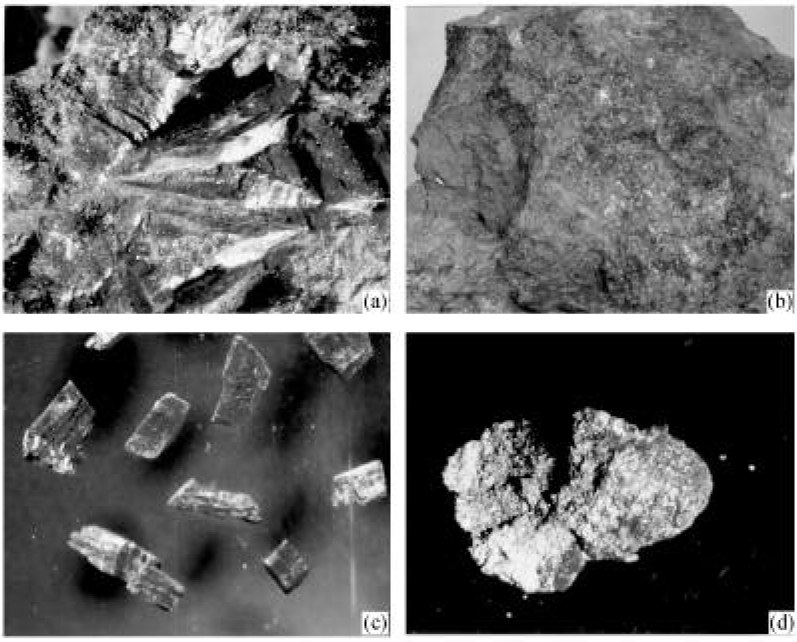

Fig. 2.(a) Drusy lorandite ore, specimen, ×2; (b) lorandite ore (red), specimen, ×2; (c) slaty crystal of lorandite monomineral, specimen, ×2; (d) crystal stock of lorandite (red) and pyrite (yellow), specimen, ×2.

2.2 Tl, Hg and As in wild plants

Three kinds of perennial wild plant growing on the ore-host beds of the Zaofanshan Hg-Tl deposit were collected and analyzed for their Tl, Hg and As contents (table 2). Analytical results show that the contents of Hg are the highest, followed by Tl and As, with the average contents and variation ranges being 13 717.345×10^{-9} (180×10^{-9}—58 194×10^{-9}), 51.624×10^{-9} (11.747×10^{-9}—305.658×10^{-9}) and 12.455×10^{-9} (5.558×10^{-9}—38.467×10^{-9}). Their enrichment factors are 171.47, 0.12 and 0.007, respectively. The contents of the three elements in wild plants largely depend not only on the geochemical properties of the elements themselves, but also on the abundances of the equivalent elements in the rocks (soils) where the wild plants grow. In the siltstones and argillaceous siltstones where the wild plants grow, the average contents of Hg, Tl and As and

Table 1 The contents of Hg, Tl and As in the vegetable samples (10^{-9})

No.	Vegetable	Hg	Tl	As
		Variation range	Variation range	Variation range
E-1	wild cabbage leaf	107—442.2	21—420.458	1.342—6.159
E-2	overgrown leaf of wild cabbage	1 251.2	1 614.339	2.880
E-3	wild cabbage stem	56—668.7	12.50—114.011	1.245—2.745
E-4	wild cabbage root	107—5 910.6	7.5—142.22	4.220—11.300
E-5	beta vulgaris var, cicla L. leaf	1 414.2	3.75	3.690
E-6	beta vulgaris var, cicla L. stem	523	51.50	2.585
E-7	beta vulgaris var, cicla L. root	2 526	29.75	5.505
E-8	lettuce leaf	3 001	15.75	6.705
E-9	lettuce stem	1 010.4	33.00	4.945
E-10	lettuce root	1 375	15.07	7.942
E-11	fragrant-flowered garlic leaf	835.6	13.50	3.620
E-12	fragrant-flowered garlic stem	500.5	12.50	4.455
E-13	fragrant-flowered garlic root	1 992.9	12.75	6.795
E-14	cabbage leaf	2 066	32.50	
E-15	cabbage root	209	47.50	
E-16	radish leaf	420	69.70	
E-17	radish stem	76	60.00	
E-18	radish root	166	98.00	
E-19	pumpkin pulp	64	23.00	
E-20	pumpkin seed	42	10.00	
E-21	sweet potato	56	8.50	
E-22	potato	180.1	19.50	1.455
	enrichment factor	11.001	0.255	0.003
	Hg:Tl:As		8:1:0.044	

Analytical unit: State Key Laboratory of Environmental Geochemistry, Institute of Geochemistry, the Chinese Academy of Sciences.

Table 2 The contents of Hg, Tl and As in wild plants ($\times10^{-9}$)

No.	Wild plant	Hg	Tl	As
1	Lycopodium selago L. leaf	4 501.8	15.500	8.285
2	Lycopodium selago L. stem	10 147.5	17.752	8.296
3	Lycopodium selago L. root	58 194.0	35.924	23.321
4	Lycopodium selago L. leaf	4 500.4	13.746	10.227
5	Lycopodium selago L. stem	11 612.7	39.583	38.467
6	Lycopodium selago L. root	47 089.3	23.224	18.155
7	Gleichenia Linearis Carke leaf	223.7	14.244	6.827
8	Gleichenia Linearis Carke stem	180.0	11.747	5.793
9	Gleichenia Linearis Carke root	500.4	13.247	6.434
10	dry pteris decursivo-pinnata O. Kuntze leaf	2 091.4	305.658	5.558
11	dry pteris decursivo-pinnata O. Kuntze stem	11 849.6	77.235	5.644
12	relative enrichment factor	171.47	0.12	0.007

Analytical unit: State Key Laboratory of Environmental Geochemistry, Institute of Geochemistry, Chinese Academy of Sciences.

their variation ranges are 28.575×10^{-6} (2.4×10^{-6}—72×10^{-6}), 33.575×10^{-6} (1.3×10^{-6}—126×10^{-6}) and 40×10^{-6} (10×10^{-6}—65×10^{-6}), respectively. Their enrichment factors (table 3) are 357.5, 78.14 and 22.22, respectively.

2.3 Hg, Tl and As in chicken organs

The contents of Hg, Tl and As in chicken organs tend to decrease progressively with the average contents of Hg, Tl and As (69.02×10^{-9}, 1.427×10^{-9}, and 0.210×10^{-9}, respectively, see table 4). The minimum content of Hg (30.38×10^{-9}) is detected in chickens' heart and the maximum content (138.40×10^{-9}) in chickens' gizzard; the minimum content (0.328×10^{-9}) of Tl is recognized in cockscomb and the maximum content (6.410×10^{-9}) of Tl in chicken bones; the minimum content (0.003×10^{-9}) of As is found in cockscomb and the maximum content (0.394×10^{-9}) of As in chicken lung. The contents of Hg, Tl and As in chicken feather vary in quite a different manner from those in various chicken organs. In chicken feather Hg is the highest in content, followed by As and Tl. The following are their average contents: Hg 1015.04×10^{-9} (955.73×10^{-9}—1045.10×10^{-9}); As 8.318×10^{-9} (8.040×10^{-9}—8.506×10^{-9}), and Tl 1.050×10^{-9} (1.046×10^{-9}—1.052×10^{-9}). As is clear in table 4, the contents of Hg, Tl and As, especially Hg and As, in chicken feather are obviously higher than in other organs. Moreover, the contents of Hg, Tl and As in chicken feather are respectively 14.71, 0.74 and 39.70 times the average contents of the organs. Therefore, the contents of Hg, Tl and As in chicken feather can be regarded as the indices for determining the contents of Hg, Tl and As in chicken organs.

Table 3 The contents of Hg, Tl and As in the basement rocks (soils) where wild plants grow （$\times10^{-6}$）

Element	Abundance (Taylor, 1964)	Argillaceous siltstone	Siltstone	Banded argillaceous siltstone	Ribbon argillaceous siltstone	Average	Enrichment factor
As	1.8	60	65	25	10	40	22.22
Tl	0.43	1.3	5	126	2	33.6	78.14
Hg	0.08	72	2.4	20.7	19.2	28.6	357.5

Table 4 The contents of Hg, Tl and As in the various organs of chicken($\times10^{-9}$)

Sample	No.	Chicken organ	Hg	Tl	As
Chicken organs	96K-1	heart	30.38	1.068	0.288
	96K-2	lung	52.33	0.625	0.394
	96K-3	flesh	45.38	0.424	0.191
	96K-4	skin	120.84	0.791	0.222
	96K-5	bone	60.53	6.410	0.119
	96K-6	gizzard	138.40	1.103	0.286
	96K-7	intestine	57.90	0.668	0.173
	96K-8	cockscomb	46.40	0.328	0.003
Average value			69.02	1.427	0.210
Chicken feather	96K-9	yellow hen feather	955.73	1.046	8.407
	96K-10	white hen feather	1 045.10	1.050	8.506
	96K-11	yellow cock feather	1 044.30	1.052	8.040
Average value			1 015.04	1.050	8.318

Analytical unit: the AAS Group of the State Key Laboratory of Environmental Geochemistry, Institute of Geochemistry, Chinese Academy of Sciences

3 Tl, Hg, As and Cd in urine, hair and nail

3.1 The contents of Hg, Tl and Cd in human urine

Urine is the most sensitive indicator of trace elements in food chain uptaken by human beings. Urine was sampled from Hg and Tl-poisoned patients and normal villagers, and was analyzed for Hg, Tl As and Cd (table 5). The analytical results show that the content of Tl in villagers' urine is obviously high; especially in the urine from those Hg- and Tl-poisoned villagers who had lived for a long time on such drinking water of which the Hg and Tl contents exceed the quality standards of potable water, the content of Tl may be as high as $1\ 220\times10^{-9}$—$2\ 660\times10^{-9}$, and is 1 220—2 660 times the quality standard of potable water. Urine samples collected from those villagers including Hg- and Tl-poisoned ones who use the standard potable water instead of Hg- and Tl-rich water in recent years have been identified and the results show that the content of Tl is remarkably reduced, mostly less than 150×10^{-9}. Although the villagers who still rely on Tl-contaminated water do not display remarked symptoms of Hg- and Tl-induced diseases, the contents of Tl in their urine are still high, mostly within the range of 370×10^{-9}—660×10^{-9}. Evidently, the content of Tl in urine largely depends on categories of food uptaken by the villagers, particularly on the content of Tl in drinking water. With the exception of some villagers whose urine is slightly high in Hg content, the content of Hg in urine collected from most villagers is less than 1×10^{-9}, i.e. lower than the quality standard of potable water. The contents of As and Cd in urine are precisely lower than the quality standards of potable water. It is not hard to see that urine collected from the villagers in the studied area show high Tl and low Hg, As and Cd. These features can also be used as effective indices to identify the degree of contamination cuased by Hg and Tl. Usually, the content of Tl in urine from those seriously Hg- and Tl-diseased patients is, in most cases, larger than 1000×10^{-9} while the content of Tl in urine from those slightly Tl-diseased patients varies mostly within the range of 100×10^{-9}—1000×10^{-9}. The content of Tl in urine collected from normal villagers is mostly less than 100×10^{-9}.

Table 5 The contents of Hg, Tl, As and Cd in urine collected from villagers living in the Lanmuchang Tl mining district ($\times10^{-9}$)

Water type	No.	Tl	Hg	As	Cd	Note
Seriously Hg-Tl-poisoned patients, living on Tl-contaminated water for a long time	96B-7	2 530	0.52	2.34	0.20	male, 54 old, losing long the sight of both eyes
	96B-8	2 660	0.03	2.20	1.53	male, 45 old, losing long the sight of both eyes
	96B-9	1 220	0.31	5.32	1.58	male, 73 old, losing long the sight of both eyes
	96B-10	1 880	0.73	0.39	1.00	male, 35 old, losing long the sight of both eyes
Slightly Hg-Tl-poisoned patients, long relying on Tl-contaminated water	96B-2	410	0.31	0.01	2.90	male, 45 old
	96B-4	660	0.03	4.42	1.72	male, 14 old
	96B-1	380	0.078	2.01	2.00	female, 42 old
	96B-3	370	0.078	0.32	0.22	female, 17 old
	95B-3	149.5	7.05	27.08		female, 63 old
No symptoms of Hg-Tl disease, Tl-contaminated water replaced by standard potable water	96B-6	100	2.41	0.10	0.97	female, 64 old
	95B-2	105.6	3.32	4.21		male, 64 old
	96B-5	80	0.93	0.10	0.63	male, 65 old
	95B-1	77.7	2.8	6.65		male, 44 old
Standard potable water[4]		1	1	50	10	

Analytical unit: The AAS Group of the Central Analysis Laboratory, Institute of Geochemistry, the Chinese Academy of Sciences.

3.2 Hg, Tl and As in human hair

Hair samples were collected from two groups of villagers (seriously Hg-Tl-poisoned patients group, and slightly Hg-Tl-poisoned patients) in the mining district and were analyzed for their Hg, Tl and As contents (table 6). The analytical results showed that there is only a slight difference in contents of Hg, Tl and As in hair between the two groups of patients. The contents of Hg, Tl and As in hair for the first group of patients and their variation ranges are Hg 890.05$\times10^{-9}$ (334.1$\times10^{-9}$—1547.5$\times10^{-9}$), Tl 2.947$\times10^{-9}$ (1.372$\times10^{-9}$—5.586$\times10^{-9}$) and As 8.431$\times10^{-9}$ (6.099$\times10^{-9}$—12.235$\times10^{-9}$); those for the second group: Hg 1 107.014$\times10^{-9}$ (195.4$\times10^{-9}$—1 527$\times10^{-9}$), Tl 2.241$\times10^{-9}$ (1.120$\times10^{-9}$—4.332$\times10^{-9}$) and As 6.163$\times10^{-9}$ (4.188$\times10^{-9}$—7.851$\times10^{-9}$). Our analyses showed that the contents of Hg, Tl and As in the hair of healthy villagers are low, Hg only 0.2 and 0.16 time 1 and 2 respectively, Tl 0.20 and 0.27 and As 0.05 and 0.073 of the two groups. That is to say, the contents of Hg, Tl and As in the hair of group 1 and group 2 in the Tl mining district are respectively 4.9, 6.1; 4.9, 3.8; and 18.8, 13.7 times those of the healthy group. As can be seen in table 6, variations in the contents of Hg, Tl and As in human hair have no obvious bearing on the age and sex of the patients. Evidently, the content of Hg in human hair from the mining district is far lower than that of the seriously poisoned group in Spain along the southern coast of the Atlantic Ocean (lower than its geometric mean value by a factor of 9—10)[8].

Table 6 The contents of Hg, Tl and As in human hair ($\times10^{-9}$)

Group	No.	Sex	Age	Hg	Tl	As
Group 1 Seriously Tl-poisoned patients (losing the sight of both eyes)	95G-2	male	50	529.2	2.537	8.288
	96G-6	female	27	1547.5	5.586	12.235
	96G-7	male	73	684.4	1.587	6.099
	96G-8	male	51	1 239.9	3.432	8.124
	96G-9	male	45	334.1	1.372	8.899
	96G-10	male	35	1 006.2	3.167	6.941
Mathematic mean				890.05	2.947	8.431
Geometric mean				784.54	2.636	8.228
Group 2 Slightly poisoned patients	95G-1	male	42	1 217.4	4.332	7.851
	95G-3	female	16	1 427.5	2.097	6.804
	96G-1	male	40	1 091.0	1.842	5.368
	96G-2	female	28	195.4	1.384	4.188
	96G-3	male	24	1 317.1	1.120	6.384
	96G-4	male	57	973.7	1.164	5.324
	96G-5	male	43	1 527	3.750	7.219
Mathematic mean				1 107.01	2.241	6.163
Geometric mean				955.195	1.965	6.044
Group 3 Contrast group	96G-11	female	59	181.7	0.596	0.448

Analytical unit: The AAS Group of the State Key Laboratory of Environmental Geochemistry, Institute of Geochemistry, the Chinese Academy of Sciences

3.3 Hg, Tl and As in human nail and toenail

Nail and toenail samples of seriously Hg-Tl-poisoned and slightly Hg-Tl-poisoned patients were collected from the Tl mining district and were analyzed for their Tl, Hg and As contents (table 7). The analytical results showed that the inhabitants there have been more or less affected by Hg and Tl pollution, as is evidenced by the fact that the contents of Hg, Tl and As in nail and toenail samples from seriously Hg-Tl-poisoned patients are n to $n\times10$ times higher than those of healthy or non-poisoned inhabitants. The average contents of Hg, Tl and As in nails and toenails collected from the serious patients are: Hg 1660.76$\times10^{-9}$ (511.9$\times10^{-9}$—4878.5$\times10^{-9}$), Tl 13.92

$\times 10^{-9}$ (2.970×10^{-9}—32.235×10^{-9}), As 8.48×10^{-9} (2.871×10^{-9}—12.456×10^{-9}), with the average values 83.5, 10.1 and 2.5 times those of healthy inhabitants; the average contents of Hg, Tl and As in nails and toenails collected from the slightly Hg-Tl-poisoned patients are: Hg 531.4×10^{-9} (410.8×10^{-9}—598.1×10^{-9}), Tl 8.534×10^{-9} (5.138×10^{-9}—13.943×10^{-9}), As 3.452×10^{-9} (2.370×10^{-9}—3.752×10^{-9}), with the average 26.7, 6.2 and 1.35 times those of healthy inhabitants.

Table 7 The contents of Hg, Tl and As in human nails and toenails ($\times 10^{-9}$)

No.	Nail or toenail	Age	Hg	Tl	As	Remark
95A-1	nail	63	4 878.5	6.120	11.536	losing the sight (female)
95A-2	toenail	63	1 014.6	32.235	12.456	losing the sight (female)
95A-7	nail	50	972.7	2.970	2.871	losing the sight (male)
95A-8	toenail	50	511.9	11.990	7.089	losing the sight (male)
95A-10	toenail	44	926.1	16.269		losing the sight (male)
Average			1 660.76	13.917	8.488	seriously Hg-Tl-poisoned patient
95A-4	nail	64	598.1	13.943	2.370	slightly (male)
95A-5	toenail	60	585.3	6.522	3.752	slightly (male)
95A-6	nail	60	410.8	5.138	4.234	slightly (male)
Average			531.4	8.534	3.452	slightly Hg-Tl-poisoned patient
9510-1	nail	60	5.974	1.134	2.946	healthy (male)
9510-2	toenail	60	33.800	1.620	3.718	healthy (male)
Average			19.887	1.377	3.332	contrast

Analytical unit: State Key Laboratory of Environmental Geochemistry, Institute of Geochemistry, the Chinese Academy of Sciences.

As can be seen from table 7, as for the same Hg-Tl-poisoned patient, the content of Hg in nail is obviously higher than in toenail whereas the contents of Hg, Tl and As in toenail are remarkably higher than in nail, just as with the case for healthy inhabitants.

4 Results and discussion

The Lanmuchange Tl deposit is the only independent Tl deposit ever reported in the world. The mineralization involves two stages, i. e. the bio-enrichment stage and the hydrothermal reworking stage. The major associated elements in the deposit are Hg, As, W and Au. The former two can be mined and utilized and the latter two are the main mineralizing elements. In the Tl ores formed as a result of bio-enrichment there have been a number of paleontological fossils recognized such as foraminiferae, bryozooids and spongy. But these fossils have all been replaced by ore-forming hydrothermal solutions containing Tl, Hg, As and S, hence forming Tl minerals in the form of bio-pseudomorphs, such as lorandite and christite. Such a rare metallogenic mechanism is the first case so far reported. As viewed from the ore-host beds of this Tl deposit, the forming age of paleontological fossils in Tl ores and the sulfur isotopic composition of ore minerals which is corresponding to that of Late Permian seawater, evidently the mineralization due to bio-enrichment took place during the Late Permian, i. e. during the Late Hercynia.

The contents of Tl, Hg and As in plants and animals in the Tl mining district show that Hg is the highest, followed by Tl, and As is lowest. Their contents are obviously controlled by the geological-geochemical and bio-geochemical environments in which living organisms lived, especially by the high background values of Tl, Hg and As in water, soil and rock (and ore) in the Tl mining district.

The contents of Tl, Hg and As in living organisms are generally high in the mining district. Particularly in those plants growing in weathered soils developed in the locations where orebodies and mineralized beds occur, the contents of Tl, Hg and As are abnormally high. It is not hard to see that the contents of Tl, Hg and As in living organisms in the mining district are not only the indices for identifying the degree of contamination caused by Tl, Hg and As, but also the markers for the prospecting of ores, especially blind orebodies.

Based on the contents of Tl in villagers' urine we have established the preliminary criteria for distinguishing seriously Hg-Tl-poisoned patients from slightly Hg-Tl-poisoned patients and healthy inhabitants in the Tl mining district, i. e. Tl>1 000 $\times 10^{-9}$——serious Hg-Tl-poisoning, (100—1000) $\times 10^{-9}$ slight Hg-Tl-poisoning and <100 $\times 10^{-9}$ normal poisoning. The contents of Hg in nail and toenail samples collected from villagers living in the Tl mining district are $n \times 10$(27—28) times those of the healthy group and those of Tl and As are several to more than ten times those of the healthy group. Moreover, for the same villager, his (or her) toenail contains higher Tl and As than his (or her) nail. The contents of Hg, Tl and As in villagers' hair samples are respectively 4.9—6.1, 3.8—4.9 and 13.7—18.8 times those for the contrast group. The contents of Tl and As in hair of seriously Hg-Tl-poisoned patients are higher than those of slightly Hg-Tl-poisoned patients. The contents of Hg, Tl and As in the hair of the two groups of patients are: Hg 890.05 $\times 10^{-9}$, 1 107.01 $\times 10^{-9}$; Tl 2.947 $\times 10^{-9}$, 2.241 $\times 10^{-9}$; and As 8.431 $\times 10^{-9}$, 6.162 $\times 10^{-9}$, respectively.

Ore deposit geochemical, environmental geochemical and biogeochemical studies have shown that the key factors leading to the environmental pollution of the mining district, the high contents of Tl and Hg in living organisms and the occurrence of Hg-Tl diseases are the exposure of primary ores on the Earth's surface during the exploitation of Tl deposits and thereafter the release of Tl, Hg, As and other elements in the process of hypergenic weathering-leaching of the ores and their participation in the circulation of the rock/ore-soil-water-living organism-human body system, which has therefore resulted in the high contents of Tl and Hg in human bodies and animals as well as in living organisms and the occurrence of a series of Hg-Tl diseases.

The formation of the Lanmuchang independent Tl deposit is due to both the special metallogenic conditions in the low-temperature ore-forming domain of southwestern China and the geochemical properties of the element Tl itself[10—14]. The associated elements Hg, As and Au in Tl deposits or the associated element Tl in Hg, As and Au deposits possess the characteristics of a sulfophile element association. For example, the Nanhua Tl deposit of Yunnan Province is closely associated with As (realgar and orpiment) deposits, so the former is referred to as the Nanhua As-Tl deposit[3]. Also, in the Lannigou Au deposit of Guizhou Province we have found such associated elements as Hg, Sb and As[12]. In low-temperature reworked deposits there has been an element association of Hg, As, Tl, W and Au due to W mineralization. With the exception of the Lanmuchang Tl deposit, no report of this kind has been made in other deposits. It is the involvement of W-bearing granitic intrusives in mineralization at the hydrothermally reworking stage that led to the occurrence of tungsten mineralization. The discovery of W-bearing granitic intrusive dikes by the author and the scheelite-bearing granitic rocks by the Guizhou Bureau of Geology and Mineral Resources provide strong evidence for the involvement of the W-bearing granitic intrusive rocks in mineralization.

The isotopic composition of sulfur in the Lanmuchang Tl deposit is characterized by heavy sulfur enrichment and is close to that of Late Permian seawater, indicating that bio-enrichment metallogenesis took place during the Hercynian and that biogenic sulfur (more light sulfur) was converted into inorganic sulfur (more heavier sulfur) as a result of magmatic and tectonic activities. In this work all the samples for sulfur isotopic analysis were sulfide minerals formed during the hydrothermal-reworking stage. If such sulfide minerals as those formed in the mineralization stage of bio-enrichment, i.e. those occurring in the form of bio-pseudomorphs, could be selected, the sulfur isotopic composition of the sulfide minerals would be viewed as being enriched in heavy sulfur. As the Nanhua As-Tl deposit possesses the characteristics of bio-metallogenesis, its sulfur isotopic composition would be viewed as being obviously enriched in light sulfur[4].

It is commonly observed that the contents of Hg, Tl and As in rocks, ores, soils, water, living organisms and human bodies in the Lanmuchang mining district are remarkably higher than those in the non-mining districts. So Hg, Tl and As can be used as indicator elements for discriminating composite pollution and ore prospecting in the Tl mining district. As the Tl deposit was weathered and leached, the release of Hg, Tl and As by way of the rock/ore-soil-water-organism-human body biological chain has led to environmental pollution in the Tl mining district and the occurrence of Hg-Tl diseases there. Obviously, the environmental pollution in the Tl mining district is the result of composite contamination of Hg, Tl and As. In terms of differences both in clinic symptoms of the diseases caused by Hg, Tl and As contamination[9] and in the concentrations of Hg, Tl and As in human organs it can be concluded that the Tl-disease suffered by the villagers inhabiting the Lanmuchang Tl mining district is caused jointly by Hg and Tl[5]. For this reason, such Tl disease is also referred to as Hg-Tl disease. The clinic symptoms of As-disease are significantly different from those of Hg-Tl diseases. Moreover, it has been commonly accepted that arsenic is a trace element indispensable for living organisms. For instance, the lack of arsenic in animals will cause such diseases as growth impediment and the spring water in which the content of As is higher than 1 mg/L can be used for medical bathing[15]. Obviously As in the Tl mining district is not a factor leading to Hg-Tl diseases.

References

1. Zhang Zhong, Zhang Baogui, Thallium in low temperature ore deposits, China, Chinese Journal of Geochemistry, 1996, 15(1): 87.
2. Zhang Zhong, Long Jiangping, Zhang Baogui, The existing forms, metallogenic model and ore-searching indicators of Tl in As-, Hg-, Sb- and Au-deposits, Geological Review (in Chinese), 1995, 41(4): 363.

3. Zhang Zhong, Zhang Xingmao, Zhang Baogui, Element geochemistry and metallogenic model of the Nanhua As-Tl deposit, Geochimica (in Chinese), 1998, 27(3): 269.
4. Zhang Zhong, Zhang Baogui, Long Jiangping et al., Thallium pollution associated with mining of thallium deposits: Science in China, Series D, 1998, 41(1): 75.
5. Zhang Zhong, Zhang Baogui, Long Jiangping et al., Study on thallium environmental pollution in the process of mining of thallium deposits in China, Science in China, Series D, 1997, 27(4): 331.
6. Zhang Baogui, Zhang Zhong, Long Jiangping et al., The problems of low-temperature ore prospecting: Developments in Geochemistry (in The Proceedings of the 30th International Congress on Geology, Guiyang: Guizhou People's Publishing House, 1996, 22—26.
7. Li Guizhu, A preliminary study on the chemical composition of ores from the Lanmuchang Hg-Tl deposit and the existing forms of Tl, Xingren, Guizhou Geology (in Chinese), 1996, 13(1): 24.
8. Yang Min, Xu Changjiang (translators), Hg and methyl Hg in danger groups of human beings in the southern coast of the Atlantic (in Chinese), a Spain: Overseas Environmental Science and Technology, 1995, (2), 62.
9. Jiang Xingjin, Purification and Sterilization of Potable Water, Beijing: China Environmental Science Press, 1989, 1—63.
10. Tu Guangchi, Zhang Baogui, The Characteristics of Southwest China's minerogenetic province of low-temperature hydrothermally reworked ore deposits: developments in geochemistry, Proceedings of the 30th International Congress on Geology, Guiyang: Guizhou People's Publishing House, 1996, 1—4.
11. Tu Guangchi, On the composition of unusually super-large ore deposits and the unique features of their geological setting and forming mechanism——A preliminary study on unusually super-large ore deposits: Science in China (in Chinese), Series D, 1998, 28 (supp.): 1.
12. Zhang Zhijian, Zhang Wenhuai, Study on the organic ore-forming fluid of the Lannigou Au (Hg, Sb) deposit, Guizhou Province, Mineral Deposits (in Chinese), 1998, 17(4): 343.
13. Regional Geological Brigade of Guizhou Bureau of Geology and Mineral Resources, A report on regional geological investigation of the People's Republic of China (1∶200000) for the Xingren and Anlong regions, Guiyang: Geological Brigade of Guizhou Province, 1980, 211—212.
14. Zhang Zhong, Long Jiangping, New advance in the study of the Nanhua Tl-rich realgar deposit: Geochemical studies of Ore deposits, in The 9th International Symposium on the Genesis of Ore Deposits, Beijing, Seismological Press, 1994, 22—26.
15. Xuan Zhiqiang, A brief account of As resources in China, Geology of Chemical Mineral Resources (in Chinese), 1998, 20(3): 205.