Science in China Series D: Earth Sciences

A preliminary discussion on the bio-metallogenesis of Tl deposits in the low-temperature minerogenetic province of southwestern China

ZHANG Zhong†, ZHANG BaoGui, HU Jing, YAO LinBo & TIAN YiFu

The Key Laboratory of Ore Deposit Geochemistry, Institute of Geochemistry, Chinese Academy of Sciences, Guiyang 550002, China

Starting with the research status of bio-metallogenesis of Tl deposits and their geology, this work deals with the geological background of Tl enrichment and mineralization and the mechanism of bio-metallogenesis of Tl deposits, as exemplified by Tl deposits in the low-temperature minerogenetic province. This research on the bio-metallogenesis of Tl deposits is focused on the correlations between bio-enrichment and Tl, the enrichment of Tl in micro-paleo-animals in rocks and ores, bio-fossil casts in Tl-rich ores, the involvement of bio-sulfur in minerogenesis and the enrichment of bio-genetic organic carbon in Tl ores. Thallium deposits have experienced two ore-forming stages: syngenetic bio-enrichment and epigenetic hydrothermal reworking (or transformation). Owing to the intense epigenetic hydrothermal reworking, almost no bio-residues remain in syngenetically bio-enriched Tl ores, thereby the Tl deposits display the characteristics of hydrothermally reoworked deposits.

thallium, Tl deposit, bio-metallogenesis, bio-fossil cast, unusual enrichment of Tl, Tl metallogenetic model

China's low-temperature hydrothermal reworking minerogenetic province covers a vast area, and is characterized as being complete in ore species, diverse in type, large in scale and complicated in ore assemblage. Therefore, it can be celebrated as the most largest low-temperature hydrothermal reworking minerogenetic province throughout the world[1]. In this minerogenetic province are preserved abundant mineral resources, and the ore deposits occurring in this province are large in scale and enormous in Tl content. Either the diversity of its ore species or the complicity of its metallogenesis cannot be matched elsewhere throughout the world. This minerogenetic province contains a large number of large and super-large ore deposits of Hg, Sb, As, Pb, Zn, Sn, Au, Cd, Ge, as well as rock crystal, ice landspar, fluorite and other non-metallic ore deposits in addition to Tl deposits. Up to now, little has been reported on Tl deposits in other countries and regions except in China. So China should be said to be the first that took the lead in the study of the mechanism of bio-metallogenesis of Tl deposits. The so-called bio-metallogenesis refers mainly to the absorption and enrichment of some special elements by living organisms in the process of metabolism, the accumulation of bio-remains and skeletons as ores and metal gathering[2−4]. There has been no unity in thinking pertaining to research on bio-metallogenesis, especially on the bio-metallogenesis of hydrothermal deposits. Due to the lack of evidence for bio-metallogenesis, the research results so far acquired are more or less of assumption. As mentioned in the book *Strata-bound Deposits and Stratiform Deposits* (vols. 1−9) edited by K. H. Volf, the cases of bio-metallogenesis are full of assumption. For example, gold mineralization during Achaean and Proterozoic times in South Africa is closely related to

Received January 10, 2006; accepted March 23, 2006
doi: 10.1007/s11430-007-2010-8
†Corresponding author (email: zhangbg168@yahoo.com.cn)
Supported by the National Natural Science Foundation of China (Grant No. 40372047)

algal activities. That is to say, whenever algae were flourishing, there would occur intensive gold mineralization[5]. Some Pb-Zn deposits formed during Phanerozoic time seem to be related to reefs with respect to their temporal-spatial distributions. Such deposits are referred to as the reef-bound ore deposits. The horse-tail structure of the Dongchuan copper deposit in China is considered to be a sort of mineralized algal sheet structure[6]. Framboidal pyrite present in sulfides is also considered to be of bio-metallogenesis. In the strata-bound gold deposits discovered in the Qinling region of China evidence has been found for thallogen bio-metallogenesis and in the metallic minerals there have been observed bio-fabrics[7,8]. All this is more ore less related to bio-metallogenesis.

The available data on ore deposit science, geochemistry and biology both at home and abroad indicate that not only little has been reported on Tl deposits themselves, but also almost no data is available for bio-metallogenesis of hydrothermal deposits of Hg, Sn, Sb, Pb, Zn, Au, etc. closely related to Tl; if any, research is restricted mostly to some indirect evidence for the involvement of organic matter in metallogenesis and that from simulating experiments[7,9]. The Idrija reniform-structure Hg deposit of Yugoslavia, the Alchar Sb-As deposit of Grace, the Lengenbach Pb-Zn deposit of Swiss and the Pine Point Pb-Zn deposit of Canada can be cited as typical examples[10,11]. These deposits contain more or less thallium and their research is mostly restricted to the indirect relationships between organic matter and metallogenesis, and no special report is available on bio-metallogenesis.

Research on bio-metallogenesis is methodologically based on plaeontological research results in combination with ore deposit science, bio-chemistry, bio-physics, microbiology and geochemistry, as well as the theories and methods concerned in addition to the observation and study of natural bio-metallogenetic phenomena, for instance, biostratigraphy, bio-mineralogy, ore bio-fabrics, bio-fossil casts, etc. Its aim is to explore the bio-organic composition, type, structure and metallogenesis of metallic ore deposits in the geological history. Adopting the methods of simulating bio-metallogenesis, the uptake of rock-forming elements by modern marine (lacustrine) or artificially cultured thallophytes, as well as the processes of their enrichment and transport are simulated so as to further deduce the contributions of paleospecies to metallogenesis. Thallium ore deposits and their alike are commonly thought to be of inorganic origin, i.e., magma hydrothermal deposits or strata-bound deposits. In their studies of Tl deposits the authors found a series of bio-metallogenetic phenomena and clues, which constitute the contents and framework for the preliminary discussion of bio-metallogenesis in this work. As exemplified by the Lanmuchang and Nanhua Tl deposits, this study discusses their bio-metallogenesis.

1 Geology of Tl deposits

The Tl deposits so far discovered in China are distributed mainly in the low-temperature minerogenetic province extending in both Guizhou and Yunnan provinces, Southwest China. The deposits have been less documented and their research is mostly restricted to the composition of ore-forming materials and ecological settings. This minerogenetic province enjoys exceptional advantages of favorable metallogenetic settings and diverse paleo-marine (continental) facies biocommunities. Their evolution and thriving-decline inoculate Tl mineralization and the formation of Tl deposits. This paper is going to discuss the geological features of Tl deposits as exemplified by the marine-hydrothermal superimposed-type Lanmuchang Tl deposit in Xingren, Guizhou Province and the continental-sedimentary reworking-type Nanhua Tl deposit in Yunnan Province.

1.1 Lanmuchang Tl deposit in Guizhou Province

The mining district is located in the Pu'an rotational shear tectonically deformed zone in the Liupanshui fault depression of the Youjiang folded zone, on the southeastern side of the Mile-Shizong fault and on the southern limb of the Zaojiaping anticline, and in the tectonically N-E and E-W composite locus (Figure 1). Owing to the composite tectonics, the nose-shaped anticline at Lanmuchang extends northeastwards at 40°—60°, which is measured at 720 m in length and 250 m in width, controlling the overall distribution of Tl deposits. The ore-hosted strata are composed chiefly of Upper Permian Longtan Formation-Changxing Formation and subordinately of the Lower Triassic Yelang Formation[1)].

1) After Guizhou Provincial Regional Survey Team, 1980

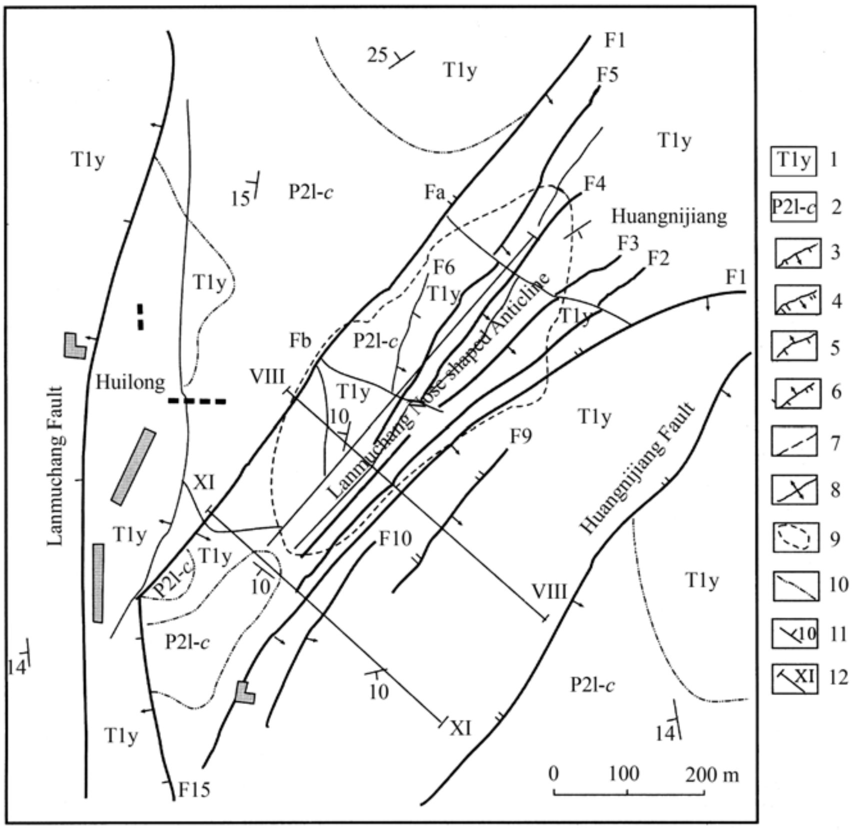

Figure 1 Geological sketch map of the Lanmuchang Tl deposit (After Guizhou Provincial Regional Survey Team, 1980). 1, Lower Triassic Yelang Formation; 2, Upper Permian Longtan Formation-Changxing Formation; 3, tensional torsion fault; 4, tensional shear fault and No.; 5, compresso-shear fault; 6, compressive fault and No.; 7, fault with unknown properties and No.; 8, nose-shaped anticline; 9, ore-bearing body and orebody distribution area; 10, measured and deduced geological boundaries; 11, attitude of strata; 12, exploration line and No.

Ore-hosted country rocks include sandstone, argillaceous limestone, sandy claystone, carbonaceous siltstone, chert limestone, limestone and shale. As the ore-hosted strata are diverse in lithology with multiple ore-bearing layers, more than twenty ore-bearing runs can be distinguished[12].

The Lanmuchang Tl deposit is controlled jointly by lithologic character and structure and generally extends along the strata; the ore-bearing bodies dip southwestwards in a vertical direction and slightly decline. The ore-bearing bodies are stratoid and lenticular in the mode of occurrence. Laterially, the ore-bearing bodies are lenticular and saddle-shaped, usually 60—240 m long and 40—80 m wide, with the maximum width of 120 m; 2—5 m in thickness with the maximum value of 17 m. The ore-bearing bodies are usually composed of several small-sized orebodies, and the small orebodies are banded, saccular, catenulate in form, generally 2—10 m long and 2—4 m wide. The ores are diverse in structure, for example, banded, disseminated, massive, nodular, stockwork-like, powdered, porous and drusy. There are two genetic types of thallium ores, i.e., syngenetic bio-sedimentation and epigenetic hydrothermal reworking. Thallium ores of the former type contain abundant foraminifers, zoaria and other bio-fossils; those of the latter type have preserved bio-fossil casts. The ores contain as much Tl as $n\times10^{-4}$—$n\times10^{-3}$. Tl-rich ores contain so much Tl as to be up to 5.22%—15.97%. The Tl minerals so far discovered include lorandite, christite, raguinite, Tl-alum, etc. (Table 1). The coexisting and associated minerals include cinnabar, pyrite, markasite, realgar, orpiment, quartz, barite, calcite, kaolinite, gypsum, melanterite, halotrichite, jarosite and limonite.

1.2 Nanhua Tl deposit in Yunnan Province

The mining district is located in the eastern-southwestern parts of the East Yunnan Depression folded zone on the South China platform, near the Malong River folded zone. Structures near the mining district are affected

Table 1 Electron microprobe analyses of Tl minerals

Mineral	Chemical formula	Element content (%)											Total
		Tl	As	S	Hg	Fe	Pb	Au	Ag	Sn	Sb	Cu	
Lorandite (8)[a)]	$TlAsS_2$	59.08	21.81	18.12	0.18	0.02	1.61	0.11	0.11	0.07	—	0.01	101.12
Christite (13)	$TlHgAsS_3$	35.29	12.23	16.57	35.46	0.10	—	—	0.08		—	0.02	99.75
Picotpaulite (6)	$TlFe_2S_3$	49.13	0.76	23.69	0.03	25.34	1.04		0.13		0.03	0.10	100.25
Hutchinsonite (7)	$PbTlAs_5S_9$	19.57	34.51	25.91	0.07	0.06	19.01		0.04		0.03	0.01	99.21
Ellisite (2)	Tl_3AsS_3	68.86	11.28	16.02	0.06	0.16	3.58		0.15		—	0.10	100.21
Raguinite (2)	$TlFeS_2$	62.86	—	19.49	0.55	16.73	—	—	—	—	—	—	99.63
Tl-pyrite (20)	$(Fe,Tl)(S,As)_2$	6.98	5.31	48.64	—	38.63	—	—	—	—	—	—	99.56

a) In the parentheses are the numbers of measured samples; indent indicates "no detection"; "—" stands for "not detected"; electron microprobe analysis accuracy =1%. Analytical unit: The Key Laboratory of Ore Deposit Geochemistry, Institute of Geochemistry, Chinese Academy of Sciences.

by the Honghe River giant fault, with the tectonic line extending north-north-westwards. The folds are represented by a synclinorium, with the axial plane mostly inclining southwestwards (Figure 2). There are three groups of faults that are roughly divided in accordance with their sizes, i.e., N-W-extending, N-E-extending and N-N-W-extending faults, of which the N-E-extending transverse faults are closely related to Tl mineralization[1)].

From the bottom to the top the ore-hosted strata in the mining district are the Dala Member (J_3^1b), the Xionghuangchang Member (J_3^1c) and the Naran Member (J_3^2a), of which the Dala Member is 242 m thick with obvious rhythm, each rhythmic layer becoming coarser and coarser from the bottom upwards, starting with sandstone and siltstone and ending with mudstone; the Naran member is 62 m thick, composed of dark purplish-red mudstone, silty mudstone intercalated with grey thin-layered argillaceous siltstone and fine sandstone; the Xionghuang member, generally called the "yellow layer", has a total length of 285 m, and it is the main Tl ore-hosted stratum. Thallium orebodies are hosted in the phase-transition zone between blackish-grey fine laminated carbonaceous argillaceous dolomite, carbonaceous argillaceous limestone and dolomitic mudstone. The ore-bearing layer not only commonly contains Tl, but also abundant paleo-fossils such as *Ostracoda*, *Pelecypoda* and fish fossils, indicative of a set of typical terrestrial clastic sediments. In the enriched bioclastic rocks thallium is highly enriched, especially in Tl-rich ores[13].

Thallium mineralization is characterized as being multi-layered and continuous, extending as long as to be up to 650—850 m. Only in the Xionghuangchang segment have there been recognized 15 small-sized mineralization horizons. The orebodies are stratoid, lenticular and veinlet-like in shape and extend in line with the strike of the strata. The orebodies show the phenomena of expansion and shrinkage along the strike. The largest ore-bearing layer is 800 m long and 1.02—1.10 m wide along the strike. The ore deposit belongs to the terrestrial sedimentation-reworking type; the ores are diverse in texture and structure, for instance, banded, disseminated, metasomatic, residual, brecciaed, massive, colloform, veined, drusy ores are recognized. In addition, banded and fine massive structures are dominant. The contents of Tl in the ores are within the range of $n\times10^{-4}$—$n\times10^{-3}$, even up to $n\times10^{-2}$ in individual cases. The Tl minerals so far discovered include hutchinsonite, picotpaulite, ellisite and Tl-pyrite (Table 1); the coexisting and associated minerals are realgar, orpment, pyrite, galena, sphalerite, dolomite, calcite, quartz, barite, etc.; the secondary minerals are picropharmacolite, gypsum, illite, geothite, etc.

2 Study on the bio-metallogenesis of Tl deposits

2.1 Bio-enrichment and its correlation with Tl

At the mean time when marine (lake) sediments were deposited, *Foraminifera* and *Ostracoda* and other vivospecies and/or remains would intake and concentrate Tl, As, S and other ore-forming elements, then forming Tl-bearing horizons on the sea floor or at the lake bottom, as well as synsedimentary Tl ores. The synsedi-

1) After No.11 Geological Party under Yunnan Provincial Bureau of Geology and Mineral Resources, 1965

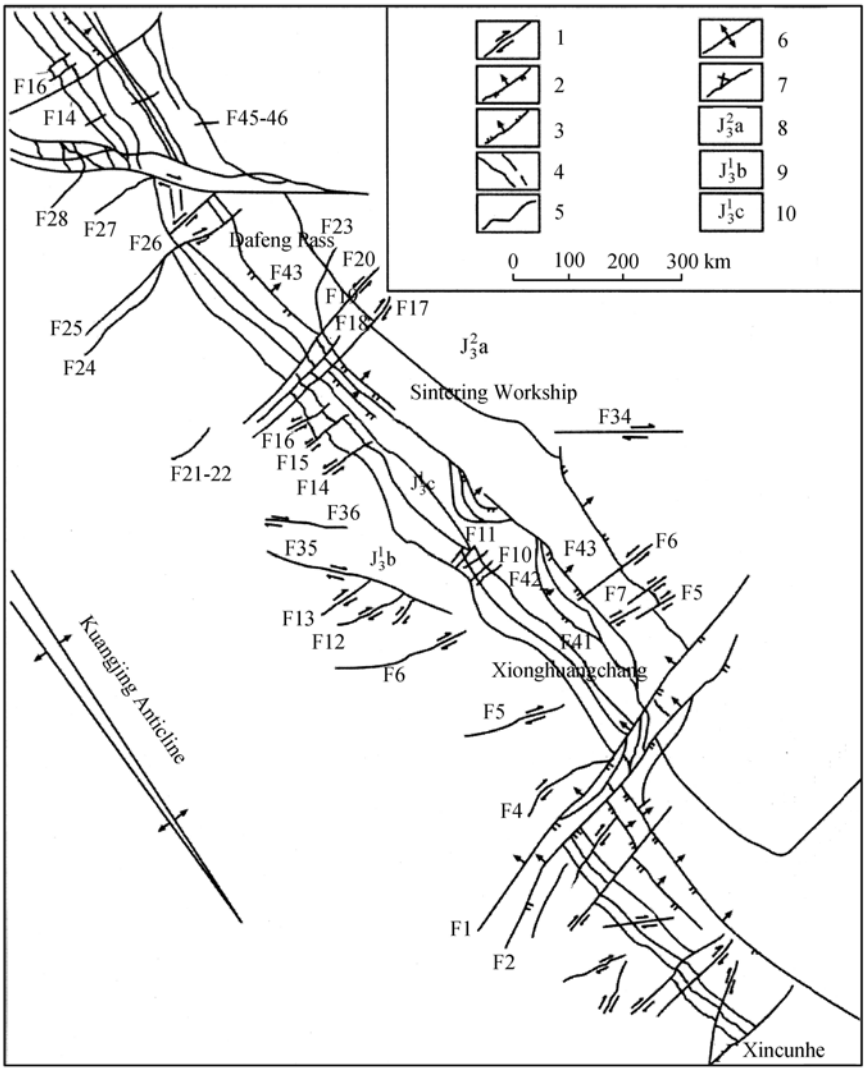

Figure 2 Geological sketch map of the Nanhua Tl deposit (after No. 11 Geological Party Under Yunnan Provincial Bureau of Geology and Mineral Resources, 1965). 1, Strike-slip fault; 2, reverse fault; 3, normal fault; 4, orebody and ore-bearing horizon; 5, geological boundary; 6, anticline; 7, diabase; 8, purple mudstone; 9, argillaceous-lime dolomite and argillaceous interbed; 10, purple mudstone-lime sandstone.

mentary Tl ores exhibit, in most cases, banded, laminated and veined structures, as well as massive and nodular structures, in consistency with the mode of occurrence of the ore-hosted strata. The ore minerals are fine-grained, mostly within the range of less than 1mm in size, and exhibit disseminated and fine clastic textures. The ores contain abundant micro-paleo-animal fossils such as foraminifers and zoaria. The contents of Tl in the ores are closely related to the amounts of bio-fossils. On the basis of the analysis of the Tl contents of rocks and ores in the Tl deposit and the statistics data on the numbers of fossils in the corresponding rock and ore thin sections, it is indicated that in the thin sections prepared from the most majority of the rock and ore samples which contain less than $(30-1500)\times10^{-6}$ Tl only a few fossils have been found, generally 0—4 in number; in those from the rock and ore samples which contain $(30-1500)\times10^{-6}$ slightly more fossils are observed, usually 1—15 in number; in the thin sections prepared from four Tl-rich ore samples ($(1900-3379)\times10^{-6}$) bio-fossils exceed 20 in number (Table 2). In the Tl-bearing rock and ore samples bio-fossils are unevenly distributed, and a variety of close-spaced bio-zones have been observed (Figure 3a—d). In the syngenetically bio-enriched rocks and ores the bio-fossils are enclosed by fine-grained quartz and hence are well preserved (Figure 3e—f). But in the hydro-

Table 2 The contents of Tl and the amounts of micro-paleo-animal fossils in ores of the Tl deposits[a)]

No.	Rock type	Tl content (10^{-6})	No. of fossils in a thin section	No.	Rock type	Tl content(10^{-6})	No. of fossils in a thin section
NH－1	purplish-red siltstone	0.1		NH－53	Tl-mineralized siltstone	4	1
NH－7	siliceous limestone	0.1	1	NH－52	Tl-mineralized siltstone	7	2
NH－9	argillaceous limestone	0.7		NH－55	Tl-mineralized siltstone	8	4
NH－10	dolomitic mudstone	0.7	2	NH－56	Tl-mineralized dolomite	3	1
NH－14	dolomitic mudstone	0.8	3	NH－59	brecciaed tl ore	19.7	2
NH－19	argillaceous limestone	2.7	1	NH－02	banded tl ore	32.8	1
NH－20	sandy mudstone	0.4		NH－05	laminated tl ore	76.3	2
NH－21	purplish-red siltstone	0.3		NH－08	weathered tl ore	71.5	5
NH－22	calcareous mudstone	0.4	3	NH－02－3	laminated tl ore	80.9	3
NH－23	silty mudstone	0.2	1	NH－02－2	banded tl ore	85.0	2
NH－25	argillaceous limestone	0.3		NH－02－1	banded tl ore	83.6	8
NH－26	silty mudstone	0.1		NH－61	Tl-rich ore	226	8
NH－27	calcareous mudstone	0.5	3	NH－64	brecciaed tl ore	249	10
NH－28	argillaceous limestone	0.1		NH－3	brecciaed tl ore	279	5
NH－29	argillaceous dolomite	0.3	4	NH－65	oxidized tl-rich ore	964	7
NH－30	calcareous mudstone	0.9		NH－13	massive tl-rich ore	1500	15
NH－38	argillaceous siltstone	0.3		NH－15	laminated tl-rich ore	1900	＞20
NH－57	calcareous siltstone	0.3		NH－56－2	Tl-rich ore	1889	＞20
NH－58	argillaceous dolomite	1.5	2	NH－56－4	Tl-rich ore	2161	＞20
NH－67	argillaceous dolomite	2.7	1	NH－56－5	Tl-rich ore	3379	＞20
	Average	0.67	1.05		Average	650.94	＞7.3

a) Atomic Absorption Spectrometry, accuracy: 2%. Chemical analysis: Analysis Center of the Institute of Geochemistry, Chinese Academy of Sciences.

thermally metasomatic Tl ores the bio-fossils are conversed to Tl minerals via metasomatism, only bio-fossil casts are preserved (Figure 4a—d). In the siliceous concretions are observed a variety of bio-fossil casts which were formed as a result of the metasomatism of living organisms by Tl minerals (Figure 4e). Lorandite of hydrothermally metasomatic origin has been detected in *Oldhamina* fossils (Figure 4f).

2.2 Thallium enrichment by micro-paleospecies in rocks and ores

As viewed from the analysis of the Tl contents of rocks and ores, monominerals (quartz and calcite) and micro-paleofossils, it is seen that the Tl contents of fossils contained in the rocks [$(20—60)\times10^{-6}$], the monominerals [$(320－570)\times10^{-6}$] and Tl (mineralization) ores (rocks) [$(300－550)\times10^{-6}$] are 8－100, 422.2－549.5 and 2.1－13.4 times those of the Tl-hosted rocks and ores, respectively (Table 3). From the results of this analysis it is deduced that the high contents of Tl in the micro-paleo-animal fossils are ascribed mainly to the intake and concentration of the dispersed Tl in sea (lake) water in the process of metabolism of these marine (lake) creatures. That is because in the special sedimentary ore-forming environments living organisms have a strong adaptibility to the surroundings, it is highly possible for them to intake a sufficient amount of Tl to form Tl ores. Trudinger P. A. et al. considered that the contents of some elements which were enriched in some micro-paleo-organisms could be so high as to be 10×10^5 times those of seawater[14]. The contents of Tl in quartz, calcite and pryite in the surroundings of micro-paleo-animal fossils in thin sections are mostly $(1－2)\times10^{-6}$, far lower than those in the micro-paleo-animal fossils. The contents of Tl in rocks and ores [$(20－570)\times10^{-6}$] are so high as to reach the index for Tl mineralization or metallogenesis[15,16]. All this provides strong evidence for the bio-metallogenesis of thallium. That is because in their vital process the living organisms persistently intook nutrients from the surroundings, and via metabolism, large amounts of beneficial and/or harmful elements would find way into the bodies of living organisms.

Marine geological investigations and ocean drilling revealed that there occur hydrothermo-sedimentary sulfide deposits near the mid-ocean-ridge black chimneys. In addition, there were found autotrophic bio-communi-

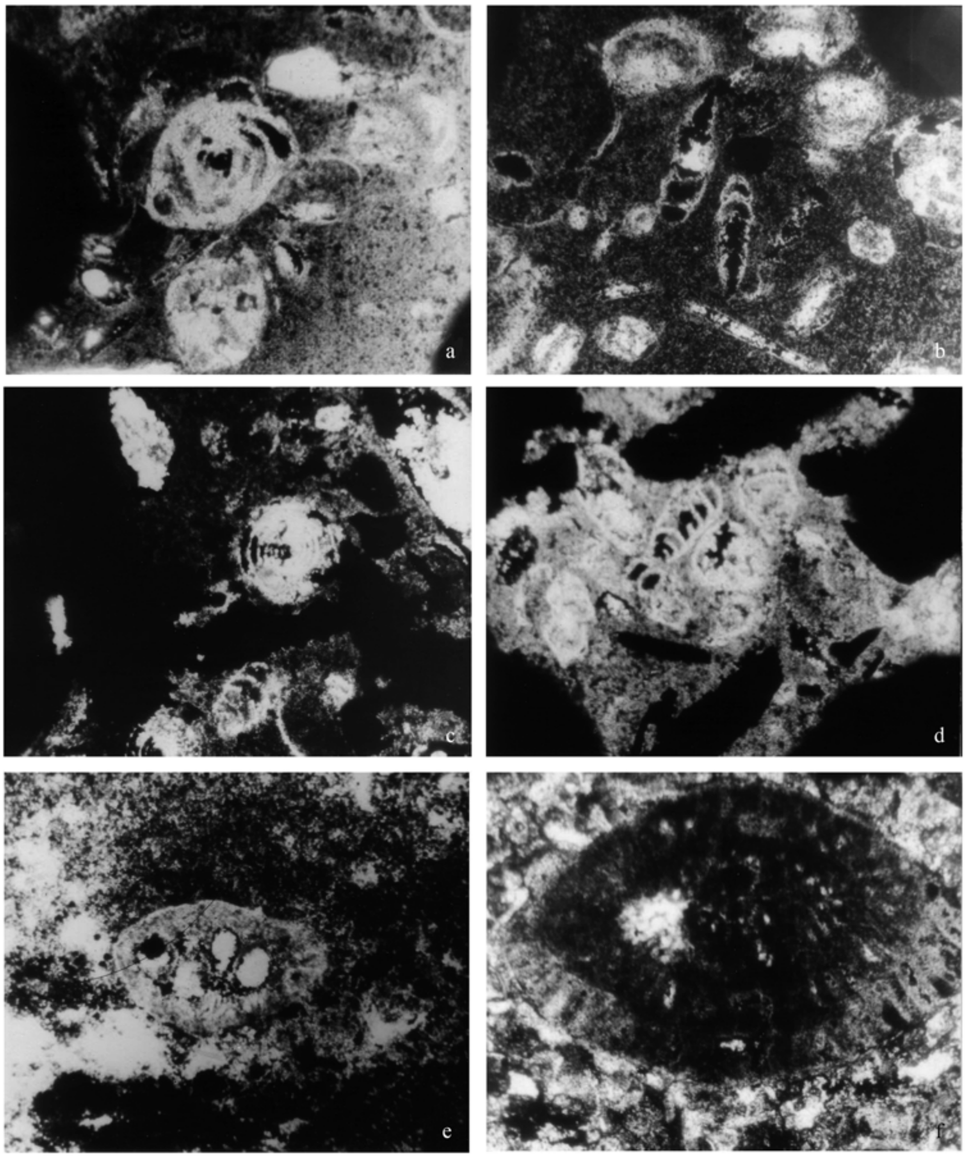

Figure 3 a, *Eotuberitina* sp. etc., enclosed by micro-fine-grained quartz, thin section, ×30; b, *Archaeodiscus* sp. etc., enclosed by micro-fine-grained quartz, thin section, ×30; c, *Multidiscup* sp.-concentrated zone, thin section, ×30; d, *Lingulina* sp.-concentrated zone, thin section, ×30; e, silicified (white) *Polypora* sp. etc., thin section, ×30; f, silicified (white) *Nanlingella* sp., thin section, ×30.

ties, called the volcanic-vent biocommunities, which do not rely on photosynthesis but on the food and energy provided by the hot-water system, including bacteria, algae, worms, bivalves, fish, etc. These creatures are very abundant near the seafloor hot springs and fumaroles and they are closely related to the formation of hydrothermo-sedimentary massive sulfide ore deposits[17]. All these data are beneficial to the study of the mechanism of bio-metallogenesis of Tl deposits in China.

2.3 Bio-fossil casts in Tl-rich ores

Bio-fossil casts are one of the indicators of biometallogenesis. In Tl-rich ores micro-paleo-animal fossils have been found completely replaced by Tl minerals as observed in the polished sections in which Tl contents reach 1%—10%, and their somatic outlines are still maintained either in mineral form or in mineral outline, i.e., bio-fossil casts. Paleo-bio-fossils responsible for bio-fossil casts have been substantially determined, which are dominated by foraminifers and zoaria, with the number of species reaching almost 20 (Table 4). The discovery of these bio-fossil casts is helpful for the explanation of bio-metallogenesis because bio-fossil casts are the Tl minerals, which were formed during the late

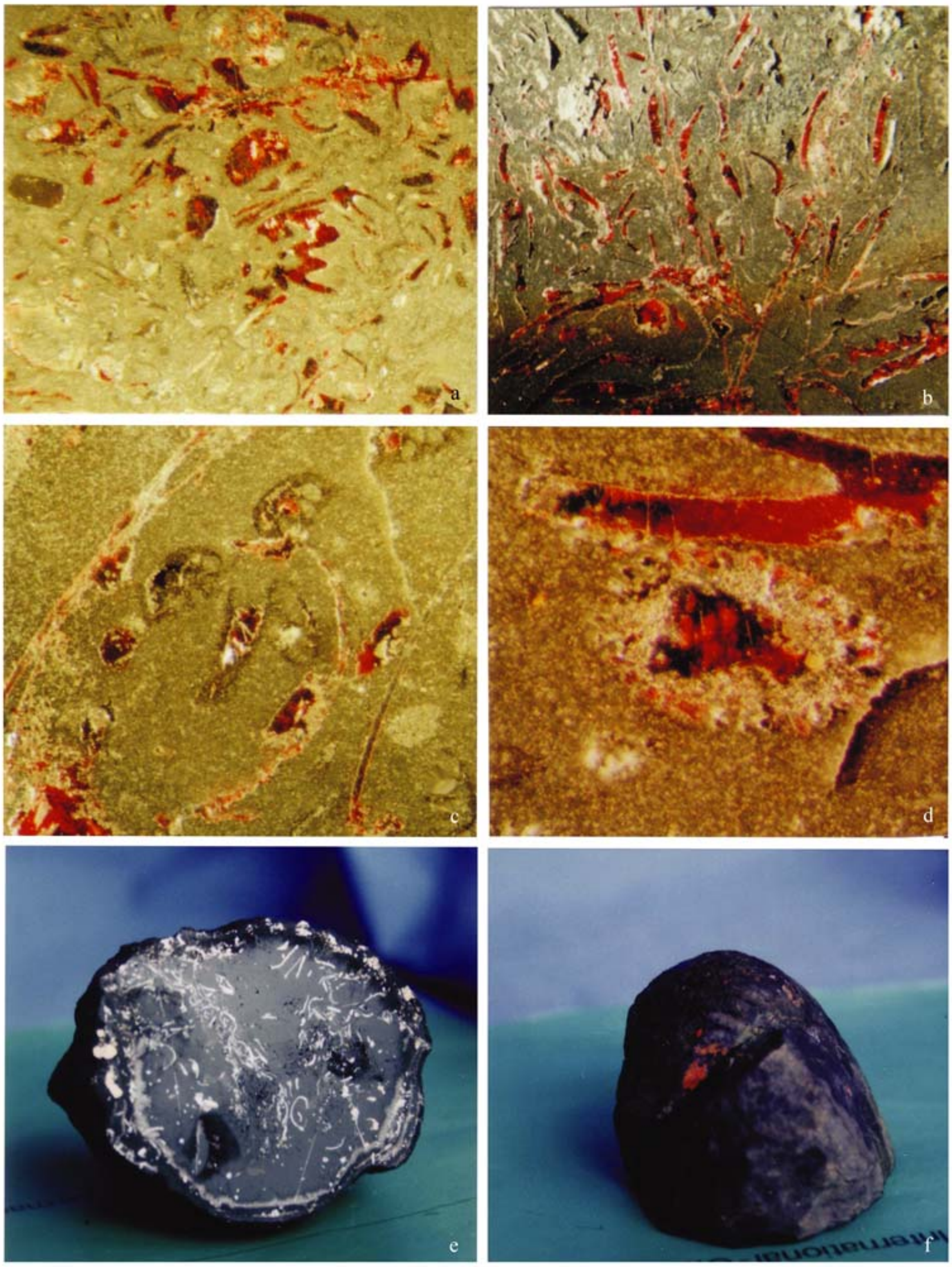

Figure 4 a, Bio-fossils are metasomatized into Tl mineral fossil casts (red), polished section, ×5; b, bio-fossils are metasomatized into Tl mineral fossil casts (red), polished section, ×5; c, Polypora in siliceous rocks replaced by lorandite (red), polished section, ×27; d, *Paleofusulina* in siliceous rocks replaced by lorandite (red), polished section, ×245; e, Tl mineral bio-fossil casts (white) in siliceous rock concretions (grey), polished section, original size; f, *Oldhamina* fossils replaced by lorandite (red), specimen, original size.

stage of Tl hydrothermal metallogenesis when Tl-bearing ore-forming hydrothermal solutions strongly metasomatized intravital organisms and/or their remains, making them maintaing the original fabrics. Either the process in which living organisms intake Tl to form Tl ores in the process of metabolism or the accumulation of bio-remains and bio-skeletons leads to Tl mineralization is designated to bio-metallogenetic series[18]. All this allows us to have further realized that the intensive reworking and metasomatism of early Tl deposits of bio-genesis by late Tl-bearing hydrothermal solutions obscured the overall picture of living organisms in early Tl ores so that it is hard to disclose the phenomenon of bio-metallogenesis. Therefore, research on ore deposits of this type has long been fettered by the theory of magma hydrothermal metallogenesis.

Table 3 Comparison of the contents of Tl in rocks and ores with those of micro-paleo-animal fossils ($\times10^{-6}$) a)

Tl deposit	Sample No.	Rock and ore	Tl contents in rocks and ores	Tl contents in fossils	Tl in fossils / Tl in ores
Nanhua (river and lake facies, sedimentation-reworking type)	N-1	silty dolomite	1.26	20	15.9
	N-2	silty dolomite	1.30	31	13.8
	N-3	laminated argillaceous dolomite	0.33	33	100
	N-4	laminated argillaceous dolomite	0.79	45	57
	N-5	laminated argillaceous dolomite	0.73	33	45.2
	N-6	purplish-red argillaceous sandstone	0.43	34	79.1
	N-7	Tl mineralized rock	90	300	3.3
	N-8	Tl mineralized rock	25	330	13.2
	N-9	Tl mineralized rock	74	410	5.54
Lanmuchang (marine facies, hydrothermally superimposed type)	L-225	argillaceous limestone	2	60	30
	L-422	argillaceous siltstone	1.3	34	26.2
	L-423	argillaceous limestone	5	40	8
	L-424	argillaceous siltstone	2	42	21
	L-425	Tl ore	126	470	3.7
	L-426	Tl ore	201	412	2.1
	L-36	Tl mineralized rock	65	340	5.2
	L-37	Tl mineralized rock	84	240	2.9
	L-38	banded mineralized rock	42	520	13.4
	L-39	banded mineralized rock	49	510	10.4
	L-40	Tl ore	214	550	2.6
	L-41	quartz	1	530	530
	L-42	quartz	0.91	500	549.5
	L-43	calcite	0.64	320	500
	L-44	calcite	1.35	570	422.2

a) Atomic Absorption Spectrometry, accuracy: 2%. Analytical unit: Analysis Center of the Institute of Geochemistry, Chinese Academy of Sciences.

Table 4 Micro-paleo-biofossil casts a)

Category	Species	Age
Foraminifer	*Archaeodiscus* sp.	C—P
	Neodiscus sp.	P
	Eotuberitina sp.	C.P
	Multidiscus semiconcavus Wang	P_2
	Geinitzina sp.	P-T_1
	Lingulina sp.	P_2—Present
	Pachyphloia sp.	P
	Nodosaria sp.	C—Present
	Multidiscus sp.	P_{1-2}
	Hemigordius sp.	P_2
	Palaeofusulina sp.	P_2
	Nanlingella sp.	P_2
Zoaria	*Polypora* sp.	P
	Fenestella sp.	P
	Bryozoans fragment	P_2
Sponge	*Amblysiphonelloids* fragment	P_2
Brachiopoda	*Oldhamina* sp.	P_2

a) Analytical unit: Nanjing Institute of Geology and Paleontology, Chinese Academy of Sciences.

2.4 Involvement of bio-sulfur in the sulfur isotopic composition of minerals

The remarkable indicator of the involvement of bio-sulfur in the sulfur isotopic composition of minerals is the light sulfur isotopic composition. It is a typical example that minerals from the Nanhua Tl deposit are enriched in light sulfur isotopes. Either primary minerals or secondary minerals are both enriched in light sulfur isotopes (Table 5). The δ^{34}S values of the Nanhua Tl deposit vary between –21.04‰ and –33.38‰ with an average value of –27.20‰. Ore minerals are also enriched in light sulfur isotopes, which is closely related to the involvement of bio-sulfur in metallogenesis.

The formation of Tl deposits underwent two stages, i.e., primary bio-sedimentation and epigenetic hydrothermal reworking. There are significant differences inS/Fe ratio for pyrite formed during these two stages. The S/Fe ratio (1.18) in biogenetic pyrite is greater than that (1.15) in pyrite of epigenetic hydrothermal rework-

Table 5 Sulfur isotopic composition of the Nanhua Tl deposit and S/Fe ratios in pyrite a)

No.	Mineral	$\delta^{34}S$ (‰)	Genesis of pyrite	
			Biological	Hydrothermal
840724	realgar	−23.05		
840725	realgar	−23.05	Fe 45.79%	Fe 46.6%
840726	realgar	−29.91		
840727	realgar	−23.31	S 53.98%	S 53.4%
840728	realgar	−23.22		
840729	realgar	−22.36	S:Fe=1.18	S:Fe=1.15
840730	realgar	−24.82		
840735	realgar	−23.05		
95061	realgar	−32.87		
95062	realgar	−32.77		
95063	realgar	−27.87		
95064	realgar	−24.78		
95065	realgar	−32.93		
95066	realgar	−34.57		
95067	realgar	−33.38		
95068	realgar	−26.80		
840738	gypsum	−21.04		
95069	gypsum	−31.33		
95070	gypsum	−22.17		
95090	epsomite	−31.64		
95091	epsomite	−26.25		
Average		−27.20		

a) SF_{60} method, mass spectrometric accuracy: ±0.2‰. Analysts: Feng Jiayi and Gen Longnian of the Open Laboratory of Ore Deposit Geochemistry, Institute of Geochemistry, Chinese Academy of Sciences.

ing origin. Similarly, the S/Tl ratio (0.33) in biogenetic lorandite (bio-genetic fossil cast) from the Lanmuchang Tl deposit is obviously greater than that (0.31) of lorandite of hydrothermal origin (Table 6). All this indicates the existence of organic sulfur, i.e., biogenetic sulfur, in both biogenetic pyrite and lorandite.

2.5 Enrichment of Tl ores in biogenetic organic components

Samples collected from the Nanhua Tl deposit (NH—8, NH—63, NH—66) and those from the Lanmuchang Tl deposit (95C—10A, 95C—2A, 95C—7B) were analyzed for organic components (Table 7). The analytical results showed that ores from both the Tl deposits are enriched in organic components. The contents of kerogen vary from 0.21% to 0.44%, and those of total hydrocarbons, 0.9—1.9 mg. As viewed from the fact that biogenetic ores from both the Tl deposits are abundant in micro-paleo-animal (fossils) and reworking-genetic ores have preserved micro-paleo-animal fossil casts and other bio-metallogenetic markers, it is indicated that organic components in the ores stemmed largely from micro-paleo-organisms, which belong to biogenetic organic matter.

3 Summary and discussion

3.1 Abundant material source and favorable bio-metallogenetic environment

China’s Tl deposits usually occur in the minerogenetic province of “low-temperature hydrothermal reworking deposits so called by Prof. Tu Guangchi. That is because in this province there exist ore-forming material sources for a variety of low-temperature ore species (e.g. Hg, Sb, Pb, Zn, Au, Ag, As,. Tl, Cd, Ge, etc.) and favorable ore-forming conditions, which made the metal thallium unusually enriched to form Tl ore deposits[20,21]. The formation of Tl deposits is not only related to their common ore-forming geological settings, but also to the special environment of Tl bio-metallogenesis due to the existence of a diversity of paleo-marine (terrestrial) bio-communities.

3.2 Unusual enrichment and sulphophility and arsenophility

Thallium metallogenesis is the inevitable result of unusual enrichment of Tl. In their study of Tl deposits the authors put forward on a trial basis that the unusual enrichment of Tl refers to the contents of Tl commonly reaching what ($n\times10^{-4}$) is required for Tl mineralization or being 100 times greater than its crustal abundance (0.75×10^{-6}). The unusual enrichment of Tl to form ores is not only controlled by a specific ore-forming environment, but also constrained by its sulphophile and arsenophile geochemical properties[22].

3.3 Two modes of intaking thallium in the process of bio-metallogenesis

Studies have shown that in the process of Tl metallogenesis living organisms intook Tl mainly through two modes. One is that living organisms intook Tl via metabolism and the other is that bio-remains extracted Tl. In the period of bio-sedimentation-metallogenesis of Tl, there existed abundant ore-forming elements and numerous living organisms, especially living micro-paleo-animals, in sea (lake) water, thus creating favorable conditions for Tl metallogenesis. But in the late hydrothermally superimposed ore-forming stage large amounts of ore-forming hydrothermal solutions adsorbed and absorbed Tl-bearing ore fluids via remains left behind by dead organisms, making the Tl ores formed during

Table 6 S/Tl ratios in lorandite of different origins

Deposit name	Lanmuchang Tl deposit in China		Alchar Sb-As deposit in Grace[19]	Carlin gold deposit in Nevada, the United States
Mineral genesis	Biogenesis (Zhang B G et al., 2000)(2)[a)]	Hydrothermal genesis (Chen D Y, 1989)(8)	Hydrothermal genesis (Zhang S F, 1957)	Hydrothermal genesis (Chen D Y, 1989) (5)
S	19.30	18.12	18.7	18.8
Tl	59.29	59.08	59.4	59.5
As	21.35	21.81	21.9	21.6
Total	99.94	99.01	100	99.9
S:Tl	0.33	0.31	0.31	0.31

a) In the parentheses are the numbers of samples.

Table 7 Separation of organic extracts and group components in the ores from the Lanmuchang and Nanhua Tl deposits[a)]

Sample No.	Ore type	C_{org} (%)	Amount of rock and ore used (g)	Chloroform bitumen (A) (mg)	Extraction rate (10^{-6})	Group component: Saturated hydrocarbon	Group component: Aromatic hydrocarbon	Group component: Non-hydrocarbon	Group component: Bitumen	Total hydro-carbon (mg)	Non-hydrocarbon + bitumen (mg)	Non-hydrocarbon + bitumen / Total hydrocarbon	Amount of sulfur dissolved in organic ex-tract liquid (g)	Amount of natu-ral mercury for desulfurization (mL)
NH-8	Tl ore	0.25	162.734	4.2	25.809	1.10	0.50	1.87	0.73	1.60	2.60	1.63	0.23	3
NH-63	Tl ore	0.21	153.627	6.8	44.263	1.10	0.80	3.70	1.20	1.90	4.90	2.58	0.20	3.5
NH-66	Tl ore (semi-weathered)	0.31	171.718	6.0	34.941	0.90	0.20	2.30	2.60	1.10	4.90	4.45	0.33	2.5
95C-10A	Tl ore	0.22	163.831	3.1	18.922	0.80	0.10	0.96	1.24	0.90	2.20	2.44	0.25	2.0
95C-2A	Tl ore	0.44	186.540	3.3	17.691	1.0	0.20	0.80	1.30	1.20	2.10	1.75	0.41	3.0
95C-7B	Tl ore	0.23	143.345	2.5	17.440	0.80	0.30	0.60	0.80	1.10	1.40	1.27	0.25	2.5

a) Kerogen preparation- chemical separation method, organic extraction -sorbitic extraction method, group component separation column chromatography. The measuring accuracy of organic element automatic analyzer: C 0.3% , H 0.5% and N 0.5%. Analytical unit: The State Key Laboratory of Organic Geochemistry, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences.

bio-sedimentation-metallogenesis become higher in grade.

3.4 Two-stage model for Tl bio-metallogenesis

According to the model of Tl metallogenesis based on the mode of intaking Tl by living organisms and hydrothermally metallogenetic characteristics, two metallogenetic stages can be roughly distinguished, i.e., the bio-enrichment metallogenesis stage and the hydrothermal superimposation stage, both of which are closely related to bio-metallogenesis. In the former stage living organisms and their remains intook sufficient amounts of Tl, leading to the unusual enrichment of Tl to form Tl ores; in the latter stage, on the basis of bio-enrichment of Tl, the metasomatism of late ore-forming hydrothermal solutions made thallium further enriched and superimposed to form Tl ores. Obviously, the Tl deposits are significantly different genetically from the magma hydrothermal deposits, the former experienced two ore-forming stages, i.e., early bio-enrichment-metallogenesis and late hydrothermal reworking-metallogenesis. Due to relatively intense late hydrothermal reworking-metallogenesis, the early bio-metallogenetic characteristics have been completely obscured and almost no sing of bio-enrichment-metallogenesis can be seen. Therefore, in the long past many geological workers have mis-regarded bio-genetic Tl deposits as those of hydrothermal origin[23,24].

3.5 Bio-genesis of Tl deposits and ore prospecting

A series of bio-metallogenetic phenomena have been found in the geological and geochemical studies of Tl deposits, for instance, micro-paleo-animals (fossils) absorbed and enriched the element Tl to form ores in the process of metabolism, bio-remains were accumulated to form ores, bio-fossil casts are preserved in Tl ores, and bio-genetic sulfur and organic matter were discovered in Tl ores. All these phenomena provide direct and indirect evidence suggesting that Tl metallogenesis is closely related to living organisms. Precisely, in search of Tl ores importance should be attached to routine geological prospecting theories and methods, but also to the bio-geochemical principles and ore prospecting indicators.

1 Tu G C, Zhang B G. The characteristics of Southwest China's minerogenetic province of low-temperature hydrothermally reworked ore deposits. In: Institute of Geochemistry, Chinese Academy of Sciences, Developments in Geochemistry ——A Contribution to 30th International Geological Congress. Guiyang: Guizhou Science and Technology Press, 1996. 133－139

2 Ye L J. Mineralogenesis of Biological Organic Matter (in Chinese). Beijing: Oceanic Press, 1996. 227－230

3 Fu J M, Qin K Z. Geochemistry of Kerogens (in Chinese). Guangzhou: Guangdong Science and Technology Press, 1995. 1－637

4 Fornari D J, Embley R W. In: Humphris S E, Zierenberg R A, Mullineaux L S, et al. eds. Seafloor Hydrothermal Systems: Physical, Chemical, Biological, and Geological Interactions. Washington D C: American Geophysical Union, 1995. 1－46

5 Volf K H. Strata-bound and Stratiform Deposits (Vol. 7) (in Chinese). Beijing: Geological Publishing House, 1981. 1－63

6 Zhu S Q, Huang H S. Geology of Strata-bound Deposits (in Chinese). Beijing: Metallurgical Industry Press, 1988. 22－37

7 Lin L. Simulating experiment on enrichment of gold by bacteria and algae in the process of minerogenesis. Geochimia (in Chinese), 1998, 27(6): 559－565

8 Wu Y Y. Bio-fabrics of metallic minerals and bio-chemical processes. Geology-Geochemistry (in Chinese), 1997, (1): 95－96

9 Hu M A. Minerogenesis in relation to bacteiral activities as exemplified by two Pb-Zn deposits in Europe. Mineral Deposits (in Chinese), 1997, 16(1): 61－69

10 Powell T G, Macpeen R W. Precipitation of sulfide ore and organic matter: Sulfate reaction at Pine Point. Can Sci Reprint Series, 1984, 224(6): 63－66

11 Volf K H. Handbook of Strata-bound and Stratiform Ore Deposits (Vol. 9). Amsterdam: Elsevier Scientific Publishing Company, 1981, 417－488

12 Chen D Y. The first discovery of Tl-rich orebodies in China's Hg-Tl coexisting ore deposits and a preliminary study on their genesis. Bulletin of Guizhou Institute of Technology (in Chinese), 1989, 18(2): 1－19

13 Zhang Z, Zhang X M, Zhang B G. Geochemistry and metallogenetic model of the Nanhua Sn-Tl deposit. Geochimia (in Chinese), 1998, 27(3): 269－275

14 Trudinger P A, Bubela B. Microorganism and the natural environment. Miner Deposits, 1967, 2:147－157

15 Tu G C. Low-temperature Geochemistry (in Chinese). Beijing: Science Press, 1996. 8－15

16 Zhu S. Mineral Deposits in China (Vol. 2), Metallic Ore Resources (in Chinese). Beijing: Science Press, 1999. 631－635

17 Juniper S K, Fouquet Y. Filamentous iron-silica deposits from modern and ancient hydrothermal sites. Con Mineral, 1988, 26: 859－869

18 Open Laboratory of Ore Deposit Geochemistry. Ore Deposit Geochemistry (chap.13), Biological and Organic Mineralogenesis (in Chinese). Beijing: Geological Publishing House, 1997. 314－338

19 Zhang S F. Mineralogy (in Chinese). Shanghai: Shangwu Publishing House, 1957. 316

20 Tu G C. A preliminary discussion on the composition, geological background and some unique characteristics of unusual large-sized ore deposits－A preliminary discussion on unusual super-large ore deposits. Sci China Ser D-Earth Sci (in Chinese), 1998, 28(sup.): 1－6

21 Tu G C, Gao Z M, Hu R Z, et al. Geochemistry of Dispersed Elements and Their Metallogenetic Mechanisms (in Chinese). Beijing: Geological Publishing House, 2003. 1－68

22 Zhang B G, Hu J, Wang S X. Geochemistry and bio-metallogenesis of Tl (Tl-bearing) deposits in the low-temperature minerogenetic province of southwestern China. Bull Mineral Petrol Geochemi (in Chinese), 2000, 19(4): 341－342

23 Zhang Z, Chen G L, Zhang B G, et al. The Lanmuchang Tl deposit and its environmental geochemistry. Sci China Ser D-Earth Sci, 2000, 43(1): 50－62

24 Zhang Z, Zhang B G, Tang C J, et al. The main geochemical biological metallogenic and reworking independent Tl deposits. Chin J Geochem, 2000, 20(1): 45－51