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Occurrence characteristics and enrichment regularity of indium in pyrite: A case study of Dachang tin ore-field

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Abstract: To reveal the occurrence state and enrichment regularity of the dispersed element indium in pyrite, the petrology, mineralogy, geochemistry, and mineral physics were researched detailedly. The results suggest that the structure of pyrite is mainly composed of massive structure, disseminated structure, vein structure, reticular structure, comb structure and so on. Generally, the pyrite coexists with sphalerite, marmatite, pyrrhotite, chalcopyrite, galena, and arsenopyrite. And the texture of pyrite primarily consists of the metasomatic texture, solid solution texture, idiomorphic−hypidiomorphic granular texture, and disseminated texture. The content of indium in pyrite ranges from 0.491×10^{-6} to 65.1×10^{-6} with an average value of 14.38×10^{-6}. Yet, the indium content in the Gaofeng deposit is higher than that in the Dafulou and Tongkeng deposit, showing a particularly significant supernormal enrichment. Besides, the cadmium content in pyrite is also higher than other dispersed elements, and similarly the abnormal enrichment of cadmium in the Gaofeng deposit is also very significant. An obvious positive correlation exists between In and Cd, or Tl, but a negative correlation between In and Re. It is difficult to find out a positive or negative correlation between In and Ga. The element zinc is of great importance to the enrichment of indium, which can possibly facilitate to the migration and crystallization of dispersed element indium.

Key words: dispersed element indium; pyrite; lattice structure; enrichment regularity; cassiterite-sulfide deposit; Dachang ore-field

1 Introduction

Generally, the dispersed elements mainly consist of eight elements like cadmium (Cd), gallium (Ga), indium (In), germanium (Ge), selenium (Se), tellurium (Te), rhenium (Re) and thallium (Tl) [1−3], and these elements are always characterized by the low content, extremely rare independent mineral, great difficulty to significant enrichment, belonging to urgent needed and dire lacked resources [4,5].

Dispersed element indium (In) is a rare metal element, and also a kind of strategic metal, whose content in the earth’s crust is very low and often scattered in geological body [6]. Indium has very unique physical and chemical properties [7], such as low melting point, high boiling point and good conductivity. Therefore, indium is widely used in high-tech fields like electronic computer, energy, electronics, photoelectricity, national defense military, aerospace, nuclear industry and the modern information industry, which has become increasingly important in the national economy, and is also one of the most important support materials in modern electronic industry [8].

Research on indium element began in the 1950s, mainly focused on geochemical characteristics, occurrence state, and thermal dynamics of indium element. According to the existing data, the indium

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enrichment shows the obvious specificity of the ore deposit type and mineral type [9], and the indium has obvious trend of enrichment in the zinc-rich and tin-rich deposit. In China, the indium-rich deposits are mainly the cassiterite sulfide deposit and tin-rich Pb−Zn deposit [10,11]. However, LIU and CAO [12] pointed out that the sphalerite is the best mineral for indium enrichment, yet entering sphalerite lattice for indium only under certain conditions. ZHANG et al [13] found out that the indium doesn't enrich in different types of lead, zinc, copper, iron, manganese and other mineral deposits, but it showed supernormal enrichment characteristic in the cassiterite sulfide deposit and tin-rich lead−zinc polymetallic deposit, and was mainly enriched in sphalerite. ZHANG et al [14] also found out that the industrial indium-rich deposit is primarily of tin-rich sulfide deposit, so the finding is synchronous for both of them.

So far, the study of indium resources is mainly concentrated in the economic significance and application value [15], etc. However, its geological characteristics, genesis and background are seldom researched, and the existing research work is mainly focused on its mineralogy [16], but the researchers are less. Furthermore, the relevant literature information, which is related to geological characteristics and genesis of indium, is also very limited. So, for the purpose of finding new indium resources, much more effort should be spared on scientific research, such as coming up with the favor geological conditions for indium, and establishing indium metallogenic pattern and prospecting model [17], so as to guide the prospecting practice. Therefore, in order to further develop the indium deposit geological theory, it's very urgent to establish a scientific metallogenic model of indium to guide the ore-prospecting. Through long-term research, TU et al [18] found out that, under certain geological and geochemical conditions, not only enrichment but also supernormal enrichment of dispersed element can occur and it is also possible to mineralize independently, the dispersed elements independent deposit can be enriched by the form of independent mineral, but more complex geological process is needed, indicating quite a demanding metallogenic condition. In China, a series of disperse elements independent ore deposits have been found, such as Dashuigou tellurium deposit in Sichuan, Yutangba selenium deposit in Hubei, Lincang germanium deposit in Yunnan, Lanmuchang thallium deposit in Guizhou, La'erma independent selenium deposit, Nanhua independent thallium deposit, Dulong cadmium deposit, Muchuan independent rhenium deposit, Niujiaotang zinc−cadmium deposit in Guizhou and Xiangquan independent thallium deposit in Anhui. There are also some reports about independent dispersed element deposits in other countries [19,20], such as Apex Ga−Ge deposit in the US, Pekka Haka Se deposit in Bolivia, Tsumeb Ge deposit in Namibia. However, the independent indium deposit or predominantly indium-rich deposit has not been found.

China has the world's largest indium geological reserve, and is also currently the largest native indium producer and exporter, but the distribution of proven indium resources is not uniform, mainly in south China folded belt and ancient Asia folded belt, including Guangxi, Yunnan, Inner Mongolia, Guangdong, Qinghai, Hunan, Jiangxi, Guizhou and Sichuan provinces, among which the provinces of Guangxi, Yunnan, Inner Mongolia and Guangdong have approximately 80% of the total indium reserves [3,18]. The reserve of Dachang ore field in Guangxi has already exceeded 5000 t (Fig. 1), ranking the first place in the world. The ore-field is an important tin-polymetallic base in China, with a number of world-class large and super-large cassiterite sulfide deposits [21], and also are characterized by high degree of research, abundant basis data, typical deposit features [22], and indium supernormal enrichment, the mineralization information of core and tunnel is fresh and colorful, being the best natural laboratory for researching on indium-rich deposit.

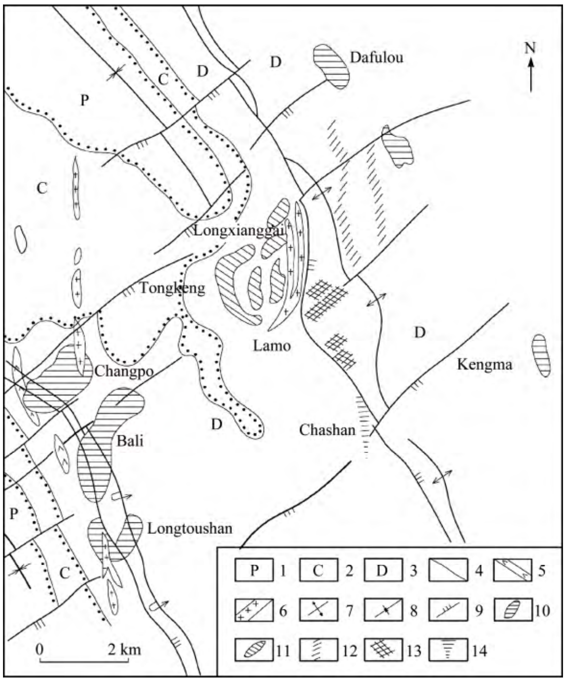

Fig. 1 Mineralization zones of Dachang ore field (compiled from China Nonferrous Metals Industry Corporation, 1987) (1 — Permian limestone and siliceous; 2 — Carboniferous limestone; 3 — Devonian limestone, shale and siliceous; 4 — Parallel unconformity stratigraphic contact; 5 — Diorite porphyrite; 6 — Granite and granite porphyry; 7 — Anticline axis; 8 — Syncline axis; 9 — Faults; 10 — Tin ore; 11 — Zn−Cu ore; 12 — Scheelite veins; 13 — Wolframite veins; 14 — Antimony veins)

However, it is extremely urgent to find a new breakthrough point, deepen the understanding of indium supernormal enrichment, and provide a scientific basis for the new breakthrough in prospecting of indium-rich deposit. The industrial mineral in the Dachang ore-field mainly consists of cassiterite, marmatite, pyrite, pyrrhotite, arsenopyrite, jamesonite, etc [23]. Hidding abundant geological information in pyrite, the detailed genetic mineralogy study contributes to extract of ore-forming process information, which is of great significance to reveal the genesis and guide ore prospecting. So, this paper took cassiterite sulfide ore deposit in Dachang ore field as an example, systematically studied the occurrence, distribution and enrichment of dispersed element indium in pyrite, and discussed the enrichment mechanism and key restrictive factors, just aiming to provide new data and evidence for the research on indium-rich deposit, and further enrich and develop the metallogenic theory of dispersed element indium.

2 Samples and analytical methods

Pyrite is one of the dominating mineral in the Dachang ore-field, which is only secondary to cassiterite and sphalerite in general. To ensure the scientific research work, the samples were collected from the latest underground tunnel from the Tongkeng and Gaofeng ore deposit, where the samples were fresh and not be weathering. Based on the detailed field geological observations and intensive microscopic identification, the results show that the structure of pyrite is mainly massive structure (Fig. 2(a)), disseminated structure (Fig. 2(b)), vein structure, reticular structure, comb structure and so on, usually associating with sphalerite, marmatite, pyrrhotite, chalcopyrite, galena, arsenopyrite, etc, and the texture of pyrite mainly consists of metasomatic texture (Fig. 3(a)), solid solution texture, idiomorphic−hypidiomorphic granular texture, disseminated texture (Fig. 3(b)), etc, such as the replacement of pyrite by arsenopyrite, and pyrrhotite.

Usually, the mineral crystal shape of pyrite was well developed with different and varying sizes (Fig. 2(a)), perhaps indicating a kind of extensional metallogenic environment, and the paragenetic assemblage of pyrite−sphalerite−pyrrhotite is the most common in this ore-field.

In this study, ten samples, which were collected from the Tongkeng (7 samples), Gaofeng (2 samples), and Dafulou (1 sample), were analyzed by inductively coupled plasma mass spectrometry (ICP−MS) and X-ray diffraction (XRD). The ICP−MS analysis is to detect the content of indium and other element in the single pyrite in less than 200 meshes powder form in CNNC Beijing

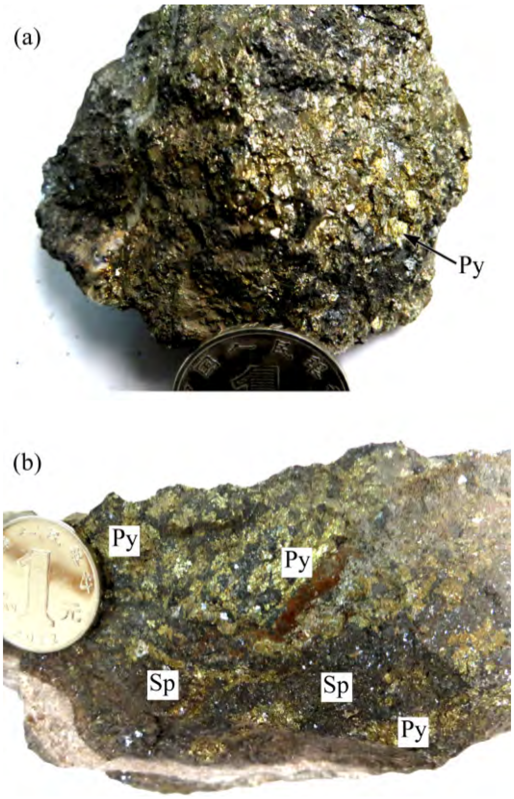

Fig. 2 Structure of pyrite in Dachang tin-polymetallic ore-field, Guangxi, China: (a) Massive structure of pyrite; (b) Disseminated structure of pyrite

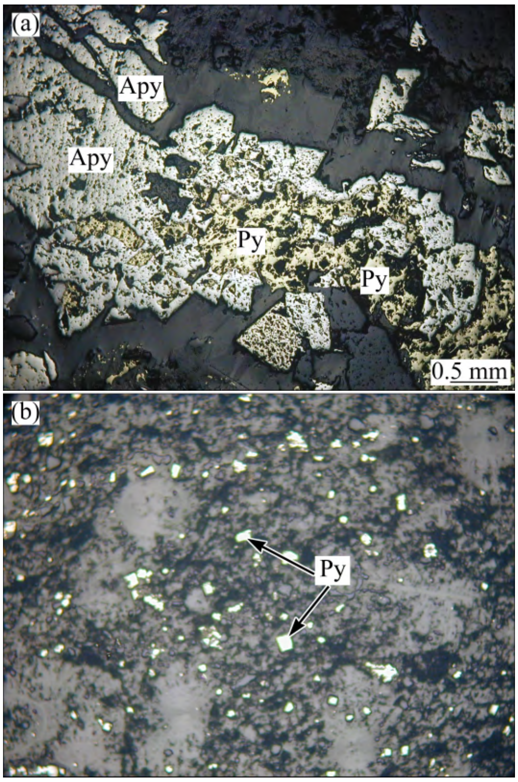

Fig. 3 Microstructure feature of pyrite in Dachang tin-polymetallic ore-field, Guangxi, China: (a) Replacement of pyrite by arsenopyrite; (b) Disseminated texture of pyrite

Research Institute of Uranium Geology, China, and the powder XRD analysis is just to measure and calculate the cell parameters and establish the crystal texture of pyrite in School of Materials Science and Engineering, Central South University, China, by D/Max 2500 type instrument, which adopts the copper target under the operating condition of 40 kV voltage and 250 mA current.

3 Results

3.1 ICP−MS analysis of trace elements

As shown in Table 1, the content of indium in pyrite ranges from 0.491×10^{-6} to 65.1×10^{-6}, with an average value of 14.38×10^{-6}, among which three values are larger than this average value.

And, according to the sources of samples, the content of indium from the Dafulou and Tongkeng ore deposit is lower than that from the Gaofeng ore deposit (Fig. 4), whose average value is 50.5×10^{-6}. So, in the Gaofeng ore deposit, the supernormal enrichment of indium in pyrite is particularly significant that is coincident to the predecessor research results. In addition to the indium, the content of cadmium in pyrite is also higher than other dispersed elements, such as Ga, Re, Tl. It is from 0.354×10^{-6} to 63.5×10^{-6} with an average value of 20.7×10^{-6}. Obviously, with a certain similarity, the value of cadmium content from the Gaofeng ore deposit is higher than that from the other two deposits, showing the prominent supernormal enrichment of cadmium to some degree (Fig. 5). That is to say, in the Dachang ore-field, the dispersed elements indium and cadmium show the synchronous supernormal enrichment, which maybe indicate the potential relationship between them in the process of mineralization, including reactivation, migration, preferential occupation, enrichment and so on. Generally, the contents of Ga, Re, Tl are lower than those of indium and casmium, among which the contents of Ga and Tl range from 0.197×10^{-6} to 1.87×10^{-6}, from 0.071×10^{-6} to 1.09×10^{-6}, respectively. Yet, most of the Re content is lower than 0.002×10^{-6}. And, the main ore-forming elements, Zn, Cu, Pb, Sb, W and Mo, are listed in Table 1. Obviously, the contents of Zn, Pb and Sb are higher than those of other elements (Fig. 6), ranging from 41.4×10^{-6} to 4037×10^{-6}, from 24.5×10^{-6} to 43967×10^{-6}, from 32.9×10^{-6} to 11095×10^{-6}, respectively. Especially, the content of lead in pyrite is the highest in the main ore-forming elements. The ratio of $w(\mathrm{Ga})/w(\mathrm{In})$ ranges from 0.01 to 1.39, with an average value of 0.29, which is regarded as one of the important discriminating standards to the genesis of sphalerite.

3.2 XRD analysis of lattice structure

The results of XRD analysis are listed in Table 2. It is easy to find out that the lattice parameter ranges within a small scope.

The values of parameters a, b and c are from 5.41684 to 5.43559 Å, from 5.41787 to 5.43171 Å, from 5.41585 to 5.45322 Å, respectively, and the average values of a, b and c are 5.42373, 5.42491, and 5.42371 Å, respectively. From the results, most of these values are larger than the standard value of pyrite (5.4170 Å), indicating possibly the potential influence of trace elements on lattice of minerals, which is usually caused by the isomorphism of the trace elements and dispersed elements, especially the content of cobalt, nickel and their ratio of $w(\mathrm{Co})/w(\mathrm{Ni})$. Undoubtedly, the isomorphism or enrichment of other elements in pyrite can also have a direct effect on the cell parameters even including the lattice−gold. The diffraction pattern of the samples is shown in Fig. 7.

Table 1 Trace element contents of pyrite in Dachang tin ore-field, Guangxi, China

Sample	Content/10^{-6}											$w(\mathrm{Ga})/w(\mathrm{In})$
	In	Cd	Ga	Re	Tl	Zn	Cu	Pb	Sb	W	Mo	
DFP-1	0.491	0.354	0.274	0.029	0.072	41.4	69.9	24.5	1239	0.666	1.84	0.56
TKP-3-2	0.674	2.54	0.197	<0.002	0.093	385	189	5205	32.9	0.177	2.89	0.29
TKP-4-2	2.15	10.7	0.314	<0.002	0.071	1775	77.4	272	108	0.18	3.57	0.15
TKJ-3-2	1.18	5.92	0.251	<0.002	0.085	933	77.8	585	318	0.177	1.78	0.21
TKW-8-2	4.66	24.2	0.804	<0.002	0.18	3828	118	10725	2139	0.327	1.18	0.17
TKW-9	1.35	24.1	1.87	0.005	1.09	4037	129	43967	7857	0.114	13.7	1.39
TKF-6-2	28.8	34.4	0.413	<0.002	0.389	3629	1504	1755	675	0.189	4.31	0.01
TKG-2-2	3.54	10.2	0.287	<0.002	0.199	1283	496	1506	1539	3.7	2.54	0.08
GFM-3-2	65.1	63.5	0.711	0.003	0.404	6731	71.4	14630	9996	0.16	1.39	0.01
GFM-4-2	35.9	31.1	0.555	0.003	1.07	2490	51.8	16158	11095	0.125	1.14	0.02

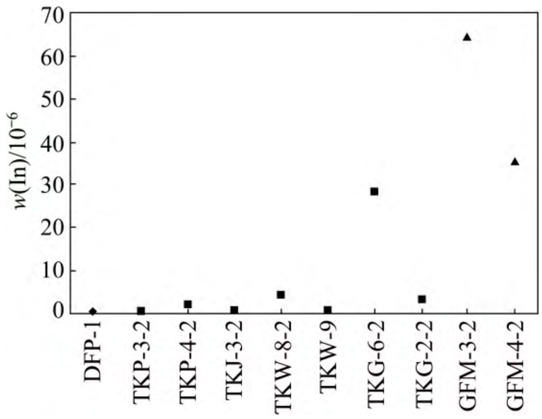

Fig. 4 Content of indium in different ore deposits from Dachang ore-field, Guangxi, south China

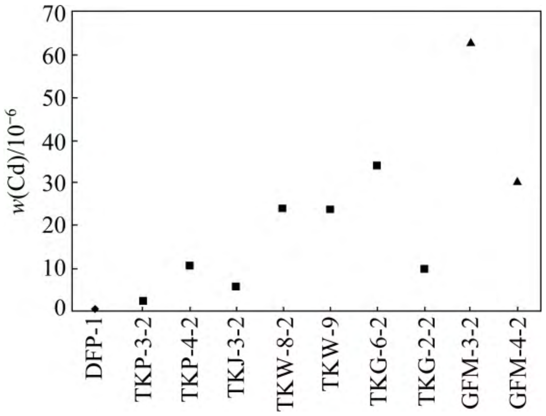

Fig. 5 Content of cadmium in different ore deposits from Dachang ore-field, Guangxi, south China

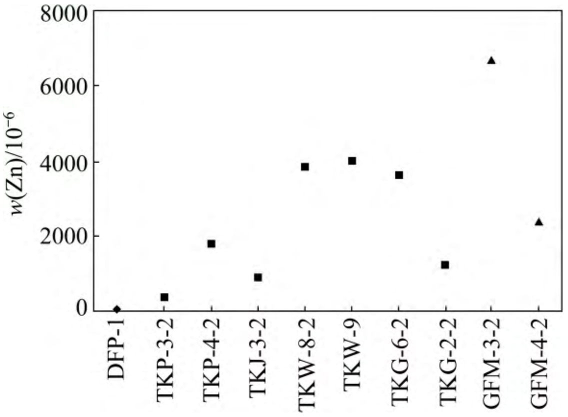

Fig. 6 Content of zinc in different ore deposits from Dachang ore-field, Guangxi, south China

Table 2 Lattice parameters of pyrite from Dachang tin ore-field, Guangxi, China

Sample	a/Å	b/Å	c/Å	α/(°)	β/(°)	γ/(°)
DFP-1	5.43559	5.43134	5.45322	89.779	90.165	90.078
TKP-3-2	5.42056	5.42011	5.42197	89.943	89.841	90.016
TKP-4-2	5.4199	5.42732	5.41939	90.055	90.022	89.886
TKJ-3-2	5.41684	5.42687	5.42013	89.925	90.02	90.029
TKW-8-2	5.42418	5.42542	5.41826	89.916	89.989	90.119
TKW-9	5.42132	5.43171	5.42204	89.968	90.014	90.083
TKF-6-2	5.42303	5.41842	5.42067	89.993	89.867	89.934
TKG-2-2	5.42366	5.42472	5.42262	89.818	89.986	89.915
GFM-3-2	5.42546	5.41787	5.41585	90.168	89.906	89.933
GFM-4-2	5.42682	5.4253	5.42291	89.98	89.912	89.844

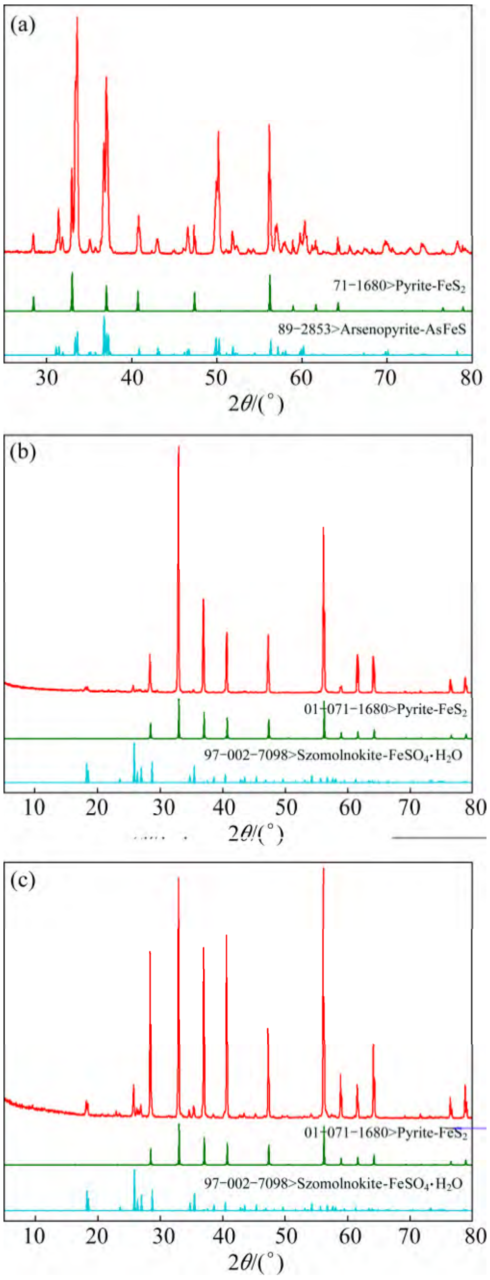

Fig. 7 XRD analysis of pyrite from Dachang tin-polymetallic ore-field, Guangxi, China: (a) Sample DFP-1; (b) Sample TKP-3-2; (c) Sample TKP-4-2

4 Discussion

4.1 Occurrence characteristics of indium

For a long time, the dispersed elements are considered as the associated components of mineral deposit, and the previous related study was mainly focused on the content, occurrence, enrichment regularity and comprehensive recovery, yet without receiving the attention it deserves. Yet, the indium enrichment shows the mineral type specificity, and a large amount of indium enriches in sphalerite in the form of ion substitution.

The electronic configuration of indium is $4d^{18}5s^{2}5p^{1}$, which tends to form trivalent cations. With 18 electrons in the outer shell of indium ion, it is usually classified as chalcophile element or chalcophile element, showing the ionic state of +1 and +3, but the latter is easy to form the more stable complexes. In nature, indium has two isotopes of ^{113}In and ^{115}In, whose relative abundance is 4.33% and 95.67%, respectively. But ^{115}In shows the radioactivity with a half-life of 5×10^{14} years and emits beta radiation to become a stable product of ^{115}Sn. Usually, the ionic radius of a stable In^{3+} is 0.81 Å, which is close to that of Sn^{4+} (0.71 Å), Zn^{2+} (0.74 Å), Fe^{2+} (0.72 Å), Cu^{2+} (0.72 Å), and Sb^{2+} (0.76 Å), but there is great difference with Pb^{2+} (1.24 Å).

As one of the dispersed elements, the independent mineral of indium is fairly rare, let alone the independent ore deposit, and the indium is usually hosted in the other metal deposits in the form of disperse element. The occurrence states of indium mainly consist of isomorphism, independent mineral, and adsorbing on other mineral surface. The previous researches show that in the process of mineralization the indium always enters the indium-rich mineral crystal lattice in the form of ion substitution, rarely a large number of indium independent minerals, and also less adsorption form. LIU et al [12] found out that there is close relationship between indium and tin, zinc, and indium is most accessible to enter tetrahedron coordination lattice sulfide minerals, such as sphalerite, stannite, and tetrahedrite. And, the recent research suggests that the entering mineral sequence of indium is roughly sphalerite, cassiterite, chalcopyrite, pyrite, stibnite, and galena. GU et al [24] pointed out that the dispersed element generally scattered in the other rock-forming and ore-forming minerals in the form of isomorphism or mechanical mixing, and experienced quite a special geochemical mechanism in some special geological conditions to tend to aggregate and form the ore deposit with a great potential economic value. LI et al [25] found out that the most probable occurrence state of indium is isomorphism in the Dachang ore-field of Guangxi, mainly hosted in sphalerite, followed by jamesonite and chalcopyrite.

The ionic radius of In^{2+} (0.92 Å) is close to that of Fe^{2+} (0.83 Å), which leads to the entering of indium to pyrite and partly replaces Fe^{2+}. And, the indium content of mineral without Fe^{3+} is lower than that contains Fe^{3+}, but there is great ionic radius correlation between In^{3+} and Fe^{3+}. It is generally believed that in the granite the indium content falls with the decline of iron, which leads to a relative steady of $w(\mathrm{Fe})/w(\mathrm{In})$ ratio without anything to do with the content of indium. So, the low content of iron in the granite is necessary to result in the low indium content to keep their stable ratio. Despite of the multiple factors to promote dispersed element enrichment, complexity of ore-forming process, and difference of different elements, it is the similar geochemical properties and behaviors that lead to the existence of dispersed element in the main form of isomorphism, and the property of some elements is analogous to indium, such as Sn, Cd, Ga, Tl, and Fe, Zn, Cu, Pb [26]. And, LIU et al [12] also found that there is also very close relationship between indium and Fe^{3+} in the rock forming minerals. According to indium content analysis result of some rock forming minerals, the order from high to low is hornblende (4×10^{-6}−8×10^{-6}), pyroxene (2×10^{-6}−5×10^{-6}), biotite (1×10^{-6}−2×10^{-6}), and feldspar−muscovite ($<1\times10^{-6}$).

4.2 Enrichment pattern of indium

The previous research suggested that the enrichment of indium is not high in different types of Pb−Zn deposits, and there also isn't the indium enrichment in the different types of copper ore deposit, let alone the indium-rich iron deposit. Generally speaking, the iron ore deposit is not a perfect place for indium enrichment.

On the basis of discovered indium-rich ore deposit, the cassiterite−sulphide deposit and tin-rich Pb−Zn deposit are the most indium-rich, such as Guangxi Dachang, Yunnan Gejiu and Dulong, Hunan Qibaoshan, and Inner Mongolia Meng'entaolegai, among which the most obvious difference between Meng'entaolegai and other Pb−Zn deposit is that the former contains more than 2000 t comprehensive recovery tin, and it locates at the high value area of indium geochemical background, very likely to be a large mineralization concentrated region of indium-rich deposit. In the different type of ore deposits, indium and tin have the relationship of synchronous growth, and indium-rich deposits are also rich in tin at different levels. And, LUO et al [27] pointed out that it exists a positive correlation relationship between indium and tin, and both of them simultaneously experienced activation, migration, and precipitation, in the weak alkaline metallogenic environment indium tends to enrich, yet in the hydrothermal system tin facilitated indium to enter and migrated together. Under the condition of oxidation, indium seems to show siderophile affinity and enriched in the limonite, indicating similar chemical and geochemical features, and the oxidizing condition is one of the key factors to the enrichment of indium in Dachang ore-field.

Currently, it is generally recognized by the academic circles that tin may play an important role in indium enrichment but not fully known [28]. In the vast majority of indium-rich deposits, indium doesn't enter cassiterite largely. Indium-rich deposit is also tin-rich depsoit, yet in the pure Pb−Zn ore deposit the indium content is rather low in sphalerite. And, the main enrichment regularity is that a plenty of indium enriches in the sphalerite but little in other minerals, which is called the mineral specificity. So, in the tin-containing sulfide deposits, only when the occurrence of sphalerite largely, an extensive enrichment of indium will only be possible.

The Meng'entaolegai ore deposit in the north China region, locating in the central of granite batholith and restricted by the fracture, is one of the few indium-rich deposits. ZHANG et al [29] found out that in Meng'entaolegai ore deposit the indium content of ore is 46−340 g/t, and indium and gallium are simultaneously enriched in the sphalerite, among which the indium content in black sphalerite is generally 500−1500 g/t, to a maximum of 2100 g/t. And, ZHANG et al [13] also thought that, due to the similarity of geochemical property of both indium and tin, indium is likely to enter into the hydrothermal system only when indium exists, but in the process of precipitation indium and tin go their separate ways, among which the former largely enters the tetrahedron sphalerite. However, LI et al [25] found out that in different areas there is a difference in the ways of the indium-rich ore deposit types and mineral combination, yet as for the different genetic deposits there is no clear relationship between the indium grade and tonnage.

The indium source is often discussed but with great differences, which even can determine indium enrichment pattern and scale to some extent. Despite all this, the relevant geological and geochemical researches were conducted thoroughly and continually to reveal the fundamental problem to dispersed elements supernormal enrichment. LI et al [25] pointed out that in the Dachang ore-field the indium source is possibly related to granitic magmatism, which was indium-rich and experienced remelting, emplacement into the upper crust, condensing crystallization, and the ore-forming fluid carried mineralization elements from the magma, such as In, Zn, Cu, and Sn, because of the influence of the fluid−rock interaction and the migmatization of both magmatic fluid and atmospheric precipitation, indium ultimately separated out, forming sphalerite, chalcopyrite and jamesonite. However, the mechanism differs from the indium-rich deposit in Japan, whose indium source mainly derived from argillaceous rock. Yet, LIU et al [30] discovered the enrichment of indium in gold ore deposit, with a content of 5×10^{-6}–17×10^{-6}, meeting the requirements of the industrial comprehensive utilization. It is generally believed that indium only enriches in the hydrothermal sulfide mineralization, especially the sphalerite, yet in this type of gold deposit, which occur only a little sulfide and few sphalerite, the enrichment mechanism is worth further research, but the detailed geochemistry and mineralogy research suggested that the indium enrichment is related to the marcasite, in which indium scattered in the form of impurity composition. Undoubtedly, the factors to cause enrichment and the relationship between indium and gold are still so far unclear, which hopefully develops the basic theory and open the ore−prospecting ideas.

From this study, in pyrite, besides the dispersed element indium, the other dispersed elements also have a certain level of occurrence, such as Cd, Ga, Tl, and Re. On the basis of the relationship between indium and other diapersed element (Fig. 8), it shows relatively obvious positive correlation between indium and Cd, or Tl, yet a negative correlation between In and Re. And, the correlation between indium and Ga is difficult to determine, without obvious positive or negative correlation. LI et al [25] thought that the indium distribution in different sulfide and oxide is heterogeneous, even in the different ore, which shows prominent selectivity in many ways of precipitation, enrichment and distribution, but the favorite minerals mainly consist of sphalerite, jamesonite and chalcopyrite, showing a close relation to the precipitation of S and Fe.

4.3 Key constraint factors to mineralization

Currently, the known indium associated ore deposits are closely related to the oceanic crust edge, and on regional scale the indium associated ore deposits are consistent with the world's major tin metallogenic belt, such as Central Europe, Northeastern Australia, South America, Eastern Asia, Western United States, and Eastern Canada. The world's most important indium associated metallogenic belt is located next to the subduction zone edge of western pacific plate, especially along the subduction zone edge of East and Southeast Asia. The second is located at the eastern edge of South America plate, such as Bolivia and Peru, stretching north into the western edge of the North America plate. The third is Alpine orogenic belt in central Europe. However, the close association between indium associated deposit and tin ore belt suggests a possible similarity for both the plate subduction and tin mineralization.

Nowadays, the discovered indium resource mainly distributes at the continental margin tin ore belt, such as Central Europe, South Australia, South America, East Asia, Western America, and Eastern Canada [31]. All over the world, there are several metallogenic provinces of indium-rich deposit, which is usually closely related to ocean, plate boundary and orogenic belt. Even in the same metallogenic province, some metallogenic period is favor to the enrichment of indium, which is generally

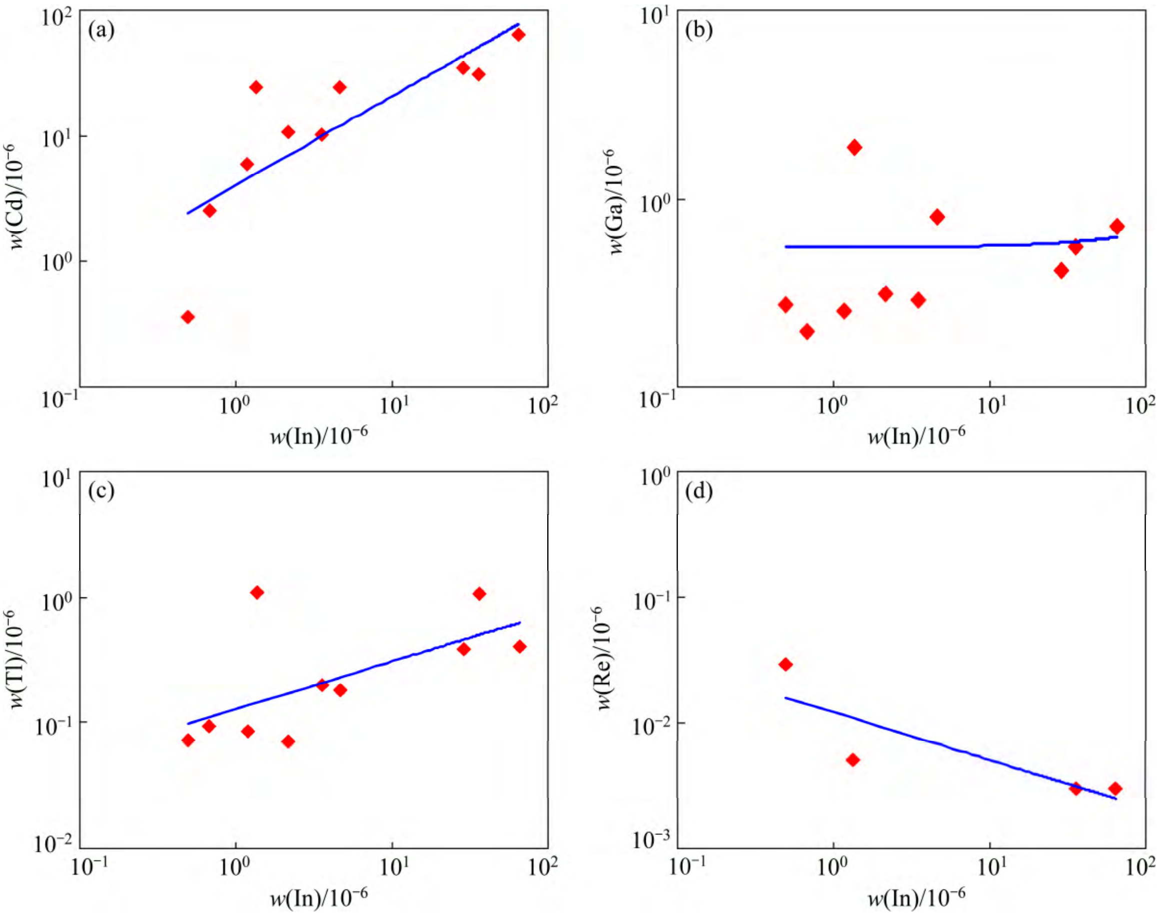

Fig. 8 Correlation of indium and other elements in pyrite from Dachang tin-polymetallic ore-field, Guangxi, China

strongly linked to the strongest orogenic activity and subduction collision orogenic event.

In China, the discovered indium resource is also characterized by maldistribution, mainly concentrated in South China and Pal−Asia fold belt, such as Guangxi, Yunnan, Inner Mongolia, Guangdong, Qinghai, Hunan, Jiangxi, Guizhou, and Sichuan [31]. TU et al [18] thought that on the basis of the tectonic environment, the indium-rich deposit is mainly located at the ancient continental margin, among which the south−southwest margin of Yangtze plate belongs to the most important large or super-large indium deposit concentrated areas. But beyond that, at the north margin of North China platform, the large scale indium-rich deposit is also discovered. About the special distribution pattern, whether it is related to the tectonic evolution of palaeo continent margin or the indium background value, it is still not well understood and needs further study.

The indium-rich deposits, which formed in the same period with the strongest orogenic belt, and regional mineralization related to subduction and collision, mainly distribute in the related magmatism and significant geothermal gradient active oceanic crust, continental margin, and orogenic belt [31,32]. The dispersed element mineralization requires special geological background and long geological process, and it usually seems to be the result of superposition of multi-phase geological processes [18,24].

GU et al [24] pointed out that it is the most vitality frontier areas in modern metallogeny study that explores the supernormal enrichment of elements and the formation mechanism of large or super-large deposits from a metallogenic continental dynamics perspective, and the occurrence of large or super-large deposits usually indicate an unique metallogenic characteristics and rather specific continental dynamics background.

To strengthen the prospecting, use multidisciplinary basis theory and new methods, and explore new prospecting theory and ideals, especially the dispersed elements independent deposit metallogenic theory is an important direction that needs to develop and deepen urgently [33]. Some scientific problems that relate to the metallogenic environment and deep dynamics remain to be further research, for example, the relationship between indium-rich deposit and tectonic environment, deep geodynamics, which type of tectonic position is favorable to the enrichment or super-richening of indium, the typical indium-rich deposit is restricted by what special tectonic setting and experienced what kind of metallogenic dynamics process. The above-mentioned problems are very crucial to ensure the sustainable development of indium resources and possibly affect the indium exploration and development around the world.

The indium concentrated distribution in western margin of Yangtze block is quite possibly closely related to the special geotectonic location and geological tectonic evolution history, and the continental margin tectonic evolution of western Yangtze plate and crust−mantle replacement, fluid activity, and elemental fractionation controlled by those tectonic process restrict the basic styles of dispersed metal mineralization and the temporal−spatial distribution of deposit [24].

As shown in Fig. 9, the correlation between indium and the main metallogenic elements is not very significant in general, in spite of this, the relationship between indium and zinc is clearer than the others, showing a significant positive correlation. It is easy to find out that the content of indium increases with the increase of zinc content, which suggests that the zinc plays rather important to the enrichment of indium. That just shows a good agreement with the mineral specialty of indium, that is to say, the sphalerite is the best mineral for its occurrence. So, it would be easy to deduce that the storage of sphalerite in cassiterite−sulfides deposit

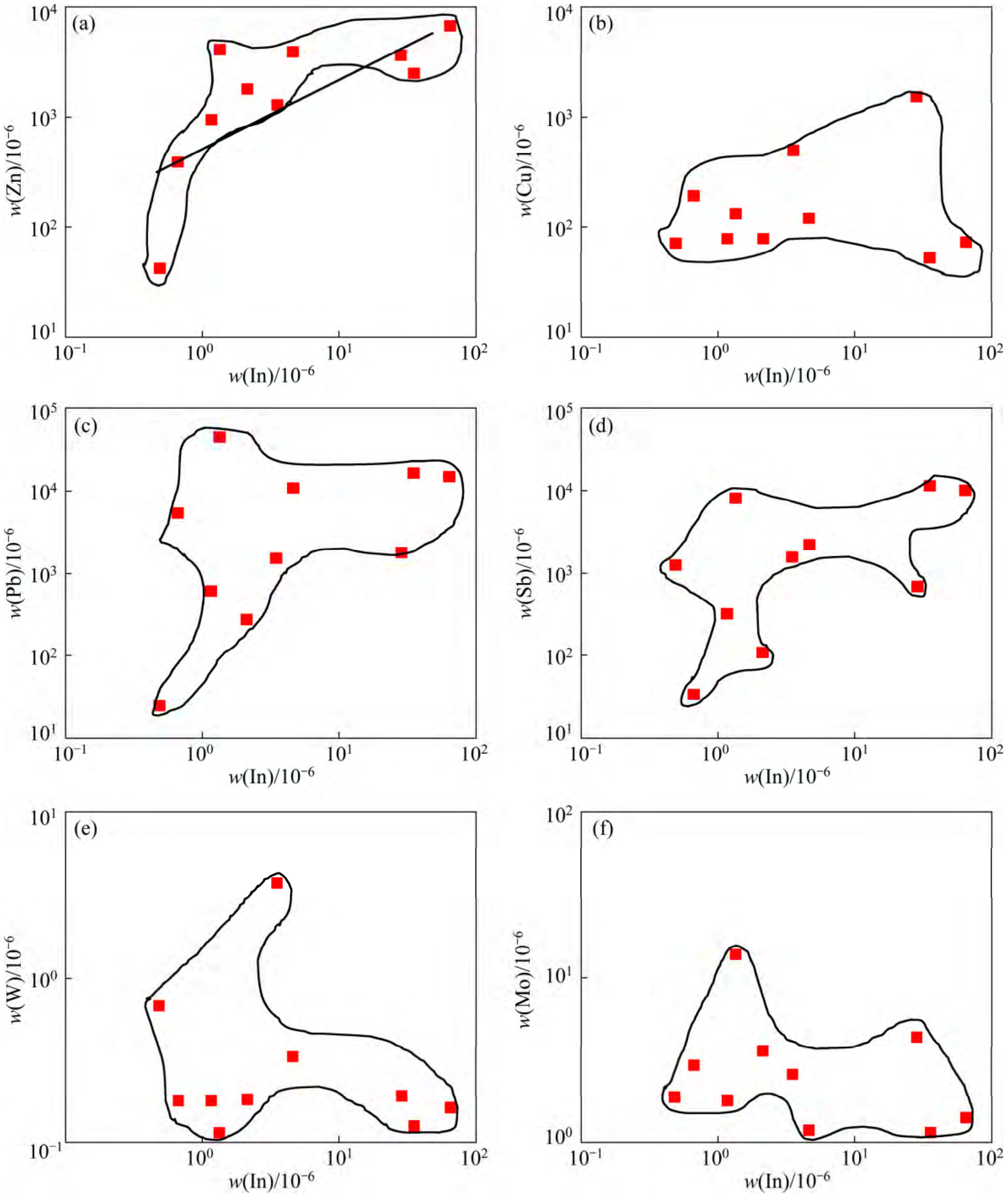

Fig. 9 Correlation of indium and other elements in pyrite from Dachang tin-polymetallic ore-field, Guangxi, China

determines largely the potential resources. Undoubtedly, about the ore prospecting of indium, the sphalerite is an important indicator and evaluation criterion, finding more sphalerite implying more potential indium resource.

The control factors of dispersed element indium have been recognized to a certain extent through recent years. LI and ZHAN [34] thought that there is a dependent relationship between indium and horizontal zoning of deposit, ore-forming temperature. DAI et al [35] found out that in the Dachang ore district the content of indium in the ore-host strata is high and varies in different lithology, yet in the ore it just shows positive correlation relationship between indium and tin or cadmium, and a negative correlation between indium and zinc. LI et al [36] found out that in the Dachang ore-field the indium was mainly derived from the magma that related to continental crust, and was the product of emplacement of the cretaceous granitic magma, suggesting indium-rich possibly in the magmatic source region. LUO et al [27] thought that in the Dachang ore-field the enrichment of indium was controlled by the mineralizing temperature, oxidation environment, and magmatite, which can be used as the prospecting indicator for indium-rich ore exploration in the future. Yet, according to the results of this study, besides of zinc, the other elements, such as Cu, Pb, Sb, W, and Mo, don’t show obvious correlation with the dispersed element indium (Fig. 9). So, the occurrence and distribution of these elements can’t restrict and affect the enrichment of indium and they are also impossible to be used as the ore guiding and evaluation index for the indium resource. Maybe, in the process of metallogenesis, both zinc and indium enter the pyrite simultaneously, and the occurrence of zinc in pyrite is very favorable to the enrichment of indium. And, whether the similar situation exists in other minerals, consisting of chalcopyrite, jamesonite cassiterite, arsenopyrite, and pyrrhotite, the relevant researches are also very necessary to further reveal the enrichment regularity and develop the metallogenic theory of indium, making up for the imperfect inadequate of dispersed elements step by step.

Recently, DAI et al [35] also pointed out that in the formation process of the Dachang ore deposit, the tin, magma, and the variations of physical and chemical conditions played an important role in indium enrichment. Undoubtedly, to understand indium enrichment fundamentally, there is a popular belief that the metallogenic dynamics research is particularly critical. Therefore, GU et al [24] thought that the continental dynamics background research of disperse elements ore-concentration area is very critical to reveal the material source, geodynamic background, and controlling factors, especially, that is favorable to understand the relationship between the relevant geological and geochemical processes, and the regional tectonic development history, crust−mantle interaction, earth spheres evolution, element geochemical fractionation.

5 Conclusions

1) In pyrite, the content of indium ranges from 0.491×10^{-6} to 65.1×10^{-6}, with an average value of 14.38×10^{-6}, yet the indium content of the Gaofeng deposit is higher than that of the other two deposits, showing the most significant supernormal enrichment feature. Similarly, the cadmium from Gaofeng deposit is also characterized by a higher content than the others.

2) The isomorphism is the main occurrence type for the dispersed element indium while there may be other forms. The relatively obvious positive correlation exists between indium and cadmium, or thallium, yet a negative correlation between indium and rhenium. However, the correlation is unconspicuous between indium and gallium.

3) The zinc is of great importance to the enrichment of indium, which just shows a good agreement with the mineral specialty of indium. Possibly, the occurrence of zinc in pyrite is very favorable to the enrichment of indium. However, the dispersed element indium doesn’t show an obvious positive or negative correlation with other elements, such as Cu, Pb, Sb, W, and Mo.

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黄铁矿中铟的产出特征与富集规律：以大厂锡矿田为例

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摘 要：为了揭示黄铁矿中分散元素铟的产出状态与富集规律，开展了详细的岩石学、矿物学、地球化学、矿物物理学等方面的研究工作。结果表明，黄铁矿通常与闪锌矿、铁闪锌矿、磁黄铁矿、黄铜矿、方铅矿以及毒砂等共生，主要呈块状构造、浸染状构造、脉状构造、网状构造、梳状构造等，黄铁矿结构主要为交代结构、固溶体结构、自形−半自形粒状结构以及浸染状结构等。黄铁矿中的铟含量介于 0.491×10^{-6}~65.1×10^{-6} 之间，平均含量为 14.38×10^{-6}，然而，该矿田中的高峰矿床黄铁矿铟含量高于大福楼矿床以及铜坑矿床的烟含量，具有更为显著的超常富集特征。另外，黄铁矿中的分散元素镉含量较其余分散元素高，且高峰矿床黄铁矿中的镉矿物同样地比其他矿床富集更为明显。铟与镉以及铟与铊之间均表现出明显的正相关关系，但是，铟与铼之间则为负相关关系，而铟与镓之间不具有显著的正相关或负相关关系。大厂锡石硫化物矿床的主成矿元素锌可能更加有利于分散元素铟的迁移与结晶，对于铟的富集成矿作用至关重要。

关键词：分散元素铟；黄铁矿；晶格结构；富集规律；锡石硫化物矿床；大厂矿田

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