



## Original Article

## Temporal and spatial distribution and genesis of primary indium deposits around the world

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### Abstract

Because rare dispersed elements including indium play an increasingly extensive and indispensable role in the field of modern high technology, the exploration, development and research of its resources are in full swing. The abundance of indium in the earth's crust is extremely low, and its original independent deposits have not been found so far. Indium is mainly parasitic in bulk non-ferrous metal deposits in the form of associated by-products. Because of its origin, the genetic types of indium deposits are as diverse as those non-ferrous metal deposits it parasitizes. The distribution of indium in geological time and earth space is uneven. The formation of indium ore deposit is closely related to tectonic-magmatic activity. It is the product of plate tectonic movement, continental rifts and mantle plumes or mantle hotspots in the interior of ancient continents. The emergence of indium ore deposit is inseparable from magmatic activity, especially granite magmatic activity. Ore-forming materials mainly come from the upper mantle and/or deep crust. Indium deposits formed under high temperature conditions have enrichment mechanisms. In addition to the enrichment factors of traditional metal deposits, the enrichment of nano-scale indium minerals through the nano effect is also a very important enrichment method. The indium deposits formed at the end of the differentiation and evolution of granite magma may not be enriched in one go, but is the result of multiple enrichments.

**Key words:** Rare metal indium; primary associated deposit; genetic type; global temporal and spatial distribution; genesis

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## 1 Introduction

Indium is a rare dispersed element. Like most other dispersed elements, the general public knows very little about indium. After all, an element like indium, which is extremely low in abundance in the earth's crust, is not as closely related to people's daily lives as iron, aluminum and copper. To paraphrase a line from a poem by Bai Juyi, a great poet of the Tang Dynasty in China:

A maiden of the Yangs to womanhood just grown, In inner chambers bred, to the world was unknown.

The "maiden of the Yangs" here is the subject of this article, indium.

There is an old saying among the ancient Chinese: things are precious because they are rare. This summary is appropriate for rare dispersed elements such as indium. The progress of science and technology and the widespread application of indium in modern high-tech fields have greatly improved the status and price of rare dispersed metals such as indium that were previously unknown to people. After being developed and utilized, indium can also be described by an ancient Chinese proverb:

After ten years' hard study noticed by none, his fame fills the land once honors are won.

Indeed, today's indium and its related products have different applications in many fields, especially in the fields of high technology and military defense. Its unique physical and chemical properties allow it to play a great role in different industries.

Because of this, there has been a global boom in indium ore deposits prospecting, exploration, development and research.

In view of this, this article will analyze the origin of indium deposits based on summarizing the temporal and spatial distribution patterns of indium deposits around the world and exploring their ore-controlling factors, so as to contribute to finding more and better natural indium ore resources.

## 2 Types of primary indium deposit

As far as we know, most of the rare dispersed elements, including indium, such as thallium, germanium, selenium, tellurium and rhenium, do not have their own independent primary deposits, but exist as associated and/or trace components in bulk non-ferrous metal deposits such as copper, lead, zinc and tin. In other words, indium ore deposit is what this article calls a parasitic mineral.

Tellurium originally had a similar fate to all other rare dispersed elements, that is, it was produced in non-ferrous metal deposits such as copper in the form of associated or symbiotic trace components. However, this situation of tellurium was completely broken in the 1990s by the discovery and development of the Dashuigou independent tellurium deposit located on the southeastern edge of the Qinghai-Tibet Plateau<sup>1-7</sup>.

There is no doubt that the discovery of the only independent tellurium deposit in the world has not only broken the traditional geochemistry and mineral geology that rare dispersed elements cannot form independent deposits, but also brought great hope to find other independent deposits of rare dispersed elements.

But so far, no primary independent deposits of indium have been found. All indium deposits currently being explored and developed are associated and/or deposits. That is, indium, as an associated and/or symbiotic trace element, exists in traditional bulk deposits such as copper, lead, zinc, tin, gold and silver, and is extracted as a by-product for human use.

Therefore, the so-called genetic type of indium deposits is actually the genetic type of deposits such as copper, lead, zinc, tin, gold and silver that people are more familiar with.

Based on the research results of predecessors and the author's personal research and development experience, the genetic types of primary associated indium deposits are briefly summarized in Table 1<sup>8-21</sup>. As for the global distribution of these different genetic types of indium deposits, please see Figure 1.

As can be seen from Figure 1, like most other minerals, the distribution of indium ore deposits in the world is seriously uneven, but concentrated in certain areas of the continental plate. Of course, these specific areas must be areas with superior metallogenic geological settings and conducive to the production of such minerals. According to the current calculation results, the world's associated indium deposits are mainly concentrated in a few countries

such as China, Peru, the United States, Canada and Russia. Among them, the indium reserves of the first three countries account for about 72.0%, 3.3% and .5% of the global total respectively<sup>22-23</sup>.

**Table 1.** Genetic types and representative deposits of associated indium deposits around the world<sup>8-21</sup>

Deposit type	Primary ore mineral	Main In-bearing minerals	Representative deposit
Skarn	Sn, Zn, Cu, Ag, Bi, As	sphalerite, chalcopyrite and andradite garnet	Dachang, Dulong, Yejiwei, and Qibaoshan in China
V(H)MS	Cu, Zn	sphalerite and chalcopyrite	María Teresa deposit in Peru, Gaiskoye deposit in Russia, Neves-Corvo in Portugal, and the Geco deposit in Canada
(Sn)PXV	Cu, Zn, Sn, Ag	Fe-rich sphalerite and stannite	Toyoha deposit in Japan; the Huari Huari, Potosi, and Bolivar mines in Bolivia
SEDEX		galena, sphalerite, chalcopyrite, and pyrite	Broken Hill in Australia; Dabaoshan mine in China
Epithermal vein	Zn, Pb, Cu, Au, Ag	gold, enargite, covellite, pyrite, sulphide, rhodonite, chalcopyrite and stannite	epithermal deposits in Argentina & Peru; Ayawilca in Peru; Ashio and Ikuno mines in Japan
Granite-related	Sn, Zn, Cu,	sphalerite, chalcopyrite, stannite, k�esterite,	Tigrinoe & Pravourmiiskoe in Russia; Isabel and Baal Gammon deposits in Australia; Cho Don in China; Colquiri in Bolivia
Porphyry Sn	Sn, Zn, Cu	sphalerite, stannite	Central Andean Sn belt from southern Peru through Bolivia to northwest Argentina; the Mount Pleasant deposit in Canada
Porphyry Cu	Cu, Co, Au, Re, Ag	chalcopyrite	The Bingham Canyon/Kennecott Copper mine, and the Santa Rita mine in USA
MVT	Pb, Zn	sphalerite, galena, pyrite, and marcasite	the Lisheen Zn-Pb deposit in Ireland
SSC	Cu	chalcocite, bornite, chalcopyrite, digenite, djurleite, anilite, galena, and sphalerite	the Waterloo mine in Australia
IOCG	Cu, Au, Fe, Ag, Co,	pyrrhotite, pyrite, chalcopyrite, bornite,	the Copper Blow Project in NSW, Australia; the
	Ni, Bi, Se, Te, U, REE, F, Ba, Mo	chalcocite, sakuraiite	Chaparra IOCG, Peru
MSCD	Cu, Pb, Zn, Ag	sphalerite, pyrite, Chalcopyrite, galena,	the Waterloo, Queensland, Australia

Note: V(H)MS - Volcanic-hosted massive sulphide; SEDEX - sedimentary exhalative mineral deposits; (Sn)PXV - (Sn) polymetallic xenothermal/epithermal veins; MVT - Mississippi valley-type Zn-Pb; SSC - Sediment-hosted stratiform Cu; IOCG - Iron-oxide copper gold; MSCD - Metamorphosed sandstone-shale copper deposits

Europe also widely develops hydrothermal vein-type associated indium deposits related to granite, such as the South Crofty area in southwest England (1 t) and the West Shropshire ore field (1 t), the Freiberg area in Germany (45 t), the Langban deposit in Sweden (1 t), and the Wiborg batholith in Finland (Werner et al., 2017)<sup>12</sup>. However, compared with similar indium deposits in other countries such as China, the resources of the above-mentioned European indium deposits are relatively much less.

The uneven distribution of different minerals on the earth's surface depends on the different geochemical properties of different elements on the one hand, and on the other hand, it is related to the earth's differentiation and evolution process and later tectonic-magmatic activities.

### 3 Metallogenic environment

A deep understanding of the formation environment of a mineral deposit is an important basis for exploring its origin and is also the only way to find more similar mineral deposits.



**Figure 1.** Map of the world's typical indium deposits<sup>8-9</sup>

Note: For the meaning of the abbreviations in the figure, please refer to the footnotes of Table 1

### 3.1 Geotectonic

Regarding the tectonic location of primary indium deposits, Schwarz-Schampera & Herzig (2002)<sup>24</sup> believed that the formation of indium deposits is closely related to plate subduction, collision and orogenic activities. Therefore, they are mainly distributed at the edges of active oceanic or continental plates, and near orogenic belts where geothermal gradients change sharply due to tectonic-magmatic activities.

This is true. An indisputable fact is that one of the most important indium mineral belts in the world is right next to the edge of the subduction zone on the west side of the Pacific plate (Figure 1)<sup>8-9</sup>. This indium mineral belt includes the Toyoha (4651 t), Ashio (1,240 t), Ikuno (1,094 t) and Akenobe (875 t) indium deposits in Japan, and the Ulsan indium deposit (90 t) in South Korea.

Another indium mineral belt is centered in Bolivia and Peru on the eastern edge of the South American plate and extends northward to the western edge of the North American plate (Figure 1). As far as we know, the indium resources in this indium mineral belt are mainly concentrated in Bolivia, accounting for nearly 20.0% of the global total<sup>12</sup>. The indium mineral genetic types are also very diverse, including epithermal silver-tin polymetallic deposits such as Huaru Huaru (5,601 t), Potosi (4,030 t) and Bolivia (2,311 t); and SEDEX-type indium-bearing lead-zinc deposits such as Malku Khota (2,431 t).

The third indium belt is centered in the Alpine orogenic belt in central Europe and extends to western Russia. The countries and indium deposits covered include Neves Corvo (3,480 t) in Portugal, Tellerhäuser (2,286 t) and Erzgebirge (1,470 t) in Germany, and VMS-type copper-zinc-(lead) deposits such as Gaiskoye, Podolskoye (485 t) and Sibaiskoye (1,000 t) in Russia. The Gaiskoye associated indium deposit is the largest indium deposit known in the world thus far, about 9,120 t) (Figure 1).

Other important indium deposits in other parts of the world include Broken Hill (2,659 t) in Australia, Mount Pleasant (1,246 t) and Kidd Creek (1,900 t) in Canada, and Kingman (1,109 t) in the United States.

Large associated indium deposits in ancient continents far from the plate subduction zones are most likely related to the activity of mantle plumes and/or mantle hotspots. For indium-bearing massive sulfide deposits in volcanic rocks

and exhalative sedimentary rocks, the favorable tectonic background is the back-arc environment and rift environment, and the favorable surrounding rocks are felsic rather than mafic rocks.

Relevant statistics show that associated indium deposits in China are highly concentrated in the eastern section of the Central Asian Orogenic Belt and South China<sup>21</sup>. Therefore, at present and for a long time before, the exploration, development and research of indium deposits in China are mainly concentrated in the southwestern margin of the Yangtze Platform in the country.

Tu et al. (2004) concluded that China's indium-rich deposits are mainly located on the edge of ancient continents. Among them, the south-southwestern margin of the Yangtze Plate is the country's most important distribution area of large and super-large indium-rich deposits<sup>25</sup>. The area includes the Dachang tin polymetallic ore field located in the southwestern margin of the Jiangnan Ancient Continent and the northern fault depression basin of the Hercynian-Indosinian passive continental margin rift basin, as well as the western end of the South China folded belt, the Yangtze Massif, and the Ailao Mountains. The Dulong tin polymetallic deposit is located at the intersection of three major structural units in the folded belt. On the northern edge of the North China Plate, there are also some large-scale indium-tin-rich polymetallic deposits distributed, such as the Meng'en Tolgoi (>500 t, Zhang et al., 2006)<sup>26</sup> in Inner Mongolia and Oi deposit (>768 t, Ishihara et al., 2008)<sup>27</sup>.

Obviously, the local concentrated development of indium deposits is also affected and controlled by the special structural geological environment at the edge of the ancient continent (Zhang et al., 2003; Cheng, 2013)<sup>28-29</sup>.

Other areas and deposits containing indium in China include: the Cambrian indium-bearing gold deposit in the western Qinling Mountains (Liu et al., 1998)<sup>30</sup>; the Chahe tin deposit in Sichuan (Guo et al., 2006)<sup>31</sup>; the indium-bearing deposits in the Bangong Lake-Nujiang River metallogenic belt in Tibet, such as the Lawu skarn copper-zinc deposit (Zhao et al., 2010)<sup>32</sup>; the high-sulfur gold-copper deposit in Zijinshan, Fujian, which contains roquesite (CuInS<sub>2</sub>) (Wang et al., 2014)<sup>33</sup>; and the copper-tin-indium deposit in the Saishitang-Rilonggou ore field in Qinghai (Liu et al., 2016)<sup>34</sup>. Indium minerals or indium mineralization have also been discovered in deposits such as Qibaoshan (Liu, 2017)<sup>35</sup>, Xianghualing (Liu et al., 2017)<sup>36</sup> and Yejiwei (Liu et al., 2018)<sup>37</sup> in Hunan Province.

An interesting phenomenon is that the world's important indium metallogenic belts coincide with the world's main tin mineralization belts. For this reason, Chen & Zhao (2021) concluded that<sup>28</sup>, the important source of indium is tin polymetallic deposits associated with granite. If this statistic is representative enough, then the tin deposit itself is one of the important prospecting signs of associated indium ores.

Werner et al. (2017) believed that<sup>12</sup>, Australia, Russia, Canada and other countries have a large number of large and super-large lead-zinc deposits. It is speculated that the indium resources in these countries have considerable prospects.

### 3.2 Ore-forming rock

Schwarz-Schampera & Herzig (2002) concluded that the hydrothermal system with the highest indium content usually appears in the back-arc rift environment and related island arcs, and is closely related to the developed bimodal volcanic activity and volatile-rich magma<sup>20</sup>. Partial melting and assimilation of the ancient crust may play an important role in the enrichment of incompatible elements indium in high-fraction arc magma.

Chen & Zhao (2021) concluded through research that an important source of indium is tin polymetallic deposits related to granitic magma<sup>38</sup>. During the evolution of the magma-hydrothermal system, tin and indium are enriched simultaneously. During this period, if the main carrier minerals of indium, such as biotite and hornblende, crystallize and separate, the mineralization potential of indium will be greatly weakened. After entering the ore-forming fluid, indium is mainly transported in the form of chloride, fluoride and hydroxide. Fluid temperature, pH, and the type and concentration of metal ligands are important factors controlling indium migration and precipitation. When indium precipitates from the fluid, the four-fold coordinated In<sup>3+</sup> is more similar to the four-fold coordinated metal ions in base metal sulfides such as sphalerite, chalcopyrite and tetrahedrite, causing a large amount of indium to enter the sulfide by isomorphic substitution and separate from tin. The precipitated indium-containing minerals may be reactivated, migrated and diffused in the later geological process, leading to the re-enrichment of indium. The enrichment of indium is closely related to tin, most likely due to the similar geochemical properties of indium and tin. In the supergene environment, indium and tin are retained in clay-rich sedimentary rocks undergoing chemical weathering due to reduced activity. This sedimentary rock will form a large number of mica minerals after

metamorphism. The decomposition of biotite, a common carrier of indium and tin, under high temperature conditions may be the fundamental reason for the simultaneous enrichment of indium and tin in the deposit.

However, indium in some newly discovered tin-poor magmatic hydrothermal deposits is also abnormally enriched.

#### 4 Metallogenic era

According to statistics from Werner et al. (2017)<sup>12</sup>, China's indium resources account for 18.2% of the world's total. These are mainly associated indium deposits of skarn-type tin polymetallic deposits, such as Dachang (8,775 t) in Guangxi, Dulong (5,124 t) and Gejiu (>4,000 t) in Yunnan, which were formed in the Late Cretaceous. Zheng et al. (2023) found that 85% of the associated indium deposits were formed in the Mesozoic, and the number of deposits before the Mesozoic was relatively small<sup>21</sup>.

Xu & Li (2018) selected 34 relatively typical indium-rich deposits from 101 publicly published in the world for relevant statistical analysis and research<sup>9</sup>. The total indium resources of these 34 indium deposits accounted for more than 95% of the known global indium resources at that time. In order to reflect the relationship between the mineralization of indium and geological evolution in different geological periods, Figure 2 shows the corresponding relationship between the genetic type, formation age and resource volume of these 34 indium deposits. As can be seen from Figure 2, the global large-scale indium mineralization is concentrated in the three geological periods of the Neogene, Cretaceous and Devonian. The corresponding indium ore genetic types of these three important indium mineralization periods are epithermal-tin polymetallic vein type, skarn type and VMS type.

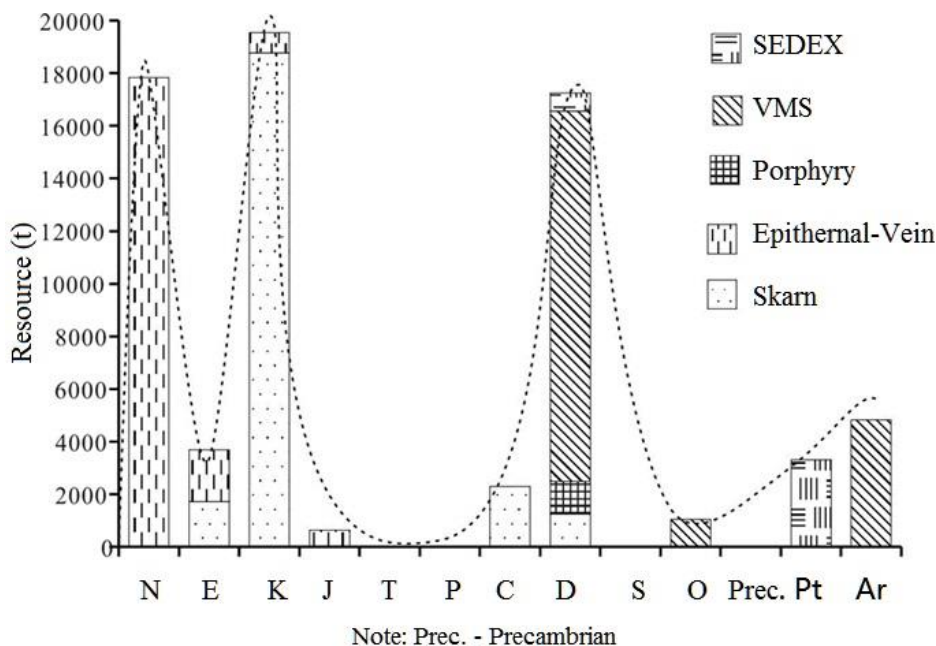


Figure 2. Distribution diagram of indium ore resources in different geological periods around the world<sup>9</sup>

#### 5 Deposit geology

All the currently known associated indium deposits in the world are produced in igneous rocks, especially granite intrusive and/or its surrounding rock contact zones. The formation of these indium deposits has a close genetic and direct spatial connection with tectonic-magmatic activities.

As for the carrier minerals of indium, no matter how the indium deposits are formed, that is, no matter what their genetic type is, indium is without exception mainly found in sphalerite<sup>21</sup>. This is already a consensus in the global geological community.

At present, more than 20 independent indium minerals have been identified in the world, including native indium (In), roquesite (CuInS<sub>2</sub>), sakuraiite ((Cu,Zn,Fe)<sub>3</sub>(InSn)S<sub>4</sub>), dzhaldindite/jaldindite (In(OH)<sub>3</sub>), indite (FeIn<sub>2</sub>S<sub>4</sub>), dzhaldindite (In(OH)<sub>3</sub>), indite (FeIn<sub>2</sub>S<sub>4</sub>), ishikaraitite (Cu,G,Fe,In,Zn)S, abramovit (Pb<sub>2</sub>SnInBiS<sub>7</sub>), ramdohrite (Pb<sub>5,9</sub>Fe<sub>0,1</sub>Mn<sub>0,1</sub>In<sub>0,1</sub>Cd<sub>0,2</sub>Ag<sub>2,8</sub>Sb<sub>10,8</sub>S<sub>24</sub>), znamenskyite (Pb<sub>4</sub>In<sub>2</sub>Bi<sub>4</sub>S<sub>13</sub>), cadmoindite (CdIn<sub>2</sub>S<sub>4</sub>), laforetite (AgInS<sub>4</sub>), damiaoite (PtIn<sub>2</sub>), yixunite (Pt<sub>3</sub>In), abramovite (Pb<sub>2</sub>SnInBiS<sub>7</sub>), yanomamite (InAsO<sub>4</sub>·2H<sub>2</sub>O), polywurtzite ((Cu,Fe,Zn,Ag)<sub>3</sub>(Sn,In)S<sub>4</sub>) or ((Cu, Zn, Fe, In, Sn)S), and three unnamed minerals ZnCdIn<sub>2</sub>S<sub>7</sub>, ZnCdIn<sub>2</sub>S<sub>5</sub> and CdInS<sub>4</sub>. Ishikaraitite was first discovered by Márquez-Zavalía in the Capillitas deposit in northwestern Argentina in 2014 and named after Japanese scholar Dr. Shunso Ishihara.

China has currently discovered five of them, among which roquesite is the most common and widely distributed indium independent mineral in China's associated indium deposits. The remaining indium independent minerals, such as native indium and dzhaldindite/jaldindite, only appear in small quantities in specific associated indium deposits<sup>21</sup>.

Tables 2 and 3 list the simple compounds of indium and the most widely distributed indium-containing minerals, respectively.

**Table 2.** Simple compounds of indium<sup>39</sup>

Compound	Mineral name	Chemical formula
Nitride	indium nitride	InN
Sulfide	indium sulphide	InS
	diindium trisulphide	In <sub>2</sub> S <sub>3</sub>
Selenide	indium selenide	InSe
	diindium triselenide	In <sub>2</sub> Se <sub>3</sub>
Telluride	indium telluride	InTe
	diindium tritelluride	In <sub>2</sub> Te <sub>3</sub>
Hydride	indium hydride	InH
Fluoride	indium trifluoride trihydrate	InF <sub>3</sub> ·3H <sub>2</sub> O
	indium fluoride	InF
	indium trifluoride	InF <sub>3</sub>
	indium trifluoride nonahydrate	InF <sub>3</sub> ·9H <sub>2</sub> O
Chloride	indium chloride	InCl
	indium dichloride	InCl <sub>2</sub>
	indium trichloride	InCl <sub>3</sub>
Bromide	indium bromide	InBr
	indium dibromide	InBr <sub>2</sub>
	indium tribromide	InBr <sub>3</sub>
Iodide	indium iodide	InI
	indium triiodide	InI <sub>3</sub>
	diindium tetraiodide	In <sub>2</sub> I <sub>4</sub>
Oxide	indium oxide	InO
	diindium trioxide	In <sub>2</sub> O <sub>3</sub>

**Table 3.** Most widespread minerals containing indium<sup>39</sup>

Name	Formula	Crystal System	Mindat Localities
Roquesite	CuInS <sub>2</sub>	Tetragonal	62
Ramdohrite	Pb <sub>5.9</sub> Fe <sub>0.1</sub> Mn <sub>0.1</sub> In <sub>0.1</sub> Cd <sub>0.2</sub> Ag <sub>2.8</sub> Sb <sub>10.8</sub> S <sub>24</sub>	Monoclinic	43
Dzhalindite	In(OH) <sub>3</sub>	Isometric	18
Sakuraiite	(Cu,Zn,Fe) <sub>3</sub> (In,Sn)S <sub>4</sub>	Isometric	15
Indium	In	Tetragonal	10
Laforêtite	AgInS <sub>2</sub>	Tetragonal	3
Cadmoindite	CdIn <sub>2</sub> S <sub>4</sub>	Isometric	3
Indite	FeIn <sub>2</sub> S <sub>4</sub>	Isometric	2
Yanomamite	InAsO <sub>4</sub> ·2H <sub>2</sub> O	Orthorhombic	2
Damiaosite	PtIn <sub>2</sub>	Isometric	2

Note: This list of minerals containing indium is built from the mindat.org locality database.

This is based on the number of localities entered for mineral species and is therefore slanted

towards minerals interesting to collectors with less coverage of common

rock-forming-minerals so it does not give an undistorted distribution of Indium mineral species.

It is more useful when comparing rare species rather than common species.

As the third largest cassiterite sulfide deposit in China, the Dulong tin-zinc polymetallic deposit in Yunnan China has been proposed by some researchers as a composite control of granite, structure and stratigraphy<sup>40-42</sup>. The late Yanshanian granitic magmatism is the provider of the main ore-forming materials and ore-forming energy, and is the key to the formation of the deposit. The structure and stratigraphy provide favorable channels, space and physical-chemical environment for the migration, enrichment and precipitation of ore-forming materials. The deposit is of magmatic hydrothermal origin.

As for the large-scale polymetallic massive sulfide deposits such as Gejiu and Bainiuchang in eastern Yunnan, China, many early researchers believed that they were typical magmatic hydrothermal deposits. Recently, some researchers have found through systematic studies of sulfide minerals in these deposits that these so-called typical magmatic hydrothermal deposits are actually massive sulfide deposits of submarine jet deposition, because oolitic, spherical and strawberry-like textures, as well as banded and lamellar structures were found in these ore bodies<sup>40</sup>.

Guo et al. (2006)<sup>31</sup> found through research that the indium content in the Chahe tin polymetallic ore area in Sichuan, China is very high, up to  $186.5 \times 10^{-6}$ . In addition, through the correlation analysis of indium and other ore-forming elements, it was found that indium in the area has a significant positive correlation with Zn, Cu, Fe, Cd, Sn, and Ga. It is speculated that indium may exist in the sulfides and/or (tin) oxides of these metals. Further electron probe analysis found that indium in the study area is mainly present in sphalerite, with a maximum content of  $500 \times 10^{-6}$ .

Zhao et al. (2010)<sup>32</sup> found that the average grade of indium in 18 deposits (showings) located in the Bangong Lake-Nujiang River metallogenic belt and adjacent areas in Tibet, China, meets the requirements of associated industrial grade. All samples with high indium content were collected from skarn-type deposits with a belt-like distribution. The indium minerals are mainly dzhalindite and native indium. The Lawu polymetallic deposit in Dangxiang County in the area, which is currently being mined, has an average indium content of  $45.44 \times 10^{-6}$  and a maximum of  $166 \times 10^{-6}$ .

Wang et al. (2014) discovered the relatively rare indium-independent mineral roquesite for the first time in China when studying the mineral composition of deep ore in the Zijinshan copper-gold deposit in Fujian, China<sup>33</sup>. Roquesite is usually found in medium- and high-temperature hydrothermal deposits. High-temperature minerals such as kiddcreekite, hemusite, colusite, mawsonite, stannite and molybdenite appear in the copper ore bodies in the southeastern section of the Zijinshan copper-gold deposit, indicating that the mineralization temperature in the deep part of the Zijinshan deposit is relatively high, and the contents of In, Sn, Pb, Zn, Mo and W in the ore-forming fluid are also relatively high.

## 6 Mineralization mechanism

Plate tectonic movement and orogenic movement are the most important driving forces for the formation of associated indium deposits and their host deposits.

These powerful forces not only produce strong tectonic-magmatic activities, but also drive the activation, enrichment and migration of various metal minerals and trace elements including various independent indium minerals. These ore-forming materials, which mainly come from the upper mantle and deep crust, not only gradually enrich in the process of magma differentiation, but also gradually reach a certain concentration with the increase of active liquid components. After finally rising to a certain part of the upper crust, due to changes in various physical and chemical conditions such as temperature and pressure, pH, salinity, sulfur fugacity and oxygen fugacity, they emplace in suitable structure and the contact zone between the intrusive and the sedimentary rock to form deposits of different genetic types.

As a copper-loving (sulfur-loving) element, indium is usually distributed in the mantle and crust in the form of  $\text{In}^{3+}$  (Smith et al., 1978)<sup>43</sup>. In the absence of sulfides during crustal differentiation, indium can show the characteristics of lithophile elements (Jenner and O'Neill, 2012)<sup>44</sup>. In the process of magma fractionation, indium is an incompatible element. Therefore, in the late stage of magma crystallization fractionation, most of the indium is retained in the solution. At this point, the fractionation evolution of indium is likely to be similar to that of tin, and it is highly volatile and can migrate in high-temperature gases such as HCl and HF at up to 940 °C (Kovalenker et al., 1993)<sup>45</sup>.

The content of indium in the mantle is about  $18 \pm 3 \times 10^{-9}$  (Witt-Eickschen et al., 2009)<sup>46</sup>,  $0.08 \times 10^{-6}$  in meteorites (Anders & Grevesse, 1989)<sup>47</sup>,  $0.05 \times 10^{-6}$  in the continental crust and  $0.072 \times 10^{-6}$  in the oceanic crust (Taylor & McLennan, 1985)<sup>48</sup>.

Liu (1984) pointed out that in most cases, high temperature conditions are conducive to the enrichment of indium<sup>49</sup>. The research results of most indium deposits also reveal that they are usually formed under high temperature conditions<sup>50-54</sup>. The increase in temperature may be conducive to improving the binding ability of indium with complex ions, and reach the maximum at 300~350 °C<sup>55</sup>.

Statistics show that the indium content in tin-rich sulfide deposits is relatively high, averaging above  $80 \times 10^{-6}$ . It shows that tin plays an important role in the enrichment of indium<sup>25,28,56</sup>. Zhang et al. (2007) pointed out by comparing China's indium-rich and indium-poor lead-zinc deposits that tin and indium are co-enriched and migrated in the ore-forming fluid until they are separated in the mineralization precipitation process<sup>57</sup>. Liu et al. (1984) found that a common feature of indium-rich minerals in crystal structure is that they all have a tetrahedral structure<sup>49</sup>. It is inferred that the tin-containing hydrothermal system is conducive to the enrichment and migration of indium, so indium can reach a higher concentration in the ore-forming solution. However, in the final precipitation process, after indium and tin parted ways, a large amount of indium entered into sphalerite with hexahedral coordination (Tu Guangchi, 2004)<sup>25</sup>.

Although existing statistics show that the vast majority of indium-rich ( $\text{In} > 100 \times 10^{-6}$ ) deposits in the world are closely related to tin-rich magmatic hydrothermal systems, while the grade and reserves of indium in tin-poor deposits are relatively low<sup>9</sup>. And some researchers have concluded that the tin-rich ore-forming fluid is the main controlling factor for the abnormal enrichment of indium metal in the deposit and its high grade and high reserves. But this does not mean that tin mineralization contributes to the mineralization enrichment of indium, at least the author of this article holds such a view. It can only be said that the mineralization geological conditions and physical and chemical conditions of indium and tin happen to be extremely close or very similar. On this point, more representative statistics and relevant in-depth research can draw more convincing conclusions.

The tin-rich indium deposits are mainly granite-related skarn type, shallow low-temperature hydrothermal type and hydrothermal vein type<sup>9</sup>. Representative deposits include the tin-rich copper-zinc deposits in Dulong, Dachang, Gejiu in China; Japan, Bolivia, Mount Pleasant in Canada; the Iberian pyrite belt in Portugal, and related deposits in the Russian Far East.

The indium deposits without tin are mainly VMS and SEDEX Cu-Pb-Zn deposits, but the grade and reserves of indium in these deposits are relatively low. Representative deposits include the Langban exhalative sedimentary Fe-Mn (Pb-Zn-Cu) deposit in Bergalagen, Sweden, and some base metal massive sulfide deposits in Siberia, Russia<sup>9</sup>.

Indium is an incompatible element in the process of magma fractionation. Therefore, in the late stage of magma crystallization fractionation, most of the indium tends to remain in the melt, and its fractionation evolution may be similar to that of tin (Kovalenker et al., 1993)<sup>45</sup>. Therefore, indium mineralization is often closely related to highly differentiated granites.

## 7 Discussion

Relevant studies have shown (Chen et al., 2008; Datta et al., 2009) that as a highly volatile sulfur-loving element, indium shows moderate to high incompatibility in mantle melt<sup>58-59</sup>. Due to its volatility, indium can be combined with sulfur in the form of gas and is widely used in nanomaterials.

Considering that the above-mentioned indium deposits around the world are mostly, if not all, formed in high-temperature environments, indium can be combined with sulfur in the form of gas to reach the nanometer level. It is certain that, like other rare dispersed elements, the enrichment of indium is closely related to the nano effect, which is the nano effect enrichment and mineralization mechanism proposed by the authors of this article<sup>1</sup>.

The formation of indium deposits is inseparable from tectonic-magmatic activities. For example, a large number of indium-rich tin polymetallic deposits related to young volcanic activities in Bolivia show the affinity of indium with volcanic-magmatic systems (Sugaki et al., 1983)<sup>60</sup>. In epithermal mineralization systems, the close relationship between indium and magmatic activity is more obvious, such as the Pinguino indium deposit related to Jurassic magmatic activity in the Deseado Massif area of Argentina (Jovic et al., 2011a, 2011b, 2011c)<sup>61-63</sup>. The close connection between granite intrusions and indium mineralization further shows that the formation of indium ore deposits cannot be separated from the help of igneous rocks. In other words, tectonic-magmatic activity is one of the most important factors in the formation of indium deposits. The relevant evidence is as follows:

Valkama et al. (2016a) confirmed that indium-containing polymetallic veins were developed in the rapakivik granite developed in the Sarvixviken area of Finland<sup>64</sup>. The world's second polymetallic skarn mineralization system (Sn, W, Mo, Be, In) was discovered in the Pitkaranta region of Russia, which is related to the rapakivi granites in the region. Shimizu & Morishita (2012) studied the Toyoha deposit in Japan and concluded that indium mineralization is closely related to porphyry dykes and/or stocks formed in the late magmatic period<sup>54</sup>.

Zhang et al. (2003) proposed that the Meng'en Tolgoi, Jubankeng, Gejiu and other deposits in China are closely related to magmatic activity, and indium may be mainly derived from magmatic activity<sup>28</sup>. The indium content of muscovite plagioclase granite in the Meng'en Tolgoi deposit in China is  $1 \times 10^{-6} \sim 7 \times 10^{-6}$ , which is 10~70 times the Clark value (Li et al., 2007)<sup>65</sup>. The high indium content ( $>0.14 \times 10^{-6}$ ) in the east and west dykes in the Dachang mining area in Guangxi China also indicates that the indium and tin in Dachang originated from the magmatic source related to granite<sup>66</sup>. Skarn-type indium mineralization also confirms its genetic relationship with magmatic activity, the most typical of which is Dachang mine in Guangxi, and Dulong mine in Yunnan, China (Werner et al., 2017)<sup>12</sup>.

There are also a large number of examples of indium mineralization related to magmatic rocks in other countries, such as the Vaulry and Charrier mines in France (Cantinolle et al., 1985)<sup>67</sup>, the Mangabeira mine in central Brazil (Moura et al., 2014)<sup>68</sup>, and the Mount Pleasant mine in Canada (Sinclair et al., 2006)<sup>69</sup>.

These deposits are almost all related to A-type or S-type granites. A-type and S-type granites are usually closely related to metal mineralization such as tungsten, tin, molybdenum, and rare metals, and often show the characteristics of highly differentiated granites (Wu et al., 2017)<sup>70</sup>. Except for the Late Cretaceous and a small amount of Late Jurassic in China, the formation age of granites in other countries is mostly concentrated in the Proterozoic and Carboniferous-Devonian<sup>9</sup>. Of course, not all S-type and A-type granites are accompanied by indium mineralization.

## 8 Conclusions



Indium mineralization, which mainly exists as an associated or paragenetic component of traditional bulk nonferrous metal mineral deposits, has a variety of genetic types. Indium deposits basically have the genetic types of other endogenous metal minerals.

The formation of indium deposits is inseparable from tectonic-magmatic activities. Especially plate tectonic movement, orogeny, continental rifting, mantle plume and mantle hotspot activities.

Large-scale tectonic-magmatic activities are the huge driving force for the formation of indium deposits. Especially the granitic magmatic activities in the mantle source and/or deep crust not only provide metallogenic power, but also provide the source of ore-forming materials.

Considering the extremely low abundance of indium in the earth's crust, the enrichment of indium ore-forming materials may not be completed in one go, but is jointly promoted by different geological processes and other processes including the nano effect; that is, the result of multiple enrichments. Indium mineralization, which mainly originates from the upper mantle and occurs under high temperature conditions, has excellent natural conditions for the enrichment of nano-scale ore-forming materials.

With the continuous deepening of research, it is not ruled out that new genetic types of associated indium deposits will be discovered in the future, such as sedimentary rock type, metamorphosed sedimentary rock type, etc. It is also not ruled out that the world's first primary independent indium deposit will be discovered under special geological background somewhere on the earth.

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#### Data availability

The data that support the findings of this study is available from the author upon reasonable request.

#### Declaration of competing interest

The author declares that he has no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

#### Use of AI tools declaration

The author declares that he has not used Artificial Intelligence (AI) tools in the creation of this article.

