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Viewpoint

Critical Metals Ga, Ge and In in the Global Pb-Zn Deposits: Current Understanding, Challenges and Perspectives

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BACKGROUND

A spectrum of strategically critical metals, such as gallium (Ga), germanium (Ge) and indium (In), with promising applications in green and high-tech fields, are produced as by-products of zinc ores in a variety of Pb-Zn deposits, such as magmatic-hydrothermal porphyry-skarn-vein type, Volcanogenic Massive Sulfide (VMS), Mississippi Valley-Type (MVT) and Sedimentary Exhalative (SEDEX) (Li et al., 2023; Zhai et al., 2019; Frenzel et al., 2016; Tu et al., 2004). The increasing demands for these strategic critical metals have driven a new rush of exploration and associated research for Pb-Zn deposits globally. In consideration of economic importance, scarcity in nature and supply risk of Ga-Ge-In metals, the global major economies, such as China, the USA, European Union, Australia, Canada and Japan have defined Ga, Ge and In as critical metals. To sustain the supply of the critical metals, a proportion of government organizations, research institutions and mining companies have launched a series of initiatives targeting for exploration for critical mineral resources (Table 1; Kelley, 2020; Mathieux et al., 2017; Schulz et al., 2017).

China is endowed with Ga, Ge and In resources, and supplies over 50% of the global Ga, Ge and In metals for two decades (Liu et al., 2022; Wen et al., 2020). To sustain China's dominant role of supplying for critical resources in the global market, the Chinese Government has launched a series of national strategic research programs focusing on critical mineral resources since 2020 (Table 1). Among these Chinese national major programs, the genesis and exploration of the critical metals of Ga, Ge and In in various Pb-Zn deposits are one of the research focuses. It thus can be viewed that the critical mineral resources have become an important part of the strategic development of China (Zhai et al., 2019), and therefore developing new genetic models for critical mineral deposits through research is urgently needed for guiding effective mineral exploration.

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Table 1 Main projects on the globally critical metals research

Institution	Projects on critical metals research	Duration
US Geological Survey	Critical mineral resources of the United States—Economic and environmental geology and prospects for future supply	Since 2017
European Union	Report on Critical Raw Materials and the Circular Economy	Since 2017
Geoscience Australia, Geological Survey of Canada and US Geological Survey	Critical Minerals Mapping Initiative (CMMI)	Since 2019
Ministry of Science and Technology, China	Development and Utilization of Strategic Mineral Resources	2021–2026
National Natural Science Foundation of China	Extreme Enrichment and Ore-forming Dynamics of Strategic and Critical Metals	2019–2026
Ministry of Natural Resources, China	New round of breakthrough strategic actions in mineral exploration	2021–2026

CURRENT UNDERSTANDING

Currently, most of Ga, Ge and In for industrial utilization are extracted from the by-products of various Pb-Zn ores, and existing research has reported the close association of accumulation of Ga, Ge and In with the formation of base-metal sulfides deposits (e.g., Liu et al., 2022; Zhao et al., 2022; Wen et al., 2020).

In particular, sphalerite, the primary zinc sulfide ore mineral, hosts the vast majority of Ga, Ge and In in its crystal structure in various Pb-Zn deposits (Ye et al., 2011; Cook et al., 2009). Below are some of our current understandings of Ga, Ge and In associated with various Pb-Zn deposit styles.

(1) Occurrence status of Ga, Ge and In

Gallium, Ge and In rarely form independent ore minerals of their own, but instead, they are commonly incorporated into the crystal lattice of host minerals through coupled substitutions and extracted as by-products (Tu et al., 2004). The by-product dependence of Ga, Ge and In is significantly different from those of the major industry metals such as Pb and Zn that occur as major elements in their ore minerals.

(2) Enrichment regularity of Ga, Ge and In

The abundance of Ga, Ge and In in the continental crust is relatively low, i.e., 16 ppm for Ga, 1.3 ppm for Ge, and 0.05 ppm for In, respectively (Schulz et al., 2017 and references therein). To reach the minimum industrial grade of about 100 ppm, a very high enrichment index, up to two to four orders of magnitude, is required. The geological processes contributing to this "Extreme Enrichment" or "Extraordinary Enrichment Process" (Zhai et al., 2019) remain largely unknown.

The enrichment of Ga, Ge and In in Pb-Zn deposits is selective. Gallium and Ge tend to be enriched in some of the relatively low-temperature hydrothermal deposits such as Mississippi Valley-Type (MVT) and sedimentary exhalative (SEDEX) deposits (Frenzel et al., 2016). By contrast, indium enrichment occurs in some of the relatively high-temperature hydrothermal deposits, such as magmatic-hydrothermal porphyry, skarn and vein type, and volcanogenic massive sulfide (VMS) deposits (Frenzel et al., 2016).

(3) Regional metallogeny of Ga, Ge and In

Gallium, Ge and In enrichment display a significant regional variation. Among the Chinese Pb-Zn deposits, the Sichuan-Yunnan-Guizhou-Hunan regions are extremely enriched in Ga, Ge and In, but other regions such as Xinjiang and Qinling Orogen are relatively depleted in Ga, Ge and In (Wen et al., 2020).

At a regional scale, the Pb-Zn deposits from different ore districts have similar geological features, whereas individual Pb-Zn deposits exhibit great variations in contents of Ga, Ge, In (Yu and Zheng, 2019). For the numerous MVT Pb-Zn deposits in South China, the Zhulingou deposit is extremely enriched in Ge, and the Fankou deposit is extremely enriched in Ga, and the Huayuan deposit is depleted in Ga, Ge and In (Luo et al., 2022).

Even at a deposit scale, the enrichment of Ga, Ge and In demonstrates great heterogeneity. In the Fankou MVT Pb-Zn deposit, the shallower Pb-Zn orebodies in the northern Jinxingling section are extremely in Ga, but the deeper southern Dongtang section is relatively depleted in Ga (Hu et al., 2023 and references therein). In the Baoshan skarn deposit (Hunan Province, South China), the earlier stage, higher temperature and deeper space facilitate indium precipitation (Wu et al., 2023).

RESEARCH CHALLENGES

Our current understanding of the enrichment mechanism of Ga, Ge and In in Pb-Zn deposits is still preliminary. The challenges lie in the absence of a basic understanding of the geological and geochemical processes in terms of the sources, transport and precipitation mechanisms of Ga, Ge and In. More specifically, we listed the following research challenges.

(1) Uncertainty of ore-control factors

The mechanisms of selective enrichment of Ga, Ge and In in Pb-Zn deposits at regional scale remain unclear (Jiang and Wang, 2022; Liu et al., 2022). Those Pb-Zn deposits commonly share similarities in geology settings, however, only certain deposits demonstrate extreme enrichment of Ga, Ge and In to the economic level. The variation could either be source-controlled, or caused during the evolution of ore-forming processes, or a combination of both.

(2) Uncertainty of favorable geological conditions

How the physiochemical parameters, such as the temperature, salinity and redox condition of ore-forming fluids that have a major control on the solubility and precipitation of Pb and Zn, affect the efficiency of Ga, Ge and In mineralization remains largely unknown and requires experimental study (Zhai et al., 2019). To which extent the control of lithology and structure on the precipitation of Ga, Ge and In in Pb-Zn deposits is also unknown. Understanding of the role of organic matters in sourcing and transporting Ga, Ge and In is of great importance to exploration.

(3) Uncertainty of metallogenic models

Comparisons of the mechanisms of Ga, Ge and In enrichment at deposit and regional scales are needed. Such knowledge carries great importance to guide effective exploration of Ga, Ge and In, as well as develop a genetic model of Ga, Ge and In extreme enrichment.

(4) Uncertainty of exploration models and guidance

The geology observation and geochemical analysis to the development of industrially applicable models are critical for guiding exploration of Ga, and Ge and In associated with Pb-Zn deposits. This would require close industry-academic collaborations on sample and data sharing, interpretation of results, human resources exchange, and pilot testing.

FUTURE PERSPECTIVE

With the increasing demand in high-tech and green technologies, we are facing great challenges in sustaining the supply of so-called ‘critical metals’ globally. China leads the global production of not only Pb and Zn resources but also the associated by-products of Ga, Ge and In (Chang et al., 2019; Leach and Song, 2019; Zhang et al., 2013). The exceptional endowment of Pb-Zn resources with associated Ga, Ge and In metals in China provides a natural laboratory for studying the enrichment mechanism of Ga, Ge and In. We herein propose to strengthen the metallogenic theory and develop novel exploration methods for Ga, Ge, In resources associated with Pb-Zn deposits in the following aspects:

(1) The progress of the metallogenic theory could build on a multiple-scale geological survey on the Chinese Pb-Zn deposits enriched in Ga, Ge and In. It aims at revealing the spatio-temporal distribution of Ga-Ge-In and the geological control on their enrichment. The multiple-scale investigation will need to cover the geological features of Ga-Ge-In enriched Pb-Zn deposits in a “global → ore belt → ore deposit → ore → mineral →atom/ion” contexts (Fig. 1). The aim is to answer a fundamental question of what geological conditions are favorable for the Ga-Ge-In mineralization.

(2) Traditional and novel *in-situ* micro-analytical techniques, including the EMPA (electron probe X-ray microanalyzer), LA-ICP-MS (Laser ablation inductively coupled plasma mass spectrometer), SEM (scanning electron microscope), TEM (transmission electron microscope), SRXAS (synchrotron radiation X-ray absorption spectroscopy) and APT (atomic probe tomography), should be jointly applied with cautions to understand the occurrence status and incorporation mechanisms of Ga-Ge-In into the Pb and Zn ore minerals. Note that the geochemical characterization should always be built upon a well-described geological observation.

(3) New research paradigms are being shaped. Multidisciplinary approaches, such as theoretical calculation, numerical modelling and simulation experiments, will aid in gaining new perspectives on Ga, Ge and In mineralization. Combing geological observation with the modelling results, it is possible to gain an improved understanding of the source of Ga, Ge and In, their transport and precipitation mechanisms in ore-forming fluids, as well as the ideal physicochemical conditions for fluids to effectively carry and deposit Ga, Ge and In.

A high-quality and real-time updated database of Ga, Ge, In resources in China and globally is critical to enhance big data-driven discovery of new resources. Applying machine learning, artificial intelligence and data mining techniques to the database will help to identify and predict geological and geochemical features to guide exploration for Ga-Ge-In metals in Pb-Zn deposits and develop a genetic model for Ga, Ge and In mineralization that is broadly applicable.

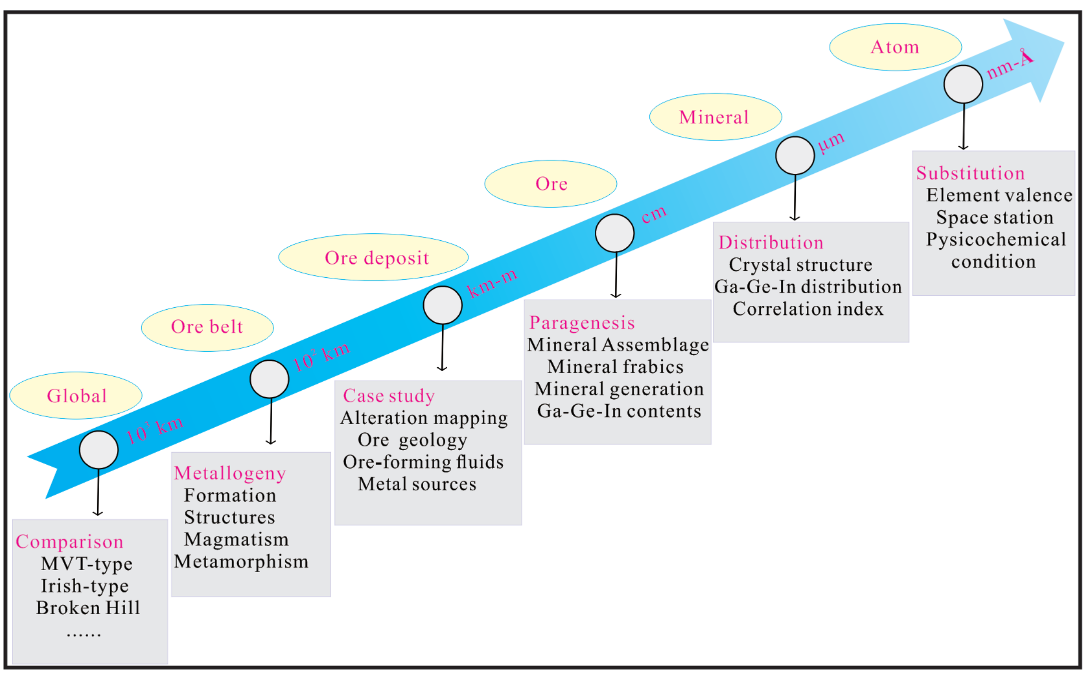

Figure 1. Multiple scale investigation and corresponding methodology (modified from Zheng et al, 2022).

A series of more targeted, high-precision and effective exploration technologies for Ga-Ge-In metals in various Pb-Zn deposits need to be developed. Different from the major industry metals, Ga, Ge and In are dispersed in various Zn-Pb sulfide minerals and their occurrence is often heterogeneous. A combination of geological, geophysical, geochemical and remote-sensing techniques is encouraged to be tested for pilot studies at mining sites.

Besides, understanding the entire value chain of Ga, Ge and In is important to develop sustainable initiatives to the supply of critical metals in general. This goes beyond understanding the geology of Ga, Ge and In, but also extends to the Pb-Zn mining industry, mineral processing, metallurgy, material applications and re-sourcing Ga, Ge and In from electronic devices and mining wastes.

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Conflict of Interest

The authors declare that they have no conflict of interest.

REFERENCES CITED

Chang, Z., Shu, Q., Meinert L., 2019. Skarn deposits of China. In: Chang, Z. S., Goldfarb, R. J., eds. Mineral Deposits of China. *Lancaster: Society of Economic Geologists SEG Special Publication*, 22: 189–234. https://doi: 10.5382/sp.22.06

Cook, N. J., Ciobanu, C. L., Pring, A., et al., 2009. Trace and Minor Elements in Sphalerite: A LA-ICPMS Study. *Geochimica et Cosmochimica Acta*, 73(16): 4761–4791. https://doi. org/10.1016/j.gca.2009.05.045

Frenzel, M., Hirsch, T., Gutzmer, J., 2016. Gallium, Germanium, Indium, and other Trace and Minor Elements in Sphalerite as a Function of Deposit Type—A Meta-Analysis. *Ore Geology Reviews*, 76: 52–78. https://doi.org/10.1016/j.oregeorev.2015.12.017

Hu, Z. B., Zheng, Y., Guo, L. X., et al., 2023. The World-Class Carbonate-Hosted Fankou Zn-Pb Deposit in China. Part I. Structural Analysis: Evolutionary Three-Order Thrusting Structures Control on the Localization of Zn-Pb Orebodies. *Ore Geology Reviews*, 157: 105463. https://doi.org/10.1016/j.oregeorev.2023.105463

Jiang, S. Y., Wang, W., 2022. What are the Super-Enrichment Mechanisms for Strategic Critical Metal Deposits? *Earth Science*, 47(10): 3869–3871 (in Chinese with English Abstract)

Kelley, K. D., 2020. International Geoscience Collaboration to Support Critical Mineral Discovery: U.S. Geological Survey Fact Sheet 2020–3035. US Geological Survey

Leach, D., Song, Y., 2019. Sediment-Hosted Zinc-Lead and Copper Deposits in China. In: Chang, Z. S., Goldfarb, R. J., eds., Mineral Deposits of China. Society of Economic Geologists SEG Special Publication, *Lancaster*, 22: 325–409

Li, X. M., Zhang, Y. X., Li, Z. K., et al., 2023. Discrimination of Pb-Zn Deposit Types Using Sphalerite Geochemistry: New Insights from Machine Learning Algorithm. *Geoscience Frontiers*, 14(4): 101580. https://doi.org/10.1016/j.gsf.2023.101580

Liu, Y., Hou, Z., Yue, L., et al., 2022. Critical Metals in Sediment-Hosted Pb-Zn Deposits in China *Chinese Science Bulletin*, 67: 406–424 (in Chinese with English Abstract)

Luo, K., Cugerone, A., Zhou, M. F., et al., 2022. Germanium Enrichment in Sphalerite with Acicular and Euhedral Textures: An Example from the Zhulingou Carbonate-Hosted Zn(-Ge) Deposit, South China. *Mineralium Deposita*, 57(8): 1343–1365. https://doi.org/10.1007/s00126-022-01112-4

Mathieux, F., Ardente, F., Bobba, S., et al., 2017. Critical Raw Materials and the Circular Economy–Background Report. Publications Office of the European Union, Luxembourg, ISBN 978-92-79-74282-8. https://doi.org/10.2760/378123jrc108710

Schulz, K., DeYoung, J., Seal, R., et al., 2017. Critical Mineral Resources of the United States—Economic and Environmental Geology and Prospects for Future Supply: U. S. Geological Survey Professional Paper 1802, 797, https://doi.org/10.3133/pp1802

Tu, G., Gao, Z., Hu, R., et al., 2004. The Geochemistry and Ore-Forming Mechanism of the Dispersed Elements (in Chinese). Geological Publishing House, Beijing. 1–424

Wen, H. J., Zhu, C. W., Du, S. J., et al., 2020. Gallium(Ga), Germanium (Ge), Thallium(Tl) and Cadmium(Cd) Resources in China. *Chinese Science Bulletin*, 65(33): 3688–3699 (in Chinese with English Abstract)

Wu, Y., Yu, P., Chen, X., et al., 2023. In Submission. Earlier Stage, Higher Temperature and Deeper Space Facilitate Indium Precipitation in a Skarn System, as Exemplified by the Baoshan Pb-Zn Polymetallic Deposit, South China. *Ore Geology Reviews*, ORGEO-S-23-0054

Ye, L., Cook, N., Ciobanu, C., et al., 2011. Trace and Minor Elements in Sphalerite from Base Metal Deposits in South China: A LA-ICPMS Study. *Ore Geology Reviews*, 39(4): 188–217. https://doi.org/10.1016/j.oregeorev.2011.03.001

Yu, P. P., Zheng, Y., 2019. Pb-Zn-Cu Accumulation from Seafloor Sedimentation to Metamorphism: Constraints from Ore Textures Coupled with Elemental and Isotopic Geochemistry of the Tiemurt in Chinese Altay Orogen, NW China. *Gondwana Research*, 72: 65–82. https://doi.org/10.1016/j.gr.2019.02.007

Zhai, M. G., Wu, F. Y., Hu, R. Z., et al., 2019. Critical Metal Mineral Resources: Current Research Status and Scientific Issues. *Bulletin of National Natural Science Foundation of China*, 33(2): 106–111 (in Chinese with English Abstract)

Zhang, C. Q., Rui, Z. Y., Chen, Y. C., et al., 2013. The Main Successive Strategic Bases of Resources for Pb-Zn Deposits in China. *Geology in China*, 40(1): 248–272 (in Chinese with English Abstract)

Zhao, T. P., Chen, C., He, X. H., et al., 2022. A Synthesis of the Geology, Spatial-Temporal Distribution and Enrichment Mechanism of Granite-Related Indium Deposits in China. *Ore Geology Reviews*, 146: 104932. https://doi.org/10.1016/j.oregeorev.2022.104932

Zheng, Y., 2022. Large-Scaled Structure-Alteration-Mineralization Mapping of the Hydrothermal Deposits: Basic Principle and Precautions. *Earth Science*, 47(10): 3603–3615 (in Chinese with English Abstract)

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