

中国镓矿分布规律、成矿机制及找矿方向

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摘 要: 金属镓资源是我国优势资源, 但随着国内外需求量不断增大, 我国金属镓的后备资源逐步短缺。本文系统搜集了我国富镓矿床研究和勘查成果资料, 初步总结了我国富镓矿的分布规律、成矿机制和找矿方向。研究认为, 我国镓矿主要伴生在铝土矿、煤矿和铅锌矿之中, 以铝土矿中伴生镓最为重要。依据不同成矿作用将我国具有工业价值的富镓矿床划分为沉积型铝土矿、堆积型铝土矿、红土型铝土矿、煤矿床和碳酸盐岩型(MVT)铅锌矿等 5 种伴生镓矿床类型, 并总结了不同类型镓矿床的时空分布规律。时间上, 我国富镓矿床在元古宙、古生代、中生代和新生代均有发育, 以石炭纪—三叠纪、侏罗纪—白垩纪和第四纪为主。其中, 富镓铝土矿主要形成于石炭纪、二叠纪和第四纪, 以石炭纪最为重要; 富镓铅锌矿主要形成于震旦纪和寒武纪; 富镓煤矿主要形成于石炭纪和二叠纪。空间上, 我国富镓矿床主要分布在晋豫成矿区、右江成矿区、扬子陆块西南成矿区、川—滇—黔成矿带、湘西—鄂西成矿带、湘东—赣西成矿带和华北陆块北缘成矿区等 7 个区带中。不同类型富镓矿床的成矿机制不同, 一般在风化-沉积作用下形成富镓铝土矿, 镓与铝常以类质同象形式存在; 在生物化学沉积作用下形成富镓煤矿, 镓常以无机态、有机态和混合形式存在, 在我国多以无机态的形式赋存于勃姆石、硬水铝石等矿物中; 在热液作用下形成富镓铅锌矿, 镓可能以类质同象形式进入以闪锌矿为主的硫化矿物晶格中。根据不同镓矿的成矿作用、富集过程和地质背景, 建立了煤矿、铅锌矿和铝土矿中镓富集成矿的理想模型, 并对铝土矿、煤矿和铅锌矿中伴生镓矿进行了找矿预测, 提出了找矿方向和重点找矿区域, 其中以沉积型、堆积型铝土矿的找矿为主攻方向, 并可兼顾煤矿和铅锌矿等其他伴生镓矿床。

关键词: 镓; 铝土矿; 煤矿; 铅锌矿; 成矿区带; 找矿方向

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Distribution, Metallogenic Mechanism and Prospecting Direction of Gallium Deposits in China

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Abstract: Gallium metal resources are dominant resources in China, but gallium reserves in China are gradually declining with increasing global demand. This study systematically collected the research and exploration results pertaining to gallium-rich deposits in China and preliminarily summarized the distribution, metallogenic mechanisms, and prospecting directions of gallium-rich deposits in China. The results indicated that gallium ore

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in China is mainly associated with bauxite, coal, and lead-zinc mining, with gallium in bauxite being the most important. According to the different modes of mineralization, gallium-rich deposits of industrial value in China can be divided into five types of associated deposits, sedimentary bauxite, accumulative bauxite, lateritic bauxite, coal mine deposits, and Mississippi Valley-type (MVT) lead-zinc deposits. The spatiotemporal distributions of these different types of gallium deposits were summarized. In terms of time, gallium-rich deposits in China developed in the Proterozoic, Paleozoic, Mesozoic, and Cenozoic, but mainly in Carboniferous–Triassic, Jurassic–Cretaceous, and Quaternary. Among these, gallium-rich bauxite mainly formed in the Carboniferous, Permian, and Quaternary, with the Carboniferous period being the most important. Gallium-rich lead-zinc deposits mainly formed in the Sinian and Cambrian periods. Gallium-rich coal mines mainly formed in the Carboniferous and Permian periods. Spatially, the gallium-rich deposits in China are mainly distributed in seven zones: the Jin–Yu metallogenic zone, Youjiang metallogenic zone, southwest metallogenic zone of the Yangtze landmass, Sichuan–Yunnan–Guizhou metallogenic zone, western Hunan–West Hubei metallogenic zone, eastern Hunan–West Jiangxi metallogenic zone, and the northern margin of the North China landmass. The different types of gallium-rich deposits have different metallogenic mechanisms. Generally, gallium-rich bauxite forms under weathering and sedimentation. Gallium and aluminum often exist in isomorphic forms. Gallium-rich coal mines form as a result of biochemical deposition. The gallium often exists in inorganic, organic, and mixed forms. In China, it is mainly hosted in inorganic form within boehmite, diasporite, and other minerals. Gallium-rich lead-zinc ore forms from hydrothermal fluids. Gallium in these deposits often substitutes within the lattice of sulfide minerals, dominantly sphalerite. Based on the mineralization, enrichment processes, and geological backgrounds of the different gallium deposits, this study established ideal models of gallium-rich deposits and integrated ores in coal mines, lead-zinc mines, and bauxite and considered the prospects of these deposits. Prospecting directions and key prospecting areas were proposed. The prospecting of sedimentary and accumulative bauxite should be the main direction, but other associated gallium deposits such as those of coal mines and lead-zinc mines can be considered.

Key words: gallium; bauxite; coal mine; lead-zinc mine; mineralization zone; prospecting direction

关键金属是当今世界发展所必需的原材料,可以推动我国战略新兴产业的发展,也是目前矿产勘查工作的重点矿种。我国的关键金属大致包括稀有金属、稀散金属、稀土金属和部分其他金属(翟明国等, 2019; 文博杰等, 2019)。镓(Ga)是典型的八种稀散元素之一,具有熔点低(29.78 ℃)、沸点高(2403 ℃)的特点,是自然界中温度区间最大的金属元素。被广泛用于半导体工业、太阳能工业、磁性材料工业等领域(Frenzel et al., 2016; 赵飞燕等, 2017; 赵汀等, 2017; Lu et al., 2017),尤其在半导体工业领域,砷化镓占全球镓消耗量的80%(李德先和王锦, 2020)。为此,欧盟和美国先后将镓列为关键矿产。镓资源是我国战略性储备资源之一,2020年我国粗镓产量占全世界90%以上(USGS, 2021)。镓的地壳丰度为 15×10^{-6} ,在自然界极少形成独立矿物,基本以伴生形式存在于铝土矿、煤矿、铅锌矿等矿床中。前人对镓的研究大多集中在镓在铝土矿、铅锌矿和煤矿矿石之中的空间分布规律与特征等方面。而富镓矿床的成矿区(带)、成矿机制和今后的找矿方向等方面研究甚少,这极大的制约了对富镓矿床的开发与利用。鉴于此,本文拟对我国富镓矿床的成矿系列、富集规律等进行归纳总结,以

期对未来找矿工作提供理论支撑。

1 镓资源概况

1.1 全球镓资源特征

全球已探明镓的储量约23万吨,其中,我国占比超80%(敦妍冉等, 2019)。全球伴生镓资源远景储量超过100万吨。镓资源大多伴生于铝土矿之中,主要分布于非洲(32%)、大洋洲(23%)、南美洲(21%)、亚洲(18%)和其他区域(6%)(Munson, 1994; Moskalyk, 2003)。我国典型的富镓铝土矿床有杜家沟铝土矿、大竹园铝土矿和贵港铝土矿等(汤艳杰等, 2001; 王佳奇, 2013; 李沛刚等, 2014)。铅锌矿同时也是世界上最主要的镓伴生矿藏之一(USGS, 2017),已确认伴生于铅锌矿中的Ga资源约19万吨,除南极洲尚未发现之外,另外几大洲均有铅锌矿分布(图1),典型矿床有美国Central Tennessee矿床(Bonnet et al., 2016),瑞典Zinkgruvan矿床(Jansson et al., 2016),中国凡口铅锌矿和银山铅锌矿(邓卫等, 2002)。此外,世界上煤炭资源中镓的总资源量约为1000万吨(Thakur, 2017),2010年我国在准格尔煤田发现与煤伴生的超大型镓矿床,勘探储备为85.7万吨(张云峰等, 2014)。

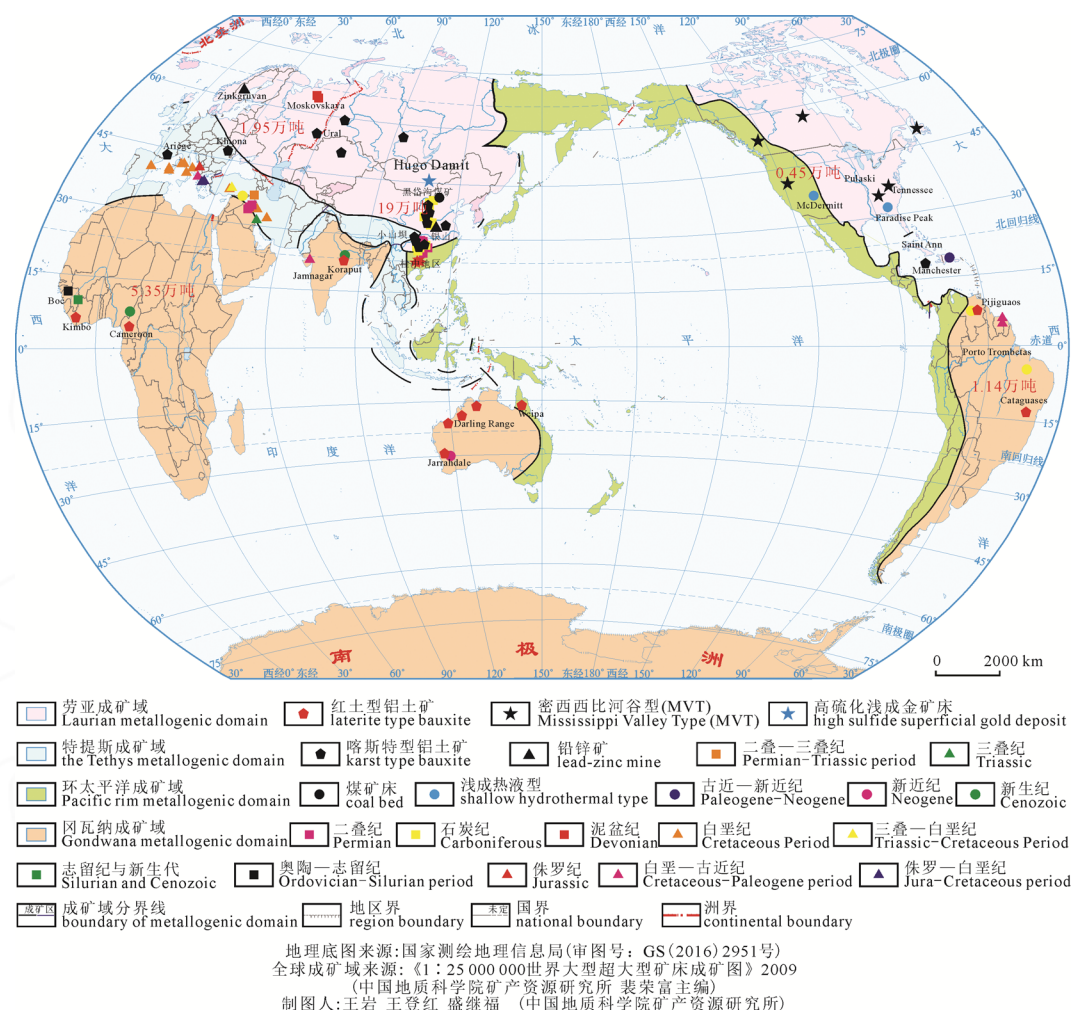


图 1 世界典型伴生镓矿床与镓资源分布
Fig. 1 Typical deposits associated with gallium and the distribution of gallium resources in the world

我国镓资源主要伴生在铝土矿之中, 含量一般为 $50 \times 10^{-6} \sim 250 \times 10^{-6}$, 镓资源量超过总量的 50%, 矿床类型以沉积型铝土矿为主(涂光炽等, 2004)。煤矿和铅锌矿也是我国伴生镓的主要来源, 如在内蒙古准格尔煤田发现了超大型伴生镓矿床, 其中镓的含量达到了 $30 \times 10^{-6} \sim 70 \times 10^{-6}$ (煤中镓的工业品位为 30×10^{-6}), 载镓矿物主要为硬水铝石和勃姆石(代世峰等, 2014), 在铅锌矿中镓主要赋存于闪锌矿中, 镓含量大于 100×10^{-6} , 少量镓赋存于方铅矿中(温汉捷等, 2020)(铅锌矿中镓的工业品位为 100×10^{-6})。因此本文将不同类型矿床中超过其伴生镓工业品位的矿床定义为富镓矿床。

1.2 世界典型富镓矿床

镓和铝、锌、铁等元素在化学和结晶化学性质上相近, 决定了他们之间密切的共存关系。不同的物理化学条件下镓的富集形式也不相同。伴生镓矿床的成矿作用主要有岩浆作用、伟晶岩作用、气成-热液作用、热液作用、风化作用、沉积作用六种(孙大中, 1960; 刘英俊, 1982; 温汉捷等, 2020)。镓具有亲石、亲硫和亲铁的地球化学性质, 按照镓的赋

存状态可将世界上含镓矿床划分为明矾石矿床、高硫化浅成金矿、火山成因硫化物矿床、铅锌矿矿床、密西西比河谷型(MVT)、多金属沉积型、铝土矿矿床喀斯特型、铝土矿矿床红土类型、表生铁帽和煤等(表 1, USGS, 2017; 敦妍冉等, 2019; 温汉捷等, 2020)。其中, 以铅锌矿、铝土矿和煤矿三类矿床为主。目前, 仅在非洲的(Tsumeb)Cu-Pb-Zn 金属矿床发现了唯一的原生镓矿物(硫镓铜矿)。

1.3 我国主要富镓矿床类型

镓极少独立成矿, 仅在某些矿床中形成工业富集, 从而形成镓含量相对较高的矿床。本文依据矿床成矿作用(热液作用、风化-沉积作用和生物化学沉积)将成因类型和工业类型进行有机融合, 并根据矿床成矿地质背景、镓的富集规律等特征, 将我国具有重要工业意义的富镓矿床的类型划分为 5 种, 并按照主矿种进行了矿床命名(表 2, 叶庆同等, 1991; 陈毓川和毛景文, 1995; 翟裕生等, 1996; 王登红等, 2002, 2020; 陈毓川等, 2016, 2022)。此外, 镓还可在沉积铁矿床、碱性伟晶岩矿床和经过气成-热液作用形成的云英岩型矿床和含铌钽矿化

表 1 世界典型伴生镓矿床
Table 1 Typical gallium-associated deposits in the world

国家	矿区或矿床	Ga/×10 ⁻⁶	富镓矿床类型	资料来源
美国	Paradise Peak Au-Hg	84	明矾石矿床	Eng et al., 1991
美国	McDermitt	34	明矾石矿床	Schulte and Foley, 2013
蒙古	Hugo Damit porphyry copper-Gold	17	高硫化浅成金矿床	Khashgerel et al., 2008
澳大利亚	Jarrahdale	69	红土型铝土矿	Anand et al., 1991
喀麦隆	Bamboutos Mount	39	红土型铝土矿	Hieronymus et al., 2001
几内亚	Kimbo	—	红土型铝土矿	Schwarz, 1997
澳大利亚	Weipa	—	红土型铝土矿	Bárdossy and Aleva, 1990
印度	Koraput	10	红土型铝土矿	Bárdossy and Aleva, 1990
委内瑞拉	Pijiguaos	75	红土型铝土矿	Tosiani et al., 1990
巴西	Cataguases	48	红土型铝土矿	Bárdossy and Aleva, 1990
中国	扶绥东门铝土矿	41	喀斯特型铝土矿	余文超, 2017
中国	黔北大竹园铝土矿	48	喀斯特型铝土矿	李沛刚等, 2014
中国	豫西杜家沟铝土矿	52	喀斯特型铝土矿	汤艳杰等, 2001
俄罗斯	Ural 铝土矿	49.8	喀斯特型铝土矿	Zakrutkin, 1974
法国	Ariège	55	喀斯特型铝土矿	Caillère, 1976
希腊	Khiona	38	喀斯特型铝土矿	Valeton, 1983
牙买加	Saint Ann	60	喀斯特型铝土矿	Blackwood et al., 1982
中国	凡口铅锌矿	60	铅锌矿	邓卫等, 2002
中国	银山铅锌矿	52	铅锌矿	黄松等, 1998
瑞典	Zinkgruvan 铅锌矿	2.3	铅锌矿	Jansson et al., 2016
美国	Central Tennessee	67	(MVT)	Bonnet et al., 2016
美国	East Tennessee	57	(MVT)	Bonnet et al., 2016
中国	黑岱沟煤矿	44.6	煤矿床	张复新和王立社, 2009
中国	海拉尔盆地	25.8	煤矿床	麻涛等, 2015
美国	Utah APEX	—	表生铁帽型	Dutrizac et al., 1986
西班牙	Rio Tinto	—	火山成因硫化物矿床	Tornos, 2006

的碱质蚀变花岗岩矿床等矿床中富集成矿,但这些矿床在我国出露较少,且缺乏代表性矿床(温汉捷等, 2020),所以本文暂未考虑。

(1)与风化-沉积作用有关的富镓矿床

与该成矿作用有关的富镓矿床的类型是铝土矿。镓含量较高的铝土矿多经历风化淋滤、沉积和成岩作用成矿。该类矿床共生矿产有耐火黏土、铁和煤等,同时多伴生 Li、Ga、Sc 和 REE 等三稀元素(刘英俊, 1982; 涂光炽等, 2004; 金中国等, 2019)。矿体一般呈似层状、透镜状和漏斗状(高兰等, 2015; Zhu et al., 2019)。其中,古风化壳沉积型铝土矿,是目前我国最主要的铝土矿类型,分布地域广,但主要集中在华北陆块和扬子陆块之间。古风化壳沉积型铝土矿的资源量约占全国 80%,是目前我国镓金属最主要的来源之一,典型矿床有贵州大竹园、山西庞家庄、河南杜家沟等。

(2)与生物化学沉积作用有关的富镓矿床

与该成矿作用有关的富镓矿床的类型是煤矿。我国煤中镓资源主要成矿时代有华北石炭—二叠纪、华南二叠纪和西北侏罗纪(宁树正等, 2019)。煤矿在经历了不断地风化作用-剥蚀作用以及地下水腐蚀的过程,导致了富镓矿石不断的细碎屑化,并

通过各阶段的高岭土和泥化作用去除了 K、Ca、Na、Mg、Si 等杂质(张复新和王立社, 2009)。典型富镓煤矿床有内蒙古黑岱沟、山西平朔、重庆南武等。

(3)与热液作用有关的富镓矿床

与该成矿作用有关的富镓矿床是铅锌矿。我国富镓铅锌矿类型主要为碳酸盐岩型(MVT)。该类矿床主要受中-低温热水和盆地盐卤影响而成矿,与岩浆作用关系不大,多伴生 Ag、Cd、Au、Cu 等金属元素(涂光炽, 1984; 刘英超等, 2008; Ding et al., 2016; 唐攀科等, 2018; Zhou et al., 2022),可以形成层状、脉状和筒状的矿体,方铅矿和闪锌矿是矿石中主要的矿物组合,且有少量黄铁矿和黄铜矿。我国该类型铅锌矿分布广泛,但超大-大型矿床主要分布于我国西北、西南和华南等地区,典型富镓矿床有广东凡口、安徽荷花山等。

2 中国富镓矿床时空分布特征

2.1 空间分布

中国的富镓矿床分布区域较广,但大-中型的富镓矿床分布相对集中。如,我国有 19 个省区市探明铝土矿资源,29 个省区市发现了铅锌矿资源(张长青等, 2014; 高兰等, 2015)。近年来,随着地质调查

项目的实施和技术的发展,在铝土矿、铅锌矿和煤矿中陆续发现一大批伴生的镓资源,使我国金属镓资源量不断增加。本文参照徐志刚等(2008)《中国成矿区带划分方案》,根据铝土矿、铅锌矿和煤矿等各类型矿床的分布特征,以及含镓物源和相应的富集成矿作用将我国富镓矿床分为 7 个成矿区带:晋豫成矿区、右江成矿区、扬子陆块西南成矿区、

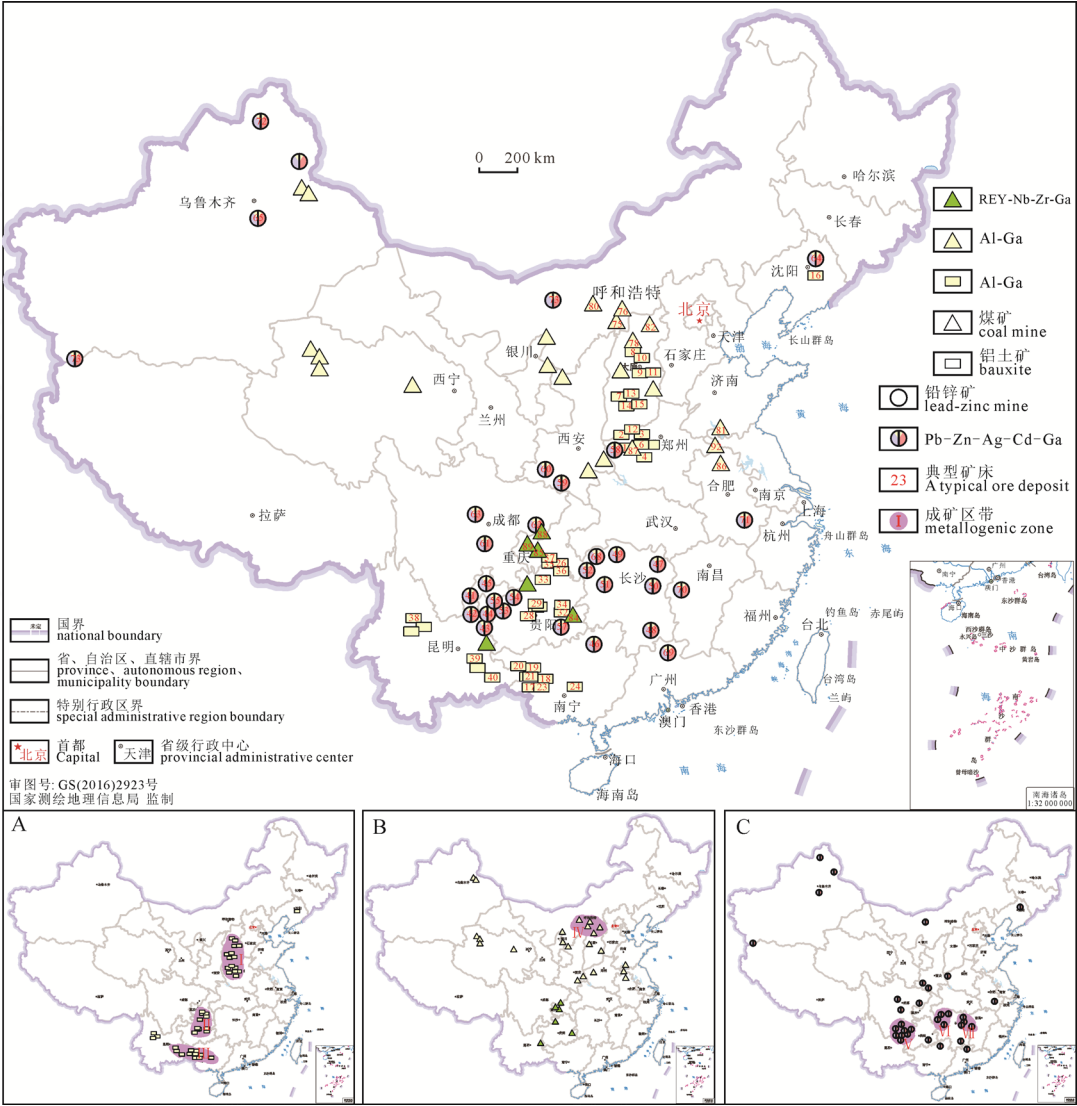
川—滇—黔成矿带、湘西—鄂西成矿带、湘东—赣西成矿带、华北陆块北缘成矿区。

2.1.1 铝土矿中伴生镓成矿区

我国伴生镓的铝土矿的主要类型为沉积型铝土矿、其次为堆积型铝土矿,少见红土型铝土矿。因此,本文研究主要集中于沉积型铝土矿,堆积型铝土矿和红土型铝土矿作为潜在研究对象。我国铝

表 2 我国典型伴生镓矿床
Table 2 Typical gallium-associated deposits in China

成矿作用	矿床类型	典型矿床
与风化-沉积作用有关	1. 沉积型铝土矿	贵州大竹园、山西庞家庄、河南杜家沟
	2. 堆积型铝土矿	云南鹤庆、广西新圩
	3. 红土型铝土矿	广西贵港、海南蓬莱
与沉积作用有关(生物化学沉积)	4. 煤矿床	内蒙古黑岱沟、山西平朔、重庆南武
与热液作用有关(与盆地卤水作用有关)	5. 碳酸盐岩(MVT)	广东凡口、安徽荷花山



I—晋豫成矿区; II—扬子陆块西南成矿区; III—右江成矿区; IV—华北陆块北缘成矿区; V—川—滇—黔成矿带;
VI—湘西—鄂西成矿带; VII—湘东—赣西成矿带。
I—Jinyu metallogenic area; II—southwest metallogenic area of Yangtze block; III—Youjiang metallogenic area;
IV—mining area in the northern margin of the North China Continent; V—Sichuan—Yunnan—Guizhou metallogenic belt;
VI—western Hunan—western Hubei metallogenic belt; VII—metallogenic belt of east Hunan and west Jiangxi.

图 2 我国伴生镓矿床与富镓矿床成矿区带
Fig. 2 Gallium-associated deposits and Ga-rich metallogenic belts in China

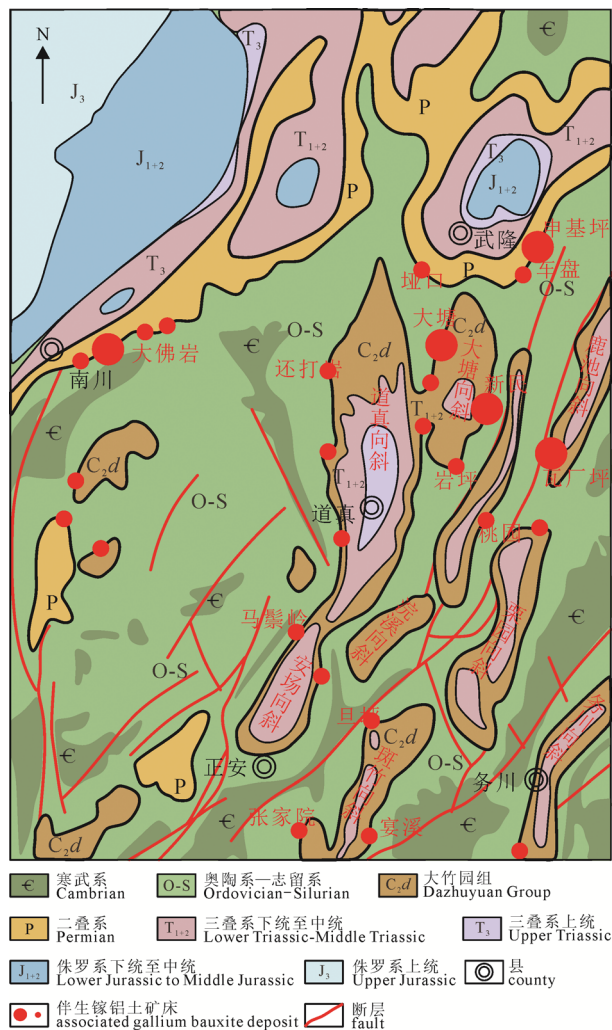
土矿中伴生镓成矿区带划分见图 2。

晋豫成矿区(I): 位于我国华北陆块, 主要涉及山西省和河南省。目前, 该成矿区已发现铝土矿中伴生镓资源占我国铝土矿中镓资源的 50% 以上。Ga 主要赋存于石炭系本溪组铝土矿中, 属地台型沉积的一水硬铝石型铝土矿(汤艳杰等, 2002; 李昌盛等, 2017), 石炭系本溪组地层直接覆盖在马家沟组的碳酸盐岩之上, 本溪组之下为铝土岩地层, 区内铝土矿床含矿岩系是一套以铝铁质黏土岩为主的滨海、海湾与泻湖环境所形成的陆源碎屑沉积。其中, 河南新密市张沟—桐树园铝土矿富集区呈北东—南西向展布, 古地理环境为泻湖潮坪沼泽相及滨岸潮坪沼泽相; 另外一个铝土矿集区王沟—范城镇铝土矿位于禹州市, 该区含矿岩系延伸超过 60 km, 矿体厚度约为 11~16 m, 受禹州向斜控制, 古地理环境为泻湖潮坪沼泽相。华北大块受构造运动影响整体抬升成陆, 之后发生强烈的风化-剥蚀作用, Mg、K、Ca、Si、S 等元素不同程度的被淋滤出去, 镓与铝一起迁移, 在基底稳定之后富集成矿(孙莉等, 2018)。山西伴生镓铝土矿主要分布于华北陆块(克拉通)中部, 主要赋存于中奥陶系碳酸盐岩古风化壳侵蚀面之上的上古生代晚石炭世早期太原组(湖田段)底部。该区铝土矿的含矿岩系同样为晚石炭世本溪组, 岩性组合自下而上可以分为“山西式”铁矿层—铝土矿层—黏土岩层, 该成矿区北部和南部地区镓含量较低, 中部地区镓含量较高, 各类型矿石中镓含量由高到低依次为豆鲕状→土状-半土状→碎屑状→致密状(廖士范和梁同荣, 1991; 陈平和柴浩然, 1997)。

扬子陆块西南成矿区(II): 该成矿区包含渝南—黔北赋镓带和黔中赋镓带。镓主要富集在石炭系大竹园组和九架炉组地层中(刘平, 1995)。其中, 黔中赋镓带位于上扬子台褶带, 黔中隆起南部, 古地理环境为黔中泻湖海盆地(莫江平和郦今放, 1991), 区域地壳频繁的升降运动, 对镓在铝土矿中的聚集起了巨大作用。在铝土矿成矿过程中铝和镓存在于成矿母岩之中, 随着铝土矿层形成和在受到后期沉积地层的压覆之下形成伴生镓矿床。含矿岩系包括三个主要特征岩性段: 上段为碎屑岩岩系、中段为含铝岩系、下段为含铁岩系, 其上覆地层为石炭系下统摆佐组, 下伏地层为寒武系中—上统娄山关组(刘幼平等, 2016)。矿石按照结构类型划分为土状、半土状、碎屑状和致密状, 以碎屑状铝土矿居多但镓含量低, 如修文小山坝矿石中 Ga 含量由高到低为: 豆鲕状→土状→碎屑状(叶霖等, 2007)。黔北—渝南赋镓带主要位于扬子板块中部, 扬子板块自寒武纪形成以来处于稳定的陆内环境(张启明等,

2012)。含铝岩系为上石炭统大竹园组, 上覆地层为中二叠统梁山组或栖霞组, 下伏地层为上石炭统黄龙组或下志留统韩家店组(韩忠华, 2008)。该区的铝土矿矿石类型主要为土状-半土状、碎屑状、致密状、豆鲕状矿石。该区各矿石类型富 Ga 规律与黔中修文小山坝明显不同, 如大竹园矿区各类型矿石中镓含量由高到低为: 致密状夹碎屑状→碎屑状→半土状→豆鲕状→致密状。黔北—渝南铝土矿含矿岩系沉积时代应该为中二叠世的梁山组和大竹园组。调查发现在大塘、新民、旦坪、桃园、宴溪、瓦厂坪、渝南大佛岩和武隆申基坪等地的铝土矿中存在不同程度镓富集, 其中, 黔北大竹园的伴生镓资源量可以达到 5400 t(李沛刚等, 2014)。根据该区铝土矿及其伴生镓分布特征认为, 黔北务正道地区和渝南武隆—南川一带的道真向斜、桃园向斜、安场向斜、浣溪向斜、栗园—鹿池向斜、大塘向斜、张家院向斜、新模向斜等具有较好的找镓前景(图 3; 李沛刚等, 2013; 李再会等, 2013)。

右江成矿区(III): 该区伴生镓的铝土矿主要分



布于云南和广西。云南铝土矿的赋矿层位在滇东南, 为晚二叠世龙潭组, 滇东南晚二叠世吴家坪早期处于滨海环境, 有利于铝土矿的形成。滇东南铝土矿主要为原生沉积型和次生堆积型铝土矿, 沉积型铝土矿位于丘北县, 文山天生桥等, 堆积型铝土矿主要位于砚山县阿猛、西畴县木者—铁厂地区。伴生镓主要赋存在堆积型铝土矿中。广西是全国第二大铝土矿资源省份, 含矿岩系为晚二叠世合山组。桂西一带有少量红土型铝土矿分布。桂西的铝土矿矿体大多散布于那坡—德保、靖西—田阳, 包括田东县和平果县一带(覃丰等, 2019), 该区铝土矿赋存于二叠系茅口组灰岩的侵蚀面之上, 二叠系合山组之下(王文鹏, 2016), 代表性矿床有靖西禄垌、桂西平果、桂西田阳、靖西大甲和靖西新圩等铝土矿。

我国的沉积型铝土矿为产于碳酸盐岩上或产于砂岩、页岩、泥灰岩、玄武岩侵蚀面上的铝土矿矿床, 铝土矿层的通常伴随着富铁矿物或煤层(炭质页岩)。从上到下通常是“页岩(炭质页岩, 煤)-铝-铁”结构。如, 华北地台石炭系本溪组底部的铝土矿(“山西式”铝土矿), 矿层主要位于灰岩之上和铁质、炭质泥岩(劣煤, 煤)共生形成了煤-铝-铁共生组合, 三者含矿系内部此消彼长, 底部铁质层为黄铁矿和菱铁矿; 贵州二叠系梁山组、广西上二叠统

合山组(图 3)含矿层都是区域性的“煤-铝-铁”结构(水兰素和常全明, 1999; Zhang et al., 2013; 高兰等, 2015; 唐波等, 2021; 姬果等, 2021)。有学者认为“煤-铝-铁”的形成伴随着强烈的风化作用, 是在强酸性-碱性转化条件下形成的, 有利于发生脱硅、去铁、富铝等一系列化学反应。“煤-铝-铁”三层结构在铝土矿中明反映现了含矿岩系垂向上的岩性差别, 并且铝土矿的上覆岩系和基岩之中镓的含量与其他地方相比偏低, 但在含铝岩系和铝土矿层中的镓含量较高(图 4)。且不同的含铝岩系中镓的含量也存在着差别, 如黔中小山坝镓在铝土矿层的中下部, 富镓岩性主要为铝土矿(岩), 而在豫西杜家沟本溪组则是铝质黏土岩和下部的铝土矿。

通过对比我国主要伴生镓铝土矿成矿带, 发现不同的铝土矿床中镓含量变化范围较大, 如杜家沟含量 $44 \times 10^{-6} \sim 130 \times 10^{-6}$ 、大竹园 $12.26 \times 10^{-6} \sim 132.56 \times 10^{-6}$ 、修文小山坝 $21.88 \times 10^{-6} \sim 72.59 \times 10^{-6}$ (叶霖等, 2008; 汤艳杰等, 2001; 李沛刚等, 2014), 且同一矿床之中不同类型矿石中镓的平均含量也有明显不同, 如大竹园铝土矿土状-半土状铝土矿中镓平均含量为 52.97×10^{-6} , 碎屑状铝土矿中镓平均含量为 65.46×10^{-6} , 致密状铝土矿中镓平均含量为 47.59×10^{-6} 。

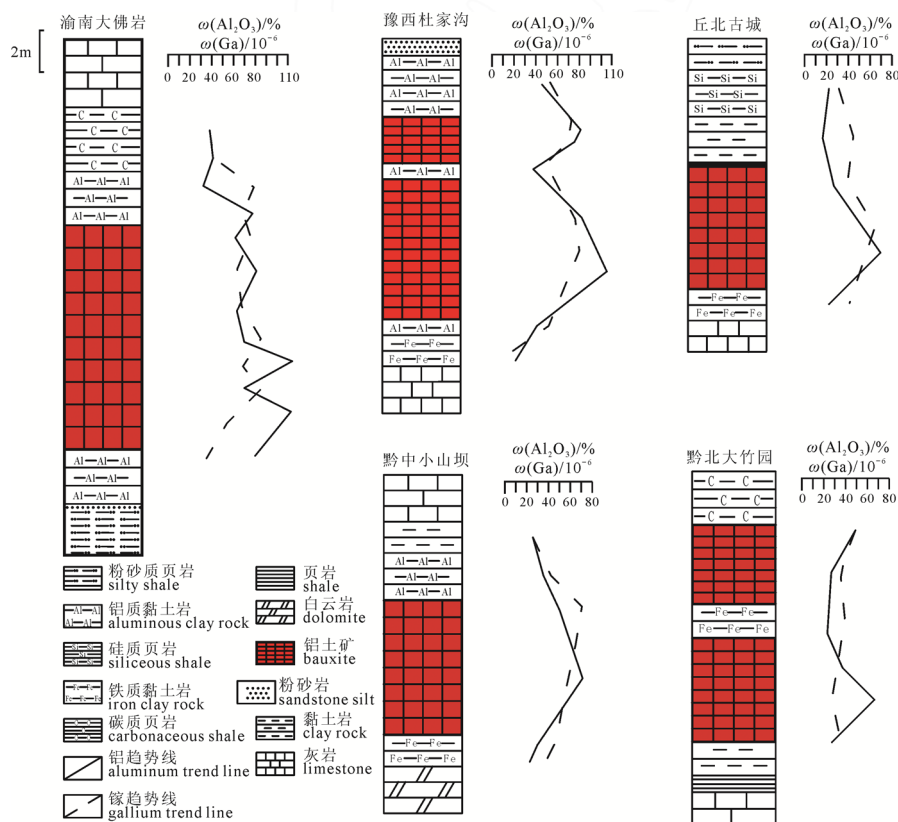


图 4 沉积型铝土矿典型剖面及镓含量变化图

(数据来源: 汤艳杰等, 2001; 叶霖等, 2008; 于蕾, 2012; 陈阳等, 2013; 崔滔, 2013)

Fig. 4 Profile of sedimentary bauxite and gallium content change

(Data sources: TANG et al., 2001; YE et al., 2008; YU, 2012; CHEN et al., 2013; CUI, 2013)

2.1.2 煤矿中伴生镓成矿区

我国富镓煤矿的空间分布特征目前还不是很明显,宁树正等(2019)划分了我国煤中金属元素矿床资源带。Dai et al.(2016)把我国煤中伴生镓的元素组合分成了两类: Al-Ga 和 REY-Nb-Zr-Ga。其中, Al-Ga 主要分布于我国华北地区和西北地区, REY-Nb-Zr-Ga 主要分布于我国西南地区。

华北陆块北缘成矿区(IV): 该区存在的伴生镓煤矿主要有黑岱沟、阿刀亥和宁武煤矿(图 5)。其中, 准格尔黑岱沟煤矿位于鄂尔多斯东北缘, 是目前我国发现唯一的与煤伴生的超大型镓矿床, 基底为奥陶统灰岩, 主要含煤地层为石炭系太原组、二叠系山西组, 上覆地层有上、下石盒子组、石千峰组等, 黑岱沟 6 号煤层是三角洲沉积体系下形成(Dai et al., 2006; 张复新和王立社, 2009; 宁树正等, 2017)。煤矿中主要矿物有碳酸盐矿物、硫酸盐矿物和黏土矿物等, 其中 Ga 主要赋存于高岭石和勃姆石等矿物中(高桂梅等, 2023)。

内蒙古大青山煤田阿刀亥矿区位于阴山纬向构造中段, 受强烈构造作用控制, 主要赋矿地层为石炭系、二叠系栓马桩组(关腾, 2013), 上覆地层为杂怀沟组和石叶湾组, 下伏地层为寒武奥陶系灰岩夹白云质灰岩(钟蓉和陈芬, 1985), 该区煤层为陆相沉积。阿刀亥矿区的矿物主要有高岭石、勃姆石、硬水铝石和磷钼铝石(邹建华等, 2012), 其中, 富镓矿物以勃姆石和硬水铝石为主。煤中镓与铝土矿中镓分布规律相似, 镓与铝紧密共生, 因此, 可以初步通过 Al_2O_3 含量去判断镓含量。

煤中伴生的镓可以赋存在有机质和无机质之中。如, 准格尔黑岱沟煤矿富镓矿物主要为勃姆石和高岭石, 镓与铝主要来自于准格尔盆地北偏东的本溪组铝土矿(代世峰等, 2014), 属于沉积成因。而阿刀亥煤矿中富镓矿物主要为勃姆石和硬水铝石, 其形成是煤层中的三水铝石在岩浆热液的烘烤下脱水所形成的。在我国滇东煤层中, 镓还可以以离子形式吸附于泥炭、腐殖酸等有机物中(Dai et al., 2010; Qin et al., 2015)。但无论镓以有机态、无机态或者混合形式存在, 对其含量上的差异性还需要进

一步研究(表 3)。

2.1.3 铅锌矿中伴生镓成矿带

川—滇—黔成矿带(V): 位于我国西南扬子地台和塔里木盆地西缘。主要出露地层有震旦系、寒武系、泥盆系、石炭系、二叠系, 次有志留系、奥陶系和三叠系。川—滇—黔成矿带遭受新生代构造活动影响较大, 是成矿作用发育的主要区域之一(叶霖等, 2011)。矿床主要分布在震旦系碳酸盐岩上部(张长青等, 2013)。区内的铅锌矿经过了多期次发育、岩浆活动和构造运动的共同作用下, 主要形成了岩浆型和沉积改造型铅锌矿, 其中沉积改造型铅锌矿占全国总资源量的 10.6%。矿石矿物主要以闪锌矿、方铅矿和黄铁矿为主, 脉石矿物有方解石、石英等。目前, 在川—滇—黔成矿带发现了老厂、富乐、五指山、洞子沟、桥儿沟和大梁子等一批大中型富镓铅锌矿床。

湘西—鄂西成矿带(VI): 位于我国扬子地台西南和北缘, 是我国重要的铅锌矿成矿带, 主要包括洛塔、保靖、花垣和凤凰四个铅锌矿田, 已经探明了洛塔、保靖等多个大-超大型铅锌矿床(吴涛等, 2021)。成矿带内主要含矿层位为震旦系陡山沱组和寒武系清虚洞组。洛塔矿田中唐家寨铅锌矿床含镓矿物闪锌矿中平均镓含量为 $1\ 320 \times 10^{-6}$, 远超过铅锌矿中镓工业回收的最低品位。长登坡、辰溪和花垣铅锌矿床镓含量均超过工业品位, 极具开发利用价值。代表性矿床有湖南长登坡、湖南辰溪等铅锌矿床。

湘东—赣西成矿区(VII): 位于扬子地台的次级构造单元——江南台隆, 区内出露地层为新元古代—第四纪。区内伴生镓矿床基底主要是由碎屑岩构成。主要矿床类型为 MVT 型铅锌矿。该区已发现的伴生镓的铅锌矿矿床较少, 但在骊山和清水塘显示了一定的镓资源潜力。

从统计数据来看, 我国伴生镓的铅锌矿主要分布于川—滇—黔成矿带和湘西—粤西成矿带, 镓资源潜力大。在闪锌矿之中镓含量多高于其工业品位, 但在黄铁矿或其他矿物之中低于地壳丰度。从根本上显示了镓的富集是由于与铅锌矿中的锌相关矿物

表 3 煤中 Ga 的赋存状态和来源(改自: Qin et al., 2015)
Table 3 Occurrence type and source of Ga in coal (modified from Qin et al., 2015)

赋存状态	Ga 含量/($\times 10^{-6}$)	Ga 的载体	Ga 的来源	矿床实例	参考文献
无机态	12~76	勃姆石	陆源碎屑	准格尔黑岱沟煤矿	Dai et al., 2006
	5.7~38	硬水铝石	陆源碎屑	大青山阿刀亥煤矿	Dai et al., 2012
	41.91~66.42	硅酸铝盐矿物	陆源碎屑	南武开发煤矿	李聪聪等, 2018
有机态	48	——	陆源碎屑	滇东月亮田煤矿	王佩佩, 2017
	33.0~106	离子吸附	火山作用	中国滇东煤层	Dai et al., 2010
混合形式	7.4~54	勃姆石和有机化合物	陆源碎屑	准格尔哈尔乌素煤矿	Dai et al., 2008

表 4 我国典型伴生镓矿床
Table 4 Typical gallium-associated deposits in China

编号	矿区	含矿层位	Ga 含量/($\times 10^{-6}$)	数据来源
1	豫西杜家沟(铝土矿)	石炭系本溪组	44~130	汤艳杰等, 2001
2	豫西渑池贯沟	石炭系本溪组	21.5~75.4	袁爱国, 2010
	豫西渑池	石炭系本溪组	19.9~40.9	王燕茹等, 2012
3	豫西贾家洼	石炭系本溪组	75~92	汤艳杰等, 2002
4	豫西宝丰县边庄	石炭系本溪组	14.9~44.9	康微, 2013
5	豫西偃师夹沟	石炭系本溪组	67~90	汤艳杰等, 2002
	豫西偃师夹沟	石炭系本溪组	24.6~86.4	袁爱国, 2010
7	山西交口庞家庄	石炭系本溪组	0.22~27.8	孟健寅等, 2011
8	山西宁武宽草坪	石炭系本溪组	9.27~71.03	孙思磊, 2011
9	山西太原阳曲	石炭系本溪组	11.77~59.67	杨中华等, 2011
10	山西原平石墙	石炭系本溪组	18.59~38.59	杨中华等, 2011
11	山西阳泉	石炭系本溪组	17~105.5	廖士范和梁同荣, 1991
13	山西交口南岭上	石炭系本溪组	36.6~74.7	陈平和柴浩然, 1997
14	山西交口回龙	石炭系本溪组	7.18~56.41	杨中华等, 2011
15	山西上务头	石炭系本溪组	14.09~33.29	于磊, 2017
16	辽宁本溪	石炭系本溪组	20.13~47.19	高仁文和邓晓峰, 2014
17	靖西禄垌	第四系	34~40.4	张佳莉等, 2016
18	桂西平果	第四系	34~48	张佳莉等, 2016
19	桂西平果	第四系	48.50~54.60	Wei et al., 2013
20	桂西田阳	第四系	11.4~84	蔡书慧等, 2012
21	靖西大甲	第四系	17.62~37.19	俞缙等, 2009
	靖西大甲	第四系	45.2~59	Wei et al., 2013
23	靖西新圩	第四系	65.74~79.26	刘枝刚, 2005
24	广西贵港	第四系	33.63~1314	王佳奇, 2013
25	桂西平果	第四系	19.03~68.97	乔龙, 2016
26	黔北大竹园	石炭系大竹园组	12.26~96.57	李沛刚等, 2014
	黔北大竹园	石炭系大竹园组	24.21~132.56	李沛刚等, 2014
28	黔中清镇燕垌	石炭系九架炉组	47~760	廖士范和梁同荣, 1991
29	黔中小山坝	石炭系九架炉组	32.3~50.7	Wen et al., 2021
	黔中小山坝	石炭系九架炉组	40.6~61.5	Wen et al., 2021
	黔中小山坝	石炭系九架炉组	21.88~72.59	叶霖等, 2008
32	福泉高洞	石炭系九架炉组	27.6~57.1	金中国等, 2018
33	遵义老瓦山	石炭系九架炉组	12.99~37	崔滔, 2013
34	凯里苦李井	二叠系梁山组	15.19~43.17	李再会等, 2013
35	黔北新民	二叠系梁山组	25.1~120	黄智龙等, 2014
36	黔北瓦厂坪	二叠系梁山组	15.19~60.84	黄智龙等, 2014
37	南川大佛岩	二叠系梁山组	20.4~71.4	李再会等, 2013
38	云南鹤庆	三叠系中窝组	8.15~26.49	王行军等, 2018
39	丘北古城	二叠系龙潭组	12.4~50.13	于蕾, 2012
40	文山天生桥	二叠系龙潭组	9.82~48.75	焦扬, 2014
41	云南省茂租(铅锌矿)	震旦系灯影组	~100(*)	张荣伟, 2013
42	云南省麒麟场	石炭系摆佐组	23.65~53.34(*)	Han et al., 2015
43	云南省锡宜	侏罗系象山组	10.10~98.24(*)	Li et al., 2020
44	云南省富乐	二叠系茅口组	5~358(*)	司荣军等, 2011
45	渝南老厂坪	寒武系清虚洞组	10.1~234(*)	王皓宇等, 2021
46	广西省泗顶	泥盆系融县组	20~250(*)	曹江帅, 2018
47	湖南省骊山	冷家溪群	17.0~381(*)	Yu et al., 2021
48	湖南省宝山	石炭系石磴子组	700~900(*)	张天栋等, 2021
49	湖南省长登坡	寒武系清虚洞组	10.2~126(*)	张沛等, 2021
50	湖南省清水塘	寒武系清虚洞组	100~1100(*)	Liu et al., 2022
51	湖南辰溪黄泥界	震旦系陡山沱组	16.63~63.5(*)	陈佳和孔令湖, 2012
52	湖南省花垣	寒武系清虚洞组	10.07~172.21(*)	隗含涛等, 2021
53	贵州省五指山	寒武系清虚洞组	20.7~158(*)	叶太平等, 2019
54	贵州省牛角塘	寒武系清虚洞组	18.43~64.61(*)	程涌等, 2022

续表 4

编号	矿区	含矿层位	Ga 含量/($\times 10^{-6}$)	数据来源
55	贵州省洞子沟	寒武系清虚洞组	12.438~55.276(*)	陈翠华等, 2019
	贵州省天桥	寒武系清虚洞组	16.03~48.71(*)	李珍立等, 2016
57	贵州省龙井街	寒武系清虚洞组	43.1~45.3(*)	耿忠武, 2018
58	河南省赤土店	震旦系煤窑沟组	10.64~36.09(*)	田浩浩等, 2015
59	陕西省楠木树	震旦系灯影组	60~370(*)	尹力, 2016
60	陕西省马元	震旦系灯影组	11.18~639.6(*)	胡鹏等, 2014
61	四川省桥儿沟	震旦系灯影组	11.9~65.3(*)	孟洪振, 2016
62	四川省大梁子	震旦系灯影组	12.29~374.04(*)	Yuan et al., 2018
63	四川省银厂沟~骑骡沟	震旦系灯影组	15~37(*)	李伟, 2011
	江西银山	侏罗系	19(*)	黄松等, 1998
64	辽宁省新岭	辽河郡大石桥组	14.7~426(*)	Sun et al., 2021
65	新疆哈尔达板	哈尔达板组	11.97~40.7(*)	Jiang et al., 2021
66	云南老厂	石炭系	23~69(*)	叶霖等, 2012
67	湖南省栗山	侏罗系-白垩系	11.3~186(*)	郭飞等, 2020
68	湖南洛塔唐家寨	奥陶系	~1320(*)	吴涛等, 2021
69	广东省凡口	泥盆系	74.5~550(*)	张先容, 1993
70	江西省蔡家坪	侏罗系	12.6~30.4(*)	Dai et al., 2014
71	安徽省荷花山	三叠系	600~1900(*)	Liu et al., 2018
72	新疆阿舍勒	泥盆系	—	吴玉峰等, 2016
73	新疆火烧云	侏罗系龙山组	—	袁鑫等, 2022
74	内蒙古甲乌拉	晚侏罗世—早白垩世	—	曹艳华和刘翼飞, 2020
75	准格尔哈尔乌素(煤矿)	石炭—二叠系太原组	25~70	秦勇等, 2009
76	准格尔黑岱沟	石炭—二叠系太原组	12~65.4	Dai et al., 2006
77	准格尔官板乌素	石炭—二叠系太原组	3.4~59	Dai et al., 2012
78	宁武平朔	石炭—二叠系太原组	8.27~68.22	刘帮军等, 2014
	宁武平朔	石炭—二叠系太原组	7.96~36.8	Di et al., 2022
80	大青山阿刀亥	石炭—二叠系太原组	5.7~38	Dai et al., 2012
81	藤县蒋庄	石炭—二叠系太原组	6.6~171	黄文辉等, 2011
82	大同北部	石炭—二叠系山西组	12.9~35.4	王钧瀚等, 2010
83	山东滕县	石炭—二叠系山西组	~80	李春阳, 1991
84	黔东南凯里	二叠系梁山组	19~44	易同生等, 2007
85	渝东南芦塘	二叠系吴家坪组	2.19~40.3	邹建华等, 2022
86	淮北芦岭	二叠系石盒子组	35.73~53.93	李影影, 2019
87	河南登封	二叠系石盒子组	3~40	杨伟林和朱绍军, 1993
88	华蓥山绿水洞	二叠系龙潭组	6.19~78.50	雒洋冰, 2014
89	重庆南武天宝	二叠系龙潭组	23.33~51.53	李聪聪等, 2018
	重庆南武开发	二叠系龙潭组	41.91~66.42	李聪聪等, 2018
91	准格尔黑岱沟	石炭—二叠系太原组	12~76	刘大锐等, 2018
92	淮北朱庄	石炭—二叠系山西组	66.5~168	李洋和李伍, 2022

注: —表示微量元素数据较低; *表示测试方法为 ICP-MS; 1~40 铝土矿; 41~73 铅锌矿; 74~92 煤矿。

的地球化学性质相似造成的。

2.2 时间分布

我国的富镓矿床从元古宙、古生代、中生代到新生代均有形成, 以石炭纪—三叠纪、侏罗纪—白垩纪和第四纪为主(图 5)。其中, 我国富镓铝土矿形成的主要时代为石炭纪、二叠纪和第四纪, 以石炭纪最为重要, 形成的富镓铝土矿超过 70%; 富镓铅锌矿的主要成矿时代为震旦纪和寒武纪; 富镓煤矿的主要成矿时代为石炭纪和二叠纪。

不同时代形成的富镓矿床类型不同, 震旦纪—泥盆纪主要形成低温热液矿床(碳酸盐岩型); 石炭

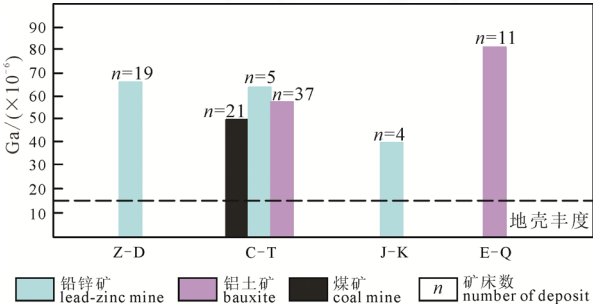


图 5 我国伴生镓矿床成矿时代矿床数量/Ga 平均含量直方图

Fig. 5 Histogram of ore deposit number/average Ga content of Ga-rich ore deposits in China during the metallogenic period

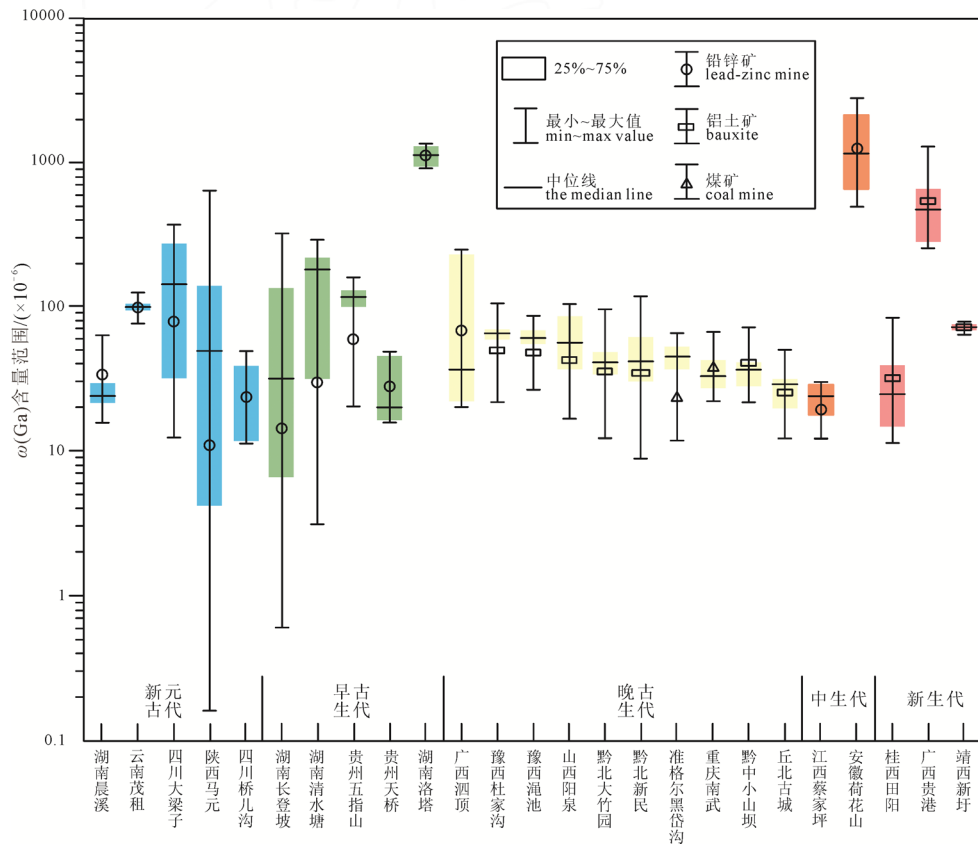
纪—三叠纪主要是由风化-沉积作用所形成的富镓铝土矿和富镓煤矿; 侏罗纪—白垩纪地壳趋于稳定, 为铅锌矿主要成矿时代, 以沉积作用为主的外生矿床为主(刘英超等, 2022), 但侏罗纪形成的铝土矿和煤矿中镓的含量都较低, 未统计在内。新生代主要为铝土矿中伴生的镓矿, Ga 的平均含量高于石炭纪—二叠纪形成的铝土矿, 主要分布在我国西南地区和东南沿海地区。目前, 我国震旦纪—泥盆纪、石炭纪—三叠纪和新生代的富镓矿床数量、规模和含量达到 Ga 工业品位, 找矿潜力巨大。

全国范围内, 富镓矿床主要发育于早、晚古生代和早中生代(图 6)。新元古代的富镓矿床均为富镓铅锌矿, 多分布于稳定的地台边缘, 矿床形成与岩浆活动无明显关系, 富镓铅锌矿多属于碳酸盐岩

(MVT)型。典型矿床有云南茂租、四川大梁子、湖南辰溪和陕西马元。

早古生代的富镓矿床多为铅锌矿, 主要为碳酸盐岩型(MVT)与少量矽卡岩型铅锌矿。川—滇—黔成矿区在晋宁运动之后产生了结晶基底和变质基底, 进而在晚震旦世, 区内形成了一套新的碳酸盐岩地层, 主要的含矿层位是震旦系灯影组白云岩, 其次为寒武系、志留系碳酸盐岩和碎屑岩(张长青等, 2013)。区内主要为中-小型矿床和矿点, 超大-大型铅锌矿较少。典型矿床有湖南长登坡、湖南清水塘、贵州五指山、贵州天桥和湖南洛塔。

晚古生代形成的富镓矿床分布广泛, 以华北陆块和扬子板块为主, 富镓矿床类型逐渐增多, 主要有沉积型铝土矿、煤矿、碳酸盐岩(MVT)型铅锌矿等,



数据来源: 茂租据张荣伟, 2013; 四川大梁子据 Yuan et al., 2018; 陕西马元据胡鹏等, 2014; 四川桥儿沟据孟洪振, 2016; 湖南长登坡据张沛等, 2021; 湖南省清水塘据 Liu et al., 2022; 贵州省五指山据叶太平等, 2019; 贵州天桥据李珍立等, 2016; 湖南洛塔据吴涛等, 2021; 广西泗顶据曹江帅, 2018; 豫西杜家沟据汤艳杰等, 2001; 豫西浍池据王燕茹等, 2012; 山西阳泉据廖士范和梁同荣, 1991; 黔北大竹园据李沛刚等, 2014; 黔北新民据黄智龙等, 2014; 准格尔黑代沟据秦勇等, 2009; 重庆南武据李聪聪等, 2018; 黔中小山坝据叶霖等, 2008; Wen et al., 2021; 丘北古城据于蕾, 2012; 江西蔡家坪据 Dai et al., 2014; 安徽荷花山据 Liu et al., 2018; 桂西田阳据蔡书慧等, 2012; 广西贵港据王佳奇, 2013; 靖西新圩据刘枝刚, 2005。

Data sources: Maozu from ZHANG, 2013; Daliangzi of Sichuan from Yuan et al., 2018; Mayuan of Shaanxi from HU et al., 2014; Qiaogou of Sichuan from MENG, 2016; Changdengpo of Hunan from ZHANG et al., 2021; Qingshuitang of Hunan from Liu et al., 2022; Wuzhishan of Guizhou from YE et al., 2019; Tianqiao of Guizhou from LI et al., 2016; Luota of Hunan from WU et al., 2021; Siding of Guangxi from CAO, 2018; Dujiagou of west Henan from TANG et al., 2001; Mianchi of west Henan from WANG et al., 2012; Yangquan of Shanxi from LIAO and LIANG, 1991; Dazhuyuan of north Guizhou from LI et al., 2014; Xinmin of north Guizhou from HUANG et al., 2014; Heidaigou of Junger from QIN et al., 2009; Nanwu of Chongqing from LI et al., 2018; Xiaoshanba of middle Guizhou from YE et al., 2008; Wen et al., 2021; Ancient City of Qiubei from YU, 2012; Caijiaping of Jiangxi from Dai et al., 2014; Hehuashan of Anhui from Liu et al., 2018; Tianyang of west Guangxi from CAI et al., 2012; Guigang of Guangxi from WANG, 2013; Xinxu of Jingxi from LIU, 2005.

图 6 铅锌矿、煤矿和铝土矿中 Ga 富集特征

Fig. 6 Ga enrichment characteristics in lead-zinc ore, coal mines, and bauxite

以沉积型铝土矿为主,主要分布在山西(断隆)成矿区和豫西成矿区。典型矿床有广西泗顶、豫西杜家沟、豫西渑池、山西阳泉、黔北大竹园、黔北新民、黔中小山坝和丘北古城等。

中生代是我国铅锌矿的重要形成时期。在印支期和燕山期时,华南华北板块聚合和特提斯洋盆闭合,主要形成陆相火山岩型和碳酸盐岩(MVT)型富镓铅锌矿。在燕山期时,铅锌矿形成主要受太平洋板块俯冲作用的影响,在我国东部的铅锌矿受岩浆作用影响显著,主要形成了矽卡岩型、各类围岩脉型等铅锌矿。它们主要分布在湘东—赣西成矿带和湘西—鄂西成矿带。典型矿床有广东凡口、安徽荷花山铅锌矿等。

第四纪的富镓矿床大部分为铝土矿,由原生沉积的铝土矿经历过后期的风化、沉积和成矿作用进一步形成品位较高、具有重要工业意义的铝土矿矿床。矿床类型以红土型铝土矿和堆积型铝土矿为主,其中,红土型铝土矿多分布于中国东南部沿海地区,堆积型铝土矿主要分布于云南、广西等省份。典型的富镓矿床有桂西田阳、桂西平果、靖西新圩、丘北古城等。

3 镓的富集成矿机制

3.1 寄主矿物

沉积型铝土矿典型剖面图及镓含量变化(图 4)表明,镓主要分布于含铝岩系中,分布状态与铝相似,富镓铝土矿中 Al_2O_3 和镓含量呈明显的正相关关系,即镓的含量随 Al_2O_3 含量增加而增加(图 7)。这是由于在铝土矿形成过程中,镓与铝紧密伴随(Ga^{3+} —— $0.62\text{\AA}$)与(Al^{3+} —— $0.57\text{\AA}$)离子半径相近,镓与铝之间容易发生类质同象(刘英俊, 1965; 汤艳杰等, 2002; 刘平, 2007; Schulte and Foley, 2013),推测镓以分散状态进入含铝矿物的矿物晶格之中。

近年来,我国学者发现了煤中镓异常富集和存在一些有巨大经济价值的富镓矿床(Dai et al., 2006, 2008, 2012, 2018; 秦勇等, 2009; 王文峰等, 2011; 宁树正等, 2019)。统计数据表明,煤矿之中镓与铝的含量呈现正相关(图 7)。镓在煤矿中赋存形式有有机态、有机态和混合形式但在中国多以无机态为主,载体矿物主要有勃姆石、硬水铝石等(Dai et al., 2012; 代俊峰等, 2021)。如,黑岱沟煤矿中镓主要寄主矿物为勃姆石(代世峰等, 2006),淮北朱庄的主要寄主矿物则为一水硬铝石和高岭石(李祥和李伍, 2022)。

前人研究表明,并非所有的铅锌矿床都属于富镓矿床,与岩浆作用有关的铅锌矿床中镓含量小于与热液作用有关的铅锌矿床(Zhang, 1987)。镓具有

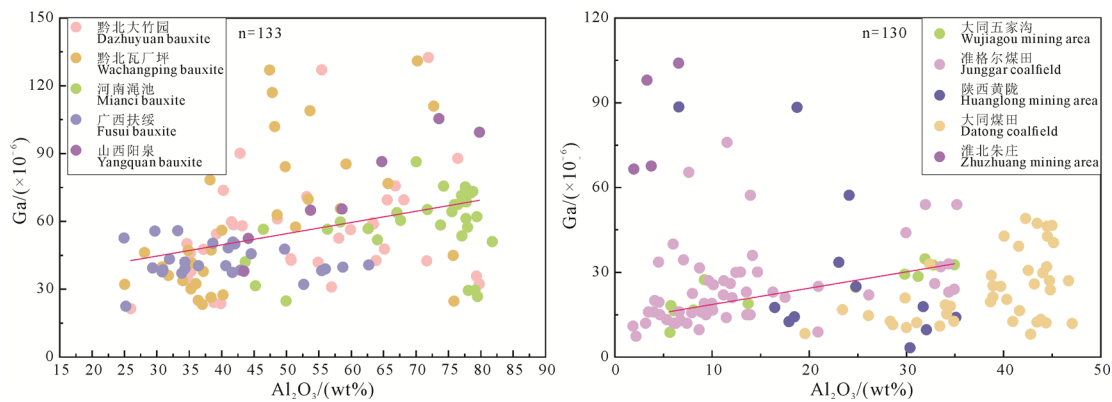
亲硫(铜)的地球化学属性,且 Ga^{3+} 是最稳定的价态,与 Zn^{2+} 和 Fe^{2+} 属于 6 配位,推测铅锌矿中,镓以类质同象的形式进入以闪锌矿为主的硫化矿物晶格(涂光炽等, 2004; Jansson et al., 2016)。

3.2 成矿机制

岩浆活动对铅锌矿床成矿主要有两种影响,一是供应物质来源,二是为成矿供应热源(李建源, 2015)。铅锌矿成矿之前,地幔隆起导致地壳拉张,然后基性-超基性岩侵入,之后岩浆侵入则带入了成矿元素,在热液作用下,矿床与容矿层也发生了改变。

煤中镓富集过程主要分为四个:①成矿物质准备阶段;②成矿物质迁移阶段;③成岩作用阶段;④后期改造阶段(陈磊, 2019)。准格尔煤田中一水软铝石和一水硬铝石等含镓矿物的主要来源是本溪组铝土矿,铝土矿在遭受风化剥蚀之后搬运到聚煤盆地之中,含镓矿物释放。在第一阶段结束时,含镓物质随着溶液进行移动,在这一过程中镓以类质同象的形式进入含铝矿物的矿物晶格之中,含铝物质通常以 $\text{Al}(\text{OH})_3$ 胶体的形式存在。随后, $\text{Al}(\text{OH})_3$ 胶体被带入煤炭沼泽之中,在成岩作用下压实脱水后形成铝硅酸盐矿物。成煤阶段后期构造运动导致岩浆侵入,在岩浆热液的烘烤下煤层中的镓进行再分配,如勃姆石进一步形成硬水铝石(Dai et al., 2012)。此外,地表水渗流使得原煤层中的镓可能被黏土矿物吸附,或者与含铝矿物发生类质同象,从而发生富集。

铝土矿形成可以分为三个阶段:成矿物质形成阶段、成矿物质迁移阶段和后期改造阶段(Bárdossy and Aleva, 1990; Bogatyrev and Zhukov, 2009)。含矿岩系中镓的分布以及迁移富集与铝的关系密切。在成矿物质形成的过程之中,母岩受到强烈的风化作用和淋滤作用而溶解其中的铝硅酸盐矿物,在酸性条件下长石类岩石会溶解(樊钰超和齐永安, 2017),其中的 Si 及大量碱性成分被排出和淋失,镓与铝固定于残余的风化产物之中,铝以三水铝石、勃姆石的形式与铁的氧化物、氢氧化物相对聚集,为沉积型铝土矿的形成提供了原始的铁-铝物质。在成矿物质迁移阶段,风化母岩之中 Si 和大部分碱性元素已经被分选出去,部分 Fe、Al、S 留了下来,然后海水侵入发生沉积作用,高铁高硫铝土矿形成。随着地壳发生升降运动,高铁高硫铝土矿由于沉积分异作用对矿物的晶体结构进行了改造,镓以类质同象的方式,进入一水硬铝石、一水软铝石、蒙脱石等矿物的晶体结构之中,或者吸附在黏土矿物和铝、铁的氢氧化物表面。另外,部分的 Fe、Al 与 Ga 则以离子的形式,从铝土矿中淋滤出来后继续向下迁

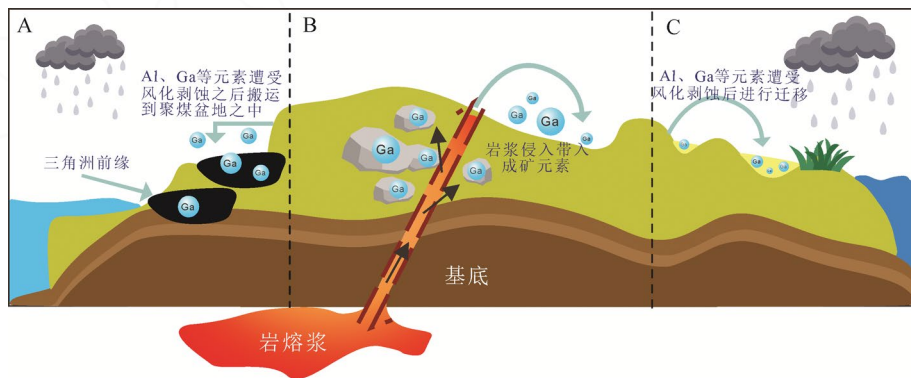


数据来源: 黔北大竹园据李沛刚等, 2014; 河南渑池据袁爱国, 2010; 广西扶绥据余文超, 2017; 山西交口据陈平和柴浩然, 1997; 黔北瓦厂坪据黄智龙等, 2014; 大同五家沟据李进孝等, 2020; 准格尔煤田据刘大锐等, 2018; 袁月, 2015; Dai et al., 2008; 淮北朱庄据李祥和李伍, 2022; 山西黄陇据张勇, 2013; 大同煤田据 Shao et al., 2022。

Data sources: Dazhuyuan of Qianbei County from LI et al., 2014; Mianchi of Henan Province from YUAN, 2010; Fusui of Guangxi from YU, 2017; Jiaokou of Shanxi from CHEN and CHAI, 1997; Wachangping of Northern Guizhou from HUANG et al., 2014; Wujiagou of Datong from LI et al., 2020; Junggar coalfield from LIU et al., 2018; YUAN, 2015; Dai et al., 2008; Zhuzhuang of Huaibei from LI and LI, 2022; Huanglong of Shanxi from ZHANG, 2013; Datong Coalfield from Shao et al., 2022.

图 7 铝土矿、煤矿中 Ga 与 Al_2O_3 相关性图(左: 铝土矿, 右: 煤矿)

Fig. 7 Correlation between Ga and Al_2O_3 in bauxite and coal mine (left: bauxite, right: coal mine)



A—煤矿; B—铅锌矿; C—铝土矿。

A—coal; B—lead-zinc ore; C—bauxite.

图 8 煤矿、铅锌矿和铝土矿中 Ga 富集成矿理想模型

Fig. 8 Ga enrichment in coal, lead-zinc ore, and bauxite

移, 富集于底部, 就构成了底部的低铁低硫型铝土矿。在后成岩作用阶段, 变质作用阶段以及表生风化淋滤作用阶段, 铝土矿层经过逐步的脱硫、去硅、除铁, 最终形成高品质的铝土矿。镓与铝关系密切二者一起迁移、一起堆积、一起富集, 但由于镓的地球化学性质比铝更活泼, 在元素迁移阶段过程之中二者分离, 在碱性环境之中镓优先于铝沉积下来, 导致富镓层位产出的比富铝层位略低一些(图 8)。

4 找矿方向

4.1 铝土矿中伴生镓资源找矿方向

镓作为一种战略性大宗矿产, 若要保障其国内资源安全, 加强镓的找矿工作是必然的选择。前文已述及, 全球超过 50% 的镓来自铝土矿之中, 其次为煤矿和铅锌矿(敦妍冉等, 2019)。这说明铝土矿是镓最主要的来源, 而我国铝土矿类型超过 80% 为古风化壳沉积型, 其次为堆积型铝土矿(15%), 红土

型铝土矿资源量占比最少(廖士范和梁同荣, 1991; 高兰等, 2015)。因此, 关于我国伴生镓资源的找矿可以以沉积型铝土矿和堆积型铝土矿做为主攻方向, 兼顾煤矿和铅锌矿等其他伴生镓矿床。重点在河南、山西、广西、重庆、云南和贵州等省份开展。

4.1.1 华北地区

晋豫成矿区是我国铝土矿资源量最多的区域, 其中伴生镓资源也是极其可观的。早古生代, 华北板块与华南扬子板块之间的秦岭海继续存在。加里东期, 华北板块继续抬升并经历长时间的风化、剥蚀与夷平。直到中石炭世, 因受海西运动海侵的影响, 地壳开始缓慢下降, 然后进行海陆交互相沉积(刘国栋等, 2021)。古风化壳中硅、铝、铁等物质因受海泛剧烈影响, 被海水冲刷到古陆附近的低洼地带富集。经过长时间的沉积构成了我国最著名的含铝岩系“山西式铁矿”。近年来, 地勘基金、整装勘查以及地方单位自筹资金等各类勘查项目, 华北

地区伴生镓铝土矿床找矿工作已经取得重大突破。如山西孝义发现一处特大型铝土矿床,其中伴生镓资源量达到了4 417.71 t;山西中阳县下枣林矿区发现特大铝土矿之中估算伴生镓资源量2 113.6 t;在豫西礼庄寨铝土矿中发现伴生镓资源量1 041 t;豫西新安县郁山发现伴生镓资源量1 739 t等。因此,可以对山西省孝义、吕梁市兴县、临沂市汾西和长治市沁源,河南省平顶山宝丰县、三门峡渑池县、陕县、郑州新密县、登封市和洛阳市偃师等地区的铝土矿开展伴生镓资源调查和勘查工作。富镓矿物以硬水铝石为主的铝土矿床,其中伴生镓的含量基本上超过了工业品位(温汉捷等, 2020)。由于镓元素主要赋存于含铝矿物,镓与铝呈强正相关关系,所以矿区里应主要研究铝土矿中的铝含量,如果铝土矿铝含量较高则有寻找到伴生镓矿的可能。

4.1.2 西南地区

扬子陆块西南成矿区是我重要的古风化壳沉积型铝土矿产区,该区晚古生代全球大地构造运动再一次活跃起来,早二叠世冰期-间冰期发生的海平面运动。在此期间,海平面的频繁变化使我国的铝土矿成矿作用呈现加强的趋势。华南板块的古纬

度位于热带辐合带内,在冰期海平面下降,大量基岩暴露且经历剥蚀,同时期低地下水水位将导致垂向淋滤作用控制下的铝土矿化作用产生(余文超, 2017)。2011年以来,尤其是在该区设立国家级整装勘查区以来,也取得了一系列重要进展。如:贵州大竹园铝土矿查明伴生镓金属量5 448.25 t;新民铝土矿伴生镓远景资源储量7 534 t(欧德琳和周静, 2010; 苏之良等, 2021)。因此,贵州省务一正一道地区和重庆市南川区、武隆县等地区的铝土矿为扬子陆块西南成矿区Ga找矿的重点远景区。

右江成矿区是我国堆积型铝土矿主要分布带。铝土矿堆积于第四纪的岩溶洼地中,经过岩溶作用后所形成的,但不会在岩溶作用时终止,在之后还会进入红土化阶段。矿石呈现出大小不一的块、砾、碎屑状堆积于松散的红土之中,其上可能覆盖有松散红土。堆积型铝土矿剖面大致可以分为三层(刘枝刚, 2005; 张佳莉等, 2016):底部黏土层、中部矿层和顶部黏土层(顶部或无覆盖层)。镓在矿层中上部含量较高,在铁质岩和铝土矿中明显富集。镓作为铝土矿的伴生矿,其平均含量已经达到了镓元素的伴生工业指标要求(表5)。如,云南文山、砚山和丘

表5 我国伴生镓铝土矿中镓平均含量
Table 5 Average gallium content in gallium-associated bauxite in China

成矿区	成矿带(矿区)	$\omega(\text{Ga})/\times 10^{-6}$ (样品数量)				
		铁质岩	铝土矿	铝土岩	铝质黏土岩	黏土岩
晋豫成矿区	交口—汾西	24.42(3)	39.9(14)	38.7(6)	32.5(7)	37.38(7)
	临县—中阳	—	45.6(3)	45.05(2)	—	43.75(2)
	沁源	—	56.2(3)	59.5(2)	—	—
	宁武—原平	25.1(7)	51.55(7)	29.1(2)	31.05(7)	36.2(6)
	朔州	—	59.45(4)	—	—	35.5(2)
	孝义—汾阳	23(2)	69.85(6)	47.76(5)	—	45.6(3)
	阳泉	—	71.86(11)	49.63(3)	—	34.05(4)
	三门峡—渑池—新安	3.61(1)	60.27(20)	38.75(8)	51.7(3)	52(1)
	汝州—宝丰—鲁山	—	60(6)	—	30.32(1)	—
	蒿萁	—	18.77(10)	28.15(2)	36.34(2)	—
扬子陆块西南缘	宜阳—汝阳	54.88(4)	40.12(9)	37.48(8)	37.14(8)	21.12(3)
	大竹园	51.02(8)	52.65(47)	45.59(12)	6.18(10)	—
	瓦厂坪	26.33(1)	64.85(18)	80.46(5)	37.77(12)	2.32(1)
	新民	55.9(2)	47.34(22)	54.11(8)	28.17(11)	3.11(1)
	小山坝	17.7(1)	22.5(2)	—	24.55(6)	17.7(1)
	凯里—瓮安—福泉	—	36.05(10)	—	22.2(7)	—
	遵义—息烽	—	22.48(4)	42.11(2)	35(2)	30(1)
	新木—宴溪	—	54.10(18)	—	31.85(8)	6.57(3)
右江成矿区	文山	31.89(7)	67.14(1)	28.6(1)	38.7(2)	—
	砚山	—	59.09(1)	—	—	—
	丘北	35.72(5)	41.62(3)	25.26(3)	32.63(10)	—
	靖西新圩	75.39(3)	70.14(5)	—	—	—
	靖西大甲	47.57(3)	25.46(21)	—	—	37.7(1)

数据来自: 廖士范和梁同荣, 1991; 陈平和柴浩然, 1997; 刘枝刚, 2005; 叶霖等, 2008; 袁爱国, 2010; 孟健寅等, 2011; 孙思磊, 2011; 王燕茹等, 2012; 于蕾, 2012; 崔滔, 2013; 冯跃文, 2013; 康微, 2013; 李再会等, 2013; 李玉娇等, 2013; 田茂军, 2013; 王佳奇, 2013; Wang et al., 2012; 邓国仕等, 2014; 黄智龙等, 2014; 李沛刚等, 2014; 焦扬, 2014; Yu et al., 2014; 程琰勋等, 2015; 赵晓东等, 2015; 乔龙, 2016; 温静静等, 2016; 樊钰超和齐永安, 2017; 余文超, 2017; 负孟超等, 2017; 白俊豪等, 2018; 金中国等, 2018; 王行军等, 2018。

北县等地, 广西大甲、新圩、平果和德保等地区的铝土矿均有可能形成伴生镓矿。

4.2 煤矿中伴生镓资源找矿方向

我国煤矿中伴生镓资源找矿应重点从华北地区和西北地区入手, 华北地区和西北地区的煤中伴生镓资源量高于西南, 且通过统计数据可以发现华北地区煤中伴生镓含量高于西南地区(表 4)。其中准格尔 6 号煤层中 Al_2O_3 的含量为 28.54%~64.9%, 平均含量为 40.76%, 且镓的含量为 $\sim 92 \times 10^{-6}$ (张复新和王立社, 2009; 伍泽广等, 2013; 代俊峰等, 2021)。准格尔煤田中大部分矿井中伴生镓元素超过了煤中伴生镓工业品位。准格尔煤田黑岱沟煤矿位于鄂尔多斯东北缘, 区内断层规模不大, 矿床受到小型的褶曲构造影响。在黑岱沟煤矿之中发现火山晶屑和火山灰, 二者提供了易分解的铝、镓物源, 铝和镓在煤层或夹矸之中富集。黑岱沟煤田是在三角洲沉积体系中形成的巨厚煤层, 三角洲平原有利于泥炭沼泽化, 容易形成巨厚煤层, 导致铝元素更容易富集在煤田之中, 形成高铝煤炭, 而镓与铝共同迁移, 所以在三角洲体系下的煤层更容易发现伴生镓资源。

4.3 铅锌矿中伴生镓资源找矿方向

不是所有类型的铅锌矿床都是富镓的。我国富镓矿床大多数为碳酸盐岩(MVT)型, 该类矿床很少发育在裂谷之中, 多形成于造山带前陆盆地和褶皱之中, 且矿床形成与岩浆活动无明显关系, 主要受到中-低温热液作用形成矿床(宋玉财等, 2017; Liu et al., 2018), 伴生镓含量较高的铅锌矿床多为低温热液型和经过沉积改造的矿床(袁莹等, 2011; 温汉捷等, 2020)。铅锌矿中镓主要与闪锌矿有关, Ga 以类质同象的形式取代 Zn 进入闪锌矿的矿物晶格之中。统计数据显示, 湘东—粤东矿集区的铅锌矿矿床之中伴生的 Ga 含量明显高于其他区域(表 4)。

5 结论

(1) 经过对前人研究分析和对比, 本文总结划分出了五个富镓矿床类型, 依次为: 沉积型铝土矿型、堆积型铝土矿型、红土型铝土矿型、煤矿型、碳酸盐岩(MVT)型。在上述富镓矿床类型之中, 已知赋存其他成矿元素有 Sc、Li、Cd、In、REE 等。目前对开发新矿山的限制导致了寻找替代资源, 常规矿床中金属储量的减少, 以及这些有价值金属在现代技术中的应用日益增多, 可以把目光投入到矿床中提取以及利用稀散金属元素。

(2) 我国镓矿床均为伴生矿, 根据其赋存矿床划分成矿带可划分为: 晋豫成矿区、右江成矿区、扬

子陆块西南成矿区、川—滇—黔成矿带、湘西—鄂西成矿带、湘东—赣西成矿带、华北陆块北缘成矿区。成矿作用类型有风化-沉积、生物化学沉积、热液作用等。富镓矿床主要成矿于石炭纪、二叠纪、侏罗纪和第四纪。风化-沉积作用形成的富镓矿床主要成矿时代为石炭系。晋豫成矿区、右江成矿区、扬子陆块西南成矿区可以成为风化-沉积型 Ga、Li、Sc、REE 等稀有金属找矿远景区。湘西—鄂西成矿带、湘东—赣西成矿带和川—滇—黔成矿带为碳酸盐岩(MVT)型 Ga、Cd、In 等稀有元素找矿远景区。

(3) 我国富镓矿床分布广泛, 形成时期较多, 主要形成时期为早、晚古生代和中生代。在空间分布上也相对集中于川—滇—黔地区、湘粤地区和晋豫等地区。我国伴生镓资源的找矿可以以沉积型铝土矿和堆积型铝土矿做为主攻方向, 兼顾煤矿和铅锌矿等其他伴生镓矿床。

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