

黑色岩系型战略性关键矿产资源研究进展 及主要科学问题

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摘要: 本文对近年来黑色岩系型战略性关键矿产的分布规律和超常富集机制等方面的研究进展进行了归纳总结, 并对战略性关键矿产资源研究进行了展望。黑色岩系分为黑色页岩、煤系地层和富碳质磷块岩等沉积地层, 其中黑色页岩中发生超常富集的关键金属有Se、Te、Re、Cd、Tl等稀散金属, 以及PGE、Co等稀贵金属; 煤系中可见Ga和Ge的超常富集(形成独立的Ga、Ge矿床), 同时也可见稀土金属、稀贵金属的富集; 磷块岩中常显著富集稀土, 尤其是中重稀土。黑色岩系中的关键金属主要源自大陆风化、海水、热液以及生物摄取。在风化沉积作用中, 硫化-还原水体环境形成的泵吸效应, 有机质的还原作用, 富有机质沉积体系中有有机质、铁锰氧化物、磷灰石、黏土矿物等的络合和吸附是关键金属发生富集的主要机制。黑色岩系可为热液叠加过程提供成矿金属, 调节热液体系的氧逸度和硫逸度, 促进超大型战略性关键矿产的形成。此外, 黑色岩系富集的金属在地球层圈物质循环中的聚散行为还可对其他相关成矿系统产生影响。黑色岩系中战略性关键金属的超常富集与大陆边缘、裂谷等环境下缺氧-硫化的沉积事件相关。大气氧含量的变化、超大陆的聚合和裂解、洋流环流模式的改变、冰期以及大规模火山活动导致的海洋缺氧事件等区域地质事件均可控制黑色岩系型战略性关键金属形成及时空分布的主要因素。黑色岩系是表生风化沉积中的一种重要类型, 今后应更加重视黑色岩系等表生风化沉积作用在战略性矿产资源形成中的重要性, 建立和发展相关的成矿理论。

关键词: 黑色岩系; 战略性关键矿产资源; 超常富集机理; 成矿过程

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Research progresses and main scientific issues of strategically critical minerals in black rock series

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Abstract: In this paper, research progresses on the distribution and supernormal enrichment mechanism of strategically critical minerals in black rock series in recent years have been summarized, and the prospect of researches on strategically critical mineral resources has been provided. The black rock series include sedimentary strata of black shale, coal-bearing strata and carbon-rich phosphorite. Especially, critical metals which were supernormally enriched in black shale include rare metals of Se, Te, Re, Cd, Tl as well as rare and precious metals of PGE, Co and others. The supernormal enrichment of Ga and Ge, commonly occurred in coal-bearing strata, led to the formation of independent Ga/Ge deposits. The enrichment of rare earth metals and rare precious metals also

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occurred in coal-bearing strata. Rare earth elements, particularly medium and heavy rare earth elements, were significantly enriched in phosphorites. The strategically critical metals in black rock series were mainly derived from continental weathering products, seawater, hydrothermal fluid, and the uptake of biological organisms. In the weathering and sedimentation processes, the main mechanisms responsible for the enrichment of critical metals include the pumping effect caused by the vulcanization-reduction water column, organic matter reduction, and complexation and adsorption of organic matters, iron and manganese oxides, apatite and/or clay minerals in organic-rich sedimentary systems. The black rock series can serve as a source of ore-forming metals for the hydrothermal overprinting process, regulate the oxygen and sulfur fugacities in hydrothermal systems, thereby facilitate the formation of super-large strategically critical mineral resources. In addition, it is crucial to acknowledge that metal accumulation and dispersion behaviors within the black rock series may have significant influences on other related metallogenic systems. The supernormal enrichment of strategically critical metals in black rock series is commonly associated with anoxic-vulcanization sedimentary events in continental margin and rift basin environments. Regional geological events, such as variations of atmospheric oxygen contents, the assembly and breakup of supercontinents, changes of ocean current circulation patterns, and ocean anoxia events caused by the glaciation, and large-scale volcanic activities, are likely primary factors controlling the formation and temporal and spatial distribution of strategically critical metal deposits within black rock series. The black rock series is of a significant sub-type of rocks formed through the epigenetic weathering and sedimentation process. In the future, more attention should be paid to the importance of rocks formed through the epigenetic weathering and deposition processes, such as the black rock series, in the formation of strategically critical mineral resources, and related metallogenic theories of strategically critical minerals should be established and developed.

Key words: black rock series; strategically critical minerals resources; supernormal enrichment mechanisms; metallogenic process

0 引言

黑色岩系是指含有机碳(>0.5%)及硫化物(铁硫化物为主)较多的深灰-黑色的硅岩、碳酸盐岩、磷块岩和泥质岩(含层凝灰岩)及其变质岩石的组合体系,是含有大量黏土级碎屑颗粒、具有纹层结构通常形成于洋盆或陆缘盆地内的还原性岩石(Wignall, 1991, 1994; 范德廉等, 2004; Johnson, 2017)。黑色岩系在地质历史时期广泛分布,与海水、大气、生物演化以及重要的沉积矿产紧密相关,所记录的古气候、缺氧事件、成矿作用等信息是重建古海洋及古大气演化特征及驱动机制的重要信息(图1; Wignall and Twitchett, 1996; Wen et al., 2009; Johnson et al., 2017; Zhang, 2023)。此外,黑色岩系还赋存了巨量的矿产资源,是沉积喷流型和火山块状硫化物型矿床的一种重要赋矿围岩(Goodfellow and Jonasson, 1984; Zierenberg et al., 1998; Barrie et al., 1999; Goodfellow et al., 2003; Sáez et al., 2011),同时也是最重要的油气烃源岩(Levan and Pawlewicz, 2017; Zhang, 2023)。全球目前发现储量位居前列的铅锌矿床(McArthur River矿床; Spinks et al., 2021)、重晶石矿床(大河边重晶石矿床; Zhou et al., 2018)、铁矿床(Carajas铁矿; Cabral et al., 2013)都发育在与黑色岩系相关的沉积地层中。因此,

自20世纪80年代中后期开始,国际上先后开展了“含金属黑色页岩”“有机质与矿产资源”“重要环境中的有机质”等国际地质对比计划(IGCP)(范德廉等, 2004),对黑色岩系进行系统研究,直至今日仍方兴未艾。

黑色岩系对战略性关键矿产资源的富集同样令人瞩目。战略性关键矿产资源是指现今社会必需、但安全供应存在较高风险的矿产资源,主要包括稀有金属(Li、Be、Rb、Cs、Nb、Ta、Zr、Hf、W、Sn等)、稀土金属(La、Ce、Pr、Nd、Sm、Eu、Gd、Tb、Dy、Ho、Er、Tm、Yb、Lu、Sc、Y)、稀散金属(Ga、Ge、Se、Cd、In、Te、Re、Tl)和部分稀贵金属(PGE、Co等)(翟明国等, 2019; 侯增谦等, 2020)。大多数关键金属元素的地壳丰度都很低(一般为ppm级以下),形成可供开采的矿床往往需要数百倍甚至上万倍的富集(翟明国等, 2019; 蒋少涌等, 2019; 侯增谦等, 2020)。黑色岩系由于往往沉积于大陆边缘盆地、裂谷盆地等构造环境,并可作为良好的地球化学障,是战略性矿产资源形成超常富集的重要载体。黑色岩系对氧化还原敏感元素以及部分亲硫元素可以发生显著富集,包括Mo、Ni、V、U、P、Cu、Zn、Pb、Co、Cd、Re、Se、Hg等(Lott et al., 1999; Jiang et al., 2007; Lehmann et al., 2007; Xu and Mao, 2021)。此外,部分黑色岩系还含有相当高含量的稀土金属、铂族金属、Au、Ag及Li、Cs等稀有金属(Yi et al., 2017;

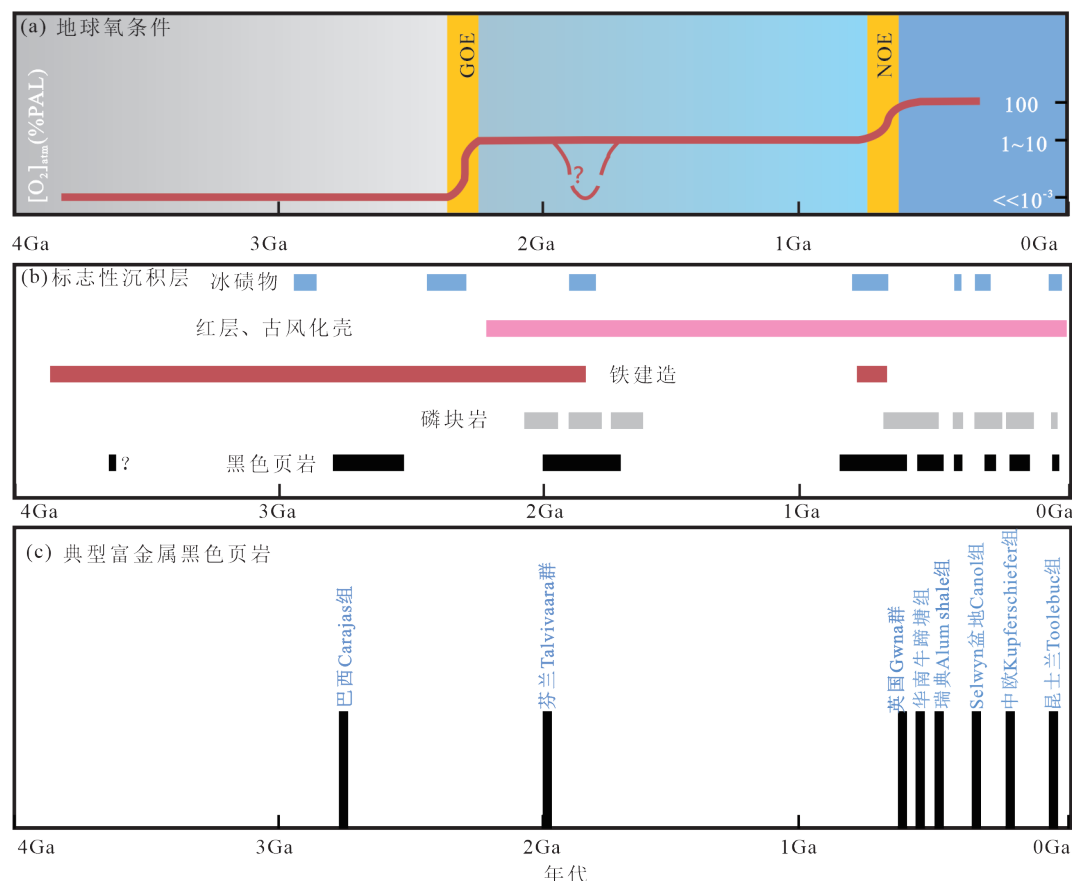


图1 黑色岩系等特征性沉积层与地球氧条件的对应关系(a、b修改自Canfield et al.,2013;Lyons et al.,2021)

Fig.1 The temporal distribution of black rock series and other typical sedimentary strata on earth, as well as their corresponding relationships with oxygen conditions (a and b,modified from Canfield et al.,2013;Lyons et al.,2021)

Takaya et al.,2018;Ling et al.,2021;Yang et al.,2021;Zhao et al.,2023)。因此,黑色岩系对稀散金属、稀土金属、稀有金属及稀贵金属都可能形成超常富集,显示出黑色岩系在战略性关键矿产资源的成矿或超常富集过程中具有特殊的成矿作用。富集战略性关键矿产资源的黑色岩系分布范围广、从晚太古界到下白垩统都有分布,典型黑色岩系包括巴西晚太古界Carajas组、芬兰早元古界 Talvivaara 组、英国晚元古界Gwna群、中国华南下寒武统牛蹄塘组、波罗的海盆地上寒武统一下奥陶统Alum Shale组和Dictyonema Shale组、Selwyn盆地中泥盆统Canonl组、中欧上二叠统Kupferschiefer组、昆士兰下白垩统Toolebuc组(表1)。大面积分布的富金属的黑色岩系显示出巨大的战略性关键矿产资源成矿潜力,Poul Emsbo在美国地质年会中提到黑色岩系中的部分关键矿产资源的品位和储量可能超过地球上任何其他金属矿床(Emsbo,2022)。黑色岩系的分布与大气、生物演化及重要的沉积矿产紧密相关(图1),正确解译黑色岩系型战略性关键矿产资源的富集过程、与重大地质事件及表生环境之间的耦合关系,对建立此类资源成矿理论十分关键。不少学

者已对这类战略性关键矿产资源的成矿作用开展了较深入的研究,取得重要成果。本文概述了全球范围内黑色岩系型战略性关键矿产资源的主要矿床类型和分布特征,以及成矿过程、超常富集机理的认识。在此基础上,初步探讨了此类成矿作用在战略性关键矿产资源研究中的启示,并为未来工作提出展望和建议。

1 黑色岩系型战略性关键矿产的分布特征

1.1 稀散金属

稀散金属是指在地壳中丰度很低,在岩石中极为分散,形成矿物并大量堆积的几率很低,成矿需要苛刻条件且很难形成独立矿床的一类元素,包括Cd、Ga、In、Tl、Ge、Se、Te、Re(涂光炽,2004)。黑色岩系是稀散金属发生超常富集的重要载体,可以对稀散金属发生高度富集。全球富稀散金属的黑色岩系沉积期集中在古元古代、寒武纪、泥盆纪、二叠纪及石炭纪(Johnson,2017)。范德廉等(2004)对我国中元古界到下二叠统黑色岩系中稀散元素含量进行了系统研究,发现早二叠世、早寒武世、泥盆纪和早震旦世是稀散元素大

表 1 典型富集战略性关键矿产资源黑色页岩的分布及地质特征

Table 1 The distribution and geological characteristics of typical black shales with enriched strategically critical mineral resources

地层	时代	产状	典型矿床	沉积环境	主要富集的 战略性关键矿产	参考资料
巴西 Carajas组	~2.7 Ga	条带状铁建造的顶部、底部以及呈夹层分布于其中	—	裂谷盆地	Co	Klein and Ladeira, 2002; Cabral et al., 2013
芬兰 Talvivaara群	2.0~1.9 Ga	黑色页岩层延伸超过100 km, 厚度~600 m; 矿层厚度40~400 m	Kuusilampi/ Kolmisoppi	大陆边缘缺氧-硫化沉积盆地	Cd/Se/Co/PGE	Loukola-Ruskeeniemi and Heino, 1996; Loukola-Ruskeeniemi and Lahtinen, 2013; Kontinen and Hanski, 2015; Johnson, 2017
英国 Gwna群	580~570 Ma	地层延伸超过200 km, 厚度5~10 cm	—	深海缺氧盆地	Te/Se/Co	Sato et al., 2015; Armstrong et al., 2018
华南 牛蹄塘组	~521 Ma	黑色页岩层延伸超过1500 km, 厚度30~150 m; 矿层厚度3~20 cm	张家界/ 遵义/ 织金	被动大陆边缘缺氧-硫化盆地	Cd/Se/Re/PGE/ Co	Jiang et al., 2007; Wen et al., 2009; Xu et al., 2011, 2013; Xu and Mao, 2021; Lehmann et al., 2022
波罗的海盆地 Alum Shale组和Dictyonema Shale组	晚寒武世—早奥陶世	黑色页岩厚度主要为15~35 m	—	大陆边缘缺氧盆地	Se/Te/Re/PGE/ Co/ REE/Cs	Wignall, 1994; Vyalov et al., 2013; Lecomte et al., 2017
Selwyn盆地 Canonl组	中—晚泥盆世	黑色页岩层厚度~5m; 矿层厚度1~10 cm	Nick/ PeelRiver/ MonsterRiver/ EaglePlains	被动大陆边缘缺氧盆地	Cd/Se/Re/Tl/PGE/ Co	Orberger et al., 2007; Pagès et al., 2018; Gadd et al., 2019, 2020
中欧 Kupferschierfer组	245~264Ma	黑色页岩层产出稳定, 出露面积大, 厚度0.4 m至数米	Rudna/ PolkowiceSieroszo- wice/ Lubin	裂谷盆地边缘缺氧盆地	Re/Se/Ge/ Cd/ Co/ PGE	Alderton et al., 2016; Horn et al., 2021; Foltyn et al., 2022
昆士兰 Toolebuc组	中白垩世	黑色页岩厚度小于35 m	—	缺氧海底	Cd/ Re	Hirner and Xu, 1991; Lewis et al., 2010

量富集的时期,Se、Te、Re、Cd、Tl在这些时期均有显著富集,这与全球富金属黑色页岩的沉积期相一致。黑色岩系对稀散金属的富集具有两个典型特征,一是可以形成独立矿床,如临沧Ge矿床、渔塘坝Se矿床、沐川Re矿床;二是可以对多种稀散金属发生同步富集,华南下寒武统牛蹄塘组、加拿大育空地区Selwyn盆地内中泥盆世Canonl组、中欧上二叠统Kupferschierfer组黑色页岩均富集Se、Re、Cd、Tl等。依据矿床的产出特征和成因,可以将黑色岩系型稀散金属矿床分为黑色页岩型、煤型和热液叠加型三类。

1.1.1 黑色页岩型 黑色页岩是狭义上的黑色岩系,由于黑色页岩大多形成于洋盆或者大陆边缘盆地的还原性底部水体(Arthur and Sageman, 1994),因此黑色页岩的沉积可以对Se、Re、Te等氧化还原敏感元素发生高度富集。Se、Te、Cd等的亲有机质性也促使其在富有机质的黑色页岩中发生一定程度的富集。目前已经资源化利用或潜在可利用的黑色页岩沉积层包括芬兰早元古界Talvivaara群(Cd、Se)、英国晚元古界Gwna群(Te、Se)、华南下寒武统牛蹄塘组(Se、Re、Cd)、波罗

的海盆地上寒武统到下奥陶统Alum Shale组和Dictyonema Shale组(Se、Te、Re)、华南上奥陶统-下志留统五峰组和龙马溪组黑色页岩(Re)、Selwyn盆地中—上泥盆统Canonl组(Cd、Se、Re、Tl)、上扬子下二叠统茅口组(Se)和中欧上二叠统Kupferschierfer组(Re、Se、Ge、Cd)(表1)。稀散金属在黑色页岩中的赋存方式主要为有机质结合态及硫化物(闪锌矿、黄铁矿等)形式(Wen et al., 2006; Fan et al., 2011; Gregory et al., 2015; 温汉捷等, 2007)。Wen等(2006)发现湖北恩施渔塘坝硒矿床中的硒主要以单质硒形式存在,呈纳米级分布,并被干酪根紧密地黏附或包裹。华南下寒武统牛蹄塘组富集的Re主要赋存在硫碳钼矿中, Cd主要赋存于闪锌矿中(Zhou et al., 2024)。

黑色页岩中稀散金属可能源自海水、热液以及生物残骸:①海水来源。大陆边缘半封闭受限制的沉积盆地具有极低的沉积速率和极少的陆源碎屑供给,这种盆地的海水具有表层氧化及底层缺氧的分层特征,盆地底部还原、富硫的环境可以形成“泵吸效应”,从而使海水中的金属大量富集沉淀在富有机质的黑色页岩

中(Mao et al., 2002; Lehmann et al., 2007, 2016; Xu et al., 2013; Frei et al., 2020; 徐林刚等, 2022)。②热液来源。富金属黑色页岩层产出与区域伸展断层相关, 在拉张构造环境中, 热液可以沿着拆离断层对流循环并上涌至海底, 所萃取出地层及岩浆中的成矿物质在还原性沉积盆地中沉淀富集(Jowitt and Keays, 2011)。富金属的黑色页岩具有大量硫化物矿物以及钼冰长石等热液矿物组合, 且富金属黑色页岩往往与相邻普通页岩具有不一致的Se、Cd、Zn同位素信号, 反映稀散金属主要受海底热液喷流活动所控制(Covey and Glascock, 1989; Lott et al., 1999; Jiang et al., 2007; Pašava et al., 2008; Wen and Carignan, 2011; Fan et al., 2011, 2020; Yi et al., 2017; Zhou et al., 2018, 2023; Han et al., 2020, Han et al., 2022)。③生物残骸。Se、Cd等元素具有亲营养性, 可以被生物摄取利用, 会随着浮游生物等微生物的凋亡在沉积物中发生一定程度的富集(Wen and Carignan, 2011; Janssen et al., 2014)。部分磷块岩沉积层对Se发生富集, 摩洛哥Yousoufia地区的磷酸盐沉积层Se含量为 44×10^{-6} , 美国爱达荷州Champ矿床Se含量为 23×10^{-6} , 秘鲁Bayovar-Sechura磷酸盐矿床矿石硒含量为 2.4×10^{-6} (Bech et al., 2010a, 2010b); 我国贵州瓮安磷矿磷块岩的平均Se含量为 7.45×10^{-6} , 最高含量为 68.86×10^{-6} (Long et al., 2020)。Long等(2020)发现瓮安陡山沱组磷块岩中的Se主要富集在真核生物化石*Megasphaera*的细胞核部位。

1.1.2 煤型 煤和含煤建造可以高度富集Ga、Ge、Re、Se等稀散金属, 尤其是对Ga和Ge的富集更为显著。已有较多煤矿对Ga和Ge进行开发利用, 其资源量较大。煤型稀散金属矿主要产在褐煤和次烟煤中, 煤层夹矸或顶底板岩石中也可以形成富集。

全球煤型Ge矿主要分布在中国和俄罗斯远东地区, 是全球工业用Ge的主要来源。典型矿床包括云南临沧(Ge金属量1620 t, 品位 850×10^{-6})、内蒙古乌兰图噶(Ge金属量1700 t; 品位 274×10^{-6})、内蒙古伊敏煤田五牧场(Ge金属量>4000 t, 品位 $>100 \times 10^{-6}$)及俄罗斯远东地区的Spetzugli矿床(Ge金属量1665 t, 品位 700×10^{-6})(Dai et al., 2021, 2022)。白垩纪是重要的煤型Ge矿富集期(Dai et al., 2022)。在临沧和乌兰图噶矿床中, Ge在煤中主要以有机质结合形成螯合物的形式赋存(Etschmann et al., 2017; Wei and Rimmer, 2017; Dai et al., 2021), 褐煤因为其中有机质的侧链和官能团发育, 可以络合更多的Ge(Qin et al., 2018)。在乌兰图噶矿床中还可可见少量锆的氧化物或草酸盐矿物(Zhuang et al., 2006; Seredin et al., 2013)。Ge主要源

自沉积盆地周缘花岗岩, 长期的热液淋滤作用形成了富Si-Ge的热液流体并进入到泥炭沼泽中, 从而形成Ge的富集(代世峰等, 2020)。

煤可以对Ga发生富集。富Ga煤系的Ga含量大都为 $20 \times 10^{-6} \sim 40 \times 10^{-6}$, 相应煤灰中Ga的含量为 $100 \times 10^{-6} \sim 600 \times 10^{-6}$ (Seredin et al., 2013)。我国典型的富镓煤矿为内蒙古准格尔煤田的黑岱沟矿(Ga金属量5.4万t, 品位 $12 \times 10^{-6} \sim 76 \times 10^{-6}$)、官板乌素矿(Ga品位 $7.4 \times 10^{-6} \sim 54 \times 10^{-6}$), 内蒙古大青山煤田的阿刀亥矿(Ga品位 $5.7 \times 10^{-6} \sim 38 \times 10^{-6}$), 山西安武煤田平朔矿(Ga金属量超过15万t, 品位 $\sim 30 \times 10^{-6}$), 河北邢台煤田个泉矿(Ga金属量305 t)(Dai et al., 2008, 2012a; Zhao et al., 2009; Sun et al., 2013; Qin et al., 2015)。从时间分布上看, 我国富Ga煤矿主要分布在石炭纪—二叠纪和侏罗纪煤层中(秦勇等, 2009; Zhao et al., 2009; Qin et al., 2015)。秦勇等(2009)分析了我国石炭系—二叠系以及侏罗系煤层的5079个样本, 发现其中最富Ga样品的Ga含量可高达 1500×10^{-6} , 预测出16个大型和6个中型富Ga煤矿, Ga资源量达120.85万t。此外, Ga在煤层中还可以赋存在勃姆石、磷铝钙石、磷锆铝矿及一些黏土矿物中(Dai et al., 2018; Shao et al., 2018), 可以呈Ga-卟啉等有机化合形式存在(Bennett and Czechowski, 1980; Dai et al., 2012a; Qin et al., 2015), 少量Ga可以被腐殖酸或泥炭吸附, 或赋存在煤层的闪锌矿内(Swaine, 1990; 王文峰等, 2011)。煤中Ga的来源是沉积盆地临近已有铝土矿或铝土质沉积等陆源碎屑的引入(Dai et al., 2008)。

1.1.3 热液叠加型 沉积喷流型(SEDEX)矿床和火山块状硫化物矿床(VMS)大多形成于大陆边缘盆地及裂谷盆地, 矿体往往与盆地底部沉积的黑色岩系紧密共生或者空间毗邻, 这些黑色岩系在热液流体成矿过程中可以作为良好的地球化学障或屏障层(Large, 1992; Broadbent et al., 1998; Leach et al., 2005; Sáez et al., 2011; Wilkinson, 2014; Hannington, 2014)。从已有稀散元素矿床的产出来看, 在适宜条件下, 黑色页岩与SEDEX、VMS等热液体系在稀散金属成矿方面存在互馈机制, 形成稀散金属超常富集的矿床。其中重要的互馈形式主要体现在金属来源方面, 黑色岩系预富集的稀散金属可以被叠加热液体系进一步富集, 相应的是热液中的稀散金属也可能被黑色岩系所富集。目前比较典型的热液叠加于黑色岩系形成巨量稀散金属成矿的实例包括加拿大Finlayson Lake地区VMS矿床的Se矿化(Layton-Matthews et al., 2013)、澳大利亚McArthur Zn-Pb矿床的Ti矿化(Spinks et al., 2021)、澳大利亚Merlin矿床的Re矿化(Babo et al., 2017)及华

南下寒武统牛蹄塘组Cd-Se矿化(Wen and Carignan, 2011; Zhou et al., 2024)。

加拿大Finlayson Lake地区的VMS矿床:区内分布有许多泥盆纪—石炭纪形成的VMS矿床,其中Gp4F矿床贫Se, Kudzu Ze Kayah矿床对Se有中等程度富集, Wolverine矿床富Se。这三个矿床位置相近, Gp4F矿床和Kudzu Ze Kayah矿床赋存于360~356 Ma的长英质火山岩及沉积岩内; Wolverine矿床赋存于356~346 Ma的长英质火山岩、侵入岩及同期沉积岩,沉积岩中有碳质泥页岩(黑色页岩)夹层(Layton-Matthews et al., 2013)。三个矿床不同矿化带的Se平均含量分别为 5×10^{-6} ~ 18×10^{-6} , 76×10^{-6} ~ 518×10^{-6} 和 305×10^{-6} ~ 2729×10^{-6} ,其中Wolverine矿床的黄铜矿-黄铁矿带Se含量最高,可达 5865×10^{-6} (Layton-Matthews et al., 2013)。

澳大利亚McArthur Zn-Pb矿床:McArthur矿床位于北澳Carpentaria锌矿带的McArthur-Isa盆地内, Zn-Pb硫化物矿体赋存在(1640±3)Ma的Barney Creek组,主要赋矿层为其中的HYC黄铁矿化页岩层。HYC黄铁矿化页岩层的岩性为纹层状含白云质粉砂岩结核的碳质泥页岩,具有黄铁矿化,矿石中Tl含量最高可达 444×10^{-6} (Kunzmann et al., 2019; Spinks et al., 2021),其中黄铁矿的Tl含量为 176×10^{-6} ~ 919×10^{-6} ,是Tl的主要寄主矿物, Tl主要富集在早期黄铁矿周围的后期生长边等晚阶段黄铁矿之中(Mukherjee and Large, 2017; Spinks et al., 2021)。

澳大利亚Merlin矿床:Merlin矿床位于澳大利亚Cloncurry区,是目前发现的Re品位最高、储量最大的Re独立矿床,早期控制的资源量为6.4 Mt, Mo和Re平均品位分别为1.5%和 26×10^{-6} (Babo et al., 2017)。近年来在其邻区新发现了一些富Re矿床(如Kalman矿床),显示区域内巨大的Re成矿潜力(Babo et al., 2017)。Merlin矿床赋存在Kuridala群(1690~1650Ma),赋矿围岩岩性为互层千枚岩和碳质板岩、钙硅酸盐岩和硅化变粉砂岩, Mo-Re矿化充填在碳质板岩和钙硅质岩石的界面及层间角砾之中。辉钼矿Re-Os年龄显示Re成矿年龄为(1536±6)Ma(Babo et al., 2017)。Re主要源自隐伏长英质岩体分异的富Re热液以及区内富Re的碳质板岩,碳质板岩层在成矿中还起到还原障及提高硫逸度的作用(Babo et al., 2017)。

华南下寒武统牛蹄塘组Cd-Se矿化:华南下寒武统牛蹄塘组黑色页岩中发育一套Ni-Mo-Se多金属硫化物层,沿北东向断裂带零星分布,可能受深大断裂构造控制(Mao et al., 2002; Jiang et al., 2007)。在遵义Ni-Mo-Se多金属矿区,硫化物层沿走向连续延伸几千

米,东部矿区的平均厚度为5~30 cm,西部矿区的平均厚度为20~50 cm。在所有的金属中, Mo、Ni、Se的浓度最高,达到工业级。矿石储量为24万t Mo、15万t Ni和大约0.8万t Se。Se在黑色页岩和矿石中的平均含量分别为 99×10^{-6} 和 1900×10^{-6} 。化学分步提取、电子探针和透射电镜分析显示,矿石中高达72%的总硒与硫化物相有关,其中MoSC(Kao et al., 2001; Orberger et al., 2007)和针硫镍矿中分别含有0.65%和0.35%的硒。而黑色页岩中高达71%的总硒与有机质有关(Fan et al., 2011)。遵义Ni-Mo-Se多金属硫化物层中Se含量为 1069×10^{-6} ~ 2621×10^{-6} ,平均为 1807×10^{-6} 。围岩中的Se含量为 27×10^{-6} ~ 419×10^{-6} 。围岩($\delta^{82}\text{Se}=0.13\text{‰} \pm 0.87\text{‰}$)和矿石层($\delta^{82}\text{Se}=0.60\text{‰} \pm 0.60\text{‰}$)之间,以及干酪根组分($\delta^{82}\text{Se}=0.7\text{‰} \pm 1.5\text{‰}$)和硫化物组分($\delta^{82}\text{Se}=0.67\text{‰} \pm 0.47\text{‰}$)之间的硒同位素组成也没有系统的差异。Auclair等(1987)发现热水系统可以提供大量的硒。此外, Rouxel等(2004)的研究表明,在大西洋中脊Lucky Strike热液区,早期热液硫化物的 $\delta^{82}\text{Se}$ 值与整体地球或地幔的值非常接近(~0‰),也与遵义矿石中硫化物的值非常相近。上述研究表明,热液过程中硒的沉淀不会导致溶液相和固相之间发生显著的同位素分馏,溶解态的硒可能以 H_2Se 的形式和热液中的 H_2S 一起迁移,然后以硒化物或者以类质同象的形式进入硫化物的方式沉淀。因此,遵义Ni-Mo-Se矿石中的Se可能来源于热液系统,但不能排除其他金属起源于海水的可能性(Wen and Carignan, 2011)。

与Se相似,华南下寒武统牛蹄塘组黑色页岩对Cd也有显著富集。Cd含量在位于盆地相、斜坡相及台地相的重晶石沉积层、钼矿层和Ni-Mo-Se多金属硫化物层分别高达 200×10^{-6} 、 191×10^{-6} 及 879×10^{-6} (Lehmann et al., 2016; Han et al., 2017; Xu and Mao, 2021; Zhou et al., 2024)。Cd在这些超常富集的黑色岩系中均主要赋存在闪锌矿中。近年来,在大河边重晶石矿床下伏的陡山沱组中发现了区域广泛分布的与重晶石同期成矿的铅锌矿化(温汉捷等, 2017; Zhou et al., 2018),矿床地质特征、矿物学产出以及S-Pb-Cd同位素组成均表明这两种矿化属于同一成矿系统(Zhou et al., 2018, 2024)。Cd同位素揭示,处于盆地相和斜坡相的重晶石沉积层及钼矿层属于受有限的 H_2S 供应所产生的瑞利分馏($\delta^{114/110}\text{Cd}$ 分别为 $0.00\text{‰} \pm 0.13\text{‰}$ 和 $0.00\text{‰} \pm 0.14\text{‰}$),热液中残余富重Cd同位素组成的 Cd^{2+} 随洋流迁移到硫化物后形成闪锌矿沉淀,因此沉积于台地相的Ni-Mo多金属硫化物层具有集中且最高的 $\delta^{114/110}\text{Cd}$ 值($0.35\text{‰} \pm 0.03\text{‰}$)(Frei et al., 2020; Frei et al., 2021; Lehmann et al., 2022; Zhou et al., 2024)。

1.2 稀贵金属

稀贵金属包括铂族元素(Ru、Rh、Pd、Os、Ir、Pt)、Co和Cr等金属元素(翟明国等, 2019; 蒋少涌等, 2019)。黑色岩系可以对稀贵金属元素发生富集, 主要是对Pt、Pd和Co发生显著富集。芬兰Talvivaara群、华南下寒武统牛蹄塘组、波罗的海盆地Alum Shale组和Dictyonema Shale组、Selwyn盆地Canonl组、中欧Kupferschiefer组的黑色页岩都对PGE和Co具有超常富集(Jowitt and Keays, 2011; 徐林刚等, 2022); 煤系也可以对Pt、Pd发生一定程度的富集, 在部分煤灰中还可以提取利用(Seredin et al., 2013)。

1.2.1 黑色页岩型 当前已发现对稀贵金属富集达到工业利用意义的黑色页岩层位有芬兰Talvivaara群、华南下寒武统牛蹄塘组、Selwyn盆地Canonl组及中欧Kupferschiefer组。华南下寒武统牛蹄塘组黄家湾矿床PGE+Au的品位约为 1000×10^{-9} , Pt和Pd的最高含量分别为 619×10^{-9} 和 679×10^{-9} (Mao et al., 2002; Jiang et al., 2007); Selwyn盆地Canonl组Nick矿床PGE品位为 $251 \times 10^{-9} \sim 1050 \times 10^{-9}$, 部分硫化物矿石Pt+Pd品位最高可达 1600×10^{-9} (Orberger et al., 2007)。PGE和Co大部分以类质同象或矿物包裹体形式赋存在方硫铁镍矿、方硫镍矿、辉砷镍矿、黄铜矿和黄铁矿等硫化物晶格内(Orberger et al., 2007)。

1.2.2 煤型 煤系也可以富集稀贵金属。相对于Pt和Pd的克拉克值(Pt: 0.5×10^{-9} , Pd: 1.5×10^{-9} ; Rudnick and Gao, 2003), 全球煤系Pt和Pd的均值为 35×10^{-9} 和 7×10^{-9} , 煤灰中的均值分别为 130×10^{-9} 和 374×10^{-9} , 皆显示出有轻微-相对显著的富集(Ketris and Yudovich, 2009)。美国肯塔基州西部煤田中PGE含量可以高达 210×10^{-9} , 我国贵州晚古生代煤田中受热液活动影响的煤层Pt和Pd含量最高值分别为 2430×10^{-9} 和 5180×10^{-9} (Dai et al., 2003), 显示出超常富集的特点。稀贵金属在含煤盆地中可以富集在煤系、煤层顶底板、夹矸以及其中的热液脉体之中。已有研究指出, PGE在煤层中的赋存状态包括: ①无机化合物。美国肯塔基州西部9号煤矿中Pt以无机化合的形式赋存在煤素质内, 我国华北和西南煤田中Pt和Pd主要赋存在无机物中(Dai et al., 2003); ②有机化合物。贵州普安煤田11号煤矿及内蒙古乌兰图嘎煤系中有报导有机态赋存的PGE分布(Dai et al., 2012b); ③硫化物。贵州普安煤田2号煤矿中的PGE主要赋存在煤系之中的热液黄铁矿(杨建业, 2007)。④自然铂、自然钯以及Pt-Pd合金。俄罗斯远东地区煤矿中有报导自然铂和自然钯分布(Seredin et al., 2013)。

1.3 稀土金属

稀土元素是镧系元素和钇的统称。在黑色岩系中, 对稀土最为富集且具工业利用价值的为磷块岩型稀土矿床。自前寒武纪-寒武纪过渡时期以来, 不同时期几乎都有磷块岩分布(范德廉等, 2004; 陈毓川, 2007; Emsbo et al., 2015)。Emsbo等(2015)通过对美国同时期磷块岩中稀土资源量的评估, 认为蕴藏的稀土资源量已超过其他类型的稀土资源。此外, 磷块岩还存在对中重稀土选择性富集的现象(Balaram, 2023; Bonnet et al., 2023), 进一步提升了该类型稀土资源的重要性。富稀土的磷块岩沉积时期集中在前寒武纪-寒武纪过渡时期以及古生代, 中生代和新生代的远少于古生代的(陈满志等, 2019)。前寒武纪-寒武纪过渡时期作为全球最早的大面积成磷事件, 巨量稀土被固定在埃迪卡拉系及下寒武统, 扬子地台南部在此时期形成了大量富稀土的磷块岩(东野脉兴, 2001)。以贵州织金戈仲伍组为例, 所赋存的稀土氧化物资源量超过3.5百万吨(Yang et al., 2021)。稀土在磷块岩中主要赋存在氟磷灰石晶格中, 主要是替代Ca, 少量稀土可以被黏土矿物和磷灰石吸附(谢俊, 2020; Yang et al., 2021; Bonnet et al., 2023)。

此外, 现代海洋沉积物中也发现有大量富稀土的磷块岩沉积物, 主要沿大西洋和太平洋西的西部大陆边缘的大陆架和斜坡相广泛分布。这类磷块岩可以出现在三种环境(Hein et al., 2016; Vysetti, 2023): ①大陆边缘、台地、斜坡或洋底高原, 以结核或结壳形式堆积在洋底; ②海山, 特别是古老(白垩纪)海山, 如西北大西洋; ③泻湖沉积物。磷块岩沉积层稀土含量可高达 2000×10^{-6} , 稀土主要赋存于氟磷灰石和铁锰微结核(Emsbo et al., 2015)。

除磷块岩沉积外, 现代洋底还发现有大量富稀土泥岩或黏土沉积。据Kato等(2011)报道, 太平洋中部及东南部深海沉积物中都发现了富稀土沉积物, 估算资源量是陆地的千余倍。随后陆续见有在印度洋、西太平洋等区域发现相似类型稀土资源的报道(Kato et al., 2011; Yasukawa et al., 2014; Takaya et al., 2018)。这类富稀土深海软泥主要沉积在远离大陆的碳酸盐补偿深度面以下, 边缘海或浅海沉积物中不发育富稀土沉积, 因此也被称为“深海稀土”(石学法等, 2021; 黄牧等, 2022)。全球已发现的富稀土深海沉积物可以分为4个成矿带: 西太平洋稀土成矿带、中-东太平洋稀土成矿带、东南太平洋稀土成矿带和中印度洋海盆-沃顿海盆稀土成矿带等(石学法等, 2021)。深海稀土以中-重稀土元素相对富集为特征。稀土主要赋

存相态包括铁锰氧化物或氢氧化物的吸附(Kato et al., 2011)、结晶铁相(Liu et al., 2023)、沸石矿物的吸附(石学法等, 2021)、磷灰石吸附或类质同象进入磷灰石晶格(Deng et al., 2022)。

煤型稀土也是一种潜在的稀土资源。世界煤及煤灰稀土含量均值分别为 68.4×10^{-6} 和 485×10^{-6} , 中国煤中稀土含量均值为 138×10^{-6} (代世峰等, 2020)。Seredin和Dai提出煤或煤灰中稀土元素氧化物超过 1000×10^{-6} , 就可以考虑煤中稀土开发利用的可能性(Seredin and Dai, 2012)。据报道, 俄罗斯远东地区煤矿、美国肯塔基煤田、我国华北石炭纪-二叠纪煤以及西南晚二叠纪煤都对稀土有一定程度的富集(黄文辉等, 2019)。煤灰中的稀土可以进一步富集, 如黑岱沟、哈尔乌素、官板乌素以及阿刀亥矿床煤灰的稀土氧化物含量均值分别为0.15%、0.14%、0.11%以及0.98%(Dai et al., 2006)。代世峰等(2020)根据稀土元素的富集成因, 将煤型稀土矿床分为碱性火山灰作用型、热液流体型、沉积岩源区供给型3种类型。煤中稀土主要的赋存方式有如下几种: ①赋存在陆源碎屑或火山碎屑引入的富稀土矿物中, 如锆石、独居石、磷灰石、磷钇矿(Seredin and Dai, 2012; Seredin et al., 2013); ②赋存在成岩阶段或后期热液叠加形成的矿物, 如铝磷酸盐矿物、磷酸盐矿物和碳酸盐矿物(Wang, 2009; Seredin et al., 2013); ③赋存在有机质中, 此种形式在低灰分低阶煤中多见(Seredin and Dai, 2012; 邹建华等, 2012); ④被黏土矿物或铁锰氢氧化物吸附(Seredin and Dai, 2012; Finkelman et al., 2018)。

1.4 稀有金属

黑色岩系对稀有金属发生显著性富集的是碳质黏土岩和煤系, 主要对锂、铍发生超常富集。近年来, 温汉捷等(2020)在我国西南地区发现新类型的碳酸盐黏土型锂资源, 锂超常富集的黏土岩目标层位主要包括黔中下石炭统九架炉组、滇中下二叠统倒石头组、桂西上二叠统合山组(温汉捷等, 2020; Ling et al., 2021; 廖家隆等, 2022; Zhao et al., 2023)。华北上石炭统本溪组黏土岩也有锂超常富集的现象(张英利等, 2023)。富锂岩系主体为含碳质的黏土岩, 伴有铝土质黏土岩、铝土矿、黄铁矿的岩性组合, 局部夹有煤线或劣质煤。富锂沉积层岩石组合具有相似性, 剖面从老到新发育: ①铝土质黏土岩, 局部含铁质; ②致密状铝土质黏土岩; ③豆鲕状铝土质黏土岩; ④疏松土状黏土岩, 其中致密状铝土质黏土岩和豆鲕状铝土质黏土岩是锂最为富集的有利岩性(温汉捷等, 2020)。根据滇中盆地下二叠统倒石头组富锂黏土岩系钻孔工程所揭露的情况, 黏土岩中 Li_2O 平均含量为0.3%, 最高达

1.7%, 显示对Li发生了超常富集。除锂外, 此种富锂岩系往往还可以对Ga及稀土发生一定程度的富集。Li主要以吸附态或类质同象形式赋存于蒙皂石和绿泥石族矿物中(温汉捷等, 2020; 崔焱等, 2022)。

煤系可以对锂形成富集。世界煤中Li含量的均值为 12×10^{-6} , 我国煤中Li含量均值为 31.8×10^{-6} (Ketris and Yudovich, 2009; Dai et al., 2012a)。孙玉壮等(2014)将煤中伴生锂的工业品位确定为 120×10^{-6} 。富锂的煤矿主要包括俄罗斯远东地区煤矿、我国华北石炭纪-二叠纪煤矿、华南晚二叠世煤矿。内蒙古准格尔煤田和山西晋城矿区是我国富锂煤最集中的矿区。准格尔煤田哈尔乌素煤矿煤灰中Li含量均值为 633×10^{-6} , 锂资源量达110万t(代世峰等, 2020); 山西平朔矿区4、9、11号煤层中锂最高含量达到 960×10^{-6} , 估算锂资源量107.25万吨(Sun et al., 2013), 均已达大型锂矿床的规模。山西晋城煤田煤层 Li_2O 平均含量为0.23%, 俄罗斯远东地区Partizansk含煤盆地泥化玄武岩岩基的 Li_2O 平均含量为0.1%(Seredin and Finkelman, 2008)。除煤层外, 煤矿中的Li还可以富集在煤层夹矸以及顶底板岩石中, 如俄罗斯Partizansk含煤盆地中Li主要富集在泥化的玄武岩岩基中(Seredin and Finkelman, 2008)。Li在煤系中的赋存形式包括: ①高岭石、绿泥石、蒙脱石及勃姆石等黏土矿物(Dai et al., 2012a; Zhao et al., 2018); ②多硅锂云母、磷酸锂铁矿、铁锂云母及锂云母等高温矿物(Sun et al., 2010); ③有机结合态, 此种方式不多见, 目前仅见于挪威Longyearbyen矿区以及我国伊敏煤矿(Lewińska-Preis et al., 2009; 梁虎珍等, 2013)。

相对于锂, 煤系对铍的富集同样引人注目。世界煤中Be含量均值为 1.6×10^{-6} , 我国煤中Li含量均值为 2.11×10^{-6} (Ketris and Yudovich, 2009)。富铍煤系主要分布在美国、俄罗斯、中国、比利时、捷克、德国等的含煤盆地中(Yudovich and Ketris, 2006; Seredin and Finkelman, 2008; Dai et al., 2015)。俄罗斯远东地区Kuzbass盆地的Spetsugli煤矿富铍煤对铍富集程度高, 煤中Be含量为 $100 \times 10^{-6} \sim 200 \times 10^{-6}$, 煤灰中为 $500 \times 10^{-6} \sim 900 \times 10^{-6}$ (Seredin and Finkelman, 2008); Krylovsk和Verkhne-Bikinsk含煤盆地中-新生代煤层顶底板的BeO含量为0.1%~0.26%(Seredin and Finkelman, 2008)。我国富铍煤矿中也发现有铍的富集, 如临沧铍矿煤层Be含量可以高达 2000×10^{-6} , 临沧大寨铍矿床的铍资源量为224 t(代世峰等, 2020); 乌兰图噶煤矿富铍煤中Be平均含量为 25.7×10^{-6} , 煤灰中为 267×10^{-6} (Dai et al., 2012b)。铍在富铍煤中主要是与有机质结合(Eskenazy, 2006; Seredin and Finkelman,

2008), 如在临沧锆矿中发现以含水硫酸盐矿物形式存在的铍($\text{BeSO}_4 \cdot \text{H}_2\text{O}$; Dai et al., 2015)。

2 黑色岩系型战略性关键矿产资源超常富集机理

2.1 还原(-硫化)水体环境形成的泵吸效应

从已有最具典型富金属黑色页岩的沉积环境而言, 早元古界Talvivaara组、晚元古界Gwna群、下寒武统牛蹄塘组、中泥盆统Canon1组、上二叠统Kupferschiefer组都沉积于大陆边缘缺氧-硫化的沉积盆地, 黑色页岩高TOC含量显示沉积时期的海洋具有高生物生产力, 并受到同时期强烈地陆地风化汇入影响(Meyer and Kump, 2008; Large et al., 2015; Johnson, 2017)。大陆边缘形成的受限制盆地具有较低的垂向混合速率, 导致海水水体形成氧化还原分层结构(Li C et al., 2020)。有机质在海水中与溶氧、 NO_3^- 、 Mn^{4+} 、 Fe^{3+} 、 SO_4^{2-} 等发生氧化还原作用, 在陆边缘形成的受限制盆地的深部还原性水体中主要与 SO_4^{2-} 发生反应, 促进深部水体形成富硫化氢的环境(Libes, 2009; Li Q et al., 2020)。硫化的深海可以对海水中亲硫元素进行富集, 使得Mo、Zn、Cd和Cu等氧化还原敏感元素(Re、Se、Te等)被硫化物固定, 硫化物和有机碳沉积形成富金属的黑色页岩(图2; Goodfellow and Jonasson, 1984; Goodfellow, 1987; Shanks et al., 1987; Lyons and Severmann, 2006; Gomes and Johnston, 2017; Armstrong et al., 2018), 形成泵吸效应, 最终形成富金属的黑色页岩层。与此相似, 部分湖湘沉积水体由于形成氧化还原梯度, 也促进氧化还原敏感元素在底部还原性沉积层发生富集(Dai et al., 2016; Li Q et al., 2020; Xu et al., 2020; Wang et al., 2022)。

早元古界Talvivaara组的金属富集与大氧化事件导致的大气及表层海水氧含量增加, 提升了大陆风化以及海洋的生产力, 有机碳的沉积速率增强, 同时含氧表面和缺氧深水之间强烈的氧化还原梯度, 有助于将大量金属输送到海底并形成缺氧硫化的深部水体环境(Anbar and Knoll, 2002; Canfield, 2005; Young et al., 2013; Large et al., 2015), 因而导致黑色页岩中的金属发生显著富集(Johnson, 2017)。晚元古界Gwna群对Se、Te、Co等的富集也受控于相似的地质条件, 在新元古代晚期大氧化事件的影响下(NO₂, 0.85~0.54Ga), 导致沿着Gondwana大陆边缘有机碳埋藏速率加快(Campbell and Squire, 2010; von Strandmann et al., 2015), 在次级盆地中, 底部还原、硫化的水体环境对Co、Se、Te等战略性关键金属发生富集(Armstrong et al., 2018)。扬子地台东南缘在埃迪卡拉纪-早寒武世

处于分层海洋模式, 其斜坡-深水盆地为还原环境, Xu等(2013)认为极低的沉积速率和极少的陆源碎屑供给等极端环境是此时期形成Ni-Mo-多金属层的必要条件。从沉积相来看, 扬子地台东南缘在早寒武世台地相的底部海水形成硫化楔(Li C et al., 2010, 2020), 因此扬子地台东南缘的下寒武统台地相-斜坡相具有Ni-Mo-PGE硫化物沉积, 斜坡和盆地相形成以重晶石和钒矿层为主的沉积层, 但其中硫化物的量要远低于台地相的多金属硫化物层(Han et al., 2017, 2022; Zhou et al., 2018, 2023), 从而印证了硫化-还原水体对氧化还原敏感元素的富集作用。其中, 相对于正常海水, 扬子地台东南缘下寒武统Ni-Mo-PGE硫化物沉积对Pt、Pd等的富集系数可以高达 10^7 倍(Mao et al., 2002)。现代海洋沉积体系中存在类似的实例, 黑海和地中海东部缺氧沉积盆地具有富有机质的金属沉积层, 其中Co、Se、Mo、U、V和Cu等元素发生富集(Nijenhuis et al., 1998; Dean and Arthur, 2011)。需要强调的是, 硫化水体的泵吸效应是富金属黑色页岩中金属沉淀的一种重要机制, 但并不是金属的来源仅是海水, 也可能是热液流体或者洋底火山活动的带入(Jiang et al., 2007; Pašava et al., 2008; Pi et al., 2013)。

2.2 有机质还原作用

有机质埋藏后形成的沉积层往往具有强还原性(Canfield et al., 1993)。这些沉积地层中的有机质在沉积岩容矿型硫化物矿床中起着还原剂的作用, 例如密西西比河谷型(MVT)Pb-Zn矿床、沉积喷流型(SEDEX)Pb-Zn矿床、砂岩型Cu矿床中广泛存在有机质与硫化物的共生结构, 显示有机质与硫化物的沉淀相关联(Ho and Mauk, 1996; Sun and Püttmann, 2000; Logan et al., 2001; Leach et al., 2005; Szmihelsky et al., 2021; Poetz et al., 2022)。其中重要的原因之一是有机质参与了硫酸盐的还原作用, 包括海洋中产生富 H_2S 的水体环境也与此紧密相关, 形成硫化物沉淀所需要的 S^{2-} , 进而将水体中的亲硫元素进行富集。此外, Re、Se、Te等氧化还原敏感元素在氧化性流体中的活性高(主要呈 ReO_4^- 、 SeO_4^{2-} 等形式), 是流体迁移和富集的重要形式(Parnell et al., 2015)。有机质还可以对硒酸盐(SeO_4^{2-})、亚硒酸盐(SeO_3^{2-})、铼酸盐(ReO_4^-)等离子进行还原, 形成 Se^{2-} 、 Te^{2-} 、 Re^{2+} 等离子, 从而促进类质同象替代硫或与 S^{2-} 键合(Morford et al., 2012; Parnell et al., 2015; Sheen et al., 2018; Missen et al., 2020; 温汉捷等, 2019), 或者形成Se、Te的单质(Wen et al., 2006)。以硒为例, 渔塘坝矿床大约70%的硒都呈自然硒形式(Wen and Carignan, 2011), 且这些自然硒在干酪根中主要以超微包裹体被吸附(温汉捷等,

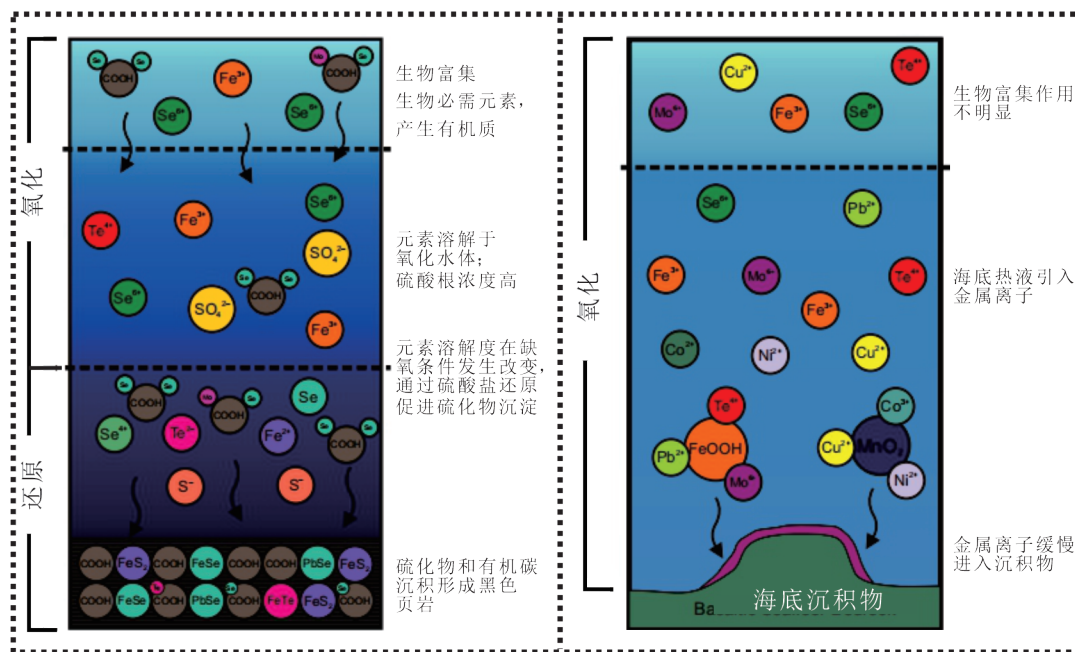


图2 硫化-还原分层的水体结构(a)和氧化水体结构(b)对金属的富集模式 (Armstrong et al., 2018)

Fig.2 Comparison of metal enrichment models for the vulcanization-reduction stratified seawater column (a) and the oxic seawater column (b) (after Armstrong et al., 2018)

2003)。富 Se^{4+} 、 Se^{6+} 的流体向下渗滤的过程中,由于有机质的强还原作用,使得高价态硒主要被还原成0价(自然Se),部分被还原成 Se^{2-} 呈硒化物或类质同象形式存在(图3)。砂岩型铀矿对硒的富集模式与此类似,氧化性大气水萃取出砂岩层和硫化物的氧化还原敏感元素,在流体氧逸度降低或与还原性沉积层反应条件下,导致硒化物(一般为白硒铁矿)和含硒硫化物沉淀(Howard III, 1977)。此外,无论是中元古界还是三叠系红层,其中还原性球体结构均显示出对Te具有更高层次的富集,这些还原性球体由生物活动等产生的有机质聚集形成,也支持有机质形成的还原障对Te发生明显富集作用(Parnell et al., 2016, 2018)。

2.3 富有机质沉积体系的络合和吸附

有机质可以对Re、Se、Ge、Ga、Be、PGE等元素进行络合,进而在黑色岩系中富集。已有研究表明,Re、Se属于亲有机元素,含 ReO_4^- 的水溶液与石油接触,大部分Re从水溶液进入有机相(Mahdaoui et al., 2015); Ge和Be在煤层中与有机质结合可能是最重要的赋存方式(Eskenszy, 2006; Seredin and Finkelman, 2008; Dai et al., 2021), Pt-Pd在煤层中也可以形成有机化合物的方式发生富集(Seredin and Finkelman, 2008),泥炭时期腐殖酸的络合作用是铂族金属富集的关键因素;由于生物活动中硒可以替代硫形成含硒的氨基酸,通过此方式进入细菌、藻类、真菌和植物体内,生物的沉积埋藏使得硒被固定下来,贵州瓮安陡山沱组磷块

岩中真核生物化石核部富硒(Long et al., 2020)。这些实例都显示有机质的络合富集可以促进黑色岩系对部分战略性关键金属进行一定程度的富集。

2.4 岩浆作用及陆源碎屑输入提供部分金属来源

岩浆作用中,由于In、Cd、Se、Te、Re、Be、Li具有亲气性,因此可以在火山喷气中以氧化物或者氢化物的形式被富集(Wahrenberger et al., 2002; Hofstra et al., 2013; Rosca et al., 2022)。全球年度火山喷出的硒含量约为100~1800t(Mather et al., 2004; Rosca et al., 2022),基拉韦厄火山在1983—1985年期间喷发了约10t硒(Greenland and Aruscavage, 1986),里巴利岛和夏威夷岛火山灰自然硫中硒可分别高达18%和5.18% (Sindeeva, 1964; USGS, 2017)。Kudryavyy和Merapi火山喷气中富集In、Cd、Cu等元素(Wahrenberger et al., 2002)。此外,长英质火山灰以及碱性岩火山灰中稀有、稀土等大离子亲石元素含量较高,俄罗斯远东地区新生代煤系以及我国西南地区上二叠统宣威组含煤岩系对铈-锆-稀土-镓的富集可能与同期大规模碱性火山灰喷发相关(Dai et al., 2016; 代世峰等, 2020)。随着喷气冷凝流体、火山喷气、火山灰等汇入或沉降滞留、低能水体环境,其中富集的战略关键金属被带入到沉积体系,提高相应金属发生富集成矿的可能性。蚀源区对黑色岩系关键金属的富集同样不可忽视,陆源碎屑输入也可以为部分黑色岩系提供金属来源。煤中Ga的富集可能与沉积盆地临近已有铝土矿或铝土

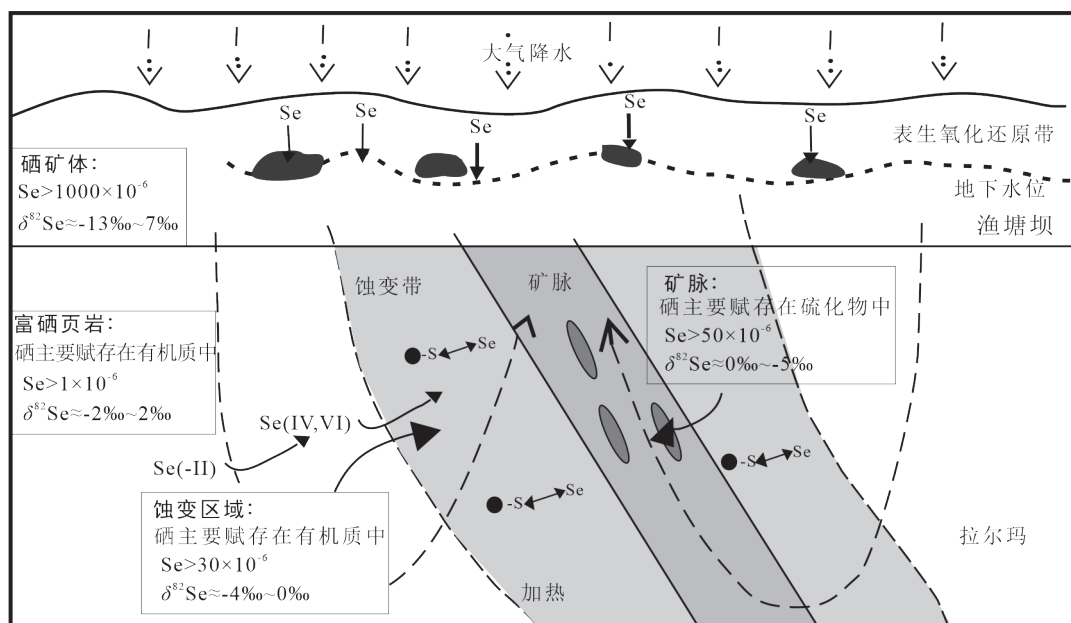


图3 渔塘坝和拉尔玛富硒黑色页岩中硒的富集模式 (Wen and Carignan, 2011)

Fig.3 A selenium enrichment model for black shales in the Yutangba and Laerma areas (after Wen and Carignan, 2011)

质沉积等陆源碎屑的引入有关, 沉积盆地邻区花岗岩、碱性岩等风化引入也会提升黑色岩系对Ge、Li、稀土等关键金属的富集程度 (Dai et al., 2008)。

2.5 黑色页岩及热液叠加过程对战略性关键矿产资源富集的促进意义

从构造环境而言, SEDEX及VMS型矿床与黑色岩系都容易在大陆边缘盆地和裂谷盆地中形成。黑色岩系大都会成为热液体系的屏障层或仅作为空间上的耦合 (Sáez et al., 2011)。SEDEX、VMS等热液体系与黑色岩系的组合往往赋存了大型—超大型战略性关键矿产资源, 例如加拿大Finlayson Lake地区VMS矿床Se矿化、澳大利亚McArthur Zn-Pb矿床的TI矿化、澳大利亚Merlin矿床Re矿化、华南下寒武统牛蹄塘组Cd-Se矿化。黑色岩系在热液叠加过程中对战略性关键金属成矿的促进作用, 主要体现在以下两方面:

(1) 黑色岩系在热液叠加过程中可以提供成矿物质。Wolverine矿床在Finlayson Lake地区泥盆纪—石炭纪形成的VMS矿床中最富硒 (Layton-Matthews et al., 2013)。相较于Gp4F矿床和Kudz Ze Kayah矿床, Wolverine矿床矿区含有较多的黑色页岩, 并具有最高的Se含量和最负的 $\delta^{82}\text{Se}$ 值, 表明该矿床Se的大量富集有黑色页岩的补给 (Layton-Matthews et al., 2013)。澳大利亚Merlin矿床是目前全球发现的最大的铼独立矿床, 其Re部分源自赋矿围岩Kuridala群中的碳质板岩 (Babo et al., 2017)。

(2) 黑色岩系可以调节热液体系的氧逸度和硫逸度, 促进战略性关键金属发生超常富集。澳大利亚

McArthur Zn-Pb矿床的TI富集与氧化性的含矿热液同碳质泥页岩的持续反应, 原碳质泥页岩及黄铁矿中的TI被热液活化, 持续的氧化还原反应导致热液氧逸度降低, 促进富TI黄铁矿沉淀, TOF-SIMS面扫在该矿床中可以看见富 ^{205}TI 黄铁矿在早期黄铁矿边部形成生长边 (图4; Spinks et al., 2021)。我国华南下寒武统牛蹄塘组Ni-Mo-PGE硫化物层对硒和镉的富集程度要远高于同层位处于深水相的钒矿层和重晶石层, 主要是受控于台地相黑色页岩与硫酸盐之间发生硫酸盐还原反应形成硫化楔, 从而导致热液带入的硒和镉被硫化楔捕获, 形成硫化物层 (Wen and Carignan, 2011; Zhou et al., 2023)。Williams-Jones和Vasyukova (2022) 认为富碳质沉积层受到富钴热液流体叠加是形成富钴矿床的主要原因。

3 对战略性关键矿产资源研究的启示和展望

3.1 表生风化沉积作用在战略性矿产资源成矿过程及对理论建立的重要性

黑色岩系对部分战略性关键矿产资源的富集有潜力超过任何其他类型的金属矿床 (Emsbo, 2022)。全面解析黑色岩系型战略性关键矿产资源成矿机制, 研究有机质和无机质相互作用及成矿过程, 对于建立战略性关键矿产资源超常富集理论具有重要意义。例如, 黑色岩系中的磷块岩型稀土资源, 不仅单个矿床资源量大, 而且大多还富集中-重稀土元素, 在全球范围内广泛发育。结合目前已发现的深海软泥型稀土资源

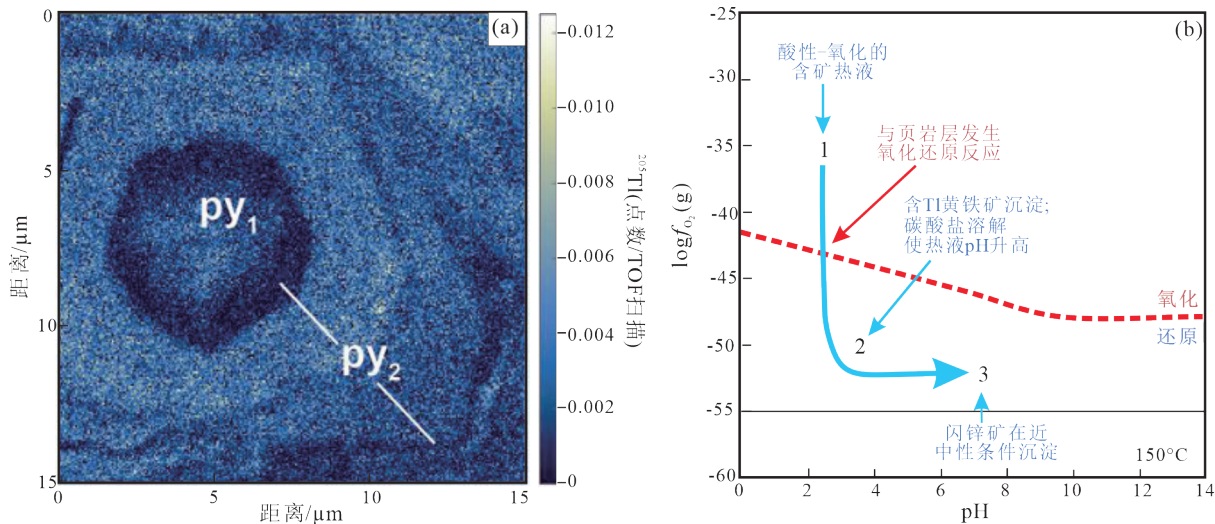


图4 McArthur River矿床富Tl黄铁矿TOF-SIMS ²⁰⁵Tl面扫描图像(a)及沉淀机制(b) (Spinks et al., 2021)

Fig.4 The TOF-SIMS mapping image of ²⁰⁵Tl in pyrite crystal (a) and the deposition mechanism (b) of Tl-enriched pyrite in the McArthur River deposit (after Spinks et al., 2021)

成矿机制的认识,研究二者之间的成矿作用的异同,对于全球稀土资源量的系统评价、稀土资源的增储具有重要战略意义。此外,煤型镓、锗已经可以进行工业利用,煤型铍及黑色页岩型钴、铌、钽都显现出巨大的资源潜力,对这类矿床成矿机制的准确认识可以建立相应资源勘查评价模型,如果发现新类型的矿床,有可能颠覆传统的资源供给布局。例如,近年来在美国、墨西哥、塞尔维亚、埃及等地相继发现了与火山岩有关的黏土型锂矿床(Benson et al., 2017, Benson et al., 2023),温汉捷等(2020)在我国西南地区发现新类型的碳酸盐黏土型锂资源。这两种黏土型锂矿床都属于风化-沉积型锂矿床,赋矿层位分布面积广、产出层位稳定、厚度较大、开采成本低(大部分可露天开采)等特点,具有巨大的资源前景。

黑色岩系是表生风化沉积中的一种重要类型。长期以来,学者们围绕岩浆-热液成矿作用以及中低温热液成矿作用相关的战略性关键矿产资源成矿作用开展了大量研究。相对而言,表生成矿作用中战略性关

键矿产资源成矿体系的研究和认识还很薄弱。但近年来越来越多与风化沉积相关的战略性关键矿产资源被发现,显示出表生风化沉积过程在战略性关键金属超常富集具有重要作用(温汉捷等, 2020; 代世峰等, 2020; 蒋少涌和王微, 2022; 何宏平和杨武斌, 2022; Emsbo, 2022; Jiang et al., 2023)。风化沉积过程中,如何将源区成矿物质进行搬运? 其中的搬运介质是什么,形式如何? 进行分异、沉淀的机制和受控条件是什么? 包括到最终形成富矿沉积层,其中涉及的成矿作用类型多样,远比以前认识的复杂。但一旦条件具备,往往可以对战略性关键金属发生超常富集,可以形成大型-超大型矿床,且易形成稀有-稀土-稀散元素共生矿床,有望突破传统认识形成新的范式以及增加资源量的潜力。表2列出了风化沉积型战略性关键矿产资源前景。

3.2 低丰度元素超常富集过程的驱动机制

战略性关键金属元素的地壳丰度很低,大多为ppm级以下,成矿需要达到数百至上万倍的超常富集,

表 2 风化沉积型战略性关键矿产资源前景

资源潜力	稀土金属	稀贵金属	稀有金属	稀散金属
最具重要工业价值	离子吸附型	红土型钴矿	盐湖型锂(铷、铯) 风化坡积型铌矿床 滨海锆砂矿	煤型锆矿床 煤型镓矿床
具有潜在工业价值	磷块岩型 深海软泥型	红土型铬矿	风化淋滤型铷矿 煤型铍矿	铝土岩型镓矿床 黑色页岩型铌矿床 黑色页岩型钽矿床
具有重要资源前景	碳酸盐风化壳型 玄武岩风化壳型 煤型	玄武岩风化壳 黑色页岩型钴、PGE	碳酸盐黏土型锂矿床 火山岩黏土型锂矿床	铁锰结核型

可见成矿需要极苛刻的条件(涂光炽,2004)。这些低丰度元素的超常富集驱动机制,是正确认识战略性关键金属成矿机制及勘查评价的首要问题(温汉捷等,2019;翟明国等,2019;蒋少涌和王微,2022;苏慧敏等,2023)。从已有对黑色岩系型战略性关键金属富集过程的认识来看,风化沉积是驱动战略性关键金属富集的方式之一;此外,不容忽视的是,黑色岩系富集的金属在地球层圈物质循环中聚散行为对其他相关成矿系统产生了影响。

铼主要在黑色岩系和斑岩型矿床中发生超常富集(Sinclair et al.,2009;Sheen et al.,2018;杨志明等,2020;McFall et al.,2021)。然而,不同类型斑岩型矿床对铼的富集程度差异很大,辉钼矿中铼含量最高的为斑岩型Cu-Au矿床,其次依次为斑岩型Cu矿床、斑岩型Mo-Cu矿床,最低的为斑岩型W-Mo矿床(Sinclair et al.,2009;Millensifer et al.,2014),其中的内在控制因素还不清楚。就辉钼矿而言,辉钼矿的铼含量随着成矿年龄变年轻具有逐渐升高的趋势,尤其是从300Ma以来形成的辉钼矿中的铼含量增幅更加明显,反映了陆壳风化带带入的铼增多,对应大气氧含量升高的地质过程(Golden et al.,2013)。相应的,全球不同时期黑色页岩铼的含量随着大气氧条件的增加而升高(Sheen et al.,2018),具有与辉钼矿相似的变化规律。因此,是否大气氧含量的增大促进了铼风化带入黑色岩系,洋底黑色页岩中富集的铼随着洋壳俯冲被带入到地幔楔,促进产生的岩浆具有更高含量的铼,从而形成不同体系之间的互馈机制,并导致斑岩型矿床中铼含量的差异性,是值得关注的科学问题。

Yierpan等(2020)发现,洋底黑色页岩富集的硒可以随俯冲被带到地幔。俯冲板片脱水可以导致上覆地幔富挥发分(水、CO₂、S、Se、Te等),由于硒的挥发性强于碲,板片中黑色岩系富集的硒较早被带入到岩浆过程,因此导致美国西部新生代浅成低温热液矿床具有从西到东可以分为富硒带和富碲带,出现硒和碲的解耦(Saunders and Brueseke,2012)。黑色页岩中富集的硒、碲、铼、PGE等金属亦可以在弧岩浆底垫过程中随硫化物饱和不混溶而进入下地壳,在后碰撞环境下形成富硒、碲、铼、PGE的斑岩型矿床(杨志明等,2020;McFall et al.,2021)。

3.3 黑色岩系型战略性关键矿产资源成矿与主要地质事件的关系

越来越明显的是,富金属黑色岩系在地史时期的某几个时间段集中产出,且具有全球可对比性,如早元古代、晚元古代、早寒武世、泥盆纪、二叠纪和白垩纪。因此,富金属的黑色页岩是否存在时间上的演化规律,

或者地球动力学过程会影响它们的演化?富金属黑色岩系沉积需要水体具有较高的生物生产力、较强的大陆风化速率、还原-硫化的水体环境,这些因素共同促使黑色页岩层等可以富集金属。地球大气经历了两次显著的增氧事件,分别为中元古代大氧化事件和晚元古代末期新氧化事件。自显生宙以来,地球整体处于富氧状态,但大气氧含量仍然在剧烈波动(Large et al.,2019)。富战略性关键金属黑色页岩的产出时代来与地球大气增氧事件具有很好的协变关系(图1)。大气氧含量的增加,一方面会促进大陆岩石风化,硫酸盐、磷,特别是氧化还原敏感元素Se、Te、Re等汇入海洋中的通量显著提升(Parnell et al.,2016,2018;Sheen et al.,2018);另一方面,还可以增强海洋表层生产力,有机碳的沉积速率加快,导致底部水体出现还原甚至硫化环境(Anbar and Knoll,2002;Canfield,2005;Armstrong et al.,2018),为黑色岩系型战略性关键金属成矿奠定物质基础以及提供沉积条件。

此外,黑色岩系的形成可能还受到一些大规模地质事件的影响。Condie等(2001)认为,元古宙和太古宙形成的黑色页岩可能与超级地幔柱和超大陆的聚合有关。主要观点为:地幔柱可以释放大量CO₂进入大气和海洋中,促进海洋碳埋藏速率加大;CO₂含量的剧增对全球气温、风化样式和速率都会产生影响。这种影响方式在生命活动微弱的元古宙和太古宙早期可能确实存在。在生命活动增强后,大气氧含量对黑色岩系沉积的影响更显著。但特定时期超大陆的聚合和裂解、洋流环流模式的改变、冰期以及大规模火山活动导致的海洋缺氧事件等(Wignall and Twitchett,1996;Tribouillard et al.,2006;Trabucho-Alexandre et al.,2012;Kunert and Kendall,2023;Zhang,2023),都可能在板块尺度或者特定的沉积盆地对黑色岩系型战略性关键金属的富集造成影响。如何从复杂的地质构造环境和重要的地球动力学过程中厘定出黑色岩系型战略性关键矿产资源富集的关键要素,有助于解决黑色岩系型关键金属超常富集理论等重大科学问题。

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·招聘信息·

【编者的话】为丰富信息量,体现学会为广大会员和科技工作者服务的宗旨,本刊特设“招聘信息”栏目。该栏目将辑近期国内主要地学科研单位、高校人才需求的有关信息,方便广大会员和有流动需求的科技工作者查询。同时欢迎我会会员和广大科技人员为本刊提供信息。来稿邮箱:kjdhtb@vip.skleg.cn.

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