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沉积型锂资源成矿作用特征*

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摘 要 沉积型锂资源作为可利用锂资源的重要组成部分，由于其储量大、分布范围广而备受关注，但对于锂的赋存状态、赋矿沉积岩的沉积特征、成矿物质来源等成矿作用特征观点不一。通过对国内外沉积型锂资源成矿作用的综合分析，文章尝试总结出沉积型锂资源的成矿作用规律。综合国内外沉积型锂资源（矿床）的特征分析，沉积型锂资源主要赋存于黏土岩、铝质黏土岩及铝土矿中，部分分布于绿豆岩（凝灰岩）以及砂岩、泥岩等碎屑岩。锂在其中的赋存状态多样，主要以类质同象或离子吸附形式赋存在绿泥石、蒙脱石、高岭石和伊利石等黏土矿物中，个别为可开采的独立含锂矿物。多数沉积型锂资源沉积在湖相、泻湖相等低能的还原环境中，富锂岩石主要来源于岛弧类长英质火山岩和少量碎屑岩-碳酸盐岩，且源区母岩经历强烈的风化作用，沉积物可能经历再旋回的搬运过程。富锂岩石源于大陆岛弧环境，沉积于被动大陆边缘、裂谷或克拉通盆地。火山岩和含锂地层下伏的碳酸盐岩均可能是沉积型锂资源中锂的来源，成矿源区的不同造成了沉积型锂资源成矿作用的差异。

关键词 地球化学；沉积型锂资源；赋存状态；沉积环境；沉积物源；成矿作用
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Metallogenic characteristics of sedimentary lithium resources

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Abstract

As an important part of available lithium resources, sedimentary lithium resources have attracted much attention because of their large reserves and wide distribution. However, different views on the occurrence state of lithium, the sedimentary characteristics of ore-bearing sedimentary rocks, the sources of ore-forming materials and other metallogenic regularities occur. To analysis the mineralization of sedimentary lithium resources, we attempt to summarize the metallogenic regularities of sedimentary lithium resources. Based on the comprehensive analysis of the mineralization of domestic and foreign sedimentary lithium resources, it is considered that sedimentary lithium resources mainly occur in clay rocks, aluminous clay rocks and bauxite, and some are distributed in mungbean (tuff), sandstone, mudstone and other clastic rocks. Lithium occurs mainly in the form of isomorphism or ion adsorption. Lithium minerals are mainly clay minerals such as chlorite, semectite, kaolinite and illite, and a small amount of independently exploitable lithium minerals. Most sedimentary lithium resources were deposited in low-energy reduction environments such as lacustrine and lagoon. Lithium-bearing rocks were mainly transported from island arc felsic magmatic rocks and a small amount of clastic rocks and carbonate. The parent rocks

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in the source area had experienced strong weathering, and the sediments may undergo recycling transportation. Lithium-rich rocks were sourced from continental island arc environment and deposited in passive continental margin, rift or craton basin. Magmatic rocks and carbonate rocks underlying lithium-bearing strata may be the source of lithium in sedimentary lithium resources. Different metallogenic source areas also lead to different mineralization of sedimentary lithium resources.

Key words: geochemistry, sedimentary lithium resources, occurrence state, sedimentary environment, source rock of sediments, mineralization

锂是重要的关键金属元素，也是战略新兴矿产资源之一。近年来，随着新能源的发展，锂资源的需求量也急剧增长。全球锂资源主要分布在智利、玻利维亚、中国、阿根廷、美国及澳大利亚（Kesler et al.，2012）。锂矿床按照成因类型分为内生和外生2类：内生型细分为花岗伟晶岩型、花岗岩型、云英岩型和岩浆热液型，可能存在花岗岩风化壳型锂资源（李建康等，2014）；以维拉斯托锡锂多金属矿床为代表的隐爆角砾岩型锂矿（李泊洋等，2018；Zhu et al.，2021）在成因上也可归属为内生型锂矿床；外生型包括盐湖型和地下卤水型（李建康等，2014），现在的沉积型锂资源也属于外生型。根据地质特征，锂矿资源主要分为硬岩型（花岗岩型和花岗伟晶岩型）、盐湖卤水型和沉积型（源自火山沉积物的富锂蒙脱石黏土）3大类（李建康等，2014；刘丽君等，2017；Bowell et al.，2020）。中国锂矿资源类型主要为硬岩型（花岗伟晶岩型为主，花岗岩型次之）和盐湖卤水型，因此，硬岩型和卤水型锂矿长期以来得到地质学家的广泛关注（例如，李建康等，2014；Li et al.，2015；王登红等，2017；许志琴等，2018；高春亮等，2020）。中国的硬岩型锂矿床主要分布在新疆、四川和福建等省（区），以新疆可可托海、柯鲁木特锂铍铌钽矿床、四川甲基卡、可尔因和扎乌龙锂铍铌钽矿床、福建南平锂铌钽矿床等为代表（刘丽君等，2017）。中国的卤水型锂矿主要分布在青藏高原中的盐湖中（刘丽君等，2017）。塞尔维亚贾达尔（Jadar）盆地沉积型锂矿床（Stanley et al.，2007）、美国McDermitt沉积型锂资源（世界第五大沉积型锂矿，Li_2O品位为0.29%、储量达2.0 Mt，Gruber et al.，2011）和中国云贵地区黏土型锂资源（温汉捷等，2020）的发现，使得沉积型锂资源受到越来越广泛的关注。

但是，根据国内外沉积型锂资源的勘查开发现状可以发现，目前沉积型锂资源的开发利用程度较低，除了贾达尔矿床外，绝大部分矿床并未进行工业化开采（于沨等，2019）。现阶段中国已发现的沉积型锂资源主要赋存于富锂的凝灰岩和黏土岩类，尤其是近年来在华南地区新发现众多的碳酸盐黏土型锂资源（崔燚等，2018；温汉捷等，2020）。与此同时，在中国的沉积型大宗矿产和能源矿产中也均伴生有大量的锂金属，具有较大的找矿潜力，如铝土矿中常伴生有品位较高的锂（钟海仁等，2019）；不同地区的聚煤盆地中也富集大量的锂、镓、稀土元素等矿产资源（代世峰等，2014；朱华雄等，2016；孙富民，2018；宁树正等，2020；廖家隆等，2020）。近年来，随着中国选冶技术的不断发展，黏土岩或者铝质岩中提锂技术也逐渐成熟（任方涛等，2013；李荣改等，2014a；2014b；Gu et al.，2020a；2020b），使得沉积型锂资源的全面、综合开发利用可行性得以提高，沉积型锂资源可能将成为锂矿资源找矿突破的新方向。

前人对沉积型锂资源的分布特征及资源潜力等方面进行过较多的研究（刘丽君等，2017；钟海仁等，2019；于沨等，2019），但是对于沉积型锂资源的沉积特征、物质来源及成矿背景等方面的研究相对薄弱。因此，本次通过详细对比国内外沉积型锂资源的地质特征，系统总结沉积型锂资源的富锂岩石的沉积特征及成矿背景等，为沉积型锂资源的勘查和开发利用提供支撑。

1 沉积型锂资源的地质特征及分布

富锂黏土岩矿床定义为非常规锂矿（Kesler et al.，2012）或沉积型锂矿，目前占世界锂资源总量<3%（Dessemond et al.，2019）。广义的沉积型锂资源一般指产于沉积岩、尚不具备独立工业开采而具有市场竞争价值的锂矿床，包括产于铝土矿、煤矿、高岭土矿床等伴生矿产利用的矿床（刘丽君等，2017）。

沉积型锂资源的赋矿岩石主要为凝灰岩和黏土岩类，少量为碎屑岩类（页岩、粉砂岩、细砂岩和粗砂岩），其中，黏土岩类包括黏土岩、铝质黏土岩以及铝

土矿等。国外沉积型锂资源的赋矿岩石以凝灰岩和碎屑岩类为主,如美国内华达州McDermitt/Kings Valley地区的沉积型锂资源的赋矿围岩为中新世中期的凝灰岩(Benson et al.,2017),而塞尔维亚贾达尔盆地中沉积型锂矿床的赋矿围岩主要为页岩、粉砂岩、细砂岩和粗砂岩(赵元艺等,2015)。中国沉积型锂资源的赋矿岩石主要为凝灰岩和黏土岩,其中富锂凝灰岩主要是扬子周缘地区中三叠世雷口坡组底部分布的绿豆岩,因其色似绿豆而得名,属于一种特殊的凝灰岩,主要分布于上扬子地区龙门山-大巴山地区及康滇隆起带(图1)。该类富锂凝灰岩厚度一般不大,在重庆铜梁地区厚度仅1~3 m(孙艳等,2018)。已有的研究表明,绿豆岩中锂含量差异较大,重庆铜梁地区$w(\mathrm{Li})$为663×10^{-6}(孙艳等,2018),峨眉山地区$w(\mathrm{Li})$为127×10^{-6}~518×10^{-6}(芦云飞等,2020),而四川谢家湾、重庆温泉镇、贵州辅处和贵州马落菁等地区雷口坡组样品平均$w(\mathrm{Li})$为267×10^{-6}(马圣钞等,2019)。

中国的富锂黏土岩类主要分布在黔北-渝南、黔中、滇东南-桂西、山西和豫西等地区(图1)。这些地区的铝土矿及含铝岩系的黏土岩及铝质黏土岩中均不同程度的富集锂(钟海仁等,2019),例如,黔中地区铝土矿和铝土岩$w(\mathrm{Li})$为75×10^{-6}~7392×10^{-6}(崔燚等,2018;刘平等,2020),豫西铝土矿$w(\mathrm{Li})$为65×10^{-6}~3531×10^{-6}(温静静等,2016;王滑冰等,2021)。

中国华南地区富锂黏土岩主要分布于黔北-渝南、黔中及滇东南-桂西地区,其中黔北-渝南地区富锂岩石主要分布于下二叠统大竹园组铝土矿(岩)(崔滔等,2014)。贵州大竹园铝土矿3个钻孔平均$w(\mathrm{Li})$大于2500×10^{-6}(王登红等,2013)。黔中富锂岩石分布于下石炭统九架炉组,岩石中锂表现出亲铝土矿和铝土岩,而疏绿泥石黏土岩的特征,而且致

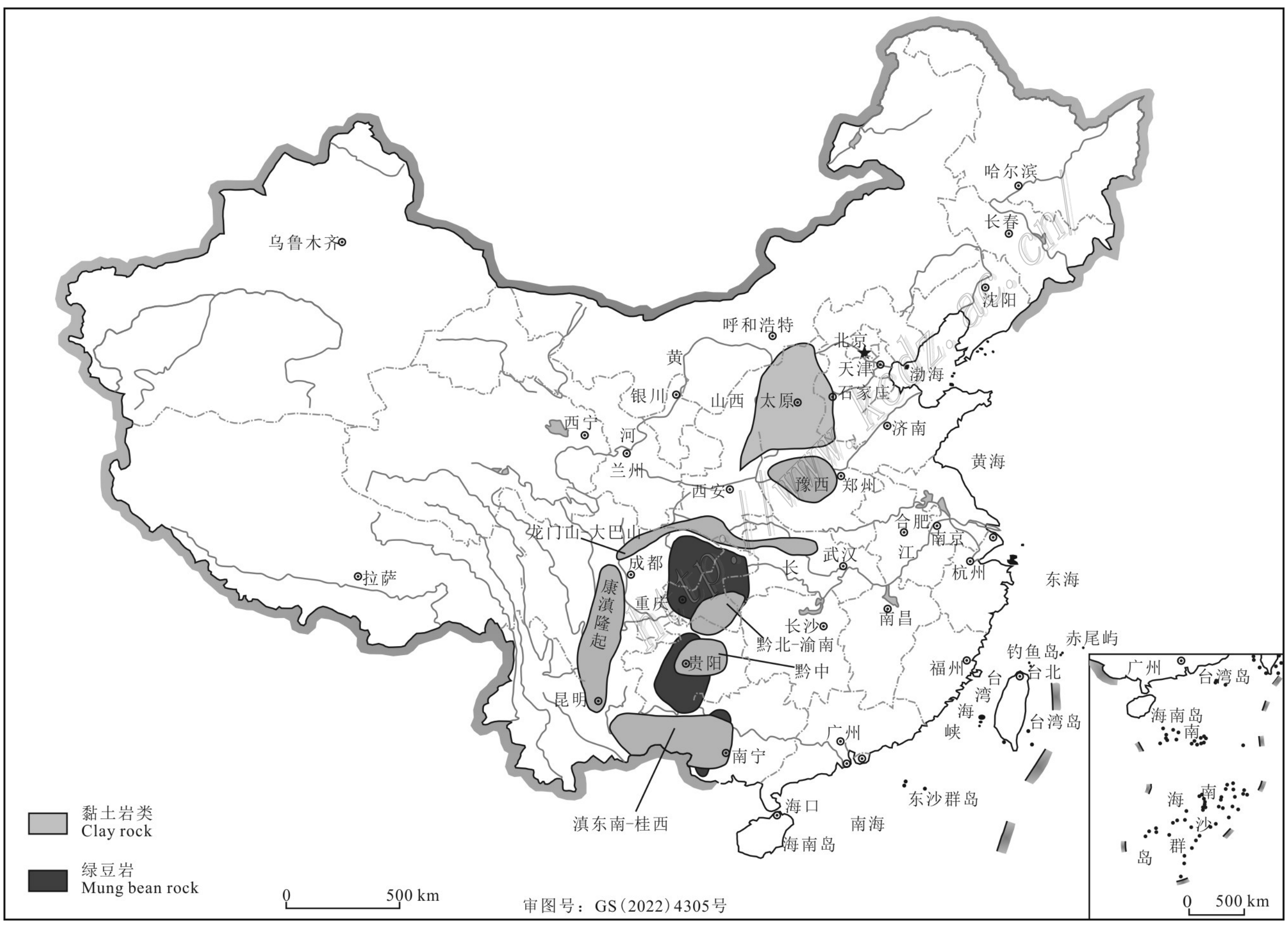

图1 中国铝土矿床及伴生沉积型锂矿潜在分布范围(据钟海仁等,2019;马圣钞等,2019修改)

Fig. 1 Potential distribution of major bauxite deposits and sedimentary lithium deposits in China (modified after Zhong et al., 2019; Ma et al., 2019)

密状铝土矿石中平均锂含量及富集程度高于碎屑状、土状矿石，如遵义后槽区铝土矿岩系中w(Li)为28×10^{-6}~249×10^{-6}，而修文铝土矿岩系平均w(Li)为52×10^{-6}（刘平等，2016），黔中小山坝锂基本富集在高岭土黏土岩中，w(Li)为204×10^{-6}~608×10^{-6}，鲕状铝土矿和碎屑铝土矿w(Li)较高，平均400×10^{-6}，而土状铝土矿中w(Li)很低，低于10×10^{-6}（叶霖等，2008）。滇东南-桂西沉积型锂资源赋存在上二叠统龙潭组（合山组）下部，含锂岩系的层序自下而上为铁质岩-铁铝质岩-铝土矿-铝质黏土岩-黑色碳质泥岩夹煤线（王行军等，2015a）。铝质岩、铝土矿等w(Li)变化较大，介于$(3$~$1207)\times10^{-6}$，且锂的含量由铝质黏土岩→菱镁矿→泥质铝土矿→铁质铝土矿→铝土矿→铁铝质岩→铁质岩依次降低（王行军等，2015b）。华南地区碳酸盐岩型锂资源主要以黔中下石炭统九架炉组和云南早二叠统倒石头组为代表（温汉捷等，2020），主要含锂岩石类型为黏土岩。九架炉组黏土岩平均w(Li)为2145×10^{-6}，最高达7384×10^{-6}（崔燚等，2018）；倒石头组黏土岩平均w(Li)为3000×10^{-6}，最高达$11\,000\times10^{-6}$（温汉捷等，2020）。

华北地区沉积型锂资源主要分布于豫西和山西地区上石炭统本溪组。沉积型锂资源与区域内的铝土矿具有相同的分布范围，主要分布于河南陕县-渑池-新安地区、嵩箕地区、济源-焦作地区和汝州-宝丰-鲁山地区及山西吕梁等地区。但不同地区锂含量变化较大，如陕县-渑池-新安地区4个铝土矿样品的w(Li)均高于30×10^{-6}，近一半样品的w(Li)超过$30\,000\times10^{-6}$（梁涛等，2013）；嵩箕地区铝土矿w(Li)为15×10^{-6}~243×10^{-6}，个别为678×10^{-6}，而铝质黏土岩w(Li)为283×10^{-6}~1260×10^{-6}（温静静等，2016）；焦作地区的黏土矿中w(Li)高达3531×10^{-6}（王滑冰等，2021）。汝州-宝丰-鲁山的铝土矿、铝质黏土岩和铁质黏土岩w(Li)为23×10^{-6}~1004×10^{-6}，平均224×10^{-6}，多数w(Li)低于250×10^{-6}（王莉等，2017）；山西地区本溪组铝土矿中w(Li)整体较低（杨军臣等，2004），但个别地区铝土矿（特别是铝土矿底部的黏土岩或者铝土矿夹层黏土岩）w(Li)较高，Li主要赋存在黏土岩特别是铁质黏土岩中，6个矿区铝土矿中w(Li)为9×10^{-6}~795×10^{-6}，平均为210×10^{-6}（杨中华，2011）。

可见，中国的沉积黏土型锂资源主要分布于晚古生代地层中，与同区域内的铝土矿具有相似的空间分布特征，锂含量变化较大，锂富集与黏土岩密切相关，尤其是铝质黏土岩中锂含量较高。

2 沉积型锂矿床锂赋存状态

沉积型锂矿床中的锂主要呈类质同象或离子吸附态和独立矿物相赋存在黏土矿物或其他矿物。沉积型锂矿床可开采、具有经济价值的独立含锂矿物极少，目前仅塞尔维亚贾达尔矿床出现的羟硼硅钠锂石具有开采价值（赵元艺等，2015）。此外，无论赋矿围岩是凝灰岩或是黏土岩，锂均以类质同象或离子吸附形式出现。如当赋矿围岩为凝灰岩时，即绿豆岩，岩石中的Li呈离子形态被黏土矿物吸附，形成锂蒙脱石（孙艳等，2018），且随着成岩作用的进行，蒙脱石逐渐向伊利石进行转变，形成锂伊利石（Lin et al.，2020）。美国McDermitt沉积型锂资源早期被认为锂主要以锂蒙脱石（$Na_{0.3}(Mg,Li)_3Si_4O_{10}(OH)_2$）形式存在（Glanzman et al.，1979；Rytuba et al.，1979），但最近成果表明，锂主要以锂伊利石形式存在（Castor et al.，2020）。

对于中国沉积型锂资源，虽然也是以类质同象或离子吸附形式出现，但是含矿矿物却变化多样。如沈丽璞等（1986）在河南某铝土矿发现锂绿泥石，呈现轮廓清楚、卷曲的叶片状或偶见花球状，单晶形态为细小鳞片状集合体。宋云华等（1987）认为，河南铝土矿中黏土岩的锂以锂绿泥石和含锂黏土矿物（如高岭石、伊利石和叶蜡石等）形式存在，其中含锂黏土矿物中以高岭石最多；李荣改等（2014a）在河南某地黏土矿中发现锂主要以锂绿泥石状态出现，且锂绿泥石集合体中包含一水硬铝石、伊利石等矿物；王新彦等（2020）对河南渑池某含锂铝土矿矿石的研究显示，高岭石、伊利石等矿物中锂更为富集，锂主要是以类质同象形式赋存在高岭石和伊利石等黏土矿物中，由于锂与铝等亲石元素离子半径接近，导致一水硬铝石等矿物中也含少量锂元素。贵州小山坝九架炉组铝土矿（岩）中伴生的锂主要以不成对类质同象替换（$Al^{3+}+Li^{+}\rightarrow Si^{4+}$）方式而赋存，部分锂以类质同象替换$Mg^{2+}$的形式赋存，而在铝土矿（岩）中以独立矿物形式和简单离子吸附形式存在的锂非常少（梁厚鹏，2018）。山西铝土矿中伴生Li主要呈离子吸附状态存在于一水硬铝石等铝矿物和高岭石、伊利石等铝硅酸盐矿物（杨军臣等，2004）；黔北中二叠统梁山组铝土矿床中的锂主要以吸附态形式赋存于重矿物（如锆石、金红石、磷钇矿等）的表面，独立矿物极少量（金中国等，2015）；黔北务正道新民大竹园

组锂以吸附形式主要赋存在高岭石中,伊利石、三水铝石和勃姆石也富集少量锂(龙珍等,2021)。华南地区碳酸盐黏土型锂矿床中锂主要以吸附方式赋存于富镁的黏土矿物——蒙脱石(温汉捷等,2020)中,锂在蒙脱石中很可能以离子吸附状态存在(姚双秋等,2021)。此外,锂绿泥石也是该碳酸盐黏土型锂资源的重要载体矿物之一,该类锂绿泥石可能为成岩过程中叶蜡石、伊利石等黏土矿物与富锂、镁的滨海浅层地下卤水或孔隙水/地下水反应形成(凌坤跃等,2021)。

因此,中国的沉积型锂资源中锂主要以类质同象和离子吸附形式出现,且主要赋存在绿泥石、蒙脱石、高岭石、伊利石中,少量可以赋存在一水硬铝石、三水铝石、勃姆石及部分重矿物中。

3　沉积型锂矿床的沉积特征

沉积环境对锂的富集具有重要的控制作用,还原、低能、滞留、局限的古地理环境有利于锂的富集(温汉捷等,2020),如美国内华达州McDermitt/Kings Valley及北美地区的沉积型锂矿床形成于封闭盆地的蒸发性湖泊环境,包括干盐湖和破火山口(Benson et al.,2017);贾达尔盆地富锂岩石由页岩、粉砂岩、砂岩等组成,上下与灰岩、凝灰岩和湖相蒸发岩等构成完整的沉积序列(图2),富锂岩石的沉积环境主要为三角洲-湖泊-碳酸盐台地(Matenco et al.,2012)。

对于中国的沉积型锂矿床,不论赋矿岩石是凝灰岩还是黏土岩,总体也呈现为还原、低能、滞留的沉积环境。如扬子地区富锂绿豆岩所属的雷口坡组,早期的沉积环境为潟湖(李凌等,2012)、局限台地(孙春燕等,2018)或潮坪(龚大兴等,2015),气候以干燥炎热为主,而沉积后期逐渐向温暖湿润变化;沉积水体整体为微咸水-咸水环境;水体氧化还原状态为亚氧化-还原状态(芦云飞等,2020)。

华南地区早石炭世含锂的九架炉组的沉积序列显示出滨海、淡化潟湖等特征,滨海相沉积物主要为砂岩、页岩和碳质泥岩等,泻湖相沉积物包括暗绿色

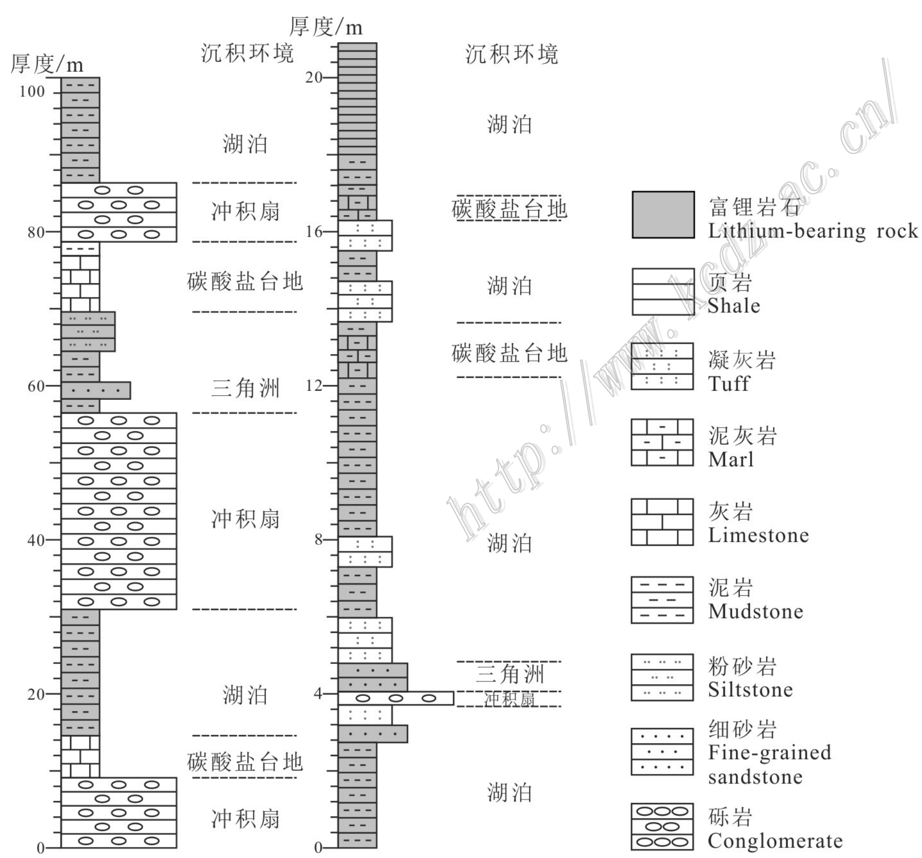

图2　贾达尔盆地富锂岩石沉积序列(据Obradović et al.,1997)

Fig. 2　Sedimentary successions of Li-enriched clastic rocks in the Jadar basin (after Obradović et al., 1997)

黏土岩、铁质黏土岩(杨明德,1989;莫江平等,1991)。但华南部分地区九架炉组则为沼泽相和潮坪-台地相,如遵义后槽区铝土矿岩系的沉积环境则为沼泽、泥炭沼泽、洪泛漫流等(刘平等,2016)。滇中地区倒石头组沉积环境主要为潮坪-局限台地(马永生等,2009)或局限台地(金玉玕等,1985)。

华南地区早二叠世大竹园组沉积时期,沉积环境包括冲积扇、湖泊和潮坪(杜远生等,2014;刘辰生等,2014;罗俊生等,2016),自下而上总体由陆相过渡到海陆过渡相。富锂的铝土矿和铝土岩沉积相为冲积平原上串珠状分布的湖泊相,顶部富锂碳质页岩沉积环境为潮上带泥沼坪(刘辰生等,2015)。此外,根据黔北钻井岩芯和探槽资料显示,富锂铝土矿沉积的湖泊环境进一步划分为滨湖和浅湖(刘辰生等,2018)。华南滇东南地区晚二叠世含锂地层龙潭组形成于海陆交互相(王行军等,2015a),桂西晚二叠世富锂的合山组沉积环境为潮坪-泻湖(李惠等,2016)。

华北地区含锂黏土岩类主要为本溪组,岩相古地理显示主要由泥坪、泻湖、障壁岛等组成(房尚明,1992),山西本溪组主要形成于古陆、古岛边缘的沼泽、泻湖环境(甄秉钱等,1986;王银川等,2011)。而豫西地区本溪组的沉积环境为滨岸泻湖(陈守民等,2011)、滨海-泻湖(孙越英等,2006)或滨海-泻湖-沼泽(李战明等,2012;组新许等,2019)。

为了更好地分析中国不同地区沉积型锂矿床赋矿围岩的沉积特征,文章分别选择黔中九架炉组、黔北大竹园组、滇东南龙潭组、桂西和平果地区合山组、山西本溪组和豫西本溪组的富锂黏土岩的地球化学数据从风化作用和沉积再旋回2个方面对赋矿围岩的沉积特征进行对比分析。

(1) 风化作用

由于富锂岩石粒度较细,风化作用、搬运作用以及成岩作用等过程对其成分影响较大(Johnson,1993)。因此,碎屑岩的化学成分可以反映物源区母岩风化的相关信息。中国不同地区富锂黏土岩类岩石的化学蚀变指数CIA(Chemical Index of Alteration;Nesbitt et al.,1984)均较高(图3a),介于78~99,表明富锂黏土岩类岩石经历强烈风化作用。富锂黏土岩类大多数位于高岭石、绿泥石和水铝矿附近(图3a),且数据点落在斜长石与高岭石、伊利石矿物成分的连线附近,说明源区的化学风化主要是斜长石向黏土矿物(高岭石、伊利石等)的转换过程,样品处于强烈风化阶段。碎屑岩的成分成熟度指数ICV(Index of Compositional Variabiliyty;Armstrong-Altrin et al.,2015)反映化学成分接近终极产物的化学特征,且ICV<0.84表明包含大量蚀变矿物(如高岭石、伊利石和白云母等),样品成熟度高;ICV>0.84表明包含大量长石、角闪石和辉石等矿物,样品的成分成熟度低(Cox et al.,1995)。CIA-ICV图解显示(图3b),中国所有富锂黏土岩类ICV小于0.85,成熟度较高。而且ICV值较低表明风化程度增强,这与Al_2O_3-(Na_2O+CaO)-K_2O图解(图3a)得出的结论一致。

(2) 沉积再旋回作用

在风化过程中,岩石中U会丢失,Th/U值将随着风化程度的增加而增加,因此Th/U值与风化程度有关(McLennan et al.,1995)。中国富锂黏土岩的Th/U值多数高于上地壳的Th/U值(3.8),表明源区处于中等以上风化程度(图4a),只有个别地区黏土岩的Th/U值较低。从风化程度看,富锂黏土岩母岩风化强度高,且成分成熟度高。Zr/Sc-Th/Sc图解(图4b)显示,桂西合山组经历沉积再旋回作用,而其他地区黏土岩很少经历再旋回作用。这一结果也可能是由于这些地区黏土岩的物质来源于较老源区,Th/Sc值偏低,偏离沉积物再旋回线(Basu et al.,1990;McLennan et al.,1993)。

4 沉积型锂矿床的物质来源

沉积型锂矿床由于赋矿围岩不同,成矿物质来源也不同。对于赋矿围岩为凝灰岩的沉积型锂矿床,成矿物质主要为来源于火山作用。美国内华达州McDermitt/Kings Valley及北美地区沉积型锂矿床的形成主要是流纹岩岩浆和火山灰受到大气降水和地底热流等热液流体作用而形成,锂成矿物质主要来自于流纹质熔岩和火山灰(Benson et al.,2017;图5)。中国华南地区的富锂绿豆岩,具有酸性火山岩的特点,源岩为英安岩、流纹岩(图6a;孙艳等,2017;2018;马圣钞等,2019;鞠鹏程等,2020;李宸等,2020;Lin et al.,2020)。

当沉积型锂矿床的赋矿围岩为黏土岩或碎屑岩时,成矿物质的源区较为复杂,但均与下伏岩石具有密切联系。如贾达尔盆地富锂岩石由页岩、粉砂岩、砂岩等组成,并与灰岩、凝灰岩和湖相蒸发岩等构成完整的沉积序列(图2),但下伏凝灰岩为其主要的物质来源(赵元艺等,2015)。目前研究显示,中国大部

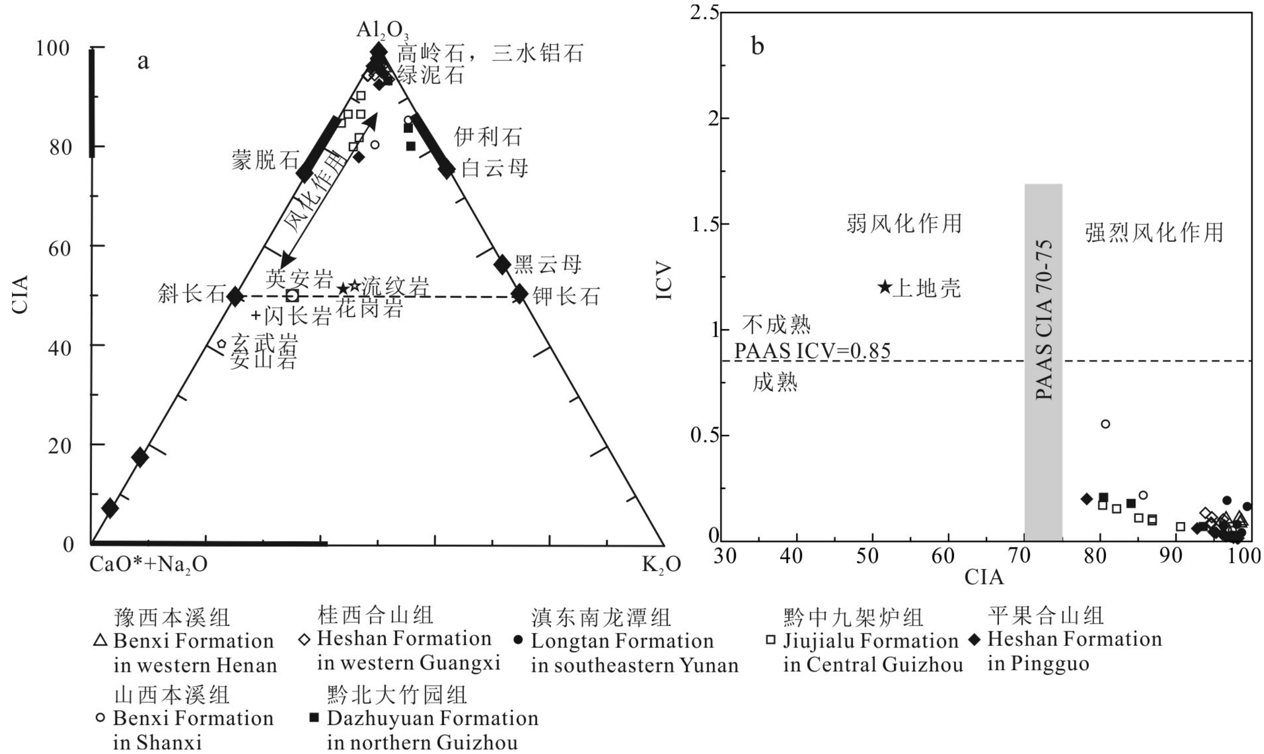

图3　中国富锂黏土岩风化程度Al_2O_3-(Na_2O+CaO*)-K_2O图解(a,据Nesbitt et al.,1984)和风化程度(CIA)-成熟度(ICV)图解(b,据Long et al.,2012)

注:PAAS为后太古宙平均页岩,豫西本溪组为三门峡七里沟实测样品,桂西合山组数据引自姚双秋等,2021;滇东南龙潭组引自王行军等,2015a;黔中九架炉组引自崔燚等,2018;平果合山组数据引自凌坤跃等,2021;山西本溪组引自孙思磊等,2012;黔北大竹园组引自李沛刚等,2014

Fig. 3　Al_2O_3-(Na_2O+CaO*)-K_2O plots showing the weathering trend (a, after Nesbitt et al., 1984) and CIA versus ICV plot showing the intensity of weathering and maturity of the siliciclastic sediments of the lithium-bearing rocks in China (b, after Long et al., 2012)

Note: PAAS- Post-Archaean Average Shale. Data adopted are as follows: Benxi Formation in western Henan Province measured, Heshan Formation in western Guanxi Province from Yao et al.,2021, Longtan Formation in southeastern Yunnan Province from Wang et al., 2015a, Jiujialu Formation in central Guizhou Province from Cui et al., 2018 , Heshan Formation in Pingguo from Ling et al., 2021, Benxi Formation in Shanxi Province from Sun et al., 2012, and Dazhuyuan Formation in northern Guizhou Province from Li et al., 2014

分沉积型锂与下伏碳酸盐岩有关,如华南九架炉组富锂黏土岩与下伏上寒武统娄山关组白云岩有密切成因联系(Ling et al.,2017;崔燚等,2018;张明等,2018;凌坤跃等,2019;温汉捷等,2020),山西铝土矿中含锂的铁质黏土岩也与铝土矿的风化源岩即基底奥陶系碳酸盐岩所夹黏土岩和泥质白云岩有关(柴东浩等,2001)。但是,除了碳酸盐岩的风化作用提供部分锂外,区域内的岩浆岩也提供部分成矿物质,如河南巩义地区本溪组的碎屑锆石U-Pb年龄指示北秦岭加里东期中酸性花岗质侵入岩也是物源区之一(Zhu et al., 2014; Wang et al., 2016; 曹高社等, 2018; Zhao et al., 2019),偃龙地区本溪组的物质源区不仅是华北板块南部北秦岭造山带,部分甚至来自华北板块北部内蒙古隆起(Cai et al., 2015;刘凌之,2018)。

除了上述的碳酸盐岩和长英质岩浆岩外,泥质岩和基性岩也可以为沉积型锂矿床提供成矿物质。如黔北务正道以韩家店组泥质岩为基底的古隆起区经历长期的化学风化和剥蚀,为大竹园组含矿岩系提供丰富的成矿物质来源(刘平,1993;雷志远等,2013;余文超等,2014)。滇东南-桂西地区的黏土岩稀土元素特征显示物源主要来自峨眉山玄武岩,少量来自下伏碳酸盐岩(Deng et al.,2010;侯莹玲等,2014;张启明等,2015;姚双秋等,2021)。但相对来说,沉积型锂矿床中富锂碎屑岩的物质来源主要为长英质火成岩,少量为砂岩和泥岩(图6b、c)。

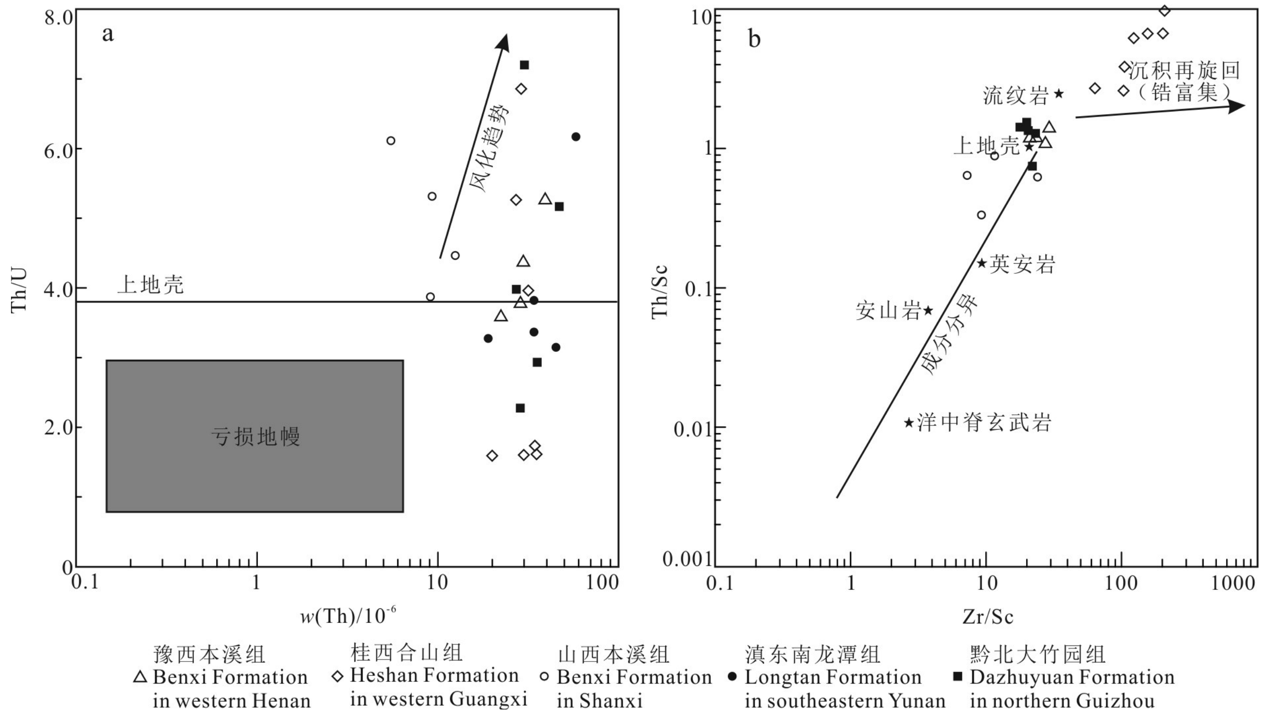

图 4　中国富锂黏土岩的 Th/U-w(Th)图解（a，据 McLennan et al.，1993）和 Zr/Sc-Th/Sc 图解（b，据 McLennan et al.，2003）

Fig. 4　Plots of Th/U ratio versus w(Th) abundances (a, after McLennan et al., 1993) and Zr/Sc-Th/Sc diagram (b, after McLennan et al., 2003) lithium-bearing rocks in China

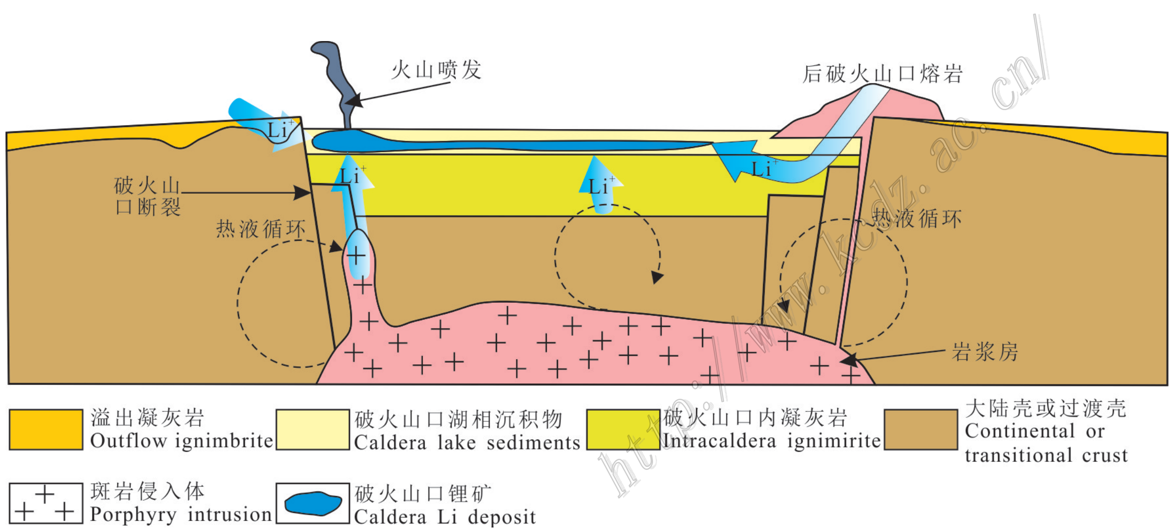

图 5　富锂沉积型锂资源的成矿物质来源及形成模式图（据 Benson et al.，2017）

Fig. 5　Schematic model for the source of ore-forming materials and formation of caldera-hosted Li clay deposits (after Benson et al., 2017)

5　沉积型锂矿床的成矿背景

赋矿岩石的类型决定了沉积型锂矿床沉积于不同的构造类型盆地。当赋矿岩石为火山岩，沉积型锂矿床沉积于板内和岛弧类型的盆地。如美国内华达州 McDermitt 锂矿床的破火山口沉积于陆内裂谷（Smith et al., 1968；图 5）。贵州大寨地区中三叠统关岭组的绿豆岩和四川雷口坡组底部绿豆岩具有长英质岛弧岩浆的特征，表现出与大洋俯冲消减作用

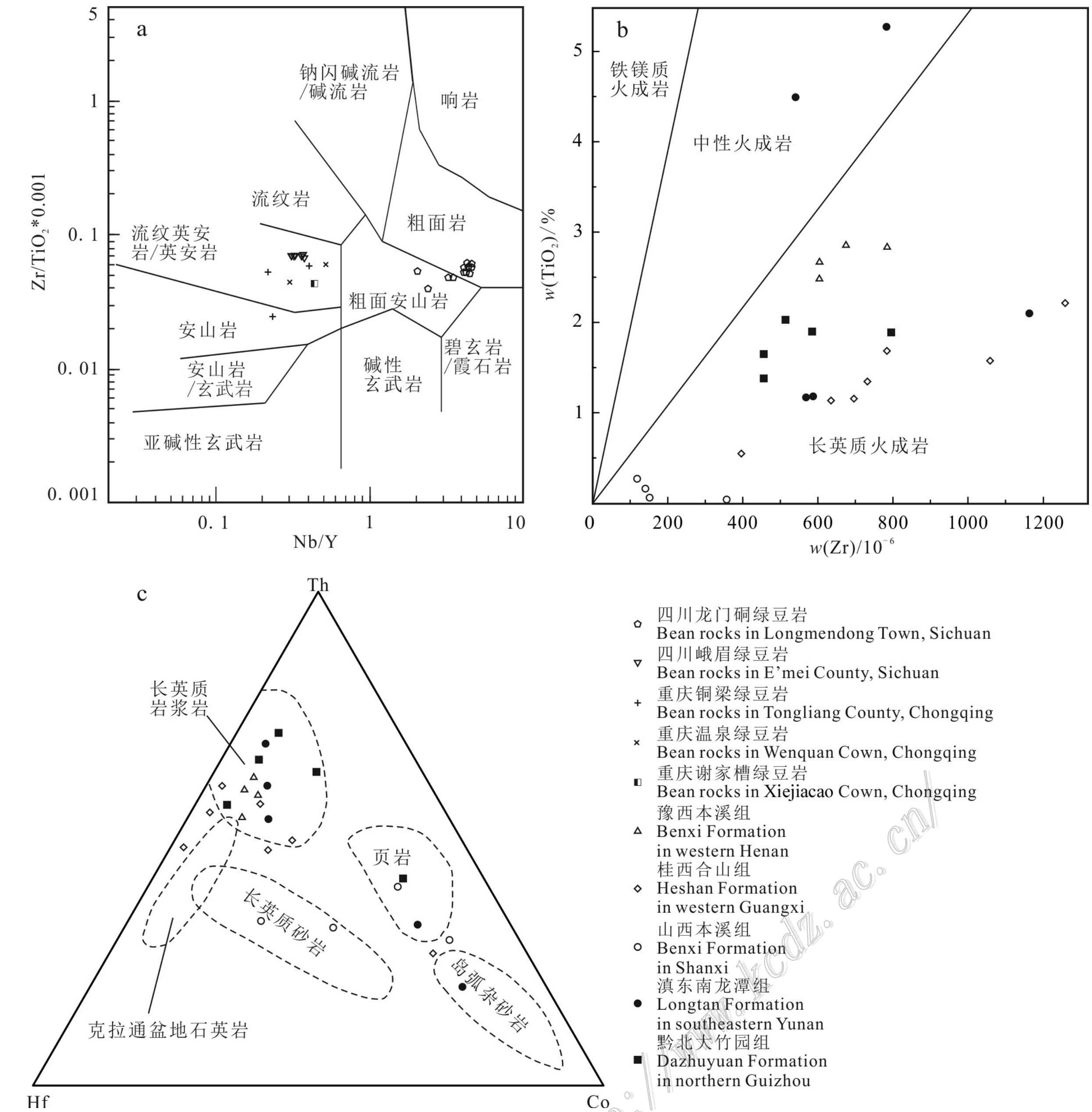

图6　不同地区富锂绿豆岩和碎屑岩源岩判别图

a. Nb-Zr/TiO_2图解(Winchester et al.,1977);b. Zr-TiO_2判别图解(据 Hayashi et al.,1997);c. Th-Hf-Co判别图解(据 Talyor et al.,1985)

注:图a数据重庆铜梁引自孙艳等,2018;重庆温泉引自鞠鹏程等,2020;四川龙门硐引自芦云飞等,2020;四川峨眉引自李宸等,2020;谢家槽引自 Lin et al.,2020。图b和c数据来源见图3

Fig. 6　Discrimination diagrams illustrating provenance of lithium-bearing bean rocks and clastic rocks

a. Nb-Zr/TiO_2 diagram (Winchester et al., 1977); b. Zr-TiO_2 diagram (after Hayashi et al., 1997); c. Th-Hf-Co discrimination diagram (after Talyor et al., 1985)

Note: Data of diagram adopted are as follows: Tongliang in Chongqing from Sun et al., 2018; Wenquan in Chongqing from Ju et al., 2020; Longmendong in Sichuan Province from Lu et al., 2020; Emei in Sichuan Province from Li et al., 2020; Xiejiacao in Chongqing from Lin et al., 2020. Data of b and c diagrams are adopted in Fig. 3

有关的岛弧/陆缘弧火山岩相似的地球化学特征,为华南火山活动的产物(王宁祖等,2019;李宸等,2020)。谢家槽地区绿豆岩地球化学特征显示源岩为流纹安山岩/安山岩类,并且源岩形成于板内构造

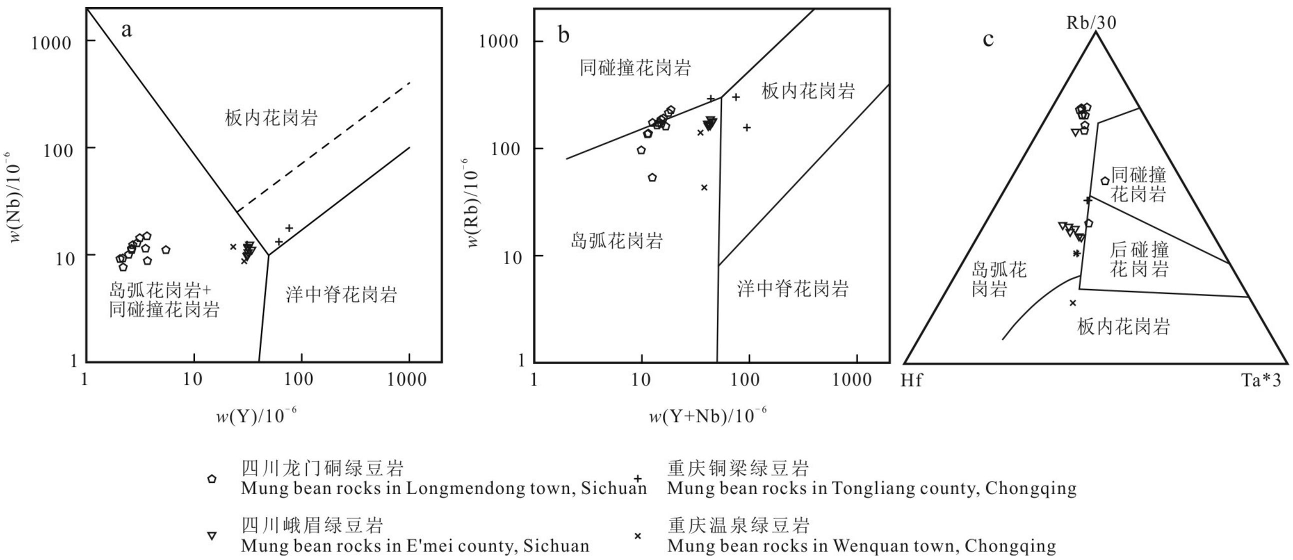

图7 扬子周缘中三叠世绿豆岩构造环境判别(底图据Pearce et al.,1984,数据来源见图6a)

Fig. 7 Tectonic setting of Middle Triassic mung bean rocks in the Yangze block (base map after Pearce et al., 1984, data are adopted in Fig. 6a)

环境(Lin et al.,2020)。重庆温泉、四川谢家湾绿豆岩可能为峨眉山地幔柱演化晚期阶段壳源物质参与的中-酸性岩浆活动后续热液-沉积事件的产物(马圣钞等,2019)。但根据绿豆岩的微量元素特征可以发现,华南绿豆岩大多数形成于岛弧环境,少量数据落于板内环境(图7)。

赋矿岩石为黏土岩或碎屑岩,沉积型锂矿床可以沉积于裂谷、被动大陆边缘和克拉通坳陷盆地,如塞尔维亚贾达尔盆地的富锂岩石沉积于裂谷盆地。中国的沉积型锂矿床的源岩主要形成于大陆岛弧,少量为被动大陆边缘(图8),富锂地层则主要沉积于被动大陆边缘和克拉通坳陷盆地。如华南地区早石

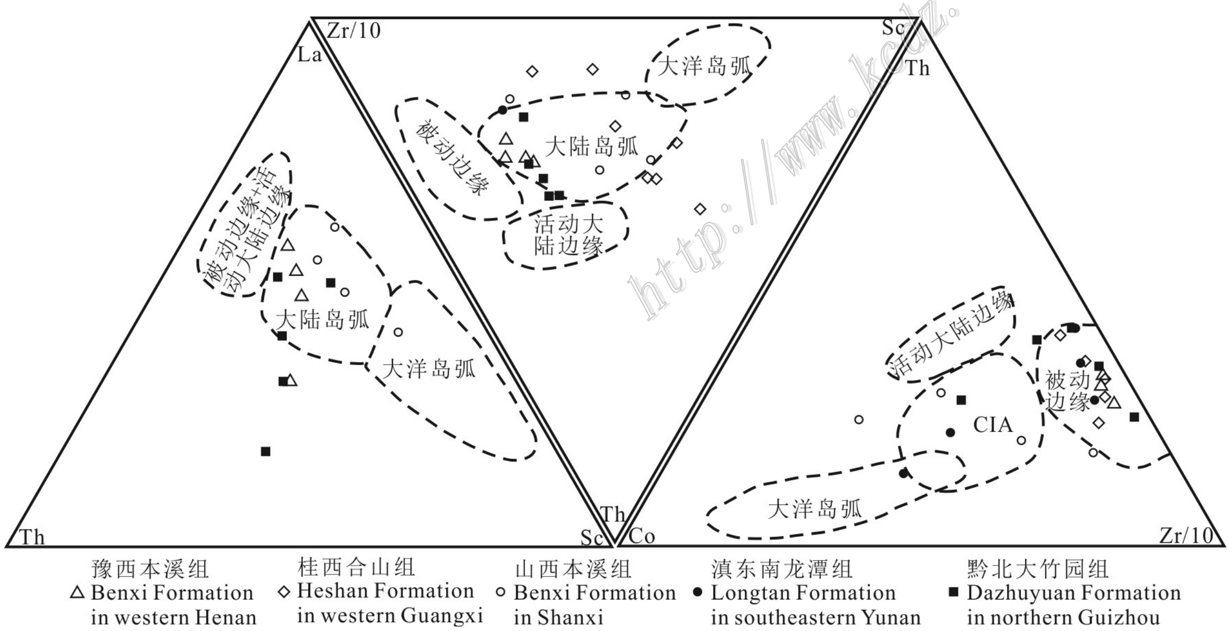

图8 中国富锂碎屑岩沉积构造环境判别图(据Bhatia et al.,1986,数据来源见图3)

Fig. 8 Tectonic discrimination plots of the lithium-bearing clastic rocks in China (after Bhatia et al., 1986, data are adopted in Fig. 3)

表1 沉积型锂矿床成矿规律

Table 1 Metallogenic regularity of sedimentary lithium deposits

岩石类型	分布地区	成矿时代	地层	沉积环境	成矿来源	源岩背景	成矿背景
凝灰岩	美国McDermitt/Kings Valley	中新世中期		湖泊	流纹岩和火山灰	大陆裂谷	大陆裂谷
黏土岩	豫西、山西	晚石炭世	本溪组	滨岸-泻湖	岩浆岩为主	大陆岛弧	克拉通盆地
黏土岩、铝土矿	滇中、黔中	早石炭世	九架炉组	陆相洪积作用及湖泊	碳酸盐岩	大陆岛弧	被动大陆边缘
黏土岩、铝土矿	黔北-渝南和黔东南	晚石炭世—早二叠世	大竹园组	冲积扇、湖泊和潮坪	页岩、灰岩和白云岩	大陆岛弧	被动大陆边缘
黏土岩、铝土矿	滇东南-桂西	晚二叠世	合山组吴家坪组和龙潭组	潮坪-泻湖	玄武岩和碳酸盐岩	大陆岛弧	被动大陆边缘
凝灰岩	扬子周缘	中三叠世	雷口坡组		长英质火山岩	大陆岛弧	克拉通盆地
页岩、粉砂岩、细砂岩和粗砂岩	塞尔维亚贾达尔	中新统		湖泊	凝灰岩		凹陷盆地

炭世至早二叠世九架炉组和倒石头组沉积期受古特提斯洋演化影响,沉积于被动大陆边缘(Chen et al., 2018; Wang et al., 2018),桂西地区晚二叠世富锂岩石也沉积于被动大陆边缘(Lehrmann et al., 2007)。华北地区晚石炭世的沉积地形是南高北低、西高东低的准平原化盆地,富锂岩石沉积于弱伸展背景下的克拉通坳陷盆地(周丽,2005;解东宁,2007)。

根据富锂岩石的地质特征,文章总结沉积型锂矿床成矿地质特征(表1)。沉积型锂矿床多沉积于水动力较弱的环境(潟湖、沼泽或湖泊),形成于克拉通盆地或者被动大陆边缘环境,物源以岛弧性质的长英质岩浆岩为主,源区经历强烈风化作用,沉积物成熟度较高。

6 沉积型锂资源成矿作用初探

目前对于沉积型锂资源成矿作用过程还不清楚,但根据锂的物质来源,沉积型锂资源的成矿作用总体可以分为2种:①火山岩受流体淋滤、交代,形成锂的富集;② 碳酸盐岩风化、沉积。

对于第1种成矿作用,主要基于沉积型锂资源的物质主要来源于火山岩。Hofstra等(2013)认为当A型或S型花岗质岩浆喷发,火山灰沉积在封闭的汇水盆地(drainage basin)。随着火山喷发,压力逐渐降低使得流体饱和、形成囊泡和玻屑,锂扩散至玻屑表面。大气降水水解玻屑,从火山灰中淋滤锂,搬运至盆地,在干旱条件下蒸发形成盐坪,使得锂进一步富集,富锂卤水与盆地沉积物反应,形成富锂黏土矿(图9)。美国McDermitt地区、塞尔维亚贾达尔盆地及华南地区绿豆岩中锂都是以类似作用形成。

美国McDermitt地区的沉积型锂资源,主要是中酸性熔岩喷发,富锂的挥发分物质包裹在玻屑凝灰岩外部或者被浮石捕获,形成以凝灰质沉积物组成的火山口。火山口垮塌之后,剩余的岩浆形成富锂的热液流体,在封闭的火山口盆地中与大气降水混

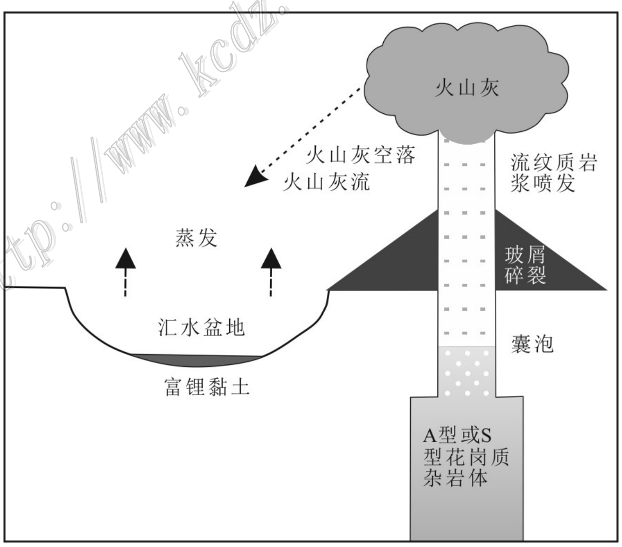

图9 黏土型锂资源形成模式示意图(据Hofstra et al., 2013修改)

Fig. 9 The formation mechanism of Li-bearing clay type deposits (modified after Hofstra et al., 2013)

合形成混合的成岩流体，热液流体和成岩流体进一步淋滤盆地周围的流纹质熔岩和火山灰，经沉积作用形成富锂沉凝灰岩（Castor et al.，2020）。中国扬子周缘地区富锂的绿豆岩也是由岩浆喷发形成大量的火山灰，在海洋环境中，火山灰经过成岩作用，形成以蒙脱石和绿泥石等黏土矿物为主的绿豆岩。在成岩作用阶段，随着埋藏深度、孔隙水（尤其是K^+含量）和时间的变化，蒙脱石逐渐向伊利石转变，逐渐形成伊蒙混层和伊利石。当热演化温度达到180℃，孔隙水（海水）以及热液流体等淋滤富锂绿豆岩，促使蒙脱石向伊利石进行转变（Lin et al.，2020）。塞尔维亚贾达尔盆地的沉积锂资源也是新近纪火山喷发后，形成大量的凝灰岩，大气降水或者同沉积断裂附近的流体淋滤凝灰岩，携带富锂沉积物进入湖泊，形成富锂碎屑岩（赵元艺等，2015）。

第2种成矿作用方式则主要认为锂来源于含锂地层下伏的不纯碳酸盐岩，以华南地区碳酸盐黏土型锂资源为代表。温汉捷等（2020）认为当不纯碳酸盐岩经历风化作用，为后期沉积型锂资源锂富集提供物质基础，当这些含锂风化物在还原、低能、滞留、局限的古地理环境中沉积，并在碱性环境中使锂以吸附方式存在蒙脱石等黏土矿物中，从而形成沉积型锂资源。至于更具体的过程和成矿机制还有待于进一步研究。

7 结 论

（1）沉积型锂资源主要富集在黏土岩、铝质黏土岩及铝土矿中，部分分布于凝灰岩（绿豆岩）以及砂岩、泥岩等碎屑岩；锂主要以离子吸附或类质同象形式赋存于锂蒙脱石、锂伊利石等黏土矿物及锂绿泥石中，少量为独立含锂矿物。

（2）富锂沉积岩形成于还原环境，主要来源于岛弧类长英质火山岩和少量碎屑岩-碳酸盐岩，但经历强烈风化作用，经历再旋回的搬运作用。

（3）富锂岩石的源区来自大陆岛弧环境，沉积于被动大陆边缘、裂谷或克拉通盆地。在构造、物源以及气候等多因素影响下，富集成矿。

（4）沉积型锂资源中的锂既可以来自于火山岩，也可来源于下伏的碳酸盐岩。后期流体对火山岩的淋滤、交代和碳酸盐岩的风化作用均可形成沉积型锂资源。成矿源区的不同造成成矿作用的差异。

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