

海绿石的成因、指相作用及其年龄意义

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摘要: 海绿石以独特的绿色自生色和球粒形状与围岩形成明显反差, 关于其成因、演化、沉积和地层学意义目前存在3种普遍被认可并被采用的观点。海绿石是典型的海相沉积自生矿物, 原地海绿石是“慢速、弱还原、较深水环境”的典型指相矿物之一, 通常是海侵相的产物, 含海绿石的地层在浅海沉积中常被作为海侵时期“凝缩段”及其相关沉积的识别标志之一, 是沉积年代学中 K-Ar、⁴⁰Ar/³⁹Ar 年龄理想的测定对象。在采用海绿石作为典型指相矿物的过程中, 应注意海绿石可以形成于多种沉积环境中, 只有原地海绿石才能作为海侵时期“凝缩段”及其相关沉积的识别标志, 海绿石年龄往往呈“年轻化”或“老化”, 没有火成岩定年准确, 只有成熟、富钾的海绿石才是最好的定年对象。

关键词: 海绿石; 指相矿物; 凝缩段; 沉积年代学

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Genesis, diagnostic role and age significance of glauconites

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Abstract: With its unique green color and pellet-like shape, glauconite contrasts remarkably with the surrounding rocks. Currently there are three generally adopted concepts: glauconite is a kind of typical marine sedimentary mineral, special in-situ glauconite is one of the diagnostic minerals indicative of slow depositional rate, weak reduction and deep-water environment, glauconites are often deposited during the transgressive period, and therefore the glauconite-bearing formations in shallow sediments are often regarded as condensed section in the transgressive period. Glauconites are ideal measurement objects of K-Ar and ⁴⁰Ar/³⁹Ar ages. Their genesis, evolution, and sedimentary as well as stratigraphic significance have been widely used. It should be noted that glauconites can be formed in a variety of sedimentary environments, only in-situ glauconites can be used to identify the condensed section, but its age may be younger or older than the real age.

Key words: glauconite; diagnostic mineral; condensed section; depositional chronology

海绿石常以独特的绿色自生色和球粒形状与围岩形成明显的反差。目前许多学者将海绿石矿物应用于沉积环境(Chacrone *et al.*, 2004; 徐勇航等, 2010; 王俊涛等, 2011; 赵霞飞等, 2011; 陈世悦

等, 2012) 层序地层(Harris and Whiting, 2000) 盆地构造演化(Berra *et al.*, 2007) 沉积岩定年(Taylor and Curtis, 1995; 李明荣等, 1996; Téllez Duarte and López Martínez, 2002; Godet *et al.*, 2011) 等方

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面的研究,因此详细地了解海绿石这种指相矿物的矿物学、沉积学、成因及其年龄研究具有十分重要的实践和理论意义。

1 海绿石的矿物学、沉积学分类

海绿石(glaucanite)是一种富钾、富铁、含水的二八面体层状铝硅酸盐矿物,晶体结构属于云母类矿物,一般化学式为 $(K, Na, 1/2 Ca)_x(Al, Fe^{2+}, Fe^{3+}, Mg, Ti)_2(Si_{4-x}, Al_x)O_{10}(OH)_2$ 通常 $0.4 < x < 1$, 在八面体位置中 $\Sigma Fe > AK$ (Nesse, 1991)。

较多学者利用 X 射线衍射分析研究了海绿石的矿物学特征(Odin and Fullagar, 1988; Rao *et al.*, 1995; Muller *et al.*, 2000; Giresse and Wiewióra, 2001),部分学者研究了海绿石演化与 X 衍射分析参数之间的关系(Odin and Matter, 1981; Kim and Lee, 2000; Pasquini *et al.*, 2004; Amorosi *et al.*, 2007)。Odin 和 Matter(1981)将 $d(001)$ 值估算为 001 和 020 反射之间的距离,该值接近于 001 峰的位置(Amorosi *et al.*, 2007)。事实上,001 衍射的半峰宽被认为是海绿石成熟度的较好的评价指标(图 1)(Amorosi *et al.*, 2007)。图 1 中,随着海绿石成熟度的增加,001 衍射峰的位置发生变化并且峰宽(FWHM)逐渐减小;垂直灰线指示 001 衍射峰的位置大约在 1 nm,说明它是高度演化的海绿石质云母。海绿石和铁伊利石(Fe-illite)、铁铝蒙脱石(Fe-Al smectite)矿物成分相似,因此根据主要矿物成分很难区分它们,但 Meunier 和 El Alban(2007)根据 $4M^+/Si-Fe$ /八面体阳离子总数区分了这些矿物。沉积体系的物理和化学条件对含铁粘土矿物的矿物学和地球化学特征有着强烈影响。高盐泻湖环境有利于形成铁伊利石(Fe-illite),而开放的海相条件有利于形成海绿石(Berg-Madsen, 1983; El Albani *et al.*, 2005; Meunier and El Albani, 2007)。如果沉积环境处于大量淡水输入、明显降低铁离子移动性的氧化条件时,那么形成的海绿石缺铁;如果沉积环境处于浅海氧化条件时, K^+ 活动性进一步降低,海绿石富铝(Berg-Madsen, 1983)。到目前为止,仅少量学者研究了海绿石颗粒的主要元素和微量元素特征(Valeton *et al.*, 1982; Ireland *et al.*, 1983; Jarar *et al.*, 2000),对海绿石的化学成分与成熟度之间的关系研究仍然相对较少。Amorosi 等(2007)研究了西欧 25 个地点、覆盖了各种成熟度的白垩纪至

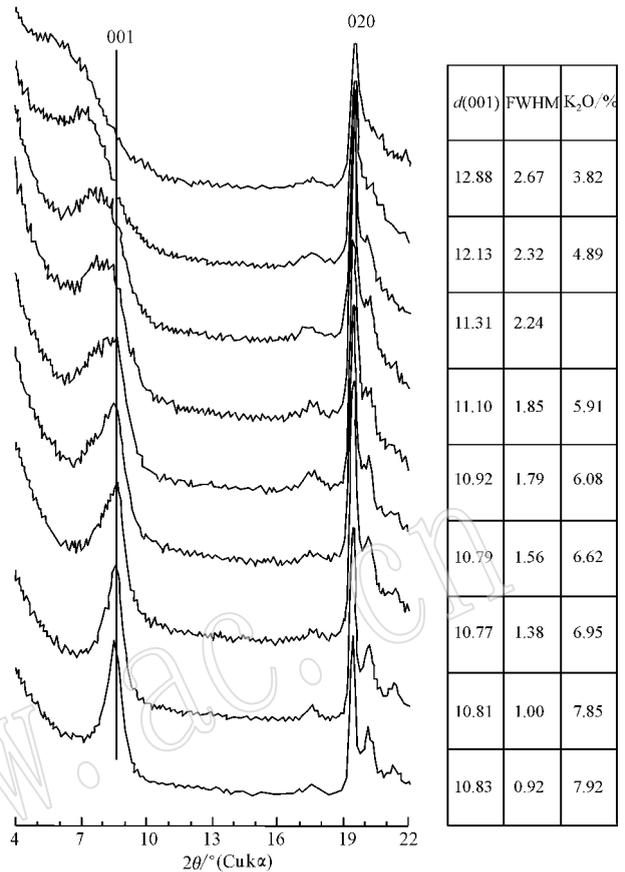


图 1 不同演化阶段海绿石 XRD 模式的对比

(Amorosi *et al.*, 2007)

Fig. 1 The comparison of the XRD models for different evolution phases of glauconite (after Amorosi *et al.*, 2007)

上新世深海海绿石的全岩主要矿物成分,发现这些海绿石的 Fe_2O_3 含量为 22% ~ 26%, K_2O 含量为 6% ~ 8.5%。

海绿石广泛地分布在现代沉积物和古代海相沉积岩之中,在古代沉积岩中有多种多样的产状。根据成因,海绿石可以分为原地海绿石和异地海绿石两种类型(Amorosi, 1995, 1997)。原地海绿石未经过搬运作用的改造,保留了其形成时的物理化学条件、沉积特征以及古海洋条件方面的信息(Stille and Clauer, 1994),对其研究可以揭示海绿石形成时的古环境。以底层形式(薄膜状覆盖层或结壳层等)产于不整合面或硬底面上的海绿石通常属于原地海绿石(Mei *et al.*, 2008; 梅冥相等 2008)。异地海绿石经过其他作用被搬离其形成地点,进一步分为准原地(或层内)和碎屑(或层外)海绿石。准原地海绿石成熟度低至中等(Amorosi, 1995),虽然经过搬运而远离其形成地点,但还是保存在同时代沉积中(图

2)。海绿石常以颗粒或碎屑的形式产出因而容易被搬运(Ordin, 1988),碎屑海绿石是指那些从更老的地层中改造而来的海绿石颗粒。

2 海绿石的形成环境

对现代海洋表层沉积物取样分析表明,海绿石是典型的浅海环境的指相矿物,主要形成于沉积作用缓慢的外陆架和大陆斜坡上部,水深 50~500 m (一般为 100~200 m, 200 m 左右为最适宜形成深度),水温一般为 15~20℃,正常盐度,次氧化至缺氧条件($Eh \sim 0$),pH 值 7.5~8.5(Ordin and Matter, 1981; Odin and Fullagar, 1988; Amorosi, 1995, 1997; Kitamura, 1998; Chafetz and Reid, 2000;

Harris and Whiting, 2000; Giresse and Wiewióra, 2001; Wiewióra *et al.*, 2001; Rousset *et al.*, 2004; Velde, 2004; El Albani *et al.*, 2005; 赵全基等, 1992; 陈丽蓉, 1994; 陈华胄等, 1997; 梅冥相等, 2008),同时海相的低能条件有利于海绿石的形成(Amorosi, 2003)。

地质历史中海绿石的发育主要有早古生代和晚中生代两个峰期,这些海绿石主要形成于温带、亚热带气候条件下,分布于各个分散的克拉通地块中,与海平面升高和大陆架地区低的沉积速率有关(Huggett *et al.*, 2005)。

尽管现代海绿石仅形成于不足 500 m 的海底(Amorosi, 2003),但古代海绿石却明显地可以形成于多种沉积环境中,如高盐泻湖(El Albani *et al.*, 2005;

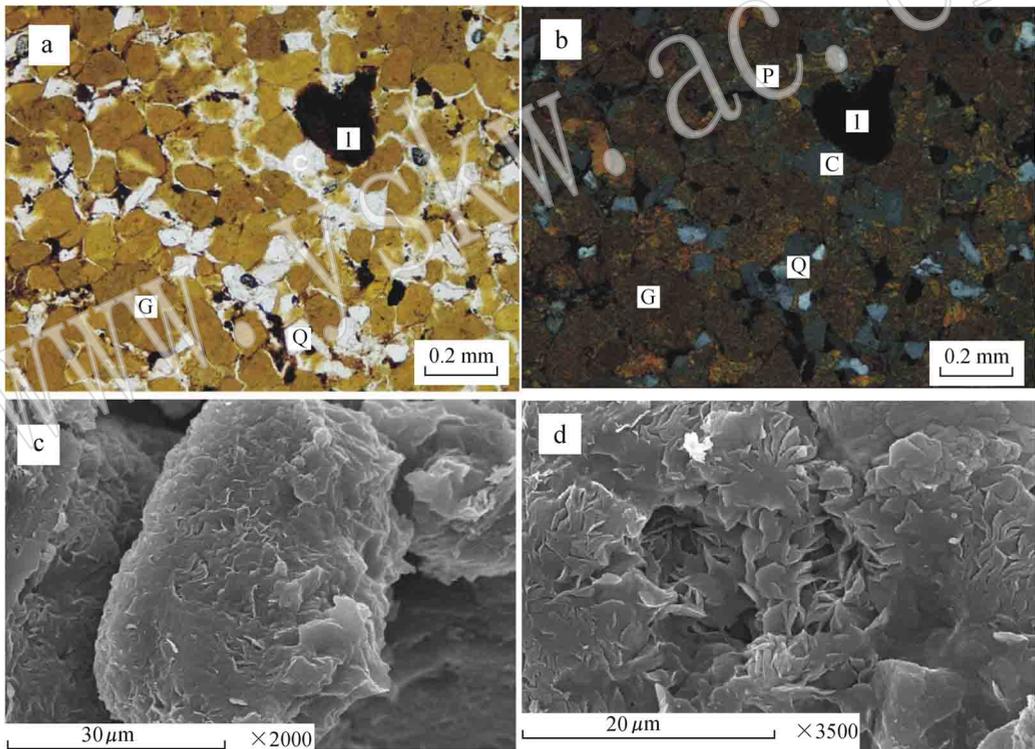


图 2 埃及 Bahariya Oasis 赛诺曼阶沉积物中海绿石的显微特征(Baioumy and Boulis, 2012)

Fig. 2 Microscopic characteristics of glauconite in the Bahariya Oasis Cenomanian sediments of Egypt (after Baioumy and Boulis, 2012)

a—具碎屑石英颗粒的粘土(C)和氧化铁(I)基质中,发育细-中粒、分选中等-好、褐黄-黄绿色海绿石球粒(G)以及分散的绿色海绿石斑点,粘土基质和分散的绿色海绿石斑点表明自生成因,而圆形、分选中等-好、颗粒形态、含碎屑石英表明层外成因,故为准原地海绿石(单偏光); b—a 的正交偏光; c—椭圆形球粒状海绿石(SEM); d—c 中球粒的放大,球粒由极细小的片状物组成(SEM)

a—fine-middle grained, moderately-well sorted, brown yellow-yellow green glauconite spherulite (G) and dispersed green glauconite spots in clay (C) and iron (I) matrix with detrital quartz; clay matrix and dispersed green glauconite spots suggest authigenic origin, whereas circle, moderate-well sorted, grain shaped and detrital quartz-containing character implies external origin, thus indicating quasi-autochthonous glauconite (plane-light); b—crossed nicols of a; c—glauconite is elliptic spherulite (SEM); d—the enlargement of the spherulite of c, showing that the spherulite is composed of extremely small sheets (SEM)

Santanu Banerjee *et al.*, 2012) 浅海陆棚和潮坪 (Huggett and Gale, 1997; Chafetz and Reid, 2000; Chafetz, 2007; 梅冥相等, 2008; 周锡强等, 2009) 湖泊和古土壤 (Huggett and Cuadros, 2010) 等。印度西部 Kutch 渐新统 Maniyara 组泻湖相自生海绿石在泻湖 20 m 深处最有利于形成, 在泻湖边缘最不利于形成 (Santanu Banerjee *et al.*, 2012)。美国西南部寒武系和奥陶系 (Chafetz and Reid, 2000; Chafetz, 2007) 天津蓟县剖面中元古界铁岭组第 2 段高能叠层石生物层灰岩 (Mei *et al.*, 2008; 梅冥相等, 2008; 周锡强等, 2009) 和华北克拉通南部古元古界熊耳群 (徐勇航等, 2010) 中原地海绿石都形成于正常潮下高能浅海环境。

3 海绿石的成因

关于海绿石的形成模式及是否形成于封闭体系等方面存在相当大的争论 (Hower, 1961; Odin and Matter, 1981; Clauer *et al.*, 1992; Stille and Clauer, 1994; Kelly *et al.*, 2001)。海绿石有两种较被认可的成因解释, 即 Hower (1961) 提出的层点阵理论 (Layer lattice theory) 及 Odin 和 Matter (1981) 提出的颗粒变绿理论 (Verdissement of grains)。

层点阵理论假设铁和钾同时被吸收到粘土矿物 (如高铝蒙脱石、伊利石或退变云母) 的空间格子中, 对涉及到 2:1 型粘土矿物的海绿石形成特别有用。而 Odin 和 Matter (1981) 认为海绿石质矿物首先沉淀在宿主的微孔隙 (5~10 μm 大小) 中, 在逐渐成熟过程中, 随着宿主矿物的溶蚀, 最初沉淀的海绿石质蒙脱石吸收钾而逐渐演化为海绿石质云母, 海绿石不是先成矿物的蚀变产物, 而是早期溶蚀-沉淀和后期的成熟过程产物, 简称为海绿石化作用。

颗粒变绿模式适用于广泛的海绿石宿主, 包括生物碎屑、粪球粒和矿物/岩石碎片。显生宙沉积物中, 海绿石常表现为圆形碎片或颗粒, 海绿石的形成常以粪球粒和生物碎屑为宿主 (Stille and Clauer, 1994; Kelly and Webb, 1999; Chafetz and Reid, 2000; Giresse and Wiewióra, 2001; El Albani *et al.*, 2005; Wigley and Compton, 2007; Santanu Banerjee *et al.*, 2012)。相对于生物碎屑海绿石化反应来说, 粪球粒通常富集海绿石形成必需的元素, 向海绿石转变的化学反应要更简单得多 (Chafetz and Reid,

2000)。

更重要的是, 在颗粒变绿模式中, 海绿石表面颜色指示的钾含量可成为其成熟度的指标之一。海绿石的颜色变化与其成熟和蚀变的物理化学条件有关 (Sánchez-Navas *et al.*, 2008)。在海绿石演化过程中, 随晶格中的 $\text{Fe}^{2+}/\text{Fe}^{3+}$ 值增加, 绿色会逐渐加深 (Kuzmann *et al.*, 2008; Sánchez-Navas *et al.*, 2008)。此外, 根据 K_2O 含量海绿石的形成可以分为 4 个演化阶段, 分别为: 初生阶段, 是宿主的总含铁含量富集阶段, 贫钾的初生海绿石 K_2O 含量为 2%~4%; 低成熟阶段, 宿主沉淀绿色海绿石条纹, 低成熟海绿石的 K_2O 含量 4%~6%; 成熟阶段, 宿主颗粒破裂, 使分散的 K^+ 扩散到宿主的核心, 原海绿石新生物从核心向外形成, 成熟海绿石的 K_2O 含量 6%~8%; 高成熟阶段, 根球状海绿石颗粒完全沉淀, 反映了沉积作用持续的最长时间, 高成熟海绿石的 K_2O 含量为 8%~10% (图 3) (Odin and Matter, 1981)。

海绿石的钾含量一般高于 6% (Odin and Matter, 1981; Stille and Clauer, 1994; Eder *et al.*, 2007)。在沉积物与水的接触界面附近, 首先形成贫钾的海绿石质蒙脱石, 随钾离子的不断富集逐渐演化成富钾的海绿石质云母即成熟海绿石 (Odin and Matter, 1981; Odin and Fullagar, 1988)。海绿石颗粒的矿物组成和形态与沉积速率、成岩作用、氧化还原及沉积物孔隙度有关, 较慢的沉积速率和较长的成岩作用形成的海绿石具有较高的钾含量和较复杂的颗粒形式 (El Albani *et al.*, 2005)。海相陆棚环境中常见的各种宿主如粪球粒、贝壳碎屑、有孔虫和层状硅酸盐等逐渐转变, 形成 200~500 μm 大小的海绿石球粒 (Odin and Fullagar, 1988; Huggett and Gale, 1997)。初生海绿石颗粒形状简单, 在低成熟阶段, 宿主内形成海绿石条纹; 成熟阶段和高成熟阶段, 粒状宿主破裂, 使 K^+ 扩散到球粒中心, 整个球粒形成海绿石; 在高成熟阶段, 钾达到其最大浓度, 一些裂缝愈合, 球粒形状最终变成球根状。

4 海绿石的指相作用

海绿石化过程非常缓慢, 从初生海绿石演化到成熟海绿石大概需要 1 Ma (Odin, 1988; Garzanti, 1991)。海绿石形成作用需要慢速的堆积作用环境、低的沉积物供应速率 (Amorosi, 1995, 1997), 过快的

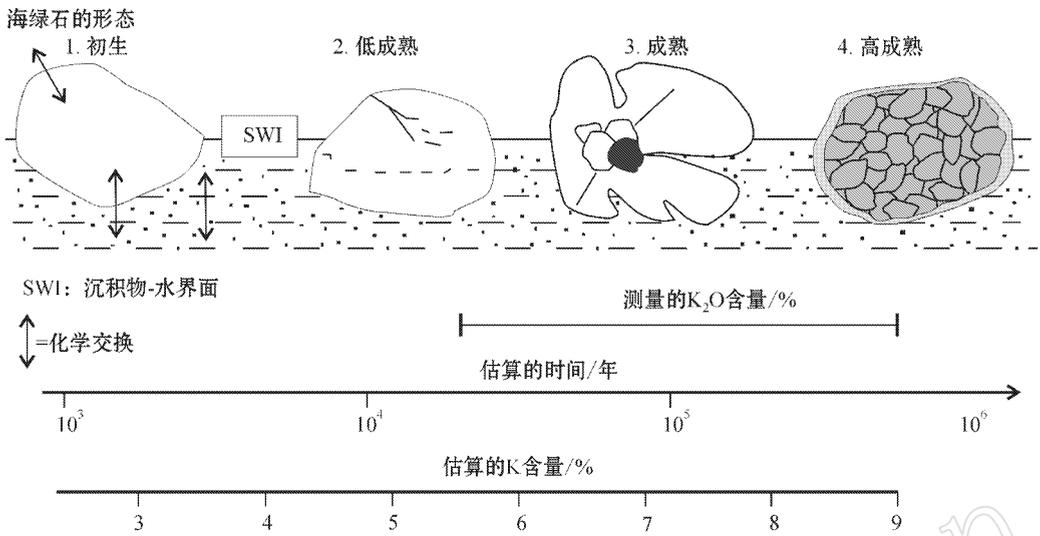


图 3 粒状宿主的海绿石化过程示意图(Odin and Fullagar, 1988)

Fig. 3 The glauconitization of the spherulite host (after Odin and Fullagar, 1988)

沉积物供应速率和埋藏作用都会使海绿石化作用停止。砂岩中高成熟原地海绿石的出现表明该地区当时沉积物供应速率长期较低,因此海绿石成熟度可以用来反映海绿石埋藏前在海底的停留时间(Odin and Matter, 1981; Odin and Fullagar, 1988)和沉积间断持续时间(Odin and Matter, 1981)。成熟度越高,在海底面停留演化时间越长,所经历的沉积间断越长,氧化钾含量大于 7% 的海绿石质矿物可能代表了具有地质意义的沉积间断(Odin and Matter, 1981; Odin, 1988)。

弱氧化至弱还原介质条件、弱碱性介质条件、一定的物质条件(特别是钾),再加上交互流动的水动力条件,便可形成海绿石(Odin and Matter, 1981)。海绿石化过程与沉积物供应速率低有关(Amorosi, 1997; Kelly and Webb, 1999; Wiewióra *et al.*, 2001; Jiménez-Millán and Castro, 2008; Huggett *et al.*, 2010),因此原地海绿石通常集中于相对薄的地层(<1~3 m)中(Amorosi, 1997)并被应用到层序地层学研究中,含海绿石地层在浅海沉积中常被作为海侵时期“凝缩段”及其相关沉积的识别标志之一(赵全基等, 1992; 陈丽蓉, 1994; Amorosi, 1995; Kitamura, 1998; Kelly and Webb, 1999; Harris and Whiting, 2000; Rousset *et al.*, 2004; Pasquini *et al.*, 2004; Amorosi *et al.*, 2007; Berra *et al.*, 2007)。如埃及 Bahariya Oasis 白垩系赛诺曼阶 Bahariya 组沉积物有原生(基质中分散的绿色粘土基质和斑块海绿石)和准原地(与大量石英碎屑混杂、圆

形、分选中等-好、清晰可辨的海绿石颗粒)两种成因海绿石,指示该地区 Bahariya 组上部为海侵体系域(Baioumy and Boulis, 2012)。藏西南札达县波林地区夏拉剖面中含原地海绿石砂岩和含碎屑海绿石灰岩中高成熟海绿石可能与早白垩世 Albian 晚期印度大陆从澳大利亚、南极大陆彻底裂解而造成该地区持续海进有关(李响等, 2011; Li *et al.*, 2012)。曹洁等(2010)表明黑龙江东部白垩系砂岩中海绿石等自生矿物与典型海侵相特征接近,说明含这些自生矿物的砂岩、粉砂岩受到海侵影响,为黑龙江省东部盆地白垩纪发生过海侵提供了矿物学依据。但 Amorosi(1995)表明,仅仅海绿石的出现并不能作为沉积层序中特定体系域的标志,对含海绿石单元层序地层学可信的解释需要海绿石的其他信息,包括成分、成熟度、演化和成因,并使用准原地海绿石的淡绿色和低-中等成熟度(K₂O 含量 4%~6%)代表高能陆棚环境海侵体系域以波浪、潮汐和风暴为主的条件。又如梅冥相等(2008)和周锡强等(2009)报道的天津蓟县剖面中元古界铁岭组第 2 段形成于高能浅海环境的叠层石生物层灰岩中的高成熟海绿石不能作为“凝缩段”的识别标志,也不是长时间地层间断的产物。海绿石在层序地层学中的广泛应用,使得判断海绿石是原地还是异地成因显得尤为重要,只有原地海绿石才能正确反映其形成时的古环境信息(Stille and Clauer, 1994; Amorosi, 1997)。对于判断海绿石是原地还是异地成因,前人给出了各种不同的判别标准(Amorosi, 1995, 1997;

Huggett and Gale, 1997) ,但不能仅依靠单一的判别标准, 需要结合多方面证据。如未成熟海绿石是一种柔软的粘土物质, 即使经过短距离搬运也会发生塑性变形(Huggett and Gale, 1997)。

5 海绿石的年龄意义

海绿石具云母型结构, 十分有利于 Ar 的保存, K^+ 含量高(通常是 6%~7%), 并且为自生成因, 在沉积岩中的时空分布范围很广, 所以海绿石是研究沉积年代学较理想的测定对象。海绿石 K-Ar、 $^{40}Ar/^{39}Ar$ 年龄常被用来解决沉积岩的沉积时间、沉积速率、成因和环境问题(Taylor and Curtis, 1995; Amorosi, 1995; Téllez Duarte and López Martínez, 2002; Godet *et al.*, 2011), 特别是对于缺乏可靠高温矿物定年计的地层, 海绿石能够给出其宿主沉积物的年龄。近 250 Ma 以来地质年代表中 40% 的绝对年龄数据是由海绿石提供的(黄宝玲等, 1998)。Téllez Duarte 和 López Martínez (2002) 利用墨西哥加利福尼亚半岛古新世 Sepultura 组碎屑沉积物中 3 个自生海绿石球粒测定的 K-Ar 年龄结果与生物地层学年代一致。不过, 海绿石 K-Ar 年龄“年轻化”, 而 $^{40}Ar/^{39}Ar$ 年龄“老化”(陈丽蓉等, 1987; 于荣炳, 1988), 原因主要是矿物结构中含有的可膨胀层引起年龄失真(李明荣等, 1994); 况且由于至少需要 1 000~10 000 年暴露才能开始海绿石化过程(Odin and Matter, 1981), 故海绿石绝对年龄没有火成岩那么准确。Gopalan (2008) 尝试对奥陶纪海绿石成功地进行了准确的 K-Ca 定年和 Rb-Sr 定年, 但是由于 K-Ca 定年较为困难, 在很大程度上限制了该方法的广泛使用。选用海绿石新鲜样品是获得理想年龄值的可靠保证, 也是必要条件。应用 K-Ar 法测定海绿石年龄时, 需要使用自生海绿石矿物(于荣炳, 1988), 并应研究海绿石的成熟度(陈丽蓉等, 1987)。只有成熟海绿石的同位素才能达到与海水的同位素平衡, 因此未成熟、贫钾的海绿石不是好的定年对象, 只有已成熟、富钾的海绿石(K_2O 含量 > 7%) 才是最好的定年对象。

6 结语

海绿石在沉积学的理论研究和实际应用中具有十分重要的意义。海绿石的成因、演化、沉积和地层

意义被广泛使用, 海绿石的形态、分布、产状、共生沉积物、矿物学特征、形成条件及形成过程可以推断和论证地质历史时期的海洋环境, 可为确定层序地层划分和区域地层对比提供有用资料。

值得注意的是, 在使用该典型指相矿物海绿石的过程中, 海绿石不仅可以形成于温暖、低能的浅海环境, 还可以形成于泻湖、湖泊等多种沉积环境中; 只有原地海绿石才能作为海侵时期“凝缩段”及其相关沉积的识别标志, 使用海绿石定年过程中, 海绿石 K-Ar 年龄“年轻化”而 $^{40}Ar/^{39}Ar$ 年龄“老化”, 因此关于海绿石的形成环境、成因及应用方面还存在较多注意事项, 在使用该典型指相矿物中应给予重视。

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