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富碳质地质样品 Re-Os 同位素体系研究进展

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摘要: Re-Os 同位素定年技术在富有机质沉积岩、低变质沉积岩、湖相沉积物、煤、油气藏样品等富碳质地质样品的尝试和成功应用,使其成为直接厘定地层沉积时代、重大地质事件发生时限和机制、古环境重建、油气藏直接定年、油气演化过程推演等研究的关键技术手段。然而,受到富碳质地质样品中极低的 Re 和 Os 丰度、采样方式以及地质作用等因素的影响,很多样品的 Re-Os 等时线年龄和初始 Os 同位素比值精度超过 10%,不能有效地评价海水 Os 的真实来源和地质作用程度,影响了对不同沉积体系及油气演化过程中 Re 和 Os 的化学行为和 Re-Os 等时线年龄地质意义的理解。由此,本文从富碳质地质样品的 Re-Os 化学行为和地质应用进展出发,对富碳质地质样品 Re-Os 同位素分析过程中的采样和取样方式、溶样方法、分离富集方式和标准物质选择四方面进行了总结和完善。指出以沉积速率为采样间距参考,通过预处理方式提高样品的均匀性,使用流程空白更低、对同位素分馏影响更小的溶样方法和分离富集方式进行 Re-Os 同位素分析,以基质匹配的地质标样进行数据监控可进一步提高样品 Re-Os 同位素分析质量,有助于不同类型富碳质地质样品 Re 和 Os 赋存机制研究、Re-Os 同位素分析技术开发及地质应用拓展。

关键词: Re-Os 同位素体系; 富碳质地质样品; 油气演化; Re、Os 化学行为; 地质应用; 富碳质地质标样要点:

- (1) 富碳质地质样品 Re-Os 同位素数据精度对其化学行为和等时线年龄地质意义解读具有重要影响。
(2) 合适的取样方式、Re-Os 分析方法和地质标样可提高富碳质地质样品 Re-Os 同位素数据精度。
(3) 丰富和完善富碳质地质样品 Re-Os 分析方法、数据库及标准物质,为富碳质地质样品的 Re-Os 赋存机制研究及广泛应用提供重要支持。

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Re 和 Os 的亲有机质特性^[1]使其在缺氧沉积环境下能够进入富有机质沉积岩中相对富集^[2-5]。在特定的地质条件下,富有机质沉积岩作为烃源岩的源岩,其富集的 Re 和 Os 在烃源岩生烃、运移、埋藏等过程中也随之转移至油气相关的地质样品中^[6-9]。Re 和 Os 在这些富含碳质地质样品中的独特富集机制,使 Re-Os 同位素体系的定年对象可以从黑色页岩^[10-18]、泥岩^[1,19-20]、片岩^[21]、板岩^[22-23]等不同类型的富有机质沉积岩及低变质沉积岩,逐

步拓展到原油^[24-28]、沥青^[29-31]、焦沥青^[32-33]、油砂^[34-35]、油页岩^[36]等油气相关的地质样品,并已经取得诸多成果。目前,富碳质地质样品的 Re-Os 同位素定年技术已经成为地层沉积时代^[6,14,37]和地层界线^[10,15-17,19,38-39]直接厘定、重大地质事件发生时限和机制^[11,40-42]、古海洋环境重建^[43-46]、油气藏直接定年^[10,26,35]、油气演化过程推演^[32-33,47-54]等研究的关键技术手段。

在富碳质地质样品 Re-Os 同位素分析过程中,

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采样取样及预处理方式^[1,12,17,55]、样品的 Re 和 Os 丰度^[56]、样品的溶样方法^[57-60]、Re-Os 分离富集方式^[61-68]以及标准物质选择^[58-60,67-74]直接影响了 Re-Os 同位素数据的准确度和精确度。尽可能地提高 Re-Os 数据质量,是研究富碳质地质样品 Re 和 Os 的富集机制,尤其是探索油气系统 Re 和 Os 化学行为的基础,对于准确理解样品 Re-Os 等时线年龄的地质意义至关重要。目前,学者们已经给出了富有机质沉积岩中 Re 和 Os 富集机制的普遍认识^[1-2],而由于油气演化过程的复杂和漫长,对于油气演化不同阶段中 Re-Os 同位素体系的分馏机制和封闭性^[7-9,75-76]仍需要深入探讨。湖相沉积物^[77-79]和煤^[80-83]的形成环境、Re 和 Os 的物质来源与海相沉积的富有机质沉积岩差异巨大,此类地质样品的 Re-Os 同位素体系研究及广泛应用仍充满挑战。

本文系统梳理了富碳质地质样品 Re、Os 的化学行为和地质应用实例,指出了目前富碳质地质样品 Re-Os 同位素体系在数据精度和实际应用中的不足。从采样方式、溶样技术、富集方式、富碳质 Re-Os 地质标样研制等方面总结归纳了进一步提高 Re-Os 同位素数据分析质量的关键因素,为不同类型富碳质地质样品的 Re 和 Os 赋存机制研究、Re-Os 同位素分析技术开发及地质应用拓展提供支持。

1 Re-Os 同位素体系在富有机质沉积岩中的赋存机制及地质应用

富有机质沉积岩的 Re 和 Os 富集机制、分异机制以及独特的 Os 同位素示踪机制在沉积时代厘定、限定重大地质事件发生时代以及古海洋环境重建等研究中取得了广泛应用。

1.1 富有机质沉积岩 Re 和 Os 赋存机制及示踪原理

Re 和 Os 的独特富集机制为富有机质沉积岩直接定年提供了可能。Re 和 Os 进入富有机质沉积岩的过程与海水中的有机质^[3-5]和沉积环境^[1-2]密切相关。在还原条件下,海水中的 Re 以 ReO_4^- 形式存在,被还原为较低价态的 Re(IV)后被有机质吸附进入富有机质沉积岩;在氧化条件下,Re 的化学行为非常保守。Os 在还原和氧化条件下分别以四价的 OsCl_6^{2-} 形式和高价的 HOsO_5^- 或 H_3OsO_6^- 存在,通过水解作用和还原作用先形成 Os(IV)氢氧化物^[2]。Os 在还原条件下被还原为 Os(III)不溶物进入富有机质沉积岩,而在氧化条件下则通过吸附或共沉淀进入黏土、硅酸盐矿物或铁锰氧化物等不含有机物

的沉积物中^[2]。另一方面,富有机质沉积岩中 Re 和 Os 的分馏对获得准确的 Re-Os 等时线年龄至关重要。已有研究显示,有机质的类型可能是富有机质沉积岩中 Re 和 Os 分馏的主要控制因素^[79,84-86],此外,多变的沉积环境^[79,85]、盐度^[86]等因素也对 Re 和 Os 的分馏也具有一定程度的影响。而海水来源的 Os 在进入富有机质沉积岩的过程中同时记录了来自大陆风化作用($^{187}\text{Os}/^{188}\text{Os} \approx 1.4$)、热液输入($^{187}\text{Os}/^{188}\text{Os} = 0.11 \sim 0.388$)和宇宙尘埃($^{187}\text{Os}/^{188}\text{Os} \approx 0.127$,接近原始地幔值)三种不同来源 Os 的相对通量变化^[87-88],并以同沉积的富有机质沉积岩初始 Os 同位素比值特征反映出来。因此,通过富有机质沉积岩 Re-Os 同位素年代学数据及初始 Os 同位素比值特征这一灵敏的示踪剂,可以有效地对地球历史上发生的重大地质事件进行时代限定和判别。

1.2 Re-Os 同位素体系应用于地层界线 and 沉积时代的厘定

富有机质沉积岩 Re-Os 同位素定年技术已经成功地提供了泥盆系—石炭系^[10]、寒武系—奥陶系^[15]、奥陶系—志留系^[20,38]、二叠系—三叠系^[39]、中—上三叠统^[16]和侏罗系—白垩系^[17]等准确的地层界线年龄,对地质年代表的更新和不同生物地层的精确对比至关重要。值得一提的是,Re-Os 同位素体系对于缺乏生物化石的哑地层或缺乏火山岩夹层的沉积地层来说具有独特优势。例如,一些学者应用 Re-Os 同位素体系对缺乏化石的贵州织金牛蹄塘组黑色页岩的沉积时代^[37]和以碳酸盐岩为主的中国南方陡山沱组地层沉积时代进行了限定^[14]。

此外,绿泥石级变质作用沉积岩中 Re-Os 的封闭性已经得到证实,通过板岩^[22-23]、片岩^[21]的 Re-Os 等时线年龄获得了准确的地层沉积时代,并借助初始 Os 同位素比值特征揭示了沉积时的风化作用强度^[23],进一步拓展了 Re-Os 同位素体系的应用方向,并为古环境重建提供了新的选择。

1.3 Re-Os 同位素体系对重大地质事件发生时代的限定及响应

富有机质沉积岩初始 Os 同位素的特征变化,可以有效地指示大气氧气水平变化和地壳风化程度从而限定大氧化事件(GOE)。通过 Os 同位素特征证实了地球演化早期大气中含氧量较低海水中的 Os 几乎没有陆源的贡献^[89],在 $1.4 \sim 0.65\text{Ga}$ 的地质时期,大气中氧含量增加使风化氧化作用增速,Os 得以进入海洋。加拿大西部 Athabasca 盆地沉积岩(沉积时代约为 1.54Ga)初始 Os 同位素比值^[41]为

0.51±0.03,也证实了这一增氧事件。利用冰期成因的黑色页岩进行 Re-Os 同位素定年研究,有效地限定了大洋缺氧事件(OAE)的发生时间和发生机制。例如,限定了 Sturtian 和 Areyonga 冰期发生的时代^[11]、Sturtian 冰期的持续时间和结束时间并证实后冰期地层经历的风化作用^[42],为“雪球地球”事件提供了丰富的信息。此外,沉积岩 Os 同位素初始值变化还印证了白垩纪^[43]和第三纪界线^[44]发生的陨石撞击事件,揭示了森诺曼阶—土仑阶之交的大火成岩省火山活动的快速爆发^[45]和镜铁山组沉积时代强烈的海底热液活动^[46]。

1.4 富有机质沉积岩 Re-Os 同位素体系在古海洋环境重建中的应用

Re、Os 的富集机制使其与有机质积累、氧化还原敏感元素及其替代指标具有较好的协同变化关系,可以有效地衡量沉积时水体的氧化还原状态进而实现对古海洋和古大气变化的多维度还原。Tripathy 等^[15]通过连续地层的总有机碳(TOC)含量、Re-Os 含量及同位素数据、Mo 含量、U 含量、富集因子和自生 Re-U 含量的相互关系还原了加拿大纽芬兰西部 Green Point 页岩在寒武系—奥陶系界线的缺氧沉积环境并限定了沉积环境范围。Xu 等^[16]通过 Re-Os 数据与 V/Mo、Mo/TOC、Re/Mo 和自生黄铁矿微粒尺寸变化之间的关系揭示了 Botneheia 到 Tschermakfjellet 组地层沉积环境由缺氧到氧化的转变。加拿大 Huronian Supergroup 沉积岩的 Os 同位素组成以及 Re、Os 和 Mo 的丰度揭示了第一次休伦冰期作用后浅海环境的氧化还原程度和大气氧气水平^[90]。

2 油气系统 Re-Os 同位素体系的化学行为及应用实例

油气系统 Re、Os 的化学行为研究一直是油气藏年代学研究的重点和难点,对理解油气藏相关样品获得的 Re-Os 等时线年龄的地质意义至关重要,是 Re-Os 同位素体系在油气系统广泛应用的重要基础。

2.1 油气生成和初次运移过程中 Re、Os 的化学行为

热模拟生烃实验^[7-8]显示,大部分的 Re 和 Os (>95%) 仍然保留在烃源岩中,仅有很小的一部分 Re 和 Os 在烃源岩产生沥青、原油和天然气的过程中向烃类流体发生转移^[6-8],因此烃源岩¹⁸⁷Re/¹⁸⁸Os 和¹⁸⁷Os/¹⁸⁸Os 值的变化很小不足以破坏烃源岩的

Re-Os 同位素体系,同时也解释了熟化作用不会影响烃源岩 Re-Os 等时线年龄的原因。

在原油生成的过程中,烃源岩中的干酪根首先热降解生成烃和沥青,不同热解阶段生成的沥青具有与烃源岩相似的¹⁸⁷Os/¹⁸⁸Os^[7]并继承了烃源岩的 Os 同位素特征。不同成熟度样品的 Re-Os 含量线性关系(图 1)显示出的不同斜率证实了在较高成熟度水平下,Re 更容易进入碳氢化合物并被烃类流体优先去除^[8],使生成的烃类具有比沉积物母体更高的 Re/Os 和¹⁸⁷Re/¹⁸⁸Os 值。这与生烃过程中含氮等杂原子会发生丢失或重新分布,使主要以杂原子配体形式存在的 Re 和 Os^[24,91]结构发生变化^[5]并以不同的速度进入烃类流体相关。当沥青的生成达到峰值后,Re 和 Os 含量呈现下降趋势,沥青开始向原油转化。排烃效率较高的烃源岩中沥青的¹⁸⁷Os/¹⁸⁸Os 显著降低^[8],Re 和放射性成因 Os 更多地进入原油使沥青和原油呈现了不同的¹⁸⁷Re/¹⁸⁸Os 特征,证实沥青向原油转化、排出的过程中发生了 Re/Os 分异,但这种分馏程度比沥青和烃源岩之间的分馏程度小得多^[8]。在排烃、运移

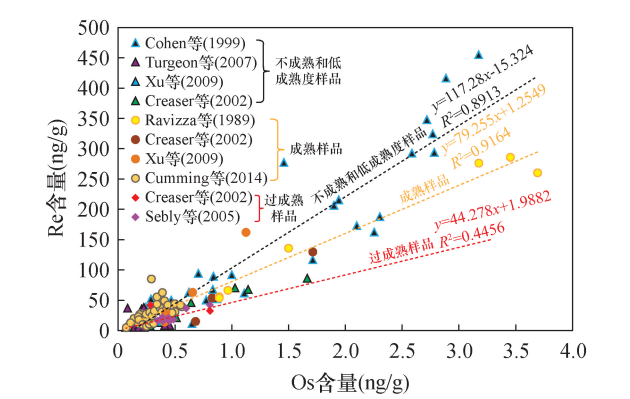


图 1 不同成熟度黑色页岩样品 Re-Os 含量及斜率(引自 Li 等^[9],2021)。黑色虚线为不成熟和低成熟样品趋势线,黄色虚线为成熟样品趋势线,红色虚线为过成熟样品趋势线

Fig. 1 Re-Os contents and slope of black shales at different maturity levels (Quoted from Li, et al, 2021^[9]). Three separate regressions of Re-Os abundance data represent immature-low mature, mature and over-mature subsets, respectively, which have slightly different slopes. The regressions of immature and low-mature samples have slightly steeper slopes compared to mature and over-mature samples. Such variations may suggest the preferential removal of Re over Os by hydrocarbon fluids at higher maturity levels.

过程中,Os 同位素可能在烃源岩与生成油气之间的浓度梯度作用下均一化^[8],也可能被烃源岩从迁移的油气中吸附^[91]而使 Os 同位素不均一,或是发生 Re 和 Os 的局部流动和重新分配^[26]。

2.2 沥青质成分变化对 Re-Os 同位素体系的影响

在脱沥青、生物降解、热蚀变和热裂解等使原油中沥青质成分变化的过程中,原油中的 Re 和 Os 也会随之迁移和分异进而影响原油的 Re-Os 同位素系统。通过脱沥青模拟实验^[48-49,69]得到了两种不同推论:Mahdaoui 等^[49]根据先沉淀出的沥青质次组分 Re、Os 含量和相似的 Re/Os 和 $^{187}\text{Os}/^{188}\text{Os}$,推测出当沥青质少量沉淀时对原油的 Re/Os、Os 同位素比值和 Re-Os 年代测定没有影响。然而,Liu 等^[48]和 DiMarzio 等^[69]发现各沥青质组分之间 Re-Os 同位素比值变化复杂,沥青质的沉淀过程会导致 ^{187}Re 和放射性成因 ^{187}Os 的失耦从而影响原油 Re-Os 等时线年龄结果。笔者认为这两种相反的结果可能与不同学者在顺序沉淀实验中使用了不同的沉淀剂而对 Re 和 Os 产生了不同程度的分馏^[49]有关,也可能与 Re 和 Os 在原油中的赋存机制相关。Re 和 Os 可能形成卟啉,而这种高极性亚组分与 Re 和 Os 的亲合力差异以及沉淀剂的极性控制了沥青质沉淀过程中原油中的 Re 和 Os 含量及同位素比值变化^[69]。此外,Re 和 Os 既可能吸附于沥青质表面,也可能封闭于沥青质内部不易和外部进行交换^[48],而沥青质与可溶质中的 Re 和 Os 也可能存在元素和同位素的分配^[24],造成脱沥青过程中原油的 Re 和 Os 含量及同位素比值存在多种变化。

Georgiev 等^[75]研究发现三叠纪—侏罗纪 Strepenosa 层段遭受严重生物降解作用的烃源岩产生的原油中可溶质组分 Re 和 Os 含量异常,不能排除生物降解作用可能对原油中 Re 和 Os 含量的复杂影响,打破了以往研究中生物降解作用对原油 Re-Os 同位素体系封闭性的认识^[7,10,50]。

而在热化学硫酸盐还原作用(TSR)和油气裂解过程中,温度是造成原油 Re-Os 同位素系统扰乱甚至重置^[50-52,92]的重要因素。低温(大约 100℃)的热液流体就可以扰乱富有机质沉积岩的 Re-Os 同位素体系^[92]和原油的聚集^[25]。TSR 作用的反应温度(100~140℃)^[51]和热裂解的温度(>150℃)^[93]均高于 Re-Os 在烃类中的封闭温度,可以破坏油气系统 Re-Os 同位素体系的封闭性。并且在 TSR 作用下,原油中的 Re 和 Os 既可能被氧化耗尽,也可能被富集在新生有机硫配体中^[92]使 Re/Os 发生变化。

2.3 油-水反应对 Re-Os 同位素体系的影响

在二次运移和充注过程中,原油不可避免地会与热液或地层水发生相互作用,并为原油提供额外的 Re、Os 来源^[9]。当热液流体经过富有机质沉积岩地层或油气藏时,Re、Os 很容易随之迁移从而改变其 Re/Os 比或同位素比值。有成矿热液流体经过的页岩其 ^{192}Os 和 Re 含量较未经热液流过的页岩有所减少,而 $^{187}\text{Re}/^{188}\text{Os}$ 和 $^{187}\text{Os}/^{188}\text{Os}$ 升高^[13]。幔源热液流体经过油气藏时,石油中的 Re 含量降低,Os 含量升高,幔源流体中的非放射性 Os 进入石油中使石油中的 $^{187}\text{Os}/^{188}\text{Os}$ 值明显降低^[25]。由于 Re 和 Os 的性质不同,Os 更倾向于进入成矿流体中,而 Re 则倾向于进入幔源流体。

地层水是如何重置原油 Re-Os 同位素体系的相关认识主要来自 Mahdaoui 等^[94]和 Hurtig 等^[67]的油-水接触实验结果。Mahdaoui 等^[94]认为,水-岩作用过程使地层水从烃源岩中获得与原油接近的 $^{187}\text{Os}/^{188}\text{Os}$ 并在整个盆地循环中达到均一,为原油提供额外的 Re、Os 来源以及重置 Re-Os 同位素体系的起点。地层水的 Re/Os 分异可借助自生黄铁矿的形成或铁的氢氧化物吸附来完成,从而达到重置 Re-Os 同位素体系的条件,Re-Os 等时线年龄即为水动力圈闭的最后时刻^[94]。Hurtig 等^[67]则认为,仅当原油与 Re、Os 含量较高的流体相互作用时,原油的初始 Os 同位素比值会向地层水的组成方向变化并且 $^{187}\text{Re}/^{188}\text{Os}$ 增大(即 Re/Os 分异)使 Re-Os 地质年代计重置,而对于 Re、Os 含量很低的流体,则不足以改变原油的 Re-Os 同位素体系,原始 Re-Os 等时线年龄信息依然保存在沥青质-原油-可溶质中。然而,现阶段的模拟实验还不能给出水岩作用下 Re 和 Os 进入地层水的条件、程度以及初始 Os 的均一化机制,仍需要优化模拟实验开展更深入的研究。

2.4 Re-Os 同位素体系在油气藏研究中的应用

加拿大西部沉积盆地中的油砂^[10]、中国西藏羌塘盆地胜利河的油页岩^[36]、英国大西洋边缘晚侏罗世的原油^[26]的 Re-Os 等时线年龄直接记录了油气生成的时间。对加拿大 Nunavut Polaris 密西西比河谷型铅锌矿伴生的沥青^[29],中国贵州晴隆锑矿床中的沥青^[31]、准噶尔盆地侏罗系的油砂^[35]、四川盆地高石梯-磨溪区灯影组的焦沥青^[32]、四川麻江、万山和米仓山古油藏中不同成熟度的沥青^[51-52]以及石墨^[53-54]等不同类型的油气样品开展的 Re-Os 同位素体系研究,限定了成矿流体运移、TSR 作用、充注、热

裂解、构造演化、热变质事件等重置 Re-Os 同位素体系的关键地质事件的发生时间,为重建油气演化过程提供了同位素年代学证据。由此可见,不同类型油气系统样品的 Re-Os 等时线年龄具有不同的地质意义,即使是同一种类型的油气系统样品也代表不同的地质意义,这与不同油气演化阶段和地质作用下 Re、Os 的化学行为密切相关。通过 Os 同位素特征及一些无机元素指纹特征(如 Pt/Pd 值)可作为油源对比工具,已经被成功应用于确定加拿大西部沉积盆地 Leduc/Nisku 组原油的烃源岩^[76]以及探索英国大西洋沿岸的原油与加拿大阿尔伯塔省油砂和烃源岩的关系^[27]。

3 富碳地质样品 Re-Os 同位素体系的局限性和挑战

3.1 富有机质沉积岩样品 Re-Os 同位素数据精度仍然有限

本文统计了国内外已发表文献中沉积时代为 2.4Ga~66Ma(古元古代~新生代)的页岩、泥岩、灰岩、板岩等 800 余件富有机质沉积岩样品 Re-Os 数据(图 2)。可以发现,富有机质沉积岩样品 Re 含量普遍在 100ng/g 以内(图 2a),大部分样品 Os 含量在 100~500pg/g 之间(图 2b),Re-Os 等时线年龄误差普遍在 10% 以内(图 2c),少数样品 Re-Os 等时线年龄误差可达到 10%~50%。通过等时线年龄得到的初始 Os 数据误差较大,仅有约 40% 左右的初始 Os 数据误差范围在 10% 以内,超过 20% 的初始 Os 数据分析误差大于 50%(图 2c)。

在 Re-Os 同位素分析中,¹⁸⁷Re 的衰变常数误差为 0.31%~1.02%^[95-97],¹⁸⁵Re 和¹⁹⁰Os 稀释剂标定误差为 0.2%~0.3%^[96-97],称量等化学操作引起的误差约为 0.3%^[98],负离子热电离质谱(NTIMS)的测量误差在 0.3‰ 左右。NTIMS 的测量精度、稀释剂标定精度和自然 Re 同位素比值精度是 Re 数据误差贡献的主要因素,Os 数据分析误差主要由稀释剂标定精度和空白贡献决定,NTIMS 的测量误差影响较小^[67]。初始 Os 同位素比值数据主要通过同源样品的 Re-Os 等时线获得,除了 Re-Os 分析过程中误差传递的影响,采样过程中的地质因素影响也会使初始 Os 同位素比值误差增加。通过分析人员提高稀释剂标定精度、降低流程空白水平,同时地质工作者选择合适的采样和取样方式减少地质因素对样品 Re-Os 数据的影响,两者相互结合才能使富有机质沉积岩样品的 Re-Os 数据精度进一步提高。

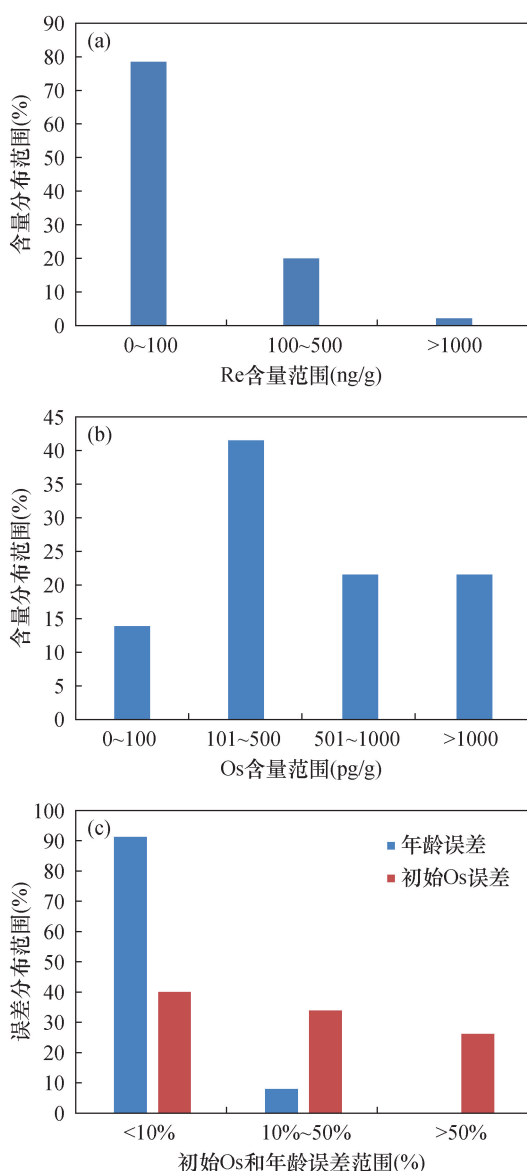


图 2 文献中已报道的富有机质沉积岩 Re-Os 同位素数据统计:(a) Re 含量范围分布;(b) Os 含量范围分布;(c) Re-Os 等时线年龄和初始 Os 值误差范围分布

Fig. 2 Re-Os isotopic data of organic-enriched sedimentary rocks from reported references: (a) Re content distribution; (b) Os content distribution; (c) Distribution of error range of Re-Os isochron age and initial Os value. The Re and Os contents of organic-enriched sedimentary rocks is generally within 100ng/g and 500pg/g, respectively. The error of the Re-Os isochron age are generally within 10%. Only about 40% of initial Os data has an error range of less than 10%.

3.2 初始 Os 同位素特征反演古环境及重大地质事件耦合关系的不足

发育在陆地近端局限盆地或盆地边缘的富有机质沉积岩易受到来自邻近陆块的陆地有机物和无机

物输入的影响而改变沉积物中 Re 和 Os 的浓度及同位素组成^[99],使沉积岩初始 Os 记录的并非完全是海水 Os 同位素比值,而是反映了区域性的、非全球性的海洋条件。只有在陆地远端、较深海水环境中发育的富有机质沉积物其初始 Os 同位素比值记录了同沉积时海水的 Os 同位素特征,而这一重要前提往往被忽略。

此外,当同时发生对海洋 Os 输入通量的改变起相反作用的不同地质事件时,不同 Os 输入通量在一定程度上会相互抵消,而不能有效地反映海水 Os 的真实来源和地质作用的程度。例如,在白垩纪—第三纪界线地质时期,同一时期发生了火山作用和高强度的风化输入作用^[100]使来自不同端元的 Os 在海水中相互抵消,从而掩盖了风化作用的程度。对于具有相似 Os 同位素比值特征的地外和幔源物质,无法仅通过 Os 同位素特征进行区分,同样需要结合地质背景或借助其他同位素分析技术及地球化学替代指标(如铂族配分曲线及 Ir 含量等)充分探究富有机质沉积岩初始 Os 同位素特征所代表的意义。

3.3 Re-Os 同位素体系在湖相沉积体系和煤的应用挑战

湖相沉积物和煤在形成过程中比海相沉积物具有更广泛的物质来源,其形成过程、经历的地质作用以及受陆源碎屑的影响也更为复杂。此外,内陆物源的沉积物往往具有更低的初始 Re 和 Os 浓度^[99],Os 同位素的滞留时间也不同,这使湖相沉积体系和煤的 Re-Os 同位素体系研究面临巨大挑战。目前,对纯湖相沉积体系^[77]和陆相煤沉积体系^[80-81]开展的 Re-Os 同位素定年尝试均未能获得有效的 Re-Os 等时线年龄,而与海侵作用相关的湖相沉积物和煤样品其 Re-Os 数据往往可以成线,Re-Os 等时线年龄代表了海侵作用的时间。例如,北冰洋罗蒙诺索夫海岭始新统湖相顶部沉积岩与海洋单元底部的 Re-Os 等时线年龄约束了该地区从湖相到海相沉积环境转变发生的时代^[78]。Cumming 等^[79]获得了美国 Uinta 盆地 Green River 湖相黑色碳质泥岩和油页岩沉积时湖水的¹⁸⁷Os/¹⁸⁸Os 特征,有效地区分了湖泊和海洋的不同沉积环境。Tripathy 等^[82]使用 Re-Os 地质年代学对来自美国西弗吉尼亚州的煤样品进行分析并获得了 325±14Ma 的 Re-Os 等时线年龄,与其上段页岩的年龄吻合被认为是海洋入侵的时间。因此,海侵作用很可能是使初始 Os 同位素组成均一化并重置 Re-Os 同位素体系的关键^[82-83]。探索 Re 和 Os 在湖相沉积物和煤中的地

球化学行为可能为湖相的沉积年龄厘定、大陆地质过程、古气候波动和陆地生物演化提供新的机会。

3.4 Re-Os 同位素定年技术在油气系统中的不足

油气类样品往往性状黏稠、具有一定的挥发性,难以准确称重和完全转移,其较高的有机质和极低的 Re、Os 丰度使封闭溶样的称样量上限仅能达到 450mg^[75],这对 Re-Os 同位素分析精度提出了挑战。目前,针对不同类型油气样品开展的 Re-Os 同位素分析方法研究和系统的采样取样方式研究仍比较欠缺,不同实验室对原油次组分的 Re-Os 同位素分析方法具有差异,同一标样获得的次组分数据也有较大区别^[71]。漫长的生油期使从烃源岩继承的¹⁸⁷Os/¹⁸⁸Os 一直在变化并且可能来自于不同演化阶段的不同层位烃源岩,而后续不同地质作用也会影响初始 Os 同位素比值,使油气演化不同阶段 Os 同位素均一化及 Re/Os 分异机制十分复杂。此外,Re 和 Os 在原油、沥青质、可溶质之间的分配行为、分馏机制也不够清晰,造成了不论是通过单一石油系统的多个原油或原油中沥青质部分进行 Re-Os 同位素分析^[7,10,24,26,29,50],还是使用同一样品的不同次组分进行 Re-Os 同位素分析^[48,75],获得的 Re-Os 等时线年龄和初始 Os 同位素比值不确定度往往较大,甚至不能成线,而 Re-Os 同位素定年技术的精度目前还不能精细地区分生油及运移成藏等过程。尚未完善的 Re-Os 同位素分析方法及 Re 和 Os 的化学行为理论,为准确理解油气样品 Re-Os 等时线年龄的地质意义增加了难度。

4 提高富碳质地质样品 Re-Os 同位素数据精度的关键因素

合理的样品采集、预处理方式与合适的 Re-Os 分析方法可以有效地减少地质因素对 Re-Os 等时线结果的影响,降低 Re、Os 分析的检出限,对提高 Re-Os 等时线精度,加深 Re-Os 等时线年龄地质意义的理解具有重要意义。

4.1 采样和取样方法

富有机质沉积岩获得的 Re-Os 等时线年龄和初始 Os 同位素比值的精度,与样品中初始 Os 同位素比值的均一性、¹⁸⁷Re/¹⁸⁸Os 的范围、样品数量和衰变常数密切相关^[79]。对于富有机质沉积岩来说,在几厘米的垂直地层范围内 Re/Os 值可以变化 2~3 倍,而横向相邻样品的 Re/Os 值通常比较相似^[1],因此合适的采样间距是提高 Re-Os 等时线年龄测量精度的关键因素之一。对于沉积速率较慢的地层

可将垂直采样间距控制在约 4Ma 并增大取样量(大于 20g)以保证 Re-Os 数据等时线上可以拉开并减少 Re、Os 元素扩散现象或失耦的影响^[1,55]。而对于沉积速率较高、海水¹⁸⁷Os/¹⁸⁸Os 快速变化的地层以及 Os 在海水中的停留时间相对较短(在低 O₂ 的元古代海洋)的地质时期来说,应将采样间距减小至约 500ka,同时增加横向样本分析,以减少样品的初始 Os 同位素比值变化。距离海岸较远的样品,可减少碎屑输入的影响以获得与沉积时海水 Os 变化更加同步的 Os_i,提高 Re-Os 数据的等时性^[17]。通过改变采样间隔仍无法有效地增加¹⁸⁷Os/¹⁸⁸Os 和¹⁸⁷Re/¹⁸⁸Os 比值变化的样品,不适合进行 Re-Os 同位素定年分析。对于原油类样品,可在分析前通过长时间充分搅拌降低样品的不均匀性,并借助和油气生成相关的无机指纹特征进行油源对比和样品筛选。对固体烃(如沥青)类样品,可在分析之前使用二氯甲烷或其他溶剂进行溶解提取,将样品的不均匀性降至最低^[12]。

4.2 溶样介质及流程空白

富碳质地质样品的 Re-Os 同位素分析一般使用逆王水^[6,11,20]和 H₂SO₄-CrO₃^[10,11,17,22]为溶样介质,在封闭的 Carius 管^[96-97,101-103]和加热条件下充分消解释放 Re 和 Os。近几年,Yin 等^[59]和 Li 等^[60]分别建立了 HNO₃-H₂O₂ 和 H₂SO₄-Na₂CrO₄ 溶样方法用于解决传统 H₂SO₄-CrO₃ 溶样方法^[5]的高 Re 空白问题,即将富碳质地质样品的溶样方法拓展至 4 种。

不同溶样方法的优缺点、空白水平及适用的地质样品总结于表 1 中。虽然不同溶样方法对富有机质沉积岩碎屑溶出程度、Re-Os 数据及等时线年龄

到底有多大影响仍没有确切的定论,但是溶样方法的流程空白仍然是保证数据准确最可控的关键因素。样品的 Re、Os 含量差异使 Os 分析误差对空白水平更为敏感,较高的 Os 流程空白会导致¹⁸⁷Re/¹⁸⁸Os 和¹⁸⁷Os/¹⁸⁸Os 受到影响而降低 Re-Os 等时线年龄的准确性^[67]。分析低含量 Re、Os 样品尤其是 Os 含量小于 50pg/g 的样品时,更需要注重空白水平对数据的影响再进行溶样方法选择。

4.3 富集方式选择

Carius 管溶样后经直接蒸馏可将 Re、Os 分离^[61-62],Os 的富集纯化一般使用微蒸馏法^[106-107],Re 的富集则使用丙酮-氢氧化钠萃取^[63]或阴离子交换法^[64-66]。以往研究普遍认为使用两种富集方式获得的结果是一致的,然而不同的富集方式可能会因为富集过程中 Re 的分馏而对¹⁸⁵Re/¹⁸⁷Re 值产生不同程度的影响。Hurtig 等^[67]和 Georgiev 等^[68]发现,使用阴离子交换富集 Re 会产生质量分馏使¹⁸⁵Re/¹⁸⁷Re 增加,而 Re 的回收率也会显著降低,导致¹⁸⁵Re/¹⁸⁷Re 测量值高于“真实”值并使计算出的¹⁸⁷Re/¹⁸⁸Os 比值偏低,Re-Os 等时线年龄比真实值偏老。富集过程中的质量分馏往往发生于 Re 含量较低的样品中,它们的¹⁸⁵Re/¹⁸⁷Re 值更容易受到测量质量、基体干扰或背景的影响,可以产生约 3%~6‰的偏离^[68]。此外,沥青不易受 Re 的富集方法影响,但是原油样品和原油中的可溶质组分更适合采用丙酮-氢氧化钠萃取法对 Re 进行富集以获得线性更好的数据^[67]。因此,我们建议对于 Re 含量很低的样品(Re 含量<1ng/g)以及油气相关样品,使用丙酮-氢氧化钠萃取法来进行 Re 富集纯化。

表 1 国内外实验室 Re-Os 同位素分析方法、流程空白及适用地质样品对比

溶样方法	优点	不足	主要适用地质样品	流程空白		数据来源
				Re 含量(pg)	Os 含量(pg)	
H ₂ SO ₄ -CrO ₃	选择性溶样 减少碎屑溶解 数据更精确	高 Re 空白 CrO ₃ 纯化困难 环保问题 有害健康	富有机质沉积 岩油气藏样品	40	<0.1	[104]
				16.8±0.06	0.43±0.06	[22]
				16.8±0.4	0.4±0.1	[8]
				10.8±1.5	0.12±0.05	[105]
逆王水	全流程空白最低 试剂易纯化	高有机碳样品 易爆炸	硫化物 富有机质沉积岩 油气藏样品 岩浆岩	0.67±0.18	0.37±0.06	[105]
				3.7±4.7	0.34±0.226	[75]
				4.3±1.8	0.36±0.22	[59]
HNO ₃ -H ₂ O ₂	全流程空白较低 试剂易纯化	易爆炸	富有机质沉积岩 岩浆岩	8~12	0.8±0.2	[59]
H ₂ SO ₄ -Na ₂ CrO ₄	全流程空白低 Re 空白水平低 试剂易纯化	环保问题 有害健康	富有机质沉积岩	1~2	0.6	[60]

4.4 富碳地质标样选择

Re-Os 同位素分析中,基质匹配的地质标样在监测 Re-Os 同位素分析流程、数据质量、分析方法验证等方面至关重要,也是开展机理研究从而进一步理解数据地质意义的关键基础。目前,国内外尚未有针对富碳地质样品专门研制的 Re-Os 同位素分析地质标样,现阶段所使用的地质标样均是在已有标样基础上经均匀性检验、实验室间数据比对后逐渐推广使用,包括美国地质调查局(USGS)页岩(SBC-1^[58,60,71]、SCo-1 和 SCo-2^[71-73]),油页岩(SGR-1b)^[59,71],钙质富有机质页岩(ShTX-1 和 ShCX-1)^[71]标样,日本地质调查局(GSJ)沉积岩标样(JCh-1 和 JMS-2)^[74]和美国国家标准与技术研究院(NIST)原油标样(NIST RM 8505)^[67-70,75],其 Re-Os 同位素数据总结于表 2。

SBC-1^[58,60,71]和 SGR-1b^[59,71]的 Re-Os 同位素数据通过不同溶样方法获得,SBC-1 标样 Re 含量较为均一,Os 含量和同位素比值略有差异(表 2,图 3 中 a~d)。这可能与 SBC-1 中存在碎屑来源 Os^[58]、Re-Os 解耦及“块金效应”有关^[105],该标样被推荐用于有机质含量较少、碎屑含量较多的富有机质沉积岩 Re-Os 数据监控。SGR-1b 即使在 0.2g 的称样量下仍具有相对均一的 Re、Os 含量及 Os 同位素比值(表 2,图 3 中 e~h),可作为油页岩样品 Re-Os 分析的标准样品进行使用^[59,71]。由于 SCo-1 标样已用尽,因此使用在同一位置采集的 SCo-2 进行页岩的数据监控。SCo-2 均

一的 Re-Os 含量及同位素比值(表 2),被推荐用于有机质含量较低样品^[92]的数据监控。NIST RM8505(表 2,图 3 中 i~l)被多次用于油气演化过程和油气样品 Re-Os 分析方法研究^[48-49, 68-69, 71,75],其较大的 Re、Os 含量差异和较为均一的同位素比值特征较适合作为 Re-Os 同位素比值标样使用。此外,Wang 等^[71]首次报道了钙质富有机质页岩标样 ShTX-1 和 ShCX-1(表 2)的 Re-Os 同位素数据,虽然数据量较少,但是其较好的均一性显现出该标样在监控钙质富有机质页岩 Re-Os 同位素数据的极大潜力。

虽然目前富碳质 Re-Os 同位素地质标样的 Re-Os 数据量仍然较少,实验室间的数据比对工作较为欠缺,但是选择与待分析样品基质匹配的标样进行数据监控,可以更加精准地监控和评价数据的有效性,而合适的标样对不同类型地质样品的方法研究、Re 和 Os 富集机制研究以及 Re-Os 等时线地质意义的理解至关重要。

5 存在问题与研究展望

三十年来,富碳地质样品 Re-Os 同位素体系为沉积时代厘定、古海洋环境演化、重大地质事件发生时间、油气演化等研究提供了诸多关键信息,对于了解地球历史具有重要意义。但是,由于 Re 和 Os 在油气系统、湖相沉积物、煤中的化学行为复杂,其地质应用仍然面临巨大挑战。因此,未来的重点研

表 2 已报道的富碳地质标样 Re-Os 同位素数据

Table 2 Reported Re-Os data of carbon-enriched geological references materials

标样编号	研制机构	标样类型	Re 含量(ng/g)	Os 含量(pg/g)	¹⁸⁷ Re/ ¹⁸⁸ Os	¹⁸⁷ Os/ ¹⁸⁸ Os	数据来源
SBC-1	美国地质调查局 (USGS)	页岩	11.11±0.14 (n=43, RSD=1.3%)	100.2±4.1 (n=43, RSD=4.1%)	883.5±46.0 (n=43, RSD=5.2%)	5.119±0.270 (n=43, RSD=5.3%)	[58, 60, 71]
SCo-2	美国地质调查局 (USGS)	页岩	1.179±0.042 (n=6, RSD=3.6%)	1167±6.8 (n=6, RSD=5.8%)	57.91±2.95 (n=6, RSD=5.1%)	1.596±0.018 (n=6, RSD=1.2%)	[71]
SGR-1b	美国地质调查局 (USGS)	油页岩	34.71±0.93 (n=24, RSD=2.7%)	0.4541±0.0235 (n=24, RSD=5.2%)	448.8±21.4 (n=24, RSD=4.8%)	1.787±0.009 (n=43, RSD=0.5%)	[59,71]
ShTX-1	美国地质调查局 (USGS)	钙质富有机质 页岩	141.6±0.2 (n=7, RSD=0.1%)	617.8±10.4 (n=7, RSD=1.7%)	1738±24 (n=7, RSD=1.4%)	4.565±0.013 (n=7, RSD=0.3%)	[71]
ShCX-1	美国地质调查局 (USGS)	钙质富有机质 页岩	13.62±0.14 (n=7, RSD=1.0%)	424.3±13.9 (n=7, RSD=3.3%)	206.8±7.1 (n=7, RSD=3.4%)	2.702±0.017 (n=7, RSD=0.6%)	[71]
JCh-1	日本地质调查局 (GSJ)	沉积岩	24.53±4.17 (n=8, RSD=17.0%)	5.604±0.375 (n=12, RSD=6.7%)	22.97±3.6 (n=8, RSD=15.7%)	0.5908±0.0189 (n=11, RSD=3.2%)	[74]
JMS-2	日本地质调查局 (GSJ)	沉积岩	126.1±4.1 (n=9, RSD=3.2%)	264.4±12.6 (n=11, RSD=4.8%)	2.540±0.156 (n=7, RSD=6.1%)	0.8138±0.0500 (n=10, RSD=6.2%)	[74]
RM 8505	美国标准局 (NIST)	原油	2.228±0.508 (n=43, RSD=22.8%)	27.06±3.63 (n=36, RSD=13.4%)	445.5±31.5 (n=36, RSD=7.1%)	1.531±0.076 (n=36, RSD=5.0%)	[67-70,75]

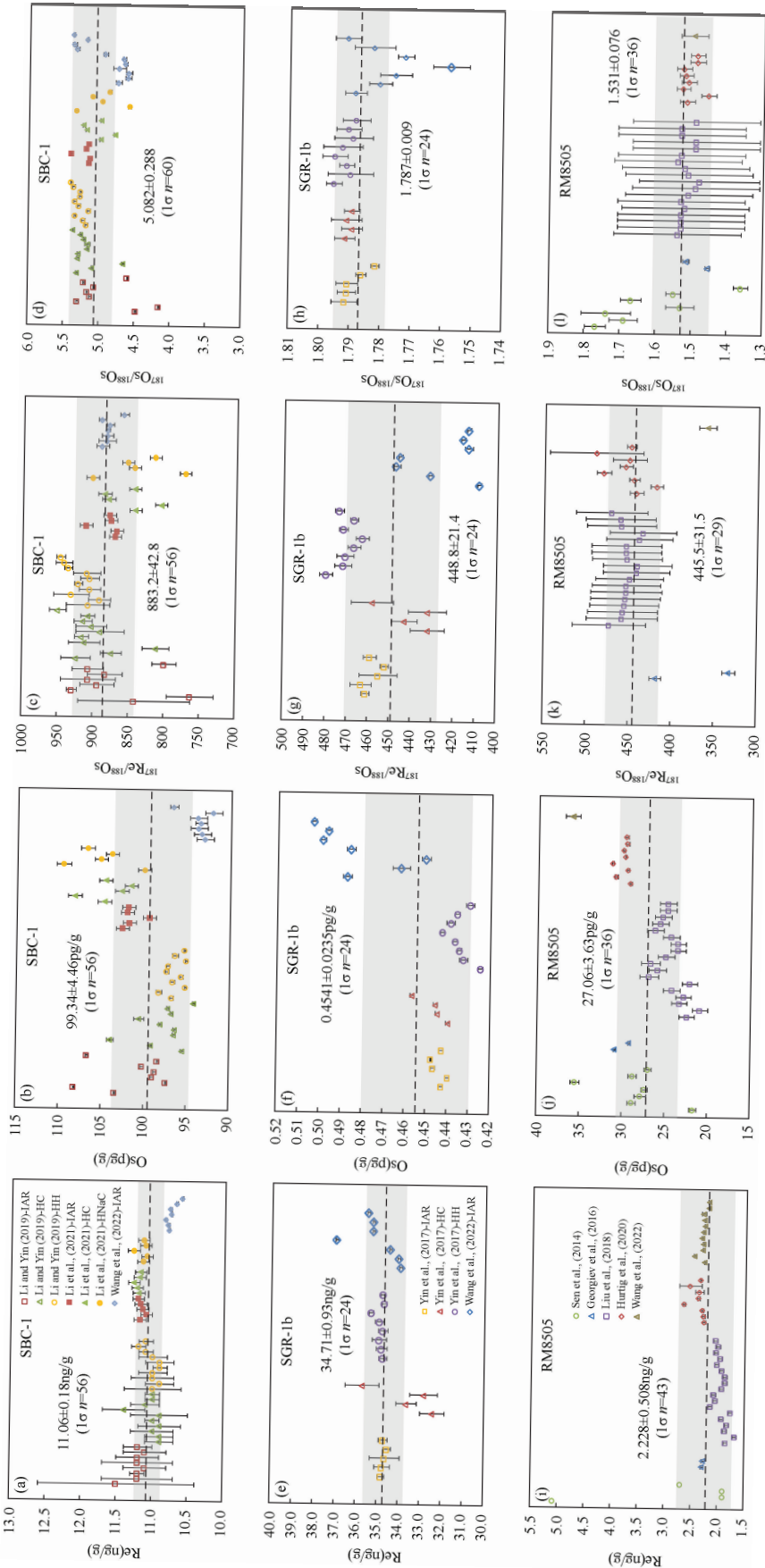


图 3 不同文献中的页岩标准 SBC-1 (a~d)、油页岩标准 SGR-1b (e~h) 和原油标准 RM8505 (i~l) 的 Re-Os 数据 (IAR、HC、HH 和 HNaC 分别代表逆王水、 H_2O_2 、 H_2SO_4 - CrO_3 和 H_2SO_4 - Na_2CrO_4 溶样法; 黑色虚线为所有数据 1 倍标准偏差)
 Fig. 3 Re-Os data of shale standard SBC-1 (a~d), oil shale standard SGR-1b (e~h) and crude oil standard RM8505 (i~l). IAR, HC, HH and HNaC represent the inverse aqua regia, HNO_3 - H_2O_2 , H_2SO_4 - CrO_3 and H_2SO_4 - Na_2CrO_4 method, respectively. The shaded areas represent 1 standard deviation (σ) of the mean value. In general, SBC-1 and SGR-1b show uniform Re and Os contents, and the isotopic ratio, which are suitable for Re-Os data monitoring of shale and oil shale samples. The RM8505 has uniform isotopic ratio which is suitable for monitoring Re-Os isotope ratio of crude samples.

究方向可以从以下几个方面展开:①丰富不同类型富碳地质样品的 Re-Os 同位素数据,为探索 Re 和 Os 在不同地质样品中的富集机制提供数据基础;②利用油源对比、无机指纹识别等多种地球化学手段探索更合适的采样方式,降低地质因素对 Re-Os 数据的影响,同时针对不同类型油气样品优化、建立匹配的 Re-Os 同位素分析技术以提高低丰度油气样品的分析精度,为深入研究油气系统 Re-Os 赋存

机制和理解 Re-Os 等时线的地质意义提供技术支持;③从中国富碳地质样品中筛选、研制 Re-Os 同位素标准物质或内部监控样,以应对国际地质标样购买困难的问题,支撑 Re-Os 分析方法优化、数据监控和拓展定年对象等研究工作。

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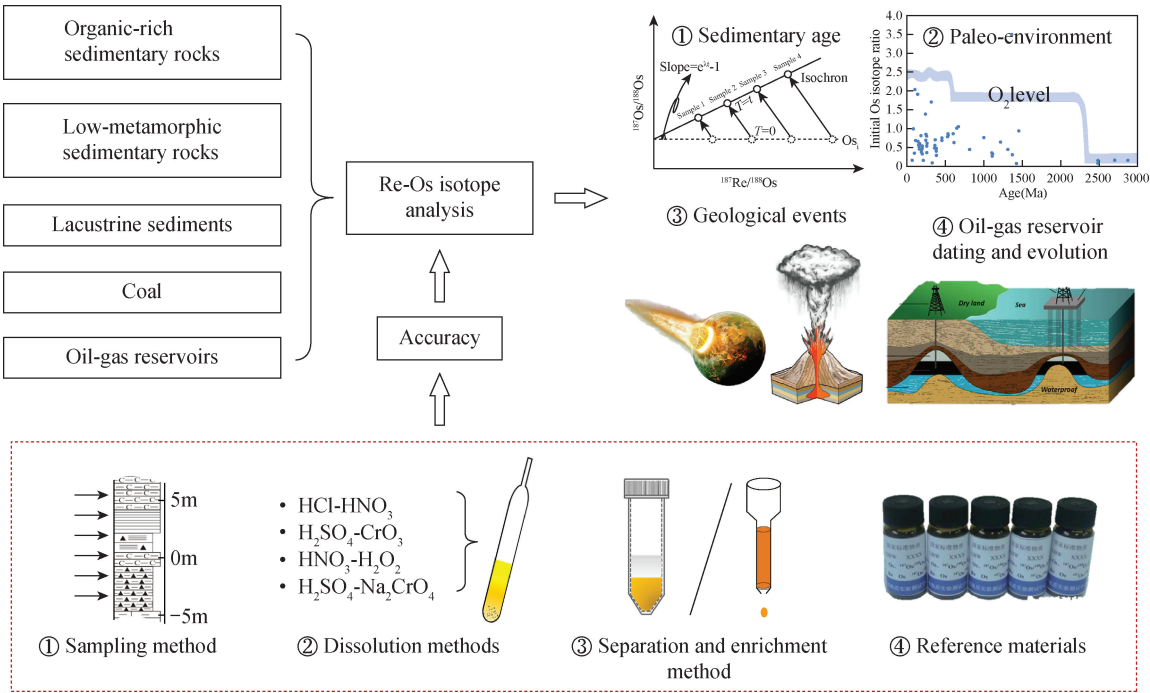
A Review of Research Progress on Re-Os Isotopic System of Carbon-enriched Geological Samples

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HIGHLIGHTS

- (1) The accuracy of Re-Os isotope data has an important influence on the interpretation of chemical behavior and isochron ages geological significance of carbon-enriched geological samples.
- (2) Appropriate sampling method, Re-Os analysis method and geological reference materials can improve the accuracy of carbon-enriched geological samples' Re-Os isotope data.
- (3) Enriching and improving Re-Os analysis methods, databases and reference materials of carbon-enriched geological samples provide important support for the study of Re-Os occurrence mechanism in carbon-enriched geological samples and wide application of Re-Os isotope dating technology.



ABSTRACT

Re and Os are relatively enriched in organic-enriched sedimentary rocks under an anoxic environment due to their organophilic property, and the seawater Os isotopic composition is recorded during the deposition of sedimentary rocks. Under certain geological conditions, the Re and Os in organic-enriched sedimentary rocks will transfer to oil-gas reservoir samples through the process of hydrocarbon generation. The enrichment mechanism of Re and Os in these carbon-enriched geological samples, such as organic-enriched sedimentary rocks, low-metamorphic sedimentary rocks, lacustrine sediments, coal, and oil-gas reservoir samples is the basis of wide geological applications. Re-Os isotopic system of organic-enriched sedimentary rocks has been applied to directly date deposition ages or stratigraphic boundary ages or oil-gas reservoirs, has been used to provide the occurrence time and explore the mechanism of major geological events, reconstructing paleo-environment, and deducing the evolution of petroleum, which has resulted in many achievements.

The accumulation mechanism of Re and Os in organic-enriched sedimentary rocks plays an important role in understanding the geological significance of Re-Os isotopic data obtained from organic-enriched sedimentary rocks. In anoxic seawater, Re and Os are reduced to lower valence states of Re(IV) and Os(III), respectively, and then Re and Os enter into organic-rich sedimentary rocks by combining with organic matter. Re and Os are enriched and fractionated during this process, enabling the Re-Os isotope system of organic-enriched sedimentary rocks to directly determine stratigraphic boundaries and sedimentary ages. The Re-Os isotope system has successfully provided accurate stratigraphic boundary ages of Devonian-Carboniferous, Cambrian-Ordovician, Ordovician-Silurian, Permian-Triassic, middle-upper Triassic, and Jurassic-Cretaceous. Furthermore, the Re-Os isotopic system has unique advantages for the strata lacking biological fossils or volcanic interlayers, which have provided the sedimentary age of the Niutitang Formation black shale in Guizhou province and Doushantuo Formation in South China. During the process of hydrogenous source Os into organic-enriched sedimentary rocks, the relative flux of Os from continental weathering, hydrothermal and cosmic dust was recorded, which was reflected as the initial Os isotopic ratio of sedimentary rocks. The coupling relationship between the variation of Os isotopic ratios, atmospheric oxygen level, crustal weathering degree, glaciation events, meteorite impact events, and Large Igneous Provinces can provide the occurrence time and explore the mechanism of major geological events in the history of the earth. The paleoseawater environment and paleoclimate during sedimentation can be further reduced in multiple dimensions by means of the coordinated variation between Re-Os isotopic data, organic matter accumulation, enrichment degree of redox-sensitive elements, and other geochemical proxies.

The behavior of Re and Os in the oil-gas system has always been the focus and difficulty in the research of oil-gas reservoir chronology, which is an important basis for understanding the geological significance and wide application of oil-gas reservoir-related samples. The chemical behavior of Re-Os varies in different stages of hydrocarbon formation and evolution. It has been found that the Re-Os isotope system of source rocks will not be destroyed during the process of hydrocarbon generation, and Re/Os fractionation and redistribution of Re and Os will occur during the process of hydrocarbon expulsion and migration. During the process of deasphaltizing, biodegradation, thermal alteration, thermal cracking and oil-water reaction, the asphaltene in crude oil will change correspondingly, and Re and Os in crude will migrate and fractionate accordingly, which will affect the closure of Re-Os isotope system, and even reset the Re-Os isotope system in crude. The different chemical behaviors of Re and Os in the process of hydrocarbon formation and evolution determine the geological significance of Re-Os isochrones obtained from oil-gas samples.

Despite the Re-Os isotope system obtaining many achievements and advances in the application of carbon-enriched geological samples, there are still many crucial problems that need to be solved, which restrict the wide application of the Re-Os isotope system. Through statistical analysis of the Re-Os data (including Re and Os contents, ages and initial Os uncertainty) of carbon-enriched geological samples from different sedimentary ages, it

is found that the Re and Os contents of organic-enriched sedimentary rocks are at the level of 10^{-9} – 10^{-12} g/g, and the error of the Re–Os isochron age and initial Os isotopic ratio of many samples exceeds 10%, especially the larger error of initial Os data. In the process of Re–Os isotope analysis, the accuracy of initial Os isotopic ratio data will not only be affected by sample content, procedural blank of chemical treatment method, error propagation and amplification during calculation, but also by geological factors in the process of sampling. The accuracy of the Re–Os data of carbon-enriched geological samples restricts the accurate identification of the paleoenvironment, the occurrence time of major geological events, the true source of seawater Os, and the degree of geological process by using the initial Os isotopic ratio and the Re–Os isochron age of organic-enriched sedimentary rocks. Moreover, the error of Re–Os isotopic data in the oil–gas system is larger than that in the organic rich sedimentary rocks. Studies on Re–Os chemical analysis methods and sampling methods for different types of oil–gas samples are still insufficient, and the fractionation mechanism of Re–Os in the process of hydrocarbon formation and evolution is still unclear. This hinders the further understanding of the chemical behavior of Re and Os, and the geological significance of Re–Os isochron ages during oil–gas evolution. In addition, the lacustrine sediments and coal have more complex material sources, geological processes, and the impact of terrigenous detrital during the formation process that is difficult to obtain effective sedimentary ages by Re–Os isotope dating at present.

On the basis of existing Re–Os isotope analysis techniques, improving the Re–Os data quality as much as possible is the key to studying the Re–Os enrichment mechanism of carbon-enriched geological samples, especially exploring the chemical behavior of Re and Os and geological significance of the Re–Os isochron age of the oil–gas system. There are four aspects that can improve the accuracy of Re–Os isotopic data of carbon-enriched geological samples.

(1) Sampling methods: In addition to collecting fresh and unweathered organic-carbon geological samples, the deposition rate can be a reference as a sampling interval. This can guarantee the samples have relatively uniform initial Os isotopic value and a wide range of the Re–Os isotopic ratios and can improve the accuracy of the Re–Os isochron and initial Os values. Through different pretreatment, such as mixing for a long time, or extracting with organic reagents improvements to the homogeneity of oil–gas samples and the quality of Re–Os data can be made.

(2) Dissolution methods: Except for the traditional H_2SO_4 – CrO_3 and reverse aqua regia method, researchers established two dissolution methods which were HNO_3 – H_2O_2 and H_2SO_4 – Na_2CrO_4 to solve the problem of high Re blank of the traditional H_2SO_4 – CrO_3 method and improve the accuracy of Re–Os data. As the principle of choosing a suitable dissolution method, the Re and Os content of the samples especially the Os content should be considered first and the method with lower procedural blank should be selected.

(3) Enrichment methods: Previous studies presumed that the $^{185}\text{Re}/^{187}\text{Re}$ data obtained by acetone–NaOH extraction method and anion resin exchange method were consistent. However, recent studies have confirmed that different enrichment methods can produce Re fractionation. The acetone–NaOH extraction method can obtain more consistent results than anion resin exchange method during Re enrichment. The acetone–NaOH extraction method is recommended for samples with Re content less than 1 ng/g and for oil–gas samples.

(4) Selection of reference materials: Matrix matched reference materials are very important in monitoring the process, data quality and method accuracy of Re–Os isotope analysis. At present, the main reference materials used are shale and oil shale standard samples (SBC-1, SCo-2 and SGR-1b) of the United States Geological Survey (USGS) and crude standard samples (NIST RM8505) of National Institute of Standards and Technology (NIST). There are also calcareous organic-enriched shales from the USGS and sedimentary rock samples from the Japan Geological Survey. According to the summarized Re–Os data obtained by different dissolution methods, SBC-1, SGR-1b and SCo-2 have relatively uniform Re/Os content and isotope ratio on the whole, which can be used for Re–Os data monitoring of shale and oil shale, respectively. The Re–Os data of calcareous organic-enriched shale standard samples have been reported recently and show good uniformity which have great potential in

monitoring Re-Os data. NISTRM8505 has relatively uniform Re-Os isotope ratio and may be more suitable for isotope ratio monitoring.

In conclusion, the Re-Os isotope system of carbon-enriched geological samples provides much key information for the determination of sedimentary age, paleomarine environment evolution, occurrence time of major geological events, and oil-gas evolution, which is significant for understanding Earth's history. It is important to improve the accuracy of Re-Os isotope data of carbon-enriched geological samples by different methods to better understand chemical behavior of Re and Os and the geological significance of Re-Os isochron age. Enriching and improving Re-Os analysis methods, databases and reference materials of carbon-enriched geological samples will provide important support for the study of Re-Os enrichment mechanism of carbon-enriched geological samples and its wide application.

KEY WORDS: Re-Os isotope system; carbon-enriched geological samples; petroleum evolution; Re-Os chemical behavior; geological application; carbon-enriched reference materials

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