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沉积岩有机碳同位素组成测定的前处理方法研究

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摘要: 沉积岩的有机碳同位素研究是地质学领域的重要内容，可为地质历史时期的古环境重建、古气候变化解析、碳循环过程理解以及能源资源勘探开发提供重要信息。由于沉积岩中的有机碳主要以干酪根的形式赋存，因此，在获取沉积岩有机碳同位素值之前，需要先对岩石样品开展干酪根提取预处理。提取过程需使用大量危险化学品，制备流程长且面临化学品使用受限等诸多挑战。因此，在实际工作中，亟需开发一种更为便捷、环保的前处理方法。本文建立了一种简易的酸处理方法，实验选取 110 件不同岩性 (灰岩、页岩、油页岩)和不同有机碳含量范围 (0.83%～35.33%) 的沉积岩样品进行该前处理方法与传统干酪根提取前处理方法的比对实验。结果表明，对于 94% 的样品，本次建立的前处理方法和干酪根提取方法获得的碳同位素值差值均小于 1.0‰，满足行业标准方法重复测定的偏差要求。表明该前处理方法可以有效地实现沉积岩样品中有机碳的分离，进而准确获取有机碳同位素值这一关键地质参数。而且，样品的有机碳含量及岩性未对测定结果产生明显影响，显示该方法对常规地质样品的适用性，可满足地质勘探调查工作需求。

关键词: 碳同位素；沉积岩；前处理方法；酸处理；干酪根

要点:

(1) 沉积岩有机碳同位素测试需以干酪根提取制备为前提，制备流程长，且面临化学品使用受限等诸多挑战，需要开发更为便捷、环保的前处理方法。

(2) 建立了一种基于稀盐酸实现沉积岩中有机碳组分有效分离的前处理方法，具有流程简洁、实验耗材易获取、样品用量少等优点。

(3) 对比了传统的干酪根提取方法与本文建立的前处理方法对不同 TOC 值、不同岩性样品有机碳同位素值测定的影响，证明了本文方法对于页岩、灰岩等常见地质样品的适用性。

中图分类号: P597.2　　**文献标识码:** A

沉积岩中的碳库包含有机碳和无机碳两类，有机碳主要赋存形式为干酪根，占据了沉积岩有机碳总量的 80% 以上，而无机碳则主要以碳酸盐的形式存在[1-2]。有机碳与无机碳的同位素值存在显著差异，具有不同地质应用意义[3-6]。目前普遍认为有机碳同位素值主要取决于有机质的来源[7-9]，受热演化作用的影响较小，在油气地球化学领域被应广泛用于区分有机质类型[10-15]。例如，以高等植物来源为主的腐殖型 (Ⅲ型) 干酪根的碳同位素值较水生植物为主的腐泥型 (Ⅰ型) 干酪根明显富集重同位素。而碳酸盐矿物则主要继承沉积水体的无机碳同位素信息[16]，可用来恢复古海洋的信息，多用于

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开展古环境重建[17-20]、地层对比等研究工作[21-29]。将沉积岩中的有机碳和无机碳同位素值开展联合应用，可以为破译地质历史时期的古环境变化、碳循环过程以及油气资源富集成藏提供重要参考信息[18,23-27]。

由于沉积岩中的有机碳主要以干酪根形式赋存，因此沉积岩有机碳同位素值的获取首先需要从岩石样品中提取干酪根，再利用同位素质谱仪对干酪根进行测定来获得有机碳同位素值[30-32]。干酪根的提取原理是先对岩石样品经过盐酸、氢氟酸等一系列的酸、碱溶液处理，去除岩石中的无机碳、矿物等成分，再经过浮选、烘干等大量处理步骤，最终获得干酪根，干酪根再通过同位素质谱仪检测才可以获取准确的有机碳同位素值。然而，干酪根的制备过程流程复杂且耗时较长，这导致了相关参数的测试周期相应延长，进而制约了沉积岩有机碳同位素数据的快速获取，影响后续地质研究及勘探评价速度。此外，在干酪根制备过程中，因使用盐酸、氢氟酸等试剂，这些试剂会对环境产生较大影响。因此，有学者提出了一种可替代的易操作的预处理方法，鉴于沉积岩中的无机碳主要以碳酸盐的形式赋存，该方法建议仅使用稀盐酸去除岩石中的碳酸盐类无机碳后，将处理后的岩石样品直接进行碳同位素分析，以此来代替干酪根制备的前处理过程[33-36]。这一方法高效，且可避免大量使用酸带来的环境问题，近年来倍受学者和测试机构关注[33-34]。但目前这一方法的研究主要围绕现代沉积物开展，而针对古代沉积岩的数据则有限，且缺乏以上两种前处理方式对沉积岩有机碳同位素值测定数据影响的系统比对，对不同岩性、不同有机质丰度样品的适用性不明确，尚不能说明这一简易前处理方法是否可以完全代替干酪根提取[37-41]。

针对以上问题，本文选取了一系列不同岩性、不同有机碳含量的沉积岩样品，分别使用简易酸处理方法和干酪根预处理的方法进行样品前处理，并利用元素分析 (EA)-同位素比质谱 (IRMS) 连续流分析方法对处理后的样品开展同位素测定对比实验，比较了两种前处理方式对不同岩性、不同总有机碳 (TOC) 含量范围的沉积岩样品的有机碳同位素测定结果的影响，明确了本方法对实际地质样品的适用性，为地质样品测定过程中合理选择前处理方法提供数据支撑，服务油气地质勘探及基础地质问题研究。

1 实验部分

1.1 样品制备

本研究在羌塘盆地采集典型剖面沉积岩样品 110 件，其中包括油页岩样品 12 件 (编号为油 1～油 12)、页岩样品 59 件 (编号为页 1～页 59)、灰岩样品 39 件 (编号为灰 1～灰 39)。采集后的沉积岩样品首先去除风化面，然后用去离子水清洗干净后放入通风橱中自然晾干。晾干后的样品经过混匀、粉碎、过筛处理，获得 100 目以下粉末样品。将每一件制备好的粉末样品分为三部分开展预处理，并分别标注。

(1) 第 1 部分样品：用于提取制备干酪根，用量约 100g，该过程参照《沉积岩中干酪根分离方法》(GB/T 19144—2010) 执行。该方法的原理主要是通过多步物理、化学的方法，去除岩石中的无机矿物和可溶有机质，提纯制备干酪根。制备流程包括：蒸馏水浸泡、盐酸或氢氟酸等多次酸处理、碱处理、黄铁矿处理、重液浮选、冷冻干燥、氯仿清洗可溶有机质、烧失量的测定等步骤。经多步反应后，制备后的干酪根样品烧失量需大于 75% 后，可存放于 60℃ 烘箱中干燥，以备后续进行干酪根碳同位素分析。

(2) 第 2 部分和第 3 部分样品：这两部分样品的预处理方式相同，用量约 5g，参照《沉积岩中总有机碳含量的测定》(GB/T 19145—2022) 的前处理过程开展。首先对盛装样品的坩埚进行高温煅烧，即在 1000℃ 条件下灼烧 2h 以上去除杂物。然后称取约 0.1g 粉末样品置于冷却的坩埚中，缓慢滴入配制好的稀盐酸溶液 (盐酸：水=1：7, *V/V*)，岩石样品与盐酸充分反应直至无气泡产生。然后用蒸馏水反复淋洗坩埚，直至滤液为中性，单次加水量需控制样品不随水溢出。洗样完毕后置于 60℃ 烘箱内干燥备用。其中，第 2 部分样品用于后期岩石中总有机碳含量的测定；第 3 部分样品用于酸处理后样品碳同位素值的测定，与第 1 部分制备的干酪根样品测试的碳同位素值开展比较。

1.2 实验方法

1.2.1 仪器与材料

总有机碳含量 (TOC) 测定仪器为 Leco CS-744 碳硫分析仪。碳同位素测定采用 EA-IRMS 联用系统，测定仪器由两部分组成：①元素分析仪，型号为 Vario MICRO cube；②同位素比质谱仪，型号为 Elementar isoprime precision。其他主要材料包括瓷坩埚、盐酸溶液 (盐酸：水=1：7, *V/V*)、锡舟。

在样品分析前, 需开展标准样品测定, 以确保仪器处于良好工作状态。在进行测量时, 每测量 10 件样品, 至少进行一次平行样品及标准样品的测定, 以监控仪器运行稳定性。在总有机碳含量测定及同位素测定过程中, 使用不同值域范围的标准物质建立标准曲线, 对测量值进行校正。

本文实验使用的标准物质名称及推荐值信息列于表 1。

1.2.2　总有机碳 (TOC) 含量的测定

本文研究的沉积岩样品的总有机碳 (TOC) 含量测定参照《沉积岩中总有机碳含量的测定》(GB/T 19145—2022) 执行, 预处理后的样品 (1.1 节中制备好的样品) 用碳硫分析仪开展 TOC 值的测定。其基本原理是: 样品在高温氧气流中燃烧, 将样品中的有机碳完全转化为 CO_2; 生成的 CO_2 再经过红外检测器检测, 并给出准确的有机碳含量。测试过程中, 标准物质及重复样测试结果满足标准方法的质量要求。

1.2.3　有机碳同位素值的测定

样品的有机碳同位素值测定参照《有机物和碳酸盐岩碳氧同位素分析方法》(SY/T 5238—2019) 执行。在锡杯中称取适量处理后的样品, 放入自动进样器, 启动元素分析仪和同位素质谱仪的采集程序, 样品经元素分析仪充分燃烧后, 生成 CO_2 并随载气流进入同位素质谱仪进行碳同位素值测定。本次实验元素分析仪燃烧管温度设定为 950℃, 还原管温度设定为 600℃。测试过程中标准物质及重复样测试结果满足标准方法的质量要求, 重复样测试误差 ≤0.5‰。

2　结果与讨论

2.1　干酪根提取和酸处理两种前处理方式获得碳同位素值的比较

表 2 总结了本文研究样品的岩性、总有机碳含量 (TOC) 以及通过两种前处理方式获得的碳同位素值。数据结果显示, 研究样品 TOC 含量的分布范围为 0.83% ~ 35.33%, 样品岩性包括灰岩、页岩、油页岩, 涵盖了油气地质勘探中较为常见的岩性种类。对所有样品测试数据开展分析, 发现通过干酪根制备预处理获得的样品有机碳同位素值 ($\delta^{13}C_{ker}$) 分布范围为−34.6‰ ~ −21.5‰, 而经过酸处理样品的有机碳同位素值 ($\delta^{13}C_{acid}$) 分布范围为−34.5‰ ~ −20.0‰。两种处理方式获得样品的 $\delta^{13}C_{acid}–\delta^{13}C_{ker}$ 值 ($\mathit{\Delta}^{13}C$) 变化范围为−2.8‰ ~ 1.8‰。

对所有样品经两种前处理方式得到的有机碳同位素值结果开展相关性分析, 发现两者数据具有良好的一致性, 相关关系满足线性规律 $y=0.97x-0.61$, 决定系数 $R^2=0.97$(图 1)。对所有样品的碳同位素值 $\delta^{13}C_{acid}–\delta^{13}C_{ker}(\mathit{\Delta}^{13}C)$ 分布范围进行统计 (图 2), 其中有 68.18% 样品的 $\mathit{\Delta}^{13}C \leqslant 0.3$‰, 89.09% 样品的 $\mathit{\Delta}^{13}C$

表 1　实验使用的标准物质及有机碳含量

Table 1　Details of reference materials and their organic carbon content.

测试项目	标准物质编号	研制单位	有机碳含量推荐值 (%) 或同位素组成 $\delta^{13}C$ 推荐值 (‰)
总有机碳含量	GBW01117	江苏省铸造热处理研究所	3.08±0.02
	501-676	美国力可公司	0.13±0.04
	501-024	美国力可公司	3.19±0.03
	502-694	美国力可公司	10.80±0.26
碳同位素组成	GBW(E)04407	石油勘探开发科学研究院	−22.43±0.3
	GBW(E)04408	石油勘探开发科学研究院	−36.93±0.3
	USGS24	美国地质调查局	−16.05±0.3
	NBS-22	国际原子能机构	−30.03±0.05

表 2　样品岩性信息及 TOC、$\delta^{13}C_{ker}$、$\delta^{13}C_{acid}$、$\mathit{\Delta}^{13}C$ 测定结果

Table 2　Lithological information of samples and measured results of TOC, $\delta^{13}C_{ker}$, $\delta^{13}C_{acid}$ and $\mathit{\Delta}^{13}C$.

样品岩性	样品数量 (件)	TOC(%)		$\delta^{13}C_{ker}$(‰)		$\delta^{13}C_{acid}$(‰)		$\mathit{\Delta}^{13}C$(‰)	
		测定值范围	平均值	测定值范围	平均值	测定值范围	平均值	测定值范围	平均值
灰岩	39	0.83 ~ 18.69	9.62	−27.5 ~ −22.2	−24.6	−27.3 ~ −22.4	−24.4	−0.3 ~ 1.1	0.2
页岩	59	0.87 ~ 35.33	11.73	−34.6 ~ −21.8	−26.3	−34.5 ~ −20.0	−26.2	−2.8 ~ 1.8	0.1
油页岩	12	6.53 ~ 21.94	14.25	−25.8 ~ −21.5	−24.0	−25.9 ~ −21.1	−23.8	−0.6 ~ 0.5	0.2

≤0.6‰，93.64% 样品的 Δ^{13}C 值均可控制在 1.0‰范围之内，满足现行标准方法中关于碳同位素测定的重复性测定误差要求。这与陈立雷等[24]关于沉积岩和海洋沉积物总有机碳同位素分析的前处理影响的研究结果具有良好的一致性，表明不同的前处理方法获得的样品碳同位素值具有良好的可比性[2,21,30]。分析其原因，沉积岩中的无机碳主要以碳酸盐的形式存在，使用稀盐酸处理样品可以去除碳酸盐，从而实现对沉积岩中有机碳组分的有效分离，进而获得样品的有机碳同位素值[27,42]。该方法与制备干酪根的方法相比，虽未经多重的酸、碱处理，但去除了大部分无机碳，测量碳同位素数据的准确性可以得到保障。

2.2　不同前处理方式对碳同位素值测定的影响分析

2.2.1　不同岩性样品碳同位素测定值的对比

为了充分说明酸处理方式的适用性，本文还对不同岩性样品的测定数据开展了对比分析。结果显示，灰岩的干酪根碳同位素值分布在−27.5‰～−22.2‰之间，页岩的干酪根碳同位素值分布在−34.6‰～−21.8‰之间，油页岩的干酪根碳同位素值分布在−25.8‰～−21.5‰之间。对不同岩性样品采用两种前处理方式得到的碳同位素数据展开对比分析，图 2 表明对于灰岩样品，两种处理方式的 Δ^{13}C 值分布范围为−0.3‰～1.1‰，这些灰岩样品中 Δ^{13}C＜0.3‰的样品占比 87.18%，Δ^{13}C＜0.6‰的样品占比 94.87%，Δ^{13}C＜1.0‰的样品占比 97.44%；对于页岩样品，两种处理方式的 Δ^{13}C 值分布范围为−2.8‰～1.8‰，页岩样品中 Δ^{13}C＜0.3‰的样品占比 57.63%，Δ^{13}C＜0.6‰的样品占比 83.05%，Δ^{13}C＜1.0‰的样品占比 89.83%；而对于油页岩，两种处理方式的 Δ^{13}C 值分布范围为−0.6‰～0.5‰，其中 Δ^{13}C＜0.3‰的样品占比 58.33%，Δ^{13}C＜0.6‰的样品占比达到 100%。

总体而言，页岩样品受不同前处理方式的影响更为明显，共有 6 件样品的差值超出了标准允许的误差范围，经分析认为出现这一现象的原因可能是页岩中的黏土矿物含量较高，遇水膨胀导致酸处理效果不佳；或者是这些样品中存在着一定数量的非干酪根态有机碳，这些组分的存在造成了两种前处理方式后样品碳同位素测量值的差异[13,32]。基于，目前该部分内容的数据较少，仍需后续继续补充实验，以准确地揭示出现这种差异的原因。

2.2.2　不同 TOC 含量样品碳同位素测定值的对比

为了说明加酸前处理方法对不同总有机碳含量 (TOC) 样品的适用性，对 TOC 含量不同的样品情况进行了对比 (图 3)。本文研究样品的 TOC 分布范

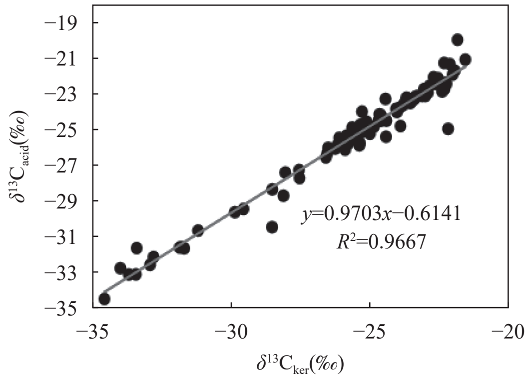

图1　样品 $\delta^{13}C_{acid}$ 与 $\delta^{13}C_{ker}$ 线性关系

Fig. 1　The linear relationship between $\delta^{13}C_{acid}$ and $\delta^{13}C_{ker}$ of samples.

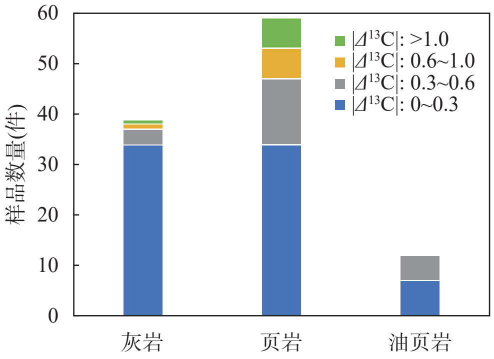

图2　不同岩性样品在不同|Δ^{13}C|范围的数量统计

Fig. 2　The quantitative statistics of samples with different lithology in different |Δ^{13}C| value ranges.

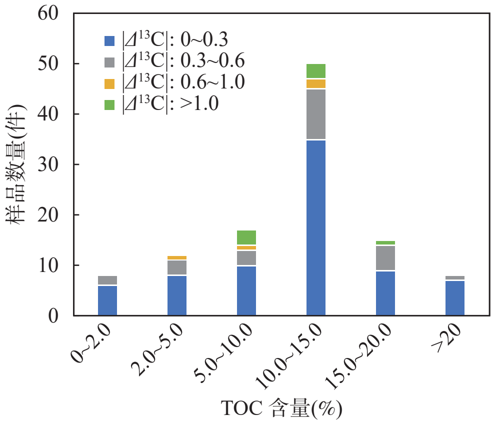

图3　不同有机碳含量样品在不同|Δ^{13}C|范围的数量统计

Fig. 3　The quantitative statistics of samples with different TOC content in different |Δ^{13}C| value ranges.

围为 0.83%～35.33%, 对应两种前处理方法处理的样品 Δ^{13}C 值变化范围为−2.8‰～1.8‰。TOC 含量＜2.00% 的样品 8 件, 这些样品中 Δ^{13}C＜0.3‰的样品占比 75.00%, 8 件样品的 Δ^{13}C 值都小于 0.6‰; TOC 含量在 2.00%～5.00% 的样品 12 件, 其中 Δ^{13}C＜0.3‰的样品占比 66.67%, Δ^{13}C＜0.6‰的样品占比 91.67%, 12 件样品的 Δ^{13}C 值都小于 1.0‰; TOC 含量在 5.00%～10.00% 的样品 17 件, 其中 Δ^{13}C＜0.3‰的样品占比 58.82%, Δ^{13}C＜0.6‰的样品占比 76.47%, Δ^{13}C＜1.0‰的样品占比 82.35%; TOC 含量在 10.00%～15.00% 的样品 50 件, 其中 Δ^{13}C＜0.3‰的样品占比 70.00%, Δ^{13}C＜0.6‰的样品占比 90.00%, Δ^{13}C＜1.0‰的样品占比 94.00%; TOC 含量在 15.00%～20.00% 的样品 15 件, 其中 Δ^{13}C＜0.3‰的样品占比 60.00%, Δ^{13}C＜0.6‰的样品占比 93.33‰, Δ^{13}C＜1.0‰的样品占比 93.33‰; TOC 含量＞20% 的样品 7 件, 7 件样品中 Δ^{13}C＜0.3‰的样品占比 87.50%, Δ^{13}C＜0.6‰的样品占比 87.50%, 全部样品的 Δ^{13}C 值都小于 1.0‰。

总体而言, 在本文研究的 TOC 含量范围内, 两种处理方法具有良好的一致性, 除个别样品外, 两种前处理方法测定碳同位素值的差值均可控制在 1.0‰以下。其中, 两种方法出现较大差异的样品 TOC 范围主要在 5.00%～15.00% 之间, 其中有 6 件样品的碳同位素值差值大于 1.0‰。经过观察与分析, 发现这些样品普遍具有较高的含油率, 在酸处理过程中, 会出现油膜包裹样品而导致酸无法与样品充分接触反应的现象, 进而导致测定结果出现偏差。

2.2.3 酸处理容器坩埚对碳同位素测定值的影响

对样品进行酸处理时, 使用的容器为瓷坩埚, 目前存在多种在售瓷坩埚, 其主要的区别在于透水效率。透水效率对盐酸溶液与样品的反应时间具有显著影响, 进而导致实验总时长发生变化。但关于透水效率是否会对碳同位素值造成影响的问题, 目前尚未有明确的研究结论。因此, 为了方便研究人员实际操作, 本文研究选取了具有三种不同透水速率的瓷坩埚 (Ⅰ型、Ⅱ型、Ⅲ型, 三种坩埚透水速率比约为 4∶3∶1) 开展对比实验, 以确定酸处理容器是否会对样品的碳同位素值产生影响。

从本次沉积岩样品中随机选取 10 件样品开展对比实验, 每件样品使用三种坩埚进行酸处理, 并对处理后的样品开展碳同位素分析。碳同位素值测定结果 (表 3) 表明, 所有样品比对结果的差值均小于 0.3‰, 满足样品测定的重复性要求。对测试数据进行单因素方差分析, 结果表明不同样品编号 δ^{13}C 样本对于三种类型的坩埚均不会表现出显著性 (p＞0.05), 意味着不同样品编号 δ^{13}C 样本对于三种类型的坩埚均表现出一致性, 未见显著差异。由此可见, 瓷坩埚的透水速率差异不会对有机碳同位素值测定结果产生明显影响, 不同漏水速率的瓷坩埚均可用于进行有机碳同位素测定的前处理。

表 3 三种坩埚酸处理取得的 δ^{13}C 测定结果

Table 3 The measurement results of δ^{13}C obtained by acid treatment with three crucibles.

样品编号	δ^{13}C 测定值 (‰)			δ^{13}C 测定平均值 (‰)	δ^{13}C 测定值 标准偏差 (‰)
	Ⅰ型坩埚	Ⅱ型坩埚	Ⅲ型坩埚		
页岩 1	−33.8	−34.1	−34.1	−34.0	0.2
页岩 2	−32.8	−32.8	−32.9	−32.8	0.1
页岩 3	−31.3	−31.4	−31.3	−31.3	0.1
页岩 4	−30.7	−30.7	−30.8	−30.7	0.1
页岩 5	−30.3	−30.5	−30.5	−30.4	0.1
页岩 6	−29.5	−29.4	−29.5	−29.5	0.1
页岩 7	−29.4	−29.3	−29.2	−29.3	0.1
页岩 8	−28.4	−28.3	−28.4	−28.4	0.1
灰岩 1	−27.2	−27.3	−27.3	−27.3	0.1
灰岩 2	−26.5	−26.6	−26.6	−26.6	0.1

3 结论

建立了基于稀盐酸溶液的沉积岩样品有机碳同位素测试前处理方法。通过对页岩、灰岩、油页岩等不同岩性及不同有机碳含量的样品进行比对实验，验证了简易酸处理法能够有效地去除沉积岩中的无机碳组分，实现与有机碳组分的分离，进而获取有机碳同位素值这个关键地质参数。该方法获得的有机碳同位素数据，与传统干酪根提取方法所得数据具有良好的可比性，证实了这种更为便捷且环保的前处理方法的有效性。

本文建立的前处理方法具有流程简洁、实验耗材易获取、样品用量少等诸多优点，能够更好地满足日常沉积岩有机碳同位素值测试需求，具有良好的应用前景。然而，部分样品仍存在酸处理测定结果与干酪根测定结果不一致的情况，因此，有必要进一步开展系统性的条件实验，深入探究其成因，并采取相应的解决措施，以更好地服务沉积岩稳定同位素研究需求。

A Pre-Treatment Method for the Determination of Organic Carbon Isotope Composition in Sedimentary Rocks

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HIGHLIGHTS

(1) The organic carbon isotope test of sedimentary rocks should be based on the extraction and preparation of kerogen, which has a long preparation process and requires the use of a significant quantity of hazardous chemicals. Therefore, more convenient and environmentally friendly pretreatment methods need to be developed.

(2) A pre-treatment method for effective separation of organic carbon components from sedimentary rocks based on dilute hydrochloric acid was established, which has the advantages of simple process, easy access to experimental consumables, and less sample consumption.

(3) The influence of the traditional kerogen extraction method and the pre-treatment method established on the determination of organic carbon isotope values of samples with different TOC values and different lithologies is compared, which proves the applicability of this method for common geological samples such as shale and limestone.

ABSTRACT: The organic carbon in sedimentary rocks is mainly in the form of kerogen, and it is necessary to extract kerogen from samples before obtaining the organic carbon isotope value. The extraction process requires a significant quantity of hazardous chemicals and a long preparation process. Therefore, in daily work, there is an urgent need to develop a more convenient and environmentally friendly pre-treatment method. A simple acid treatment method was established, and 110 sedimentary rock samples with different lithology (limestone, shale, oil shale) and different organic carbon content range (0.83%−35.33%) were selected for comparison experiments of two pretreatment methods. The results show that for 94% of the samples, the difference of carbon isotope values obtained by the acid pretreatment method established in this study and the kerogen extraction method was less than

1.0‰, which met the deviation requirements for repeated measurements, indicating that this pretreatment method can be used to accurately obtain the key geological parameter of an organic carbon isotope value. Furthermore, the organic carbon content and lithology of the samples does not influence the results, demonstrating the applicability of this method to typical geological samples and fulfilling the requirements of geological exploration and investigation. The BRIEF REPORT is available for this paper at http://www.ykcs.ac.cn/en/article/doi/10.15898/j.ykcs.202403110038.

KEY WORDS: carbon isotope; sedimentary rock; pretreatment method; acid treatment; kerogen

BRIEF REPORT

Significance: The carbon pool in sedimentary rocks comprises both organic and inorganic carbon. Organic carbon predominantly exists in the form of kerogen, which accounts for over 80% of the total organic carbon in these rocks, while inorganic carbon primarily occurs as carbonate[1-2]. There are notable differences in the isotopic values of organic and inorganic carbon, each bearing distinct geological significance[3-6]. Currently, it is widely accepted that the stable carbon isotope value of organic matter is largely determined by its source[7-9], remaining relatively unaffected by thermal evolution. This characteristic renders it a valuable tool for distinguishing types of organic matter in the field of oil and gas geochemistry[10-15].

Since organic carbon in sedimentary rocks primarily exists in the form of kerogen, it is necessary to extract kerogen from samples before obtaining the organic carbon isotope value[30-32].

The preparation process of kerogen is complex and time-consuming, which limits the rapid acquisition of organic carbon isotope data from sedimentary rocks and affects the geological research and exploration evaluations. Furthermore, a significant amount of chemical reagents are utilized in the kerogen preparation process, which can have considerable environmental impacts. Consequently, some researchers have proposed a pretreatment method that only uses hydrochloric acid to replace the pretreatment process of kerogen preparation[33-36]. This method is simple and efficient, and it has garnered significant attention from scholars in recent years. However, the current application objects of this method are mainly modern sediments, while the data for ancient sedimentary rocks are very limited. There is also a lack of systematic comparison of the impact of the two pre-processing methods on the organic carbon isotope value determination of rock samples with different lithology and TOC values. It is not clear whether this simple pretreatment method can completely replace the kerogen extraction method[33-41].

This study established a pre-treatment method for effective separation of organic carbon components from sedimentary rocks based on dilute hydrochloric acid, and experiments were conducted using samples of various lithologies and organic carbon contents, including shale, limestone, and oil shale. The results demonstrate that the organic carbon isotope data obtained through this pre-treatment method are comparable to those acquired via the traditional kerogen extraction method. This research offers a more convenient and environmentally friendly pre-treatment method for isotope research in sedimentary rocks samples.

Methods: 110 typical profile rock samples were collected from Qiangtang Basin, including shale, oil shale and limestone. Each crushed sample was divided into 3 parts for pretreatment and subsequent experimental analysis. The Part 1 sample was used for extraction and preparation of kerogen, with the sample weight of about 100g. Part 2 and Part 3 samples were used to carry out acid treatment with about 5g per sample, and the organic carbon contents and isotope values were measured respectively after treatment.

The total organic carbon (TOC) content of sedimentary rock samples was determined by a Leco CS-744 carbon sulfur analyzer. The EA-IRMS combined system was used to determine the carbon isotope value of the sample. The combustion tube temperature of the element analyzer was set at 950℃, and the reduction tube temperature was set at 600℃. During the test process, the test results of standard substances and repeated samples need to meet the quality requirements of standard methods, and the carbon isotope test error of repeated samples is less than 0.5‰.

Data and Results: The research results indicate that the Δ^{13}C value ($\delta^{13}C_{acid}$−$\delta^{13}C_{ker}$) of the samples processed by the two methods ranges from −2.8‰ to 1.8‰. A correlation analysis was conducted on the isotope values obtained using these two pre-processing methods, revealing a strong consistency between the two datasets. The correlation followed the linear relationship described by the equation y=0.97x−0.61, with a correlation coefficient of R^2=0.97 (Fig.1). Notably, the proportion of samples with Δ^{13}C values less than 1.0‰ constitutes 94% of the total samples. These samples satisfy the repeatability error requirements for carbon isotope determination based on current standards, indicating that the carbon isotope values obtained through different pretreatment methods are highly comparable[2,21,24,30].

The study conducted a comparative analysis of carbon isotope data obtained through two pre-processing methods applied to samples with varying lithology (Fig.2). It was observed that shale samples were significantly more influenced by the different pre-processing methods, and a total of six shale samples exhibit Δ^{13}C values exceeding 1.0%, significantly higher than those of other lithologies. Analysis indicates that this phenomenon may be attributed to either a relatively high clay mineral content in the shale or the presence of non-kerogen organic carbon in these samples[13,32]. However, there is currently little data in this part, and additional experiments are still needed to accurately reveal the reasons for this difference.

In addition, the article compared the conditions of samples with varying total organic carbon (TOC) contents (Fig.3). The results indicate that the TOC content does not consistently influence the differences between the two methods. Specifically, only six samples exhibit differences greater than 1.0‰, with their TOC values primarily ranging from 5.00% to 15.00%. Notably, these samples tend to have a high oil content. During the acid treatment process, an oil film forms around the samples, which hinders the acid from fully contacting and reacting with them, ultimately leading to discrepancies in the measurement results.

The study selected three crucibles with varying water permeability rates to conduct comparative experiments. The results indicate that the differences in water permeability rates of acid treatment containers do not significantly impact the organic carbon isotope values.

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