

显生宙以来汞浓度异常评估及碳汞耦合关系的初步研究

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摘 要: 在漫长的地球历史中,生物大灭绝事件屡次发生,特别是显生宙以来至少发生过5次全球性生物大灭绝,汞(Hg)作为将这些事件与大火成岩省喷发连接起来的关键线索,在地质记录中备受关注。然而,先前的研究多倾向于聚焦重大事件导致的特定时期内汞浓度异常现象,缺乏对汞在地质历史时期大尺度下演化的整体性认识。此外,总有机碳(TOC)作为沉积物中汞的主要载体,二者之间的协同演化关系也存有许多未知。因此,本研究以沉积地球化学与古环境项目数据库中汞和碳的记录和近年来5次生物大灭绝事件的文献数据为研究对象。通过观察各时期元素浓度变化,发现SGP数据库记录的最高的4个Hg峰值分别位于508、401、298和111 Ma;通过Spearman's rho相关系数和回归分析,发现沉积物中Hg与TOC的浓度之间存在正相关关系。对比前人对地质记录中汞浓度异常的解释和沉积物中Hg与TOC关系的研究,我们探讨了造成沉积物中Hg异常的可能因素,认为4个时期Hg含量的高值可能并不都是火山作用造成的;另外,我们发现碳酸盐岩和硅质碎屑岩中Hg与TOC含量的数据在分区拟合下效果最佳,说明在不同沉积环境下沉积物中Hg与TOC含量可能具有不同的耦合关系。

关键词: 显生宙;环境演化;总有机碳;汞;元素耦合

中图分类号: P595 **文献标识码:** A **文章编号:** 1672-9250(2025)01-0001-13 **DOI:** 10.3724/EE.1672-9250.2024.52.049

在地球漫长的演化历史中,极端气候事件及其导致的环境剧变曾引发了多次重大生物灾难事件,不仅对生命变迁产生了深远影响,甚至重塑了地球生态系统^[1-2]。据Sepkoski Jr统计,地球自显生宙以来至少经历了5次生物大灭绝^[3],分别在4.45亿年前的奥陶纪末、3.72亿年前的泥盆纪末(主要在Frasnian/Famennian之交)、2.52亿年前的二叠纪末、2.01亿年前的三叠纪末和6 600万年前的白垩纪末^[4-5]。虽然这些生物灭绝事件触发因素的机制尚不清楚,但区域性的大规模火山活动被认为是一个重要的原因^[6]。大火成岩省(Large Igneous Province,简称LIP)在不到100万年的时间内,不仅可以排放大规模的二氧化碳(CO₂),引发全球变暖和海洋酸化,而且还可能排放大量的二氧化硫(SO₂),造成气候强烈波动、酸雨频发以及生态系统的毒害^[7]。LIP导致的岩浆大规模侵入活动,以及随后发生的火山脱气过程,可以导致温室气体的大量增加,对大气组成造成显著的影响和扰动^[8]。显生宙LIP喷发证据表明,几乎每一次生物大灭绝事件都经历了一定程度的LIP岩浆作用^[7,9],例如,西伯利亚大火成岩省和中大西洋岩省分别被认为是驱动二叠

纪末和三叠纪末生物大灭绝的主要原因^[8,10]。

汞(Hg)元素及其稳定同位素数据常作为重建古环境和古气候特征的指标^[11-12],沉积物中Hg含量的异常升高通常被视为大规模火山作用^[13-16]与生物灭绝事件^[17-21]关系的重要指示剂。前人研究表明,火山活动除释放大量CO₂和SO₂,还会释放大量气态单质Hg注入大气-陆地-海洋系统,这是地球表层系统中Hg的主要来源^[22-25]。Pyle和Mather^[22]通过对现代火山喷发的研究,发现只有处于大爆发时期的火山才能排放超出环境背景值的Hg,而LIP活动不仅排放量远远超过普通火山,且持续时间更为长久,喷发气体在全球迅速扩散和沉积,最终在地层中留下显著记录,正是这一机制才将沉积Hg含量异常与大规模火山活动联系起来。例如,Grasby等^[18]估计Siberian Traps LIP事件(~252 Ma)排放了高达3 800 MT的Hg(相比于现代背景值增加约14倍),Percival等^[26]估计Karoo-Ferrar LIP事件在超过300~500 Ka的时间里总共排放了150 MT的Hg。然而,Hg含量异常并不绝对指示大规模火山活动,其他多种机制同样能够导致沉积物中Hg元素的富集现象。例如,全球

收稿日期: 2024-05-07; 改回日期: 2024-08-08

基金项目: 中国科学院百人计划项目。

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气候变暖易导致大规模的森林火灾或野火频发,植被燃烧也可释放相当可观的单质Hg,在沉积物中留下明显的异常记录^[27-28];寒冷地区的永久冻土层中储存有大量的Hg和碳(C),在全球变暖期间,永久冻土中的Hg可能会因为与诸如LIP事件相关的大量CO₂排放而不稳定,同时甲烷水合物也可能会失稳而释放甲烷,造成气温进一步升高,使得环境中额外的Hg通量进一步增加^[29-30];在水体缺氧环境下,大量的Hg会更倾向于与硫(S)结合形成化合物或吸附于粘土矿物在海底埋藏,这使得底层沉积物中Hg的富集效应更为显著^[12],由此海洋缺氧事件常常伴随着海底沉积物中Hg含量异常值的出现;此外,大陆岩石或土壤的风化剥蚀作用增强^[31],以及大规模冰川覆盖面积的变化^[32],均会导致全球循环中Hg通量的强烈波动。因此,虽然沉积物中的Hg含量可以作为大规模火山活动的指标,但存在其他过程会对地层中Hg的富集造成影响,不能盲目将Hg浓度异常与LIP联系起来,需要仔细评估地质事件中Hg的来源,以分析LIP岩浆活动起到了多大程度的影响^[33]。

由此可见,尽管前人对于地层中生物大灭绝事件的Hg含量变化已经有了一定程度的研究,然而目前对沉积物中Hg异常的探讨主要聚焦于生物大灭绝事件与LIP活动的联系上,缺乏对Hg在地质历史时期大尺度下演化的整体性、连续性认识^[12,34-35]。加之沉积物中Hg的多源性,这严重阻碍了我们对地层Hg信号的认识。

在沉积物中,总有机碳(TOC)通常作为Hg的主要载体,二者之间存在协同演化关系,因此TOC常作为研究Hg的迁移和富集的衡量指标^[34,36],它们的比值(即Hg/TOC)常被用作判断Hg异常事件的地球化学指标。前人的研究表明,沉积物中Hg和TOC的含量之间存在显著相关性^[37],这可能是由于有机质(OM)对Hg的吸附,对Hg在沉积物中的封存起到至关重要的作用^[12,37-39],使其能较好保存在地质记录中。进入水体的有机质通量波动,可能会强烈影响沉积物对Hg的固存能力,进而影响其在沉积物中的富集^[12,39]。通过对极地冻土、沼泽、湖泊等环境沉积物的元素浓度进行分析,Hg与TOC含量之间存在线性关系^[37-42]。然而,沉积物中Hg与TOC之间的线性关系假设并不总是成立。一些学者在陆地土壤、湖泊、永久冻土^[43-44]以及海洋沉积物^[25,45]中,发现了Hg与TOC含量的非线性关系。不管是线性关系还是非线性关系,在深时沉积地层的研究中,很可能都被当作简单的线性变化处理,从而忽视这种非线性关系的重要性。事实上已有研究表明,当沉积物中TOC含量较低时,Hg与TOC含量呈现线性增长,而TOC含量超过某一

特定阈值时,Hg含量只是在一定范围波动,不受TOC含量变化影响^[34,45-47]。

针对目前尚未充分揭示显生宙以来Hg的地质记录演化趋势及沉积物中Hg与TOC之间的耦合关系,本文对全球沉积地球化学与古环境项目(The Sedimentary Geochemistry and Paleoenvironments Project,简称SGP)数据库中显生宙以来的Hg和TOC地球化学记录并结合近年来与5次生物大灭绝事件有关的文献数据进行研究,在大时间尺度的分析框架下,探讨了沉积物中Hg含量及TOC含量(用于衡量Hg)随时间推移的演变趋势,并对Hg和TOC含量突然出现的异常高值的原因进行了推测。本文还详细剖析了沉积物中Hg与TOC含量的耦合关系,进一步揭示了Hg与TOC之间的内在联系。本研究不仅有助于我们深入理解C在Hg地球化学循环中的作用,也为解析不同环境下Hg与C耦合关系提供了重要支撑。

1 方法

SGP于2015年成立,第一阶段的数据收集于2019年结束,数据库涵盖了SGP团队贡献的数据集和来自美国地质勘探局(United States Geological Survey,简称USGS)的子数据集。数据库综合收集汇总了来自71个国家不同地质背景的82 578个样品和2 701 236个分析结果,其中约64%的数据已发表,约36%的数据尚未公开。数据中包括样品的地理位置、采样深度、分析年龄、岩性特征、所含元素浓度等重要信息。本文从SGP数据库中提取了Hg和TOC地球化学数据集,数据集中的样品主要采自北美地区,时间跨度从新太古代至新生代,尤以显生宙样品居多(占比~85%)。

本文选择数据集中显生宙沉积物样品数据(样品年龄小于540 Ma)作为分析对象,共筛选出5 288个Hg数据点和14 137个TOC数据点(Hg单位为mg/kg,TOC单位为wt.%)。为避免SGP数据库中Hg和TOC数据的不完善,代表性不够等问题,同时为与SGP数据库做对比,本研究收集了近年来针对5次生物大灭绝事件的文献数据(表1)^[11,15,25,45,48-70],共计4 232个Hg数据点和4 313个TOC数据点(Hg单位为μg/kg,TOC单位为wt.%)。在分析Hg和TOC演化趋势时,分别将Hg与TOC数据点按时间顺序分类。在分析沉积岩中Hg和TOC关系时,我们选择了同时含有Hg和TOC含量的5 125个样品数据(其中碳酸盐岩样品1 320个,硅质碎屑岩样品3 805个),分别计算碳酸盐岩样品和硅质碎屑岩样品中Hg与TOC数据的Spearman's rho(ρ)相关系数并做回归分析。Spearman's

表1 5次生物大灭绝事件中Hg的数据

Table 1 Hg data for the Big Five mass extinctions

生物灭绝事件	剖面	样本数/个	Hg /(μg/kg)			
			最小值	中位数	最大值	平均值
白垩纪末生物大灭绝	Højerup (丹麦) ^[48]	22	0.88	6.55	257.94	40.28
	Bottaccione (意大利) ^[48]	28	0.16	0.7	5.23	1.14
	Padriciano (意大利) ^[48]	18	2.9	16.75	182.5	32.29
	Bajada del Jagüel (阿根廷) ^[48]	14	8.55	12.69	16.56	12.89
	Meghalaya (印度东北部) ^[48]	26	1.6	6.5	98.6	10.9
	Jhilmili (印度中部) ^[48]	18	6.2	14.65	100.2	21.38
	El Kef (突尼斯) ^[49]	40	23.4	73.25	575.8	100.98
	Elles (突尼斯) ^[49]	71	9.2	19.2	112.7	24.24
	Elles (突尼斯) ^[50]	291	8.46	28.03	249.38	35.33
	松辽盆地 (中国北部) ^[51]	88	1.35	5.52	63.59	9.84
	Seymour Island (南极洲) ^[45]	98	10.6	21.25	48.5	23.69
	Bass River (美国新泽西州) ^[45]	60	14.5	30.5	84	33.07
	Zumaia (西班牙) ^[45]	140	1.9	7	47	10.02
	East Gilbert Creek (美国蒙大拿州) ^[45]	64	8	67	366.5	89.47
三叠纪末生物大灭绝	Partridge Island (加拿大) ^[15]	46	2.2	60	337	74.27
	Iguonane (摩洛哥) ^[15]	30	0.4	3.6	35	6.88
	St Audries Bay (英国) ^[15]	94	1.9	44	171.5	48.02
	Kuhjoch (奥地利) ^[15]	82	2.7	23	555	38.7
	Astartekloft (格陵兰) ^[15]	91	6	34.5	344.5	46.41
	Arroyo Malo (阿根廷) ^[15]	40	5	21	60	26.25
	Csővár basin (匈牙利) ^[52]	161	0.5	10.5	972.1	37.61
	Rodby (德国北部) ^[53]	40	26.2	152.8	549.9	187.45
	郝家沟 (中国新疆) ^[54]	116	2.64	28.32	100.91	34.47
	七里峡 (中国四川) ^[54]	105	1.03	60.96	1 837.38	138.76
二叠纪末生物大灭绝	St. Audrie's Bay (英国) ^[55]	80	2.6	32.15	128.39	32.11
	Buchanan Lake (加拿大) ^[56]	88	23	210.5	641	257.66
	Ursula Creek (加拿大) ^[25]	37	16.8	59.74	492.92	93.27
	Opal Creek (加拿大) ^[25]	53	19.52	59.94	142.65	62.94
	Bálvány (匈牙利) ^[25]	30	0.06	3.08	106.76	8.62
	煤山 (中国浙江) ^[25]	41	1	9.45	171.5	20.21
	大峡口 (中国湖北) ^[25]	41	0.5	34.5	535.67	84
	新民 (中国贵州) ^[25]	32	0.95	25.92	130.64	46.57
	克脚 (中国贵州) ^[25]	36	12.94	63.23	186.53	72.92
	Akkamori (日本) ^[25]	59	0.71	16.84	85	17.76
	Ubara (日本) ^[25]	28	0.77	31.31	43.86	22.26
	Gujo-Hachiman (日本) ^[25]	33	0.99	5.5	134.23	19.74
	Ursula Creek (加拿大) ^[57]	27	14.27	54.27	460.35	93.46

(续表1)

生物灭绝事件	剖面	样本数/个	Hg /(μg/kg)			
			最小值	中位数	最大值	平均值
泥盆纪末生物大灭绝	煤山 (中国浙江) ^[57]	19	1.5	14.7	346.4	39.37
	Hovea-3 (澳大利亚) ^[57]	19	39.25	96.73	437.05	124.52
	巢湖 (中国安徽) ^[58]	84	5.27	106.65	1 108.36	139.47
	上司 (中国四川) ^[58]	97	11.38	98	879	153.09
	甘溪 (中国南部) ^[58]	126	11.34	107.17	781.81	153.27
	大峡口 (中国湖北) ^[59]	39	2.4	54.3	396.2	111.85
	Island Bay (新西兰) ^[60]	40	10	60	7590	1013.5
	Kahlleite (德国) ^[61]	7	60	1 280	1 380	895.71
	Drewer (德国) ^[61]	13	20	130	280	117.69
	Cat Ba Island (越南) ^[62]	19	10	20	1 090	162.26
	Syv'yu River (俄罗斯) ^[11]	62	12.9	42.5	260.5	70
	Kahlleite (德国) ^[11]	16	5.2	20.7	2 517.3	181.72
	Lahmida (摩洛哥) ^[11]	43	6.8	153.2	1 144.9	217.43
	Catalan Coastal Ranges (西班牙) ^[63]	46	1	21	1570	142.48
	Walnut Creek (美国) ^[64]	53	3.22	20.11	52.78	20.05
	南洞 (中国南部) ^[64]	93	0.08	7.1	550.41	39.77
	Dupont GHS (美国田纳西州) ^[64]	93	0.86	115.88	224.49	115.22
	杨堤 (中国南部) ^[64]	85	0.09	4.06	32.9	5.67
	Walnut Creek (美国) ^[65]	15	22.92	35.67	56.19	35.32
	Beaver Meadow Creek (美国) ^[65]	17	18.59	29.13	53.89	30.76
奥陶纪末生物大灭绝	Joint Creek (美国) ^[65]	10	23.93	29.49	35.57	29.52
	West Valley (美国) ^[65]	30	21.69	28.92	43.37	29.71
	Irish Gulf (美国) ^[65]	20	14.54	26.65	45.66	28.1
	H-32 (美国) ^[65]	47	15.5	66.5	313.5	90.71
	Zbrza (波兰) ^[66]	62	10	165	530	167.74
	胭脂 (中国重庆) ^[67]	51	16.77	92.14	644.67	126.12
	焦页 (中国重庆) ^[67]	73	5.61	103.44	590.76	130.91
	漆辽 (中国重庆) ^[67]	70	9.09	149.65	1 458.52	185.99
	Vinini Creek (美国内华达州) ^[68]	84	6	54.5	737	123.44
	XY5 core (中国重庆) ^[68]	47	16	62	211	79.75
	丁家坡 (中国湖北) ^[69]	53	25.3	101.2	406.1	112.79
	王家湾 (中国湖北) ^[69]	119	0.4	3.2	320.5	61.14
	王家湾 (中国湖北) ^[70]	54	17.5	91.95	384.1	124.76
	Monitor Range (美国内华达州) ^[70]	158	1.7	12.15	2 963.8	49.2

rho(ρ)相关系数不假设线性共变,而是着重于指出变量之间的单调关系,因此,该系数不受线性或非线性关系的约束,可以更精确地揭示Hg与TOC含量之间的相关性。

2 结果

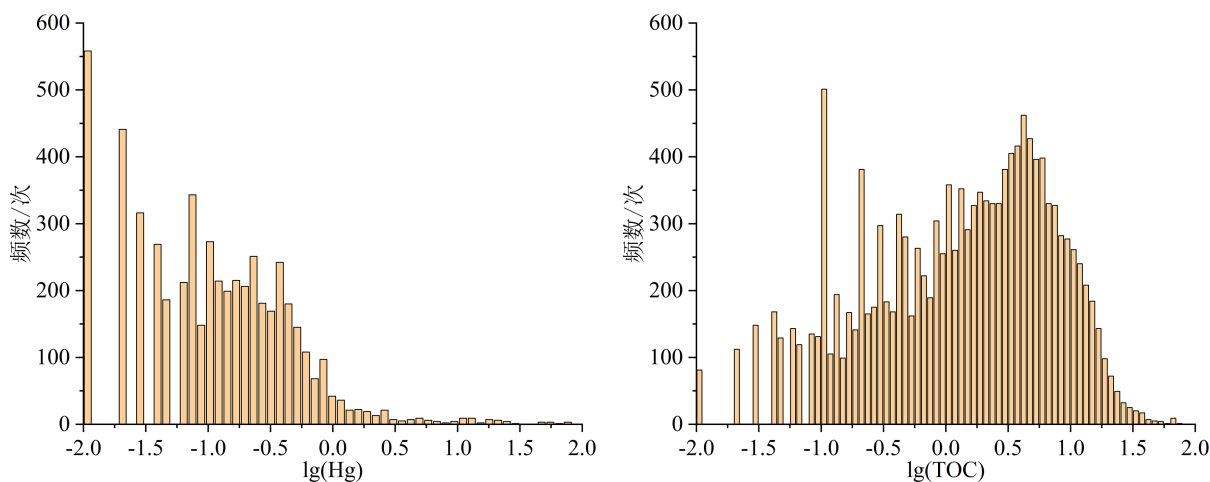
来自SGP数据库中的Hg数据呈对数偏态分布,范围为0.01~100 mg/kg,平均值为0.51 mg/kg;TOC数据近似双峰对数正态分布,范围为0.01~72.16 wt.%,平均值

为3.65 wt.%(图1)。Hg数据的对数偏态分布,可能是由于SGP数据库中Hg的数值单位较大,因此在记录时对较低的Hg值统一采取了近似值处理,导致在低值区出现集中。5次生物大灭绝事件相关文献中的Hg与TOC数据均呈对数正态分布(图2),Hg含量范围为0.06~2 963.8 $\mu\text{g}/\text{kg}$,平均值为98.94 $\mu\text{g}/\text{kg}$; TOC值范围为0.006~56.31 wt.%,平均值为1.77 wt.%.由此可见,SGP数据库中的Hg值和TOC值均较大,所记录的沉积物中Hg含量的平均值也大于前人统计出的62.4 $\mu\text{g}/\text{kg}$ [12],这很可能是由于SGP数据库收录的不完整和对低值数据近似处理导致的。

根据Hg与TOC数据点在时间轴上的分布,图3清

晰地展现了显生宙时期Hg和TOC浓度的波动,二者均呈现出多个显著的“峰值”,表现出相似的变化趋势。通过仔细分析,我们发现SGP数据库记录的最高的4个Hg峰值分别位于508、401、298和111 Ma, Hg含量分别最高可达75、100、80和60 mg/kg 。此外,除401 Ma附近因数据缺失无法确认TOC情况外,其余3个Hg峰值时期均伴随着TOC的异常现象。

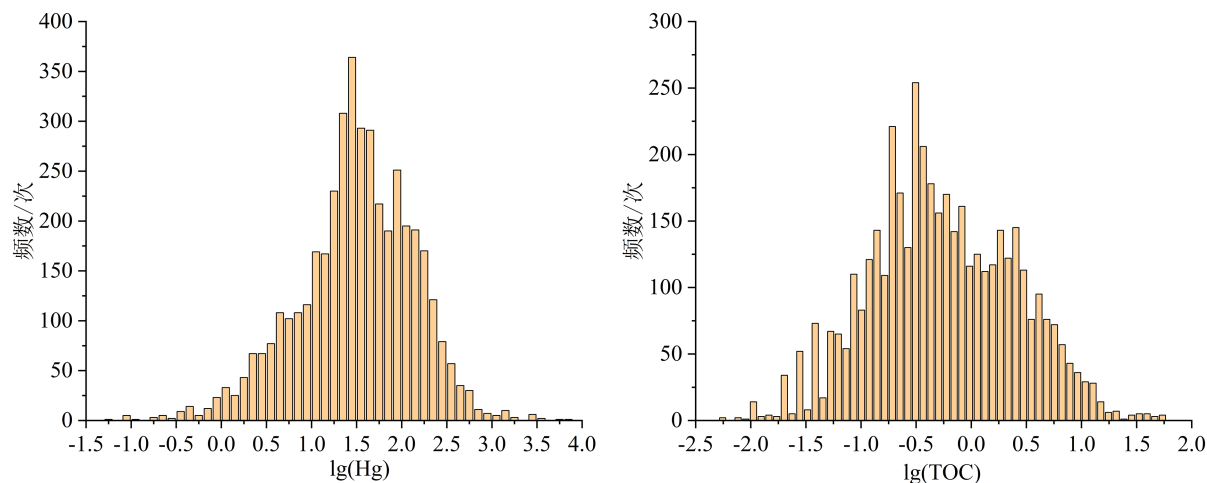
对显生宙碳酸盐岩样品和硅质碎屑岩样品中Hg与TOC的含量数据进行Spearman's $\rho(\rho)$ 相关系数计算,结果表明沉积岩中Hg与TOC含量之间存在显著的正相关关系。尤其是硅质碎屑岩中Hg与TOC的相关性($\rho=0.582, p<0.001$)相较于碳酸盐岩($\rho=0.449, p<0.001$)



Hg单位为 mg/kg , TOC单位为wt.%。

图1 SGP数据库中显生宙以来Hg和TOC值的分布特征

Fig.1 Characterization of the distribution of Hg and TOC values from the SGP database since the Phanerozoic



Hg单位为 $\mu\text{g}/\text{kg}$, TOC单位为wt.%。

图2 文献中5次生物大灭绝事件Hg和TOC值的分布特征

Fig.2 Characterization of the distribution of Hg and TOC values for the Big Five mass extinctions in literatures

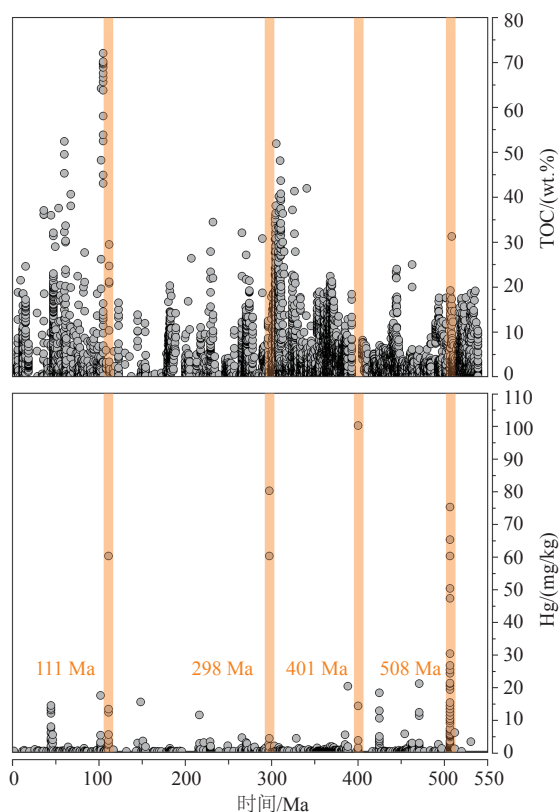


图3 显生宙以来沉积物中TOC和Hg含量随时间变化的趋势图
Fig.3 Trend plots of TOC and Hg content over time in sediments since the Phanerozoic

要更为显著(图4)。图4显示,碳酸盐岩样品和硅质碎屑岩样品中的数据点在不掩盖变化规律的情况下可划为不同区块,以代表沉积物中不同的Hg封存模式。碳酸盐岩中的数据点可分为A、B两部分,其中A区的数据TOC含量在低值区变化,Hg含量在高值区变化,B区的Hg和TOC含量均在高值区或低值区变化(图4a);硅质碎屑岩中的数据点可分为A、B、C三部分,其中A区的数据TOC含量在低值区变化,Hg含量在高值区变化,B区的TOC和Hg含量均在高值区或低值区变化,C区的数据点TOC含量在高值区变化,Hg含量在低值区变化(图4b)。

3 讨论

3.1 Hg异常的解释

Hildebrand和Boynton^[71]是最早在显生宙灭绝事件中关注Hg的研究者之一,他们报道了白垩纪-古近纪边界(K/Pg)的汞异常。此后,越来越多的学者将Hg作为LIP事件或与岩石记录中其它大规模灭绝事件在时间联系上的证据^[13-17,19-21,35]。这些研究有一个共同的发现,即显生宙地层中Hg含量的异常升高通常可指示大规模火山活动,以及与LIP紧密联系的陆地、海洋环境变化和

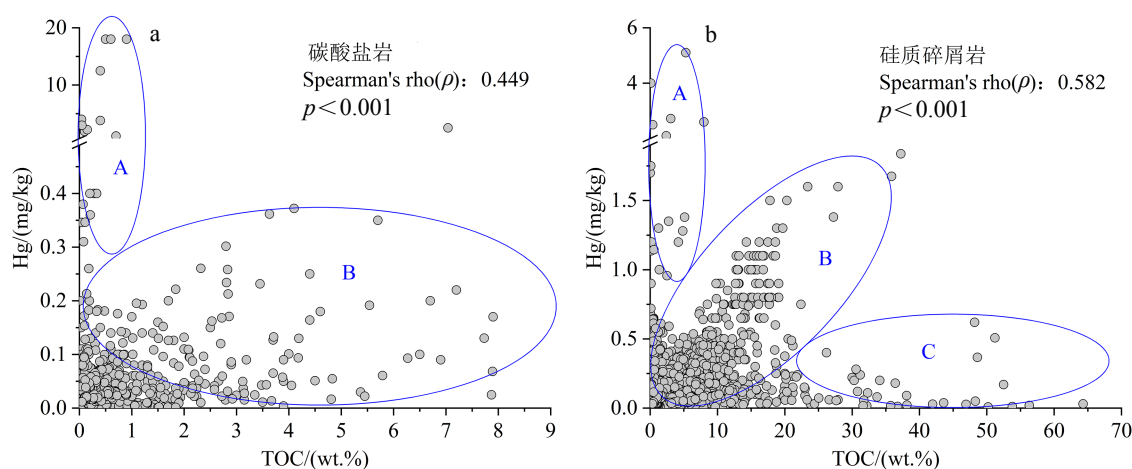
生物灭绝事件^[11,14,28,72-74]。然而,地质历史时期的每个Hg峰值,以及伴随的TOC含量变化是否一定指向LIP还有待考证,在判断这种异常的形成原因时,还要考虑其他区域或局部过程的控制。图3中Hg和TOC含量变化的相似性,说明沉积物中Hg的富集很可能与生物环境变化有关,而本研究在SGP数据库中识别出的位于508、401、298和111 Ma的4个Hg含量异常变化,表明当时的环境中很可能发生了某些地质事件以增加Hg通量,这些Hg的具体来源可能是多样的。

在508、111 Ma时期,沉积物中Hg和TOC含量的异常波动显著(图3),很可能直接或间接受到了LIP事件的影响。其中,约510 Ma开始的中寒武世Kalkarindji LIP活动影响范围广泛且持续时间较长,不仅在地质记录中留下了深刻的印记,还对当时的生物群落造成了重大冲击。Nixon等^[75]在McArthur盆地观察到整个盆地地层在中寒武世经历了一次显著加热事件,这与北和西澳大利亚克拉通寒武纪Kalkarindji LIP喷发几乎同时发生,很可能是由Kalkarindji LIP喷发以及热液岩浆的广泛侵入活动所导致。而在我国南方东津剖面杨柳岗组地层中,Liu等^[76]发现了与Kalkarindji LIP火山喷发相吻合的Hg峰值(最高达136.9 $\mu\text{g/kg}$),这次大规模火山爆发显著增强了大陆侵蚀速率,导致富含 SO_4^{2-} 等陆源物质输入的增加和深部边缘盆地 H_2S 的富集,加之随后的海洋上升流(>506 Ma)将缺氧海水带入大陆架,很可能最终导致Redlichiid和Olenellid三叶虫的大灭绝。Sundberg等^[77]在美国亚利桑那州和内华达州Tapeats砂岩中的研究结果也显示三叶虫在507.7 Ma时期灭绝。然而,本研究中508 Ma的Hg峰值(最高达75 mg/kg)远远超过Liu等^[76]在杨柳岗组地层中发现的记录,表明Kalkarindji LIP火山活动的规模可能被低估,或是该时期还存在其它Hg源。Shang和Chen^[78]通过对老挝地区Truong Son造山带(Truong Son Orogenic Belt,简称TSOB)中的岩浆岩进行研究,发现中寒武世(~507 Ma)是Tamky-Phuoc Son洋壳双向俯冲的开始阶段,引发了与特提斯造山运动有关的早古生代重大构造-岩浆事件。其他研究者也在日本^[79]、澳大利亚^[80]、捷克共和国^[81]、阿尔卑斯山脉^[82]以及摩洛哥^[83]的地层中发现早古生代中寒武世局部地区岩浆热液活动(~510~507 Ma)的痕迹,表现为洋壳俯冲引起的火山弧或活动大陆边缘系统中幔源性或复合性岩浆热液对沉积盆地的持续侵入或喷出。因此,SGP数据库中508 Ma极高的Hg峰值以及大量有机质的埋藏可能是Kalkarindji LIP持续性活动,与507 Ma左右局部海底或大陆架区域岩浆热液侵入或喷出事件相叠

加的结果(图5)。这一系列大规模火山喷发和岩浆侵入活动造成的环境累积效应,如大陆风化加剧、海洋深部缺氧与硫化、生物灭绝事件等,可能导致了有机碳快速埋藏、海洋初级生产力增加等结果,这些变化很可能与随后的晚寒武世碳同位素正偏移(Steptoean Positive Carbon Isotope Excursion,简称SPICE)事件(~497~493 Ma)存在联系^[74,84-85](图5)。此外,第2次大洋缺氧(Oceanic Anoxic Event 2,简称OAE 2)事件(约94 Ma开始)是一次全球变暖事件,以正碳同位素漂移和富有机质泥岩的出现为标志,启动于海底一个或多个大火成岩省(Large Igneous Provinces,简称LIPs)的持续喷发或岩

浆侵入,如加勒比LIP、北极高LIP、马达加斯加泛流玄武岩和第二翁通爪哇海台^[35,86-87]。本研究在OAE 2之前约111 Ma附近发现的Hg和TOC异常,可能是这一系列LIPs初始活动留下的痕迹(图5)。LIPs喷发的大量CO₂使全球快速变暖,大陆风化加强,海水温度上升,同时火山向海洋系统输送更多生物基本营养物质,导致全球海洋中溶解氧的减少和大规模有机质埋藏^[87]。在缺氧的海洋环境下,还原条件和强烈的硫化物条件使得Hg与硫化物和粘土矿物表现出高亲和力,这可能是导致更多Hg被封存在底层沉积物中的原因。

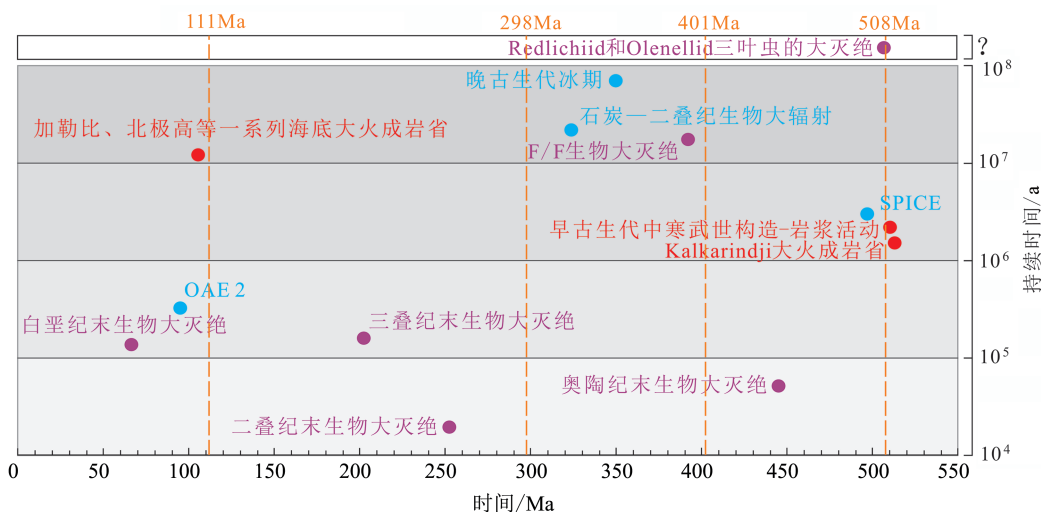
另外,并非所有的Hg峰值及其伴随的TOC浓度异



椭圆A、B、C分别代表海洋还原环境、正常环境和高初级生产力环境下的Hg封存模式。

图4 显生宙以来碳酸盐岩和硅质碎屑岩中Hg与TOC含量关系图

Fig.4 Plot of Hg versus TOC content in carbonate rocks and siliceous clastic rocks since the Phanerozoic



?-该事件持续时间未知;红色点-LIP事件^[76,78,86-87],紫色点-生物灭绝事件^[5,77,88],蓝色点-非LIP非生物灭绝事件(晚古生代冰期^[89-90]、石炭-二叠纪生物大辐射^[91]、SPICE^[84]、OAE 2^[86])。

图5 显生宙以来地球历史上部分重要地质和生物事件的起始时间和持续时间

Fig.5 In the Phanerozoic, the onset and duration of some important geological and biological events in the Earth's history

常均与LIPs活动产生联系,401、298 Ma的Hg异常值则可能由其他地质过程或事件导致(图3)。最新发现,F/F生物大灭绝事件或许早就开始于中泥盆世(392.72 Ma),一直延续到泥盆纪末(368.24 Ma),期间生物多样性持续下降^[91-92],但造成此次生物灭绝事件的成因尚不清楚。在401 Ma记录到的显著Hg峰值与F/F生物大灭绝事件在时间上较为接近,可能与其成因机制密切相关(图5)。约401 Ma的时间点附近,目前尚未发现有关LIPs的报道,仅存在一些区域性小规模火山活动^[93],由此看来此次异常记录可能是多种因素共同作用的结果。例如,Liu等^[94]发现在F/F生物灭绝事件之前,陆地野火事件频发,主要燃烧的是草本和灌木植物,推测这种大规模野火的起火源很可能是温室背景下的火山作用。本研究中的Hg峰值数据进一步支持了这一观点,并暗示此次野火事件与火山活动的联动规模可能远超先前估计。大规模的野火不仅会导致过量的Hg和C释放到环境中,还会破坏植物根系,进而增强风化作用,影响碳循环和气候^[95]。增强的风化作用会增加海洋的营养通量,促进海洋生产力的提升,反过来增加碳埋藏并降低二氧化碳分压($p\text{CO}_2$),最终在全球氧含量大幅上升的背景下导致气候变冷。这些因素相辅相成,逐渐放大之后很可能促成了F/F生物灭绝事件的发生。另一方面,298 Ma出现的Hg和TOC峰值与石炭-二叠纪生物大辐射时期相吻合(Mississippian亚纪末期-早二叠世Sakmarian末期)^[91](图5),这一时期也恰逢晚古生代冰期的第三期次(晚石炭世Moscovian-早二叠世Artinskian),即冰川大规模发育于冈瓦纳大陆及亲冈瓦纳大陆地块群之上,在到达鼎盛期后开始消亡的阶段^[89,90]。此时,陆地维管植物大量繁盛,大气氧含量急剧增长,生物多样性总体呈上升趋势。生物活动的增加意味着有机质生产效率的提高,这很可能是导致沉积物中TOC含量增加的原因。同时,大陆风化作用的加剧和全球冰川消融的开始,极有可能是造成晚古生代冰期第三期次沉积物中Hg峰值的重要因素。

综上所述,通过对SGP数据库中508、401、298和111 Ma的4个Hg异常高值分析解释,不难发现环境中Hg和TOC的来源呈现出多元化的特点。由于SGP数据库当前数据的局限性,本文对4个Hg峰值的识别和探讨相对初步,随着SGP第2阶段的工作完成,基于更为全面和详尽的数据集,届时有望得出新的见解与认识。沉积岩中Hg含量的异常积累,并非总是源于大规模火山活动的排放,其他全球性或区域性的地质过程同样扮演着重要角色,这进一步增加了Hg在地质历史记录中的复杂

性和不确定性,对于准确解读沉积物中Hg含量异常提出了更高的要求。因此,在未来的研究中,当面对沉积物中高浓度的Hg时,我们不应仅仅局限于大规模火山活动的影响,还需要结合地质时代的背景,综合考虑多种可能的因素,这样才能更准确地揭示Hg和TOC在地球系统中的迁移和固存机制。

3.2 沉积岩中Hg与TOC含量的耦合关系

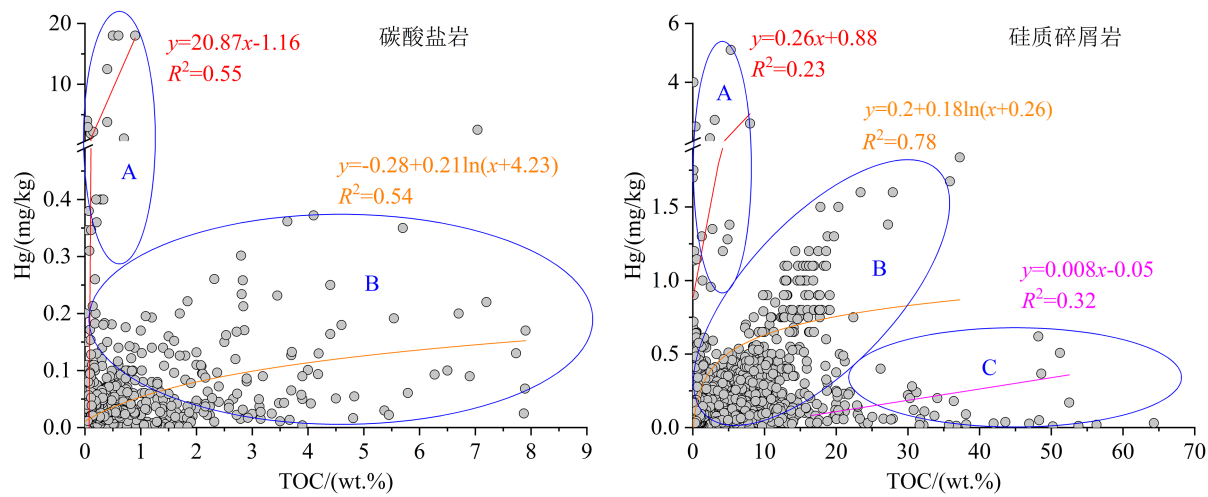
无论是现代地层还是深时地层,沉积物中检测出的Hg与TOC含量之间均存在着显著关系,这可能与TOC对Hg在沉积物中的固存机制有关^[12,34,36,39]。然而,沉积物中Hg与TOC的相互关系尚未定音,本研究通过分析显生宙以来沉积岩中Hg和TOC的浓度数据,以深入探究这一关系及其受岩性的影响程度。如图4所示,无论是碳酸盐岩还是硅质碎屑岩,大部分数据点落在B区,TOC和Hg含量在一定范围内变化,反映了在正常海洋条件和背景值范围下有机质对Hg的吸附作用;A区的数据点显示,TOC含量较低的情况下,Hg含量在较高范围变化,这可能反映了在黄铁矿埋藏率较高的还原系统中Hg的过量沉淀;相反,C区的数据点表明,尽管TOC含量数据较高,但Hg含量数据在较低范围变化,这反映了高初级生产力环境中有机质埋藏增强情况下对Hg的吸附作用,这一过程在硅质碎屑岩中表现得更为突出^[12]。碳酸盐岩和硅质碎屑岩中Hg与TOC含量数据的变化存在明显差别(图4),可能暗示岩性对沉积物中Hg与TOC的关系变化具有显著影响。这种差异的来源之一可能是硅质碎屑岩中,存在另一个或多个变量对高浓度TOC条件下Hg的固存有较强的控制作用,如碳酸钙、硫、粘土矿物等^[34],进而表现出了不同的相互关系。

目前,关于沉积岩中Hg和TOC含量变化的关系尚未有定论,既可能表现为线性特征,也可能为非线性特征,又或者兼具线性与非线性关系,其中非线性特征常常可由对数函数或双曲正切函数表达^[12,34,39]。因此,本研究对图4中的数据分别进行了线性函数、对数函数和双曲正切函数拟合(表2)。此外,如图4所示,碳酸盐岩和硅质碎屑岩中Hg和TOC含量数据表现出明显的分区特征,代表不同的沉积环境,因此本研究同时对图4中的数据进行了分区拟合(表2)。结果如表2所示,在对所有数据同时进行拟合的情况下,碳酸盐岩和硅质碎屑岩中的Hg和TOC含量之间未表现出线性关系,非线性关系中的对数和双曲正切函数关系的拟合效果也很差。然而,分区拟合的结果显示,A区中的线性关系,B区中的对数关系,C区中的线性关系或对数关系能够最有效地描述本研究显生宙地层中沉积岩内Hg和TOC含量之间

表2 沉积岩中Hg与TOC含量数据拟合结果

Table 2 Results of data fitting for Hg and TOC content in sedimentary rocks

数据拟合形式	碳酸盐岩			硅质碎屑岩		
	拟合函数	方程	R ²	拟合函数	方程	R ²
整体拟合	线性	y=0.02x+0.1	<0.1	线性	y=0.01x+0.11	<0.1
	对数	y=0.19+0.05ln(x+0.006)	<0.1	对数	y=-0.73+0.32ln(x+13.89)	<0.1
	双曲正切	y=0.23tanh(x/0.39)	<0.1	双曲正切	y=0.38tanh(x/18.04)+0.09	<0.1
分区拟合	A区	线性	y=20.87x-1.16	线性	y=0.26x+0.88	0.23
		线性	y=0.02x+0.02	线性	y=0.03x+0.06	<0.1
	B区	对数	y=-0.28+0.21ln(x+4.23)	对数	y=0.2+0.18ln(x+0.26)	0.78
		双曲正切	y=0.12tanh(x/2.82)+0.01	双曲正切	y=0.6tanh(x/9)+0.04	0.52
	C区			线性	y=0.008x-0.05	0.32
				对数	y=ln(0.93x+0.009)	0.31
				双曲正切	y=0.57tanh(x/28)	0.24



椭圆A、B、C分别代表海洋还原环境、正常环境和高初级生产力环境下的Hg封存模式;红色、橙色、紫色线条分别代表A、B、C区中的拟合曲线。

图6 显生宙以来碳酸盐岩和硅质碎屑岩中Hg与TOC含量拟合曲线图

Fig.6 Fitted curves of Hg versus TOC content in carbonate rocks and siliceous clastic rocks since the Phanerozoic

的关系特征(图6),说明在不同沉积环境下沉积物中Hg与TOC含量可能具有不同的耦合关系。

4 结论

先前的研究多聚焦于特定时期Hg浓度及其与TOC的比值,缺乏大尺度视角下沉积物中Hg含量范围的全面考察。为填补这一研究空白,本文系统梳理了SGP数据库中自显生宙以来的Hg与TOC数据,并补充了近年来针对5次生物大灭绝事件的文献数据,分别在508、401、298和111 Ma时期识别出了最高的4个Hg含量异常值。通过对这4个时期的Hg异常高值进行解释,发现508和111 Ma的Hg含量异常很可能与LIP活动有着直接或间接联系,

而401和298 Ma的Hg含量异常则很可能与陆地野火事件、大陆风化剥蚀和冰盖扩张有关。因此,沉积物中大量的Hg积累并非总是直接指向大规模火山活动,全球性或区域性的其他地质变化过程同样对沉积物中的Hg富集产生显著影响,在解读数据中的异常值时,需要综合考虑,以便更准确地揭示其背后的成因机制。

沉积岩中Hg与TOC含量的关系复杂多变。经对碳酸盐岩和硅质碎屑岩中Hg与TOC含量数据的分析,本研究观察到不同岩性中Hg与TOC的含量数据呈现出不同特征。通过对碳酸盐岩和硅质碎屑岩中的数据进行线性函数、对数函数和双曲正切函数拟合,结果显示分区拟合的效果最佳,说明在不同沉积环境下沉积物中

Hg与TOC含量可能具有不同的耦合关系。具体而言,碳酸盐岩和硅质碎屑岩中Hg和TOC含量在还原环境中可能为线性关系,在正常海洋环境下可能为对数关系,硅质碎屑岩中Hg和TOC含量在高初级生产力环境下可

能为线性关系或对数关系。然而,目前研究所用到的数据仍不够完善,随着今后数据量的不断扩充,沉积岩中乃至不同岩性中Hg与TOC或其他载体之间的关系及影响因素有望得到进一步的揭示。

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Preliminary Study on the Assessment of Mercury Concentration Anomalies Since the Phanerozoic and the Coupling Relationship Between Carbon and Mercury

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Abstract: Biological mass extinctions have occurred repeatedly throughout Earth's long history, especially since the Phanerozoic, when at least five global mass extinctions have occurred, and mercury (Hg) has attracted much attention in the geologic record as a key clue linking these events to the eruption of large igneous provinces. However, previous studies have tended to focus on Hg concentration anomalies over specific periods of time with major events occurred, and have lacked a holistic understanding of the evolution of Hg over large scales of geologic history. In addition, total organic carbon (TOC) as the main host for mercury in sediments, there are many unknowns about the co-evolutionary relationship between TOC and Hg. Therefore, this study is based on the Hg and carbon records in The Sedimentary Geochemistry and Paleoenvironments Project (SGP) database and data for the Big Five mass extinctions in recent years to solve the above problems. By observing the changes of elemental concentration in each period, this study found that Hg and TOC had similar trends during the Phanerozoic period, and the four highest Hg peaks recorded in the SGP database were found to be located at 508, 401, 298, and 111 Ma; And a positive correlation between Hg and TOC concentrations in sediments was found by Spearman's rho correlation coefficient and regression analysis. Comparing previous interpretations of Hg concentration anomalies in the geologic record and studies of the relationship between Hg and TOC in sediments, we explored possible factors contributing to Hg anomalies in sediments, and we suggest that: (1) The sources of Hg in the environment are complex and varied, and anomalous accumulations of Hg in sedimentary rocks do not always originate from the LIP, and a combination of possible factors needs to be considered when interpreting Hg concentration anomalies; (2) The relationship between Hg and TOC concentrations in different lithologies shows significant differences. Data on Hg and TOC concentrations in carbonatites and siliciclastic clastic rocks work best with zonal fitting, suggesting that Hg and TOC concentrations in sediments may be coupled differently in different depositional environments. Hg and TOC concentrations in carbonatites and siliciclastic rocks may be linear in reducing environments and logarithmic in normal marine environments, and Hg and TOC contents in siliciclastic rocks may be linear or logarithmic in high primary productivity environments.

Keywords: Phanerozoic; environmental evolution; total organic carbon; mercury; elemental coupling