

长江口邻近海域沉积物间隙水的地球化学*

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长江口及其邻近海域的水文、地质情况极为复杂,对沉积物的成岩作用和间隙水中元素的生物地球化学过程,均有显著影响。

本文作者曾于1980年7月对长江口邻近海域沉积物与间隙水的地球化学特征进行了调查,调查船为“金星”号,工作范围为 $122^{\circ}00' - 126^{\circ}08'E$, $30^{\circ}30' - 32^{\circ}31'N$,共测定18个站位(图1)表层沉积物氧化还原性质的参量及间隙水主要化学成分、营养盐和微

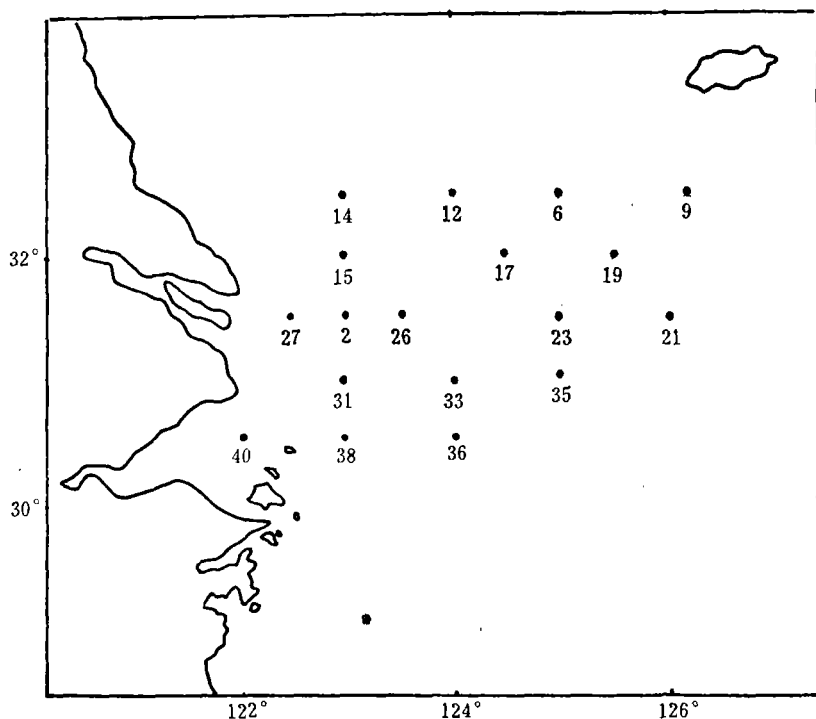


图1 调查站位

* 中国科学院海洋研究所调查研究报告第879号。
刁焕祥同志协助营养盐分析,特致谢意。
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表 1 长江口海域表层沉积物性质及间隙水的化学成分¹⁾

站 位	水 深 (m)	沉积物			间 隙 水						沉淀物特征				
		pH	Eh (mv)	Es (mv)	Cl%o	主要成分 (g l ⁻¹)			营养盐(ppm)			微量元素 (ppb)			
						Cl ⁻	SO ₄ ²⁻	Ca ²⁺	Mg ²⁺	PO ₄ ³⁻		SiO ₂	Cu(I,II)	Pb(II)	Cd(II)
2	33	7.86	400	-52		19.0	2.59	0.393	1.29	0.643	14.1	4.8	1.8	0.10	深灰色细沙,有一定数量贝壳
6	56	7.50	-391	-193	18.47	20.1	2.81	0.402	1.37	0.826	15.6	5.3	1.5	0.10	深灰色软泥,较多贝壳及沙蚕壳体
9	97	7.63	-348	-362	19.56	19.6	2.88	0.399	1.42	0.734	22.3	5.3	8.8	0.12	深灰色粉沙质软泥,少量贝壳
12	40	7.57	-545	-305	19.05	19.1	0.92	0.168	1.33	0.979	34.8	5.4	3.4	0.10	深灰色粉沙质软泥,少量贝壳及沙蚕(海面有蚤光虫)
14	35	7.50	-552	-250	18.51										细沙,有大量贝壳
15	35	8.00	308	2											
17	41	7.56	93	-125	18.57	19.1	2.57	0.407	1.30	0.673	25.0	7.2	3.4	0.08	灰色沙质泥
19	64	7.51	19	-101	18.43	19.0	2.73	0.396	1.30	0.643	25.4	7.8	2.3	0.13	深灰色软泥
21	69	7.48	-45	-71	18.43	19.0	2.69		1.34	0.704	31.9	6.6	1.7	0.15	深灰色软泥
23	47.8	7.60	54	-66	18.66	19.2	2.76	0.382		0.612	19.2	9.8	3.2	0.08	深灰色软泥,少量贝壳
26	38.5	8.10	396	-44											细沙,贝壳较多
27	22	7.96	354	-18											细沙,含大量粉碎状生物贝壳
31	50.5	7.44	-27	1	18.61	19.1	2.42	0.340	1.30	0.642	27.3	10	2.8	0.08	灰色沙质软泥
33	41.5	7.83	293	6											细沙,有贝壳
35	59	7.72	-6	4	18.51	19.1	2.81	0.385	1.31	0.581	25.0	9.9	7.7	0.13	灰色软质泥
36	56.5	7.71	18	-2	19.03	19.6				0.612	24.4	2.5	7.3	0.13	灰色软质泥,有贝壳
38	57	7.62	-50	-8	19.24	19.8	2.71	0.410	1.36	0.520	19.2	6.8	3.1	0.12	灰褐色软泥
40	11	7.02	-39	-79	10.95	11.3	0.74	0.256	0.81	0.459	16.7	9.1	2.0	0.17	褐色软泥
33*	37	8.27	321	13	18.91	19.5	2.62	0.416	1.32	0.092	1.1				
35*	55	8.15	301	15	18.40	18.9	2.57	0.410	1.29	0.086	1.0				
36*	50	7.98	305	19	19.21	19.8	2.62	0.419	1.32	0.089	1.5				
38*	53	8.07	261	-21	19.68	20.4	2.62	0.416	1.32	0.092	1.9				
40*	9	8.10	319	43	10.14	10.4	1.51	0.256	0.75	0.061	4.0				

1) 包括部分站位的底层水(*)。Eh 与 Es 为相对于标准氢电极的电位值(6,9,12,14站两者负值偏大,可能为测量误差)。Cl⁻离子含量用硝酸银滴定法测得,包括少量 Br⁻ 和 I⁻, 在此作为恒定性参量。Cu(I, II) = Cu(I) + Cu(II), 沉积物间隙水中铜离子在一定还原条件下,尚存在亚铜离子的氨基或羧基络合物^[10]。

量重金属的含量(包括部分站位底层水的测定)。文中研究了沉积物中钙、镁的碳酸盐矿物之间的转化,及钙、镁形成磷、硅酸盐矿物的地球化学平衡机制,同时也讨论了间隙水中微量重金属铜、铅、镉的碳酸盐和硫化物的溶解、沉淀作用。由此,阐明了在该海域不同区域的沉积物间隙水中所进行的若干成岩反应及有关元素的地球化学过程。

一、方法与结果

使用大洋 50 型采样器采集表层沉积物^[6], 去掉约 2cm 表层泥以防污染和海水的渗入,然后将沉积物装满广口瓶并蜡封保存,以备间隙水的制取和成分分析用。间隙水系用防污染液压活塞式间隙水采样器^[7]压取。

应用玻璃电极和铂片电极以及硫电极,以饱和甘汞电极作参比电极^[1],在现场同时插入泥样分别测量沉积物的 pH, Eh 和 Es, 测量仪器为 HSD₁ 型船用 pH 计。底层水上述参量的测定系自采水器导入一配有上述电极并可封闭的容器进行。

间隙水及底层水分析(底层水营养盐现场分析,其他均于实验室进行)系用 Mohr 硝酸银法测定氯度;用 EDTA 络合法滴定硫酸根、钙和镁离子含量^[4];用阳极溶出伏安法和 AD-1 型极谱仪测定铜、铅和镉离子;以钼蓝比色法用自动分析仪(美国 Technicon 公司 AAI 型)测定硅酸盐(活性硅酸盐)和磷酸盐(可溶性无机磷酸盐)。所得结果如表 1。

二、沉积物间隙水的地球化学特征

夏季长江冲淡水与黄海沿岸流、台湾暖流以及黑潮流系的相互交汇和影响,使东海不

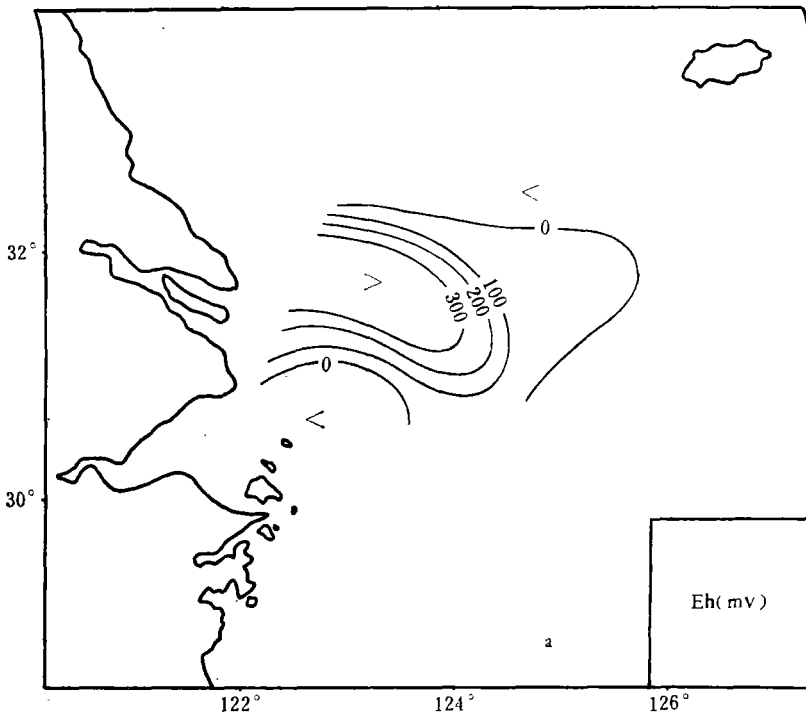


图 2a 沉积物的 Eh 分布

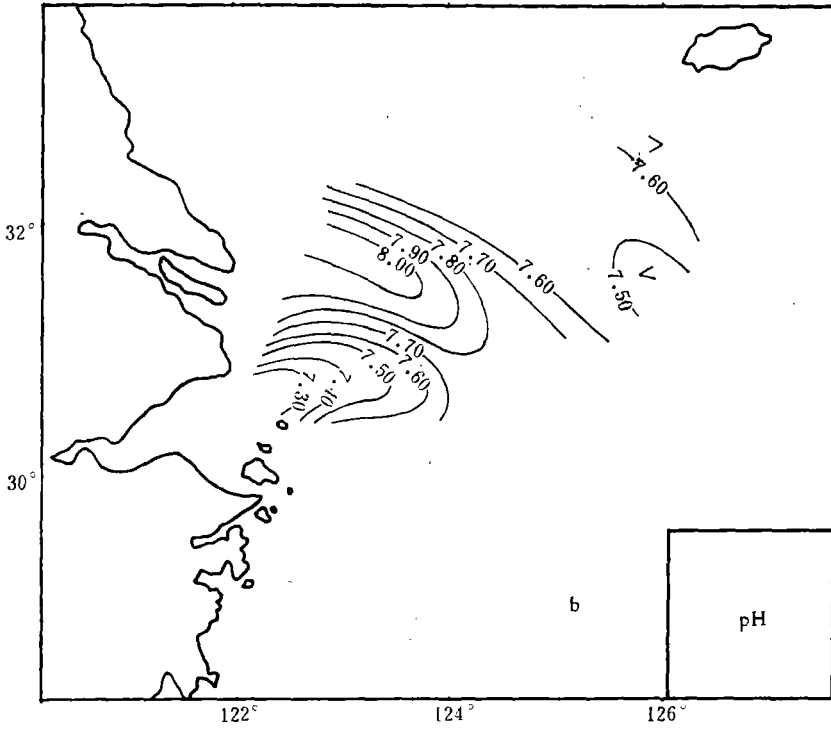


图 2b 沉积物的 pH 分布

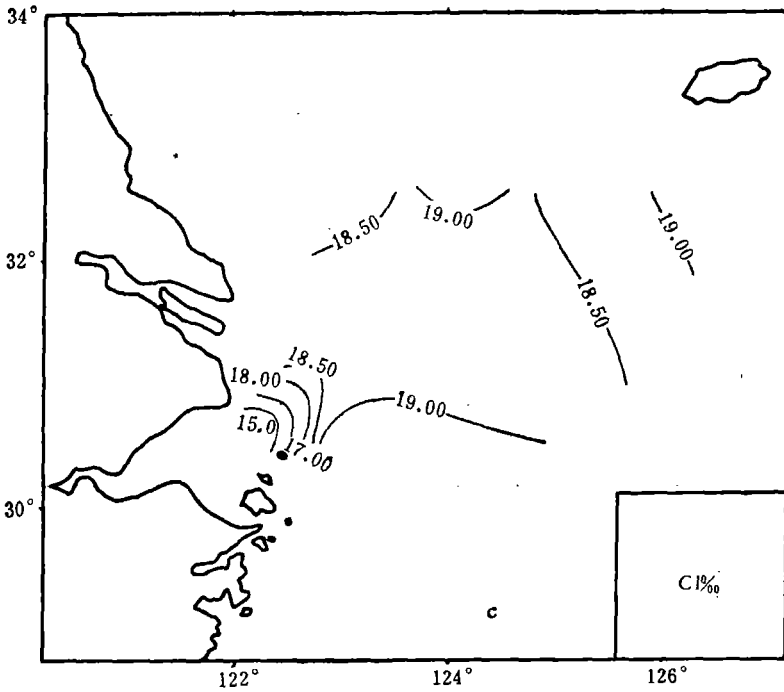


图 2c 间隙水的氯度分布

同区域的现代沉积物质的分配及其运输途径有所不同,长江口海域尤为复杂。图2说明沉积物的氧化还原性质及间隙水氯度均呈不同区域的分布特征,与水文^[1]、地质^[8]情况基本一致。

由表2可见,表层沉积物间隙水化学成分的恒定性大致为:主要成分>营养盐(硅酸盐和磷酸盐)>微量重金属。主要成分有较好的恒定性,并与底层水一致;硅酸盐与磷酸盐有一定的恒定性,但其氯度比值比底层水的大十倍左右,说明营养盐在间隙水中的再生过程;微量重金属则无一定的恒比关系,这与其生物地球化学过程的复杂性有关^[10,20,21]。此外,40号站间隙水和底层水主要成分含量由于受钱塘江及长江淡水影响而明显偏低(表1),且沉积物间隙水中的硫酸盐可能因有机物氧化、分解而消耗,故其含量及氯度比值均偏低。

三、钙、镁的沉积及其碳酸盐的转化

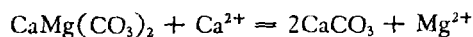
从表2中钙、镁浓度的比值,可以了解长江口海域沉积物中白云石与方解石之间的转

表2 长江口海域表层沉积物间隙水化学成分的比值

站位	$\frac{SO_4^{2-}}{Cl^-}$	$\frac{Ca^{2+}}{Cl^-}$	$\frac{Mg^{2+}}{Cl^-}$	$\frac{PO_4^{3-}}{Cl^-}$ $\times 10^{-3}$	$\frac{SiO_2}{Cl^-}$ $\times 10^{-3}$	$\frac{Cu(I,II)}{Cl^-}$ $\times 10^{-7}$	$\frac{Pb(II)}{Cl^-}$ $\times 10^{-7}$	$\frac{Cd(II)}{Cl^-}$ $\times 10^{-9}$	$\frac{[Mg^{2+}]}{[Ca^{2+}]}$
6	0.14	0.021	0.068	3.4	0.74	2.5	0.95	5.3	5.4
9	0.14	0.020	0.068	4.1	0.78	2.7	0.75	5.0	5.6
12	0.15	0.020	0.072	3.7	1.1	2.7	4.5	6.1	5.9
14	0.05	0.009	0.070	5.1	1.8	2.8	1.8	5.2	11
17	0.13	0.021	0.068	3.5	1.3	3.8	1.8	4.3	5.3
19	0.14	0.021	0.068	3.4	1.3	4.1	1.2	6.8	5.4
21	0.14			3.7	1.7	3.5	0.89	7.9	
23	0.14	0.020	0.070	3.2	1.0	5.1	1.7	4.3	5.8
31	0.13	0.018	0.068	3.4	1.4	5.2	1.5	4.3	6.3
35	0.15	0.020	0.068	3.0	1.3	5.2	4.0	6.8	5.6
36				3.1	1.3	1.3	3.7	6.6	
38	0.14	0.021	0.069	2.6	0.95	3.4	1.6	6.1	5.5
40	0.07	0.023	0.071	4.1	1.5	8.1	1.8	15	5.2
33*	0.13	0.021	0.068	0.47	0.055				5.2
35*	0.14	0.022	0.068	0.46	0.051				5.2
36*	0.13	0.021	0.067	0.45	0.073				5.2
38*	0.13	0.020	0.065	0.45	0.095				5.2
40*	0.15	0.025	0.072	0.59	0.38				4.8

*——底层水,余者见表1。14与31站间隙水中镁、钙浓度的比值,其偏高的原因尚不清楚(由表1可见,主要因钙含量偏低所致)。

化及其平衡,如:



则

$$\frac{[Mg^{2+}]}{[Ca^{2+}]} = \frac{K_D}{K_C^2} = \frac{10^{-16.7}}{10^{-8.4 \times 2}} \quad (1)$$

K_D 和 K_C 分别为白云石和方解石的溶度积 (25°C)^[14]。 K_D/K_C^2 比值接近 1, 因海水中钙、镁离子的活度系数也较相近, 而表层沉积物间隙水与海水的主要成分又较接近, 故所测镁、钙浓度比值说明表层沉积物间隙水与海水均对白云石呈明显过饱和状态。除 14 和 31 号站外, 间隙水中镁、钙离子浓度比值恒定在 5.2—5.9 之间。而底层水则大部为 5.2, 与文献[14]报道的海水镁、钙比值为 5.3 比较一致。由此说明镁在间隙水中通过与方解石(或霏石)的置换反应, 比在海水中较易转移至白云石。40 号站底层水因受镁、钙比值较低的长江淡水的影响, 其比值偏低。由长江口至外海底层水以及由底层水到沉积物间隙水中, 镁、钙比值增高, 这与长江径流搬运溶解性钙进入海洋后, 发生沉淀或逐渐形成碳酸钙并转移至海底所进行的沉积过程有关。然而钙、镁在海水中直接沉淀而形成白云石非常困难, 其在海洋中的转移及碳酸盐的成矿过程, 至今仍是地球化学中尚在研究的重要课题^[11, 6]。

四、硅与硅酸盐矿物

据 Stumm 等^[27] 和 Sillén 等^[25] 关于硅石和硅铝矿物的溶解反应及无定形(非晶形)硅石与其溶液中存在形式的平衡常数, 绘成图 3。可见无定形硅石溶解达平衡时, pH 在 9 以下, 溶解硅主要以 $Si(OH)_4$ 形式存在。Siever 也已证明, 对于 $pH < 9$ 的水, 溶解硅几乎全部以基本不离解的单体硅酸存在^[9]。关于硅酸的水合度尚不清楚, 故许多作者常以 $SiO_2(aq)$ 表示其水合^[30]。在海洋沉积物中, 除石英及粘土矿物等硅铝矿物外, 尚含有来自硅藻、放射虫、底栖海绵类残骸等生物成因的无定形硅石(如蛋白石), 对控制间隙水中溶

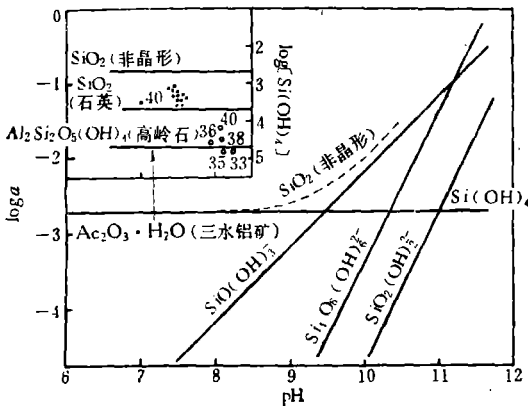


图 3 硅石和硅铝矿物的溶解度及溶解硅与 pH 的关系
 (.....表示总溶解硅; ●为间隙水;
 ○为底层水; $\gamma_{Si(OH)_4} = 1$ ^[13])

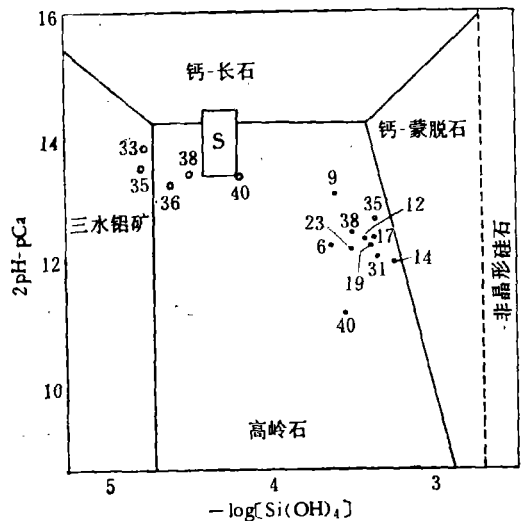


图 4 硅铝矿物稳定性关系的优势图^[27]
 (●为间隙水; ○为底层水; I 及 $\gamma_{Ca^{2+}}$ 参见表 4)

解硅的浓度,以及沉积物成岩作用的地球化学过程起着重要作用。但由图 3 左上角小图中可以看出,间隙水对无定形硅石是不饱和的(无定形硅石在水或海水中的溶解度为 $100-140\text{mg l}^{-1}$ [21],与图 3 所示一致),这可能与东海大陆架沉积物中缺少无定形硅石有关[9]。间隙水对石英则是过饱和的,而石英的沉淀和溶解速度均非常缓慢。此外,间隙水对高岭石是过饱和的;但在 33 和 35 站的外海底层水中,高岭石有转变为三水铝石的趋势。

从含钙的硅铝矿物的多相平衡模式(图 4)[27]可以看出,长江口邻近海域沉积物中的高岭石系由长石风化后,经大陆径流搬运进入海底的,这证明了东海沉积物的陆源性。同时也可看出,沉积物中蒙脱石少于高岭石,这与东海沉积物中粘土矿物 X 射线分析和电子显微镜照像的研究结果是一致的[5]。图 4 中底层水测点也说明自长江口向外(远至 33 和 35 站),高岭石趋向三水铝石转变(同图 3 所示),据 Stumm[27] 计算并指出:如果通过长期沥滤使高岭石转化为三水铝石,硅酸浓度应保持在 $10^{-4.7}\text{M}$ 以下。故在深海沉积物中常发现两者结合在一起[28]。

海洋沉积物间隙水对一些镁的硅酸盐矿物[如海泡石—— $\text{Mg}_6(\text{H}_2\text{O})_4\text{Si}_2\text{O}_3(\text{OH})_4 \cdot 8\text{H}_2\text{O}$]来讲是过饱和的,图 5[22]说明,除 40 及 6 号站外,长江口海域表层沉积物间隙水对天然有序晶体的海泡石呈饱和和过饱和状态。由于一些海泡石-坡缕石组的动力学势垒较低,故在间隙水中趋于形成这种表生沉淀物(Supergene precipitate)[14,28]。上述东海沉积

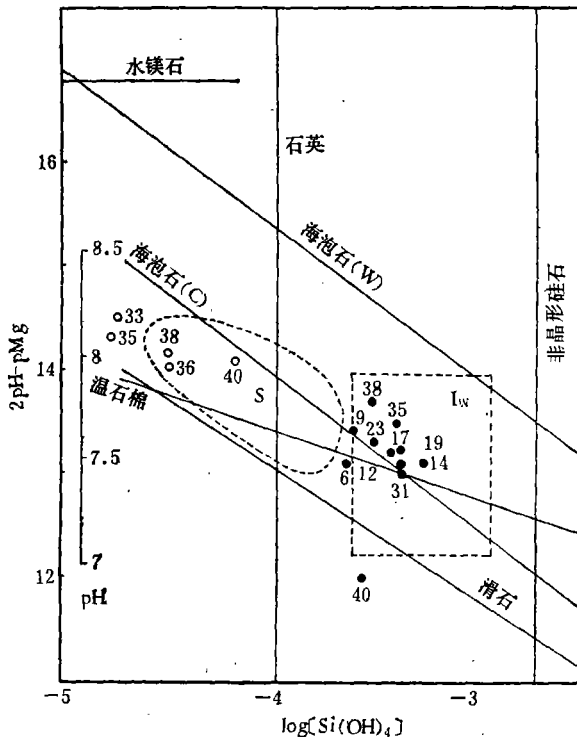
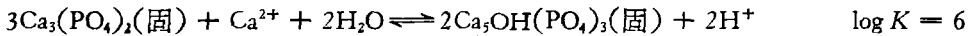
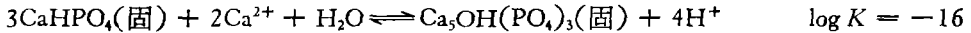


图 5 MgO—SiO₂—H₂O 体系中一些矿物的平衡溶解度[12]
 (S——海水; I_w——间隙水; W——无序固相; C——天然有序晶体;
 ●为间隙水; ○为底层水; I = 0.7, r_{Mg²⁺} = 0.217;
 I = 0.4, r_{Mg²⁺} = 0.247[22]; I 的计算见表 4)

物的分析研究结果^[5]也已证实这种矿物的存在。此外,这种粘土矿物同其他大陆造岩矿物一起,也会被传送到海洋沉积物中。图5中底层水测点说明,对石英及海泡石均呈不饱和状态,不如在间隙水中形成这种矿物容易。有人计算,在海泡石形成过程中,假若全部硅石同镁以及碳酸盐反应而生成海泡石,则从海洋中释放二氧化碳的通量,几乎等于因硅酸盐风化反应使二氧化碳转移而需要补偿的通量(硅酸盐风化每年需要 3.5×10^{12} 克分子的二氧化碳)^[12,18]。

五、磷酸盐矿物的溶解作用

Sillén^[24]的计算结果表明,在海水中羟基磷灰石 $[\text{Ca}_5\text{OH}(\text{PO}_4)_3]$ 是唯一的稳定磷酸钙矿物。有关磷酸钙固相之间的转化反应,如:



达平衡时,两反应有如下关系:

$$2\text{pH} + \log a_{\text{Ca}^{2+}} = 8 \quad (2)$$

$$2\text{pH} + \log a_{\text{Ca}^{2+}} = -6 \quad (3)$$

又知,羟基磷灰石有如表3所示不同溶解反应^[24,27]。

表3 羟基磷灰石的溶解平衡

反应方程式	logK
1. $\text{Ca}_5\text{OH}(\text{PO}_4)_3(\text{固}) + 4\text{H}^+ = 2\text{Ca}^{2+} + 3\text{CaHPO}_4^0 + \text{H}_2\text{O}$	3×10^2
2. $\text{Ca}_5\text{OH}(\text{PO}_4)_3(\text{固}) + 4\text{H}^+ = 5\text{Ca}^{2+} + 3\text{HPO}_4^{2-} + \text{H}_2\text{O}$	-5.0
3. $\text{Ca}_5\text{OH}(\text{PO}_4)_3(\text{固}) + 3\text{H}_2\text{O} = 2[\text{Ca}_2\text{HPO}_4(\text{OH})_2]_{\text{表面}} + \text{Ca}^{2+} + \text{HPO}_4^{2-}$	-8.5
4. $[\text{Ca}_2\text{HPO}_4(\text{OH})_2]_{\text{表面}} = 2\text{Ca}^{2+} + \text{HPO}_4^{2-} + 2\text{OH}^-$	-27
5. $\text{Ca}_5\text{OH}(\text{PO}_4)_3(\text{固}) = 5\text{Ca}^{2+} + 3\text{PO}_4^{3-} + \text{OH}^-$	-55.6

由表3反应式计算可知,溶解磷主要为 HPO_4^{2-} , 其次为 CaHPO_4^0 , 以及少量 PO_4^{3-} 等(如 $\text{H}_2\text{PO}_4^{15}$)。由此可根据表1中 pH, Ca^{2+} , 磷酸盐浓度及有关活度系数,并按表3中控制溶解磷的主要反应1,2和3式(尤其 $\text{pH} > 6.5$ 时)计算,得到表4结果,借以讨论羟基磷灰石的形成条件及其溶解作用。

虽然采用同 Sillén 类似的计算是近似的,但由表4第二栏结果与式(2),(3)比较,足以说明在这些间隙水条件下(尽管可能存在压力或温度校正等误差),上述生成羟基磷灰石的两个反应均应向右进行到底,羟基磷灰石在沉积物中是稳定相。并且底层水的计算结果,与 Sillén 所得的(13.4)一致。通过四、五两栏结果的比较,可见间隙水和底层水对羟基磷灰石均是过饱和的,说明除温度影响外,其磷酸盐的含量不仅受表3所示羟基磷灰石的溶解作用所影响,尚可能存在 Mg^{2+} , Fe^{3+} 等的磷酸盐络合物(如 MgHPO_4^0 , FeHPO_4^+), 以及存在有机物质在氧化或还原条件下进行分解作用所释放的磷酸盐,如:

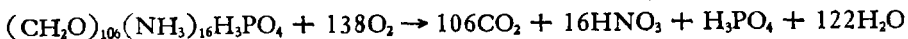
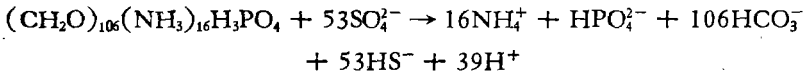


表 4 羟基磷灰石的生成条件及其溶解情况¹⁾

站 位	2pH + log $\alpha_{Ca^{2+}}$	$\frac{[PO_4 - P] - [CaHPO_4^0]}{[HPO_4^{2-}]}$ ($\times 10^{-6}M$)	log $\alpha_{HPO_4^{2-}}$	log $\alpha_{HPO_4^{2-}}$ a)	log $\alpha_{HPO_4^{2-}}$ b)
6	12.3	6.7	-6.1	-7.2	-5.8
9	12.6	8.7	-6.0	-7.3	-5.8
12	12.4	7.7	-6.1	-7.3	-5.8
14	12.0	10	-5.9	-6.6	-5.5
17	12.4	7.0	-6.1	-7.2	-5.8
19	12.3	6.7	-6.1	-7.2	-5.8
23	12.5	6.4	-6.1	-7.3	-5.8
31	12.1	6.7	-6.1	-7.0	-5.7
35	12.7	6.1	-6.2	-7.1	-5.8
38	12.5	5.4	-6.2	-7.3	-5.8
40	11.2	4.6	-6.1	-6.3	-5.7
33*	13.9	0.96	-7.0	-8.2	-5.8
35*	13.6	0.90	-7.0	-8.1	-5.8
36*	13.3	0.93	-7.0	-7.8	-5.8
38*	13.5	0.96	-7.0	-8.0	-5.8
40*	13.4	0.64	-7.0	-7.8	-5.7

1) $[PO_4 - P]$ 为表 1 分析的磷酸盐克分子浓度, $[CaHPO_4^0]$ 系由表 3 反应式 1 计算值, $\gamma_{CaHPO_4^0} = 1^{[13]}$ 。a), b) 系由表 3 反应式 2, 3 计算值。*——底层水。设 $\gamma_{CaHPO_4^0} = 1$, 间隙水主要成分恒定性较好, 故用离子强度公式: $I = 35.9997Cl\% / (1000 - 1.81578Cl\%)^{[27]}$, 则大部分站间隙水和底层水: $I = 0.7$, $\gamma_{Ca^{2+}} = 0.199$, $\gamma_{HPO_4^{2-}} = 0.133$; 40 号站: $I = 0.4$, $\gamma_{Ca^{2+}} = 0.232$, $\gamma_{HPO_4^{2-}} = 0.165^{[23]}$ 。

或



后者反应多发生在河口还原性沉积物中^[2,19]。有机物分解是磷酸盐再生的重要途径。当然,部分磷酸盐阴离子也存在为高岭石、蒙脱石以及铁、铝氢氧化物沉淀所吸附的可能性。此外,羟基磷灰石同水反应可以形成“表面络合物”(如表 3 反应 3),但这种络合物在水溶液中是不稳定的^[27],故表 4 第六栏计算结果,实际不易达到。

六、重金属在氧化、还原条件下的迁移

根据 Lu 和 Chen^[27] 研究在氧化或还原条件下,重金属溶解浓度与其碳酸盐和硫化物溶解平衡的关系(例如图 6; 铅、铜类同,略),说明长江口海域表层沉积物间隙水中镉、铅、铜的分析浓度高于其硫化物溶解平衡的浓度,而低于其碳酸盐溶解平衡的浓度。在还原性沉积物中,重金属以溶度积较小的硫化物存在,但与许多天然有机配位体的络合作用(如腐殖酸易与铜离子形成络合物)^[16,23],而使其在间隙水中的溶解度增大。在氧化条件下,重金属由于粘土矿物的吸附,或嵌入沉积物的晶体结构(如蒙脱石的层状结构)中,故在间隙水中低于以碳酸盐溶解平衡计算的浓度。此外,在一些弱氧化性沉积物表面尚有溶解氧与硫化氢之间的竞争,影响着溶解作用或沉积作用。除此,微量重金属离子在沉积物间隙水中的迁移,尚受扩散作用及生物活动的影响。

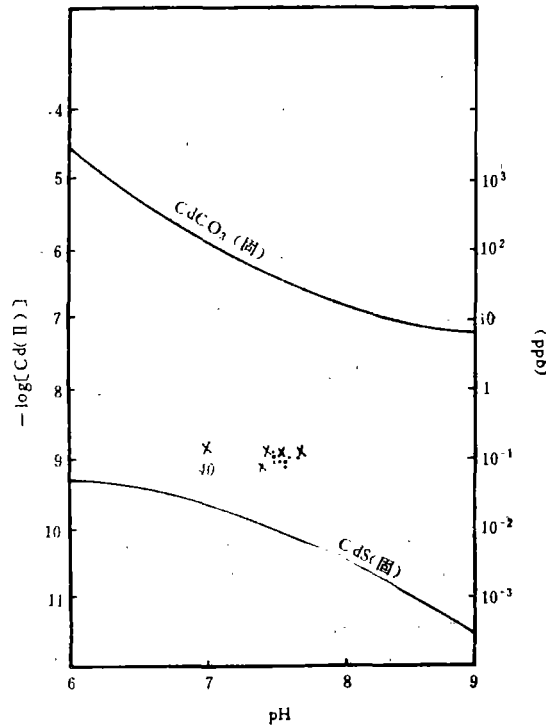


图 6 间隙水中溶解镉与其碳酸盐及硫化物的平衡
(●与×分别系沉积物 Eh 为正、负值的站)

七、结 语

通过对长江口邻近海域表层沉积物间隙水的地球化学特征的初步研究,表明沉积物间隙水的地球化学过程,存在着一定的准稳平衡。由此证明应用地球化学平衡原理,讨论和研究沉积物的来源、成岩作用及其与间隙水之间的化学交换,可以得到一些预示性的结果,为进一步的调查、研究提供参考和启迪。

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GEOCHEMISTRY OF THE SEDIMENT INTERSTITIAL WATER IN THE ADJACENT SEA AREA TO THE CHANGJIANG RIVER ESTUARY*

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ABSTRACT

The geochemical characteristics of the sediments and interstitial waters in the adjacent sea area to the Changjiang River Estuary are related to the hydrological and geological conditions of this area.

The redox parameters such as Eh, pH, and Es of the surface layer sediments in the area have been measured, and the contents of major, nutrient, and minor elements such as calcium, magnesium, sulphate, chloride (Cl%), phosphate, silicate, copper, lead, and cadmium in the interstitial waters of the surface layer sediments have been also analyzed and listed in Table 1 of this paper. Included in this Table are also the analytical results for the five station bottom layer waters. The eighteen stations observed are shown in Fig. 1.

The distribution tendencies of pH, Eh, and chlorinity as shown in Fig. 2 a-c indicate that the different mutual confluence of the Changjiang diluted water, the Huanghai Sea Coastal Current, the Taiwan Warm Current, and the Kuroshio system gives rise to the variations of the transport way and distribution of the sedimentary matter in this area.

The ratios represented in Table 2 demonstrate that the constituents in the interstitial waters of surface layer sediments are approximately in the sequence of major elements > nutrients > minor elements. The concentration ratios of magnesium to calcium in the interstitial waters lie for the most part between 5.2 and 5.9; however, those in the bottom layer waters of this area are mainly 5.2, which is compatible with the value of 5.3 as in sea water^[14]. Therefore, it would be of greater advantage to convert calcite into dolomite by the replacement of magnesium in the interstitial waters than in the bottom layer waters.

Fig. 3 explains that silicic acid is the predominating species of dissolved silica at pH < 9 in interstitial or sea water, that the interstitial waters are supersaturated and undersaturated with respect to quartz and amorphous silica as shown in the left upper diagram of Fig. 3, and that it seems to be possible to convert kaolinite into gibbsite in the bottom layer waters of station 33 and 35 far off this estuary as noted in the diagram and Fig. 1.

According to the predominance diagram for the calcium silicate minerals as presented in Fig. 4, the resulting points fall into the stability field of kaolinite, which is likely to be the weathering product of feldspar and the indicating mineral present in the sediments of this area. Therefore, we may infer that the continental shelf sediments of the East China Sea should be of terrigenous material. The tendency to convert kaolinite into gibbsite appe-

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ars to be present in the bottom layer waters of station 33 and 35 as shown in Fig. 3. If this process progressed successively, silicic acid would have been kept below $10^{-4.7}$ M^[27].

Similarly, it can be seen from Fig. 5 that, except station 6 and 40, the interstitial waters are supersaturated with respect to sepiolite(c), and that the magnesium silicate minerals such as sepiolite-palygorskite group are precipitated from the interstitial waters, and the occurrence of these minerals has already been proved by the X-ray analysis of the East China Sea sediments^[5].

As seen from Table 4 which is calculated from the corresponding data in Table 1 and 3, and by comparison of the values of 2 pH plus Ca^{2+} activity logarithm with equations (2) and (3) of this paper, it is reasonable to infer that CaHPO_4 (s) and $\text{Ca}_3(\text{PO}_4)_2$ (s) in these two reactions should be eventually transformed into $\text{Ca}_5\text{OH}(\text{PO}_4)_3$ (s). So hydroxylapatite is the sole stable phase of apatite in the sediments of this area. It follows from the last three columns of HPO_4^{2-} activity logarithms in Table 4 in which the fourth is calculated from HPO_4^{2-} concentrations in the third column, and the fifth and sixth from the formula 2 and 3 in Table 3 in sequence that the contents of soluble inorganic phosphate in the interstitial and bottom layer waters are contributed not only by hydroxylapatite dissolutions as shown in Table 3, and but also very likely by the complex formations of Mg^{2+} and Fe^{3+} with phosphate anions and the organic matter decompositions to release soluble phosphate species in oxidative or reductive condition as seen from the comparison of the fourth with the fifth columns. "Surface complex" formed as reaction 3 in Table 3 is metastable equilibrium with the aqueous solution^[27], so in fact, as in the natural waters it would be unlikely to attain the values in the final column which are calculated from this reaction equation.

The concentrations of soluble trace metals such as cadmium, lead, and copper in the interstitial waters are higher than the equilibrium concentrations of their sulfide solids and lower than that of their carbonate solids. The relationship of soluble cadmium concentrations in the interstitial waters to the equilibrium concentrations of the two solids in redox conditions is shown in Fig. 6. The results are similar to those obtained by Lu and Chen^[11] on the migration of trace metals in interfaces of seawater and polluted surficial sediments.