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CHROMIUM(III) — CHROMIUM(VI) INTERCONVERSIONS IN SEAWATER

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ABSTRACT

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The stable form of dissolved chromium in oxygenated seawater is Cr(VI). But Cr(III)-species are also present at an analytically significant level. It is shown that Cr(III) is oxidized only slowly by dissolved oxygen, and that manganese oxide is a strong catalyst for such oxidation. However, the low oceanic concentration of suspended MnO_2 impedes the conclusion that the former process is quantitatively less important than the latter one. The distribution of dissolved chromium among Cr(VI)- and Cr(III)-species is probably kinetically controlled.

INTRODUCTION

Little doubt exists that dissolved chromium in seawater is predominantly present as Cr(VI)-species. However, Cr(III)-species always seem to be present at a level of analytical significance. Based on thermodynamic data, no Cr(III) is expected to be present.

Elderfield (1970) suggested five possibilities to explain this discrepancy:

(1) published analytical results do not represent speciation in true solution;

(2) published stability constants are inapplicable;

(3) relevant species have been overlooked;

(4) there is no equilibrium with the atmosphere;

(5) kinetics of redox reactions Cr(III)—Cr(VI) are sluggish.

Indeed, many of the earlier published analytical results on chromium speciation can be discarded. In this paper we will address ourselves to the other possibilities mentioned above.

STABILITY OF Cr (III)- AND Cr (VI)-SPECIES IN SEAWATER

No important changes of stability constants of chromium complexes have been reported since Elderfield's paper. In comparison with hydrolysis and oxidation of Cr(III), complexes with chloride, fluoride, sulphate and carbon-

ate ions only play a minor role. The stability field of Cr(III), in terms of pε and pH, cannot be expanded by complexing with those inorganic ligands. Because of the low concentration of dissolved organic matter in seawater, the role of organic complexes of Cr(III) is also small.

The contribution of hydrolysis products to the Cr(III) concentration is shown in Fig. 1, based on data given in Table I. The tendency of Cr(III) to become adsorbed on mineral surfaces in the sea can be explained by the predominance of the dihydroxy complex (cf. James and Healy, 1972). At the low level of chromium concentrations in seawater (Σ Cr $\simeq$ 4—5 nM), the presence of dinuclear and trinuclear chromium(III)—hydroxy complexes can be practically ruled out. The pε—pH stability diagram for chromium in seawater is given in Fig. 2. The boundary between Cr(III)- and Cr(VI)-species is shifted by 1/3 pε-unit for every ten-fold change in the ratio. This means that for most of the acceptable data on chromium speciation in seawater pε $\simeq$ 5—6. This value is much lower than the apparent pε value for

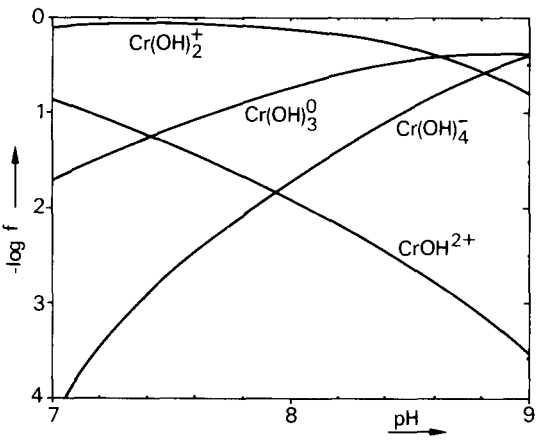

Fig. 1. pH-dependence of Cr(III) speciation relative to the total Cr(III) concentration.

TABLE I

Apparent stability constants (298 K, $I = 0.75, \gamma_{H^+} = 0.95$) calculated for pertinent reactions relevant for chromium speciation in seawater

Equation	log K^1	Reference
(1) $Cr^{3+} + H_2O \rightleftharpoons Cr(OH)^{2+} + H^+$	−4.4	Baes and Mesmer (1976)
(2) $Cr^{3+} + 2H_2O \rightleftharpoons Cr(OH)_2^+ + 2H^+$	−10.6	Baes and Mesmer (1976)
(3) $Cr^{3+} + 3H_2O \rightleftharpoons Cr(OH)_3 + 3H^+$	−19.2	Baes and Mesmer (1976)
(4) $Cr^{3+} + 4H_2O \rightleftharpoons Cr(OH)_4^- + 4H^+$	−28.2	Baes and Mesmer (1976)
(5) $HCrO_4^- \rightleftharpoons CrO_4^{2-} + H^+$	−5.8	Baes and Mesmer (1976)
(6) $Cr(OH)^{2+} + 3H_2O \rightleftharpoons CrO_4^{2-} + 7H^+ + 3e$	−69.0	Dellien et al. (1976)
(7) $Cr(OH)_2^+ + 2H_2O \rightleftharpoons CrO_4^{2-} + 6H^+ + 3e$	−62.8	comb. (1), (2), (6)
(8) $Cr(OH)_3 + H_2O \rightleftharpoons CrO_4^{2-} + 6H^+ + 3e$	−54.2	comb. (1), (3), (6)
(9) $Cr(OH)_4^- \rightleftharpoons CrO_4^{2-} + 4H^+ + 3e$	−45.2	comb. (1), (4), (6)

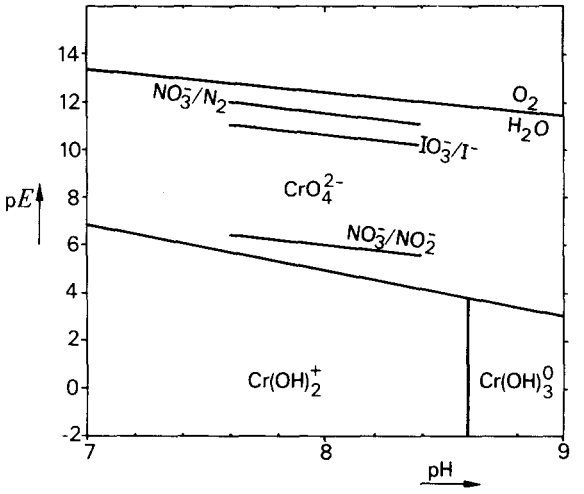

Fig. 2. pe—pH stability diagram for dominant chromium species in seawater, showing equimolar boundaries. Also indicated are equi-activity boundaries for some species in the nitrogen and iodine systems.

seawater, based on iodide—iodate and nitrate—nitrogen couples, as suggested by Liss et al. (1973). Although the metastable nitrate—nitrite redox couple comes much closer in this respect, this does not imply that the Cr(VI)/Cr(III) ratio is controlled by the complicated microbiologically induced nitrogen cycle in seawater. Recently Nakayama et al. (1981a) reported the presence of dissolved organic Cr(III)-species in the Pacific Ocean and in the Japan Sea. These species constituted about half of the dissolved chromium in their samples. In another publication Nakayama et al. (1981b) suggest that such species are inert to oxidation. If their observations are correct some relevant species have indeed been overlooked in the past.

RATE OF OXIDATION

Elderfield (1970) supposed that the kinetics of oxidation for Cr(III) to Cr(VI) are slow, which would explain the apparent absence of thermodynamic equilibrium. Emerson et al. (1979) and Cranston and Murray (1978) showed that the Cr(III)/Cr(VI) ratio responds to changes in the redox conditions. Schroeder and Lee (1975) carried out experiments on the oxidation of Cr(III) in model freshwaters. They were able to demonstrate oxidation of Cr(III) by oxygen at a slow rate, the activation energy being $92\,kJ\,mol^{-1}$. No significant differences were found for variation of pH, although protons play a role in the oxidation reaction. The same authors also tested the effect of the presence of naturally occurring mineral phases. They found that Cr(III) was strongly adsorbed onto sand, bentonite, and ferric oxyhydroxide. Only manganese dioxide had a strong effect on the oxidation; in a few days all Cr(III) was oxidized.

Similar experiments were carried out in our laboratory. In addition to artificial seawater and natural seawater from the North Sea, artificial freshwater samples in the pH range 5.5—8 were used. The oxidation of Cr(III), using an initial concentration of $100\,\mu g\,l^{-1}$, was repeatedly tested. Even after 6 weeks no Cr(VI) had been formed at room temperature, nor did raising the temperature to 310 and 320 K result in detectable oxidation of Cr(III). Adsorption of Cr(III) was measured using ^{51}Cr as a spike. The adsorption behaviour of Cr(III) during these experiments is illustrated by the curves given in Fig. 3. The results compare well with those of Nakayama et al. (1981b).

It would be speculative to apply such experimental results directly to chromium chemistry in the oceans. However, the results can be used in an order of magnitude estimation. Assuming that during the six weeks period $2\,\mu g\,Cr(III)\,l^{-1}$ was oxidized (just below the limit of detection of Cr(VI) for the applied analytical method), that the average Cr(III) concentration during this period was $50\,\mu g\,l^{-1}$, and that first-order oxidation kinetics can be applied according to

$$-\frac{d[Cr(III)]}{dt} \simeq k\,[Cr(III)]$$

where k = rate constant comprising the concentration of free oxygen, then

$$k \simeq \frac{2}{50} \times \frac{365}{42} \simeq 0.35\,y^{-1}$$

Assuming again that the Cr(III) concentration in the oceans is about $1.10^{-9}\,mol\,l^{-1}$, and the oxygen fugacity in the water column approximately equals that of the experiments, and temperature differences are neglected, then the production of Cr(VI) would be roughly

$$\frac{d[Cr(VI)]}{dt} \simeq 0.35.10^{-9}\,mol\,l^{-1}\,y^{-1}$$

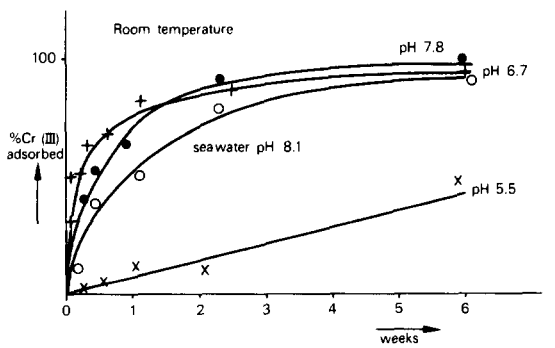

Fig. 3. Typical curves obtained by monitoring adsorption of Cr(III) onto glass container walls, showing effect of pH and ionic medium.

The fluxes of chromium in the exogenic cycle are shown in a simple diagram in Fig. 4; some relevant values are given in Table II. Steady state requires that $F_1 = F_4$ and $F_2 = F_3$.

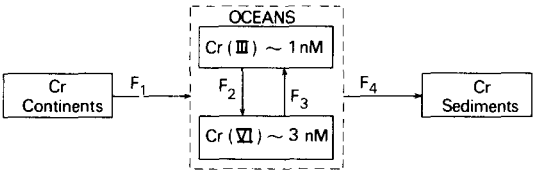

Fig. 4. Fluxes of chromium in the exogenic cycle. (Estimated concentrations of chromium species in the oceans after Nakayama et al. (1981a).)

TABLE II

Some relevant data on the hydrogeochemical cycle of chromium

Annual discharge of world rivers	$0.376 \times 10^{17}\,\mathrm{l\,y^{-1}}$
Total ocean volume	$1.3 \times 10^{21}\,\mathrm{l}$
Cr concentration in river water	$\sim 1 \times 10^{-6}\,\mathrm{g\,l^{-1}}$
Cr concentration in ocean water	$\sim 0.2 \times 10^{-6}\,\mathrm{g\,l^{-1}}$
Ocean residence time of Cr	~7000 y

From the foregoing it would follow that $F_3 \simeq 600 F_1$. This means that the fluctuations in the chromium speciation would be much greater than they actually are. Therefore either the rate constant or the Cr(III) concentration in the oceans must be much lower.

The presence of MnO_2 has, indeed, a remarkable effect on the oxidation of Cr(III). Both reagent-grade and natural MnO_2 were used in our experiments. Typical curves, representing sorption and oxidation, are presented in Figs. 5 and 6. These curves demonstrate that the presence of MnO_2 in both freshwater and seawater helps to oxidize Cr(III) in a sequence of adsorption, surface oxidation and desorption. Similar results were reported by Nakayama et al. (1981b). The kinetics of these processes are significantly slower in seawater than in freshwater, due to the competition between Cr(III) and other cations for reactive surface sites. Schroeder and Lee (1975) showed that lower concentrations of MnO_2 in suspension result in lower oxidation rates. From the results presented in Figs. 5 and 6 a rate constant of oxidation can be calculated, using the relation

$$-\frac{d[\mathrm{Cr(III)}]}{dt} \simeq k\,[\mathrm{MnO_2}]\,[\mathrm{Cr(III)}]$$

From the results of the experiments, the rate constant can be estimated as $k \simeq 2.10^5\,\mathrm{l\,mol^{-1}\,y^{-1}}$.

In order to compare these results with the oxidation of Cr(III) in the ocean, it is important to know the concentration ratio of suspended MnO_2

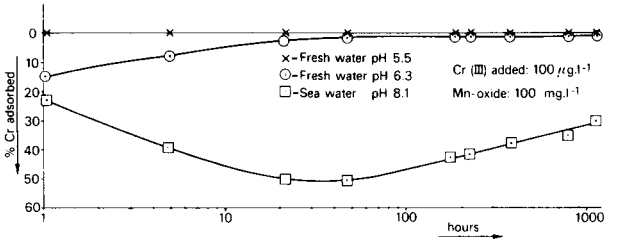

Fig. 5. Adsorption of Cr(III) by manganese oxide in freshwater and in seawater.

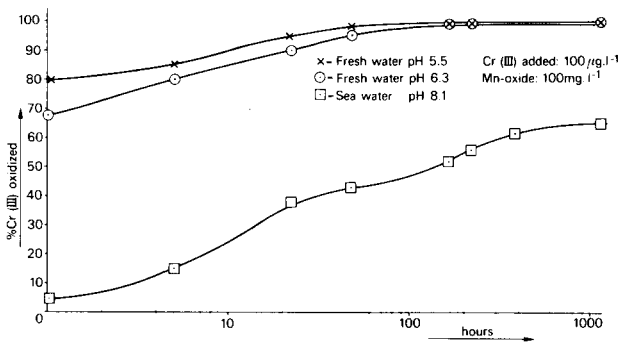

Fig 6. Oxidation of Cr(III) by manganese oxide in freshwater and in seawater.

and Cr(III). The sedimentation of manganese as MnO_2, including ferromanganese oxide coatings on sediment particles, is <10% of the manganese input in the oceans. An estimate of the MnO_2 concentration in the water column can be based on the average sedimentation rates of marine sediments, their MnO_2 content, and the settling velocities of particulate matter. Our 'order of magnitude' estimate is

$$[MnO_2] \simeq 10^{-10}\ \mathrm{mol\,l^{-1}}$$

Adopting a Cr(III) concentration of about $1.10^{-9}\ \mathrm{mol\,l^{-1}}$, the rate of catalyzed oxidation would be

$$\frac{d[Cr(VI)]}{dt} \simeq 2.10^{-14}\ \mathrm{mol\,l^{-1}\,y^{-1}}$$

This amounts to $F_3 \simeq 0.1\,F_1$, which in our opinion is not far beyond realistic expectations.

Similar rates could have been calculated for the Cr(III)—O_2—seawater system using rate constants far below the detection limits in the experiments. Based on the experiments, it is not clear whether oxidation by dissolved oxygen or by suspended MnO_2 is responsible for maintaining the oceanic chromium speciation.

Nakayama et al. (1981a,b) suggested, that ocean sediments play a major role in the oxidation of Cr(III), a theory which cannot easily be tested be-

cause one should be able to estimate the 'equilibrium concentration' of sedimentary MnO_2 per liter of near-bottom water and the residence time of that water in the near-bottom layer. In any case, sediments covered by manganese nodules are likely to play a role in the conversion of trivalent to hexavalent chromium. Chuecas and Riley (1966) reported a low efficiency of hydrous manganese oxide in co-precipitation of chromium from solution. In a series of experiments on adsorption of transition metals onto manganese oxide, we found that the solution turned yellow, demonstrating the oxidation of Cr(III) into Cr(VI). Glasby (1974) concluded that chromium in manganese nodules is almost exclusively present in the detrital phase. He mentioned that the low tendency of nodule material to absorb anions such as CrO_4^{2-} could explain this behaviour.

SINKS FOR CHROMIUM

In Table III the equilibrium concentrations of chromium with respect to the least soluble mineral phases are calculated. These data show that formation of distinct Cr(III) mineral phases is unlikely. It is known, however, that adsorption of Cr(III) onto iron hydroxides and other mineral phases in the marine environment is a very effective mechanism for its removal from seawater. Precipitation of distinct Cr(VI) mineral phases can also be ruled out. Co-precipitation with barium sulphate is possible, but according to Betechtin (1977), the chromate ion apparently has little affinity for a sulphate lattice. Therefore, the most likely sink for Cr(VI) is adsorption after prior reduction to Cr(III). This reduction could take place: (a) by biological activity in the water column; (b) by diffusion into the anoxic layers of sediments; (c) in anoxic basins.

There is as yet no evidence that the first two processes take place. Reduction in anoxic basins is demonstrated by Cranston and Murray (1978) and by Emerson et al. (1979). The latter assume that Cr(VI) is readily reduced below the oxic—anoxic boundary (although their results do not quite confirm this), but that Cr(III) is less rapidly oxidized above this boundary. They calculate a residence time of 6—20 days for Cr(III) in the oxic layer. From

TABLE III

Solubility of least soluble Cr(III)- and Cr(VI)-mineral phases in seawater (Dissociation data from Baes and Mesmer (1976) and from Charlot (1969))

Mineral Phase	pK^1 diss ($I = 0.75$)	Calculated for	Solubility (mol Cr l^{-1})	
			pH 7.5	pH 8.2
$Cr(OH)_3$	28.6		$10^{-4.65}$	$10^{-5.2}$
$CrPO_4$	20.4	$C_{P(tot)} = 2 \times 10^{-6}$	$10^{-5.22}$	$10^{-4.5}$
$BaCrO_4$	8.76	$C_{Ba} = 1.5 \times 10^{-7}$	$10^{-1.9}$	$10^{-1.9}$

their description of the chemistry along the vertical profile, i.e. their reference to a layer of manganese oxide just above the oxic—anoxic boundary, it can be expected that in such systems MnO_2, locally produced in relatively high concentrations, helps to diminish the residence time of Cr(III) as compared to a system with dissolved oxygen as the only oxidant.

CONCLUSIONS

Oxidation of Cr(III) in seawater by oxygen is a very slow process. Adsorption on manganese oxide, followed by oxidation at the surface, helps considerably to convert Cr(III) into the thermodynamically stable Cr(VI). Because of the low concentration of suspended MnO_2 in the oceans, it is not clear whether this catalyzed oxidation is quantitatively more important than the direct oxidation by dissolved oxygen; the contribution of MnO_2 in marine sediments is hard to assess. Sinks for Cr(III) are adsorption onto ferric oxyhydroxide clays, etc.; sinks for Cr(VI) are probably identical, following the reduction of Cr(VI). The marine part of the geochemical cycle of chromium is still not fully documented.

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