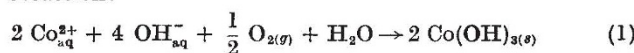## GEOCHEMISTRY

Formation of Cobalt (III) in the Amorphous FeOOH.nH₂O Phase of Manganese Nodules

RECENT discussions[1] on the nature of $3d$ transition-metal ions in sea water and in manganese nodules have rejected the possibility that oxidation of cobalt to Co (III) occurs in marine environments. A detailed electron microprobe study of manganese nodules[2] from diverse geographical localities supports the belief[3] that there is a cobalt–iron inter-element relationship in the nodules. Cobalt is enriched in the X-ray amorphous FeOOH.nH₂O phase in those nodules which contain appreciable amounts of iron. The results indicate that Co (III) and Fe (III) constitute an 'isomorphous' pair in the amorphous (Fe,Co)OOH.nH₂O phase, which may be recrystallized to geothite on treatment with hydroxylamine hydrochloride.

Thermodynamic calculations support the hypothesis that Co²⁺ in sea water may be oxidized to Co(OH)₃ under certain conditions. The model on which the calculations are based is as follows:

Reaction:

$$2\ \text{Co}^{2+}_{aq} + 4\ \text{OH}^-_{aq} + \frac{1}{2}\ \text{O}_{2(g)} + \text{H}_2\text{O} \rightarrow 2\ \text{Co(OH)}_{3(s)} \qquad (1)$$

$\Delta G^0_{298} = -52 \cdot 53$ k cal mole⁻¹ (ref. 4)

$\Delta S^0_{298} = 60$ cal deg mole⁻¹ (ref. 4)

$\Delta G^0_{275} = -51 \cdot 1$ k cal mole⁻¹ (calc.)

$K = [(a_{\text{Co}^{2+}})^2\ (a_{\text{OH}^-})^4\ (a_{\text{O}_2})^{1/2}]^{-1}$

Concentration of Co²⁺ in the Pacific Ocean[5]: 0·38–0·67 μg/l.⁻¹ or 0·645–1·138 × 10⁻⁸ m.

A typical depth for the formation of manganese nodules is 3,000 m (ref. 6)

pH of sea water at 3,000 m (ref. 7): 8·0; ([OH⁻] = 10⁻⁶ m)

Temperature of the ocean at 3,000 m (ref. 7): 2° C (275° K)

Average salinity of sea water at 3,000 m and 2° C (ref. 7): 35 g/1,000 g of sea water, corresponding to an ionic strength of approximately 0·6 m

Activity coefficient of Co²⁺ in a 0·6-M solution at 2° C (ref. 8): 0·49

Activity coefficient of OH⁻ in a 0·6-M solution at 2° C (ref. 8): 0·68

Partial pressure of oxygen at the sediment–water interface[9]: 0·25 atmosphere

Calculation: Taking [Co²⁺] as 10⁻⁸ m:
$K = [(10^{-8} \times 0 \cdot 49)^2 \times (10^{-6} \times 0 \cdot 68)^4 \times (0 \cdot 25)^{1/2}]^{-1}$
$= 3 \cdot 90 \times 10^{41}$

$\Delta G_{275} = \Delta G^0_{275} + RT \log_e K$
$= +1 \cdot 24$ k cal mole⁻¹

Therefore, reaction (1) is unfavourable when the Co²⁺ ion concentration is 10⁻⁸ M. However, the reaction has a negative free energy when the Co²⁺ ion concentration exceeds 1·3 × 10⁻⁸ M (Fig. 1). Furthermore, reaction (1), which is probably catalysed by Fe(OH)₃, is favoured by Co(OH)₃ forming a solid solution with Fe(OH)₃. Also, the reaction is more likely to proceed in oxidizing environments.

The question arises whether the Co²⁺ ion concentration in sea water ever exceeds 1·3 × 10⁻⁸ M. The cobalt-rich manganese nodules are found on the floor of the central Pacific Ocean[6] in the neighbourhood of basaltic islands, atolls, and guyots. Most basalts have cobalt concentrations
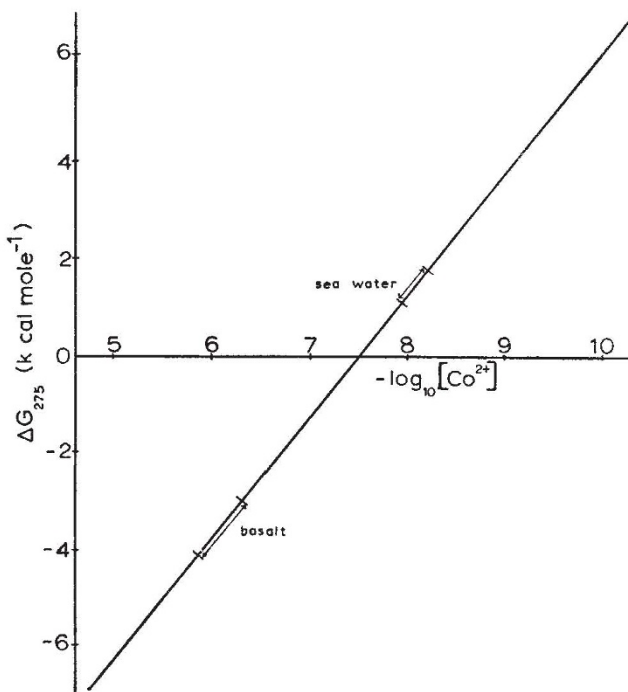

Fig. 1. Variation of ΔG_{275} with Co²⁺ ion concentration for the reaction: $2\ \text{Co}^{2+}_{aq} + 4\ \text{OH}^-_{aq} + \tfrac{1}{2}\text{O}_{2(g)} + \text{H}_2\text{O} = 2\ \text{Co(OH)}_{3(s)}$. Ranges of the [Co²⁺] in sea water and basalt are indicated

between 30 and 80 p.p.m. (ref. 10) (0·5–1·4 × 10⁻⁶ M). Therefore, submarine vulcanism with subsequent leaching of the basaltic glass or palagonite could raise the cobalt concentration of sea water above 1·3 × 10⁻⁸ M locally. This would favour reaction (1), and account for the enrichment of cobalt in the amorphous (Fe,Co)OOH.nH₂O phase of manganese nodules. The low cobalt content in manganese nodules which formed in areas adjacent to the American continent[6] may be attributed to a lack of basaltic bed-rock and to the reducing environment in the sediments.

Several simplifications are inherent in the calculations here. In particular, the effect of pressure at depth on the reaction, the variation of the ionization constant of water with temperature, and the presence of dissolved cobalt in a form (CoSO₄, CoCl₄²⁻, etc.) other than the simple Co²⁺ ion have been ignored. Nevertheless, the calculations demonstrate that oxidation of cobalt to a hydrated cobaltic oxide is a feasible process in certain marine environments. Similar calculations for nickel indicate that oxidation of Ni²⁺ to Ni(OH)₃ is unlikely ($\Delta G_{275} = +21$ k cal mole⁻¹ when [Ni²⁺] = 10⁻⁷ M).

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