

ON URANYL-CARBONATO-PEROXO COMPLEX FORMATION
IN THE SEA

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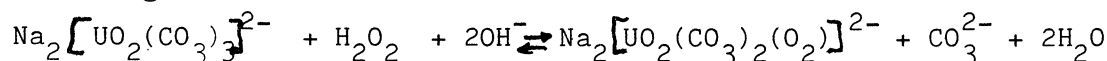
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Summary. The pH-dependent distribution curves of uranyl, based on stability constants of uranyl dicarbonato peroxo and of uranyl carbonato complexes, were calculated. Literature data on higher hydrogen peroxide levels in the photic zone of the ocean were taken into account. Preliminary experiments were done in an attempt to test and verify the theoretically predicted existence of the mixed uranyl peroxo carbonato complex.

Résumé. Les courbes de distribution d'uranyl en fonction du pH, basées sur les constantes de stabilité des complexes uranyl dicarbonate péroxide et des complexes uranyl carbonate ont été calculées. Les données existantes dans la littérature sur les niveaux d'hydrogène péroxide plus élevés dans la zone photique de l'océan ont été considérées. Les expériences préliminaires ont été effectuées en vue d'examiner et de vérifier l'existence supposée du complexe mixte d'uranyl carbonate.

In our previous research concerned with U-distribution in seawater¹ uranyl is found to be present mostly as $\text{Na}_2[\text{UO}_2(\text{CO}_3)_3]^{2-}$ what is in agreement with available literature data. The presence of higher concentrations of hydrogen peroxide - up to 10^{-5} mol dm^{-3} in the photic zone of the oceans, have been proposed by Cooper and Zika². Considering these facts we made an attempt to establish whether this could have any influence on the existing distribution of uranyl species in the seawater.

It is known that O_2^{2-} ligand and H_2O_2 can react with $[\text{UO}_2(\text{CO}_3)_3]^{4-}$ and that UO_2^{2+} has a greater affinity towards the O_2^{2-} ligand than for carbonate ligand. Under specific circumstances² the carbonate ligand can be displaced by the peroxide ion from the inner sphere of the complex according to the reaction:



If H_2O_2 is present, and under conditions of higher pH, the mixed $\text{Na}_2[\text{UO}_2(\text{CO}_3)_2(\text{O}_2)]^{2-}$ complex could be formed, with a partial displacement of the CO_3^{2-} ligand, as can be seen from the above mentioned reaction.

Considering this, both the stability constants of uranyl dicarbonato peroxo complexes were taken into account. Corresponding theoretical distributions were calculated for total uranium concentrations of 10^{-4} , 10^{-5} and 10^{-8} mol dm⁻³. At higher uranyl concentrations (10^{-4} mol dm⁻³) and a peroxide content of 10^{-5} mol dm⁻³, only one tenth of the uranium present exists as the mixed uranyl peroxo dicarbonato complex, at pH values corresponding to that of seawater (pH=8).

However, when the concentration of U approximates its actual level in seawater (10^{-8} mol dm⁻³), the theoretical distribution calculations indicate that about 50% of uranium is present as the uranyl peroxo carbonato complex.

Hence, we tried to verify experimentally the theoretically predicted existence of the mixed uranyl peroxo carbonato complex under conditions mentioned above. Preliminary results are discussed.

References

1. R. Djogić, M.Sc. Thesis, University of Zagreb, Zagreb (1982).
2. W.J. Cooper and R.G. Zika, Photochemical formation of hydrogen peroxide in surface and ground water exposed to sunlight, Science, 220 (1983) 711-712.