
Chemical Speciation and Geochemical Behaviour of Platinum in Natural Waters – A Critical Review

Antonio Cobelo-García¹, Charlotte Catrouillet²

¹Instituto de Investigaciones Mariñas (IIM-CSIC), Vigo (Galicia), Spain

²Faculté des géosciences et de l'environnement, Université de Lausanne, Switzerland

e-mail: acobelo@iim.csic.es, charlotte.catrouillet@unil.ch

Platinum (Pt) is amongst the least abundant elements in the Earth's crust, with average concentrations around or below the nanogram per gram level. However, its distribution in several environmental compartments is undergoing a significant transformation due to the considerable increase in its anthropogenic emissions over the last three decades mainly due to its use in automotive catalytic converters. During abrasion and aging of washcoat layer of the catalyst, metallic and oxide forms of Pt are emitted as particles (normally 10-30 µm) at rates up to several hundred nanogram per kilogram per vehicle [1] and then are subject to mobilization through interaction/complexation with naturally occurring ligands [2]. Accordingly, Pt concentrations well above background values have been reported in areas subject to vehicular traffic and also evidence for a long range transport and contamination has been given from the study of Greenland and Antarctic ice cores [3,4].

In this context, rivers, estuaries and coastal areas are subject to increasing Pt anthropogenic inputs. Their solution speciation and geochemistry is, therefore, much required in order to study and predict its biogeochemical behaviour (reactivity, transport, fate, toxicity). To this end, thermodynamic and kinetic models that accurately describe its interactions in the environmental compartments are needed. The solution speciation of Pt in natural waters has been, however, poorly characterised, and the available speciation calculations given in the literature are not fully consistent. The main characteristics of the information available on the geochemistry and speciation of Pt are the following: (i) stability constants with some inorganic ligands are still unknown; (ii) thermodynamic data has been derived from experiments using Pt concentrations well above ambient values. The extremely low concentrations of these elements hamper the study of their complexation at their natural concentrations; (iii) several constants with inorganic ligands are from 'old' papers and/or from the grey literature, and therefore the accuracy of the calculations is under debate; (iv) a significant fraction of the work on the inorganic complexation of Pt was made to calculate their speciation in systems with a different composition than natural waters (e.g. industrial recovery of platinum group elements from acidic solutions). Therefore, some of the reported stability constants with inorganic ligands are given at ionic strengths or temperatures different to those in natural waters; (v) an important fraction of trace elements in natural waters is known to be complexed with natural organic matter (NOM). Although several papers report the interaction of Pt with NOM [5,6], the stability constants of its complexes have not been calculated yet and only constants with few model and synthetic ligands (e.g. desferrioxamine-B, etc.) are available [2].

The present paper, therefore, constitutes a critical review of the literature dealing with the speciation and geochemistry of Pt (II and IV) in natural waters. Calculations of the 'best' estimation of their speciation will be given as well as the implications for their geochemical behaviour. Needs for future research will be outlined.

References

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