



Phosphorus speciation by coupled HPLC-ICPMS: low level determination of reduced phosphorus in natural materials

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Phosphorus is a geologically important minor element in the Earth's crust commonly found as relatively insoluble apatite. This constraint causes phosphorus to be a key limiting nutrient in biologic processes. Despite this, phosphorus plays a direct role in the formation of DNA, RNA and other cellular materials. Recent works suggest that since reduced phosphorus is considerably more soluble than oxidized phosphorus that it was integrally involved in the development of life on the early Earth and may continue to play a role in biologic productivity to this day. This work examines a new method for quantification and identification of reduced phosphorus as well as applications to the speciation of organo-phosphates separated by coupled HPLC – ICP-MS. We show that reduced phosphorus species (P1+, P3+ and P5+) are cleanly separated in the HPLC and coupled with the ICPMS reaction cell, using oxygen as a reaction gas to effectively convert elemental P to P-O. Analysis at $M/Z = 47$ producing lower background and flatter baseline chromatography than analyses performed at $M/Z = 31$. Results suggest very low detection limits ($0.05 \mu M$) for P species analyzed as P-O. Additionally we show that this technique has potential to speciate at least 5 other forms of phosphorus compounds. We verified the efficacy of method on numerous materials including leached Archean rocks, suburban retention pond waters, blood and urine samples and most samples show small but detectable levels of reduced phosphorus and or organo-phosphates. This finding in nearly all substances analyzed supports the assumption that the redox processing of phosphorus has played a significant role throughout the history of the Earth and it's presence in the present environment is nearly ubiquitous with the reduced oxidation state phosphorus compounds, phosphite and hypophosphite, potentially acting as significant constituents in the anaerobic environment.