EVALUATION OF SELECTIVE IRON EXTRACTION TECHNIQUES TO QUANTIFY IRON-BOUND PHOSPHORUS IN SEDIMENTS

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Abstract

In order to accurately characterize the role of oxidized-iron phases in sequestering phosphorus in aquatic systems, it is crucial to understand the role that iron mineralogy plays in phosphate sorption. To address this challenge, five of the selective extractants most commonly used to achieve targeted dissolution of specific iron (oxy)hydroxides (hereafter Fe_{ox}) phases in marine sediments were evaluated (i) for their specificity for particular Fe_{ox} phases, and (ii) for their ability to quantify the Fe-bound phosphate (hereafter P_{Fe}) associated with these targeted phases.

The first objective of this study was to identify the most efficient and consistent extractant to target the pool of P_{Fe} in natural sediments. Two extractants in wide use within the literature that target this pool are a near-neutral 8-hr citrate bicarbonate dithionite (CBD) (Ruttenberg 1992, Ruttenberg et al. 2009) and a near neutral 1-hr bicarbonate buffered dithionite without citrate (BD) (Jensen and Thamdrup 1993). Complete dissolution of the total Fe_{ox} pool is an essential component of accurately quantifying P_{Fe}, therefore, the dissolution of five Fe_{ox} pure-analog mineral phases that are commonly occurring in the marine environment were assessed for both extractants. Results of this study indicate that both the CDB and BD extractants are able to completely solubilize the pool of Fe_{ox}, however, while CDB achieves complete dissolution of all Fe_{ox} minerals in the recommended published extraction time of 8-hrs, an extraction time of 10-hrs is required for BD to completely solubilize the iron oxide, hematite. Because the removal of citrate greatly facilitates the spectrophotometric analysis of P, a 10-hr BD extraction is recommended to replace CDB in solid phase phosphate speciation schemes such as SEDEX (Ruttenberg 1992).

The second objective of this study was to evaluate four less aggressive extractants: hydroxylamine-HCl, 0.5M HCl, ammonium oxalate, and ascorbic acid, for their efficiency and specificity in quantifying the Fe_{ox} minerals that control P-sorption in natural sediments. These Fe_{ox} minerals are referred to as ‘easily reducible’ (hereafter ER-Fe_{ox}) and are characterized by high surface area. Dissolution of target ER-Fe_{ox} phases was confirmed through pure-analog Fe_{ox} mineral efficiency experiments. Dissolution of non-target Fe and P phases wass assessed by conducting specificity experiments using natural analog P phases and a natural Fe carbonate mineral.

Originally we considered the possibility of inserting a new extraction step into the SEDEX scheme to quantify ER-Fe_{ox} and associated P, within the extraction protocol. However, results of efficiency and specificity experiments using analog phases suggest that the extractants evaluated in this study are not suitable for insertion into SEDEX. Specifically, because the extractants evaluated target only partial dissolution of Fe_{ox} pool, this creates conditions that favor secondary P-readsorption onto residual Fe_{ox}, resulting in inaccurate quantification of P bound to ER-Fe_{ox}. Furthermore, partial dissolution of Ca-bound P by acidic ER-Fe_{ox} extractants will result in inaccurate quantification of the P_{Fe} pool, because some portion of the extracted P will have been derived from Ca-bound P phases. We also found that conducting parallel SEDEX and ER-Fe_{ox} extractions, and using P solubilized in SEDEX-Step III to correct P_{Fe} for any P contributed by Ca-bound P phases, was not a viable option because the ER-Fe_{ox} extractants only partially solubilize variable quantities of Ca-bound P. Ultimately, results of this study suggest that the best option for determining the association of P_{Fe} to ER-Fe_{ox} in sediments was to conduct separate extractions for each, and relate them after the fact. Thus, we recommend BD to solubilize P_{Fe}, and hydroxylamine-HCl after pre-extraction with sodium acetate (to remove Fe-carbonates, as recommended in Poulton and Canfield (2005)), to quantify the Fe_{ox} phases most likely to be relevant to coupled Fe-P cycling.

We applied all of the extractants examined in this study to sediment cores from two depositional environments in order to contrast the quantity of Fe and P solubilized in each extractant, and resulting Fe:P ratios, in two mineralogically distinct environments. Consistent with analog phase results of efficiency and specificity experiments, sediment profiles of Fe_{ox} and P_{Fe} generated using each of the five extractants differed substantially from one another within each sediment core. Substantial differences were also observed for each of the extractants between the two sites, suggesting that sediment mineralogy has the potential to impact greatly the end result of ER-Fe_{ox} quantified using selective extractants. Discrepancies observed in results from applying different extractants to the sediment cores assayed in this study suggest strongly that it is unwise to compare directly Fe_{ox}, P_{Fe}, and Fe:P ratios from studies that utilize different extraction protocols. A compilation of Fe_{ox}, P_{Fe} and Fe:P data from the literature support this conclusion, and allow further examination of particular aspects of depositional environments that also can influence these parameters, such as seasonal variability in redox state, salinity, and the sediment depth over which these parameters are quantified. The implication of each extractant solubilizing different Fe phases in natural sediment has particular relevance concerning our overall understanding of the pool of Fe relevant to P cycling. The pool of ER-Fe_{ox} can be used in estimating P availability in the modern ocean, and can also be used in paleocean modeling. The pool of Fe relevant to P cycling is believed to provide critical positive and negative feedbacks on atmospheric oxygen concentrations and overall oceanic productivity. This study provides a careful analysis that allows for a more informed choice when selectively extracting P_{Fe}, and the Fe relevant to P cycing.