Phosphorus speciation in Ancient Sedimentary Rocks: Modifications to the SEDEX Method

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In the last decade, there has been increased focus on the role of phosphorus cycling in the chemical evolution of Earth's atmosphere and oceans [1,2,3]. Whilst some understanding can be gained by assessing the total P concentration relative to other key elements such as Fe and Al, sequential extraction techniques have become a favoured tool for evaluating P speciation within sediments, creating a far more detailed picture of P cycling in the marine environment. The SEDEX sequential extraction method [4] has proven to be a robust method for use in modern sedimentary settings, however it is currently less well suited for application to ancient sedimentary rocks. For example, key periods of Earth's history have been dominated by ferruginous oceans (anoxic and rich in Fe^{2+}) [5], leading to increased burial of more crystalline Fe oxide phases that are not readily extracted by the conventional SEDEX method. For any extraction scheme to successfully inform our understanding of P cycling during these periods, it must include extraction of these more crystalline minerals.

Here we present modifications to the SEDEX method that improve its suitability for use with ancient sedimentary rocks. Additional extractions result in increased recovery of P associated with more crystalline iron minerals, specifically hematite and magnetite (not previously extracted). This newly adapted method allows the partitioning of P between operationally defined sedimentary reservoirs to be examined in ancient environments, but may also be applicable to modern environments enriched in more crystalline Fe minerals. We will describe the technique and report new P speciation data for a suite of rocks deposited ~1.85 billion years ago, during the onset of a critical transition to widespread euxinia along productive continental margins.

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[4] Ruttenberg (1992) *Limnol.Oceanogr.*, **37**, 1460-1482.
[5] Poulton & Canfield (2011) *Elements*, **7**, 107-112.