Article:
Thompson, J, Poulton, SW orcid.org/0000-0001-7621-189X, Guilbaud, R et al. (3 more authors) (2019) Development of a modified SEDEX phosphorus speciation method for ancient rocks and modern iron-rich sediments. Chemical Geology, 524. pp. 383-393. ISSN 0009-2541

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Figure Captions

Figure 1. Schematic of the SEDEX sequential extraction scheme for P in modern marine sediments (left figure), as described in Ruttenberg (1992). Schematic of the Fe speciation method (right figure) for ancient sediments (Poulton and Canfield, 2005). CDB – sodium citrate-dithionite-bicarbonate. CDA – sodium citrate-dithionite-acetate.

Figure 2. Recovery efficiencies for synthetic Fe minerals using different extractions performed non-sequentially. Oxalate extraction data for the composite magnetite/hematite sample are expressed relative to the Fe present as magnetite. Error bars are reported as 2 s.d. based on triplicate analyses, where sufficient sample was available. Extractions were not performed for 'l' and 'c' for the 2 h and 6 h CDA extractions, or for 'f', 'g', 'l' and 'h' for the 6 h oxalate extraction.

Figure 3. Comparison of Fe extracted from Animikie Basin (A) and Golfo Dulce (B) sediments via CDB (SEDEX procedure), with that extracted via CDA (Fe_{ox}) and ammonium oxalate (Fe_{mag}) (Poulton and Canfield, 2005). Animikie Basin Fe_{ox} and Fe_{mag} data are from Poulton et al. (2010). The RSD (n=3) for the Fe extracted by the CDB step is 3.7%. Inset figures show the Fe extracted by an 8 h CDB extraction as a proportion of the Fe recovered by the CDA and ammonium oxalate extractions. Each bar represents an individual sample. The bottom panel indicates the redox conditions under which the samples were deposited.

Figure 4. A revised method for the sequential extraction of P in ancient rocks and modern iron-rich sediments. (A) The starting point for modern sediments; (B) The starting point for ancient rocks. Total Fe-bound P is the sum of P_{Fe1}, P_{mag} and P_{Fe2}. The P_{det} step of the original SEDEX procedure has been redefined as P_{cryst}, and represents crystalline apatite which may include recrystallized CFA as well as detrital apatite of igneous or metamorphic origin (see text for details).

Figure 5. Comparison of Fe recoveries for the synthetic hematite (grey) and magnetite/hematite composite (black) samples during sequential extraction using the original SEDEX method (solid bars) and the revised method (striped bars). The oxalate and summed recoveries for magnetite are reported relative to the concentration of magnetite Fe in the magnetite/hematite composite sample, discounting the Fe extracted by the CDB extraction, which likely largely represents hematite dissolved from this sample. Hem = hematite, mag = magnetite/hematite composite sample.

Figure 6. P speciation for Golfo Dulce samples using the revised method. (A) Partitioning relative to total P. (B) Partitioning relative to reactive P (defined as the sum of all phases minus P_{cryst}). The bottom panel indicates the redox conditions in which the samples deposited.

Figure 7. P speciation for ancient marine rocks using the revised method. (A) Partitioning relative to total P. (B) Partitioning relative to reactive P (defined as the sum of all phases minus P_{cryst}). The bottom panel indicates the redox conditions in which the samples deposited. Ferr. = ferruginous. Equiv. = Equivocal, meaning the redox conditions were unable to be determined.

Table Captions

Table 1. Details of the P phases extracted by the SEDEX method (Ruttenberg, 1992).

Table 2. Sample information for all samples used.

Table 3. Reproducibility (%RSD) for each step of the revised method performed sequentially (n=6).

Figures

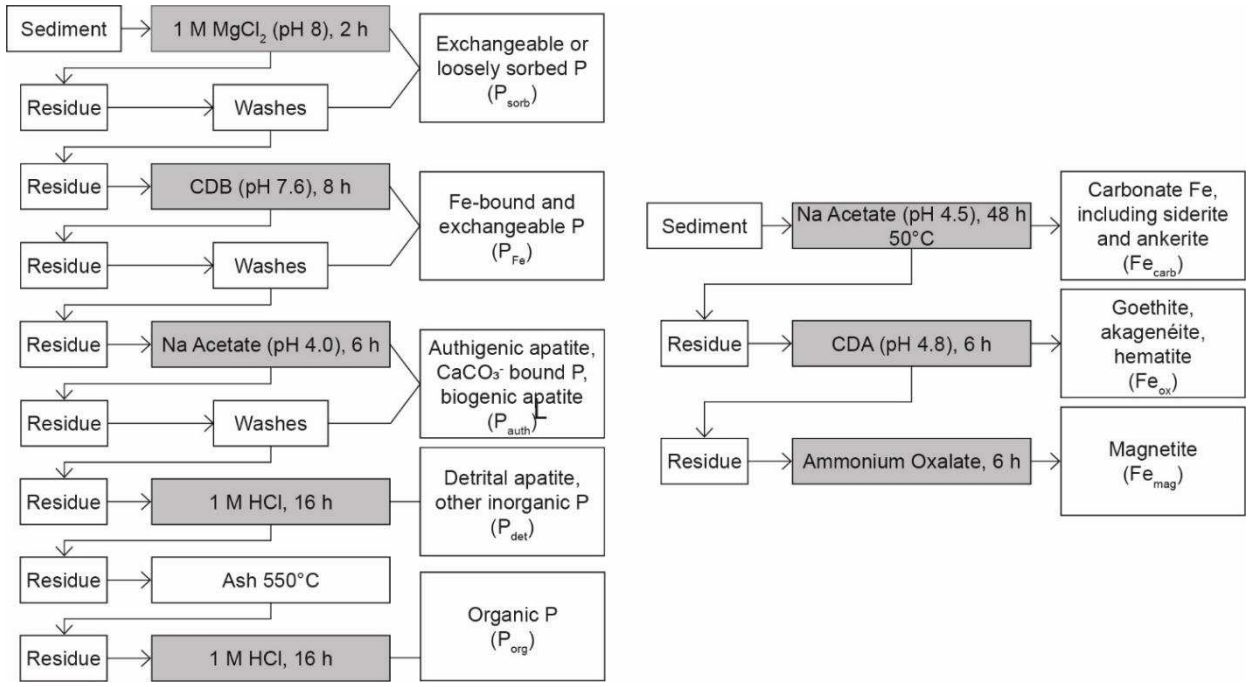

Figure 1

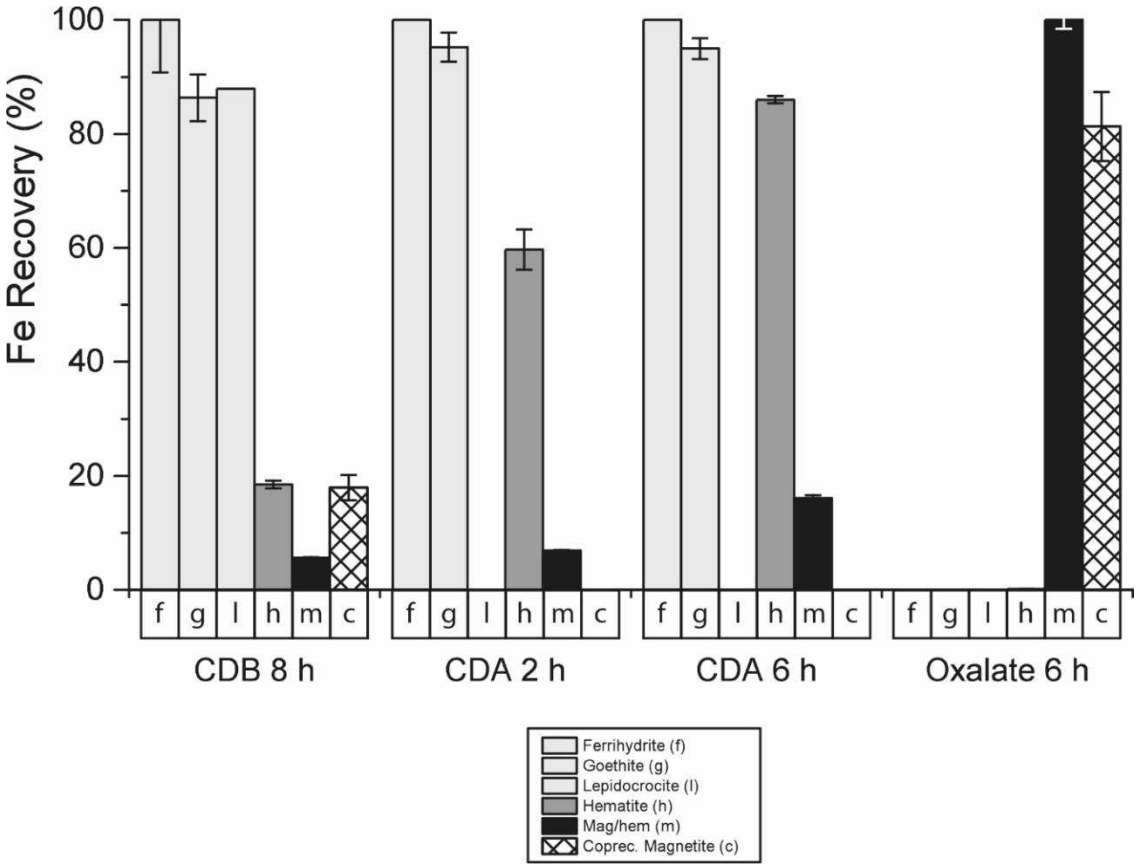
Fe Recovery (%)
100
80
60
40
20
0
f g l h m c
CDB 8 h
CDA 2 h
CDA 6 h
Oxalate 6 h
Ferrihydrite (f)
Goethite (g)
Lepidocrocite (l)
Hematite (h)
Mag/hem (m)
Coprec. Magnetite (c)

Figure 2

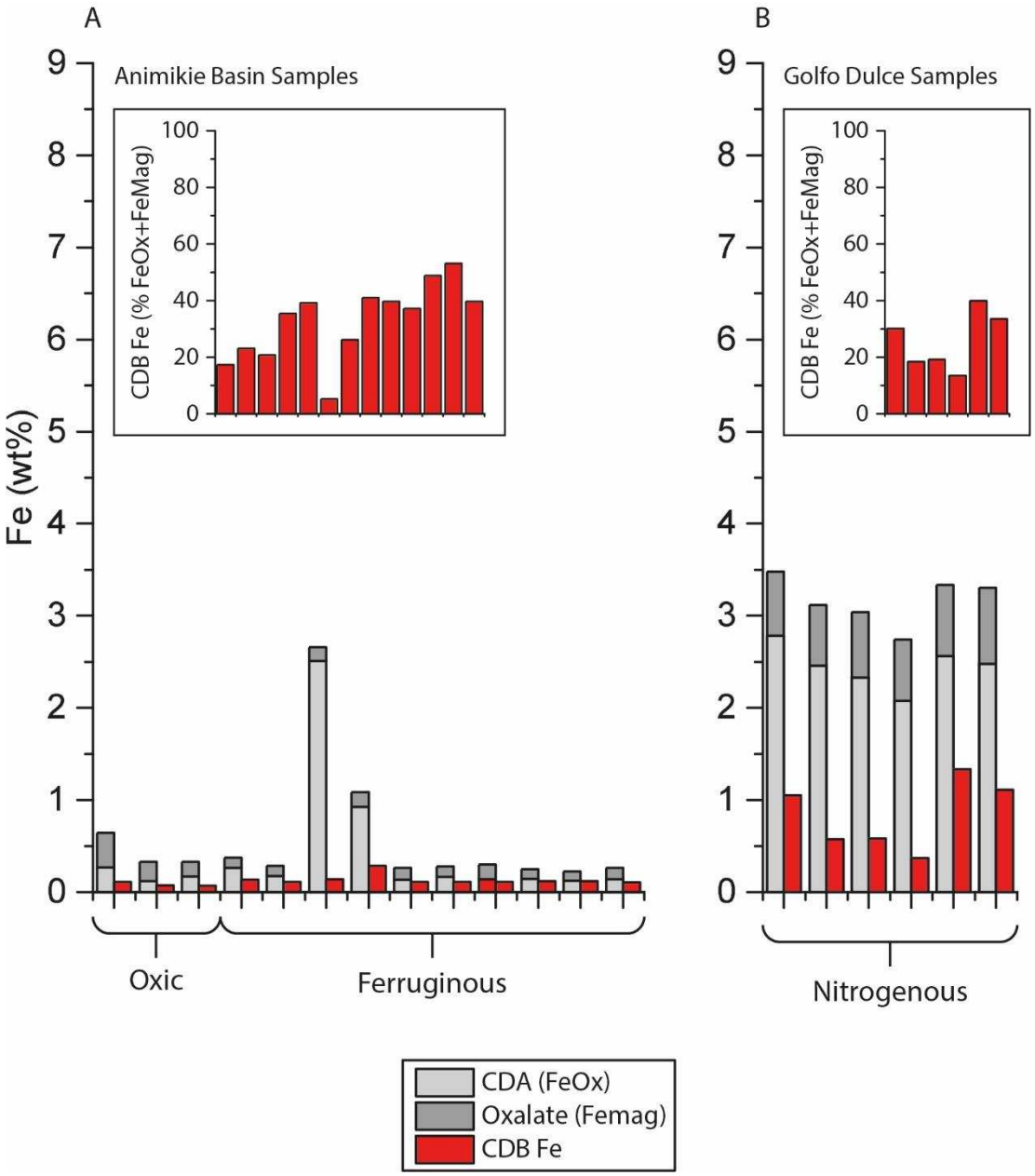
A
B
Animikie Basin Samples
Golfo Dulce Samples
Fe (wt%)
CDB Fe (% FeOx+FeMag)
Oxic
Ferruginous
Nitrogenous
CDA (FeOx)
Oxalate (Femag)
CDB Fe

Figure 3

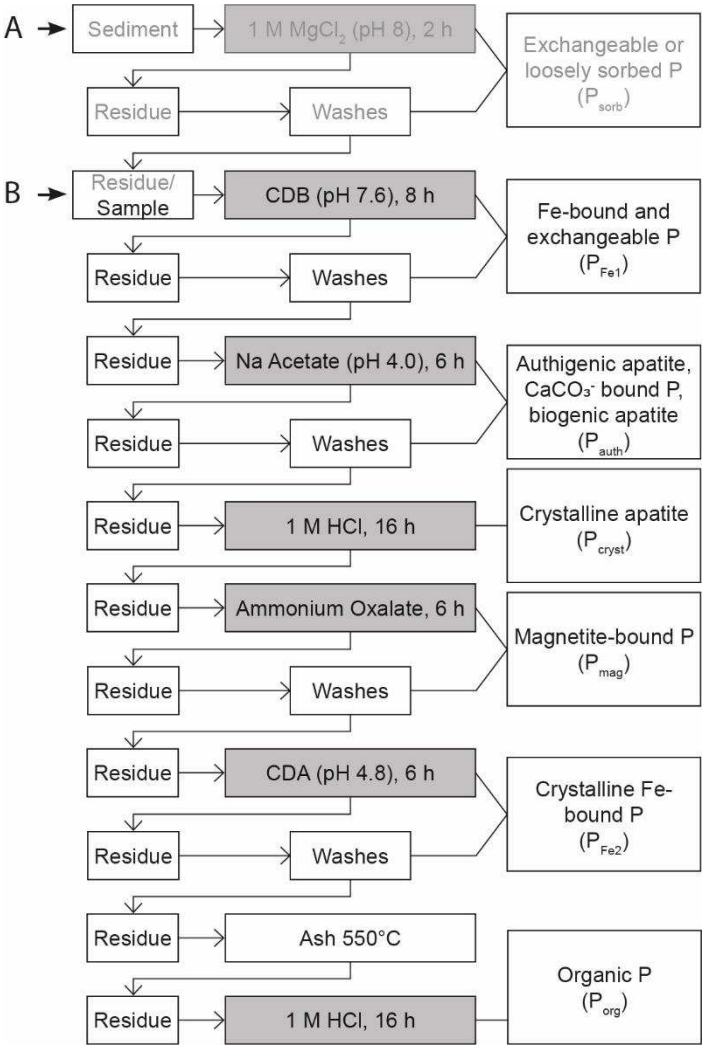
A
Sediment
1 M MgCl2 (pH 8), 2 h
Residue
Washes
Exchangeable or loosely sorbed P (Psorb)
B
Residue/ Sample
CDB (pH 7.6), 8 h
Residue
Washes
Fe-bound and exchangeable P (PFe1)
Residue
Na Acetate (pH 4.0), 6 h
Residue
Washes
Authigenic apatite, CaCO3- bound P, biogenic apatite (Pauth)
Residue
1 M HCl, 16 h
Crystalline apatite (Pcryst)
Residue
Ammonium Oxalate, 6 h
Residue
Washes
Magnetite-bound P (Pmag)
Residue
CDA (pH 4.8), 6 h
Residue
Washes
Crystalline Fe-bound P (PFe2)
Residue
Ash 550°C
Residue
1 M HCl, 16 h
Organic P (Porg)

Figure 4

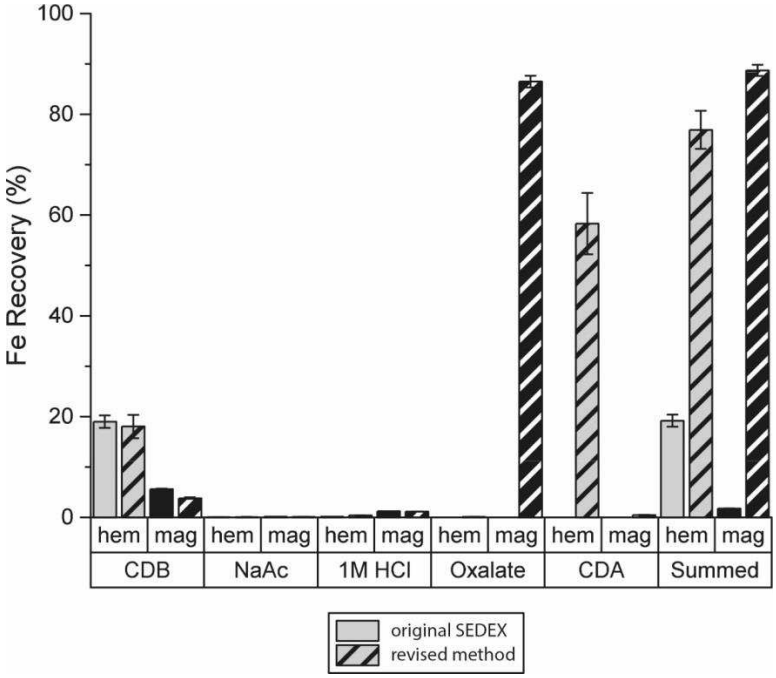
100
80
60
40
20
0
Fe Recovery (%)
hem
mag
CDB
NaAc
1M HCl
Oxalate
CDA
Summed
original SEDEX
revised method

Figure 5

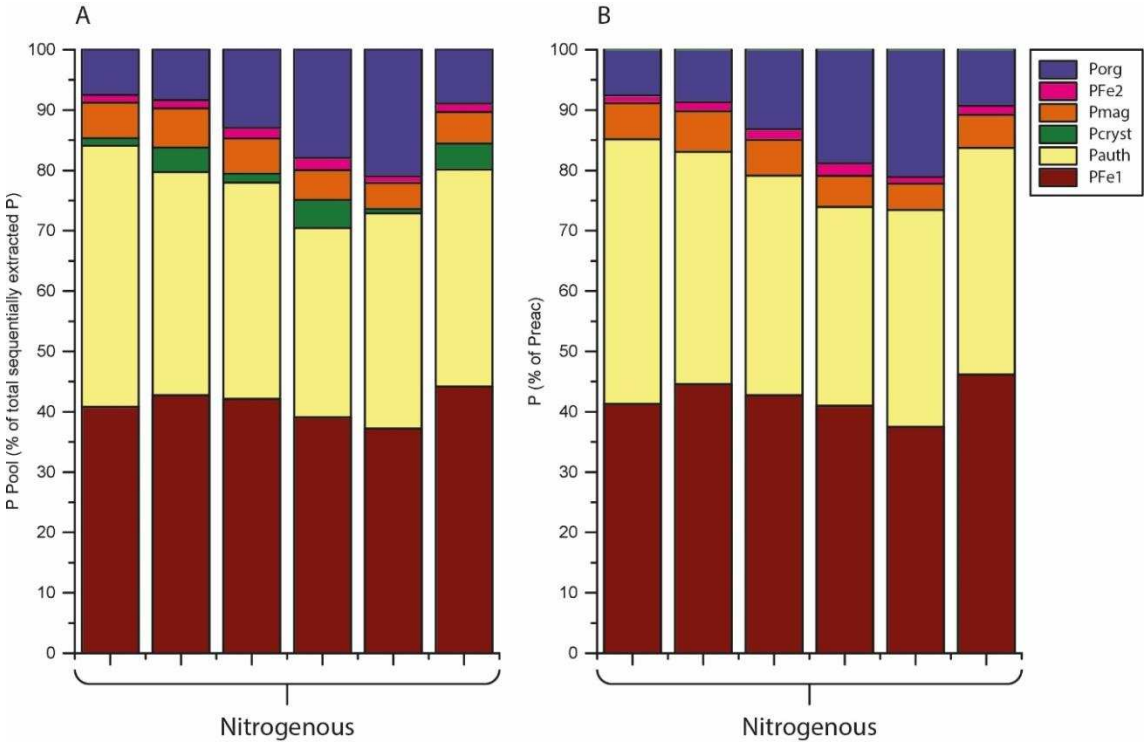
A
B
P Pool (% of total sequentially extracted P)
P (% of Preac)
100
90
80
70
60
50
40
30
20
10
0
Porg
PFe2
Pmag
Pcryst
Pauth
PFe1
Nitrogenous
Nitrogenous

Figure 6

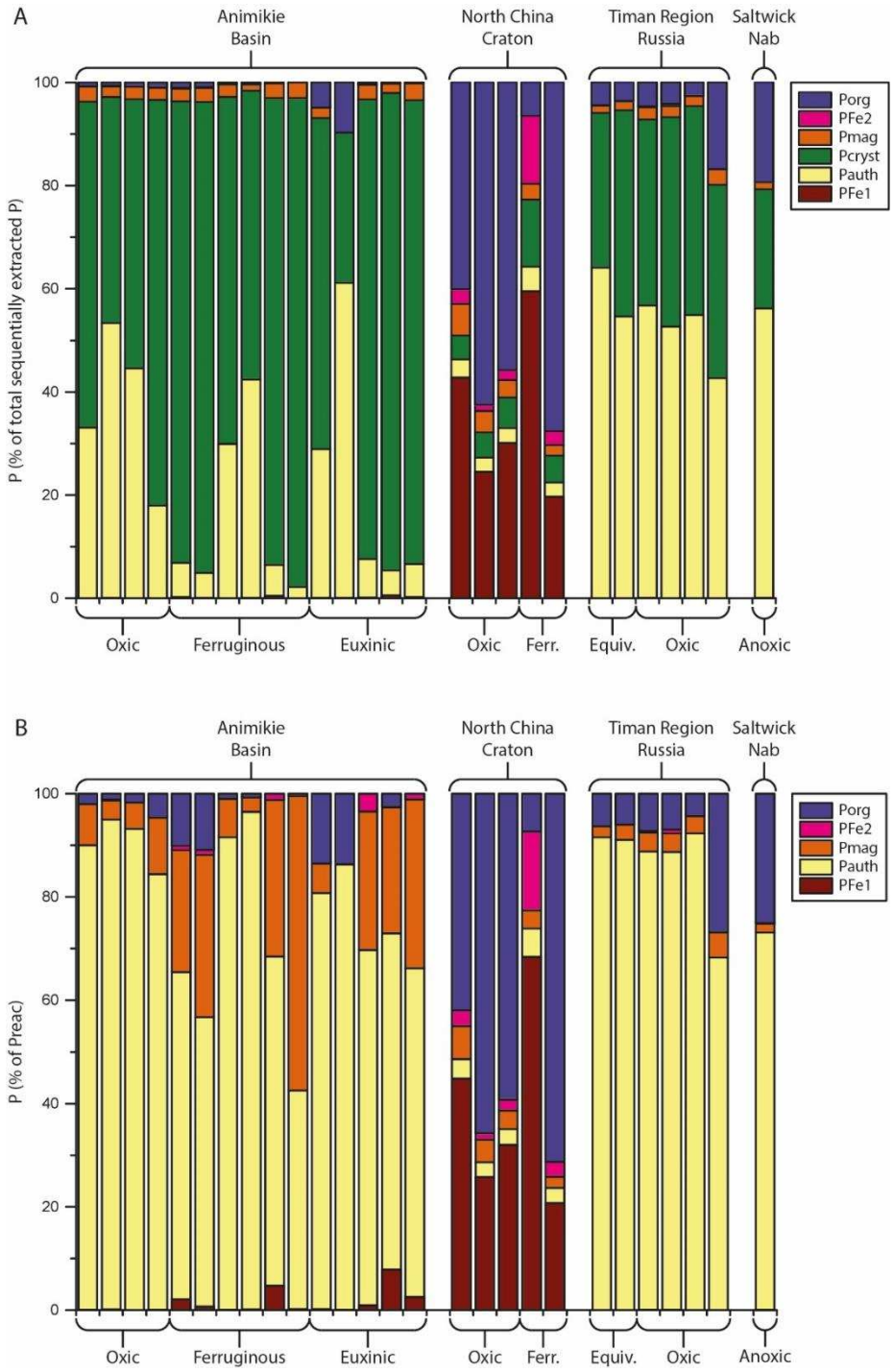
A
Animikie Basin
North China Craton
Timan Region Russia
Saltwick Nab
P (% of total sequentially extracted P)
100
80
60
40
20
0
Porg
PFe2
Pmag
Pcryst
Pauth
PFe1
Oxic
Ferruginous
Euxinic
Oxic
Ferr.
Equiv.
Oxic
Anoxic
B
Animikie Basin
North China Craton
Timan Region Russia
Saltwick Nab
P (% of Preac)
100
80
60
40
20
0
Porg
PFe2
Pmag
Pauth
PFe1
Oxic
Ferruginous
Euxinic
Oxic
Ferr.
Equiv.
Oxic
Anoxic

Figure 7

Tables

P Pool	Phases Extracted
$\mathbf{P_{sorb}}$	Exchangeable or loosely sorbed P
$\mathbf{P_{Fe}}$	Fe (oxyhydr)oxide-bound P
$\mathbf{P_{auth}}$	Authigenic apatite, $CaCO_3$-bound P and biogenic apatite
$\mathbf{P_{det}}$	Detrital apatite and other inorganic P phases
$\mathbf{P_{org}}$	Organic P

Table 1

Sample	Age	Source	Depositional Setting
Synthetic Minerals			
Ferrihydrite		Prepared according to Cornell and Schwertmann (1996)	
Lepidocrocite			
Goethite			
Hematite		BDH Laboratory Supplies	
Magnetite-hematite composite		Initially prepared according to Cornell and Schwertmann (1996)	
Magnetite co-precipitated with P		Prepared according to Cornell and Schwertmann (1996)	
Natural Mineral Samples			
Crystalline Apatite		Madagascar	
Banded Iron Formation, Isua Greenstone Belt	~3.8 Ga	Isua, Greenland	Marine
Modern Marine Sediments			
Golfo Ducle, Costa Rica	Recent	Short marine mud core	Deep tropical fjord
Marine Sedimentary Rocks			
Animikie Basin, North America	1.88-1.83 Ga	Drill core samples	Open-ocean margin
North China Craton	1.65 Ga	Field samples	Semi-restricted basin, sub tidal
Timan Region, Russia	715-542 Ma	Drill core samples	Shallow water foreland basin, low energy sub tidal
Saltwick Nab, Yorkshire, UK	183-174 Ma	Field samples	Shallow marine

Table 2

Extraction	P_{Fe1}	P_{auth}	P_{det}	P_{mag}	P_{Fe2}	P_{org}	Summed P
%RSD	3.2	5.3	2.7	7.3	2.9	8.1	1.8

Table 3