In Situ Biomineralisation for Groundwater Radionuclide Remediation

Callum Robinson[1], Sam Shaw[1], Jonathan R. Lloyd[1], James Graham[2], Jörg Rothe[3], Kathy Dardenne[3] and Katherine Morris[1]

(1)Research Centre for Radwaste Disposal, Department of Earth and Environmental Sciences, University of Manchester, Manchester, M13 9PL, UK

(2) National Nuclear Laboratory, Central Laboratory, Sellafield, Seascale, Cumbria, CA20 1PG

(3) Institute for Nuclear Waste Disposal (INE), Karlsruhe Institute of Technology, Karlsruhe 76131, Germany

MANCHESTER 1824

The University of Manchester

Radionuclide Contamination at Sellafield

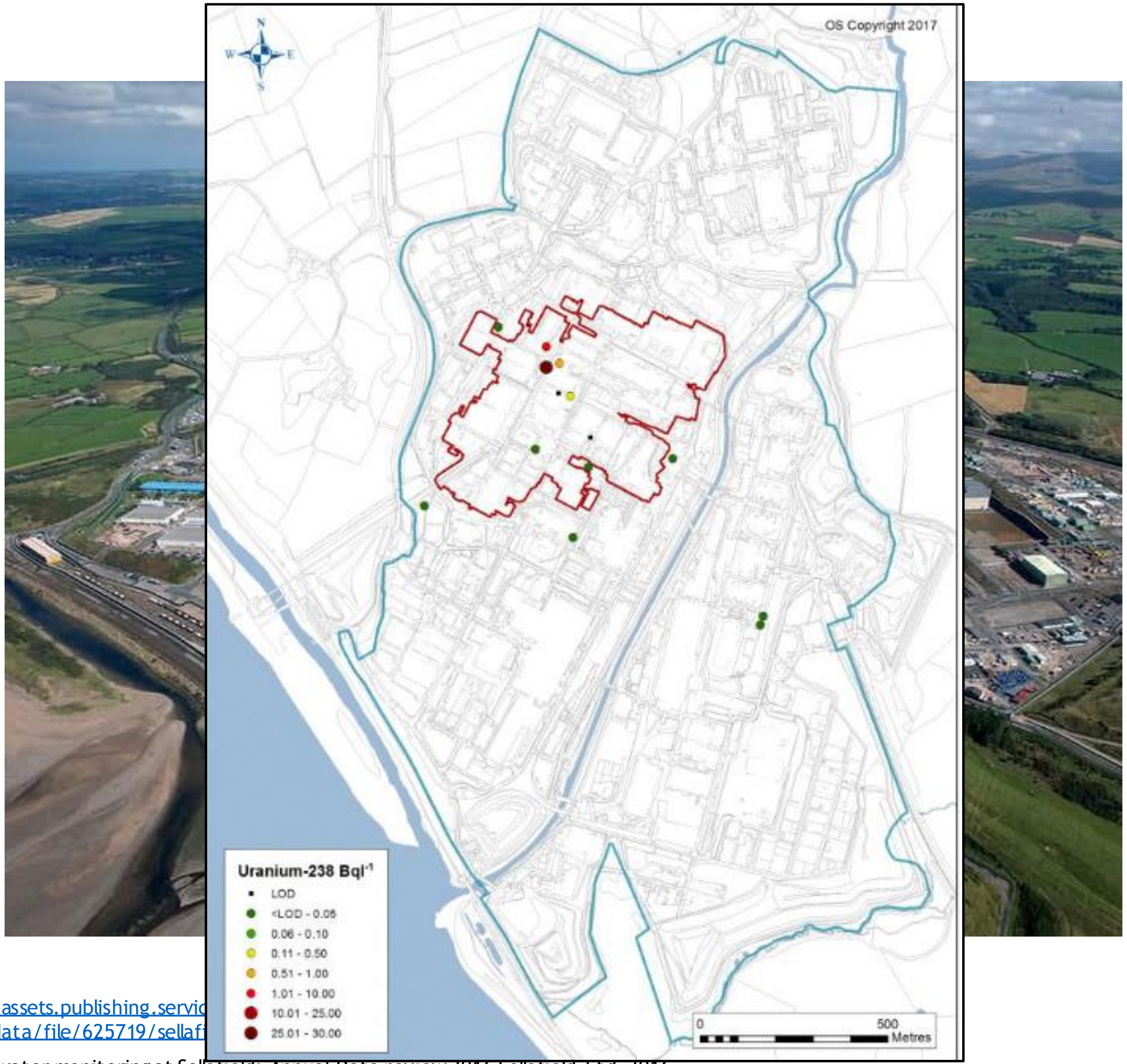
- Sellafield has legacy storage facilities and silos from historical operations
- Significant radionuclide contamination of the subsurface
- Focus of this work ^{90}Sr and U

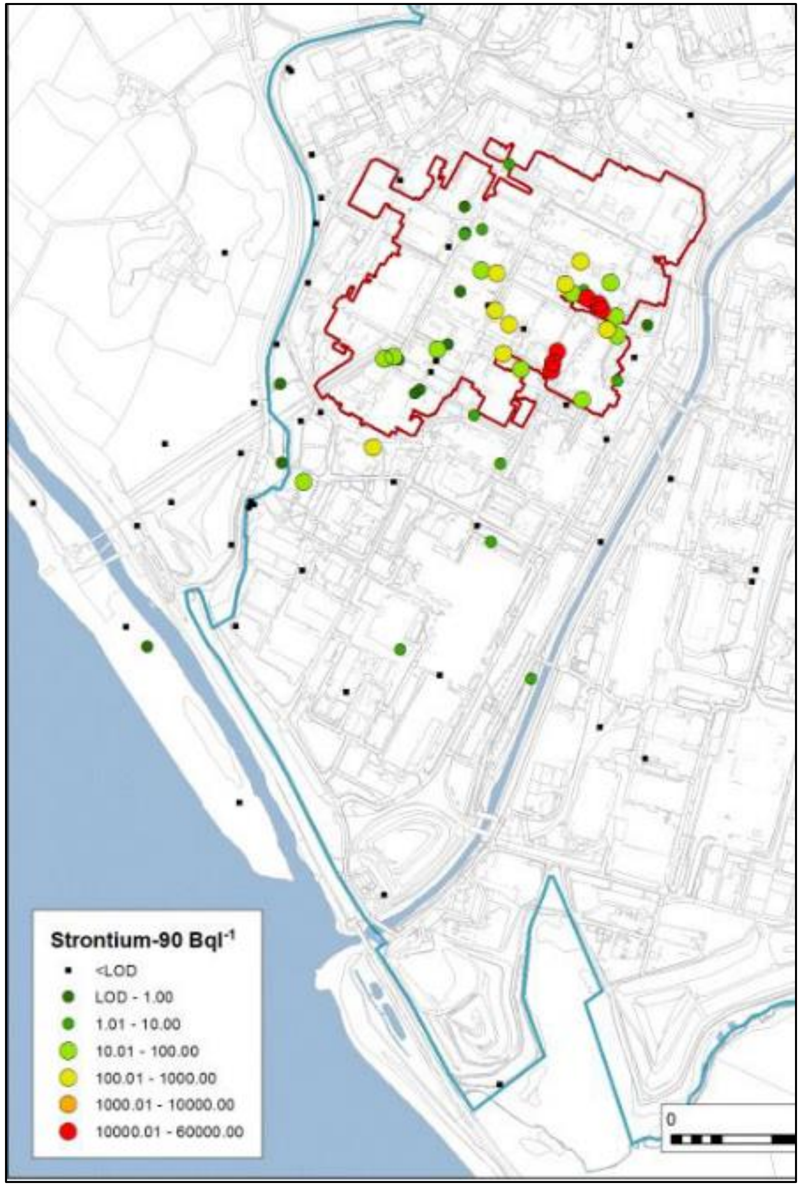
https://assets.publishing.service.gov.uk/government/uploads/system/uploads/attachment_data/file/625719/sellafield-magazine-issue-4.pdf pg21

Groundwater monitoring at Sellafield: Annual Data review 2016 Sellafield Ltd, 2016

The University of Manchester

Radionuclide Contamination at Sellafield





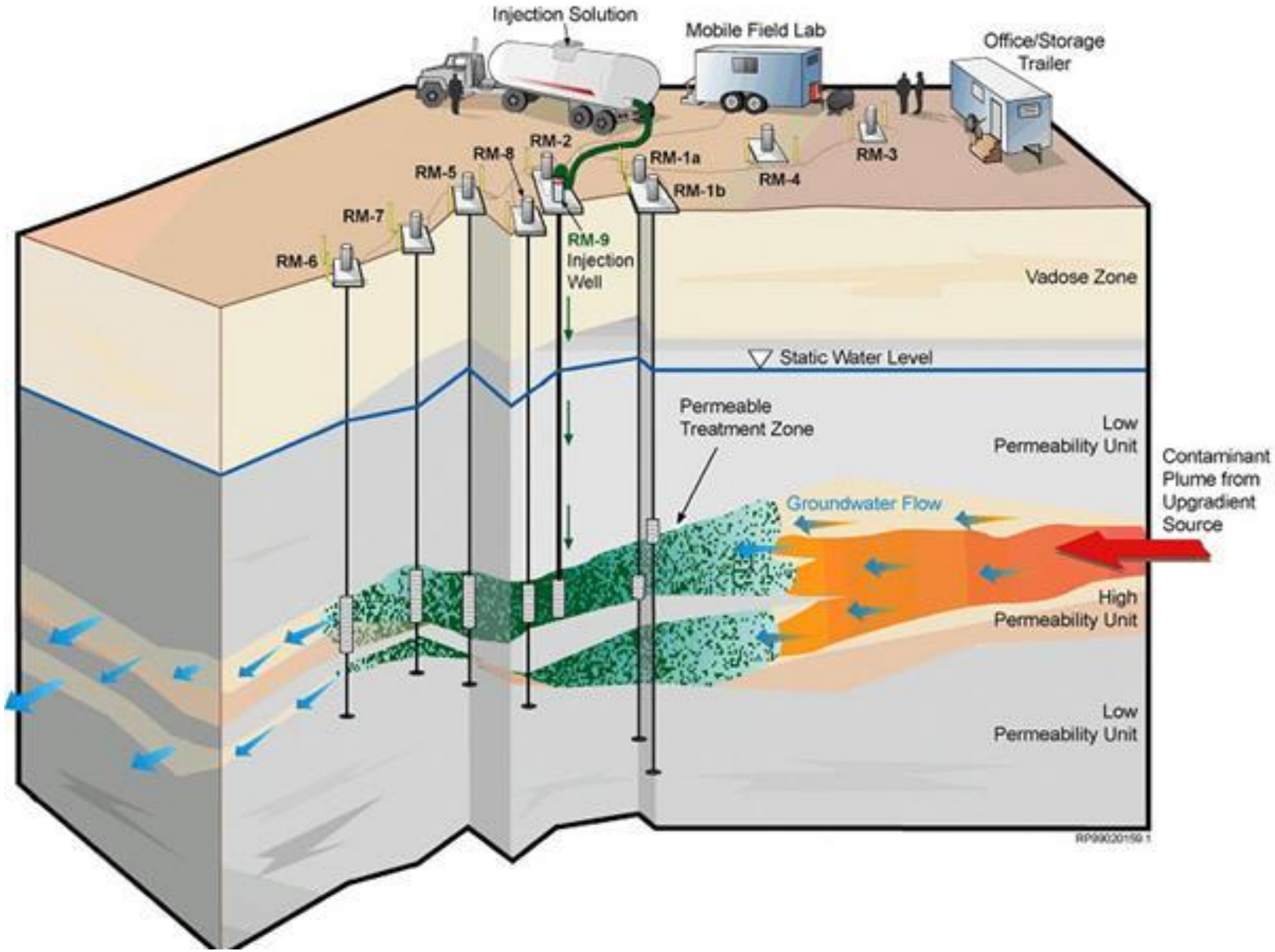
https://assets.publishing.servic
hment_data/file/625719/sellafi

Groundwater monitoring at Sellafield: Annual Data review 2016 Sellafield Ltd, 2016

Phosphate Mineralisation

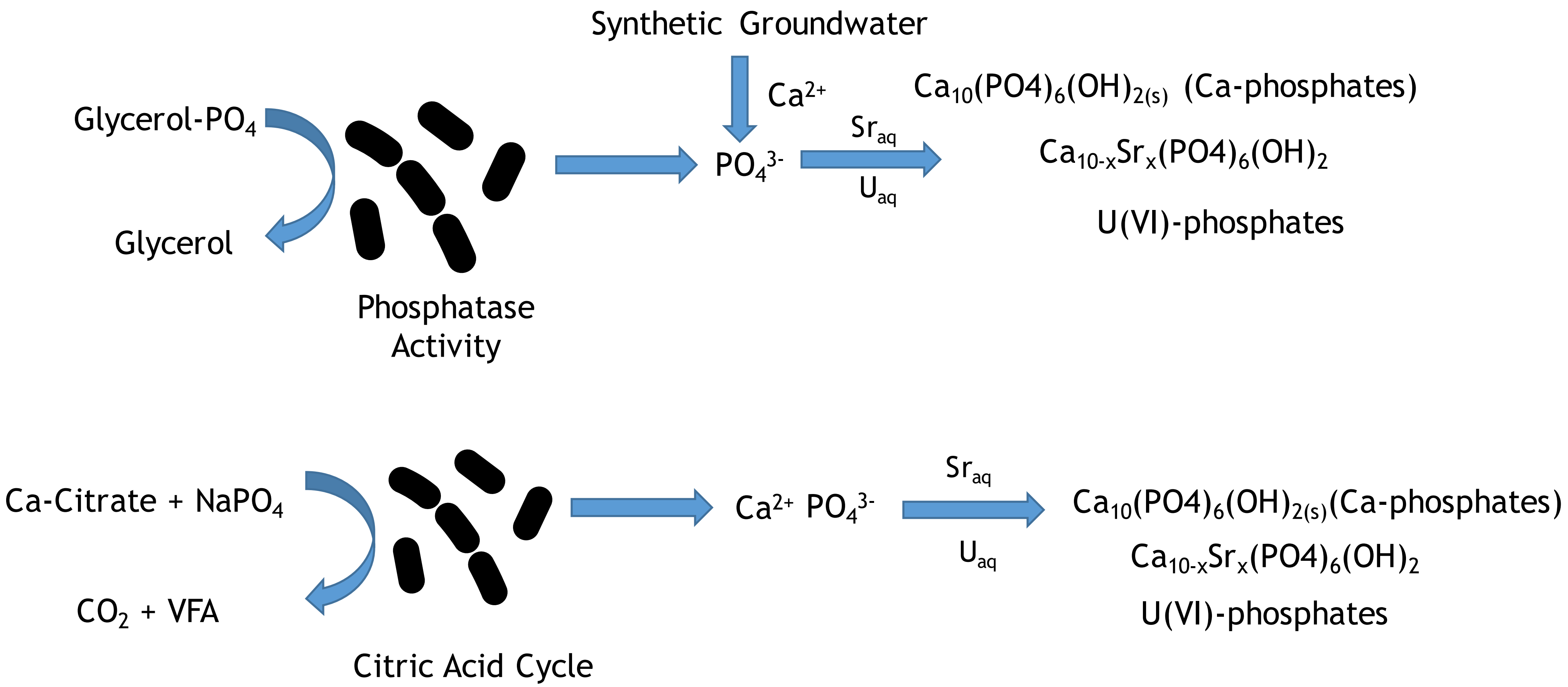
- Phosphate containing minerals such as hydroxyapatite (HAp) have been shown to incorporate ^{90}Sr within their structure
- Uranium phosphates are highly insoluble mineral phases
- Direct injection of phosphate containing solutions into the subsurface can lead to injection well clogging
- In situ, slow release phosphate delivery is promising for co-treatment of Sr^{2+} and $U^{VI}O_2^{2+}$

J. M. Hughes, Am. Mineral., 2015, **100**, 1033–1039.
Szecsody, J., Williams, M., Burns, C., Girvin, D., Moore, R., Mckinley, J., … Phillips, J. (2007). Hanford 100-N area apatite emplacement: Laboratory results of Ca-Citrate-PO4 solution injection and Sr-90 immobilization in 100-N sediments.
Cleary, J. R. Lloyd, L. Newsome, S. Shaw, C. Boothman, G. Boshoff, N. Atherton and K. Morris, *Chem Geol.*, 2019, **509**, 213–222.
Newsome, L., Morris, K., Trivedi, D., Bewsher, A., & Lloyd, J. R. (2015). Biostimulation by Glycerol Phosphate to Precipitate Recalcitrant Uranium(IV) Phosphate. Environmental Science and Technology, 49(18)
Vermeul, V. R., Szecsody, J. E., Fritz, B. G., Williams, M. D., Moore, R. C., & Fruchter, J. S. (2014). An Injectable Apatite Permeable Reactive Barrier for In Situ 90Sr Immobilization. Groundwater Monitoring and Remediation, 34(2), 28–41.



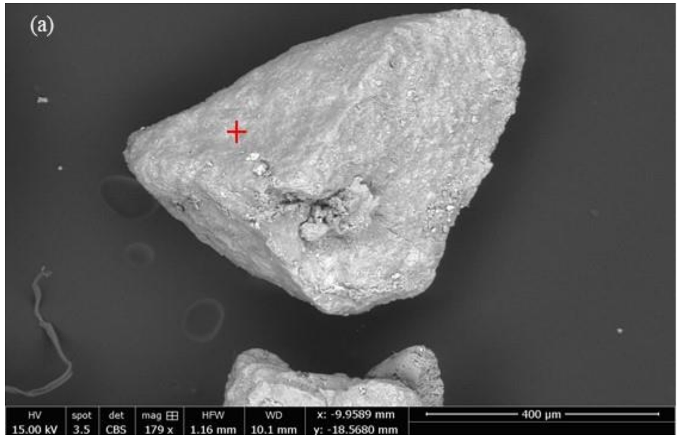
In-Situ Remediation of Soil, Sediments, and Groundwater Contaminated by Hazardous Substances. Author: Mauro Capocelli, Researcher, University UCBM – Rome (Italy) http://www.oil-gasportal.com/in-situ-remediation-of-soil-sediments-and-groundwater-contaminated-by-hazardous-substances/?print=print

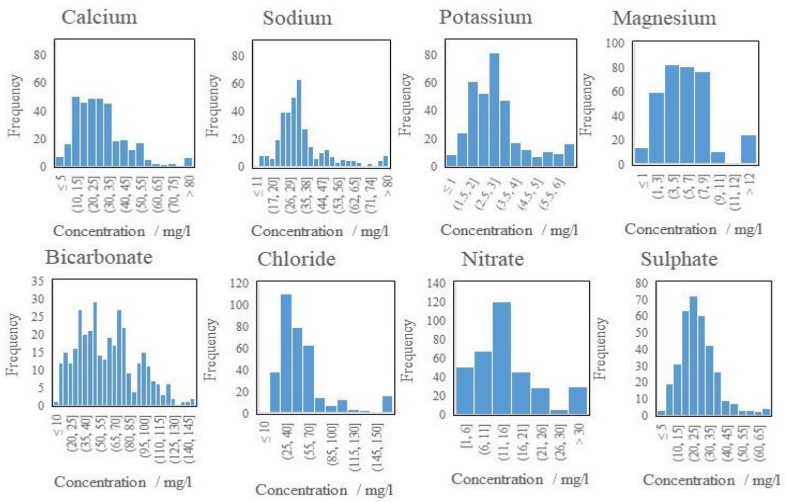
Biomineralisation



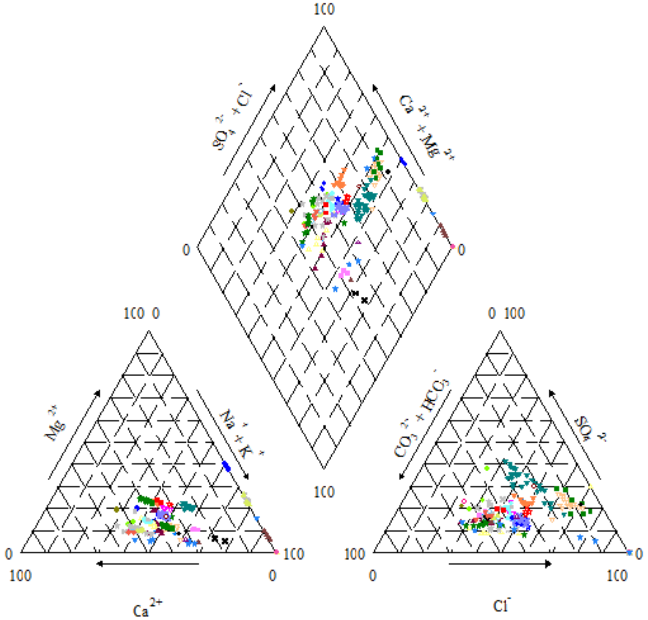
Sediment Characterisation and Synthetic Groundwater

Montage from centre of Active Face of Peel Place Quarry (NW BAY)





Sr Plume Groundwater Piper Plot



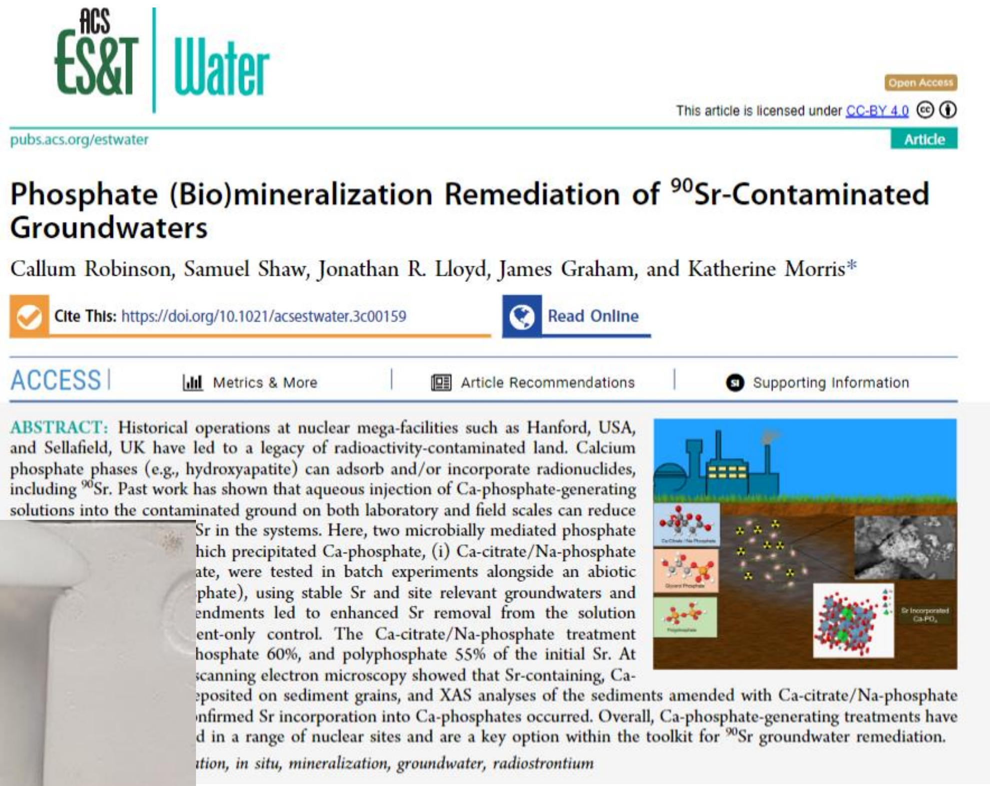
[Sellafield Ltd, Groundwater Monitoring at Sellafield: Annual Data Review 2016 2016.

Biomineralisation of Sr

- Peel Place Quarry (PPQ) Sediment
- Calder River (CR) Sediment
- Oxic Experiments
- Synthetic Groundwater
  - ➢ 1mM (88ppm) Sr Spiked

➢ Calcium citrate/sodium phosphate

➢ Glycerol phosphate



ACS ES&T Water
pubs.acs.org/estwater
Article

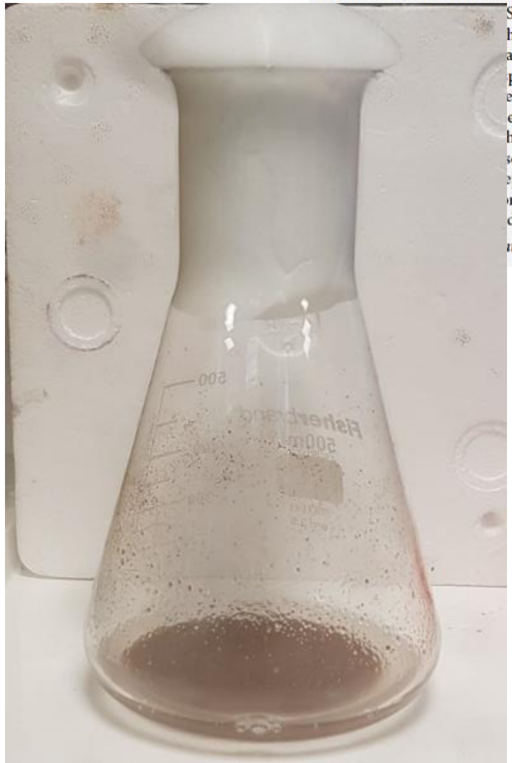
Phosphate (Bio)mineralization Remediation of ^{90}Sr-Contaminated Groundwaters

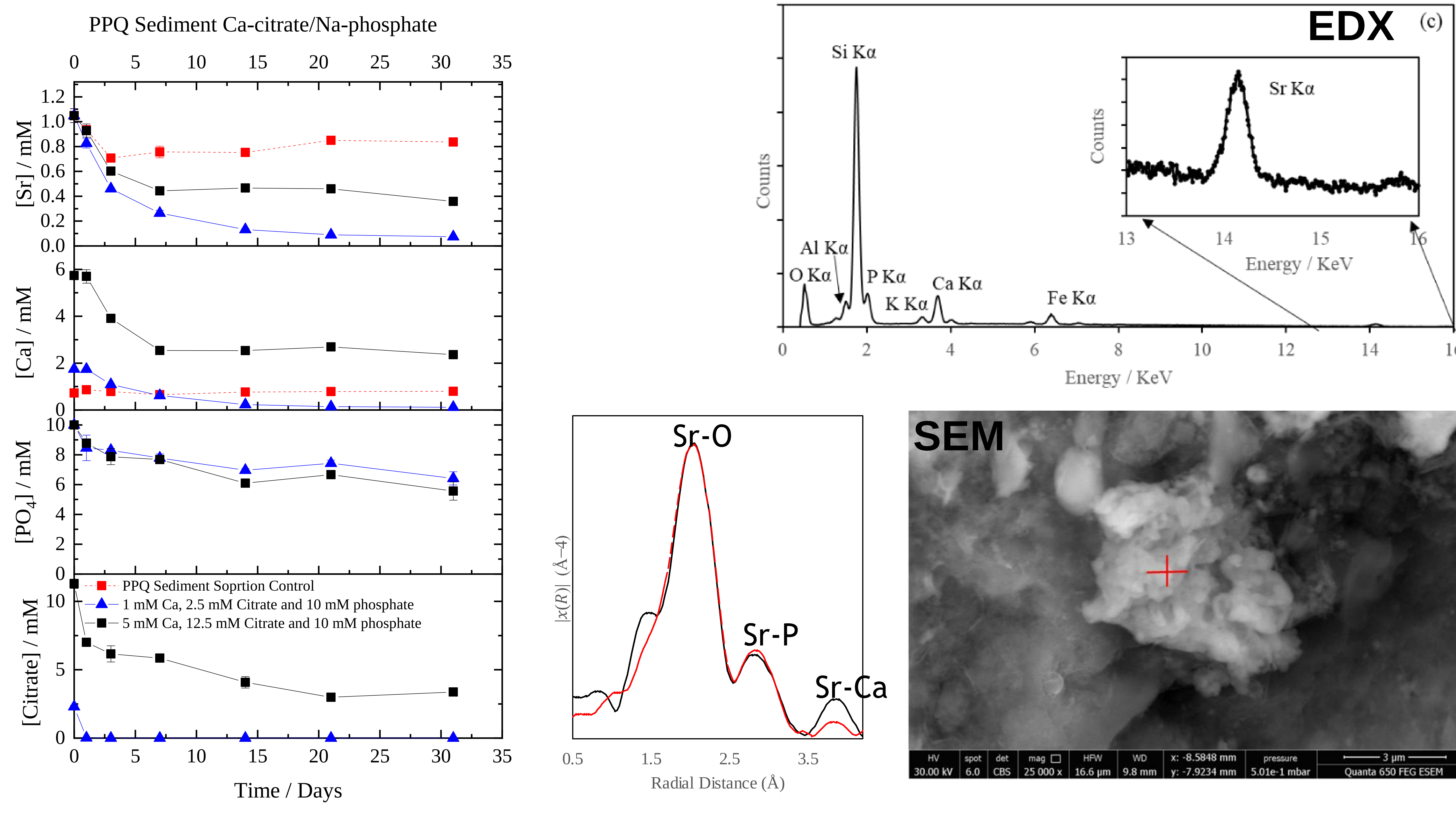
Callum Robinson, Samuel Shaw, Jonathan R. Lloyd, James Graham, and Katherine Morris*

Cite This: https://doi.org/10.1021/acsestwater.3c00159
Read Online

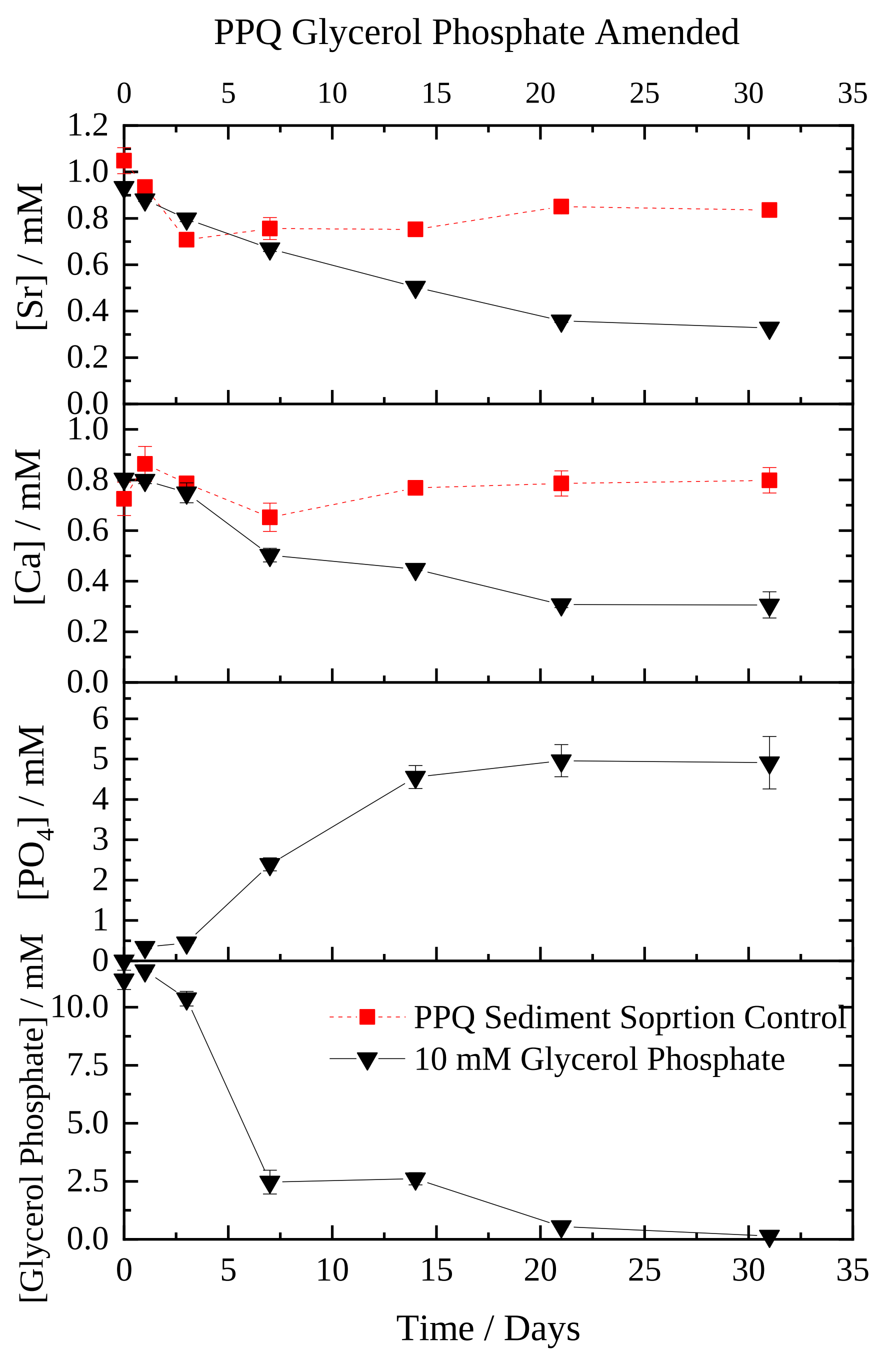
ACCESS | Metrics & More | Article Recommendations | Supporting Information

ABSTRACT: Historical operations at nuclear mega-facilities such as Hanford, USA, and Sellafield, UK have led to a legacy of radioactivity-contaminated land. Calcium phosphate phases (e.g., hydroxyapatite) can adsorb and/or incorporate radionuclides, including ^{90}Sr. Past work has shown that aqueous injection of Ca-phosphate-generating solutions into the contaminated ground on both laboratory and field scales can reduce
Sr in the systems. Here, two microbially mediated phosphate
hich precipitated Ca-phosphate, (i) Ca-citrate/Na-phosphate
ate, were tested in batch experiments alongside an abiotic
phate), using stable Sr and site relevant groundwaters and
endments led to enhanced Sr removal from the solution
ent-only control. The Ca-citrate/Na-phosphate treatment
hosphate 60%, and polyphosphate 55% of the initial Sr. At
scanning electron microscopy showed that Sr-containing, Ca-
eposited on sediment grains, and XAS analyses of the sediments amended with Ca-citrate/Na-phosphate
nfirmed Sr incorporation into Ca-phosphates occurred. Overall, Ca-phosphate-generating treatments have
d in a range of nuclear sites and are a key option within the toolkit for ^{90}Sr groundwater remediation.
ation, in situ, mineralization, groundwater, radiostrontium



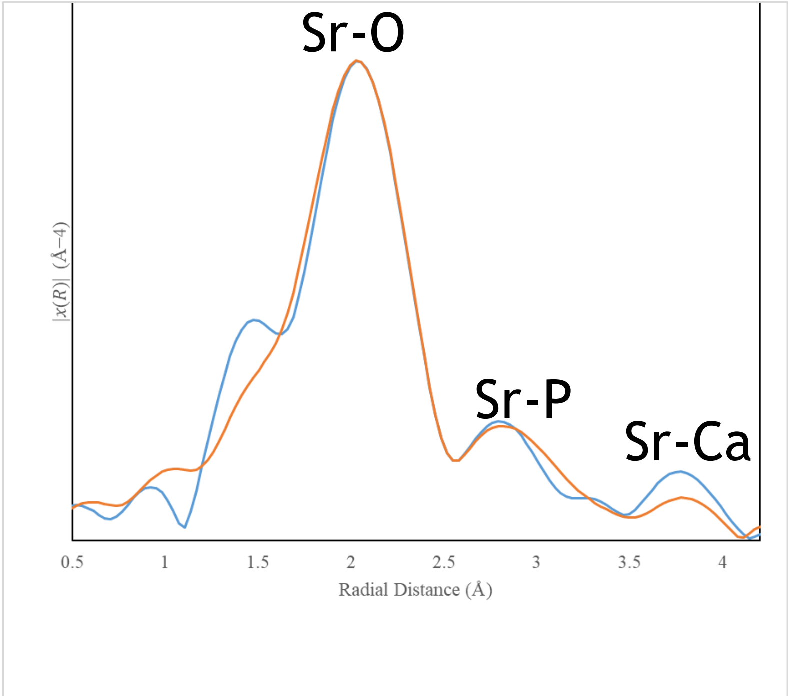


PPQ Sediment Ca-citrate/Na-phosphate
[Sr] / mM
[Ca] / mM
[PO4] / mM
[Citrate] / mM
Time / Days
PPQ Sediment Soprtion Control
1 mM Ca, 2.5 mM Citrate and 10 mM phosphate
5 mM Ca, 12.5 mM Citrate and 10 mM phosphate
EDX
(c)
Counts
Si Kα
Al Kα
O Kα
P Kα
K Kα
Ca Kα
Fe Kα
Sr Kα
Energy / KeV
Sr-O
Sr-P
Sr-Ca
|χ(R)| (Å−4)
Radial Distance (Å)
SEM
HV 30.00 kV
spot 6.0
det CBS
mag 25 000 x
HFW 16.6 µm
WD 9.8 mm
x: -8.5848 mm
y: -7.9234 mm
pressure 5.01e-1 mbar
3 µm
Quanta 650 FEG ESEM

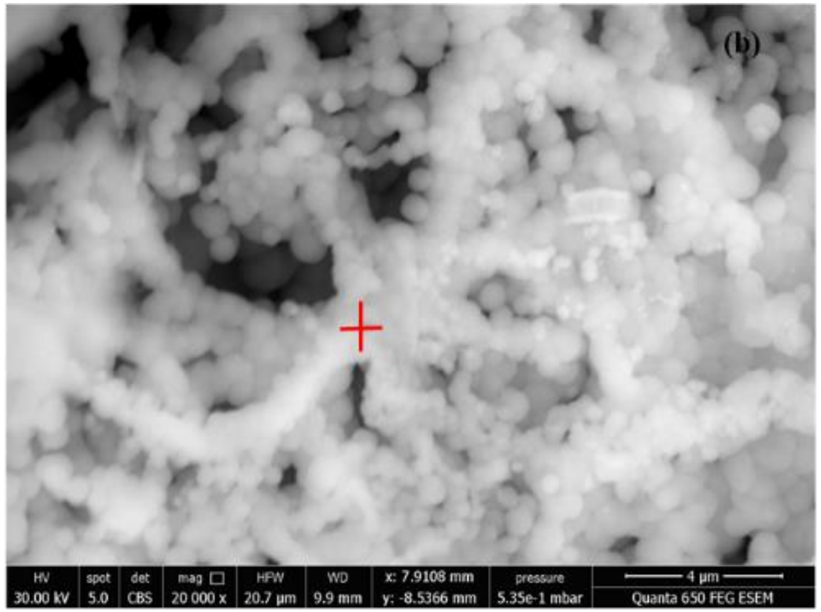


PPQ Glycerol Phosphate Amended
[Sr] / mM
[Ca] / mM
$[PO_4]$ / mM
[Glycerol Phosphate] / mM
PPQ Sediment Soprtion Control
10 mM Glycerol Phosphate
Time / Days

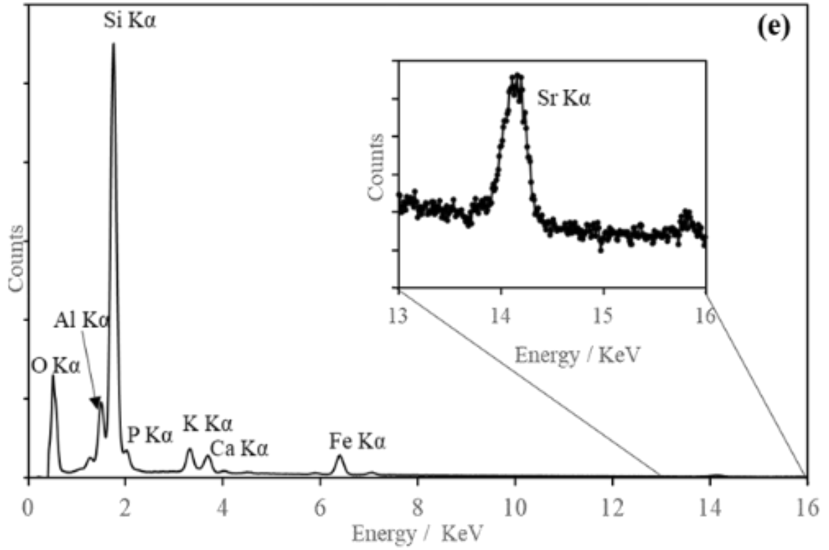
diamond



Sr-O
Sr-P
Sr-Ca
$|\chi(R)|$ (Å−4)
Radial Distance (Å)



(b)
HV 30.00 kV
spot 5.0
det CBS
mag 20 000 x
HFW 20.7 µm
WD 9.9 mm
x: 7.9108 mm
y: -8.5366 mm
pressure 5.35e-1 mbar
4 µm
Quanta 650 FEG ESEM



(e)
Si Kα
Al Kα
O Kα
P Kα
K Kα
Ca Kα
Fe Kα
Sr Kα
Counts
Energy / KeV

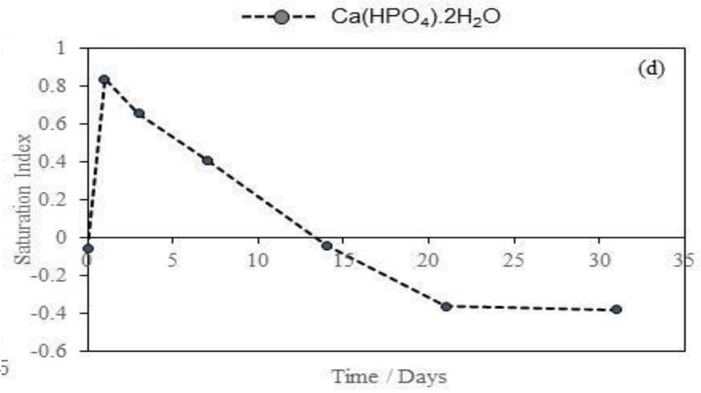
The University of Manchester

Sr Speciation during Mineralisation

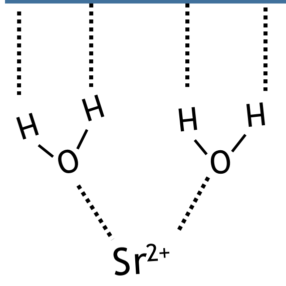
Released into solution

Ca^{2+} PO_4^{3-}

Sr^{2+}



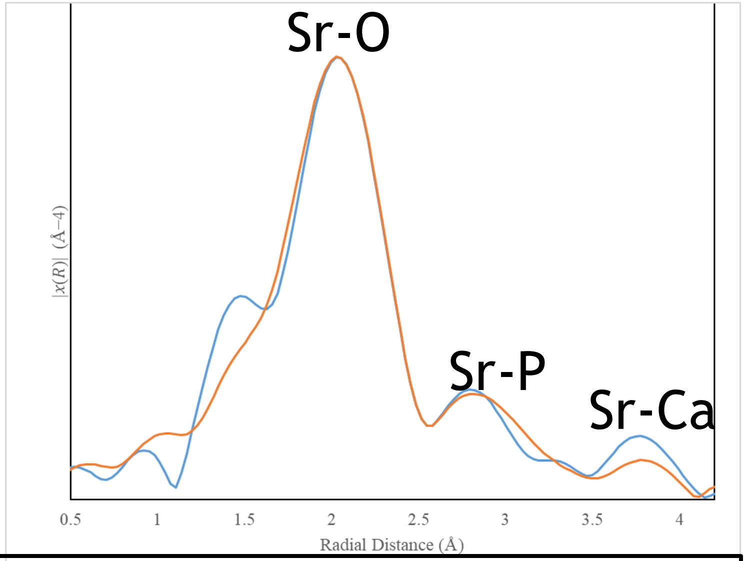
Amorphous Ca-PO_4 Phases



Rapid sorption to Ca-PO_4 phases

Recrystallisation

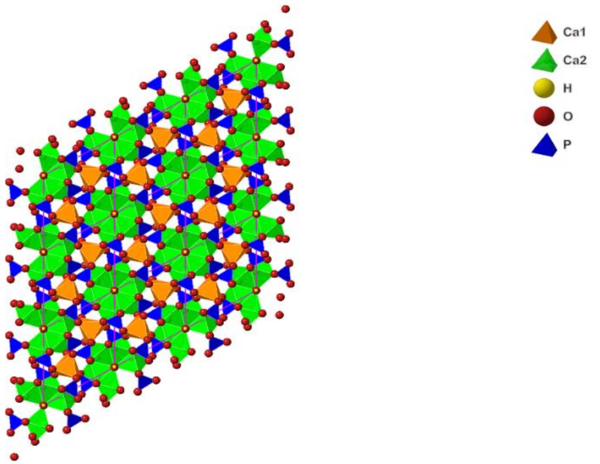
Incorporation into poorly ordered hydroxyapatite-like phase



Crystalline Ca-PO_4 Phases e.g. Hydroxyapatite

Incorporation of Sr^{2+}

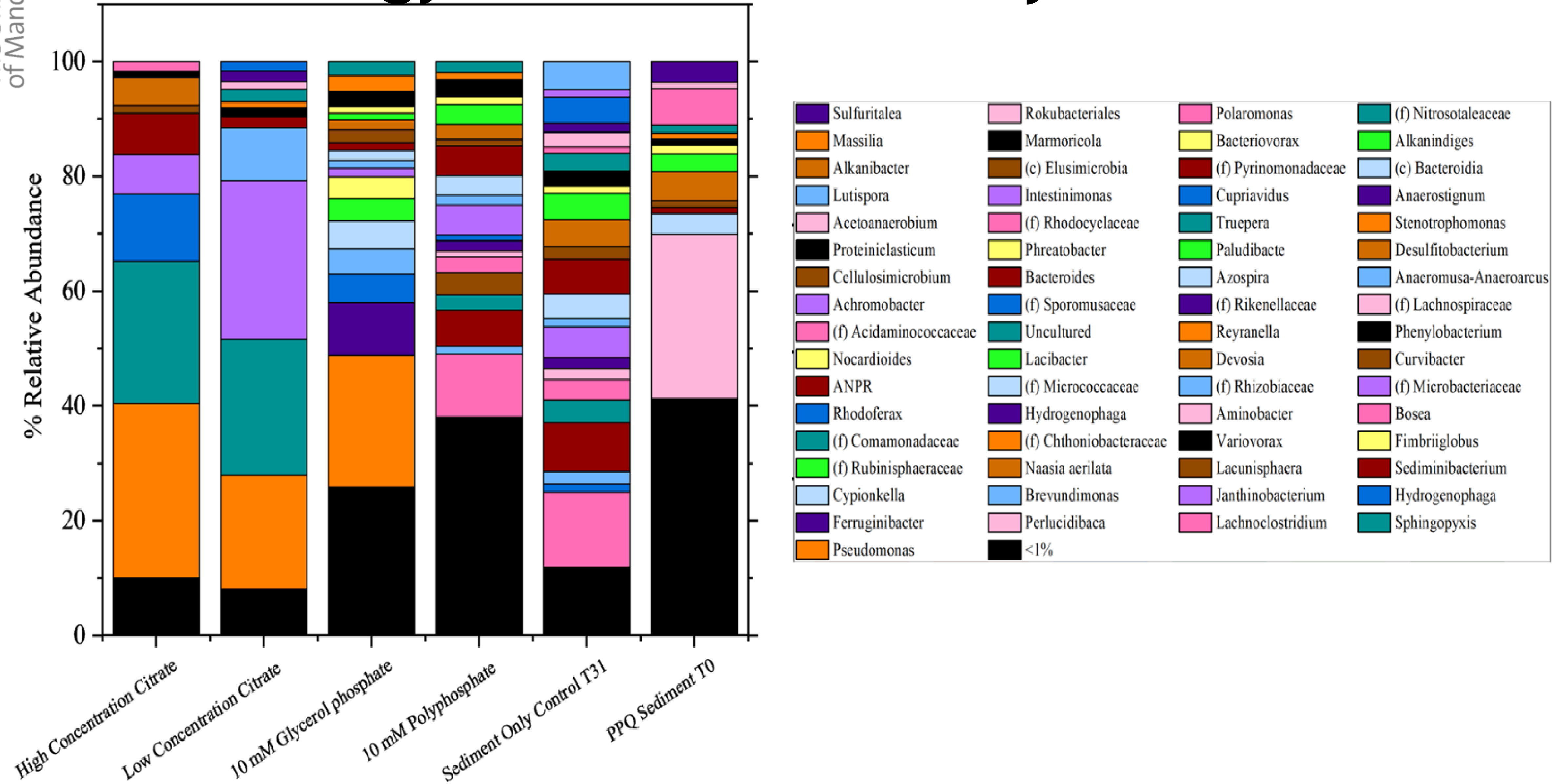
$(Ca_{10-x}Sr_x(PO_4)_6(OH)_2)$



MANCHESTER
1824

The University of Manchester

Microbiology of Sr biomineral systems



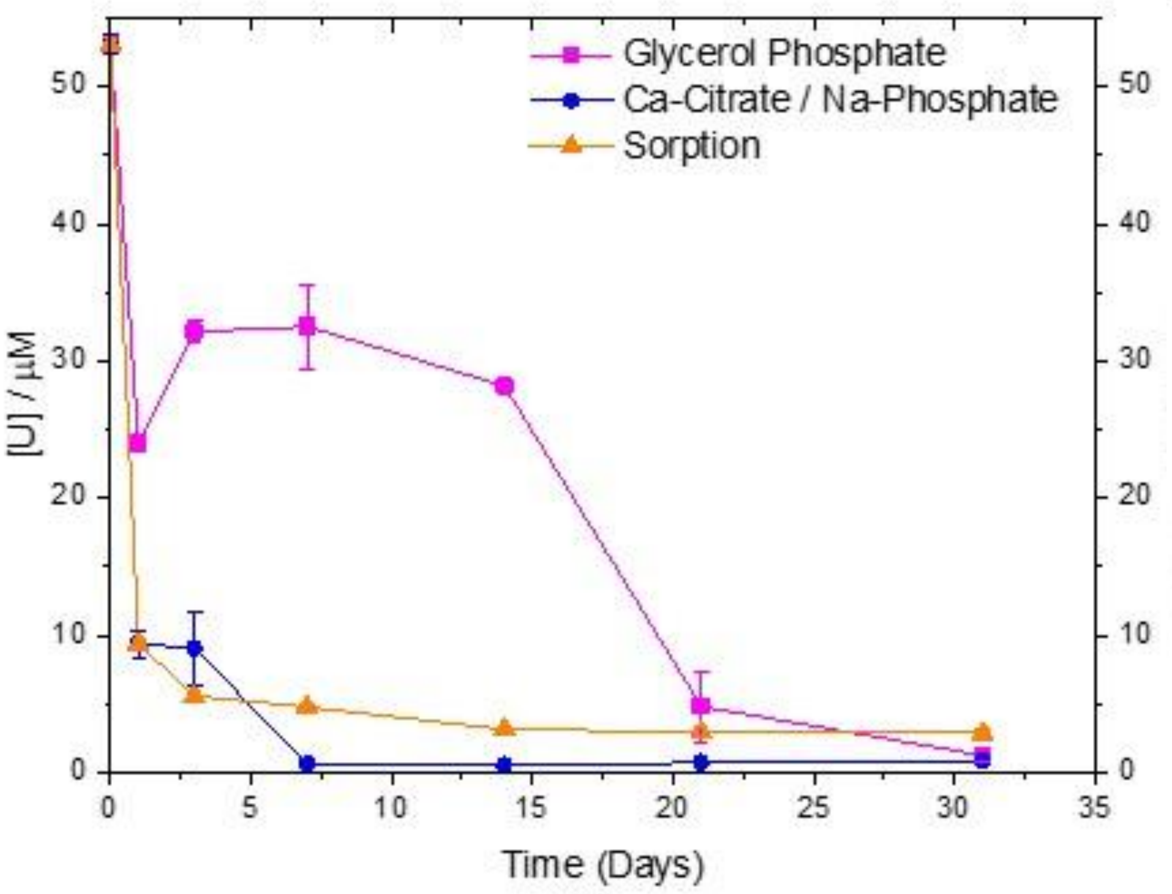
MANCHESTER 1824
The University of Manchester

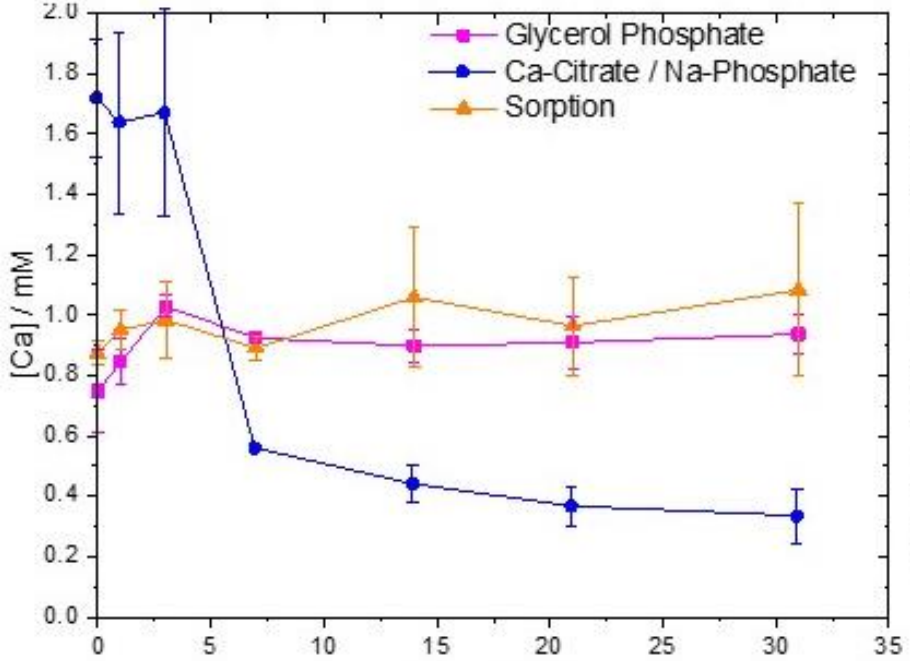
U Bioremediation at Sellafield

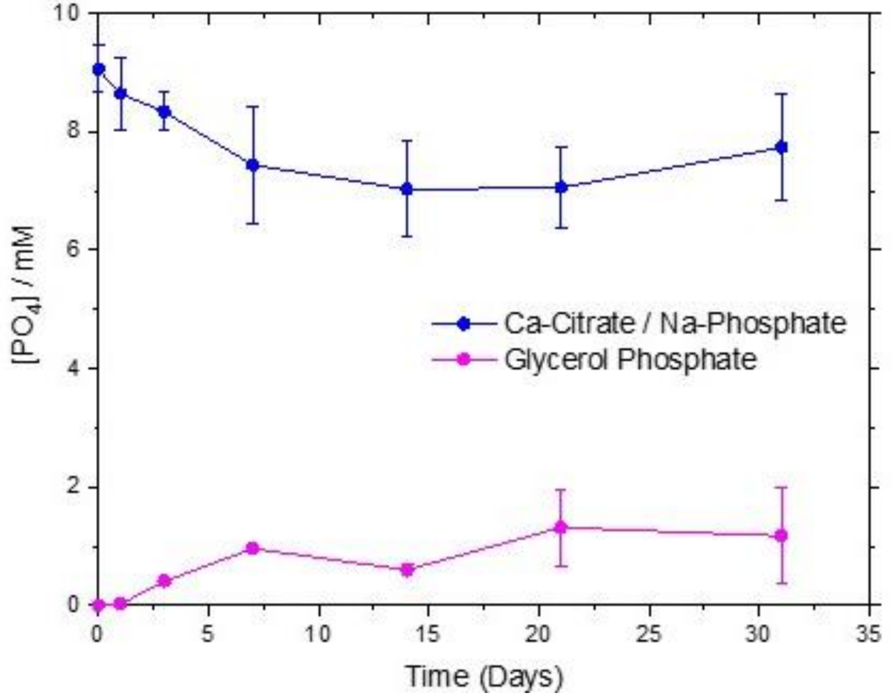
- U mobility in the environment is controlled by pH and redox
- Past work on $U^{(VI)}$ bioreduction using Fe(III)-reducing bacteria [1],[2]
- Sellafield sub-surface has oxic regions and anoxic regions[2]
- Oxic conditions present challenges to redox-driven $U^{(VI)}$ remediation
- Application of in situ phosphate technologies to $U^{(VI)}$ under Sellafield relevant conditions

[1] L. Newsome, K. Morris, D. Trivedi, A. Bewsher, and J. R. Lloyd, "Biostimulation by Glycerol Phosphate to Precipitate Recalcitrant Uranium(IV) Phosphate," Environ. Sci. Technol., 49(18), 11070–11078 (2015).
[2] L. Newsome, K. Morris, D. Trivedi, N. Atherton, and J. R. Lloyd, "Microbial reduction of uranium(VI) in sediments of different lithologies collected from Sellafield," Appl. Geochemistry, 51, 55–64 (2014).

U(VI) Biomineralisation





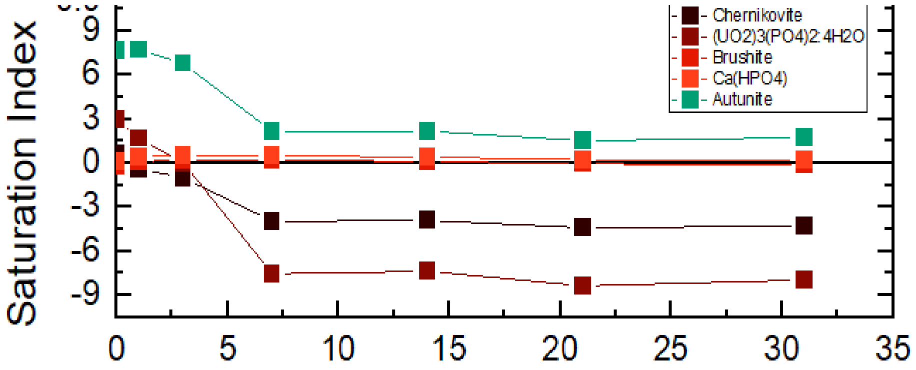


R (A)

U(VI) Phosphate Mineralisation

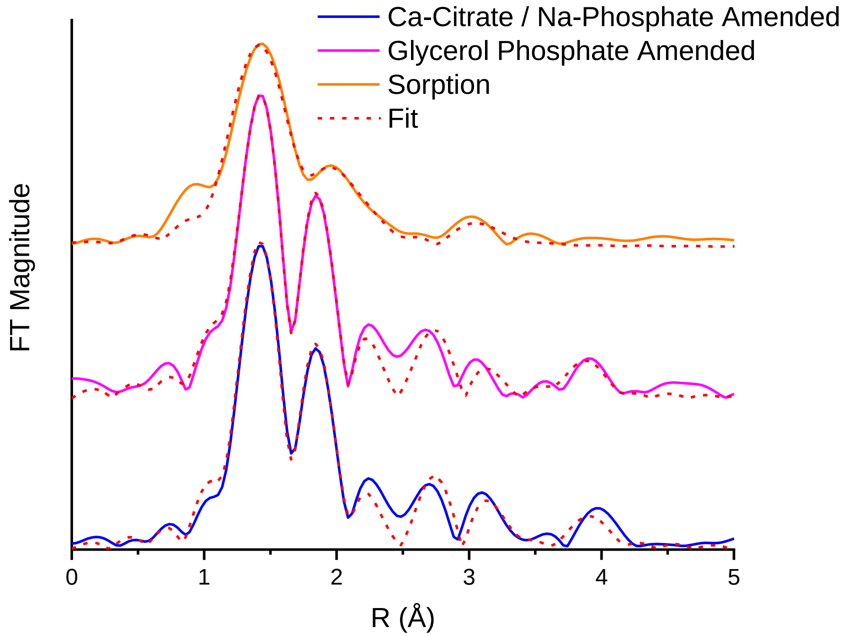
Released into solution

U(VI) PO_4^{3-}



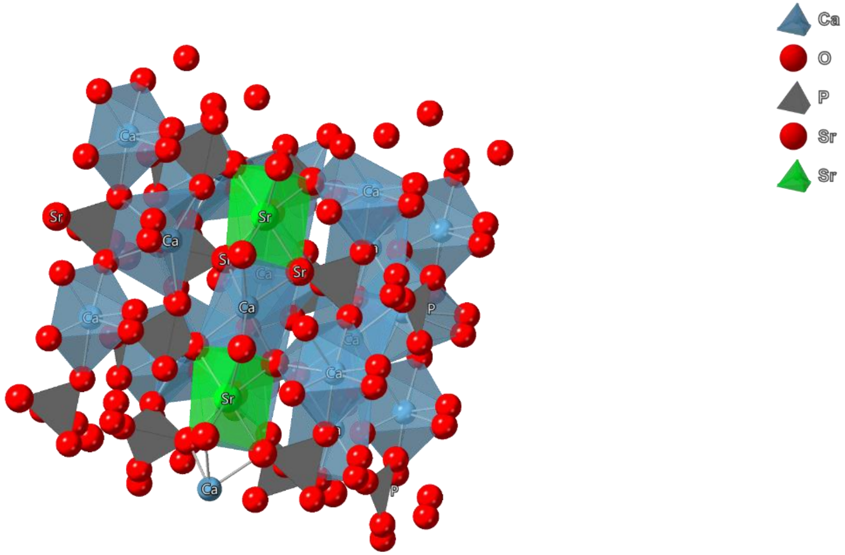
Ca-autunite, Chernikovite and Uranyl orthophosphate are predicted to be oversaturated

EXAFS analysis suggested uranyl orthophosphate is the predominate phase



Summary of Batch Oxic Microcosms

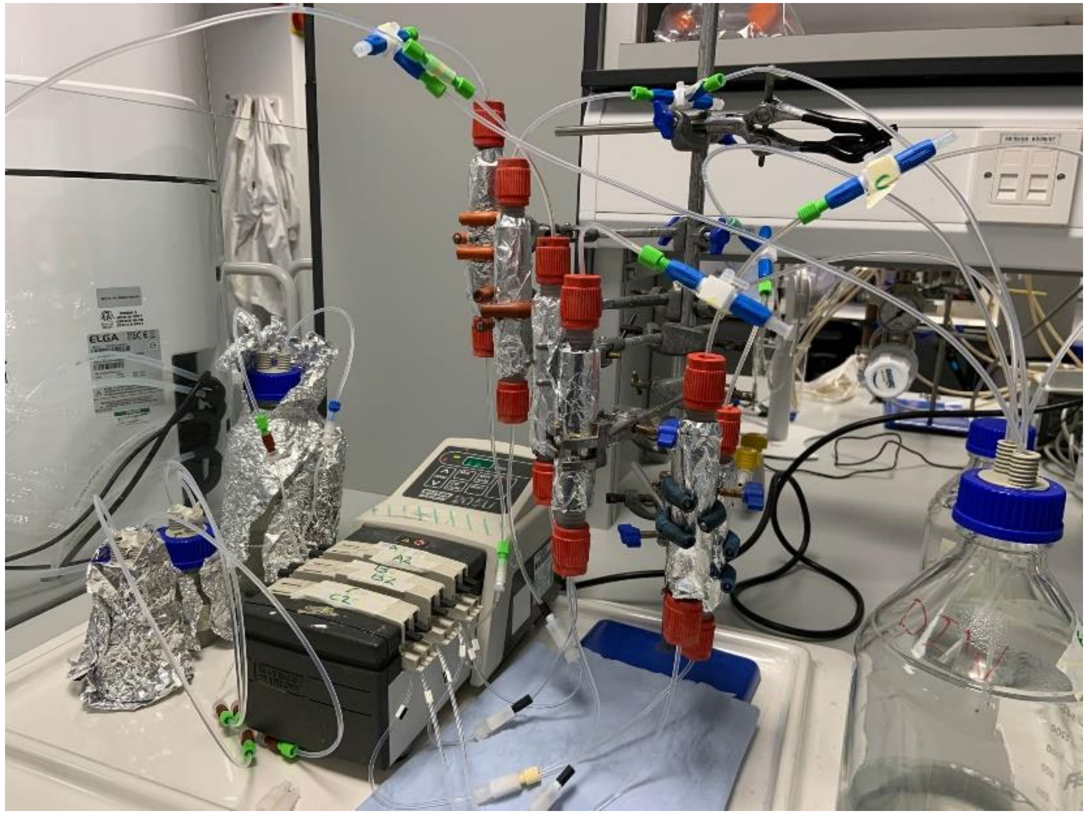
- Ca-Citrate/Na-phosphate highly successful for both U^{VI} and Sr^{2+}
- Glycerol phosphate successful for both U^{VI} and Sr^{2+}
- Sr/U bearing phosphate minerals formed in both treatments



MANCHESTER 1824

The University of Manchester

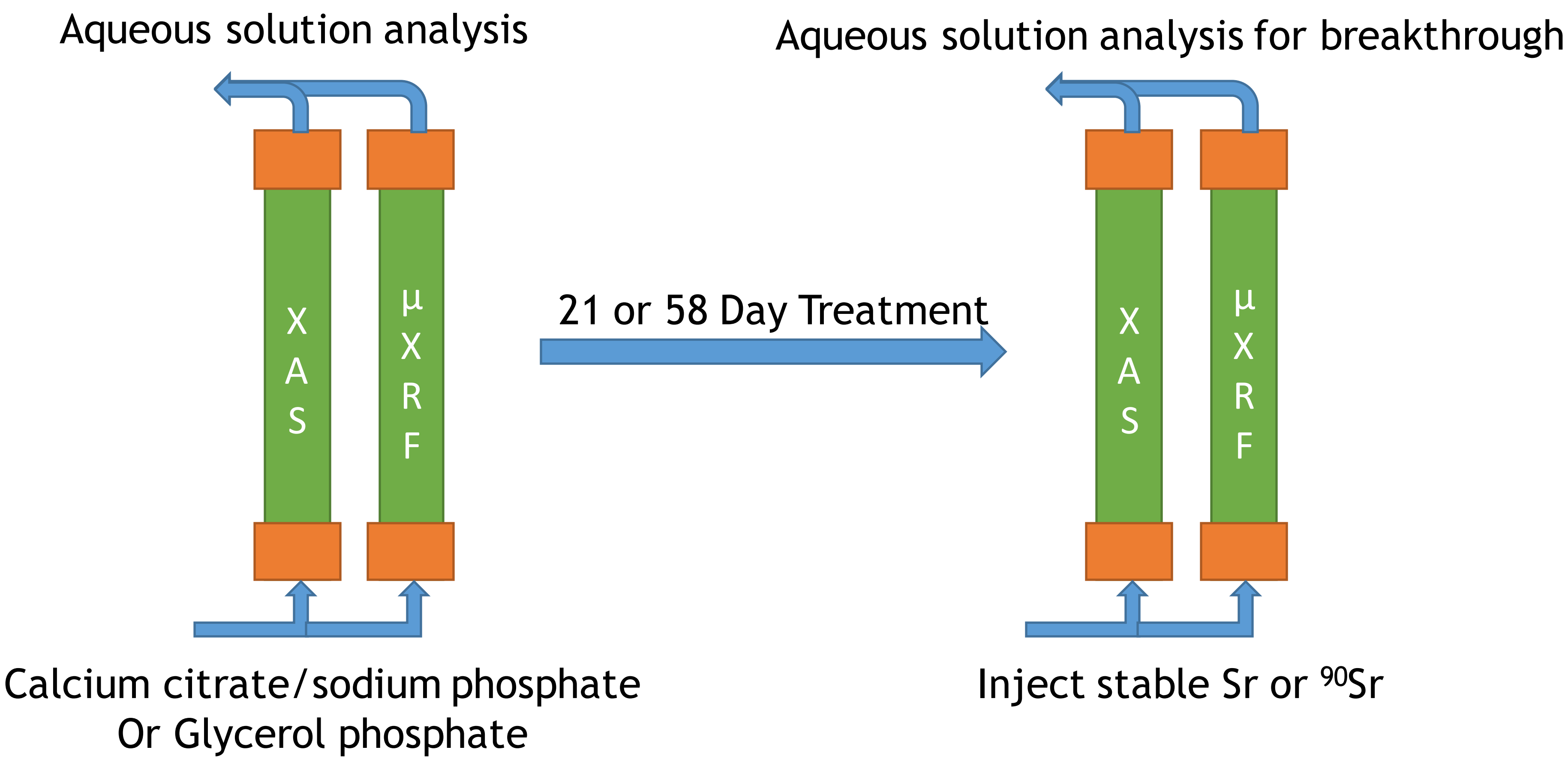
Flowing Column Experiments



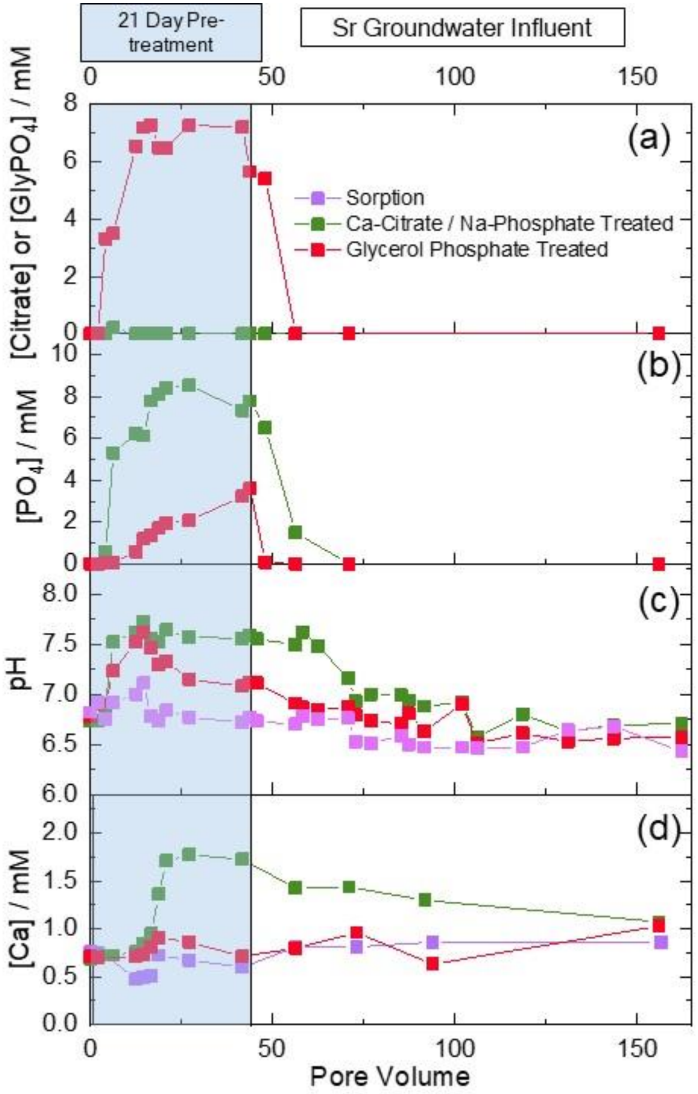
- ➢ Columns enabling ^{90}Sr experiments under flowing conditions
- ➢ Flow regime representative of Sellafield subsurface
- ➢ Treated columns for 21 days with Ca-phosphate amendments:
    - ➢ Calcium citrate/sodium phosphate
    - ➢ Glycerol phosphate

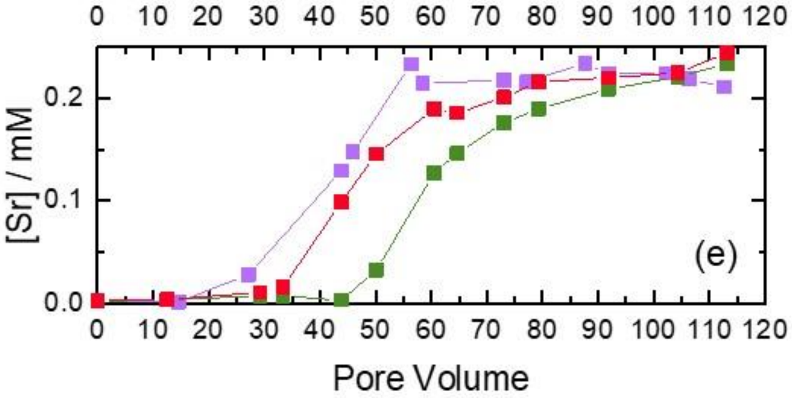
(With a lot of help from Gareth Law and Mallory Ho (Uni of Helsinki) M. S. Ho, G. F. Vettese, K. Morris, J. R. Lloyd, C. Boothman, W. R. Bower, S. Shaw, and G. T. W. Law, "Retention of immobile Se(0) in flow-through aquifer column systems during bioreduction and oxic-remobilization," Sci. Total Environ., 834(February), 155332 (2022). [M. S. Ho, G. F. Vettese, P. H. Keto, S. P. Lamminmäki, M. Vikman, E. Myllykylä, K. Dardenne, and G. T. W. Law, "Mechanisms Governing 90Sr Removal and Remobilisation in a VLLW Surface Disposal Concept," Minerals, 13(3), 436 (2023).

Flowing Column Experiments

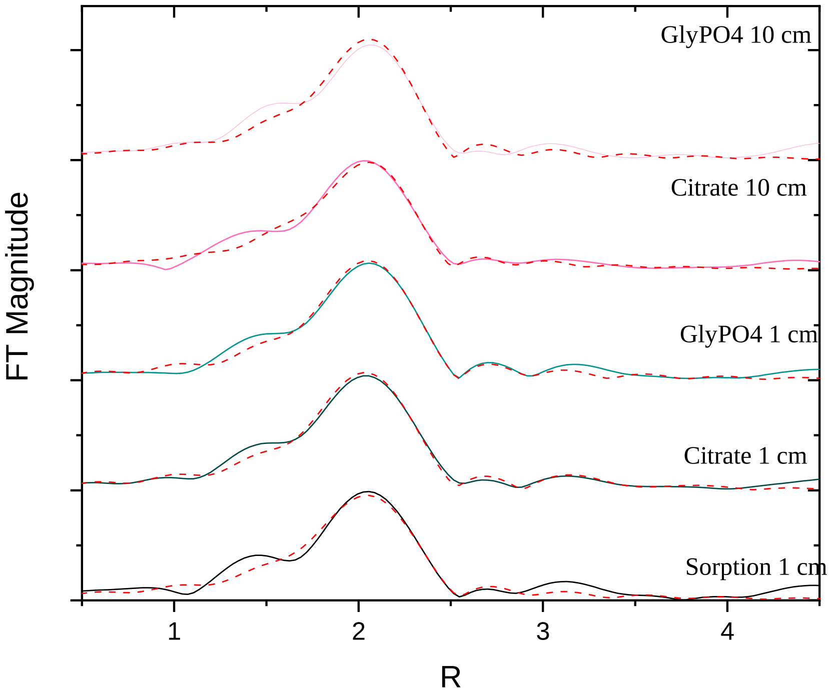


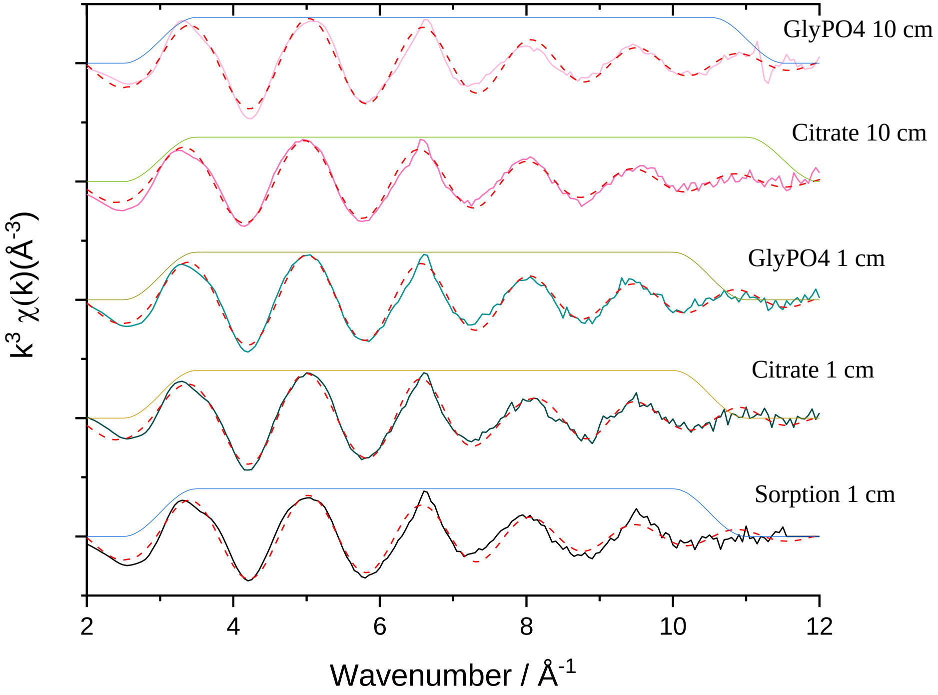
Column Results Stable Sr at 20 ppm





Solid Phase Analysis of Columns



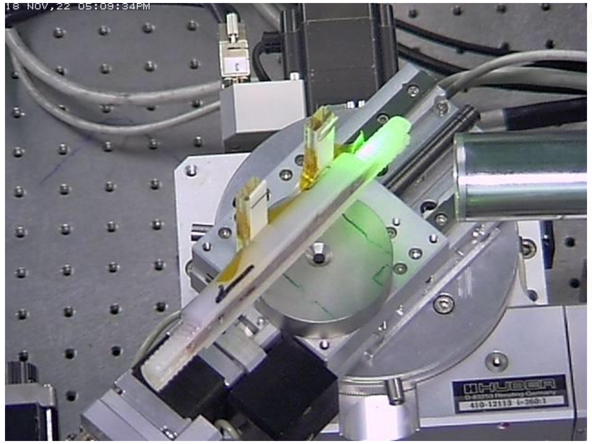


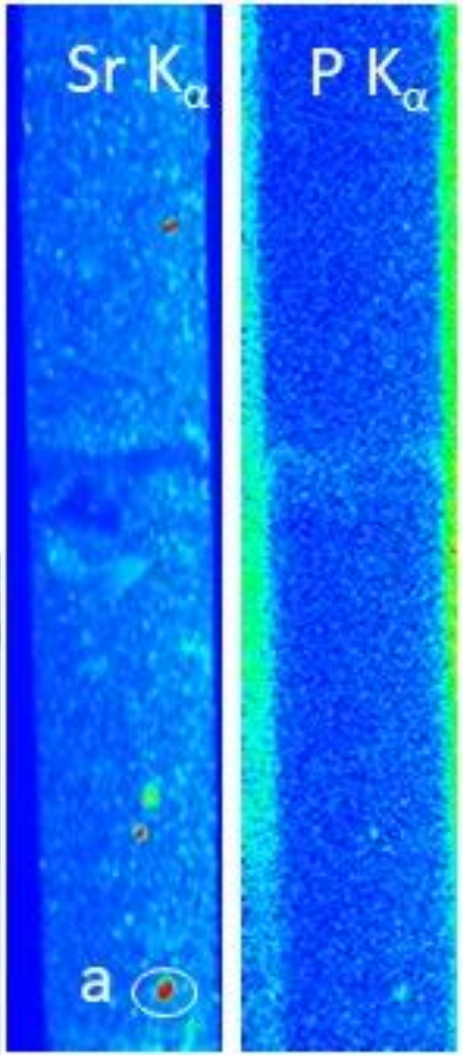
MANCHESTER
1824

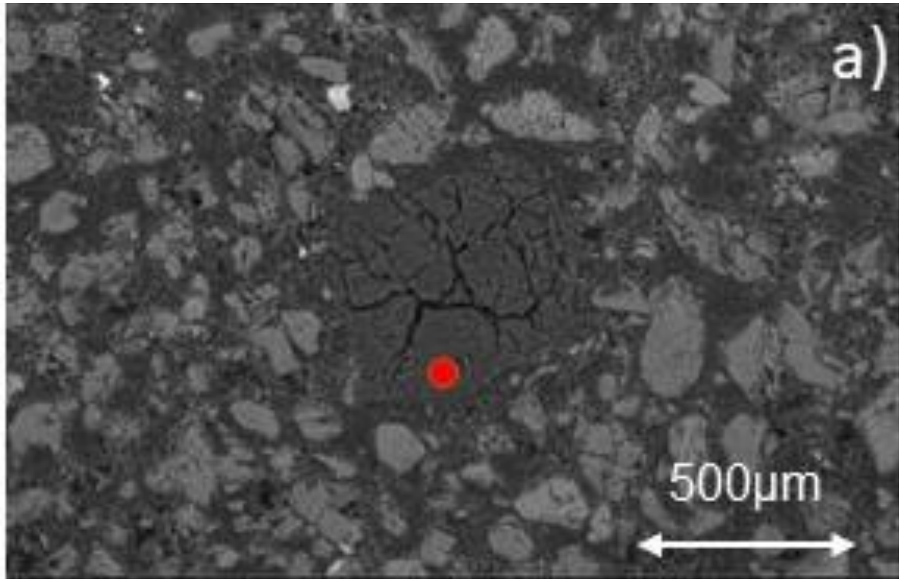
The University
of Manchester

Karlsruher Institut für Technologie

Micro Focus XRF

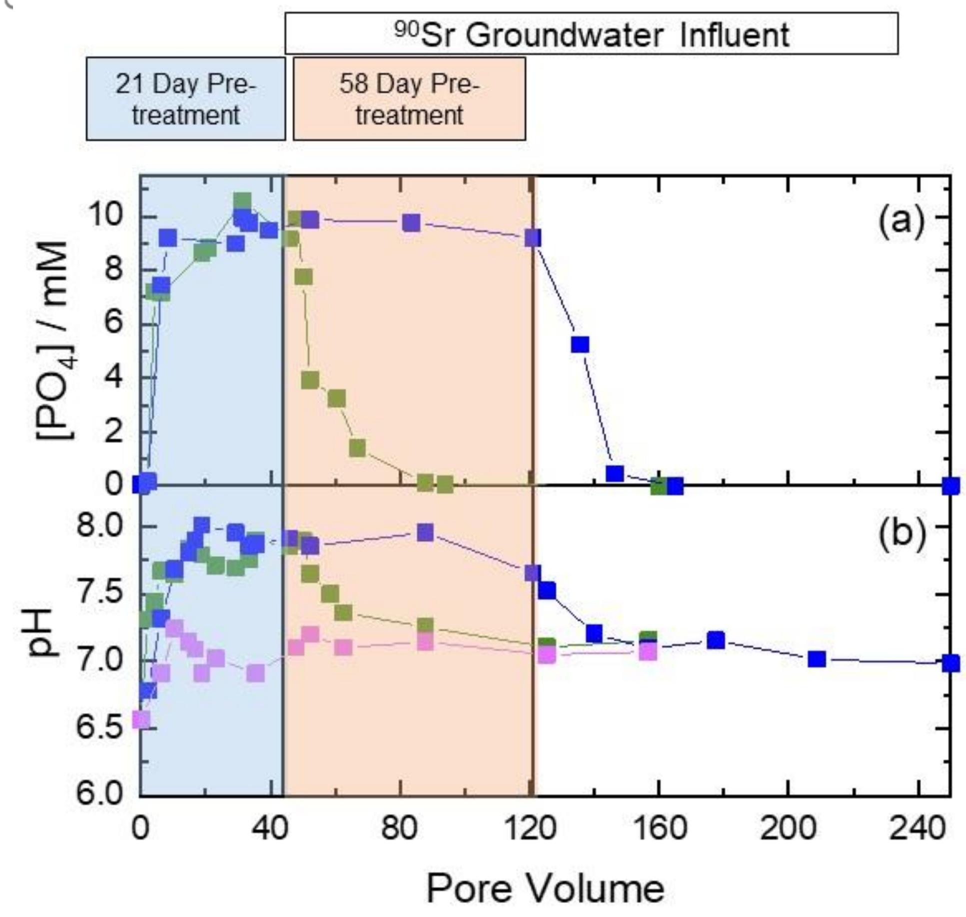


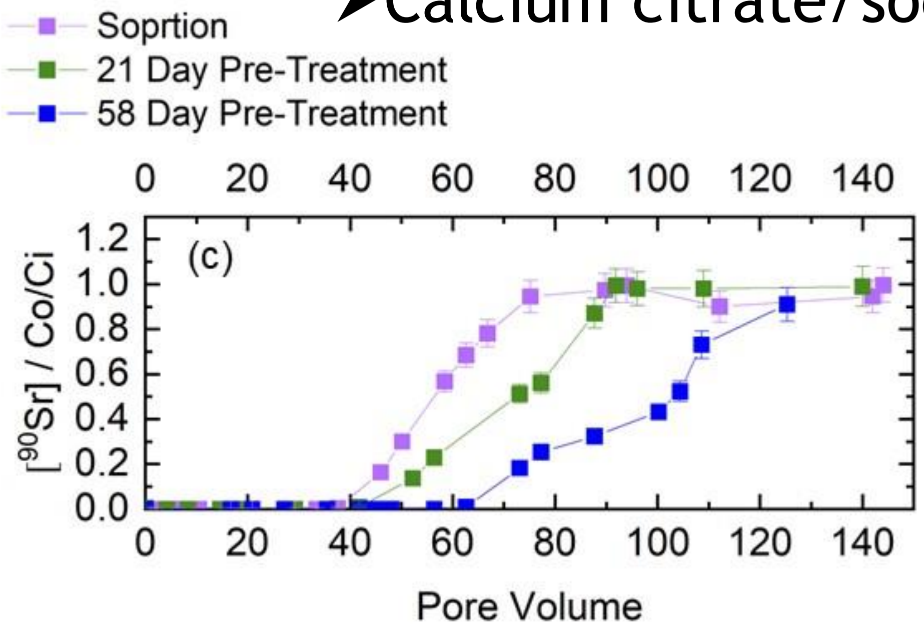




^{90}Sr Flowing Column Experiments

- Pre-treated columns for 21 and 58 days with Ca-phosphate amendment:
  - Calcium citrate/sodium phosphate





Summary of Phosphate Mineralisation Study

- Batch experiments - removal of Sr^{2+} using phosphate biomineralisation (oxic conditions)
- U^{VI} phosphate biomineralisation under Sellafield representative conditions
- Dynamic flowing column study - ^{90}Sr sequestration via in situ phosphate biomineralisation

MANCHESTER 1824

The University of Manchester

Thank You for Listening

Acknowledgments-

Prof Katherine Morris

Prof Sam Shaw

Prof Jonathan Lloyd

Dr James Graham (National Nuclear Laboratory)

Dr Lewis Hughes (SEM)

Dr Jörg Rothe (KIT)

Dr Kathy Dardenne (KIT)

Manchester Geomicrobiology Group

NATIONAL NUCLEAR LABORATORY

KIT Karlsruher Institut für Technologie

NNUF National Nuclear User Facility

UKRI Engineering and Physical Sciences Research Council

diamond

NNUF RADER