



Roinn Cumarsáide,
Fuinnimh & Acmhainní Nádurtha
Department of Communications,
Energy & Natural Resources



**Geological Survey of Ireland Research Programme
- Short Call 2015, Final Report -**

Name of Lead Investigator	Liam Morrison
Email	Liam.morrison@nuigalway.ie

Organisation name	National University of Ireland, Galway (NUIG)
Organisation type:	☒ HEI ☐ Public Sector (other) ☐ Private Sector
Department/section	Biogeoscience Research Group, Earth and Ocean Sciences and Ryan Institute

Project Title	Developing a rapid, low cost bathymetric survey methodology using multi-resolution imagery
Contract No.	2015-sc-028



2. Project information:

Title of project	Linking sources of contamination of groundwater resources with naturally occurring arsenic in meta-sedimentary rock in Ireland
Did you make any formal amendment to the project workplan / budget?	☐ yes ☒ no If yes, please specify:

Project Report (max 1500 words, excluding figures and headings):

(i) Objectives and scientific/engineering targets beyond the state of the art

Mineralogical controls on elevated As within an aquifer in Co. Louth were investigated from two 200 m bedrock cores, drilled by the GSI. The cores were logged and key targets for potential mineralogical sources of arsenic were identified by the collaborators jointly (Fig. 1). The Feede core was found to be comprised of felsic units with intrusive basalts and hornfelsed sediments, whereas the Faughart core was made of un-metamorphosed greywacke sediments with minor basaltic intrusive. This has added some level of detail to the geological bedrock understanding in the area, which has remained relatively simplistic until now. Both cores were logged and digitised graphic logs of each were created (See Appendix 2).

Sulfide minerals were identified within calcitic veins in the Faughart core, up to 1 cm diameter, (Fig. 2). These were identified as the most likely direct mineralogical sources of arsenic. Focus, however, has also been given to identifying processes such as adsorption and secondary mineral precipitation, which may attenuate, transform, concentrate or disperse contaminants. Iron oxyhydroxide coated and altered fractures were identified in the Feede core between 50 -75 m depth, (Fig. 3). These are concordant with the well depths in the area and which may represent potential sinks of arsenic, from which it is then mobilised into the groundwater. A select sample of these fractures were collected and were sealed with epoxy resin for analysis across the fracture, to directly study the processes occurring at the water-rock interface.



Figure 1. Selected images of project collaborators during sample identification and core logging at the GSI Core Store.



Figure 2. Selected images of sulfide minerals within fault gouge material containing micro-veins of calcite (left) and within individual calcite veins (right) at 54 m and 27 m depths of the Faughart core respectively.

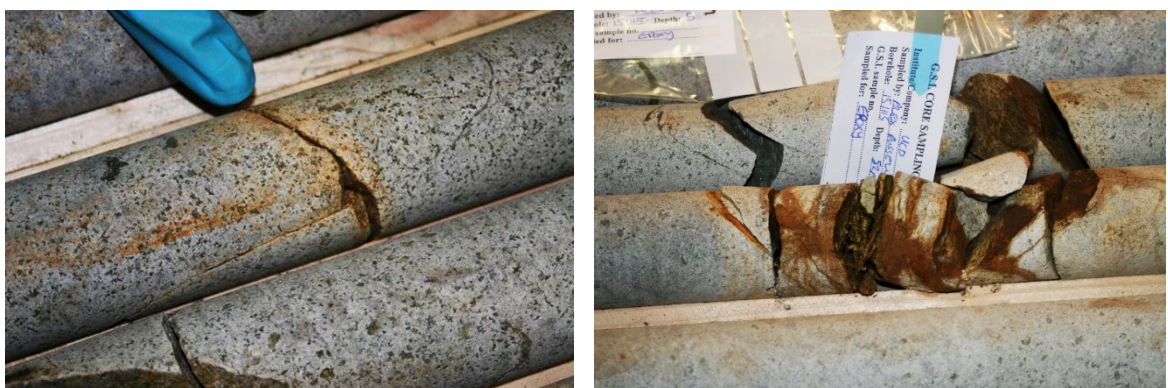


Figure 3. Selected images of iron-oxyhydroxide alterations along fractures between 50-75 m depth in the Feede core, showing direct water-rock interactions.

Analysis has been completed or is currently underway to identify the relationship between As and these mineralogical sources and/or sinks using a variety of methods. Bulk chemistry across all of the major lithologies is being analysed by acid-digestion coupled with Inductively Coupled Plasma Mass Spectrometry (ICP-MS). In addition to this X-Ray Diffraction (XRD) at Trinity College Dublin is being applied to identify mineralogical controls, including potential iron-rich clays in the altered fractures which may attenuate arsenic. Initial desktop Scanning Electron Microscopy (SEM) coupled with Energy-dispersive X-ray spectroscopy (EDS) work at UCD has suggested no arsenic is associated with the sulfide minerals present, (Fig. 4). However, continued work with a more powerful SEM at NUIG is now targeting a larger range of samples, and is particularly being applied to study the geochemistry across the iron-oxyhydroxide fractures. Transmission Electron Microscopy (TEM) is also underway on these same fractured areas for an additional level of detail.

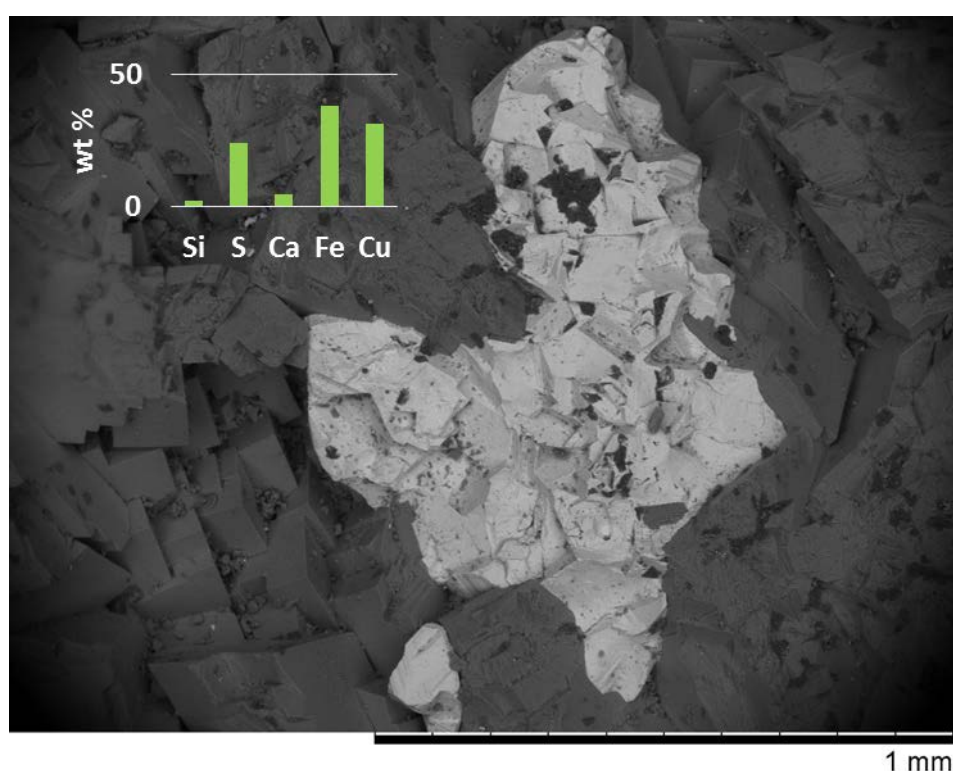


Figure 4. Scanning Electron Microscope (SEM) image of a sulfide mineral within a calcite vein in the Faughart core. Semi-quantitative initial EDS analysis suggests no arsenic is associated to the sulfide minerals, however, more detailed analysis may highlight arsenic presence.

Once all of the resulting geochemical and mineralogical data have been collated, they will be added to a GIS database, and interpreted alongside existing hydrochemical data to aid in the interpretation within a geological framework of As and metal concentrations in groundwater supplies on a regional and national level. This is the first such study in Ireland, and is applicable at an international level where the true extent of geogenic contamination within groundwater systems is only just becoming clear.

(ii) Implementation (including reference to timelines, milestones, management)

See Gantt Chart for timeline breakdown.

The administrative aspects of the project including management of finances and budget reporting were handled by Liam Morrison at the Ryan Institute (NUIG). A Project Management Team was formed within the first month of the project, consisting of Liam Morrison, Alex Russell and Frank McDermott to ensure project deliverables were progressed. An initial assessment and detailed logs of the two 200 m bedrock cores alongside an initial desk study were undertaken by PhD student Alex Russell, during March-April 2016, before samples could be collected. Subsequently to this a sampling strategy was devised, including collaboration with GSI industry partner Natalya Hunter Williams. Probable mineralogical sources of arsenic were identified and samples were collected during May 2016. Delays arose in regards to the sampling and logging of the cores due to time conflicts between the availability of Alex Russell and the limited accessibility to the GSI Core Store, as such the original implementation plan was offset.

An initial round of representative thin sections were made by Tom Culligan (UCD) in July 2016, of potential arsenic sources. This was followed by thin section preparation of all major lithologies and features sampled from the cores (August 2016). Petrographic microscopy was carried out on all of the thin sections throughout July-September 2016. Preparations for bulk chemical analysis of 44 samples were then undertaken between September-November 2016, using the rock preparation facilities at UCD. Powdered samples were sent for bulk analysis by Inductively Coupled Plasma Mass Spectrometry in November 2016. Scanning Electron Microscopy and TEM will be completed in December 2016.

Regular meetings were held between the joint research groups and industry partner (NUIG, UCD and GSI) to monitor progress and discuss findings. Meetings (over phone) between the Project Management Team occurred on a minimum of a bi-weekly basis. The outputs from this collaborative research were disseminated at the GSI Geoscience 2016 conference via three posters, one for the GSI poster sessions and a further for the iCrag poster sessions also present at Geoscience 2016 and also at the Ryan Institute Research Day in NUIG (December 2016). Plans are in place for further dissemination of the findings through a presentation at the international geochemistry conference Goldschmidt in summer 2017. This will be accompanied by the submission of a manuscript to an international peer-review journal such as *Geochimica et Cosmochimica Acta* (GCA).

[illegible]

[illegible]

(iii) Outputs (please use bullet points)

Impact/value of the project (Max 500 words):

1. Scientific Discovery and Training

2. New methodologies to Inform Policy and Governance

An improved understanding of the As mobilisation processes will help formulate policies to prevent the conditions that result in As mobilisation (e.g. avoidance of deep wells, no contamination that results in de-oxygenation of the recharge zones). The project will provide vital information on sources of arsenic and metals in groundwater informing water sampling strategies (adaptive monitoring) including for exempted supplies – e.g. in areas with bedrock suspected of high As (or other metals), which can be selectively target for As sampling, determination and field verification. Therefore saving money for the exchequer, companies and individuals. This will aid the state in meeting its obligations under European Directives such as the WFD (2000/60/EC), the Groundwater Directive 2006/118/EC, Marine Strategy Framework Directive (2008/56/EC) and the Habitats Directive (92/43/EEC).

3. Positive Societal Impact

The project has the potential to directly benefit public health and quality of life of Irish society in relation to groundwater fed public drinking water supplies, group schemes and private wells, especially where the issue seems more apparent with small abstractions. The Irish Governments' framework document, 'Our Sustainable Future (2012) provides a framework for Sustainable Development, setting out 70 measures in a range of environmental, economic and social areas required to drive sustainable development. The Framework addresses areas central to this proposal including the conservation and management of natural resources and the securing of health and wellbeing.

4. Communications and Dissemination

The results of this project have been disseminated to the wider scientific community via one national and conference and will be further disseminated via an international conference in 2017 and via publication in an international peer reviewed journal (already in preparation –Dec 2016). The results of this project will also be made available and used as part of general outreach activities in the Ryan Institute at NUI Galway (which showcased environmental, marine and energy research activities to > 50,000 members of the general public in 2013).

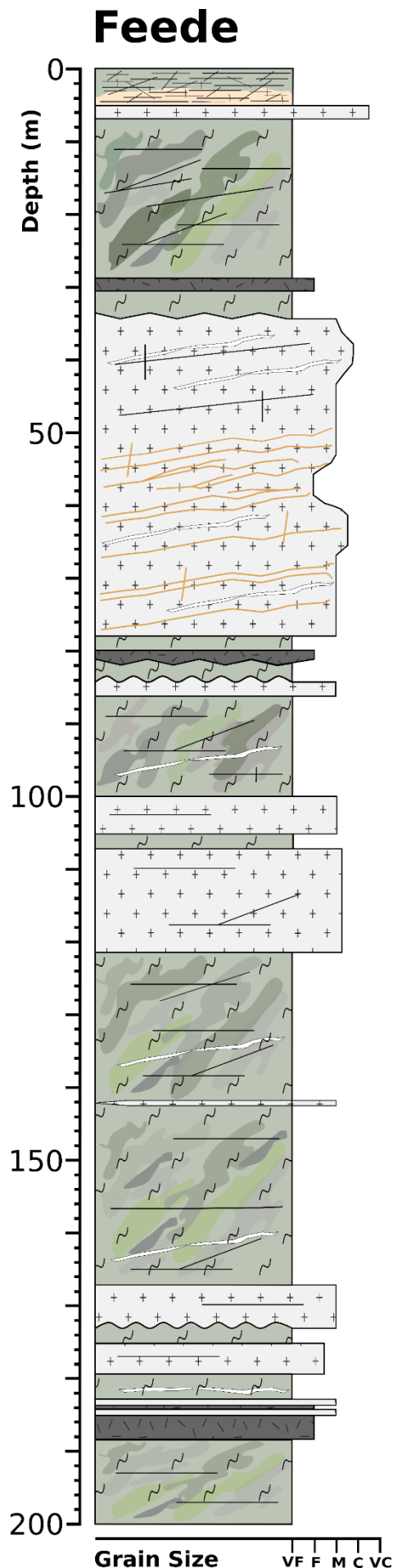
Appendix 1 – Publications & Presentations:

[Proposed Journal Manuscript Title] Russell, A. W., Morrison, L., McDermott, F. Daly, E., Henry, T., Hunter Williams, N. (2017) Arsenic groundwater contamination in North-East Ireland; identifying potential sources and sinks of arsenic. *Geochimica et Cosmochimica Acta*...

[Planned Conference Publication Title] Russell, A. W., Morrison, L., McDermott, F., Daly, E., Henry, T., Hunter Williams, N. (2017) Identifying sources of arsenic within a contaminated aquifer of North-East Ireland. Goldschmidt 2017, Paris.

Appendix 2 – Any additional information not included above:

- (i) Graphic log of the Faughart core (221 m), recovered from Co. Louth, comprised of greywacke sediments, red-mica greywacke layers and minor basaltic intrusives.
- (ii) Graphic log of the Feede core (200 m), recovered from Co. Louth, comprised of granophyric granites with hornfelsed meta-sediments and basaltic intrusives.



Key (Feede)

- Metasediments -**
Hornfelsed sediments with epidote
- Basalt -**
Fine grained intrusive with sharp contacts
- Granite -**
Granophyric textures with varying crystal sizes
- Veins -**
Primarily calcitic, with occasional quartz
- Fractures -**
Horizontal to moderate dip. Iron oxide rims present (orange)

Appendix 2.2

Graphic log of the Feede core (200 m), recovered from Co. Louth, comprised of granophyric granites with hornfelsed meta-sediments and basaltic intrusives.

Aoife, Braiden

From: Morrison, Liam <liam.morrison@nuigalway.ie>
Sent: 13 December 2016 17:08
To: GSI Research
Subject: RE: reminder: Short Call report due

Hi Aoife,

Here are the requested details.

(i) Results from SEM/TEM/ICPMS

Bulk chemical analysis of the core using ICP-MS will be completed by December 23rd 2016. Work is continuing on SEM/TEM and final results for each will be compiled into January and February 2017.

(ii) Interpretation of results towards a mechanistic understanding of As and metal sources to groundwater & (iii) Indication how this will inform monitoring strategies & template for other As-affected regions

Once ALL results have been compiled, they will then be interpreted with the aim of understanding where arsenic and trace metals may be occurring mineralogically in the area. Coupled with hydrochemical data, from previous studies, including information on parameters such as Eh, pH, DO and conductivity the mobilisation methods by which arsenic goes from source/sink and into the groundwater aqueous environment can be fully understood. This can then be compared at both a local and international level to provide insights into why arsenic may be occurring within groundwaters. Where similar geologies occur, which is certainly the case in Ireland, the findings of this study will be able to directly inform, based on hydrochemical and lithology, the likely sources and mobilisation processes of arsenic or other trace metal contaminations. The inclusion of hydrochemical data will therefore help with monitoring strategies as should Eh vs. pH be the controlling factor then this should take priority in terms of potential monitoring elsewhere.

(iv) Demonstration of the application of techniques in Ireland to investigate arsenic and metals sources and pathways

The findings of this project will be directly continued within the work of the PhD student, Alex Russell, whose project sets out to directly investigate occurrences of arsenic within Irish groundwaters and then understand the processes which have led to its occurrence.

Best wishes,
Liam.

From: GSI Research [mailto:GSIResearch@gsi.ie]
Sent: 08 December 2016 16:29
To: Morrison, Liam <liam.morrison@nuigalway.ie>
Subject: RE: reminder: Short Call report due

Hi Liam,

We have gone through your report. Could you please provide the following (or details about when they will be delivered) – these are from your original planned outputs;

- Results from SEM/TEM/CPMS
- Interpretation of results towards a mechanistic understanding of As and metal sources to groundwater
- Indication how this will inform monitoring strategies & template for other As-affected regions

- Demonstration of the application of techniques in Ireland to investigate arsenic and metals sources and pathways

Many thanks,
Aoife

From: Morrison, Liam [<mailto:liam.morrison@nuigalway.ie>]
Sent: 07 December 2016 13:22
To: GSI Research
Subject: RE: reminder: Short Call report due

Dear Aoife,

Please find my report attached.

Best wishes,
Liam.

From: GSI Research [<mailto:GSIResearch@gsi.ie>]
Sent: 07 December 2016 11:16
To: GSI Research <GSIResearch@gsi.ie>
Subject: reminder: Short Call report due

Dear Researcher,

Please remember to submit your final report for your Short Call project and invoice **by tomorrow**. If your Tax Clearance Cert has expired since your last payment please also include a current one.

We cannot process your payment until your report has been approved so please submit these as soon as possible to ensure payment.

Many thanks
Aoife



Dr Aoife Braiden Research Manager

Geological Survey Ireland, Beggars Bush, Haddington Road, Dublin D04 K7X4, Ireland.

T +353 (0) 678 2650 M +353 (0) 87 6790941 E aoife.braiden@gsi.ie www.gsi.ie/research

A division of the Department of Communications, Climate Action & Environment.

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Tá eolas sa teachtaireacht leictreonach seo (agus b'fhéidir sa chomhaid ceangailte leis) a d'fhéadfadh bheith

príobháideach nó faoi rún. Is le h-aghaidh an duine/na ndaoine nó le h-aghaidh an aonáin atá ainmnithe thuas agus le haghaidh an duine/na ndaoine sin amháin atá an t-eolas. Murab ionann tusa agus an té a bhfuil an teachtaireacht ceaptha dó bíodh a fhios agat nach gceadaítear nochtadh, cóipeáil, scaipeadh nó úsáid an eolais agus/nó an chomhaid seo. Más trí earráid a fuair tú an teachtaireacht leictreonach seo cuir, más é do thoil é, an té ar sheol an teachtaireacht ar an eolas láithreach. Deimhnítear leis seo freisin nár aims odh víreas sa phost seo tar éis a scanadh.

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**Geological Survey of Ireland Research Programme
- Short Call 2015, Final Report -**

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Date received:

Ref. No.:

☐ GSI Geoscience

☐ INFOMAR

☐ Tellus

Name of Lead Investigator	Liam Morrison
Email	liam.morrison@nuigalway.ie
Phone number	+353 91 493200 / +353 87 7741806

Organisation name	National University of Ireland, Galway (NUIG)
Organisation type: Sector	☒ HEI ☐ Public Sector (other) ☐ Private
Department/section	Biogeoscience Research Group, Earth and Ocean Sciences and Ryan Institute
Address	School of Natural Sciences, National University of Ireland, Galway, Ireland.

Project Title	Linking sources of contamination of groundwater resources with naturally occurring arsenic in metasedimentary rock in Ireland
Contract No.	2015-sc-028
Total financial support requested from GSI (as per proposal)	€23,091.20

The details presented in this report are a true and accurate reflection of the work undertaken and the associated financial expenditure. All work was carried out within the GSI Terms and Conditions and as per the Contract (unless formally amended).

Signed: _____

Lead Investigator

1. NEW Partner information – (in addition to those named in project proposal)
please copy table as needed:

Co-applicant name	Alexander Russell (PhD Student)
Role in the project	Collaborator
Organisation name	Irish Centre of Research in Applied Geosciences (iCRAG) University College Dublin (UCD)
Organisation type:	☒ HEI ☐ Public Sector (other) ☐ Private Sector
Company Registration No. (if applicable)	
Department/section	School of Earth Sciences
Address	Science Centre, Belfield, Dublin 4

Staff funded by the GSI Short Call Project (add lines if required)

Name	Male/female	Position	Expertise
N/A			

2. Project information:

Title of project	Linking sources of contamination of groundwater resources with naturally occurring arsenic in meta-sedimentary rock in Ireland
Did you make any formal amendment to the project workplan / budget?	☐ yes ☒ no If yes, please specify:

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Figure 1. Selected images of project collaborators during sample identification and core logging at the GSI Core Store.



Figure 2. Selected images of sulfide minerals within fault gouge material containing micro-veins of calcite (left) and within individual calcite veins (right) at 54 m and 27 m depths of the Faughart core respectively.

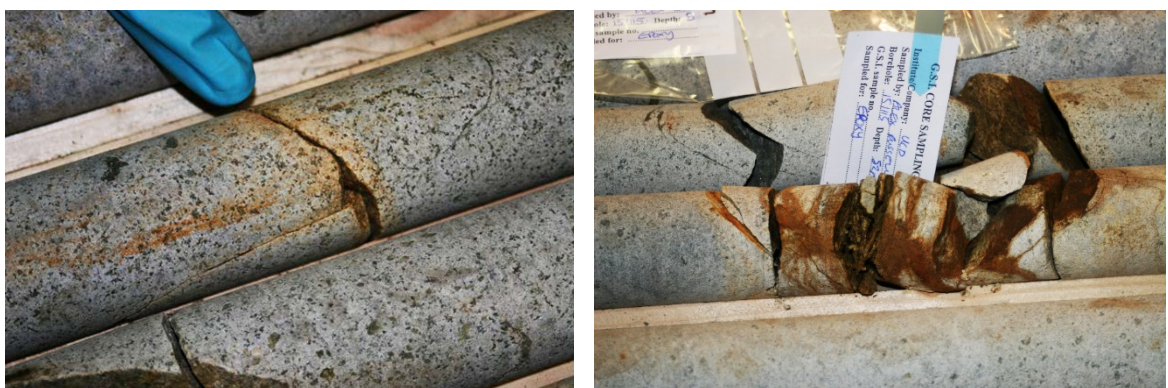


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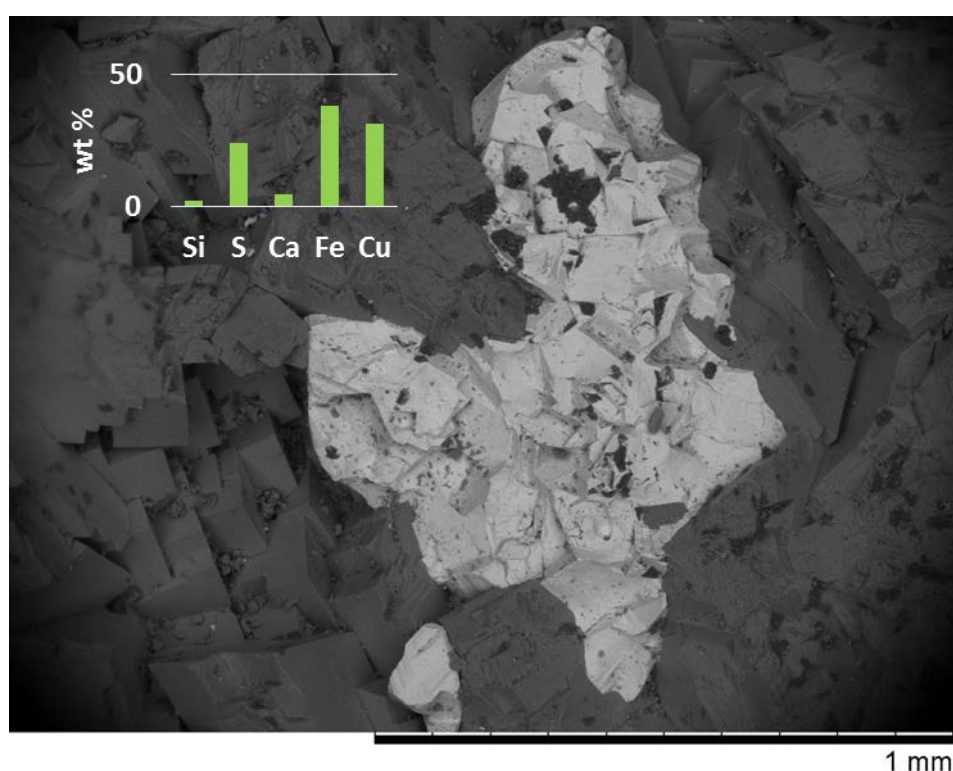


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[illegible]

2. New methodologies to Inform Policy and Governance

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3. Project Expenditure (double click on table below to activate). The GSI reserves the right to request evidence of expenditure if required.

Item	Cost €
Personnel costs	0
Student fees	0
Consumables	14963.34
Travel (incl. Fieldwork)	1622.15
Conferences	511.4
Outreach	89.45
* Funds remaining yet to be spent	3805.61
University overhead	2099.2
Other (please specify..)	0
Total	23091.15
Contribution (cash & in-kind), if applicable	0
Total requested from GSI	23091.15

Explanation of budget deviation, if applicable (max 500 words):

- A balance of €3805.62 remains unspent in the account and is primarily associated with the conferences and outreach budget sections. We would like to ensure the GSI that we intend to spend these funds on activities directly related to the project. This included cost of travelling and presenting the findings of the project at the Goldschmidt conference in Paris in 2017. Registration for this conference will open on January 2017 and we can also arrange flights and accommodation before March 2017. In addition, we would like to use the outreach funds for costs associated with colour publishing in our target journal "Geochimica et Cosmochimica Acta" for the publication of the findings in early 2017.

4. GSI Funding programme

Please provide some comments on the GSI Short Call funding programme (max 500 words):

Positive:

- Good way to fund relatively smaller budget projects, with large applications.

Negative:

- More detailed work and particularly dissemination could have been undertaken (within budget) should the project timing not have been restricted.

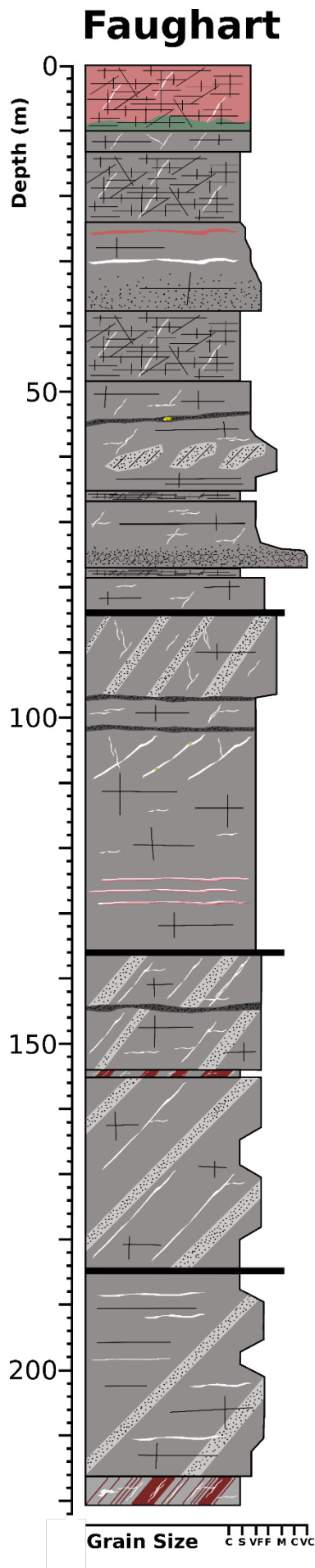
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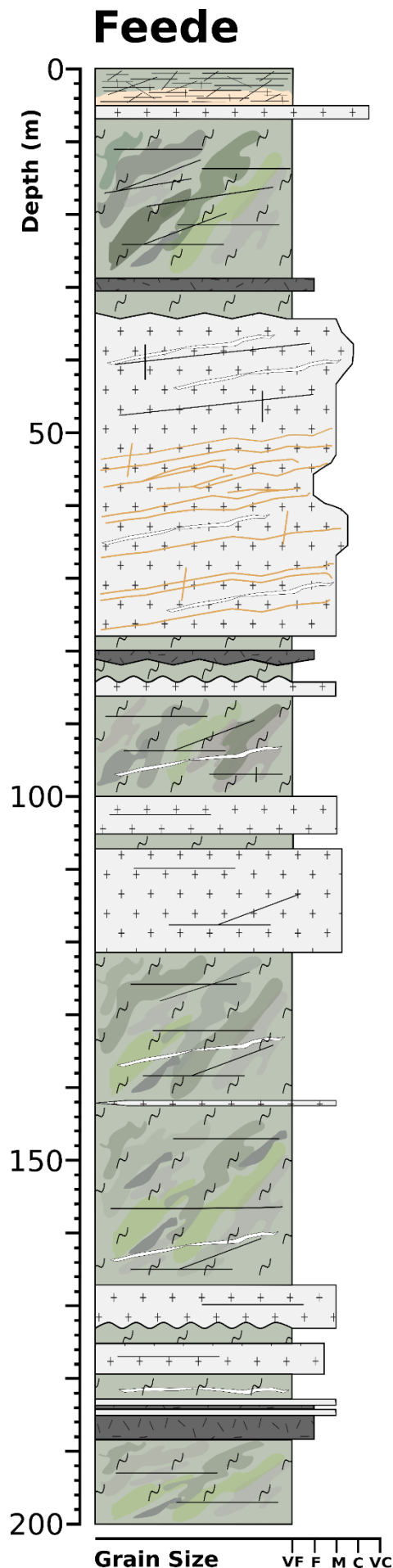


Key (Faughart)

- Basalt -**
Fine grained intrusive with sharp
- Greywacke -**
Matrix supported grey very fine to coarse sands and muds, with occasional steeply dipping beds
- Red-banded Mudstones**
Mm to cm thick steeply dipping beds of
- Fractures -**
Horizontal to moderate dip and near vertical.
- Veins -**
Calcitic, with occasional quartz (white). Red staining present also (red).

Appendix 2.1

Graphic log of the Faughart core (221 m), recovered from Co. Louth, comprised of greywacke sediments, red-mica greywacke layers and minor basaltic intrusives.



Key (Feede)

- Metasediments -**
Hornfelsed sediments with epidote
- Basalt -**
Fine grained intrusive with sharp contacts
- Granite -**
Granophyric textures with varying crystal sizes
- Veins -**
Primarily calcitic, with occasional quartz
- Fractures -**
Horizontal to moderate dip. Iron oxide rims present (orange)

Appendix 2.2

Graphic log of the Feede core (200 m), recovered from Co. Louth, comprised of granophyric granites with hornfelsed meta-sediments and basaltic intrusives.