9. A natural laboratory for critical metals investigations in the Mourne Mountains granites

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Certain metals that are vital for many modern technologies occur naturally in the Mourne Mountains Complex of County Down, Northern Ireland. These include niobium, tantalum and the rare earth elements. Using the Tellus geochemistry data and the results of more detailed sampling, we have investigated their geological sources in granite bedrock and their dispersion in stream sediments. From this research, an exploration methodology has emerged that can assist in the search for critical metals globally. Planned follow-on studies include investigations of the environmental fate of these metals and the potentially toxic elements with which they are naturally associated.

Strategic context

Many new technologies, such as those required for clean energy generation and modern communications, require a wide range of elements in their manufacture. Of particular interest are elements that are used in small quantities but are highly valued for their unusual properties. The mines that produce these economically important metals are mostly located in a few countries where political, social and environmental circumstances could potentially disrupt supply. These technology metals with a substantial supply risk are termed 'critical metals' (Moss *et al.*, 2011). The rare earth elements (REEs) exemplified the concept of criticality when in 2011 China, which controlled 97% of the global REE supply, cut its export quota and caused a shortfall in supply relative to demand (Chakhmouradian and Wall, 2012).

Supply shortages cannot be fully offset by increased recycling due to dispersion of critical metals in the environment, longevity of use in some applications, and manufacturing design and alloying with metals that inhibit separation (Steinbach and Wellmer, 2010; Bloodworth, 2014). Other mitigation strategies include substitution, reduction in use

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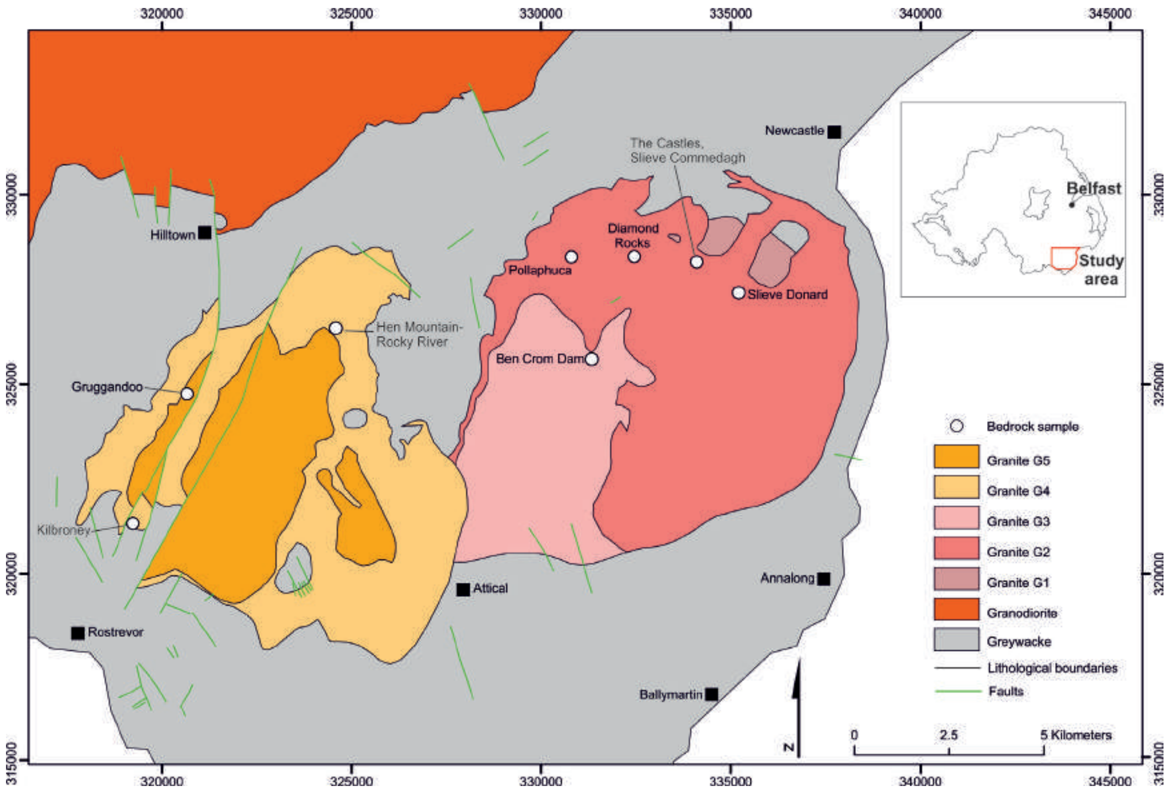

Figure 9.1. Geological map of the Mourne Mountains Complex showing locations of field investigations (and bedrock sampling sites) that were identified using the geochemical anomalies in the Tellus deep soil data. Geological linework based on Hood (1981).

through improved engineering design, development of mines in more stable countries and production as a by-product from existing operations. The Critical Metals Alliance between the British Geological Survey (BGS) and the Camborne School of Mines (CSM) is actively researching the Earth processes that concentrate the critical metals in both established and novel types of mineralisation.

The granites of the Mourne Mountains Complex (Fig. 9.1) in County Down, Northern Ireland are of interest for geological research into critical metal mineralisation because they: (1) have rock compositions related by a subalkaline acid fractional crystallisation trend (Meighan *et al*., 1984) that elsewhere in the world is associated with critical metal deposits; (2) have periodically been explored over the past 30 years for uranium, gold, tin, tantalum and niobium; and (3) are traversed by rivers with alluvial sediments containing minerals that host REE, niobium (Nb) and tantalum (Ta) metals (Moles and Tindle, 2011). There have been no previous investigations of the links between these and other metals and the variations in distribution of the combined metal budgets in the different geological settings found in the Mourne Mountains. The geochemical results of the Tellus survey, combined with knowledge of mineralisation in bedrock, and the availability of new heavy mineral concentrate samples obtained from stream sediments, provide an excellent opportunity to use the Mourne Mountains as a natural laboratory to investigate the primary geological sources of critical metals.

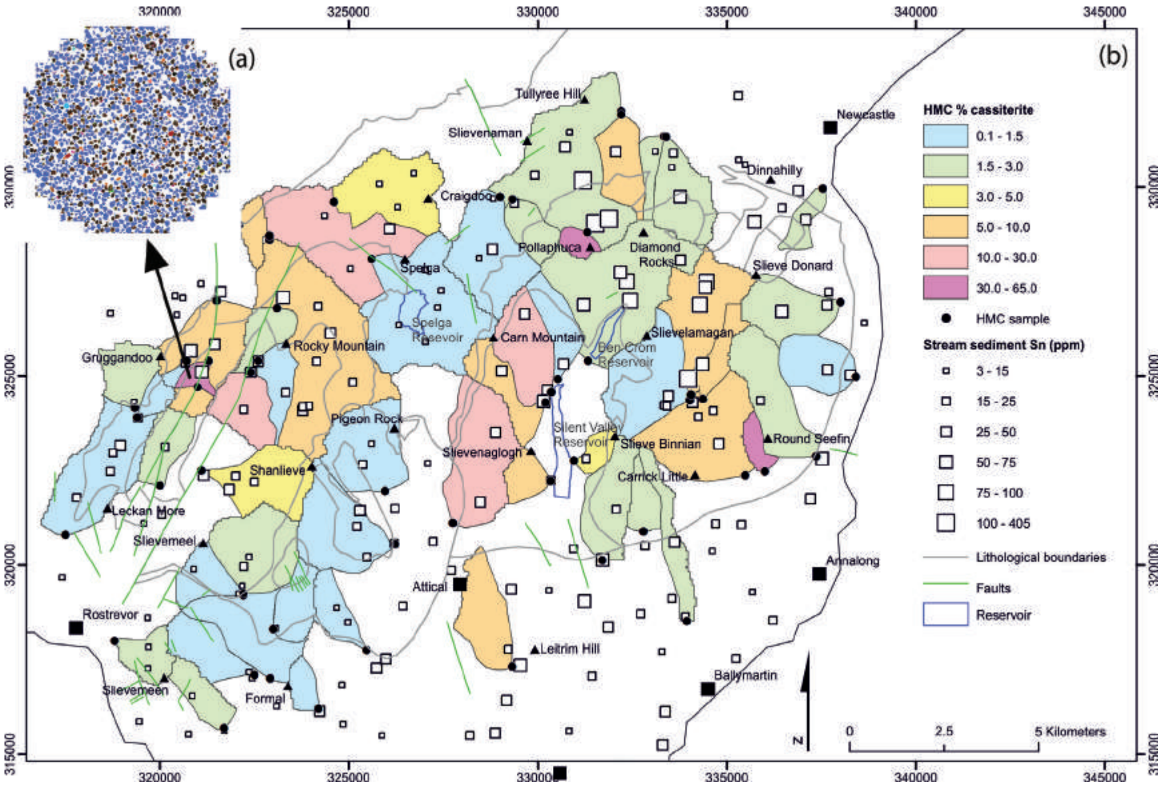

Figure 9.2. (a) False-colour QEMSCAN® image showing the dominance of coarse-grained cassiterite (65.1 vol. % of HMC) as blue grains in a 30 mm wide grain mount of HMC; (b) abundance of tin in Tellus stream sediment samples shown as proportional symbols overlain on cassiterite abundance in HMC sample catchments.

A Tellus-based critical metals survey

To construct and test a methodology for critical metals research and exploration, the Tellus stream sediment and deep soil (S-horizon) data sets were used to inform the design of two resampling programmes of heavy mineral concentrates (HMCs) and bedrock. HMCs are the dense fraction of alluvial sediments that host metal-rich minerals. Samples were obtained by sluicing sediment at each sampling site, applying the same methodology used for placer gold research (Chapman and Mortensen, 2006). Stream sediment samples and soil geochemistry surveys are regularly used in mineral exploration but the minerals that host the critical metals are relatively scarce, so small sample volumes may not be representative. The HMC samples that we collected for quantitative mineralogical analysis differ from the Tellus stream sediment samples as they are 'pure' concentrates of heavy minerals obtained by sluicing, panning and subsequent laboratory preparation. The initial volume of sediment was typically 0.5 to 1 tonne of active stream sediment, much larger than the Tellus sieved stream sediment samples, and enabling useful amounts of heavy mineral grains to be collected at each site. Fig. 9.2a shows the individual grains in an HMC sample that have been analysed for size, mineral type and mineral associations: false colours are used to denote mineral composition which in this sample is dominated by cassiterite (false-colour blue). The new data from the HMCs offer excellent precision, but our sampling was necessarily at a lower density than the Tellus stream sediments. Therefore we used both

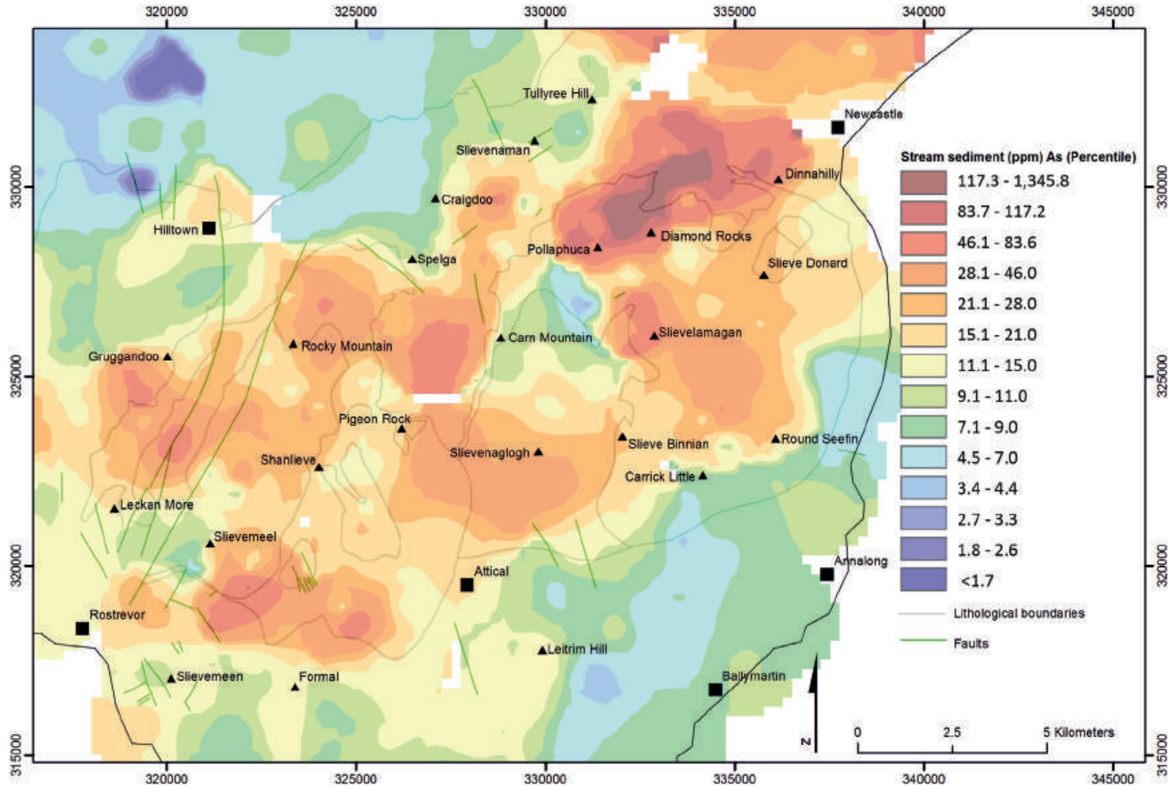

Figure 9.3. Map of gridded arsenic concentration (ppm) in Tellus stream sediment (multi-acid near-total ICP data).

data sets in combination to investigate the spatial distribution of critical and other metals in the study area.

Bedrock samples were collected at locations of representative geochemical anomalies across the Mourne Mountains (Fig. 9.1). The minerals in both the HMC and bedrock samples were analysed by electron microbeam using the QEMSCAN® process for quantitative analysis of rock and mineral textures and electron probe microanalysis (EPMA) for analysis of mineral chemistry. Using a geographic information system (GIS), HMC mineral concentrations were mapped onto catchment areas upstream of each sample-site to display spatial associations. River catchment analysis was used to correlate the HMC mineralogical data with Tellus stream geochemical data to assess the distribution of different minerals containing critical and other metals. For example, Fig. 9.2b shows that the abundance of cassiterite in HMCs varied greatly, from <1% up to 65%, with three samples containing >30% and a further four containing 10–30%. Cassiterite-rich HMC sites are widely distributed across the Mournes, indicating multiple bedrock sources. There is a reasonable correlation between HMC cassiterite abundance and Tellus stream sediment tin (Sn) concentration with relatively high Sn values (50–405 ppm) throughout the eastern Mournes granite and also in the upper Leitrim valley, but the HMC data provide more specific mineralogical information, particularly with respect to grain-size.

Principal component analysis showed that in granites of the eastern Mourne Mountains Complex there is a positive association of: (1) the niobate mineral fergusonite with zircon and iron oxide minerals and (2) the REE mineral allanite with mafic silicate minerals. Cassiterite (a tin ore mineral) and wolframite (a tungsten ore mineral) have positive association with one another in the eastern Mournes but do not have an association with niobate or REE minerals. In the western Mournes, fergusonite is associated with wolframite, and allanite with cassiterite, but wolframite and cassiterite are not associated with one another. These contrasting mineral associations are indicative of differences in the processes that formed critical metal enrichments in the western and eastern Mourne granite centres.

Bedrock samples collected (locations as white symbols, Fig. 9.1) were representative of those that host metal-rich mineralisation. The rock types included pegmatites (patches of extremely coarse-grained granite), drusy granites (containing vapour 'bubbles'), greisens (areas where fluids moved through the solid rock and altered and replaced minerals) and mineral veins (tabular features where tectonic faults acted as fluid pathways to develop secondary enrichments). Textural and chemical analysis of the rocks was used to interpret four types of anomaly that we identified in the context of polymetallic mineralisation formed by magmatic-hydrothermal processes:

1. A large curvilinear array of soil anomalies across the eastern Mournes was caused by minerals hosting niobium, REEs, uranium and thorium that crystallised from the final remnants of the most alkaline and fluorine- and water-rich magmas in the roof-zone of the granite intrusions. The REE anomalies are interesting because REE profiles in granite-related mineralisation have a higher ratio of heavy rare earth elements (HREEs) to light rare earth elements (LREEs) than in most currently operating (carbonatite-hosted) REE mines.
2. Small and isolated cerium soil anomalies that occur in the Mourne Mountains granites correlate with amorphous manganese-rich and cerium-rich masses that infilled drusy cavities. These were formed by the separation of small volumes of hydrothermal fluids from late-stage magmas, which migrated short distances through the rock. Lithium, arsenic and tin were present in trace amounts in this mineralisation.
3. A substantial anomalous arsenic plume in stream sediments (Fig. 9.3) in the eastern Mournes was formed by erosion of a greisen: an area of granitic rocks that had been affected by larger volumes of magmatic fluids with flow paths controlled by geological structures. Reactions between arsenic + halide-rich fluids and mafic silicate + diverse accessory minerals in the roof-zone granites produced an arsenic-rich greisen (observed at Pollaphuca) that hosts multiple critical metals and tin (as cassiterite).
4. Diverse, small-scale and highly variable REE anomalies in the Tellus soil data along structural features in the western Mournes correlate with vein mineralisation

> resulting from episodic migration of hydrous fluids of variable composition, probably with a smaller magmatic component than elsewhere. This finding is compatible with previous research that used stable isotope compositions to show that meteoric fluids have a minor and localised influence on granitic rocks near internal contacts and at the margins of plutons (McCormick *et al*., 1993).

Magmatic crystallisation and the migration of associated hydrothermal fluids explain the mineral associations for fergusonite, allanite and cassiterite observed in the heavy mineral concentrates, particularly in the eastern Mournes. The variation between mineral associations in the western and eastern Mournes may be a function of variable mixing between magmatic fluids and meteoric water (groundwater). Meteoric water is likely to have permeated along the north–south-trending faults that dissect the western Mourne granites. However, coarse-grained cassiterite that was observed in the HMC (Fig. 9.2a) was not found in the limited set of bedrock samples, so we do not yet have an exhaustive account of all potential types of mineralisation in the region, particularly in the western Mournes.

Significance and impact of the research

Scientific value

A geological model has been developed that describes enrichment of critical metals in the last fraction of magma, separation of fluid from this magma with a characteristic critical metal composition, and later mixing between magmatic fluids and other subterranean fluids. Focusing on critical metals has enabled us to elaborate details of processes that cannot currently be observed because they occurred in geological history and beneath the Earth's surface at elevated pressures and temperatures. For example, the diversity of primary niobium-, yttrium- and HREE-bearing minerals in the Mourne Mountains required a lengthy process of crystallisation (as described below) from a parent magma that originated in a mantle source region rich in trace metals, such as the relatively niobium-enriched Iceland Plume underlying the British Palaeogene Igneous Province (Kent and Fitton, 2000).

Figure 9.4 shows an accessory mineral assemblage that comprises zircon (red) that contains inclusions of thorium- and REE-minerals such as thorite and xenotime (pink), and is mantled by and intergrown with magnetite containing inclusions of the niobium–REE mineral aeschynite (yellow). This assemblage is intergrown with the major silicate minerals biotite (blue) and quartz (black). The rock texture shows that all the minerals crystallised at the same time in the roof-zone granites, at minimum magmatic temperatures. The simultaneous crystallisation of minerals at the lowest magmatic temperatures occurs because many of the critical metal atoms do not fit into the structures of common magmatic minerals that crystallised earlier. These lowest temperature granites enclose drusy

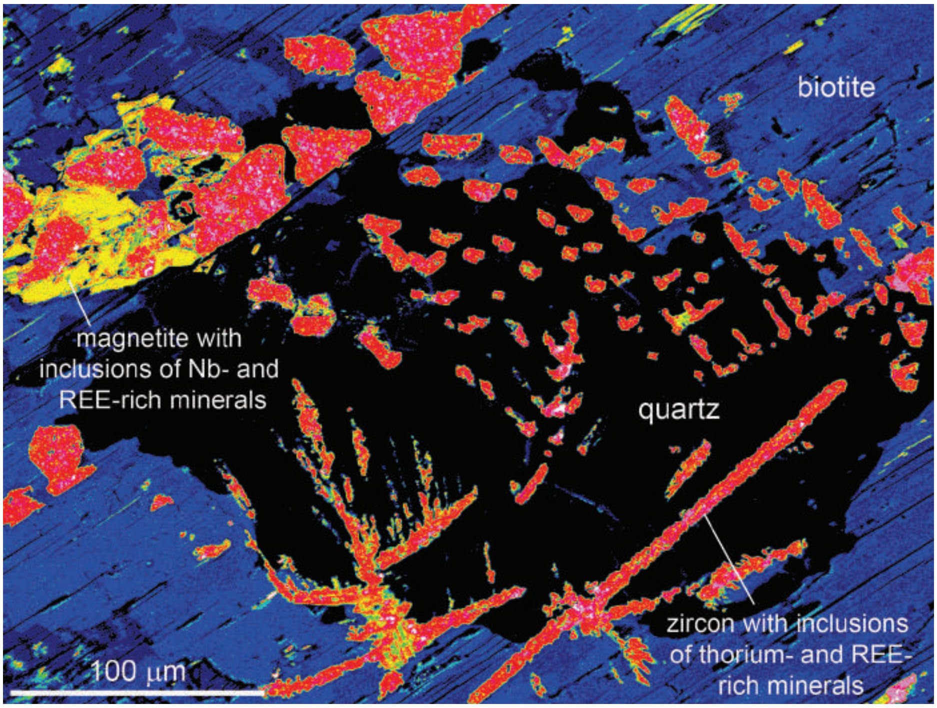

Figure 9.4. False colour element map showing an example of 'micrographic' intergrowth texture in a bedrock sample of drusy granite.

cavities filled with intriguing coarse-grained minerals including topaz, beryl, zinnwaldite, fluorite, tourmaline and stilbite. Their mineral compositions together describe the most hydrous residual materials in the magma chamber, which are very rich in fluorine, beryllium, lithium and boron. Therefore, there is a preferential separation (partitioning) of niobium + REE into magmatic minerals in the main body of the cooling granite magma, and of lithium, fluorine, beryllium, boron and occasionally tin into pockets of the very last magmas soaked in magmatic fluids. Thus, the Mourne Mountains can be used as a natural laboratory to investigate the behaviour of critical metals during the transition from silicate magma to hydrous fluid, which is fundamentally important to understanding the formation of polymetallic mineralisation globally.

The distribution of the drusy cavities demonstrates that the fluorine-rich late-stage magmatic fluids were heterogeneously distributed in small pockets in the roof-zones of granitic magma chambers, and high-temperature fluids in such magmatic environments have previously been shown to have significant compositional heterogeneity (Kamenetsky *et al*., 2002). Percolation of *in situ* magmatic fluids through roof-zone Mourne granites remobilised critical metals such as HREE and niobium over very limited distances and caused some minerals (e.g. xenotime and aeschynite) to dissolve and re-precipitate as secondary minerals. However, substantial greisens that result in a plume of arsenic enrichment in streams in the eastern Mournes (Fig. 9.3) add a further dimension to this story.

They are produced by large volumes of arsenic-rich fluids that migrated through the rock over greater distances and precipitated the LREE-enriched fluorocarbonate minerals monazite and bastnäsite, and LREE-enriched arsenic minerals arsenoflorencite and chernovite. Comparison of the mineral compositions in the greisen with those in the granite shows that the large volume fluids have a magmatic origin, and that LREEs were preferentially transported over HREEs and niobium. This pattern is consistent with experimental work which shows that HREEs are restricted to the high-temperature input zone along fluid flow paths and LREEs migrate away from it (Williams-Jones *et al.*, 2012). The size and disposition of the arsenic mineralisation suggests that a large volume of fluid was channelled over a sustained time interval along a geological fault from a substantial granitic source region beneath the present level of rock outcrop.

Economic significance

Potential ore minerals (e.g. bastnäsite, monazite and xenotime) for REEs occur throughout the Mourne granites. However, these minerals occur in comparatively low quantities and with a fine grain-size that is not favourable for disaggregation and processing. Magmatic allanite is more coarse-grained in some of the Mourne granites but it is resistant to chemical processing and it is not currently economically viable to extract REEs from it. HREE-bearing oxides such as niobate minerals have attractive REE contents but are not considered to generally occur in quantities that could constitute a sustained source, as either the primary ore minerals or a by-product (Mariano and Mariano, 2012). The development of REE recovery techniques from mineralogically complex ore deposits in Canada and Brazil may pave the way for the future development of a greater number of granite-based polymetallic projects (Chakhmouradian and Zaitsev, 2012). However, this is unlikely to include the Mourne granites because of their environmental sensitivity and because other international REE prospects have higher critical metal concentrations. On a global scale the highest critical metal concentrations occur in deposits that formed from the most intensive remobilisation of critical metals from magmatic minerals by hydrothermal fluids (Chakhmouradian and Zaitsev, 2012; Williams-Jones *et al.*, 2012). Hydrothermal activity was not as extensive in the Mourne granites, so their investigation provides a window through which to examine the early stages of formation of economic critical metal deposits and thereby a means to enhance globally relevant geological models. Ultimately the research can contribute to an awareness of the granitic environments most likely to host critical metals deposits and thus inform exploration for new deposits.

Environmental value

The survey has identified bedrock sources of natural arsenic, a potentially harmful element, and provides the baseline information for investigating heavy metal distribution in the environment. This is particularly relevant in the Mourne Mountains, whose catchments provide water to the Belfast conurbation as well as nearby rural populations. To date, the research has guided the design of further student-based projects to investigate the geological nature of the arsenic mineralisation, including both field-based research for undergraduate students and detailed postgraduate research.

Implications for further exploration and research

The Tellus stream and deep soil data sets for Northern Ireland were used to assess the potential of the Mourne Mountains for polymetallic critical metal enrichments (technology metals that are at supply risk such as REEs, tungsten and niobium). Subsequently, we used combined stream sediment, HMC and bedrock investigations to find chemical couplings of REEs with niobium, titanium and uranium associated with primary magmatic crystallisation and of REEs with tin, manganese and arsenic in metasomatic–hydrothermal mineralisation. We have identified multiple opportunities for further research to:

- locate the bedrock sources of the remaining enrichments of potential ore minerals that have been observed in the HMC data;
- investigate the processes at lowest magmatic temperatures, at the magmatic–hydrothermal transition, and during greisen formation that concentrate critical metals using the Mourne Mountains as a case study;
- instigate further mineralogical and geological research projects in cross-border locations where we believe granite intrusions have the potential to host critical metal enrichments.

The Mourne Mountains Complex is not an isolated granite complex in the British Tertiary Province and there are marked similarities between the Mourne granites and the northern Arran granite (west Scotland), particularly in the mineralogy of the drusy cavities (Hyslop *et al.*, 1999). Granites in the Republic of Ireland that are geologically much older and have a different granitic heritage are also prospective for REEs. Fluorine-rich magmas and/or late-stage hydrothermal fluids have been suggested as the agents that concentrated HREEs in the most evolved granites of the late Caledonian Galway Batholith (Feely *et al.*, 1991). The Main Donegal granite is known to host uranium mineralisation (O'Connor and Long, 1985) that has similar features to that in the Mournes, and it may be accompanied by REE-hosting minerals. Thus, the application of similar combined Tellus–HMC–bedrock surveys in other parts of Ireland and across national borders would provide a means to identify polymetallic critical metal enrichments that could be potentially economic to extract, and would provide further understanding of the occurrence of critical metals.

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