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# Te-rich protolith for PGE mineralisation in NE Scotland

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**Abstract.** The geological factors controlling the mineralisation of basic layered Ni-Cu-PGE intrusive deposits are often complex and debated at length. Many models of Ni-Cu deposit formation rely on assimilation of carbonaceous continental crust to reach sulphide saturation for ore formation, rather than through fractionation of the melt alone. The Ordovician 'Newer Basic Intrusions' in NE Scotland have historically been targeted for their Ni, Cu and minor precious metal enrichments (up to 700 ppb Au+Pt+Pd). The distribution of PGEs within these intrusions is variable, with the highest concentrations associated with sulphide-rich graphitic pyroxenites. The host rocks for these enriched intrusions are the sulphidic pelites and diamictites of the Dalradian Argyll Group. Sulphides within these strata are often enriched in tellurium, selenium and gold relative to average crustal values and there is considerable evidence for assimilation of this country rock within the ultrabasic intrusions. We propose here an ore formation model of Dalradian country rock assimilation, sulphide saturation and semi-metal enrichment of the intrusive melt. Tellurium enrichment within the melt resulted in localised PGE-telluride mineral formation, associated with graphitic xenoliths. It is possible that more extensive PGE mineralisation exists in similar settings in NE Scotland and globally.

## 1 Introduction

Ultramafic intrusive complexes are a major source of nickel (Ni), copper (Cu) and platinum group elements (PGE) globally (Bushveld Complex, Duluth, Vammala Nickel Belt, Aguablanca) (Thériault et al. 1997; Naldrett 1999; Pina et al. 2006; Ihlenfeld and Keays 2011; Makkonen et al. 2017; Samalens et al. 2017). As well as gold (Au), these deposits are often relatively enriched in other rare 'critical elements', including tellurium (Te) and selenium (Se), which are vital for the production of green technologies, such as photovoltaic cells. Understanding the mechanisms controlling accumulations of these elements is vital to identifying new deposits and securing their supply in the future. Current global production of Te and Se is primarily as a by-product of copper (Cu) refining, which limits future supply growth (Lu et al. 2015).

Here we investigate a model of PGE mineralisation in graphitic basic intrusions in NE Scotland, through crustal assimilation of sulphidic metasedimentary basement. Tellurium reserves within the metasediment-hosted Cononish Au deposit, Scotland, have recently been reexamined (Spence-Jones et al. 2018) and it is conceivable that other overlooked or unidentified enrichments in critical elements associated with metasediments may prove important as demand for these commodities increases. Accurate identification of the different mineralisation mechanisms in these complex systems is key in targeted exploration.

## 2 Geological setting

The Grampian Highlands terrane of north-east Scotland (Fig. 1), bordered to the south by the Highland Boundary Fault and the north-west by the Great Glen Fault, can be split into three simplified units - Proterozoic basement, Devonian sedimentary rocks and Ordovician to Devonian intrusives. The Proterozoic metasedimentary Dalradian Supergroup (deposited c. 800–595 Ma; Halliday et al. 1989; Thomas et al. 2007), the stratigraphy of which has been well-characterized (Fig. 2), underlies and outcrops across the region. The intrusive units of the Grampian Terrane (granites and basic-ultrabasic layered sequences) formed during the Caledonian orogeny (475–400 Ma; Oliver et al. 2008), during subduction and closure of the Iapetus Ocean. This orogenic event also caused widespread regional metamorphism of the Dalradian Supergroup (Oliver et al. 2008). The Devonian 'Old Red Sandstone' in the north of the terrane comprises clastic sedimentary deposits, associated with the formation of the Orcadian basin to the north as a result of orogenic events in the Grampian Terrane (Kendall 2017).

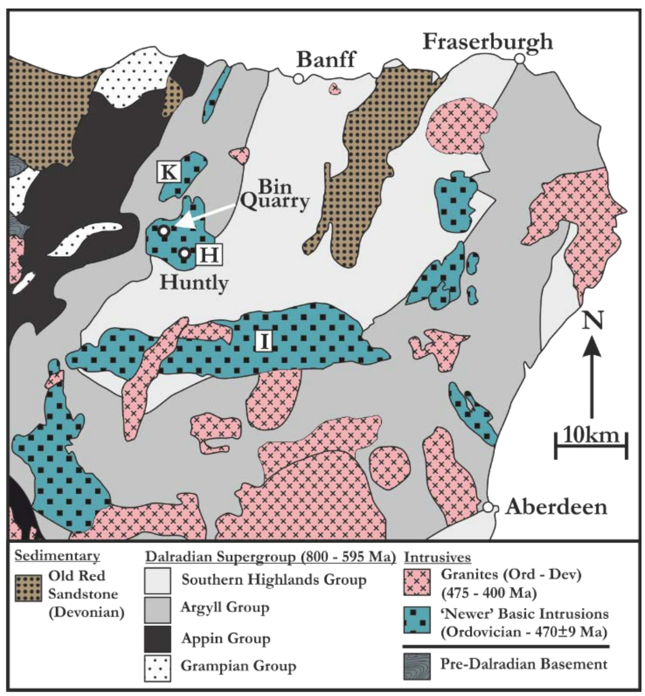


**Figure 1.** Simplified geological map of the Grampian Highlands terrane, NE Scotland: Illustrating the distribution of Proterozoic Dalradian metasediments, Caledonide intrusions and Old Red Sandstone. Intrusions: K = Knock; H = Huntly; I = Insch. Geological map after (Droop et al. 2003; Stephenson et al. 2013b). Dating ages (Halliday et al. 1989; Dempster et al. 2002; Thomas et al. 2007).

# 3 Caledonide PGE enrichment, NE Scotland

Platinum (Pt), palladium (Pd), Ni, Cu and minor Te, Au and Co enrichments have previously been identified within the 'Newer' basic intrusive bodies in NE Scotland (Fletcher 1989; Gunn and Styles 2002; McKervey et al. 2007). These are basic-ultrabasic layered cumulate intrusions of Ordovician age, emplaced within the Dalradian Supergroup metasedimentary sequence. Timing of these ultrabasic intrusions was roughly coeval with the wider S-type granitoid emplacement in the region c. 470±9 Ma (Dempster et al. 2002; Oliver et al. 2008).

Two Ni-Cu (+minor PGE and Au) deposits of the Newer Basic Intrusions were identified as potentially prospective in the late 1960s and have been extensively studied since (Fletcher 1989; Fletcher et al. 1989; Gunn and Shaw 1992; Gunn and Styles 2002; McKervey et al. 2007). They compromise the Huntly and Knock intrusions (Fig 1) with values of 0.003–3.02% Ni, 0.002–6.46% Cu and maximum values of 584 ppb Pt and 381 ppb Pd across the two intrusions (Fletcher 1989; McKervey et al. 2007), though these are highly variable. Au concentrations vary between 1–179 ppb, with most values <20 ppb. The Ni, Cu, PGE and minor Au

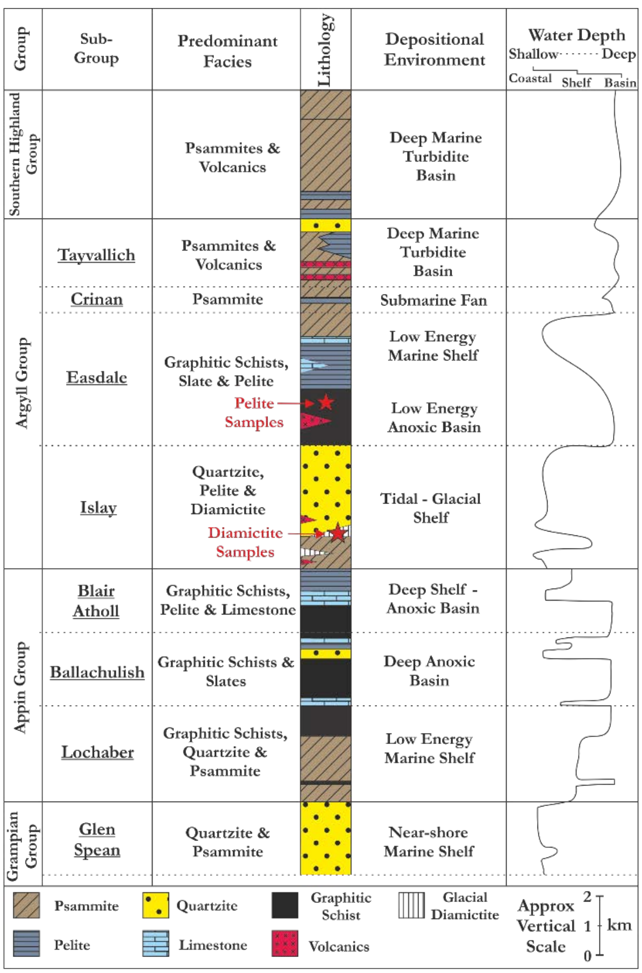


**Figure 2.** Simplified Dalradian stratigraphy in NE Scotland. After (Stephenson et al. 2013a, b)

enrichments are primarily associated the sulphides pyrrhotite, chalcopyrite and pentlandite, within sulphidic gabbronorite and graphitic pyroxene pegmatites (Fletcher 1989). Occurrences of the PGE-bismuth-telluride, merenskyite, have been identified historically and are thought to be the main phase of PGE enrichment in these deposits (Fletcher 1989; Gunn and Styles 2002). The graphitic pyroxenites have Au+Pt+Pd concentrations up to 700 ppb (Gunn and Styles 2002).

The intrusions are layered basic and ultrabasic cumulates, gabbros and serpentinites with extensive disseminated sulphides, thought to be of magmatic origin. Localised deformation and sulphide mineralisation occurs along xenolithic shear zones, with common, but discordant pyroxene porphyritic mineralisation, abundant in graphite and sulphides (McKervey et al. 2007).

Existing models for the PGE-Ni-Cu mineralisation in the Younger Intrusions are complex and propose a magmatic sulphur source, with re-mobilisation and enrichment of sulphides associated with subsequent shear deformation and hydrothermal processes. While localised graphitic pyroxenites are known to have the highest precious metal concentrations in these deposits, previous works have discounted the influence of carbonaceous crustal assimilation on PGE mineralisation (Fletcher 1989; McKervey et al. 2007). The local host rock for these intrusions is the Dalradian Argyll Group (Fig. 1; Fig. 2), which is widely carbonaceous and sulphidic, with the potential to alter the bulk sulphur and trace element content of the melt during magmatic emplacement.

# 4 Dalradian crustal assimilation

Sulphides within carbonaceous schists, pelites and glacial diamictites in the Dalradian Argyll Group have been shown to contain anomalously high concentrations of Te, Au and Se (Parnell et al. 2017, 2018). Laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) analysis of Argyll Group diamictites shows discrete Se and Te mineralisation within pyrite in these deposits (Fig. 3). SEM analysis has identified several discrete Te and Se mineral phases, including lead selenide, lead telluride, nickel telluride and bismuth telluride (Fig. 4). Given this mineralisation, these strata have the potential to act as protoliths for trace element enrichments during orogenic and magmatic processes.

Partial melting of the country rock has long been recognized as a factor during the emplacement of the Ordovician intrusive suites in NE Scotland (Ashworth 1976; Droop et al. 2003; Johnson et al. 2015). Carbon (C) isotopic analysis of graphite from Bin Quarry, Huntly intrusion (Fig. 1) provide $\delta^{13}C$ values of -25.0 to -18.0‰, which are distinct from mantle derived values of -5‰ ± 3 (Horita and Polyakov 2015). Organic C is isotopically light, with an average $\delta^{13}C$ of -25‰ (Luque et al. 2012), indicating that the graphite in the Newer Basic Intrusions is derived from crustal contamination by organic C. The Argyll Group metasediments into which the Huntly and Knock intrusions were emplaced (Fig. 1), consist primarily of deep marine, carbonaceous schists and

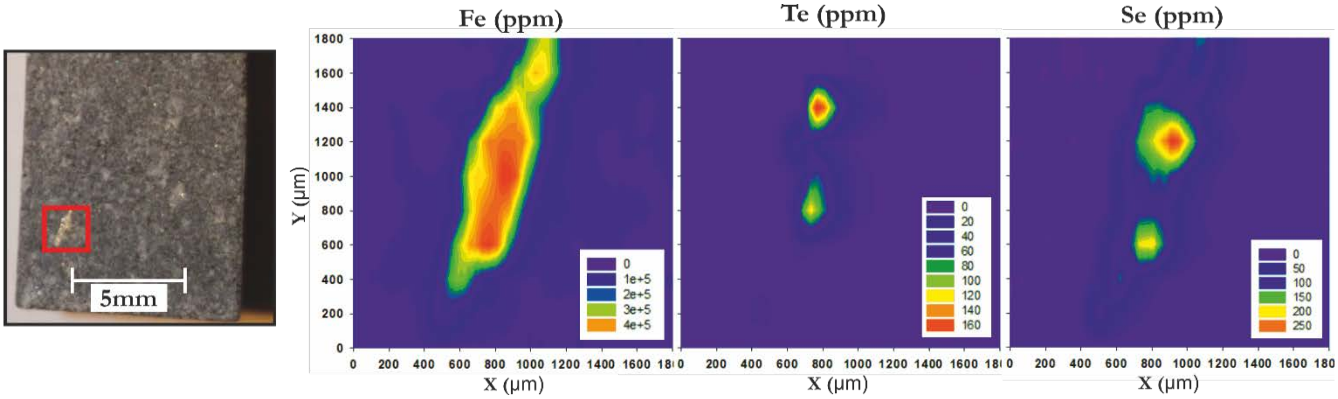


**Figure 3.** LA-ICP-MS maps of Fe, Te and Se concentration across sulphidic Argyll Gp diamictite sample. Te and Se enrichment within pyrite.

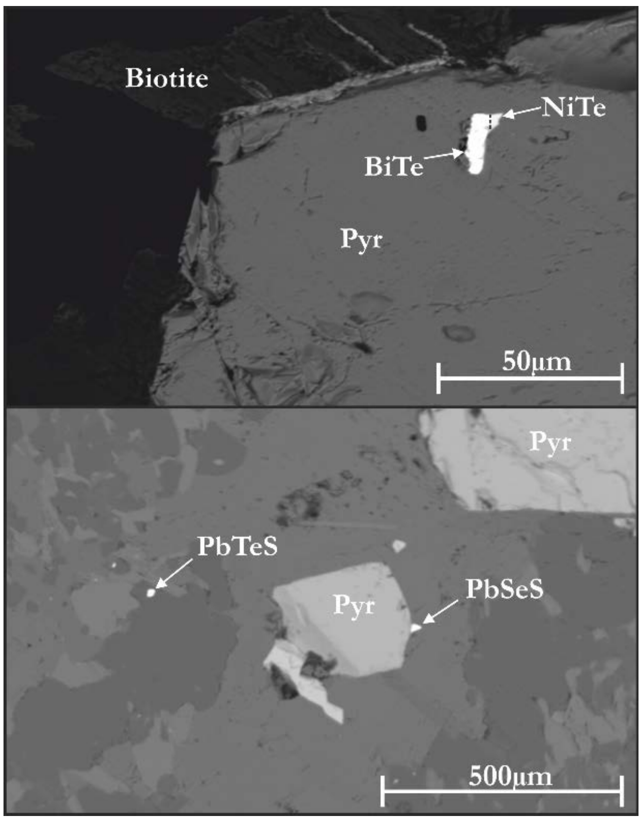


**Figure 4.** SEM imagery of discrete telluride mineralisation in glacial diamictite samples, Argyll Gp.

pelites, which are abundant in organic C (Fig. 2). Given the widespread graphitic mineralisation within the younger intrusions at Knock and Huntly, it is likely that localised crustal assimilation of the Argyll Group was significant during their emplacement.

Isotopic studies have previously concluded that the sulphur source within these intrusions is magmatic in origin, with $\delta^{34}S$ values between -1.7‰ and +6.5‰, which is comparable to typical magmatic values of 0±3‰ (Fletcher 1989). Given the variable nature of Argyll Group $\delta^{34}S$ compositions in Scotland, ranging from -15.5‰ to +11.8‰ (Parnell et al. 2017), distinguishing crustal sulphur input from primary magmatic sulphur can be difficult, as discussed in these previous studies.

The average S/Se ratio of sampled graphitic pyroxenites at Bin Quarry is 8440 (Table 1), which is significantly higher than the mantle maximum of 4350, indicating contamination of the melt by crustal sulphur (Queffurus and Barnes 2015). These S/Se values are in agreement with previous studies from the ultrabasic intrusions in the region (McKervey et al. 2007). While the predominant sulphur source in these systems may be magmatically derived, a minor or localised Dalradian crustal component cannot be discounted. Tellurium and Se concentrations in the graphitic pyroxenites average 0.86 ppm and 7.1 ppm respectively, which is significantly higher than crustal averages of 0.03 and 0.09 ppm (Rudnick and Gao 2003; Hu and Gao 2008).

**Table 1.** Bulk rock ICP-MS data for graphitic pyroxenite samples, Bin Quarry, Huntly intrusion.

| ID | Te (ppm) | Se (ppm) | S/Se | S (%) | Pt (ppb) | Pd (ppb) |
|---|---|---|---|---|---|---|
| A | 0.34 | 3.8 | 7658 | 2.91 | 2 | 11 |
| B | 1.26 | 8.9 | 8236 | 7.33 | 3 | 26 |
| C | 0.99 | 8.6 | 9000 | 7.74 | <2 | 43 |

## 5 Semi-metal input & PGE scavenging

Many models from comparable PGE-enriched Ni-Cu deposits (Duluth, Vammala, Aguablanca) propose that the assimilation of carbonaceous country rock increases the sulphide saturation in the melt, leading to precipitation of sulphides (Peltonen 1995; Pina et al. 2006; Samalens et al. 2017). Some of these models also propose that semi-metal enrichment from the country rock resulted in crystallization of accessory mineralised phases including graphite and PGE-tellurides.

Partial melting and assimilation of crustal sulphur from Dalradian sulphides is likely to have resulted in assimilation of the sulphide-hosted semi-metals (Te, Se and Au) within the Argyll Group, which would readily enter a sulphide under-saturated melt. Alternatively, partial melting of sulphidic, semi-metal enriched strata by a sulphide-saturated melt would result in semi-metal precipitation and potential scavenging of other chalcophile elements (Holwell and Mcdonald 2010).

It is conceivable that the partial melting of sulphidic Dalradian strata during emplacement of the Newer Basic Intrusions increased the trace element composition of the melt, particularly in the vicinity of the graphitic xenoliths. This increased Te content, coeval with an increase in sulphide saturation, is proposed here as a key mechanism for PGE scavenging and mineralisation in these intrusions. By comparison, precious metal concentrations at Knock and Huntly are significantly higher (max. 700 ppb Au+Pt+Pd) than those found at the Insch intrusion (Fig. 1), with a maximum of 13 ppb (Gunn and Shaw 1991). Cumulate sequences here are comparable with those at Knock and Huntly, with similar levels of shear deformation, though graphitic mineralisation is not a significant feature. The emplacement of the Insch intrusion, primarily within the Southern Highlands Group Dalradian strata (Fig.1–2), which is lacking in trace element enriched carbonaceous or sulphidic lithologies, suggests that differences in PGE content of these intrusions may relate to the varying trace element content of assimilated host rock. Therefore, crustal assimilation of Te-rich Argyll Group strata at the Huntly and Knock intrusions likely contributed to the formation of PGE minerals (specifically merenskyite) in these deposits. It is feasible that similar or more significant enrichments may be found in other intrusions emplaced within Te-enriched Dalradian country rock.

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