

## Whole-rock geochemistry for intrusion-hosted magmatic Ni-Cu-Co exploration: identifying prospective host rocks

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<https://doi.org/10.70499/BNCK6894>

### Introduction

Nickel, copper and cobalt are hot targets for today's explorers. Demand is projected to rise and keep rising with the expected upsurge in demand for the electric vehicle market. Magmatic sulfide deposits host all of these elements, plus in many cases significant quantities of platinum group elements (PGEs), so a good discovery is a holy grail for the mining industry. Even relatively small deposits by global standards, such as the Savannah deposit in the Kimberley region of Western Australia, contain billions of dollars' worth of metals (about AU\$3.5 billion for Savannah at February 2022 spot prices). The supergiant Oktyabrynsky orebody in the Norilsk-Talnakh ore camp in arctic Siberia (Russia), contains what is probably the most valuable single ore deposit of any type on the planet, with premining resources estimated at 140 ktonnes Ni, 113 ktonnes Cu and 290 tonnes PGEs (Barnes *et al.* 2020). At current prices, the pre-mining metal content of this extraordinary deposit (discovered in the 1960s) is worth well in excess of half a *trillion* Australian dollars. Therefore, important questions for the reader include what are magmatic sulfide deposits and how can we use geochemistry as a tool in exploring for them?

Magmatic sulfide deposits are analogous to nature's smelters. By the same process that has been used since prehistoric times to extract metals from ores, magmatic sulfide ores form by the interaction between immiscible sulfide-oxide liquids (mattes) with silicate magmas (slags). Scavenging of chalcophile elements – Ni, Cu, Co, Au and PGEs – and the accumulation of the matte component has produced the deposits that currently account for ~56% of the world's Ni production and over 96% of Pt and Pd production (Mudd and Jowitt 2014).

Australia (specifically Western Australia) is well-endowed with this deposit type. The Archean East Yilgarn nickel province is the third largest magmatic nickel province in the world after Sudbury (Canada) and Norilsk-Talnakh, containing well over ten million tonnes of nickel metal on a premining basis (Hronsky and Schodde 2006; Barnes and Fiorentini 2012). These deposits are hosted in komatiites, the ultra-hot lava flows that are the signature volcanic rock of the first half of Earth history. However, the komatiite belts of Western Australia have been very extensively explored, and while new deposits are discovered from time to time (such as Mincor's 2015 Cassini discovery near Widgiemooltha, 1.2 million tonnes at 4% Ni), it is relatively unlikely that giant undiscovered deposits still exist at accessible depths. Consequently, a large effort has been focussed internationally to discover the second and globally most important type of Ni-Cu-Co sulfide deposits: those hosted in deep-seated mafic-ultramafic intrusions formed by basaltic magmas. Australian explorers have had some major successes in finding these deposits in recent years, with the discovery of Nova-Bollinger (2012), Gonnevillie (Julimar) (2020) and Savannah North (2014). This category includes most of the world's giant deposits, including those at Norilsk-Talnakh and is the topic of this article.

Intrusion-hosted Ni-Cu-Co deposits are really tough targets. Explorers speak of distal footprints: the broad signal of ore forming processes that extends beyond the dimensions of the deposits themselves and effectively increases the size of the target. In many other deposit types, such as porphyry copper or orogenic gold deposits, there is a broad halo of hydrothermal alteration and anomalous geochemical signatures that occupies many times the volume of the actual orebodies. Such haloes rarely if ever exist in magmatic sulfide systems. The distal geochemical and mineralogical signals of magmatic ores can, in most cases, only be found within the magma transport network within which they form. These networks take the form of interconnected sills, dykes, conduits and magma chambers having a wide range of sizes, shapes and internal structures (Barnes *et al.* 2016a).

As research scientists, we aim to apply our understanding of ore forming processes to exploration in two main ways: improved prediction of where to look for prospective terranes, and improved detection to find the needle in the haystack at the prospect or deposit scale. These approaches are commonly combined nowadays into a "mineral system" approach, where deposits are seen holistically in a multi-scale framework from lithospheric-scale magma transport to the local mechanisms of deposit formation (Barnes *et al.* 2016a). It's now well established that major deposits tend to be located near craton margins – that is, near the edges of the ancient building blocks of the continental crust (Begg *et al.* 2010). However, this targeting only narrows down the prospective terranes to a scale of tens or even hundreds of km, so moving into the detection stage becomes rapidly harder and more expensive.

At CSIRO (Commonwealth Scientific and Industrial Research Organisation) Mineral Resources group, we have been focussed for the last few years on identifying prospective host rocks through a better understanding of the physics

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of the ore forming processes. Igneous intrusions are plentiful in prospective belts such as the Albany-Fraser orogen in Western Australia, or the Siberian Traps flood basalt sequence in arctic Russia, but the proportion of intrusions that contain orebodies can be vanishingly tiny. In the Siberian example, the ore-bearing intrusions account for less than one part per million of the total volume of basaltic magma in the province (Barnes *et al.* 2020). In the Albany-Fraser Orogen this proportion is unknown, but one volume percent ore-bearing would be a conservative order-of-magnitude guess. A typical exploration program will encounter large volumes of potentially “fertile” rocks, the challenge being to then reduce the search space to the most promising targets. The challenge, particularly in poorly outcropping or covered terranes, lies in extracting the maximum amount of useful information from drill intersections of barren rocks. Can a small number of sulfide-free samples from the distal portions of an ore-forming system (Fig. 1) be used to identify prospectivity or vector towards ore?

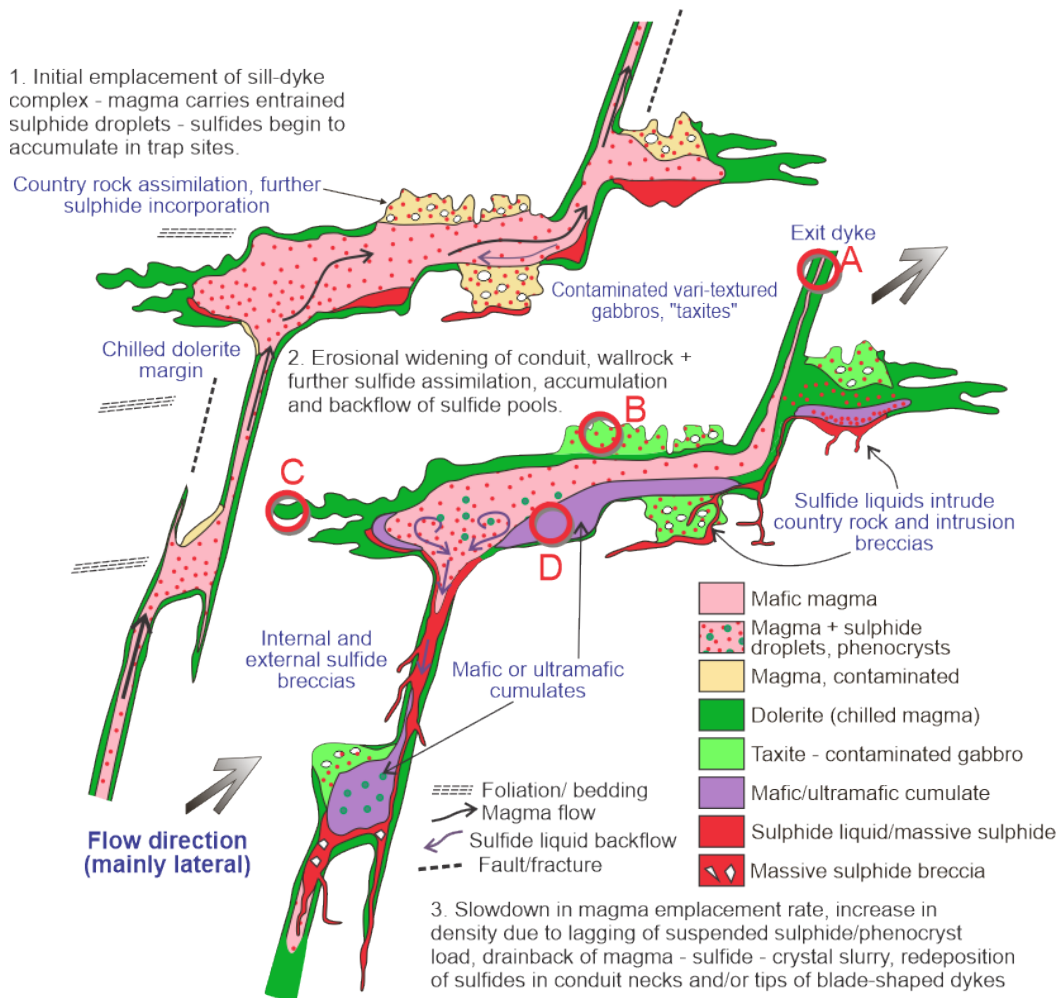


Figure 1. Schematic diagram showing two stages in the development of an intrusion-hosted Ni-Cu-Co sulfide system, modified from Barnes *et al.* (2016a). Ore deposition takes place within part of a larger sill-dyke network with multi-stage assimilation, transport and deposition (Stage 1), re-entrainment and backflow of sulfide liquid droplets and pools (Stage 2) and final deposition during drain-back at the waning stages of magmatism (Stage 3). Geochemical anomalies indicative of ore formation can be present in several components of the system. A) “exit dyke” sampling silicate melt, potentially depleted or enriched in chalcophile elements; B) contaminated marginal taxites with anomalous mineralogy and/or whole rock chemistry; C) distal margins of offshoot dykes and sills preserving early-stage emplacement and transported sulfide droplets; D) cumulate rocks in deposition sites extending beyond sulfide ores – anomalous mineral chemistry and zoning.

It is commonly accepted that ore formation happens within magmatic plumbing systems that are active over prolonged periods of time, experiencing multiple pulses of magma injection (Lightfoot and Evans-Lamswood 2015; Barnes *et al.* 2016a; Leshner 2019). The cartoon in Figure 1 illustrates this type of environment. Basaltic magma derived from the mantle flows (mostly sideways) through interconnected fracture networks in the crust (Magee *et al.* 2016). The critical sulfide component is derived by incorporating fragments of sulfide-bearing wall rock into the magma and melting them (Fig. 1, stage 1). The resulting sulfide liquid matte is very dense, and so has a strong tendency to sink out of the magma (Fig. 1, stage 1), but is also easily recycled and carried along as dispersed droplets (Leshner 2019; Yao *et al.* 2020). Based on detailed studies of the sulfide-silicate textures in the deposits themselves, and on analogies with modern volcanic systems, Barnes *et al.* (2016a) proposed that major deposits form in the waning stages of these plumbing systems where slurries of magma, sulfide droplets, crystals and rock fragments flow backwards and downwards into trap sites, often invading and intruding their own host rocks (Fig. 1) (Taranovic *et al.* 2022). How can these conceptual models be used to inform targeting decisions? How can maximum value be added to exploration data, particularly whole-rock chemical analyses and geochemical databases?

Modern exploration programs collect colossal volumes of geochemical data. Most commercial laboratories now offer ICP-MS or ICP-OES analyses of 40 or more elements per sample, and tens of thousands of samples can be (and often are) analysed during an extensive exploration program. The secret to obtaining the best value from these large datasets

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lies in using the data to answer specific questions arising from mineral system models (Fig. 1). Here are three main ones:

1. Is there evidence for the presence and/or deposition of sulfide liquid droplets?
2. Is there evidence that the magmas have been interacting with their country rocks along the flow pathway?
3. Are the samples at or close to a deposition site, where suspended silicate crystals are being deposited from the magma to form cumulate rocks?

Clearly if the answer to the first question is positive, this is by far the best geochemical indicator of magmatic ore formation. But there are many examples of near-misses where lack of evidence of sulfide in rocks from an unmineralized part of an ore-bearing intrusive system could generate a false negative. Furthermore, signals of country rock interaction, in the form of geochemical indicators of wall-rock contamination of the magma, can be flushed out by uncontaminated fresh magma within the flow pathways. On the other hand, there are very few, if any, examples of ore forming systems where there is not a positive answer to question 3 so we focus on this aspect now.

### Identifying cumulate rocks from geochemistry

Deposition sites are marked by the presence of cumulate rocks: the solid products of fractional crystallisation (Fig. 2A). Cumulates are rocks made up primarily of the crystals that were separated from the magma they crystallised from, plus a smaller component of that magma trapped between the crystals. Where they are dominantly ultramafic, i.e. made up of high proportions of ferromagnesian igneous minerals such as olivine and pyroxene, they are easy to recognise. Nevertheless, where they contain cumulus plagioclase in addition to olivine and pyroxene they can be much harder to recognise, as the cumulus mineral assemblage is not greatly different from the mineralogy produced by isochemical solidification of the magma. Ore-bearing intrusions typically contain a high proportion of cumulate rocks, such that understanding their origin and chemistry is crucial to unravelling geochemical data sets in magmatic sulfide exploration. Figure 2 shows the petrological basis for this understanding in the framework of standard phase diagrams.

The main messages from the phase diagrams are these.

1. Ultramafic rocks are not necessarily derived from ultramafic magmas. In fact, most “normal” mantle derived basalts can generate ultramafic cumulates, provided that they haven’t evolved too far from their original compositions.

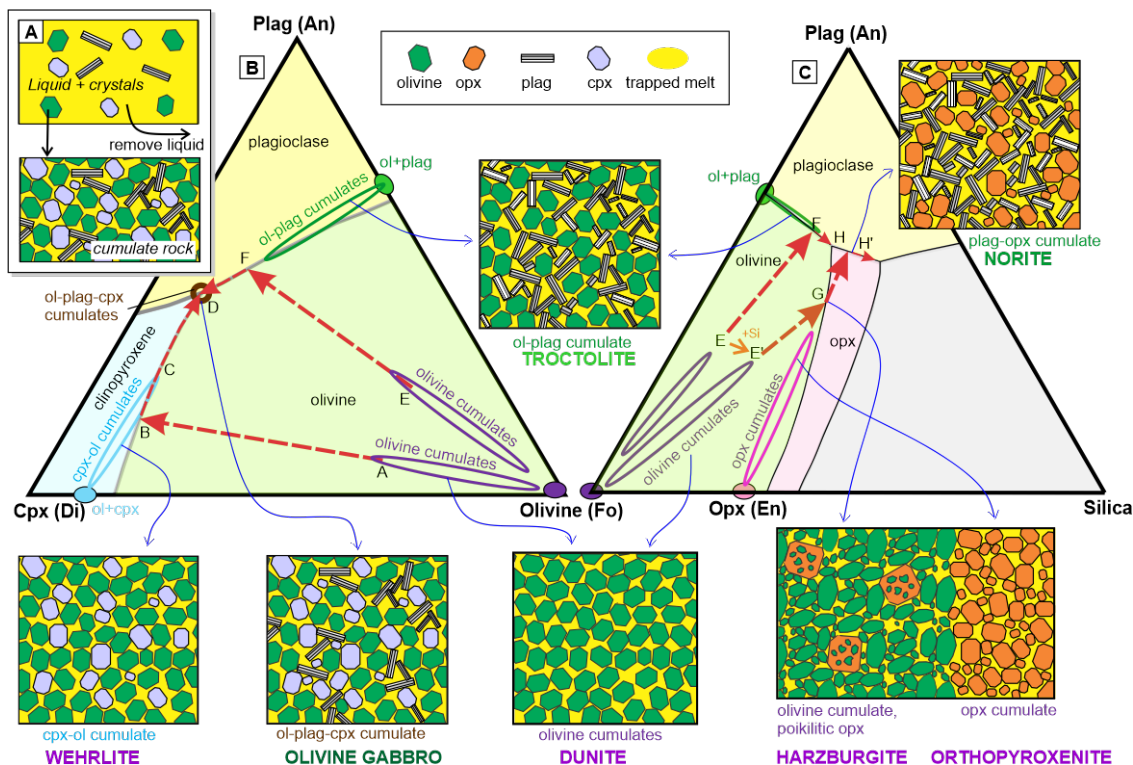


Figure 2. Phase diagrams from the “basalt tetrahedron” (Irvine 1970) showing crystallisation sequences of basaltic liquids in the simplified “basalt tetrahedron” system olivine (ol), forsterite (Fo) – clinopyroxene (cpx), diopside (Di) – plagioclase (plag), anorthite (An) – silica (Si), which includes orthopyroxene – enstatite (En). Coloured fields indicate the first phase to crystallise, red dashed line indicate the down-temperature path of evolution of the liquid during perfect fractional crystallisation (crystals removed from the liquid as they form – inset A). Cumulate fields indicate the compositions of the rocks formed as mixtures of cumulus crystals and their parent liquids.

For example in the Fo-Di-An projection (B), liquid A crystallises ol, evolves to point B, crystallises ol+cpx along path B-C, C-D. At D, plag begins to crystallise giving rise to an olivine gabbro, olivine+cpx+plag. Liquid E crystallises ol, evolves to point F, follows a path E-F-D giving ol, ol + plag (troctolite), olivine gabbro. If liquid A crystallises to a solid of its own composition, it will produce a non-cumulate rock made mostly of ol, cpx and plag. In the Fo-An-Silica projection (C), liquid E follows the same sequence as in the F-Di-An projection, giving ol, ol + plag (troctolite), olivine gabbro. However, crystallisation of a slightly more silica enriched composition E’ is complicated by a “peritectic” phase boundary where olivine reacts with the liquid to form orthopyroxene (Opx-En, enstatite)– path E’-G-H-H’ giving rise to distinctive poikilitic harzburgite, and eventually norite.

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2. A very minor change in the chemistry of the magma can cause a significant change in the cumulate rock it produces, e.g. from a peridotite (ultramafic - olivine+pyroxene) to a troctolite or a olivine gabbro (mafic) at the first appearance of plagioclase (points F, D, H in Figure 2); these phase appearances are commonly present as sharply-bounded layers in ore-hosting intrusions. They do not require new magma pulses.
3. A small change in the "starting composition" can cause a big change in crystallisation sequence: e.g. changing the starting composition from E to E' in Figure 2C, by adding a small amount of silica, causes the crystallisation path to change from dunite-troctolite-norite along the path E-F-H-H' to dunite-harzburgite-orthopyroxenite-norite along path E'-G-H'. The harzburgites formed in this way have a characteristic texture called "poikilitic" where large grains of orthopyroxene enclose many smaller, partially dissolved crystal of olivine. This is probably the most widespread rock type associated with intrusion-hosted Ni-Cu-Co deposits.
4. The further down the crystallisation path, the more the solid cumulate product chemically resembles the magma, the harder the cumulate is to recognise.

Armed with this basic understanding, whole rock geochemistry is easier to interpret. All of these rock types can be readily distinguished in geochemical data sets. For example, Figure 3 shows an easy way to distinguish a cumulate

Table 1. Data sources.

Locality/Belt	Source of data
Albany-Fraser Orogen regional and Nova-Bollinger deposit	(Smithies <i>et al.</i> 2013), (Taranovic <i>et al.</i> 2022), (Bathgate 2019)
Halls Creek Orogen and Savannah/Savannah North deposits	(Mole <i>et al.</i> 2018), (Le Vaillant <i>et al.</i> 2020), Geological Survey of WA WACHEM database, <a href="https://catalogue.data.wa.gov.au/dataset/?tags=WACHEM">https://catalogue.data.wa.gov.au/dataset/?tags=WACHEM</a>
Kimberly Craton Hart Dolerite	Geological Survey of WA WACHEM database, <a href="https://catalogue.data.wa.gov.au/dataset/?tags=WACHEM">https://catalogue.data.wa.gov.au/dataset/?tags=WACHEM</a>
Mozambique Mobile Belt, Ntaka Hill deposit	(Mole <i>et al.</i> 2017), (Barnes <i>et al.</i> 2016b)

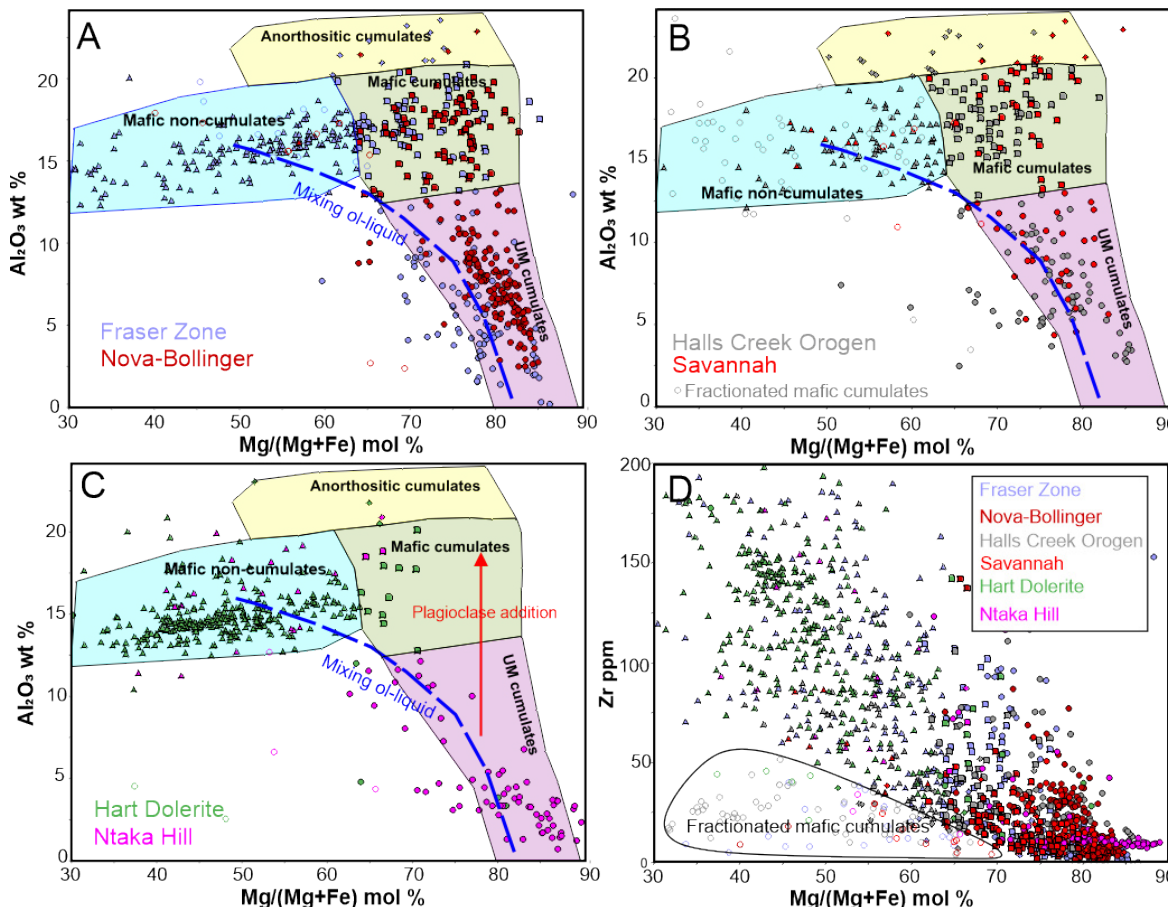


Figure 3. Discriminant plot for ultramafic (UM) and mafic cumulates and non-cumulate mafic rocks. Whole rock data,  $\text{Al}_2\text{O}_3$  wt % versus Mg number ( $\text{Mg}\#$ , molar percent  $\text{MgO}/[\text{MgO}+\text{FeO}]$ ). Cumulate rocks have higher  $\text{Mg}\#$  due to Fe-Mg minerals always having higher  $\text{Mg}\#$  than the magmas they crystallise from. Individual plots show data for (A) the Fraser Zone of the Albany-Fraser orogen, comparing regional mafic rocks with the host intrusion to the Nova deposit; (B) Halls Creek orogen data compare regional mafic-ultramafic intrusions with the Savannah deposit host intrusion; and (C) the Hart Dolerite is an

extensive unmineralised suite of dolerite sills in the Kimberley Craton, showing an almost complete absence of ultramafic cumulates and the Ntaka Hill deposit, hosted by an almost entirely ultramafic host body containing an abundance of orthopyroxene cumulates.

(D) Plot of whole rock Zr vs Mg number, showing field for mafic cumulates derived from strongly fractionated Fe-rich parent magmas. See Table 1 for data sources.

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gabbro (indicating a deposition site – position D in Figure 1 from a mineralogically similar rock that simply represents the magma crystallising to a solid of the same composition – such as might be found in a chilled margin, for example (position C, Figure 1). Spatially mapping out ultramafic and gabbroic cumulates from non-cumulate chilled liquid rocks using spatially constrained geochemical datasets provides a powerful tool for unravelling the internal structure of a potentially fertile magmatic system.

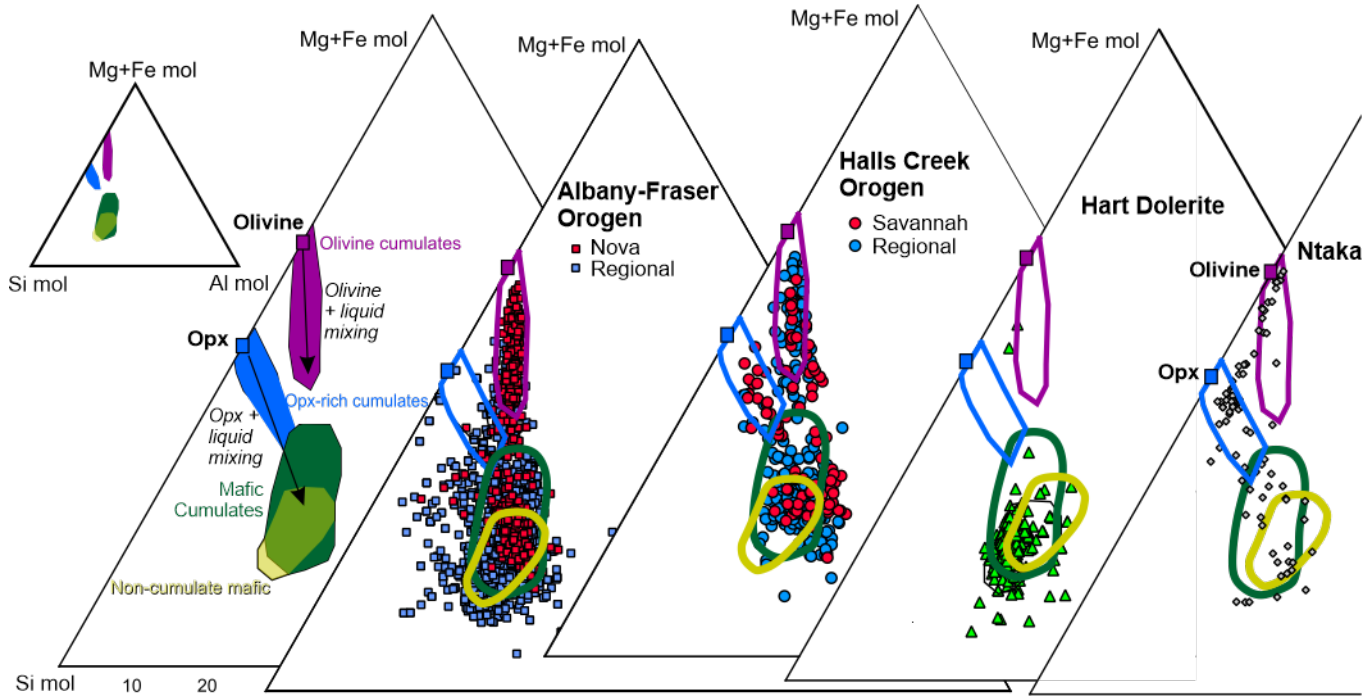


Figure 4. Triangular plot – molar ratio of MgO + FeO, SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> (see Table 2 for the calculation method) for discrimination of olivine and orthopyroxene (opx) dominated cumulates from cumulate and non-cumulate gabbros. Same data sets as Figure 3.

Table 2. Factors for calculating molar components.

Mg mol	MgO/40.3
Fe mol	[Total Fe as FeO*]/71.9
Si mol	SiO <sub>2</sub> /60.1
Al mol	Al <sub>2</sub> O <sub>3</sub> /51
Mg#	Mg mol/[Mg mol + Fe mol]

\*in cumulate rocks we neglect the component of Fe present as Fe<sub>2</sub>O<sub>3</sub>. This introduces a small positive error, up to about relative 5%, in orthocumulates.

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Not all ore-hosting intrusions contain ultramafic cumulates, where the cumulus phases are combinations of olivine, pyroxene and (usually) minor chromite, but there are very few that don't. As can be seen in Figures 3, the ore-bearing intrusions in a number of prospective belts are strongly dominated by cumulate rocks compared with other mafic rocks in the same belt, a particularly clear example being the Nova intrusions in the Albany Fraser orogen. The Hart Dolerite represents a very high-volume Large Igneous Province almost completely devoid of cumulate rocks, and has so far proved entirely barren for this deposit type. This would be typical of the signatures of unmineralized suites of mafic rocks.

Recognising ultramafic cumulate rocks is generally fairly straightforward: they are high in Mg, Cr and Ni and low in components such as Al and Ti that are not concentrated in these minerals. However, ultramafic rocks are very susceptible to alteration, which can modify their chemistry, and weathering,

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which is discussed in the next section. Orthopyroxene is a particularly useful indicator, in that most mantle-derived magmas don't crystallise much of it. The presence of orthopyroxene cumulates is a good indication that magmas have been contaminated with silica-rich country rocks (causing the shift from composition E to E' in Figure 2C), which is another

positive indicator for fertility.

Figure 4 shows a geochemical technique that allows the recognition of olivine and orthopyroxene cumulates from whole-rock geochemistry, to be used in conjunction with Figure 3. It is important to note that this method requires reliable  $\text{SiO}_2$  analyses, which are not provided in some element suites such as the standard ICP-OES package offered by many commercial laboratories. Silica is such an important component that it's generally worth spending more money to analyze it using the more comprehensive ICP-MS method, even if that is at the expense of dropping off some of the lower-abundance trace elements like Se, Te and Bi that are typically below the limit of detection in cumulate rocks. The mineralised Ntaka Hill intrusion in Tanzania (Barnes *et al.* 2019) shows up clearly as an intrusion with abundant orthopyroxene cumulates (Fig. 4).

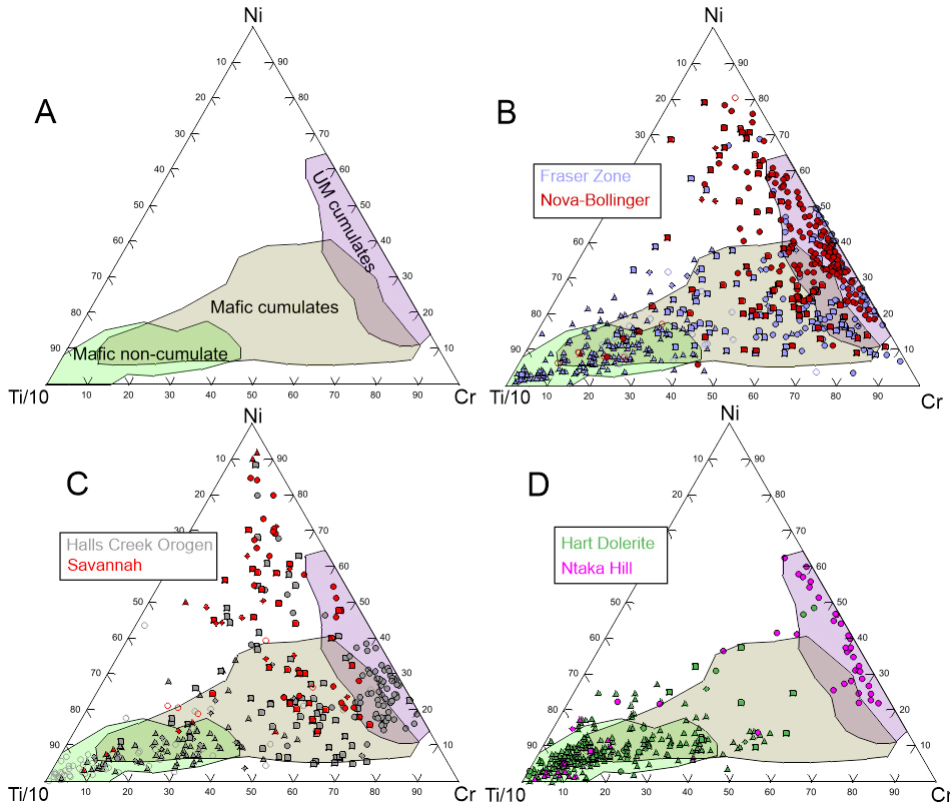


Figure 5. Ni-Cr-Ti triangular plot, same format and data sets as Figure 4.

### Weathered and/or altered rocks

Weathering and alteration commonly cause chemical changes in rocks, with the more soluble elements such as Na, K, Ca, Mg, Cu, Zn and sometimes Si being most affected. In the case of deeply weathered terranes common in Australia, exploration programs commonly sample leached rocks where some or all of these elements have been largely stripped.

The solution to this problem is to use relative proportions of the relatively immobile elements, on the assumption that the ratios of these elements to one another do not change during alteration or mild weathering. We investigated the best element combinations using a dataset from the Agnew area in Western Australia where we had excellent sampling of fresh rocks and their overlying weathered equivalents (Barnes *et al.* 2014), and found that the following elements can be reliably used in this way: the rare earths (REE), Ti, Al, Sc, Zr, Hf, Cr and, except in cases of advanced lateritic weathering, Ni. Consequently, plots using combinations of these elements such as Ni/Ti, Ni/Cr and Al/Ti, or triangular plots using combinations of these elements, as shown in Figure 5, are reliable discriminants of rock type in moderately weathered or altered rocks. This is particularly useful in identifying cumulate rocks from bottom-hole samples from percussion drilling programs. Furthermore, Ni, Cr and Ti are reliably determined by portable XRF on percussion chips or air core, making this combination particularly useful in reconnaissance greenfields exploration (Le Vaillant *et al.* 2014, 2016).

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### Concluding remarks

Successful exploration involves weighing multiple lines of evidence. In the case of magmatic sulfide deposits, the evidence might include the presence of cumulates, textural or geochemical evidence for existence of sulfide liquids, geochemical indicators of wall rock contamination using strongly incompatible lithophile elements such as light rare earth elements and Th (Leshner *et al.* 2001; Le Vaillant *et al.* 2016), pyroxene zoning (Schoneveld *et al.* 2020), anomalous chemistry in other indicator minerals like olivine and chromite (Locmelis *et al.* 2018; Barnes *et al.* 2022), and of course the presence of encouraging geophysical anomalies (Peters 2006). Any of these signals can generate false positives and negatives. The presence of high proportions of cumulate rocks in small intrusions (less than a few hundred metres in thickness) is one of the best “distal footprint” indicators, particularly if they contain traces of magmatic sulfide.

It is not possible to go into more detail about the many potential applications of whole-rock geochemical datasets in this short article, but we have prepared a set of short course notes, iGas diagram templates and Python libraries that can be examined fully on our CSIRO Magmatic Sulfides Systems website (<https://research.csiro.au/magnico/workshops-and-resources/>) for free download. We encourage readers to investigate this toolkit, and to contact us to request help with using it.

There are no silver bullets. It may be that AI-based automated decision making may take over in future in the process of weighing the evidence, but it is likely that application of sound principles of igneous petrology and geochemistry will prevail for a few decades. Either way, the best strategy is to make the most intelligent use of data to answer critical questions, rather than drowning in vast volumes of indigestible numbers. As we noted earlier, these are difficult targets to find. The upside of that is that there are almost certainly major discoveries yet to be made.

### Acknowledgments

We thank the many exploration companies who have supported CSIRO nickel-related research over the years, particularly IGO Ltd. and Panoramic Resources Ltd. for funding studies of the Nova and Savannah camps. Dr. Yulia Uvorova encouraged submission of this article. Dr. Uvarova and Dr. Margaux Le Vaillant reviewed an early draft. Thanks to Dr. Michel Houlé for his review and Beth McClenaghan for editorial handling and assistance.

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