Critical commodities in Australia

An assessment of extraction potential from ores

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Executive summary

Critical commodities, which by definition include commodities that are both economically important and have a high risk of supply disruption, are present at varying levels in a range of Australian ore deposits, and, consequently, Australia has great potential as a source of these commodities for the global market. Many critical commodities are produced as by-products of major commodities, and their production is a consequence not only of grades, but also the existence of metallurgical processes whereby the critical commodities can be extracted economically from ores and concentrates.

Production of critical commodities is a potential opportunity to extract additional value from Australia’s existing mining sector. Some critical commodities are or have been extracted as main products or co-products from Australian ores (e.g. nickel, tungsten, tin, tantalum, lithium, antimony and chromium). Other critical commodities are currently extracted as by-products from Australian concentrates by smelters in Australia and overseas (e.g. cobalt, platinum group elements, gallium, cadmium, bismuth, selenium and tellurium). The viability of this by-product extraction is not only dependent on the technical and economic viability of by-product extraction, but also on the economics of the major commodity with which the by-product critical commodity is associated.

Other critical commodities are known to be enriched in Australian mineral deposits, but are not currently produced. These include commodities that are extracted overseas and could be extracted from Australian deposits using existing technologies (e.g. vanadium, titanium, molybdenum and rhenium). This group also includes commodities that are enriched in Australian ores but are not currently extracted due to either economic or processing impediments (e.g. niobium, indium and germanium). Although there are several rare earth element deposits currently in production (e.g. Mount Weld), construction (e.g. Browns Range) or feasibility (e.g. Nolans), several major deposits in Australia are enriched in these elements, although they are not extracted. The best example of this is the Olympic Dam deposit, which is the second largest rare earth element accumulation in the world, but these metals are not extracted at present due to economic and metallurgical constraints.

This analysis has highlighted the potential for Australian production of critical commodities from existing mines, but also indicates that there are significant technological and economic impediments to realisation of this potential. It has also highlighted that the potential for critical commodity production is highly dependent upon the type and geochemical characteristics of the ores, and that additional data are required to more fully assess Australia’s potential as a critical commodity producer.
Critical commodities in Australia - an assessment of potential in ores

Scientific summary

Consideration of samples from the large range of ore samples analysed as part of the OSNACA (Ore Samples Normalised to Average Crustal Abundance: http://www.cet.edu.au/projects/osnaca-ore-samples-normalised-to-average-crustal-abundance) analytical program at the Centre for Exploration Targeting at the University of Western Australia and as certified reference materials by ORE Research & Exploration Pty Ltd (http://www.ore.com.au/) indicates that some Australian ores have potential as sources for critical commodities as by-products or 'companion metals'. Skirrow et al. (2013) found that potential sources of critical commodities can be grouped into four categories: (1) critical commodities associated with mafic orthomagmatic mineral systems, (2) critical commodities associated with felsic magmatism, (3) critical commodities associated with heavy mineral sands, and (4) critical commodities sourced as by-products of the mining of ores of major commodities. In this contribution, the first, second and fourth of these groups are discussed; the third group is not discussed due a lack of data. The viability of by-product extraction is not only dependent on the technical and economic viability of by-product extraction, but also on the economics of the major commodity with which the by-product critical commodity is associated.

Critical commodities associated with mafic orthomagmatic mineral systems. Komatiite–hosted nickel sulfide and related deposits currently produce both platinum–group elements (PGEs) and Co as by products, but PGEs are also known to be present in unconformity–related uranium deposits and some porphyry Cu deposits, and Co is known but not recovered in some sediment–hosted copper deposits. The data suggest some potential for recovery of PGEs as companion metals, although at present time such recovery is not economic.

Critical commodities associated with felsic magmatism. Molybdenum and Re are not currently produced in Australia, yet there are a number of potential sources of these metals, including deposits in which molybdenite could be recovered as the main commodity (e.g. porphyry Mo–Cu and skarn deposits) and others in which these metals could be recovered as by-products (e.g. porphyry Cu deposits and sediment–hosted deposits of various kinds). As Mo and Re are commonly recovered as by-products from porphyry Cu deposits around the world, these deposits are perhaps the best potential source of Mo and Re as companion metals in Australia, although their extraction is governed by economic and metallurgical considerations.

Pegmatite deposits in Western Australia and the Northern Territory, which are presently being assessed as Li resources, have potential for by–product Ta and Sn. The Toongi zirconia project in New South Wales, if developed, would recover Ta along with other metals including Hf, Nb, Y and rare earth elements (REEs). The Olympic Dam and Prominent Hill iron oxide copper–gold (IOCG) deposits in South Australia contain highly anomalous REE concentrations, with the Olympic Dam deposit being the second largest accumulation (after Bayan Obo, China) of these metals in the world. However, due to low grades (compared to REE-only deposits) and difficulties in producing a REE concentrate, these metals are not currently extracted at Olympic Dam.

Critical commodities sourced as by–products of the mining of ores of major commodities. At present, sphalerite (Zn) concentrates are an important source of Cd, Ga, Ge and In, with Cd currently being recovered by Australian Zn smelters. Although Cd concentrations are mostly a function of Zn grade, the concentrations of Ga, Ge and In depend strongly on deposit type, and the highest grades of Ga and In are from ores in which Zn is not the major commodity. The highest concentrations of Ga and In
in Zn–rich ores are from deposits formed from higher temperature ore fluids, and include, for example, volcanic–hosted massive sulfide (VHMS) ores. In contrast, the highest concentrations of Ge are from deposits formed by low temperature, oxidised fluids such as Mississippi Valley–type deposits and siliciclastic–carbonate sediment–hosted Zn–Pb deposits (e.g. Mount Isa and McArthur River). Intrusion-related deposits can host the highest concentrations of Ga and In.

Highest concentrations of Ga and In are from intrusion–related deposits, not from Zn–rich deposits. Gallium is most highly enriched in intrusion–related W ores and the Mount Weld REE–rich carbonatite, but extraction of Ga from these types of ores in not presently technically feasible. The highest concentration of In in the samples analysed is from intrusion–related Sn deposits, where it closely correlates with Cu, indicating that chalcopyrite may be a repository. Like Ga, recovery of In from these ore is not technically feasible at present.

Antimony and Bi, although not recovered from sphalerite concentrates, are also enriched in Zn–rich deposits. Antimony can be enriched in a large range of Zn ores types, but the most likely Australian Sb sources are orogenic stibnite deposits in which Sb would be the main recovered commodity if mined. Recovery of Sb from Zn–rich ores is at present not viable, although these ores contain significant potential companion resources of Sb. Bismuth, on the other hand, can be recovered from a range of mill products, including Pb (galena) and Cu concentrates. Like Ga and In, Bi is enriched in higher temperature deposits including VHMS deposits and some granite–related deposits.

Selenium and Te are currently recovered from anodic slimes produced during electrolytic recovery of Cu, hence Cu–rich ores are the best sources of these elements. The greatest potential for Se recovery is from some IOCG deposits and Cu–rich VHMS deposits, which are also the most promising sources of Te. Other deposit types (e.g. Zn-rich VHMS and orogenic base metal deposits) can contain elevated Se and Te, but given the constraints imposed by current extraction technologies, these sources may not be economically viable.
1 Introduction and background

In 2013, Geoscience Australia undertook an analysis of the potential economic impact of so-called 'critical commodities' on Australia's resource extraction industry (Skirrow et al., 2013). Critical commodities, as defined by Skirrow et al. (2013), are those commodities that are both economically important and have a high risk of supply disruption. Most major commodities — copper, zinc, lead, gold, iron, etc. — though economically important, do not have a supply risk as supply is available from a wide range of sources. Commodities that are most critical are those that, although produced in limited quantities, are critical for specific (generally technological) uses and have restricted sources of supply. A good example of a group of critical commodities is the rare earth elements (REEs), which are used in batteries, high-strength magnets, phosphors and other evolving technologies, but over 90% are produced by China (Skirrow et al., 2013). Many critical commodities are co- or by-products produced from ores of major commodities, and have been termed 'companion metals' by Mudd et al. (2014).

To assess the 'criticality' of commodities, Skirrow et al. (2013) compiled the results of major economically-based assessments from around the world to produce a global ranking. They found that although Australia's economy had very limited exposure to the availability of critical commodities (i.e. Australian industry is not a significant consumer of these commodities), Australia has great potential as a source of these commodities for the global market if technological and economic constraints allow.

In addition to this economically-based assessment, Skirrow et al. (2013) provided a geologically-based assessment of Australia's potential to provide these commodities based upon the mineral system paradigm. From this assessment, they concluded that the potential for specific critical commodities could be grouped according to mineral system. They indicated that mafic-ultramafic orthomagmatic mineral systems had high concentrations of, or potential for, Ni, PGEs, Cr and Co; mineral systems related to felsic magmatism had high concentrations or potential for REEs, W, Nb, Ta, Mo, Re, Be, Bi and fluor spar; and heavy mineral sand systems had high potential for Zr, Ti, REEs and Th. In addition, a fourth group of critical commodities, including Sb, In, Ga, Ge, Cd, Te and Se, were currently sourced as by-products from the processing of major commodities. Some commodities (Mn, Sr and graphite) do not fit easily into these groups.

This contribution provides a detailed analysis of the potential for critical commodities as companion metals based upon publicly available datasets. Data are for a wide range of elements, including many critical commodities, from ore-grade samples taken from a wide range of deposit types in Australia. The databases have been supplemented by re-analysis of samples for other commodities; results of all analyses are appended. These data can be used to assess the potential for critical commodities in the general groups proposed by Skirrow et al. (2013) and to assess critical commodities present in deposits that are currently being mined. As data are not available for heavy mineral sand deposits or for deposits of Mn, Sr and graphite, these deposits and associated commodities are not considered further.
2 Sources of data and analytical methods

Although data for major and trace commodities are presented for a number of deposits around Australia in individual PhD theses and papers (e.g. McGoldrick, 1982; Huston, 1988; Smith and Huston, 1992), datasets covering a wide range of major and trace elements for ore–grade samples for many different deposits have only recently become available. These datasets include the OSNACA (Ore Samples Normalised to Average Crustal Abundance) dataset (http://www.cet.edu.au/projects/osnaca-ore-samples-normalised-to-average-crustal-abundance) and ore–grade certified reference material (CRM) from ORE Research & Exploration Pty Ltd (http://ore.com.au). As part of this study these samples were analysed for an additional range of critical commodities as described below. Analytical methods and analytical results used to determine the distribution of critical elements are presented in Appendices A and B. Additional analyses of low–grade or unmineralised samples from Australia and for ore–grade samples outside of Australia can be found at the two websites. Although the original purposes of these datasets are not to determine the abundance of critical elements in ores (OSNACA's purpose is to study different ways of quantifying ore element signatures, and ORE Research & Exploration's purpose is to provide CRMs), both datasets fit the requirements of the present study and characterise a range of Australian ore deposits. The locations of the deposits from which the samples were sourced, as well as the locations of other deposits mentioned in this report, can be found in Figure 2.1. Table 2.1 lists deposits for which analytical data are available.

2.1 OSNACA data

Samples analysed as part of the OSNACA dataset were 'crowd–sourced' from mining companies, universities and geological surveys from Australia and elsewhere in the world. OSNACA provides a consistent dataset analysed by one laboratory (Bureau Veritas – Ultratrace) over a short time period for a large range of elements (see below). OSNACA presents analyses for a total of 707 samples, of which 339 are from Australia, and, of these, 306 are ore–grade or strongly mineralised. Following crushing, splitting and pulverising by standard methods, analyses were undertaken using a combination of fire assay (Au, Pt and Pd), peroxide fusion (B, Cr, Hf, Pb, S, Sb, Si, Sn, Ta, Ti, W and Zr), aqua regia (Au, B, Te, Hg, Ag and Sb), and mixed acid (hydrofluoric–nitric–perchloric)–hot box (Ag, Al, As, Bi, Ca, Cd, Co, Cs, Cu, Fe, In, K, Li, Mg, Mn, Mo, Na, Nb, Ni, Pb, Rb, Re, Sc, Se, Sn, Sr, Te, Th, Ti, U, V, W, Y, Zn and REEs) dissolution methods followed by induction plasma–optical emission spectroscopy (ICP–OES) or induction–coupled plasma–mass spectrometry (ICP–MS) scans. Brief descriptions of analytical methods and minimum detection limits are listed in Appendix A, which follows http://www.cet.edu.au/projects/osnaca-ore-samples-normalised-to-average-crustal-abundance/osnaca-analytical-techniques.

In addition to the existing analyses, this study commissioned re–reading of existing scans by Bureau Veritas on OSNACA samples to determine Be, Ga and Ge for Australian samples. Beryllium and Ga were analysed originally using mixed acid–hotbox (method MA202), and Ge by peroxide fusion (PF102), both with ICP–MS finishes. All analyses are tabulated in Appendix B.

\[x^1\] Samples sourced from the OSNACA are called OSNACA samples; CRMs from ORE Research & Exploration Pty Ltd are called OREAS samples.
2.2 ORE Research & Exploration data

The ORE Research & Exploration data (denoted hereafter as OREAS) differ from the OSNACA data in several important ways. As the data are from CRMs, the samples were analysed by multiple laboratories using many analytical techniques, with the resulting data synthesised to produce recommended values for each analyte for each different analytical method. The analyses were undertaken over a relatively long time-period, and the samples analysed using different methods for different analytes. To produce a consistent dataset, the CRMs were also analysed at Analabs–Brisbane (www.alsglobal.com) using a combination of fire assay, four acid digestion, borate fusion and HF digestion with ICP–OES, ICP–MS and XRF (X-ray fluorescence) finishes. In addition, F was analysed using a specific ion electrode, Cl was determined volumetrically, total C was determined using Leco apparatus, and LOI (loss–on–ignition) was determined by TGA (thermal gravimetric analysis) furnace. The ORE Research & Exploration certified values for the relevant analyte and
analytical method, and new analytical results where certified values are not available, are presented in Appendix B.

### Table 2.1 Deposit type and deposits for which OSNACA and OREAS data are available.

<table>
<thead>
<tr>
<th>Deposit type</th>
<th>Deposits</th>
</tr>
</thead>
<tbody>
<tr>
<td>Komatiite-associated nickel sulfide</td>
<td>Betheno, Black Swan, Blair, Cliffs, Cosmos, Goliath, Honeymoon Well, Hunt, Long, Mount Newman, Otter-Juan, Prospero and Six Mile Well</td>
</tr>
<tr>
<td>Intrusion-hosted nickel sulfide</td>
<td>Radio Hill and West Musgrave</td>
</tr>
<tr>
<td>Intrusion-hosted vanadium</td>
<td>Windarra</td>
</tr>
<tr>
<td>Epithermal gold-silver</td>
<td>Belyando, Cracow, Lake Cowal and Pajingo</td>
</tr>
<tr>
<td>Porphyry copper-gold</td>
<td>Cadia, North Parkes E22, North Parkes E26, North Parkes E48 and Ridgeway</td>
</tr>
<tr>
<td>Intrusion-related gold-copper</td>
<td>Boddington, Mount Leyshon and Telfer</td>
</tr>
<tr>
<td>Skarn, undifferentiated intrusion-related</td>
<td>Browns, Junction Reef, Lucky Draw and Sandy Creek Fluorspar</td>
</tr>
<tr>
<td>Intrusion-related tin</td>
<td>Cleveland and Renison Bell</td>
</tr>
<tr>
<td>Intrusion-related tungsten</td>
<td>Kind Island and White Rock</td>
</tr>
<tr>
<td>Pegmatite tantalum-tin-lithium</td>
<td>Greenbushes and Londonderry</td>
</tr>
<tr>
<td>Carbonatite rare-earth element</td>
<td>Mount Weld</td>
</tr>
<tr>
<td>Iron-oxide copper-gold</td>
<td>Einasleigh, Eloise, Geko, Mount Elliot, Olympic Dam, Osborne, Prominent Hill, Warrego and White Devil</td>
</tr>
<tr>
<td>Volcanic-hosted massive sulfide</td>
<td>DeGrussa, Erayinia-King, Gossan Hill, Harbour Lights, Hellyer, Henty, Hercules, Kangaroo Caves, Mount Lyell, Mount Morgan, Que River, Rosebery, Salt Creek, Scuddles, Sulphur Springs, Teutonic Bore, Tritton and Woodlawn</td>
</tr>
<tr>
<td>Sediment-hosted zinc-lead-silver - clastic dominated - siliciclastic-mafic</td>
<td>Abra, Beltana and Broken Hill</td>
</tr>
<tr>
<td>Sediment-hosted zinc-lead-silver - clastic dominated - siliciclastic-carbonate</td>
<td>Century, Dugald River, George Fisher, Hilton, HYC, Lady Loretta and Mount Isa</td>
</tr>
<tr>
<td>Sediment-hosted zinc-lead-silver - Mississippi valley-type</td>
<td>Cadjebut, Goongewa, Kapok, Magellan, Pillara, Sandy Creek and Warrabarty</td>
</tr>
<tr>
<td>Sediment-hosted copper</td>
<td>Lady Annie, Mount Isa copper, Mount Oxide and Nifty</td>
</tr>
<tr>
<td>Iron ore</td>
<td>Beebyn, Giles Mini, Koolyanobbing, Madoonga, Mount Whaleback, Spinifex Ridge iron and Windarling</td>
</tr>
<tr>
<td>Orogenic gold-antimony</td>
<td>Ballarat Last Chance, Bellvue, Big Bell, Chalice, Copperhead, Darlot, Fortnum, Frasers, Golden Kilometre, Golden Mile, Granny Smith, Griffins Find, Harlequin, Hibernian, Hill 50, Hillgrove, Junction, Jupiter, Kanowna Belle, Karonie, Kings Cross, Lancefield, Lawlers, Lindsay, Marvel Loch, Maybell, Meekatharra Prohibition, Micky Doolan Meekatharra, Mount Charlotte, Mount Morgans, Mount Olympus, Mount Olympus Peake, Nathans Labouchere, Nevoria, Ora Banda, Paddington, Porphyry, Randalls, Redeemer, Sons of Gwalla, Stawell, Sunrise Dam, Sunrise Dam, Three Mile Hill, Tick Hill, Victory, Wallaby, Warronga - Agnew, Wiluna and Youanmi</td>
</tr>
<tr>
<td>Orogenic base metal</td>
<td>Chesney, CSA, Endeavor (Elura), Prairie Downs, Ragged Hills and Woodcutters</td>
</tr>
</tbody>
</table>
2.3 Limitations of data

As many of the analytical methods involve acid digestions, the results may not reflect the total concentration of metals in the samples. This is particularly important for elements that are difficult to dissolve, such as Al, Nb, Sc, Th, Y and the REEs. Hence, results for these elements should be treated with caution. In the following discussion the analytical techniques most likely to produce complete analyses were used.

2.4 Treatment of data

To allow comparison and identify potential critical element enrichment in ores, the deposits were classified according to the scheme presented in Skirrow et al. (2013). The geochemical clusters of ore deposit types identified by Brauhart et al. (2017) were used in determining potential critical element enrichment. Only ore–grade samples were considered in the analysis, which involved both estimating 'typical' concentrations of critical commodities in ores and identifying intercorrelations between these and major and minor ore elements. It must be born in mind that due to the non–systematic methods in which the samples were obtained, 'typical' concentrations of critical commodities reported herein should be considered as guides only.

For most of the scattergrams showing the relationship between critical commodities and major ore commodities (section 4), average crustal abundances, and indicative grades at which the critical commodities have been extracted, are shown as horizontal lines. Table 2.2 summarises the sources of data used to determine these lines.
Table 2.2 Crustal abundances and recoverable grades of critical commodities.

<table>
<thead>
<tr>
<th>Critical commodity</th>
<th>Concentration in bulk continental crust</th>
<th>Grade as co–product</th>
<th>Grade as by–product</th>
<th>Basis of grade estimates</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pd</td>
<td>1.5 ppb</td>
<td>0.3 ppm</td>
<td>Grade of Kambalda Ni ore (Hudson and Donaldson, 1984)</td>
<td></td>
</tr>
<tr>
<td>Pt</td>
<td>1.5 ppb</td>
<td>0.4 ppm</td>
<td>Grade of Kambalda Ni ore (Hudson and Donaldson, 1984)</td>
<td></td>
</tr>
<tr>
<td>Co</td>
<td>26.6 ppm</td>
<td>500 ppm</td>
<td>Grade of Windabout Cu–Co–Ag deposit (2008 Gunson Resources annual report)</td>
<td></td>
</tr>
<tr>
<td>Cr</td>
<td>135 ppm</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>V</td>
<td>138 ppm</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mo</td>
<td>0.8 ppm</td>
<td>420 ppm(^a)</td>
<td>130 ppm(^b)</td>
<td>Spinifex Ridge (ASX release: Moly Mines Ltd, 13 Feb 2012); average Mo grade, porphyry Cu deposits (Singer et al., 2008)</td>
</tr>
<tr>
<td>Re</td>
<td>0.188 ppb</td>
<td>0.05 ppm</td>
<td>Typical Re grade in porphyry Cu deposits (Singer et al., 2008)</td>
<td></td>
</tr>
<tr>
<td>W</td>
<td>1 ppm</td>
<td>349 ppm</td>
<td>Inferred resource, Kara No 1 deposit (Geoscience Australia, 2013)</td>
<td></td>
</tr>
<tr>
<td>Ta</td>
<td>0.7 ppm</td>
<td>113 ppm</td>
<td>Pilgangoora Li pegmatite (ASX releases: Pilbara Minerals, 11/07/2016)</td>
<td></td>
</tr>
<tr>
<td>Sn</td>
<td>1.7 ppm</td>
<td>126 ppm(^a), 1200 ppm(^b)</td>
<td>Moonyella pegmatite (ASX release: Lithex Resources, 02/03/2012); Kidd Creek mine (Canada) (Hennigh and Hutchinson, 1999)</td>
<td></td>
</tr>
<tr>
<td>Nb</td>
<td>8 ppm</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Li</td>
<td>16 ppm</td>
<td>5654 ppm</td>
<td>Pilgangoora Li pegmatite (ASX release: Pilbara Minerals, 11/07/2016)</td>
<td></td>
</tr>
<tr>
<td>Be</td>
<td>1.9 ppm</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>La</td>
<td>20 ppm</td>
<td>12600 ppm(^a)</td>
<td>1705 ppm(^b)</td>
<td>Bayan Obo (China); Olympic Dam (Weng et al., 2015)</td>
</tr>
<tr>
<td>Cd</td>
<td>80 ppb</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ga</td>
<td>16 ppm</td>
<td>50 ppm</td>
<td>Typical grade in bauxite and Zn ores from which Ga is extracted</td>
<td></td>
</tr>
<tr>
<td>Ge</td>
<td>1.3 ppm</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>In</td>
<td>52 ppb</td>
<td>50 ppm</td>
<td>Typical grade in ores from which In has been extracted (Schwarz-Schampera and Herzig, 2002)</td>
<td></td>
</tr>
<tr>
<td>Sb</td>
<td>0.2 ppm</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bi</td>
<td>0.18 ppm</td>
<td>1600 ppm</td>
<td>200 ppm</td>
<td>Co–product grade, NICO (Canada) deposit (Canizares et al., 2009); by–product grade, Citadel mineral resource (ASX release: Antipa Resources, 19/03/2012)</td>
</tr>
<tr>
<td>Se</td>
<td>0.13 ppm</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Te</td>
<td>1.0 ppb</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\(^a\)Bulk continental crust concentrations from Rudnick and Gao (2003) except for Te, which is from www.webelements.com.

\(^b\)A co–product is a product that is produced jointly with a main product.

\(^b\)A by–product is an incidental or secondary product from processes used to produce a main product.
3 Extractive metallurgy

Many, if not most, critical commodities are produced as by–products of major commodities. For example, Ge, In and Cd are largely by–products of Zn smelting. As a consequence, the production of these commodities depends not only on their concentrations in the ores, but also upon the availability of the metallurgical processes for recovery. Table 3.1 summarises the sources and the metallurgical processes used to recover critical commodities discussed in this report.

The implications of metallurgy on critical commodity production are many and varied. For some commodities, metallurgical processes have been developed to extract specific commodities from a limited range of mineral sources. For example, at present metallurgical processes have not been developed to extract In from chalcopyrite. At present Zn–rich ores are by far the dominant source of In, even though Cu–rich ores can contain higher overall concentrations (see below).

Moreover, in some cases, high concentrations of critical commodities in mineral concentrates can be detrimental. For example, high concentrations of Ge (>50 ppm) and Sb (>1000 ppm) in Zn concentrates can result in smelter penalties due to the difficulties presented in recovering and/or disposing of these metals (Sinclair, 2005).

Hence, the geochemical data provided in this report must be used with an understanding of metallurgical processes when determining the potential for critical commodity recovery. Many critical commodities are extracted during metallurgical processing of specific concentrates, so even if a concentrate is enriched in a particular commodity, the commodity is only extractable if current commercial processes and metal prices allow extraction. The main purpose of this report is to raise awareness that critical commodities may be present in ores but are not recovered. Additional analysis, including metallurgical studies, are required to establish if any of the elements identified can be extracted economically.
### Table 3.1 Metallurgical processes used to recover critical commodities

<table>
<thead>
<tr>
<th>Commodity(ies)</th>
<th>Sources and extractive metallurgical processes</th>
<th>References</th>
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<tbody>
<tr>
<td><strong>Critical commodities present mostly in mineral systems related to mafic–ultramafic magmatism</strong></td>
<td></td>
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<tr>
<td>Ni, Co and platinum-group elements (Ru, Rh, Pd, Os, Ir and Pt) in sulphide ores</td>
<td>Flotation is used to produce Ni–Co and Cu concentrates from the ores. The concentrates are then smelted to produce metal–rich mattes, which are then leached to produce a leachate from which Ni and Co, and Cu are extracted by solvent extraction, electrowinning and/or H₂ reduction. PGEs are also refined from the mattes using hydrometallurgical methods.</td>
<td>Crundwell et al. (2011); Cole and Ferron (2012)</td>
</tr>
<tr>
<td>Ni and Co in lateritic ores</td>
<td>Saprolite ores are smelted to produce ferronickel, whereas limonitic ores are leached at high temperature and pressure, with Ni and Co recovered by solvent extraction, electrowinning and/or H₂ reduction.</td>
<td>Crundwell et al. (2011)</td>
</tr>
<tr>
<td>Cr</td>
<td>Chromite is smelted to ferrochromium using an aluminothermic reaction. Alternatively it is converted to Cr metal by roasting with chromate leached from the calcine and precipitated as sodium dichromate by reaction with sulphuric acid. The dichromate is reduced to Cr metal in two stages using C and then aluminothermal reduction.</td>
<td><a href="https://en.wikipedia.org/wiki/Chromium">https://en.wikipedia.org/wiki/Chromium</a> (accessed 17 August 2016)</td>
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<tr>
<td>V and Ti</td>
<td>Following enrichment by magnetic separation, V–Ti–bearing magnetite is smelted, with most of the V and Ti reporting to the slag. The slag is then leached and V and Ti are recovered using hydrometallurgy and then reduced to metal. This process also produces pig iron. An alternative approach to recover V is salt roasting followed by leaching of the calcine and hydrometallurgical recovery.</td>
<td>Taylor et al. (2006)</td>
</tr>
<tr>
<td><strong>Critical commodities present mostly in mineral systems related to granitic (and alkalic) magmatism</strong></td>
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<tr>
<td>Mo (and Re)</td>
<td>Following flotation, molybdenite concentrates are roasted and then leached with aqueous ammonia, with Mo extracted from this solution and then reduced to metal using H₂. Rhenium is extracted from flue dust produced during roasting by aqueous solution and precipitated by addition of potassium or ammonium chloride. Rhenium metal is produced by reduction with H₂.</td>
<td>Gupta (1992); <a href="https://en.wikipedia.org/wiki/Molybdenum">https://en.wikipedia.org/wiki/Molybdenum</a>; <a href="https://en.wikipedia.org/wiki/Rhenium">https://en.wikipedia.org/wiki/Rhenium</a> (accessed 17 August 2016)</td>
</tr>
<tr>
<td>W</td>
<td>Following various combinations of gravity separation and flotation, W concentrates are decomposed by a number of different methods, and the resulting product is reduced to W metal in a furnace.</td>
<td>Yih and Wang (1979)</td>
</tr>
<tr>
<td>Sn</td>
<td>Cassiterite, which is concentrated by gravity, and, to a lesser extent, flotation methods, is the main source of tin. Tin sulphides are more difficult to process. Cassiterite concentrates are smelted using thermocarbonic reduction to produce Sn metal.</td>
<td>Anonymous (2012)</td>
</tr>
<tr>
<td>Ta and Nb</td>
<td>Following gravity separation, Ta–Nb concentrates are leached using hydrofluoric and sulphuric acid, with the Ta and Nb extracted from the leachate using organic solvents. The metals are extracted from the solvent by addition of KF and ammonia and then reduced to metal using Na.</td>
<td><a href="https://en.wikipedia.org/wiki/Tantalum">https://en.wikipedia.org/wiki/Tantalum</a>; <a href="https://en.wikipedia.org/wiki/Niobium">https://en.wikipedia.org/wiki/Niobium</a> (accessed 17 August 2016)</td>
</tr>
<tr>
<td>Li (from spodumene-bearing pegmatites)</td>
<td>Although most Li is currently produced from brines extracted from salt lakes, principally in South America, Australia’s Li production and potential is from spodumene in pegmatite deposits. Spodumene is concentrated largely by froth flotation, and the resultant concentrate is roasted and then leached by sulphuric acid. Following removal of impurities from the leachate, Li is precipitated as a carbonate by addition of sodium carbonate to the leachate.</td>
<td>Averill and Olson (1978)</td>
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<tr>
<td>Commodity(ies)</td>
<td>Sources and extractive metallurgical processes</td>
<td>References</td>
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<tr>
<td>Be</td>
<td>The main Be ore mineral are bertrandite and beryl, which are concentrated using froth flotation. Bertrandite concentrates are leached with sulphuric acid, whereas beryl concentrates require melting prior to acid leaching. The leachate is treated to remove impurities prior to precipitation as Be hydroxide, which is then used in beryllia ceramics and in the production of Be metal.</td>
<td>Walsh (2009); <a href="http://beryllium.eu/about-beryllium-and-beryllium-alloys/facts-and-figures/beryllium-extraction/">http://beryllium.eu/about-beryllium-and-beryllium-alloys/facts-and-figures/beryllium-extraction/</a> (accessed 17 August 2016)</td>
</tr>
<tr>
<td>Fluorspar</td>
<td>Fluorspar (fluorite), which is typically concentrated using froth flotation, is directly used as a metallurgical flux, in ceramics and for HF acid production.</td>
<td>Peterson et al. (1990)</td>
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<tr>
<td>Rare–earth elements (La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm ,Yb and Lu)</td>
<td>Following concentration by gravity and magnetic methods (placer deposits) or flotation (hydrothermal deposits), REE–bearing minerals are typically dissolved in acids (or in some cases treated by NaOH to leave a REE–rich residue which is then dissolved). The REEs are then recovered from solution through ion exchange or solvent extraction, with individual REE metals produced by fused salt electrolysis and metallothermally.</td>
<td>Habashi (2013)</td>
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<tr>
<td>Critical commodities present mostly as by– or co–products from the processing of major commodities</td>
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<td></td>
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<tr>
<td>Zn, Cd, In, Ge (and Ga)</td>
<td>Zinc is recovered by both electrolysis (89% of production) and carbothermic reduction (11%). Cadmium is recovered by leaching of Zn cementate. Other trace elements (In, Ge and Ga) can be recovered by leaching of iron residue.</td>
<td>Alfantazi and Moskalyk (2003); Sinclair (2005)</td>
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<tr>
<td>Ga</td>
<td>The main source of Ga is the processing of bauxite. Gallium is recovered by electrolysis of Al hydroxide solution. Minor sources are from the processing of sphalerite concentrates (see above).</td>
<td>Moskalyk (2003)</td>
</tr>
<tr>
<td>Co (from Cu–Co deposits – sulphide ores)</td>
<td>Copper–Co concentrates produced by flotation are roasted. The resulting calcine is leached, with Cu won using electrowinning and, after impurities are removed from the leachate, Co is precipitated as a hydroxide.</td>
<td>Fisher (2011)</td>
</tr>
<tr>
<td>Sb</td>
<td>The main Sb source is stibnite, although it can be recovered from other Sb–bearing sulphides (e.g. tetrahedrite). Following flotation, Sb is recovered pyrometallurgically using volatilisation, smelting or liqution/iron precipitation.</td>
<td>Anderson (2002)</td>
</tr>
<tr>
<td>Bi</td>
<td>Bismuth–bearing sulphide minerals generally report to Pb or Cu concentrates, whereas other Bi minerals can report to W or Bi–Sn concentrates. Following smelting Bi metal is extracted from Pb bullion either from slimes produced by Pb electrowinning or from dross produced by kettle refining. Bi–bearing process residues produced during Cu smelting and refining can be added to the Pb concentrate prior to smelting. Bismuth can also also recovered from the processing of W ores.</td>
<td>Ojebuoboh (1992)</td>
</tr>
<tr>
<td>Te and Se</td>
<td>The vast majority (90%) of both Se and Te are recovered from anodic slimes produced during electrolytic refining of Cu. Selenium, Te and a number of other metals are extracted from the slimes by use of a mixture of roasting, leaching and/or chlorination.</td>
<td>Schlesinger et al. (2011); Lu et al. (2015)</td>
</tr>
</tbody>
</table>
4 Results

The combined OSNACA/OREAS dataset (Appendix B) provides information for many of the critical commodities identified by Skirrow et al. (2013). In the following discussion, each of three critical commodity families – mafic–ultramafic–related, felsic igneous–related and by–/co–product – are discussed separately. In all cases, average continental crust abundances for the commodity of interest (Rudnick and Gao, 2003) are given, and, in many cases, the grades of currently operating mines or deposits in advanced stages of feasibility (mostly Australian and mostly as by–products) are provided (Table 2.1) as a guide to grades at which it might be possible to economically extract the commodity.

4.1 Critical commodities present mostly in mineral systems related to mafic–ultramafic magmatism

Many of the critical commodities identified by Skirrow et al. (2013) are present as minor constituents in deposits associated with mafic to ultramafic magmatism. In some cases the commodities are extracted as by–products of Ni mining (PGEs and Co). In other cases (Cr and V), the critical commodities are the main or only product extracted. Although mafic–ultramafic orthomagmatic deposits are the main sources of these commodities, other classes of deposits, unrelated to mafic–ultramafic magmatism, are also potential sources.

4.1.1 Platinum–group elements

Figure 4.1 illustrates the correlation of PGEs, as represented by Pt (Fig. 4.1A) and Pd (Fig. 4.1B), with Ni in both komatiite–associated and intrusion–hosted Ni–S deposits, a relationship noted by many authors (Hoatson and Lewis, 2014, and references therein). As PGEs are recovered from the leaching of Ni and Cu mattes produced by the smelting of Ni and Cu concentrates, the recovery of these metals in Australia is largely dependent upon the economics governing Ni and Cu production from the ores. Historically, komatiite–associated Ni–S mines in Western Australia typically grade around 2% Ni or more (Hoatson et al., 2006), but since the mid–1990s, the Mount Keith mine has been in operation as a large tonnage deposit grading only 0.57% Ni. This deposit grades between <0.2 and 0.5 ppm total PGEs, significantly lower than the grades of the higher grade Kambalda deposits (2.96% Ni, 0.22% Cu and 1.19 ppm total PGEs: Hoatson and Lewis, 2014).

Although the vast majority of PGEs in Australia have been, and continue to be, produced as a by–product of Ni smelting from orthomagmatic mafic–ultramafic–associated deposits in Western Australia, PGE potential exists not only in PGE–dominant deposits, but also as a co– or by–product of other deposit types, including porphyry Cu and unconformity–related U deposits. Deposits in which PGEs are the main commodities of interest include the Munni Munni and Panton deposits in Western Australia (Hoatson and Lewis, 2014), but these deposits, although high grade, are not sufficiently large to support development. The only other significant producer of Australian PGEs have been placers in Tasmania (Adamsfield and Wilson River) and New South Wales (Fifield) from 1893 to 1934.

Another significant deposit type that can contain high PGE content is unconformity–related U deposits. At the Coronation Hill deposit in the Northern Territory, a high–grade Au–PGE resource (6.69 Mt @ 6.42 g/t Au, 0.30 g/t Pt, and 1.01 g/t Pd (pre–JORC): Mernagh et al., 1994; Hoatson and Lewis, 2014) is located in a zone that is spatially separate from the main U–Au (with minor PGE credits) zone. As
this resource is located in a prescribed reserve, mining is prohibited. Platinum–group elements have also been recognised, either through assays or mineralogical studies, at other unconformity–related U deposits in the Northern Territory, including the Ranger and Jabiluka deposits, but very limited data are available and the PGEs are not recovered.

Porphyry Cu deposits from the Macquarie Arc in New South Wales are also known to have elevated PGE contents. Hoatson and Lewis (2014) reported that discrete samples from the Copper Hill deposit can contain up to 0.91 ppm Pd. This is supported by the OSNACA/OREAS data which indicates individual assays of ore samples contain up to 0.043 ppm Pd, and a sample of Cu concentrate assayed 0.66 ppm Pd and 0.04 ppm Pt. Platinum–group elements are not currently recovered from Macquarie porphyry Cu deposits as recovery is not economically viable. If recovery techniques could be developed or grades could be increased to allow economic recovery, the Macquarie porphyry Cu deposits could represent a significant PGE resource.
4.1.2 Cobalt

In addition to PGEs, Co is also recovered as a by–product of smelting orthomagmatic Ni–Cu and lateritic Ni ores. In 2010, Western Australia produced 3852 t of Co in concentrate from Ni–dominant operations (Elias, 2013). Figure 4.1C illustrates a strong correlation between Ni and Co for orthomagmatic Ni–Cu deposits based upon the OSNACA and OREAS samples. Like PGEs, the grade of by–product Co depends strongly upon the economics of Ni production, so the recoverable Co grade will vary from deposit to deposit.

Figure 4.2A shows that other potential sources of Co in Australia include shale–hosted Cu deposits (including deposits in the Mount Isa Province, Queensland: Mount Isa Cu and Mount Oxide), and Cu–rich volcanic–hosted massive sulphide deposits (Tritton (New South Wales) and DeGrussa (Western Australia)). However, viable Co recovery depends upon what minerals host Co, which determines what product (concentrate or tails) they report to during flotation.

4.1.3 Chromium

Virtually all of the world's supply of chromium comes from chromite, which is concentrated by magmatic and/or metamorphic processes into chromitite bodies that form stratigraphic bands within layered mafic–ultramafic intrusions or pods in serpentinised mafic–ultramafic complexes. The most significant chromite producer in Australia was the Coobina mine in the Pilbara Craton of Western Australia, which, until its closure in 2013 produced 1.32 Mt of chromite ore (Bye, 1975; Australian Consolidated Minerals annual reports). As Cr is produced solely as a major commodity, it is unlikely that it can be produced as a by–product from existing mines. The highest Cr assay in the OSNACA and OREAS analyses is 4900 ppm from the Honeymoon Ni deposit, well below the grades of typical chromitites.

In addition to Coobina, chromitites are also known in Western Australia at the Munni Munni (Pilbara Craton), Panton, Lamboo (Halls Creek Orogen), Weld Range and Windimurra (Yilgarn Craton) layered mafic intrusions. Podiform chromitites associated with serpentinised mafic–ultramafic complexes are known in Tasmania (e.g. Adamsfield) and New South Wales (Coolac). In most cases these chromitite deposits are too small to justify mining, but many contain PGEs directly associated with chromitites, and have potential as PGE resources (see 4.1.1). The Coobina chromitite, however, does not contain appreciable PGE concentrations.

4.1.4 Vanadium

Most of the world's production and Australia's resources of V are from stratiform V– and Ti–bearing magnetite deposits hosted by layered mafic–ultramafic intrusions. Such deposits include Balla Balla, Speewah, Canegrass and Unaly Hill in Western Australia, and Mount Peake in the Northern Territory (Fig. 2.1). Of these, the most significant is at Balla Balla, with total resources of 456 Mt grading 45% Fe, 0.64% V2O5 and 13.7% TiO2 (Geoscience Australia, 2013). In addition to these orthomagmatic magnetite resources, a V resource has been defined at the Julia Creek shale–hosted deposit in Queensland where the V is enriched with Mo in calcareous oil shale. A total resource of 5.308 Gt grading 0.37% V2O5 and 312 ppm Mo has been defined (Geoscience Australia, 2013).
Figure 4.2. Scattergrams showing the relationship of selected critical commodities with Cu based on analyses of ore samples from Cu and Cu–Au deposits: (A) Co versus Cu, (B) Mo versus Cu, (C) Re versus Cu, (D) La versus Cu, (E) Cd versus Cu, (F) In versus Cu, (G) Sb versus Cu, (H) Bi versus Cu, (I) Se versus Cu, and (J) Te versus Cu. Crustal abundances and recoverable grades are presented in Table 2.2. For Se and Te, crustal abundances are lower than the minimum values on the respective graphs.
In the OSNACA–OREAS data, the highest V concentrations (up to 700 ppm) are associated with orogenic gold deposits; the maximum concentrations for other deposit types are less than 300 ppm (Appendix B). It is unlikely, given concentrations in vanadiferous magnetite deposits, that V can be be recovered economically from other deposit types.

4.2 Critical commodities present mostly in mineral systems related to granitic (and alkalic) magmatism

Some critical commodities, including Mo, Re, W, Ta, Nb, Li, Be and REEs, are commonly associated with felsic or alkaline magmatism. In contrast to the commodities associated with mafic–ultramafic igneous systems, many of these commodities are enriched in hydrothermal deposits, where they have been transported from the source magma by magmatic–hydrothermal fluids.

4.2.1 Molybdenum and rhenium

Global production of Mo and Re is from deposits in which Mo is the main or only commodity produced (e.g. porphyry Mo deposits) and from those in which Mo is a by–product (e.g. porphyry Cu deposits). Rhenium closely follows Mo as it is a minor constituent in molybdenite, which is the main Mo ore mineral. Although Australia does not produce Mo currently, a number of deposits in Australia are potential producers. These include deposits in which Mo is one of the major potential products (Spinifex Ridge, Western Australia (porphyry Mo–Cu); Unicorn, Victoria (porphyry Mo–Cu); Merlin, Queensland (iron–oxide copper–gold (IOCG)–related Mo–Re); and Molyhil, Northern Territory (skarn Mo–W)) and others where Mo (and Re) could be recovered as a by–product (porphyry Cu deposits in Macquarie ‘Arc’). With the possible exception of the Merlin deposit, the above deposits have a direct association with intermediate to felsic magmatism. Molybdenum can also be enriched in oil shales (e.g. Julia Creek (see above)) and some sediment–hosted U deposits (e.g. Maureen, Queensland).

Although development of Mo–dominant deposits is largely dependent on the price of Mo and other co–products and on the location of the deposit, extraction of Mo and Re as by–products is dependent on the economics of the main commodities and the viability of separating molybdenite from other minerals. The main source of by–product Mo is porphyry Cu deposits, which typically have grades of between a few to several hundred ppm Mo (Singer et al., 2008). Data from the OSNACA/OREAS dataset are compatible with the Singer et al. (2008) global dataset, with a total range in concentrations of 1–240 ppm in ore samples, and a concentration of 490 ppm in a Cu concentrate (Fig. 4.2B; Appendix B). Moreover, this concentrate is enriched in Re (0.897 ppm: Fig. 4.2C).

Other Cu–dominant deposit types that are enriched in Mo and/or Re include IOCG and VHMS deposits (including high sulfidation varieties: Figs. 4.2B and 4.2C). However, using the typical Mo grade of porphyry Cu deposits (Singer et al., 2008) as a guide, very few of the analysed samples have sufficient grade for recovery of Mo as a by–product. Even though some of the Re grades of the analysed samples significantly exceed Re grades of porphyry Cu deposits, recovery of the Re would be dependent upon the viability of Mo recovery.

Although Mo has a strong correlation with Ni in mafic–ultramafic orthomagmatic Ni–S deposits (Fig. 4.1D), it is unlikely that Mo concentrations would ever approach levels to allow economic recovery. Similarly, in Zn–rich deposits, it is unlikely that Mo and Re could be recovered, although more Cu–rich deposits from the Cobar orogenic base metal district do contain significant Mo enrichment (Fig. 4.3A), albeit with low levels (Appendix B).
Figure 4.3. Scattergrams showing the relationship of selected critical commodities with Zn based on analyses of ore samples from Zn deposits: (A) Mo versus Zn, (B) W versus Zn, (C) Sn versus Zn, (D) Cd versus Zn, (E) Ga versus Zn, (F) Ge versus Zn; (G) In versus Zn, (H) Sb versus Zn, (I) Bi versus Zn, and (J) Se versus Zn. Crustal abundances and recoverable grades are presented in Table 2.1.
The few available analyses of granite–related W deposits (King Island, Tasmania and White Rock, New South Wales) indicate some potential for by–product recovery of Mo from these deposits depending upon the metallurgical viability of extracting molybdenite from these ores (Fig. 4.4A). If the molybdenite can be extracted there is potential also for by–product Re. One of the highest–grade Mo deposit in Australia is the Molyhil skarn (4.71 Mt grading 0.13% Mo, 0.28% WO₃ and 18.1% Fe: 2013 Thor Mining Plc annual report). The limited data available suggest that, if pegmatite samples are excluded, there is an anticorrelation between Sn and both Mo and Re, suggesting that granite–related Sn deposits have low potential for Mo and/or Re.

4.2.2 Tungsten

Although Australia historically has been a major W producer, since mining ceased at the Dolphin and Bold Head lenses on King Island in Tasmania, Australian W production has been limited, with minor production from the Kara magnetite skarn in Tasmania and deposits in north Queensland. Currently all economically demonstrated resources in Australia are from deposits in which W is the major product or a co–product (Geoscience Australia, 2013). The OSNACA dataset, however, indicates potential for by–product W in intrusion–related Sn deposits in Tasmania and at the Abra deposit in Western Australia.

A very high–grade sample from the Renison Bell Sn deposit in Tasmania contains nearly 2000 ppm W, and other samples from Renison Bell and the nearby Cleveland deposits contain a few hundred ppm W (Fig. 4.4A). Venture Minerals have reported an ore reserve at the Mount Lindsay magnetite skarn, also in Tasmania, of 14 Mt grading 0.2% Sn, 0.1% WO₃, 0.1% Cu and 15% Fe (ventureminerals.com.au; accessed 28 August 2016).

At the Abra deposit, samples from the Cu–rich zone contain several hundreds to thousands of ppm W, whereas Pb–rich samples generally contain less than 100 ppm W (Fig.4.3B). Although classified as a syngenetic sediment–hosted deposit (Pirajno et al., 2016), other deposits of this style are not W–enriched. Lode gold deposits are also characterised by enrichment in W (Appendix B), but at levels that are not likely to be economic.

4.2.3 Tin

Like W, all of Australia’s economically demonstrated resources of Sn are intrusion–related deposits in which Sn is the only or major economic commodity (Geoscience Australia, 2013). However, Sn has historically been produced as a by–product from several deposit types, including pegmatites and VHMS deposits. Pegmatite fields in the Pilbara Craton and at Greenbushes in Western Australia have been significant historical producers of Sn (Blockley, 1980; Sweetapple and Collins, 2002), generally as a by–product of Ta production. The potential mining of these same pegmatites for Li (see 4.2.4) raises the possibility of the production of by–product Sn.

Although Sn has not been recovered from VHMS deposits in Australia, by–product Sn has been produced from Zn–rich ores at Kidd Creek in Canada (Hennigh and Hutchinson, 1999), and co–product Sn has been produced from Sn–Cu ores at Neves Corvo in Portugal (Relvas et al., 2006). Analyses from the OSNACA dataset indicate that Sn is commonly enriched in Australian VHMS deposits (Fig. 4.3C), even to levels recorded at Kidd Creek. Hence, there is potential for by–product Sn in some Australian VHMS deposits, if favourable metallurgy can be demonstrated.
4.2.4 Tantalum, niobium, lithium and beryllium

From the mid 1990s until 2008, when Ta production ceased from the Greenbushes and Wodgina operations in Western Australia, Australia was the main global producer of Ta. Greenbushes is currently a significant Li producer, and a number of pegmatites in the Pilbara (e.g. Pilgangoora) and Yilgarn (e.g. Greenbushes) cratons in Western Australia are either producing Li from spodumene, or are in the advanced stages of feasibility. These pegmatites historically have produced significant quantities of Nb and Be in addition to Li, Ta and Sn (Sweetapple and Collins, 2002). Hence, existing and future development of pegmatite deposits should consider the extraction of Ta, Nb, Sn and Be in addition to the main commodity Li.

Figure 4.4. Scattergrams showing the relationship of selected critical commodities with Sn and Cu based on analyses of ore samples from Sn and W deposits: (A) Mo versus Sn, (B) W versus Sn, (C) In versus Sn, (D) In versus Cu, and (E) Bi versus Sn. Crustal abundances and recoverable grades are presented in Table 2.1.

Although not analysed as part of this study, the Dubbo, or Toongi, zirconia project in New South Wales, has a mineral resource of 73.20 Mt grading 1.96% ZrO₂, 0.04% HfO₂, 0.46% Nb₂O₅, 0.14%
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Ta₂O₅, 0.14% Y₂O₅ and 0.75% REO² (2015 Alkane Resources Ltd annual report). If developed, Ta, Nb and other rare metals would be produced as a by–product of zirconia production. In addition, Lynas Corporation reports a Nb–rich mineral resource of 37.7 Mt grading 0.024% Ta₂O₅, 1.07% Nb₂O₅, 1.16% REO, 0.3% ZrO₂, 7.99% P₂O₅, 0.09% Y₂O₅ and 4.01% TiO₂ at the Mount Weld deposit in Western Australia (this is in addition to the REE resources at Mount Weld: 2015 Lynas Corporation annual report). These resource data suggest that Ta, Nb and other rare metals may be produced as by–products of zirconia and REE extraction.

4.2.5 Rare earth elements

As noted in the introduction, REEs exemplify critical commodities in that well over 90% of production of these essential commodities is from China (mostly from the Bayan Obo deposit). Australia has a number of REE projects that are in production (e.g. Mount Weld) or in advanced stages of feasibility (e.g. Nolans, Northern Territory). The potential of these deposits is well known. Less well known is the potential of other types of deposits to produce REEs as by–products, in particular IOCG deposits. Figure 4.2D illustrates that not only is the Olympic Dam IOCG deposit in South Australia enriched in REEs, but that the nearby Prominent Hill deposit is also enriched in REEs. These levels (average La concentration at Olympic Dam is 1000 ppm: K Ehrig, pers. comm., 2017) are less than 10% of the average grade of the Bayan Obo deposit (12600 ppm: Weng et al., 2015). The large size of Olympic Dam, however, makes it a major REE accumulation that is roughly half the size of Bayan Obo (e.g. Bayan Obo contains 19.4 Mt La (calculated from data in Weng et al., 2015) versus 10.4 Mt La for Olympic Dam (calculated from data provided by K Ehrig, pers. comm, 2017). Despite the size of the Olympic Dam resource, the current operators have no plans for REE extraction due to the low grade of the resource relative to other REE resources and the fine-grained character of the REE minerals, which makes production of a REE concentrate unviable (K Ehrig, pers. comm., 2017). The limited data from the OSNACA database suggest that IOCG deposits are not all REE–enriched, with other analysed deposits (those from the Tennant Creek, Northern Territory district and from the Einasleigh, Queensland deposit) having REE concentration near, or below, the average crustal abundance (Fig. 4.2D). Other than IOCG deposits and the Mount Weld deposit, no other deposits in the OSNACA/OREAS database have significant REE enrichment.

4.3 Critical commodities present mostly as by– or co–products from the processing of major commodities

In addition to the commodities that have a strong association with either mafic–ultramafic orthomagmatic or granite–related mineral systems, other critical commodities are known to be present in other mineral systems, including those associated with Zn–Pb–dominated deposits that formed in volcanic and sedimentary basins. These commodities, also known as companion commodities, are important in that they are currently, or could be, recovered using existing metallurgical processes.

4.3.1 Zinc, cadmium, gallium, germanium and indium

Sphalerite, the main Zn ore mineral, commonly contains trace to minor concentrations of Fe, Mn, Cd, Ga, Ge and In (Huston et al., 1995; Cook et al., 2009). Many of these metals are recovered during the metallurgical processing of Zn concentrates (Table 3.1), and, as such, represent existing or potential sources of critical commodities. Figure 4.3D illustrates a very strong linear relationship between Zn

² Total Rare Earth (Lanthanide) Oxide
and Cd, which is largely independent of deposit type. Cadmium is currently recovered at the Nyrstar Zn smelter in Hobart, Tasmania. Although Cu–rich deposits generally do not contain high Cd concentrations, a few examples from Cu–rich VHMS deposits contain ~100 ppm Cd. These samples, however, are of Zn–rich zones from the deposits.

Relationship between Zn and Ga, Ge and In is more complex. Although these metals are also recovered through the metallurgical processing of sphalerite (Table 3.1), their relationship to Zn concentrations is not simple, and, only in some types of deposits do they have consistent enrichment with Zn.

Gallium, which is mostly extracted during the processing of bauxite (Table 3.1; Yellishetty et al., 2017), is also recovered from the processing of sphalerite concentrates. For Zn–rich ores, Ga concentrations range from ~1 ppm to 40 ppm. Although there is not a consistent pattern, most of the higher Ga concentrations are from VHMS deposits (Fig. 4.3E). Unlike most other metals of economic interest, the concentration of Ga in ores is not significantly higher than the average continental crust value of 16 ppm (Rudnick and Gao, 2003); the main reason that Ga is recovered is its amenity for recovery during metallurgical processing. Based on the OSNACA–OREAS dataset, the highest concentrations of Ga are not from Zn–rich ores or bauxite, but from intrusion–related W ores (to 246 ppm) and the Mount Weld carbonatite (106 ppm), with pegmatite ores also having elevated (28–62 ppm) concentrations. At present, however, processes to recover Ga from these ores are not known.

The highest concentrations of Ge are in Zn–rich ores. With the exception of some granite–related deposits (Browns Creek (to 30 ppm), intrusion–related Sn (to 87 ppm) and pegmatite (to 25 ppm) deposits), Zn–poor deposits mostly contain less than 5 ppm Ge (Appendix B). Zinc-rich samples generally contain more abundant Ge, but enrichments vary between different classes of Zn deposits. The OSNACA–OREAS dataset (Appendix B) suggests that Zn–rich deposits that formed from low temperature (<200°C), oxidised fluids (Cooke et al., 2000; Huston et al., 2016: red and orange symbols on Figure 4.3F) have significantly higher Ge concentrations (mostly 10–80 ppm) than deposits that formed from higher temperature (>200°C), reduced fluids (blue and green symbols on Figure 4.3F: mostly <10 ppm). This suggests that most potential for Ge is present in Mississippi Valley–type (e.g. Lennard Shelf district, Western Australia) and shale–hosted deposits in amagmatic, carbonate–rich basins (e.g. Mount Isa Zn, Hilton–George Fisher and Century in Queensland and McArthur River in the Northern Territory), but less so in VHMS (e.g. Rosebery and Hellyer in Tasmania, Gossan Hill in Western Australia and Woodlawn in New South Wales) and sediment–hosted deposits in siliciclastic basins with coeval mafic volcanism (e.g. Broken Hill in New South Wales and Abra).

Of the metals extracted from sphalerite concentrates, the distribution of In is most complex. In Zn–rich ores, In concentrations range from 0.01 ppm to ~100 ppm, with VHMS deposits generally having the highest concentrations (Fig. 4.3G). The highest In concentrations, however, are from granite–related Sn deposits in western Tasmania, where the Renison Bell and Cleveland deposits have concentrations of up to 350 ppm (Fig. 4.4C). With a few exceptions, most other ore samples from other deposit types contain much less than 1 ppm In. Exceptions include samples from shale–hosted Cu (3–17 ppm; Mount Isa Cu, Nifty, Western Australia), some IOCG (to 10 ppm), intrusion–related Au and Cu–Au deposits (to 6 ppm) and the Weld Range carbonatite deposit (2 ppm) (Appendix B).

The higher In grades from VHMS deposits are similar to the typical grades (50 ppm) at which In has been extracted as a by–product (Schwarz-Schampera and Herzig, 2002) (Fig. 4.3G). As sphalerite concentrates are presently the main source of In (Schwarz-Schampera and Herzig, 2002), there may be potential for In recovery from sphalerite concentrates from Australian Zn–rich ores, particularly VHMS deposits.
Of potential further interest is the high concentrations of In in ores from granite–related Sn deposits in western Tasmania. Indium correlates with both Sn and Cu in these ores (Figs. 4.4C–D), raising the possibility that the host to the In is either cassiterite, chalcopyrite or Cu–Sn minerals such as stannite. A synthesis of microprobe and ore assay data from polylmetallic vein and greisen deposits around the world by Seifert and Sandmann (2006) indicate that both cassiterite and chalcopyrite can host significant In (0.5–1000 ppm and 100–7500 ppm, respectively), although at levels lower than in sphalerite (1–69000 ppm). Figure 4.4C indicates that the analysis with the highest Sn grade has only relatively moderate In concentrations, whereas In increases uniformly with increasing Cu grade. This suggests that the most likely host to the In is chalcopyrite. Chalcopyrite (CuFeS₂) is isostructural with roquesite (CuInS₂), the main In mineral, raising the likelihood that chalcopyrite can accept high concentration of In in its structure. Assuming this to be the case, and given Cu:In ratios of analyses from intrusion–related Sn deposits of 65 to 400, the concentration of In in chalcopyrite would be 8600–33 000 ppm. In contrast, samples from Cu and Cu–Au deposits have much lower In concentrations and Cu:In ratios of 500 to 2 700 000, implying that chalcopyrite from these deposits will have much lower In concentrations (1–4800 ppm). At present, In is only extracted from sphalerite concentrates, so VHMS deposits are the most likely sources of In, but if a method of extracting In from chalcopyrite can be developed, chalcopyrite from granite–related Sn deposits could be a significant source of In.

4.3.2 Antimony and bismuth

At present Sb is produced exclusively from ores in which stibnite (Sb₂S₃) is the main ore mineral, mostly from China. Historically, however, Sb has been produced from other Sb–bearing minerals such as tetrahedrite ((Cu,Fe)₁₂Sb₄S₁₃) (Anderson, 2002), raising the possibility of Sb production as a companion metal. Australia's current economically demonstrated resources of Sb stand at 159.3 kt (Geoscience Australia, 2013), most of which is from stibnite deposits at Costerfield, Victoria and Hillgrove, New South Wales.

As shown in Figure 4.3H, many ore samples from Zn deposits have high concentrations of Sb, with many analyses above 100 ppm and one approaching 1000 ppm. These Sb–rich deposits include Zn–rich VHMS, sediment–hosted massive sulfide and intrusion–related deposits. Based on these data and other data from the literature, Yellishetty et al. (2017) estimated that the stock of Sb as a companion metal could be of the order of 77 kt, with the largest potential resources at the Cannington (Queensland), Mount Isa and McArthur River deposits. Realising this potential, of course, depends on development of an economically viable method of extracting Sb from the ores.

Although Sb is most consistently concentrated in Zn–Pb–Ag deposits, other types of deposits can also be enriched in Sb. The highest Sb grade (>3% Sb) in the OSNACA/OREAS database is from a stibnite–rich sample from the Wiluna orogenic gold deposit in Western Australia. Many orogenic gold deposits contain significant stibnite and, historically, Sb has been recovered from some of these deposits. If sufficient grades and tonnages are demonstrated in such deposits, they can be mined for Sb as a major commodity, with Au as a co– or by–product (e.g. Hillgrove and Costerfield).

Some other deposit types can have irregular high concentrations of Sb (Appendix B). For example, one sample from the Honeymoon komatite–associated Ni–S deposit in Western Australia has a concentration of ~1100 ppm, but all other samples from this deposit type have concentrations below 10 ppm. Many Cu and Cu–Au deposits can have local high Sb concentrations (Fig. 4.2G), but given the metallurgy of these ores and the irregularity of the high Sb concentrations, it is unlikely that such deposits will contain viable Sb resources.

3 These values must be considered maximum concentrations.
According to Ojebuoboh (1992) Bi is currently extracted from a number of sources, including Pb and Cu concentrates and W ores. Based on the OSNACA/OREAS dataset, Bi can be enriched in many types of deposits, but the most consistent enrichment is found in granite–related deposits (e.g., skarn and intrusion–related Sn: Fig. 4.4E), some IOCG deposits (Fig. 4.2H) and some Zn–dominated deposits (Fig. 4.3I). Bismuth grades from intrusion–related Sn deposits range up to 500 ppm. The highest and most consistent grades of Bi are from IOCG deposits in the Tennant Creek district. These include analyses of up to 13.8% Bi from the White Devil deposit (not shown in Fig. 2.1), and the Tennant Creek district produced 14 kt Bi last century (Ahmad et al., 2009).

The concentration of Bi in Zn–rich deposits appears to be strongly dependent upon deposit type, with deposits that form from low–temperature, oxidised basinal fluids (red and orange symbols in Fig. 4.3I) having in general, much lower Bi concentrations than deposits formed from reduced, higher temperature fluids (blue and green symbols in Fig. 4.3I). This is the opposite relationship observed for Ge. This relationship suggests that deposits such as VHMS (e.g., Rosebery; Teutonic Bore, Western Australia), and siliciclastic–mafic sediment–hosted (e.g., Broken Hill; Cannington) deposits have much higher potential for companion Bi than deposits such as Mississippi Valley–type (e.g., Lennard Shelf district) and siliciclastic–carbonate sediment–hosted (e.g., Mount Isa, McArthur River) deposits.

4.3.3 Selenium and tellurium

Both Se and Te are recovered during electrolytic refining of Cu by roasting of anodic slimes produced during electrolysis (Table 3.1), hence production of both elements is dependent ultimately upon the processing of Cu concentrates. As a consequence, Cu– and Cu–Au–rich deposits are better targets for production of these elements as companion commodities.

Figure 4.2I indicates that many Cu and Cu–Au deposits contain significant Se enrichment. In particular, IOCG deposits can be Se–enriched, especially those from the Tennant Creek district, which historically has produced 220 t Se. The other deposits with significant Se enrichment are Cu–rich VHMS deposits: seven of the 18 analysed samples in the OSNACA/OREAS dataset contain over 100 ppm Se (Appendix B). The bulk content of other Cu and Cu–Au deposits are generally much lower (mostly <25 ppm).

Nickel–rich sulfide deposits contain low Se concentrations (Fig. 4.1E), generally below 25 ppm. Some Zn–rich — VHMS and orogenic base metal — deposits are enriched in Se, with concentrations up to 175 ppm Se. However, due to the constraints imposed by metallurgical processes, it is unlikely that this Se could be recovered, at least at present. Granite–related Sn and W deposits contain uniformly low (<5 ppm) Se concentrations.

Of all the critical commodities determined in the OSNACA/OREAS dataset, Te has the largest range of concentration, varying from <0.02 ppm to ~4000 ppm. The deposit types with the most consistently high Te concentrations are Cu–rich VHMS deposits and Cu–Au skarn deposits. Sixteen of the 18 samples of Cu–rich VHMS deposits contain ≥1 ppm Te, and nine of these samples exceed 10 ppm. These two deposit types have greatest potential for production of companion Te. Nickel deposits can also contain high Te concentrations, which generally increase with Ni, although some of the highest Te values (to 4010 ppm) are associated with relatively low–Ni grade (Fig. 4.1F). All other deposit classes are characterised by uniformly low Te (<1 ppm) concentrations.
5 Summary, conclusions and future directions

Analyses of ore samples from a range of deposits indicate that Australian ores contain relatively high concentrations of a range of critical commodities, some of which are currently extracted and others that have potential for extraction. In 2011 Australia produced ~440 kg of PGEs, exclusively as a by-product from orthomagmatic Ni–Cu deposits in the Yilgarn Craton (Geoscience Australia, 2013). However, PGEs are known to be present in other deposit types, including unconformity–related uranium and porphyry Cu deposits (Hoatson and Lewis, 2014). In particular, copper concentrates produced from porphyry Cu deposits in New South Wales might represent a PGE resource: copper concentrate from one of the deposits in this region contains 0.7 ppm Pd and Pt, but cannot be economically recovered. In addition, a number of PGE–dominant deposits, albeit small, are known in Western Australia.

The main source of Co production in Australia is also the orthomagmatic Ni–Cu group of deposits in the Yilgarn Craton, which produced ~3.9 kt Co in 2010 (Elias, 2013). Based on public data, however, other deposits in Australia are known to contain significant Co grades, in particular sediment–hosted Cu deposits, from which Co is not recovered. These deposits represent a potential untapped source of Co, but recovery will depend upon advances in metallurgical processing. Due to its importance in batteries, the demand for Co could increase substantially in the future.

Orthomagmatic deposits hosted by mafic and ultramafic igneous rocks are also the most likely potential sources of Cr and V, neither of which is currently produced in Australia. Chromitites, which are the main global sources of Cr, are known in Western Australia, New South Wales and Tasmania. It is unlikely that Cr could be produced as a companion metal due to the low concentration of Cr in ores other than chromitites. The most likely Australian source of V is orthomagmatic magnetite–V–Ti deposits that are located mostly in Western Australia. Another potential V source are large oil–shale–hosted V–Mo deposits such as at Julia Creek in Queensland.

Although Mo and Re are not currently produced in Australia, there are a number of potential sources of these metals, including deposits in which molybdenite is recovered, or will be recovered, as the main commodity (e.g. porphyry Mo–Cu, skarn and some IOCG–related deposits) and others in which these metals could be recovered as by–products (e.g. porphyry Cu deposits and sediment–hosted deposits of various types). Because Mo and Re are commonly recovered as by–products from porphyry Cu deposits around the world, these deposits are perhaps the best potential source of Mo and Re in Australia, however, the economic viability of by–product Mo–Re recovery has not been demonstrated in Australian deposits.

Historically Australia has been a significant Sn and W producer. The Renison mine in western Tasmania is a current Sn producer, and there are a number of other Sn and W prospects in various stages of exploration (Geoscience Australia, 2013). A potential boost to Australia's Sn and Ta production may come with the development of Li–bearing pegmatite bodies in Western Australia and elsewhere. Pegmatites commonly contain elevated levels of Sn and Ta, possibly allowing extraction as a by–product, or, historically as a the main product. Tantalum, Zr, Hf, Nb, Y and REE may also be extracted from the Toongi Zr deposit in New South Wales, which is at an advanced stage of feasibility.

Australia currently produces REE from the Mount Weld deposit and has other prospects at various stages of exploration (e.g. Nolans). In addition to these deposits in which REEs are the main product, some IOCG deposits (Olympic Dam and Prominent Hill) have elevated REE concentrations, which are
not currently extracted due to low grades relative to REE–only deposits and difficulties in producing a sufficiently high-grade REE concentrate. No other deposits are sufficiently enriched in REEs to consider extraction.

Cadmium, Ga, Ge and In are commonly extracted from sphalerite concentrates. Of these elements, only Cd is produced in Australia. The OSNACA/OREAS data suggest that although Cd has a relatively even distribution, the concentrations of Ge and In vary significantly between deposit types. Base metal deposits formed from low temperature, oxidised fluids (Mississippi Valley type and siliciclastic–carbonate sediment–hosted deposits) are enriched in Ge but depleted in In relative to deposits formed from higher temperature, reduced fluids (VHMS and siliciclastic–mafic sediment–hosted deposits). The highest In concentrations in the OSNACA/OREAS dataset are from granite–related Sn deposits, with the In likely hosted in chalcopyrite. This association represents a second potential source of In if an economic extraction method can be established.

Both Sb and Bi have been produced historically, but are not produced currently, in Australia. The major potential for Sb production is from stibnite deposits in which Sb could be extracted as the main product. Some types of Zn deposits have relatively high Sb concentrations, but extraction of this Sb is not viable using current technologies. Unlike Sb, existing technologies allow extraction of Bi from a number of different sources, including Cu concentrates, Pb concentrates and W ores. The OSNACA/OREAS dataset indicates that Bi can be concentrated in granite–related deposits, some IOCG deposits, and higher temperature Zn–rich deposits. These deposit types have significant potential to produce Bi as a companion metal, although it is not extracted at present using current technologies.

Selenium and Te are currently produced from anodic slimes produced by electrolytic refining of Cu. Based upon this constraint and data from the OSNACA/OREAS dataset, the greatest potential for Se extraction as a companion element is from some IOCG deposits and Cu–rich VHMS deposits, which are also the most promising sources of Te. Other deposit types can contain elevated Se and Te, but given the constraints imposed by extraction technologies, these sources may not be economically viable.

An important conclusion of this study is that production of companion commodities depends not only on concentration (grade) but, perhaps more importantly, whether viable metallurgical processing technologies are available. This analysis suggests that some critical commodities that are enriched in Australian ores cannot be recovered using present-day technologies, but that new recovery technologies may allow economic recovery in the future, particularly if the demand for the commodity of interest grows. Finally, some critical commodities may be recovered from Australian concentrates that are currently shipped overseas; assessing this possibility is beyond the scope of the report, but justifies further investigation.

This report has found that critical commodities are present at varying levels in many Australian ores, but that these are generally not recovered due to technical or economic limitations. It must be stressed that this report is preliminary, and significantly more data are required to truly assess the potential of Australian ores as sources of critical commodities. In particular, analyses of concentrates and a larger range of deposit and ore types are required. In addition, input from metallurgists is required to assess current and, potentially, develop new extraction technologies: the presence of geochemical enrichment is not sufficient for viable recovery of critical commodities.
Acknowledgements

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Ojebuoboh, F. K., 1992, Bismuth — production, properties, and applications. JOM 44, 46–49.


Appendix A Analytical methods

As most analyses used in this study were sourced from the OSNACA database, analytical methods for these analyses are presented below as described on the OSNACA website (http://www.cet.edu.au/projects/osnaca-ore-samples-normalised-to-average-crustal-abundance/osnaca-analytical-techniques). As the finish methods, uncertainties and detection limits are not provided on the OSNACA website, they are not reported here. As the OREAS certified reference materials involved a large range of analytical laboratories and methods, a description of the analytical techniques is beyond the scope of this report, and the reader is referred to analytical certificates for each certified reference material, which can be obtained from http://ore.com.au.

A.1 OSNACA Analytical Techniques

Ore samples are crushed in a steel jaw crusher with barren quartz processed between each sample. They are then pulverised to –75 µm in a steel mill, with barren quartz rinse milled in between each sample.

Analytical solutions for reading by ICP–MS and ICP–OES are prepared by the following methods. Table A.1 summarises detection limits. Accuracy equivalent to ± 2 times detection limit is achievable, up to a concentration of 10 times the detection limit, and then ± 5% of the value thereafter.

A.1.1 Pb fire assay — Au, Pt, Pd

40 grams of sample is weighed (lower weights down to 10 grams can be used if there is insufficient sample or for highly sulfidic samples). The sample is then fused for one hour at 1100°C in a ceramic pot with 165 grams of flux (a mix of borax, soda ash, flour, litharge (PbO) and a small amount of silver) with additional soda ash for silica rich samples, additional borax for basic samples, and additional KNO₃ and litharge for some sulfidic samples. During the fusion the litharge is reduced to Pb collecting the precious metals. Molten samples are poured into steel conical moulds where a lead button sinks to the bottom separating from the glass slag. The lead button is then placed on a cupel and heated to 990°C for 45 minutes during which time the Pb oxidises back to PbO flowing into the absorbent cupel leaving behind a silver prill containing all Au, Pt and Pd. The prill is then dissolved in 1 ml of concentrated nitric acid followed by 1 ml of concentrated hydrochloric acid at 110°C. The resultant solution is then made up to 10 ml with deionised water and then analysed using ICP-MS (method FA003).

A.1.2 Peroxide fusion — B, Cr, Hf, Pb, S, Sb, Si, Sn, Ta, Ti, W, Zr

0.2500 grams of sample is fused with 1.5 g of sodium peroxide in an alumina crucible for 30 minutes at 650°C. For carbon–rich samples, the temperature is raised slowly to 650°C to allow ashing for 1 hour prior to fusion. The crucible is allowed to cool and then agitated in 100 ml of deionised water for one hour, before adding 100 ml of hydrochloric acid and agitating every 10 minutes for 30 minutes in a water bath at 95°C. The solution is made up to 500 ml with de-ionised water, and analysed using ICP-OES (PF101: B, Cr, S, Si and Ti) and ICP-MS (PF102: Hf, Pb, Sb, Sn, Ta, W and Zr).
Table A.1. Minimum detection limits for OSNACA analyses

<table>
<thead>
<tr>
<th>Element</th>
<th>Minimum detection limit (ppm)</th>
<th>Element</th>
<th>Minimum detection limit (ppm)</th>
<th>Element</th>
<th>Minimum detection limit (ppm)</th>
<th>Element</th>
<th>Minimum detection limit (ppm)</th>
</tr>
</thead>
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<tr>
<td>Pb fire assay (FA003)</td>
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<td>Pt</td>
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<td>Pd</td>
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<td>Peroxide fusion (PF101, PF102)</td>
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<td>Cr</td>
<td>50</td>
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<td>2</td>
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<tr>
<td></td>
<td></td>
<td>S</td>
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<td>Sb</td>
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<td>Si</td>
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<td></td>
<td></td>
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<td>Ti</td>
<td>100</td>
<td>W</td>
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<td>Hg</td>
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<td></td>
<td></td>
<td>Sb</td>
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<td>Al</td>
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<td>Tm</td>
<td>0.02</td>
<td>Yb</td>
<td>0.05</td>
</tr>
</tbody>
</table>

A.1.3 Aqua regia — Bi, Te, Hg, Ag, Sb

4.0 grams of sample is placed in a polythene vial before 5 ml of concentrated nitric acid is added in 1 ml increments checking for violent reactions before agitating and adding a further 5 ml of nitric acid. 10 ml of concentrated hydrochloric acid is added, agitated, and left to stand for 30 minutes before heating to 95°C for two hours in a water bath. The solution is made up to 50 ml with deionised water and then analysed using ICP-MS.

A.1.4 Mixed acid (hot box) — Ag, Al, As, Bi, Ca, Cd, Co, Cs, Cu, Fe, In, K, Li, Mg, Mn, Mo, Na, Nb, Ni, P, Pb, Rb, Re, Sc, Se, Sn, Sr, Te, Th, Ti, U, V, W, Y, Zn, REEs

0.15 grams of sample is placed in a teflon tube and dissolved in 10 ml of a concentrated mixture of hydrofluoric, nitric and perchloric acids (hot–box mix). This solution is brought up to 250°C and back down to 150°C over a period of 12 hours. After allowing to cool for 5 minutes, 10 ml of concentrated hydrochloric acid is added and the sample is re–heated to 150°C for 15 minutes. 10 ml of de–ionised water is added before decanting into a polystyrene tube. The solution is made up to 20 ml with deionised water and mixed thoroughly by agitating. The solution is then analysed using ICP-OES
(MA201: Al, Ca, Fe, K, Mg, Mn, Na and P) and ICP-MS (MA202: Ag, As, Bi, Cd, Co, Cs, Cu, In, Li, Mo, Nb, Ni, Pb, Rb, Re, Sc, Se, Sn, Sr, Te, Th, Ti, U, W, Y, Zn and REEs).

A.2 Data selection

Whole-rock geochemical data are presented as raw laboratory files, and in tabular format that can be linked with metadata by sample number. In the tabular data files, a ‘preferred value’ has been selected for those elements which have been analysed by two different techniques; a robust and a sensitive technique (Table A.2. For the element tabulated below, the robust technique ensures complete digestion for samples that contain high concentrations, and the sensitive technique allows readings to lower detection limits where concentrations are low. The ‘robust cut-off’ is the value below which the sensitive technique is used in preference to the robust technique. Combining the data in this way ensures the most reliable value for each of these elements over a very wide range of concentrations.

Table A.2. Criteria for determining ‘preferred values’ for analytes with multiple analytical methods

<table>
<thead>
<tr>
<th>Element</th>
<th>Robust Technique</th>
<th>Robust LLD (ppm)</th>
<th>Robust cut-off (ppm)</th>
<th>Sensitive Technique</th>
<th>Sensitive LLD (ppm)</th>
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<td>Mixed Acid</td>
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<td>Lab selected</td>
<td>Aqua Regia</td>
<td>0.02</td>
</tr>
<tr>
<td>Te</td>
<td>Mixed Acid</td>
<td>0.2</td>
<td>Lab selected</td>
<td>Aqua Regia</td>
<td>0.02</td>
</tr>
<tr>
<td>Pb</td>
<td>Peroxide Fusion</td>
<td>100</td>
<td>&lt;1000</td>
<td>Mixed Acid</td>
<td>1</td>
</tr>
<tr>
<td>Sb</td>
<td>Peroxide Fusion</td>
<td>2</td>
<td>Lab selected</td>
<td>Aqua Regia</td>
<td>0.02</td>
</tr>
<tr>
<td>Sn</td>
<td>Peroxide Fusion</td>
<td>5</td>
<td>&lt;5</td>
<td>Mixed Acid</td>
<td>1</td>
</tr>
<tr>
<td>W</td>
<td>Peroxide Fusion</td>
<td>5</td>
<td>&lt;5</td>
<td>Mixed Acid</td>
<td>0.5</td>
</tr>
</tbody>
</table>

For Bi, Te, Ag and Sb considerable repeat assaying was performed, particularly for samples that followed samples with very high values. Fusion, mixed acid and aqua regia data were all considered before selecting the preferred value. In general, mixed acid data for Ag and fusion data for Sb were found to be reliable right down to their respective detection limits, whereas aqua–regia data have been preferred for Bi and Te at values up to five times the mixed acid detection limit. Very high results for Ag, Bi and Te have been confirmed by fusion.

Bureau Veritas – Ultratrace have confirmed data for many other elements by comparing values by different techniques. These internal checks show, for example, that the REEs have been fully digested by the mixed acid technique when the data are compared to peroxide fusion data. Gold has been analysed by fire assay and aqua–regia to the same detection limit and fire assay values are used in preference.
Appendix B Analytical results

Complete analytical results are available here.