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Alkaline leaching of brannerite.
Part 2: Leaching of a high-carbonate refractory uranium ore

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Abstract
There are several metasomatic uranium deposits in the area around Mount Isa in Queensland, containing a total of 56,400 tonnes of uranium. Many of these ores are refractory in nature, meaning that relatively high leach temperatures (>75°C) and reagent dosages (>50 g/L H2SO4) are needed to effectively extract the uranium from them. Also, these ores are hosted in alkaline rock which means that acid leaching is unlikely to be economical.

While refractory uranium ores are not typically leached in alkaline media, previous work has shown that uranium can be extracted from brannerite in alkaline media, albeit slowly. The same leaching conditions previously shown to be effective for the extraction of uranium from brannerite were repeated with a sample of refractory uranium ore from a deposit near Mount Isa in north western Queensland. Mineralogical analysis with a Tescan Integrated Mineralogical Analyser (TIMA) showed that the uranium was present as brannerite (51%) and coffinite (49%).

The ore was leached in sodium carbonate media for 24 hours. Leach temperatures of 50, 70 and 90°C, and sparging with oxygen, air and nitrogen were tested. The effect of adding ferricyanide chemical oxidant was also tested. Similar initial uranium extraction rates were observed for the Mount Isa uranium ore compared with Sierra Albarrana brannerite leached under the same conditions in earlier work. The final extractions were lower however, due to the fine-grained nature of the uranium mineralisation in the ore.

TIMA analysis on a residue produced under the most intense set of leaching conditions (90°C, O2 sparged) showed that the extent of coffinite dissolution was greater than that of brannerite dissolution during leaching. Likewise, the TIMA analyses showed that the extent of apparent uranium liberation decreased during leaching, due to poorly liberated particles remaining undissolved. These results indicate that alkaline leaching could be a viable method for the processing of these long overlooked ores provided that the uranium is sufficiently liberated.

Keywords: Uranium; Brannerite; Leaching; Alkaline; Carbonate; Kinetics.

1 Introduction
The first uranium deposits near Mount Isa in northern Queensland were discovered in 1954 (Brooks, 1958). Of the uranium deposits in Queensland, only the Mary Kathleen deposit has ever been mined.
The uranium ores of this area are high in refractory uranium minerals like brannerite (Gregory et al., 2005; Wilde et al., 2013). Early testwork on ore from the Valhalla deposit showed that leaching is slow, and acid consumption is high (Goldney et al., 1972).

There are several metasomatic uranium deposits near Mount Isa, of which Valhalla is the largest (29300 t U) followed by Skal (8400 t U) (Wilde et al., 2013). Altogether, the metasomatic uranium deposits near Mount Isa contain around 56,400 tonnes of uranium (Hutton, 2014). This is slightly more than the amount of uranium produced in Australia between 2007 and 2014 (WNA, 2015). A detailed understanding of the leaching chemistry is required if refractory uranium ores like those from Mount Isa are to be mined and processed.

The albitite uranium deposits near Mount Isa (Polito et al., 2009) are high in carbonates and other acid consuming gangue minerals. Like those in the Central Ukrainian Uranium Province surrounding the city of Kirovograd, Ukraine (Cuney et al., 2012) they formed through alteration of the original granite by alkaline fluids (Wilde et al., 2013).

Preliminary work (Gilligan and Nikoloski, 2017) has shown that alkaline leaching of brannerite is indeed possible, albeit slow. Up to 82% of the uranium from a specimen of brannerite from Cordoba, Spain dissolved over 24 hours of leaching in 1.00 M carbonate media at 90°C with 25 mM K$_3$Fe(CN)$_6$ as an oxidant.

A sample of uranium ore was obtained from a uranium deposit near Mount Isa in north-western Queensland. This ore was leached under the same conditions studied previously by Gilligan and Nikoloski (2017).

2 Materials and methods
2.1 Sample preparation
The ore sample was obtained as approximately 80 individual 150-200 gram bags. These were combined, blended and homogenised in a rotary splitter. The sample was split into eight sub-samples and recombined three times, before being split into individual 1 kg charges.

2.2 Analyses
All scanning electron microscope (SEM) imaging, energy dispersive x-ray (EDX) spectroscopy and x-ray diffraction (XRD) analyses were performed at Murdoch University according to the same methods described by Gilligan et al. (2016).

Detailed mineralogical analyses were performed with a TESCAN integrated mineralogical analyser (TIMA3 FE GMU) at Curtin University. TIMA analyses were performed on the feed material and the residue from just one leach test (90°C, O$_2$ sparged leach). For the TIMA analyses, an accelerating voltage of 25 kV was used with 5 μm between each analysis spot. 1000 counts of x-rays were gathered per spot.

All intermediate aqueous samples from the leaching tests were assayed for uranium and titanium by ICP-MS/AES by a local commercial mineral laboratory. The ore sample and leached residues were analysed by sodium peroxide fusion followed by ICP-MS/AES analysis by a local commercial mineral laboratory. All extractions were based on the calculated head grade as derived from a metallurgical balance.

2.3 Leaching experiments
The leaching conditions used in the previous study (Gilligan and Nikoloski, 2017) were modified for this study. A much larger amount of material was used, due to the lower grade and the heterogeneous
nature of the ore. A pulp density of 20% solids was used in all experiments with 150 g of ore added to 600 mL of lixiviant once the lixiviant had reached the leaching temperature.

2.3.1 Alkaline ore leaching experiments
As with the previous alkaline brannerite leaching experiments (Gilligan and Nikoloski, 2017), 70°C was selected as the baseline temperature. Certain experiments were repeated at 50 and 90°C to assess the effect of temperature. The carbonate concentration was kept constant at 0.66 M NaHCO₃ and 0.34 M Na₂CO₃.

Three sparged gases were tested at 70°C: nitrogen, air and oxygen (P₂O₅ = 0, 0.21, and 1 atm). Sparged oxygen was tested at all three temperatures, and with and without ferricyanide. All gases were of industrial grade, 99.5% purity.

Table 1. Conditions for the alkaline ore leaching experiments

<table>
<thead>
<tr>
<th>Sparged gas</th>
<th>Chemical oxidant</th>
<th>Temperature(s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nitrogen</td>
<td>--</td>
<td>70°C</td>
</tr>
<tr>
<td>Air</td>
<td>--</td>
<td>70°C</td>
</tr>
<tr>
<td>Oxygen</td>
<td>--</td>
<td>50, 70, 90°C</td>
</tr>
<tr>
<td>Oxygen</td>
<td>K₃Fe(CN)₆</td>
<td>50, 70, 90°C</td>
</tr>
</tbody>
</table>

3 Results and discussion
3.1 Ore sample characterisation
The homogenised ore sample appeared light grey, though several sub-samples were dark green or red-brown in appearance. The material is mildly radioactive, with an activity around 1.5–1.8 μSv/h.

3.1.1 Bulk chemical analysis
Analysis by sodium peroxide fusion followed by ICP-MS/AES determined the uranium content to be 2560 ppm. All elements exceeding 10 ppm in the sample are shown in Table 2. Fluorine was not among the elements analysed, though there is some evidence for its presence (see section 3.1.4).

Table 2. Bulk chemical analysis of the Mount Isa uranium ore sample.

<table>
<thead>
<tr>
<th>Element</th>
<th>%</th>
<th>Element</th>
<th>ppm</th>
<th>Element</th>
<th>ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si</td>
<td>26.09%</td>
<td>Mn</td>
<td>1150</td>
<td>Nd</td>
<td>39</td>
</tr>
<tr>
<td>Fe</td>
<td>6.63%</td>
<td>Zr</td>
<td>839</td>
<td>Sc</td>
<td>25</td>
</tr>
<tr>
<td>Ca</td>
<td>5.68%</td>
<td>Cu</td>
<td>500</td>
<td>La</td>
<td>23</td>
</tr>
<tr>
<td>Al</td>
<td>5.02%</td>
<td>Pb</td>
<td>500</td>
<td>Th</td>
<td>21.5</td>
</tr>
<tr>
<td>Mg</td>
<td>2.76%</td>
<td>V</td>
<td>400</td>
<td>Li</td>
<td>20</td>
</tr>
<tr>
<td>Na</td>
<td>2.02%</td>
<td>As</td>
<td>300</td>
<td>Rb</td>
<td>17</td>
</tr>
<tr>
<td>Ti</td>
<td>0.88%</td>
<td>Sr</td>
<td>100</td>
<td>Hf</td>
<td>14</td>
</tr>
<tr>
<td>K</td>
<td>0.27%</td>
<td>Y</td>
<td>64.0</td>
<td>Dy</td>
<td>13.0</td>
</tr>
<tr>
<td>S</td>
<td>0.26%</td>
<td>Ce</td>
<td>62</td>
<td>Gd</td>
<td>12.0</td>
</tr>
<tr>
<td>U</td>
<td>0.256%</td>
<td>Ba</td>
<td>50</td>
<td>Sm</td>
<td>10.5</td>
</tr>
<tr>
<td>P</td>
<td>0.215%</td>
<td>Cr</td>
<td>50</td>
<td>W</td>
<td>10</td>
</tr>
</tbody>
</table>
3.1.2 Bulk mineralogy by XRD

The XRD pattern of the ore contained a number of strong, clear peaks. Quartz was the most prominent mineral, followed by albite (NaAlSi$_3$O$_8$), a type of alkali feldspar (Wenk and Bulakh, 2004). Other phases identified included the phyllosilicates chlorite ([(Mg,Fe$^{2+}$,Fe$^{3+}$,Mn,Al)$_{12}$(Al,Si)$_8$O$_{20}$(OH)$_{16}$) and biotite (K(Mg,Fe)$_3$(AlSi$_3$O$_{10}$)(OH)$_2$). The carbonate minerals calcite (CaCO$_3$) and dolomite (CaMg(CO$_3$)$_2$) were also detected.

Figure 1: X-ray diffraction pattern for the ore sample. Q: Quartz, D: Dolomite, A: Albite, Ca: Calcite, Cl: Chlorite, B: Biotite.

No uranium phases were detected. Based on assays (Table 2) these phases make up less than 1% of the ore, below the typical detection limit of XRD (Youlton et al., 2011). Brannerite is typically poorly crystalline and metamict (Lumpkin et al., 2012), increasing the difficulty of detecting it by XRD.

3.1.3 SEM imaging and EDX analyses

The ore sample was supplied as a finely milled powder, with a $P_{80}$ of 32 µm as determined by laser sizing, though SEM images and TIMA analyses showed a number of particles much larger than the apparent $P_{80}$ of 32 µm. Some particles were much brighter on the backscattered electron images and some of these bright particles were targeted for EDX analyses. These EDX analyses showed that the brannerite in the Mount Isa uranium ore is of a similar composition to the Sierra Albarrana brannerite used in earlier work (Gilligan and Nikoloski, 2017; Figure 2).
Brannerite was identified as fine grains (<5 μm) associated with titanium oxide in between silica and calcite. This is consistent with earlier work which found that the uranium mineralisation in this deposit is very fine grained (Wilde et al., 2013), which led to low recoveries in early test work on Valhalla ore (Goldney et al., 1972).

### 3.1.4 Mineralogy by TIMA analysis

The major phases identified by TIMA analysis were in agreement with the XRD results. All phases identified by XRD exceeded 1.5% of the sample mass (Table 3). Many of the dolomite particles analysed contained iron, suggesting that they were actually somewhere between dolomite and ankerite (CaFe²⁺(CO₃)₂) in composition. The x-ray diffraction patterns of these minerals are nearly identical. Dolomite and ankerite are known to form a series (Wenk and Bulakh, 2004).

#### Table 3. Mineral phases exceeding 0.5% of the mass of the ore sample, as determined by TIMA.

<table>
<thead>
<tr>
<th>Phase</th>
<th>Formula</th>
<th>Mass fraction</th>
</tr>
</thead>
<tbody>
<tr>
<td>Quartz</td>
<td>SiO₂</td>
<td>37.78%</td>
</tr>
<tr>
<td>Albite</td>
<td>NaAlSi₃O₈</td>
<td>21.36%</td>
</tr>
<tr>
<td>Anorthite</td>
<td>CaAl₂Si₂O₈</td>
<td>13.19%</td>
</tr>
<tr>
<td>Chlorite - Clinchlore</td>
<td>Mg₃Al(AlSi₃O₁₀)(OH)₈</td>
<td>8.80%</td>
</tr>
<tr>
<td>Calcite</td>
<td>CaCO₃</td>
<td>5.05%</td>
</tr>
<tr>
<td>Garnet</td>
<td>Mg₄Al₃(SiO₄)₃</td>
<td>4.25%</td>
</tr>
<tr>
<td>Hematite/Magnetite</td>
<td>Fe₂O₃/Fe₃O₄</td>
<td>3.09%</td>
</tr>
<tr>
<td>Biotite</td>
<td>K(Mg,F₆)(AlSi₃O₁₀)(OH)₂</td>
<td>1.71%</td>
</tr>
</tbody>
</table>
TIMA analysis showed that 51% of the uranium was present as brannerite while the remainder was present as coffinite. The brannerite category was further broken down into brannerite and high-Si brannerite. TIMA analysis was consistent with the spot EDX analyses (Figure 2) in determining that the brannerite in this ore sample was high in silicon. These uranium bearing phases were often found together. Uranium deportment and liberation is discussed in greater detail in section 3.3.2.

3.2 Leaching kinetics
Despite the relatively quick initial rates of extraction at 90°C, final extractions in all tests did not exceed 50%. This is likely due to the fine-grained nature of the uranium mineralisation and poor liberation discussed in more detail in a later section.

3.2.1 Effect of temperature, activation energy
Temperature had a strong effect on the rate of uranium dissolution (Figure 4), though this effect was less than that observed previously when brannerite alone was leached under the same conditions (Gilligan and Nikoloski, 2017). The maximum extractions were quite close at 70 and 90°C, with this apparent extraction limit being reached faster at 90°C.
At 50 and 70°C, uranium extraction slowed significantly after the first 15 minutes of leaching. As this ore contains uranium in several different mineral phases, it is thought that this initial fast dissolution arises from the dissolution of liberated coffinite particles in the ore.

In the initial stages of leaching, the extraction of uranium from Mount Isa uranium ore had less of a dependence on temperature compared to the extraction of uranium from brannerite (Figure 5). The activation energy for the extraction from Mount Isa uranium ore (Table 4) was lower than the value calculated for the Sierra Albarrana brannerite (Gilligan and Nikoloski, 2017).

Figure 4. Uranium dissolution rates from Mount Isa uranium ore at different temperatures.
Figure 5. Arrhenius plots for the extraction of uranium from brannerite (Sierra Albarrana) and ore (Mt Isa) with different oxidants.

Table 4. Activation energy for alkaline leaching

<table>
<thead>
<tr>
<th>Material</th>
<th>Oxidant</th>
<th>$E_a$ (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mount Isa uranium ore</td>
<td>$O_2$</td>
<td>26.7</td>
</tr>
<tr>
<td>Mount Isa uranium ore</td>
<td>$O_2 + 25$ mM $K_3Fe(CN)_6$</td>
<td>27.6</td>
</tr>
<tr>
<td>Sierra Albarrana brannerite</td>
<td>$25$ mM $K_3Fe(CN)_6$</td>
<td>45.4</td>
</tr>
</tbody>
</table>

It is unlikely that this reflects the dissolution of brannerite. As the Mount Isa ore has 2-3 different uranium phases, it’s likely that the uranium dissolving in the initial stages was mostly from coffinite. Reactions in which stronger bonds are broken have higher activation energies (Langmuir, 1997), and therefore, the activation energies calculated for the leaching of less refractory phases like uraninite or coffinite (De Pablo et al., 1999) were lower than those calculated for brannerite in alkaline media (Gilligan and Nikolisoki, 2017). Anand-Rao and Suri (2014) calculated an activation energy of 29.4 kJ/mol for the alkaline carbonate leaching of a high-carbonate pyritic uranium ore between 70 and 110°C, within a similar range to the activation energies determined for uranium extraction from the Mount Isa uranium ore. The main uranium phases present in the ore studied by Anand-Rao and Suri (2014) were pitchblende and coffinite.
3.2.2 Effect of different oxidants
Comparing the rates of uranium dissolution at 70°C with nitrogen, air and oxygen indicates that higher oxygen partial pressure resulted in a higher uranium extraction. In the presence of ferricyanide, sparged oxygen was even more effective. These differences were minimal in the initial 15-30 minutes of leaching, but increased significantly later in the experiment.

![Figure 6. Uranium extraction curves at 70°C with different oxidants](image)

3.2.3 Leaching of titanium
The majority of titanium in the ore sample was present as minor gangue minerals like anatase/rutile and ilmenite, with only a small fraction present as brannerite. As a result of this, the titanium extraction was much lower than the uranium extraction. When leaching brannerite alone, titanium extraction was typically only slightly lower than the uranium extraction.

As with the alkaline leaching experiments on the Sierra Albarrana brannerite (Gilligan and Nikolski, 2017), titanium was observed to re-precipitate after initially dissolving. Both dissolution and precipitation of titanium were faster at higher temperatures (Figure 7). Precipitation started within one hour at 90°C, and took around 8 hours to start at 70°C. There was no evidence for the re-precipitation of titanium oxide at 50°C.
Calculations after Schmidt and Vogelsberger (2009) with HSC Chemistry v7.1.1 (Roine, 2011) indicate that there is no difference in Ti solubility at a pH of 9-10 from 50 to 90°C (Figure 8). The difference in the behaviour of titanium at different temperatures most likely arises from differences in precipitation kinetics. The ore contained anatase/rutile which could act as seeds to initiate titanium precipitation from a super-saturated solution. Based on the calculated solubility of anatase and the titanium content of this ore, the solution is saturated with anatase at a titanium concentration equivalent to 0.05-0.10% extraction, around the same concentration of titanium measured at the end of the 90°C leaching experiments.

Figure 7. Titanium extraction and precipitation kinetics.
3.2.4 Gangue element extraction

Of the several gangue elements present, sulphur was the element that most readily dissolved. Sulphides like pyrite are known to dissolve in alkaline media (Ciminelli and Osseo-Asare, 1995), with the dissolution of pyrite facilitated by the formation of stable complexes such as Fe(CO$_3$)$_2^-$ (Caldiera et al., 2008). Sulphides were detected in TIMA analyses on the ore, and are a minor component of the ore. Calculations with HSC chemistry v7.1.1 (Roine, 2011) indicate that pyrite is unstable under the conditions used in these leaching experiments (Figure 9).

Figure 8. Calculated solubility of anatase at 50, 70 and 90°C based on calculations in HSC Chemistry v 7.1.1 (Roine, 2011). Individual titanium species omitted for clarity.

Figure 9. Stability of iron (red) and sulphur species (blue) at 70°C.

Higher temperatures and more strongly oxidising conditions resulted in greater amounts of sulphur dissolving (Figure 10). The rate of pyrite oxidation is proportional to the square root of oxygen partial pressure.
pressure (Ciminelli and Osseo-Asare, 1995). This explains the increase in sulphur extraction with the concentration of oxygen in the sparged gas.

The acid generated by the oxidation of pyrite can cause problems with alkaline leaching. Pyrite can be removed from the ore by flotation prior to alkaline leaching (IAEA, 1980). This was done at the Beaverlodge mill in Canada (Scott, 1982; IAEA, 1993). The oxidation of pyrite is strongly thermodynamically favourable (Reaction 1 after Ciminelli and Osseo-Asare, 1995; $\Delta G^{70\circ C}$ values calculated with HSC Chemistry v7.1.1 (Roine, 2011)).

\[
\begin{align*}
\text{FeS}_2 + 3.75 \text{O}_2 + 2.5 \text{H}_2\text{O} &\rightarrow \text{FeOOH} + 4\text{H}^+ + 2\text{SO}_4^{2-} \\
\Delta G^{70\circ C} &= -1177 \text{kJ/mol} \quad \text{Reaction 1} \\
\text{FeS}_2 + 3.75 \text{O}_2 + 0.5 \text{H}_2\text{O} + 2\text{CO}_3^{2-} &\rightarrow \text{FeOOH} + 2\text{SO}_4^{2-} + 2\text{CO}_2(\text{g}) \\
\Delta G^{70\circ C} &= -1416 \text{kJ/mol} \quad \text{Reaction 2} \\
\text{FeS}_2 + 3.75 \text{O}_2 + 2.5 \text{H}_2\text{O} + 4\text{CO}_3^{2-} &\rightarrow \text{FeOOH} + 4\text{HCO}_3^- + 2\text{SO}_4^{2-} \\
\Delta G^{70\circ C} &= -1440 \text{kJ/mol} \quad \text{Reaction 3}
\end{align*}
\]

If all the sulphur in the ore was oxidised through reactions 1-3, one tonne of ore would neutralise 8.6 kg of Na$_2$CO$_3$. The iron extraction (<0.5%) was much lower than that of sulphur. After the dissolution of pyrite, it’s likely that the iron precipitated as insoluble ferric oxides/hydroxides. Calculations indicate that the solubility of iron as goethite at pH 9-10 is low. TIMA analysis showed a decrease in the pyrite content and a slight increase in the iron oxide content during leaching (see section 3.3.2).

Likewise, aluminium dissolution was minimal. The concentration of aluminium in solution was approximately 2 ppm at most, around the theoretical solubility at pH 9-10 (Figure 11).
Figure 11. Calculated solubilities of aluminium (gibbsite), ferric iron (goethite) and titanium (anatase) at 70°C.

While phosphates can be problematic in acid leaching (Laxen, 1973; Nicol et al., 1975; Ram et al., 2013; Gilligan and Nikoloski, 2016), this does not appear to be the case in alkaline leaching. Phosphorus extractions were low (<2%), likely due to the stability of apatite under these conditions. Thermodynamic calculations with HSC Chemistry v7.1.1 (Roine, 2011) indicate that apatite is the more stable phase in carbonate solutions and is therefore unlikely to dissolve.

\[
Ca_5(PO_4)_3F + 5CO_3^{2-} \rightarrow 5CaCO_3 + 3PO_4^{3-} + F^- \\
\Delta G^{70^\circ C} = +165kJ/mol
\]

Reaction 4

3.2.5 Comparison of brannerite and ore
Higher overall uranium extractions were observed for pure brannerite (Figure 12), which is likely due to it being close to 100% liberated. The initial extractions were faster for the ore sample however (Figure 13), which is likely due to the presence of coffinite, which is known to dissolve more readily than brannerite. After the more liberated and less refractory uranium bearing phases dissolved, the dissolution rate of uranium from ore was closer to that of pure brannerite. The changes in uranium deportment and liberation are discussed in the following section.
Figure 12. Comparison of uranium extraction kinetics from brannerite and ore with ferricyanide as an oxidant.
Figure 13. Comparison of uranium extraction kinetics from brannerite and ore with ferricyanide as an oxidant in the initial stages of leaching.

3.3 Leach residue characterisation

3.3.1 XRD

Apart from the apparent decrease in biotite in some residues, the XRD results for the different alkaline leaching residues were mostly identical to each other and to the feed ore, indicating that there was little to no change in the bulk mineralogy of the ore during alkaline leaching.
Figure 14. XRD patterns for residues leached at 70°C with different oxidants compared with the ore sample. Q: Quartz, D: Dolomite, A: Albite, Ca: Calcite, Cl: Chlorite, B: Biotite.

3.3.2 TIMA

Like the XRD results (Figure 14), TIMA analyses indicated minimal changes to the gangue mineralogy during leaching, with the exception of a decrease in the biotite and chlorite content (Table 5). The pyrite content decreased during leaching, in agreement with solution assays which showed that up to 70% of the sulphur in the ore dissolved during leaching.

Table 5. Mineralogy as determined by TIMA analysis before and after leaching.

<table>
<thead>
<tr>
<th>Phase</th>
<th>Formula</th>
<th>Feed</th>
<th>Leach residue - 90°C, O₂ sparged</th>
<th>Change</th>
</tr>
</thead>
<tbody>
<tr>
<td>Quartz</td>
<td>SiO₂</td>
<td>37.8%</td>
<td>41.2%</td>
<td>3.4%</td>
</tr>
<tr>
<td>Albite</td>
<td>NaAlSi₃O₈</td>
<td>21.4%</td>
<td>21.9%</td>
<td>0.6%</td>
</tr>
<tr>
<td>Anorthite</td>
<td>CaAl₂Si₂O₈</td>
<td>13.2%</td>
<td>12.4%</td>
<td>-0.8%</td>
</tr>
<tr>
<td>Chlorite - Clinoclite</td>
<td>Mg₃Al<a href="OH">AlSi₃O₁₀</a>₈</td>
<td>8.80%</td>
<td>7.42%</td>
<td>-1.37%</td>
</tr>
<tr>
<td>Calcite</td>
<td>CaCO₃</td>
<td>5.05%</td>
<td>4.51%</td>
<td>-0.53%</td>
</tr>
</tbody>
</table>
TIMA analysis showed that the deportment of uranium changed during leaching, with greater amounts of coffinite dissolving than the brannerite variants (Table 6).

Table 6. Uranium deportment before and after leaching.

<table>
<thead>
<tr>
<th>Uranium phase</th>
<th>Feed</th>
<th>Leach residue - 90°C, O₂ sparged</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coffinite</td>
<td>49.63%</td>
<td>38.74%</td>
</tr>
<tr>
<td>Brannerite</td>
<td>23.82%</td>
<td>27.71%</td>
</tr>
<tr>
<td>Brannerite (high Si)</td>
<td>26.55%</td>
<td>33.55%</td>
</tr>
</tbody>
</table>

Converting these to equivalent grades shows that coffinite dissolved to a greater extent than brannerite, which in turn dissolved to a greater extent than the high Si brannerite. The extent of coffinite dissolution was almost twice that of brannerite. Brannerite is known to be more refractory than coffinite, so it is not surprising that less brannerite dissolved compared to coffinite. These results also suggest that the presence of silicon in brannerite makes it more refractory.

Table 7. Equivalent uranium grade (ppm) in the ore and in O₂ sparged 90°C leach residue, broken down by mineral.

<table>
<thead>
<tr>
<th>Equivalent grade, based on feed grade</th>
<th>Mt. Isa U ore</th>
<th>Leach residue - 90°C, O₂ sparged</th>
<th>U extraction</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coffinite</td>
<td>1271*</td>
<td>548*</td>
<td>56.8%</td>
</tr>
<tr>
<td>Brannerite w/ high silicon</td>
<td>680*</td>
<td>475*</td>
<td>30.1%</td>
</tr>
<tr>
<td>Brannerite</td>
<td>610*</td>
<td>392*</td>
<td>35.7%</td>
</tr>
<tr>
<td>Total brannerite</td>
<td>1289*</td>
<td>867*</td>
<td>32.8%</td>
</tr>
<tr>
<td>Total uranium</td>
<td>2560^</td>
<td>1415^</td>
<td>44.7%^</td>
</tr>
</tbody>
</table>

*based on assay data; ^derived from assay data and deportments based on TIMA analysis (Table 6)

Comparing the extent and distribution of uranium liberation before and after leaching shows (unsurprisingly) that there was less liberated material in the leached residue, with more liberated uranium-bearing particles being more susceptible to leaching (Figure 15). There was a much larger decrease in the extent of liberation for coffinite than the brannerite variants during leaching. Even
coffinite that was only 10-20% liberated dissolved to some extent. This suggests a minimum level of liberation is needed for dissolution to take place. This was around 30-40% for brannerite, 50-60% for the high-Si brannerite, and around 10% for coffinite.

Figure 15. Change in the cumulative liberation of U minerals before and after leaching.

Titanium oxide coated brannerite particles were not identified in the leached residue, and the TIMA analysis showed minimal association of brannerite with rutile before or after leaching. When brannerite alone was leached at 90°C in carbonate media, the leached brannerite particles were coated in a titanium oxide layer up to 30 μm thick. This does not seem to happen when leaching ore under the same conditions. While titanium did dissolve and re-precipitate, it does not appear to be precipitating on brannerite. This means that the formation of a titanium oxide layer on leached brannerite is unlikely to be a problem when leaching refractory uranium ore in alkaline carbonate media.

4 Conclusions
A high-carbonate refractory uranium ore was leached under the same conditions previously used to leach a specimen of brannerite. TIMA analysis showed that the ore contained uranium as brannerite and coffinite. TIMA analysis of a sample of leached residue from the 90°C O₂ sparged leaching
experiment showed that the fraction of uranium associated with brannerite was higher in the residue than in the feed, indicating that coffinite was more readily leached.

Both x-ray diffraction analyses and TIMA analysis showed minimal changes to the bulk mineralogy during alkaline leaching under the most intense conditions used, apart from some dissolution of phyllosilicates.

Initial extraction rates were faster for the ore sample compared to the pure brannerite specimen, likely due to the presence of coffinite, a less refractory uranium-bearing phase. The extraction slowed however, once the liberated material had dissolved. TIMA analysis showed a change in the extent of uranium liberation during leaching, which pointed to a minimum level of liberation required for leaching to occur. This minimum was higher for brannerite than coffinite.

Tests on brannerite and a brannerite-containing ore show that alkaline leaching could potentially be a viable process for the extraction of uranium from refractory ores provided that the brannerite is sufficiently liberated. Further tests are needed with different particle size ranges. When dealing with high carbonate ores, alkaline leaching may be the most effective option. More tests are needed to determine the optimum leaching conditions and reagent dosages.

5 Acknowledgements
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Highlights

- A study of the leaching of uranium from a brannerite ore in alkaline sodium carbonate media
- The results show effect of temperatures between 50 and 90°C and residence time
- Addition of ferricyanide is shown to improve the rate of leaching when oxygen is present
- Up to 80% of the uranium was extracted from a Mount Isa uranium ore when leached at 90°C
- Results indicate that alkaline leaching could be a viable method for the processing of such ores