Characterising lithium host minerals within the lateritic duricrust, Greenbushes, Western Australia

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SUMMARY

Whilst detailed geochemical analyses have been conducted to mitigate the complications regolith cover poses to modern exploration efforts, less attention has been directed to the mineralogical associations that exist between lateritic residuum and potentially underlying intrusive-hosted Li-deposits. The characterisation of mineral hosts for Li in the lateritic duricrust would assist exploration efforts within poorly outcropping regions of Australia, by providing early indication and characterisation of potentially concealed deposits. Pisolitic laterite and lateritic duricrust from Greenbushes, Western Australia, was analysed as an example, using a suite of lab- and field mineralogical analytics, to understand the regolith mineralogical signature of buried Li ore.

The major and minor mineral phases, including the Li host minerals, in the regolith and underlying pegmatites are identified and compared. This provides insight into the distribution and mobility of Li in this setting, and the evolution of the Greenbushes ore deposit.

INTRODUCTION

The Greenbushes mine (Sn-Ta-Nb-Li), located 250 km south of Perth, is an unusually large, pegmatite-hosted, high-grade Li-resource (Kesler et al., 2012), and currently produces approximately 40% of the world's Li. The Greenbushes pegmatite swarm intrudes into the Balingup metamorphic belt (Smith et al., 1986), along the north to northwest trending Donnybrook to Bridgetown shear zone (Partington, 1990). Mining at Greenbushes commenced in the early 1900s and continued intermittently until 1964 after which it has been constant, with market dependent emphasis varying from Sn, Ta, Nb and Li (the latter as spodumene from fresh pegmatite). Surface sampling of locally undisturbed regolith, particularly lateritic pisoliths and lateritic duricrust, was carried out from 1979 to 1984 (Smith et al. 1987) over and around the Greenbushes ore deposit. The purpose was to test whether or not a geochemical halo occurred around the ore deposits. The same samples have been used within this study, providing a unique opportunity to mineralogically analyse the regolith profile that is no longer present due to the subsequent mining activity.

METHOD AND RESULTS

Hyperspectral reflectance spectroscopic data was collected using portable TerraSpec and Fourier Transform Infrared (pFTIR) devices, covering a continuous wavelength range from 350 – 14500 nm (28570 – 690 cm⁻¹), encompassing the visible, near, short-wave, mid-wave and thermal infrared wavelength regions. This, in combination with X-ray diffraction (XRD), enabled identification of sample bulk mineralogy, which overwhelmingly consisted of abundant gibbsite, poorly-crystalline kaolinite and quartz, with varying amounts of goethite and hematite. Small amounts of lithiumilite, ilmenite and boehmite were also identified in some samples. Using the Spectral Geologist (TSG™) software, mineral distribution was plotted in relation to the pegmatites. This allowed the correlation of mineralogy with geochemistry, and mineralogical vectoring towards the deposit in the wider Greenbushes area.

Scanning Electron Microscopy (SEM) analyses further confirmed the bulk mineralogical findings and provided textural and paragenetic information. Kaolinite, gibbsite and Fe-oxides were found to exist as very fine-grained mixtures within the samples, with individual phases often unresolved. Contained within this fine-grain mixture are coarser-grained quartz fragments, ilmenite and an array of trace minerals not detected by XRD or reflectance spectroscopy, including cassiterite, zircon, rutile, xiloilite and xenotime.

X-ray fluorescence (XRF) and Laser Ablation Inductively Coupled Plasma Mass Spectrometry (LA-ICP-MS) mapping showed elemental distribution within the pisolithic laterite samples. XRF was used to visualise major and heavy elements. LA-ICP-MS mapping revealed the distribution and semi-quantitative (ppm) abundance of Li and several other trace elements that form anomalies in the regolith centering on the Greenbushes deposit, including Be, As, Sn and Sb.

Laterite samples consist of either loose pisolith nodules, or pisoliths cemented in a kaolinite-gibbsite-goethite matrix. Where cement does occur, it contains higher concentrations of Li than that which occurs within the nodules it surrounds. Large fragments of minerals incorporating significant amounts of Li were also observed in the matrix. These minerals, yet to be definitively identified, do not appear to have formed in-situ and may originate from the underlying pegmatite body.

Most of the pisolith nodules are of a concretionary nature, typically consisting of an Fe-rich, Li-poor nucleus surrounded by concentric Al, Si and Fe-rich layers due to varying
proportions of kaolinite, gibbsite and Fe-oxides, with occasional quartz-rich layers (Figure 1). Lithium is enriched in the cortex, with several more generations of Li accumulation often preserved within the internal layers. Small fragments of Li-bearing minerals occur sparsely throughout. An As-bearing goethite cutan is sometimes present. The nucleus and concentric structure are absent in some pisoliths (Figure 2). These pisoliths are primarily clastic in nature with abundant quartz fragments occurring amidst finely intermixed kaolinite, gibbsite and Fe-oxide, with a Li-enriched cortex.

**DISCUSSION AND CONCLUSIONS**

Lithium host minerals known to occur in the Greenbushes pegmatites, such as spodumene, amblygonite, holmquistite and lepidolite, were not detected in the lateritic duricrust in the XRD or pFTIR data, in which they produce distinct signatures (LeGras et al., 2018). Neither could residual fragments of these minerals be detected by LA-ICP-MS analysis. Therefore, it can be concluded that the original Li-host minerals at Greenbushes are not preserved in the regolith atop the ore deposit, but that Li detected by geochemical analysis is now hosted by secondary minerals. One exception is lithiophilite, a Li-phosphate mineral which occurs in both the pegmatite and overlying lateritic duricrust. The implication for explorers is that a lack of Li orebodies at surface does not preclude the presence of a Li orebody below. Instead, attention should be given to geochemical anomalies (Smith et al., 1987). Increases in lithiophilite and ilmenite in lateritic duricrust also appear indicative of an underlying orebody.

Trace elemental mapping with LA-ICP-MS suggests a complex history of Li movement in the weathering profile, with a major late stage Li mobilisation event. Smectite, the primary crystalline weathering product of spodumene (Singh and Gilkes, 1993), was not detected in the samples. Lithium, at least in some instances, now appears to be hosted primarily by kaolinite and, in lesser quantities, gibbsite. Iron-oxides do not appear to host Li in this setting. The assignment of kaolinite and/or gibbsite as Li host minerals was generally difficult as the grain size and very fine intermixing of mineral phases in the samples is much smaller than the spatial resolution of the laboratory equipment. In future studies, infrared microspectroscopy coupled with X-ray fluorescence microscopy, using Synchrotron radiation, will potentially enable delineation and examination of the structural and chemical properties of the minerals at the required fine scale. This may help illuminate the complex weathering relationships between spodumene, smectite, kaolinite and gibbsite, and the movement of Li in the weathering system.

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**REFERENCES**


