GOLD MOBILITY WITHIN DUNE SYSTEMS ON THE BARNS PROSPECT, WUDINNA, SOUTH AUSTRALIA: A PARTIAL EXTRACTION APPROACH

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INTRODUCTION

The extensive regolith cover overlying outcropping geology hampers exploration within Australia. This regolith overburden can interact with underlying geology and take on some properties of the underlying geochemistry. Regolith geology and especially geochemistry has provided useful tools for exploration. In particular the gold-attracting capacity of regolith carbonates, or calcrete, has lead to several successes in the discovery of significant gold mineralisation in the underlying bedrock. The aims of this project are to: investigate the distribution of major and trace elements as well as identification of the mineral composition of carbonate-bearing regolith in aeolian cover on the Barns prospect, Wudinna, South Australia; and, to determine any chemical and mineralogical relationships, especially with respect to the identified correlation of gold and regolith carbonate. Selected samples were used to develop a sequential extraction method to investigate the distribution of Au in authigenic carbonates and clay minerals in the transported regolith. Results from this project will hopefully establish further understanding of the relationships of Au within the aeolian dune profile at the Barns prospect with respect to chemical and mineralogical processes.

LOCATION & GEOLOGY

The Barns Au project deposit is located approximately 25 km north of Wudinna on the Northern Eyre Peninsula. Situated on farming land, the area is easily accessible thanks to cleared natural vegetation and good road access (Figure 1). Extensive cover of the area by Quaternary units largely limits the understanding of the geology to the interpretation of drill holes and geophysical techniques. The following summary of the geology of the Wudinna area has been taken largely from Drown (2003).

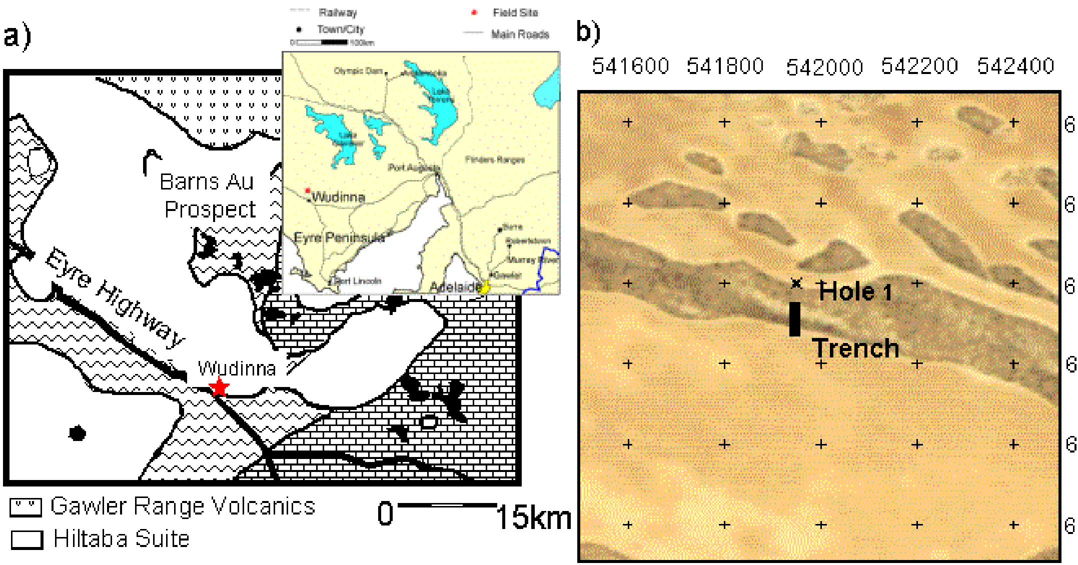

Figure 1a (left): Site location of fieldwork, inset Australian map showing location. Adapted from Drown (2003). **b (right):** Barnes Au project aerial photograph showing sand dunes, trench and hole location of analyses.

The eastern part of the complex is part of the highly metamorphosed Archaean Sleaford Complex, the west is dominated by intrusives of the 1690-1680 Ma Tunkilia Suite. The Tunkilia Suite includes moderately to strongly deformed granodioritic gneiss. Mafic granulites, felsic paragneisses and rare carbonate/magnetite-rich units form the majority of the Sleaford Complex. There are various volcanics and intrusives in the area such as the Gawler Range Volcanics (GRV) and the Hiltaba Suite intrusives dated at 1590 Ma. From the present level of exposure it can be concluded that the presently exposed units were at shallow crustal levels at

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the time of the Hiltaba-GRV event (Drown 2003).

The gold anomaly at Barns was identified through regional calcrete sampling and confirmed by subsequent shallow drilling by Adelaide Resources Ltd. The outline of the anomaly at Barns and the nearby Baggy Green follow a northwesterly trend, broadly parallel to the Proterozoic Yarlbrinda shear zone. High gold content is continuous in the saprolith underlying the aeolian sands and extends into the fresh bedrock. Primary mineralogy of the underlying bedrock consists of plagioclase, K-feldspar phenocrysts, quartz and biotite. Apatite, allanite, magnetite and zircon make up some of the accessory minerals all being identified from drilling in 2003 (Drown 2003).

SAMPLING AND ANALYTICAL METHODS

Samples of various types of calcrete and calcareous sand were taken from the aeolian sand dunes using a percussion soil corer to provide regolith cores of 32 mm diameter down to ca. 4m at the boundary of a 6 m high aeolian dune and surrounding farmland, approximately in the centre of the Barns property (see Figure 1). Further samples were taken from vertical and horizontal profiles on the walls of a ca. 6 m long trench dug into a dune by PIRSA on the Barns property. The regolith samples were analysed for whole rock components by commercial laboratories specialising in calcrete rock analysis.

Samples were analysed by XRF for major and trace elements to determine the compositional range and variation of the material from the aeolian deposits. Subsequently the < 2 μm grain size fraction was separated from the bulk quartz sand for determination of mineral composition through XRD, following the observation that the > 2 μm size fraction consisted mainly of quartz sand. The separation and chemical processes applied to the different size fractions follow closely to those described by Moore & Reynolds (1989).

Based on the results of the XRD and XRF analyses, a sequential extraction method was designed to further identify the distribution of Au within the different mineral and size fractions. The selected sample (BNS54) was chosen for its homogeneous distribution of gold content of 14 ± 2 ppb in several sample splits, suggesting that gold was present in non-particulate form and was evenly distributed throughout the sample. The total content was considered high enough for the sequential extraction procedure. Approximately 1 kg of sample was split into 3 parts and the extraction was carried out on a bulk sample and separates of > 2 μm and < 2 μm size fractions. After the grain size separation each fraction was split into 6 even sized samples, each to undergo the respective steps of the extraction procedure. After each step each the remaining residue was analysed for major and trace elements and Au.

The selective extract procedure involved the following steps:

1. Addition of 20 ml 1M $CaCl_2$ and 1M acetic acid twice to remove possible dolomite fraction;
2. Addition of 20 ml 1M $MgCl_2$ and 1M acetic acid to remove calcite fraction;
3. Wash with 20 ml 1M acetic acid 4 times to completely remove carbonates;
4. Addition of 0.5M hydroxylamine hydrochloride and 0.5M HCl to remove Fe and Mn oxides by reduction of the oxides in an acid environment;
5. Finally 4M HCl was added to the sample to remove crystalline Fe oxides.

After each process step the residual sample was washed and dried and sent for analysis for Au, Ag, Al, As, Ba, Bi, Ca, Co, Cr, Cu, K, La, Mg, Mn, Mo, Na, Ni, P, Pb, Rb, Sr, Te, Th, Ti, U, V, W, Yb, Zn & Zr. The chemical properties of dolomite cause it to readily dissolve after calcite, which is why in this process overloading of the solution with $CaCl_2$ will cause the calcite to remain as a solid while dolomite is dissolved. The opposite occurs when removing calcite; the solution is saturated with MgCl to ensure dolomite remains undissolved.

RESULTS

Major and trace element XRF and aqua regia digest ICP-MS and ICP-OES analyses established a consistent positive correlation of Au with Ca and Mg but also K and Al (see Figure 2a). Gold abundance ranges from 3 ppb at surface level to 18 ppb at a depth of 2 m and the other metals seem to follow this relationship. The relationship confirmed the results from previous studies (e.g., Drown 2003, Schmidt Mumm & Reith 2004). Other relationships seen in the down-hole data include a negative correlation of Au with Ni to depth and a reliable co-variation of Au and Ti.

The next step was to separate the < 2 μm grain size fraction according to the routines described by Moore & Reynolds (1989). Findings for this are displayed in Table 1a. The total amount of < 2 μm grain size fraction systematically increased with depth in the drill core. The major minerals identified in the samples were kaolinite and smectite in the form of montmorillonite; quantitative estimates of the mineral content as determined using SIROQUANT are listed in Table 1b. Carbonate content in the samples could not be quantified, as the removal of carbonates is required before orientated samples for clay analysis can be run. However the XRD spectra derived before carbonate removal show strong domination by a calcite and ankerite phase.

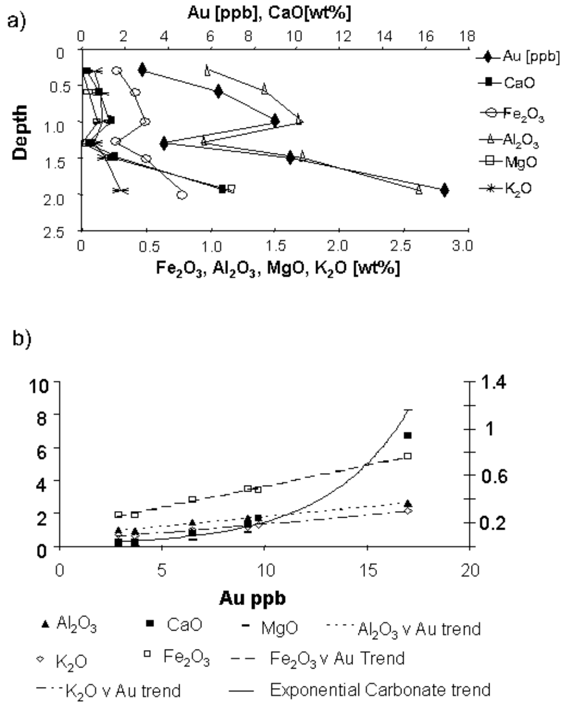

Figure 2a (above): Au and metal oxide abundances with depth in the initial drill hole. Note the distinct co-variation of Au with the metal oxides. **b (below):** Correlation of major elements and Au in the drilled profile. The most prominent difference is that CaO and MgO follow an exponential trend while Al_2O_3, Fe_2O_3 and K_2O follow more linear relationships with Au.

Further samples were taken along vertical profiles on the eastern and western face of the trench, (Figure 3a & c) and along a horizontal profile on the eastern face of the trench (Figure 3b). Analytical results of the sample profiles on the eastern face (Figure 4) were summarised to get a more consistent image of the compositional variation within the dune. Geochemistry on further samples that were taken from the trench in the dune location (Figure 1) further support the relationships of Au with Al, K, Ca, Mg, and also with Cu, all increasing in concentration with depth.

Along the walls of the trench dug into the aeolian dune 4 zones of different composition could be distinguished upon visual inspection (from top to bottom):

1. Organic rich root zone. The top 10-20 cm contains spinifex roots and abundant organic detritus from trees and shrubs;
2. Depleted leached zone. Ranging in thickness from 1.5 to 3 m, depending on the location in the dune, this zone is highly leached of elements and can be seen as almost white quartz sand with only some minor organic root zones from the bigger trees. It is extremely visibly distinct from the above and below horizons;
3. Enrichment zone. Visible in the trench as an orange horizon, this zone is concentrated in the elements leached from the upper zones. This zone is transitional between the depleted zone above and the carbonate zone below, showing some relationship between the formation of the two zones;
4. Carbonate zone. Two distinct types of carbonate occur: a fine powder that is dispersed throughout this zone; and a stronger cemented powder zone that forms around root zones penetrating to depth.

Table 1a: Wt. % of clay in each sample after grain size separation increasing with depth. **b**: Quantitative estimates of clay minerals from SIROQUANT program.

	21001	21002	21003	21004	21005	21006	Error
Depth (m)	**0-0.3**	**0.3-0.6**	**0.6-1.0**	**1.0-1.3**	**1.3-1.5**	**1.5-1.95**	
Quartz	7	4	4	6	4	4	1
Kaolin	48	42	46	50	46	39	5
Smectite	38	48	44	37	40	47	5
Anatase	1	1	1	1	1	<1	1
Goethite	<1	<1	<1	<1	1	1	1
Mica	6	5	5	5	7	4	1
Dolomite	-	-	-	-	-	6	1
Total	100	100	100	99	99	101	
> 2 µm weight	19.20	19.58	19.49	21.18	18.90	16.80	
< 2 µm weight	0.57	1.13	1.63	0.59	1.77	4.06	
Wt. % Clay per sample	2.88	5.46	7.72	2.71	8.57	19.45	

Figure 5a shows the depth relationships of the vertical profile on the eastern face of the trench. These results reiterate the patterns of element distribution as determined in drill hole 1. Samples taken from root zone carbonate and adjacent non-carbonate sand show distinct compositional differences. Au is clearly enriched in the root zones characterised by high CaO and MgO contents.. Each zone of root growth has extensive carbonate production surrounding it and this carbonate is enriched in Au as shown in Figure 5b.

The major component of the project was to analyse the distribution of the Au within the calcrete. Results showed firstly that Au is most readily dissolvable out of the Mn and Fe oxide phases. Figure 6a shows < 2 µm results relative to initial sample. Compared to the removal of Mn & Fe oxides, removal of dolomite and a lesser extent calcite shows little change in Au amounts. Al and K stay constant with respect to each other accept in removal of calcite where we see change in the relationship and a greater depletion of Al with respect to K. Zr remains constant throughout the whole removal process which would be expected as it is incorporated within a resistant mineral and should not be associated within one particular phase.

In the > 2 µm fraction Au concentrations change very little throughout all extractions (see Figure 6b). After each extraction the main elemental change is that of calcium and magnesium, while the other metals change very little. Unlike the < 2µm phase Au concentration is not much lower than the Mn, Fe hydroxides.

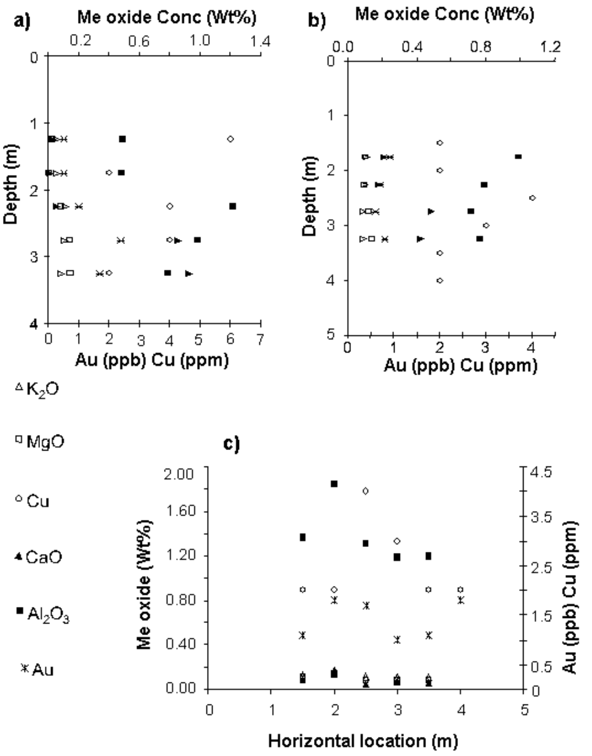

Figure 3a: Vertical profiles of western face showing concentration of metal oxides in wt. %, Au in ppb and Cu in ppm respectively. Note the correl-ation between CaO, K_2O and Au. **b:** Vertical profile of eastern face of dune. **c:** Horizontal profile of dune face.

DISCUSSION OF RESULTS

Results from the project have shown that apart from the well established correlation of gold with Ca and Mg, Au also shows a distinct co-variation with K throughout the sampled drill hole sand profiles. The K source was shown to be fine-grained authigenic smectite and kaolinite, in particular, in samples deeper in the profile. The increase of smectite/kaolinite concentration through the profile further illustrates the correlation observed between Au and Al within the profiles. This relationship is also reflected in the samples taken from the Enrichment Zone of the trench (see Figure 3c). However as shown in Figure 2 the correlation between MgO, CaO and Au is much stronger than that demonstrated with Al_2O_3 and K_2O, suggesting that Au is more strongly correlated to the carbonate-forming process. At high concentrations of CaO, MgO and K_2O, the correlation with Au follows a linear trend for K_2O, although with respect to MgO and CaO the trend is exponential in higher concentrations (see Figure 2). This could be interpreted as demonstrating a gradual accum-ulation of Au with authigenic smectite and kaolinite but the more closely linked accumulation through (co-)precipitation of Au and carbonate. The exponential relationship of CaO and MgO to Au implies that the precipitation of carbonates scavenges available Au from the (undersaturated) mineral-forming solution but continues beyond this. It is at this stage where carbonate is formed that expands to CaO/Au ratios beyond the observed correlation prevailing at low Au and CaO concentrations. Thus the solution is exceeding its capacity to provide Au and creates an exponential type relationship in precipitation.

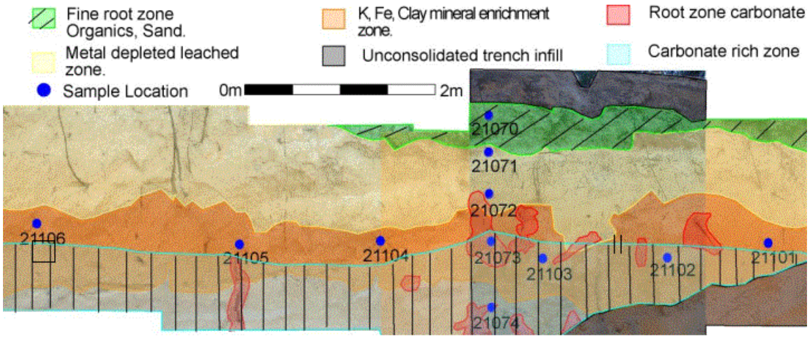

Figure 4: Annotated photo mosaic of the eastern face of dune showing sample locations and interpretation of internal differentiation of the dune from field observations.

Butt (1997) demonstrated the properties of a lateritic soil environment and the elemental relationships. These elemental relationships do not apply in the case of the investigated dune system. Field observations and chemical analyses have shown that there is chemical stratification within the dune structure and, from visual evidence on site (Figure 4), layering can be observed. Reduced metal content within the Depleted Zone and enrichment of clay minerals and consequently metals with depth, culminating in the highest contents in the Enriched Zone suggest secondary movement and authigenic mineral growth. If the clay minerals were simply deposited as aeolian clays the dunes would have an internal, primary stratification. The observation of metal content increasing with depth suggests a combination of processes being involved: Firstly the removal of aeolian clays from the upper regions (depositional zone) of the dune and the subsequent deposition lower in the strata (illuviation) and secondly field observations, chemical relationships between upper and lower regions of the profile and the XRD analysis suggest that there is authigenic mineral growth of mainly carbonates and smectites.

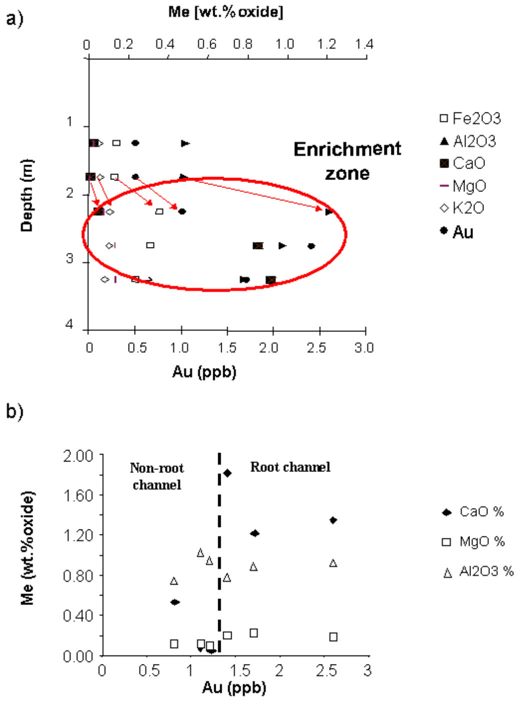

Figure 5a (top): Depth versus. concentration plot through the vertical profile of the dune eastern face highlighting the area of enrichment seen in Figure 4. **b (bottom):** Plot showing root zone carbonates against non-root zone carbonates within proximity of each other highlighting the relationship of Au with calcite in the root zones. A similar but less distinct relationship exists with Mg-containing carbonate. No systematic relationship is evident for Al_2O_3.

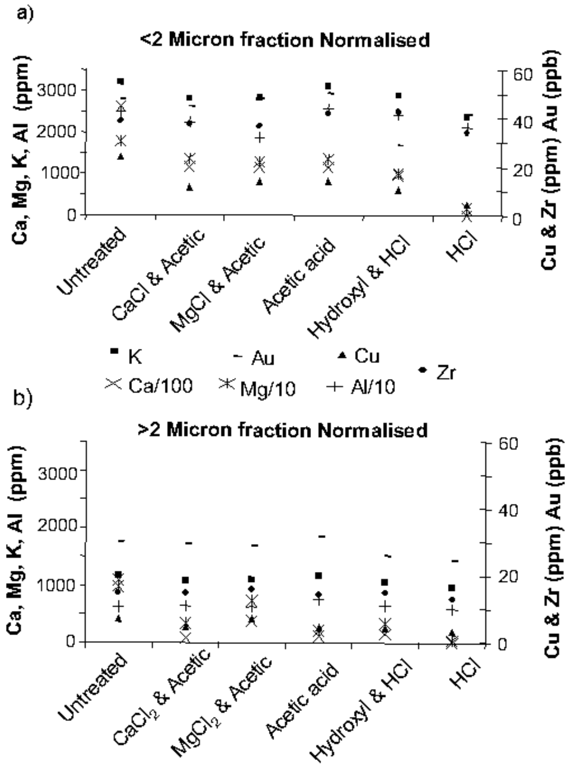

Figure 6a (top): < 2 µm fraction showing results of whole rock ICP-MS and ICP-OES analyses following each step of the partial extraction, highlighting relationships between Al, Au, Ca, Cu, K, Mg & Zr. Note: changes in concentrations must be compared to the original (Untreated sample). **b (bottom):** > 2 µm fraction results following the same process.

The formation of the carbonate at depth is dependent on the availability of CO_2 and Ca or Mg. There are two sources of calcium: aeolian blown marine Ca; or Ca derived through weathering and leaching of the bedrock. We can assume that Ca is abundant in the bedrock. Roots from trees that reach down into the profile will enhance the availability of CO_2 due to bioactivity surrounding the root zones and whenever this is released then Ca from either source can precipitate $CaCO_3$ (Schmidt Mumm & Reith 2004) as $CaCO_3$. This explains the stronger accumulations of regolith carbonate around the root zones of the trees in the profile. Figure 5b shows root zones and their adjacent non-carbonate zones demonstrating the ability of carbonate and Au to precipitate around roots.

The aeolian sands would not provide much in the way of metal ions as the samples from the upper horizons show. Trees in this arid environment must search for nutrients and water, therefore, they must have long roots to get sufficient water to survive. These roots can reach down to near saprolite areas and extract waters, which comprise small amounts of metal ions. As these trees die and the organic material breaks down the metals are leached down the profile in humic acids and precipitated when the chemistry changes at the point of contact with the carbonate.

Assuming this is how the Au and other metal ions get into this carbonate phase it can be examined as to where in the carbonate the is Au situated. Completion of analysis from the sequential extraction Au is relatively even throughout the sample except when Fe oxides are removed. There are differing trends in either grain size fraction analysed. The < 2 μm phase clearly shows a depletion of Au when Fe and Mn oxides are removed and a weaker depletion when dolomite is removed. Looking at the relationship between Al and K, it remains constant throughout. When there is removal of one species the other is removed proportionately. Studying the distribution after the $MgCl_2$ & acetic acid wash, much more Al is removed, suggesting that the alumina species is attached more to the calcite phase or more likely that in the alumina layer of the clay Mg can substitute with Al. There is much less Au in the > 2 μm separate than the < 2 μm phase, suggesting again the relationship with the < 2 μm clay materials and hence the association seen with Al and K. Because of the strong relationship between Au, Ca, Mg, K and Al, it can be theorised that these elements all precipitate out of solution together. The results in the extraction data where the only substantial loss in Au is after application of hydroxylamine hydrochloride and hydrochloric acid suggest that although there is a strong co-precipitation relationship for the Au, carbonate and clays, dissolution is not a reversible reaction. This is, however, only under the current experimental procedures.

CONCLUSIONS & DISCUSSION

Although some answers have been found such as a qualitative relationship with the Fe oxides and clay minerals, further work must be done to try and quantify the processes going on in this system. The leach process undertaken in this study does not take into account pH or oxygen fugacity buffering nor does it have any time constraints to take in effects of kinetics on Au dissolution. However, from the process undertaken thus far it is concluded that the Au precipitation in the dune chemistry is not reversible under these experimental parameters. If natural factors and also time constraints are considered then perhaps Au is re-dissolvable in the profile. However, the concentration increase of Au in the enrichment horizon indicates that Au is possibly not so mobile once precipitated and hence this is why there is an anomaly seen.

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