

Geochemical controls on uranium precipitation in calcrete palaeochannel deposits of Namibia

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ABSTRACT: Palaeo-river channels containing calcrete are important potential hosts for economic uranium mineralization in many parts of southern Africa particularly Namibia. The main feature of these deposits are the dominance of the mineral Carnotite $[K_2(UO_2)_2(VO_4)_2 \cdot 3(H_2O)]$ as the main uranium host in these channels. However other phases such as andersonite $(Na_2K_3UO_3(CO_3)_3(H_2O)_6)$, liebigite $(Ca_2UO_2(CO_3)_3(H_2O)_{10})$, rutherfordine (UO_2CO_3) , swartzite $(CaMgUO_2(CO_3)_3(H_2O)_{12})$, tyuyamunitite $(Ca(UO_2)_2(VO_4)_2 \cdot 5-8H_2O)$, and urancalcarite $[Ca(UO_2)_3(CO_3)(OH)_6 \cdot 6H_2O]$ are also present in minor amounts. These minerals are associated with epigenetic calcite, dolomite, gypsum, palygorskite, and strontianite. Typically a complex stratigraphy of calcite as transported and epigenetic calcite can be observed in the deposits. Uranium precipitation can occur more than once in the paragenesis indicating carnotite can be dissolved and re-precipitated in the palaeochannel possibly in response to fresh alkaline groundwater. Clear evidence exists that carbonates, gypsum, and uranium minerals are precipitated interstitially in the granite dominated detrital that fills the channel. Grade in these channels is typically higher at shallow depth with often the highest grade being at surface indicating that evaporation may play a role in precipitating uranium. Mineral equilibrium calculations, based on known mineralogy and groundwater chemistry have been used to construct geochemical models to understand ore genesis and assist exploration for carnotite hosted calcrete deposits. Multiple phases of calcite and carnotite formation are indicated in mineral paragenesis and an explanation for this may be that there has been frequent re-working of the deposit by inflowing groundwater. In addition, high evaporation in the near surface environment generate conditions for another mechanism for carnotite formation. Species activities and mineral saturation have been determined. These demonstrate that for many of the deposits carnotite is close to saturation or is only weakly undersaturated demonstrating that recent or even seasonal dissolution and re-mobilization of uranium may occur in these deposits leading to wide hydrogeochemical halos for trace levels of uranium in groundwater around these deposits. However inherent difficulties in the analysis of trace levels of metals in high salinity groundwater typical of palaeochannels may limit application in exploration.

KEYWORDS: uranium, hydrogeochemistry, geochemical modelling, Namibia

INTRODUCTION

The discovery of the calcrete hosted surficial uranium deposits of Namibia demonstrated the presence of widespread uranium in calcrete filled palaeochannels (Hambleton-Jones 1984) and similar mineral deposits have been observed elsewhere in Southern Africa, USA and Australia (Carlisle 1978; Hambleton-Jones 1978; Mann & Deutscher 1978). The host rocks are typically lenticular bodies of alluvium, soil or detrital material cemented by calcite, gypsum, palygorskite, and other mineral phases. Uranium mineralogy is dominated by the mineral Carnotite $[K_2(UO_2)_2(VO_4)_2 \cdot 3(H_2O)]$ as the main mineral in these channels. However other phases such as andersonite $(Na_2K_3UO_3(CO_3)_3(H_2O)_6)$, liebigite $(Ca_2UO_2(CO_3)_3(H_2O)_{10})$, rutherfordine (UO_2CO_3) , swartzite $(CaMgUO_2(CO_3)_3(H_2O)_{12})$, tyuyamunitite $(Ca(UO_2)_2(VO_4)_2 \cdot 5-8H_2O)$, and urancalcarite $[Ca(UO_2)_3(CO_3)(OH)_6 \cdot 6H_2O]$ are also present in minor amounts (Bowell *et al.* 2008). In Namibia the presence of authigenic gypsum in the surface calcrete increases with proximity to the Atlantic Ocean and this has been identified as an important factor in considering genesis of these deposits (Hambleton-Jones & Toens 1978). The genesis of carnotite-hosted calcrete deposits has been studied in both Namibia and in Australia and several mechanisms have been invoked, including evaporative controls weakening uranyl-carbonate species and decreasing pH close to the

groundwater table (Mann & Deutscher 1978; Carlisle 1978), physical and chemical attenuation through common ion effect and interaction with clay minerals and capillary driven diffusion mechanism similar to chemical dilatancy (Cameron *et al.* 2002). In order to determine the major geochemical controls on these deposits and the implications this may have for regional exploration geochemical modelling has been undertaken using groundwater chemistry from four deposits in Namibia.

GEOLOGY

The Namib Desert is underlain by bedrock complex of Late Proterozoic Damaran Belt unconformably overlying a 2 billion year old (Giga-annum or Ga) Mesoproterozoic basement complex of granite-gneiss (Kukla *et al.* 1991). The Damaran beds consist of metamorphosed arsenites and argillites of the Nosib Group overlain by pelitic rocks of the Swakop Group. Folding combined with regional granite intrusions occurred in the Pan African Orogeny (800 to 500 million years ago). Some of these orogenic granites are uraniumiferous. The sequence was intruded by both late to post tectonic 528Ma granites and most importantly by a series of post Karoo age (124-137Ma), anorogenic, peralkaline, slightly peraluminous, and topaz bearing granites with moderately elevated background uranium counts (e.g., Rössing; Basson & Greenway 2004). The latter younger granites (Spitzkoppe) are related to the break up of

Gondwanaland (130 – 80Ma) and constitute the ultimate source rocks for Trekkopje Project mineralization, with background contents of 20-30ppm uranium in places.

Between 80Ma and 50Ma, the Namib rocks were eroded to a smooth peneplain (the Namib Unconformity). Namib Group Tertiary and Quaternary sedimentary debris was deposited in east-west to southwest trending paleochannels incised into Karibib marbles and schists on that Cretaceous age unconformity. From mid Tertiary to present, the central Namib region has maintained profoundly arid climatic conditions for the last 50 or more million years. Uplift initiated the post African erosion surface that filled valleys and channels with poorly sorted angular material, with little evidence of chemical weathering or organic debris. Host rocks are paleo-channel deposits of cobbles, gravels, and local sands composed of the regional rock types. Calcrete formation is widespread throughout the region particularly in alluvium channels and paleoriver beds. The major calcrete channels in central western Namibia are shown in Figure 1.

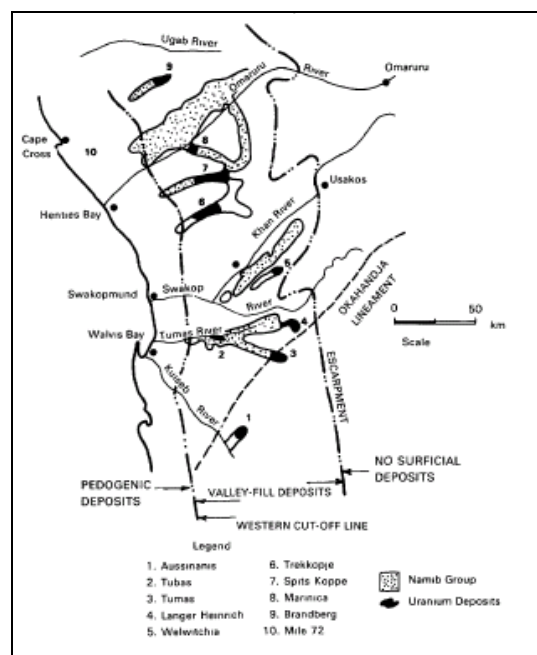


Fig. 1. Distribution of calcrete-hosted carnotite deposits in central Namibia (from Hambleton-Jones 1984).

HYDROGEOCHEMISTRY OF CARNOTITE HOSTED CALCRETE DEPOSITS

Data has been obtained from published sources and listed data held in the library of the Geological Survey of Namibia. This data has been used to assess the geochemical environment in the vicinity of channel fill and pedogenic uranium-bearing calcrete deposits. The data has been analysed by various methods and laboratories so direct comparison of the data has to be treated with caution. A summary table of the geochemistry of waters from each of the deposits is given in Table 1.

Table 1. Hydrogeochemistry of representative groundwater analysis, Calcrete Uranium deposits, Namibia (average of available data).

Element	Trekkopje	Langer Heinrich	Tubas	Mile 72
pH	6.62	7.8	7.57	7.81
Eh, mV	64	107	137	455
Carbonate, mg/L	174	473	575	88.3
Sulfate, mg/L	2090	2240	3250	1270
Chloride, mg/L	6750	3000	6580	6790
Sodium, mg/L	4110	970	2640	3070
Potassium, mg/L	121	387	822	1160
Calcium, mg/L	665	429	1460	890
Uranium, mg/L	0.212	0.316	0.182	0.019
Vanadium, mg/L	0.038	0.121	0.061	<0.005

The deposit with the highest salinity is Mile 72, followed by Tubas, Trekkopje, and Langer Heinrich. The reason behind this obviously can be related to distance from the sea with Trekkopje and Langer Heinrich the furthest from the coast, Tubas being 40 km and Mile 72 at the coast. Uranium is present in many of the groundwaters (Table 1). In terms of a correlation, a positive correlation can be observed for uranium with redox potential (Eh), high carbonate and lower sulfate and chloride, pH, and potassium in groundwaters (Fig. 2).

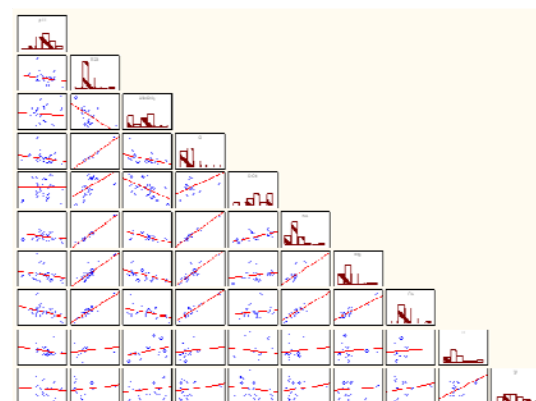


Fig. 2. Matrix plot for key groundwater parameters, calcrete-hosted carnotite deposits, Namibia.

GEOCHEMICAL CONTROLS

The speciation of uranium and vanadium has been determined for groundwaters from the calcrete-hosted carnotite deposits. These were completed in Geochemists Workbench v.7 using in-program database supplemented by additional data from Gorman-Lewis *et al.* (2008). The chemistry of groundwater for Namibian calcretes promotes the stabilization of the species, $UO_2(CO_3)_2^-$ (Fig. 3) and for vanadium, $VO_2(OH)_4^-$.

The uranyl dicarbonate species is extremely stable in aqueous solutions but by evaporation can

become sufficiently concentrated by evaporation to generate the low solubility mineral carnotite in the pH range 6 to 8, the natural range of pH values in the Namibian groundwaters.

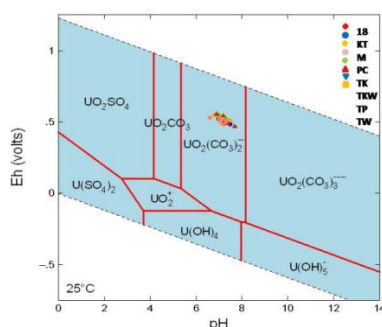


Fig. 3. Eh-pH diagram for the system U-H-O-S-Cl-C at 298 K.

At the prevailing pH in the Namibian groundwaters, the predicted solubility of carnotite is low and close to saturation. From one hole in the Tubas deposit, carnotite saturation is close to 0 and predicted to be over saturated around the water-table zone and in the near-surface upper 2m of the gypcrete. Where Eh is positive carnotite is predicted to be near-saturation. This indicates that carnotite accumulation at or above the regional water-table can occur by upward diffusion of uranyl carbonate species with possible precipitation due to nucleation on clay minerals or gypsum, as evidenced in the Tubas river.

MECHANISMS OF FORMATION

Understanding the formation of carnotite in calcrete is important with respect to not just understanding the formation of the deposits but also has implications for exploration of such deposits (Nash *et al.* 1981; Hambleton-Jones *et al.* 1984). A number of mechanisms have been proposed to explain the precipitation of Carnotite in calcrete formations (Boyle 1984). These include, reduction, sorption, uranyl complex dissociation, changes in redox state of constituent metals, evaporation, variation in CO₂ partial pressure, pH, mixing of different groundwaters and colloidal precipitation.

The source of uranium mineralization is erosion of uraniferous granites in the region followed by transportation of uranium in mildly oxidizing saline alkaline groundwater solutions in constricted drainages to semi-closed basins with variable evaporative conditions. The Quaternary erosion cycle was marked by uplift of coastal areas and marine regression with planation and incision of the post African erosion surface, with river valleys becoming younger towards the coast (Nash & McLaren 2003). This regional uplift across the Southern African subcontinent resulted in renewal of deposition of coarse sedimentary debris into incised drainage ways, creating the current drainage channels (Ringrose *et al.* 2005). Precipitation fluctuations in this period are believed to have effected uranium deposition, dissolution, and re-deposition.

In the fluvial-type deposits, such as Langer Heinrich or Trekkopje, most likely high carbonate fluids are responsible to mobilize uranium as uranium (VI) and deposition is in response to changes in a_{HCO_3} , pH, or redox similar to mechanisms proposed for Australian calcrete hosted carnotite deposits (Mann & Deutscher 1978b; Hartleb 1988). This form of carnotite is primarily due to remobilization of carnotite "upstream" and to de-complexing of uranyl-carbonates in waters of higher salinity. Uranium analyses and solubility indices suggest that the carnotite up stream is at present re-dissolving and that a different mechanism was primarily responsible for its original precipitation. The slow moving and upward welling groundwater undergo chemical and redox (reduction/oxidation state) changes allowing for precipitation of uranium as carnotite near surface. Carnotite occurs within the margins of the "chemical delta" formed as the drainage system forms, as observed for trace-element distribution in modern inland deltas (Ringrose *et al.* 2005).

In zones close to or at the water table the primary driver for remobilization appears to be high salinity and evaporative driven chemical dilatancy such as in the shallow calcrete deposits, for example Mile 72. A possible comparative mechanism has been proposed by Cameron *et al.* (2002) to explain the development of surface geochemical anomalies in areas with a thick vadose zone. Results of soil and groundwater analyses from an integrated study at the Spence porphyry copper deposit in northern Chile, which is buried beneath 50 to 100 m of Miocene gravels, are consistent with the vertical movement of saline metal-rich groundwater along fractures (Cameron *et al.* 2002). Copper in groundwater is restricted to the mineralised area due to the tendency of Cu²⁺ released by oxidation of sulfides to adsorb to Fe hydroxide colloidal particles and coatings, whereas elements that dissolve as anions (e.g., As, Mo, Se, and Re), are dispersed widely. Field measurement of the conductivity of soil-water slurries showed two zones of salt (NaCl) enrichment, one directly over the deposit and the other 1 km away. Trenching of the soils in these zones revealed vertical fractures in the gravels, whereas trenching in a background area showed no fractures. The fracture zones appear to have formed by reactivation of basement faults. Elements present in the soils above the fracture zones are the same as those enriched in groundwater near the deposit and indicate redistribution of elements by groundwater movement to the surface during earthquakes, followed by evaporation and further redistribution by rain.

The correlation to calcrete-gypcrete deposits is that saline groundwater may mobilize uranium both laterally and vertically through cyclic diffusion and pumping in a similar, albeit on a smaller scale. This may occur in response to recent marine transgression-regression episodes or even seasonally high salinity incursions in coastal groundwater.

Field measurements in sedimentary fluvial-type calcrete deposits also suggest that present-day groundwater in these areas may also display potential to both dissolve and precipitate uranium in

the near surface. Chemical dilatancy and evaporation-driven diffusion that promote de-complexing, diffusion, and re-precipitation mechanisms are seen to play integral parts in the continued chemical re-working and modification of these calcrete-hosted carnotite deposits.

IMPLICATIONS FOR EXPLORATION

The development of relatively large, but weak geochemical halos associated with calcrete-hosted carnotite deposits can be utilized on a regional scale through the application of aerial radiometric surveys and in more detailed prospect level evaluation by direct geochemical analysis of groundwater coupled with borehole geology and down hole radiometric surveys. The proximity to such superficial deposits of uranium can be gauged by groundwater uranium content. In addition for blind deposits the development of a Carnotite Saturation Index has been applied in Australia as a more sensitive approach based on several parameters (Mann & Deutscher 1978). This index can be defined as;

$$CSI = \log \frac{[U][V][K]}{1.13 \times 10^{-4} [HCO_3]^{-2}}$$

Where uranium and vanadium concentrations are in µg/L and potassium and bi-carbonate are in mg/L. Where the CSI is equal to zero then groundwater chemistry and carnotite saturation are in equilibrium and the mineral has the potential to be present. The assessment of groundwater chemistry in the vicinity of calcrete-hosted carnotite deposits indicates that a wide geochemical halo exists and that this halo can be identified during exploration. In Australia direct analysis of groundwater and the CSI have been demonstrated as suitable methods for exploration. In Namibia, in reality although the approach may be useful for higher grade deposits, such as Langer Heinrich, in reality the low uranium and vanadium chemistry in most groundwaters in proximity to calcrete-hosted carnotite deposits and difficulties in detecting trace levels of these metals will limit application. In addition for many of the Namibian deposits direct surface mapping of carnotite is possible for most of the known deposits so surface radiometrics and geological mapping will continue to provide a more cost-effective and reliable method of exploration for this class of deposit in Namibia and throughout Southern Africa.

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