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INTRODUCTION

Groundwater is a potentially useful sampling medium for successful mineral exploration. It is also one of the agents important in weathering processes and the geochemical evolution of regolith, given its reactive nature and ability to transport elements and dissolved gases. The aims of this study are to understand potential mineralisation signatures in an area with known base metal, e.g., Cu and Zn, and Au deposits and to understand the geochemical controls on groundwater composition.

SITE DESCRIPTION AND METHODOLOGY

The Hermidale area is situated in western New South Wales (Figure 1). The landscape consists of plains, rises and low hills in the western and southwestern parts of the area. The oldest rocks that outcrop are from the Ordovician Girilambone Group, which consists of rhythmically bedded, poorly sorted, fine to coarsegrained quartzose sandstone with subordinate quartzo-feldspathic sandstone, siltstone and chert together with minor intercalated basic volcanics and minor conglomerate, marl and serpentinite (Gilligan & Byrnes 1995). These rocks have been weathered to saprolith that forms the rises and low hills (Chan et al. 2002). In the Hermidale area, the Girilambone Group is overlain by shallow marine volcanic sediments of the Kopyje Group (Late Silurian-Early Devonian Babinda and Florida volcanics; Suppel & Gilligan 1993). There are also shallow alluvial deposits overlying the Girilambone and Kopyje Groups that are mainly associated with the present-day drainage pattern of Whitbarrow and Pangee Creeks, which generally flow to the north and northeast of the study area (Chan et al. 2002). Paleochannels are identified, based on aeromagnetic data, and show the same patterns as present day drainage. The aeromagnetic data also indicate NNW- trending bedding or structures, but no faults have been identified in the area. The climate of the area is sub-arid, with average monthly maximum temperatures ranging from 13°C to 20°C in winter and 28°C to 39°C in summer. Average monthly minimum temperatures range from 2°C to 8°C in winter and 14°C to 24°C in summer, measured at Cobar.



Figure 1: Location map of the Hermidale area in NSW and the locations of the drill holes for which there are groundwater samples.

The area has undergone a detailed drilling programme (Chan *et al.* 2002) where 48 air core holes (coded as Cobar Air Core, CBAC) were drilled in the Hermidale–Bobadah area. Groundwater was detected in 14 boreholes (Figures 2 and 3). However, only five drill holes remained open for sampling (CBAC150,

CBAC154, CBAC158, CBAC160 and CBAC173; Figure 1). The water depth, electrical conductivity (EC), pH and water temperature were measured on site. Water samples were filtered with 0.45 μ m filters and separated into 500 mL for cation analyses (acidified with 2 mL concentrated HNO₃) and 500 mL for anion analyses (unacidified).

The alkalinity of the unacidified samples was measured by titration in the laboratory and cation and anion concentrations were measured by conventional methods using Inductively Coupled Plasma-Optical Emission Spectroscopy (ICP-OES) at Bureau of Rural Science (BRS), and ICP-Mass Spectroscopy (ICP-MS) at University of Canberra, for major (Na, K, Ca, Mg, S, SiO₂, Cl⁻, SO₄²⁻, NO₃⁻) and trace elements (Al, As, B, Ba, Br, Co, Cr, Cu, F⁻, Fe, Li, Mn, Ni, P, Sr, Ti, V, Zn). Four water samples were analysed for ³⁶Cl at the Department of Nuclear Physics of the Australian National University. Details of the methods of ³⁶Cl analysis and a description of the Accelerator Mass Spectrometer used are outlined by Fifield *et al.* (1987).

RESULTS AND DISCUSSION

HYDROGEOLOGY

The water levels indicate an aquifer that consists of weathered phyllitic siltstone interbedded with phyllitic sandstone, rather than overlying transported sandy gravel (Figures 2 and 3), and the groundwater flow rate is slow. The water levels also mirror topography (Figures 2 and 3), suggesting that the aquifer is unconfined and that the general flow direction is from southwest to northeast (Figure 4).



Figure 2: Inferred lithologic and hydrogeologic cross-section between CBAC140 and CBAC158 in the northern part of the Hermidale area (see Figure 2 for location).



Figure 3: Inferred lithologic and hydrogeologic cross-section between CBAC173 and CBAC182 in the southern part of Hermidale area (see Figure 4 for location).

ELECTRICAL CONDUCTIVITY, pH AND TEMPERATURE

Electrical conductivity (EC) ranges from 7,200 μ S/cm to 31,600 μ S/cm, the pH ranges from 6.4 to 7.1 and the temperature ranges from 23°C to 27°C (Figure 4). The EC is variable, but is lowest in the southwest and north, which may indicate proximity to recharge areas as those samples are from holes in the highest parts of the landscape. The EC is higher in the samples inferred to be downstream of the lower-EC samples, which may indicate mixing with higher salinity water or evaporation, both of which are consistent with element ratios (e.g., Na/Cl, Cl/Br; Khider 2004). The easternmost sample (CBAC158; Figure 4) has an intermediate salinity, but it comes from the overlying gravel layer and is probably not downstream of the other samples, and is therefore unrelated to them. It is possible that it has a lower salinity than the other samples taken from approximately the same depth and in the phyllitic material because of mixing with recharging fresher water. The pH and temperature decrease along the inferred flow path, but differences are small and probably not significant.

The groundwater in the Hermidale region is chloride-rich (Khider 2004), where it is dominated by Cl^{-} , with lesser SO_{4}^{--} and HCO_{3}^{-} , and the main cation is either sodium or potassium.



Figure 4: Generalised hydraulic contours (m) in the Hermidale area (dashed lines) and measured water chemistry parameters. Sold lines indicate locations of the cross-sections in Figures 2 and 3.

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The ratio ³⁶Cl/Cl is plotted against chloride in Figure 5, together with representative trends for the processes indicated. The ³⁶Cl/Cl ratios are relatively high in CBAC 173 and CBAC 150, lowest in CBAC 160 and intermediate in CBAC158. The ratio decreases along the inferred flow path, although the easternmost sample (CBAC 158) has a higher ratio. The high values indicate the water is proximal to recharge, and the lowest value in CBAC 160 is probably a result of evaporation and mixing of groundwaters along the flow path. The intermediate ratio at CBAC 158 could be a result of mixing with a less saline and lower chlorine ratio water, or the groundwater is from a different source than to the east. Note that the groundwater from CBAC 158 could be from the transported gravel layer (Figures 4, 5).

WATER-REGOLITH INTERACTION

In order to understand the changes in the hydrogeochemistry and the interaction between groundwater and regolith, we plotted the measured element concentrations in the groundwater on activity-activity diagrams and calculated mineral saturation indices for all samples. We used Geochemist's Workbench Release 6.0 (Bethke 2005) with the thermo.dat database of thermodynamic properties for all calculations.



Figure 5: ³⁶Cl/Cl versus chloride for the Hermidale groundwater samples. Process trends are shown by arrows (Bird *et al.* 1991).

WEATHERING OF SILICATE MINERALS

The water samples plot in the muscovite stability field on a log a K^+/H^+ versus log a Mg^{++}/H^+ diagram (Figure 6), which is consistent with the observed presence of muscovite in that borehole (detected by XRD). In addition, analysis of weathering trends shows that the weathering of saprolite in the Hermidale area is not advanced, based on the Chemical Index of Alteration.

STABILITY OF COPPER AND ZINC ORE MINERALS

The waters are undersaturated with respect to oxidised copper minerals, assuming all the copper is oxidised (dissolved and solid). Although Eh was not measured in these samples, other samples from the area had an average Eh of 350 mV. At these conditions the water compositions plot in the cuprite stability field (Figure 7A), which is consistent with the presence of cuprite observed in two regolith samples from the boreholes. Zinc minerals are undersaturated, even at an Eh of 350 mV (Figure 7B).



Figure 6: Hermidale groundwater compositions and calculated mineral stability fields. Diagram is calculated assuming quartz saturation.

SATURATION INDICES

Spatial distributions of saturation indices may be useful in vectoring to ore. Figure 8 shows examples of $ZnSiO_3$ (chosen to avoid the complications of variables such as Eh and CO_2), malachite ($Cu(OH)_2CO_3$) and tenorite (CuO). In general the saturation index increases from S to N, with the exception of drill hole 173. Mineralisation is known to the north of drill hole 150, so the change in SI appears to indicate the position of the mineralisation, even though the inferred flow paths are from SW to NE (Figure 4). The changes in SI could result from other aspects, such as fluid mixing and/or evaporation (Khider & McQueen 2005).



Figure 7: Hermidale groundwater compositions, mineral stability fields and aqueous species predominance areas. Diagrams are calculated assuming representative conditions of the Hermidale samples. A: a _{Cu species} = 5.4×10^{-8} and pe = 5.9; and, B: a _{Zn species} = 3.6×10^{-7} and a _{HCO3} = $10^{-2.5}$



Figure 8: Calculated saturation indices of: A - $ZnSiO_3$; B – malachite; and, C - tenorite in Hermidale groundwaters.

CONCLUSIONS

Groundwater is moving slowly through the regionally extensive phyllitic siltstone-sandstone layer of *in situ* regolith. Water levels mirror topography, indicating an unconfined aquifer system, and groundwater is flowing in general to the northeast in the Hermidale area. Salinity and ³⁶Cl/Cl values indicate that mixing of groundwater is likely. The waters are undersaturated with respect to oxidised copper minerals; however, using redox conditions from nearby groundwater samples, cuprite is predicted to be stable, and observed in some regolith samples. The waters are undersaturated with respect to most zinc minerals. Calculated saturation indices of ZnSiO₃, malachite and tenorite appear to show a vector towards known mineralisation in the area.

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