

THE APPLICATION OF MMI™ GEOCHEMISTRY IN CARBONATE ENVIRONMENTS

Currently there is a great deal of interest in various parts of the world, in sampling carbonate environments. MMI™ geochemistry has been applied in many of these situations, although it is true to say there is further application work to be done to cover all of these environments. This technical paper has been compiled at this time to indicate the findings to date, and to outline some of the results and constraints of performing geochemistry in carbonate environments.

In conjunction with the field trials, a number of laboratory based experiments have been undertaken identifying, and in some cases, quantifying the parameters which influence the mobilisation and accumulation of metal ions near surface. This specific work has been the subject of two research projects undertaken at the Geochemistry Research Centre in Perth, and supported by mining companies, MMI™ technology and the West Australian State Government. At this point, findings of the first project M219 are available for publication whilst those of M267 remain confidential to the sponsors.

There are a number of different carbonate environments. Pedogenic carbonate, calcrete or caliche, are the terms frequently used to describe surficial soils over a variety of bedrock types, which have accumulations of carbonate in the upper part of the profile. They are frequently observed in areas with arid to semi-arid climates, i.e. desert regimes. These desert regimes also are sometimes host for groundwater calcretes, or carbonate deposits related to evaporation or partial evaporation of groundwaters containing carbonate salts. Transgressive carbonate units, e.g. of marine carbonates from the tertiary, often cover ore deposits of interest. Finally, limestones are often important host rock units for important ore styles and types, e.g. Carlin- type Au, or Mississippi Valley Pb-Zn deposits.

The decrease of solubility of many metals with increase in pH (increase in carbonate content) is well documented (e.g. Mann & Deutscher (1997) and Mann & Deutscher (1980)). However, it is important to note, that the decrease is never to zero, and most metals retain significant solution concentrations, particularly in the pH range pH=2 to pH=6. At pH values from pH=7 to pH=8, the relatively insoluble carbonates of metals such as Cu, Pb, and Zn limit the solubility of these elements to the tens to hundreds of ppb range.

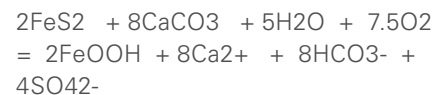
Carbonate environments are known accumulators of metals such as gold. In former times, when analytical detection limits were of prime consideration, this was an attribute of some value. However, with current instrumentation easily capable of ppb detection in soils, reproducibility of the sampling medium is of prime concern. Techniques which utilize the accretion of metals in a particular substrate run an inherent risk of "nugget effects" from bound and mechanically transported metal providing "false anomalies".

The MMI™ technique is one specifically designed to detach the unbound form of metals from the soil. As such, it has the aim and the observed capability to accurately outline the active source areas of metal input to the soil layer, and the ability to discriminate against bound and transported metal. This has been documented in relation to laterite profiles (e.g. TB6 The Application of MMI™ geochemistry in deeply weathered lateritic environments). It has the potential to be also a very useful technique in a range of carbonate environments.

GEOCHEMICAL WINDOWS IN CARBONATE TERRAINS

Neutralization of CaCO₃ in the Vicinity of Weathering Ore Deposits

As pointed out by Mann and Webster (1990), 2.4 tonnes of oxidizing pyrite will be responsible for the neutralization of 8 tonnes of calcium carbonate. The reaction stoichiometry:



240g 800g

dictates this will happen provided the reaction goes to completion. Specific gravities of the relevant minerals would suggest that on most occasions the volumetric equivalents would be even more dramatic, i.e. oxidizing pyrite can account for in excess of three times its own volume of carbonate. Where mineral deposits in carbonate terrain are, or have in the past contained oxidizing sulphides, particularly pyrite, dissolution of carbonate, and alteration of the prevailing geochemistry is an inevitable outcome. In that oxidation in this case requires oxygen, the process is usually a near- surface one,

with important consequences for the surficial geochemistry.

Surface Geochemistry Patterns

Ions can be transported to the surface, from weathering environments by a number of processes – gaseous, diffusion and capillary rise are amongst the most likely mechanisms. In normal circumstances the ions must exceed the capacity of either a physical or chemical barrier to absorb or dilute the effect of the metal flux, before recognizable geochemical contrast (an anomaly) is observed at the surface. This can, and does happen over geological time. However, if hydrogen ions also migrate towards the surface, along with other metallic products of the weathering, as many observations now seem to suggest, several important and fundamental changes to the surface geochemical patterns are likely to be observed. Even if only partial dissolution of the carbonate within the vicinity of the deposit is achieved, the pH within the “neutralization envelope” will be lower, i.e. more acidic, than the immediately surrounding, or un-neutralized terrain. It is believed that the same processes which provide for sharp MMI™ geochemical patterns above mineralization, will provide relatively sharp pH contours in the soils above an oxidizing deposit. Many metals have pH dependent solubilities, and mobility and migration within the neutralization envelope will be enhanced. Thus, a geochemical window, or zone of enhanced mobile ion activity will be produced within the carbonate terrain within a relatively short period of time.

This is not to say that geochemical responses can be obtained in all carbonate terrains - quite clearly if the amount of carbonate is large compared to the hydrogen and metal ion producing capacity of the deposit, movement of ions away from the deposit will be restricted, and the deposit will remain ‘blind’ to any type of geochemistry at the surface. This

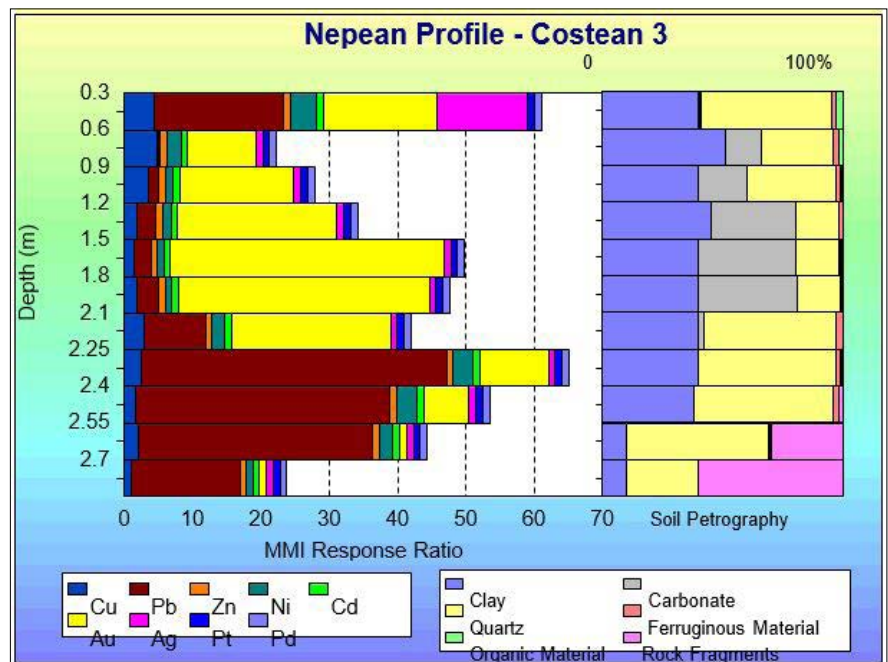


Figure 1: MMI™ Responses

is particularly true for the base metals Cu, Pb, Zn, and Cd, which themselves form relatively insoluble hydroxy-carbonates at pH 7-8.

Similarly, active alluvial and aeolian environments will affect the geochemical signatures in a physical sense. However, there is a volume of field (e.g. Smee (1997)), experimental, and theoretical evidence which now suggests that useful signatures can be obtained in a number of carbonate terrains, due to the formation of “geochemical windows”.

MMI™ RESPONSES

The MMI™ response for various elements, as a function of depth in a carbonated profile at Nepean, Western Australia is shown in Figure 1. Whilst it is evident that a considerable amount of Au, with an MMI™ Au signal occurs deeper in the profile along with carbonate, the sample with optimum response for all metals is the sample nearest the surface.

In this case, the profile consists of about 1m of transported granitic sands with occasional carbonate fragments, overlying a carbonated upper saprolite

zone, which has recognizable weathered rock fragments from about 2.5m below surface. Unweathered rock and fresh mineralization in this profile is some 80m below surface.

The surface sample at this location (over mineralization) contains MMI™ signatures for Au, Ag, Ni, and Pb, which are anomalous with respect to surface samples over background. The ability of MMI™ at this location (Nepean, near Coolgardie in the Eastern Goldfields of Western Australia) to outline the nickel sulphide mineralization at depth has been previously documented (Mann et al, 1993). The contrast between MMI™ geochemistry, and conventional geochemistry at Nepean is shown in Figure 2.

The ability of MMI™ geochemistry to assist in early drill targeting of primary sources in complex lateritic terrains has been demonstrated at the Golden Web Deposit (semi-arid environment) and at the La Salle Concession, Venezuela (tropical environment). At Nepean, the ability of MMI™ to do this in a predominantly carbonated profile for Pb, Au, Ag, and Ni is also evident. Whilst, thick

carbonate environments may provide barriers difficult for penetration of the base metals Cu, Pb, and Zn, there is no reason to assume that the modest amounts of carbonate as represented by pedogenic carbonates (i.e. caliche or calcrete environments) will preclude the formation of useful MMI™ geochemical anomalies for these elements. However, as always, great care needs to be taken with interpretation, and orientation surveys are recommended prior to the widespread use of MMI™ in any terrain.

CONCLUSIONS

Applications in Carbonate Terrains

Two important factors emerge from our work in carbonate terrains to date:

- (i) the optimum sampling location is near surface (5-15cm below surface); and
- (ii) where correctly sampled, MMI™ has the ability to provide higher resolution geochemistry than conventional techniques.

The prime application for MMI™ geochemistry in all types of carbonate terrains is more precise drill targeting of mineralisation hidden or obscured beneath transported surficial layers.

Often the more anomalous values defined by conventional or total element determinations are not directly linked to primary or source mineralisation at depth. The development of false or displaced geochemical anomalies can be a function of:

- (i) local chemical conditions in a weathering profile that can influence hydromorphic mobilisation, dispersion and subsequent re-deposition of elements; and
- (ii) the selective physical dismantling of the landscape exposing different components of a profile.

MMI™ geochemistry has been specifically designed to respond to the strongest source of mobile metal ions, that is, the metal ions that are

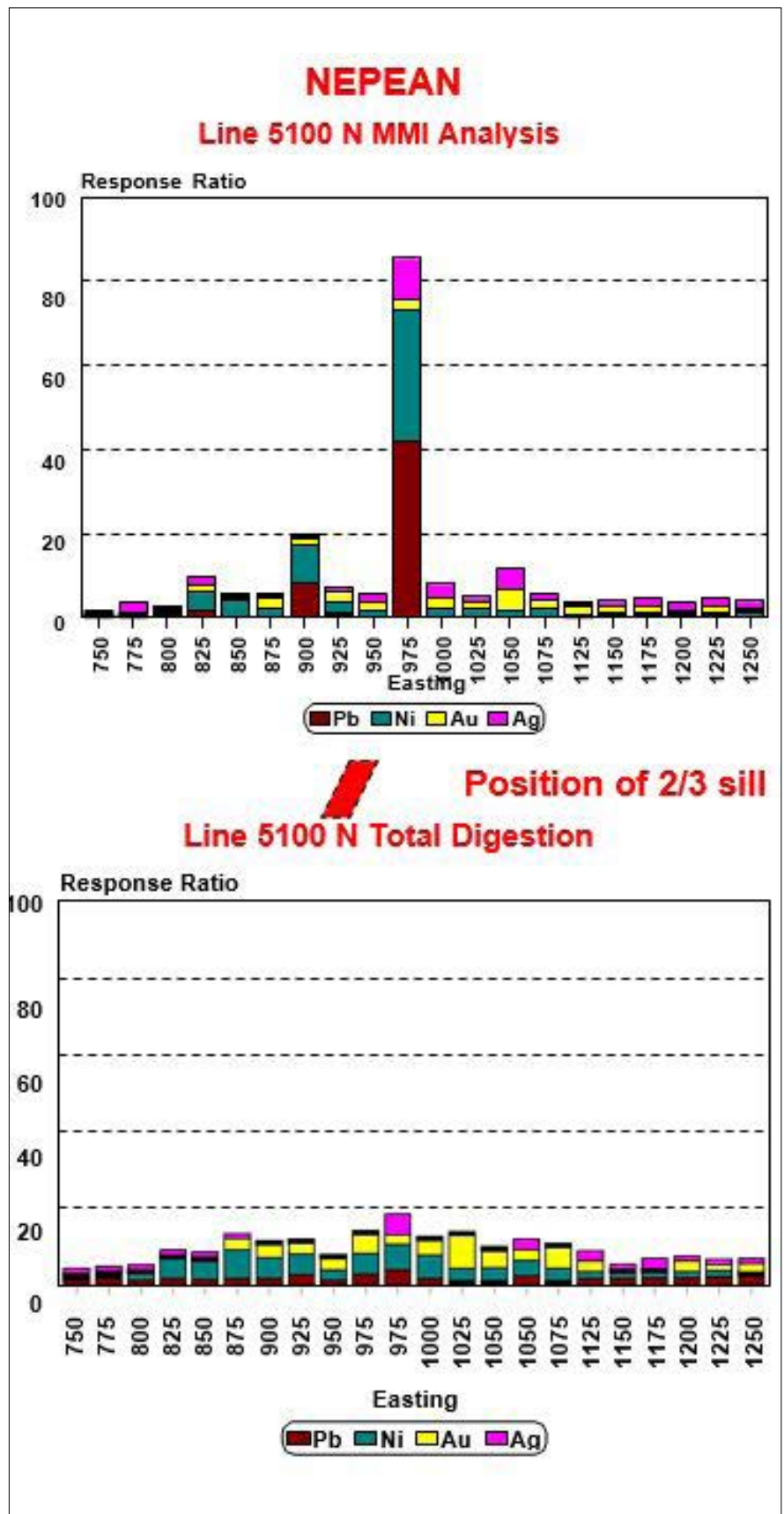


Figure 2: MMI™ Geochemistry and Conventional Geochemistry at Nepean

interstitial or very weakly attached to soil particles. By measuring the mobile component of metals in the soils, the technique pinpoints the most active source of metal ions, prior to the elements being transported any significant distance from source and becoming more strongly bound within the soil matrix by pedogenic processes. Given that the conventional (bound) geochemical anomaly requires mobile ions as a pre-cursor (see Mann et al, 1998), it is doubtful that conventional geochemical anomalies will be developed in carbonate environments that do not have an associated active mobile ion issue to the surface.

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