

TOWARDS UNDERSTANDING THE FERRUGINOUS COMPONENT OF THE REGOLITH

Kenneth G McQueen

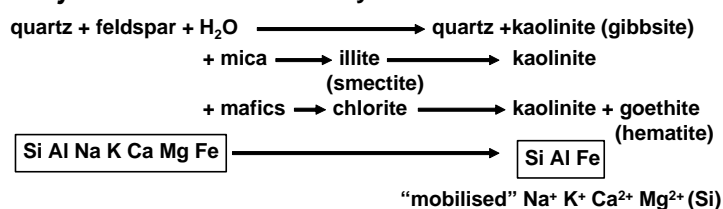
CRC LEME, Australian National University Canberra

kmq@ems.anu.edu.au

INTRODUCTION

The Earth is a wet, iron-rich planet and for much of its history has had an oxidising atmosphere. Oxidation of ferrous (Fe^{2+}) to ferric iron (Fe^{3+}), followed by hydrolysis and formation of insoluble oxide/oxyhydroxide minerals from soluble species is a major aspect of weathering and the regolith. Iron oxides/oxyhydroxides (principally goethite and hematite) are major end products of near surface chemical weathering and because of their ability to take up a wide range of cations these minerals exert a significant control over the fate of many trace elements, including target and pathfinder elements used in geochemical exploration (Figure 1).

Major Elements: control by mineral transformations



Trace Elements: dispersed-sequestered to specific hosts

Clays

Iron oxides/oxyhydroxides*

Manganese oxyhydroxides

Primary resistate phases

Stable weathering accessories

- ability to host a wide range of trace elements
- abundant in strongly weathered and oxidised profiles

Figure 1: The basics of element fractionation during chemical weathering of silicate rocks.

It is important to understand the mineralogical-chemical characteristics and evolution of ferruginous weathering products because:

- they are a major component of the surface and near surface regolith, affecting its chemistry and landscape stability;
- they can provide a record of certain environmental and chemical conditions (e.g. Eh);
- they have advantages/disadvantages as a geochemical sampling medium in mineral exploration.

SOME CHEMICAL CONSIDERATIONS

The most abundant iron oxides/oxyhydroxides in the regolith are goethite ($\alpha\text{-FeOOH}$) and hematite ($\alpha\text{-Fe}_2\text{O}_3$). Both these minerals are very stable under ambient conditions. Ferrihydrite (ca. $\text{Fe}_5\text{HO}_8 \cdot 4\text{H}_2\text{O}$) is a widespread but unstable compound in surface environments, generally transforming into more stable iron oxides/oxyhydroxides. Although not as abundant as goethite and hematite, lepidocrocite ($\gamma\text{-FeOOH}$) is common in non-calcareous soils and other ferruginous weathering products (Cornell and Schwertmann, 1996). Maghemite ($\gamma\text{-Fe}_2\text{O}_3$) is commonly present at and near the surface, particularly in ferruginous lag, where it is thought to form from the other iron oxides/oxyhydroxides by heat transformation.

Minor and trace elements can be incorporated into iron oxides/oxyhydroxides by the following mechanisms:

- adsorption/desorption followed by structural substitution or neo-formation of trace-element specific minerals;
- isomorphous substitution from a precursor phase (e.g. ferrihydrite to goethite);
- coprecipitation/introduction of new trace-element specific minerals;

- overgrowth and inclusion of other resistate minerals.

Under aqueous conditions, heavy metal cations (and complexes) adsorb onto the surface of iron oxides/oxyhydroxides by interaction with deprotonated, surface hydroxyl groups to form mono- and binuclear inner sphere complexes (Cornell and Schwertmann, 1996; Figure 2). The extent of this adsorption is strongly pH dependant, increasing with increasing pH over a narrow range. Increased temperature and addition of anions (e.g. thiosulfate, chloride) can also enhance cation adsorption, in the latter case by formation of mixed metal/ligand surface complexes (e.g. Schindler, 1990; Gunton, 2004). The available mineral surface area is a major control on the level of adsorption. Adsorption characteristics are different for the different iron minerals (e.g. in typical near surface environments and soils the relative strengths of metal adsorption on goethite are $\text{Cu} > \text{Pb} > \text{Zn} > \text{Co} > \text{Ni} > \text{Mn}$ and for hematite $\text{Pb} > \text{Cu} > \text{Zn} > \text{Co} > \text{Ni} > \text{Mn}$; McKenzie, 1980).

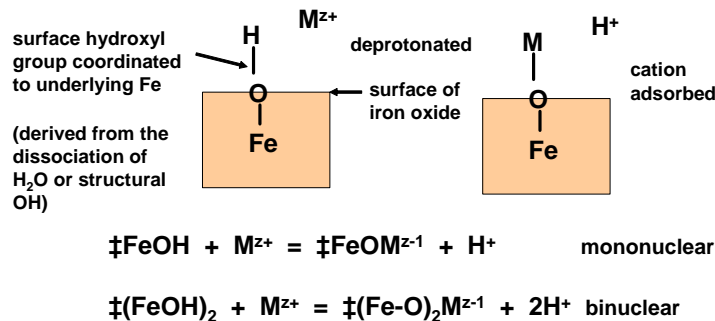


Figure 2: Summary of heavy metal cation adsorption onto the surface of iron oxides/oxyhydroxides under aqueous conditions.

Under dry conditions, surface Fe atoms in the iron oxides/oxyhydroxides may be coordinatively unsaturated with respect to hydroxyl groups, affecting the level of adsorption. Periodic wetting and drying may therefore have an effect on the adsorption capabilities and behaviour of the minerals. During deposition of iron oxides/oxyhydroxides adsorption is probably a preliminary step in the substitution of cations for Fe^{3+} .

A wide range of cations can isomorphously substitute for Fe^{3+} in iron oxides/oxyhydroxides including, Al, Cd, Co, Cr, Ga, Ge, Mn, Ni, Pb, Sc, Zn in goethite and Al, Cu, Cr, Ga, Ge, In, Mn, Rh, Si, Sn, Ti in hematite (Cornell and Schwertmann, 1996). Isomorphous substitution commonly changes the cell dimensions of the iron oxides/oxyhydroxides. The main controls on substitution possibilities are ionic radius and charge characteristics of the substituting elements.

FERRUGINISED LANDSCAPES

The formation of iron oxides/oxyhydroxides by weathering processes can have major effects on landscape evolution. This occurs through:

- induration of porous lithologies, surfaces and structures by chemically and physically stable iron oxide (mainly hematite);
- formation of iron oxide dominant rocks/regolith, such as ironstones, gossans, ferricretes and duricrusts.

Ferruginisation involves both vertical and lateral transport of dissolved iron in groundwater and in some cases surface water. The ferruginous component can also be added mechanically as detritus (e.g. aeolian dust and fluvial sediments). Ferruginous materials may be contributed to the soil, concentrated in surface lag and recycled through different components and levels of the landscape as the latter evolves.

Ferruginous induration and deposition commonly occur below the surface and in low parts of the landscape and these resistant materials may then become topographically inverted. They form chemically and physically stable features that can persist for long periods. Ferruginisation can armour the landscape (e.g. ferruginous duricrusts). Under arid and semi-arid conditions hematite is inherently more stable and probably more persistent than goethite. Many porous, ferruginised lithologies are quartz-rich and this adds to their stability. In these landscapes ferruginised materials can dominate what is available at the surface for observation and sampling. They dramatically affect the chemical characteristics of surface and near surface regolith. Ferruginised surfaces may also become buried.

FERRUGINOUS MOTTLING

Ferruginous mottling is a feature of many weathering profiles above the water table. These mottles are yellow to reddish brown segregations with more abundant iron oxides/oxyhydroxides. They take many forms including:

- light staining or impregnation/cementation of saprolite by minor amounts of the iron minerals;
- more concentrated nodular and concretionary accumulations of goethite/hematite with well defined outlines;
- goethite/hematite infillings of fractures, cavities and porous zones or beds.

The mottles form by patchy or localised precipitation of Fe^{3+} oxidised from Fe^{2+} and complexes dissolved in deep and shallow groundwater. The initial precipitate is probably ferrihydrite, which then transforms to goethite-hematite. In many cases biological activity plays a role in precipitation. Infilling of pore space may be followed by replacement of clays to produce more iron-enriched masses (Nahon, 1991). Ferrollysis (which lowers the pH) assists the dissolution of clay minerals. The relative proportions of goethite and hematite depend largely on the level of local hydration. Typically goethite is more common deeper in the weathering profile and closer to the water table, whereas hematite is generally more abundant at and near surface. More concentrated accumulation of iron oxides/oxyhydroxides results in nodules and pisoliths.

Strong mottling results in significant local enrichment in Fe^{3+} . Adsorption/incorporation of other elements typically results in an overall increase in their abundance in the ferruginous mottles but relative to Fe these enrichments may be small, particularly in environments where the elements are present at background concentrations (e.g. Figure 3). The dominant process is clearly oxidative deposition of Fe^{3+} and accumulation of iron oxide/oxyhydroxide from a large source volume. Other dissolved elements are extracted from solution and their level of adsorption/substitution varies with the type of host iron oxide/oxyhydroxide as well as their concentration. In some cases minor and trace elements are precipitated as secondary minerals incorporated into and protected by the ferruginous mottles (e.g. secondary sulfates phosphates, chlorides and manganese minerals).

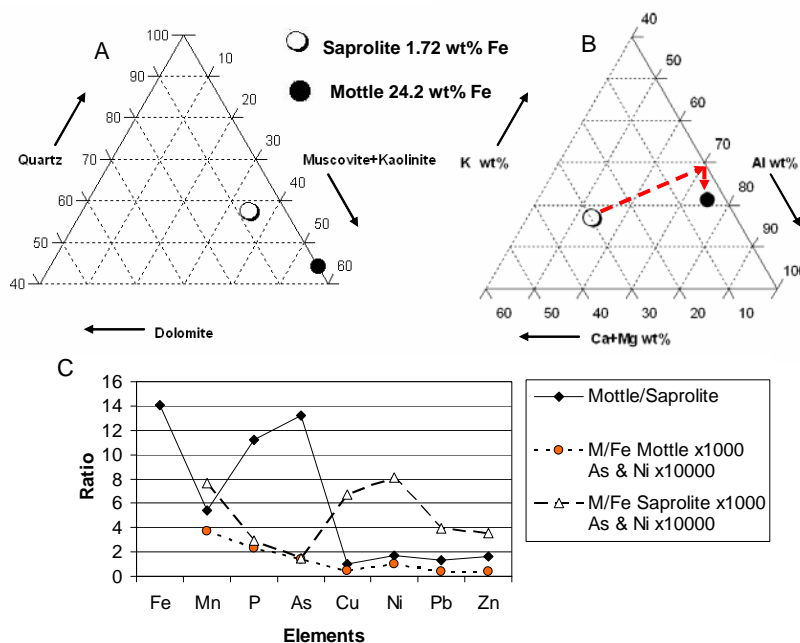


Figure 3: Compositional differences between ferruginous mottled and adjacent non-mottled saprolite/saprock from Pine Tree Tank quarry northeast of Cobar. Bedrock is fine grained, quartz-rich sandstone (ca. 40% quartz). A. shows the major (non-iron) mineral differences. B. shows major element differences (less Fe and Si) C. line plots show ratios of element abundance, including relative enrichment and ratios of elements over iron for the mottled and non-mottled material.

In mineralised environments, ferruginous mottles can fix target and pathfinder elements that may be leached from the surrounding saprolite or introduced by groundwater. If these elements become substituted/incorporated they are then less leachable compared to adsorbed or weakly bound cations (e.g. on clays). The mottles are therefore a useful sampling media if appropriate threshold values and

the history and degree of transport of the elements can be established. A number of parameters indicate that goethite is generally the better ferruginous sampling medium.

IRONSTONES, FERRICRETES AND FERRUGINOUS DURICRUSTS

Surficial and near-surficial accumulations of iron oxides/oxyhydroxides can form where groundwater flow has been focussed and where dissolved Fe^{2+} can be oxidised to Fe^{3+} (e.g. along structures or where groundwaters are exposed). This can produce massive ironstones or ferruginous, cemented sands and gravels, generally referred to as ferricretes. Extreme or prolonged concentration of iron oxides/oxyhydroxides by precipitation or residual enrichment above or within deeply weathered profiles gives rise to ferruginous duricrusts.

These ferruginous materials can scavenge and trap available cations in a similar fashion to ferruginous mottles. It is important to know the source vectors of the precipitating groundwater to interpret any geochemical anomalies present. For example, elements may have been transported in a vertical, residual or lateral sense. Some ironstones and ferricretes superficially resemble gossans and many have been “tested” by early prospectors. In mineralised environments they can occur with, and even mask gossans.

WEATHERED ORE PROFILES AND GOSSANS

Weathering profiles through ores exposed at the surface or intersected by the water table generally show strong ferruginisation (depending on iron content and extent of weathering). In these profiles there is a progressive change in the major mineral hosts for ore and associated elements from primary minerals (mainly sulfides and oxides) below the weathering front, to supergene assemblages around the water table, to secondary oxides and oxysalts (sulfates, carbonates, phosphates, arsenates) in the lower oxidised zone, to residual iron and manganese oxides/oxyhydroxides in the upper oxidised zone. This trend is reflected by an increasing positive correlation between many of the elements and Fe up the profile (e.g. McQueen and Munro, 2003). Due to their greater overall abundance, the ferruginous minerals generally retain the bulk of the remnant (unleached) ore elements. Goethite is an important host for Zn, Cu, As and to a lesser extent Pb, Bi and Sb. Hematite, where predominant, is an important host for Cu, Pb, As and Sb. The relative proportions of the major iron oxides/oxyhydroxides vary within the profile depending on chemical conditions (pH, Eh, activity of H_2O and O_2) during profile evolution and position relative to the surface and water table (Figure 4). Transformations between the iron oxides/oxyhydroxides result in release/redistribution of adsorbed and substituted elements.

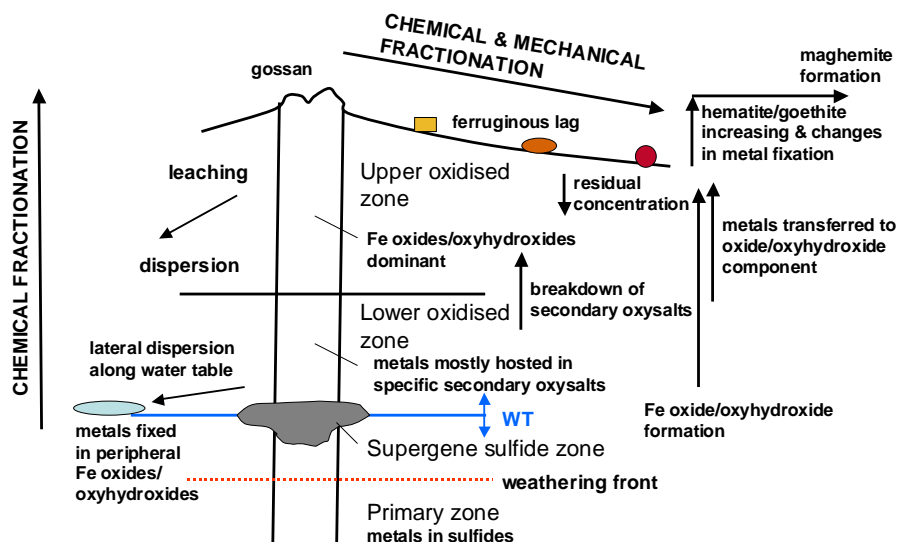


Figure 4: Schematic summary of a well developed weathering profile through sulfide mineralisation, showing major mineralogical transitions, the distribution of different ferruginous components and their role in hosting target and pathfinder metals.

Changes in mineral hosts, accompanied by element leaching, vertical and lateral dispersion and selective sequestering by particular minerals in different parts of the weathering profile, result in an overall chemical fractionation. The nature of this fractionation varies with the style of mineralisation and history of weathering. Once the profile is exposed at the surface, erosion results in mechanical dispersion of the gossan and its contained ore and pathfinder elements. Further transformations in the

ferruginous component (notably conversion of goethite-hematite assemblages to hematite±maghemite) are accompanied by additional chemical fractionation of the associated ore and pathfinder elements.

FERRUGINOUS LAG

The most chemically and physically resistant components of the regolith commonly form a layer of surficial lag, particularly in areas where normal surface runoff is unable to remove the coarser or more dense fractions. In deeply weathered, arid or semi-arid environments much of this lag is highly ferruginous. It can be derived from all the various ferruginous materials of the regolith but especially the underlying mottled zone, or where present, ferruginous duricrust. Lag has been widely used as a sampling medium in geochemical exploration (generally the 3-15 mm size fraction) on the assumption that it retains ore and pathfinder elements present in the underlying bedrock.

Detailed investigations in the Cobar area of western New South Wales have established that lag undergoes physical and chemical maturation as a result of mechanical reworking, transport, conversion of residual goethite to hematite, loss of soluble components and precipitation of additional hematite (McQueen and Munro, 2003; McQueen *et al.*, 2004). This maturation is accompanied by significant fractionation of trace elements. The contents of some elements including Th, Hf, Pb, As, Sb, Bi, Ba and Cr systematically increase with increasing Fe (and hematite) content and with degree of rounding and physical maturation of the lag. This results in significant concentration of these elements. Thorium shows the strongest correlation with Fe and hematite and is a good marker for the fractionation. Other elements (including Cu and Zn) do not show this relationship and in some cases are negatively correlated with hematite content. The mechanisms for this control on element fractionation in ferruginous lag are not fully known. For some elements, positive correlation with Fe reflects residual concentration in separate resistate minerals (e.g. Ba in barite) that accumulate with residual hematite. Sequential leaching experiments also indicate that most concentrating elements are largely bound in the crystalline component of the lag and appear to be dispersed within hematite (Cairns *et al.*, 2001, McQueen *et al.*, 2004). Significant amounts of Cu and Zn are present in exchangeable or loosely bound forms (including in the amorphous and manganese oxide components).

Fractionation of pathfinder and ore elements needs to be taken into account when interpreting lag geochemical data, particularly where the lag contains variable mixtures of different lag types. Normalisation against Fe content for those elements that concentrate with hematite is one approach to reducing this geochemical noise. Typical background trends for elements against Fe can be recognised and preliminary results indicate that these are different from trends found in areas of known mineralisation and for lag sourced from gossan (Figure 5). This suggests that regional templates could be constructed for background ratio trends, which could then be applied to lag geochemical data to isolate and detect truly anomalous values.

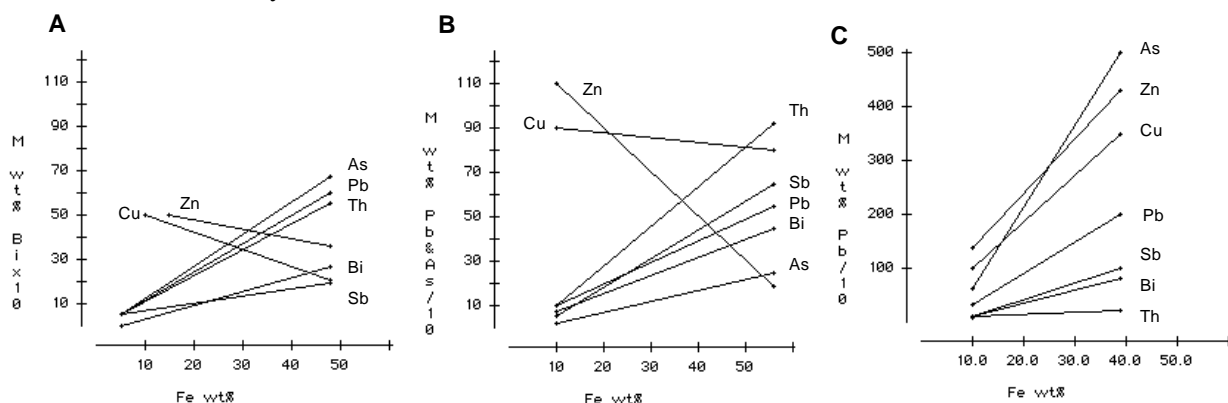


Figure 5: Ratio trends for some target and pathfinder elements in ferruginous lag from the Cobar area, NSW. A. is for lag from a background (unmineralised) site. B. is lag from the Cu-Pb-Zn mineralised CSA area. C is lag derived from gossan near the CSA mine (note plotted values have been increased by an order of magnitude for Bi in A and reduced by an order of magnitude for Pb and As in B and for Pb in C).

CONCLUSIONS

Ferruginous materials are a major but diverse physical and chemical component of the regolith. To effectively use these materials in mineral exploration it is important to understand their origin and mineral-chemical characteristics in the context of their landscape setting and the landscape evolution. Interpreting source locations of target and pathfinder elements in ferruginous materials depends on identifying the history, directions and extent of hydromorphic and mechanical transport of the elements during and after formation of the host iron oxides/oxyhydroxides. Possibilities include:

- “*in situ*” incorporation of elements from either mineralisation or the primary dispersion halo into adjacent or nearby iron oxides/oxyhydroxides in the weathering profile;
- limited lateral hydromorphic dispersion of dissolved elements along the water table (or palaeo water tables) and incorporation into precipitated iron oxides/oxyhydroxides;
- extensive lateral dispersion of dissolved elements by groundwater to sites where iron oxides/oxyhydroxides have precipitated and where the elements are adsorbed/incorporated;
- mechanical transport and reworking of eroded ferruginous materials containing target and pathfinder elements;
- subsequent incorporation of cations into transported ferruginous materials from a local or distal source.

Trace element fractionation can occur as ferruginous materials undergo transformation near and at the surface. This needs to be taken into account when interpreting geochemical data derived from these materials, particularly hematite-rich ferruginous lag.

More research is required to fully understand the mineral-chemical and biological controls on trace element behaviours and distributions in the ferruginous regolith.

Acknowledgments: The work reported here was supported by the Australian Government’s Cooperative Research Centre Program within CRC LEME. I thank my co-workers and students from CRC LEME, particularly, Keith Scott, David Gray, Ravi Anand and Dougal Munro, who have helped with the data collection, geochemical analysis and comments. Bear McPhail read and made useful comments on the abstract.

REFERENCES

- Cairns, C.J., McQueen, K.G. and Leah, P.A., 2001. Mineralogical controls on element dispersion in regolith over two mineralised shear zones near the Peak, Cobar, New South Wales. *Journal of Geochemical Exploration*, **72**, 1-21.
- Cornell, R.M. and Schwertmann, U., 1996. *The Iron Oxides*. VCH Publishers, New York, 573 pp.
- Gunton, C., 2004. Adsorption: Should we care? In: Roach I.C. (ed.) *Regolith 2004*. CRC LEME, pp. 112-116.
- McKenzie, R.M., 1980. The adsorption of lead and other heavy metals on oxides of manganese and iron. *Australian Journal of Soil Research*, **18**, 61-73.
- McQueen, K.G. and Munro, D.C., 2003. Weathering-controlled fractionation of ore and pathfinder elements at Cobar, NSW. In: Roach, I.C. (ed.) *Advances in Regolith*. CRC LEME, pp. 296-300.
- McQueen, K.G., Munro, D.C., Gray, D. and Le Gleuher, M., 2004. Weathering-controlled fractionation of ore and pathfinder elements Part II: The lag story unfolds. In: Roach, I.C. (ed.) *Regolith 2004*. CRC LEME, pp. 241-246.
- Nahon, D.B., 1991. *Introduction to the Petrology of Soils and Chemical Weathering*. John Wiley, New York, 313 pp.
- Schindler, P.W., 1990. CO-adsorption of metal ions and organic ligands: Formation of ternary surface complexes. In: Hochella, M.F. and White, A.E. (eds), *Mineral-Water Interface Geochemistry*. Reviews in Mineralogy 23, Mineralogical Society of America, Washington, pp. 281-309.