## 2.5.16

## Hydrogeochemistry and transport of weathering/oxidation products of buried mineralisation

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1-D and 2-D coupled reactive transport modelling is used to understand the dispersion of weathering and oxidation products of sulfide mineralisation in two areas of weathered bedrock and shallow transported cover. Of these, one area is well characterised through extensive industry and researchbased drilling and geophysical data acquisitions. The other area is considerably larger and datasets are more widely spaced, but it does have a high-quality groundwater composition dataset. In the models, sulfides are oxidised by varying redox and salinity conditions to simulate the regional groundwater systems. Transport is through unaltered bedrock, weathered bedrock and transported sediments in saturated and unsaturated systems. Reactions are constructed to simulate the effects on shallow and deep mineralisation. Using hydrogeological models constructed from geophysical and drillhole data, the 3-D hydrostratigraphic framework incorporating mineralogical data is used to parameterise and test models and model outcomes. Water-rock interactions along the flow path include dissolution/precipitation reactions, ion exchange and adsorption. Transport includes diffusion, advection, dispersion and mixing. Model results often match hydrogeochemical and geochemical data in terms of relative amounts but the lack of detailed knowledge of the permeability structure restricts their predictive capability. Groundwaters that have oxidised sulfide mineralisation retain a chemical signature of the mineralisation. In particular, the oxidation of sulfides above or below the water table results in small though significant differences in the composition of the local and regional groundwater. Although the modelled dispersion patterns are strongly dependent on permeability and mineralogy of the weathered bedrock and transported sediments, the general associations match field data. In the central New South Wales Gidginbung Volcanics Cu-Au mineralisation trend, oxidation of the primary mineralisation results in a net in situ concentration of metals in the regolith and the aqueous reaction products accumulate primarily in ferruginous paleochannels associated with the transported sediments. In the Curnamona Sub-basin Pb-Zn and Cu-Au province, mixing, ion exchange and adsorption should result in the rapid attenuation of mineralisation signatures in groundwaters but also introduce the potential for distinctive element ratios to be used to distinguish the geochemical and hydrogeochemical dispersion patterns.

## 2.5.21

## Reactive fronts at the nanoscale: The nature and origin of a coupled dissolution-precipitation interface

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A mineral replacement process is initiated and controlled by a nanoscale fluid layer which forms the interface between the parent and product phase. Whenever a fluid is in contact with a mineral surface with which it is out of equilibrium, dissolution of the surface will tend to occur. The nanoscale topographic heterogeneity of any surface is such that some sites are further out of equilibrium, and hence more reactive, than others. Under temperature conditions where some dissolution takes place, a layer of fluid immediately in contact with the surface, formed by mixing components from both the parent solid and original fluid, may become supersaturated with respect to a different more stable phase or phases. Nucleation of the product phase(s) will be entirely controlled by the structural relationships between parent and product, and may take place as an epitaxial two dimensional nucleus. This initial step sets in place the coupling between the dissolution and precipitation, and defines the replacement mechanism. The surface precipitation enhances the rate of dissolution ('autocatalysis') and hence of precipitation rate. In the presence of even thin films of fluid, such reactive fronts operate in a wide range of replacement processes, including isochemical replacements such as polymorphic transformations and coarsening of exsolution lamellae, to cases where there is a significant compositional difference between parent and product. In the latter cases, the rate control is most likely to be mass transport through the fluid phase to and from the interface. This may take place through the interfacial fluid film, or through the parent phase if porosity is generated by the replacement.

Such replacement processes are dynamic and all-pervasive in rocks where any energy input (such as deformation or heat) or fluid input disturbs the equilibrium. Examples of experimental replacement processes in soluble salts observed by *in situ* microscopy will be related to observation of replacement processes in granitic rocks. The replacement of plagioclase by potassium feldspar will be described together with some possible consequences to the origin of the relationships between different granitic rock types.