METAL-ORGANIC INTERACTIONS AND ANDEAN DEFORMATION

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Summary

Close associations occur between migrated organic matter (bitumen) and metalliferous minerals in several Andean regions, including western Argentina (uranium/copper), Chile (copper) and Peru/Columbia (vanadium). These associations represent diverse styles of mineralization, some of which may have been enhanced by fluid migration controlled by compressional deformation.

Introduction

The occurrence of organic materials in ore deposits is widespread. In many examples the organic materials played a geochemical role in the concentration of metals, although they are not always enriched in metals. Some organic matter however is highly enriched in metal(s). Metal concentration can be envisaged in several types of organic material, which represent different stages in the geological evolution of organic matter. Living organisms use and may take up a large number of elements including metals. The decay of dead organisms yields organic acids and other compounds that may complex with metal ions. The degradation of sulphur-rich organic matter by anaerobic bacteria, and bacterial sulphate reduction both yield hydrogen sulphide which can help to precipitate metals as sulphides within organic-rich sediment. Mixed sequences of organic-rich and organic-poor sediment contain redox boundaries that facilitate metal precipitation. Finally, epigenetic organic materials (migrating oil, bitumens, pyrobitumens) can cause the reduction and/or complexing of metals. At each of these stages it is possible for the organic material to become metal-enriched. Metal enrichments in organic matter may therefore be useful as pathfinders in the exploration for metalliferous ores.

Metal enrichments

Many elements are concentrated by biological activity. Numerous metals are utilized by micro-organisms in enzymes or other metabolic activity, and some organisms can concentrate them by several orders of magnitude (e.g. Robbins 1983). Much data show that terrestrial plant matter in particular accumulates metals. For example peat bogs concentrate uranium and other metals through adsorption and the binding action of humus. Plants growing on mine waste take up substantial quantities of metals. Determinations of metals in young coniferous trees suggest that they can be used as a sampling medium during geochemical prospecting (King *et al*. 1984).

After death, the degraded tissues of organisms may still absorb metals, and metal concentrations in organic-rich sediments in an anoxic environment are much higher than those in the overlying water column. Further enrichment of metals can occur during the diagenesis of the organic-rich sediment. Metals are already being mobilized during early diagenesis, and transported or deposited according to redox conditions. The relative importance of metals may change, because some organometallic complexes are quite stable during diagenesis, while others break down as the temperature rises. Vanadium and nickel complexes are particularly stable and these metals will substitute for others which are progressively lost (Lewan and Maynard 1982). Vanadium and nickel are also important components of petroleum and bitumens, in which they are concentrated within certain organic fractions, particularly the heavy fractions rich in asphaltenes and sulphur. In addition to vanadium and nickel, elements often concentrated within petroleum and bitumens include copper, cobalt, molybdenum, lead, manganese and iron.

Metal exploration

The metal enrichments in organic materials can be significant to metal exploration in four main ways:

(i) The organic material could be enriched in metal that has been taken up from groundwaters flowing off a metal deposit, i.e. the organic matter is younger than the ore deposit. The enrichments in living plants are examples of this.

(ii) The organic material may contain metal enrichments which are a signature of more limited levels of enrichment in the host sediments. If the enrichments in the sediments were later remobilized and concentrated into an ore deposit, the organic sampling medium is older than the ore deposit.

(iii) The organic material could be so enriched in the metal that it constitutes the actual ore. Further metal enrichments could occur in the vicinity, or the metal may be restricted to the organic material.

(iv) The organic material could be an epigenetic product (bitumen, pyrobitumen) generated at the same time as the ore deposit, particularly in a hydrothermal environment. Traces of the ore metal may occur as a signature within the organic material.

Metal enrichments in bitumens

Metals which occur within bitumens could have been:

(i) inherited from the hydrocarbon source rock as organometallic complexes;

(ii) scavenged by migrating hydrocarbon-bearing fluids; or
(iii) deposited in the bitumens at the site of mixing of metal-bearing and hydrocarbon-bearing fluids.

Very high metal enrichments within bitumens necessitate the existence of microscopic inclusions of ore minerals within bitumens. Such inclusions could be formed in numerous ways (Parnell 1988):
(i) remnants of minerals partially replaced by bitumen;
(ii) ore minerals physically transported by flowing oil;
(iii) coeval precipitation of bitumen and ore mineral inclusion from a common fluid;
(iv) precipitation following absorption of metal to a concentration above what can be accommodated as organometallic complexes;
(v) infill of fractures and cavities formed during devolatilization.

Vanadiferous bitumens, Peru

A strong enrichment of vanadium in bitumens from Argentina to Venezuela could relate to a regional crustal vanadium anomaly, but is most likely to reflect common derivation from a regionally important source rock in the Cretaceous. There are a large number of solid bitumen veins in Central Peru which are ubiquitously enriched in vanadium. These bitumen veins occur predominantly within the Lower Cretaceous black shale Pariatambo Formation in a 350 km long belt extending from San Marcos in the north to Huancayo in the south. The presence of appreciable amounts of vanadium within the bitumens was first discovered in the late 1800s and subsequent investigation by various workers (see Hernandez 1955) revealed that this organo-metallic association was widespread throughout Central Peru, and vanadium extraction was economically viable at Minas Ragra.

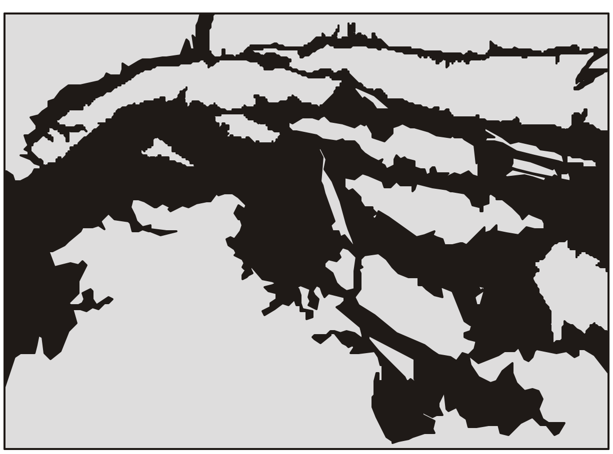

Fig. 1. Line drawing of bitumen (black) within host limestone, La Lucha Mine, Peru. Note spalled host rock fragments and rotated clasts within bitumen. Field width 3m.

The bitumen deposits occur both as bedding parallel veins and as veins crosscutting the enclosing shale and limestone horizons. They occur almost without exception in strongly folded areas. The marked lithological contrast between the more ductile bituminous shaly Pariatambo Formation and the massive limestone formations at its base (Chúlec) and top (Jumasha) resulted in intense disharmonic folding of the Pariatambo Formation with respect to the units above and below. It is considered that this deformation enhanced hydrocarbon generation from the shale. The resultant hydrocarbons migrated along bedding planes and fractures, into space provided by dilation, sometimes under considerable pressure. Evidence of vigorous emplacement of a viscous hydrocarbon is best seen at La Lucha Mine, where thick bitumen veins containing suspended, spalled limestone slabs up to a metre in length and rotated, smaller limestone clasts within the bitumen (Fig. 1). Thin bitumen stringers filled to their tips run both parallel and normal to larger feeder veins. Bitumen emplacement is believed to have occurred towards the end of the Incaic Orogeny (Paleogene) which resulted in the intense folding which is widespread in Central Peru.

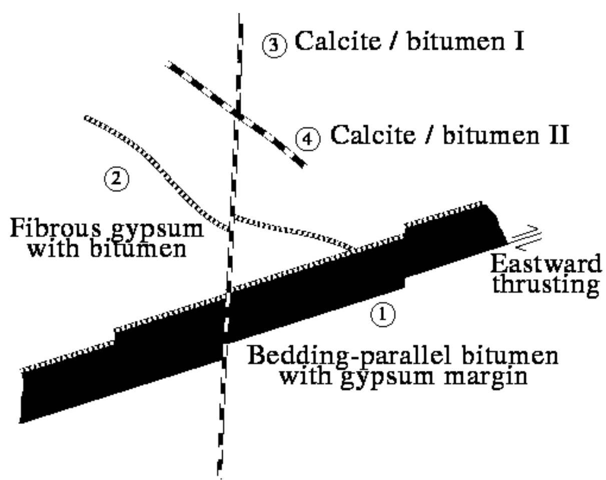

Fig. 2. Schematic representation of 4 successive bitumen-bearing phases and relationship with thrusting, in vertical section, La Valenciana Mine, Argentina.

The black shales of the Pariatambo Formation contain appreciable amounts of vanadium (0.2 to 0.8%). It is believed that this vanadium was incorporated into the shales by organo-metallic complexing, or as sulphides. The vanadium enrichment in the bitumen veins may be

attributed to the subsequent transport of this syn-sedimentary vanadium with the migrating hydrocarbon.
The concentration of vanadium to economic levels in bitumen at Minas Ragra, Peru, is associated with excessive availability of organically-bound sulphur in the bitumen, which allowed vanadium sulphide precipitation. The sulphur in turn may have been derived from evaporite beds. Sulphate reduction in the presence of organic matter probably also influenced other types of sulphide mineralization in central Peru.

Ores and bitumen, Neuquen Basin

Solid bitumen veins in the Neuquen Basin occur in the Argentinian pre-Cordillera in a region over 500km length and 100km width, parallel to the Andean trend. The basin part of a system of sub-Andean foreland basins with thick Jurassic-Cretaceous fill. In the late Miocene, the foreland basin experienced compression, forming westward-dipping, north-south oriented thrust zones (Uliana and Legaretta 1993). The bitumen veins occur particularly in the Mendoza Group outcrop, which includes the source rock Vaca Muerta Formation: the veins are concentrated at the west margin of the basin where the strata are thickest, indicating that the host rocks are the source of the veins.
Bitumen emplacement occurred vigorously, and caused brecciation and spalling of the host rocks. The bitumen was also viscous, and supports rock debris ranging in size from sand grains up to metre-scale slabs. Brecciation, bedding-parallel injection, and wall rock impregnation suggest high fluid pressures during emplacement. High fluid pressure may have been created by substantial hydrocarbon generation from rich source rocks in a low-permeability (shale-rich) sequence, and probably caused the fractures into which the bitumen migrated. The fractures do not show evidence for earlier flow of fluids before bitumen emplacement, i.e. there are no mineral linings.
Several features are evidence for the relationship between bitumens and thrusting: (1) bitumen was emplaced along surfaces that exhibit bedding-parallel movement and associated ductile deformation, (2) bitumens exhibit internal slickensides that indicate deformation continued after solidification of the parent oil. At least in some cases the slickenside surfaces are thrust planes, (3) cross-cutting thrust planes in bedding-parallel bitumen veins contain a younger (less viscous) phase of bitumen, (4) hydrocarbons occur in gypsum beds, which were major decollement surfaces during thrusting, and (5) petrographic features suggest high pore fluid pressures during bitumen emplacement. In summary, the bedding-parallel veins facilitated decollement during thrusting that took place during and after bitumen emplacement. Thrusting occurred in southwestern Argentina throughout the Tertiary, but was most active in south Mendoza during the Miocene (Kozlowski et al. 1993). The timing of emplacent relative to thrusting and oil migration constrains bitumen emplacement to the Eocene-Oligocene.

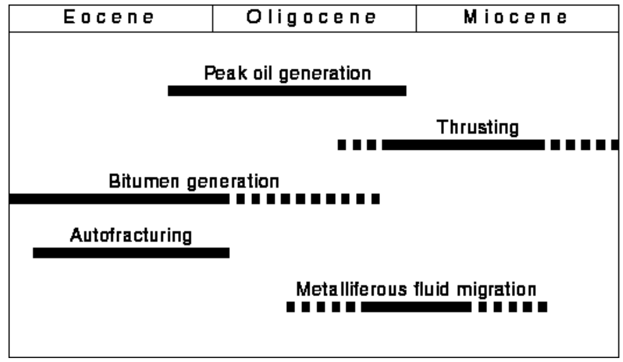

Fig. 3. Proposed time relationships between deformational events and bitumen and mineral precipitation, Neuquen Basin, Mendoza.

The bitumen veins exhibit enrichments in vanadium and nickel (Kett 1948). Electron microscopy shows that they contain inclusions up to 5 microns size of vanadiferous iron oxide and the vanadian clay roscoelite. These phases are equally distributed through the bitumen and appear to be authigenic precipitates rather than later mineral precipitates. The vanadium probably originated as organically-bound metal, as found in many heavy oils. The widespread occurrence of vanadium-rich Mesozoic source rocks (e.g. Breit and Wanty 1991) explains why many bitumens in Jurassic-Cretaceous rocks are subsequently enriched.
In two sandstone-hosted deposits in the Neuquen Basin, Argentina, paragenetic relationships of bitumen with copper minerals (Fortuna IV mine) and uranium/copper minerals (Cerro Huemul mine) indicate that metal precipitation occurred after bitumen emplacement. At Fortuna IV, chalcopyrite, malachite and azurite occur in sandstone wallrocks, which is black due to bitumen impregnation. Veins of solid bitumen appear to have been forcefully injected into the host sandstones, attributable to high pore fluid pressure. Malachite occurs at bitumen vein margins, suggesting that mineralization postdated bitumen emplacement when copper-rich groundwaters encountered the bitumen at a later time. At Cerro Huemul, copper-uranium precipitation in a paleo-oil reservoir has been radiometrically dated at 29Ma (Ferreyra and Lardone 1990). This indicates bitumen emplacement during or earlier than the Oligocene (Fig. 3). Thrusting overlapped and followed bitumen emplacement and was enhanced by bituminous surfaces (Parnell and Carey 1995). Thus metal migration and thrusting occurred at a broadly similar time (Oligocene-Miocene).

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