

## **Pisolite Type Azurite/Malachite Ore in Sandstones at the Base of the Miocene in Northern Sardinia: The Authigenic Hypothesis**

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**Abstract :** Mineralized formations in the bottom sediments of a Miocene transgression have been discovered in Sardinia. The mineral assemblage consists of copper sulphides and oxidates suggesting fluctuations of redox conditions in neutral to high-pH restricted shallow-water coastal basins. Azurite/malachite has been observed as authigenic and occurs as loose spheroidal crystalline particles associated with the transitional-littoral horizon forming the bottom of the marine transgression. Many field observations are consistent with a supergenic circulation of metals involving terrestrial groundwater-seawater mixing. Both clastic materials and metals come from Tertiary volcanic edifices while the main precipitating anions, carbonates, and sulphides species are of both continental and marine origin. Formation of Cu carbonates as a supergene secondary 'oxide' assemblage, does not agree with field evidences, petrographic observations along with textural evidences in the host-rock types. Samples were collected along the sedimentary sequence for different analyses: the majority of elements were determined by X-ray fluorescence and plasma-atomic emission spectroscopy. Mineral identification was obtained by X-ray diffractometry and scanning electron microprobe. Thin sections of the samples were examined in microscopy while porosity measurements were made using a mercury intrusion porosimeter. Cu-carbonates deposited at a temperature below 100 C° which is consistent with the clay minerals in the matrix of the host rock dominated by illite and montmorillonite. Azurite nodules grew during the early diagenetic stage through reaction of cupriferous solutions with CO<sub>2</sub> imported from the overlying groundwater and circulating through the sandstones during shallow burial. Decomposition of organic matter in the bottom anoxic waters released additional carbon dioxide to pore fluids for azurite stability. In this manner localized reducing environments were also generated in which Cu was fixed as Cu-sulphide and sulphosalts. Microscopic examinations of textural features of azurite nodules give evidence of primary malachite/azurite deposition rather than supergene oxidation in place of primary sulfides. Photomicrographs show nuclei of azurite and malachite surrounded by newly formed microcrystalline carbonates which constitute the matrix. The typical pleochroism of crystals can be observed also when this mineral fills microscopic fissures or cracks. Sedimentological evidence of transgression and regression indicates that the pore water would have been a variable mixture of marine water and groundwaters with a possible meteoric component in an alternatively exposed and subaqueous environment owing to water-level fluctuation. Salinity data of the pore fluids, assessed at random intervals along the mineralised strata confirmed the values between about 7000 and 30,000 ppm measured in coeval sediments at the base of Miocene falling in the range of a more or less diluted sea water. This suggests a variation in mean pore-fluids pH between 5.5 and 8.5, compatible with the oxidized and reduced mineral paragenesis described in this work. The results of stable isotopes studies reflect the marine transgressive-regressive cyclicality of events and are compatible with carbon derivation from sea water. During the last oxidative stage of diagenesis, under surface conditions of higher activity of H<sub>2</sub>O and O<sub>2</sub>, CO<sub>2</sub> partial pressure decreased, and malachite becomes the stable Cu mineral. The potential for these small but high grade deposits does exist.

**Keywords :** sedimentary, Cu-carbonates, authigenic, tertiary, Sardinia

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