

Geochemical analysis of Fe, Zn and Ni sulphides in calcareous black shales, Puyango, Ecuador

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Introduction

Critical elements (V, Cu, Ni, Zn, among others) are known to concentrate in marine black shales deposits during their formation, primarily through deposition under anoxic to euxinic conditions and early diagenetic processes [1]. Consequently, this study was initiated to analyze the mineralogy and chemical compositions of minerals sulphides hosted by marine black limestones and calcareous black shales of Puyango deposit (V, U, Zn), Ecuador [2].

Methods, Discussion of Results

The mineral occurrence of Puyango, Ecuador, contains high values of several critical metals: vanadium (mean 2051 mg/Kg; maximum 7220 mg/Kg), zinc (mean 939 mg/Kg; maximum 5610 mg/Kg), nickel (mean 255 mg/Kg; maximum 1160 mg/Kg), among others. It is hosted in black calcareous shales and black limestones from the Puyango Formation of Cretaceous age. Analysis of selected samples were carried out by Electron Probe Microanalysis (EPMA), identifying Fe, Zn, Ni and Cu sulphides: pyrite (including framboid pyrite), sphalerite, millerite and chalcopyrite (in smaller quantities).

Preliminary results indicate anoxic to euxinic conditions during sedimentation, according to elemental ratios in bulk composition of black calcareous shales and black limestones by ICP-MS: (U/Th > 4.8), (V/(V+Ni) > 0.6), (V/Cr > 4.8) [3,4].

[1] Breit, G. and Wanty, R. Vanadium accumulation in carbonaceous rocks: A review of geochemical controls during deposition and diagenesis, *Chemical Geology*. **91** (1991) 83-97.

[2] Manrique, J., et al., Origin of the vanadium-uranium geochemical anomalies in the limestones of the Puyango Formation, La Sota (Ecuador): preliminary results, *Andean Geology*. **49** (2) (2023) 75-92. [3] Jones, B. and Manning, D. Comparison of geochemical indexes used for the interpretation of palaeoredox conditions in ancient mudstones. *Chemical Geology*. **111** (1994), 111–129. [4] Tribouillard, N., et al., Trace metals as paleoredox and paleoproductivity proxies: An update. *Chemical Geology*. **232** (2006) 12–32.