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GEOCHEMICAL PROSPECTING STUDY OF THE VANADIUM-URANIUM MINERALIZATION OF PUYANGO, ECUADOR

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INTRODUCTION

A geochemical prospecting study has been carried out in the Puyango sector, Loja province, Ecuador to determine uranium and vanadium anomalies and identify the main mineral phases that make up the mineralized rocks, through chemical analysis using portable X-ray fluorescence (pXRF), gamma spectrometry, petrographic analysis and X-ray diffraction (XRD). Maximum eU values of 136 ppm were detected by gamma spectrometry in situ and maximum values of V₂O₅ of 1.60%. The mineralization is hosted mainly in black bituminous limestones of Cretaceous age belonging to the Ciano and Puyango Formations of the Alamor - Lancones marine basin [1]. These rocks are composed mainly of calcite, quartz, illite, apatite, uranospathite and minor amounts of phyllosilicates and vanadium minerals such as sherwoodite, rossite and ronneburgite. The hypothesis of the formation of this mineralization is that both vanadium and uranium were deposited in a reducing environment, in marine waters under euxinic, anoxic to sub-oxic conditions, this is evidenced by V/Cr - V/V + Ni ratios and by the presence of organic matter in the samples, in which these elements can be linked in compounds such as porphyrins, where V can complex.

METHODS AND RESULTS

Mineralogical analysis.

Petrographic and mineralogical analyzes by X Ray Diffraction (XRD) it was obtained that the main minerals that make are calcite (CaCO₃) (61 -88%), quartz (SiO₂) (6 -22%), fluorapatite (Ca₅(PO₄)₃(F)), uranospathite (Al_{1-xx}[(UO₂)(PO₄)]₂(H₂O)_{20+3xF1-3x}) (1-3%), sherwoodite (Ca₉Al₂V₅+4V₅+24O₈₀•56(H₂O)) and, smaller amounts of rossite (CaV₂O₆), ronneburgite (K₂MnV₄O₁₂), illite ((K,H₃O)(Al,Mg,Fe)₂(Si,Al)₄O₁₀[(OH)₂(H₂O)]), biotite (K(Mg,Fe)₃[AlSi₃O₁₀(OH,F)₂], kaolinite (Al₂Si₂O₅(OH)₄), chloritoid ((Fe,Mg,Mn)₂Al₄Si₂O₁₀(OH)₄), chamosite ((Fe,Mg,Fe)₅Al(Si₃Al)O₁₀(OH,O)₈) and, glauconite ((K,Na)(Fe,Al,Mg)₂(Si,Al)₄O₁₀(OH)₂).

Chemical analysis.

Chemical analysis was done by portable X Ray Fluorescence (pXRF), according to this the background of the concentration of U is 49 ppm, reaching a maximum value of 153 ppm in black bituminous limestones. In relation to vanadium, the background value was statically determined in the area of 1500 ppm of V₂O₅, with a maximum value of 23100 ppm.

Anomalous values were determined statistically P₂O₅ (4.52%), Zn (3340 ppm), Mo (219 ppm), Cu (165 ppm), Cd (131 ppm) and, Se (21 ppm). High concentrations of other uranium pathfinder elements and geochemically associated to this and to vanadium are detected: sub-anomalous values As (95 ppm), Bi (68 ppm), Ni (337 ppm) and, Pb (72 ppm).

In situ Gamma Spectrometry.

Gamma spectrometry analysis in situ was made with a portable gamma spectrometer, according to which anomalous values of eU (86 ppm) were detected, with a maximum value of eU (136 ppm). This evidence U mineralization associated with the in black bituminous Cretaceous limestones, since this technique is useful to delimit radioactive elements mineralization [2].

DISCUSSION AND CONCLUSION

Mineralogy analysis.

According to the geochemical prospecting carried out, the majority of the rocks correspond to bituminous limestones, of Cretaceous age of the Puyango Formation, since most of the samples are composed of calcite (CaCO_3) (61 - 88%) and to a lesser extent quartz, phosphates and phyllosilicates (clays and micas).

The petrographic analysis showed that the majority of the samples correspond to micritic limestones and sparitic limestones with foraminiferous fossils.

The mineralogical studies show the uranium and vanadium to be present in the following forms:

- Fluorapatite (28-75%).
- Uranospathite (2-3%).
- Sherwoodite (1-2%).
- Rosiite and ronneburgite (<1%).

Uranospathite may have been formed by weathering and chemical alteration of the primary phosphate (uraniferous apatite) [3].

The minerals that contain vanadium (sherwoodite, rossite and ronneburgite), are vanadates with V^{5+} and V^{4+} in their crystalline structures, in addition there may be V^{3+} in clay minerals such as illite, since it can replace Al^{3+} during diagenesis [4]. This occurs similarly in vanadium deposits in black shales and, vanadium accumulations in carbonaceous rocks in general [5-6].

The samples contain organic material of marine origin according to the sedimentation environment, so it is likely that vanadium is also linked to organic matter, in compounds such as porphyrins [7-8].

Chemical analysis and statistics.

The chemical analyzes it was obtained that the U and Ca correlates with the P, indicating that the minerals that host are the apatite and uranospathite. There are strong correlations between V-Ni, V-U, V-Mo, V-Zn probably associated with organic matter, which may be geochemically associated with porphyrins [7-8].

By calculating elementary relationships $\text{V/Cr} - \text{V/V} + \text{Ni}$ ratios, the sediments were deposited under under euxinic, anoxic to sub-oxic conditions [9], thus the hypothesis of the formation of this mineralization is that both vanadium and uranium were deposited in a reducing environment, in marine waters and by the presence of organic matter in the samples, in which these elements can be linked in compounds such as porphyrins, where V can complex [7-8].

Several authors [10] have indicated that the sediments of the Puyango Fm. were deposited in a marginal marine basin, formed between the Celica arc volcanic to east and Amotape - Tahuin Massif in the west, which corroborates the results obtained through elementary relations.

Gamma analysis interpretation.

According to the analysis of in situ gamma spectrometry, anomalous values of eU (86 ppm) and a maximum value of eU (136 ppm) were detected in bituminous limestones. The values of eTh reached a maximum of 31 ppm detected in shales, with a background value of 5 ppm, which evidences the low mobility of Th in the conditions of formation of the mineralization, due to its geochemical properties. The eU / eTh ratio was calculated for the samples analyzed and the values fluctuated between 0.06 - 18.80, which shows the mineralized areas with high values of the ratio.

Conclusions.

The geochemical prospecting study of the Puyango sector using chemical, mineralogical and gamma spectrometry analysis, determined that there is a V-U mineralization associated with black bituminous limestones, which are part of Fm. Puyango of Cretaceous age.

There are anomalous values of P_2O_5 (4.52%), Zn (3340 ppm), Mo (219 ppm), Cu (165 ppm), Cd (131 ppm) and, Se (21 ppm), in addition sub anomalous values of uranium pathfinders elements: As (95 ppm), Bi (68 ppm), Ni (337 ppm) and, Pb (72 ppm).

The host minerals of uranium are apatite and uranospathite, that is (the last) formed by the weathering and chemical alteration of the primary phosphate.

The minerals that contain vanadium are the sherwoodite and in a smaller proportion rossite and ronneburgite, which are vanadates with V^{5+} and V^{4+} in their structures, in addition there may be V^{3+} in clay minerals such as the illite, since this can replace Al^{3+} during diagenesis.

Mineralogical and geochemical analysis should be done through SEM to identify with greater precision the mineral phases that contain vanadium, as well as its association with organic matter.

According to the calculation of the eU/eTh ratio for the samples analyzed by in situ gamma spectrometry, the values fluctuated between 0.06 - 18.80, which shows the mineralized areas with high values of the ratio.

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Country or International Organization

Ecuador

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