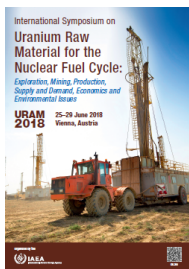


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GEOCHEMICAL AND MINERALOGICAL CHARACTERIZATION OF THE URANIFEROUS PHOSPHATE ROCKS OF THE NAVAY FORMATION, TÁCHIRA STATE, VENEZUELA

Wednesday, 27 June 2018 17:00 (1 hour)

INTRODUCTION

Through the CRP IAEA T11007 a geochemical and mineralogical characterization study of the uraniferous phosphate rocks of the Navay Formation, Táchira state, Venezuela. Phosphates deposit associated with sandstones in the top levels of the Navay Fm. (Upper Cretaceous) in southwest of Táchira state, Venezuela, was discovered in early 1978 by radiometric surveys, conducted by Ministry of Energy and Mines by The National Commission of Nuclear Affairs (CONAN). This consists of siliceous shales, calcareous shales, uraniferous phosphatic sandstones and, cherts ("ftanites") [1]. To date there have been studies on the feasibility of exploiting to produce phosphate fertilizers. There have been no studies on uranium mining.

METHODS AND RESULTS

Mineralogical analysis.

Petrographic and mineralogical analyzes by X Ray Diffraction (XRD) it was obtained that the main minerals that make are fluorapatite/chlorapatite ($\text{Ca}_5(\text{PO}_4)_3(\text{F},\text{Cl})$), collophane or carbonate fluorapatite which is a compositional variant of apatite ($\text{Ca}_5(\text{PO}_4)_3\text{F}$), uranospathite ($\text{Al}_{1-x}[\text{UO}_2(\text{PO}_4)]_2(\text{H}_2\text{O})_{20+3x}\text{F}_{1-3x}$), quartz (SiO_2) (4 – 88 %), calcite (CaCO_3) (10 – 35 %), montmorillonite ($(\text{Na},\text{Ca})_0,3(\text{Al},\text{Mg})_2\text{Si}_4\text{O}_{10}(\text{OH})_2$) (maximum 6 %), and, microcline (KAlSi_3O_8) (maximum 1,43 % %) mainly.

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

- Fluorapatite –carbonate fluorapatite (28-75%).
- Uranospathite (2-3%).

Chemical analysis.

Chemical analysis was done by several techniques: portable X Ray Fluorescence (pXRF), Total Reflection X-Ray Fluorescence (TRXRF) and, Inductively Coupled Plasma –Atomic Emission Spectroscopy (ICP AES). According to this the background of the concentration of U is 102 ppm, reaching a maximum value of 160 ppm in a calcareous phosphatic sandstone, what is within the average range of U in marine phosphate rocks (50-300 ppm U) [2].

Sub anomalous values were determined statistically Cd (82 ppm), Cu (261 ppm), Zn (268 ppm), Sr (1832 ppm), Zr (510 ppm) and, anomalous values of Cr (1653 ppm). In addition, maximum values of majority, minority and trace elements were detected: MgO (12.40 %), Al_2O_3 (9.60 %), K_2O (3.07 %), Fe_2O_3 (1.25 %), MnO (0.05 %), TiO_2 (0.35 %), S (1.31 %), Cl (1.07 %), V (82 ppm), Ni (2083 ppm), Pb (86 ppm), Co (199 ppm) and, Rb (91 ppm).

According to the chemical composition of the samples, most correspond to phosphate rocks (median 17.25 % and maximum 24.81 % of P_2O_5), quartz sandstones (median 25.60 % and maximum 88.70 % of SiO_2) and phosphate limestones (median 27.88 % and maximum 70.40 % of CaO) [3].

Gamma Spectrometry.

Gamma spectrometry analysis was also done on several samples of the deposit, in which ^{226}Ra was detected, which may be present in the apatite either replacing the Ca^{2+} (geochemical affinity) or by the radioactive decay of the ^{238}U series. Other isotopes of this decay series were detected (^{214}Pb and ^{214}Bi).

DISCUSSION AND CONCLUSION

Mineralogy composition.

Fluorapatite has been identified as the main phosphate mineral, which in some cases contains carbonate in its structure (CO_3^{2-}), which is common in this group of minerals where carbonate ions can replace phosphate ions (PO_4^{3-}) [4]. The U is hosted in the apatite because the U^{4+} (ionic radio 0.97 Å) can replace the Ca^{2+} (ionic radio 0.99 Å) [5]. The presence of uranospathite has been detected by XRD, which is a secondary phosphate of Al and U belonging to the autunite group formed as a result of the weathering of primary phosphates in humid environments [6]. The presence of autunite and wavelite is not ruled out, which have been identified in samples from La Lucha River in Táchira state [1].

The mineralogy is typical of marine phosphatic deposits. Some samples in thin sections were studied by petrography, where they determined that the samples correspond to sandstones phosphatizing, limestones phosphatizing and micritization of peloids.

The fossil *Orthokarstenia ewaldi* of lower Cretaceous period Maastrichtian age, which indicates a shallow marine environment, was identified by means of petrographic analysis, it is a foraminifera associated with this type of environment [7-8]. The Navay deposit is sandy phosphorites type, formed during the lower Cretacic, probably by currents upwelling, which produced the deposit of these sediments. Constitute a lithological facies deposited in shallow waters while cutting lines and is locally Campanian-Maastrichtian age [9].

The Navay Formation is a lateral equivalent of the La Luna Fm. in western Venezuela, which contains black phosphorites and black shales hydrocarbon-generating [10].

Chemical composition.

The chemical analyzes it was obtained that the U and Ca correlates with the P, indicating that the mineral that host is the apatite. There are strong correlations between P - Y (0.72) which may indicate the presence of yttrium in the mineral phosphates, Ca - Mg (calcite), Ca - Sr (substitution of Sr^{2+} by Ca^{2+}), Si with Al and K (silicates as microcline and clays such as montmorillonite), Fe - S (possibly forming sulphides), Fe-V (associated in detrital oxides and/or in organic matter), S - V (possibly in organic matter), U with V and Ni (probably associated with organic matter, as well as the strong V - Ni correlation, which may be geochemically associated with porphyrins [11-12].

In several samples yttrium (Y) was detected, which is associated with phosphates, this may be due to ionic substitutions of Y^{3+} (ionic radio 0.93 Å) in the structure of the apatite by Ca^{2+} (ionic radio 0.99 Å). It is recommended to perform REE analysis using ICP-MS or another analytical technique, since they could not be detected using the techniques used in this research. The REE can be included in the phosphate minerals, due to their geochemical affinity [2].

By calculating elementary relationships $\text{V/Cr} - \text{V}/\text{V}+\text{Ni}$ V/Ni , Navay sediments were deposited under oxic conditions, without replacement, using the Ni/Co ratio, several samples indicate that these sediments were deposited under sub-oxic to anoxic conditions [13-14]. This difference may be due to the fact that there were redox changes during sedimentation, as a result of upwelling currents that brought oxygen-poor water from the bottom to the surface. On the other hand, there may be remobilization, that is, secondary dispersion of several of these elements are redox sensitive and under oxidative conditions by weathering, they have been oxidized and/or dispersed in the deposit.

Gamma spectrometry analysis.

According to the analysis of gamma spectrometry of surface samples and cores, a concentration of average activity of ^{226}Ra of 2100 Bq/kg was detected, in addition to other isotopes of the decay series of ^{238}U were detected. The ^{226}Ra was measured (by the ^{214}Pb and ^{214}Bi measure) and ^{234}Th directly through issuance of 63 keV. The low contrast concentrations activity of the isotope ^{232}Th series and ^{40}K not detected by this technique.

This implies that there are low concentrations of thorium in the deposit, what corresponds to geochemical environments of this type, in which the U is mobilized as U^{6+} (uranyl ion UO_2^{2+}), fixed in the apatite as U^{4+} under reducing conditions, while the Th^{4+} is immobile in superficial environments, for which its concentration is low in this type of deposits.

By the analysis of gamma spectrometry ^{226}Ra was detected, as well as other isotopes of the decay series of the ^{238}U , however, no isotopes of the ^{232}Th or ^{40}K series were detected.

Conclusions.

The mineralogy of Navay Fm. is typical of marine phosphatic deposits with fluorapatite/chlorapatite, collophane or carbonate fluorapatite which is a compositional variant of apatite ($\text{Ca}_5(\text{PO}_4, \text{CO}_3)\text{F}$), uranospathite, quartz and, calcite mainly.

The presence of autunite and wavelite is not ruled out, which have been identified in samples from La Lucha River in Táchira state, in outcrop Navay Fm.

The mineralogical studies show the uranium to be present in the following forms: apatite (28-75%) and, uranospathite (2-3%).

The fossil *Orthokarstenia ewaldi* of lower Cretaceous period Maastrichtian age, which indicates a shallow marine environment, was identified by means of petrographic analysis

According to chemical analysis the background of the concentration of U is 102 ppm, reaching a maximum value of 160 ppm in a calcareous phosphatic sandstone, so it can be considered a deposit of uranium as unconventional according to the U grade.

Statistically sub anomalous values were determined Cd (82 ppm), Cu (261 ppm), Zn (268 ppm), Sr (1832 ppm), Zr (510 ppm) and, anomalous values of Cr (1653 ppm), these are considered elements of interest because of their association geochemical with uranium and phosphates.

In several samples yttrium (Y) was detected (Y max. 144 ppm), which is associated with phosphates, it is recommended to perform REE analysis using ICP-MS or another analytical technique, since they could not be detected using the techniques used in this research.

By calculating elementary relationships $V/\text{Cr} - V/V+\text{Ni}$ V/Ni , Navay sediments were deposited under oxic conditions, but using the Ni/Co ratio, several samples indicate that these sediments were deposited under sub-oxic to anoxic conditions, this difference may be due to the fact that there were redox changes during sedimentation, as a result of upwelling currents that brought oxygen-poor water from the bottom to the surface.

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