Article

Influence of the Rift Molango on the mineralization of platinum group elements and light rare earths into a sedimentary exhalative ore deposit

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Abstract: This paper describes the influence of the ancient Rift Molango, Mexico, during the origin of the sedimentary exhalative ore deposits, according to the tectonic, chemical, climate and biological evolution of the place where these deposits were formed through time. The mineralization found in these deposits contains elements of the platinum group and some light rare earths, showing two types of mineralizations; philonian and sedimentary, both of lower Jurassic age (Plienbanchian). The sedimentary ore deposits, show a philonian lithology that has traces of hydrothermal remobilization of chalcopyrite, quartz, biotite and muscovite, containing sperrilite, calaverite, native platinum, gold and silver; as well as some light rare earths. Meanwhile, in the sedimentary outcrop there are values of platinoids (8 ppm of Pt, 10 ppm of Pd, and 5 ppm of Au), and light rare earths into the monazite minerals (Ce, La, Nd, Th, (PO_4)) and bastnaesite minerals. By means of XRD it was possible to identify medium temperature minerals such as pyrite, albite, quartz, and also carbon; high temperature mineral, such as monazite and low temperature minerals, such as jarosite, chalcopyrite and bornite. In conclusion, the behavior of both mineralizations has a very close relationship with a transgressive event during the lower Jurassic; the high contents of siliciclasts, the presence of exhalative roots, the deficiency of sulfur and a mega structure Rift type, allow to classify them according to their genesis as exhalative sedimentary type (SEDEX).

Keywords: platinum; light rare earths elements; sedimentary ores; SEDEX

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1. Introduction

The occurrence of mineral deposits of the platinum group has been described in the Yukon in Canada [1], where the exploration of platinoids in blackboards is carried out, and there are included deposits of different origins. The association of V-Cr-PGE is known in exhalative deposits [2], and also the chromifera spinels associated with Pd minerals have been described in Nairme, Australia [3]. Pasava [4] suggests that the PGE anomalies have their origin in exhalative deposits related to volcanism in rift zones in the presence of organic matter. Consequently, the main characteristics of the massive vulcanogenic sulfide (VMS) deposits [5] and SEDEX, are scarcely known in Mexico [6] as well as those of other deposits sedimentary that have been studied recently, being these objects of artisanal production; such as those described in the mid-2000s in eastern Mexico that are of the RED BED and KUPFERSHIEFER type. However, its main economic attractiveness is based on the potential contents of Cu and Ag.

The largest occurrence of rare earth elements (REE) is in Asia, where about 95% of total production is in the People's Republic of China. Particularly the Bayan Obo deposits, of high grade, igneous type of carbonatite with about 80% of LREEs [7], but the typical in these deposits is a low content of HREEs.

The first attempts in exploration to find strategic minerals and in particular rare earths in Mexico, occurred in the middle of the eighties for the prospection of phosphorites located in western Mexico, particularly in Baja California, using the traditional method of exploration. In addition, the first reports on its occurrence date from the first half of 1990, in the El Picacho Complex [8], in Tamaulipas in eastern Mexico; there, the presence of an intrusive tertiary age complex of nepheline-foidolites and rare earth mineralization has been reported.

Likewise, at the beginning of the 2000s, geochemical studies were performed on Precambrian rocks in eastern Mexico, in the Grenvillian basement of Gneiss Huiznopala [9], where anomalies were obtained positive Eu and low concentrations of Y, Zr, Nb, Th and U. Similarly, anomalies were found in the Complejo Oaxaqueño [10], from the southeast of Mexico. It should be mentioned that there are still no reports of deposits in production of rare earths in Mexico, and similarly there is no report of the occurrence of platinoids (PGE).

On the other hand, exhalative deposits are known in Mexico in Rift zones and an example of this is the one located in eastern Mexico, where there is a giant syngenetic reservoir of marine affinity manganese [11], of the SEDEX type (in Molango, Hidalgo) and is by far the largest known deposit by researchers from the United States [12], with 3 MT of measured reserves, proven reserves of 200 MT and estimated at 1500 MT, of a degree of 10%, which is a sample of the potential mineral contents of these SEDEX-type deposits.

Traditionally, platinum deposits are related to V, Cr and Ni (as trace elements) and because in Mexico there is not much evidence of these tracers, but the analysis have always been done on ultramafic rocks. It is for this reason, that there has been no exploration in any type of deposit to look for elements of the platinum group, leaving only the sedimentary deposits as the last option to be able to determine its occurrence.

In the manganese district of Molango, the zone containing stratigraphic and structural remains is located, which allows us to infer the presence of an old Rift that shows a heterochronic stage of proto and neo-jurassic transgression, according to Cantú-Chapa [13], which is related to the SEDEX mineralization. On the other hand, it is worth mentioning that the SEDEX deposits in Cuba [14] occur in stratigraphic lithological sequences and tectonic characteristics very similar to those of these deposits, located in the Rift Molango. Thus, the following deposits, their respective content and tonnage, are examples of this type of deposits that lie in the San Cayetano Formation, a stratigraphic equivalent to the Huayacocotla Formation [15].

Similarity, there is structural evidence of a Triassic Rift -Jurassic in this area [17,18,19,20] and whose basement is of Grenville age, which contains evidence of different tectonic stages as is

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reported in the North Qaidam orogen, Western China [21]. Moreover, it is inferred that the origin of the mineralization of PGE´s, base metals and rare earths may be related to fluvial sediments associated with a hydrothermal activity linked to the Rift that could give rise to the Gulf of Mexico, a region of study that has been defined as an old Jurassic Triassic Rift [6]. The foregoing is important, because it is widely accepted that exhalative sedimentary deposits (SEDEX) and other stratiform sedimentary deposits, occur in such environments.

Similarly, the fact that Mexico has traditionally been a producer of gold and silver, led to the search only for deposits rich in these metals and for its ease of exploitation and superficial occurrence; deposits that were mainly of epithermal and mesothermal igneous type during the tertiary. Thus, low-content marine and continental sedimentary deposits have received little attention, but this type of deposits has base and precious metals such as Cu, Pb, Zn, Au and Ag in small quantities [20], and elements from the group of Platinum and other strategic elements. However, advances in the study of new metal extraction processes have achieved efficient results in the extraction of Au, Ag and Cu, from deposits with low values of these metals [22] and considering the large volumes of sedimentary deposits, its exploitation has now become profitable.

In terms of extractive metallurgy and exploitation, the times are changing because REE ores have a different arrangement of fine-grained refractory minerals that hinder the benefit for their physical concentration by over-grinding. For the mining and extractive metallurgy processes, they are comparatively low cost processes [23]. Another alternative for obtaining REE and minimal amounts of PGE is offered by underwater nodules [24].

The nature of the emergent continental zones and the marine transgressions, provided an adequate environment to give origin to exhalative sedimentary deposits in marine rocks, as well as sedimentary deposits in continental rocks, since the type of deposit generates different lithologies and deposit environments; both, oxidants (continental) and reducers (marine). It was with this methodology that indirect exploration was proposed and based on the results of previous works [5], with which was considered the existence of land anomalies of LREs and PGE minerals in eastern Mexico and the results presented here, show that the potential resources of PGE are similar to other deposits in the world [14].

2. Materials and Methods

The location of the SEDEX deposit described here was carried out using the method described by E Cerecedo et al [5], where indirect exploration method has been described. Then, samples were taken from ore deposit using a channel sampling method avoiding contamination of samples.

Samples so obtained, were homogenized and quartered to get a homogeneous sample to be characterized. The characterization carried out in this work was executed in order to obtain accurate data of the mineralogical phases present, for which an analysis of general phases was proposed by means of X-ray diffraction (XRD).

Likewise, the characterization studies were complemented by Scanning Electron Microscopy (SEM) to identify texture, granulometry and morphology of the detected phases; in the same way, the analysis by mapping and EDS helps us to determine the semi-quantitative composition of some of

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the previously identified phases. Finally, an Inductively Couple Plasma Spectrometry (ICP) analysis was done to find the average total rock composition of the mineralized phase, where the positive anomalies of the light rare earth and mineral contents of the platinum group (PGE) were found.

3. Results

In the study area, the mineralization is located in the lower Jurassic (Huayacocotla Formation of Pleinsbachian age); Figure 1 shows the two lithologies of the production unit, philonian and sedimentary, and this formation is divided into three members:

The intermediate member is constituted by conglomerates, sandstone and slate and is characterized by the presence of ammonites.

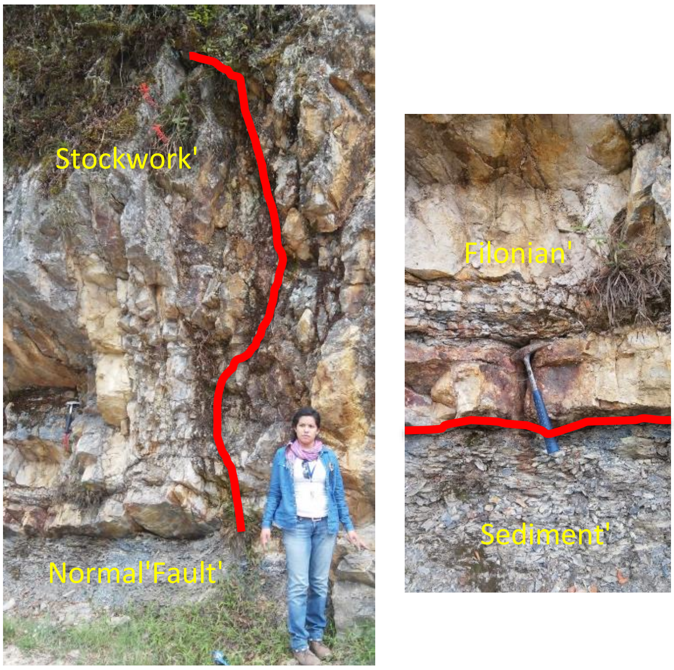

Figure 1.Lithology of the production unit

Furthermore, the upper member consists of sandstone, siltstone, slate, some conglomerates and fossil plants. In this last horizon near the top of the Huayacocotla Formation, the producer mining horizon was found, and in the initial portion of the transgressive cycle some exhalative roots could be located and are shown in the Figure 1, where the contact between the two lithological, sedimentary lithology is observed in contact whit philonian lithology.

In the study area, there was only one producer mining horizon located in the middle part, and close to the top of the Huayacocotla Formation of Pleinsbachian age of the lower Jurassic. However, in the initial portion of the transgressive cycle some exhalative roots could be located. and Figure 2 (a) shows the exhalation roots mineralization of stockwork type, jarosite 2(B), and disseminated pyrite (C).

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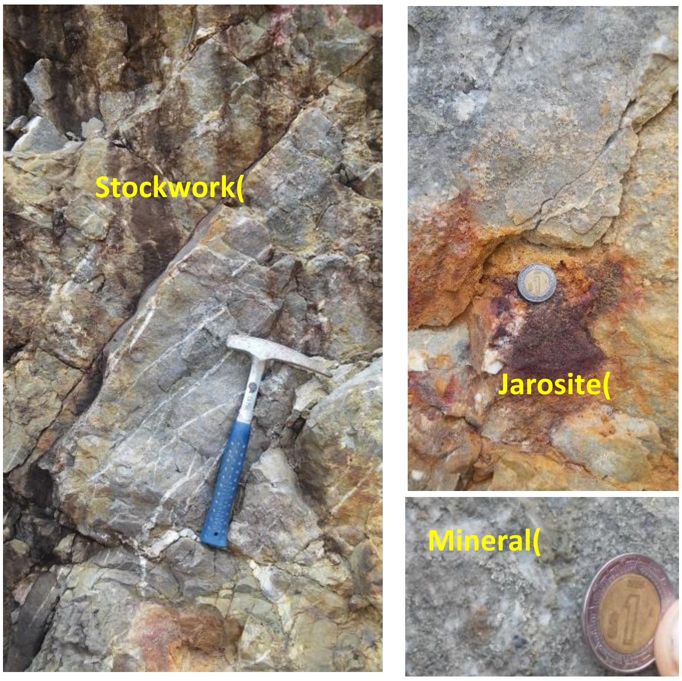

Figure 2. Mineralization zone

In the Huayacocotla formation of Pleinsbachian age, there is an outcrop of two members where can be observed the three lithologies of the mentioned formation, that consist of the intermediate member constituted by conglomerates, sandstone and slate, and is characterized by the presence of ammonites. It is worth mentioning that in this area, the existence of an inverse fault is considered, Figure 3 (A), in contact whit the mineralization figure 3 (B), because the intermediate member that has ammonites rides the upper member inorganic carbon Figure 3 (C), area that is made up of sandstone, siltstone, slate, some conglomerates and fossil plants. In this last horizon near the top of the Huayacocotla Formation the producer mining horizon was found.

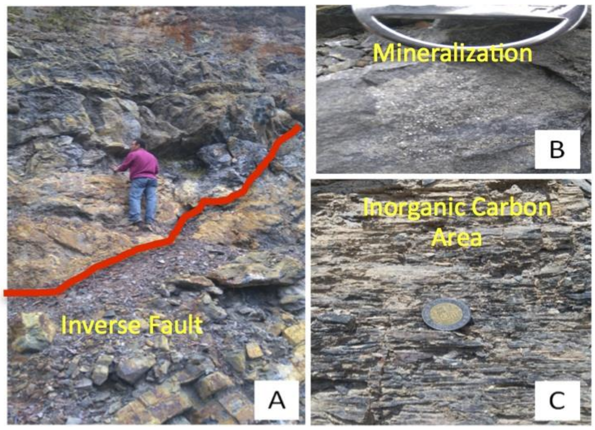

Figure 3. Huayacocotla Formation

The SEDEX base metal deposits are located only in the intermediate unit of transgressive lithology of shale, and sandstone in rhythmic intervals, which overlie the shale unit with plants of

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the Huayacocotla Formation. While in the unit with shale with high carbon content, is where the greatest presence of monazite is observed, possibly at the base of the intermediate unit, and the exhalative roots appear.

Possibly, at the base of this outcrop there is a small interval of the oldest limestone unit that in its complete sequence includes conglomerate, sandstone, siltstone, and shale with gap intervals, with reworked fossils, sandstone exoclastics, rock fragments volcanic and in a smaller proportion of limestone rocks, the size of the measured clast was from 5 to 100 cm in a sandy matrix, the size of the clasts of the conglomerate and the clasts suggest a continental affinity.

The intermediate unit represents a marine transgression because in the fieldwork it was observed that it consists of sandstone and shale in rhythmic sequence, in the conglomerates the size is not larger than 10 cm, and the main characteristic of this unit is the presence of marine ammonites at the base of this unit, mainly in the shale. In this unit near the top, the exhalative roots of the outcrop were observed.

In the study area, thicknesses of 350 meters were measured at 900 meters from the Huayacocotla Formation and the thickness of the producing horizon surfaced 100 meters, the upper shale unit with plants outcrops 250 meters of sedimentary rocks and increases in some areas with rock outcrops volcanic at 350 meters, the intermediate portion is greater than 250 meters thick, and the basal portion has been observed at about 450 meters.

In the production unit, sandstone lenses were observed, and meanwhile, in the unit that overlies it, sandstone lenses were observed, and some rich in organic matter that mark a continental deposit environment.

The mining geological behavior is different in the Huayacocotla Formation, since the SEDEX mineralization is only attributed here to the lithology of the intermediate portion, and that infrayace to the shale unit with plants. In Figure 4, the hydrothermal system that host epithermal veins are characterized by length scales on the order of 15 km and heat and mass flux of fluid that is steady relative to the timescale of vein formation, the inset is illustrative of the localization of veins by faults in the system. The hydrothermal system for vein zones in the processes of heat extraction applied to a wide range of deposits of styles of surface bark deposits associated with fragile deformation. The range of epithermal veins, deposits of massive sea floor sulphides, mesothermal veins in cortical zones, high temperature veins and hypothermic stockork.

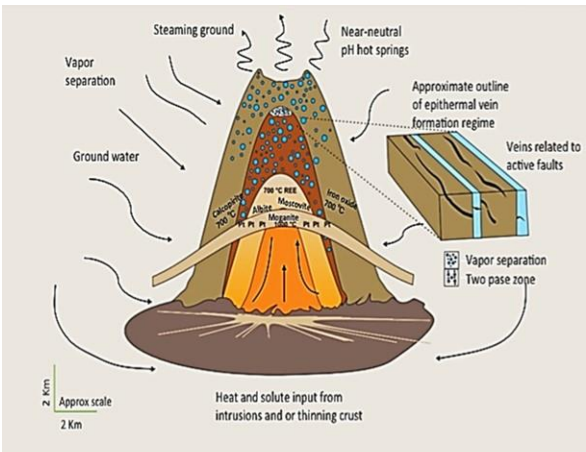


Figure 4. The hydrothermal system and veins

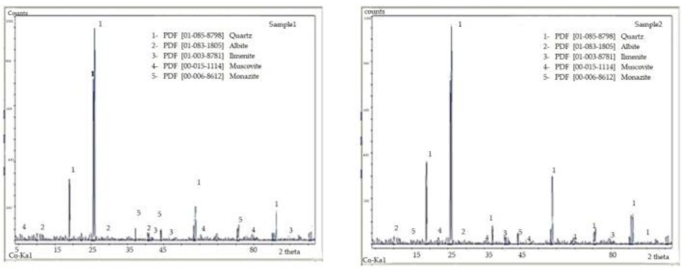
2.3. CHARACTERIZACION OF SEDEX ORE BODY

The preliminary characterization of the SEDEX type found was based on the mineralogical description by XRD, as well as the morphological identification and some semi-quantitative point analyzes with the use of SEM - EDS, as well as mapping to be able to identify the distribution of contents at a depth in the samples of holes made from 0 - 9 meters. Finally, a total rock analysis was carried out by fire test, IPC - masses.

X – Ray Difraction

The results of X-ray diffraction are shown mainly in figure 5 (a, b), showing the presence of high and medium temperature minerals, such as monazite, mogonite-type quartz, muscovite and albite. Highlights the presence of ilmenite that could be associated with rare earths.

Figure 5a shows chalcopyrite minerals that are evidence of hydrothermal remobilization, confirming that the type of deposit found is SEDEX.



a) b)

Figure 5. XRD spectra of; a). Medium temperature minerals; and b). High temperature minerals

Finally, Figure 5b shows the distribution and identification of the minerals using XRD, which are found in the extracted drill core. It can be noted that there are minerals of high, medium and low temperature distributed through the lithological column (Figure 6), confirming the existence of thermal pulses.

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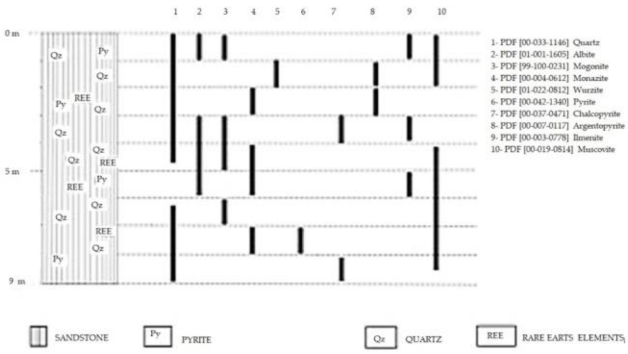

Figure 6. Lithological column obtained by XRD data

The quartz is distributed through the column from 1 to 4.75 m, and from 6 to 9 m with an absence of 4.75 m to 6 m, having a density of 3.83 g/cm^3, which indicates that we have an alpha quartz with a temperature of 597 ° K, that is also found in the form of mogonite at 1 m, 4 m and 5 m depth, with a density of 2.55 g/cm^3 and a high temperature of 1354 ° K. The albite is found from 1 m to 1.75 m and 4 m 6.75 m, with absence at 2 m, 3 m, 7 m, 8 m and 9 m, is distributed more to the center of the column, with a density of 2.6 g/cm^3.

Scanning Electron Microscopy (EDS & Mapping)

The characterization carried out by scanning electron microscopy, and mappings analysis, allowed us to corroborate the presence of REE of the samples analyzed as can be seen in the Figure 7, shows an image of which corroborates the presence of the cerium element (Ce), which is a rare earth, is also observed.

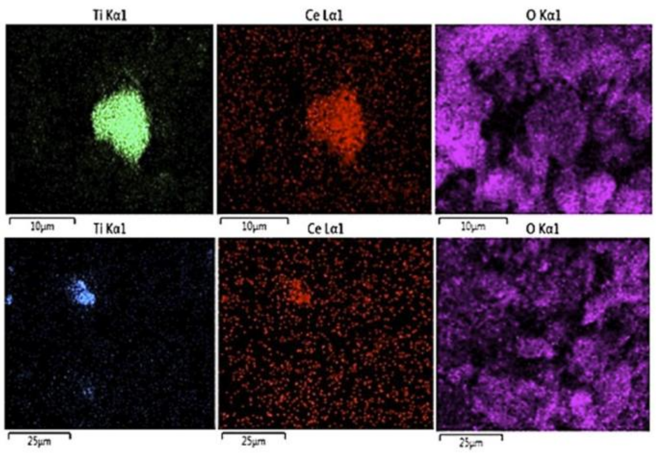

Figure 7. Mapping of SEDEX ore body

In Figure 7, can be observed contains of elements such as oxygen (O), thallium (Tl). On the other hand, Figure 8; shows contains of elements such as titanium (Nd), and cerium (Ce).

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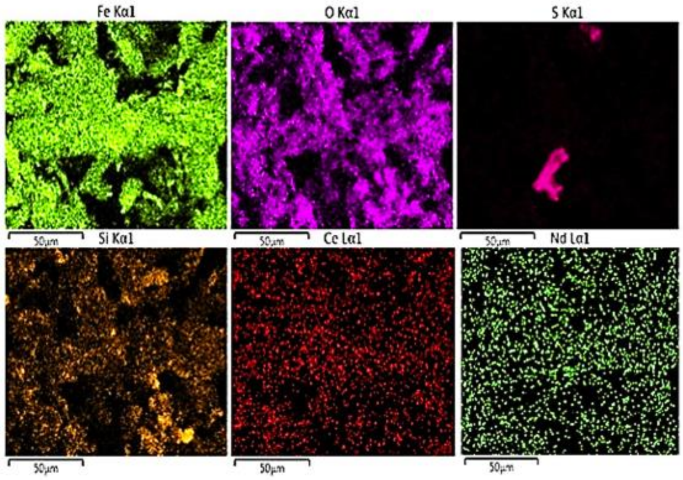
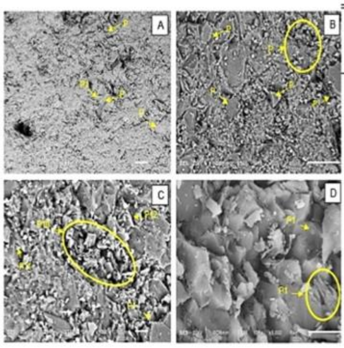


Figure 8. Mapping of mineral SEDEX.

Likewise, Figures 9 and 10 show some micrographs of the original mineral, showing the points where its semi-quantitative composition was obtained, which was done with the scanning electron microscopy technique (MEB) in conjunction with EDS.



Elementos	Zona 1 (wt %)	Zona 2 (wt %)
C	59.07	2.37
O	0	57.85
Mg	0.2	0.06
Al	4.92	2.82
Si	33.72	35.52
K	1.25	0.73
Ti	0.21	0.1
Fe	0.62	0.56

Figure 9. SEM images and EDS microanalysis got from SEDEX mineral (SEM-SE & SEM-EDS)

In Figure 9, can be observed a sinuous surface constituted by particles of the order of 6.6 μm to 21 μm showing euhedral structures, the images show almost similar microstructures, with a variation in the types of shapes, where can be identified euhedral, anhedral and subhedral forms, with smooth surface microstructures, fibrous and sinuous and a wide distribution of sizes no greater than millimeters. Images at x5000 are shown in figure 9 (A),(B).

On the other hand, in the detailed image of Figure 9 (C) and (D), it was possible to identify the presence of elements such as C, Si and Al.

The analyzes carried out by EDS, show an association between silicon (Si) and oxygen (O) with a wide distribution, marking the most oxidizing zones, while potassium (K) and aluminum (Al) are relationed to 1m, 4m, 6m and 8 m deep.

Alternatively, there is also a relationship between iron (Fe) and titanium (Ti), at 1 m, 4 m and 6 m depth, inside the column. But also iron (Fe) has a relationship with magnesium (Mg).

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Finally, the relationship that exists between silicon (Si) and aluminum (Al) at 1 m, 4 m, and at 6 m depth, that are areas of neutral pH.

According the above, with the results of ICP (total rock), allows confirming the presence of these strategic elements in the SEDEX type deposit, described here. Which constitutes the potential basis to consider this deposit economically attractive.

Table 1 shows the average chemical composition of the sample, where the contents are shown in majority, minority and trace elements, and can be appreciated the presence of the elements of rare earths.

Table 1 Average chemical composition by ICP

Element	Units	Concentration
Ce, Nd, La, Eu, Gd, Sm, Y	ppm	0.4 - 20.5
Au, Pd, Pt	ppm	0.05 - 10
Ti, Si, Mg, Fe, Al, K	%	0.08 - 40.8

The Figure 10 shows a XRD spectra and an image of al Au-Ag-Pt alloy, obtained by cupellation to determinate the contents of platinum and gold (using Ag as catalyst). The obtained results by this essay show that mineral contents are 5 g/t of Pt and 10 g/t of Au.

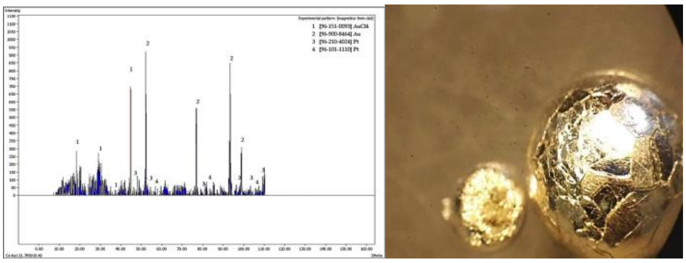

Figure 10. Cupellation results to determine Pt and Ag contents in mineral

3. Discussion

There are two controversial aspects in this work; the classification of the deposit and the mineral association. In the first case, it is considered to be SEDEX-type mineralization because two types of mineralization are recognized: philonian and stratiform, in the philonian exhalation roots are observed the stockwork towards the base, which of course, do not cut the top of the sedimentary sequence, so here it is inferred that they can correspond to the emission channels.

Meanwhile, the stratiform mineralization is concordant with lutitic, slate sediments of submarine origin, that is the same that in some zones showing great schistosity, reason why it could be inferred that the age of this mineralization is previous to the development of the mountains and hills in this area, with which it is found associated the schistosity and pyrite. Additionally, it is inferred here that perhaps due to reductive conditions, the precipitation of the sulfides observed in

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the hand specimen was favored, such as the finely disseminated pyrite, which in some cases shows framboidal crystallization and botroidal growths, showing that its formation corresponds to a chemical nature, formed in a submarine media. So all this approaches to a SEDEX mineralization of the Selwyn type, because the nature of the Huayacocotla Formation of lower Jurassic age is of the siliciclastic type of a reducing environment. Finally, the low amount of nickel and other metallic contents such as chromium, as well as other elements of ultrabasic affinity are present in this mineralization, and the additional results found allow this site to be classified as SEDEX. However, considering these results and the improtant contents of platinum in metallic form; this deposit can be subclassified as a more regional sub type.

4. Conclusions

The mineralogy of the outcrop, presents a clear and continuous mineralogical zoning that is reflected by the contents of Au, Pt, V, Cr, Cu, Ag, Zn, Pb and Ba. Meanwhile, in the stratiform body vertical zonation with pyrite and chalcopyrite at the base and wurzite towards the top and sperrilite are recognized, while, in the fillonian deposit based on the concentration profiles obtained by XRD, it shows the existence of two pulses, which can be inferred by the presence of high temperature minerals obtained according to the results of XRD. The high temperature exhalative minerals are ilmenite, monazite, and mogonite, which contrasts with medium temperature minerals that mark the end of the pulse, such as those of the albite type ($AlSi_30_8$), that were detected and chalcopyrite as the typical mineral of re mobilization hydrothermal solutions.

The characterization through SEM-EDS and Mapping, allowed establishing the presence of REE and PGE, the latter not previously known in Mexico. On the other hand, the analysis by ICP is concordant with the aforementioned analyzes confirming the presence of PGE and REE. Likewise, the SEDEX deposit has felsic affinity as presented by the low contents of transition trace elements such as V, Cr, Co, Cu, Ni.

It was also observed anomalies of V, and Cr that can be associated with metal contents of the platinum group.

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Conflicts of Interest: The authors declare no conflict of interest.

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