Rare Earth Elements and carbon nanotubes in coal mine sediments around spontaneous combustions

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Abstract

Increasing population growth and rise global energy petition have made congregation the requests of energy generation and safety a major challenge global. In another hand nanogeoscience is commencing to develop a viable remediation approach of attention in coal mine drainage (CMD) around spontaneous coal combustion (SCC). On the ecological context, nanophases (minerals and/or amorphous phases) are more reactive than bulk compounds, a property that powerfully influences the fate of pollutants in topsoils and drainages. In this work petrographic and geochemical investigations of selected CMD sediments were conducted. Potential hazardous elements (PHEs) sediments control the geochemistry of CMD around SCC. But, the physico-chemical developments governing major elements (e.g. Al, Fe, Si, Mn) transference and sedimentation in those ecosystems are not completely comprehended. For example the substitution of As, Cd, Hg, and Se in pyrite was most apparent in the CMD sediments. The sampled CMD contained carbon nanotube (CNTs) structures and many others C-nanophases. The CNTs contained several elements, including Hg, Pb, F, Cl, and halogens. While CNTs are known to be produced from coal fires of varying ranks, this seems to be the first report of naturally occurring CNTs. This work also denotes the occurrence of historical NPs-locations in near vicinity to all other, as for illustration deposits of C-NPs and non-crystalline compounds appear only nano-meters separately from each other on the contradictory sides of non-altered amorphous phases. In addition, non-conventional sources, including CMD hosting elevated concentrations of Rare Earth Elements and Yttrium (REY), have been explored as attractive secondary sources for elements recovery. Consequently, in this study we investigate CMD from abandoned coal mines in the South America as a potential REY resource. It is suggested that more work is required on CMD and a few research areas are proposed for future research.

Keywords: Carbon nanotubes, Potential hazardous elements, Spontaneous coal combustion, Potential hazardous elements, Sediments drainages

1. Introduction

The worldwide population continues to grow, and principally in the shadow of climate change and air pollutions, the requests for more and better-distributed energy generation have created an ongoing global challenge (Landim et al., 2016; Schneider, I.L. et al., 2016; Agudelo-Castañeda et al., 2017, 2016). Coal is a combustible organic rock, which is transformed from plant debris with complex biochemical, physical, chemical and geochemical processes over a long period of geologic time (Silva et al., 2011a,b). In addition to the sedimentary factors, the formation and distribution of coal seams have undergone complex structural changes in the later period, resulting in the complexity and diversity of the occurrence of coal seams. Among them, affected by tectonism such as faulting, folding, and slipping, tectonic stress may have destroyed the original structure of coal, causing the coal to be severely crushed or even pulverized.

Nanomineralogy (including minerals and amorphous phases) has become a good strategy of attention as a viable tool in spontaneous coal combustion (SCC) areas, where it aims to increase efficiency in energy generation, pathogen evaluation and keys, and water property (Ribeiro et al., 2010; Civeira et al., 2014, 2016a,b,c). Additionally to these needs, nanophases (NPs), have been caused to act as pollutant scavengers and could be affected to an extensive variety of supplementary requests (Rojas et al., 2019; Saikia et al., 2014, 2015, Oliveira et al., 2014). While there are numerous scientific studies those attentions on the scavenging capability of NPs, few have utilized this to coal mining areas. Geochemical characteristics, such as nano-size, extraordinarily high surface to volume ratios, and greater geochemical activity, build NPs supreme potential hazardous elements (PHEs) and hazardous organic compounds sorbents (León-Mejía et al., 2018, 2016; Gasparotto et al., 2018). Given this situation, we need to seek a better understanding of how economically important constituents, such as critical elements, fresh compounds for activated carbonaceous matters, many collective and manufacturing substances, and nanometer phases, can be recovered or produced from coal (Silva et al., 2013; Kronbauer et al., 2013). Securing potentially sustainable domestic sources of these commercially critical elements has become increasingly important, requiring the diversification of supplies to include recovery of REY from recycling and alternative resources such as CMD. Rare earth elements (REE) and yttrium (hereafter REY) are a group of 16 elements comprising the lanthanides and yttrium that exhibit similar physicochemical characteristics and tend to co-occur in nature. Scandium is chemically similar to the lanthanides and yttrium, and is sometimes included in the REEs, but it does not occur in the same geologic settings (Silva et al., 2020) and is not considered further in this study. The REE are generally sub-divided based on their atomic numbers into light-REE (LREE), also called the "cerium group," including lanthanum (57) to europium (63); middle-REE (MREE), including Sm, Eu, Gd, Tb, and Dy, and heavy-REE (HREE) including gadolinium (64) to lutetium (71), also called the "yttrium group". Yttrium (Y, $Z = 39$) is not a lanthanide, however, is usually grouped with the HREY because of their geochemical similarities. Carbon nanotubes and other C-nanophases are a type of C-allotropes with various characteristics and unique characteristics (e.g. Fe-magnetism, superconductivity, adsorption, including others), which types them of meticulous importance in diverse fields of utilization, such as geomedicine, materials sciences, energy, and care compounds (Montellano et al., 2011). Up to now, C-nanotubes have not been detected in coals. The SCC can produce C-nanophases, producing an environmental exposure. Nevertheless, as a result of their unification into mine engineering and user crops, health and ecological contact should expansion in the coming decades.

Coal mining containing NPs are corporate in the most mining disturbed zones of Earth, involving in and around SCC (Dias et al., 2014; Cutruneu et al., 2014). Aluminum, C, Fe, and Mn-NPs are of meticulous coal scientific attention because they have robust redox and sorption characteristics that can limit the geomobility of PHEs within SCC, even below a range of redox circumstances and coal power plants (Ribeiro et al., 2010, 2013a,b), and increasing PHEs geomobility. Besides their ability to remove PHEs from natural systems, NPs, particularly Al, C, Fe, Mn-NPs have also been studied (Sehn et al., 2016; Silva et al., 2010). The last years have appreciated the presence of ample methodical information validating the mechanism utilized by sulphate-rich coal drainages in both Fe and Al series on Earth (Nordin et al., 2018) surface atmospheres. Coal mine drainage (CMD) products from the geochemical contacts between oxygen/water, Fe-sulphides, and bacteria, occasioning in high proportions of dissolved PHEs (Nordin et al., 2018) and suspended NPs (Civeira et al., 2016). The CMD sediments geochemistry is habitually ordered by Fe^{3+} , PHEs, and sulphates complexes reactions. These complexes PHEs compounds play a fundamental function in the development of management procedures dealing with drainages recuperation (Ayora et al., 2016).

The present work aims to distinguish minor NPs (minerals and amorphous compounds), C-nanotubes containing Al-Fe-Si and trace PHEs, but also to provide a basis for further studies of carbon nanotubes, graphenes, and other new products from CMD around SCC. To date, the natural occurrence of C-nanotubes in CMD sediments samples has not happened described. The objective of this work is to discuss certain features of the geochemistry and, in particular, the nano-meter-scale structure of the CMD sediments. For this aims it procedures a compilation of electron microscopies (scanning, FE-SEM, and transmission, HR-TEM) and microscopies preparations/analysis by focused ion beam (FIB) to describe development and alteration geoprocesses of NPs during early modification periods of CMD sediments. In turn, this could establish the basis for further studies of SCC.

2. Materials and Methods

In the present work, we studied the nanophases and ultra-fine particles characteristics of REY in CMD sampled at CMD sites across Santa Catarina State (Brazil). We also report REY data for solid matrices, which could represent parent-weathering materials for the generation of CMD, including: (1) samples of raw coal collected from an underground coal mine (raw coal), coal mining materials feeding preparation facilities (feed coal), refuse coal mining materials after preparation (coal refuse), and prepared coal output from a coal preparation facility in southern Illinois (prepared coal), and (2) Permian mafic igneous rocks from southern Illinois. Twenty-six CMD sediments samples around spontaneous coal combustion (previously reported by Cutruneu et al, 2014; Dias et al., 2014), were collected from Santa Catarina State, Brazil. Previous authors of these CMD sediments provide the geologic quality framework for this investigation (Nordin et al., 2018). However do not provide CMD NPs identifications around SCC. The studied sites were selected to represent a range of drainages geochemistries (e.g., Eh, pH, sulfate, and hazardous elements contents). The selected CMD included strong acidic discharges (pH 2.1 to 4.9) as well as circumneutral and alkaline discharges with pH up to 7.5. The wide range of discharge geochemistry is representative of CMD on a basin-scale. Aspects about chemical composition, geology, temperature, redox potential, electrical conductivity, and pH values can be found in previous studies (Silva et al., 2011a, 2013; Nordin et al., 2018).

The massive array of NPs occurrences in the CMD sediments around SCC areas constituents has never been explained and deduced before, yet they divulge considerable about the historical and present reaction of coal zones with the hydrosphere and air quality. More precisely, this material was utilized by the present scientists to (I) interpret historical variations in the geochemical ecosystem of a topsoil; (II) comprehend the geomobility of the PHEs in CMD around spontaneous coal combustions and (III) describe association mechanisms of PHEs by NPs surface coatings (Silva et al., 2011b,c,d,e,f). As such, a supplementary main of this work is to exam whether the analytical approach of FE-SEM, FIB and transmition microscopy (for mineralogical and element description of the NPs) can be applied to interpret the structure of geochemical progressions on the top of modified CMD sediments and soils hat leads to the generation of important NPs (Oliveira et al., 2017, 2018a,b; Silva et al., 2010, 2009b). For these reasons, an illustrative quantity of CMD sediment was ground to ultrafine powder, studied by X-ray powder diffraction by a Phillips PW1830 diffractometer with Cu Kλ radiation, with mineral identification by indication to the ICDD Powder Diffraction File (ICDD, 2019); Geochemical of the CMD sediments samples were studied by a FIB, Zeiss Model ULTRA plus FE-SEM, with charge compensation for all applications on conductive as well as non-conductive samples, and a 200-keV JEOL-2010F HR-TEM, prepared with an Oxford energy dispersive X-ray detector and a scanning (STEM, to produce chemical compositional maps). The utilized FE-SEM was prepared with an energy-dispersive X-ray spectrometer (EDS) and the ultrafine particles and NPs investigations were based on the morphology, structure, and chemical configuration by secondary electron and back-scattered electron modes and the EDS spectra (Sehn et al., 2016; Arenas-Lago et al., 2013; Quispe et al., 2012; Cerqueira et al., 2012, 2011; Dalmora et al., 2016). EDS spectra recorded in TEM image mode were quantified using ES Vision software that uses the thin foil method to convert X-ray counts of each element into atomic or weight proportions. Electron diffraction patterns of the minerals were recorded in selected area electron diffraction(SAED) or microbeam diffraction(MBD) mode and the *d* spacings were associated to the International Center for Diffraction Data(ICDD, 2019) non-organic compound powder diffraction file (PDF) database to recognize the minerals (Ramos et al., 2017). Occurred an association of SAED and FFT analysis, geochemical dispersal maps, semi-quantitative geochemical studies, and textural topographies of NPs earlier reported in the previouslly studied NPs (Oliveira et al., 2019a,b; Silva et al., 2009, 2010, 2011b; Kinyemi et al., 2019; Duarte et al., 2019).

3. Results and discussion

3.1 General nanomineralogy

Diverse secondary NPs have been recognized in modified CMD sediments around previously studied SCC areas (Dias et al., 2014; Cutruneo et al., 2014). Varying on temperature or the geocomposition of the CMD, these NPs can be quartz, carbonates, sulphides, sulphates, clays, and amorphous Al-C-K-Mg-Mn-Si NPs. The obtained XRD and microscopic results showed that it is significant to contemplate that, due to the discovery that the physic-chemical and physical properties of NPs vary as an occupation of NPs dimension in the nanometer range, these variations probably arise from differences in surface and surface atomic configuration as a occasion of size as well as shape and superficial structure. In this study it was confirmed that these variations significantly affected important PHEs. This one broadening recognition enriches our opinion of how NPs impact the ecosphere, planet, and air quality around several SCC areas (Duarte et al., 2019).

The selected CMDs sediments XRD mineralogy indicates that it has abundant amorphous, gypsum, jarosite, kaolinite, and quartz (e.g. Figure 1) with minor quantities of sulphates, suphides, carbonates, and clays. The detected mullite, secondary minerals (e.g. jarosite, gypsum, and goethite), C-nanotubes, and several amorphous NPs by HR-TEM and FIB-SEM/EDS most probable formed through the contact of topsoil with SCC with the surface waters and CMD sediments. Utilized HR-TEM (and STEM-EDS spectra) examination shows that acid CMD samples (e.g. Figure 2) around SCC contain jarosite in association with pryrite, ferrydrite, schwertmannite, and amorphous nanospheres. Generally, hematite mixed with magnetite and ferrydrite with some amorphous phases occurs in the studied CMD samples. The EDS analysis in the spherical areas indicates the presence of PHEs (e.g. As, Hg, Cd, Cr, Pb, U). Modified and intact amorphous NPs are frequently rimmed by nano- to micrometer size ultrafineparticles which also happen (in many cases) within the matrix of modified amorphous phases. In particular circumstances, modifications rims are completely composed by major elements containing trace PHEs. Previous authors showed that, in low-pH, sulfate-rich waters, SO_4^{2-} is the primary ligand for REY forming predominantly mono-sulphate complexes (LnSO4+; where Ln is a lanthanide element) and $Ln(SO_4)_2^-$ and free ionic (Ln^{3+}) species contributing minor amounts to dissolved REY speciation (Pérez-López et al., 2010). Since SO_4^{2-} was the most abundant anion in studied Santa Catarina State CMD regardless of the pH CMD and the SO_4^{2-} concentrations were an order-of-magnitude higher than those of the other anions, we conclude that REY-sulfate complexes were the dominant dissolved REY species in CMD analyzed in this study, with limited partitioning into the solid Fe-precipitates (Nordin et al., 2018). Collectively, these results suggest that in addition to pH CMD other key factors controlled the abundance and patterns of REY enrichment in studied CMD. Such factors could have included the bedrock geology, alteration mineralogy, biogeochemical processes at the CMD site, input of REY from outside systems, and CDM geochemical.

Detected FIB-SEM subdivision depicts rare elements geochemically (Figure 3) diverse layers principally constituted of complexes crystalline and amorphous phases, which include on common higher proportion of titanium than those detected by EDS. The structure and dimension of these sheets range from linear to curvilinear and irregular and from tenth's to hundreds of nanometers. By FIB-SEM/EDS was possible to confirm the both iron-sulfides (i.e. marcasite and pyrite) contain trace substituted PHEs. Elements with arsenic, Co, Cu, Cd, Ga, Hg, Ni, Pb, and Se were ubiquitous trace constituents of the acid CMD sediments. EDS measurements coupled to HR-TEM/SAED and FE-SEM results indicate that pyrite grains are the most As- (size range of 0.2 - 15 µm = 0.3-1.8% and size range of 2 - 94 nm = 0.2-3.8%), and Se- (size range of 0.1 - 8 µm = 0.2-0.7% and 2 - 91 nm = 0.3-1.9%) rich. Previous studied working with As replacement for sulfur in Fe-sulphide demonstrated prolonged lattice factors and chemical alterations between arsenic-rich and arsenic-poor dominions, both of which should de-stabilize arsenian Fe-sulfide comparative to pure pyrite (Kolker et al., 2007). The Pb content of the sampled CMD sediments were notably higher than in other CMDs. Both regions were subjected to SCC (Cutruneo et al., 2014; Dias et al., 2014), a possible factor in Pb and As enrichment in CMD sediments. The alteration described in those studies seems to have been largely confined to the metamorphism of coal cleaning rejects and not to sulfide and other mineralization. On the other hand, several chemical compounds like lead, selenium, thorium, and arsenic may or may not display an analogous sediments behavior to Al^{3+}-rich compounds.

Several CMDs sediments contain complex amorphous Al-Fe-O-Si-agglomerates containing hazardous elements (V, Sb, and Ti). Their formation was probably the result of chemical reactions of the decomposition of the Fe-sulfides that become sulfates (like jarosite and schwertmanite) and iron oxides (e.g. hematite and magnetite). The resulting sulfuric acid attacked the aluminum-silicate minerals present in CMDs samples, generating the amorphous NPs. A recent work (Echigo et al. 2012) is appreciated because it confirmed that to evaluate the size requirement of NPs georeactivity, it is vital to account for the effects of NPs morphology, the occurrence of defects or organizational disorder, and the aggregation state. Positively, all of these features will be significant in the studied CMDs sediments in immobilizing pollutants. There would look to be fascinating explanations to propose that the sorption behavior of amorphous and crystalline NPs is not only a role of surface area, but additionally of NPs size. Dark-field STEM pictures and EDS-STEM geochemical disseminations plans signify that the lath constituted of an alluminium-iron-oxigen-silicon-bearing NPs has a higher quantity of iron and PHEs (e.g. Figure 3). Additionally, HR-TEM pictures of the boundary between the primary (e.g. sulphides and carbonates) and secondary NPs (e.g. ferrihydrite/hematite) combines display the incidence of an alteration area on the surface of the anterior NPs (Figure 4).

The results presented in this study propose that such distinctive landscapes most likely generated done the dispersal of studied CMDs water into the amorphous compounds in dry circumstances, the fractional suspension of the amorphous phases and the decantation of the PHEs hooked on Al-Fe-Si-rich mixed NPs amorphous and crystalline spherical Al-Si-O-K-Ca-As-Pb-clays (Figure 5). The diffusion of CMDs water towards amorphous/iron-rich zone boundary was probable likely through the Al-Si-concentrates pockets. Conversely, proportions of dispersal may have been small due to the dry ecological circumstances, and the incidence of Si-NPs pockets with aperture areas perhaps in the sub nanometer range. The reduced diffusion rate through the changed iron concentrates zones of the amorphous NPs had most possible also a result on the mass conversation. This work performances that Al, Si, and iron NPs (hydr/oxides, hydrous amorphous silica and sulphates) are the principal secondary materials of the spontaneous coal combustion alteration of the studied area. While iron NPs have been before detected by Cutruneo et al., 2014, the micro/nano-scale investigations in the present work divulge for the initial time the geochemical evolution for their configuration and their structural and association to PHEs, minerals, and amorphous compounds. Iron oxides (e.g. hematite and magnetite) happens totally in greater CMD precipitates, and spherical NPs and comprehends a greater quantity of Al, Ca, Mg, K, Si, S, and Ti. Magnetite NPs appear in several amorphous phases (Si-Al-K-S-Ti-rich matrices) within layers of diverse quantity of PHEs and on the exterior of the ferrihydrite/hematite. Additionally, well-expressed lathes of clays happen in agglomerates within and adjacent to Al-Si-S-rich zones.

3.2 Carbon nanotubes containing PHEs

The existence of CNTs, PHEs and several amorphous NPs in studied CMD sediments and linked topsoils containing SCC is generally coordinated by the action of coal fires in the topsoil, the disposal of major minerals compounds, hazardous coal carbonaceous compounds, and pH/Eh. The utilized chemical data for both aqueous (e.g., CMD) and solid matrixes show evidence for two main factors controlling the REY concentrations and carbon nanotubes patterns in studied CMD, namely (1) the overall composition of the source materials, and (2) the degree of alteration of the weathering coal mine wastes. The both factors also had a significant effect on the carbon nanotubes critical-ΣREY composition as well as the content of metals of economic value (e.g., chromium, cobalt, vanadium, zinc) occurred in Santa Catarina CMDs. In opportunity, these elements are persuaded by atmosphere, CMD around coal spontaneous combustion, natural vegetation, and depth of burial (Dias et al., 2014). Previous mineralogical works of the studied area indicated minor abundances of NPs including fullerenes. In this work, the nonappearance of measureable amounts of fullerene CMD sediments is in agreement with the chemical structures of the FIB and transmition microscopy sections. An important mention is about the unequivocal NPs categorization by the applied multi-analytical approach was difficult because of their exceptionally poor atoms assemblage and for they were perceptive to the utilized analytical approach. In addition, this study show the PHEs distributed between the CMD sediments constituents of the studies area.

The CMDs all contained mostly spherical carbon nanotubes (CNTs) structures (Figure 6). Certainly, graphitic structures are well documented in SCC (Gredilla et al., 2019; Silva et al., 2012) and other rocks at that metamorphic level. To date, though, no significant natural occurrences of CNTs have been recorded in CMD sediments around SCC. Thus, while this study is the first time such CNT has been reported in the literature, it is expected to motivate future studies that utilize or take advantage of naturally occurring CNTs from coal from different geological formations, in order to achieve greater economic value for the spontaneous coal combustion areas.

The detected CNT particles by applied advanced microscopies almost always contained associated inorganic elements, including PHEs such as arsenic, cadmium, mercury and thorium, or more benign elements such as Si, Al, and K, among others. The multiple crystallinities varied from particle to particle and from CMD sediments samples to CMD sediments samples, however many times the same particle presented different ordering, as marked in Figure 6B. Aside from the ubiquitous occurrence of PHEs associations with organic matter, including Mo and Ni with Fe-rich particles, Al>K>S>Ti>Ca≈Ni are create to be associated with the CNTs. Among the halogens, F, Cl, and Br were the most easily detected in CNTs. While F and Cl were detected by EDS in the same areas, in most occurrences. the organic matter contained only one of these three halogens. Flourine and bromine were also detected in amorphous Al-Si-K-Na-K-Mg-rich NPs in the sampled CMD sediments.

The studied coal geochemical area is very complex (inorganic predominant NPs sedimentation) but at the similar time intricate since C-nanotubes, graphenes, and PHEs leaching and sink activities are coordinated by resuspended complex NPs, neo-formed new precipitates on the CMD sediment superficial generations. After a description and FIB explorations of the diverse sediments sections of this termogeochemical area, the co-incidence of major elements (e.g. aluminum, iron and silicon) in the C-nanotubes precipitates was ratified. Instantaneously, an extreme decrease in size of the inorganic NPs was detected as a consequence of the unexpected leaching of the original CMD by a SCC creek.

3.3 Community perceptions

Ecological and social works have debated the impact of CMD. Manager to the implication generated by CMD have tended towards a technocratic investment in temporary to long-term solutions. However, the health effects of CMD (Nordin et al., 2018) remain neglected in research and policy arenas because of the lack of documented evidence. As a result, this renders the problem invisible, while the impact is deleterious for poor communities. Such communities suffer the effects of CMD principally through a perpetual risk posed by water contamination. Moreover, they are voiceless and excluded from matters affecting their well-being. This work was carried out with a community in Santa Catarina State, near the coal mining fields. It tested their understanding and perceptions of human and ecological health risks associated with CMD. The goal was to uncover the knowledge of the research participants of the existence of CMD and of its impact on their physical health and well-being. Qualitative methods were employed to measure knowledge, attitudes, and perceptions and to analyse the diseases inventory of the study population. Findings suggest that communities located near mines are affected by mining externalities that pose a threat to their health. It was also discovered that such communities are excluded from any planning and decision-making by local mining authorities. This case study presents strong evidence in favour of empowering marginalised communities by including them in decision-making, actively facilitating their participation, and exposing them to environmental health education to increase their awareness and reduce the risks caused by coal mining areas.

4. Summary

The compilation of advanced microscopies technology with XRD permitted for the first time to interpret the fundamental geochemical mechanisms for the materialization of complexes NPs in CMD sediments around a spontaneous coal combustion area. The present work provide a basis for the identification of naturally occurring nanominerals, C-nanoparticles in CDM seidments and for studies of their impact on the properties of the spontaneous coal combustions around CMD. Among the chemical properties of the Brazilian coals, the enrichment of Pb and As CMD sediments corresponds to expectations with respect to metamorphism by hydrothermal fluids. Some of the variability in the concentration of chalcophile elements lies in their varied concentrations in forms of pyrite and marcasite and in the occurrence of metalloid forms with As, Co, Cu, Cd, Ga, Hg, Ni, Pb, and Se. Several inorganic elements, including Hg and the halogens, are associated with the CNTs. To the greatest of our information, this is the initial study of naturally occurring CNTs in SCC area. Future works of comparable ecosystems will allow elucidation of the presented results as well to construct the bridge between major elements-concentrate CMD sediments development and a probable alteration to NPs leading to the definitive formation of other more constant phases. Synthesis of nanomineralogical data suggests that mine activity probably played a key role in producing CMD enriched in carbon nanotubes, hazardous elements, and most importantly, in critical-REY. Specifically, the presented data point towards two sources of REY enrichment in Santa Catarina CMD, namely coal mine wastes containing solid matrixes (1) with high Al and Si contents (e.g. aluminum-silicates) and (2) impact of CMD solutions concentrated in hazardous elements and REY.

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Captions

Figure 1. Typical XRD of studied CDM.

Figure 2. Amorphous and minerals assemblage around SCC.

Figure 3. Monazite and amorphous NPs detected by FIB-SEM sections works.

Figure 4. Sulfates and sulfides in CDM occurs in various forms: (A) nanocrystals (jarosite); (B) in association with Fusinites syngenetic (pyrite); (C) with gypsum association; (D) as pyrite framboids; (E and F) as cubic crystals (pyrite + marcassite).

Figure 5. Mixed amorphous and crystalline spherical Al-Si-O-K-Ca-As-Pb-clays.

Figure 6. Spherical carbon nanotubes (CNTs) structures.