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NANOMINERALOGY APPLIED TO HIGH-TECH CRITICAL METAL ORE RESEARCH

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1. INTRODUCTION

1.1. Nanoscience of High-Tech Critical Metals

Metals are key ingredients in our evolution as society, and essential for the transition from an economy relying on fossil fuels to one on renewable resources. With a rising global population, the demands of metals specific for these new technologies will grow even more, thus becoming highly critical for many countries (hereafter High-Tech CM). Europe has high import dependency of most of these High-Tech CM necessary for the green technologies, and specially for Co, Ni, and Cu as well as the noble metals (Au, Ag, platinum-group elements (PGEs: Os, Ir, Ru, Rh, Pt and Pd)). Recycling of these High-Tech CM from both mine and electronic waste does not meet the current and near future necessities even assuming a 100 % of recycling efficiency. Thus, the increase and diversification of High-Tech CM production from known and indigenous mineral resources available in nature are of major importance for their secure and sustainable supply to potential suppliers. An innovative approach to tackle this cutting-edge scientific-technological problem is to examine the source, distribution and enrichment mechanisms of High-Tech CM applying nanoscience research. This is now possible with the advent of new generation of powerful instrumental for nanoscale analysis, that allow the easy detection and characterisation of all types of nanomaterials in natural ore samples (Fig. 1).

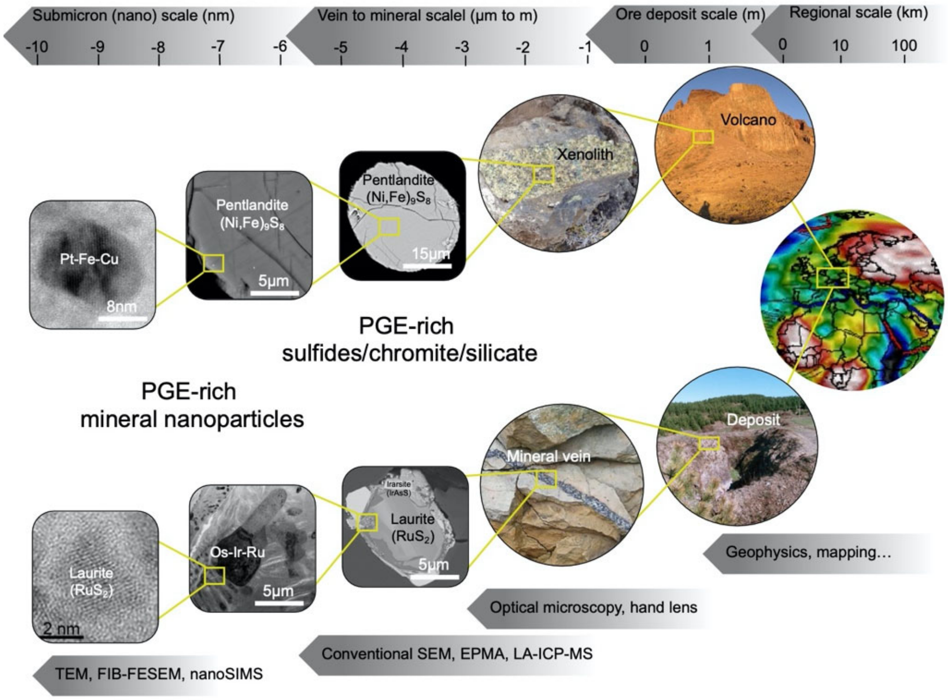

Figure 1. Nanoparticles of platinum-group minerals in mineral deposits with reference to the dimensional scale of the Earth Sciences. The horizontal scale on top is depicted in 10× meters, and shows ~10 orders of magnitude difference between the scale of ore body (upper right) and that of metal nanoparticles (left). Techniques suitable for each dimensional range are also shown (see the text for acronyms).

The results acquired over almost three decades by using combination of techniques for mineral microanalysis and characterisation (i.e., reflected light, field-emission scanning electron microscopy (FE-SEM), electron probe microanalysis (EPMA), laser-ablation inductively-coupled plasma mass spectrometry (LA-ICP-MS), secondary ion mass spectrometry (Nano-SIMS), atom probe tomography (APT), high-resolution transmission electron microscopy-scanning transmission electron microscopy (HRTEM-STEM), and transmission electron microscopy – energy-dispersive X-ray spectrometry (TEM-EDS)) show that traces of some High-Tech CM (Co, Ni, Cu, Au, Ag, and PGEs) can be incorporated as both lattice-bound and into nanomaterials in some ore (i.e., sulphides and oxides) and their associated gangue minerals (i.e., magmatic olivine, pyroxenes or amphibole as well as hydrothermal quartz, chalcedony or sericite). Nanomaterials in natural ore deposits are akin to those manufactured by industry may include atomic clusters, mineral nanoparticles (NPs, when they also exist in larger micrometre-scale sizes), nanominerals (only existing within this size range), nanofluids and nanomelts (e.g., [1-3]). Traditionally, in the field of economic geology, we have used the prefix nano- to denote to one-billionth (i.e., a factor of 10^{-9}) [1]. This definition contrasts to what is used in physics and engineering, where nano- applies to particles with one or more dimensions from 1 to 100 nm (10^{-9} to 10^{-7} m) – i.e., the size where particles have singular physicochemical properties due to their high surface-area-to-volume ratio and atomic bonds that do not exist at the micron scale.

1.2. A role of nanoscale processes for High-Tech CM enrichment in ore systems?

Ore deposits are rock volumes containing metals in sufficient concentration and quantity that permit their economic exploitation. Briefly, an ore deposit forms if there is a source of metals, a transporting medium, and a geological trap in which metals are concentrated [4], although they can be also seen as the result of an optimal combination of common geological factors, namely ([5]): (1) source fertility (defined as the source for the metals and their ligands); (2) geodynamic trigger; (3) pathway (favourable lithospheric structure allowing transport by focussed fluids/melts flow); (4) transport medium (melts and/or aqueous fluids); (5) deposition (trap allowing the selective crystallisation/precipitation in a confined area); and (6) preservation of the mineral system. In this communication, I will show how an ever-increasing body of work made over the last four decades has provided impressive results allowing us to realise that nanoscale processes may play a key role in metal transport, deposition and partitioning within a wide range of conditions in the Earth's upper mantle and crust where ore deposits form.

2. HYDROTHERMAL ORE SYSTEMS

The disulfide pyrite (FeS_2) is undoubtedly the most abundant ore mineral in a wide range of hydrothermal mineral deposits, where Au is extracted as the main or by-product component - sediment-hosted, Carlin-type, intrusion-related gold (IRG), "orogenic", epithermal, Au-porphyry, and volcanogenic massive sulphide (VMS) deposits (see [6, 7] and references therein). Unlocking the so-called "invisible" (or refractory) form of Au in pyrite has attracted much of the attention of researchers over the past four decades. Pioneering studies carried out in the late 1980s already suspected that "invisible" gold could be related to the presence of Au^0 NPs in pyrite instead of the incorporation in the crystallographic nature of pyrite, as revealed by depth-profiling analysis of element concentrations by SIMS and LA-ICP-MS (e.g., [8, 9]). Almost contemporarily, Au^0 NPs were identified in gangue minerals (quartz and chalcedony) applying SEM to samples from the epithermal Seeper deposit of Nevada [10]. However, many Au^0 NPs hosted in these minerals are smaller than 100 nm in size, making them "visible" only recently when more "modern" and sensitive techniques could be used, including synchrotron X-ray fluorescence microscopy (XFM), APT, high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) or HRTEM-EDS microscopy. In particular, the application of HRTEM and image analysis have revealed that pyrite not only contains nanoparticles of native gold (hereafter Au^0 NPs) but also this metal combined with Ag (i.e., electrum) or other metals (e.g., Te, Pb) preferentially in As-rich domains of pyrite – i.e., arsenian pyrite defined as a pyrite containing from a few ppm to tens wt% As [7, 11]. In fact, a wide suite of NPs may accompany Au^0 NPs in pyrite, including sulphides such as galena [PbS], cinnabar [HgS], chalcopyrite [$CuFeS_2$], arsenopyrite [AsFeS] and the tellurides nagyagite [$Pb(Pb,Sb)S_2(AuTe)$] and merenskyiite [$PdTe_2$] as well as a large suite of unidentified compounds comprising combinations with the (semi)-metals Te, As, Bi, Sb and Se (hereafter TABS) (e.g., [12-14]). It is worth noting that in some hydrothermal pyrites (and in their host gangue minerals), spheroidal Au^0 NPs may be present alone [15] or coexisting with other drop-like inclusions made up of base-metals (Cu, Co, Ni, Fe) and TABS [16-18], evidencing the key role of TABS nanomelts in scavenging Au, Ag and other high-Tech CM from the hydrothermal fluid. This is consistent with the experimental results of in-situ melting of pyrite matrices in dry and liquid cells coupled to HRTEM, showing the lower melting point of Au-(Ag) nanoparticles compared to bulk counterparts (e.g., Au particles of < 4 nm melt at 370 °C instead of 1,064 °C of the bulk; see cited works in [19]). On this line, textural observations in magmatic-hydrothermal deposits (porphyry-epithermal, skarns, magnetite apatite (MtAp)-iron oxide gold copper (IOCG)), combined with experimental [20] and thermodynamic [21] modeling, point out that these Au-rich TABS melts might form by: (1) direct transference from magmas to the hydrothermal fluids during fluid unmixing, (2) immiscibility from hydrothermal fluids due to the breakdown of TABS-bearing aqueous complexes, or (3) adsorption–reduction operating on mineral surfaces due to fluid-rock interaction.

All the aforementioned observations suggest that the classical transport models of metals in aqueous fluids as dissolved species might reflect only a part of the picture. Until recently, the experimental inference that tens ppb of the noble metals Au, Ag and PGEs could be transported in hydrothermal fluids dissolved as chloride- and bisulphide-bearing aqueous complexes [22-24] has prevailed in all the proposed models. However, these results were somehow biased because metal contents were measured using a combination of techniques (EPMA, EDS-SEM, ICP-MS and Raman) that might be not accurate enough to resolve the potential existence of nanomaterials in the experimental run precipitates. In addition, mass balance calculations indicate that such low abundances may explain the high-grade concentrations (tens of ppm) of Au, Ag and PGEs in veins from common magmatic-hydrothermal (e.g., porphyry copper deposits, PCDs) and hydrothermal (e.g., epithermal or orogenic) ore-systems. Nonetheless, aqueous complexation of metals is more difficult to reconcile with the formation of ultra-high-grade "bonanza-type" ore zones, which show hyper-enrichment in noble metals up to wt% in few mm to cm. This is fully consistent with the aforementioned identification of nanomelts enriched in High-Tech CM in pyrite and its gangue minerals, as well as metal-bearing NPs in colloidal suspensions – i.e., solid NPs with charged surfaces dispersed in an electrolyte solution – identified by ICP-MS and FIB-HRTEM analysing fossil [25-27] and modern geothermal fluids [28, 29]. Analyses of fluid inclusions with a combination of SEM plus LA-ICP-MS from some epithermal [30] and orogenic gold [31] deposits reveal extremely high Au contents (up to 6,000 ppm) in agreement with experimental works (e.g., [31]), thus indicating that suspensions with Au NPs can concentrate up to ~5,000 times more Au than fluids with dissolved species.

Another key target that has attracted much of the researchers specialising in hydrothermal pyrite, is the mineralogical expression of Co, Ni and Cu found in trace amounts in it. This is because Co/Ni/Cu ratios in this sulphide have been increasingly used as a tool to decipher the chemical evolution of hydrothermal systems and ore deposits at various scales [35, 36] and, by extension, as a vectoring tool for mineral exploration. Studies applying a range of techniques (e.g., instrumental neutron activation analysis (INAA) and atomic absorption; [37]) have concluded that Co, Ni and Cu could incorporate in pyrite via: 1) isovalent substitution of Ni^{2+}, Co^{2+} and Cu^{2+} for Fe^{2+}; and 2) heterovalent substitution of Cu^{+} for Fe^{2+}. However, [13] documented a suite of unidentified Ni and Cu-rich NPs (i.e., Cu-Fe-S, Au-Ag-As-Ni-S, Fe-As-Ag-Ni-S and Fe-As-Sb-Pb-Ni-Au-S in a matrix of pyrite in Carlin-type (Lone Tree, USA) and epithermal (Pueblo Viejo, Dominican Republic) deposits using a variety of techniques including, FESEM, SAED and HRTEM (Fig. 2). These results are consistent with more recent works that also revealed the presence of undefined Cu-rich NPs in metal-rich pyrites from the Chinese Dexing porphyry Cu deposit by means of SIMS [38] or nano-sized tetrahedrite [$(Cu,Fe)_{12}Sb_4S_{13}$] in VMS deposits of the Iberian Pyrite Belt using FIB-HRTEM [3]. In a more recent work, [39] have documented micron-to-nanoscale zoning of Ni, Co, and Cu in hydrothermal pyrite associated with basic rocks of the Betic Cordillera.

The application of a combination of micro- and nano-analytical techniques (i.e., FESEM, EPMA, FIB and HRTEM), reveal that nano-scale zoning corresponds to a combination of alternating layers (~500 nm thickness) of pyrite (FeS_2) with cattierite (CoS_2) and/or carrollite ($CuCo_2S_4$), and discrete nanoparticles of 80 - 120 nm carrollite ($CuCo_2S_4$), chalcopyrite ($CuFeS_2$) and violarite ($FeNi_2S_4$) (Fig. 3). These new findings have profound impact in our current understanding of the true nature of complex oscillatory Ni-Co-Cu microzoning that is commonly observed in hydrothermal pyrite.

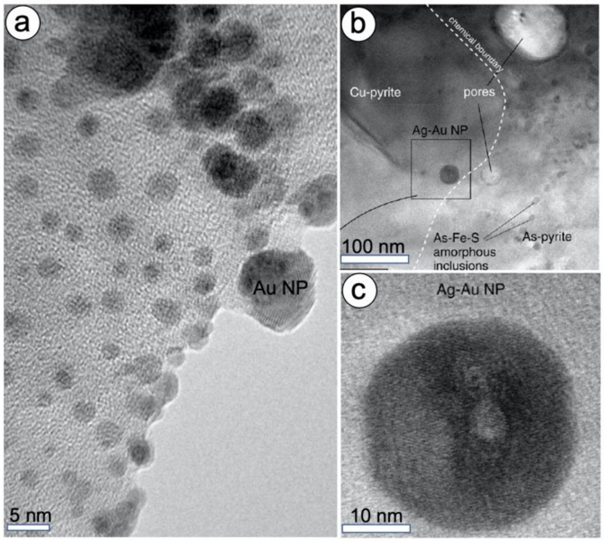

Figure 2. HRTEM images of spheroidal gold and electrum NPs in a) sericite from the epithermal deposit of Round Mountain in Nevada, USA [33], and b and c) pyrite from the epithermal-VMS deposit of Pueblo Viejo in the Dominican Republic [13].

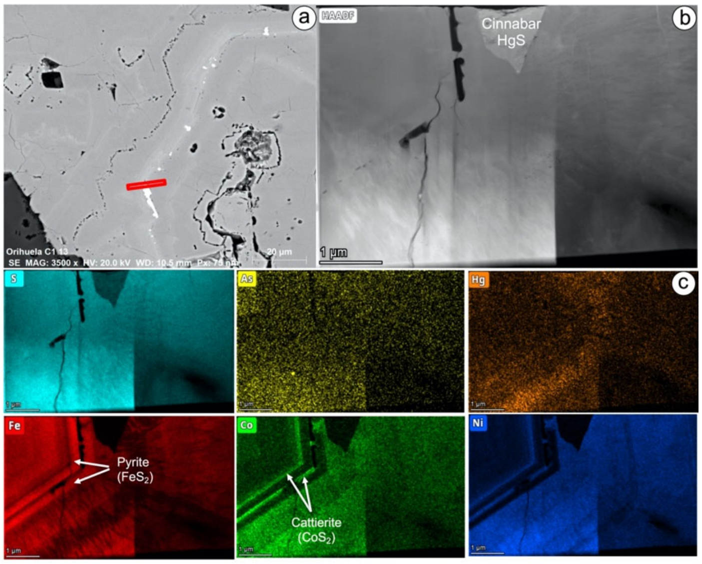

Figure 3. a) Backscattered electron image of a zoned pyrite associated to basic rocks from the Betic Cordillera; the image was obtained using FE-SEM and the red rectangle shows the location of the FIB thin foil extraction. b) HAADF image of the thin foil cut containing zoning microstructure and cinnabar microinclusion. c) EDS-STEM compositional maps of the thin foil showing alternating bands of pyrite (FeS_2) and cattierite (CoS_2). A more detailed description and interpretation of the nanoscale structure of other pyrite grains analysed in the same locality can be found in [39].

3. MAGMATIC ORE SYSTEMS

The most prominent enrichments of High-Tech CM in ores originated by magmatic processes occur in sulphide ± chromite ores associated with layered mafic-ultramafic complexes within or at the boundaries of cratons, and in the mantle and mantle-crust sections of ophiolites [40].

In sulfide-saturated systems, Ni-Cu-Fe-(Co) sulphide melts usually separate from silicate magmas by liquid immiscibility at high T (~ 1,200 ºC) when sulphide saturation is achieved, collecting most noble metals (PGE, Au and Ag) and semimetals (TABS: Te, As, Bi, Sb) owing to their extremely high disulphide/silicate partition coefficients (> 104). Since early 1970's, there has been a status quo that PGE and TABS are hosted in mineral products of the crystallisation of sulphide melts (mainly pyrrhotite, pentlandite, chalcopyrite; [40]). In this widely accepted model, upon immiscible segregation of a sulphide melt from a basaltic magma, the High-Tech CM PGEs should concentrate with the sulphides owing their high sulphide/silicate partition coefficients. In the early 1990's a group of South African researchers [41-42] challenged this model suggesting a disruptive hypothesis involving PGE nanomaterials for the formation of PGE "Reef-style" deposits associated with the large layered intrusions of the Bushveld Complex in South Africa and the Great Dyke of Zimbabwe. In their paper published in 1995, Marian Tredoux and colleagues worded "PGE might occur in magmas as metallic clusters of 50 - 100 atoms, rather than as cations or any molecular species. Clusters could be stabilised by an outside 'envelope' of ligands (e.g., S, As, Sb, Te) and this might lead to their incorporation into a sulphide melt or chromite (if available); however, the association between the PGE clusters and the sulphide would be a mechanical rather than chemical one". However, this "PGE cluster model" met ab initio with much scepticism because the prevailing model for PGE ore deposit formation was based nearly exclusively on chemical partition coefficient. Almost 20 years later, the experimental works carried out by members of Marian Tredoux's research team (i.e., the PhD thesis of Bianca Kennedy in 2013 [43]) confirmed the existence of these PGE "nanomaterials" in magmatic sulphides, which were imaged and characterised using scanning Auger microscopy (SAM) in combination with time-of-flight secondary ion mass spectrometry (ToF-SIMS). The undoubtedly confirmation was provided by [44] synthesized nano-metre sized Pt-As compounds cogenetic with monosulphide solid solution (i.e., MSS; $Fe_{1-x}S$) that they characterised and imaged using HRTEM, providing additional support for the possible existence of PGE-rich NPs in magmatic systems. Eyes were finally opened to the community when [45] and [46] applied FEG-SEM, and FIB combined with HRTEM to pyrrhotite and pentlandite from PGE-rich ores of the Bushveld complex in South Africa. These two teams of researchers recognised that PGE in the sulphides occur as: (1) homogenous solid solution, (2) patchily distributed solid solution, (3) ordered within the pentlandite structure, substituting for Ni and/or Fe (superlattice), and very interestingly, as (4) discrete nano-inclusions (< 50 nm) of PGM (PtTe, PtBi, Pd-Pd-Sn, Pt-Fe-Cu, unidentified arsenides of Ru-Rh-Pt and sulphides of Ru-Rh-Os, Ru-Rh-Pt-Ir, and Ru-Rh-Pt sulphide) with no orientation relationship with the host sulphide mineral. Subsequently, an increasing number of works have documented PGE-(Au)-TABS NPs with crystallography both related and unrelated to their host magmatic base metal sulphide (BMS) [47-50], giving the ultimate evidence that PGE-rich NPs may form in wide range of conditions within magmatic systems (Fig. 4).

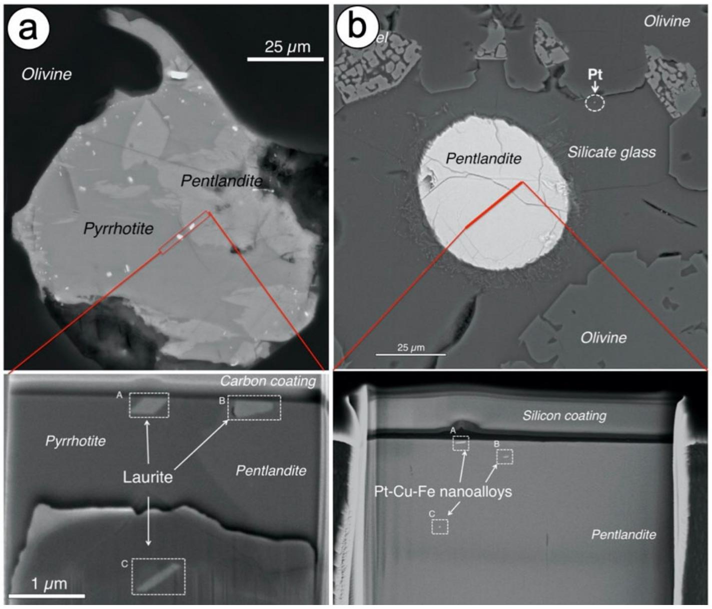

Figure 4. FESEM and FIB images of PGE NPs in sulphides and silicate glasses from mantle-derived xenoliths of the Argentinian Patagonia [48]. a) Euhedral nanocrystals of laurite (RuS_2) are hosted in both pyrrhotite and pentlandite. Note that the HRTEM analyses (not shown) of these mineral NPs show orientations different from their host base metal sulphides (BMS), suggesting crystallisation prior to the hosting sulphides. b) Pt-rich nanoalloys found in both sulphide (pentlandite) bleb and glass. Note the tiny Pt NPs revealed under FIB in pentlandite which were not resolvable by FESEM.

New advances in the PGE nanoworld also include the nanoscale characterization of micrometre-sized inclusions of PGM sulphides and alloys hosted in chromite ores associated to mantle rocks from either subcontinental [51] and oceanic [52] mantle. A specific feature revealed by HRTEM observations by [51] from Os-rich laurites of the Ojén massif in southern Spain is that Os is not hidden in the laurite lattice of Os-rich laurites but forming fringes (10 – 20 nm thickness) of almost pure erlichmanite within a homogenous laurite matrix. It cannot be detectable if the whole PGM grain is imaged using conventional FE-SEM and EPMA elemental mapping. Another unprecedented observation in the work carried out by [52] was the rather complex structure of the cores and rims of some micrometre-sized zoned laurite grains hosted in chromitites. In the oscillatory zoned grains of laurite hosted in chromitites from Cuban ophiolite they studied, micrometre-sized cores of the zoned grains consisted, down to the nanoscale, of an aggregation of much smaller cores (< 1 μm), which are in turn wrapped by bands thinner than 10 nm; these nanostructures were neither detected using conventional instruments (Fig. 5). The nanoscale studies also allowed to identify that micron-sized laurite and erlichmanite grains may contain a plethora of nano-sized inclusions such as pentlandite, millerite, Os-Ir alloys. The immediate consequence of the results provided in these works were the following. Firstly, they question the conventional definition of the intermediate terms of the solid solution defined only using in-situ single-spot EPMA analysis or BSE images obtained using SEM, i.e., Os-poor or Os-rich laurite, between the pure species laurite (RuS_2) and erlichmanite (OsS_2). Secondly, it is clear that it can only be adequately assessed by detailed TEM studies. Secondly, zoning in laurite grains could form at both the micron- and nano-sized scales.

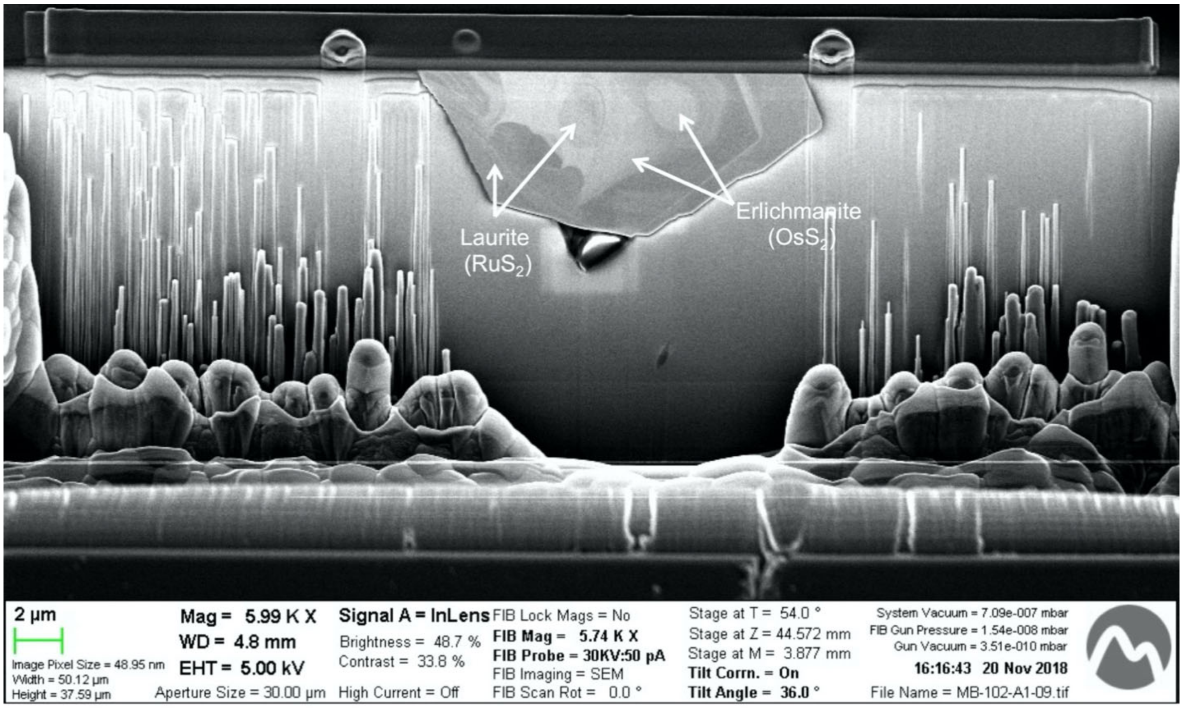

Figure 5. FE-SEM image of a thin-foil being milled. The thin foil was cut perpendicular to a zoned laurite grain found as inclusion in a chromite crystal forming the Monte Bueno chromite ore deposit, in the eastern Cuban ophiolites. Note that the micrometre-sized PGM show a very complex internal structure with various erlichmanite cores, which is only revealed during FIB thin foil preparation. A more detailed description and interpretation of the nanoscale structure of this grain can be found in [52].

Finally, post-magmatic alteration of magmatic PGM also reveal an unseen complexity at the nanoscale realm. [53] realized that Os-and Ir-bearing laurite (RuS_2) from the Loma Baya chromite ores from Mexico have experienced partial desulphurisation during hydrous metamorphism, giving rise to the neo-formation of nanometric (< 50 nm) particles of Ru-Os-Ir alloys "visible" under FE-SEM. In contrast, a subsequent short-lived thermal event that promoted dehydration in the chromitite had the opposite effect, producing a significant coarsening of metal nanoparticles to dimensions larger than a micrometre. In an ensuing work, [52] have analysed the in-situ transformation of Ru-Os-Ir sulphides to alloys during serpentinisation of silicate matrix of chromite ores from the Monte Bueno Mine, in eastern Cuba. Combining high-magnification and HAADF images and the corresponding EDS spectra, the elemental mappings acquired using HRTEM, these authors showed that micrometre-sized aggregates of desulphurised laurite ± Os-Ir-Ru alloys consist of intergrowth of nano-sized (< 5 nm) laurite with ad Ru-Os-Ir-(S-As) and Ru-Os-Ir alloys (50 - 100 nm) within a Fe-Mn oxide/hydroxide matrix. This microstructure and the coexistence of these nanoparticles within the Fe-Mn oxide/hydroxide matrix was interpreted as the result of an alteration sequence whereby magmatic laurite was desulphurised and decomposed into smaller laurite nanoparticles, which in turn were progressively transformed to Ru-Os-Ir-(S-As) particles and, finally, to Ru-Os-Ir nanoalloys. Using a similar approach (EPMA, SEM, FIB-HRTEM) [54] have recently analysed laurite-erlichmanite grains associated with PGE-bearing pentlandite in the intergranular space of the chromite Kızıldag ophiolite in southern Turkey. These authors also observed that the interaction of primary sulphides with low temperature aqueous solutions produce secondary PGMs and base metal mineral assemblages with complex nanostructures. Thus, they documented “secondary” intergrowths made up of Os-Ru nanophases (Os-Ru nanoparticle and $OsRu_3$ nanoalloy) + awaruite ($FeNi_3$) + trevorite (Fe_2NiO_4) in nodular chromitite, Os-rich laurite + Os-Ir(Ru) alloy/oxide + pentlandite + millerite (NiS) in banded and massive chromitite, and Ru(Ir) oxide + heazlewoodite (Ni_3S_2) in disseminated chromitite.

More recently, [55] have investigated oxygen-bearing Pt-rich PGMs within fractures in chromite grains from chromitite bodies on Ouen Island, New Caledonia. These authors also showed how desulphurisation of primary Pt-rich sulphides may also produce complex nanoscale intergrowths of PGE alloys and Fe oxyhydroxide. Application of FEG-SEM and EPMA revealed that a complex micrometre-sized zoning of the PGM, consisted of irregular cores of Pt(-Pd-Ni-Fe) sulphides surrounded by mantles of O-bearing Pt-Fe-Ni(-S) compounds and outermost rims of Pt-Fe-Cu(-Pd) alloys. In addition, the STEM-EDS, HRTEM, and HAADF observations revealed a nanoporous structure in the relict S-poor Pt(-Pd-Ni-Fe) sulphide core and its wrapping Pt-Fe-Ni oxidised alloy mantle. Such a nanoporous structure consisted of nanometric needles of Pt(-Pd-Ni-Fe)-S compounds and is mantled by Ni-Fe alloys (tetrataenite (FeNi) and antitaenite (Fe_3Ni)) embedded in an O-bearing Pt-Fe matrix (Fig. 6). Cano and co-workers argued that the latter phases could be fine intergrowths of Pt^0 or isoferroplatinum with ferrihydrite, such as those reported by based on X-ray microbeam absorption spectra on micrometre-sized Pt-rich “oxides” from the nearby Pirogues mineralisation by [56]. All these micro- to nanoscale textural and compositional evidence from O-bearing PGMs supports a mobilisation of S from cooperite (or malanite), following the sequence of desulphurisation: PGE-Fe-Ni sulphide → S-poor Pt(-Pd-Ni-Fe) sulphides → Ni-Fe alloys + Pt-Fe-O → tulameenite.

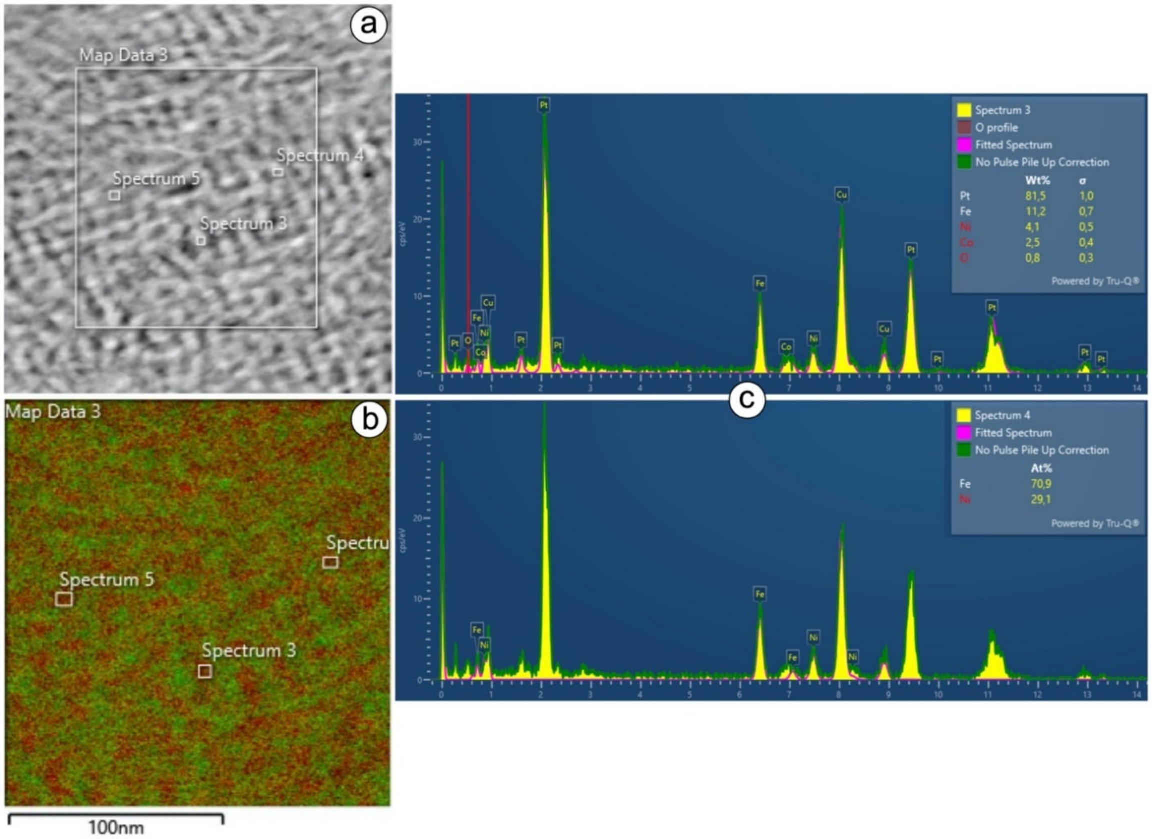

Figure 6. Nanoscale structure of a micrometric oxygen-bearing Pt-rich PGM grain from chromite ores of the New Caledonia ophiolite. Note that at the nanoscale the structure consists of a) an aggregate of Pt-Fe and Fe-Ni alloy as seen in the HRTEM image, b) the X-ray EDS STEM maps, and c) single-spot analysis. A more detailed description and interpretation of the nanoscale structure of this PGM grain can be found in [55].

4. CONCLUSION

Summarising the track-record of reports now available in the literature it is possible confirm the existence of a High-Tech CM nanoworld, still hiding important information for our understanding of the enrichment of these valuable metals in a variety of mineral ore systems. This is clearly a fertile field for further investigation, where new hypothesis of ore genesis must be evaluated taking in account that nanomaterials (clusters of atoms, NPs, nanofluids and nanomelts) may play a key role for the transference and partitioning of a specific suite of High-Tech CM (i.e., PGE, Au, Ag, Co, Cu, Ni, Te, Bi, Sb and Nb) in magmatic and hydrothermal ore systems and their transitions. Clarifying how these nanomaterials form and act will help to overcome the enigmatic paradox on how common magmas and hydrothermal fluids, with relatively low budget of dissolved metals, produce over enrichments of economic importance. This information is now accessible with the advent of a new generation of micro- and nano-analytical techniques, including FEG-EPMA, LA-ICP-MS, micro-Raman, FESEM, EBSD, FIB, HRTEM, nanoSIMS and ATP.

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