



# Supergene minerals with Indium (In) in the San Roque polymetallic project, North Patagonian Massif, Argentina

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## ABSTRACT

San Roque (40°45'54"S; 65°48'07"W) is a mining project located in the eastern sector of Northpatagonian Massif, Río Negro province, Patagonia, Argentina. In this project the polymetallic mineralization has epithermal characteristics and is hosted in the Jurassic volcanites, volcanoclastites and sedimentary rocks of the Marifil Volcanic Complex. It was defined as a low to intermediate sulfidation epithermal system in which the ore mineral association mainly consists of native gold, low Fe In-bearing sphalerite, chalcopyrite and galena. This contribution documents the geochemical data and the mineralogical studies carried out in representative samples of two drillholes that intercepted Del Indio Structure in the supergene oxidation zone. This structure represents one of the most explored epithermal manifestations of the project. According to the observations with a scanning electron microscope and semi-quantitative analyses, the main supergene minerals that concentrate In, Cu, Zn, Pb, Ga, Mn, P, As and Cl are attributed to hematite, plumbojarosite, coronadite and motttramite, which are hosted by coarse-grained epiclastic subfacies from the Marifil Volcanic Complex, described in this contribution as polymictic orthobreccia. It is also documented, for the first time, a supergene mineral-association together with base and precious metals, by oxidation of the polymetallic epithermal mineralization in the San Roque project. The veinlets, stockwork and, in a lesser extent, disseminated mineralization style of the hypogene ore, with In-bearing sphalerite and pyrite as the predominant sulfides, combined with the porosity and limited acid-buffering capacity of the host rock, favored the penetration of acidic, and oxidizing relatively V-rich meteoric waters, giving rise to the and subsequent oxidation process.

**Keywords:** Critical metals, supergene ore, vanadate, Jurassic, Patagonia.

## RESUMEN

*Minerales supergénicos con Indio (In) en el proyecto polimetálico San Roque, Macizo Nordpatagónico, Argentina.*

San Roque (40°45'54"S; 65°48'07"W) es un proyecto minero ubicado en el sector oriental del Macizo Norpatagónico, provincia de Río Negro, Patagonia, Argentina. En este proyecto la mineralización tiene características epitermales y polimetálicas y está alojada en las volcanitas, volcanoclastitas y sedimentitas del Jurásico correspondientes al Complejo Volcánico Marifil. Fue definido como un sistema epitermal de baja a intermedia sulfuración en el cual la asociación mineral de mena consiste principalmente en oro nativo, esfalerita con In y pobre en Fe, calcopirita y galena. En esta contribución se documentan datos geoquímicos y estudios mineralógicos realizados en muestras representativas de dos sondajes que interceptaron la Estructura Del Indio en la zona de oxidación supergénica. Esta estructura representa una de las manifestaciones epitermales más exploradas del proyecto. De acuerdo a las observaciones con microscopio electrónico de barrido y análisis-semicuantitativos, los principales minerales supergénicos que concentran In, Cu, Zn, Pb, Ga, Mn, P, As y Cl se atribuyen a hematita, motttramita, plumbojarosita y coronadita, que se alojan principalmente en facies epiclasticas de grano grueso del Complejo Volcánico Marifil, descritas en esta contribución como ortobrechas polimicticas. Asimismo, se presenta por primera vez, una asociación mineral supergénica portadora de In, metales base y preciosos, generada a partir de la oxidación de la mineralización epitermal polimetálica en el proyecto San Roque. El estilo vetiforme, en stockwork y diseminado de la mineralización primaria con esfalerita con In y pirita, como los sulfuros predominantes, combinado con la porosidad y la capacidad limitada de la roca de caja de actuar como *buffer* geoquímico, favorecieron la percolación de fluidos meteóricos ácidos, oxidantes, relativamente ricos en V, que dieron lugar al posterior proceso de oxidación.

**Palabras clave:** Metales estratégicos, mena supergénica, vanadatos, Jurásico, Patagonia.

## INTRODUCTION

The San Roque project is located in the eastern sector of the North Patagonian Massif, in Río Negro province, Argentina (Fig. 1a, b). It is an epithermal and polymetallic deposit (Dill et al. 2013a, Jovic et al. 2015, Padelletti Di Marco 2023) that covers an area of approximately 74,000 hectares. It is characterized by epithermal manifestations that occur as quartz and sulfide veins, veinlets, and stockworks with strong structural control. Geochemical exploration by mining companies revealed that the sulphide-rich epithermal mineralization shows relatively high levels of Au, Ag, Zn, Pb, Mo and In. One of the most interesting elements, in view of the economic potential (in addition to the Au and Ag contents), is the presence of In, which registers concentrations up to 1,500 ppm in hypogenic ore and almost 15,000 ppm in the supergene zone (Falls and Montgomery 2012). Currently, the available data for deposits with In which are affected by supergene processes is particularly limited and the San Roque project is not the exception, since until now there has not been a suitable study with the characterization of the mineral phases that concentrate economically important metals (In, Pb, Ag, Zn, Mo, Cu, Au) in the supergene zone. Although these metals are not critical elements in Argentina, they can be considered of strategic economic importance due to their critical nature worldwide (USA, European Union, China, United Kingdom), which ultimately indicates the importance attached to them for the industry promoting their exploration and eventual economic use (Zappettini 2021).

Supergene deposits are the subject of increasing interest for mining industries, driven by an increasing demand for metallic elements for new technologies. In this context, the near-surface location and the weathered and easily exploitable host rocks, are advantages over hypogene mineralization due to their relatively easy and rapid accessibility and extraction (Verhaert et al. 2020 and references therein). An additional benefit of secondary ores is their higher metal content, compared to primary sulfides (Sillitoe 2005), although their complex mineralogy can also represent a challenge for ore processing. Supergene minerals formed through these processes and their stability in exogenous settings play a key role in mobility of chemical elements of economic importance. For this reason, the study of these minerals contributes to elucidate mechanism of metals transport and accumulation under natural conditions. Also, it contributes to a better understanding of the geochemical behavior of In – among others metals - in near-surface portions of the Earth's crust. This stands for more than relevant information for exploration and exploitation

of metals in this region of Argentina.

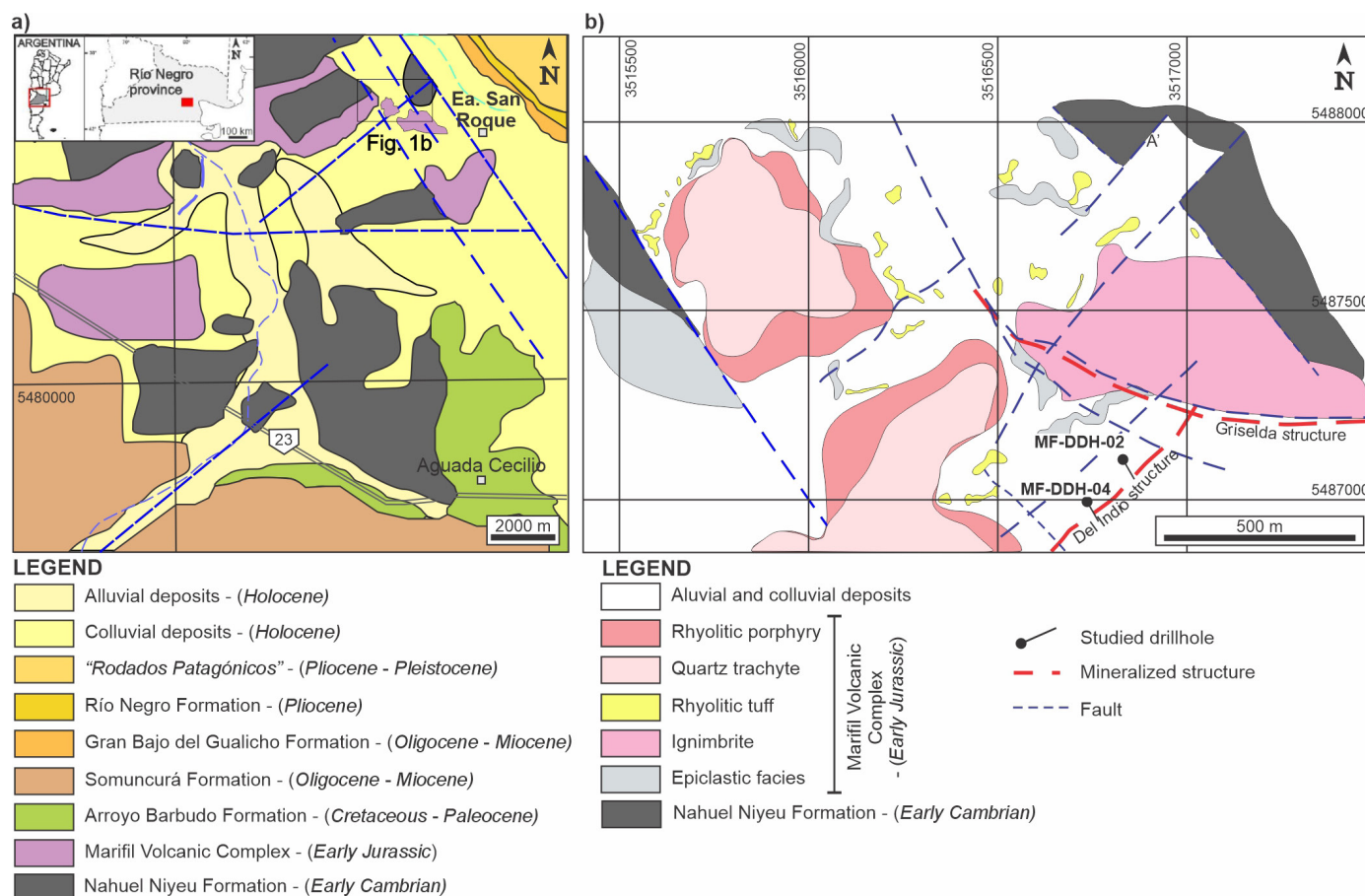
Within the San Roque project, Del Indio Structure is one of the most explored epithermal structure, it has a general NE-SW strike and a length of 300 m (Fig. 1b). The supergene zone is best represented along this structure, since a complex weathering profile incorporating part of the orebody was described. This paper documents a detailed study of newly collected samples belonging to the In-rich oxidation zone in Del Indio Structure, where the supergene mineral associations are described and semiquantitative mineral compositions are presented. In addition, we also characterize the epiclastic host-rocks of the mineral associations and the interpretation of strategic metals.

## GEOLOGY OF THE SAN ROQUE PROJECT

The San Roque polymetallic (Au-Ag-Cu-Pb-Zn) project is characterized by quartz and sulfides veins, veinlets and stockworks with epithermal features, containing critical metals such as In, Mo, Ga (Dill et al. 2013a; Jovic et al. 2015, Padelletti Di Marco et al. 2023). They are mainly hosted in acidic volcanic and epiclastic rocks of jurassic age belonging to the Marifil Volcanic Complex (Cortés 1981, Dill et al. 2013a) and locally, in the paleozoic metamorphic basement of the Nahuel Niyeu Formation (Greco et al. 2015; Fig. 1a, b).

The studied area comprises a volcano-sedimentary basin (~2 km-diameter) bounded by foliated metasediments of the metamorphic basement rocks (Nahuel Niyeu Fm.). Overlying the metamorphic rocks, there is a sedimentary sequence consisting of breccias and conglomerates, both matrix-supported and clast-supported, as well as coarse to fine-grained sandstones and siltstones. Besides, volcanic pyroclastic and coherent facies are interbedded with reworked epiclastic facies. In addition, subvolcanic facies of high-level trachyte and rhyolite porphyry stocks intrude the basement rocks and the volcano-sedimentary sequence. The latter represents an active magmatism coeval with volcanoclastic sedimentation attributed to the Marifil Volcanic Complex (Pankhurst et al. 2000, Martinez et al. 2001; Fig. 1a, b).

Locally, fossiliferous marine sedimentary rocks of the overlying cretaceous to paleocene Arroyo Barbudo Formation are exposed (Fig. 1a). Tertiary basaltic flows of the Somuncurá Formation built up an extensive plateau cropping out southward the San Roque project near the Aguada Cecilio town (Fig. 1a). According to Kay et al. (2007), the basaltic flows were extruded in an intraplate setting during an extensional



**Figure 1.** a) Geological map of the northeast sector of the Northpatagonian Massif and location of the San Roque project. Modified from Martínez et al. (2001). b) Geological map of San Roque project in Del Indio and Griselda structures area. Modified from Falls and Montgomery (2012).

processes linked to a local thermal instability of the mantle. The effusions developed mainly in the Oligocene (33 to 26 Ma), although the available ages cover a wide temporal range (Ardolino et al. 1981, Cordenons et al. 2020). In the northeast of the San Roque project, miocene-oligocene marine sedimentary rocks of the Gran Bajo del Gualicho Formation, continental sandstones of the Río Negro Formation and polymictic conglomerates corresponding to the "rodados patagónicos" unit are exposed (Fig. 1a). Holocene is represented by alluvial and colluvial deposits (Martínez et al. 2001; Fig. 1a, b).

A series of northeast and northwest trending faults have been interpreted from surface topography, geophysical data, geological mapping and drillcore intersections (Fig. 1b). These faults are thought to control the extent of the half-graben basin, the hydrothermal activity, as well as the porphyritic intrusions. Field relationships interpreted from drilling and mapping strongly suggest that faulting and hydrothermal activity responsible for veining and mineralization were broadly contemporaneous (Falls and Montgomery 2012).

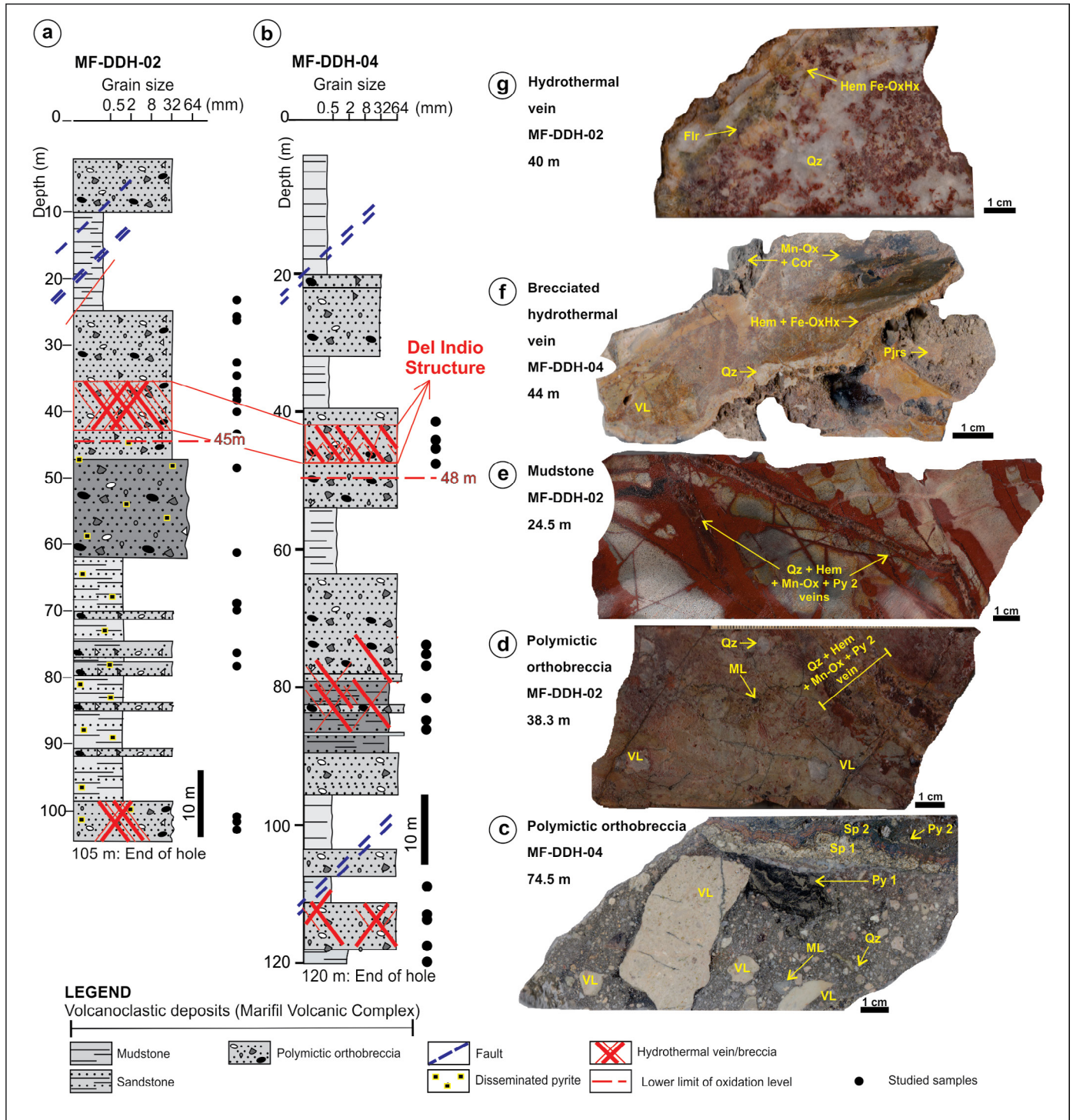
## Epithermal polymetallic hypogenic mineralization in Del Indio structure

Based on hydrothermal breccias and veins characteristics, fill textures, quartz-sericitic alteration, Fe-poor sphalerite with fluid inclusions homogenization temperatures (215° to 248 °C, Gómez et al. 2008; 243 to 273 °C, Padelletti Di Marco et al. 2023), low to moderate salinity of the fluids (4.7 to 6.5 % NaCl eq. Gómez et al. 2008; 5.11 to 5.57 % NaCl eq. Padelletti Di Marco et al. 2023), mineralization was defined as an epithermal system of low to intermediate sulfidation. Ore mineralogy consists in native gold, sphalerite, galena, chalcopyrite, and minor amounts of others Cu-sulfides and sulfosalts, while gangue minerals mainly comprise quartz, with subordinate calcite and fluorite (Gómez et al. 2008, Dill et al. 2013a, Padelletti Di Marco et al. 2023). According to the hydrothermal alteration that occurred in detrital and magmatic Al-bearing minerals, and the development of illite >> kaolinite ± chlorite as patches or pervasive alteration in the rocks, as well as voids and cracks filling, it was interpreted that the hydrothermal fluids followed feeders and conduits, and also they

diffused in the pores of the host volcanoclastic and epiclastic rocks, resulting in a hydrothermal assemblage with very low acid buffering capacity (Padelletti Di Marco 2023).

The hypogenic polymetallic mineralization in Del Indio

structure occurs as veinlets, stockworks and locally hydrothermal breccias in intervals of variable thickness (apparent thickness 7 to 20 m) hosted in the volcanoclastic sequence (Fig. 2 a, b). The hydrothermal veins and veinlets are between 0.5



**Figure 2.** a-b) Columnar lithological profiles of the analyzed drillholes. c) Hand sample of the polymictic orthobreccia subfacies extracted from the hypogene zone, MF-DDH-04 drillhole. d) Hand sample of the polymictic orthobreccia subfacies extracted from the supergene zone, MF-DDH-02 drillhole. e) Hand sample of the mudstone subfacies extracted from the supergene zone, MF-DDH-02 drillhole. f) Hand sample from a hydrothermal breccia located in the zone of supergene alteration, MF-DDH-04 drillhole. g) Hand sample from a quartz and oxidized sulfides vein located in the zone of supergene alteration, MF-DDH-02 drillhole. Qz: quartz, Hem: hematite, Mn- Fe-Ox-Hx: Mn-Fe oxy-hydroxides, Mott: mottramite, Py: pyrite, Cor: coronadite, Fcor: ferricoronadite, Pjrs: plumbojarosite. Fir: fluorite, VL: volcanic lithic, ML: metamorphic lithic.

and 5 cm thick while the brecciated sectors have an apparent thickness of up to 10 cm. The veinlets are continuous, with sharp edges, generally lack internal symmetry and show alteration halos in the host rocks. The syn-mineralization episode is characterized by the precipitation of two generations of sphalerite: banded sphalerite (Sp 1) and colloform sphalerite (Sp 2) associated with pyrite, chalcopyrite and galena (Fig. 2c). Edges of chalcopyrite crystals are usually replaced by bornite, covellite, anilite, or tetrahedrite group minerals. Quartz, carbonates and fluorite precipitated as late filling of the cavities during the post-mineralization episode (Padelletti Di Marco et al. 2023).

## SAMPLING AND ANALYTICAL METHODS

In the field, a detailed sampling of the cores of two drill-holes (MF-DDH-02: 3516788E, 5487020N and MF-DDH-04: 3516736E, 5486975N) that intercepted Del Indio structure at different depths was carried out. The drill holes have a NW-SE orientation, an inclination of  $-60^\circ$  and depths of 105 and 120 m, respectively (Figs. 1b, 2a, b). Based on geochemical information provided by Marifil Mines S.A. mining company, sampling was focused on intervals with anomalous metals contents.

Rock samples from the selected drillholes were analyzed for 41 elements at the Alex Stewart laboratory in Mendoza using four-acid digestion and emission spectrometry (ICP-ES). A statistical analysis of the geochemical data was carried out by estimating the Pearson correlation coefficient ( $r$ ), as a quantitative method to determine the degree of correlation between the analyzed elements. Ranges were established to define low ( $r = 0.1 - 0.4$ ), moderate ( $r = 0.4 - 0.7$ ), high ( $r = 0.7 - 0.9$ ) and perfect ( $r = 0.9 - 1$ ) positive correlations. Box and whisker plots were performed in order to identify the chemical elements with anomalous contents. Then, based on these results, the anomalous elements were selected to make the litho-geochemical profiles.

A total number of 13 thin and polished sections of representative rock-samples were prepared in the Petrology Laboratory of the INGEOSUR, CCT CONICET Bahía Blanca and were analyzed with a Nikon Eclipse E600 petrochalcographic microscope. A JEOL JSM 35 CP scanning electron microscopy (SEM), equipped with an energy dispersive X-ray spectroscopy detector (EDS) belonging to the CCT-CONICET Bahía Blanca was used to analyze the chemical composition of the mineral phases in 7 representative petrochalcographic samples and rock fragments. In addition, compositional maps

were performed in the analyzed samples in order to show the distribution of chemical elements in each mineralogical phase of interest.

## RESULTS

### Host rocks of supergene polymetallic mineralization

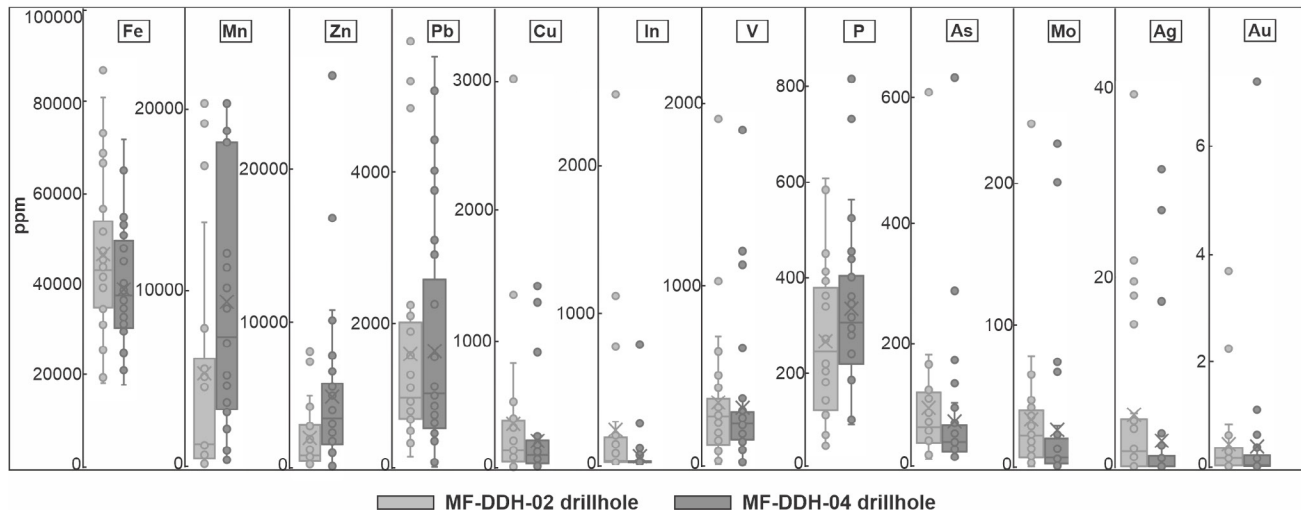
The studied drillholes from Del Indio Structure intercepted a succession of epiclastic facies interbedded with volcanoclastic facies from the Marifil Volcanic Complex. The lithological characteristics and the size of the fragments in the epiclastic facies allowed to define two subfacies as the principal rocks in the supergene zone: a) polymictic orthobreccia and, b) mudstone (Fig. 2a, b, d, e).

The polymictic orthobreccia is light gray or dark green in color at greater depths (Fig. 2c), while at shallower depth it is pinkish-brown in color (Fig. 2d). It has a matrix-supported to clast-supported texture, where the clastic fraction constitutes 10 to 60 % by volume (% vol.) of the rock. The lithoclasts are angular to rounded with sizes between 0.2 and 5 cm and they predominantly correspond to acid volcanic rocks with a porphyritic texture and aphanitic groundmass (up to 35 %). Subordinately, smaller lithoclasts (maximum 0.5 cm) of pelitic rocks and foliated metamorphic rocks can be distinguished (Fig. 2c, d). Locally, idiomorphic to hypidiomorphic clasts of quartz (2 to 10 % vol.) and feldspar (3 % vol.) can be distinguished with sizes that vary between 400 and 800  $\mu\text{m}$  (Fig. 2c, d), the latter partially or totally replaced by illite >> kaolinite  $\pm$  chlorite. The matrix (25 to 75 % vol.) is fine to medium sand size and includes the same components mentioned previously. Besides up to 15 % ferruginous cement can be distinguished (Fig. 2c, d).

The mudstone subfacies was intersected throughout the drillhole and occurs as interbedded levels between the coarse-grained lithologies (Fig. 2e). They present a massive to finely laminated fabric with greenish-gray, dark brown and grey color, and no evidence of bioturbation. The clasts may vary in grain-size from clay ( $\sim 1.5 \mu\text{m}$ ) to coarse silt ( $\sim 50 \mu\text{m}$ ) and are mainly composed of quartz, feldspars, illite, and disseminated framboidal pyrite. At the contacts between the two different lithologies of the epiclastic facies, a higher concentration of iron oxides veinlets is observed.

### Whole-rock geochemistry

With the aim of determining the distribution and/or variation in concentration of chemical elements, box-and-whisker plots were constructed (Appendix A; Fig. 3) in order to de-



**Figure 3.** Boxplots showing the chemical variation in studied drillholes.

fine which of them show chemical outliers along the oxidation zone. Bulk-ore metals grades show a wide range in concentration, as shown in diagrams in figure 3. In general, metals show a high dispersion with a positively skewed asymmetric distribution; while Fe and Mn show a more symmetric distribution.

Rock sample descriptions and analyses of the litho-geochemical profiles in the studied drillholes indicate a complex chemical weathering profile that reaches a current depth of 45 and 48 m in MF-DDH-02 and MF-DDH-04 drillholes, respectively (Fig. 4a, b). In both drillholes the oxidation zone includes Del Indio structure, which represents the high-grade zone.

In MF-DDH-02 drillhole (Fig. 4a), the oxidation zone contains the highest concentrations of Fe (8.06 wt. %), Mn (>2 wt. %), Zn (7786 ppm), Pb (5705 ppm), Cu (3013 ppm), In (2435 ppm), V (1917 ppm), As (609 ppm), P (607 ppm), Sr (333 ppm), Mo (241 ppm), Ga (15 ppm), Ag (5.6 ppm), Au (3.65 ppm). Below the oxidation level, the Cu, In, V, As, Sr, Mo, Bi, Ga, Ag, Au contents are very low, sometimes below the limit detection, which agrees with the scarcity of hydrothermal veins described in the transitional and hypogenic zones. Fe, Zn and Pb present variable concentrations below the oxidation level with maximum values in those samples that present hydrothermal veins and veinlets. Sulfur and Cd have similar geochemical profiles, both elements are scarce to undetectable through the oxidation zone and show a sharp increase in their concentrations below it.

In MF-DDH-04 drillhole the highest contents of Fe (7.24 wt. %), Mn (> 2 wt. %), Pb (5530 ppm), V (1857 ppm), As (633 ppm), P (816 ppm), Sr (270 ppm), Mo (227 ppm) and Au (7.2 ppm) are in the oxidation zone (Fig. 4b). Besides, the highest concentrations of Ag (31.3 ppm), Cu (1290 ppm) and In (780

ppm) are associated with Del Indio Structure intercepted between 42.6 and 46.3 m depth; Zn, Cd and Ga present low to undetectable concentrations (0.21 wt.%, 6 ppm and 15 ppm, respectively). Below the oxidation level (from 48 m to the end of the drillhole; Fig. 3), the highest contents of Zn (2.55 to 14.81 wt.%), S (4.24 to 9 wt.%), Cu (578 to 4490 ppm), In (206 to 1160 ppm), Cd (154 to 888 ppm), Ga (< 65 ppm) and Ag (6.7 to 60.7 ppm) are also present. These elements are preferentially concentrated in a sector intercepted at a depth of 74 m, with an apparent thickness of 4.5 m, and which corresponds to an interval with abundant veins and irregular veinlets filled by representative sulfides of the hypogene zone (Fig. 2c).

Pearson's correlation coefficients were calculated with the geochemical data of all samples above the oxidation level (Appendix A). In MF-DDH-02 drillhole, the Pearson correlation coefficients indicate several perfect positive correlations, among which are highlighted: In - Bi ( $r = 0.99$ ), In - V ( $r = 0.93$ ), As - Mo ( $r = 0.96$ ), As - Cu ( $r = 0.93$ ), Cu - Mo ( $r = 0.96$ ) and V - Bi ( $r = 0.91$ ). In the MF-DDH-04 drillhole there are also numerous perfect positive correlations: Ag - Cu ( $r = 0.98$ ), Ag - Mo ( $r = 0.93$ ), As - Au ( $r = 0.93$ ), As - In ( $r = 0.97$ ), As - Mo ( $r = 0.92$ ), As - V ( $r = 0.91$ ), Au - Bi ( $r = 0.95$ ), Au - In ( $r = 0.97$ ), Bi - In ( $r = 0.93$ ) and Cu - Mo ( $r = 0.93$ ).

### Supergene mineralogy in the oxidation zone

Above the oxidation level the supergene alteration zone was recognized (Fig. 4a, b). This zone is characterized by a supergene mineral-association that may occur as: a) fine-grained aggregates that fill dissolution cavities and microfractures in the polymictic orthobreccia, b) replacing hypogenic minerals in quartz vein/veinlets and c) forming patchy aggregates in the finer grained rocks (Fig. 2). The recognized

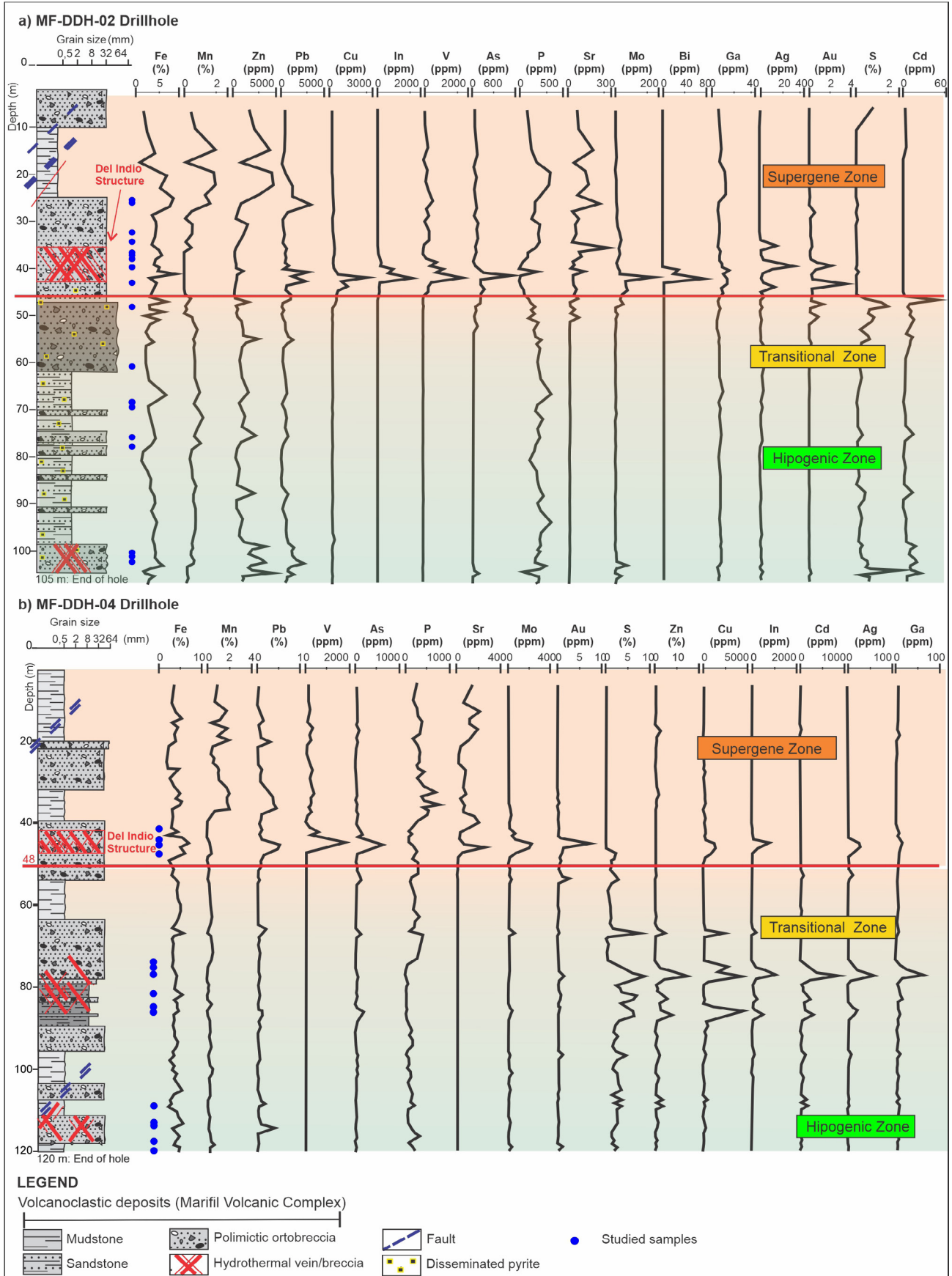


Figure 4. Litho-geochemical profiles corresponding to a) MF-DDH-02 and b) MF-DDH-04 studied drillholes.

minerals containing anomalies in In and other metals of economic interest are described below in decreasing order of abundance (Fig. 5).

**Hematite:** is a moderately abundant to abundant mineral that is present in most samples along the supergene zone. It occurs as patches, cavity and microfractures fillings, and as sulfide replacement (Fig. 5a-c). Hematite and Fe oxy-hydroxides stain veins and veinlets filled with quartz and sulfides (mainly pyrite) with a reddish color. The presence of empty spaces and cavities resulting from the dissolution of primary sulfides is common (Fig. 5a). Under the microscope, crystalline aggregates are fine-grained and have massive, skeletal, fibrous, spherical, botryoidal and mammillary habits with banded texture, where the bands have a thickness that varies between 10 and 250  $\mu\text{m}$  (Fig. 6). In some cases, idiomorphic crystals of pyrite are partially to totally pseudomorphically replaced by hematite (Fig. 5c). The semi-quantitative chemical analyses carried out on hematite crystals ( $n = 27$ ; Appendix B, table 1), together with images of backscattered electrons with distribution of concentrations of chemical elements (chemical maps), allowed to determine that this mineral concentrates in addition to Fe (35.4-60.4 wt.%), other metallic elements such as Pb (up to 11.3 wt.%), V (up to 2.5 wt.%), Cu (up to 2.5 wt.%), Zn (up to 1.7 wt.%), As (up to 1.7 wt.%), In (up to 1.3 wt.%), Mn (up to 0.9 wt.%) (Fig. 6).

**Manganese oxides:** are also widely distributed along the supergene zone. Macroscopically they are observed as dense, massive, black to black-brown aggregates in oxidized ore samples, closely associated with quartz veins and veinlets and with hematite and/or Fe-oxy-hydroxides (Fig. 5d). Under the polarizing microscope with reflected light they occur as common fine-grained colloform aggregates with light and dark bands showing different shades of gray (Fig. 5e). Coronadite, ideally  $\text{Pb}(\text{Mn}^{4+}_6, \text{Mn}^{3+}_2)\text{O}_{16}$  belongs to the coronadite group, and the hollandite supergroup, it was found in samples from drillcore MF-DDH-04. Coronadite fills vugs in quartz veinlets and occurs as botryoidal aggregates with a rough appearance (Fig. 5f). Manganese and Pb contents may vary between 30.4 to 55.9 wt.% and 16.8 to 28.5 wt.%, respectively ( $n = 13$ , Appendix B, table 2). It contains accessory amounts of Cu (0.9 – 2.58 wt%), V (1.3 – 2 wt.%, and only minor contents of Al, Si. Some analyses ( $n = 3$ ) registered Fe contents (6.7 to 11.1 wt.%), and this could be attributed to the presence of ferricoronadite  $\text{Pb}(\text{Mn}^{4+}_6\text{Fe}^{3+}_2)\text{O}_{16}$  (Chukanov et al. 2016).

**Mottramite:** ideally  $\text{PbCu}(\text{VO}_4)(\text{OH})$ , belongs to the adelite-descloizite group, a large group of minerals of the general form  $\text{AB}(\text{XO}_4)(\text{Z})$ , which contains intermediate-size divalent cations (Ca and Pb) at the A site, divalent transition metals

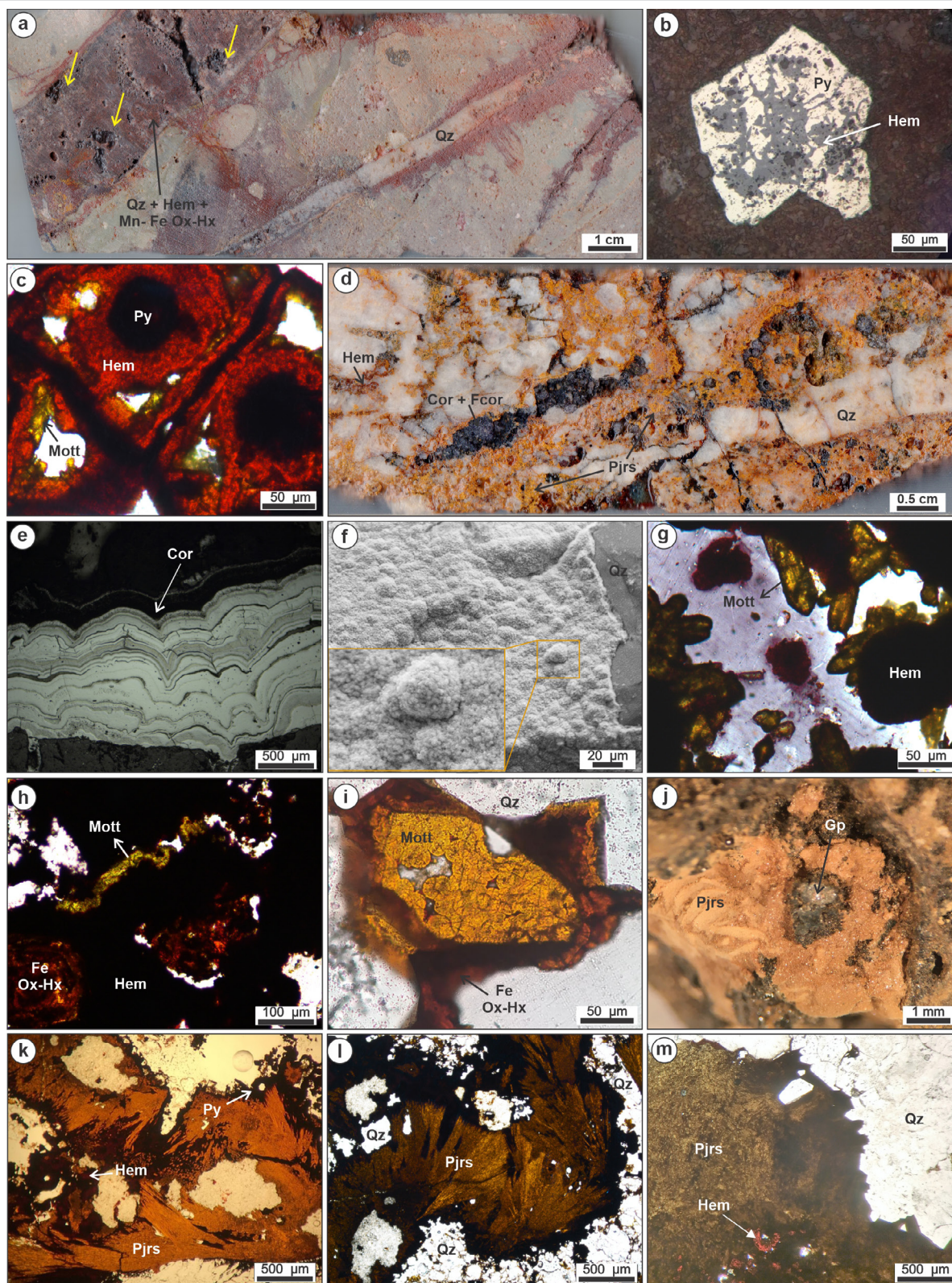
(Cu, Zn, Fe, Mn, Mg, Co and Ni) in site B. X represents the structural site for elements such as P,  $\text{As}^{5+}$  and  $\text{V}^{5+}$  and Z represents the structural site for OH, F, Cl (Richmond 1940). Although mottramite is not an abundant mineral, it was identified in most of the studied samples along the supergene zone. This vanadate occurs as fine-grained ( $< 60 \mu\text{m}$ ) late idiomorphic fibrous or prismatic crystals that grow on colloform hematite aggregates (Fig. 6), and in late cavities within totally or partially pseudomorphically replaced pyrite crystals (Fig 5g, h). Locally, mottramite occurs as colloform aggregates that fill microfractures (Fig. 5h) and cavities in volcanoclastic rocks (Fig. 5i). It is transparent to subtranslucent with a variable green to yellow color with slight pleochroism. Lead is the dominant cation at the A site (47.2 to 57.4 wt.%,  $n = 8$ ). B site is predominantly occupied by Cu (6.7–13 wt.%). Vanadium is the dominant chemical element at the X site (10.2 to 12.1 wt.%). Iron, Zn, and Mn are also present with maximum values of (10.2; 5.5 and 1 wt.%, respectively; Appendix B, table 3). From the chemical map images and EDS analysis it is possible to observe that mottramite concentrates minor amounts of In, Ga, P and Cl, the latter two, probably occupying X and Z sites, respectively (Fig. 6i-l).

**Plumbojarosite:**  $\text{Pb}_{0.5}\text{Fe}^{3+}_3(\text{SO}_4)_2(\text{OH})_6$  is a relatively scarce mineral in samples from the supergene zone, but, in all the studied samples is always associated with Fe-oxy-hydroxides (Fig. 2f, Fig. 5j, k). It occurs as fine-grained ( $< 1 \text{ mm}$ ) crystalline aggregates with a radial fibrous habit closely associated with pyrite oxidation, forming anhedral grains around pyrite crystals and intergrown with hematite (Fig. 5k). Under the polarizing microscope with transmitted light are reddish-brown in color, with weak pleochroism. From the semi-quantitative chemical analyses ( $n = 8$ ; Appendix B, table 4) it was determined that the Pb content varies between 5.8 and 11.5 wt.%, while Fe and S concentrations vary between 14.5 to 23.1 wt.% and 5.7 to 8.4 wt.%, respectively. The subordinate participation of K (1.2 - 2.2 wt.%), As (0.7 - 1.2 wt.%) and In (up to - 0.4 wt.%) was also determined (Fig. 7).

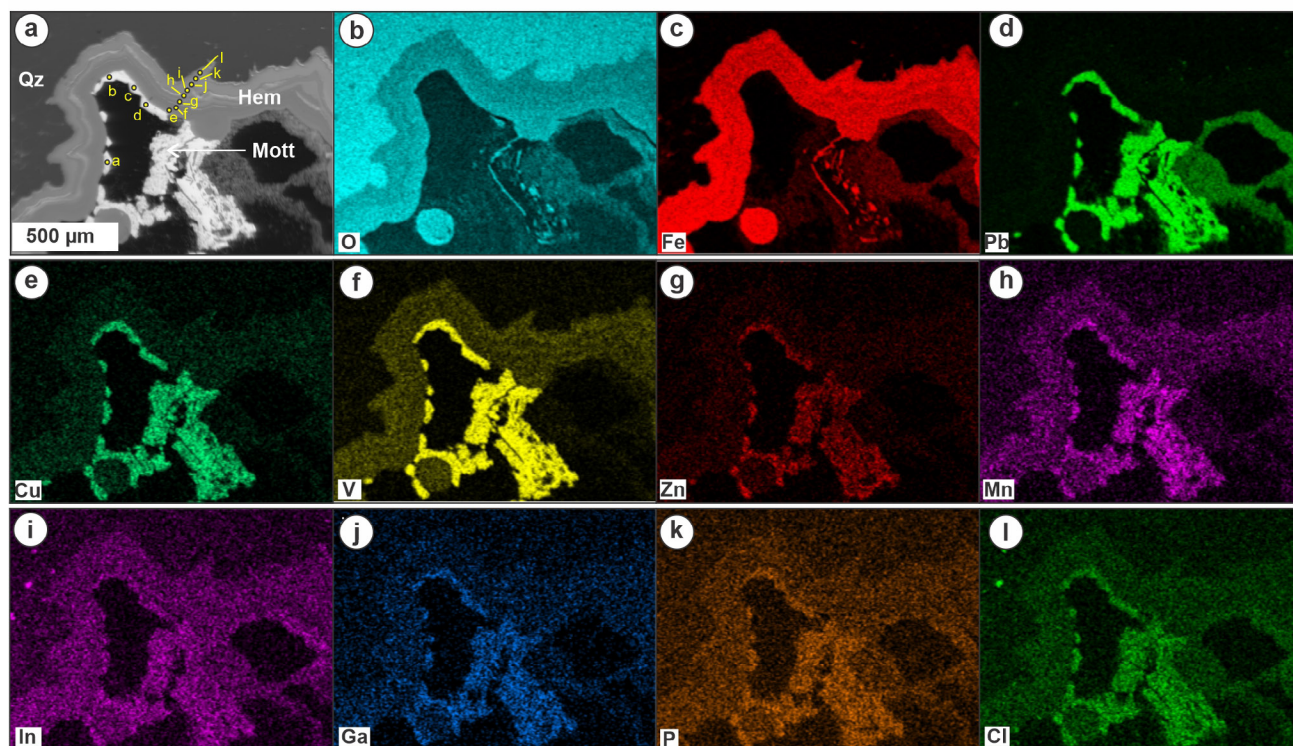
## DISCUSSION

In the San Roque project, the mineralogical, textural, and chemical characteristics of the supergene minerals described in this contribution provide strong evidence for an origin from oxidation of hypogenic polymetallic mineralization, partial mobilization of chemical elements, and open space re-precipitation, as well as in situ replacements (e.g. pseudomorphic hematite after pyrite leaving only relics cores of that mineral). The presence of an oxidizing environment and fluids leaching





**Figure 5.** Quartz and sulphide veins with intense oxidation hosted in the polymictic orthobreccia subfacies. The yellow arrows indicate dissolution cavities. b) Photomicrograph of subhedral pyrite crystals partially replaced by hematite. c) Photomicrographs of hematite crystals with pyrite core and late mottramite crystals. d) Quartz hydrothermal vein with dissolution voids and open spaces partially filled by supergene minerals. e) Late colloform coronadite aggregates. f) Backscattered electron image of coronadite in secondary electrons mode. g) Late prismatic crystals of mottramite that grow on late cavities and within hematite. h) Microfractures filled by late mottramite. i) Colloform aggregate of mottramite. j) Plumbojarosite fine-grained aggregate in the polymictic orthobreccia. k-m) Plumbojarosite and hematite crystals under the transmitted light microscope. Qz: quartz, Hem: hematite, Mn-Fe Ox-Hx: Mn-Fe oxy-hydroxides, Mott: mottramite, Py: pyrite, Cor: coronadite, Fcor: ferricoronadite, Pjrs: plumbojarosite, Gp: gypsum.



**Figure 6.** Backscattered electron images with distribution of chemical element concentrations (chemical maps) of hematite and mottramite. Yellow circles indicate the semi-quantitative analyses position (Appendix B, Table 3).

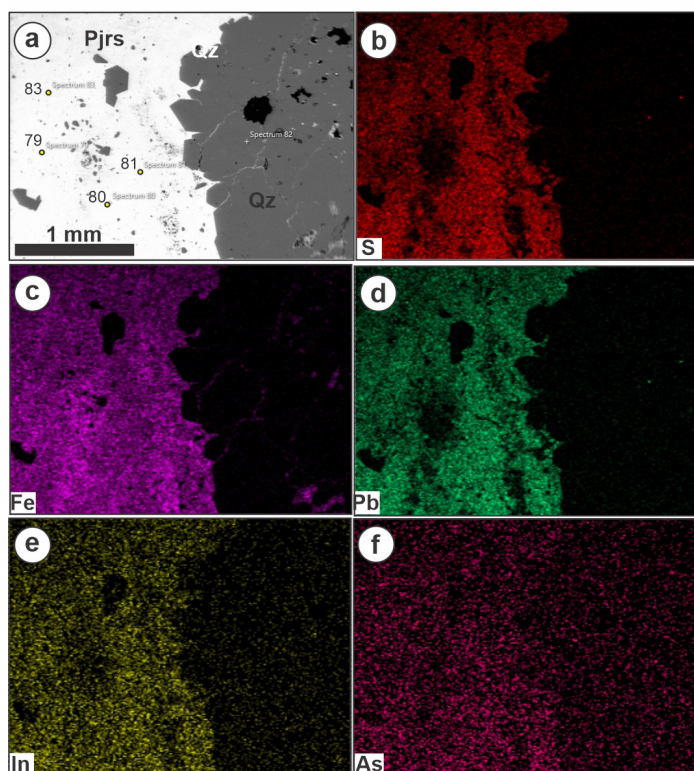
the primary ore are the main factors leading to the formation of supergene ores (Choulet et al. 2014, Boni and Mondillo 2015, Verhaert et al. 2017, Sillitoe 2019). Other factors that may have played a role in the formation of the supergene zone in the San Roque project include uplifting of the area and fracturing with exhumation and subsequent weathering of host rocks and increasing climatic aridity, or a combination of all these. In San Roque area, the exhumation process happened after the Jurassic (Martinez et al. 2001), and an increase in aridity as a product of the uplift of the Patagonian Andes, would have depressed the regional water tables, facilitating the oxidation of primary minerals and the formation of supergene minerals such as those documented in this contribution.

The importance of the porosity and the permeability of the host rocks, together with the structural control evidenced by the presence of faults/fractures may facilitate the percolation of meteoric waters since they represent main controls for the circulation of supergene fluid flows (Sillitoe 2019). This was evidenced in this study, since according to the distribution of the chemical elements along the volcano-sedimentary columns intercepted by the studied drillholes (Fig. 4), the highest concentrations of metals were found in the epiclastic levels of coarser granulometry, associated with fault and/or fractures zones.

Another factor that favored the formation of the supergene

minerals described here is related to the mineralogy of the host rocks. The epiclastic rocks described in this contribution are mostly composed of clasts of volcanic origin characterized by an acidic mineral association with abundant quartz, K-feldspars relicts and secondary minerals such as illite, minor kaolinite and traces of chlorite, and also fragments of the metamorphic basement rocks, providing a final association with very low acid buffering capacity.

Supergene metal deposits contribute significantly to the world's supply of selected base metals (Cu, Zn, Ni, Co) and structural metals (Al, Fe, Ni, V, Reich and Vasconcelos 2015). Zones of supergene sulfide oxidation are widely developed at several Au-Ag epithermal deposits in the Deseado auroargentiferous province, Deseado Massif located in Patagonia, Argentina (Schalamuk et al. 1997; Fernández et al. 2008; Sillitoe 2019), and had influenced the increase of metal grades (e.g. Mina Marta, Páez et al. 2016; Veta Eureka West, Cerro Negro project, Permuy Vidal 2014; Veta Julia, Virginia project, Luna 2021). In the San Roque project, the hypogenic minerals that contain In are sphalerite >> roquesite and Cu-sulfides and sulfosalts, while in the supergene zone only dzhalindite ( $\text{In}(\text{OH})_3$ ) was described (Dill et al. 2013a). According to observations with SEM and semi-quantitative analyses of the San Roque project studied samples, the main supergene minerals that concentrate In are attributed to hematite, plumbojarosite and



**Figure 7.** Backscattered electron images with distribution of chemical element concentrations (chemical maps) of plumbojarosite.

mottramite.

Semi-quantitative analyses on hematite crystals revealed very variable Fe contents (35.4-60.4 wt.%), together with the presence of other metallic elements such as In, V, Cu, Zn, Pb. This provides evidence of the ability of this mineral to trap and/or assimilate metals during its formation by replacement of the primary ore, mainly pyrite, at room temperature and near-neutral pH (Wood and Samson 2006). It has been proposed that the metal retention capacity of hematite and other Fe-oxi-hydroxides could have been enhanced by the presence of sulfates in the depositional environment (Swedlund et al. 2009). Hematite and Fe-oxi-hydroxides with In and Ga contents, among others, were described in the oxidized ores of the Kabwe Zn-Pb deposit (formerly known as 'Broken Hill'), located in central Zambia (Mondillo et al. 2018). These authors proposed that during the last stage of supergene alteration of sulfides, the more immobile In and Ga were residually incorporated into the newly formed Fe-oxi-hydroxides.

Mottramite is a vanadate typically found in oxidized zones of vanadium bearing supergene deposits, but may also be abundant within and/or around Cu, Pb, Zn sulfides ores (Yans et al. 2017 and references therein). It forms at low temperatures (40-50°C), in arid, acidic and slightly reduced environments, such as the boundary between the phreatic and vadose zones (Boni et al. 2007). However, Dill et al. (2013b)

suggested that vanadates are most stable under strongly oxidizing and neutral pH conditions. The association of mottramite, hematite and Fe-Mn-oxi-hydroxides at the San Roque project implies that the hypothesis of Dill et al. (2013b) is more adequate in this case, and it was also proposed for other polymetallic deposits with supergene alteration and mottramite formation (Verhaert et al. 2020). The occurrence of mottramite irregularly scattered in the studied samples from the supergene zone of Del Indio Structure as microveinlets / microfractures crosscutting the oxidized mineralization (Fig. 5h), overgrowing walls of cavities in skeletal hematite (Fig. 5c, g), precipitating with late colloform/botryoidal hematite aggregates (Fig. 6), corroborates the observation of Boni et al. (2007) and Verhaert et al. (2020) that vanadates such as mottramite often form during late phases in the supergene history.

Schwellnus (1945), Verwoerd (1953), van der Westhuizen et al. (1989), and Boni et al. (2007), proposed that mottramite forms by recombination of V mobilized from host rocks and/or sulfides, with residual Cu and Pb amounts deriving from primary sulfides. In Patagonia, mottramite was described in a kaolin deposit located in the southeast of Los Menucos town (Marfil et al. 2002). These authors suggest that vanadium mobilized from hydrothermally altered rhyolitic tuffs of the Sierra Colorada Formation, whose V content is ~ 100 ppm, precipitated as isolated crystals directly related to alunite from hydrothermal solutions or acid hot springs. The hypogenic ore in the San Roque project is not enriched in V, as well as the host rocks below the oxidation level (Fig. 4). For this reason, considering the relative's V contents in the rocks of the region, and their proximity to the San Roque project area (Fig. 8), it is shown that all the volcanic units of the Meseta de Somuncurá have high contents of V (especially those with trachybasalt, basaltic trachyandesite or basaltic-andesite lithologies), therefore, they may be the main source of V for this region. Since the tertiary lava-flows of the Somuncurá Formation are widely extended in the Río Negro province and they are the closest to the San Roque project located southward of the project area (Fig. 1a) we suggest that this formation can be the main possible source of V. In this sense, Reimann and de Caritat (2012) mentioned that basaltic rocks show, in fact, the highest V concentrations among the most diffused crustal rock types. This is also the case for the lithologies in the surroundings of San Roque project (Fig. 8). Finally, the peculiar V concentrations in the supergene zone in San Roque project is also favored by their chemical-physical conditions, since V according to Wright and Belitz (2010) is highly mobile in oxidized and alkaline conditions. In this way, the vanadate's formation in the San Roque project would have occurred during or after basalts extrusion which began to be extruded during the early

Oligocene (Cordenons et al. 2020 and references there in).

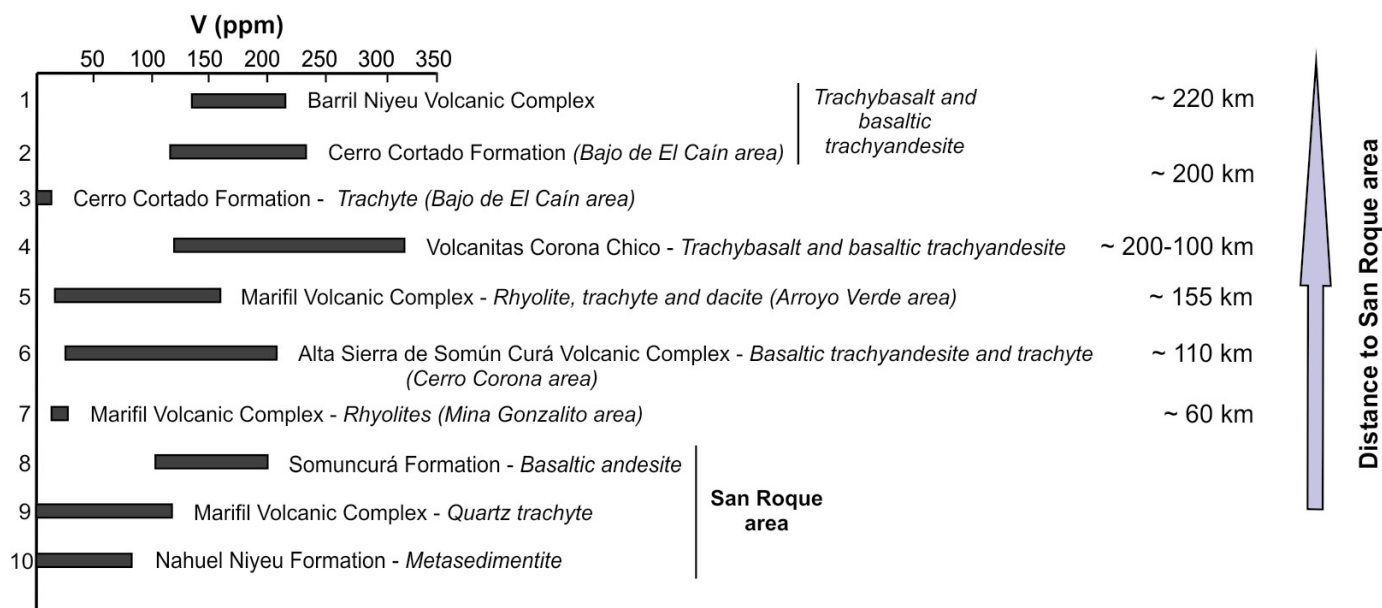
In the studied samples, plumbojarosite has a local distribution and occurs as patches and replacements in the host rock, associated with Fe-Mn-oxy-hydroxides and hematite. The presence of plumbojarosite indicates high concentration of Pb available in the system, low pH environments, it generally represents mature Pb phases, and was described in the supergene oxidized zone of Pb-Zn deposits (Scott 1987, Davis et al. 1993, Basciano and Peterson 2010). Plumbojarosite was not observed as cavity infillings indicating their formation was not by direct precipitation from weathering solutions, for this reason, its formation is inferred to the related replacement in situ of unstable hypogene minerals under an oxidizing environment, such as sulfides. This would also explain the In contents observed in this mineral, since sulfate complexes and metal ions involved in sulfates precipitation are originated from the hypogenic sulfides, whereas Na and Al most probably derived from silicates of the host rocks.

These results, among others described in other deposits from Patagonia and the world (e.g. Moura et al. 2007, López et al. 2015), show that In behaves as an immobile metallic element under oxidizing conditions. The stability of In in the supergene zone was explained by the extremely low solubility of this element at pH values between ~4.5 and ~9, and in a low temperature range (Ogawa et al. 2012; Schwarz-Schampera and Herzig, 2002).

Coronadite usually occurs as a primary mineral in hydrothermal veins or can crystallized from hot springs, also might

be of secondary origin in oxidized zones above the manganese-bearing rocks or can be found in bedded sedimentary deposits (Vlasáč et al. 2021). In this contribution, coronadite most likely has a secondary origin due to their textural features and mineral association described in all samples. In turn, the low Mn contents present in the samples located in deeper zones, below the supergene oxidation zone (Fig. 4), indicate that the primary sulfides and host rocks are not enriched in this element.

Neither Au, Ag nor electrum were identified in the studied samples. Likewise, these metals were not detected as inclusions or as trace elements in other minerals based on the analytical techniques used in this research. Nonetheless, their presence was confirmed in the whole-rock geochemical analyses provided by the mining company (Figs. 3, 4). On the other hand, among the cavities of the Fe-oxy-hydroxides of rock samples from the MF-DDH-04 drillhole (sample 7469; 44 m depth, Au: 7.2 ppm), abundant small crystals (10 to 25 µm), with yellow to silver colors and high reflectance, have been observed. Some of them, have been individualized as gold and/or electrum grains (Guido and Jovic 2007; in a private report prepared for Marifil Mines S.A). Also, it is important to note that in the studied supergene zone, Au and In show a perfect positive geochemical correlation (Appendix A). In turn, these elements also have perfect and high positive correlations with Ag, As, Cu, Mo, V, Bi and Sn, which suggests that they could be used as guide elements for the exploration of both metals. Probably, during the early stages of the supergene alteration,



**Figure 8.** Graph showing the variations in the vanadium content ranges in the lithologies present in the San Roque project and in Northpatagonian massif region. Fm.: Formation. The references of the geological units are ordered according to the distance from the area of the San Roque project, as follows: 1: Asiain et al. (2019); 2: Asiain et al. (2021); 3: Ferracutti et al. (2022); 4: Asiain et al. (2017, 2019); 5: Pavón Pivetta et al. (2020); 6: Maro y Remesal (2012); 7: Pugliese et al. (2021); 8: Asiain et al. (2017); 9 y 10: Marifil S.A. (private report).

the mineralogy of the host volcanoclastic succession combined with the veinlet/stockwork/disseminated style of mineralization of hypogene minerals and the high potential of pyrite to produce highly oxidizing agents (Plumlee 1999), enhanced oxidation process resulting in liberation of microparticulate Au. Gold, could also have been mobilized with chloride complexes that can occur in arid supergene environments (Reich and Vasconcelos 2015).

## CONCLUSIONS

In the San Roque project, a supergene alteration process has affected the upper portion of the epithermal mineralization, hosted in the polymictic orthobrecha epiclastic subfacies from the Marifil Volcanic Complex. The porosity and the permeability of the host rocks, together with the structural control with the presence of faults/fractures, facilitate the percolation of meteoric waters, and therefore, the supergene fluids flow. Rock heterogeneity between the mudstones and the coarser grained polymictic orthobreccia played a critical role in the development of the supergene mineralization. The veinlets, stockwork and, in a lesser extent, disseminated mineralization style of the hypogenic ore, with In-bearing-sphalerite and pyrite as the predominant sulfides, combined with the porosity and limited acid-buffering capacity of the polymictic orthobreccia, favored the percolation of slightly acidic, oxidizing and relatively V-rich meteoric waters and the subsequent oxidation process. Hematite and Fe-Mn-oxy-hydroxides predominate at the uppermost part of the deposit, whereas secondary minerals as mottramite and plumbojarosite are present in minor amounts. These supergene minerals concentrate metals of strategic economic importance such as In, Pb, Cu, V, Mo, which behaved immobile in this oxidizing environment.

The peculiar V concentration in the supergene zone in San Roque project was favored by their chemical-physical conditions, since V is highly mobile in oxidized and alkaline conditions. The V source is related with the Somún Curá Magmatic Province, especially with the Somuncurá Formation, therefore, vanadates in the San Roque project must have formed during or after early Oligocene.

Despite the perfect positive geochemical correlation between In and Au in the supergene zone represented in the studied drillholes and notwithstanding the fact that Au and/or electrum grains have been already identified in other locations of the San Roque project, they were not found in the studied samples of the supergene zones represented in both drillholes that intercepted Del Indio Structure. This absence may be related with the highly oxidizing environment that en-

hanced the liberation of Au microparticles and mobilized Au with chloride complexes common in arid supergenic systems.

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