REVISION 2

THE NATURE OF Zn-PHYLLOSILICATES IN THE NONSULFIDE MINA GRANDE
AND CRISTAL ZINC DEPOSITS (BONGARÁ DISTRICT, NORTHERN PERU): THE
TEM-HRTEM AND AEM PERSPECTIVE

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RUNNING TITLE: Zn-phyllosilicates in the nonsulfide deposits of Bongará (Peru)
Zn-phyllosilicates are common minerals in nonsulfide Zn deposits and can give crucial information on the genesis of these oxidized mineralizations. They seldom represent the prevailing economic species but might have a significant impact on mineral processing. This study has been carried out on the Mina Grande and Cristal Zn-sulfide/nonsulfide deposits, which occur in the Bongará district (Amazonas region, northern Peru). The Cristal and Mina Grande orebodies are hosted by the sedimentary (prevailingly carbonate) successions of the Pucará Group (Condorsinga formation, Lower Jurassic), in an area affected by Neogene tectonics and characterized by Late Miocene and Pliocene-Early Pleistocene uplift phases (Andean and Quechua tectonic pulses). The Cristal deposit consists of both sulfide (sphalerite with minor pyrite and galena) and nonsulfide concentrations. The nonsulfides consist of smithsonite, hemimorphite, hydrozincite, chalcophanite, goethite and greenockite, locally associated with Zn-bearing phyllosilicates. The Mina Grande deposit consists almost exclusively of Zn-oxidized minerals in limestone host rocks. The nonsulfides association consists of hydrozincite, hemimorphite, smithsonite, fraipontite and Fe-(hydr)oxides, also containing a clayey fraction. The study deals with TEM-HRTEM and AEM investigations on clayey materials, in order to determine their crystal-chemical features and the origin of the complex Zn-clays-bearing parageneses. In both deposits, Zn-bearing illites (1M₀ and 2M polytypes) and I/S clay minerals (I3) are the main detected phases, with few compositions close to (Zn-bearing) muscovite. In the clayey fraction at Mina Grande, fraipontite, a Zn-bearing mica called K-deficient hendricksite, and (Zn-bearing) kaolinite also occur. Zn-illites and smectites (always containing Zn in variable amounts) characterize the mineral association at Cristal. The investigated compositional gap between di- and tri-octahedral Zn-phyllosilicates gives indications on the genetic relationships between them and advances on the knowledge of these species. The present work gives an insight into the Zn-bearing phyllosilicates systems, by determining the amount/mode of metal
incorporation in their lattices and understanding the relationships of natural occurring clay-rich complex associations, which can act as models for possible synthetic counterparts.

**Keywords:** Zn-phyllosilicates; Bongará; Cristal; Mina Grande; Peru; TEM-HRTEM; AEM

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**INTRODUCTION**

Zn-phyllosilicates are quite rare minerals, which can be found in most nonsulfide Zn deposits. In this kind of ores, mainly derived from the weathering of primary sulfide concentrations, the Zn-clays generally represent minor concentrations in the mineral assemblage, but they can also be the prevailing economic minerals as in the world-famous Skorpion deposit in Namibia (Borg et al. 2003; Emselle et al. 2005; Kärner 2006; Boni and Mondillo 2015; Buatier et al. 2016; Choulet et al. 2016; Arfè et al. 2017; Balassone et al. 2017). Zn-clay minerals, formed in slightly acidic to neutral conditions, are also commonly found in contaminated soils at mining and smelting sites (Manceau et al. 2000; Juillot et al. 2003).

Sauconite (Ross 1946; Newman and Brown 1987), one of the most common clay minerals in nonsulfide deposits (Large 2001; Hitzman et al. 2003; Boni, 2005, 2009a,b; Mondillo et al. 2014; Boni and Mondillo 2015), is a trioctahedral saponite-like smectite with Zn in octahedral coordination. Experimental studies on its synthesis and stability (i.e., Kloprogge et al. 1999; Higashi et al. 2002; Petit et al. 2008; Pascua et al. 2010) demonstrated that sauconite can precipitate from solutions of silicic acid, variously mixed with Zn-compounds (Zn-chlorides, Zn-oxides, or Zn-hydroxides) and Na- and Al compounds, at a pH interval of 6–12 and temperatures ranging between 20 and 200 °C. Among the other Zn-phyllosilicates, the mineral fraipontite, belonging to the kaolinite-serpentine group and the serpentine subgroup (Fransolet and Bourguignon 1975), and baileychlore, a member of the chlorite group (Rule and Radke 1988), also occur in some nonsulfide
ore deposits. Recently, Mondillo et al. (2015) and Balassone et al. (2017) studied the Zn-
phyllosilicates from Accha and Yanque (Peru) and Skorpion (Namibia), respectively, by means of
transmission electron microscopy - high resolution TEM (TEM-HRTEM) analyses. Kaufhold et al.
(2015) characterized the Zn-bearing smectites from the Silver Coin Mine (USA). Buatier et al.
(2016) and Choulet et al. (2016) described Zn-clays consisting of interstratified fraipontite/smectite
(fraipontite-prevailing), closely associated to willemite ores in several nonsulfide Zn deposits from
the Moroccan High Atlas, formed by direct precipitation of meteoric and/or hydrothermal fluids.
Generally speaking, Zn-clays are not only an ore resource but also a drawback, because they can
negatively affect the industrial treatment to a various extent (Choulet et al. 2016, and references
therein). Hence, their detailed mineralogical study is particularly useful from the perspective of
industrial and economic evaluations.
Zn-phyllosilicates had been already detected in the Mina Grande and Cristal sulfide and nonsulfide
deposits, located in the Bongará area in northern Peru (Arfè et al. 2017a,b, 2018; Arfè 2018;
Mondillo et al. 2018a,b). In these mineralizations, sulfide minerals are mostly represented by
sphalerite and by minor galena and pyrite, weathered to a nonsulfide assemblage mostly consisting
of smithsonite, hemimorphite, and hydrozincite. Arfè et al. (2017b, 2018) and Arfè (2018) detected
variable amounts of different Zn-phyllosilicates in the complex mineral assemblages of the
Bongará mining district. A first detailed mineralogical identification of the Zn-rich clayey
assemblages of the Mina Grande and Cristal supergene deposits was carried out by Arfè et al.
(2017a) by combined scanning electron microscopy with energy dispersive X-ray spectroscopy
(SEM-EDS) and X-ray powder diffraction (XRPD). According to the latter work, the main sheet
silicates occurring in both deposits were considered I/S (illite/smectite) mixed layers, partly altered
or overprinted by sauconite. Fraipontite (the Zn-member of the kaolinite-serpentine group) has been
found only at Mina Grande, locally associated with minor zaccagnaite (a rare hydrated Zn-Al
carbonate, member of the hydrotalcite supergroup and quintinite group; Merlino et al. 2001; Lozano
et al. 2012; Mills et al. 2012), whereas a Zn(Mn) mica similar to hendricksite (a Zn-Mn trioctahedral potassic mica; Robert et al. 1985) was detected at Cristal.

However, due to the micro- to nano-sized nature of the Bongará phyllosilicates, as well as to the presence of diffuse impurities, typically consisting of Fe(Mn)-(hydr)oxides (i.e. goethite, chalcophanite, etc.), some questions still remained open, thus requiring a specific study of the clay fraction. The issues in need of a better clarification concerned: (i) a more accurate characterization of the widespread Zn-layered silicate varieties generically identified as Zn- micas (or illites), as well as of the I/S interstratified clay minerals, (ii) the ascertainment of hendricksite-type mica, (iii) the definition of the smectite(s) types and of other possible clays (or also other possible Zn- minerals), (iv) if the occurrence of fraipontite should be confined only to Mina Grande deposit.

In order to answer these questions and determine the true nature of the Zn- phyllosilicates, we have carried out detailed TEM and scanning TEM (STEM) and HRTEM investigations down to the nanoscale on the clay-rich fraction of a few selected samples already studied by Arfè et al. (2017a). This approach has allowed to analyze the purest mineralogical phases and has consequently helped resolving the issues above exposed. The present research was also aimed at identifying the processes accounting for the genesis of the Zn-phyllosilicates, with implications to their potential for zinc recovery.

**GEOLOGY AND MINERALIZATION OF THE BONGARÁ AREA**

Bongará is a province of the Amazonas Region in Peru, located approximately 740 km north of Lima and 245 km northeast of the coastal city of Chiclayo. It is situated on the western margin of the Subandean foreland basin of northern Peru, within the mountainous terrain of the Subandean fold-and-thrust belt (Fig. 1a) (Arfè et al. 2018). The geology of the northern Andes, where Bongará is located, underwent two important orogenic cycles (Benavides-Caceres 1999), i.e. the pre-Andean...
(Precambrian to Palaeozoic) and Andean (Early Jurassic to Present) cycles. The sedimentary Pucará Basin developed in correspondence of the current Eastern Cordillera, within a NW-trending sinistral shear zone (Mégard 1987; Benavides-Caceres 1999; Rosas et al. 2007). The basin started to be filled with up to 3000 m thick continental siliciclastics of the Mitu Group (Middle to Late Triassic) (Arfè et al. 2017a, 2018), which include red sandstones, mudstone, polymictic conglomerates and rare pyroclastic rocks (Fig. 1b). At the same time, it underwent a fault-controlled subsidence, which was gradually followed by a regional subsidence associated with NW to NNW-trending sinistral shear zone from Late Triassic to Early Jurassic (Mégard 1984; Benavides-Caceres 1999; Rosas et al. 2007). From Late Triassic to Early Jurassic, the sediments of the Pucará Group filled the basin with shallow-to deep-water marine carbonates, unconformably deposited over the sediments of the Mitu Group (Fontboté 1990; Reid 2001; Rosas et al. 2007). The Pucará Group Units are stratigraphically subdivided in basal Chambará Formation consisting of thinly bedded limestone and silty shale, overlying bituminous calcareous Aramachay Formation and uppermost Condorsinga Formation with its bioclastic and cherty limestone (Brophy et al., 2012). During Toarcian, a regional uplift promoted erosion and karstification of the top of the Condorsinga carbonates (Mondillo et al. 2018a), leading to the formation of cavities and depressions. As a consequence, the continental sequences of the Sarayaquillo Formation (Upper Jurassic to Cretaceous), which consist of red shales, sandstones and marls (Arfè et al. 2017b; Arfè 2018), were deposited in various colluvial, alluvial and lacustrine environments together with gypsum beds (Rosas et al. 2007) in angular unconformity above the Condorsinga Formation (Fontboté 1990; INGEMMET 1995). The lower Cretaceous in the Bongará area is characterized first by a major marine transgression, which led to the deposition of siliciclastic rocks of the Goyllarisquizga Group, and then of argillaceous limestones with nodular silty mudstones (Mondillo et al. 2018a) of the Chonta-Chulec Formation. The area of interest for this study has been affected by Neogene tectonics from 20.5 to 1.6 Ma,
characterized by Late Miocene and Pliocene-Early Pleistocene uplift phases, among which the Andean and Quechua tectonic pulses (Arfè et al. 2017a,b, 2018; Arfè 2018; Mondillo et al. 2018a).

The Pucará Basin includes many types of ores in central and northern Peru (Kobe 1977, 1982, 1990a,b; Dalheimer 1990; Fontboté 1990; Reid 2001), mainly corresponding to Mississippi Valley-type (MVT) Zn-Pb deposits. The most intensive exploration in the Bongará area was carried out in the Charlotte Bongará permit (which includes the Mina Grande and Cristal occurrences) in the north, and in the Florida Canyon permit, in the south. These deposits consist of stratabound Zn-Pb nonsulfide/sulfide concentrations (Wright 2010; Boni and Mondillo 2015). The formation of supergene nonsulfide mineralization is closely related to the tectonics of the area, which led to uplift, uncapping, weathering and alteration of several exhumed sulfide orebodies (Arfè et al. 2017b).

Mina Grande and Cristal are hosted by Mesozoic limestones and dolostones of the Condorsinga Formation. The Mina Grande deposit consists totally of nonsulfides, derived from the weathering of MVT ores. The mineralization contains supergene zinc minerals such as smithsonite, hemimorphite, hydrozincite but also of Zn-phyllosilicates. Mina Grande was partly mined in open-pit in three different areas (A, B and C Phases) and is currently under exploration. The Cristal deposit is a mixed sulfide and nonsulfide mineralization, with the latter resulting from alteration and dissolution of the sulfide protore. The presence of sulfides still in place at Cristal (Mondillo et al. 2018a) combined with the absence of any obvious recent karstic activity, suggests that supergene alteration acted in two different ways in the two respective localities (Arfè et al. 2018).

MATERIALS AND METHODS

The transmission electron and analytical electron microscopy (TEM-AEM) study was conducted on four samples (ZB-1, ZB-2, CR07-13, CR13-7) collected from the Mina Grande and Cristal
nonsulfide deposits (Fig. 2), during a field survey carried out in 2016. These (sub)samples come from drill cores and hand-specimens already mentioned in Arfè et al. (2017a). In order to select the richest clayey fractions of the samples for successive TEM-AEM investigations, preliminary mineralogical analyses were carried by combined X-ray powder diffraction (XRPD) and SEM-EDS at the Dipartimento di Scienze della Terra, dell’Ambiente e delle Risorse (DiSTAR) University of Naples Federico II, Italy (XRD equipment: Seifert–GE ID3003 diffractometer, with CuKα radiation, Ni-filtered at 40 kV and 30 mA, 3–80 °2θ range, step scan 0.02°, time 10 s/step, and Rayflex (GE) software package; SEM-EDS equipment: JEOL JSM5310 electron microscope with Oxford EDS, INCA X-stream pulse processor with 4.08 Inca software, operating conditions at of 15 kV and 20 mm working distance).

Textural observation of clays at the micro- and nanoscale and chemical analyses were performed on thin sections by combining TEM with high resolution transmission electron microscopy (HRTEM), scanning transmission electron microscopy (STEM) and high-angle annular dark field (HAADF) investigations, carried out at the Centro de Instrumentación Científica (CIC) of the University of Granada (Spain). Copper rings were attached to representative selected areas of the matrix of thin sections prepared with Canada balsam and after ion-thinned, using a Fischione Model 1050 ion mill, and carbon coated. Ion milling was performed at 4 kV and ±10°, until the first hole and ±7° during 20 min for final cleaning. We used a Titan TEM with XFEG emission gun, spherical aberration image corrector and HAADF detector, working at 300 kV, with a resolution of 0.8 Å in the TEM mode and 2 Å in the STEM mode. Qualitative vs. quantitative chemical identification of minerals and chemical maps were obtained by AEM-EDX (energy dispersive X-ray spectroscopy) analyses using the Super-X system. Quantitative analyses, presented in Tables 2-5, were obtained using albite, biotite, muscovite, spessartine, olivine, titanite, and hemimorphite as standards, measured using the same protocol as samples (Abad and Nieto 2003), to obtain K-factors for the transformation of intensity ratios to concentration ratios, according to Cliff and Lorimer (1975). In
order to avoid contamination problems (mainly due to widespread goethite and other oxy-
hydroxides), several chemical analyses were rejected, and only those as pure as possible have been
accepted. Electron diffraction patterns (selected area electron diffraction, SAED) were carried out,
whenever possible, in the same areas investigated by TEM-AEM. Additional investigations on
particle morphology and quantitative chemical analyses were obtained by using a TEM Philips
CM20 (CIC, Granada), operating at 200 kV, with an EDAX solid-state EDX detector. Lifetime of
the analyses was 100 s; areas producing dead time higher than 5% were rejected to ensure the thin
character required by the Cliff and Lorimer (1975) approximation. Analyses were obtained using
STEM mode, from powdered portions deposited on a holey C-coated Au grid. This mode of
preparation disperses individual grains of minerals onto the grid surface. Albite, biotite, muscovite,
spessartine, olivine, titanite, and hemimorphite standards were measured using the same protocol as
the samples.

Ideal chemical formulae of the main minerals quoted in this work are listed in Table 1.

RESULTS

The TEM-AEM study has pointed out that the main phyllosilicate detected in the clay-rich fractions
of the supergene assemblage of Bongará is being identified as illite, which always contains Zn
(±Fe,Mn) in variable amounts (Tables 2-5), hence corresponding to a Zn-bearing illite. These
chemical variations describe a particular outline and represent, in our opinion, a key point for the
definition of this kind of Zn-sheet silicates, as it will be discussed more in detail in the following
paragraphs. Taking into account that AEM allows determining the ratios between the various
elements, it is required to normalize the obtained chemical compositions to the basic formula of the
investigated minerals. Hence, on the basis of the composition of Zn-bearing illites, we have mainly
distinguished two varieties:
- Zn(Fe)-poor and Al\textsuperscript{VI}-rich varieties, in brief indicated hereafter as Zn-illites, and considered as diocahedral. Their structural formulas have been calculated on the basis of 6 (IV+VI) cations, as suggested by Nieto et al. (2010) for diocahedral species of illite;

- Zn(Fe)-rich and Al\textsuperscript{VI}-poor varieties, which we have considered as a mixture of diocahedral/trioctahedral species and abbreviated to MDT Zn-illites hereafter (see also Discussion). For these mixed compositions, the structural formulas have been recalculated on the basis of 11 oxygens.

Other significant Zn-bearing mineral/associations have been detected in minor to trace amounts in the two sampled occurrences (Mina Grande and Cristal), and are described in the following paragraphs.

**Mina Grande**

Tables 2 and 3 show representative AEM analyses of Zn-illite and MDT Zn-illite in the Mina Grande samples (ZB-1 and ZB-2), with the second variety definitely prevailing over the first one.

Zn-illite shows the tetrahedral cations in the range 3.06-3.14 apfu for Si (average, av. hereafter, equal to 3.10 apfu) and 0.86-0.94 apfu for Al\textsuperscript{IV} (av. 0.90 apfu); regarding the octahedral cations, Zn is in the interval 0.31-0.40 apfu (av. 0.36 apfu), Mg 0.19-0.26 apfu (av. 0.23 apfu), Fe 0-0.01 apfu (av. 0.01), Ti 0-0.03 apfu (av. 0.02 apfu), whereas Al\textsuperscript{VI} is in the range 1.31-1.49 apfu (av. 1.40 apfu). The interlayer cation K varies in the range 0.70-0.75 apfu (av. 0.73 apfu). Fig. 3a shows a common texture of Zn-illite, often associated with fraipontite mainly occurring as cavity fillings. The SAED-HRTEM investigations (Fig. 3b) demonstrate that illite is characterized by lattice fringes and 00l spots in the SAED with d-spacings always around 10 Å. The rest of the rows (non-00l) in the SAED, which could allow the identification of the mica polytypes, are represented by continuous lines, indicating a disordered polytype 1\textit{M}\textsubscript{d}. The lattice fringe images of Fig. 3c show misorientation among the packets, typical of illite. The various packets have different
crystallographic orientation, at less [100] and [110] zone axis have been identified from partial
periodicity which can be recognized along some layers and allows identification of very local order,
corresponding to 1M polytype of illite. In the FFT of the image 3c (inset), together with those
orientations, also [010] can be identified. The misorientation among the various packets is
responsible of the disordered character of the polytype identified for the whole area in the SAED.
However, in the same image the textures can be interpreted as belonging to illite/smectite mixed
layers (I/S) of I3 type, due to the minor presence of smectite layers, characterized by different
contrast and spacing (12 Å), separated by at less 3 illite layers. Smectite layers collapse variably
between 17 and 10 Å, being the latter their most frequent value, in the vacuum of the microscope,
principally depending on their local interlayer composition. Periodicity of 52 Å
(4 illite layers + 1 smectite layer) can be also identified in the FFT. Fig. 3e shows a chemical map
of a Zn-illite (+fraipontite, Fe,Ti-oxy-hydroxides) area and its typical EDX spectrum, with the small
but always present peak of Zn.
Compositions referred as to MDT Zn-illite (Tables 2 and 3) show the tetrahedral cations in the
range 2.57-3.17 apfu for Si (av. 2.90 apfu) and 0.83-1.43 apfu for AlIV (av. 1.10 apfu); in the
octahedral site, Zn is in the interval 0.29-1.44 apfu (av. 0.77 apfu), Mg 0.15-0.46 apfu (av. 0.26
apfu), Fe up to 0.81 apfu (av. 0.37 apfu), Ti up to 0.52 apfu (av. 0.20 apfu) and AlVI is in the range
0.43-1.42 apfu (av. 0.92 apfu), whereas K is in the interval 0.48-0.90 apfu (av. 0.62 apfu). Fig. 4a
shows a textural image of an area of sample ZB-1 particularly rich in MDT Zn-illite; its electron
diffraction pattern is shown in the bottom-right inset of Fig. 4a, and represents rows with spacings
of 10 Å. Figs. 4b,c,d,e also shows the association of MDT Zn-illite with fraipontite and Fe,Ti,Mn-

1 The notation I3 refers to the nomenclature for interstratifications as reported by Vázquez et al. (2016) and Bauluz et
al. (2000). Indeed, according to these authors, ordering in interstratified I/S, ordinarily characterized by its Reichweite
value (R) based on X-ray diffraction data, representing long-range ordering averaged over all the layers that scatter X-
radiation; TEM images can identify short-range ordering of interlayers within I/S packets, and the Reichweite
nomenclature results inappropriate for specific layer sequences as observed by TEM. Hence the notation I,n, analogous
to the Reichweite nomenclature, can be employed but applied only to specific layers, where n is the number of illite-like
layers associated with a given smectite-like (see Vázquez et al. 2016, and references therein, for further details).
oxy-hydroxides. The 1:1 phyllosilicate is often in individual recognizable crystals significantly bigger than those of micas, reaching a maximum length of 3 μm.

Fig. 5 shows a remarkable feature involving these Zn-layered silicates and observed in an area of approximately 1 μm². Figs. 5a and 5b, respectively, illustrate a textural image and the related chemical map of sample ZB-2, where illites show variable amounts of Zn in the packets; here they occur with fraipontite and subordinate kaolinite and Fe-Ti-oxides. If the AEM map of Fig. 5b is compared with the chemical mappings of selected elements of Fig. 5c, the illite-rich area is significantly well-defined by the K map and displays a complex textural organization. Indeed, in this zone, while K is homogeneously distributed, Zn is highly heterogeneous, resulting in fine intergrowths between MDT Zn-illite, with 1.28 apfu of Zn (see analysis. # 3.cuan-MAP1 of Table 3, and EDX spectrum 2 of Fig. 5d), and Zn-illite, with 0.31 apfu of zinc (see analysis # 6.cuan, Table 3, and EDX spectrum 1 of Fig. 5d). The inference of this particular compositional and textural organization, relevant to the origin of Zn-phyllosilicates, will be discussed more in detail in the section "Discussion". High resolution TEM investigation of this zinc illite (inset in Fig. 5) illustrates stacking of 10 Å periodicity, which is in agreement with this type of sheet silicate.

Another second distinctive finding in the Mina Grande samples is a well-defined Zn-mica (illustrated in Tables 2, 3 and Fig. 6), having an octahedral population with Zn in the range 1.55-1.89 apfu (av. 1.66 apfu), Fe 0.13-0.20 apfu (av. 0.15 apfu) and Mg up to 0.14 apfu (av. 0.15 apfu), (Tables 2 and 3); Si is the range 2.87-2.92 apfu (av. 2.89 apfu) and AlIV 1.08-1.13 apfu (av. 1.11 apfu), whereas K shows an interval of 0.57-0.70 apfu (av. 0.64 apfu) (Tables 2 and 3). In accordance with the guidelines reported in the classification of micas (Rieder et al. 1998), hendricksite is characterized by Zn>1.5 apfu and K<1. Hence the Zn-mica detected here can be defined as hendricksite, even if this mica typically shows an “illitic” character (lower K amounts, presence of AlIV). For this reason, we named it K-deficient hendricksite. Fig. 6 shows Zn-phyllosilicates dispersed particles in sample ZB-2, composed of K-deficient hendricksite, Zn-illite...
and fraipontite, with the qualitative chemical spectra of selected areas of the zinc mica and serpentine.

Fraipontite was detected in the Mina Grande samples. Fig. 3d shows stacking of 7 Å periodicity, typical of this Zn phyllosilicate. Fig. 4c illustrates an association of fraipontite and MDT Zn-illite at the nanoscale; the electron diffraction pattern in the inset suggests an epitaxial or topotaxial relationship between the two minerals, as they share the c* parameter. Due to the paragenetic relations between these 2:1 and 1:1 phyllosilicates, it is reasonable to assume that fraipontite grew onto illite. Chemical compositions of fraipontite (Tables 2 and 3) show tetrahedral cations within a range of 1.08-1.40 apfu for Si (av. 1.23 apfu) and 0.60-0.92 apfu for AlIV (av. 0.76 apfu); the octahedral cations range from 2.19 to 2.96 apfu for Zn (av. 2.54 apfu), from 0.34-0.68 apfu for AlVI (av. 0.50 apfu) and from 0.04 to 0.14 apfu for Fe (av. 0.10 apfu).

Kaolinite was detected in very subordinate amounts only in sample ZB-2 (Table 3). In the tetrahedral site Si is in the range of 2.00-2.10 apfu (av. 2.05 apfu), whereas the octahedral population is composed of 1.44-1.66 apfu AlVI (av. 1.54 apfu), as well as of small amounts of Mg (0.13 apfu) and Zn (0.12-0.70 apfu, av. 0.14 apfu).

Finally, Fig. 7a and 7b respectively show HAADF and chemical mapping of an area of sample ZB-2 where tiny cavity-lining and tapering crystals of supposed zaccagnaite can be observed together with Zn-illite, fraipontite and oxides (Table 1). These crystals are Zn-rich and appear morphologically slightly different from fraipontite crystals; the EDX spectrum displays high Zn, C and O peaks, compatible with a zinc carbonate, whereas the chemical map of Si indicates the virtual absence of this element in the areas of possible zaccagnaite occurrence. Even though smithsonite/hydrozincite could also be a reasonable option, the occurrence of zaccagnaite in the Mina Grande samples has been already proved by Arfè et al. (2017a). Because of the nano-sized dimension of these crystals and the close association with fraipontite, it was impossible to obtain chemical analyses and SAED-HRTEM images for validating this phase.
Similarly to Mina Grande, also in the Cristal samples CR07-13 and CR13-7 (Fig. 2) illites, both Zn- and MDT Zn-illites, are always the prevailing minerals detected in the supergene assemblage. Here the varieties referred as Zn-illite prevail over the MDT types (Tables 4 and 5), if compared with Mina Grande. Furthermore, differently from Mina Grande, and in agreement with Arfè (2018), K-deficient hendricksite and fraipontite have been not detected, at least in the investigated samples.

In the Cristal Zn-illites (Tables 4 and 5), the tetrahedral cations are in the range 3.18-3.66 apfu for Si (av. 3.36 apfu) and 0.42-0.82 apfu for Al\textsuperscript{IV} (av. 0.64 apfu); in the octahedral site, Zn is in the interval of 0.04-0.27 apfu (av. 0.10 apfu), Mg 0.16-0.32 apfu (av. 0.29 apfu), Fe up to 0.21 apfu (av. 0.11), whereas Al\textsuperscript{VI} is in the range 1.41-1.11 apfu (av. 1.50 apfu). Regarding the interlayer cation K, it varies in a range of 0.34-0.72 apfu (av. 0.61 apfu). As illustrated in Tables and 5, few values of K indicate compositions close to a (Zn-bearing) muscovite, rather than illite. In particular, if we consider three analyses of sample CR07-13 (Table 4, # anl. 5, anl. 11 and 1.cuan-MAP2) and two analyses of sample CR13-7 (Table 5, # 3.cuan-MAP4 and 11.cuan-MAP5) in relation to the ideal muscovite formula established by Rieder et al. (1998), these compositions fulfill the condition of the interlayer cation (K) amounts in the range 0.7-1.0 apfu (or $I \geq 0.85$ apfu), as well as the condition of Si = 3.0-3.1 apfu in the majority of cases; however, the $\text{VI}_{\text{Al}}$ values of these analyses do not fully satisfy the standard muscovite ranges reported by Rieder et al. (1998) (1.9-2.0 apfu), and also most of the calculated $\text{VI}_{\text{R}^2+}/(\text{VI}_{\text{R}^2+} + \text{VI}_{\text{R}^3+})$ ratios are slightly higher (0.30 apfu on average) than the muscovite range (i.e. <0.25 apfu). These Zn-bearing muscovites show the following ranges: Si 2.89-3.39 apfu (av. 3.19 apfu) and Al\textsuperscript{IV} 0.61-1.811 apfu (av. 0.81 apfu), with Al\textsuperscript{VI} 0.90-1.66 (av. 1.50 apfu), Zn 0.07-0.15 apfu (av. 0.11 apfu), Mg 0-0.29 apfu (av. 0.18 apfu), Fe up to 0.84 apfu (av. 0.29) and Mn 0-0.65 apfu (av. 0.12 apfu) in the octahedral site. The interlayer cation K is in the range 0.81-1.07 apfu (av. 0.95 apfu).
Fig. 8 shows the chemical mapping of Zn-illite, which can contain differently Zn-enriched packets varying from Zn of 0.04 apfu (see analysis # 3.cuan-MAP1 of Table 4 and EDX spectrum 1 of Fig. 8c) to Zn equal to 0.21 apfu (see analysis # 1.cuan-MAP1 of Table 4 and EDX spectrum 2 of Fig. 8c). The SAED-HRTEM investigation is reported in Fig. 8b, where rows with stacking of 10 Å periodicity can be observed.

Subordinate MDT Zn-illite (Tables 4 and 5) shows the tetrahedral cations in the range 2.67-2.93 apfu for Si (av. 2.78 apfu) and 1.07-1.33 apfu for Al\textsuperscript{IV} (av. 1.22 apfu); the octahedral cations vary from 0.51-0.60 apfu for Al\textsuperscript{VI} (av. 0.54 apfu), 0.39-0.86 apfu for Zn (av. 0.65 apfu), 0.28-0.98 apfu for Mn (av. 0.72 apfu), 0.60-1.07 apfu for Fe (av. 0.86 apfu) and up to 0.26 apfu for Mg (av. 0.09 apfu). Compared with the same varieties detected at Mina Grande, these illites are Mn-bearing and Ti-free. Due to the rarity of MDT type, it was not possible to find suitable crystalline particles for recording their lattice fringes images and/or electron diffraction patterns of acceptable quality.

Fig. 9a and 9b show typical textural images of the Zn-illite at Cristal. The top right inset of Fig. 9a shows the electron diffraction pattern with differences of orientation among the various packets; rows with periodicity of 14 Å can be due to smectite. In the right inset of Fig. 9b, the less visible row corresponds to [100] (20 Å, 2\textit{M} polytype), and the more visible to [010]. Diffraction points corresponding to (h0l) have systematic extinctions for \textit{l} odd, therefore they do not allow the polytype identification. The left inset of Fig. 9b also illustrates the SAED pattern of a disordered polytype (1\textit{M}\textsubscript{d}). Fig. 9c and 9d respectively illustrate lattice image of packets with I/S mixed layers having minor proportion of smectite layers (I3) and slightly disoriented packets, typical of illite.

Fig. 10 illustrates another characteristic of the zinc phyllosilicates at Cristal; here smectite occur both as nanoscale interleaved (Fig. 10a) phase with Zn-illite and in larger particles (Fig. 10b); high resolution TEM images show that the small packets are internally ordered with stacking of 10 Å (Zn-illite) and 13 Å (slightly collapsed smectite) periodicities. Smectites detected in the Cristal samples correspond to beidellite, which always contain small amounts of Zn (0.02 apfu) and
sauconite (see the EDX spectra of Fig. 10 and Table 5). As shown in Fig. 10b, sauconite seems also
to replace zinc illite. Finally, a composition attributable to montmorillonite, with small but
detectable Zn amount (0.14 apfu) was also locally found (Fig. 10a and Table 5).

**Overall crystal-chemical features of the Bongará phyllosilicates**

Bivariate diagrams of selected elements of the detected phyllosilicates are reported in Fig. 11. In the
Al_{tot} vs. Si diagram (Fig. 11a), zinc illites are generally enriched in these elements compared with
MDT Zn-illites, even though some Si-depleted compositions fall in the field of the latter illites. K-
deficient hendricksite entirely plots in the area of MDT Zn-illite, being indistinguishable from these
illites in terms of Si and Al_{tot} contents. Fraipontites cluster in a well-constrained field, as well as
kaolinites. Sauconite compositions are characterized by variable Si and Al amounts, as already
observed by Mondillo et al. (2015) and to a lesser extent by Balassone et al. (2017), and possibly
attributable, at least in part, to interstratifications with illite layers.

The Zn vs. Al VI plot (Fig. 11b) shows a positive correlation of EDX data, illustrating a distinction
between dioctahedral and trioctahedral species; MDT Zn-illite compositions fall in a quite wide
area, placed between the Zn-illite and the K-deficient hendricksite fields. MDT Zn-illite is variable
in term of both Zn and Al VI, whereas Zn-illites show an evident chemical variability mainly in term
of Al VI content. Hendricksite is better constrained if compared with the diagram of Fig. 11a (even
though only three compositions were measured at Mina Grande). Obviously, fraipontite/sauconite
and kaolinite/beidellite/montmorillonite occupy the opposite sides of trioctahedral and dioctahedral
compositional fields, respectively.

Fig. 11c illustrates the Zn vs. K diagram, which shows a similar trend as the previous plot; the
dioctahedral and trioctahedral compositions fall in well-defined fields, with MDT Zn-illite
compositions scattered between the Zn-illite and the K-deficient hendricksite fields. The major
chemical variability of Zn-illite is related to the K cation, differently from MDT Zn-illite
compositions, which are more variable in terms of both Zn and K contents. Indeed, while in bivariate plots of Fig. 11a and 11b compositions approaching muscovite cannot be distinguished from the other Zn-illites, in the diagram of Fig. 11c mica-related compositions are obviously better constrained, due to their higher K amounts. Dioctahedral smectites plot in the Zn, K-poor side.

In the $M^+\cdot4Si-3R^{2+}$ ternary diagram (Fig. 12a), used for discriminating the dioctahedral and the trioctahedral compositions (Meunier 2005), our Zn-illites are scattered along the mixing line of muscovite-sauconite-fraipontite ideal compositions and rather plot into an intermediate domain between the muscovite and sauconite poles. As illustrated in Tables 4 and 5, some compositions more correctly plot close to muscovite end-member, whereas other Zn-illites, as well as MDT Zn-illites are more scattered, indicating that clays are generally mixed compositions. In this plot, K-deficient hendricksite also plots along the muscovite-sauconite join and into the MDT Zn-illite field, in slightly different position if compared with the ideal hendricksite. Fraipontite plots very close to the theoretical compound, whereas other clay minerals, i.e. smectites and kaolinite, are more scattered due to their chemical variability (i.e. Zn in kaolinite).

In the K-Zn-Al$_{VI}$ ternary diagram of Fig. 12b all Zn-illites plot into an intermediate area between ideal muscovite and K-deficient hendricksite; Zn-illite, MDT Zn-illites and K-deficient hendricksite occupy three different domains, fairly well-defined but continuous, indicating that zinc clays are dominantly a mixture of two end-members sensu lato approaching theoretical muscovite and hendricksite, that we have considered to be respectively Zn-illite and K-deficient hendricksite (see the next paragraph). As might be expected, compositions close to (Zn)muscovite plot in a better defined, K-rich, area. Fraipontite again plots in a restricted field, confirming its homogenous composition, as well as smectites (both dioctahedral and trioctahedral), even if based on few point-analyses.

**DISCUSSION**
Mineral identification

Guggenheim et al. (2006) listed illite as a dioctahedral species in the interlayer-deficient mica group. However, following the proposal by Rieder et al. (1998), Guggenheim et al. (2007) subsequently considered illite to be only a series name. Besides showing a variety of chemical compositions, many illite samples are essentially mixed-layer structures, with smectite usually making up the other component although the presence of interstratified smectite layers is difficult to detect when their proportion is less than 10%. The chemical composition of illite has been extensively studied by many authors (i.e. Środon and Eberl 1984; Brigatti and Guggenheim 2002; Meunier and Velde 2004; Meunier 2005; Nieto et al. 2010; Escamilla-Roa et al., 2016), and according to the International Mineralogical Association (IMA) nomenclature committee the term illite should be used to designate interlayer-cation-deficient (<0.85 apfu) micas (Rieder et al. 1998). Then, following the nomenclature suggested by Rieder et al. (1998), illite has a general formula $K_{0.65}Al_{2.0}\square Al_{0.65}Si_{3.35}O_{10}(OH)_2$, with $\frac{\text{VI}R^{2+}}{\text{VI}R^{2+} + \text{VI}R^{3+}} \leq 0.25$, and can refer to a relatively large volume in compositional space, as a counterpart to glauconite. To summarize, we established that the Zn-illite investigated in the present study, and often reported by Arfè et al. (2017a,b) simply as Zn-mica, is very similar to illite *sensu* Reider et al. (1998); its mean formula can be expressed as:

$$K_{0.67}(Al_{1.45}Ti_{0.01}Mg_{0.26}Fe_{0.06}Zn_{0.22})_2(Si_{3.3}Al_{0.7})_4O_{10}(OH)_2\cdot nH_2O$$

The occurrence of Mg and Fe is a common characteristic for illite, but, if we compare the theoretical formula of illite with this case of study, the remarkable aspect is that its packets also show variable Zn concentration (e.g. Fig. 8). In the ordered illite polytype (mainly observed at Cristal), the apparent disorder is only due to the small dimension of the packets with different orientation and does not reside in the packet itself, as normally observed in illite. At Mina Grande, instead, a true disordered polytype ($1M_4$) has been found. Besides, the minor occurrence of smectite...
layers, attributable to R3 type I/S mixed layers, has also been observed in the investigated samples (Figs. 3 and 9). Compositions ascribed to Zn-bearing muscovite, found in the Cristal samples only, can be expressed by the average formula $K_{0.95}(Al_{1.30}Mg_{0.18}Fe_{0.29}Mn_{0.12}Zn_{0.11})_2(Si_{3.19}Al_{0.81})_4O_{10}(OH)_2\cdot nH_2O$.

Many mixed compositions between Zn-illite and K-deficient hendricksite, i.e. MDT Zn-illites, are recognized in this study. K-deficient hendricksite has the following average empirical formula:

$K_{0.64}(Al_{0.86}Mg_{0.15}Fe_{0.15}Zn_{1.66})_2.82(Si_{2.89}Al_{1.11})_4O_{10}(OH)_2$.

From the TEM study, this mica appears to be Mn-free, differently from Arfè et al. (2017a,b) and Mondillo et al. (2018a), who found Mn in some Zn-micas from Cristal. Considering that when studying these assemblages at a finer scale (TEM-HRTEM), the mica particles, as well as other zinc silicates, appeared to be often pervaded by Fe(Mn)-(hydr)oxides (Fig. 13), it is possible that previous EDS-WDS analyses could have been carried out on micas with very fine intergrowths of Fe- and Mn-(hydr)oxides. The simple fact that we found a hendricksitic mica at Mina Grande only and not at Cristal, contrary to Arfè et al. (2017a,b) and Mondillo et al. (2018a), can be also due to either a heterogeneous nature of the samples or to an intrinsic limit of the sample selection for TEM analyses, which investigated a restricted area in each specimen.

In this study, fraipontite was detected at Mina Grande only, in agreement with Arfè et al. (2017a,b), and has the following empirical formula obtained by AEM study:

$(Zn_{2.54}Fe_{0.10}Al_{0.50})_3.14(Si_{1.24}Al_{0.76})_2O_5(OH)_4$.

Fraipontite commonly occurs in pore spaces and as well-crystallized individuals with dimension in the range 0.2-3 μm, free of inclusions of other minerals (e.g. Figs. 3 and 4). This rare Zn-clay also
crystallized onto the illite surface; indeed, sometimes these two minerals are also in epitaxial/topotaxial relation, with illite acting as a template for the zinc serpentine (Fig. 4c). Contrary to the fraipontite-bearing nonsulfide zinc deposit of Bou Arhous in Morocco (Choulet et al., 2016), at Mina Grande interstratified fraipontite/sauconite minerals were not detected in the fraipontite-rich fractions.

Rare trioctahedral and dioctahedral smectites were also found in the Cristal clay fractions. Sauconite has been found in this location in agreement with the findings of Arfè et al. (2018), who described this smectite as mica replacement, as well as occurring in vugs and fracture fillings; its average composition is:

\[ \text{K}_{0.28}(\text{Zn}_{2.34}\text{Mg}_{0.12}\text{Fe}_{0.07}\text{Mn}_{0.33})_3.02(\text{Si}_{3.38}\text{Al}_{0.62})_4\text{O}_{10}(\text{OH})_2\cdot n\text{H}_2\text{O}. \]

The average composition of the Accha and Yanque sauconite (Mondillo et al. 2015) is

\[ (\text{Ca}_{0.15}\text{K}_{0.05})_{0.20}(\text{Zn}_{2.10}\text{Mg}_{0.26}\text{Al}_{0.40}\text{Fe}_{0.15}\text{Mn}_{0.02})_{2.87}(\text{Si}_{3.5}\text{Al}_{0.5})_4\text{O}_{10}(\text{OH})_2\cdot n\text{H}_2\text{O}. \]

Compared with the latter occurrences, K is the only interlayer cation in the Cristal sauconite, and is also richer in Zn and Mn and poorer in Al**VI** and Mg.

Together with sauconite, already reported by Arfè et al. (2017a,b, 2018) and Arfè (2018), the first recorded occurrence of beidellite can be observed in the same location, always with a small Zn amount (0.02 apfu). This clay has the following average formula:

\[ \text{K}_{0.19}(\text{Al}_{1.81}\text{Mg}_{0.24}\text{Zn}_{0.02})_{2.07}(\text{Si}_{3.7}\text{Al}_{0.3})_4\text{O}_{10}(\text{OH})_2\cdot n\text{H}_2\text{O}. \]

If compared with the composition of the Zn-bearing beidellites found in the Accha and Yanque nonsulfide zinc ore deposits (Mondillo et al. 2015), i.e.

\[ (\text{Ca}_{0.05}\text{K}_{0.15})_{0.20}(\text{Al}_{1.6}\text{Zn}_{0.25}\text{Mg}_{0.1}\text{Fe}_{0.15})_{2.1}(\text{Si}_{3.6}\text{Al}_{0.4})_4\text{O}_{10}(\text{OH})_2\cdot n\text{H}_2\text{O}, \]

the Cristal beidellite shows...
interlayer cation only represented by K, lower Zn, higher Mg contents and lacking of Fe. Moreover, also a Zn-bearing montmorillonite (0.14 apfu of Zn) occurs at Cristal, perfectly in line with what was observed in all the Bongará layered silicates. Finally, the kaolinite of Mina Grande has an average formula (Al$_{1.54}$Zn$_{0.41}$Mg$_{0.13}$)$_{2.08}$Si$_{2.05}$O$_{5}$(OH) and shows K in trace amount (0.13 apfu), which indicates minor contamination by surrounding illite in the investigated site and explains the anomalous octahedral and tetrahedral sums found.

The compositional gap between di- and trioctahedral Zn-phyllosilicates

The first major division in the classification of phyllosilicates is between their dioctahedral and trioctahedral varieties. This is due to the different structural configurations of their respective octahedral layers, with concomitant effects on the corresponding linked tetrahedral layers. In the trioctahedral ones, divalent cations (typically Mg and Fe$^{2+}$) occupy the three possible positions, accounting for a total charge of 2x3 = 6. On the other hand, in the dioctahedral ones, trivalent cations (generally Al, but also frequently Fe$^{3+}$) occupy only two positions, giving 3x2 = 6 charges. Due to their greater charge, trivalent cations strongly attract anions, producing a smaller octahedron than the divalent ones in the trioctahedral structures, and, certainly smaller than the vacant positions in dioctahedral ones. Therefore, the general structure of the two kinds of layers is significantly different, with three roughly similar octahedrons in the trioctahedral layers, in opposition to two smaller ones and one big irregular position (usually named the M1 site) in the dioctahedral structures (Moore and Reynolds 1997).

As a result, the phyllosilicates always correspond to one of the two types of structures, with a consequential compositional gap between both of them, with a very limited possibility of a solid solution. Therefore, phyllosilicates which have an intermediate composition are rare in nature. The cases of midway chemistry are solved by the existence of nanodomains, as the case of smectites, which appear continuous at the clay particle scale, but are made of associated different lattices or
clusters at a finer scale, producing a wide miscibility gap (Grauby et al. 1993; Yamada et al. 1999), or in alternation of the two types of layers, as in sudoite or the limited occurrence of di-trioctahedral interstratified minerals. Therefore, due to the structural constrains, at the unit cell level, a phyllosilicate is either dioctahedral or trioctahedral.

In this context, the compositional maps in Fig. 5b and 5c can be considered a graphic representation of the compositional gap between dioctahedral and trioctahedral 2:1 phyllosilicates for the case of Zn varieties. In the phyllosilicates, due to their crystal-chemical characteristics, atomic radio and charge, Zn plays a similar role to Mg and Fe$^{2+}$. Therefore, as a major element it tends to form trioctahedral phyllosilicates, similar to Mg in phlogopite, saponite, serpentines or tri-chlorites. These would be the equivalent cases of hendricksite, sauconite, fraipontite or baileychlore. However, Mg and Fe (together with other divalent cations, e.g. Mn) can also enter in minor proportion in the typical Al dioctahedral phyllosilicates as muscovite-illite, montmorillonite-beidellite or kaolinite. In a similar way, Zn has been detected in this study in all the aforementioned cases (note that the only exception is baileychlore, which does not occur at Bongará). Zn-bearing varieties of illite (muscovite), beidellite, kaolinite and montmorillonite, have been found together with their trioctahedral counterparts, i.e. K-deficient hendricksite, fraipontite and sauconite, in which Zn is the major or the quite unique octahedral cation.

A special consideration needs the case of illite/micas, which are the major constituents of the studied samples. The Cristal and Mina Grande samples mainly consist of Zn-illites. Since they have been formed in a low-temperature environment, these mica-like compositions are genetically conditioned to form as their low-temperature variety, hence to crystallize as illite (Merriman and Peacor 1999; Vázquez et al 2016). Nevertheless, the composition of the fluid from which the micas were grown should have had a Zn content greater than the amount acceptable by the crystal chemistry of dioctahedral illite/mica. Due to the compositional gap between zinc dioctahedral and trioctahedral phyllosilicates, the resultant product was an extremely fine intergrowth of the two
varieties: a Zn-illite and its trioctahedral equivalent, i.e. K-deficient hendricksite with Zn as the major octahedral cation. As pointed out by the AEM study, most of the obtained analyses have been unable to resolve the intergrowth, due to its nano-sized nature, under the 20 nm scale (Fig. 5a), resulting in many mixed compositions, i.e. the so-called MDT Zn-illite, as shown in the bivariate plots of Fig. 11 and in the ternary diagrams of Fig. 12. However, the high spatial capabilities of the modern TEMs have allowed obtaining in some limited areas detailed chemical information (as shown in Fig. 5b and 5c), able to reveal the dual nature of the intergrowths (Fig. 5d).

The trioctahedral Zn-rich limb of the gap for the low-temperature micas (illite) is difficult to classify due to the lack of previously described equivalents. It shares with hendricksite the major component and the trioctahedral nature. Usually, hendricksite contains also a high quantity of Mn (Robert and Gaspérin 1985; Sharygin 2015), but according to the IMA classification of micas (Rieder et al. 1998), this characteristic is not a limiting condition for its classification. Our analyses fulfill the condition of Zn>1.5 apfu, hence the mineral with the studied composition could be considered as hendricksite, but this is not considered one of the K-deficient micas in the IMA classification. Indeed, according to Rieder et al. (1998), the trioctahedral phyllosilicate corresponding to an interlayer-deficient mica is named wonesite, which has a formula Na$_{0.5}$Mg$_{2.5}$Al$_{0.5}$AlSi$_3$O$_{10}$(OH)$_2$; in the IMA database, the chemical formula of this mineral is reported as (Na,K,☐)(Mg,Fe,Al)$_6$(Si,Al)$_8$O$_{20}$(OH,F)$_4$. The term wonesite is used in the sense of trioctahedral equivalent of illite in the clay literature although, admittedly, following Rieder et al. (1998), it appears as a Na, instead of K, variety. In conclusion, we have indicated the trioctahedral Zn-equivalent of illite as a K-deficient hendricksite. Alternatively, a valid name could be Zn(K)-wonesite, even though a proper term was not predicted in the IMA classification as, to our knowledge, this phase had not been previously described in literature.

Origin of the Bongará Zn-phyllosilicates assemblage
Illite is a widespread mica-related clay mineral, uncommon as a surface-derived weathering product, generally formed diagenetically from other clay minerals, such as smectite and kaolinite at temperatures higher than 70 °C (Einsele 2000). According to Meunier (2005), the range of physical conditions for illite formation are from 20 °C, in surface soil conditions, to below 300 °C, under diagenetic or hydrothermal environments. During diagenesis, with increasing burial, the degree of crystallinity of illite increases, leading to more stable structures. Most studies on illitization report that, as I/S interstratified clays become illitic, the interlayer arrangements change from random (R0) to short-range (R1) ordered, and then to long-range (R3) ordered (e.g. Nieto et al. 1996; Vázquez et al. 2014, and references therein). This occurs at temperatures from 75 to 120 °C. The transition from R1- to R3-ordered I/S occurs up to 175 °C, or in other cases at also higher T (Vázquez et al. 2014, and references therein).

In the context of nonsulfide Zn(Pb) ores, the zinc-rich clays are frequently detected in supergene deposits, although few studies have provided a clear identification of their nature. In addition, the origin of zinc clays and their place within the ore evolution remain poorly understood (Choulet et al. 2016).

The AEM study and the TEM-HRTEM textural evidences of the studied samples suggest that Zn-bearing illite, together with the I3 I/S detected both at Cristal and Mina Grande, could be deposited from a Zn-bearing fluid in a temperature range of 170-200 °C. Considering that Mondillo et al. (2018a), using the mineral geothermometer GGIMFis and the trace element data in sphalerite from the Cristal prospect calculated a possible precipitation temperature (TGGIMFis) of 225±50 °C (slightly higher than in the genesis of typical MVT deposits; Paradis et al., 2007), the studied Zn-illite could have formed during (and/or just after) sulfide precipitation; these TOT sheet silicates hosted Zn$^{2+}$ cations in the octahedral site to various degrees, up to hendricksite-like mineral. Regarding Mina Grande, Arfè et al. (2017b) hypothesized that both a Zn-bearing mica and fraipontite could have formed during the hydrothermal alteration of siltstone or sandstone.
interbedded within the host limestone, in association with the emplacement of sulfides. The
evidences obtained in this study seem to support this genetic model.

Regarding fraipontite, its textural arrangement observed by means of TEM-HRTEM suggests that
this mineral occurs as a newly formed phase from direct precipitation from Zn(Si,Al)-rich fluids
(possibly low temperature hydrothermal), likely at expense of Zn-bearing illite. According to recent
studies (i.e. Arfè et al. 2017a; Buatier et al. 2016; Choulet et al. 2016), this TO clay mineral may
have formed either during the hydrothermal process that generated the Zn sulfides, or in the early
stages of supergene alteration, which took place under acidic conditions associated with the
alteration of sulfides. In both cases, when the buffering of the carbonate host rock turned the
environment from acidic to alkaline (pH>7), the fraipontite became unstable and zaccagnaite started
to form at its expenses. Arfè et al. (2017a) described by XRD analysis the occurrence of the 3R-
polytype zaccagnaite at Mina Grande; they inferred that this particular fraipontite-zaccagnite
association could suggest an origin related to weathering processes. However, the present study was
not able to definitively confirm or reject this inference about the nature of zaccagnaite and of its
origin from a crystal-chemical point of view, because of the tiny size and paucity of their crystals in
the samples analyzed.

IMPLICATIONS

This study reveals that the whole of virtually Zn-free phyllosilicates in the Bongará district (Peru)
do contain zinc in variable amounts. Among these minerals, Zn-illites are the most widespread in
the investigated Zn-rich clayey materials. Considering that deciphering the nature of clay minerals
is pivotal for direct implications in the mining industry dealing with base metal recovery/processing
of Zn and other metals in nonsulfide deposits (Arfè et al. 2017, and references therein), Zn-bearing
illites might not be considered as barren material indeed. In addition, this study indicates that zinc is
located within the octahedral sites in each component of the layered silicate forming an intricate
mineral assemblage (as also observed in other studies, e.g. Choulet et al. 2016; Balassone et al. 2017). Hence it cannot be recovered easily and can only be released by leaching techniques such as solvent extraction, which is relatively efficient for a given clay species like sauconite (Cole and Sole 2002; Boni 2005; Boni et al. 2009a,b; Boni and Mondillo 2015). At Bongará, as in other worldwide occurrences (Choulet et al. 2016), the subordinate occurrence of interstratified clay minerals can have effects in ore liberation, requiring advances for an efficient separation technique and a better selectivity of solvents used.

Clay minerals are efficient sinks for base and heavy metals in the geosphere (Churakov and Dähn 2012), and the knowledge of the uptake mechanism of these elements on clays, among which there are illite and smectite, can have many important applications in a number of fields of material sciences, including, for instance, protection from industrial pollution and waste, clay based-polymer nanocomposites, heterogeneous catalysts etc. (e.g. Srivastava et al. 2005; Gu and Evans 2007, 2008; Montoya et al. 2018; Zhang et al. 2017). Hence the present work can contribute to an insight into Zn-bearing phyllosilicate systems, by determining the amount/mode of metal incorporation in their lattices and understanding the relationships of naturally occurring complex clay-rich associations, which can act as models for synthetic counterparts.

Finally, this research provides an advance in understanding the compositional gap between dioctahedral and trioctahedral layer silicates, with regard to Zn-poor and Zn-rich clays/micas of Bongará, which corresponds to their di- and tri-octahedral varieties respectively. In this case of study, Zn plays in phyllosilicates an equivalent role to Mg and Fe$^{2+}$, with minor presence in the dioctahedral species, together with trioctahedral minerals in which Zn is the major octahedral cation. Among others, this is the case of K-deficient hendricksite - or, if any, Zn(K)-wonesite - the low-temperature variety of Zn trioctahedral mica, whose composition has been firstly described in the current study. It can be predicted that other similar examples will be discovered when appropriate (metal-bearing) systems are examined more closely down to the nanoscale.
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LIST OF FIGURES CAPTIONS

FIGURE 1. (a) Geological map of the Bongará district within the Northern Andes morphostructural units B (modified from Arfè et al. 2017b), with location of Mina Grande and Cristal ore fields. (b) Stratigraphic column of the succession in the Bongará area (modified from Brophy 2012).

FIGURE 2. The studied samples from the nonsulfide Mina Grande and Cristal zinc deposits, Bongará (Peru), scale bar is equal to 2 cm.

FIGURE 3. Sample ZB-1 (Mina Grande): (a) textural images of Zn-illite (Zn-Ilt), with fraipontite (Frp). (b) HRTEM image of Zn-Illite in the yellow frame in the image (a), corresponding to a basically disordered polytype, with misorientation among the packets typical of illite (or I3 I/S...
mixed-layer); the SAED in the inset shows the [100] pattern with reflections (00l) at 10 Å of MDT Zn-illite and 9 Å average period in the b* direction. Rows corresponding to (02l) and (04l) are basically ill-defined diffuse lines, typical of disordered polytypes. (c) HRTEM of another area in yellow circle of (a), with the white fringes likely corresponding to a I3 I/S mixed layer. FFT (inset) shows the misorientation among the layers of the various packets and spacing which correspond to c*, b* and a* of illite and c* of the I3 I/S (4 illite + 1 smectite layers, in crimson). (d) HRTEM image of fraipontite close to Zn-illite, indicated by the sky-blue circle of image (a). (e) Chemical map of Zn-illite (Zn-Ilt), fraipontite and Fe-Ti-oxides (Fe-ox, Ti-ox) of a different zone from the previous ones, with the EDX spectrum referring to Zn-illite of the white frame area. Hereafter the Cu peak visible in the EDX spectra comes from the copper ring used for TEM sample preparation (mineral abbreviations mainly in agreement with Whitney and Evans 2010).

FIGURE 4. (a) Textural image of an area in Sample ZB-1 formed by MDT Zn-illite only (MDT Zn-Ilt, see text for acronym explanation); in the inset, SAED [100] + [010] patterns of illite (c* = 10Å, a* = 5.2 Å and b* = 9 Å) related to the yellow circle area; (02l), (20l) and (04l) rows are continuous diffuse lines, typical of disordered polytypes. (b) Sample ZB-1, MDT Zn-illite with fraipontite (Frp) and Fe,Ti oxide (Fe-ox, Ti-ox). (c) Sample ZB-2, smooth transition zone of MDT Zn-illite/fraipontite; the inset reports the electron diffraction pattern mainly taken in the left side of the investigated area, displaying rows with the fraipontite (7 Å) and illite (10Å) spacing, in parallel orientation (see text). (d) Sample ZB-1, chemical map of MDT Zn-illite of a different zone from those reported in (a) and (b), with Fe,Ti(Mn) oxide and fraipontite. (e) STEM-EDX spectra 1 and 2 of MDT Zn-illite and fraipontite in image (d).
FIGURE 5. Sample ZB-2 (Mina Grande): (a) textural and (b) chemical map of a zinc illite area (both MDT Zn-Ilt and Zn-Ilt, see text for further explanation), with fraipontite (Frp), kaolinite (Kln), Fe-(hydr)oxides (Fe-ox) and rutile (Ti-ox); the top right inset shows the lattice fringes of the zinc illite area in the white circle. (c) Selected chemical maps (K, Zn and Mg) of the investigated site in (a) and (b). (d) Qualitative EDX spectra of the two areas indicated in image (b). Images a, b and c show the intergrowth between the trioctahedral and dioctahedral micas at the ~20 nm scale.

FIGURE 6. Sample ZB-2: (a) Particles deposited onto a copper grid (CM20 instrument), showing Zn-illite (Zn-Ilt), K-deficient hendricksite (Hnk, see text for explanation), fraipontite (Frp) and Fe(Mn)-oxy-hydroxides (Fe,Mn-ox). (b) Qualitative EDX spectra of K-deficient hendricksite and fraipontite, related to the areas in the red frames of image (a).

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characteristic of 2M polytype. (c) HRTEM image of interstratified I/S type, with minor
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**FIGURE 10.** Sample CR13-7 (Cristal): (a) chemical map of Zn-illite (blue areas) interleaved with
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**FIGURE 11.** Bivariate plots of (a) Al\textsubscript{tot} vs. Si, (b) Zn vs. Al\textsuperscript{VI} and (c) Zn vs. K, expressed in terms of
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**FIGURE 12.** (a) 4Si-M\textsuperscript{+}–3R\textsuperscript{2+} diagram, showing the compositional variations of di- and trioctahedral
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**Figure 13.** Chemical mappings of the typical infiltration of Fe-Mn (hydr)oxides in zinc silicates at very fine scale: (a) Fe(Mn)-ox (mainly Mn-bearing goethite) with Zn-illite (Zn-Ilt); (b) chalcophanite with hemimorphite (sample CR13-7).

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**Table 1.** Theoretical formulae of Zn-bearing phyllosilicates and other selected minerals cited in the text (IMA database, http://rruff.info/ima/).

**Table 2.** Selected structural formulae of phyllosilicates from sample ZB-1, in atoms per formula units (apfu), calculated on the basis of 11 oxygens for MDT Zn-illite and K-deficient hendricksite, 6 octahedral+tetrahedral cations for Zn-illite (as in Nieto et al. 2010) and 7 oxygens for fraipontite.

**Table 3.** Selected structural formulae of phyllosilicates from sample ZB-2, in atoms per formula units (apfu), calculated on the basis of 11 oxygens for MDT Zn-illite and K-deficient.
hendricksite, 6 octahedral+tetrahedral cations for Zn-illite (as in Nieto et al. 2010) and 7 oxygens for fraipontite and kaolinite.

Table 4. Selected structural formulae of phyllosilicates from sample CR07-13, in atoms per formula units (apfu), calculated on the basis of 11 oxygens for Zn-illite MDT and 6 octahedral+tetrahedral cations for Zn-illite and muscovite (as in Nieto et al. 2010).

Table 5. Selected structural formulae of phyllosilicates from sample CR13-7, in atoms per formula units (apfu), calculated on the basis of 11 oxygens for Zn-bearing illite MDT, sauconite, beidellite and montmorillonite and 6 octahedral+tetrahedral cations for Zn-bearing illite and muscovite (as in Nieto et al. 2010).