



UNIONE EUROPEA
Fondo Sociale Europeo



UNIVERSITÀ
DEGLI STUDI
FIRENZE
Da un secolo, oltre.

DOTTORATO DI RICERCA IN _____ *Scienze della Terra* _____

CICLO XXXVII - PON ex DM1061

Capture and recovery of heavy metals in trap minerals:
incorporation mechanisms of Tl, Pb and Zn in pyrochlore and
hollandite structures

Settore Scientifico Disciplinare
GEOS-01/A

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Deinde quaeritur de Angelis per comparisonem ad corporalia.

(Thomas Aquinas, *Summa Theologiae*, I, q. 51, pr.)

Abstract

The dispersion of heavy metals in water poses a significant risk to human health and severely impacts the natural environment. Given their inherent toxicity, developing effective strategies to remediate contaminated water is crucial. A solution to this problem could come from mineralogy. The aim of this work is to investigate the ability of pyrochlore and hollandite to remove heavy metals from water environments. Its focus is on the ion exchange mechanisms and on the relations between the incorporated heavy metal ions and the host structure.

The crystal structure of pyrochlores and hollandites consists of an octahedral framework defining tunnel microporosities, where a wide range of ions and small molecules can be hosted and exchanged with the external environment. Their ion exchange properties make them promising materials for water remediation, as they can effectively incorporate hazardous heavy metals directly into their structure tunnels.

Two pyrochlores with the compositions $[K_{1.1(1)}(H_2O)_{0.4}\square_{0.5}]Ta_2[O_{5.1}(OH)_{0.9}](H_2O)$ (falling in the field of microlite) and $[Na_{0.7(1)}(H_2O)_{0.3}\square_{1.0}]W_2O_6[(H_2O)_{0.3}(OH)_{0.7}]$ (elsmoreite), and a hollandite $[K_{1.4(1)}\square_{0.6}]Mn_8O_{16}$ (cryptomelane) were synthesized in the form of microcrystalline powders and used through imbibition experiments solutions containing Tl(I), Pb(II) and Zn(II) with concentrations ranging from 0.01 to 1M.

The chemical composition of both treated and untreated samples was given by PIXE analysis; the eventual presence of water species occurring in the tunnel environment was detected by means of FTIR measurements. All the three sorbent materials were able to incorporate conspicuous amounts of Tl, in the range of 1-1.2 *apfu* for the most concentrated solutions. Microlite and cryptomelane incorporated Pb and Zn at lower levels, around 0.2-0.3 *apfu*, while elsmoreite showed very limited ability to absorb the latter metals.

XRD analysis showed that the octahedral frameworks remain quite stable after the ion exchanges, while the tunnel environment may undergo drastic changes in electron density distribution due to the uptake of metals. Water species were found to play an important role in pyrochlores, since they can stabilize the structure by balancing the charge of other ions and participate in the ion exchange reactions.

Despite the strong disordering phenomena occurring in the tunnels, EXAFS analysis allowed to achieve a quite accurate overview of the local structure of the selected heavy metals. The results showed that heavy metal ions do not occupy conventional crystallographic sites, but they are rather displaced along the tunnel axis or towards the tunnel walls, with disorder occurring around a constellation of satellite positions.

Finally, a series of preliminary imbibition experiments using 10-20 ppm solutions of Tl(I), Pb(II) and Zn(II) was performed. The analysis of the residual solutions revealed that in most cases the three sorbents can remove up to 99% of metal in less than one minute.

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1. Introduction

1.1. Definition of Heavy Metals: a disclaimer.

Before introducing the work, a disclaimer is needed. 'Heavy metal' is a term used for decades in scientific literature despite the lack of an official scientific definition. It is usually employed to group metals with high atomic weight, often associated with environmental concerns and potential hazards for living organisms.

As reported by Duffus (2002), the oldest scientific use of the term 'heavy metal' dates to 1936, in the English translation of the third Danish edition of the Bjerrum's *Inorganic Chemistry* (Bjerrum, 1936). In the textbook, heavy metals are described as metals with elemental densities above 7 g/cm³. To date, a great number of authors provided many definitions formulated in terms of elemental density or atomic weight (e.g. Bennet, 1986; Parker, 1989; Morris, 1992; Rand et al., 1995; Nies, 1999). Nevertheless, the International Union of Pure and Applied Chemistry (IUPAC), in a technical report prepared by Duffus in 2002, asserted that 'heavy metal' is a meaningless and misleading term, which has never been defined by the IUPAC or any other authoritative body, and that there is no correlation between the specific gravity of a metal and the toxicity or other physicochemical properties which the term often implies. Duffus (2002) concluded that a new classification of metals firmly based on their chemical properties is needed and that terms such as 'heavy metal' should be abandoned. In the subsequent years, more authors (e.g., Pourret, 2018; Hodson, 2004) brought to the attention the necessity of banning the term 'heavy metal' from the scientific literature, suggesting its replacement with more adequate and less misleading terms, like 'potentially toxic elements' and 'trace metal elements' (Pourret and Hursthouse, 2019; Pourret et al., 2021). Finally, Chapman (2007) recommended to use this term for music and not for science. On the opposite side, Batley (2012) and Ali and Khan (2017), upheld the term 'heavy metal' and tried to end the long-standing controversy proposing more comprehensive definitions.

Specifically, Batley (2012) grouped among the heavy metals the transition metals from Sc to Zn, Y to Cd and La to Hg, and the metals in Group IIIA and IVA, that are Ga, In, Sn, Tl and Pb; while Ali and Khan (2017) defined heavy metals as "naturally occurring metals having atomic number greater than 20 and an elemental density greater than 5 g/cm³."

A further side was represented by Hübner et al. (2010), which pointed out that 'heavy metal' is a too common and widespread term to be efficiently and completely banned from the scientific literature, suggesting the pragmatic approach to define a set of elements based on their linguistic spreading rather than by rigorous scientific criteria.

Far from the intention of giving a comprehensive definition but just driven from the necessity and the sake of pragmatism, since it is widespread in both scientific and environmental regulation literature, the term 'heavy metal' has been used throughout this work referring to the transitional metals from Sc to Zn, Y to Cd, and Hf to Hg, and the post transitional metals Ga, In, Sn, Tl, and Pb. In addition, the alkaline metal Cs and the metalloids As and Sb are included due to their high toxicity level and widespread environmental concerns. The possibility of including actinides, lanthanides (either entirely or partially) and other elements could be evaluated, but in the course

58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu
90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr

Some heavy metals, like Fe and Cu, in appropriate quantities are vital nutrients for biological

Heavy metals can also interact directly with nuclear proteins causing conformational changes in

5

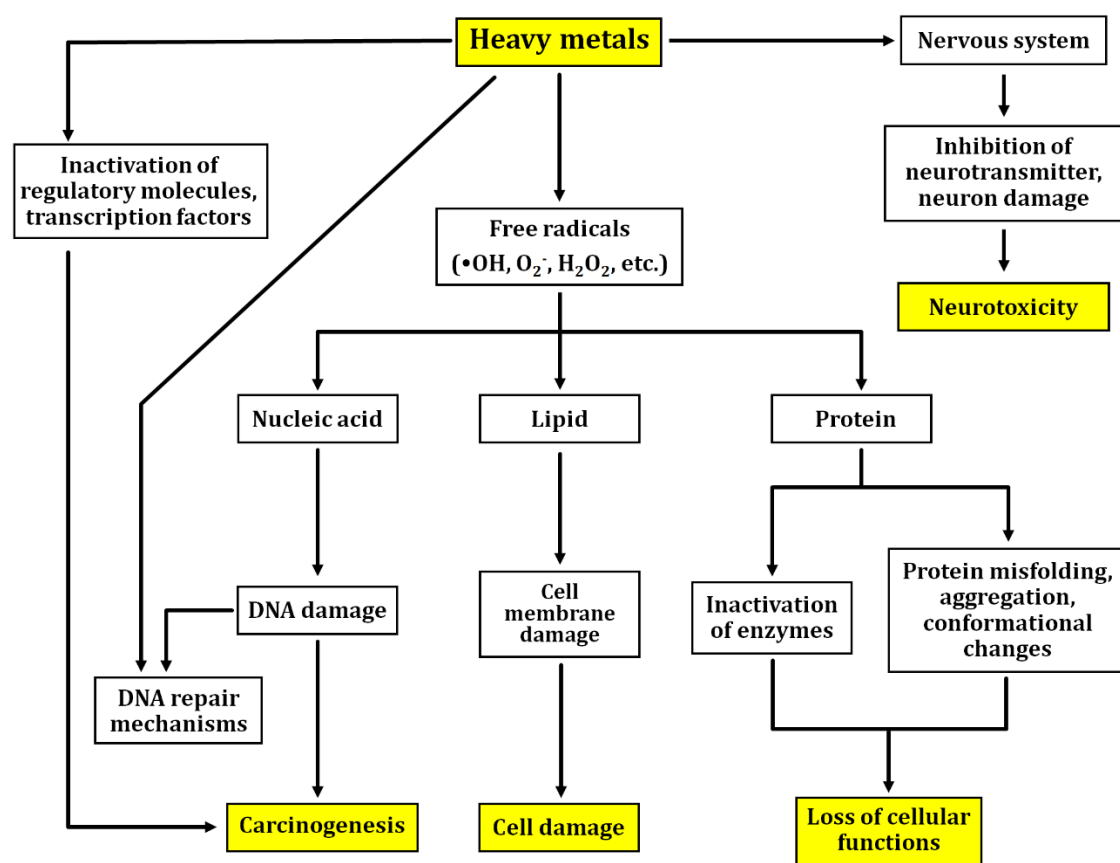


Figure 2. Scheme illustrating the major harmful effects of heavy metals on human beings (from Engwa et al., 2019; aesthetic modified).

The dispersion of heavy metals in the environment can be due to natural reasons, such as volcanic eruptions and leaching of natural rock bodies, but anthropic activity is by far the major source (Nagajyoti et al., 2010). Indeed, industrial activity, mining drainage and urban sewage are the leading causes of heavy-metal contamination of water. Nevertheless, heavy metals are not only dangerous, problematic wastes. They are also essential for many technological applications. Therefore, their dispersion in the environment can be seen not only as a dramatic concern for human health and the natural environment, but also as a waste of valuable resources that, with the growth of the human population and the related industrial activities, are progressively becoming scarce to found in their pristine, natural reservoirs. In this perspective, the scientific community and the ecological world industry have spent, and are still spending, a lot of effort to decontaminate and protect the natural environment from heavy metals pollution and recover valuable materials.

In the past years, to mitigate the widespread occurrence of heavy metals in wastewater and freshwater reservoirs, many treatment technologies have been proposed. The most prominent techniques employed for the removal of toxic pollutants are chemical precipitation, ion exchange, adsorption, biosorption, membrane filtration, coagulation and flocculation, flotation and electrochemical treatments (Fu and Wang, 2011; Shrestha et al., 2021).

Among the various methods employed to address this issue, the use of minerals has emerged as a promising approach. Certain minerals, owing to their physicochemical properties, exhibit a remarkable ability to bind and sequester heavy metals from aqueous matrices. The properties of the material, then, reflect the type of mechanism involved in the sequestration. The two principal removal methods involving minerals are chemical adsorption and ion exchange.

Adsorption is a process related to the particle surface dynamics and consists of the immersion of an adsorbent material in the contaminated solution. Due to physicochemical interactions among the charged surfaces of the particles and the ions spread in the external environment, the latter ions can adhere onto the surface of the particles themselves (Langmuir, 1918). This property, depending on the nature of the structure -not necessarily crystalline- and on the chemical composition of the particles, can be used for the heavy metal ions removal. Following adsorbents regeneration processes, the metals can be recovered and the adsorbents itself reused (e.g., Lata et al., 2015).

Ion exchange is a reversible interchange of ions amid an insoluble solid and a surrounding solution. The reaction involves the crystal structure of the solid particles, which contains weakly bonded ions that can be exchanged with the external environment without compromising the integrity of the crystal structure itself. Minerals with good ion exchange properties are mostly characterized by layered structures or frameworks defining interconnected microporosities (i.e. tunnels). The interlayer gaps and the tunnels are occupied by a population of ions and small molecules that can therefore be exchanged with the external environment. The cleaning strategy then consists in the release of harmless ions, like K^+ and Ca^{2+} , and the sorption of toxic species from the aqueous environment. The exchange reversibility can allow the release of the heavy metals in controlled conditions and their recovery throughout different physicochemical processes such as precipitation. Mineral like zeolites (having tunnel microporosities) and clay minerals (showing a layered structure) have been extensively investigated in the past years due to their excellent ion exchange properties and successfully applied for heavy metals removal from aqueous environments (e.g., Yuna, 2016; Gu et al., 2019).

This work is specifically focused on the ion exchange method, and it is aimed at investigating the ability of minerals belonging to two distinct supergroups, pyrochlore and hollandite supergroups, to remove heavy metals from aqueous solutions. The crystal structures of pyrochlores and hollandites consist of stable frameworks defining tunnels, where a wide range of cations and small molecules can be hosted and exchanged. Their ion exchange properties are well known and, in the past years, many synthetic compounds having pyrochlore or hollandite structures have been produced with the most different chemical compositions and exploited for quite a lot of applications. For example, both structural types have been studied as potential materials for battery applications based on the reversible intercalation of cations such as Li^+ , K^+ , Na^+ and Zn^{2+} in the tunnel microporosities (e.g., Dai et al., 2000; Matsutami et al., 2015; Le et al., 2021; Tashlanov et al., 2025).

In the past years, different studies have been conducted on the utilization of these kind of structures also for the removal of toxic ions. Due to their high thermal stability, resistance to

ionization and extreme pH conditions, pyrochlores with different chemical composition have been synthesized and studied for the separation of caesium, cobalt and strontium radionuclides from radioactive liquid waste (e.g., Möller et al., 2001, Möller et al., 2002; Mu et al., 2015). In the latter works, the authors showed that pyrochlores can incorporate radioactive ions in the tunnels of their crystal structure and revealed that slight variations in the chemical composition of the framework, conveniently doped with different metals, can increase the efficiency and the selectivity of the exchange.

Han et al. (2014) proposed a niobium tungsten oxide $[\text{KNbWO}_6 \cdot \text{H}_2\text{O}]$ with the pyrochlore structure for the selective removal of Pb^{2+} by ion exchange in solutions containing other metal ions such as Co^{2+} , Mn^{2+} and Cd^{2+} . The latter work demonstrated that pyrochlore can remove specific ions with a high selectivity, increasing thus the versatility and the efficiency of the ion exchange method.

The present study draws inspiration from a series of works reporting the incorporation of thallium by different natural pyrochlores. Jäger et al. (1959) and Bindi et al. (2006) used a standard flotation method (Vassar et al., 1925) involving the utilization of the Clerici solutions, which is made of equal part of thallium formate $[\text{Tl}(\text{HCO}_2)]$ and thallium malonate $[\text{Tl}(\text{C}_3\text{H}_3\text{O}_4)]$, to separate pyrochlore fragments from other gangue minerals. Following chemical and structural analysis revealed that the pyrochlores samples incorporated part of the thallium contained in the Clerici solution within the tunnel of their crystal structure. Harris (1965) intentionally soaked a natural bariopyrochlore in a thallium nitrate $[\text{TlNO}_3]$ solution to demonstrate the mobility of the tunnel ions. Recently, on the thrust of the latter discoveries, Taddei et al. (2024) investigated the ability of a hydroxy-pyrochlore [ideally $(\text{H}_2\text{O}, \square)_2\text{Nb}_2(\text{O},\text{OH})_6(\text{H}_2\text{O})$], to incorporate thallium and its effect on the average structure of the mineral.

Hollandites have also been tested for the removal of heavy metals and radionuclides. In particular, natural and synthetic cryptomelanes [ideally $\text{K}(\text{Mn}^{4+}_7\text{Mn}^{3+})\text{O}_{16}$] have been used by many authors in ion exchange experiments involving different toxic cations. For example, Tsuji and Komarneni (1993), with the aim of removing radioactive $^{60}\text{Co}^{2+}$ from circulation waters of nuclear power plants, studied the ion-exchange ability and selectivity of a synthetic cryptomelane for divalent metal ions reporting the following selectivity order: $\text{Pb} \gg \text{Mn} > \text{Co} > \text{Cu} > \text{Hg} > \text{Cd} > \text{Zn} > \text{Ni}$. O'Reilly and Hochella (2003) investigated the lead sorption efficiency of different manganese oxides, including cryptomelane; Lu et al. (2007) studied the ability of natural cryptomelane to remove divalent cadmium; Li et al. (2015) used a Co-doped cryptomelane to remove divalent lead and trivalent chromium from wastewater; Wick et al. (2019) investigated the incorporation mechanisms of thallium in layered and microporous manganese oxides, again including cryptomelane, revealing that Tl^+ can replace K^+ in the tunnels of the hollandite structure. Lastly, Ghaly et al. (2022) evaluated the utilization of cryptomelane nano-powders for the scavenging of cobalt, caesium and lead, revealing that it is an efficient sorbent media for the removal of the latter ions and that can be regenerated and reused several times.

1.3. Aim and Workflow

Nearly all the scientific works that look at pyrochlores and hollandites as traps for heavy metals or radionuclides are focused on the effects of the sorbent materials on the contaminated solutions rather than the effects of the incorporation on the sorbents crystal structure. Namely, they are focused on the analysis of the solutions, while the crystal structure investigations are mostly limited to a brief characterization of the untreated sorbent materials. The variations of the metal concentrations in the target solutions are evaluated to determine the efficiency of the removal process; Langmuir or the Freundlich isotherms models are used to express the sorption of the metals and the reaction kinetics (e.g., Lu et al., 2007; Mu et al., 2015).

Only few works address the topic from a structural standpoint. Nevertheless, given the extreme variability and complexity of pyrochlore and hollandite minerals, it is critically important to achieve a deep understanding of the heavy metal incorporation mechanisms and the resulting effects on their crystal structures. A strong structural characterization of the sorbent systems can also lead to an enhancement of the metal removal methods and help the development of future applications. For all these reasons, the focus of this work is mainly on the structure of pyrochlores and hollandites; its aim is to shed light on the incorporation mechanisms of heavy metals and to investigate the structural response following the incorporation.

The first step to achieve the aforementioned aim was, of course, to obtain the sorbents materials. Instead of using natural samples, synthetic analogues of minerals were produced in the form of microcrystalline powders. In particular, a sample of hollandite, with the composition of cryptomelane, and two different pyrochlores, with compositions falling in the microlite and elsmoreite group field, were synthesized. The main differences between the two pyrochlores are the valence and type of cation hosted in the framework: Ta^{5+} for microlite and W^{6+} for elsmoreite. The purpose was indeed to evaluate the effects of cations with different valences within the framework on the ion exchange properties. Although all these names (pyrochlore, elsmoreite, microlite, hollandite, cryptomelane) are mineral groups or mineral species names (and then they should be used only for natural specimens), for the sake of simplicity they are utilized in the course of this work to refer also to their synthetic analogues.

The decision to use synthetic materials is due to the extreme complexity of the natural specimens. As it will be explained in more depth in the chapters dedicated to the review of their crystal structures, pyrochlore and hollandite can accommodate a wide range of ion species in both framework and tunnel sites, and natural samples are usually characterized by the coexistence of many different elements, making thus difficult to evaluate the effect of each component on the sorbent materials properties. Even small amounts of an additional element within the structure can indeed affect the physicochemical properties of the whole crystal structure (e.g., Mu et al., 2015). For this reason, we decided to synthesize structures with the simplest possible chemistry: one cation for the framework and one (plus inevitable water and hydroxyls) for the tunnel sites. Another downside of natural pyrochlores and hollandites is the rarity of exploitable deposits. In case they were to be used for heavy metal removal at an industrial scale, the quantities of required

materials would be considerable, probably in the order of tons. However, pyrochlores are accessory minerals, found as small crystals or aggregates in pegmatites and carbonatites, and rarely they accumulate in exploitable reservoirs. Just a dozen of pyrochlore deposits is known all around the world and only three are currently mined as a source of niobium: the Catalão and Araxá mines in Brazil and the Niobec mine in Canada (Gibson et al., 2015). Manganese oxides with the hollandite structure are relatively common in soils (e.g., Chukhrov and Gorshkov, 1981) and deep-sea manganese nodules (e.g., Halbach et al., 1992), but they are extremely difficult to separate or even to identify due to their poor crystallinity and inherent association with other manganese oxides and silicates such as birnessite $[(\text{Na},\text{Ca})_{0.5}(\text{Mn}^{4+},\text{Mn}^{3+})_2\text{O}_4 \cdot 1.5\text{H}_2\text{O}]$, pyrolusite $[\text{Mn}^{4+}\text{O}_2]$, todorokite $[(\text{Ca},\text{K},\text{Na},\text{Mg},\text{Ba},\text{Mn})(\text{Mn},\text{Mg},\text{Al})_6\text{O}_{12} \cdot 3\text{H}_2\text{O}]$ and braunite $[\text{Mn}^{2+}\text{Mn}^{3+}_6(\text{SiO}_4)_8\text{O}_8]$.

On the other hand, synthetic samples of both pyrochlores and hollandites can be produced with a good grade of crystallinity and reproducibility, and with just minor or no impurities in every research facility using simple lab equipment. In addition, even if the amounts of material produced in this work were quite small (few grams), with adequate readjustments the synthesis processes could be scaled up to an industrial level.

The choice to use fine powders instead of, for example, single crystals is related to the inherent increase in sorption capacity with the decrease in particle size. The ion exchange process is directly linked to the surface area of the sorbents material, as it determines the probability, and then the frequency, of the exchange reactions and the time required for the transport of the ions through the tunnels to the binding sites. The incorporation process is then more efficient for materials with higher specific surfaces (that is the total surface area of a material per unit mass), such as fine powders. In addition, due to their large size, the single crystals are inherently limited in their capacity to fully characterize the complete process of exchange and the resulting distribution of the metal within the particle. Lastly, the synthesis of fine powders is a relatively easy process, as it does not require challenging procedures for the growth of the crystallites.

The heavy metals selected for the ion exchange experiments are Tl(I), Pb(II) and Zn(II). Lead was chosen because it is a very common and highly toxic pollutant. Thallium is less common than lead, but it can be fatal even at very low concentrations (see 3.1). Moreover, a concerning Tl contamination was found in the tap water in the Valdicastello Carducci and Pietrasanta area, northern Tuscany: a fact that has reawakened public attention to the dangers of this particular metal and led to numerous investigations into defining and resolving the problem (e.g. Campanella et al, 2016). The choice fell on Tl(I) and Pb(II) also because it was considered interesting to evaluate eventual differences in the behaviour of the sorbent materials (and then in the incorporation mechanisms of the metals) facing cations with different charge and dimensions (ionic radii). Zinc was selected because it is a common byproduct of many industrial processes and a valuable resource, worthy to be recovered and reintroduced in the industrial cycle (e.g., Xu et al., 2022).

The latter three heavy metals were then used in imbibition experiments involving microlite, elsmoreite and cryptomelane powders. Each sorbent material was then contacted with a solution containing a single heavy metal for a fixed amount of time. Highly concentrated solutions (in the

range of 0.01-1 M) were used to maximise the extent of the reactions, and then the effects of the ion exchange on the crystal structure of the sorbent materials. The exposure time of the powders to the heavy metal solution (one day for each experiment) was considered long enough to ensure the reaction equilibrium was reached.

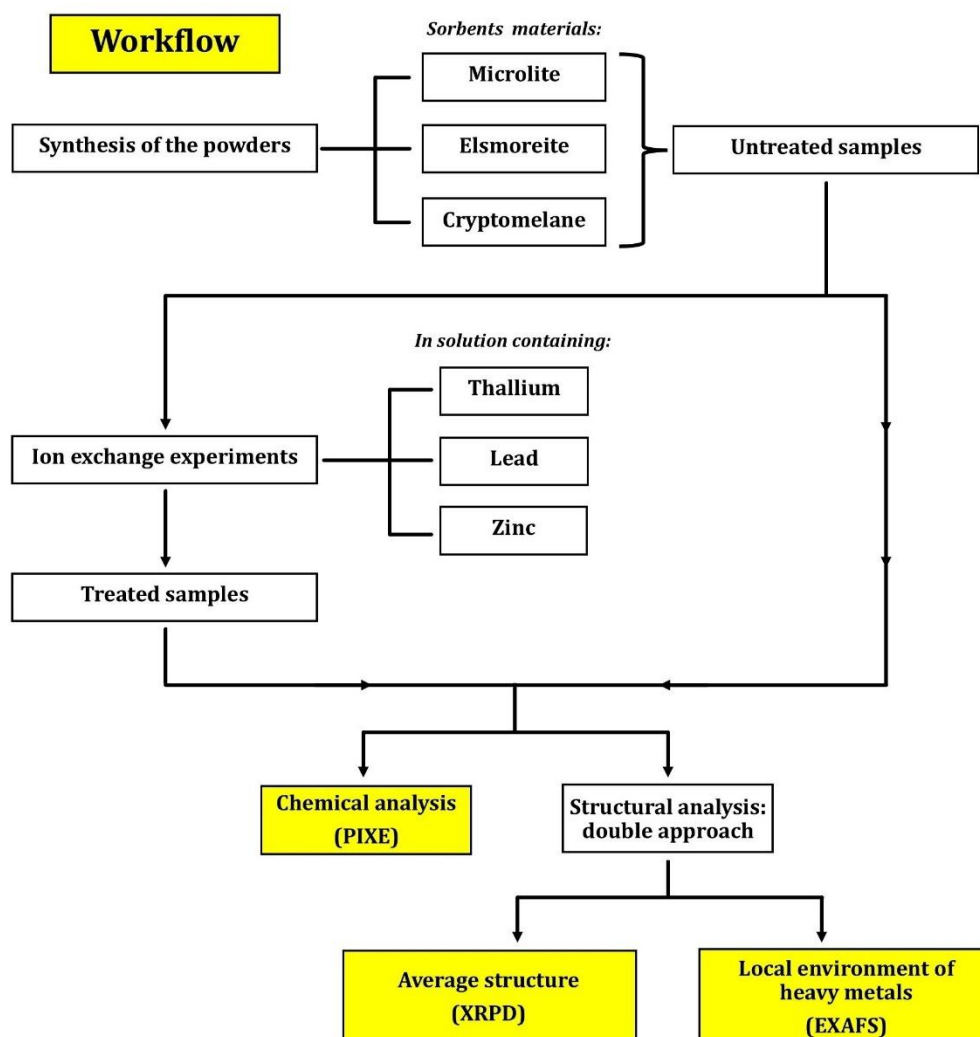


Figure 3. Scheme of the workflow.

Before and after the heavy metal treatment, the chemical composition of the powders was measured by means of Particle Induced X-ray Emission (PIXE). For the structural investigations, a double approach was applied. The average structure of the sorbent materials was analysed by means of X-ray Powder Diffraction (XRPD). The Rietveld refinements conducted on the XRPD patterns provided a description of the variations in the average structure (variations in cell parameters and tunnel sites populations brought by the ion exchanges). Then, the local environment of the heavy metals was investigated using X-ray Absorption Spectroscopy (XAS). In particular, Extended X-Ray Absorption Fine Structure analyses (EXAFS) allowed to assess the average coordination of the heavy metals within the tunnels of the different crystal structures. The

work strategy is summarized in the scheme reported in Fig. 3. The experimental details are reported in chapter 4; the results and the discussion on the characterization of microlite, elsmoreite and cryptomelane before and after the ion exchange experiments are showed in chapters 5, 6 and 7, respectively.

After the structural investigations, to complement the present work, a batch of experiments using diluted heavy metals solutions were performed. The aim of these experiments was to test the removal performance of sorbent materials in conditions close to those found in polluted water environments (i.e., low, but still highly dangerous, heavy metal concentrations). In this case, the focus was not on the sorbent material but rather on the exchanging solutions, the heavy metal concentration variations were measured employing an Ion Coupled Plasma-Mass Spectrometer (ICP-MS). The details and the results of the latter experiments are reported in Chapter 8.

Before proceeding to the experimental sections (Chapters 4-8), it was deemed necessary to provide the reader with a series of preliminary information regarding the sorbents materials, that is to say pyrochlores and hollandites (Chapter 2), and three heavy metals (Tl, Pb and Zn) employed in the present work (Chapter 3).

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2. The Crystal Structure and Chemistry of the Sorbent Materials

2.1. The Crystal Structure and Chemistry of Pyrochlore

Pyrochlore is a supergroup of minerals which includes a wide variety of high field-strength element oxides. The name of the supergroup comes from the mineral pyrochlore [ideally $(\text{Na,Ca})_2\text{Nb}_2\text{O}_6(\text{F,OH})$], which in turn derives from the ancient Greek $\pi\upsilon\rho$ (fire) and $\chi\lambda\omega\rho\acute{o}\varsigma$ (green). Such name was given by J.J. Berzelius in 19th century to a cubic mineral, found by N.O. Tank, that turned green when heated to the flame (Wöhler, 1826).

The crystal structure of pyrochlore was described for the first time by Gaertner (1930) and consists of a corner-sharing octahedra framework interconnected with an intricate interweaving of tunnels where a wide range of ions and small molecules can be hosted (Fig. 1a). The ideal unit cell (Fig. 1b) is cubic, face centred, with space group $Fd-3m$ ($Z = 8$).

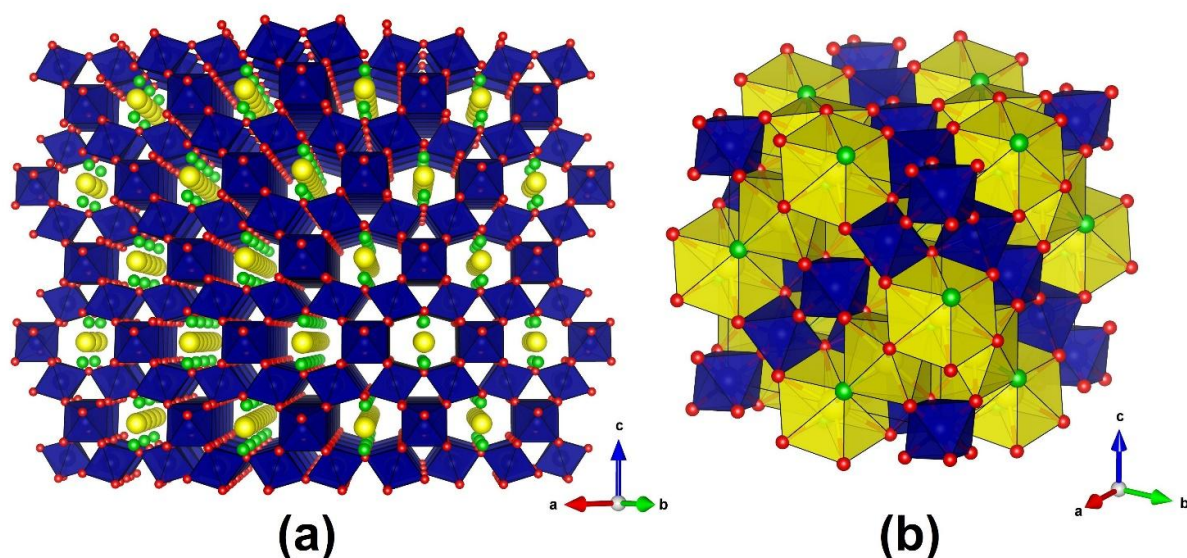


Figure 1. Overall structure highlighting the tunnels (a) and unit cell (b) of pyrochlore.

Colour scheme: A = yellow; B = blue; X = red; Y = green.

The general formula for the supergroup members is $^{VIII}A_{2-m}^{VI}B_2^{IV}X_{6-w}^{IV}Y_{1-n}$.

A is a large-radius cation, such as Na^+ , K^+ , Ca^{2+} , Ba^{2+} , Sr^{2+} , Pb^{2+} , Sb^{3+} , Sc^{3+} , Y^{3+} , Ree^{3+} , U^{4+} and Th^{4+} , or a small molecule such as water. It is located within the tunnels, coordinated by six X anions of the octahedral framework and, eventually, up to two Y anions. Usually, A site is partway vacant ($2 > m > 0$), sometimes it is empty ($m = 2$). A-cation-absent varieties of pyrochlores are called *defect* pyrochlores.

B is usually a high field-strength element, such as W^{6+} , Ta^{5+} , Nb^{5+} , Sb^{5+} , V^{5+} , Ti^{4+} , Zr^{4+} , and Hf^{4+} , but it can also be a less-charged ion, like Fe^{3+} , Al^{3+} and Mg^{2+} . It is coordinated by six X anions forming a BX_6 octahedron.

X is mainly O^{2-} or, less frequently, F^- , Cl^- or OH^- . Despite most of the pyrochlores being transition metal oxides (i.e., O^{2-} and/or OH^- in X), a few chlorides and fluorides pyrochlores are known (e.g., Ledesert and Raveau, 1987; Calage et al., 1987). Normally, X site is entirely filled, but it can be partially vacant in highly altered samples, with $0 \leq w \leq 0.7$ (Lumpkin and Ewing, 1992; Lumpkin and Ewing, 1995).

Y is usually an anion such as O^{2-} , OH^- and F^- , or a water molecule. It can also be partially vacant. It is placed at the intersection of three tunnels, coordinated by four A cations. Y site can eventually host very large-radius monovalent cations (usually with ionic radius $> 1.3 \text{ \AA}$) like K^+ , Cs^+ or Rb^+ , that may be too large to accommodate in the A site (Ercit et al., 1993; Agakanov et al., 2021). Pyrochlore varieties where the A site is predominantly vacant and the cations are located only in the Y site are called *inverse* pyrochlores. Their general formula is $\square_2B_2X'_6Y'$, where Y' represents the cations that would normally be in A but are instead found in the Y position. (Ercit et al., 1993). Due to the variability of their crystal chemistry, the nomenclature of pyrochlores is quite complex. During the past century, a series of classifications were proposed: Ginzburg et al. (1960), van der Veen (1963), Bonshtedt-Kupletskaya (1966) and Hogarth et al (1977). The latter authors classified sixteen mineral species and grouped them in three subgroups based on the atomic proportion of Nb, Ta and Ti in the B site:

- Pyrochlore Subgroup ($Nb + Ta > 2Ti$ and $Nb > Ta$);
- Microlite Subgroup ($Nb + Ta > 2Ti$) and $Ta \geq Nb$);
- Betafite Subgroup ($2Ti \geq Nb + Ta$).

The current classification was proposed by Atencio et al. (2010), and subsequently updated by Atencio (2021) to include new mineral species. The Atencio classification defines the Pyrochlore Supergroup, which is, in turn, divided into five group depending on the dominant cation of the dominant valence in B site:

- Pyrochlore Group if the dominant cation is Nb;
- Microlite Group if the dominant cation is Ta;
- Roméite Group if the dominant cation is Sb;
- Betafite Group if the dominant cation is Ti;
- Elsmoreite Group if the dominant cation is W.

The list of Pyrochlore Supergroup mineral species is reported in (Table 1) divided in their respective groups, as stated by Atencio (2021).

In addition to the minerals, a broad variety of crystalline compounds having the pyrochlore structure has been synthesized in the past years. The compositional flexibility of the crystal structure allows the accommodation of a wide range of ion combinations and mixed sites populations. In addition to the naturally occurring W^{6+} , Ta^{5+} , Nb^{5+} , Sb^{5+} , and Ti^{4+} the B site can be occupied by almost any other high strength-field element, such as Zr^{4+} ; Ir^{4+} , Sn^{4+} , $Ru^{4+,5+}$, $Mo^{4+,5+}$, $Te^{4+,6+}$, Os^{6+} , Re^{6+} (e.g., Singh et al., 2002; Abbot et al., 2019; Converse et al., 2022) and, in high pressure and temperature conditions, even by smaller ion, such as Si^{4+} , Ge^{4+} and Mn^{4+} (e.g., Reid et al., 1977; Shimakawa et al., 1999;). Similarly, the A site can host a wide range of cations with different oxidation states such as Tl^+ , Zn^{2+} , Co^{2+} , Cd^{2+} , Bi^{3+} and trivalent rare earth elements (e.g.,

Uma et al., 2000; Moritomo et al., 2001; Singh et al., 2002; Liu et al., 2010; Shapiro et al., 2012; Fuentes et al., 2024).

Table 1. classification of the pyrochlore supergroup according to Atencio (2021). Atomic species that have no relevance in the nomenclature are indicated with the generic letter A.

Pyrochlore Supergroup		
<i>Pyrochlore Group</i>	<i>Microlite Group</i>	<i>Roméite Group</i>
Oxycalciopyrochlore $\text{Ca}_2\text{Nb}_2\text{O}_6\text{O}$	Hydroxykenomicrolite $(\square, \text{A})_2\text{Ta}_2\text{O}_6(\text{OH})$	Hydroxycalcioroméite $(\text{Ca}, \text{A})_2\text{Sb}^{5+}_2\text{O}_6(\text{OH})$
Hydropyrochlore $(\text{H}_2\text{O}, \square, \text{A})_2\text{Nb}_2\text{O}_6(\text{H}_2\text{O})$	Oxystannomicrolite $\text{Sn}_2\text{Ta}_2\text{O}_6\text{O}$	Fluorcalcioroméite $(\text{Ca}, \text{A})_2\text{Sb}^{5+}_2\text{O}_6\text{F}$
Cesiokenopyrochlore $(\square, \text{A})_2\text{Nb}_2\text{O}_6\text{Cs}$	Oxystibiomicroite $(\text{Sb}^{3+}, \text{A})_2\text{Ta}_2\text{O}_6\text{O}$	Hydroxyferroroméite $(\text{Fe}^{2+}, \text{A})_2\text{Sb}^{5+}_2\text{O}_6(\text{OH})$
Fluorcalciopyrochlore $(\text{Ca}, \text{Na}, \text{A})_2(\text{Nb}, \text{Ti})_2\text{O}_6\text{F}$	Fluorcalciomicrolite $(\text{Ca}, \text{A})_2\text{Ta}_2\text{O}_6\text{F}$	Oxycalcioroméite $\text{Ca}_2\text{Sb}^{5+}_2\text{O}_6\text{O}$
Fluornatropyrochlore $(\text{Na}, \square, \text{A})_2\text{Nb}_2\text{O}_6\text{F}$	Fluornatromicrolite $(\text{Na}, \text{A})_2\text{Ta}_2\text{O}_6\text{F}$	Oxylumboroméite $\text{Pb}_2\text{Sb}^{5+}_2\text{O}_6\text{O}$
Hydrokenopyrochlore $(\square, \text{A})_2\text{Nb}_2\text{O}_6(\text{H}_2\text{O})$	Hydrokenomicrolite $(\square, \text{A})_2\text{Ta}_2\text{O}_6(\text{H}_2\text{O})$	Fluornatroroméite $(\text{Na}, \text{A})_2\text{Sb}^{5+}_2\text{O}_6\text{F}$
Hydroxycalciopyrochlore $(\text{Ca}, \text{A})_2\text{Nb}_2\text{O}_6(\text{OH})$	Hydroxycalciomicrolite $(\text{Ca}, \text{A})_2\text{Ta}_2\text{O}_6(\text{OH})$	
Hydroxynatropyrochlore $(\text{Na}, \text{A})_2\text{Nb}_2\text{O}_6(\text{OH})$	Kenoplumbomicrolite $(\text{Pb}, \text{A})_2\text{Ta}_2\text{O}_6\square$	<i>Betafite Group</i>
Hydroxykenopyrochlore $(\square, \text{A})_2\text{Nb}_2\text{O}_6(\text{OH})$	Oxynatromicrolite $(\text{Na}, \text{A})_2\text{Ta}_2\text{O}_6\text{O}$	Oxycalcibetafite $(\text{Ca}, \text{A})_2\text{Ti}_2\text{O}_6\text{O}$
Hydroxymanganopyrochlore $(\text{Mn}^{2+}, \text{A})_2\text{Nb}_2\text{O}_6(\text{OH})$	Oxycalciomicrolite $\text{Ca}_2\text{Ta}_2\text{O}_6\text{O}$	Oxyuranobetafite $(\text{U}, \text{A})_2\text{Ti}_2\text{O}_6\text{O}$
Hydroxylumbopyrochlore $(\text{Pb}, \text{A})_2\text{Nb}_2\text{O}_6(\text{OH})$	Oxybismutomicrolite $(\text{Bi}, \text{A})_2\text{Ta}_2\text{O}_6\text{O}$	
Fluorstrontipyrochlore $(\text{Sr}, \text{A})_2\text{Nb}_2\text{O}_6\text{F}$	Hydromicrolite $(\text{H}_2\text{O}, \text{A})_2\text{Ta}_2\text{O}_6(\text{H}_2\text{O})$	<i>Unassigned members</i>
Fluorkenopyrochlore $(\square, \text{A})_2\text{Nb}_2\text{O}_6\text{F}$		Fluornatrocoulsellite $(\text{Na}, \text{A})_2\text{Mg}_2\text{F}_6\text{F}$
Oxynatropyrochlore $(\text{Na}, \text{A})_2\text{Nb}_2\text{O}_6\text{O}$	<i>Elsmoreite Group</i>	Hydrokenoralstonite $\square_2\text{Al}_2\text{F}_6(\text{H}_2\text{O})$
Oxylumbopyrochlore $\text{Pb}_2\text{Nb}_2\text{O}_6\text{O}$	Hydrokenoelsmoreite $\square_2\text{W}_2\text{O}_6(\text{H}_2\text{O})$	
Oxyttropyrochlore-(Y) $(\text{Y}, \text{A})_2\text{Nb}_2\text{O}_6\text{O}$	Hydroxykenoelsmoreite $(\square, \text{A})_2\text{W}_2\text{O}_6(\text{OH})$	
Kenoplumbopyrochlore $(\text{Pb}, \text{A})_2\text{Nb}_2\text{O}_6\square$		

Due to their properties resulting from their structural features and crystal-chemical diversity, synthetic pyrochlores have been investigated and adopted for many technological applications. Pyrochlores have been studied as material for batteries, solid oxide fuel cells and various electronic applications (e.g., Ren et al., 2001, Oh et al., 2012; Gardner et al., 2010; Anantharaman et al., 2021). Defect pyrochlores have been extensively tested as catalysts for environmental remediation and hydrogen generation from water splitting (e.g. Jitta et al., 2015). Titanate- and zirconates-pyrochlores have been developed for long-term radwaste disposal due to their ability to immobilize long-lived radionuclides and resist to prolonged exposure to radiations (e.g. Ewing et al., 2004; McMaster et al., 2018).

The crystallographic positions of the four sites of the pyrochlore structure (Table 2) are fixed by the symmetry except that of the X site, which has a single variable parameter along the x-direction (Ercit et al., 1994; Vanderah et al., 2005). The crystal structure of pyrochlore is therefore described by only two variables: the cell parameter a and the x coordinate of the X site. The geometry of the A and B sites depends on the latter variable. If $x = 0.375$, the A ion lies at the centre of a perfect cube, while BX_6 is distorted to a trigonal antiprism. If $x = 0.3125$, the A cube is deformed to a trigonal scalenohedron, while B lies in a perfect octahedron (Chakoumakos, 1984).

Table 2. Positional parameters for pyrochlores. In black are reported the conventional 4 sites; in blue the additional tunnel sites given by Ercit et al., 1993.

Site	Wyckoff position	x	y	z
A	$16d$	0.5	0.5	0.5
B	$16c$	0	0	0
X	$48f$	x	0.125	0.125
Y	$8b$	0.375	0.375	0.375
A'	$32e$	x	x	x
Y'	$32e$	x	x	x
Y''	$96g$	x	x	z

In the ideal pyrochlore, all the tunnel occupants are placed only in A and Y. Nevertheless, due to disorder phenomena and stereochemical constraints caused by electrostatic repulsion between adjacent ions, they may have a more diffuse distribution within the tunnels, and additional sites can be found close to the conventional A and Y positions. Ercit et al., 1994 reported the occurrence of three additional sites: the A' site, that lies near the A sites and Y' and Y'' sites near the Y site (Fig. 2). Their positional parameters are reported in Table 2.

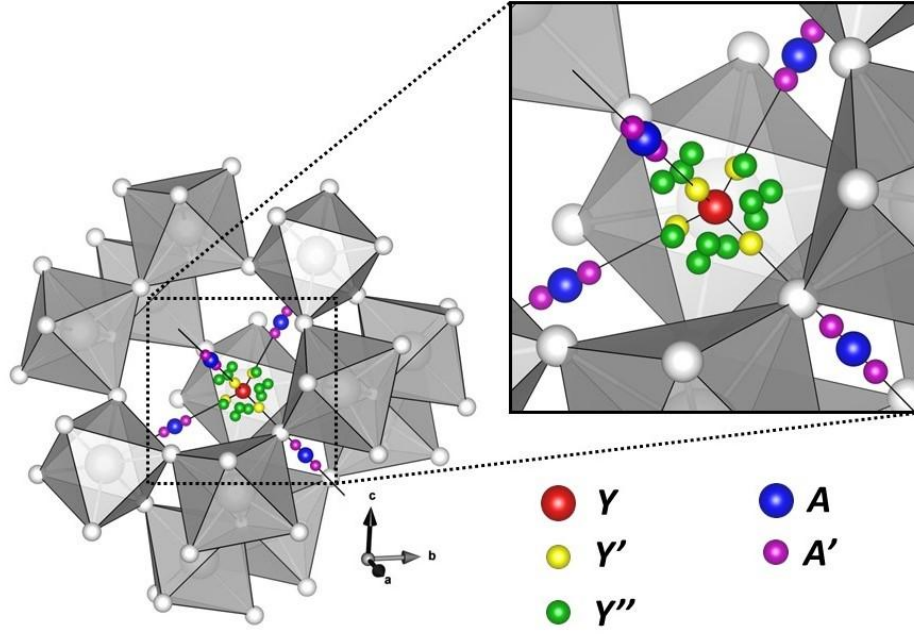


Figure 2. Conventional and additional crystallographic positions within the tunnels.

Despite most pyrochlores being cubic, it is not unusual to find structures showing lower symmetries. A common decrease in symmetry is from cubic, $Fd-3m$, to rhombohedral, $R-3m$. This type of crystallographic operation splits the A, B and X sites, such that the structure can be crystallographically represented as $(A1)_3(A2)_1(B1)_3(B2)_1(X1)_6(X2)_6Y_2$ (Mills et al., 2017), and can be due to a cation ordering that can occur in both A and B sites. For example, the synthetic pyrochlore $CsTe_2O_6$ crystallizes in the space group $R-3m$ because of the ordering of Te^{4+} and Te^{6+} in the B sites with the ratio 1:3 (Siritanon et al., 2011), while in the natural ‘parabariomicrolite’, now considered a hydrokenomicrolite (Atencio 2016), a Microlite Group pyrochlore according to the nomenclature rules of Atencio (2010), the same thing seems to happen due to the ordering of large cations and vacancies in the A site (Ercit et al., 1986). In addition, the synthetic pyrochlores of the $Mn_2Ln_3Sb_3O_{14}$ series (Ln = lanthanide and Y) show a rhombohedral $R-3m$ lattice due to the ordering Mn:Ln in the A sites and Mn:Sb in the B sites, again with the ratio 1:3 (Fu and Ijdo, 2014). In addition to ordering phenomena, geometrical deformation of the crystal structure can be responsible for a rhombohedral cell. For example, Subramanian et al. (1984) reported the occurrence of a synthetic pyrochlore, $Mn_2Sb_2O_7$, whose rhombohedral distortion has been attributed to the displacement of the A-X network, presumably due to the small size of Mn^{2+} in A. Trigonal $R-3$ distortions have been also mentioned in literature. Mills et al. (2016) reported the occurrence of two different polytypes of hydrokenoelsmoreite (an Elsmoreite Group pyrochlore) crystallizing in space group $Fd-3m$ and $R-3$. The trigonal form shows a doubling in the unit cell along the unique threefold axis due to ordering of Na and $(\square, H_2O)$ in the A site, such that the general crystallographic formula can be written as:

$$(A1)_3(A2)_2(A3)_3(B1)_1(B2)_1(B3)_6(X1)_6(X2)_6(X3)_6(X4)_6(Y1)_2(Y2)_2.$$

Another *R*-3 trigonal pyrochlore of the Elsmoreite Group, called hydroxykenoelsmoreite, has been described by Mills et al. (2017). In this case, there is no doubling of the unit cell and the decrease in symmetry is attributed to the concomitant effects of the ordering of Fe³⁺ and W⁶⁺ in B sites and the occurrence of small rotations of the coordination polyhedra.

Due to the microcrystalline nature of the samples, many pyrochlores -and among them the rhombohedral ones- have been described using X-ray powder diffraction rather than single-crystal X-ray diffraction (e.g., Subramanian et al., 1984; Ercit et al., 1986). Bonazzi and Bindi (2007), in their work on the crystal structure of ingersonite [Ca₃Mn²⁺Sb⁵⁺₄O₁₄], which is isostructural with the synthetic weberite-3T polytype (trigonal, space group *P*3₁21) and related to the pyrochlore structure type, revealed that only few weak reflections allow the distinction between the P lattice of the ingersonite and the R lattice of a rhombohedral pyrochlores. According to the latter authors, from powder diffraction alone, it could result difficult, if not impossible, to discriminate a trigonal ingersonite from a rhombohedral (or even an eventual trigonal) pyrochlore.

A decrease in symmetry can also occur still remaining in the cubic system. For example, Andrade et al. (2017) described the pyrochlore hydroxycalciumicrolite [Ca_{1.5}Ta₂O₆(OH)] that crystallize in the space group *P*4₃32 due to the long-range ordering of Ca and vacancies on the A sites.

2.2. The Crystal Structure and Chemistry of Hollandite

Hollandite is a mineral supergroup which includes a wide variety of Mn and Ti oxides. It takes its name from the mineral hollandite [ideally Ba(Mn⁴⁺₆Mn³⁺₂)O₁₆], so named by Lewis L. Fermore in 1906 after Thomas Holland, director of the Geological Survey of India (Nayak, 1964). The crystal structure of hollandite was described for the first time by Byström and Byström (1949). The ideal unit cell (Fig. 3a) is tetragonal, body centred, with space group *I*4/*m* and corresponds to that of synthetic α-MnO₂ (Johnson et al., 1997).

The general formula for the minerals of the hollandite supergroup is A²⁺[M⁴⁺₆M³⁺₂]O₁₆ or A⁺[M⁴⁺₇M³⁺]O₁₆, where:

- A is a mono- or divalent cation such Ba²⁺, Pb²⁺, Sr²⁺, K⁺, Na⁺, Tl⁺.
- M⁴⁺ can be either Mn⁴⁺ or Ti⁴⁺.
- M³⁺ can be Mn³⁺, Fe³⁺, Cr³⁺, V³⁺, Al³⁺.

The Hollandite Supergroup is divided in two groups, depending on the dominant M⁴⁺ cation: the coronadite group, if the main M⁴⁺ cation is Mn⁴⁺, and the priderite group if it is Ti⁴⁺ (Biagioni et al. 2023). A list of the Hollandite Supergroup mineral is reported in Table 3.

Despite not being included in the formal supergroup, other minerals showing a hollandite structure exist. For example, libermannite [KAlSi₃O₈] and lingunite [NaAlSi₃O₈] are high-pressure polymorphs of K-feldspar and albite, respectively, both showing a tetragonal *I*4/*m* hollandite structure (Chen et al., 2000; Ma et al., 2018). Another example is the mineral akaganéite [(Fe³⁺,Ni²⁺)₈(OH,O)₁₆Cl_{1.25}], also known as β-FeOOH: a common soil mineral found also as a

corrosion product of natural iron minerals and steel artefacts showing a distorted monoclinic hollandite structure (Post and Buchwald, 1991).

In addition to the minerals, a number of synthetic analogues with very diversified compositions has been developed over the past years, for the purpose of using them as ionic conductors (e.g., Beyeler, 1976), catalysts (e.g., Li and King, 2005), materials for battery applications (e.g., Tompsett and Saiful Islam, 2013) and radwaste immobilization (e.g., Ringwood et al., 1979).

Table 3. The hollandite supergroup minerals divided in coronadite and priderite groups.

Coronadite Group	Priderite Group
Coronadite [Pb(Mn ⁴⁺ ₆ Mn ³⁺ ₂)O ₁₆]	Priderite [K(Ti ⁴⁺ ₇ Fe ³⁺)O ₁₆]
Ferricoronadite [Pb(Mn ⁴⁺ ₆ Fe ³⁺ ₂)O ₁₆]	Mannardite [Ba(Ti ⁴⁺ ₆ V ³⁺ ₂)O ₁₆]
Hollandite [Ba(Mn ⁴⁺ ₆ Mn ³⁺ ₂)O ₁₆]	Henrymeyerite [Ba(Ti ⁴⁺ ₆ Fe ³⁺ ₂)O ₁₆]
Ferrihollandite [Ba(Mn ⁴⁺ ₆ Mn ³⁺ ₂)O ₁₆]	Mannardite [Ba(Ti ⁴⁺ ₆ V ³⁺ ₂)O ₁₆]
Cryptomelane [K(Mn ⁴⁺ ₇ Mn ³⁺)O ₁₆]	
Strontiomelane [Sr(Mn ⁴⁺ ₆ Mn ³⁺ ₂)O ₁₆]	
Manjiroite [Na(Mn ⁴⁺ ₇ Mn ³⁺)O ₁₆]	
Thalliomelane [Tl(Mn ⁴⁺ ₇ Mn ³⁺)O ₁₆]	

The M cations are octahedrally coordinated by six oxygen atoms and lie in special position (x; y; 0) on the mirror plane perpendicular to the fourfold axis of the tetragonal structure. MO₆ octahedra share edges to form double chains in the fourfold axis direction, and corners with further double chains of octahedra, thus creating a solid octahedral framework. The latter describes an array of 2x2 octahedra wide tunnels which extends along the fourfold axes of the crystal structure, and is occupied by the A cations (Fig. 3b). MO₆ octahedra can be distorted for two main reasons: (1) due to the Jahn-Teller effects, which causes the differential elongation of the M-O distances, and (2) due to the electrostatic repulsion between the M cations within the octahedral chains, which results in the off-centre shifts in opposite directions of the M cations themselves (Cheary, 1986a; Kaltak et al., 2017). Cell parameters and tunnels size depend mainly on the average M cation size (Post et al., 1982; Cheary, 1986a). Each tunnel is confined by four walls of MO₆ octahedra double chains and is surrounded by other four tunnels, that share an octahedral wall with it. Due to their tunnel feature, hollandite supergroup minerals are classified

among the tunnel oxides (Pasero, 2005). Synthetic hollandites are usually placed among the octahedral molecular sieves (OMS) (De Guzman et al., 1994).

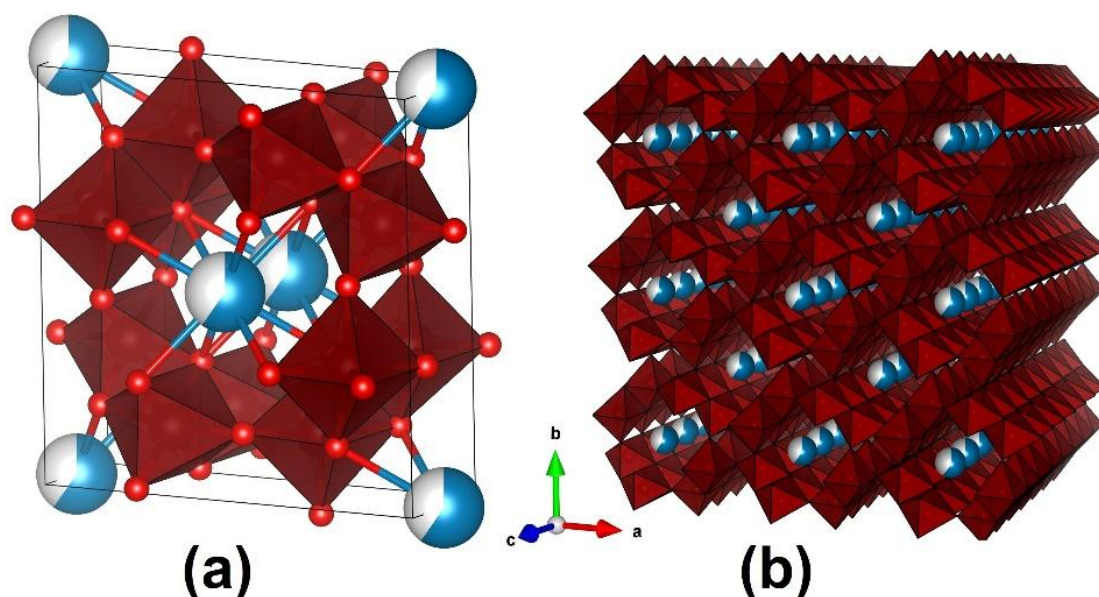


Figure 3. Unit cell of hollandite (a) and overall structure highlighting the tunnels (b).

Colour scheme: M = dark red; A = cyan; O = red.

A cations are coordinated by eight oxygen atoms forming a distorted prism. Larger cations generally occupy the central, highly symmetrical positions $2a$ and $2b$, that lie on the fourfold axis of the tetragonal unit cell, while smaller cations are displaced in the more peripheral $8h$ and $8h'$ positions (Fig. 4), which are shifted toward the tunnel walls (Tumurugoti et al., 2020).

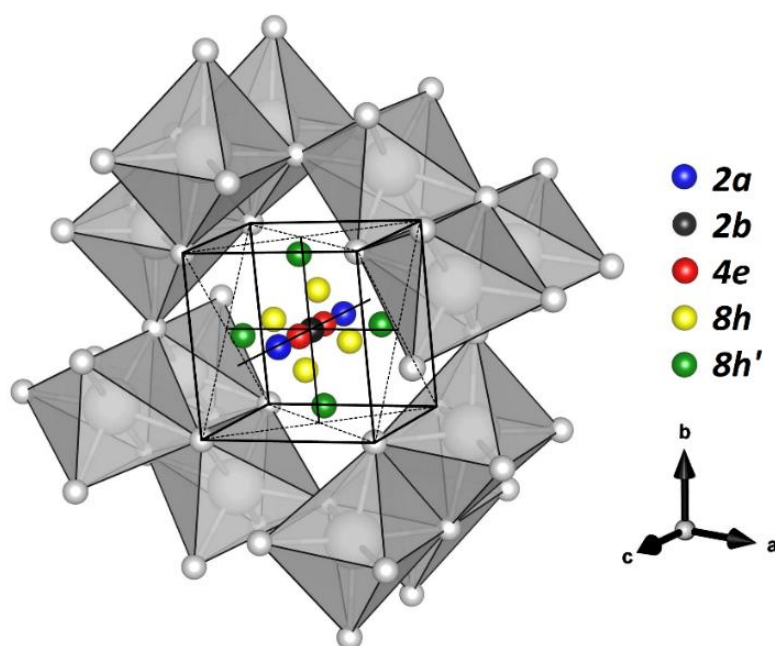


Figure 4. Possible crystallographic positions within the tunnel's oxygen cage. From Tumurugoti et al. (2020), slightly modified.

If the A cation is small enough, the octahedral walls undergo twisting distortion, that can lead to a reduction in symmetry from tetragonal, space group $I4/m$ (Fig. 5a), to monoclinic, space group $I2/m$ (Fig. 5b). Indeed, due to the deformation of the lattice, the square section of the tunnels is distorted in a lozenge shape; the volume of the tunnels decreases, allowing for smaller cations to fit better within the oxygen cages (Post et al. 1982; Nistor et al. 1994). In general, the symmetry of a hollandite can be determined by the relative size of the ions occupying the tunnels compared to those forming the octahedral framework. For high r_A/r_M ratios, the tetragonal symmetry is preferred, while low r_A/r_M promotes a reduction to the monoclinic symmetry (Post et al., 1982). A decrease in symmetry can be also associated with charge localization (e.g., the formation of Mn^{3+} centres), or the distortion of the MO_6 octahedra due to the occurrence of the Jahn-Teller effect (Kaltak et al., 2017).

In tetragonal hollandites MO_6 octahedra, even when they are distorted, are all identical, while in monoclinic hollandites there are two different types of octahedra and only those of the opposite walls are identical (Cheary, 1986b). The lowering of the symmetry from tetragonal to monoclinic causes the splitting of both octahedral and oxygens sites (Table 4).

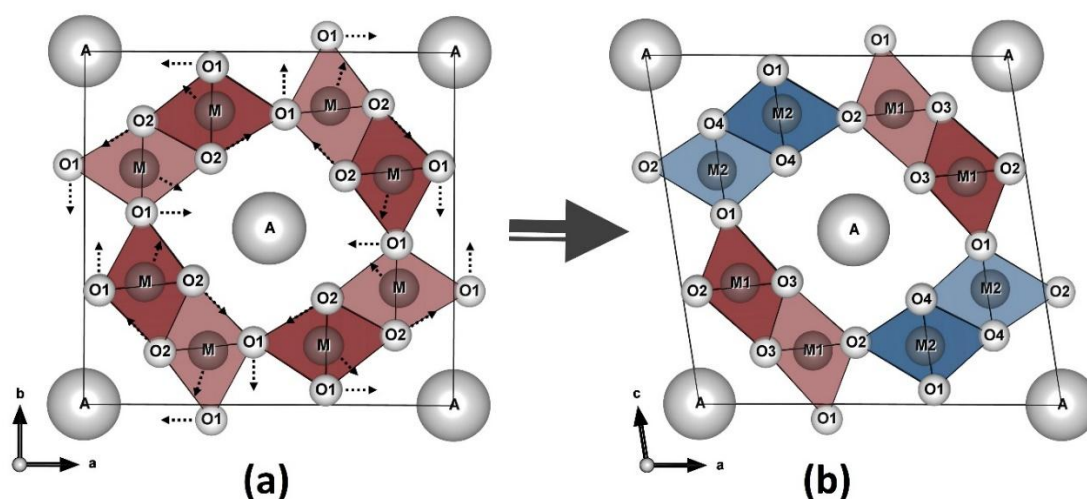


Figure 5. (a) Unit cell of tetragonal ($I4/m$) hollandite. Dotted arrows show the atomic displacement that led to the monoclinic cell. (b) Unit cell of monoclinic ($I2/m$) hollandite. From Tumurugoti et al. (2020); aesthetic modified.

Monoclinic to tetragonal transitions can occur in both natural and synthetic hollandites when they are heated (e.g., Nistor et al., 1994) or irradiated with heavy ions (e.g., Grote et al., 2019).

Single crystal X-ray and neutron diffraction structure refinements often show large thermal motions in the A sites, with thermal ellipsoid stretching along the tunnel axis, and the displacement of the tunnel cations from the conventional A position, thus suggesting the occurrence of positional disorder phenomena (Fournès et al., 1977; Sinclair et al., 1980; Post and Bish, 1989).

The reasons of the disorder are still not very clear. According to Post et al. (1981), the displacement could be explained by the relationships between the geometry of the tunnel cavity and the ionic

radius of the tunnel cations. Therefore, a cation could be shifted along the tunnel axis to optimize its distances with the framework oxygens. For example, in the cryptomelane studied by the latter authors, K^+ lies in the A site at $\sim 2.88 \text{ \AA}$ from eight framework oxygens. In this case, the K-O distance is very close with that predicted using the ionic radii sum of Shannon (1976). On the other hand, Sr-O distances wouldn't be acceptable considering the smaller Sr^{2+} placed in the A site. In fact, Sr^{2+} turns out to be shifted of $\sim 0.6 \text{ \AA}$ along the tunnel axis, resulting in an average Sr-O distance of $2.65 \text{ \AA}$, which is coherent with that predicted using the ionic radii sum. In other words, each type of cation could choose its position to better fit within the tunnel cavities. In addition, according to Post and Burnham (1986), the displacement can be also affected by interactions among tunnel cations in neighbouring tunnels. Nonetheless, the magnitude of the displacement from the centre of the tunnel generally increases with the decreasing of the ionic radius of the A cations.

Table 4. Positional parameters for tetragonal (space group $I4/m$) and monoclinic (space group $I2/m$) hollandites.

Site	Wyckoff position	x	y	z
<i>space group $I4/m$</i>				
A	$2b$	0	0	$\frac{1}{2}$
M	$8h$	x	y	0
O1	$8h$	x	y	0
O2	$8h$	x	y	0
<i>space group $I2/m$</i>				
A	$2b$	0	$\frac{1}{2}$	0
M1	$4i$	x	0	z
M2	$4i$	x	0	z
O1	$4i$	x	0	z
O2	$4i$	x	0	z
O3	$4i$	x	0	z
O4	$4i$	x	0	z

Post and Burnham (1986), on the basis of a structure-energy calculations model, revealed that the minimum-energy positions of tunnel cations in the hollandite structure are a function of the configuration of the lower-valence cations in the octahedral site. In other words, the distribution of the cations within the tunnels could be driven by the disordered allocation of the trivalent cations in the octahedral sites. According to the same authors, the electrostatic repulsion among adjacent tunnel occupants could also play an important role in the displacement of the occupants from the conventional A position.

The cation displacement is important for the definition of the tunnel maximum occupancy. Since their spacing is too short, two neighbouring A sites can't be simultaneously occupied. As a result, if all the cations are allocated precisely in A, the maximum occupancy of the site can't exceed $1/2$ (Fig. 6a). Nevertheless, the increased interaction distance due to a cation displacement can minimize the electrostatic repulsion between neighbouring cations, thus increasing the tunnel

occupancy. For example, Post and Bish (1989) found out that Pb cations in coronadite are displaced away from filled and toward vacant sites in adjacent unit cells along a tunnel (Fig. 6b). As a result, the Pb occupancy of the tunnel sites increases up to $2/3$.

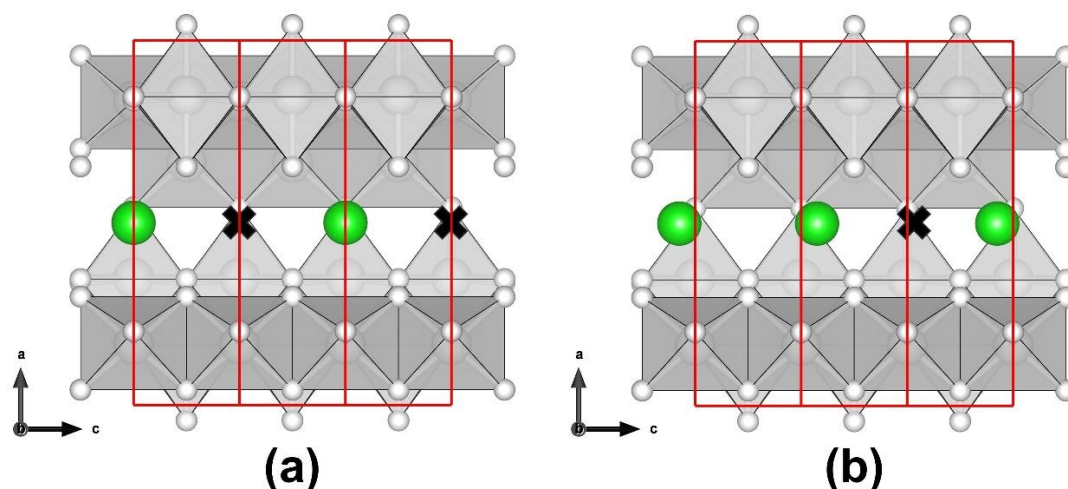


Figure 6. Distribution of cations in three unit cells (red rectangles) along the hollandite tunnel. The green circles represent the tunnel cations while the black crosses the vacancies. In (a) the A cations are placed at their conventional position and only half of the sites are occupied. In (b) the A cations are shifted from their conventional position, thus minimizing the repulsion forces and allowing a site occupancy of $2/3$. Modified after Post and Bish (1989).

The maximum tunnel occupancy also depends on the cation size and charge. In general, the hollandite structure can accommodate smaller and monovalent cations better than larger and divalent ones. For example, the tunnel occupancy in large, divalent Ba-bearing hollandites seldom reaches 1 tunnel cation per unit cell, while in smaller, monovalent Na-bearing hollandites it can reach up to 1.5 cations per unit cell, that is $3/4$ of the full tunnel occupancy (Post and Bish, 1989).

2.3. References

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3. The three employed Heavy Metals: Thallium, Lead and Zinc.

3.1. Thallium

Thallium is the 81st element of the periodic table, a post-transitional metal belonging to the p-block with an average atomic weight of 204.4 u and a $[\text{Xe}]4f^{14}5d^{10}6s^26p^1$ electron configuration. In addition to the metallic form, it can be found in two oxidation states: Tl(I) and Tl(III). The trivalent cation has a chemical behaviour close to that of other elements of the same group, B^{3+} , Al^{3+} , Ga^{3+} and In^{3+} , while the monovalent one resembles more the alkali metals, especially K^+ and Rb^+ . In aqueous solutions, Tl^+ is the more common and stable form, while Tl^{3+} is unstable and tends to be slowly reduced to the monovalent state (Delvalls et al., 1999; Peter and Viraraghavan, 2004; Yang et al., 2022).

Monovalent thallium is often found replacing potassium by isomorphic substitution in common minerals, such as potassium feldspar, plagioclase, mica, alunite and jarosite. While its average concentration in continental earth's crust is approximately 0.5 mg/Kg (Wedepohl, 1995), Tl can be found replacing K in rock-forming minerals in pegmatites and igneous rocks with concentrations in the order of magnitude of tens of mg/Kg (e.g., Akintola and Adekeye, 2008). Nevertheless, due to its sulphur-binding properties, sulphide minerals, where it can be found associated with Fe, Pb, Zn, Cu, Hg, As and other metals, are the best environment for Tl^+ (Xiong 2009; Liu et al., 2019). Particularly, its concentrations can exceed thousands of mg/Kg in Zn-Pb deposits and Fe-sulphides such as pyrite (e.g. Duchesne et al., 1983; George et al., 2019). Tl^+ may be also present in coal, with concentrations that range from 0.5 to 3 mg/Kg (Smith and Carson, 1977). Its occurrence is attributed to the presence of metal sulphides within the coal, mainly Tl-bearing pyrite particles (Finkelman, 1995).

Tl^+ is hence contained mostly in other-metal minerals as a trace element, and phases where it represents a major constituent are very rare. Again, they are represented mainly by sulphides, where Tl^+ is associated with As, Sb, Pb, Hg and other elements with a good affinity for sulphur.

In thallium sulphides, Tl^+ is bounded with S atoms with interatomic distances usually ranging from 2.7 to 3.3 Å, forming distorted polyhedra with different coordination numbers. For example, in the mineral biagioniite $[\text{Tl}_2\text{SbS}_2]$ Tl is found in three different coordinations: linear, triangular and tetrahedral (Fig. 1a) (Bindi et Moëlo, 2020). In carlinite $[\text{Tl}_2\text{S}]$, Tl is found in trigonal pyramidal coordination, with Tl-S bounds in the range 2.85-3.05 Å (Radtke and Dickson, 1975). In lorándite $[\text{TlAsS}_2]$, Tl is coordinated by five sulphur atoms forming a flattened pyramid (Fig. 1b) (Fleet, 1973); in hutchinsonite $[\text{TlPbAs}_5\text{S}_9]$ it is present in sixfold coordination forming a heavily distorted octahedron (Fig. 1c) (Matsushita and Takéuchi, 1994); and in simonite $[\text{TlHgAs}_3\text{S}_6]$ it forms a 7+2 irregular polyhedron (Fig. 1d) (Engel et al., 1982). The high degree of distortion of the Tl coordination polyhedra of the sulphides may be attributed to presence of an electron pair in monovalent thallium.

Thallium has been also found associated with manganese and iron oxides, usually as a trace element (e.g., Cabral et al., 2002; Huang and Fu, 2023). Of particular interest for the purpose of this thesis is thalliomelane $[\text{Tl}(\text{Mn}^{4+}_{7.5}\text{Cu}^{2+}_{0.5})\text{O}_{16}]$, a mineral of the Hollandite Supergroup where Tl^+ is instead reported as a major constituent, occupying the tunnel microporosities of the crystal structure, where it is coordinated by eight oxygen atoms to create an eightfold cuboid-like coordination (Fig. 2a) (Gołębiowska et al., 2021).

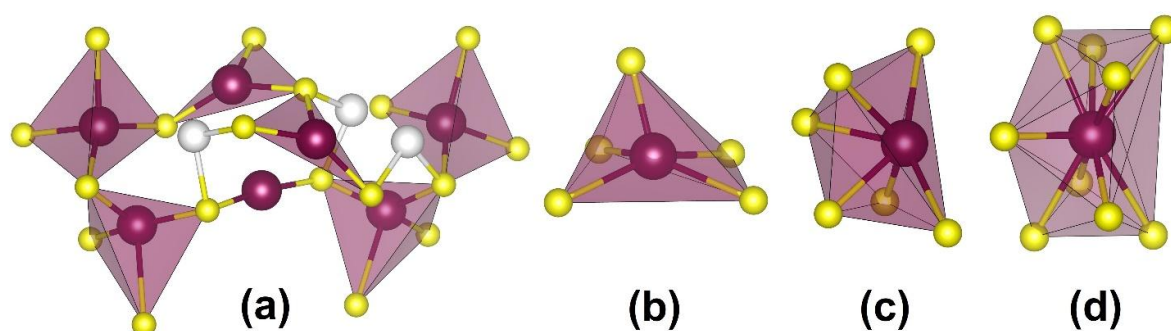


Figure 1. Coordination environment of thallium in different sulphide minerals: detail of the biagionite structure showing the three type of Tl coordination (a); lorándite (b); hutchinsonite (c) and simonite (d).

Colour scheme: Tl = raisin purple; S = yellow; Sb = white.

If natural Tl oxides are very rare, in the past years several thallium-containing oxides have been synthesized (e.g., Shannon et al., 1967; Bhattacharya et al., 2002; Moeinian and Akhbari, 2016). Among them a series of pyrochlores have been produced and described. Fourquet et al. (1979) reported different synthetic Tl pyrochlores, such as $\text{TlNb}_2\text{O}_5\text{F}$, $\text{TlTa}_2\text{O}_5\text{F}$, TlNbWO_6 , TlTaWO_6 , TlSbWO_6 , that have been produced by high temperature solid state routes as part of the PhD thesis of Michel, in 1974, and Fourquet, in 1977. The latter author described the coordination environment of thallium in the phase $\text{TlNb}_2\text{O}_5\text{F}$, outlining the displacement of Tl from the supposed $8b$, that is the Y site, position to a set of two $32e$ positions, the A' and Y' sites (Fig. 2b). Another thallium-containing synthetic pyrochlore is TlMn_2O_7 , which was the subject of numerous studies due to its magnetic properties (e.g., Singh, 1997; Hwang and Cheong 1997; Shimakawa and Kubo, 1999). In this case, thallium results to be trivalent and it takes a position at the centre of the hexagonal MnO_6 rings, that is in the conventional A site (Shimakawa and Kubo, 1999). Regarding trivalent thallium, the number of its minerals is very small. Just few, very rare oxides, such as avicennite $[\text{Tl}_2\text{O}_3]$ and amgaite $[\text{Tl}_2^{3+}\text{Te}^{6+}\text{O}_6]$, and chlorides, like chrysothallite $[\text{K}_6\text{Cu}_6\text{Tl}^{3+}\text{Cl}_{17}(\text{OH})_4 \cdot \text{H}_2\text{O}]$ and kalithallite $[\text{K}_3\text{Tl}^{3+}\text{Cl}_6 \cdot 2\text{H}_2\text{O}]$, are known.

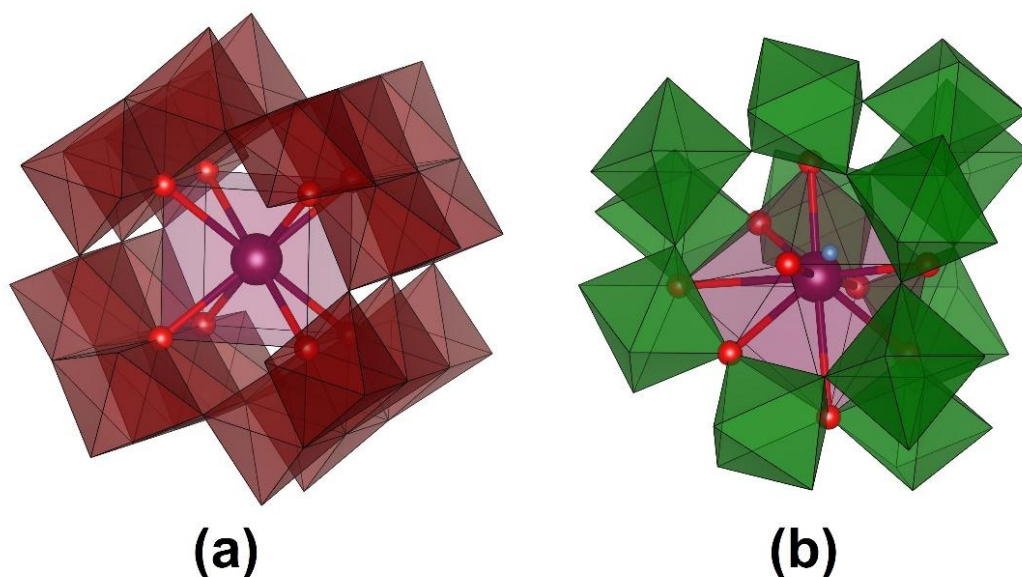


Figure 2. Coordination environment of Tl in thalliomelane (a) and TlNb₂O₅F pyrochlore (b). The light blue dot in (b) represent the position of the 8b site, while the thallium atom is placed in one of the surrounding 32e sites.

Colour scheme: Tl = raisin purple; O,F = red; MnO₆ = dark red; NbO₆ = green.

Thallium is a highly toxic element, that can be lethal even in low amounts. It can be introduced in the human body by ingestion, inhalation or through the skin. When it happens, it is absorbed rapidly by mucosa and spread to the tissue by the blood stream (Cvjetko et al., 2010). The lethal dose is estimated between 0.5 and 1 g, or 10 to 15 mg/Kg of body mass for a single ingestion, but death can occur even at lower dosage (Moeschlin, 1980; Manzo, 2007; Cvjetko et al., 2010). The excretion rate is very slow, and the metal tends to persist and accumulate in the organism even at low levels of exposure (Cvjetko et al., 2010).

Acute thallium intoxications may lead to many, non-specific symptoms involving multiple systems of the human organism. They include various gastrointestinal disturbance, nervous systems, neuromuscular and cardiac disorders, damages to the optic nerve, pain in abdomen, back, arms and legs, sleep disorders, weakness, hallucinations, confusion, delirium, convulsion and coma (Galván-Arzate and Santamaria, 1998; Rodriguez-Mercado and Altamirano-Lozano, 2013).

The only distinguishing symptom of an acute Tl intoxication is alopecia. It is hypothesized that, due to its affinity with sulphur, thallium may bind with the sulfhydryl group of cysteine (Fig. 3), preventing the keratinisation of hair proteins and then causing the loss of hair (Cvjetko et al., 2010 and references therein). Hair loss begins roughly ten days after the intake while the complete epilation occurs after one month (Mulkey and Oehme, 1993).

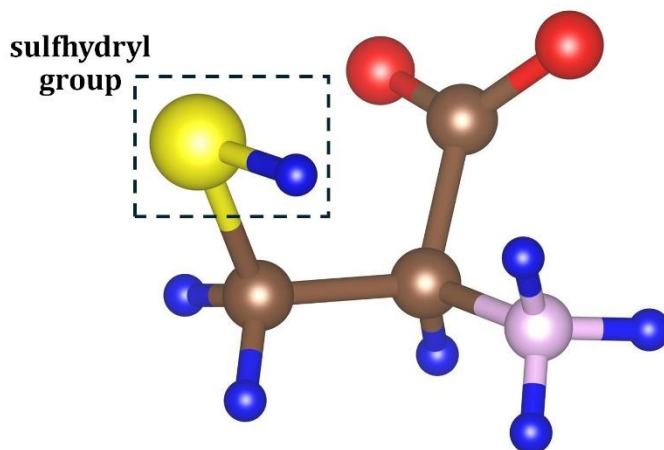


Fig 3. Structure of cysteine [$C_3H_7NO_2S$]. The dotted rectangle underlines the sulfhydryl group -SH.
Scheme of colours: C = brown; H = blue; N = pink; O = red; S = yellow.

The variety of the symptoms reflects the complexity in the thallium behaviour and its ability to spread all over the human body, reason why the mechanisms that mediate thallium toxicity are still poorly understood.

It is believed that, due to their similarity, thallium may follow the same distribution pathways of potassium, thus altering many K-related biological processes. Tl can enter cells through potassium uptake channels, inhibiting the activity of many K-dependent enzymes (such as Na^+/K^+ -ATPase, that mediate the synthesis of ATP), altering the permeability of cellular membranes, damaging DNA and proteins, inducing oxidative stress on mitochondria and, *in extrema ratio*, killing the cell itself (Genchi et al., 2021).

Thallium can also bind with sulfhydryl groups of many proteins, enzymes, and other molecules compromising their functions and increasing oxidative stress in the cell (Mulkey and Oehme, 1993). The above-mentioned deactivation of cysteine causing alopecia is quite an example.

If many cases of acute intoxication reported in scientific literature, only few investigations were focused on the effects of sublethal doses of Tl in chronic exposures resulting from environmental contamination. In a study conducted on rats, Galván-Arzate et al. (2000) revealed that, even in low doses, Tl can lead to an important toxic response due to lipid peroxidation (oxidative degradation of lipids), which can play an important role in organ dysfunction and tissue damage. According to Bramanti et al. (2019), low doses of thallium (in the order of 1-100 $\mu\text{g/L}$) can induce changes in neuronal morphology and mitochondrial activity. Duan et al. (2020) stated that thallium exposure at low concentration can lead to early dysfunction on multiple organs in children. In their work, they reported the case of six children living near coal and metal sulphide mines with a Tl urinary concentration ranging from 13.4 to 60 $\mu\text{g/L}$ and suffering of permanent liver, renal and myocardial damages.

For a long time, thallium couldn't find much room in the global economy. In the twenties of the past century, it was introduced as pesticide and rodenticide, but it was banned in 1965 by the USA government due to the occurrence of several accidental poisonings (Chamberlain et al., 1958; Riyaz et al., 2013). In recent years, the interest for this element has risen and today it finds some application in tech industry and medical diagnostics. It is used as catalyst for the synthesis of organic compounds, as constituent of semiconductors and high-temperature superconductors, in the production of optical lenses, laser equipment, scintillator crystals, photocells and low temperature thermometers (Genchi et al., 2021; Liu et al., 2019). In radiology, ^{201}Tl (TlCl) is used as a radiological contrast agent for scintigraphy imaging (Genchi et al., 2021).

All these applications require very low amounts of thallium, and its production is quite scarce. Since 1985, the world annual production of Tl usually ranges from 10 to 16 tons (Cvjetko et al., 2010; Liu et al., 2019). Thallium is mostly exploited as a by-product during the mining of Pb, Zn, Co, As, Au and Hg ore deposits. The only mine exclusively dedicated to the extraction of this metal is the Xiangquang deposit, Anhui province, China, where hydrothermal orebodies, containing lorándite, hutchinsonite and Tl-bearing pyrite, provide a metal reserve of about 250 t (Zohu et al., 2005). In Europe, the Alshar deposit, Republic of North Macedonia, hosts significant amounts of lorandite, with an estimated Tl reserve of approximately 500 t (Volkov et al., 2006). Although mining activities were discontinued at the beginning of the twentieth century, this mineralization could gain new interest in light of the recent Critical Raw Materials Act (European Commission 2023).

If some authors (e.g., Xiao et al., 2004) pointed out concerns related to 'natural' contaminations due to the mobilization of Tl from outcropping rock bodies, sulphide ore mining related activities and coal-fired power plants have been identified as the main sources of Tl pollution. During the smelting processes of the metal ores and the combustion of coal, Tl originally contained in the solid mineral phases vaporises and condenses on the surfaces of fly ash particles in the cooler parts of the burner. As a result, the concentrations of Tl dramatically increase from the raw material to the final waste. For example, Liu et al. (2016) reported an increase of Tl from 15.1-87.7 mg/Kg in Zn-Pb ore materials from Northern Guangdong Province, China, to 3280-4050 mg/Kg in electrostatic dust and 13300 mg/Kg in acidic waste. According to the same authors, Tl compounds bound to the surface of ashes are also very leachable and can be easily released in water or soil systems during the disposal or the recycling of the industrial wastes.

Regarding the coal combustion in power plants, Antón et al. (2013) found that the content of Tl in ashes increases with the decreasing particle size, with the higher concentrations found in particles with a diameter of less than 7.3 μm . Such tiny particles can bypass conventional retention devices, be released in the atmosphere and then inhaled by living beings or precipitate, contaminating soil and water systems.

Cement plants are another relevant source of thallium pollution (Kazantis et al., 2000). The emission of thallium is mainly due to the roasting of Tl-containing pyrite that is used as ferric iron additive. Once again, during the cement production Tl binds to fly ash particles after it is released from pyrite (Brockhaus et al., 1981; Dolgner et al., 1983).

The overall industrial annual emissions of thallium were estimated to be 2000-5000 tons before the year 2000 (Kazantis et al., 2000), but they could be dramatically increased in the recent years due to the growth of mining and industrial activities in various regions of the world.

In unpolluted water environments, Tl amounts are usually very low. Tl concentration in seawater has been found to range from 12 to 16 ng/L, showing a relatively constant distribution through the world's oceans (Flegal and Patterson, 1985). In uncontaminated freshwater they usually range from 5 to 10 ng/L (Peter and Viraraghavan, 2004), with a world average concentration in rivers of 6 ± 4 ng/L (Nielsen et al., 2005).

Environmental standards for Tl are very restrictive. In Italy, the maximum Tl concentration is set at 1 µg/L for wastewater (Ministero dell'Ambiente e della Tutela del Territorio, 2003) and at 2 µg/L for groundwater (Ministero dell'ambiente e della Tutela del Territorio e del Mare, 2006). An official limit for drinking water does not yet exist but, following the thallium contamination in aqueduct pipelines in Pietrasanta and Valdicastello Carducci (Lucca Province, Tuscany, Italy), the Istituto Superiore di Sanità (ISS) set a temporary maximum contaminant level of 2 µg/L (Lucentini et al., 2018).

In the USA, the maximum admissible Tl concentration in drinking water set by the United States Environmental Protection Agency (USEPA) is 2 µg/L (USEPA, 2018); the one adopted in China is 0.1 µg/L (SEPA, 2006).

In the past years, several thallium water contaminations have been reported all over the world. Chem et al., (2000) found high Tl concentrations, up to 24 µg/L, near coal-fired power plants in the eastern region of Canada. Shortly after, Chem (2001) drew a map of Tl contamination in Canadian waters, revealing that Tl concentrations in waters surrounding power plants were 20 times greater than the estimated background values.

As a consequence of an extremely rapid growth in mining and industrial activities, a number of main rivers in China have been contaminated with thallium. For instance, Liu et al. (2019) reported several cases of waterbodies contamination: the Beijiang River of Guangdong (2010), the Hejiang River of Guangxi (2013), many main rivers in the Xinyu and Jiangxi prefectures (2016), the Jiang River in Sichuan and Shanxi provinces (2017), the Lu River across Hunan Province and Jiangxi Province (2018).

In Italy, Tl was found in 2014 in tap water distributed in the areas of Pietrasanta and Valdicastello Carducci, leading to a Do Not Drink order to the population and a detailed investigation summarized in a conspicuous collection of scientific papers (e.g. Campanella et al., 2016; Campanella et al., 2017; Biagioni et al., 2017; D'Orazio et al., 2017). The source of thallium was identified in two abandoned mines (Arsiccio and Pollone mines) containing Tl-bearing pyrite orebodies with Tl concentrations up to 1100 mg/Kg (D'orazio et al., 2017). The concentrations of Tl in the spring water were between 5 and 37 µg/L; those measured in tap water ranged from 2 to 10 µg/L (Campanella et al., 2016).

3.2. Lead

Lead is the 82nd element of the periodic table, a post-transitional metal with an average atomic weight of 207.2 u and a $[\text{Xe}]4f^{14}5d^{10}6s^26p^2$ electron configuration. In addition to the metallic form, lead can be found in two oxidation states: Pb(II) and Pb(IV). Divalent lead is the most widespread form in the environment, especially in water systems, and the most important for inorganic chemistry and toxicology, while tetravalent lead is relatively common in organic chemistry. Lead is a chalcophile element and tends to accumulate in sulphide deposits, especially in association with zinc. The main lead mineral is galena $[\text{PbS}]$, usually found in association with other metal sulphides such as sphalerite $[(\text{Zn},\text{Fe})\text{S}]$ and chalcopyrite $[\text{CuFeS}_2]$ in hydrothermal veins or low-temperature, carbonate-hosted Pb-Zn deposits. Besides sulphide ores, Pb is extracted from several other minerals, such as litharge $[\text{PbO}]$, cerussite $[\text{PbCO}_3]$ and anglesite $[\text{PbSO}_4]$ (Casas and Sordos, 2006).

Depending on the ligands and the crystal structure of the host mineral, lead can be found in many different coordination environments. For example, in galena (Fig. 1a) lead is sixfold coordinated by S atoms, forming a regular octahedron with Pb-S distances of about 2.97 Å (Noda et al., 1987), while in cerussite (Fig. 1b) it is placed within an irregular octahedron surrounded by nine oxygens atoms belonging to the CO_3^{2-} groups, with Pb-O distances ranging from 2.58 to 2.77 Å (Ye et al., 2012). In oxides, the interatomic distances are shorter. In litharge (Fig 1c), Pb is fourfold coordination with oxygens atoms at about 2.3 Å to form a PbO_4 pyramid (Boher et al., 1985), while in plattnerite $[\text{PbO}_2]$ (Fig 1d), where lead is in its tetravalent form, the Pb-O distances of the slightly deformed Pb octahedron are about 2.15 Å (Bolzan et al., 1997).

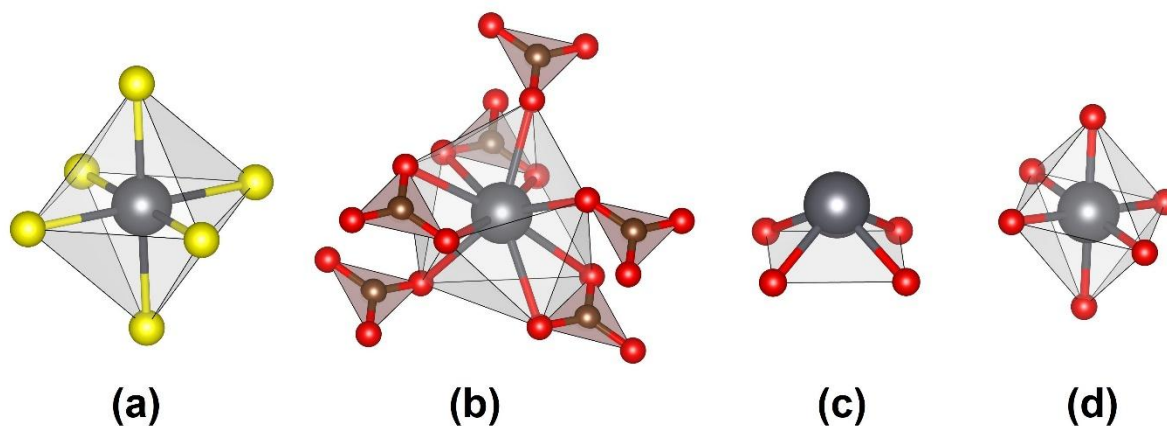


Figure 1. Coordination environment for Pb in galena (a), cerussite (b), litharge (c) and plattnerite (d). Colour scheme: Pb = grey; S = yellow; O = red; C = brown.

To date, two lead-containing minerals of the hollandite supergroup are known: coronadite $[\text{Pb}(\text{Mn}^{4+}_6\text{Mn}^{3+}_2)\text{O}_{16}]$ and ferricoronadite $[\text{Pb}(\text{Mn}^{4+}_6\text{Fe}^{3+}_2)\text{O}_{16}]$, both belonging to the coronadite group. In coronadite and ferricoronadite, Pb is placed within the tunnel axis of the hollandite structure, slightly shifted along the tunnel to the conventional A position (Post and Bish, 1989). Pb

hence results at the top of a distorted PbO_4 pyramid (Fig. 2a). Such coordination, close to that showed in litharge, is attributed to the effect of the Pb^{2+} stereoactive lone pair.

In addition to the natural Pb-bearing hollandites, a lead-vanadium oxide $[\text{Pb}_{1.6}\text{V}_8\text{O}_{16}]$ with the hollandite structure was produced and studied for its magnetic properties by Maignan et al. (2010), while a similar compound $[\text{Pb}_{1.32}\text{V}_{8.35}\text{O}_{16.7}]$ was synthesized by Mentre and Abraham (1996).

The latter authors described a $I2/m$ crystal structure with the tunnel occupied by Pb and part of the V atoms. Here, lead atoms are distributed in two different sites: a $4g$ site, comparable to that found in the coronadite described by Post and Bish (1989), and a $4i$ site, shifted towards the tunnel's octahedral walls (Fig 2b). Pb in the $4i$ position results again at the top of a PbO_4 pyramid, showing the effects of the lone pair, which is oriented towards the tunnel axis.

Regarding pyrochlores, different lead-containing mineral species have been described in the past years. They are hydroxyplumbopyrochlore $[(\text{Pb}, \square)_2\text{Nb}_2\text{O}_6(\text{OH})]$, oxyplumbopyrochlore $[\text{Pb}_2\text{Nb}_2\text{O}_6\text{O}]$, kenoplumbopyrochlore $[(\text{Pb}, \text{A})_2\text{Nb}_2\text{O}_6\square]$, belonging to the pyrochlore group, and kenoplumbomicrolite $[(\text{Pb}, \square)_2\text{Ta}_2\text{O}_6(\text{O}, \text{OH}, \square)]$, of the microlite group. In both pyrochlore and microlite group members, Pb is placed in the conventional A tunnel site, surrounded by six oxygen of the octahedral framework and two O^{2-} or OH^- allocated in the Y sites (Fig. 2c) (e.g., Atencio et al., 2018; Li et al., 2020).

More compounds having a pyrochlore structure have been synthesized with Pb in the tunnels and different metals in the octahedral framework. Among the others, $\text{Pb}_2\text{Ir}_2\text{O}_{6.5}$ (Kennedy, 1996) and $\text{Pb}_2\text{Ru}_2\text{O}_{6.5}$ (Tachibana et al., 2006) are worthy of note due the slight displacement along the tunnel axis of Pb from the conventional A position.

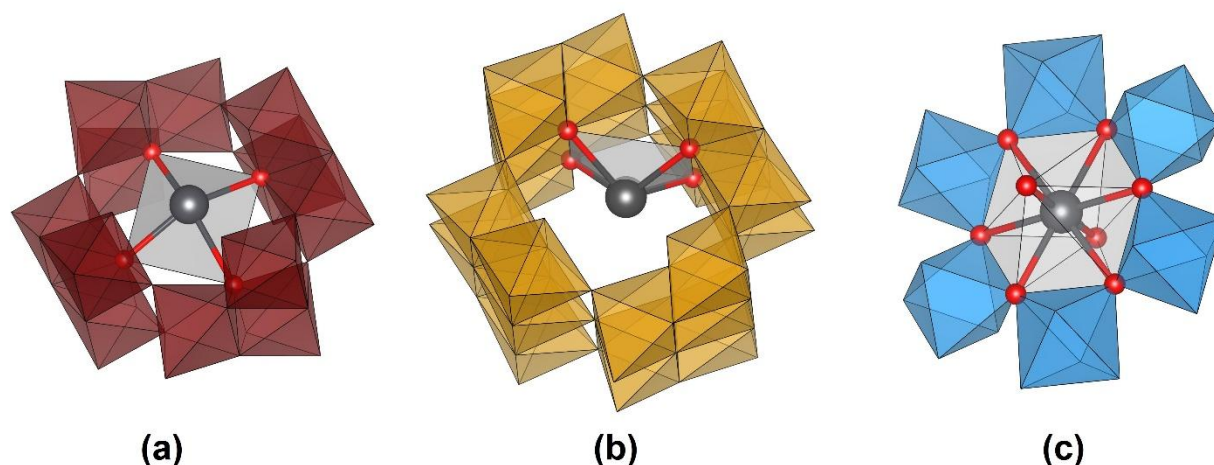


Figure 2. Coordination environment of Pb in coronadite (a), $\text{Pb}_{1.32}\text{V}_{8.35}\text{O}_{16.7}$ synthetic hollandite (b) and natural pyrochlores (c).

Colour scheme: Pb = grey; O = red; MnO_6 = dark red; VO_6 = orange; $(\text{Ta}, \text{Nb})\text{O}_6$ = light blue.

Lead is a highly toxic element which presents a serious risk for human health. It can be absorbed by ingestion of contaminated food and water, by inhalation of polluted air and by skin contact with lead-containing materials.

Acute intoxications are related to short but intense exposure, with blood Pb levels reaching up to 100-120 µg/dl (Flora et al., 2006; Carocci et al., 2016). The first symptom of Pb acute intoxication is a feeling of malaise, accompanied by constipation and digestive disturbance, then slight colic and anaemia occur, followed by polyuria and albuminuria. At the early stage of poisoning, the most diagnostic sign is the so-called Burton's line, a slight blue line that appears at the junction of the teeth with the gums. If the assumption of lead continues, the countenance assumes an ashen grey colour; cachexia, severe pain in abdomen and acute colic may develop, followed by nephropathy, muscular paralysis, convulsion and, ultimately, death (Prendergast, 1910; Charkiewicz et al. 2020).

Nowadays, thanks to the public health and environmental protection laws, severe lead poisonings are rare. Nevertheless, repeated exposures to low dosages over a prolonged period can be very threatening due to bioaccumulation phenomena.

After the exposure, lead spreads throughout the body by the blood stream, accumulating in soft tissue, liver, kidney, lung, bones, and cardiovascular, nervous and reproductive systems (Sirivarasai et al., 2015; Manisalidis et al., 2020). Elimination processes can be very slow. If the elimination from blood and soft tissues can take 20-30 days, the bones can retain lead for years. For example, the biological half-life of Pb in trabecular bone is estimated in 10-20 years (Jakubowski, 2014; Charkiewicz et al., 2020).

Lead can interfere with multiple biochemical processes due to its capacity to replace other bivalent cations. It can reduce the activity of enzymes, hinder the synthesis and the functioning of proteins, interrupt the cell haemostasis, undermine inflammatory response and alter the cell signalling (Charkiewicz et al. 2020; Raj and Das, 2023). An important mechanism for Pb toxicity involves its ability to generate oxidative stress, which in turn can lead to the production of free radicals either through the depletion of antioxidants or the production of radical species (Klein et al., 1991; Silbergeld et al., 2000). Chronic exposure can thus result in the development of cancer, especially renal cancer, due to the inclination of lead to accumulate and affect the kidneys (Goyer, 1993; Silbergeld et al., 2000).

The adverse effects of Pb, such as anaemia and renal malfunctioning, can occur even with blood concentrations as low as 10 µg/dL, while a prolonged exposure to low levels of lead can result in blood levels of 40–60 µg/d (Flora et al., 2006), exposing the individual to a decisive risk of renal failure and cardiovascular diseases. Blood levels of 20-29 µg/dL (or even lower than 10 µg/dL) have been associated with increased myocardial infarction and stroke mortality (Lustberg and Silbergeld, 2002; Menke et al., 2006).

Lead has been known and used by mankind since the Neolithic age. The first evidence of lead smelting has been found in Asia Minor and dates back to 7000-6500 BC (Boldyrev, 2018). Before the Roman age, the ancient populations of the Mediterranean and Middle East areas utilized lead mainly to produce ornamental or votive artefacts, as a constituent of eye paints or as a form of currency. In those times, lead was obtained mainly as a byproduct of silver-bearing galena [PbS]. Romans were the first to make extensive use of lead. Due to its resistance to alteration and

malleability, they utilized lead to make pipes and siphons for urban plumbing systems and aqueducts (Waldron, 1973).

Romans and ancient Greeks used lead as a sweetener and preservative for wine, which was intentionally stored in leaden vessel with this purpose or even corrected using lead acetate. In addition, sweetener syrups for wine and food were prepared boiling unfermented grape juice in lead kettles (Needleman, 1999; Kaufman, 1997).

The utilization of leaden containers to store wine protracted up to the 18th century, exposing the consumers to a deadly disease called *colica Pictonum*, that has been very common for centuries and so widespread to touch epidemic levels (Eisinger, 1982).

From the Middle Age to the Industrial Revolution, lead has been mainly used to produce stained glass (e.g., Mecking, 2013), pigments (e.g., Gonzalez et al., 2023), cosmetics (e.g., Littler 2020), bullets for firearms and components for printing presses (e.g., Boldyrev, 2018).

If at the beginning of the Industrial Revolution the world lead production was estimated at around 100000 tons (Casas and Sordos, 2006), in the contemporary age it is in the order of millions of tons. More specifically, the annual lead mine production is estimated at around 4.5 million tons, while the total annual production (mine and secondary, that is recycle, production) is about 12.8 million tons. Identified world lead resources are more than 2 billion tons (USGS annual report, 2024).

Pb finds room in many fields, even if the current trend is to reduce its utilization due to health and environmental concerns. For decades, it was used in paint and as an additive in petrol, becoming one of the most diffuse and worrisome toxic metal in the 20th century (Shy, 1990). Today, the most diffuse application of lead is by far in lead-acid batteries, which rival with lithium-ion batteries in the power storage race (Lopes and Stamenkovic, 2020; Ryś et al., 2024). According to the USGS lead statistic and information, the 85% of the reported lead consumption in the USA in 2023 is accounted by the lead-acid battery industry (USGS, 2024). Due to its durability and low maintenance costs, lead is commonly used in the form of sheets in building industry for flashings, complete roofing systems and vertical wall cladding; because of its water and corrosion resistance it is utilized for pipes in industrial plants and as sheathing material for undersea powder cables. Among the other applications, due to the massive use of X-ray based techniques throughout this work, it is worth to be mentioned the utilization of lead sheets and leaded glass as a radiation shielding material. Nevertheless, due to its toxicity, when it is possible and economically convenient, lead tends to be replaced by other, safer materials, such as aluminium, steel, zinc and polymers (Casas and Sordos, 2006).

Mining and ore smelting processes are among the main sources of lead pollution. Other major sources are lead containing fuels, manufacture of lead-acid batteries, fertilizers and pesticides, coal-powered plants and other industrial activities. Minor sources, less dangerous for the global environment but still very hazardous for the metropolitan human population, are urban waste, sewage, lead-based paints, old toys and furniture, lead solders in water pipes (Komárek et al., 2008; Yang et al., 2020; Raj and Das, 2023).

The average concentration of lead in the earth crust is about 20 mg/kg (Flora et al., 2006). In soil, it is concentrated in the superficial horizons, with natural contents ranging from 1 to 200 mg/Kg, mostly contained in organic matter or bound to iron and manganese oxides and hydroxides (Swaine, 1955; Ettler et al., 2005).

In atmosphere, lead is present mostly in submicrometric aerosols which can be transported by winds over long distances (Komárek et al., 2008).

Lead can enter waterbodies (waters streams, lakes, groundwaters) by leaching of Pb-containing solid waste (e.g., mining waste in slag heaps) and contaminated soils, industrial wastewaters and deposition of windborne particulate (Castro et al., 2011). Natural concentrations of lead in continental surface water are in the range of 1-3 µg/L (Flora et al., 2006), while in the ocean water, the concentrations range from 1 to 15 ng/Kg (Schaule and Patterson, 1981).

Due to its toxicity, environmental limits for Pb in water are very restrictive. In Italy, the maximum Pb concentration is set at 5 µg/L for all the waters intended for human consumption (D.lgs 18/23). Lead is particularly dangerous for children, especially in those younger than five years. This is mainly because Pb can interfere with the fast, natural development of the nervous system. In children, levels of less than 50 ng/L can lead to impairments in neurocognitive and behavioural development (Mayans, 2019).

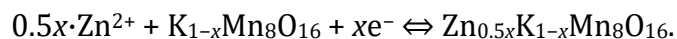
3.3. Zinc

Zinc is the 30th element of the periodic table, a transitional metal of the d-block having an average atomic weight of 65.37 u and a [Ar]3d¹⁰4s² electron configuration. In nature, zinc is usually found in sulphide ores, in association with iron, lead and copper in minerals such as sphalerite, galena, pyrite, bornite and chalcopryrite, and in non-sulphides series of oxidised Zn, Pb-ore minerals (e.g., Prokin and Buslaev, 1998; Boni and Mondillo 2015).

In both sulphides and oxides, zinc is usually found in tetrahedral coordination. For example, in sphalerite [ZnS] and wurtzite [(Zn,Fe)S], it forms ZnS₄ tetrahedra with Zn-S interatomic distances of about 2.3 Å (Evans and McKnight, 1959; Skinner, 1961), while in zincite [ZnO] the Zn-O distances of the ZnO₄ tetrahedra are about 2 Å (Kihara and Donnay, 1985). In the carbonate smithsonite, Zn is in sixfold coordination with the oxygens of the CO₃²⁻ groups, with Zn-O distances of 2.1 Å. In silicate minerals, such as hemimorphite [Zn₄Si₂O₇(OH)₂ · H₂O] and willemite [Zn₂SiO₄], it is again in tetrahedral coordination, with Zn-O distances comparable with those of the zincite (Klaska et al., 1978; Libowitzky et al., 1997).

No natural zinc hollandite or pyrochlore exist. Zinc-containing hollandites were synthesized for radioactive caesium disposal, but Zn is hosted in the octahedral framework and not in the tunnel sites (e.g., Grote et al., 2019).

Mn oxides with hollandite structure have been extensively studied for hydrated Zinc Ion Batteries (ZIBs). In these materials, Zn is inserted into the tunnels via ionic exchange reactions. For example, Cui et al. (2018) described the intercalation of Zn in a synthetic cryptomelane following the reaction ratio:



Le et al. (2021) investigated the effect of the Zn intercalation on the structure of the manganese hollandites. According to their Density Function Theory (DFT) model, zinc would not occupy the conventional A position in the centre of the tunnel, but it is shifted toward the octahedral walls, thus forming a ZnO_5 tetragonal pyramid (Fig 1).

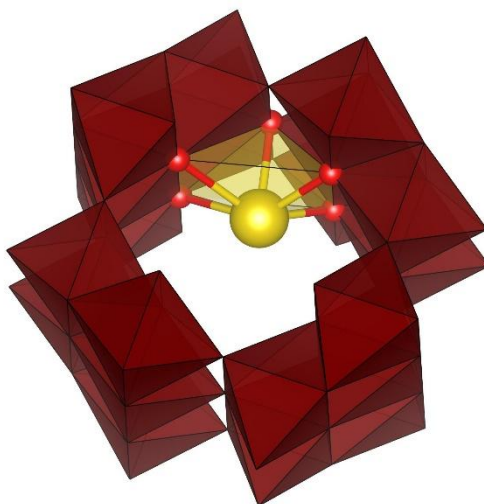


Figure 1. Coordination environment of Zn in synthetic cryptomelane according to Le et al. (2021).

Colour scheme: Zn = yellow; O = red MnO_6 = dark red.

Some synthetic zinc-containing pyrochlores have been produced. For example, some authors, like Liu et al. (1993), Wang et al., (1997) and Ren et al. (2000), reported the synthesis of different bismuth zinc niobate pyrochlores, with Zn allegedly disordered in both tunnel and framework sites, or hosted in the octahedral framework alone, but their structures were not deeply investigated. Arfoy et al. (2025) reported a novel zinc-doped yttrium titanate pyrochlore solid solution, where Zn is hosted in the framework sites. All those compounds were produced with high temperature procedures, suggesting that, at least in HT conditions, Zn would rather occupy the framework octahedra than the tunnel sites.

Compared with thallium and lead, zinc is quite harmless. Rather than toxic, it is considered an important micronutrient, essential for numerous biological functions (Hambidge, 2000; Chasapis et al., 2020). On the average, the dietary intake is in the range of 5-20 mg/d and the tolerable upper intake level has been set by the US Food and Nutrition Board at 40 mg/d for adults older than 19 years (Nriagu, 2007).

Long-term, high-dose exposures can interfere with the uptake of copper, so, many toxic effects are more due to copper deficiency than to a zinc surfeit, and they occur only when the intake of zinc is much higher than that of copper.

Despite acute intoxications being rare, the high exposure by inhalation of zinc oxide-containing fumes can lead to the so-called metal fume fever, while the immediate symptoms of an ingestion of 1-2 g or more of zinc may include abdominal pain, nausea, vomiting, epigastric pain and bloody diarrhoea (Porea et al., 2000; Nriagu, 2007; Plum et al., 2010). In addition, intakes of 50–300 mg

in excess of normal dietary doses may have harmful effects on lipid metabolism and serum cholesterol balance (Nriagu, 2007).

Even if zinc is not considered carcinogenic and an adequate amount of zinc is important for the efficiency of the immune system, high uptakes can result in immunodepression, which in turn can increase the risk of cancer.

Zinc ores have been used since the 4th millennium BC to produce the copper-zinc alloys, that is brass. Nevertheless, due to the high volatility of zinc at high temperatures (at the temperature necessary to smelt it from its ores it is already a gas), it was not known as a metal for several millennia (Craddock, 1987). Metallic Zn was produced for the first time in India around the 13th century by collecting and cooling zinc vapours from a covered crucible in condensation recipient. In Europe it was identified as a metal only in the 16th century by Philippus Theophrastus Paracelsus and Georgius Agricola, and isolated as a pure metal only in the 18th century by Andreas Sigismund Marggraf. The first zinc smelting plant was opened in England in 1743; in the 19th century the industrial production of Zn was by then diffused in all of Europe and USA (Schönnenbeck and Neumann, 2015).

Nowadays, in front of identified world resources of about 1.9 billion of metric tons, zinc production ranges from 12 to 13 million of metric tons. In 2023, the biggest world producer of zinc is China, with 4 million of metric tons, followed by Peru and Australia, with 1.4 and 1.1 million of metric tons respectively (USGS annual report, 2024).

Zinc is mainly used for steel coating (galvanisation), to produce copper and aluminium alloys, in the building industry as a covering material, for rechargeable Zn-battery production and in chemical industry (Schönnenbeck and Neumann, 2015; Shy et al., 2020). In addition, zinc and its compounds, are utilized for a multitude of electronic, chemical, biomedical, biotechnological applications.

The average Zn contents in rocks range from 10 to 120 mg/Kg, with higher values for shales and magmatic rocks (40-120 mg/Kg) and lower in sandstones, limestones and dolomites (10-30 mg/Kg), while those in uncontaminated agricultural soils vary from 10 to 300 mg/Kg with a mean value of 50-55 mg/Kg (Barber, 1995; Kabata-Pendias, 2000; Alloway, 2009). In the oceans, the Zn concentrations range from 0.1 to 10 nM (Bruland and Lohan, 2006; Bermin et al., 2006, Sinor et al., 2012), while in the European rivers are estimated in the range 1.3–14.6 µg/L (Van Sprang et al., 2009; Noulas et al., 2018). By comparison, zinc concentrations in drinking water needs to overcome 15 mg/L to produce acute intoxication in adult human beings (Nriagu, 2007).

Nevertheless, if Zn in water seems to be quite harmless for humans and for the macrofauna and flora, relatively high metal concentrations (in the order of few mg/L) can affect the aquatic microbial ecosystems, such as zooplankton and bacterivorous protozoa (Seto et al., 2013) or bacteria and algae in periphyton communities (Paulsson et al., 2000).

The metal can be introduced in water by natural processes, such as leaching of Zn containing rocks and soils, but the anthropic activities play a leading role in Zn contaminations. Among the major Zn water pollution source are mine drainage, industrial activities (especially the manufacturing of industrial chemicals), urban sewages and runoff, coal-fired power stations (Noulas et al., 2018).

Mine drainages are particularly relevant due to the very high concentrations of Zn, that can easily exceed 1000 mg/L (e.g., Carranza et al., 2016). In Italy, the drainage of wastewaters in sewage systems and surface waters is allowed only for Zn concentrations lower than 1 mg/L and 0.5 mg/L, respectively (D. Lgs 152/06). In line with the World Health Organization guideline, the limit of zinc in drinking water is 3 mg/L (D. Lgs. 339/99).

3.4. References

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4. Experimental Section

4.1. Particle Induced X-ray Emission (PIXE) and Particle Induced Gamma-ray Emission (PIGE)

Compositional analyses using particle induced X-ray emission (PIXE) and particle induced Gamma-ray emission (PIGE) techniques were performed at the INFN LABEC laboratory in Florence (Chiari et al., 2021), which houses a 3 MV Tandem accelerator equipped with a beamline specifically designed for low-currents, non-destructive measurements on thick samples in an external beam setup (Chiari et al., 2023).

Before the measurements, from 10 to 20 mg of treated and untreated microlite and cryptomelane powders were mixed with ~35 mg of cellulose in an agate mortar and compacted in 1.3 cm² pellets employing a manual hydraulic press machine. The same sample preparation was used for the elsmoreite powders, but ~50 mg of KBr were utilized instead of cellulose.

A proton beam with an initial energy of 3.00 MeV was extracted into the atmosphere through a 200 nm thick Si₃N₄ membrane, and samples were positioned at 8 mm from the extraction window. After accounting for energy loss in the Si₃N₄ window and the atmospheric path, the proton energy at the sample surface was evaluated to be 2.95 MeV. The beam spot was defined by a circular collimator, 0.5 mm in diameter, placed in vacuum before the extraction window, and the beam was scanned over the surface of the samples using a micrometric stepper motor, enabling continuous scanning over a 5 mm line to minimise the impact of potential local inhomogeneities.

The beam current, indirectly measured using a rotating chopper (Chiari et al., 2002), was maintained at 50-100 pA to ensure that the dead time remained below a few percent (<5%) and peak pile-up effects were negligible. Each measurement lasted 300 s. The experimental setup for PIXE-PIGE measurements included two X-ray detectors for PIXE: a small-area Ketek Silicon Drift Detector (SDD) with a 10 mm² active area (collimated to 3.5 mm²) and a helium flow to reduce low-energy X-ray absorption for light element analysis (Na-Ca) and a large-area Ketek SDD with a 150 mm² active area and a 450 µm Mylar absorber for mid-heavy and trace elements (>Ca). Additionally, an ORTEC High-Purity Germanium (HPGe) gamma-ray detector with 20% relative efficiency and a mechanical cooler was used for PIGE measurements.

PIXE spectra were processed using GUPIXWIN software (Campbell et al., 2010), with Na as the lightest detectable element. Instrumental parameters for quantitative analysis were calibrated using X-ray spectra from external reference materials: NIST 1412 and BCR 126A for the small- and large-area SDDs, and NIST 610 for the large-area SDD exclusively. PIGE was employed to determine Na concentration using the nuclear reaction $^{23}\text{Na}(p,p'\gamma_{1-0})^{23}\text{Na}$, which produces gamma rays with 441 keV energy. The gamma-ray peaks of interest in the PIGE spectra were fitted with a gaussian function to obtain the peak area. Quantitative analysis of Na was then carried out through a comparison of the gamma-ray yield with those obtained from the measurements of thick NIST 1412 and BCR 126A glass standards. The sources of the estimated uncertainties are peak fitting

and spectral deconvolution, as statistical contributions, and the calibration procedure with external standards as systematic contribution.

4.2. Fourier Transform – Infrared Spectroscopy (FTIR)

Infrared data were collected for untreated samples and those treated with 1M heavy metal solutions. FTIR reflection absorption spectra were acquired employing a Nicolet RaptIR microscope attached to a Nicolet iS50 FTIR spectrometer (Thermo Fisher) and equipped with a Polaris IR source, KBr beam splitter and a liquid-nitrogen-cooled MCT detector.

Before the analysis, the samples were dried in oven at 80°C for 2 hours to remove eventual humidity adsorbed onto the powder particles. IR spectra were collected in reflectance mode, pressing the powders against a high-refractive-index plate. The measurements were conducted in the spectral range of 6000-850 cm^{-1} with a resolution of 4 cm^{-1} . The data analysis was carried out using the OMNIC Paradigm software provided by Thermo Fisher. Sixty-four scans were averaged for each spectrum.

4.3. X-ray powder diffraction (XRPD)

X-ray Powder Diffraction (XRPD) experiments were conducted at the ID11 Material Science beamline of the European Synchrotron Radiation Facility (ESRF), Grenoble, France (Wright et al., 2020). Before the measurements, the powders were grinded in an agate mortar and loaded in Kapton capillary tubes with an internal diameter of 0.5 mm.

2D diffraction patterns were acquired in the Experimental hutch 1 (EH1) using a FReLoN 16 bit dynamic CCD camera with a frame resolution of 2048x2048 pixels and a pixel size of 14 microns. The measurements were performed in 16 bunch filling mode with an average current of 75 mA. The energy was set at 65 KeV ($\lambda = 0.1907457 \text{ \AA}$), right below the K absorption edge of W (69.525 KeV) and Ta (67.416 KeV) to avoid absorption phenomena in tungsten- and tantalum-containing samples. The energy was selected using a double bent crystal monochromator operating in horizontal Laue geometry, while the beamline was focused utilizing a vacuum transfocator. To minimise iso-orientation phenomena, the capillary was kept spinning.

A CeO_2 standard was used to calibrate the setup; the sample-detector distance was kept at 530 mm, while the acquisition times were $\leq 1\text{s}$. The XRD profiles were obtained by averaging fifty frames in the Q range 0.429417- 8.711628 $\text{\AA}^{-1}$ with a resolution of $2.8 \times 10^{-3} \text{ \AA}^{-1}$. The data integration was performed using the software pyFAI (Ashiotis et al., 2015).

4.4. X-ray Absorption Spectroscopy (XAS)

X-ray Absorption Spectroscopy (XAS) experiments were conducted at the BM08 LISA CRG beamline (d'Acapito et al. 2019) at the European Synchrotron Radiation Facility (ESRF), Grenoble, France. The beamline consists in three lead hutches: one optics hutch (OH) that contains the main optical elements (a monochromator placed between two focussing mirror) and two experimental hutches, EH1 and EH2, containing the instrumentation for the experiments.

Before the analysis, the powders were mixed with cellulose, compacted in 1.3 cm² pellets using a manual hydraulic press machine and sealed in Kapton tape. The amount of material in each sample was such as to keep the total absorption (μ) between 1.5 and 0.1 for transmission mode, and to keep the edge step slightly around 0.01 for fluorescence mode. XAS investigations were conducted at Ta L₃-edge (9.881 KeV), W L₃-edge (10.207 KeV), Tl L₃-edge (12.658 KeV), Pb L₃-edge (13.035 KeV) and Zn K-edge (9.659 KeV) in 7/8 multibunch, with a typical current of 200 mA. Ta, W, Pb and Zn metal foils were used as standard for energy calibration, while a Se metal foil (Se K-edge = 12.658 KeV) was used to calibrate the energy of Tl spectra. A fixed exit monochromator equipped with a pair of Si (111) flat crystals was used to scan energy in the selected sampling interval, while a couple of silicon mirrors with a 15 KeV energy cut off was used for harmonic rejection and to focus the X-ray beam.

The employed scan setup is reported in Table 1.

Table 1. Scan setup used for both transmission and fluorescence XAS spectra collection.

Energy range [†]	Energy step
From -200 to -30eV	10 eV
From -30 to +30 eV	0.5 eV
From +30 eV to the end of the spectrum	0.05 Å ⁻¹
[†] Where the theoretical absorption edge is placed at 0 eV.	

Transmission spectra were collected in EH1 using ion chambers filled with N₂, while fluorescence measurements were acquired in EH2 using a liquid nitrogen-cooled HpGe detector. In EH2 the X-ray beam is focussed to a size of ~150 μ m, thus maximising the flux of photons, which is the best solution for fluorescence measurements. In EH1, since the beam is slightly out of focus, the wider beam (with a size of few millimetres) provides a better averaging of the sample, which is essential for transmission acquisitions.

All the measurements were conducted in vacuum (approx. 10⁻⁴ mbar). In order to prevent beam damage, a cold finger LN2 cryostat was used to set the measurement temperature to 80 K.

Two to four spectra were averaged for each sample in order to reduce the level of noise in the signal and achieve statistically good profiles.

Unfortunately, it was not possible to measure the EXAFS signal of Zn-treated samples of microlite and elsmoreite due to the strong interference between the Zn K-edge (9.659 KeV) and the Ta L₃-edge (9.881 KeV), found in microlite as a major framework constituent and in elsmoreite as a small impurity. As a result, only the Tl L₃-edge and Pb L₃-edge EXAFS spectra were collected for the pyrochlore samples. In elsmoreite samples, the W L₃-edge was also measured.

XAS data were processed through Athena software (Ravel and Newville, 2005), while Artemis (Ravel and Newville, 2005) was used to fit the EXAFS spectra. The software FEFF (Ankudinov et al., 1998) was employed to calculate the theoretical paths included in the EXAFS fitting procedures.

4.5. Inductively coupled plasma-mass spectrometry (ICP-MS)

Inductively coupled plasma-mass spectrometry (ICP-MS) analyses were performed at the Centro Ricerche Ecotec, Uta, Cagliari province, Sardegna, Italy. The measurements were conducted using a spectrometer ICP-MS NexION® 2000B (PerkinElmer) equipped with a triple quadrupole mass analyser. Selective interference suppression was achieved using the Kinetic Energy Discrimination (KED) mode using helium as collider gas. Element determination in the analysed samples was performed by comparison with external standards, using a calibration curve.

4.6. References

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5. Incorporation Mechanisms of Heavy Metals in Microlite

In this chapter, the results of the ion exchange experiments involving the KTP synthetic microlite are presented. The first sections (from 5.1 to 5.6) cover the synthesis of the sorbent material, the ion exchange experiments with thallium, lead and zinc and the chemical and structural characterization of both treated and untreated samples. The second part (5.7) is instead left to the discussion of the results, with a particular emphasis on the average structures of both treated and the untreated samples, and the local coordination environment of thallium and lead incorporated in the microlite structure.

5.1. Synthesis

Microlite powders were synthesized via hydrothermal route following the protocol stated by Goh et al. (2002) with minor modifications. Briefly, 2.5 mmol of tantalum (V) oxide [Ta_2O_5 , 99% trace metals basis, Sigma-Aldrich] were loaded in a 25ml Teflon-lined hydrothermal reactor containing 14 ml of a 4M KOH aqueous solution. The reactor was sealed and heated to 175°C in a muffle furnace for 16 hours. The product of the reaction, a white, wet slurry, was filtered, washed with 50 ml of deionized water and then dried at 60°C for 3 hours in an oven. Secondary electron images of the samples were acquired with a scanning electron microscope (SEM) EVO 40 (Carl Zeiss), using a 10 KV current with 20 pA of intensity. Microlite powders consist of octahedral microcrystals ranging from 200 to 800 nm in size (Fig.1).

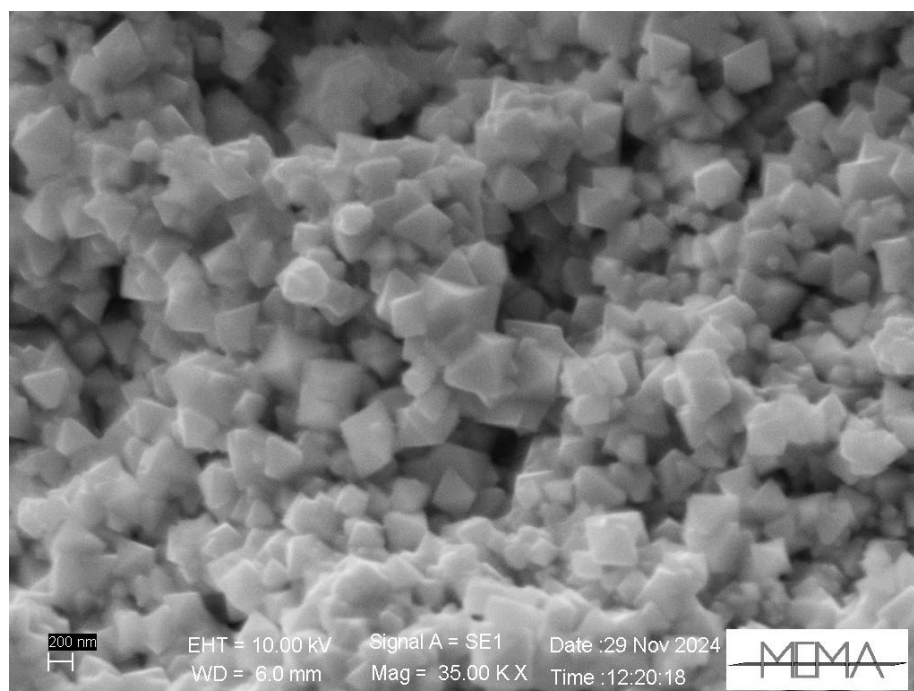


Fig. 1 SEM secondary electron image of microlite powders prepared via hydrothermal synthesis.

5.2. Ion Exchange Experiments

200 mg of microlite powders were plunged into 5 ml of 1 and 0.1M aqueous solutions of thallium (I) formate [HCO_2Tl , 97%, Sigma-Aldrich], lead (II) nitrate [$\text{Pb}(\text{NO}_3)_2$, ACS reagent, $\geq 99.0\%$, Sigma-Aldrich] and zinc (II) nitrate hexahydrate [$\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, reagent grade, 98%, Sigma-Aldrich] contained in 15 ml Falcon tubes, manually stirred with a stainless steel spatula for a few seconds and then left stationary. After one day of imbibition, the powders were filtered and washed three times with 5 ml of deionized water to remove eventual soluble salts precipitated from the intergranular moisture, left under the fume hood overnight to roughly dry and then kept in an oven at 70°C for 2 hours to complete drying.

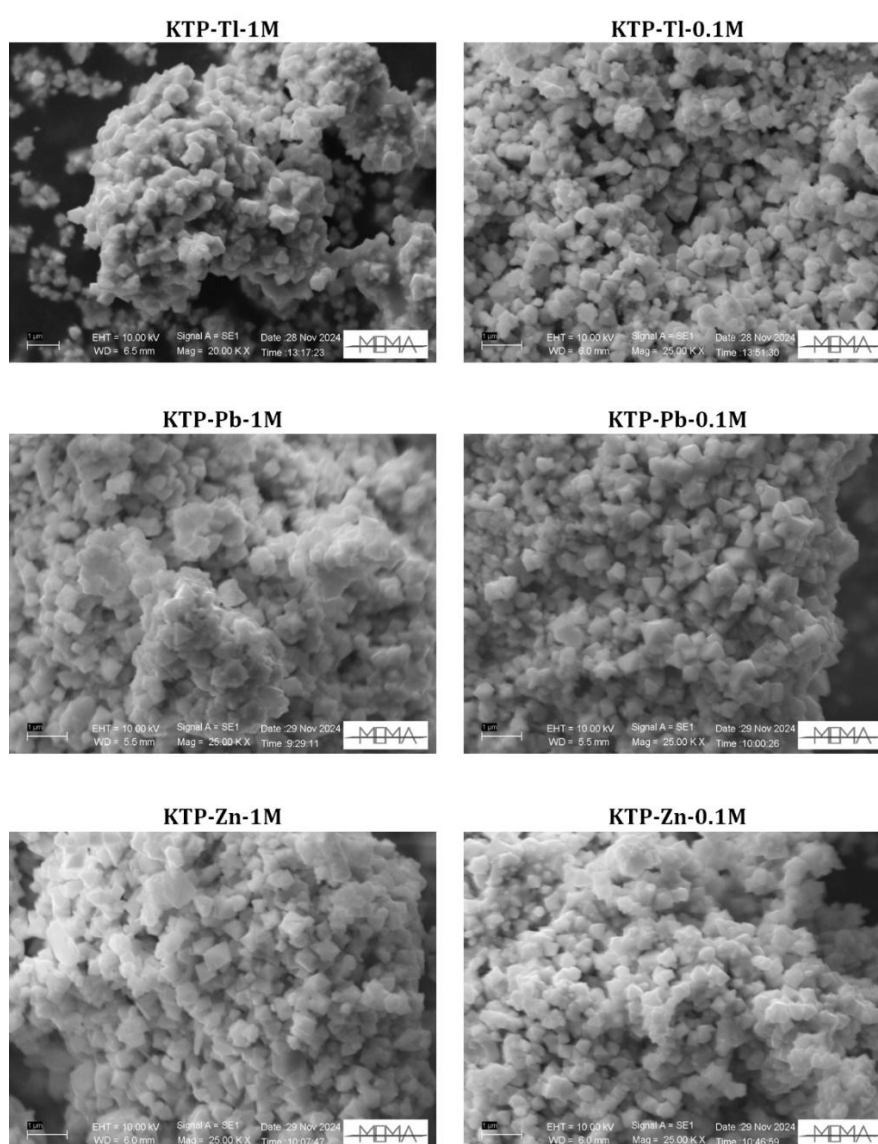


Fig. 2 SEM secondary electron images of microlite powders after the treatment with 1M and 0.1M solutions of Tl, Pb and Zn.

The untreated microlite is called KTP, standing for potassium tantalum pyrochlore, while the symbol of the heavy element used for the treatment and the concentration of the solution is added to the treated samples. For example, the sample plunged in the 1M thallium solution is called KTP-Tl-1M.

SEM investigations revealed that the morphology of the powders resulted unchanged after the contact with the heavy metal solutions (Fig. 2). Nevertheless, in Tl-treated sample a change in the colour of the material has been observed. Upon contact with the thallium solution, the microlite powders almost instantly developed a yellow tint. The colour was slightly more vibrant for the sample treated with the 1M solution, suggesting that the colour intensity may depend on the thallium content.

5.3. Chemical Analysis

The relative concentrations of potassium, tantalum, thallium, lead and zinc were measured by means of PIXE (Table 1). In the errors calculations, a further relative 10% was added to the percentage error values reported in Table 1 due to systematic uncertainties inherent to the PIXE measurements.

The normalization of the PIXE results, the estimation of the water content and the attribution of the different ions/molecules to the different crystallographic sites are discussed in section 5.7.

Table 1. PIXE analytical results of treated and untreated microlite powders.

sample	K (wt%)	Ta (wt%)	Tl (wt%)	Pb (wt%)	Zn (wt%)	total
KTP	10.70	89.30	0.00	0.00	0.00	100
err (%)	2.9	0.33	–	–	–	
KTP-Tl-1M	2.64	57.68	39.68	0.00	0.00	100
err (%)	19	0.31	0.41	–	–	
KTP-Tl-0.1M	4.64	59.49	35.87	0.00	0.00	100
err (%)	12	0.29	0.41	–	–	
KTP-Pb-1M	4.94	82.06	0.00	12.99	0.00	100
err (%)	2.7	0.34	–	0.86	–	
KTP-Pb-0.1M	6.76	85.96	0.00	7.28	0.00	100
err (%)	2.3	0.23	–	1.2	–	
KTP-Zn-1M	5.41	89.77	0.00	0.00	4.82	100
err (%)	2.8	0.37	–	–	0.79	
KTP-Zn-0.1M	6.57	90.06	0.00	0.00	3.38	100
err (%)	2.7	0.37	–	–	0.95	

5.4. Infrared Analysis

Infrared data were collected for the untreated microlite and for the powders treated with 1M heavy metal solutions. All the IR spectra (Fig. 3) exhibit a broad absorption band from 2500 to 3800 cm^{-1} , which is typical of the O-H stretching vibration, and a finer peak at about 1625-1650 cm^{-1} , which is imputable to the H-O-H bending vibration of water molecules (Goh et al., 2002; Andrade et al., 2013). The intense, sharp peak at about 2360 cm^{-1} is instead the characteristic band of carbon dioxide from air.

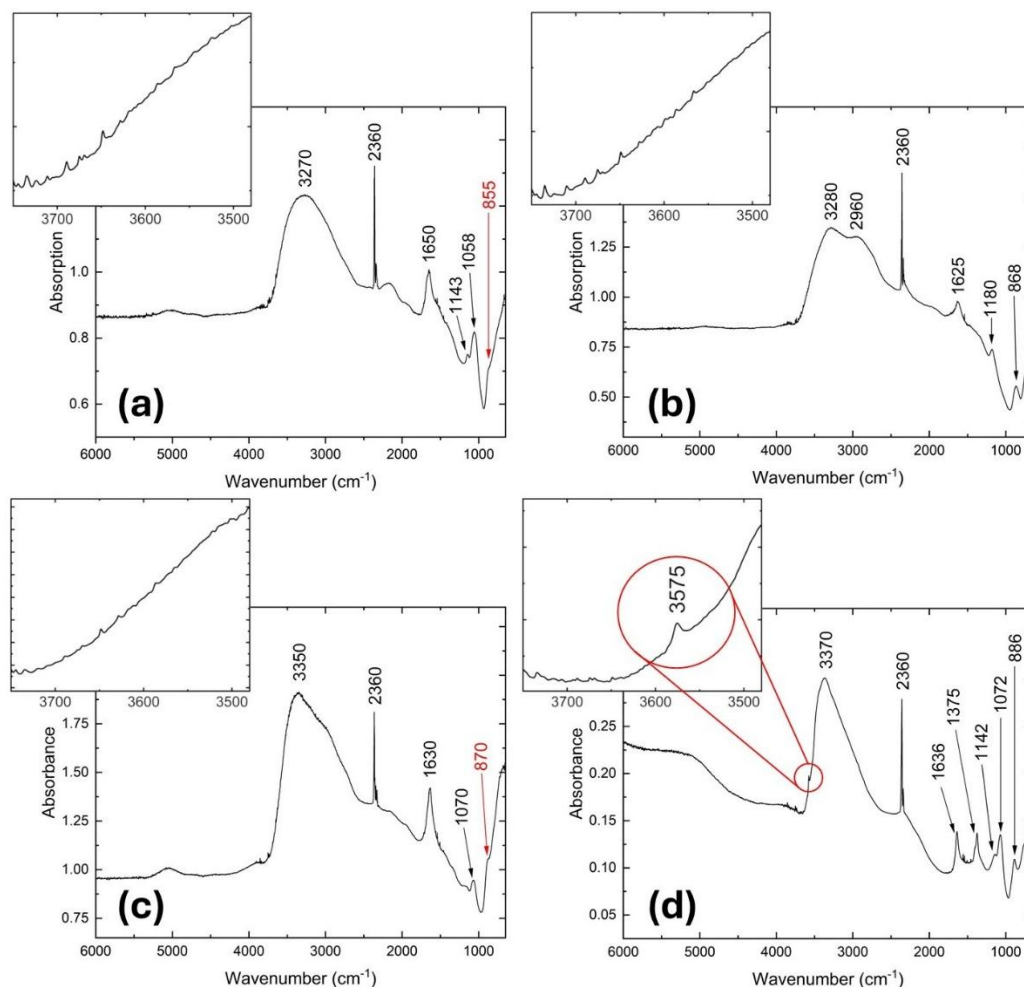


Figure 3. FTIR spectra of (a) KTP untreated microlite, (b) KTP-Tl-1M, (c) KTP-Pb-1M and (d) KTP-Zn-1M. A magnification of the FTIR spectra in the 3480-3750 cm^{-1} range is reported in the top-left panels. The wavenumber found above each band corresponds to its absorbance maximum.

The untreated KTP and the KTP-Pb-1M samples show a shoulder at about 850-890 cm^{-1} (indicated with red arrows in Fig. 3a and Fig. 3c), which takes the form of a weak peak in the KTP-Tl-1M (Fig. 3b) and KTP-Zn-1M (Fig. 3d) samples, at 868 and 886 cm^{-1} respectively. The bands in this range correspond to Ta $\cdots$ O-H bending vibrations (Andrade et al. 2013), thus suggesting the presence of hydrogen cations bound to the framework oxygens. Moreover, in the KTP-Zn-1M spectra, a minuscule but clear peak at 3575 cm^{-1} , corresponding to the stretching vibration of hydroxyl groups in the framework, arises from the flank of the broad and much more intense O-H band

(Duan et al., 1998). The other samples also show something resembling peaks in the same range, but they are confused in the background noise.

The bands in the range 1140-1180 cm^{-1} were attributed to Ta-O octahedron vibrations (Yang et al., 2014), while those at about 1055-1075 cm^{-1} to overtones and combination modes (Andrade et al., 2017). In the KTP-Zn-1M sample a further peak at about 1375 cm^{-1} is clearly visible (Fig. 3d), but its attribution is unclear. A possible explanation involves the presence of NO_3^- , which presents absorption bands just at 1375 cm^{-1} (Grady et al., 1995; Bahrami et al., 2011). The zinc solutions were prepared using the soluble salt $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, which releases Zn^{2+} and NO_3^- ions once contacted with water. Then, nitrate ions could have been involved in the ion exchanges or adsorbed in the active sites on the microcrystals surface. Nevertheless, no other evidence can be presented in support of this hypothesis, as the other techniques employed in this study are not sensitive to the specific presence of nitrate ions. In addition, a nitrate containing reagent [$\text{Pb}(\text{NO}_3)_2$] was also utilized for the preparation of the lead solutions, but nothing more than a slight shoulder can be seen at about 1350 cm^{-1} in the KTP-Pb-1M sample. In alternative, an amorphous nitrate phase could have been precipitated by the exchanging solutions to form a residue too small to be detected by synchrotron XRD measurements. Even in this instance, though, there's no experimental evidence to back up the hypothesis.

5.5. Rietveld Refinements

Structural refinements were carried out in the space group $Fd-3m$ using the software Topas (Coelho, 2018), setting the origin on the position $16c$ (B site).

A minor impurity of Ta_2O_5 , probably a residual of the starting reagent, was found in KTP as well as in all the treated samples; and it was added to the Rietveld refinements as a $Pccm$ orthorhombic phase with $a = 6.190(3) \text{ \AA}$; $b = 3.661(1) \text{ \AA}$; $c = 7.775(2) \text{ \AA}$.

The tunnel environment of the untreated microlite was initially refined using the conventional A ($16d$) and Y ($8b$) sites. The presence of residual electron density in the tunnel region suggested a more complex atoms distribution. Two additional sites were then added to the refinement: the A' ($32e$) and Y' ($32e$) sites (Ercit et al., 1994). The electron density resulted distributed along A, A' and Y' sites, while the Y site remained empty. The occupancy factors of the tunnel sites (A, A' and Y') were refined, while those of the framework sites (B and X) were set at 1 (fully occupied). At this point of the refinement, no significant residual was evident in the ΔF -map, and both tunnel and framework sites thermal parameters were refined isotropically. The XRD profile with fit and residuals of the untreated microlite is reported in Fig. 4.

The same procedure was used to refine the all heavy metal-treated samples. For the Tl-treated samples, the refinement of the Y' coordinates brought this site closer to A than Y, leading to a tight distribution of three sites in roughly 2 $\text{\AA}$. Therefore, for the thallium treated samples, Y' was called A'' to underline its close relationship with A, rather than with Y.

Scattering curves for neutral atoms, taken from the international Tables for Crystallography (Wilson, 1992), were used as follow: B = Ta and X = O for all the samples; A, A' and A'' = Tl vs. $\square$ for

the Tl-treated samples; A, A' and Y' = Pb vs. $\square$ for the Pb-treated samples; A, A' and Y' = Zn vs. $\square$ for the Zn-treated samples.

The XRD profiles with fit and residuals of KTP-Tl-1M, KTP-Tl-0.1M, KTP-Pb-1M, KTP-Pb-0.1M, KTP-Zn-1M and KTP-Zn-0.1M are reported in Figure 5, 6, 7, 8, 9 and 10, respectively.

Rietveld refinement results are reported in Table 2. A selection of bond distances and angles are instead reported in Table 3.

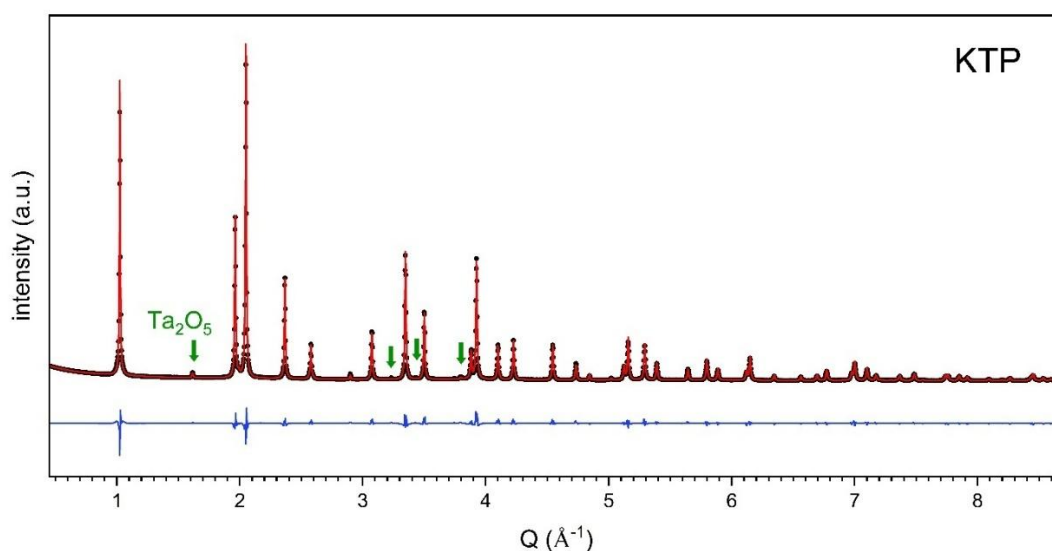


Figure 4. XRD profile of the untreated KTP microlite: measured (black points), calculated (red lines) and the difference (blue lines). Green arrows indicate the small peaks of the Ta_2O_5 impurity.

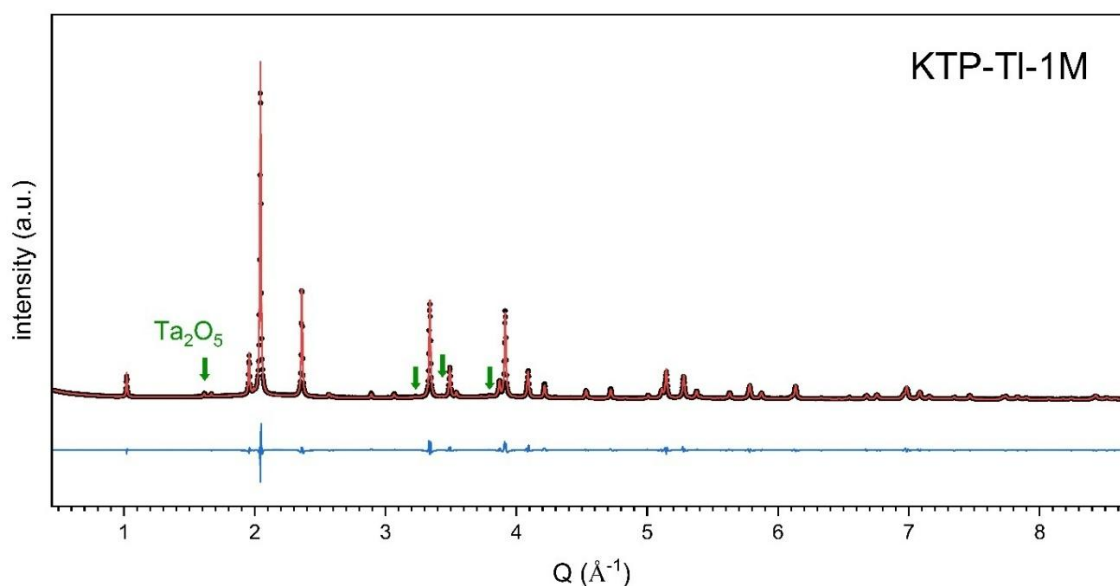


Figure 5. XRD profile of KTP-Tl-1M: measured (black points), calculated (red lines) and the difference (blue lines). Green arrows indicate the small peaks of the Ta_2O_5 impurity.

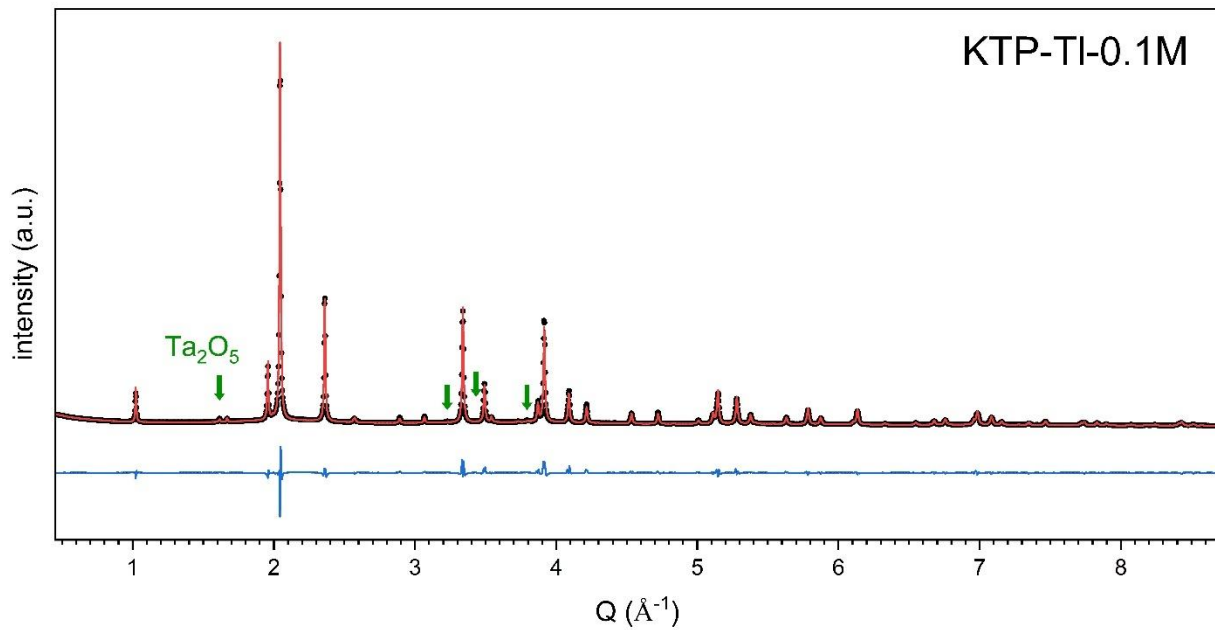


Figure 6. XRD profile of KTP-Tl-0.1M: measured (black points), calculated (red lines) and the difference (blue lines). Green arrows indicate the small peaks of the Ta_2O_5 impurity.

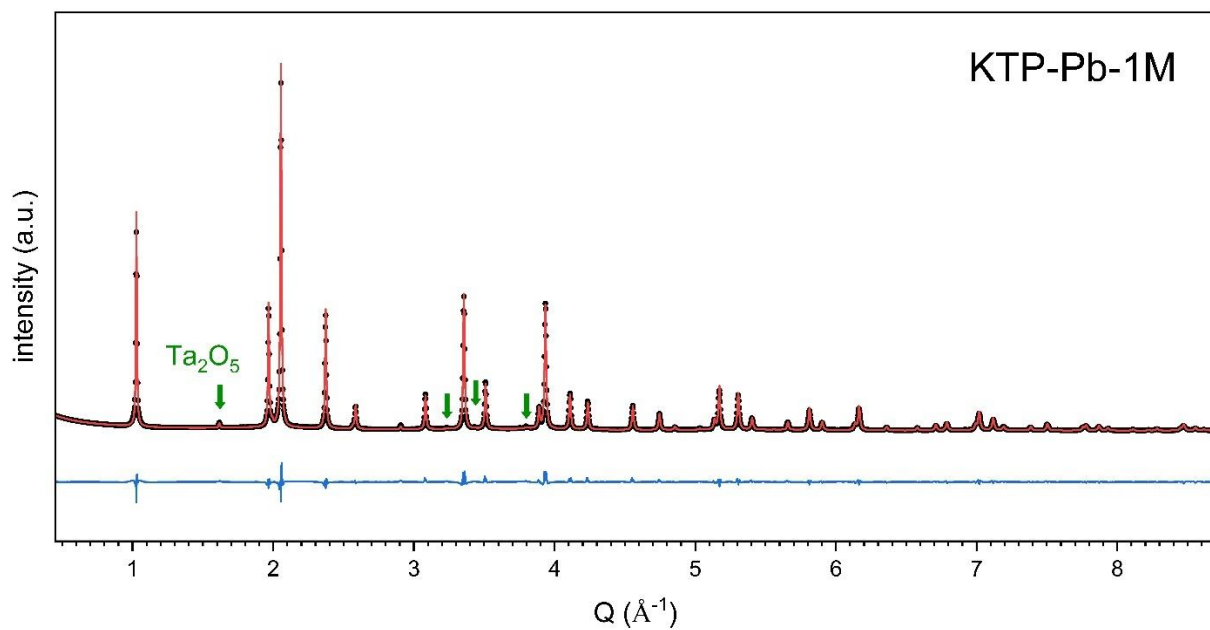


Figure 7. XRD profile of KTP-Pb-1M: measured (black points), calculated (red lines) and the difference (blue lines). Green arrows indicate the small peaks of the Ta_2O_5 impurity.

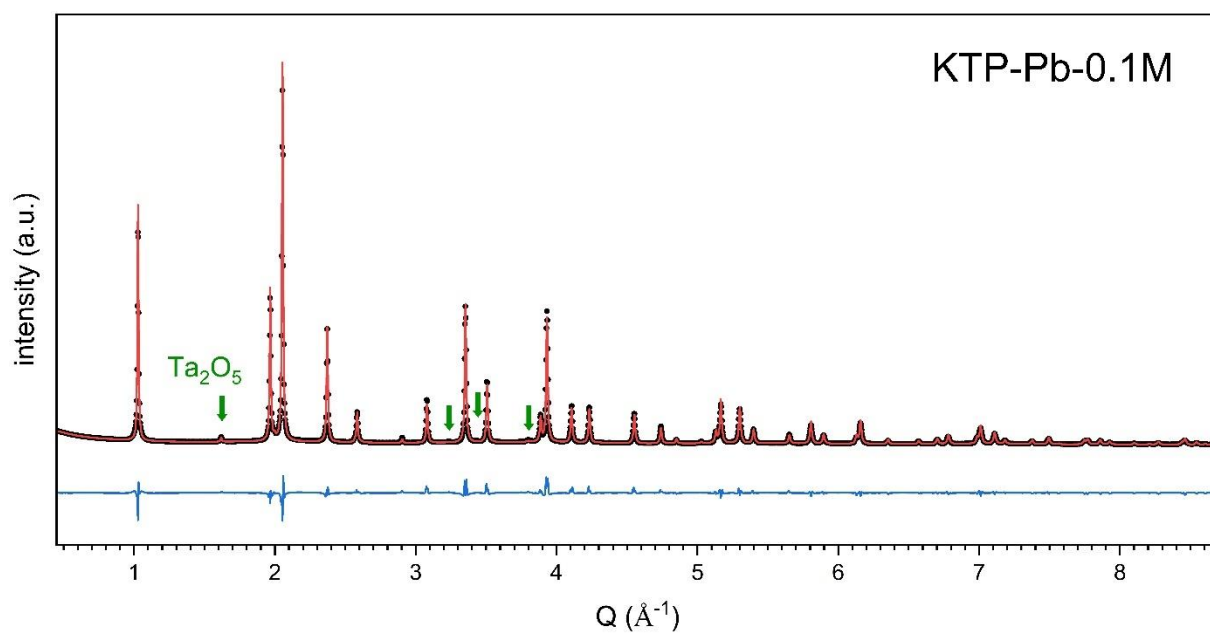


Figure 8. XRD profile of KTP-Pb-0.1M: measured (black points), calculated (red lines) and the difference (blue lines). Green arrows indicate the small peaks of the Ta_2O_5 impurity.

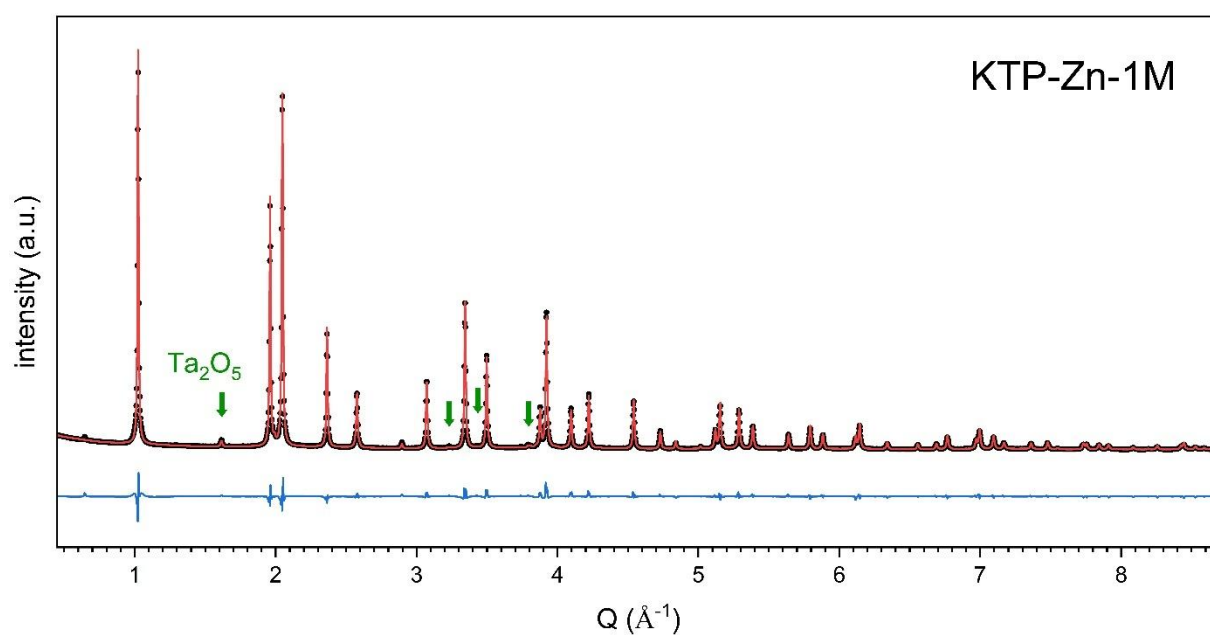


Figure 9. XRD profile of KTP-Zn-1M: measured (black points), calculated (red lines) and the difference (blue lines). Green arrows indicate the small peaks of the Ta_2O_5 impurity.

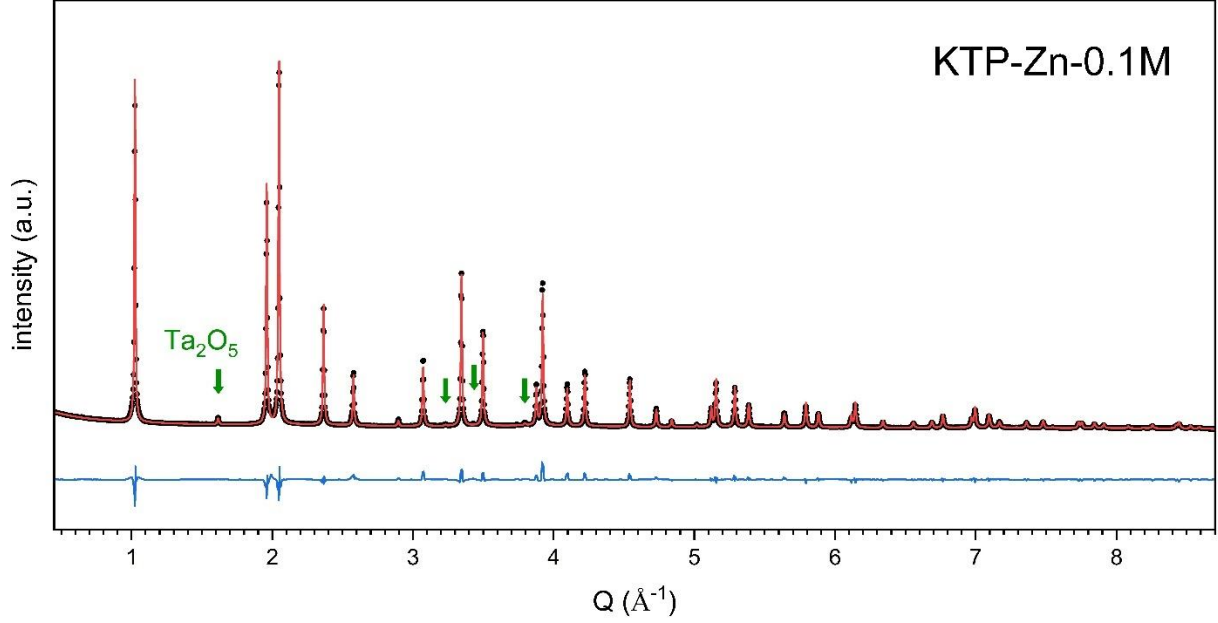


Figure 10. XRD profile of KTP-Zn-0.1M: measured (black points), calculated (red lines) and the difference (blue lines). Green arrows indicate the small peaks of the Ta_2O_5 impurity.

Table 2. Rietveld refinements results: unit cell a parameter and volume; (x , $\frac{1}{8}$, $\frac{1}{8}$) coordinate of X ; (x , x , x) coordinates of the A' and Y' sites; isotropic thermal parameters (B) and occupancies ($Occ.$) for the different sites; weighted profile R -factor (R_{wp}).

	KTP	KTP-Tl-1M	KTP-Tl-0.1M	KTP-Pb-1M	KTP-Pb-0.1M	KTP-Zn-1M	KTP-Zn-0.1M
a (Å)	10.61798(4)	10.64526(5)	10.64356(6)	10.59158(5)	10.60751(6)	10.62645(4)	10.62638(5)
V (Å ³)	1197.09(2)	1206.34(2)	1205.76(2)	1188.18(2)	1193.55(2)	1199.95(1)	1199.93(2)
$x_{48f}(X)$	0.3144(6)	0.3131(6)	0.3151(6)	0.3149(6)	0.3175(7)	0.3145(5)	0.3190(6)
$x_{32e}(A')$	0.526(5)	0.528(1)	0.528(1)	0.523(5)	0.529(19)	0.546(5)	0.521(14)
$x_{32e}(Y')$	0.573(2)	0.557(1)	0.559(1)	0.577(2)	0.570(2)	0.583(3)	0.565(2)
$Occ.$ (A)	0.48(9)	0.20(1)	0.18(1)	0.18(2)	0.18(2)	0.19(2)	0.13(13)
B (Å)	1.7(4)	1.5(1)	1.1(1)	2.2(1)	3.1(2)	3.7(6)	2.6(4)
$Occ.$ (A')	0.127(9)	0.143(4)	0.140(4)	0.029(9)	0.010(6)	0.056(10)	0.07(6)
B (A')	1.0(1)	1.5(1)	1.5(1)	2.2(1)	3.1(2)	4.9(1)	2.6(4)
$Occ.$ (Y') [†]	0.10(5)	0.111(7)	0.107(6)	0.0321(19)	0.043(4)	0.07(1)	0.137(11)
B (Y') [†]	1.7(4)	4.5(3)	5.0(4)	5.0(9)	5.0(8)	3.7(6)	5.0(7)
B (X)	1.0(1)	1.0(2)	1.0(2)	1.0(2)	1.0(2)	1.0(1)	1.0(2)
B (B)	1.18(1)	1.0(1)	1.1(1)	1.16(2)	1.23(2)	1.45(1)	1.46(2)
R_{wp}	5.61	5.16	5.69	5.37	6.99	5.15	6.06

$$R_{wp} = \left[\frac{\sum_i w_i (y_{C,i} - y_{O,i})^2}{\sum_i w_i (y_{O,i})^2} \right]^{\frac{1}{2}} \text{ (Young, 1993).}$$

[†] A'' instead of Y' for Tl-treated samples.

B and X sites were considered fully occupied by Ta and O, respectively, and their occupancies were set at 1.

Table 3. Selected bond distances and angles.

	KTP	KTP-Tl- 1M	KTP-Tl- 0.1M	KTP-Pb- 1M	KTP-Pb- 0.1M	KTP-Zn- 1M	KTP-Zn- 0.1M
Bond distances of the BX ₆ octahedron (Å)							
B-X (x6)	1.998 (2)	1.998(2)	2.005(3)	1.995(2)	2.007(3)	2.000(2)	2.016(2)
X-X (s.)	2.84(1)	2.83(1)	2.86(1)	2.84(1)	2.89(1)	2.85(1)	2.92(1)
X-X (u.)	2.806(3)	2.820(3)	2.809(3)	2.797(3)	2.789(4)	2.808(3)	2.787(3)
Bonds distances of the tunnel sites (Å)							
A-X (x6)	2.722(4)	2.739(5)	2.723(5)	2.711(4)	2.695(5)	2.723(4)	2.689(4)
A'-X (x3)	2.695(6)	2.714(5)	2.696(6)	2.681(5)	2.666(17)	2.732(17)	2.655(7)
	(x3)	2.83(3)	2.86(1)	2.84(8)	2.80(3)	2.83(12)	2.97(6)
Y'-X † (x3)	2.70(1)	2.79(1)	2.75(1)	2.78(1)	2.80(1)	2.92(2)	2.77(1)
	(x3)	3.21(2)	3.07(2)	3.05(1)	3.07(1)	3.16(2)	3.31(4)
A-Y' † (x2)	2.86(2)	2.97(1)	2.96(2)	2.95(2)	2.80(3)	2.66(4)	2.86(2)
A'-A'	2.97(16)	2.94(4)	2.93(4)	3.06(11)	2.9(5)	2.37(11)	3.1(3)
Bond angles (deg.) and bond angle variance (deg. ²)							
X-B-X (u.)	89.2(3)	89.8(3)	89.0(3)	89.0(3)	88.0(3)	89.2(3)	87.4(3)
X-B-X (s.)	90.8 (3)	90.2(3)	91.0(3)	91.0(3)	92.0(3)	90.8(3)	92.6(3)
B-X-B	140.0(4)	140.7(4)	139.6(4)	139.7(4)	138.2(4)	139.9(3)	137.4(4)
B-X-A	104.4(1)	104.1(1)	104.5(1)	104.4(1)	104.8(1)	104.4(1)	105.1(1)
σ ² (BX ₆)	0.65	0.07	1.20	1.03	4.37	0.71	7.30

u. = unshared edge of the octahedron; s. = shared edge between B and A polyhedra.

Bond angle variance (σ²) was calculated according to the formula proposed by Robinson et al. (1971).

† A'' instead of Y' for Tl-treated samples.

5.6. X-ray Absorption Spectroscopy Analysis

X-ray absorption spectroscopy (XAS) analysis was performed on the Tl- and Pb-treated samples, at the L₃-edge of thallium and lead, respectively. The X-ray absorption near edge structure (XANES) spectra of Tl-treated samples were compared with those of thallium (I) chloride [TlCl] dissolved in an aqueous solution (Scheckel et al., 2004), thallium (I) sulphate [Tl₂SO₄] and thallium (III) oxide [Tl₂O₃] (Biagioni et al., 2020)(Fig. 11), revealing that Tl contained in the KTP microlite is Tl⁺. In fact, the Tl⁺ compounds feature a single absorption peak at about 12.665 KeV, while Tl³⁺ in Tl₂O₃ shows two shoulders on rising absorption followed by a peak at about 12.680 KeV (Fig. 11a). The differences between the near edge structures of Tl⁺ and Tl³⁺ are more evident in the XANES derivative (Fig. 11b), where the Tl-treated and Tl⁺ references show a single, relatively sharp peak, while the absorption edge of Tl₂O₃ is represented by three different broad bands.

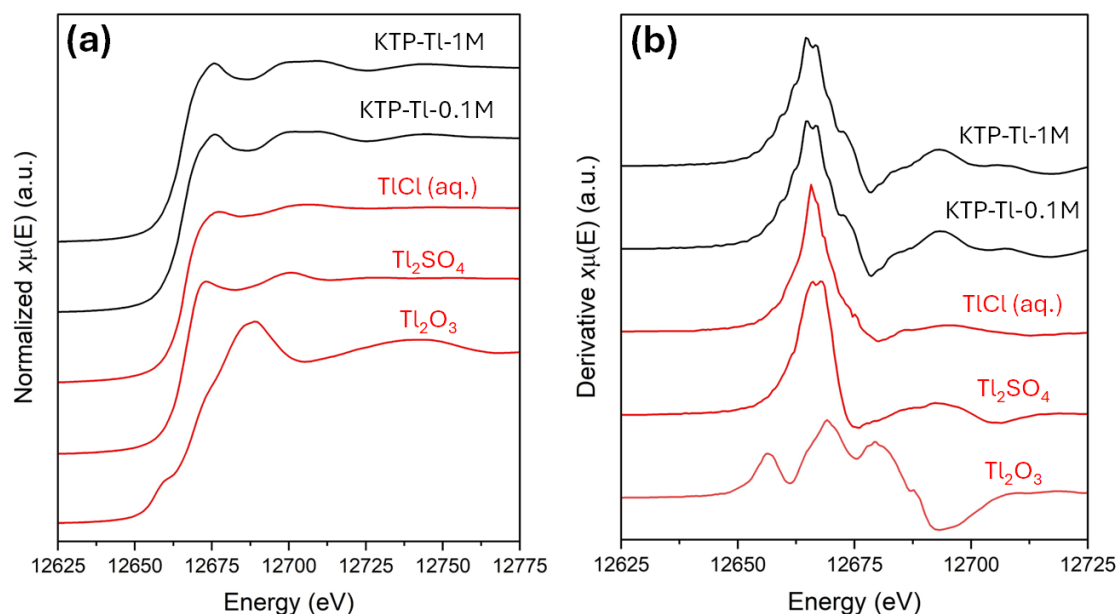


Figure 11. XANES spectra (a) and their derivative (b) of the microlite samples treated with Tl (in black) and thallium references (in red).

The direct comparison between the XANES profile of Pb-treated samples and lead (IV) oxide [PbO₂], lead (II) oxide [PbO] and metallic lead references (Fig 12) was not fruitful. The peak broadness of the XANES derivatives of the samples and the small difference in terms of energy between the edges of the Pb²⁺ (13037.5 eV) and Pb⁴⁺ (13038 eV) references did not allow for a simple attribution to either of the two valence states. Nevertheless, some considerations were made on the rising absorption features and the position of the maximum absorption intensity. According to Bargar et al., (1997), the L₃-XANES spectra of Pb²⁺ are very sensitive to the first shell coordination environment and to the nature of the chemical bond (ionic or covalent). The two shoulders on rising absorption shown by PbO and PbO₂ references are due to 2p → 6s and 2p → 6d electronic transitions which are typical of Pb-O covalent bonds. Featureless XANES spectra are instead typical of ionic-bounded Pb²⁺ (Bargar et al., 1997), thus hinting at the divalent nature of the lead contained in the Pb-treated samples.

In addition, the maximum of absorption intensity is at about 13.054 KeV for PbO, while it shifted to 13.058 KeV in the PbO₂ reference. This shift to higher energies is typical of many redox-sensitive elements, including Pb (Syverson et al., 2019). The maximum of absorption intensity of the Pb-treated samples is at the same energy of PbO (13054 eV), while that of Pb₂O is placed at higher energies (13058 eV) (Fig. 12a). This is a further indication that the lead in the samples may be bivalent.

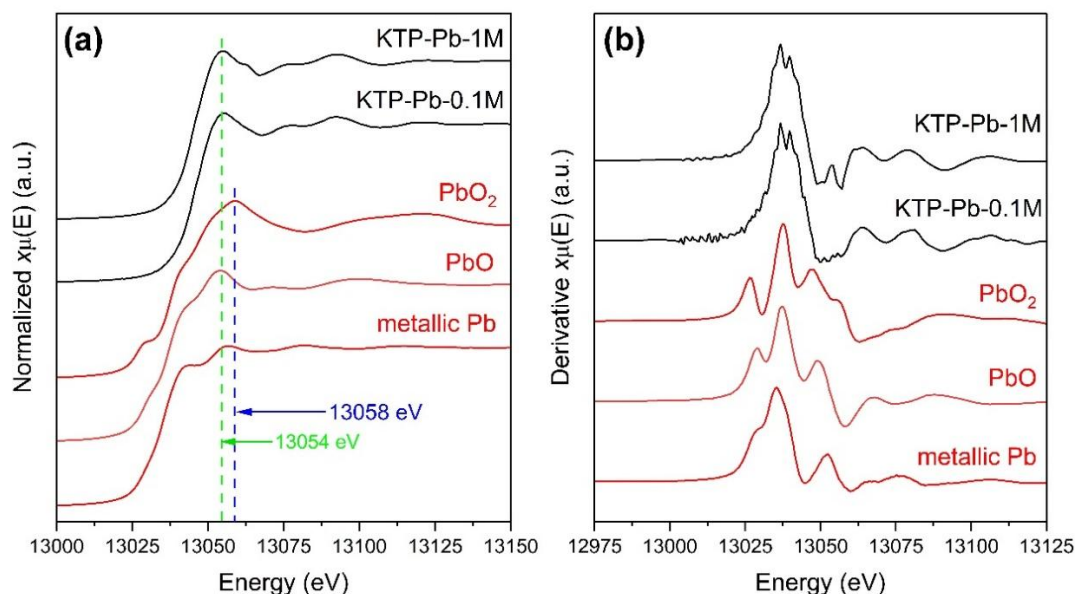


Figure 12. XANES spectra (a) and their derivative (b) of the microlite samples treated with Pb (in black) and lead references (in red).

Extended X-ray absorption fine structure (EXAFS) was performed to investigate the coordination environment of Tl and Pb in the KTP microlite structure. The structural model utilized to calculate the theoretical paths was that of the untreated KTP sample obtained from the Rietveld refinements, suitably modified by removing the satellite site A' and replacing the original potassium in the A site with the different heavy metals (HMs) as central scatterer atoms. Multiple sets of single scattering paths (typically HM-O and HM-Ta) with different interatomic distances (R) were calculated using the software FEFF (Ankudinov et al., 1998) and used in the fitting process. The first step of the data analysis was the fitting of the first shell considering the heavy metals (HM) in the conventional A position, that is with six oxygens represented by a single path with a coordination number (N) of 6 and interatomic distances in the range 2.7-2.8 Å. Since the first and second shell of all the samples were unable to be modelled independently, an HM-Ta path with N = 6 was added to the fit.

At this point different tests were performed to evaluate an eventual asymmetrical coordination considering:

- The HM shifted along the tunnel axis (i.e., A', A'' and Y' positions). Several pairs of HM-O paths (each with N = 3) with different interatomic distances were then selected on the basis of the supposed shift extent and used in the fitting procedure.
- The HM displaced off the tunnel axis toward the tunnel walls. Several combinations of HM-O paths with different R and N were used considering a heavy metal's approach to the octahedral framework.

In both cases, the paths combinations were based on the expected bond valence sum (BVS) for Tl⁺ and Pb²⁺. HM-Ta paths were adjusted on the basis of the first shell asymmetry. Once the first and second shell were assessed, additional paths were included to the fit in order to model more remote environments. For both Tl-treated samples, the best fit was obtained considering a single

2.78 Å Tl-O path with N = 6 for the first shell and a 3.75 Å Tl-Ta path with N = 6 for the second shell. Each of the several attempts to split the coordination of the first shell considering the aforementioned asymmetries did not produce any result.

For KTP-Tl-1M, after the first and the second, a third shell consisting of a single Tl-O path with N = 6 was found to improve the quality of the fit. On the opposite, the fitting of a third shell did not provide acceptable results for KTP-Tl-0.1M. The EXAFS results of the Tl-treated samples are reported in Table 5 and Fig. 13.

Table 5. Tl L_3 -edge EXAFS analysis results for the two Tl-treated samples.

KTP-Tl-1M				KTP-Tl-0.1M		
S_0^2	1.0(4)			S_0^2	1.0(3)	
E_0	-8.0(3.0) [†]			E_0	-7.4(2.0) [†]	
R-factor	0.021			R-factor	0.072	
BVS	1.16			BVS	1.16	
Path	Tl-O	Tl-Ta	Tl-O	Path	Tl-O	Tl-Ta
Distance (Å)	2.78(5)	3.75(9)	4.15(6)	Distance (Å)	2.78(3)	3.75(3)
N	6	6	6	N	6	6
σ^2 (Å ²)	0.023(7)	0.026(17)	0.021(7)	σ^2 (Å ²)	0.019(6)	0.015(4)

S_0^2 = amplitude reduction factor; E_0 = threshold energy; N = coordination number; σ^2 = Debye-Waller factor (Å²).

R-factor = $(\sum_i |y_{obs} - y_{calc}|) / (\sum_i y_{obs})$ (Roy and Gurman, 1999).

BVS = bond valence sum for the first shell: $V_i = \sum_j S_{ij}$ with $S_{ij} = \exp\left(\frac{R_0 - R_{ij}}{b}\right)$; R_{ij} = distance between i and j atoms; R_0 and b values taken from Brese and O'Keeffe (1991).

[†] The E_0 values are high, but overall acceptable. However, the uncertainties on the refined distances reflect the intrinsic problems of the fit (e.g., Kelly and Ravel 2007).

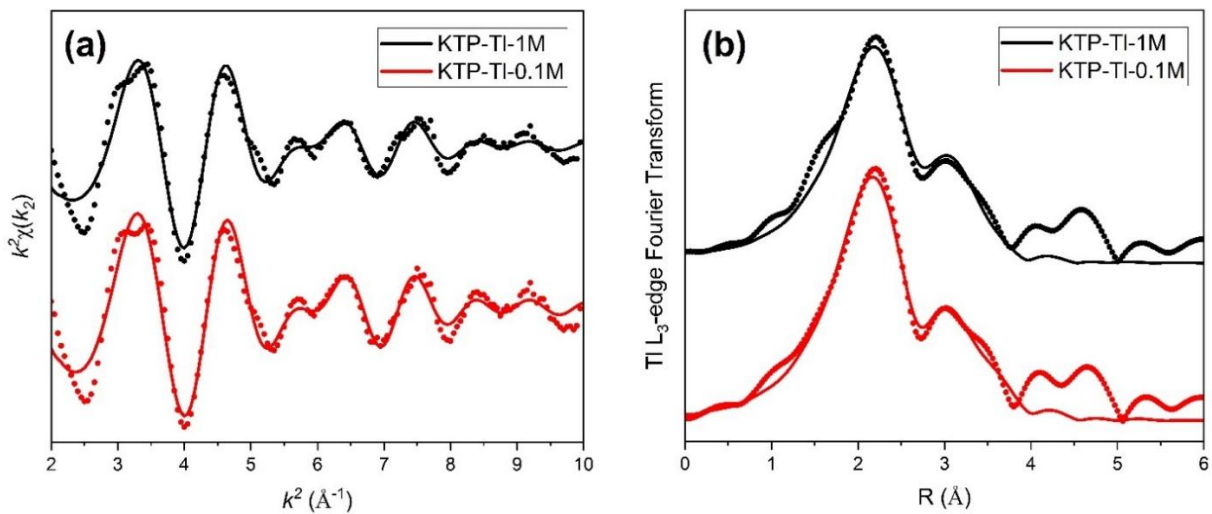


Figure 13. Tl L_3 -edge EXAFS (a) and Fourier transform (b) of the Tl-treated samples. Experimental data are displayed by symbols and fit by solid lines.

The KTP-Pb-1M EXAFS spectrum resulted strongly affected by signal dampening after $4 \text{ \AA}^{-1}$ (Figure 14a), making the data analysis very challenging. The fitting of a first shell assuming Pb located in the conventional A or A', even considering the presence of two oxygens placed in Y' sites, failed completely. Many tests were thus performed employing different sets of Pb-O and Pb-Ta paths considering an asymmetrical disposition of Pb within the tunnel environment, but all the fits were characterized by high values of the amplitude reduction factor (S_0^2). Constraining S_0^2 to values in the range 0.7-1.1 did not produce reasonable results.

The best result, illustrated in Fig. 14 and summarized in Table 6, was obtained considering:

- four distinct Pb-O path, each with $N = 2$ and interatomic distances in the range 2.4-2.9 $\text{\AA}$, for the first shell.
- a single Pb-Ta path with $N = 6$ for the second shell.
- two additional Pb-O paths with $N = 6$ and 12 and interatomic distances up to $\sim 5.2 \text{ \AA}$.

The high errors in the fitting parameters and, especially, the anomalous S_0^2 value, suggest being very cautious in the results interpretation. The low quality of the Pb EXAFS spectra was definitely evident in the KTP-Pb-0.1M sample, whose analysis did not produce any consistent results, since both the fitted parameters and graphical output were unsatisfactory.

Table 6. Pb L_3 -edge EXAFS analysis results for KTP-Pb-1M.

KTP-Pb-1M				
S_0^2	1.5(5)			
E_0	1.7(6)			
R-factor	0.011			
BVS	2.15			
Path	Pb-O	Pb-O	Pb-O	Pb-O
Distance ($\text{\AA}$)	2.41(3)	2.56(3)	2.71(3)	2.86(3)
N	2	2	2	2
σ^2 ($\text{\AA}^2$)	0.016(8)	0.010(10)	0.008(9)	0.014(15)
(average first shell Pb-O distance = 2.64 $\text{\AA}$)				
Path	Pb-Ta	Pb-O	Pb-O	
Distance ($\text{\AA}$)	3.81(2)	4.34(3)	5.12(4)	
N	6	12	6	
σ^2 ($\text{\AA}^2$)	0.024(7)	0.032(11)	0.012(9)	
S_0^2 = amplitude reduction factor; E_0 = threshold energy; N = coordination number; σ^2 = Debye-Waller factor ($\text{\AA}^2$). R-factor = $(\sum_i y_{obs} - y_{calc}) / (\sum_i y_{obs})$; from Roy and Gurman (1999). BVS = bond valence sum for the first shell: $V_i = \sum_j S_{ij}$ with $S_{ij} = \exp\left(\frac{R_0 - R_{ij}}{b}\right)$; R_{ij} = distance between i and j atoms; R_0 and b values taken from Krivovichev (2012).				

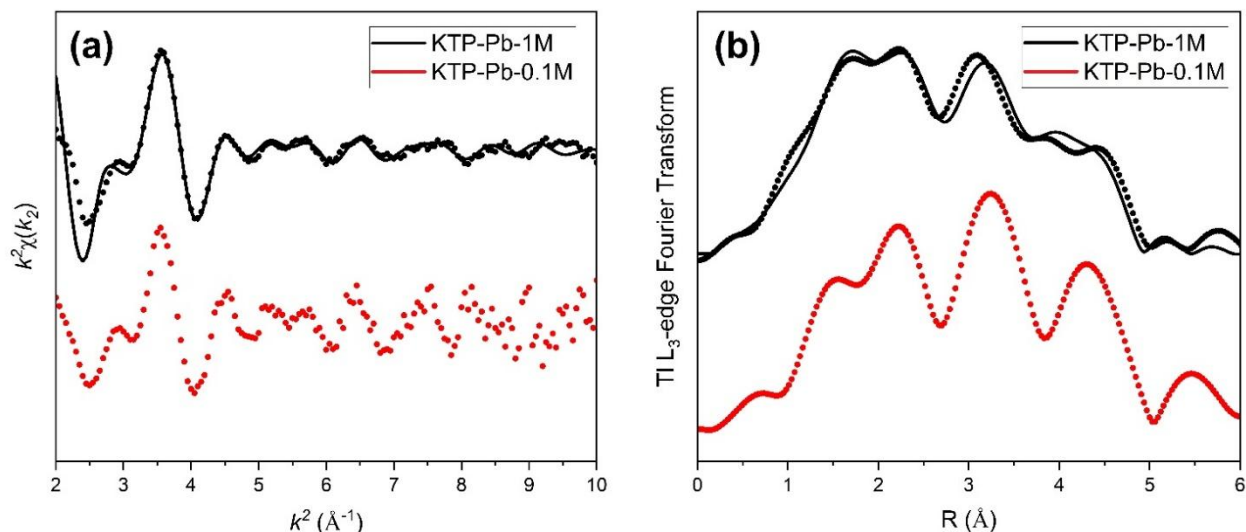


Figure 14. Pb L_3 -edge EXAFS (a) and Fourier transform (b) of the Pb-treated samples. Experimental data are displayed by symbols and fits by solid lines. Since the fit was not possible, for the KTP-Pb-0.1M sample only the data are reported.

5.7. Discussion

In this section is reported the discussion about the incorporation mechanisms of the three heavy metals in the microlite structure. First the crystal structure and chemistry of the untreated KTP microlite is introduced (5.7.1). Then, the effects of the heavy metal incorporation on the average structure, the local coordination environment and the ion exchange reactions are discussed in three consecutive sub-sections (5.7.2, 5.7.3 and 5.7.4), one for each heavy metal. A further paragraph (5.7.5) is dedicated to the final remarks.

5.7.1. Crystal Structure and Chemistry of the untreated KTP Microlite

The KTP microlite is cubic, space group $Fd-3m$. Its unit cell parameter a is 10.61797(7) Å, in good agreement with the synthetic potassium tantalum pyrochlore reported by Duan et al. (1998), which was produced following a similar procedure and showed a cell parameter of 10.6193(3) Å. The K:Ta ratio measured by PIXE is about 0.55; the elemental mass percentage was normalized on the basis of ΣB cations = 2 (where B, the framework cations site, was considered fully occupied by Ta), thus giving a potassium content of 1.1(1) atom per formula unit.

Large monovalent cations like K^+ can occur in both conventional A and Y sites depending on the ratio between tunnel A and framework B cations. At high values of A:B ratio (A occupancy ≥ 0.5) potassium tends to occupy the A positions, while at lower A:B ratio (A occupancy < 0.5), potassium is preferentially located in the Y site (English et al., 1980; Grins et al., 1980; Ercit et al., 1994).

Following the latter principle, since 1.1 *apfu* would correspond to an A occupancy > 0.5, K⁺ should be assigned to the A site. Nevertheless, the tunnel environment is complexified by the presence of a satellite site (A') placed at about 0.5 Å from A (Fig. 15).

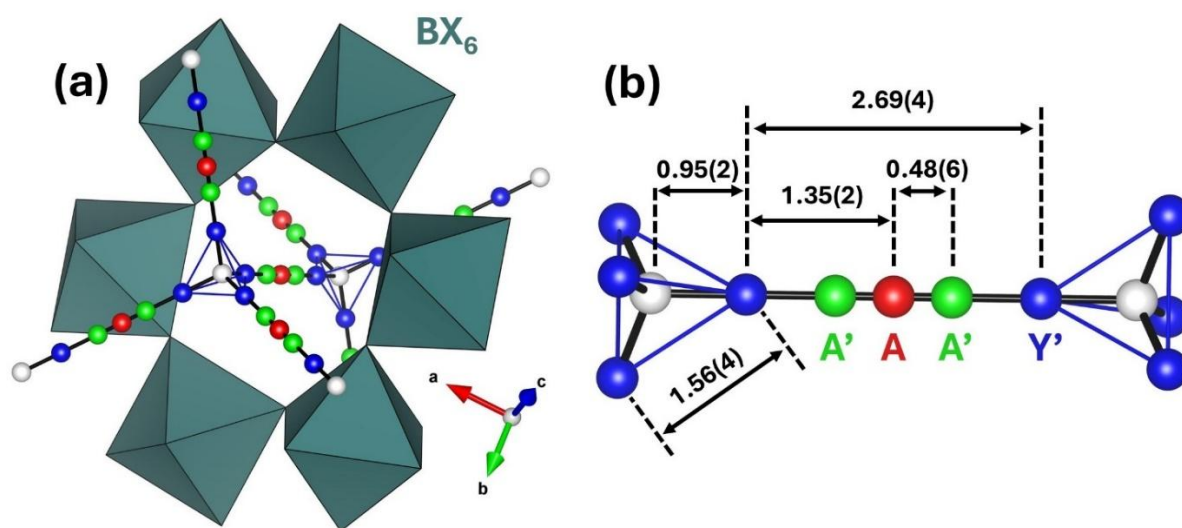


Figure 15. Relative disposition of A, A', Y' and empty Y (a) and interatomic distances of the tunnel sites for untreated KTP (b). Colour scheme: A = red; A' = green; empty Y = white; Y' = blue; BX₆ = grey.

The short distance between A and A' suggests the occurrence of positional disorder phenomena in this section of the tunnel, with a continuous but inhomogeneous atomic distribution (with an electron density maximum in proximity of the A site) rather than an actual localization of atoms in defined crystallographic sites. As a consequence, since the attribution of potassium to a precise crystallographic position would be quite impractical, if not wholly erroneous, K⁺ was just considered disordered between A and A'.

Comparing the number of electrons in the tunnel sites obtained by the Rietveld refinement with that calculated from PIXE results (Table 7), a discrepancy of ~14 e⁻ can be noticed. This discrepancy can be attributed to the occurrence within the tunnels of water molecules, whose presence has been evidenced also by the results of the FTIR measurements.

Notably, water has been found positionally disordered off the ideal 8(b) Y site in both natural and synthetic Ta-bearing pyrochlores (Groult et al., 1982; Ercit et al., 1986). That was consistent with the Rietveld refinement results of the KTP microlite, where Y was found empty, while an average of roughly 9 electrons were found in a close position, the 32(e) Y' site (Table 7).

Since one molecule *pfu* of H₂O corresponds to an electron number of 8, Y' was considered occupied by such an amount of water, which is also the maximum capacity of the site. Indeed, since the Y'-Y' distances are too short (~1.5 Å), only one of the four Y' sites arranged in tetrahedral configuration around the empty Y site can be occupied (Fig. 15 a, b). As a consequence, only ¼ of the 32(e) sites can be filled, thus giving a maximum occupancy of 1 molecule *pfu*.

*Table 7. Number of electrons measured by XRD and PIXE
for the KTP microlite*

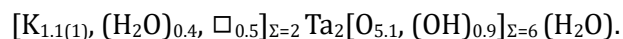
Measured by XRD		Obtained by PIXE	
n. e ⁻ (A)	18(3)	n. e ⁻ (K)	21(2)
n. e ⁻ (A')	8(4)		
n. e ⁻ (Y')	9(1)	Δe^-	14
Σe^-	35(8)		
Δe^- = difference between the average number of electrons measured by XRD and that found by PIXE.			

The difference between the number of electrons in A and A' found by refining their occupancy factors ($\sim 26 e^-$) and that brought by 1.1(1) *apfu* of potassium measured by PIXE ($\sim 21 e^-$) suggested the presence of water in the latter sites. Nevertheless, the large uncertainties inherent in the combination of Rietveld refinements and PIXE measurements did not allow an accurate assessment of the water content. Some crystallochemical considerations were then needed.

A and A' sites form an A'-A-A' row along the tunnel axis, with A placed in the centre of a hexagonal ring of six BX₆ octahedra and A' slightly shifted along the tunnel axis from the position of A (Fig. 15a). Since it occupies a 16(*d*) position in a crystal structure with Z = 8, the A site has a maximum occupancy of 2 *apfu*, while that of A', which is placed in a 32(*e*) position, is 4 *apfu*. Therefore, from a pure crystallographic perspective, the sum of the maximum occupancies of A and A' sites should be 6 *apfu*. Nevertheless, as the A-A' distances are just $\sim 0.5 \text{ \AA}$, only one site can be occupied in a single A'-A-A' row. As a result, the sum of the maximum occupancies of A and A' can't exceed 2 *apfu*, that is $\frac{1}{3}$ of the theoretical value (Fig. 15b). In this particular case, the utmost capacity of the A'-A-A' row is further limited by the close proximity of the adjacent Y' site. Every Y' of a YY'₄ tetrahedron adjoins a different A'-A-A' row. If one of the four Y' site is occupied by a water molecule, its closer A'-A-A' row must be empty, while the other three can be occupied. Having the Y' sites occupied by one water molecule *pfu*, at least $\frac{1}{4}$ of the A'-A-A' rows must be vacant and the sum of the maximum occupancies of A and A' drops to 1.5 *apfu*. As the A and A' sites are occupied by about 1.1 *apfu* of K, the maximum water content in the latter sites is roughly 0.4. At this point, it is logical to assume that A and A' sites were filled at the maximum of their capacity with 1.1 *apfu* of potassium and 0.4 water molecules *pfu*. Given the latter assumption, the resulting total water content in the tunnel environment is about 1.4 *apfu*, in perfect agreement with that found by Goh et al. (2002), on whose procedure is based the synthesis employed in this work.

The positive charges brought by tunnel K⁺ and framework Ta⁵⁺ are not enough to balance six *apfu* of O²⁻. As no sign of H₃O⁺ was detected by FTIR measurements, the electric neutrality can be provided only by the presence of hydroxyl groups in the octahedral framework. A comparable case was reported by Groult et al. (1982) and Catti et al. (1992), which showed that protons in the synthetic HTaWO₆·xH₂O pyrochlore are not located in the tunnel sites, but at the edge of the (Ta,W)O₆ octahedra forming hydroxyl groups with the framework oxygens. In our synthetic

microlite, the presence of hydroxyl ions bound to tantalum was outlined by infrared measurements and justified by the use of a concentrated solution of KOH in the synthesis procedure. The formula was therefore balanced assigning adequate amounts of framework OH⁻, yielding:



5.7.2. Incorporation Mechanisms of Thallium in Microlite

The normalization of the Tl and K⁺ concentrations found by PIXE on the basis of ΣB cations = 2 yielded a thallium content of 1.2(1) and 1.1(1) *apfu* and a potassium content of 0.4(1) and 0.7(1) *apfu* for KTP-Tl-1M and KTP-Tl-0.1M, respectively. The KTP microlite shows high affinity for Tl, and its different concentrations in the solutions have only minor effects on the amount of sorbed metal, which is 466(39) mg/g for KTP-Tl-1M and 427(39) mg/g for KTP-Tl-0.1M. The affinity for thallium can be explained by the similarities between Tl⁺ and K⁺, which are both monovalent cations with comparable ionic radii (1.51 Å for ^{viii}K⁺ and 1.59 Å for ^{viii}Tl⁺) (Shannon, 1976).

The incorporation of thallium had various effects on the sorbent material. The first and most obvious change observed was the powder's colour shifting from white to yellow. According to English et al. (1980), the yellow colouring may be attributed to transition from the filled 6s band to the empty 6p band of monovalent thallium due to Tl-Tl interaction along the tunnels. The rapidity of the colour transition, which occurred in just a couple of seconds, suggests that the ion exchange reaction occurred almost instantly.

Turning now to structural responses, after the ion exchange the unit cell parameter increases from 10.61797(4) Å to 10.64526(5) Å for KTP-Tl-1M and 10.64356(6) Å for KTP-Tl-0.1M, with a respective variation of 7.7‰ and 7.2‰ in unit cell volume (Table 2). The latter variation in unit cell is consistent with the uptake of conspicuous amounts of Tl⁺, which, since it is slightly larger than K⁺, tends to expand the tunnel sections where it is hosted in order to better fit in the tunnel itself. Indeed, while the Ta-O interatomic distances in the BX₆ octahedra remain practically identical, those between two opposite Ta atoms of the BX₆ hexagonal rings increase from 7.508(1) Å to 7.527(1) Å and 7.526(1) Å for KTP-Tl-1M and KTP-Tl-0.1M, respectively.

As Y and eventual Y' were found totally vacant, the tunnel environment of the Tl-treated samples can be described by a single ~2.1 Å long A''-A'-A'-A'' row hosting all tunnel occupants (Fig. 16). The electron density distribution is not uniform along the A''-A'-A'-A'' row but seems to show a relative maximum in correspondence of A' (Table 8), which lies at about 0.5 Å from A, slightly shifted from the centre of a BX₆ hexagon along the tunnel axis (see Fig 16). It is then quite clear that incorporated Tl⁺ and residual K⁺ do not occupy single, precise crystallographic positions, but they are instead disorderly distributed along the tunnel axis, with a slightly greater probability to be found nearby the A' sites rather than around A and A''.

The concomitant occurrence of significant amounts of K within the tunnels did not allow a precise description of the local environment of Tl by means of XRD. However, some consideration can be made on the basis of the results of the Rietveld refinements. Since Y and eventual Y' are empty (and then they do not host anions which can bind to Tl), the coordination of Tl is limited to the six inner oxygen anions of the BX_6 hexagon. The interatomic distances between Tl and the framework oxygens depends on the position of the Tl itself along the A''-A'-A'-A'' row. Considering Tl disordered among A, A' and A'' sites, the average Tl-O distance would be ~ 2.81 Å. The latter value, considering the six-fold coordination of thallium, gives a Bond Valence Sum (BVS) of about 1.07, which is in good agreement with the +1 charge of the monovalent thallium. The latter scenario is very close to that resulting from the EXAFS investigations. Indeed, the first shell of Tl in both Tl-treated samples was successfully modelled using six ~ 2.78 Å Tl-O distances.

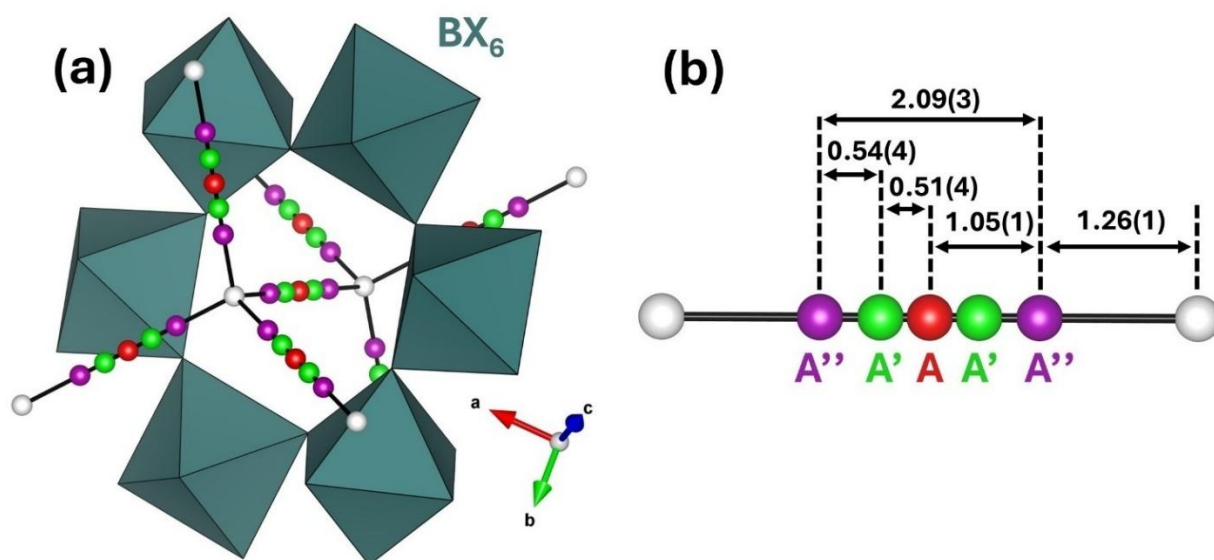


Figure 16. Relative disposition of A, A', A'' and empty Y (a) and interatomic distances of the tunnel sites for KTP-Tl-1M (b). Colour scheme: A = red; A' = green; A'' = purple; Y = white; BX_6 = grey.

The strong static disorder affecting Tl (and, more in general, all the tunnel environment) had a remarkable effect on the EXAFS signal, whose fits showed anomalous uncertainties in the amplitude reduction factor (S_0^2) and high values of Debye-Waller factors (σ^2). As S_0^2 is strongly correlated to the coordination numbers (Roy et al., 1997), the latter parameters had to be considered with some caution. Nonetheless, the BVS calculated for the first shell, which is 1.16, supports the hypothesis of a sixfold coordination for Tl.

Furthermore, according to EXAFS results, the second shell of Tl consists of six Ta atoms at ~ 3.75 Å for both KTP-Tl-1M and KTP-Tl-0.1M samples. The XRD analyses provided an average Tl-Ta distances of ~ 3.82 Å, which is slightly longer than that found by EXAFS. The second shell environment is hence further evidence of Tl being surrounded by a ring of six TaO_6 octahedra. From XRD, A' and A'' result respectively ~ 4.06 and ~ 3.90 Å far from a set of six oxygen atoms (plus

a further set of six oxygens at $R > 4.5 \text{ \AA}$), while A is surrounded by a set of twelve equidistant O atoms at $\sim 4.26 \text{ \AA}$. The KTP-Tl-1M EXAFS signal revealed the presence of oxygen atoms at about $4.15 \text{ \AA}$. The N of the path used in the fit (Table 5) was set to six. Nonetheless, tests conducted with different N values did not provide significantly different results. As a consequence, it was not possible to determine a reliable coordination number for the third shell.

In conclusion of this digression, EXAFS and XRD results are thus in good agreement, showing Tl atoms placed along the tunnel axis, surrounded by a hexagonal TaO_6 ring.

The crystallochemical effect of the thallium incorporation is accounted for the dehydration of the Y cage: if the A''-A'-A'-A'' rows are filled at the maximum of their occupancy, the distance between the rows occupants is not enough to allow the presence of H_2O in middle sites. That also explains the expulsion of an electrically neutral molecule during an exchange reaction that should involve only ions. A substantial dehydration consequent to Tl^+ incorporation was previously reported for natural hydropyrochlore (Taddei et al., 2024).

Despite the dehydration of the Y cage, since the presence of the H-O-H bending vibration mode was detected by FTIR measurements, residual H_2O molecules could have remained in the A''-A'-A'-A'' rows. The high level of disorder highlighted by the XRD did not allow to evaluate the precise amount of water hosted in the tunnels. Nonetheless, assuming that the maximum occupancy of the A''-A'-A'-A'' row (considering a crystal structure with $Z = 8$) is 2 *apfu* (that is to say assuming that only one atom/molecule can be hosted in a single A''-A'-A'-A'' row) and that the tunnels are filled up at the maximum of their capacity, approximately 0.4 and 0.2 molecules *pfu* of water can be estimated as the tunnels water content for KTP-Tl-1M and KTP-Tl-0.1M, respectively. Considering the tunnels occupied by the latter amounts of H_2O and by the quantities of Tl and K measured by PIXE, the number of electrons brought by all these occupants is in fair agreement with that found by refining the occupancy factor of the tunnel sites (Table 8).

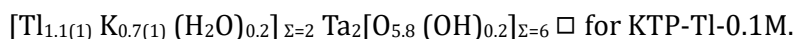
Table 8. Number of electrons measured by XRD and PIXE for the Tl-treated samples. Values for the untreated KTP are also reported for comparison.

	KTP	KTP-Tl-1M	KTP-Tl-0.1M
Measured by XRD			
n. e ⁻ (A)	18(3)	32(2)	28(2)
n. e ⁻ (A')	8(4)	46(1)	45(1)
n. e ⁻ (Y'/A'') ⁺	9(1)	36(2)	35(2)
$\Sigma \text{ e}^-$	35(8)	114(5)	108(5)
Obtained by PIXE			
n. e ⁻ (K)	21(2)	8(2)	13(2)
n. e ⁻ (Tl)	–	97(8)	89(8)
$\Sigma \text{ e}^-$	21(2)	105(10)	102(10)
$\Delta^{\dagger}$	14	9	6

⁺ A'' instead of Y' for Tl-treated samples.

[†] Difference between the number of e⁻ found in the tunnel sites by XRD and the sum of e⁻ brought by the tunnel cations obtained by PIXE.

The amount of released K^+ (approximately 0.7 and 0.4 *apfu* for KTP-Tl-1M and KTP-Tl-0.1M, respectively) is not enough to balance the charges of sorbed Tl^+ (about 1.2 and 1.1 *apfu* for KTP-Tl-1M and KTP-Tl-0.1M, respectively). The expulsion of H^+ ions could be accounted for the maintenance of the ion exchange reaction electroneutrality. As previously explained, the presence of protons (i.e. H^+ ions) bound to the framework's oxygens is required to counterbalance the negative charges brought by 6 *apfu* of framework O^{2-} . Part of H^+ could be involved in the ion exchanges, and released to counterbalance the positive charges provided by the inbound Tl^+ . All that being said, it is possible to write the chemical formulae for the $[K_{1.1(1)}, (H_2O)_{0.4}, \square_{0.5}]_{\Sigma=2} Ta_2[O_{5.1}, (OH)_{0.9}]_{\Sigma=6} (H_2O)$ microlite treated with Tl solutions:



In summary, the incorporation mechanism of Tl involves the dehydration of the Y cage and the loss of potassium from the original A'-A-A' rows. To balance the electrical charges brought by Tl^+ , part of the H^+ ions originally bound to the framework oxygens are also expelled from the tunnel environment.

5.7.3. Incorporation Mechanisms of Lead in Microlite

The Pb and residual K concentrations in the microlite powders were normalized on the basis of ΣB cations = 2, giving a potassium content of 0.56(5) and 0.73(7) *apfu*, and a lead content of 0.28(3) and 0.15(1) *apfu* for the samples treated with 1M and 0.1M lead solutions, respectively. The lead contents found by PIXE correspond to a Pb sorption amount of 110(12) and 59(4) mg/g for KTP-Pb-1M and KTP-Pb-0.1M, respectively.

After the incorporation of Pb, a slight decrease in the tunnel diameter was observed, as testified by the slight reduction of the interatomic distances between two opposite Ta atoms of the BX_6 hexagonal rings from 7.508(1) Å to 7.489(1) Å and 7.501(1) Å for KTP-Pb-1M and KTP-Pb-0.1M, respectively. This trend is consistent with the substitution of K^+ with the smaller Pb^{2+} ($^{VIII}K^+ = 1.51$ Å; $^{VIII}Pb^{2+} = 1.29$ Å) (Shannon et al., 1976). The contraction of the tunnel environment is evident also by observing the unit cell parameters, which decrease from 10.61797(4) to 10.59158(5) and 10.60751(6) Å for KTP-Pb-1M and KTP-Pb-0.1M, with a variation of -7.5‰ and -3.0‰ in cell volume, respectively (Table 2).

In KTP-Pb-1M, the number of electrons found in Y' by refining the occupancy factor of the site remains roughly constant after the ion exchange, suggesting that Y' remains occupied by one molecule of H_2O *pfu*. On the opposite, the increase of the number of electrons in A from ~18 to ~30 suggests that most of Pb is located around this site.

A more detailed description of the coordination environment of lead was provided by EXAFS. The first shell of Pb in KTP-Pb-1M was described employing four different Pb-O paths, with interatomic distances ranging from ~ 2.41 to ~ 2.86 Å (Table 6). Each path was assigned a coordination number of 2. The resulting bond valence sum, 2.15, is in good agreement with the +2 charge of the divalent lead, while the sum of N is consistent with the Pb being coordinated by six framework oxygens in X and two water oxygens in Y'. Despite that, due to the very high S_0^2 value (~ 1.5), the N numbers cannot be considered completely reliable.

Considering the tunnel geometry, the wide range of interatomic distances used to describe the first shell is inconsistent with lead being hosted in either the A or A' sites (Table 3). The two shortest Pb-O paths (~ 2.41 and ~ 2.56 Å) suggest instead an approach of the lead atoms towards the tunnels walls, and then a more asymmetrical coordination environment. Such a displacement can be explained considering the size of Pb^{2+} , which could be too small to fit in the coordination polyhedra of A and A'. A shift from the tunnel axis towards the oxygen atoms of the octahedral framework could be required for lead to better fit in the tunnel environment.

The asymmetry of the resulting coordination can be also explained by the effects of the stereoactive lone pair of lead. Considering the lone pair oriented toward the walls of the tunnel, the electrostatic repulsion with the framework oxygens would push the Pb^{2+} ion against the opposite walls.

Just as the first shell is asymmetrical, so should the second one be. Nonetheless, due to the high number of variables needed to model such a complex environment, the attempts to split the second coordination sphere using different paths with different interatomic distances did not yield any good result. Therefore, a single Pb-Ta path with $N = 6$ and an interatomic distance of ~ 3.81 Å was employed to describe the second shell.

Additional oxygen atoms were found beyond 4 Å. In particular, Pb-O paths with interatomic distances of ~ 4.34 and 5.12 Å may be related with further ~ 4.24 and 5.35 Å sets of O atoms belonging to the TaO_6 hexagonal ring reported by XRD analysis.

Lead is not the only occupant of the A site and, more generally, of the A'-A-A' rows. Indeed, 0.28 *apfu* of Pb correspond to about $23 e^-$, while $\sim 30 e^-$ were found in A and ~ 10 in A' (Table 9). As in the case of the untreated microlite, residual K (about 0.56 *apfu*, according to PIXE results) and water molecules can be assumed to be disordered along the A'-A-A' rows.

The precise amount of water in the A'-A-A' rows could not be accurately determined. Nevertheless, an estimation is possible through a series of considerations. As in the case of the untreated KTP, $\frac{1}{4}$ of the A'-A-A' rows is vacant and the sum of the maximum occupancies of A and A' is 1.5 *apfu*. According to the PIXE measurements, about 0.28 *apfu* of Pb and 0.56 *apfu* of K, for a total of ~ 0.84 *apfu*, are placed in the A'-A-A' rows. Considering the rows filled at the maximum of their capacity (1.5 *apfu*), the amount of water disordered between A and A' should be about 0.66 *apfu*.

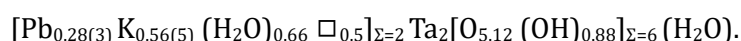
Comparing the number of electrons found by Rietveld refinements for A and A', and that for the amount of Pb and residual K the results are quite close. Indeed, $40(6) e^-$ are found in A and A', while the sum of electrons brought by Pb and K is $34(3)$, giving a difference of about $6 e^-$, corresponding to ~ 0.75 *apfu* of water. The high uncertainties refined in the number of electrons

do not allow to consider accurate the so estimated water content. Nonetheless, these considerations on the differences in the number of electrons suggest a water occupancy up to the maximum capacity of the A'-A'-A' rows. If this is true, the KTP-Pb-1M A'-A'-A' rows show an increase in the water content with respect to the untreated KTP. The increase can be estimated in about 0.26 *apfu*, which is close to the amount of incorporated Pb and twice the quantity of expelled K (~0.54 *apfu*, according to PIXE results).

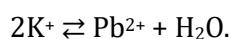
Table 9. Number of electrons measured by XRD and PIXE for the Pb-treated samples. Values for the untreated KTP are also reported for comparison.

	KTP	KTP-Pb-1M	KTP-Pb-0.1M
Measured by XRD			
n. e ⁻ (A)	18(3)	30(3)	30(3)
n. e ⁻ (A')	8(4)	10(3)	3(2)
n. e ⁻ (Y')	9(1)	10(1)	14(1)
Σ e ⁻	35(8)	50(7)	47(6)
Obtained by PIXE			
n. e ⁻ (K)	21(2)	10.5(1)	14(1)
n. e ⁻ (Pb)	–	23(2)	12(1)
Σ e ⁻	21(2)	33.5(3)	26(2)
Δ [‡]	14	16	21
‡ Difference between the number of e ⁻ found in the tunnel sites by XRD and the sum of e ⁻ brought by the tunnel cations measured by PIXE.			

At this point, a chemical formula for the KTP-Pb-1M sample can be provided:



The ratio between the expelled K⁺ and the incorporated Pb²⁺ and H₂O suggested the following ion exchange mechanism:



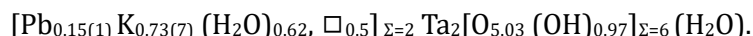
The expulsion of two K⁺ counterbalances the introduction of each Pb²⁺, while water participates to the reaction as a neutral species. The H⁺ ions bound to the framework oxygens do not appear to be involved in the reaction.

The 2:1 ratio in the 2K⁺ → Pb²⁺ exchange mechanism ought to result in a unit cell volume decrease exceeding the value obtained by XRD (Table 2). Nonetheless, this is prevented by the incorporation of water in the A'-A'-A' rows. With a diameter of about 2.7-2.8 Å (Pu et al., 2020), water molecules are indeed larger than both K⁺ and Pb²⁺ ions, and their occurrence in the tunnels counteracts the contraction effects of the divalent lead.

In KTP-Pb-0.1M, A' is almost empty and most of the electron density is condensed in the A site. The number of electrons found in A by Rietveld refinements ($\sim 30 e^-$) is consistent with the site occupied with all the Pb ($\sim 0.15 \text{ apfu}$) and K ($\sim 0.7 \text{ apfu}$) measured by PIXE and approximately 0.7 water molecules *pfu*. The number of electrons of the Y' site seems too high (approximately $14 e^-$) to be occupied only by H₂O, thus suggesting the presence of small amounts of lead or potassium. This could be also true for the KTP-Pb-1M sample, which, despite its Y' electron number being quite coherent with that of approximately one H₂O *pfu*, could still host small amounts of Pb or K. However, due to the alleged small amounts of lead and the limits inherent in the Rietveld analysis, the quantification of a precise Pb:H₂O ratio in Y' is not feasible and all the lead was considered located around the A site.

As mentioned above, due to the poor quality of the signal, the EXAFS analysis of KTP-Pb-0.1M did not provide any reasonable fit. However, the similarities between the EXAFS spectra of KTP-Pb-1M and KTP-Pb-0.1M suggest a similar Pb local environment for both samples.

The following chemical formula is proposed for the KTP-Pb-0.1M sample:



The exchange mechanism proposed for KTP-Pb-0.1M is the same reported above for KTP-Pb-1M.

5.7.4. Incorporation Mechanisms of Zinc in Microlite

The Zn and K concentrations in KTP-Zn-1M and KTP-Zn-0.1M obtained by PIXE measurements were normalized on the basis of $\Sigma \text{B cations} = 2$, thus giving a potassium content of 0.56(5) and 0.67(6) *apfu* and a zinc content of 0.30(3) and 0.21(2) *apfu* for the samples treated with 1M and 0.1M zinc solutions, respectively. The zinc contents found by PIXE correspond to a Zn sorption amount of 37(4) and 26(2) mg/g for KTP-Zn-1M and KTP-Zn-0.1M, respectively.

In contrast with what expected from the incorporation of a small cation such as Zn²⁺ in replacement of the larger K⁺ ($^{VIII}\text{K}^+ = 1.51 \text{ \AA}$; $^{VIII}\text{Zn}^{2+} = 0.9 \text{ \AA}$) (Shannon et al., 1976), the unit cell parameters of Zn-treated KTP show slight increases from 10.61797(4) to 10.62645(4) Å for KTP-Zn-1M and 10.62638(5) Å for KTP-Zn-0.1M, with a cell volume variation of approximately +2.4‰ for both samples. Despite the different amounts of incorporated metal, the increment of the edge of the cubic unit cell is almost the same for both samples, suggesting that this variation is not related with the amount of Zn in the tunnels.

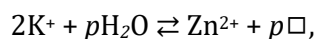
As it happens for the Pb-treated samples, the ion-exchange reaction in KTP-Zn-1M does not seem to involve Y', whose occupancy remained constant after each treatment, while more evident variations were observed in the A'-A-A' rows. The sum of the electron numbers found in A and A' by Rietveld refinements is coherent with all the K⁺ ($\sim 0.6 \text{ apfu}$) and Zn²⁺ ($\sim 0.30 \text{ apfu}$) measured by PIXE being positionally disordered in the A and A' site. No water results therefore hosted in the A'-A-A' row. Having said all that, the chemical formulae for the Zn-treated samples can be written:

$[\text{Zn}_{0.30(3)} \text{K}_{0.56(5)} \square_{1.14}]_{\Sigma=2} \text{Ta}_2[\text{O}_{5.16} (\text{OH})_{0.84}]_{\Sigma=6} (\text{H}_2\text{O})$ for KTP-Zn-1M;

$[\text{Zn}_{0.21(2)} \text{K}_{0.67(6)} \square_{1.12}]_{\Sigma=2} \text{Ta}_2[\text{O}_{5.09} (\text{OH})_{0.91}]_{\Sigma=6} (\text{H}_2\text{O})$ for KTP-Zn-0.1M.

The high number of vacancies and the assumed lack of water in the A'-A-A' row could play some role in the expansion of the structure observed by XRD, as the absence of a cation or a molecule around the A position may produce a relaxation of the BX₆ hexagonal ring.

The ratio between released K⁺ and incorporated Zn²⁺ is close to 2:1, thus suggesting the following ion exchange mechanism:



where p is the amount of water originally hosted in the A'-A-A' row (~ 0.4 apfu).

The behaviour of KTP-Zn-0.1M was not easy to evaluate because of the high errors on A' and Y' number of electrons (Table 10). For analogy with KTP-Zn-1M, all Zn²⁺ and K⁺ were considered disordered in the A'-A-A' rows, while Y' was deemed to remain full of water molecules. Due to the high errors in the A' site electron density (Table 10), it was not possible to estimate the water content of the A'-A-A' rows which, again for analogy with the sample treated with 1M solution, were considered anhydrous.

Table 10. Number of electrons measured by XRD and PIXE for the Zn-treated samples. Values for the untreated KTP are also reported for comparison.

	KTP	KTP-Zn-1M	KTP-Zn-0.1M
Measured by XRD			
n. e ⁻ (A)	18(3)	12(1)	16(1)
n. e ⁻ (A')	8(4)	8(2)	8(8)
n. e ⁻ (Y')	9(1)	7(1)	8(7)
Σ e ⁻	35(8)	27(4)	32(16)
Obtained by PIXE			
n. e ⁻ (K)	21(2)	11(1)	13(1)
n. e ⁻ (Zn)	–	9(1)	6(1)
Σ e ⁻	21(2)	20(2)	19(2)
$\Delta^\dagger$	14	7	13

$\dagger$ Difference between the number of e⁻ found in the tunnel sites by XRD and the sum of e⁻ brought by the tunnel cations measured by PIXE.

5.7.5. Final Remarks

The KTP microlite powders were able to incorporate good amounts of all three heavy metals, but with substantial differences in terms of sorption amounts, incorporation mechanisms and structural response to the incorporation.

Among the three metals, the KTP microlite seems to have a particular affinity for thallium, which, as already mentioned, can be explained considering the similarities in terms of electrical charge and ionic radius of Tl^+ and K^+ .

Pb^{2+} and Zn^{2+} were incorporated in quite similar amounts (the disparities in the sorption amount reported in Table 11 are mainly due to the different atomic weight of lead and zinc). The metal uptake in KTP-Pb-1M and KTP-Zn-1M is approximately $\frac{1}{4}$ of that in KTP-Tl-1M, between $\frac{1}{6}$ and $\frac{1}{8}$ if we consider the ratio among the 0.1M-treated samples. This difference in the sorption ability can be attributed to the differences in ionic radius and valence state. The exchange reaction requires the expulsion of two K^+ cations to balance the incorporation of one Pb^{2+} or Zn^{2+} cation, thus halving the amount of lead and zinc that can be tolerated by the structure in comparison with Tl^+ .

Pb^{2+} and Zn^{2+} are smaller than the original K^+ , thus implying the demand for some adjustments in the local coordination of the divalent ions. From EXAFS, it has been noticed that Tl^+ tends to occupy a central position within the tunnels, signifying that it fits quite well in the tunnel environment. On the opposite, due to its lower ionic radius, Pb^{2+} resulted shifted towards the tunnel walls.

Because of the strong interference between the Zn K-edge (9.659 KeV) and the Ta L_3 -edge (9.881 KeV) in the EXAFS signal, no information on the local environment of Zn could be obtained by EXAFS analysis. Nonetheless, due to its similarity with Pb^{2+} , Zn^{2+} is expected to have a similar coordination. This hypothesis is corroborated by the findings of Levin et al. (2002), which described the crystal structure of a synthetic $\text{Bi}_{1.5}\text{Zn}_{0.92}\text{Nb}_{1.5}\text{O}_{6.92}$ pyrochlore, where the Zn and Bi were displaced from the ideal A position towards the tunnel walls. In the case of the Zn-treated microlite samples, since the ionic radius of Zn^{2+} is lower than that of Pb^{2+} , the coordination environment of zinc may be even more asymmetrical than that of lead, which Zn ions pushed closer to the oxygens of the octahedral framework.

From the results summarised in Table 11, it is also evident that the sorption of Pb^{2+} and Zn^{2+} has a strong correlation with the concentration of the exchanging solutions (at least in highly concentrated solutions), while the amounts of incorporated Tl^+ are almost identical for the samples contacted with 1M and 0.1M solutions.

Regarding the exchange ratios of ions, the exchange reactions of lead and zinc appear to be quite similar. Indeed, the incorporation of both Pb^{2+} and Zn^{2+} requires the expulsion of two K^+ . The uptake of Pb^{2+} , however, involves the incorporation of one water molecule, while that of Zn is responsible for the dehydration of the A'-A-A' rows.

In any case, the ion exchange reactions of lead and zinc do not involve the Y' site, which seems to remain occupied by one *apfu* of water, but only the A'-A-A' rows. The incorporation of Tl^+ instead

results in the complete dehydration of the Y cage. In addition, the wide distribution of the electron density within the tunnel environment suggests the occurrence of remarkable displacement disordering phenomena affecting Tl^+ , which results distributed along a $\sim 2\text{\AA}$ row of sites.

Table 11. Summary of the chemical formulae and sorption amounts of the whole sample set.

Sample	Chemical formula	q_e
KTP	$[\text{K}_{1.1(1)} (\text{H}_2\text{O})_{0.4} \square_{0.5}]_{\Sigma=2} \text{Ta}_2[\text{O}_{5.1} (\text{OH})_{0.9}]_{\Sigma=6} (\text{H}_2\text{O})$	–
KTP-Tl-1M	$[\text{Tl}_{1.2(1)} \text{K}_{0.4(1)} (\text{H}_2\text{O})_{0.4}]_{\Sigma=2} \text{Ta}_2[\text{O}_{5.6} (\text{OH})_{0.4}]_{\Sigma=6} \square$	466(39)
KTP-Tl-0.1M	$[\text{Tl}_{1.1(1)} \text{K}_{0.7(1)} (\text{H}_2\text{O})_{0.2}]_{\Sigma=2} \text{Ta}_2[\text{O}_{5.8} (\text{OH})_{0.2}]_{\Sigma=6} \square$	427(39)
KTP-Pb-1M	$[\text{Pb}_{0.28(3)} \text{K}_{0.56(5)} (\text{H}_2\text{O})_{0.66} \square_{0.5}]_{\Sigma=2} \text{Ta}_2[\text{O}_{5.12} (\text{OH})_{0.88}]_{\Sigma=6} (\text{H}_2\text{O})$	110(12)
KTP-Pb-0.1M	$[\text{Pb}_{0.15(1)} \text{K}_{0.73(7)} (\text{H}_2\text{O})_{0.62}, \square_{0.5}]_{\Sigma=2} \text{Ta}_2[\text{O}_{5.03(8)} (\text{OH})_{0.97}]_{\Sigma=6} (\text{H}_2\text{O})$	59(4)
KTP-Zn-1M	$[\text{Zn}_{0.30(3)} \text{K}_{0.56(5)} \square_{1.14}]_{\Sigma=2} \text{Ta}_2[\text{O}_{5.16} (\text{OH})_{0.84}]_{\Sigma=6} (\text{H}_2\text{O})$	37(4)
KTP-Zn-0.1M	$[\text{Zn}_{0.21(2)} \text{K}_{0.67(6)} \square_{1.12}]_{\Sigma=2} \text{Ta}_2[\text{O}_{5.09} (\text{OH})_{0.91}]_{\Sigma=6} (\text{H}_2\text{O})$	26(2)
q_e = sorption amount (mg/g) of heavy metals in KTP. The water and hydroxyl content was estimated on the basis of crystallochemical considerations.		

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6. Incorporation Mechanisms of Heavy Metals in Elsmoreite

The results of the experiments conducted on synthetic elsmoreite are covered in the present chapter. In the first part of the chapter (5.1-5.6), the synthesis procedure, the ion exchange experiments, and the chemical and structural characterization are described. The second part (5.7) is instead dedicated to the discussion of the results, with a particular focus on the average structures of both the treated and untreated samples, and the local coordination environment of thallium and lead incorporated within the microlite structure.

6.1. Synthesis

Elsmoreite powders were synthesized following the protocol of Günter et al. (1989) with slight modifications: 1 mL of a 37% HCl solution was added to 13 mL of deionized water. When 7.5 mmol of sodium tungstate dihydrate [$\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$, ACS reagent, $\geq 99\%$, Sigma Aldrich] were poured to the solution, a sudden and effervescent reaction occurred. The result was a clear solution with pH=7. The pH was adjusted to a value of 3.5 by adding dropwise a 37% solution of HCl.

The solution was then loaded in a 25 mL Teflon-lined hydrothermal reactor and heated to 155°C in a muffle furnace for 72 hours. After the reaction, a white powder was retrieved at the bottom of the Teflon vessel, immersed in a clear solution with pH=5. The powders were filtered, washed with 50 mL of deionized water and dried at 70°C for 7 hours in an oven.

Secondary electron images of the samples were acquired using a scanning electron microscope (SEM) EVO 40 (Carl Zeiss), using a 10 KV current with 20 pA of intensity. Elsmoreite powders consist of crystallites ranging from approximately 200 nm to 5 μm in size (Fig. 1). The crystals have rounded edges and sometimes are twinned.

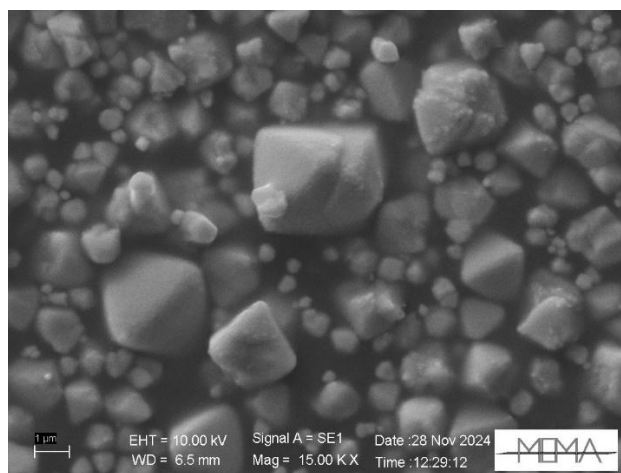


Fig. 1 SEM secondary electron image of elsmoreite powders prepared via hydrothermal synthesis.

6.2. Ion Exchange Experiments

200 mg of elsmoreite powders were immersed into 5 ml of 1 and 0.1M aqueous solutions of thallium (I) formate [HCO_2Tl , 97%, Sigma-Aldrich], lead (II) nitrate [$\text{Pb}(\text{NO}_3)_2$, ACS reagent, $\geq 99.0\%$, Sigma-Aldrich] and zinc (II) nitrate hexahydrate [$\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, reagent grade, 98%, Sigma-Aldrich] contained in 15 ml Falcon tubes. The plunged powders were manually stirred for few seconds using a stainless steel spatula and then left stationary. After one day of imbibition, the powders were filtered and washed three times with 5 ml of deionized water to remove eventual soluble salts precipitated, left under the fume hood overnight to roughly dry and then kept in an oven at 70°C for 2 hours to complete drying.

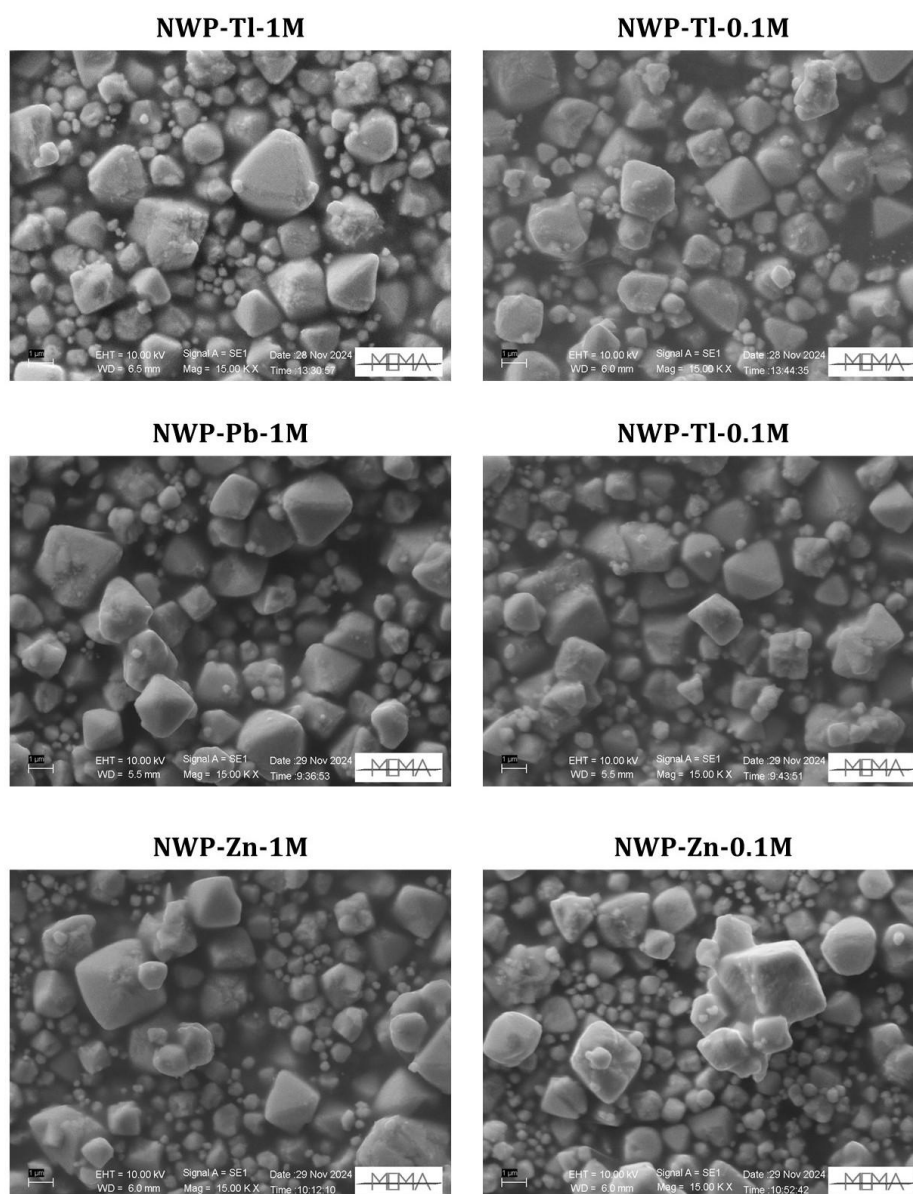


Fig. 2. SEM secondary electron images of elsmoreite powders after the treatment with 1M and 0.1M solutions of Tl, Pb and Zn.

The untreated elsmoreite is called NWP, standing for sodium tungsten pyrochlore, while the symbol of the heavy element used for the treatment and the concentration of the solution is added to the treated samples. For example, the sample plunged in the 0.1M zinc solution is called NWP-Zn-0.1M. As expected, no morphological changes have been shown by SEM investigations on the treated samples (Fig. 2).

6.3. Chemical Analysis

The relative concentration of tungsten, thallium, lead and zinc were measured by means of PIXE, while those of sodium by PIGE (Table 1). In the *apfu* errors calculations, a further relative 10% was added to the percentage error values reported in Table 1 due to systematic uncertainties inherent to PIXE and PIGE measurements.

The normalization of the chemical data, the estimation of the water content and the attribution of the different ions/molecules to the different crystallographic sites are discussed in section 6.7.

Table 1. PIXE and PIGE analytical results of treated and untreated elsmoreite powders.

sample	Na (wt%)	W (wt%)	Tl (wt%)	Pb (wt%)	Zn (wt%)	total
elsmoreite	3.9	96.1	0.0	0.0	0.0	100.0
err (%)	13.0	0.7	–	–	–	
NWP-Tl-1M	0.7	64.4	34.9	0.0	0.0	100.0
err (%)	22.0	0.7	0.9	–	–	
NWP-Tl-0.1M	0.5	65.8	33.7	0.0	0.0	100.0
err (%)	36.0	0.3	0.7	–	–	
NWP-Pb-1M	3.6	92.3	0.0	4.1	0.0	100.0
err (%)	12.0	0.7	–	2.3	–	
NWP-Pb-0.1M	3.0	93.7	0.0	3.3	0.0	100.0
err (%)	13.0	0.7	–	2.8	–	
NWP-Zn-1M	4.2	95.5	0.0	0.0	0.2	100.0
err (%)	13.0	0.7	–	–	66.0	
NWP-Zn-0.1M	3.8	96.0	0.0	0.0	0.2	100.0
err (%)	12.0	0.4	–	–	70.0	

6.4. Infrared Analysis

Infrared data were collected for the untreated elsmoreite and for the powders treated with 1M heavy metal solutions. All the IR spectra (Fig. 3) resulted quite similar. They exhibit:

- A marked peak at about 960-970 cm^{-1} , which can be imputable to W=O stretching vibration (Guery et al., 1997).
- A peak in the range 1600-1625 cm^{-1} due to the H-O-H bending vibration in H_2O molecules.
- A sharp peak at 2360 cm^{-1} , which is the typical band of the carbon dioxide from air.
- A broad band in the range 2600-3800 cm^{-1} , which is characteristic of the O-H stretching vibration.

- A broad peak at about 5180 cm^{-1} , which is the stretching + bending combination band of water (e.g., Ma et al., 2021).

In conclusion, the FTIR analysis revealed the clear presence of water in the structure of all the elsmoreite samples.

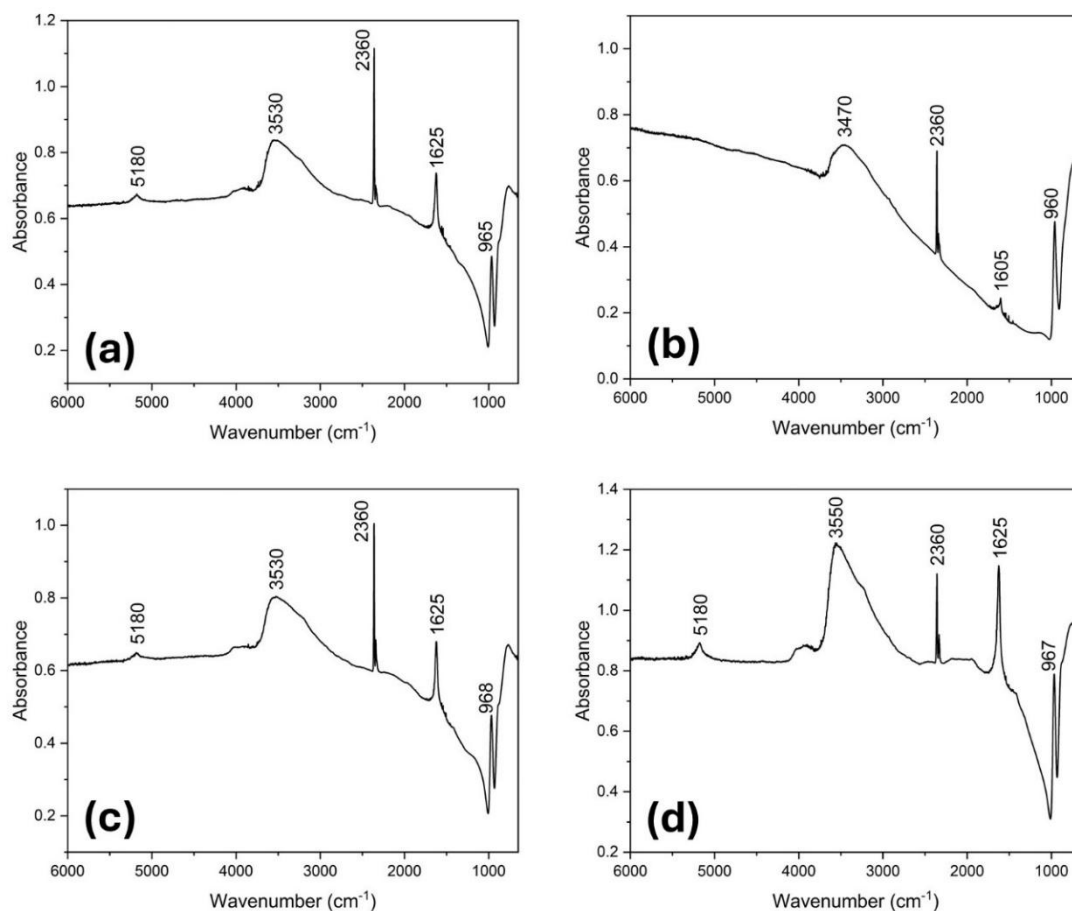


Fig 3. FTIR spectra of (a) NWP untreated microlite, (b) NWP-Tl-1M, (c) NWP-Pb-1M and (d) NWP-Zn-1M. The wavenumber found above each band correspond to its absorbance maximum.

6.5. Rietveld Refinements

The diffraction pattern of NWP elsmoreite was comparable to that measured by Reis et al. (1992) for a rhombohedrally distorted tungsten sodium pyrochlore phase, produced by a similar synthesis protocol. The reduction of the symmetry from the conventional cubic, $Fd-3m$ structure can be inferred considering a slight asymmetry of the peaks (Fig. 4) that would be expected to split upon a rhombohedral distortion. Due to the small extent of the distortion and experimental uncertainties, Reis et al. (1992) could not determine the rhombohedral space group. They instead provided a unit cell parameter of $a = 10.333(2)$ Å based on the cubic cell.

The rhombohedral space group employed in the Rietveld refinements is $R-3m$, which was deduced by group-subgroup relations using the Isodistort software (Campbell et al., 2006; Stokes et al., 2016). Since Mills et al. (2016) reported the occurrence of a sodium-bearing natural elsmoreite,

crystallizing in $R-3$, a refinement test was performed using the latter rhombohedral space group, but it did not provide any significant improvement in the fit. As a consequence, since no evidence for a further reduction in symmetry was recorded, the space group $R-3m$ was used in the refinement of both treated and untreated NWP samples.

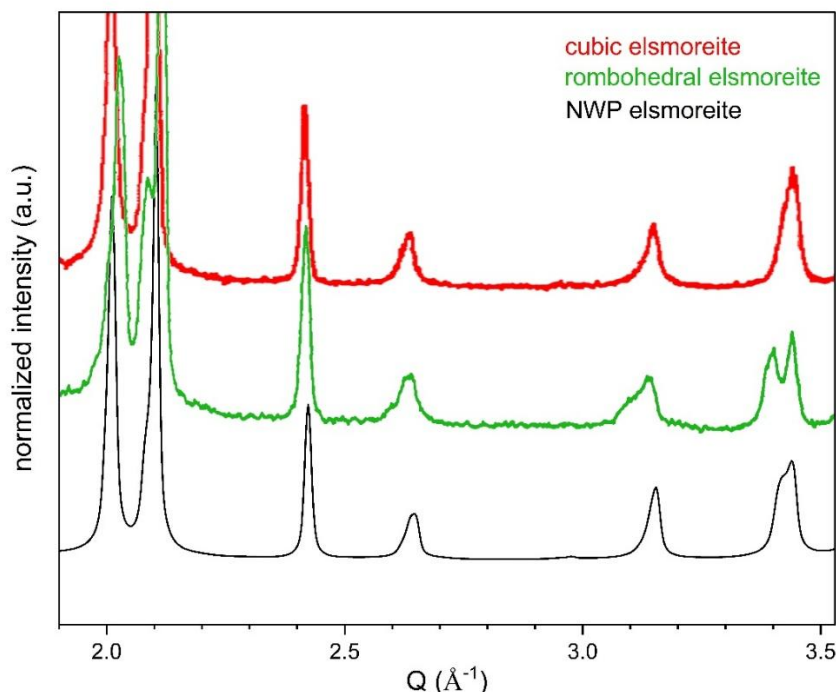


Figure 4. Comparison between the powder diffraction patterns of NWP elsmoreite (black) and the cubic (red) and rhomboherdally distorted (green) elsmoreites reported by Reis et al. (1992).

The rhombohedral distortion leads to the splitting of A, B and X site in A1 and A2; B1 and B2; X1 and X2 sites, respectively. The latter sites were then used for the refinement of the untreated NWP, and for the Pb- and Zn-treated samples.

The XRD patterns of the Tl-treated samples showed a broad hump (Fig. 6 and 7), which has been attributed to the occurrence of an amorphous material, probably formed during the ion exchange experiments. The hump was included in the background, which was fitted using a conventional Chebyshev profile function.

In the Tl-treated samples, after the inspection of the ΔF -map, a clear residual near Y was found, suggesting the occurrence of some positional disorder around this site. After the addition of a satellite site, Y' ($6c$), the fit resulted improved. Small electron density residuals were also observed in all the samples at about $1 \text{ \AA}$ from A1. The addition of a further site near A1 did not produce any improvement in the fit. So, in order to limit the number of variables of the refinement, the latter site was not considered in the XRD data analysis. Therefore, for the refinement of the Tl-treated samples, four tunnel sites were employed: A1, A2, Y and Y'.

The refinement of the framework sites occupancies yielded values of about 1 for all the samples, thus suggesting that the framework sites are totally filled. To reduce the number of variables, their occupancies were not refined, but considered = 1 in all the final refinements.

The software Topas (Coelho, 2018) was used for the Rietveld refinements; scattering curves for neutral atoms, taken from the international Tables for Crystallography (Wilson, 1992), were used as follow: B = W and X = O for all the samples; A1, A2 and Y = Na vs. □ for the untreated NWP; A1, A2, Y, Y' = Tl vs. □ for the Tl-treated samples; A1, A2 and Y = Pb vs. □ for the Pb-treated samples; A1, A2 and Y = Zn vs. □ for the Zn-treated samples.

The Rietveld refinements results are summarized in Tables from 2 to 7; the XRD profiles are shown in Figures from 5 to 11.

Table 2. Rietveld refinement results: unit cell parameters, volume, volume percentage difference between treated and untreated samples, and R-factor (R_{wp}).

	$a(\text{Å})$	$c(\text{Å})$	$V(\text{Å}^3)$	$\Delta V(\%)$	$R_{wp}(\%)$
NWP	7.3065(3)	18.0860(11)	836.16(8)	-	9.81
NWP-Tl-1M	7.2868(4)	18.0973(17)	832.17(13)	-0.48	6.98
NWP-Tl-0.1M	7.2845(6)	18.0971(19)	831.66(15)	-0.54	8.93
NWP-Pb-1M	7.3048(3)	18.0945(11)	836.16(9)	0.00	8.51
NWP-Pb-0.1M	7.3040(3)	18.1018(10)	836.33(8)	0.02	8.23
NWP-Zn-1M	7.3014(3)	18.0843(10)	834.92(8)	-0.14	8.55
NWP-Zn-0.1M	7.3033(3)	18.0853(10)	835.40(8)	-0.09	8.23

$R_{wp} = \left[\sum_i w_i (y_{C,i} - y_{O,i})^2 / \sum_i w_i (y_{O,i})^2 \right]^{\frac{1}{2}}$ (Young, 1993); $\Delta V(\%) = [(V_t - V_0)/V_0] \cdot 100$, with V_t = unit cell volume after the ion exchange experiment, V_0 = unit cell volume of the untreated NWP.

Table 3. Wyckoff positions, occupancy (Occ.), coordinates (x, y, z) and isotropic thermal parameters (B_{iso}) for the untreated NWP elsmoreite.

Site	Wyckoff position	Occ.	x	y	z	$B_{iso}(\text{Å}^2)$
A1	3b	0.48(12) [†]	0	0	0.5	1(4)
A2	9e	0.40(4) [†]	0.5	0	0	1(2)
Y	6c	0.95(5) [†]	0	0	0.645(2)	5(1)
B1	3a	1 [†]	0	0	0	2.42(4)
B2	9d	1 [†]	0.5	0	0.5	2.42(4)
X1	18h	1 [†]	0.790(3)	0.210(3)	0.269(2)	1.7(4)
X2	18h	1 [†]	0.545(3)	0.455(3)	0.132(1)	1.7(4)

[†] Not refined. [‡] Refined: Na vs. □.

Table 4. Wyckoff positions, occupancy (Occ.), coordinates (x, y, z) and isotropic thermal parameters (B_{iso}) for the Tl-treated NWP elsmoreite samples.

Sample	Site	Wyckoff position	Occ.	x	y	z	B_{iso} ($\text{\AA}^2$)
NWP-Tl-1M	A1	$3b$	$0^\dagger$	0	0	0.5	1.0(7)
	A2	$9e$	$0.04(1)^\dagger$	0.5	0	0	1.4(1)
	Y	$6c$	$0.52(2)^\dagger$	0	0	0.641(1)	5.0(2)
	Y'	$6c$	$0.37(2)^\dagger$	0	0	0.404(2)	5.0(2)
	B1	$3a$	$1^\dagger$	0	0	0	3.35(7)
	B2	$9d$	$1^\dagger$	0.5	0	0.5	3.35(7)
	X1	$18h$	$1^\dagger$	0.789(4)	-0.789(4)	0.268(2)	1.9(5)
	X2	$18h$	$1^\dagger$	0.541(4)	-0.541(4)	0.135(2)	1.9(5)
NWP-Tl-0.1M	A1	$3b$	$0.07(3)^\dagger$	0	0	0.5	1(3)
	A2	$9e$	$0^\dagger$	0.5	0	0	1(3)
	Y	$6c$	$0.69(2)^\dagger$	0	0	0.641(1)	5.0(5)
	Y'	$6c$	$0.23(2)^\dagger$	0	0	0.578(3)	5.0(5)
	B1	$3a$	$1^\dagger$	0	0	0	2.8(1)
	B2	$9d$	$1^\dagger$	0.5	0	0.5	2.8(1)
	X1	$18h$	$1^\dagger$	0.795(9)	-0.795(9)	0.273(5)	2.8(8)
	X2	$18h$	$1^\dagger$	0.524(8)	-0.524(8)	0.156(5)	2.8(8)

† Not refined. ‡ Refined: Tl vs. □.

Table 5. Wyckoff positions, occupancy (Occ.), coordinates (x, y, z) and isotropic thermal parameters (B_{iso}) for the Pb-treated NWP elsmoreite samples.

Sample	Site	Wyckoff position	Occ.	x	y	z	B_{iso} ($\text{\AA}^2$)
NWP-Pb-1M	A1	$3b$	$0.06(1)^\dagger$	0	0	0.5	1(3)
	A2	$9e$	$0.10(1)^\dagger$	0.5	0	0	3.5(1)
	Y	$6c$	$0.11(1)^\dagger$	0	0	0.639(3)	5.0(1)
	B1	$3a$	$1^\dagger$	0	0	0	2.55(5)
	B2	$9d$	$1^\dagger$	0.5	0	0.5	2.55(5)
	X1	$18h$	$1^\dagger$	0.790(3)	-0.790(3)	0.269(2)	1.9(4)
	X2	$18h$	$1^\dagger$	0.544(3)	-0.544(3)	0.132(2)	1.9(4)
NWP-Pb-0.1M	A1	$3b$	$0.09(1)^\dagger$	0	0	0.5	1.0(2)
	A2	$9e$	$0.10(1)^\dagger$	0.5	0	0	5.0(1)
	Y	$6c$	$0.13(1)^\dagger$	0	0	0.650(1)	5.0(1)
	B1	$3a$	$1^\dagger$	0	0	0	2.61(4)
	B2	$9d$	$1^\dagger$	0.5	0	0.5	2.61(4)
	X1	$18h$	$1^\dagger$	0.793(2)	-0.793(2)	0.269(1)	2.0(4)
	X2	$18h$	$1^\dagger$	0.541(2)	-0.541(2)	0.126(1)	2.0(4)

† Not refined. ‡ Refined: Pb vs. □.

Table 6. Wyckoff positions, occupancy (Occ.), coordinates (x, y, z) and isotropic thermal parameters (B_{iso}) for the Zn-treated NWP elsmoreite samples.

Sample	Site	Wyckoff position	Occ.	x	y	z	B_{iso} ($\text{\AA}^2$)
NWP-Zn-1M	A1	3b	0.20(3) [†]	0	0	0.5	1(2)
	A2	9e	0.18(1) [†]	0.5	0	0	4.3(2)
	Y	6c	0.38(1) [†]	0	0	0.649(1)	5.0(1)
	B1	3a	1 [†]	0	0	0	2.57(4)
	B2	9d	1 [†]	0.5	0	0.5	2.57(4)
	X1	18h	1 [†]	0.793(2)	-0.793(2)	0.269(1)	1.9(4)
	X2	18h	1 [†]	0.542(2)	-0.542(2)	0.125(1)	1.9(4)
NWP-Zn-0.1M	A1	3b	0.15(4) [†]	0	0	0.5	1(4)
	A2	9e	0.14(1) [†]	0.5	0	0	1.0(1)
	Y	6c	0.33(1) [†]	0	0	0.640(2)	5.0(1)
	B1	3a	1 [†]	0	0	0	2.59(4)
	B2	9d	1 [†]	0.5	0	0.5	2.59(4)
	X1	18h	1 [†]	0.791(3)	-0.791(3)	0.269(1)	1.9(3)
	X2	18h	1 [†]	0.541(3)	-0.541(3)	0.135(1)	1.9(3)

† Not refined. ‡ Refined: Zn vs. □.

Table 7. Selected bond distances (reported in $\text{\AA}$), and Bond angle variance (σ^2) for the BO_6 octahedra

BO ₆ octahedra	B1 octahedron		B2 octahedron		
	B1-X1 (x6)	σ ² (B1X ₆)	B2-X1 (x2)	B2-X2 (x4)	σ ² (B2X ₆)
NWP	1.95(3)	4.59	1.93(3)	1.99(2)	42.76
NWP-Tl-1M	1.94(4)	9.75	1.92(3)	1.98(3)	19.93
NWP-Tl-0.1M	1.95(9)	6.74	1.96(9)	1.99(5)	79.49
NWP-Pb-1M	1.95(3)	5.00	1.93(3)	1.99(2)	30.87
NWP-Pb-0.1M	1.98(3)	1.95	1.92(3)	2.04(1)	82.94
NWP-Zn-1M	1.98(3)	1.40	1.92(3)	2.04(1)	94.47
NWP-Zn-0.1M	1.95(3)	2.67	1.93(3)	1.99(2)	24.24

Tunnel sites	A1-X2 (x6)	A2-X2 (x2)	A2-X1 (x4)	Y-A1	Y-A2	Y-Y'
NWP	2.75(3)	2.45(3)	2.69(3)	2.62(4)	2.15(1)	-
NWP-Tl-1M	-	2.49(4)	2.70(3)	-	2.16(1)	0.80(4)
NWP-Tl-0.1M	2.43(8)	-	-	2.53(3)	-	1.14(6)
NWP-Pb-1M	2.73(3)	2.48(3)	2.69(3)	2.52(6)	2.17(1)	-
NWP-Pb-0.1M	2.73(2)	2.34(3)	2.67(2)	2.71(3)	2.13(1)	-
NWP-Zn-1M	2.74(2)	2.32(3)	2.67(2)	2.70(3)	2.13(1)	-
NWP-Zn-0.1M	2.69(3)	2.49(3)	2.68(3)	2.53(4)	2.16(1)	-

σ^2 = Bond angle variance calculated according to the formula proposed by Robinson et al. (1971).

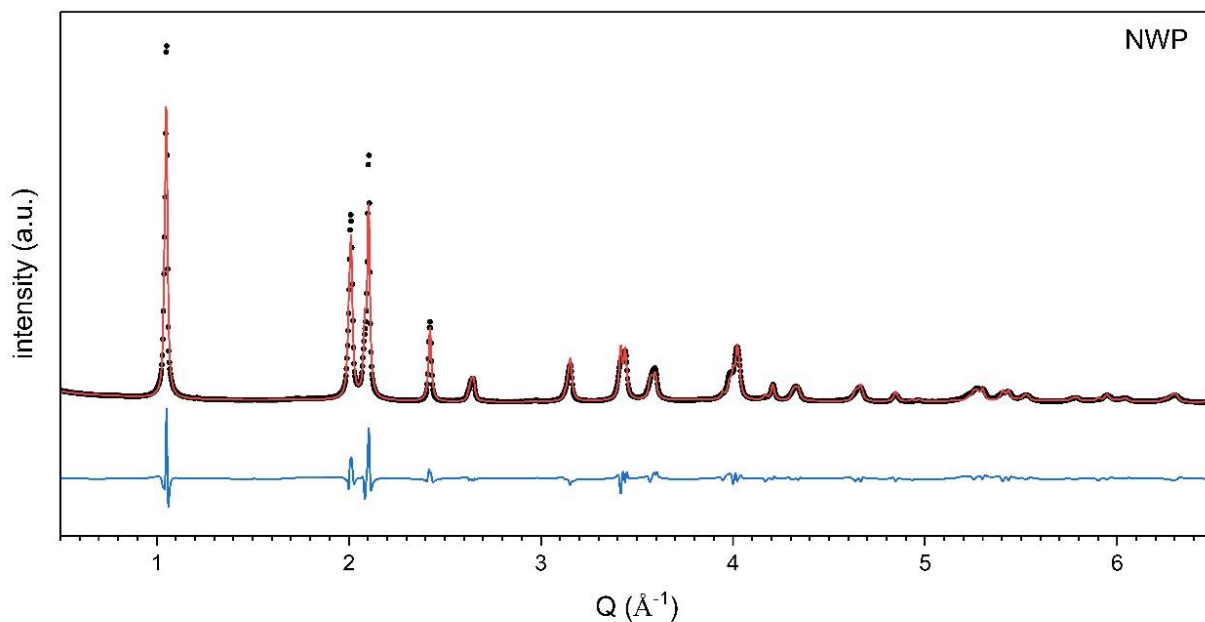


Figure 5. XRD profile of the untreated NWP elsmoreite: measured (black points), calculated (red lines) and the difference (blue lines).

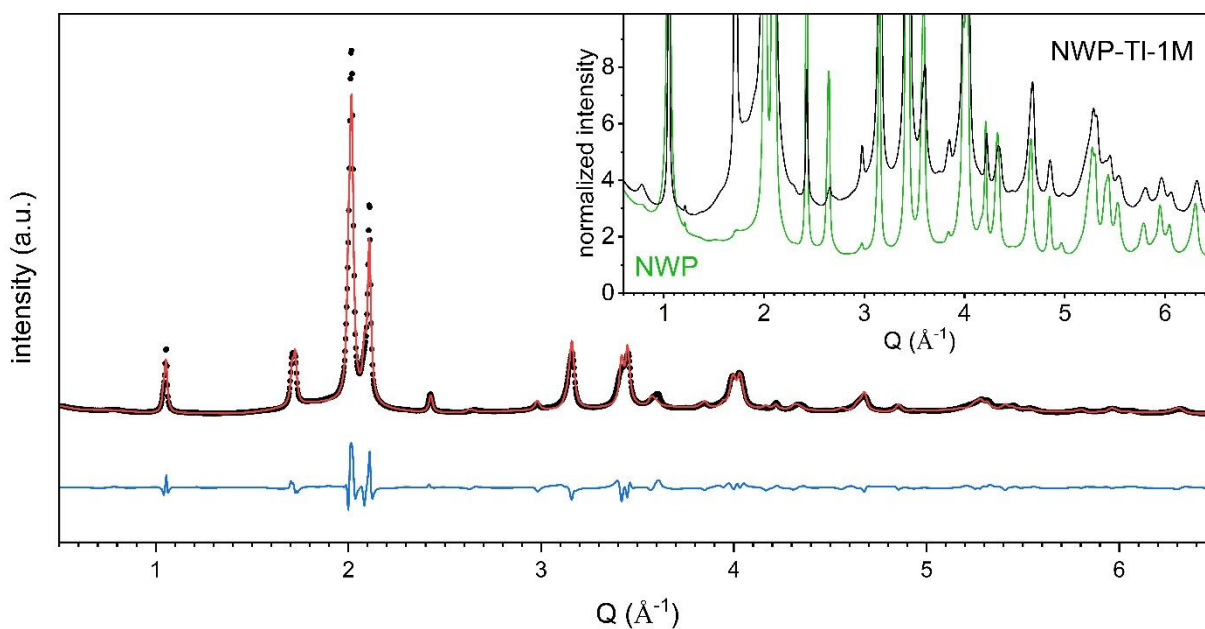


Figure 6. XRD profile of NWP-TI-1M: measured (black points), calculated (red lines) and the difference (blue lines). An enlargement of the XRD patterns for the present sample (in black) and the untreated NWP (in green) is shown in the top right inset to emphasizes the amorphous hump.

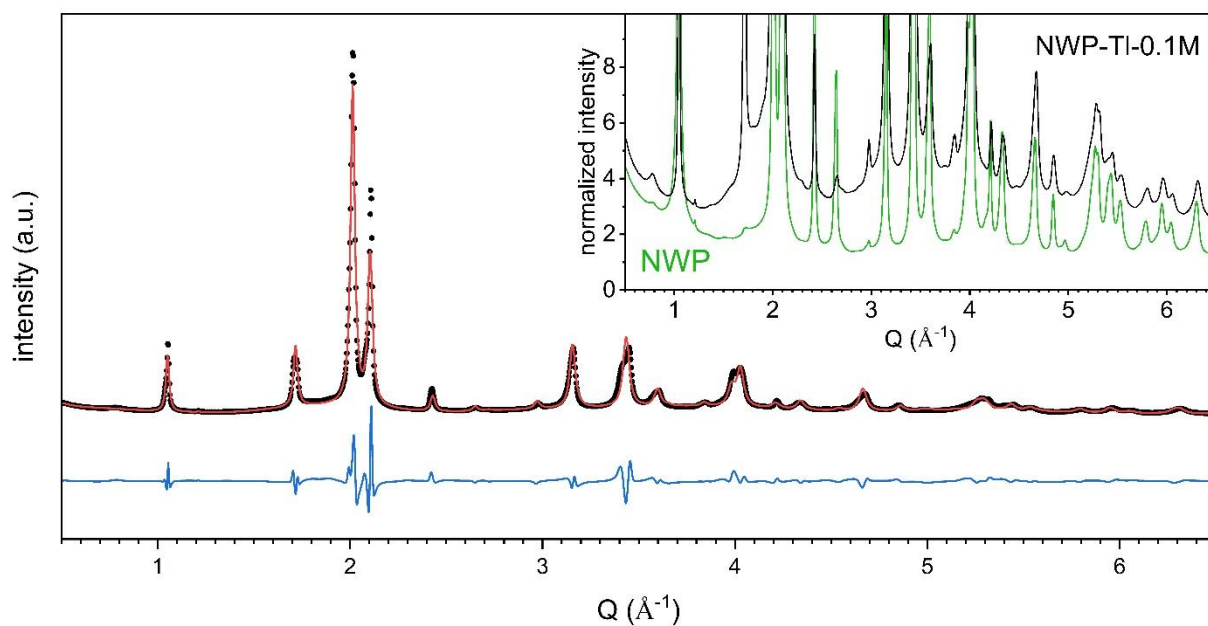


Figure 7. XRD profile of NWP-Tl-0.1M: measured (black points), calculated (red lines) and the difference (blue lines). An enlargement of the XRD patterns for the present sample (in black) and the untreated NWP (in green) is shown in the top right inset to emphasize the amorphous hump.

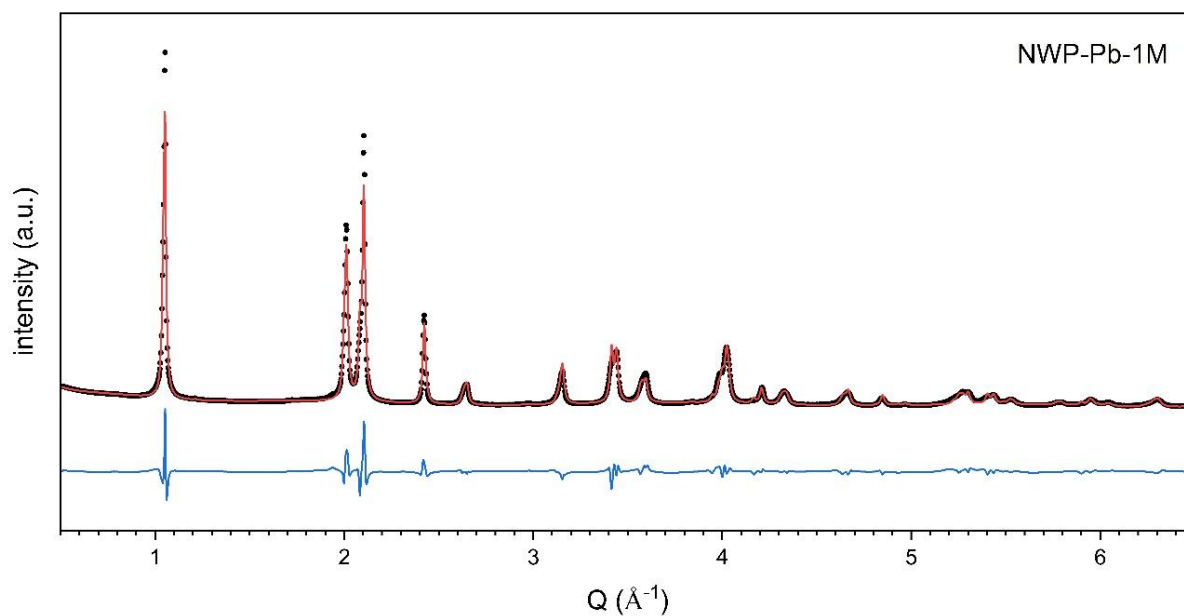


Figure 8. XRD profile of NWP-Pb-1M: measured (black points), calculated (red lines) and the difference (blue lines).

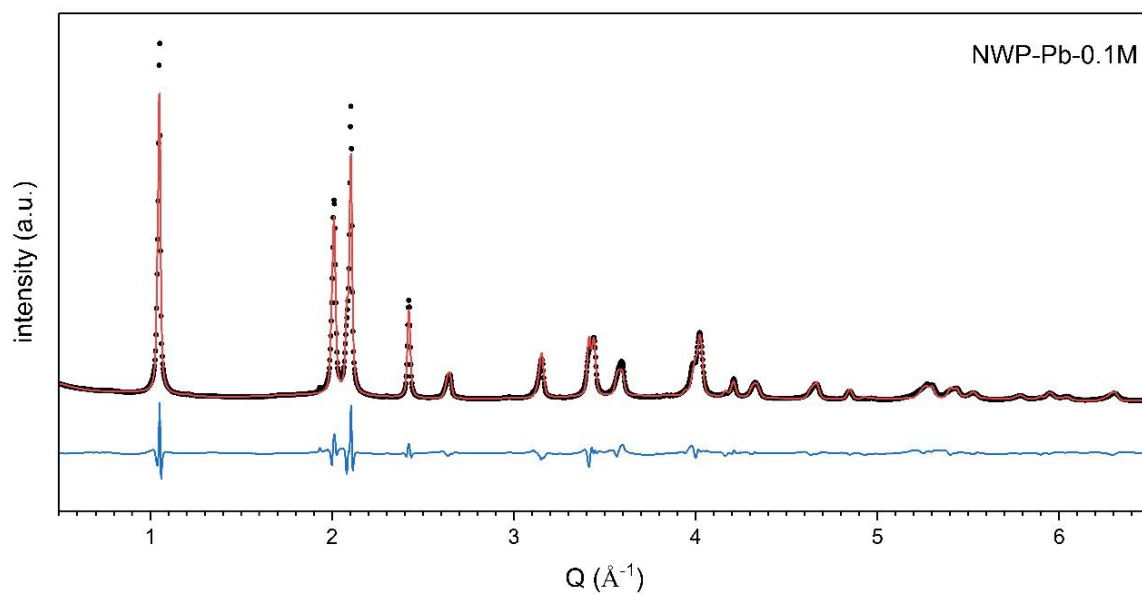


Figure 9. XRD profile of NWP-Pb-0.1M: measured (black points), calculated (red lines) and the difference (blue lines).

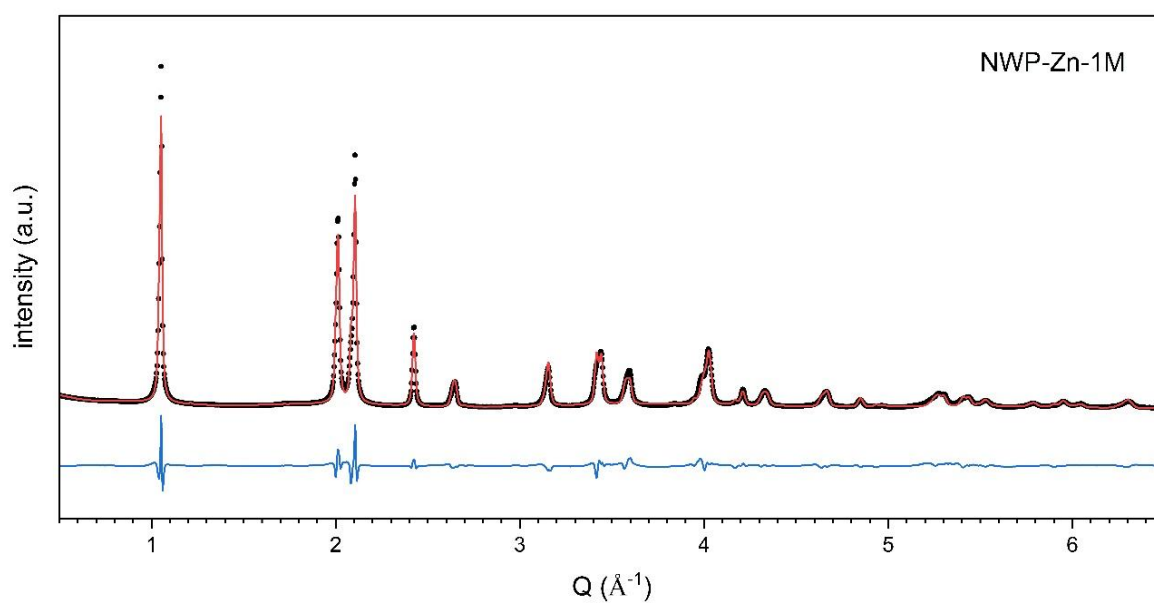


Figure 10. XRD profile of NWP-Zn-1M: measured (black points), calculated (red lines) and the difference (blue lines).

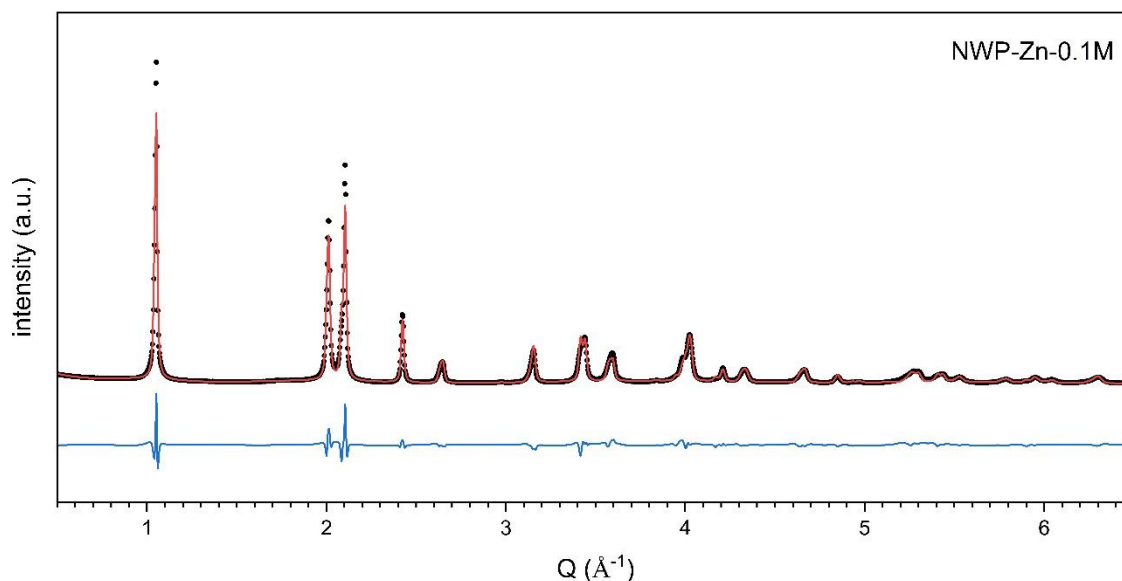


Figure 11. XRD profile of NWP-Zn-0.1M: measured (black points), calculated (red lines) and the difference (blue lines).

6.6. X-ray Absorption Spectroscopy Analysis

X-ray absorption spectroscopy (XAS) analysis was performed on the Tl- and Pb-treated samples, at the L_3 -edge of thallium and lead, respectively.

The X-ray absorption near edge structure (XANES) spectra of Tl-treated samples were compared with those of thallium (I) chloride [TlCl] dissolved in an aqueous solution (Scheckel et al., 2004), thallium (I) sulphate [Tl₂SO₄] and thallium (III) oxide [Tl₂O₃] (Biagioni et al., 2020) (Fig. 12).

The Tl-samples XANES feature an adsorption edge at about 12666 eV, which is perfectly aligned with that of Tl(I) in aqueous thallium (I) chloride and thallium (I) sulphate, while the edge of Tl(III) in Tl₂O₃ is found at higher energies (~12669 eV). In addition, the XANES derivatives emphasized the similarity of the near edge structure of Tl in the treated samples and monovalent thallium compounds, which consist of sharp peaks sometimes showing a slightly splitted top, while that of Tl₂O₃ is represented by three different broad bands (Fig 12b).

The XANES profiles of Pb-treated samples were compared to lead (IV) oxide [PbO₂], lead (II) oxide [PbO] and metallic lead (Fig 13). The absorption edge of the Pb-treated samples was affected by a high level of noise (Fig. 13b), which did not allow a straightforward comparison with the references. Nonetheless some consideration were made on the rising absorption features and the position of the maximum absorption intensity.

Despite the noise, the XANES derivatives of the samples do not seem to show any particular feature. According to Bargar et al. (1997), featureless XANES spectra are typical of ionic-bounded Pb²⁺. As a result, the lead present in the Pb-treated materials is suggested to be divalent.

In addition, the maximum absorption intensity of Pb-treated samples is at approximately 13054 eV, in good agreement with that of divalent Pb in PbO reference, which occurs at the same energy, while the peak of Pb(IV) in PbO₂ is shifted to higher energies (~13058 eV). As a result of the latter considerations, all the Pb contained in the elsmoreite samples was considered divalent.

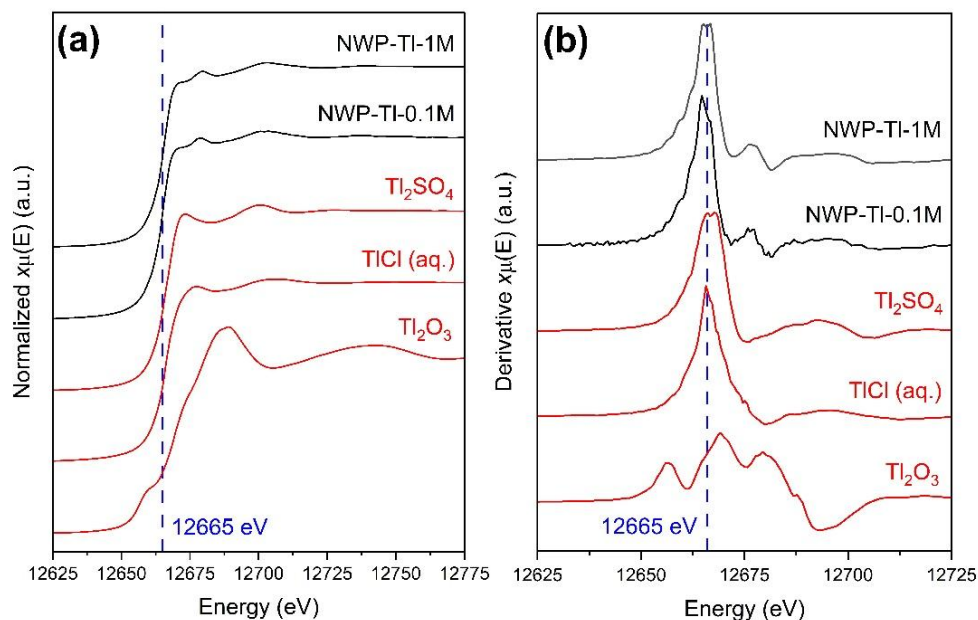


Figure 12. XANES spectra (a) and their derivative (b) of the elsmoreite samples treated with Tl (in black) and thallium references (in red). The blue dotted line indicates the adsorption edge of monovalent thallium.

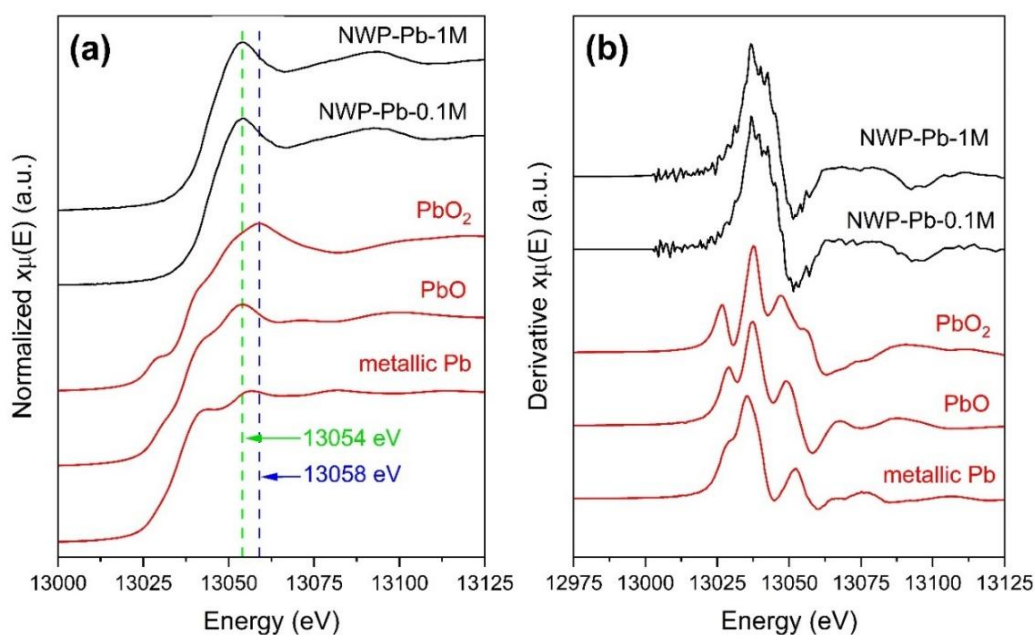


Figure 13. XANES spectra (a) and their derivative (b) of the elsmoreite samples treated with Pb (in black) and lead references (in red). The green dotted line at about 13054 eV corresponds to the maximum absorption intensity of Pb(II) while the blue dotted line at about 13058 eV that of Pb(IV).

XAS analysis at the tungsten L_3 -edge was also performed on both 1M-treated and untreated samples to assess the oxidation state of the framework cation before and after the ion exchange experiments. The edge shape of the tungsten XANES and the position of their maximum absorption intensity are coherent with that of the W(VI) in the WO_3 reference for all the samples. Therefore, the tungsten in NWP results hexavalent: and so it stays after the ion exchange reactions. The tungsten absorption profile (Fig. 14a) of all the samples shows an intense white line, which is typical of the W L_3 -edge (Yamazoe et al., 2008). According to the latter authors, the splitting of the white line, showed by all the samples, can be attributed to the splitting of the 5d orbitals by the ligand field due to a distortion of the WO_6 octahedra. The energy gap between the peaks (which can be better seen in the derivatives of the profiles reported in Fig. 14b) is indeed correlated with splitting of the d orbitals caused by the distortion of the octahedral symmetry. Therefore, based on this parameter, the observed splitting of the white line strongly suggests that the WO_6 octahedra in the NWP samples have a rather undistorted octahedral symmetry.

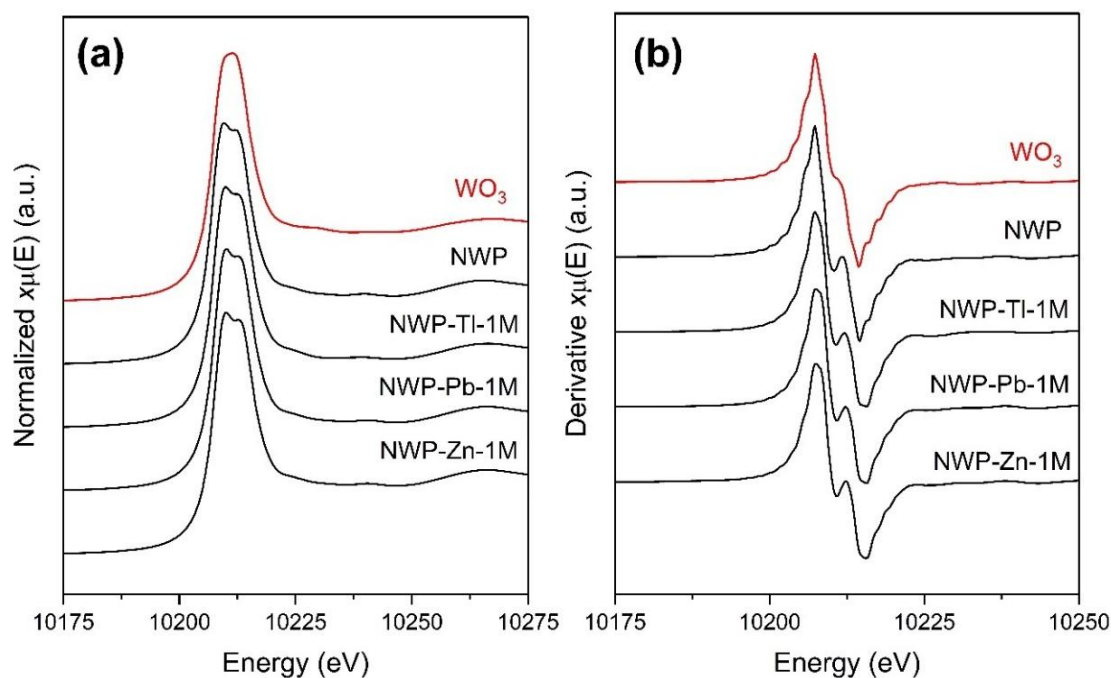


Figure 14. XANES spectra (a) and their derivatives (b) of tungsten L_3 -edge. WO_3 is used as reference in red, the samples in black.

Extended X-ray absorption fine structure (EXAFS) analysis was carried out to evaluate the coordination environment of Tl and Pb in the NWP elsmoreite structure.

The NWP-Tl-1M EXAFS spectrum was affected by a severe signal dampening after $4 \text{ \AA}^{-1}$, which in turn was probably responsible, along with the substantial disorder of the thallium atoms, for the loss of structured signal after $7.5\text{--}8 \text{ \AA}^{-1}$. As a consequence, the corresponding Fourier-transform was characterized by a very broad band in the range $1\text{--}4 \text{ \AA}$ (Fig. 15b).

Despite the weakness of the signal, the modelling of the first two coordination shells was still possible. The structural model utilized to calculate the theoretical paths was that of the untreated NWP sample obtained from the Rietveld refinements, suitably modified by removing the Y site and considering the Tl in Y' as central scatterer atom. Multiple sets of single scattering paths (Tl-O and Tl-Ta) with different interatomic distances (R) were calculated using the software FEFF (Ankudinov et al., 1998) and used in the fitting process. Different combinations of interatomic distances and coordination numbers (N) were tested to model the first shell considering a thallium configuration similar to that found in Y'. The initial guessed R and N values employed in the fit were chosen to comply with the bond valence sum of Tl⁺.

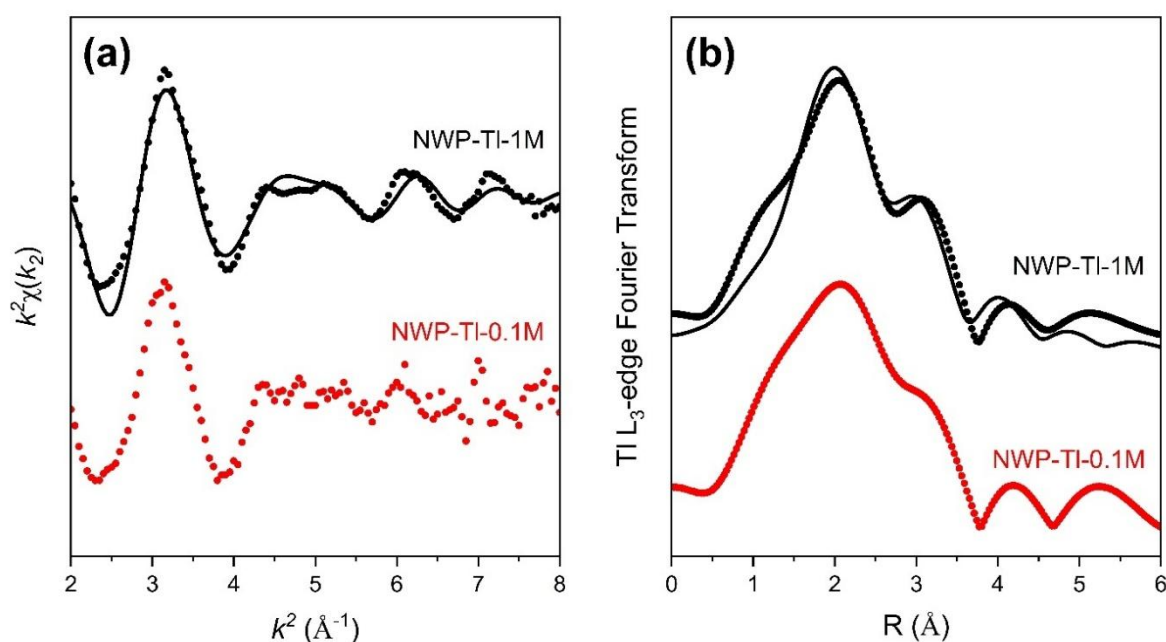


Figure 15. Tl L₃-edge EXAFS (a) and Fourier transform (b) of the two Tl-treated samples. Experimental data are displayed by symbols and fit by solid lines. NWP-Tl-1M is reported in black, NWP-Tl-0.1M in red. Since the fit was not possible, for the NWP-Tl-0.1M sample only the data are reported.

The best fit was achieved employing two Tl-O paths, both with N = 3 and interatomic distances of about 2.7 and 2.9 Å. Following the scheme of the first shell, two Tl-W set with N = 3 and interatomic distances of about 3.8 and 4.0 Å were employed for the second shell. The best fit, whose results are reported in (Table 8), shows high values of σ^2 factors and high errors on R and S_0^2 , which can be however justified considering the strong disordering phenomena affecting Tl.

Further tests considering Tl around the Y position did not produce any result.

Signal dampening and the high level of noise in the NWP-Tl-0.1M (Fig. 15) did not allow a quantitative analysis of the EXAFS signal. Nonetheless, the similarity between the two spectra suggests that the coordination environment of Tl in NWP-Tl-0.1M may be similar to that of NWP-Tl-0.1M.

Table 8. Tl L₃-edge EXAFS analysis results for the NWP Tl-treated samples.

NWP-Tl-1M				
S ₀ ²	1.0(4)	R-factor	0.04	
E ₀	1.2(2.4)	BVS	1.13	
Path	Tl-O	Tl-O	Tl-W	Tl-W
R (Å)	2.66(4)	2.91(4)	3.83(7)	4.03(7)
N	3	3	3	3
σ ² (Å ²)	0.02(2)	0.02(2)	0.01(1)	0.01(1)
(average first shell Tl-O distance = 2.79 Å)				
S ₀ ² = amplitude reduction factor; E ₀ = threshold energy; R = interatomic distance; N = coordination number; σ ² = Debye-Waller factor (Å ²). R-factor = (Σ _i y _{obs} - y _{calc})/(Σ _i y _{obs}) (Roy and Gurman, 1999). BVS = bond valence sum for the first shell: V _i = Σ _j S _{ij} with S _{ij} = exp($\frac{R_0 - R_{ij}}{b}$); R _{ij} = distance between i and j atoms; R ₀ and b values taken from Brese and O'Keeffe (1991).				

The EXAFS spectra of Pb-treated samples show a loss of structured signal after 7.5-8 Å⁻¹, which was attributed to disordering phenomena in the tunnel environment involving lead (Fig. 16a).

The theoretical paths were calculated using the structural model of the untreated NWP obtained from the Rietveld refinements. To model the first shell of Pb, several combinations of Pb-O paths with different N and R were tested. The combinations where selected to match with the coordination environment of the three tunnel sites (also considering possible displacements from the theoretical crystallographic positions) and the BVS expected for Pb²⁺. For both Pb-treated samples, the best, as well as the only acceptable fit was achieved using a single Pb-O-path with R = 2.55-2.6 Å and a coordination number set to 7.

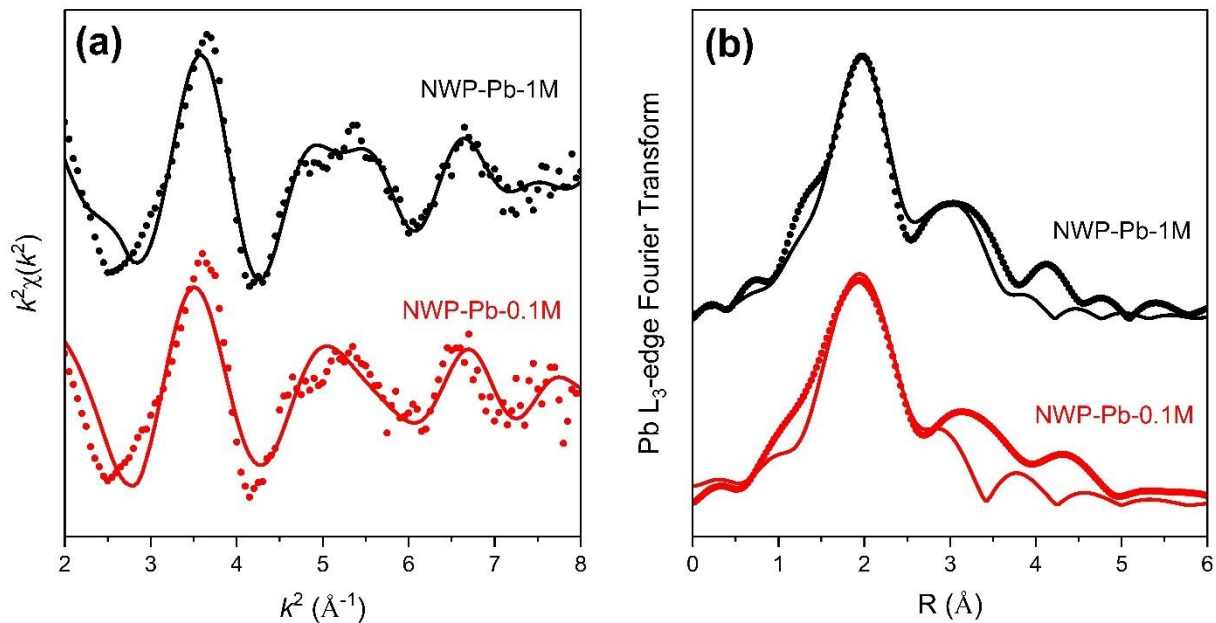


Figure 16. Pb L₃-edge EXAFS (a) and Fourier transform (b) of the two Pb-treated samples.

Experimental data are displayed by symbols and fit by solid lines.

NWP-Pb-1M is reported in black, NWP-Pb-0.1M in red.

For the second shell, a Pb-W path with $R = 3.6\text{-}3.65 \text{ \AA}$ and $N = 6$ was employed. For the NWP-Pb-1M sample, a farther oxygen shell at about $4 \text{ \AA}$ could be modelled with a single Pb-O path with a coordination number of six. The worse data quality of the NWP-Pb-0.1M did not allow the description of the coordination environment of lead after the second shell.

The occurrence of strong disordering phenomena is also responsible for the high values of the amplitude S_0^2 , σ^2 and the errors in the interatomic distances (Table 9).

Table 9. Pb L_3 -edge EXAFS analysis results for the NWP Pb-treated samples.

NWP-Pb-1M			
S_0^2	0.9(4)	R-factor	0.055
E_0	1.3(3.1)	BVS	2.11
Path	Pb-O	Pb-W	Pb-O
R ($\text{\AA}$)	2.55(4)	3.60(17)	4.00(7)
N	7	6	6
σ^2 ($\text{\AA}^2$)	0.018(8)	0.03(2)	0.001(1)
NWP-Pb-0.1M			
S_0^2	0.9(6)	R-factor	0.154
E_0	3.3(4.2)	BVS	1.95
Path	Pb-O	Pb-W	
R ($\text{\AA}$)	2.59(7)	3.66(13)	
N	7	6	
σ^2 ($\text{\AA}^2$)	0.02(1)	0.02(2)	
S_0^2 = amplitude reduction factor; E_0 = threshold energy; R = interatomic distance; N = coordination number; σ^2 = Debye-Waller factor ($\text{\AA}^2$). R-factor = $(\sum_i y_{obs} - y_{calc}) / (\sum_i y_{obs})$ (Roy and Gurman, 1999). BVS = bond valence sum for the first shell: $V_i = \sum_j S_{ij}$ with $S_{ij} = \exp\left(\frac{R_0 - R_{ij}}{b}\right)$; R_{ij} = distance between i and j atoms; R_0 and b values taken from Krivovichev (2012).			

6.7. Discussion

In this section the discussion about the incorporation mechanisms of the three heavy metals in the elsmoreite structure is reported. First the crystal structure and chemistry of the untreated NWP elsmoreite is introduced (6.7.1). Section 6.7.2 is dedicated to the discussion of the structural effects of Tl incorporation, while section 6.7.3 focuses on those produced by Pb and Zn. A further paragraph (6.7.5) is dedicated to the final remarks.

6.7.1. Crystal Structure and Chemistry of the untreated NWP Elsmoreite

The NWP elsmoreite is a Na-bearing rhombohedral pyrochlore (space group $R\bar{3}m$). The Na:W ratio measured by PIXE is about 0.35; the normalization on ΣB cations = 2 yielded the sodium content, which is 0.7(1) atoms per formula unit.

The framework of NWP consists of units of $B1X1_6$ and $B2(X1_2X2_4)$ octahedra which alternate along the c axis by sharing X1 corners. Both B1 and B2 are fully occupied by tungsten; X1 and X2 by

oxygen. W in B1 is coordinated by six O atoms, with interatomic distances of 1.95(3) Å, while B2 by four O (in X2) at 1.93(3) Å and two O (in X1) at 1.99(2) Å (Table 7). The latter bond lengths are slightly longer but still consistent with those reported by Mills et al. (2016) for two natural hydrokenoelsmoreite samples, whose W-O distances were in the range of 1.92-1.94 Å, with an average of 1.93 Å.

The electron density distribution in the tunnel environment has been modelled using three sites: A1 and A2, derived from the splitting of the conventional A site of the cubic pyrochlore, and Y, which does not split after the symmetry reduction but just changes its Wyckoff position (from 8b to 6c) and, slightly, its overall coordination environment. Y is placed at the centre of a large cage of WO₆ octahedra (with Y-O distances ranging from 3.1 to 4.2 Å) formed by the intersection of three tunnels. The A sites are found at the centre of two different hexagonal rings. A1 is surrounded by six X2 oxygen atoms, belonging to as many B₂O₆ octahedra, with six identical A1-O distances of 2.75(3) Å. A2 is instead ringed by two framework oxygens at 2.45(3) Å and additional four at 2.69(3) Å, belonging to B₁O₆ and B₂O₆ octahedra, respectively. A summary of the most significant interatomic distances for NWP can be found in Table 7.

The electron density distribution within the tunnel environment was very complex to model by means of XRD, and quite difficult to decipher. Some assumptions based on crystallochemical considerations were then needed.

The number of electrons refined in Y (~10) (Table 10) and the large volume of its coordination environment suggested that the latter site may be fully occupied by water molecules or hydroxyl groups. The amount of OH⁻ in Y is considered to be such as to balance the positive charges brought by ~0.7 *apfu* of Na measured by PIXE.

The large coordination of A1 is not very suitable for Na⁺, since the six ~2.75 Å distances with the oxygen framework are larger than the usual Na-O distances, which typically range from 2.2 to 2.7 Å (Mills et al., 2016; Gagné and Hawthorne, 2016).

Table 10. Number of electrons measured by XRD and PIXE for the NWP elsmoreite.

Obtained by XRD		Measured by PIXE	
n. e ⁻ (A1)	3(1)	n. e ⁻ (Na)	8(1)
n. e ⁻ (A2)	7(1)		
n. e ⁻ (Y)	10(1)	Δe ⁻	12
Σ e ⁻	20(3)		
Δe ⁻ = difference between the average number of electron measured by XRD and that found by PIXE.			

It is therefore reasonable to assume that A1 is also occupied by water molecules, since 3 electrons were here refined (Table 10), which is comparable to 0.3-0.4 H₂O molecules *pfu*.

The A2-O distances, ranging from 2.4 to 2.7 Å are more appropriate for sodium. Moreover, the number of electrons in A2 corresponds to about 7 electrons, in good agreement with the ~ 8 brought by the ~ 0.7 apfu of Na measured by PIXE. Nonetheless, the latter site is only 2.15(1) Å far from Y, which was stated to be fully occupied by water species. Considering Na in A2, its complete coordination would then be formed by two O atoms at 2.15(1) Å, other two at 2.45(3) Å and four at 2.69(3) Å, thus giving a bond valence sum (BVS) of about 1.38 (Gagné and Hawthorne, 2016). The latter value is evidently too high for a monovalent cation such as Na⁺.

In order to enable Na⁺ to fit in A2, a displacement of the Y occupants from their crystallographic position, thus increasing the A2-Y distance, may be hypothesized. For example, a ~ 0.95 Å shift of the Y occupants along the *c* axis would result in a 0.35 Å increase in the A2-Y bond distances, thus giving back a BVS in perfect agreement with the theoretical value of 1.00. Given the geometry of the tunnel and the relations between the different tunnel sites, the shifting of one Y would allow the simultaneous occupation of three A2 sites by displacing or, more likely, by vacating one A1 site (Fig. 17b). Such a disposition of sites would also justify the low occupancies of the A sites, the sum of which is about 1 apfu, that is half of the theoretically predicted value.

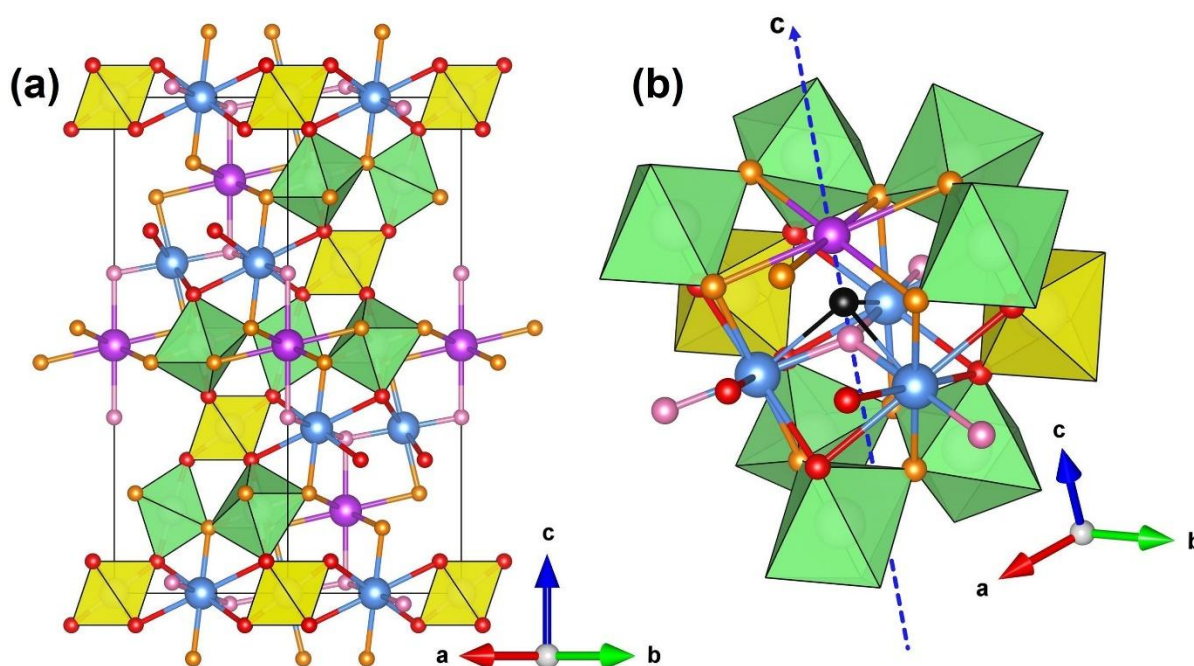
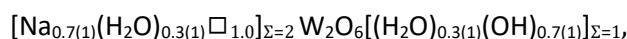


Figure 17. Unit cell of the NWP elsmoreite (a) and detail of the Y cage environment (b). The black sphere in (b) represent the hypothetical site resulting from a ~ 0.95 Å shift of the Y occupants along the *c* axis (highlighted in blue). Colour scheme: B1 octahedron = yellow; B2 octahedron = green; X1 = red; X2 = orange; Y = pink; A1 = purple; A2 = light blue

An evidence supporting this hypothesis could come from the ΔF -map, which showed small electron density residuals at about 1 Å from A1 and 1.5 Å from the Y site (along the [001] direction), thus indicating a more complex distribution between A1 and Y. Nevertheless, the latter

residual was not included in the Rietveld refinement as it did not produce any improvement in the fit.

In conclusion, given the aforementioned reasons, sodium was entirely attributed to the A2 site, while A1 and Y was considered occupied by water species, thus yielding the following formula for the untreated NWP pyrochlore:



6.7.2. Incorporation Mechanisms of Thallium in Elsmoreite

The NWP elsmoreite is able to incorporate considerable amounts of Tl, up to 350-400 mg per gram of sorbent. The normalization of the Tl concentrations on the basis of ΣB cations = 2 yielded a thallium content of 1.0(1) and 0.9(1) *apfu* for NWP-Tl-1M and NWP-Tl-0.1M, respectively. The quantity of Tl incorporated by the two Tl-treated samples is very similar, thus implying that the different concentrations of Tl in the exchanging solutions have only minor effects on the amount of sorbed metal (at least considering high concentrations of Tl).

The incorporation of thallium induced a significant rearrangement of the tunnel environment. In both Tl-treated samples, Y shows a satellite site, which was called Y' (Fig. 18). The latter site is found at ~ 0.8 Å from Y in NWP-Tl-1M and ~ 1 Å in NWP-Tl-0.1M. The strong electron density maxima inside the Y cage (Table 11) clearly indicate that Tl is distributed between Y and Y'. The number of electrons associated with Y and Y' closely match that of thallium obtained by PIXE (Table 11), thus suggesting that the occupancy of the latter sites is close to their maximum capacity ($Y+Y' = 1$ *apfu*).

Table 11. Number of electrons measured by XRD and PIXE for the Tl-treated samples. Values for the untreated NWP are also reported for comparison.

	NWP	NWP-Tl-1M	NWP-Tl-0.1M
Obtained by XRD			
n. e ⁻ (A1)	3(1)	0	3(2)
n. e ⁻ (A2)	7(1)	5(1)	0
n. e ⁻ (Y)	10(1)	52(1)	56(1)
n. e ⁻ (Y')	-	33(1)	17(1)
Σ e ⁻	20(3)	90(3)	76(4)
Measured by PIXE			
n. e ⁻ (Na)	8(1)	2(1)	1(1)
n. e ⁻ (Tl)	-	81(8)	73(8)
Σ e ⁻	8(1)	83(9)	74(9)
$\Delta^\dagger$	15	7	2

† Difference between the number of e⁻ found in the tunnel sites by XRD and the sum of e⁻ brought by the tunnel cations measured by PIXE.

The occurrence of two so close sites suggests that thallium is positionally disordered within the cage, rather than effectively constrained in two specific positions. Moreover, the Y cage is too large to host a Tl⁺ ion just in the Y position, which lies in the geometrical centre of the cage itself. Indeed, the interatomic distances between Y and the framework oxygens, which range from 3 up to 4 Å, are not in agreement with those predicted by the bond valence sum theory. A slight displacement of the Tl⁺ cations from Y towards the cage walls is therefore required to achieve a coordination in line with the BVS theory.

The Y' site is instead closer to the octahedral framework. For example, in NWP-Tl-0.1M, Y' results surrounded by three O atoms at ~2.7 Å and other three at ~2.9 Å (Fig. 18b). Considering a Tl⁺ ion placed in Y', its BVS would be about 1.1, in good agreement with the theoretical values of 1.

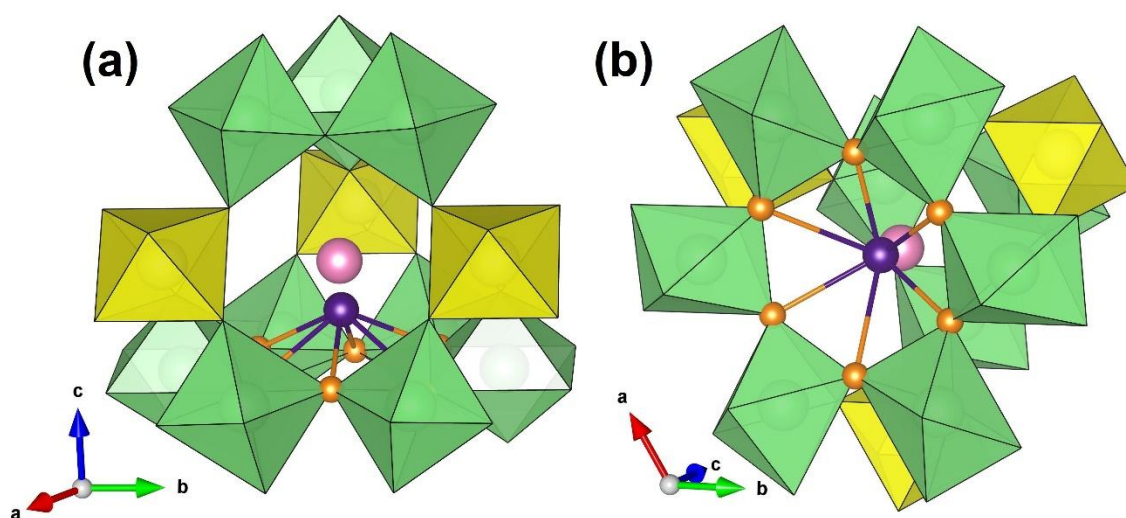


Figure 18. Two different perspective of the Y cage containing the Y (pink) and Y' (violet) sites. In (a) is highlighted the position of Y' in relation to Y; in (b) the coordination of Y' with six framework oxygen atoms.

Colour scheme: B1 octahedra = yellow; B2 octahedra= green; X2 oxygens= orange.

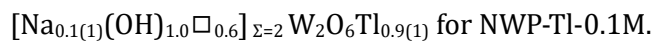
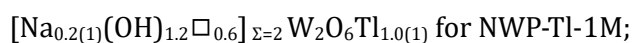
According to EXAFS, Tl shows an asymmetrical environment, with two set of oxygen atoms at 2.66(4) and 2.91(4) Å, both with a coordination number of three. The second shell shows an asymmetry similar to that of the first shell, with two sets of tungsten atoms at 3.83(7) and 4.03(7) Å, both with N = 3 (Table 8). The latter scenario resembles the environment of Y' resulting from the XRD analysis. More generally, it is consistent with an overall displacement of the Tl atoms from the centre of the Y cage (which coincides with the Y site) towards the framework WO₆ octahedra. In summary, the two close sites, Y and Y', described by the XRD model are probably, as highlighted by EXAFS, just a hint of a complex, asymmetrical coordination environment, which is just averaged in two position by the model itself.

The incorporation mechanism of thallium is quite complex. All the water and hydroxyl molecules originally contained in Y have been replaced by thallium. Simultaneously, considerable amounts of sodium have been expelled from the A2 site (based on PIXE, about 0.5-0.6 *apfu* for both

samples). Since the extrusion of Na⁺ alone is not sufficient to balance the electrical charge introduced by approximately 0.9-1 *apfu* of Tl⁺ and the original hydroxyls that ensured the electrical neutrality of the tunnel environment are no longer present in the Y cage, an adequate amount of OH⁻ is needed in the A sites to balance the positive charges brought by thallium and residual sodium cations.

Nonetheless, probably due to the substantial disorder of Tl, the Rietveld refinements did not provide an accurate description of the electron density in A1 and A2. Indeed, during the refinements, the number of electrons of the A sites resulted quite unstable and very sensitive to those of Y and Y'. As a consequence, as it resulted to be the most probable scenario, the charge balancing was formally attributed to OH⁻ ions disordered around the two A sites.

Said all that, the following chemical formulae for the two Tl-treated elsmoreite samples are proposed:



After the ion exchange experiments with thallium solutions, a decrease in the unit cell volume of about 0.5% was observed in both Tl-treated samples (Table 2).

The latter variation may be attributed to a contraction of the tunnel width along the *a* direction, probably due to the loss of Na⁺ from the A2 site. Indeed, the B1-A2 distances, along the *a* direction, slightly decrease from 3.6532(2) to 3.6434(3) and 3.6422(5) Å after the treatment with the 1M and 0.1M thallium solution, respectively. The incorporation of Tl in the Y cage results in a slight enlargement of the cage itself. For example, after the treatment with the 1M thallium solution, the average Y-W distance increases from 4.30 to 4.31 Å. This variation affects the length of the *c* axis, which increases from 18.086(1) to 18.097(2) Å, but is not enough to compensate for the decrease in the *a* axis. As a consequence, the volume of the unit cell decreased after the Tl incorporation.

The XRD patterns of both NWP-Tl-1M and NWP-Tl-0.1M show a broad hump which was attributed to an amorphous phase (Figs. 6 and 7). Despite that, SEM investigations did not show any relevant change in the morphology of the elsmoreite microcrystals, nor the onset of new, morphologically distinct phases after the ion exchange experiments (Fig. 2). The shape and intensity of the hump is similar for the two Tl-treated samples, thus indicating that the differences in the metal concentration of the exchanging solutions did not affect significantly its formation.

If the amorphous phase had incorporated significant amounts of thallium, the concentrations of this metal obtained from PIXE should be higher than those derived from the refinement of the tunnel site occupancies (in particular the Y and Y' sites). Nonetheless, the results of PIXE and XRD are quite in good agreement, thus suggesting that (1) any eventual metal incorporation into the amorphous phase did not exceed the experimental uncertainties, or (2) the amounts of Tl incorporated by the amorphous phase are comparable with those of the crystalline pyrochlore. Although the presence of the amorphous phase seems not to have significantly interfered with the

structural analyses, further studies on the topic are considered essential to obtain a complete description of the system under investigation.

6.7.3. Incorporation Mechanisms of Lead and Zinc in Elsmoreite

The NWP elsmoreite was able to incorporate only small quantities of Pb, in the range of 20-35 mg/g, and almost no Zn. The normalization of the heavy metal concentrations measured by PIXE on the basis of ΣB cations = 2 yielded a Pb content of 0.08(1) and 0.06(1) *apfu* for NWP-Pb-1M and NWP-Pb-0.1M, respectively, and a Zn content of just about 0.014 and 0.012 *apfu* for NWP-Zn-1M and NWP-Zn-0.1M, respectively. The low affinity of the elsmoreite structure for these ions can be explained considering the high electrical charge of W^{6+} in the framework, which could constitute a major barrier to the entry of divalent cations like Pb^{2+} and Zn^{2+} into the tunnels.

Due to the low amounts of incorporated Pb^{2+} and Zn^{2+} , no noticeable variations in the average structure of elsmoreite were observed by XRD after the ion exchange experiments (Table 2). Pb and Zn were attributed to the A sites (A1, A2 or both) due to their small ionic radii (Ercit et al., 1986; Ercit et al., 1993), while Y is considered filled with water molecules and hydroxyl ions. The amount of H_2O in the A sites is considered virtually unchanged from the untreated NWP.

Table 12. Number of electrons measured by XRD and PIXE for the Pb- and Zn-treated samples. Values for the untreated NWP are also reported for comparison.

	NWP	NWP-Pb-1M	NWP-Pb-0.1M	NWP-Zn-1M	NWP-Zn-0.1M
Obtained by XRD					
n. e ⁻ (A1)	3(1)	3(6)	4(1)	3(1)	2(1)
n. e ⁻ (A2)	7(1)	12(1)	12(1)	8(1)	6(1)
n. e ⁻ (Y)	10(1)	9(1)	11(1)	11(1)	10(1)
Σe^-	20(3)	24(8)	27(3)	22(3)	18(3)
Measured by PIXE					
n. e ⁻ (Na)	8(1)	7(1)	6(1)	8(1)	8(1)
n. e ⁻ (HM ⁺)	-	7(1)	5(1)	<1	<1
Σe^-	8(1)	14(2)	11(2)	8(1)	8(1)
$\Delta^\dagger$	12	10	16	14	10

+ HM = heavy metal (Pb or Zn).

† Difference between the number of e⁻ found in the tunnel sites by XRD and the sum of e⁻ brought by the tunnel cations measured by PIXE.

The coordination of Pb was investigated through EXAFS analysis. The fits show high errors on the amplitude reduction factors (S_0^2), and high Debye-Waller (σ^2) factor values, which are probably related with the extreme disorder occurring in the tunnel environment. Despite this, a good description of at least the first and second Pb shells was achieved. Pb resulted coordinated by seven oxygen atoms with Pb-O distances in the range 2.55-2.6 Å in both NWP-Pb-1M and NWP-

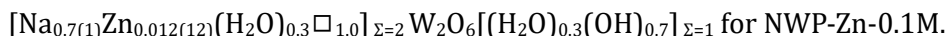
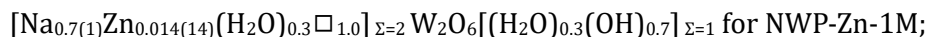
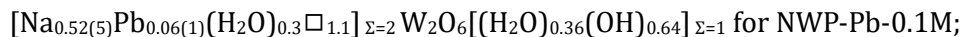
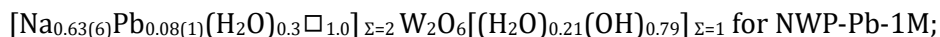
Pb-0.1M. The latter interatomic distances are in good agreement with those of A2, which is surrounded by six oxygens atoms of the octahedral framework with an average A2-O distance of 2.57 Å. The seventh oxygen of the Pb first shell likely represents a hydroxyl anion or the oxygen of a water molecule located along the same tunnel, adjacent to the scatterer atom.

The second shell of lead was characterized by six W atoms at 3.6-3.65 Å. The latter environment is again consistent with Pb contained in A2, which is placed at the centre of a hexagonal ring consisting of six WO₆ octahedra with an average A2-W distance of 2.67 Å (Fig. 17b).

The third shell found in the NWP-Pb-1M sample ($R \sim 4$ Å; $N = 6$) may be attributed to other oxygen atoms belonging to the WO₆ of the hexagonal ring.

Ultimately, the local environment of Pb described by EXAFS is consistent with the A2 site found by XRD, thus suggesting that lead can be placed close to this site.

The chemical formulae proposed for the Pb- and Zn-treated samples are reported as follow:



6.7.4 Final Remarks

The NWP elsmoreite is able to incorporate conspicuous amounts of Tl⁺, but only minor quantities of Pb²⁺ and Zn²⁺. The selectivity can be explained by considering the valence of the studied heavy metals relative to that of the framework cation. Indeed, the high field strength of W⁶⁺ could constitute a barrier that prevents the divalent cations from accessing the binding sites available in the structure's tunnels, allowing the incorporation of only monovalent cations like Tl⁺.

This result was deemed highly relevant for the general aim of the present work, as the selectivity of elsmoreite for monovalent cations could significantly improve the removal efficiency of particular, selected elements in a water environment characterized by a wide assortment of competitor ions.

The incorporation mechanism of Tl⁺ is very different from those of Pb²⁺ and Zn²⁺. The latter divalent cations are likely allocated around the A sites, replacing the original occupants of these sites, with only minor effects on the Y cage environment (these, of course, may be also due to the small amounts of incorporated metals). Tl⁺ is instead disordered within the Y cage, where the incorporation occurs at the expense of H₂O molecules. It is expected that, employing more diluted solutions, as the available Tl⁺ would not be able to fill all the Y cages, the extent of the dehydration

would be minor. Additionally, the incorporation of Tl in the Y cages results in the loss of Na⁺ from A2 and the incorporation of OH⁻ anions to balance the excess of positive charges brought by Tl⁺.

6.8. References

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Chapter 7. Incorporation Mechanisms of Heavy Metals in Cryptomelane

The results of experiments on synthetic cryptomelane will be covered in this chapter. The synthesis, the ion exchange experiments and the chemical and structural characterization of the materials are presented in the first part of the chapter (7.1-7.6). The second part is instead left to the discussion on the experimental results (7.7). Special attention was given to the average structures of both treated and untreated samples, alongside the local coordination environment of the thallium, lead and zinc incorporated within the cryptomelane structure.

7.1. Synthesis

Cryptomelane powders were obtained by a two-step procedure. First, K-birnessite [$\text{K}(\text{Mn}^{4+}, \text{Mn}^{3+})_2\text{O}_4 \cdot 1.5\text{H}_2\text{O}$] was synthesized following the sol-gel procedure developed by Ching et al. (1995), with slight modifications. Briefly, 5 g of glucose monohydrate [$\text{C}_6\text{H}_{12}\text{O}_6 \cdot \text{H}_2\text{O}$, BP-USP, ACEF] were dissolved in 20 ml of deionized water. Then, 3 g of potassium permanganate [KMnO_4 , ACS reagent, $\geq 99.0\%$, Labkem] were dissolved in 50 ml of deionized water. The potassium permanganate solution was added to the glucose solution and mixed vigorously for 20-30 seconds. At this point, a sudden exothermic reaction occurred, and a dark-brown gel was obtained. The gel was left to cool for 2 hours and then dried at 110°C overnight in an oven. The resulting brown xerogel was grinded in an agate mortar and then calcinated at 400°C for 2h in a muffle furnace, producing a grey ash, which was grinded and washed thoroughly with deionized water. The resulting wet paste was dried at 80°C for 4 hours in an oven. The resulting fine brown powder is tentatively identified as birnessite, by analogy with the observations of Ching et al. (1995).

The second step of the procedure consisted in the thermal treatment at 600°C for 6 hours in a muffle furnace of the birnessite powders. The resulting dark brown powders were washed thoroughly with deionized water to remove eventual soluble K-Mn byproducts, which are occasionally associated with Mn oxides obtained from solid-state high temperature reactions (e.g., Kim et al., 1999) and then dried at 80°C for 4 hours in an oven. The result was a cryptomelane powder.

Secondary electron images of the cryptomelane powders were acquired with a scanning electron microscope (SEM) EVO 40 (Carl Zeiss), using a 10 KV current with 20 pA of intensity.

The sample consists of irregular, sub-micrometric particles dispersed over round-shaped, cloud-like, micrometric masses (Fig. 1). At higher magnification, some particles show a needle-like shape, which is characteristic of hollandite, while others appear irregular and rugged (Fig. 2). The cloud-like masses are vaguely similar to those reported by Cheney et al. (2008) for a brown birnessite nanomaterial. This is not surprising, as the hollandite reported in this study has been obtained after a birnessite precursor. In the present work, the cloud-like masses are found both isolated or linked together to form bigger uneven crusts, either free or covered by the irregular

and needle-like particles. At higher magnifications they appear as aggregates of individual smaller corpuscles (Fig. 3), which are not clearly discernible at the SEM scale.

The complexity of the sample morphology can be explained considering the employed synthesis procedure, which involves several steps: from amorphous Mn oxides dispersed in a xerogel, to birnessite ashes and, finally, cryptomelane.

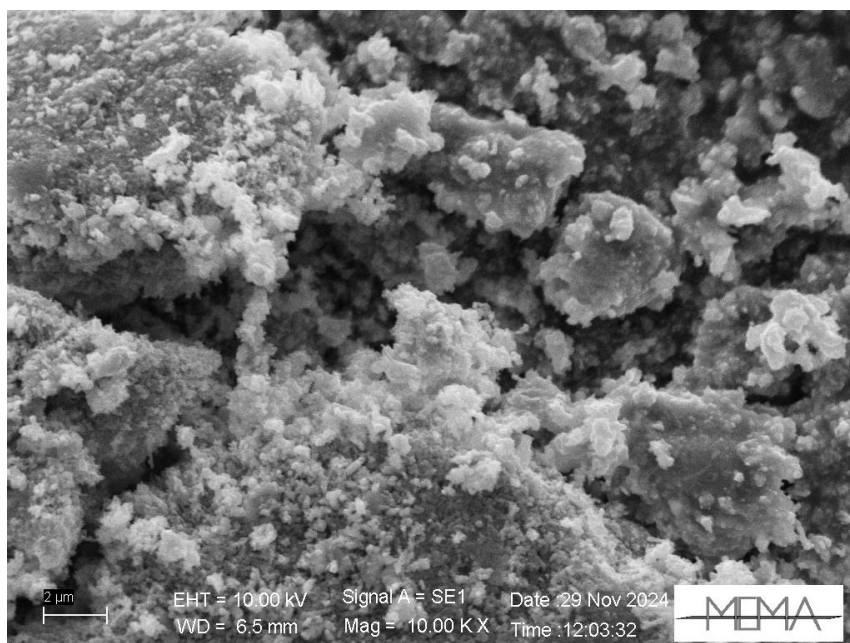


Figure 1. Overall appearance of the cryptomelane sample by a SEM secondary electron image.

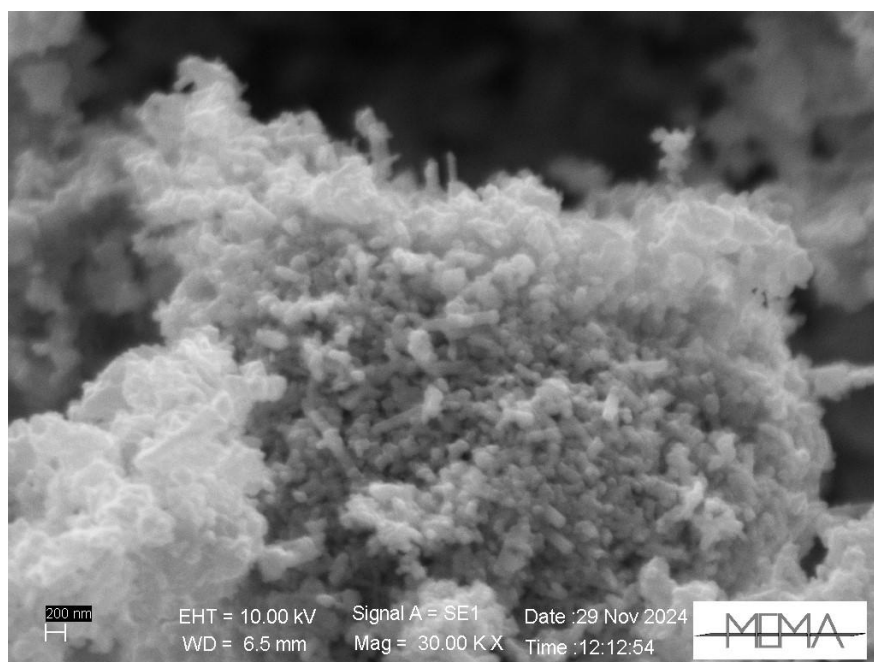


Figure 2. SEM secondary electron image of an aggregate of particles showing needle or rugged shapes.

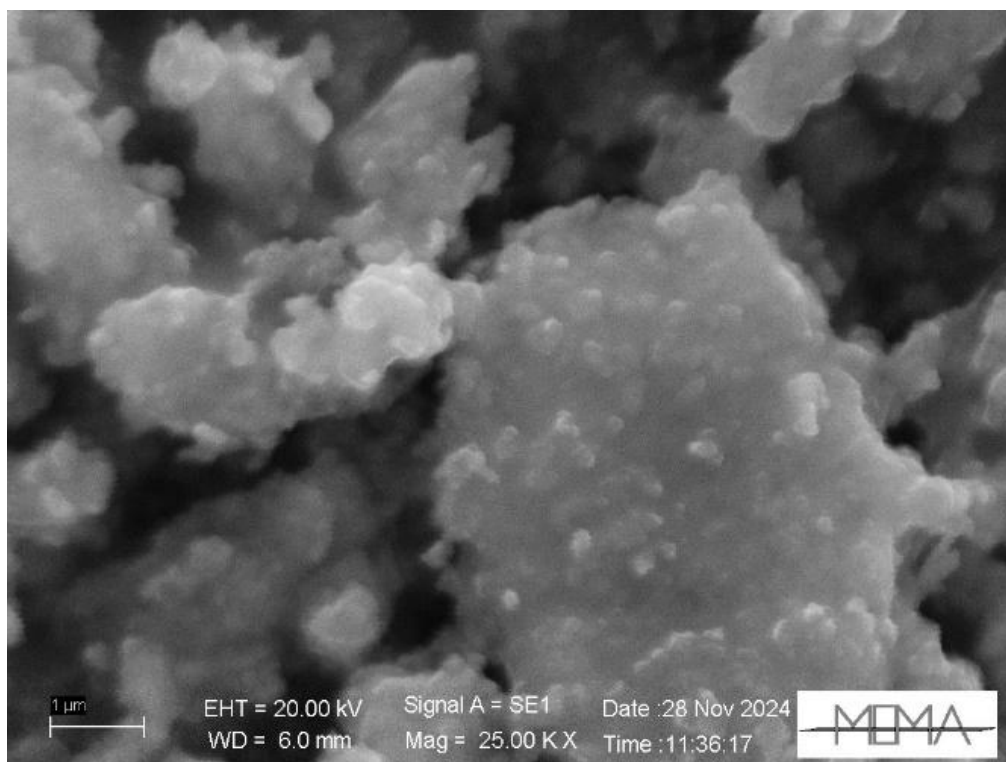


Figure 3. SEM secondary electron image of a cloud-like aggregate of particles.

7.2. Ion Exchange Experiments

100 mg of cryptomelane powders were immersed into 5 ml of 1, 0.1 and 0.01M aqueous solutions of thallium (I) formate [HCO_2Tl , 97%, Sigma-Aldrich], lead (II) nitrate [$\text{Pb}(\text{NO}_3)_2$, ACS reagent, $\geq 99.0\%$, Sigma-Aldrich] and zinc (II) nitrate hexahydrate [$\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, reagent grade, 98%, Sigma-Aldrich] contained in 15 ml Falcon tubes, manually stirred with a stainless steel spatula for a few seconds and then left stationary. After one day of imbibition, the powders were centrifugated and washed three times with 5 ml of deionized water to remove eventual soluble salts precipitated from the intergranular moisture. Then, they were left under the fume hood overnight to roughly dry and then kept in an oven at 70°C for 2 hours to complete drying.

The untreated cryptomelane is called KMH, standing for potassium manganese hollandite (that is quite the mineralogical definition of cryptomelane), while the symbol of the heavy element used for the treatment and the concentration of the solution is added to the treated samples. For example, the sample plunged in 0.01 M lead solution is called KMH-Pb-0.01M.

SEM investigations revealed that the complex morphology of the powders resulted unchanged after the treatment with the heavy metal solutions (Fig. 4).

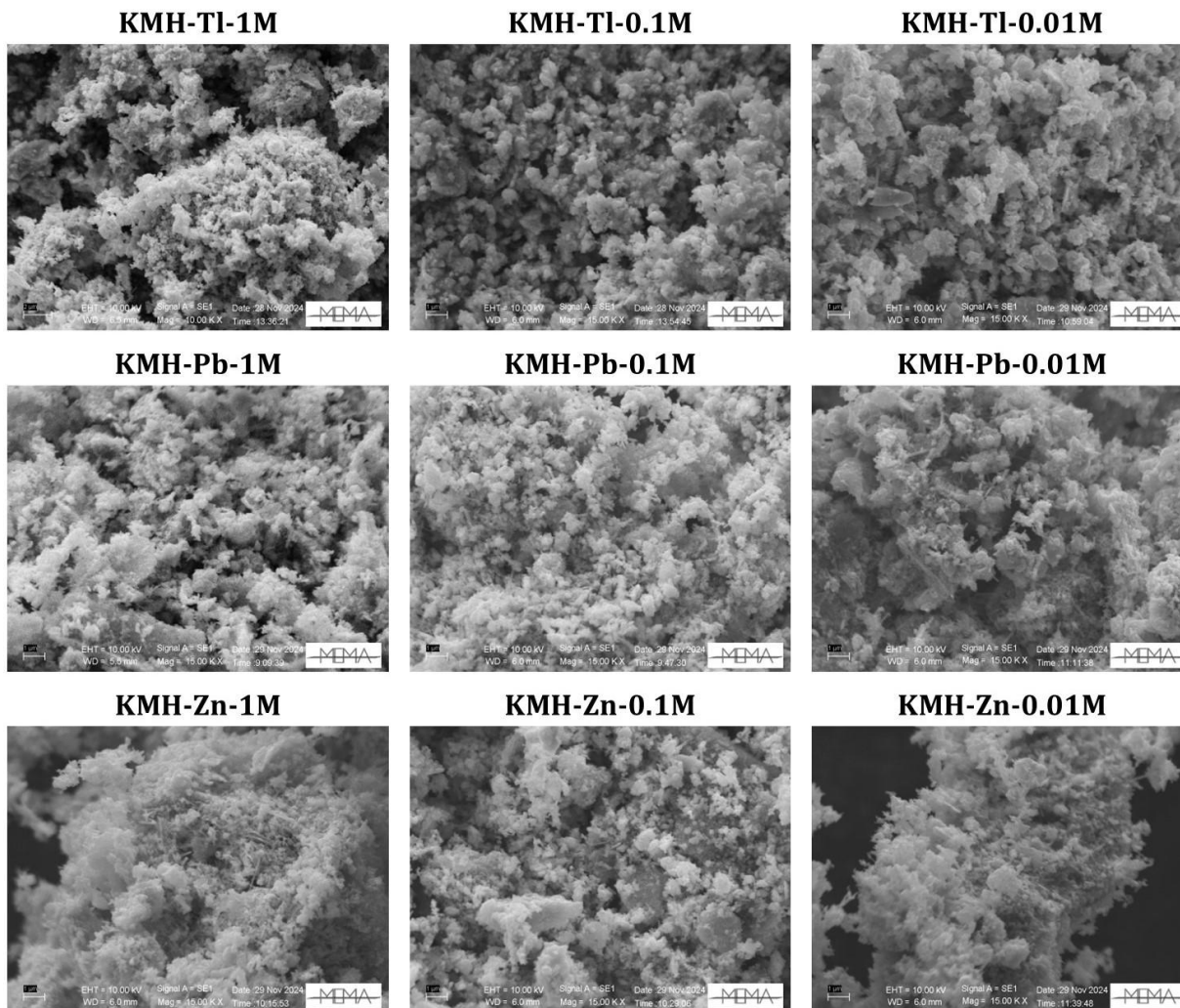


Figure 4. SEM secondary electron images of cryptomelane powders after the treatment with 1M, 0.1M and 0.01M solutions of Tl, Pb and Zn.

7.3. Chemical Analysis

The relative concentrations of potassium, manganese, thallium, lead and zinc were measured by means of PIXE (Table 1). In the errors calculations, a further relative 10% was added to the percentage error values reported in Table 1 due to systematic uncertainties inherent to the PIXE measurements. The normalization of the chemical data is discussed in detail in section 7.7.

Table 1. PIXE analytical results of treated and untreated cryptomelane powders.

sample	K (wt%)	Mn (wt%)	Tl (wt%)	Pb (wt%)	Zn (wt%)	total
cryptomelane	10.8	89.2	0.0	0.0	0.0	100
err (%)	1.8	0.9	–	–	–	
KMH-Tl-1M	2.2	60.9	36.9	0.0	0.0	100
err (%)	4.7	0.5	0.5	–	–	
KMH-Tl-0.1M	2.2	61.2	36.5	0.0	0.0	100
err (%)	5.6	0.7	0.7	–	–	
KMH-Tl-0.01M	7.2	85.7	7.1	0.0	0.0	100
err (%)	3.2	1.9	2.2	–	–	
KMH-Pb-1M	6.4	83.3	0.0	10.4	0.0	100
err (%)	2.4	0.4	–	1.1	–	
KMH-Pb-0.1M	6.8	83.5	0.0	9.7	0.0	100
err (%)	2.4	1.5	–	1.8	–	
KMH-Pb-0.01M	7.3	86.5	0.0	6.2	0.0	100
err (%)	2.3	2.1	–	2.7	–	
KMH-Zn-1M	7.3	89.9	0.0	0.0	2.8	100
err (%)	2.2	0.9	–	–	0.7	
KMH-Zn-0.1M	7.5	89.9	0.0	0.0	2.5	100
err (%)	2.4	1.1	–	–	0.6	
KMH-Zn-0.01M	7.6	90.2	0.0	0.0	2.2	100
err (%)	2.4	1.1	–	–	0.3	

7.4. Infrared Analysis

Infrared data were collected for the untreated cryptomelane and for the powders treated with 1M heavy metal solutions. The only significant feature of the IR spectra of the samples is an absorption band at about 2360 cm^{-1} (Fig. 5), which is the characteristic band of carbon dioxide from air. As no bands related to the presence of water molecules, nor H_3O^+ and OH^- are displayed, the samples are considered anhydrous.

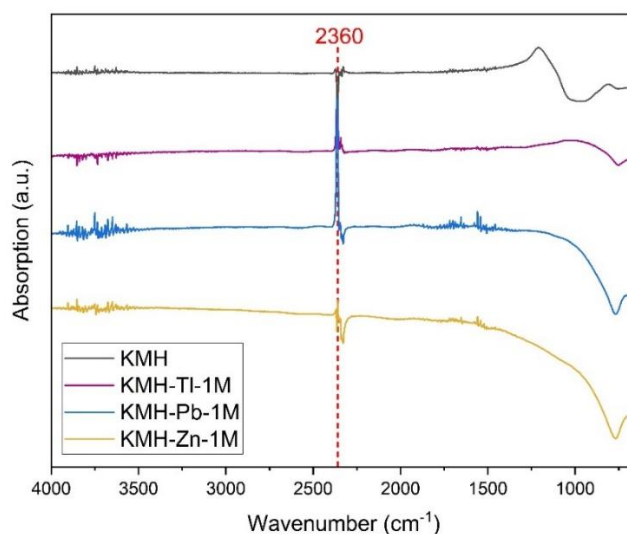


Figure 5. FTIR spectra of the untreated cryptomelane and the powders treated with 1M heavy metal solutions.

7.5. Rietveld Refinements

Rietveld refinements were carried out using the software Topas (Coelho, 2018). Initially, the structure of the untreated KMH cryptomelane was refined in the tetragonal space group $I4/m$. Nevertheless, since the hollandites are often reported as both tetragonal $I4/m$ and monoclinic $I2/m$, a test with the latter space group was also performed. As the lower symmetry provided a significant improvement in the fit of the peaks intensities (reflected by the decrease of the R_{wp} parameter from 3.79 to 2.93%), the monoclinic space group $I2/m$ was used instead of the tetragonal $I4/m$ in all the Rietveld refinements.

A test was performed including a birnessite phase in the refinement of the KMH cryptomelane. Birnessite, also known as δ - MnO_2 , is a manganese oxides with a layered structure, whose diffraction pattern is characterized by two intense peaks at $Q = 0.854$ and $1.707 \text{ \AA}^{-1}$ -corresponding to the (001) and (002) reflections, respectively (both with a relative intensity > 95) followed by a sequence of minor peaks (relative intensity < 15) at higher Q . On the other side, the KMH cryptomelane shows double peaks at about $0.90 \text{ \AA}^{-1}$, corresponding to the (10-1) and (101) reflections, and 1.80 - $1.81 \text{ \AA}^{-1}$, corresponding to the (20-2) and (202) reflections.

No peak imputable to a birnessite phase was actually recorded in the KMH sample XRD pattern. Nonetheless, the signal of minor amounts of birnessite could have been hidden under the broad profiles of the cryptomelane peaks. Since K-birnessite was a precursor material in the synthesis procedure that led to the KMH cryptomelane, a test including a birnessite phase was considered appropriate to evaluate the eventual effects of a possible impurity. However, as the fit including birnessite did not show any improvement, the latter phase was not included in the fits of either the untreated KMH or the treated samples. In summary, if an undetected impurity of birnessite is present in the cryptomelane powders, it should not affect the refinements results.

The XRD pattern of KMH-Tl-1M and KMH-Tl-0.1M samples showed a broad hump that has been attributed to the occurrence of an amorphous material, probably formed during the ion exchange experiments. To improve the background fitting, additional peaks were then added to the conventional Chebyshev profile function. Moreover, the KMH-Tl-1M sample showed five additional peaks (corresponding to $d = 3.04$; 2.63 ; 2.24 ; 1.86 and $1.58 \text{ \AA}$) which were not related to the hollandite phase, but they are imputable to an impurity of Tl (III) oxide $[Tl_2O_3]$ with the avicennite crystal structure, again formed during the ion exchange experiment (Radtke et al., 1978). The avicennite phase was then added to the model, refining unit cell parameters, scale factor and adding sensible constraints on thermal parameters. The resulting amount of avicennite was below 3%, indicating a minor contribution to the diffraction pattern and preventing a more accurate quantification (Fig. 7).

The tunnel environment of the untreated cryptomelane and the Pb- and Zn-treated KMH was refined using the conventional A ($2a$) site, while that of the Tl-treated samples required the addition of a satellite $4g$ site, called A', since the ΔF -map showed significant residuals along the tunnel axis, in the immediate vicinity of A.

Scattering curves for neutral atoms, taken from the international Tables for Crystallography (Wilson, 1992), were used as follow: M = manganese and O = oxygen for all the samples; A and the

eventual A' = Tl vs. □ for the Tl-treated samples; Pb vs. □ for the Pb-treated samples; Zn vs. □ for the Zn-treated samples. The Rietveld refinements results are summarized in Tables 2, 3, 4 and 5; the XRD profiles are shown in Figures from 6 to 15.

Table 2. Unit cell parameters, volume, volume percentage difference between treated and untreated samples, and R-factor (R_{wp}) of the Rietveld refinements.

samples	a (Å)	b (Å)	c (Å)	β (°)	V (Å ³)	ΔV (%)	R_{wp} (%)
KMH	9.8840(10)	2.8596(2)	9.8027(10)	90.22(1)	277.06(4)	–	2.93
KMH-Tl-1M	9.8728(12)	2.8635(2)	9.9129(12)	89.90(2)	280.24(5)	1.15(2)	3.14
KMH-Tl-0.1M	9.8801(13)	2.8631(2)	9.9064(14)	89.93(1)	280.23(6)	1.14(2)	3.83
KMH-Tl-0.01M	9.8324(8)	2.8591(1)	9.8780(8)	89.86(1)	277.68(3)	0.22(1)	2.70
KMH-Pb-1M	9.8138(9)	2.8580(2)	9.8736(9)	89.82(1)	276.93(4)	-0.05(2)	3.46
KMH-Pb-0.1M	9.8132(9)	2.8579(2)	9.8729(9)	89.83(1)	276.89(4)	-0.06(1)	2.87
KMH-Pb-0.01M	9.8154(9)	2.8584(2)	9.8745(8)	89.83(1)	277.04(4)	-0.01(1)	2.84
KMH-Zn-1M	9.8116(9)	2.8577(2)	9.8704(8)	89.82(1)	276.75(4)	-0.11(1)	2.95
KMH-Zn-0.1M	9.8129(9)	2.8578(2)	9.8710(8)	89.82(1)	276.82(4)	-0.09(2)	3.27
KMH-Zn-0.01M	9.8133(9)	2.8580(2)	9.8723(8)	89.83(1)	276.89(4)	-0.06(1)	1.80
$R_{wp} = \left[\sum_i w_i (y_{c,i} - y_{o,i})^2 / \sum_i w_i (y_{o,i})^2 \right]^{\frac{1}{2}}$ (Young,1993); ΔV (%) = $[(V_t - V_0)/V_0] \times 100$, with V_t = unit cell volume after the ion exchange experiment, V_0 = unit cell volume of the untreated KMh.							

Table 3. Atomic coordinates (x, y, z), occupancies (Occ.) and isotropic thermal parameters (B_{iso}) of the KMh cryptomelane.

Site	Wyckoff position	Occ.	x	y	z	B_{iso} (Å ²)
KMh cryptomelane						
A	2a	0.64(1) [‡]	0	0	0	3.7(5)
M1	4i	1 [†]	0.8472(7)	0	0.3365(8)	1.64(3)
M2	4i	1 [†]	0.3272(7)	0	0.1498(8)	1.64(3)
O1	4i	1 [†]	0.655(2)	0	0.294(2)	1.03(14)
O2	4i	1 [†]	0.594(1)	0	0.031(2)	1.03(14)
O3	4i	1 [†]	0.308(2)	0	0.353(2)	1.03(14)
O4	4i	1 [†]	0.043(2)	0	0.329(2)	1.03(14)
† Not refined. ‡ Refined: K vs. □.						

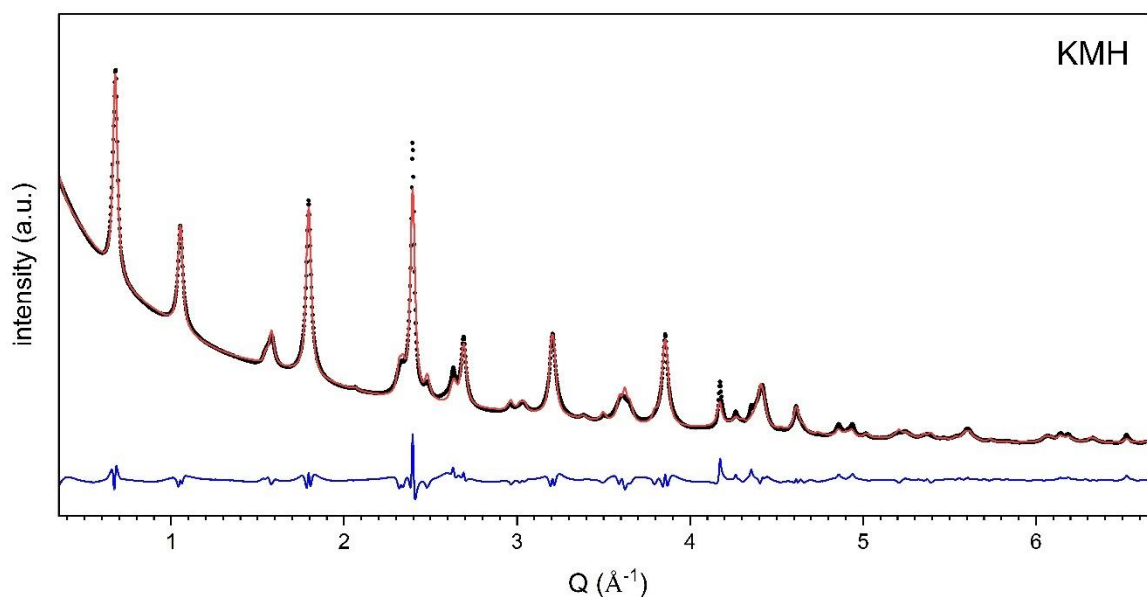


Figure 6. XRD profile of the untreated KMH cryptomelane: measured (black points), calculated (red lines) and the difference (blue lines).

Table 4. Atomic coordinates (x, y, z), occupancies ($Occ.$) and isotropic thermal parameters (B_{iso}) of the Tl-treated samples.

Sample	Site	Wyckoff position	Occ.	x	y	z	$B_{iso} (\text{\AA}^2)$
KMH-Tl-1M	A	$2a$	0.12(1) [‡]	0	0	0	1(3)
	A'	$4g$	0.27(5) [‡]	0	0.856(17)	0	5.0(3)
	M1	$4i$	1 [†]	0.8520(10)	0	0.3268(9)	1.00(10)
	M2	$4i$	1 [†]	0.3372(12)	0	0.1466(11)	1.00(10)
	O1	$4i$	1 [†]	0.657(3)	0	0.308(4)	1.00(19)
	O2	$4i$	1 [†]	0.695(2)	0	0.048(3)	1.00(19)
	O3	$4i$	1 [†]	0.325(4)	0	0.341(3)	1.00(19)
	O4	$4i$	1 [†]	0.035(3)	0	0.3961(18)	1.00(19)
KMH-Tl-0.1M	A	$2a$	0.03(4) [‡]	0	0	0	1.0(2)
	A'	$4g$	0.18(2) [‡]	0	0.853(10)	0	1.0(2)
	M1	$4i$	1 [†]	0.8435(12)	0	0.3334(14)	4.34(12)
	M2	$4i$	1 [†]	0.3317(14)	0	0.1380(10)	4.34(12)
	O1	$4i$	1 [†]	0.649(4)	0	0.294(3)	1.8(2)
	O2	$4i$	1 [†]	0.5842(15)	0	0.0360(18)	1.8(2)
	O3	$4i$	1 [†]	0.294(4)	0	0.342(4)	1.8(2)
	O4	$4i$	1 [†]	0.0453(19)	0	0.3244(18)	1.8(2)
KMH-Tl-0.01M	A	$2a$	0.03(7) [‡]	0	0	0	3.1(4)
	A'	$4g$	0.10(4) [‡]	0	0.87(3)	0	3.1(4)
	M1	$4i$	1 [†]	0.8489(8)	0	0.3340(9)	1.57(7)
	M2	$4i$	1 [†]	0.3290(8)	0	0.1443(6)	1.57(7)
	O1	$4i$	1 [†]	0.654(2)	0	0.314(2)	1.25(16)
	O2	$4i$	1 [†]	0.6078(12)	0	0.0398(17)	1.25(16)
	O3	$4i$	1 [†]	0.301(2)	0	0.339(2)	1.25(16)
	O4	$4i$	1 [†]	0.044(2)	0	0.3184(15)	1.25(16)

† Not refined. ‡ Refined: Tl vs. □.

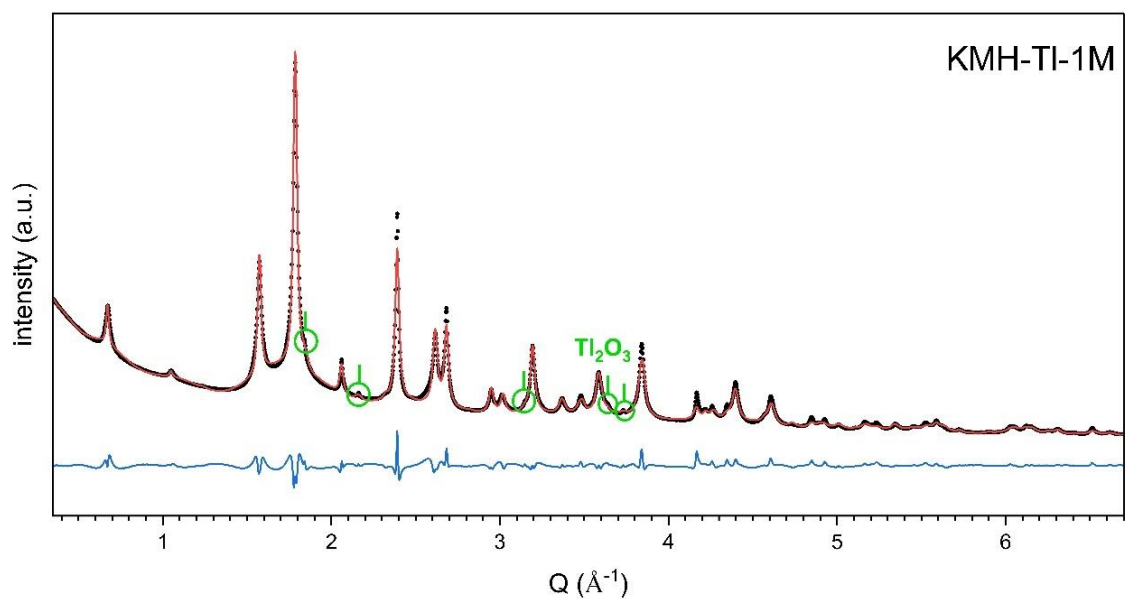


Figure 7. XRD profile KMH-Tl-1M: measured (black points), calculated (red lines) and the difference (blue lines). The green circles indicate the weak peaks of the avicennite (Tl_2O_3) phase precipitated during the ion exchange experiments.

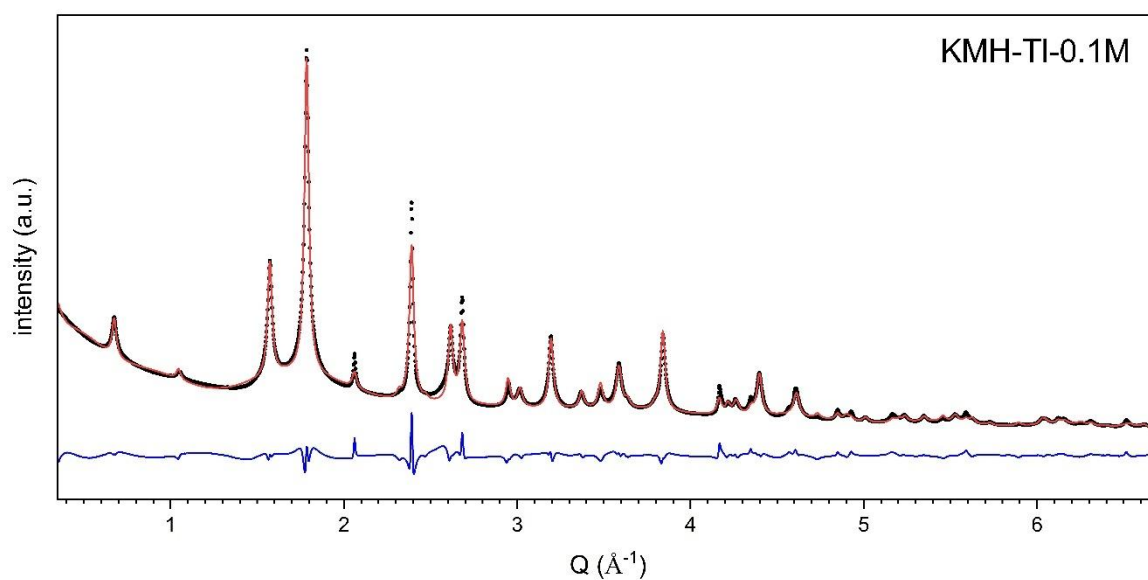


Figure 8. XRD profile KMH-Tl-0.1M: measured (black points), calculated (red lines) and the difference (blue lines).

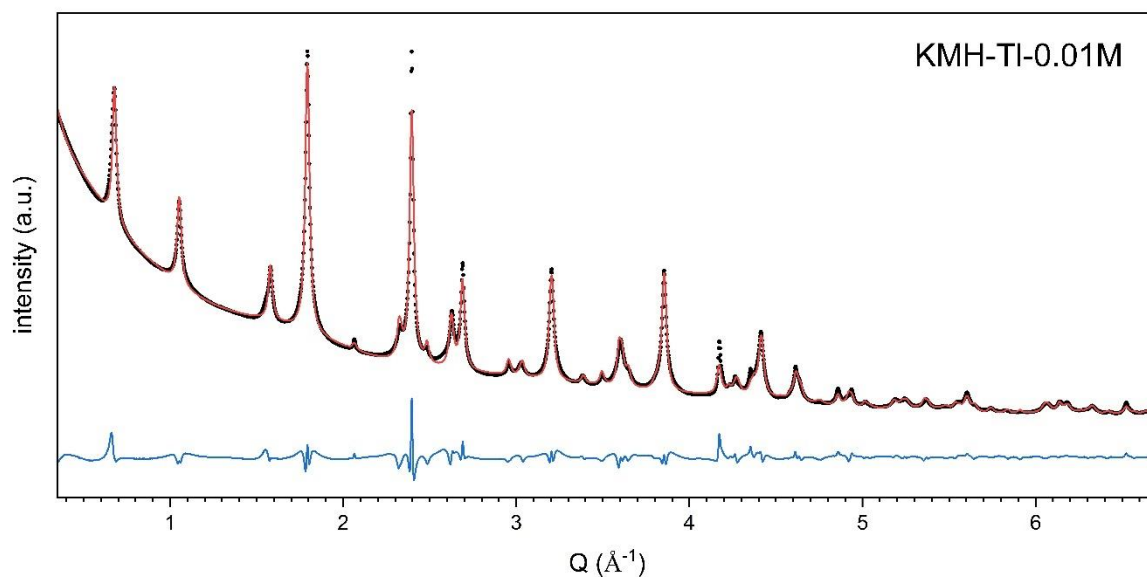


Figure 9. XRD profile KMH-Tl-0.01M:
measured (black points), calculated (red lines) and the difference (blue lines).

Table 5. Atomic coordinates (x, y, z), occupancies (Occ.) and
isotropic thermal parameters (B_{iso}) of the Pb-treated samples.

Sample	Site	Wyckoff position	Occ.	x	y	z	B_{iso} (Å ²)
KMh-Pb-1M	A	2a	0.18(1) [‡]	0	0	0	5.0(4)
	M1	4i	1 [†]	0.8519(7)	0	0.3282(7)	1.00(7)
	M2	4i	1 [†]	0.3291(7)	0	0.1446(6)	1.00(7)
	O1	4i	1 [†]	0.657(3)	0	0.305(2)	2.12(15)
	O2	4i	1 [†]	0.6091(14)	0	0.040(2)	2.12(15)
	O3	4i	1 [†]	0.313(2)	0	0.342(3)	2.12(15)
	O4	4i	1 [†]	0.048(2)	0	0.3195(18)	2.12(15)
KMh-Pb-0.1M	A	2a	0.17(1) [‡]	0	0	0	5.0(4)
	M1	4i	1 [†]	0.8551(6)	0	0.3347(7)	1.07(8)
	M2	4i	1 [†]	0.3283(6)	0	0.1470(6)	1.07(8)
	O1	4i	1 [†]	0.661(3)	0	0.318(2)	1.31(16)
	O2	4i	1 [†]	0.6158(14)	0	0.0400(17)	1.31(16)
	O3	4i	1 [†]	0.3049(19)	0	0.340(2)	1.31(16)
	O4	4i	1 [†]	0.047(2)	0	0.2992(15)	1.31(16)
KMh-Pb-0.01M	A	2a	0.16(1) [‡]	0	0	0	5.0(3)
	M1	4i	1 [†]	0.8516(6)	0	0.3291(7)	1.03(7)
	M2	4i	1 [†]	0.3280(7)	0	0.1445(6)	1.03(7)
	O1	4i	1 [†]	0.657(3)	0	0.305(2)	2.12(14)
	O2	4i	1 [†]	0.6097(13)	0	0.0394(19)	2.12(14)
	O3	4i	1 [†]	0.312(2)	0	0.344(3)	2.12(14)
	O4	4i	1 [†]	0.047(2)	0	0.3194(17)	2.12(14)

† Not refined. ‡ Refined: Pb vs. □.

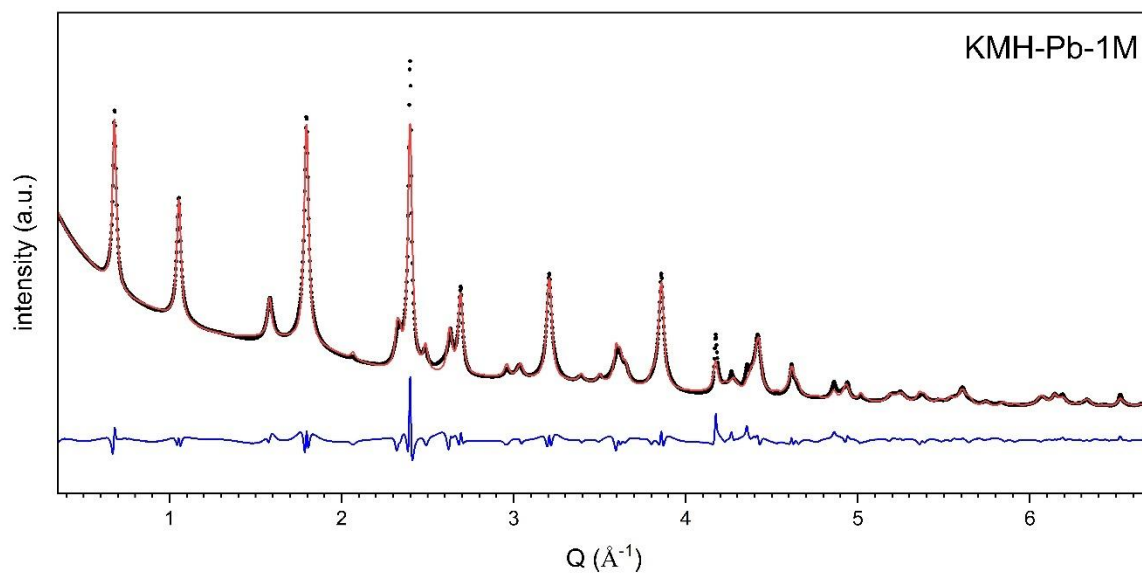


Figure 10. XRD profile KMH-Pb-1M:
measured (black points), calculated (red lines) and the difference (blue lines).

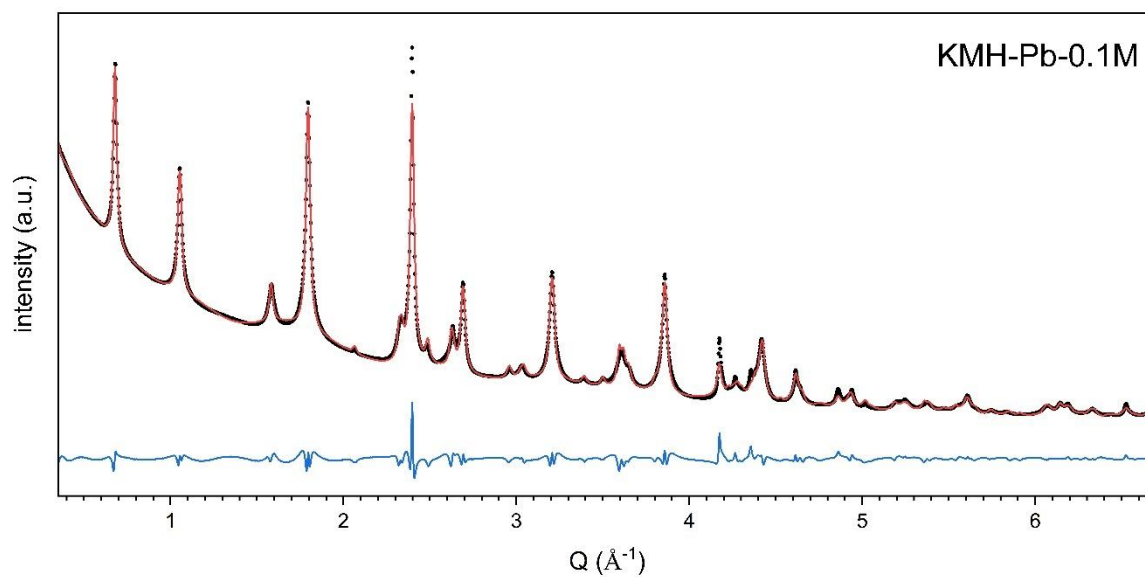


Figure 11. XRD profile KMH-Pb-0.1M:
measured (black points), calculated (red lines) and the difference (blue lines).

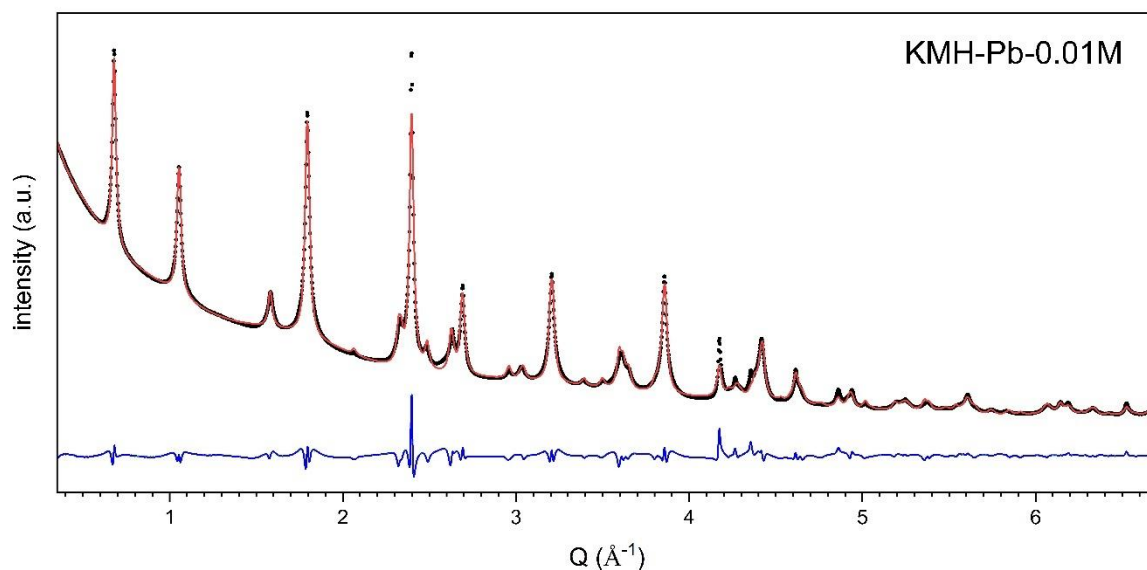


Figure 12. XRD profile KMH-Pb-0.01M:
measured (black points), calculated (red lines) and the difference (blue lines).

Table 6. Atomic coordinates (x, y, z), occupancies ($Occ.$) and isotropic thermal parameters (B_{iso}) of the Zn-treated samples.

Sample	Site	Wyckoff position	Occ.	x	y	z	B_{iso} ($\text{\AA}^2$)
KMh-Zn-1M	A	$2a$	$0.35(1)^\ddagger$	0	0	0	3.6(4)
	M1	$4i$	$1^\dagger$	0.8527(7)	0	0.3277(6)	1.24(7)
	M2	$4i$	$1^\dagger$	0.3297(7)	0	0.1442(6)	1.24(7)
	O1	$4i$	$1^\dagger$	0.658(3)	0	0.306(2)	2.33(16)
	O2	$4i$	$1^\dagger$	0.6036(14)	0	0.0382(19)	2.33(16)
	O3	$4i$	$1^\dagger$	0.308(2)	0	0.349(3)	2.33(16)
	O4	$4i$	$1^\dagger$	0.048(2)	0	0.3213(18)	2.33(16)
KMh-Zn-0.1M	A	$2a$	$0.35(1)^\ddagger$	0	0	0	4.5(4)
	M1	$4i$	$1^\dagger$	0.8524(7)	0	0.3299(7)	1.29(7)
	M2	$4i$	$1^\dagger$	0.3278(7)	0	0.1443(6)	1.29(7)
	O1	$4i$	$1^\dagger$	0.657(3)	0	0.307(2)	2.12(15)
	O2	$4i$	$1^\dagger$	0.6034(13)	0	0.0359(18)	2.12(15)
	O3	$4i$	$1^\dagger$	0.304(2)	0	0.350(3)	2.12(15)
	O4	$4i$	$1^\dagger$	0.047(2)	0	0.3174(16)	2.12(15)
KMh-Zn-0.01M	A	$2a$	$0.36(1)^\ddagger$	0	0	0	3.9(4)
	M1	$4i$	$1^\dagger$	0.8516(7)	0	0.3294(7)	1.38(7)
	M2	$4i$	$1^\dagger$	0.3278(7)	0	0.1433(6)	1.38(7)
	O1	$4i$	$1^\dagger$	0.657(3)	0	0.307(2)	2.46(15)
	O2	$4i$	$1^\dagger$	0.6024(13)	0	0.0379(19)	2.46(15)
	O3	$4i$	$1^\dagger$	0.308(2)	0	0.346(3)	2.46(15)
	O4	$4i$	$1^\dagger$	0.047(2)	0	0.3210(17)	2.46(15)

† Not refined. ‡ Refined: Zn vs. $\square$.

Table 7. Selected interatomic distances (in Å) for the M1, M2, A and eventual A' polyhedron.

M1 octahedron	M1-O1 (x2)	M1-O1 (x1)	M1-O2 (x2)	M1-O4 (x1)	<M1-O>	σ^2
KMH	1.92(1)	1.94(3)	2.02(1)	1.93(2)	1.96	176.01
KMH-Tl-1M	1.96(3)	1.94(4)	1.95(3)	1.94(4)	1.95	87.77
KMH-Tl-0.1M	1.96(5)	1.91(3)	2.06(2)	1.99(3)	1.98	224.51
KMH-Tl-0.01M	2.05(2)	1.93(3)	1.95(1)	1.92(3)	1.97	76.39
KMH-Pb-1M	1.94(2)	1.93(4)	1.97(2)	1.93(3)	1.95	78.66
KMH-Pb-0.1M	2.08(2)	1.91(3)	1.91(1)	1.91(3)	1.97	45.6
KMH-Pb-0.01M	1.95(2)	1.93(3)	1.97(1)	1.92(3)	1.95	78.04
KMH-Zn-1M	1.95(2)	1.92(4)	1.99(1)	1.92(3)	1.96	89.99
KMH-Zn-0.1M	1.97(2)	1.93(4)	2.00(1)	1.91(3)	1.96	85.19
KMH-Zn-0.01M	1.97(2)	1.92(4)	1.99(1)	1.92(3)	1.96	93.55
M2 octahedron	M2-O2 (x1)	M2-O3 (x2)	M2-O3 (x1)	M2-O4 (x2)	<M2-O>	σ^2
KMH	1.94(2)	1.96(1)	2.00(3)	1.93(1)	1.95	72.03
KMH-Tl-1M	1.95(4)	1.92(4)	2.16(4)	1.96(3)	2.02	60.17
KMH-Tl-0.1M	1.91(3)	1.90(3)	2.06(5)	1.91(2)	1.94	153.79
KMH-Tl-0.01M	1.92(2)	1.92(2)	1.94(3)	1.93(2)	1.93	95.60
KMH-Pb-1M	1.92(3)	2.00(2)	1.95(4)	1.90(1)	1.95	80.23
KMH-Pb-0.1M	1.92(2)	1.94(1)	1.92(3)	1.96(1)	1.94	93.77
KMH-Pb-0.01M	1.91(2)	1.99(2)	1.98(4)	1.92(1)	1.95	75.13
KMH-Zn-1M	1.91(2)	1.97(2)	2.03(4)	1.90(1)	1.95	73.06
KMH-Zn-0.1M	1.90(2)	1.93(1)	2.04(4)	1.92(1)	1.94	75.09
KMH-Zn-0.01M	1.91(2)	1.96(2)	2.01(4)	1.92(1)	1.95	84.93
A and A' polyhedron	A-O1 (x4)	A-O3 (x4)	A'-O1 (x2)	A'-O1 (x2)	A'-O3 (x2)	A'-O3 (x2)
KMH	2.91(2)	2.77(2)	-	-	-	-
KMH-Tl-1M	2.84(4)	2.75(4)	2.65(4)	3.06(5)	2.56(4)	2.98(5)
KMH-Tl-0.1M	3.25(2)	2.94(4)	2.71(4)	3.12(4)	2.76(4)	3.17(4)
KMH-Tl-0.01M	2.78(2)	2.90(2)	2.60(4)	2.98(6)	2.74(4)	3.10(6)
KMH-Pb-1M	2.85(3)	2.80(3)	-	-	-	-
KMH-Pb-0.1M	2.78(3)	2.87(2)	-	-	-	-
KMH-Pb-0.01M	2.85(3)	2.80(3)	-	-	-	-
KMH-Zn-1M	2.84(3)	2.80(3)	-	-	-	-
KMH-Zn-0.1M	2.83(3)	2.82(3)	-	-	-	-
KMH-Zn-0.01M	2.83(3)	2.81(3)	-	-	-	-
σ^2 = Bond angle variance calculated according to the formula proposed by Robinson et al. (1971).						

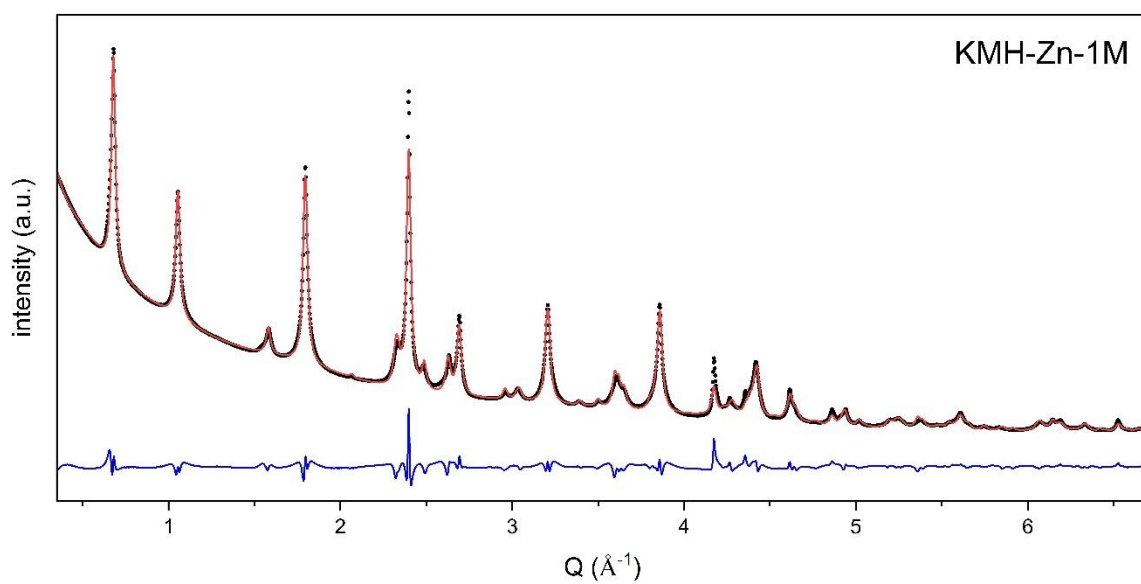


Figure 13. XRD profile KMH-Zn-1M:
measured (black points), calculated (red lines) and the difference (blue lines).

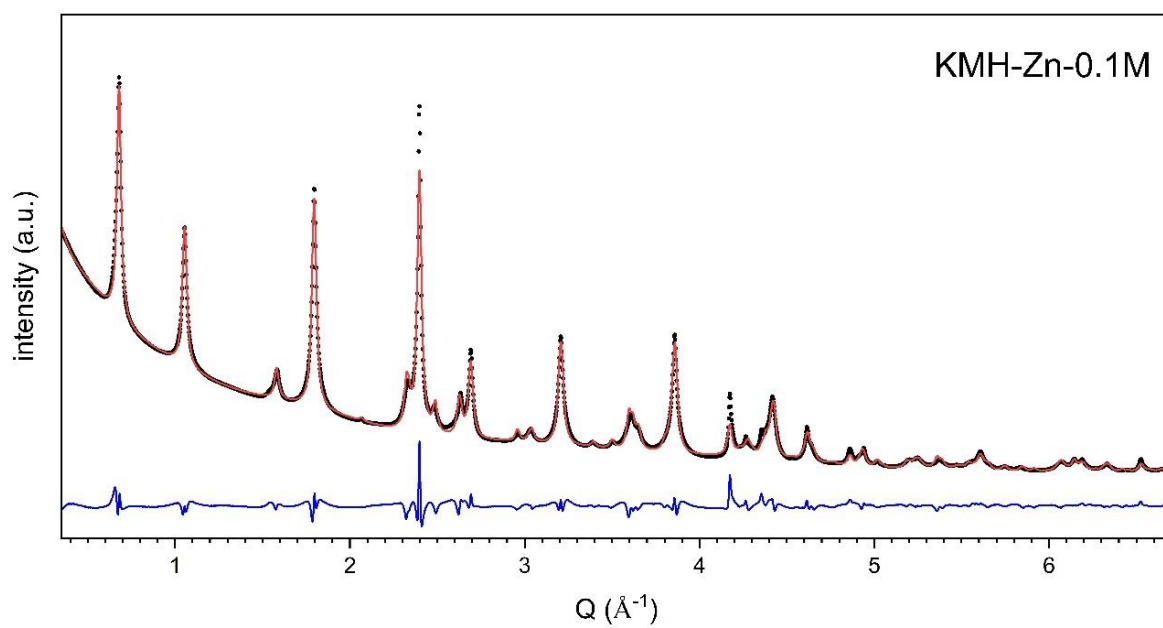


Figure 14. XRD profile KMH-Zn-0.1M:
measured (black points), calculated (red lines) and the difference (blue lines).

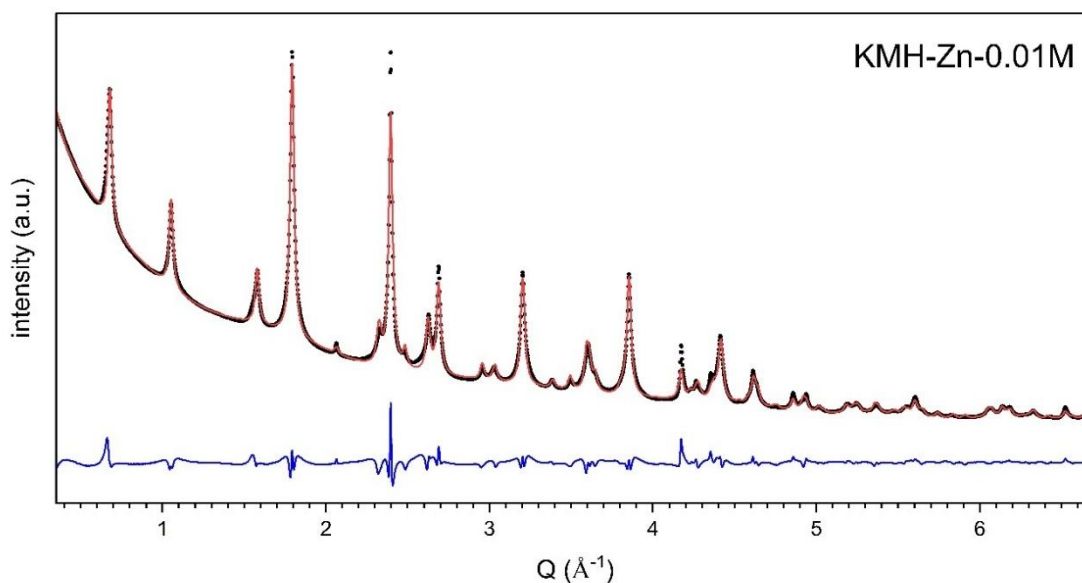


Figure 15. XRD profile KMH-Zn-0.01M:
measured (black points), calculated (red lines) and the difference (blue lines).

7.6. X-ray Absorption Spectroscopy Measurements

X-ray absorption spectroscopy (XAS) analysis was performed on the Tl, Pb and Zn-treated samples, at the L₃-edge of thallium and lead, and the K-edge of zinc, respectively.

The X-ray absorption near edge structure (XANES) spectra of Tl-treated samples were compared with three thallium compound references: thallium (I) chloride [TlCl] dissolved in an aqueous solution (Scheckel et al., 2004), thallium (I) sulphate [Tl₂SO₄] and thallium (III) oxide [Tl₂O₃] (Biagioni et al., 2020) (Fig. 16). The XANES of the Tl-treated samples show a peak at about 12674 eV, in good agreement with the Tl⁺ references. As a consequence, the thallium contained in the Tl-treated samples is considered monovalent. Despite the presence of Tl³⁺ contained in the avicennite precipitate, the XANES spectrum of KMH-Tl-1M shows no features attributable to trivalent thallium, indirectly confirming that the avicennite content is very low.

The XANES spectra of the Pb-treated samples were compared with three lead model compounds, each one containing lead with a different oxidation state: lead (IV) oxide [PbO₂], lead (II) oxide [PbO] and metallic lead (Fig 17). The edge environment of the Pb-treated samples shows evident differences compared to those of the references. Indeed, none of the Pb-treated samples XANES spectra derivatives display any clear pre-edge and post-edge features (Fig 17b), which are instead typical of PbO (at about -8 and + 12.5 eV, respectively) and PbO₂ (at about -11 and +12 eV, respectively) (Rao and Wong, 1984). Nevertheless, the analysis of the edge position (in Fig. 18 a comparison between the L₃ absorption edge of KMH-Pb-0.1M -taken as an example- and those of PbO and PbO₂ is reported) indicates that lead contained in the cryptomelane samples is divalent. This in turn implies that no oxidation, which could be expected according to different authors (e.g.,

Risch et al., 2017; Pan et al., 2019 and Wang et al., 2020), occurred during the ion-exchange process.

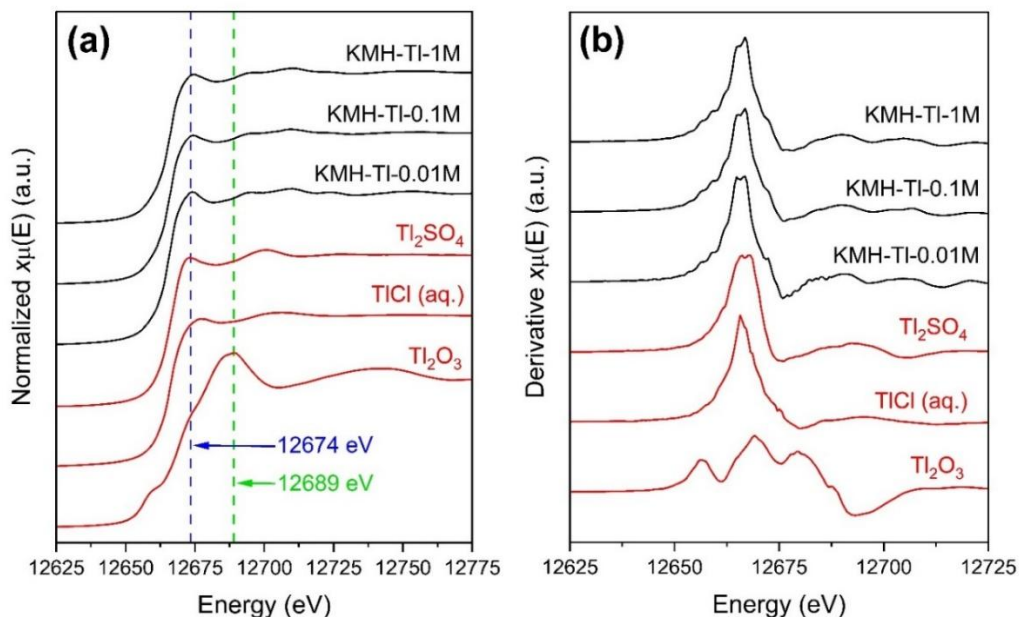


Figure 16. XANES spectra (a) and their derivatives (b) of the cryptomelane samples treated with Tl (in black) and thallium references (in red). The dotted blue line in (a) indicates the peak of the Tl(I) at about 12674 eV of the KMH-Tl samples, while the green dotted line the peak of the Tl(III) at 12689 eV of the Ti_2O_3 reference.

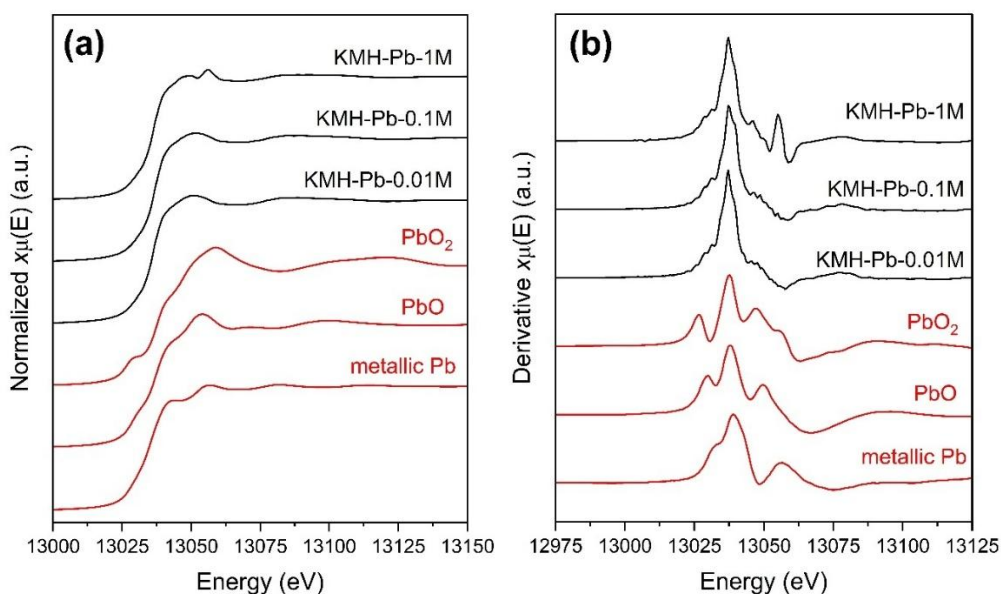


Figure 17. XANES spectra (a) and their derivatives (b) of the cryptomelane samples treated with Pb (in black) and lead references (in red). The dotted blue lines in (a) indicates the top of the XANES spectra of the cryptomelane samples (in blue), PbO (in green) and PbO_2 (in purple) at about 13051, 13054 and 13059 eV, respectively. Please note that a normalization problem gives rise to a spurious peak in the descending part of the absorption maximum in KMH-Pb-1M. This problem was caused by the high fluorescence emission of Pb, which affected the normalization in the XANES region.

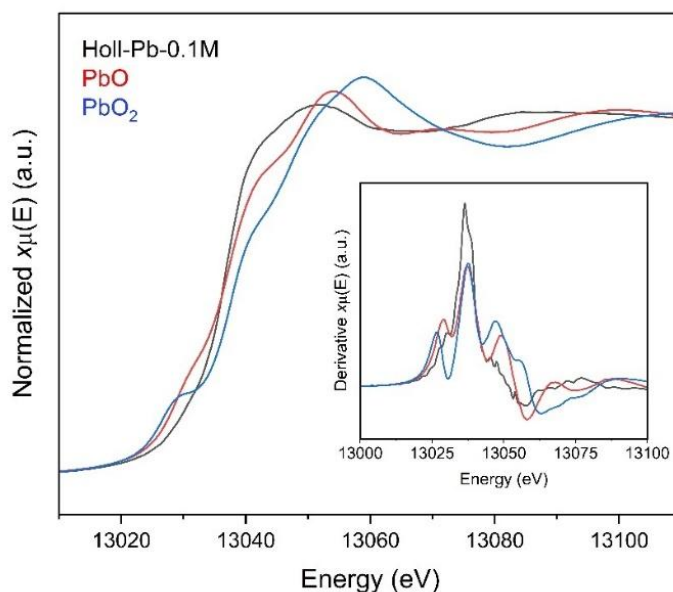


Figure 18. Comparison by the absorption Pb L_3 -edge of Holl-Pb-0.1M (taken as an example) and those of Pb(II) and Pb(IV) references, PbO and PbO₂, respectively.

The profile of the XANES spectra of zinc do not show any clear feature that can allow a comparison with those of the references (Fig. 19). Nonetheless, the absorption edges of the samples result in line with that of the ZnO, while that of the metallic zinc is placed at a slight lower energy.

However, Zn can be found only in the divalent and metallic state, and it is very improbable to find metallic zinc incorporated in a Mn oxide. All the zinc contained in the KMH samples was therefore considered Zn²⁺.

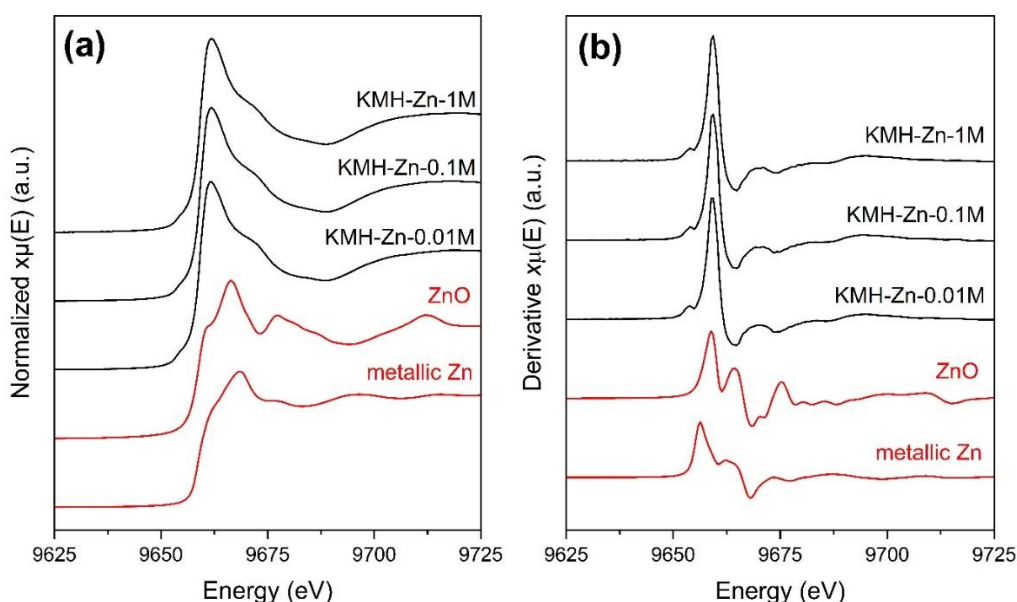


Figure 19. XANES spectra (a) and their derivatives (b) of the cryptomelane samples treated with Zn (in black) and zinc references (in red).

Extended X-ray absorption fine structure (EXAFS) was utilized to investigate the coordination environment of the three heavy metals in the KMH cryptomelane structure.

The structural model employed to calculate the theoretical paths was that of the synthetic tetragonal ($I4/m$) cryptomelane reported by Vicat et al. (1986), suitably modified by replacing the original potassium with the different heavy metals (HMs) as central scatterer atoms. Multiple sets of single scattering paths (typically HM-O and HM-Mn) with different interatomic distances (R) were calculated using the software FEFF (Ankudinov et al., 1998) and employed in the fitting process.

The first step of the data analysis of the Tl-treated samples was the fitting of the first shell considering a tetragonal structure and the thallium placed in the conventional A position, that is with two Tl-O paths with a coordination number (N) of 8 and 4, and interatomic distances in the range 2.7-2.8 and 3.3-3.4 Å, respectively. Since the first and second shell of all the samples were unable to be modelled independently, two Tl-Mn paths (N = 4 and R = 3.5-3.7 Å; N = 8 and R = 4.0-4.1 Å) were added to the fit. At this point, the monoclinic distortion and the displacive disorder of the Tl in the site A and A' found after the XRD analysis were considered. The first shell was then modelled with three Tl-O paths (with N = 4 and R of approximately 2.70, 2.95 and 3.30 Å), while the second shell with three Tl-Mn paths (with N = 4 and R of about 3.65, 3.90-4.00 and 4.15-4.25 Å).

Thirdly, further Tl-O and Tl-Mn paths were added in the attempt to fit farther coordination shells. In the KMH-Tl-1M sample, a single Tl-Mn path with N = 8 and R ~4.6 Å was found to improve the quality of the fit, while the addition of further paths resulted in destabilization of the fit. In KMH-Tl-0.1M and KMH-Tl-0.01M two different Tl-O paths with R in the range 4.1-4.5 Å and a Tl-Mn path with R ~ 4.7-4.9 Å were successfully added after the first and the second shell.

Despite the Fourier Transform functions of all the Tl-treated samples showed a further peak at about 5 Å (Fig 20b), the environment at such a distance resulted too chaotic to be modelled.

The EXAFS results of the Tl-treated samples are reported in Fig. 20 and Table 8.

For the Pb- and Zn-treated samples the approach was different. In comparison with potassium and thallium, lead and zinc are smaller cations. In eightfold coordination, the ionic radii of Zn^{2+} and Pb^{2+} are 0.9 and 1.29 Å, while those of K^+ and Tl^+ are 1.51 and 1.59, respectively (Shannon, 1976). If the A site environment, which lies in the centre of the hollandite tunnel, is quite suitable for the large monovalent cations, it may result too large for the smaller divalent cations. Indeed, preliminary fits considering Pb and Zn in an environment comparable to that of the A site did not produce any results.

On the other hand, various authors suggested that different cations, just on the basis of their size, can occupy different positions within the tunnel of the hollandite structure (e.g., Mentre and Abraham, 1996; Tompsett and Islam, 2013; Tumurugoti et al., 2021; Le et al., 2021). In particular, Mentre and Abraham (1996) found that Pb, in a synthetic hollandite with a VO_6 framework, can be displaced from the conventional position in the centre of the tunnel towards the walls of the octahedral framework. A similar displacement phenomenon was suggested by Le et al. (2021) for zinc in a synthetic Mn-hollandite on the basis of Density Functional Theory (DFT) calculations. As

a consequence, a model considering a positioning of Pb and Zn close to the octahedral walls, with typical interatomic distances (Pb-O in the range of 2.3-2.7 Å and Zn-O in the range of 1.9-2.3 Å) was used in the EXAFS fits. The interatomic distances and the coordination number of the first shell in the input model were set to achieve a bond valence sum (BVS) of ~2. The final results of the fit are reported in Table 9 and 10, and Fig. 21 and 22, for Pb and Zn respectively.

Table 8. Tl L_3 -edge EXAFS analysis results for the KMH Tl-treated samples.

KMH-Tl-1M									
S ₀ ²	0.7(4)	R-factor		0.03					
E ₀	2.0(3.6)								
Path	Tl-O	Tl-O	Tl-O	Tl-Mn	Tl-Mn	Tl-Mn	Tl-Mn		
R (Å)	2.69(5)	2.94(5)	3.28(6)	3.66(5)	3.96(5)	4.26(5)	4.63(7)		
N	4	4	4	4	4	4	8		
σ ² (Å ²)	0.01(1)	0.02(2)	0.01(1)	0.008(4)	0.014(8)	0.02(1)	0.022(9)		
(average first shell Tl-O distance = 2.97 Å)									
KMH-Tl-0.1M									
S ₀ ²	0.8(3)	R-factor		0.013					
E ₀	6.3(1.8)								
Path	Tl-O	Tl-O	Tl-O	Tl-Mn	Tl-Mn	Tl-Mn	Tl-O	Tl-O	Tl-Mn
R (Å)	2.73(3)	2.98(3)	3.28(3)	3.67(2)	3.93(3)	4.18(3)	4.36(9)	4.46(9)	4.89(11)
N	4	4	4	4	4	4	8	4	8
σ ² (Å ²)	0.02(1)	0.02(1)	0.01(1)	0.01(1)	0.01(1)	0.01(1)	0.05(2)	0.05(2)	0.04(2)
(average first shell Tl-O distance = 3.00 Å)									
KMH-Tl-0.01M									
S ₀ ²	0.9(6)	R-factor		0.03					
E ₀	0.8(3.9)								
Path	Tl-O	Tl-O	Tl-O	Tl-Mn	Tl-Mn	Tl-Mn	Tl-O	Tl-O	Tl-Mn
R (Å)	2.68(5)	2.94(5)	3.20(4)	3.62(4)	3.87(4)	4.07(4)	4.15(12)	4.25(13)	4.70(8)
N	4	4	4	4	4	4	8	4	8
σ ² (Å ²)	0.007(9)	0.007(9)	0.038(7)	0.008(5)	0.008(5)	0.008(5)	0.03(2)	0.03(2)	0.017(10)
(average first shell Tl-O distance = 2.94 Å)									

S_0^2 = amplitude reduction factor; E_0 = threshold energy; R = interatomic distance; N = coordination number; σ^2 = Debye-Waller factor (Å²). R-factor = $(\sum_i |y_{obs} - y_{calc}|) / (\sum_i y_{obs})$ (Roy and Gurman, 1999).

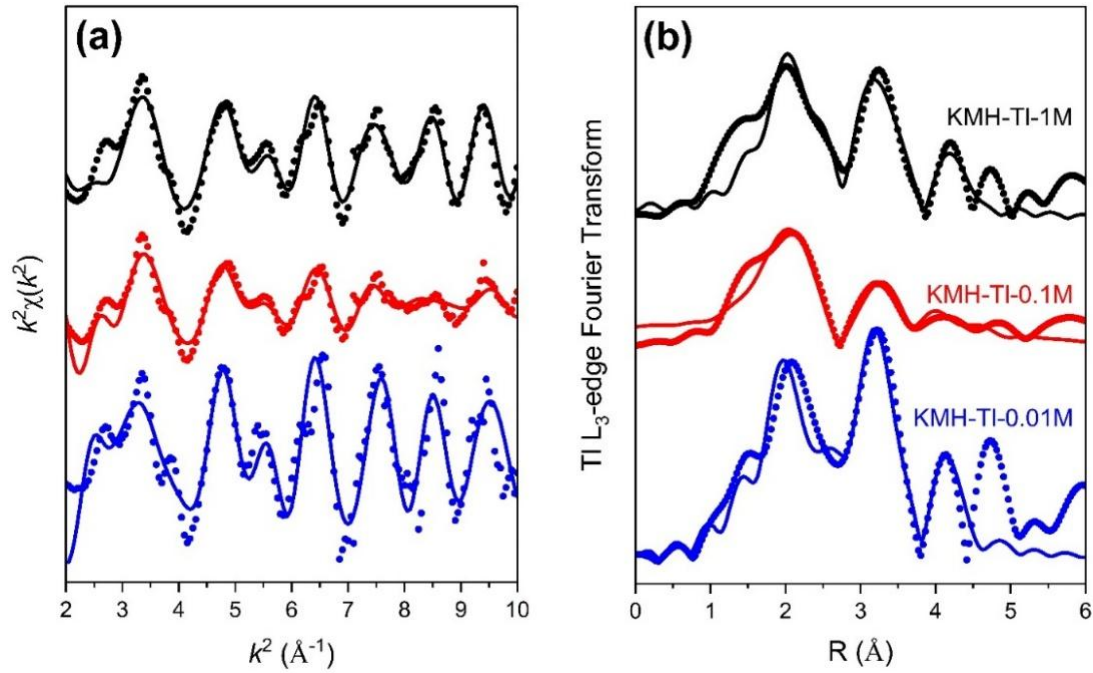


Figure 20. Tl L_3 -edge EXAFS (a) and Fourier transform (b) of the three Tl-treated samples. Experimental data are displayed by symbols and fit by solid lines. KMH-Tl-1M is reported in black, KMH-Tl-0.1M in red and KMH-Tl-0.01M in blue.

Table 9. Pb L_3 -edge EXAFS analysis results for the KMH Pb-treated samples.

KMH-Pb-1M				KMH-Pb-0.1M			
S_0^2	1.0(4)			S_0^2	1.1(7)		
E_0	2.1(2.8)			E_0	3.2(4.4)		
R-factor	0.015			R-factor	0.026		
BVS	2.06			BVS	1.92		
Path	Pb-O	Pb-O	Pb-Mn	Path	Pb-O	Pb-O	Pb-Mn
R (Å)	2.33(3)	2.59(6)	3.74(4)	R (Å)	2.37(5)	2.62(11)	3.76(6)
N	2	4	4	N	2	4	4
σ^2 (Å ²)	0.009(5)	0.027(9)	0.023(6)	σ^2 (Å ²)	0.01(1)	0.03(2)	0.02(1)
(average first shell Pb-O distance = 2.50 Å)				(average first shell Pb-O distance = 2.54 Å)			
KMH-Pb-0.01M							
S_0^2	1.1(9)						
E_0	2.5(5.4)						
R-factor	0.057						
BVS	1.94						
Path	Pb-O	Pb-O	Pb-Mn				
R (Å)	2.36(6)	2.62(11)	3.75(8)				
N	2	4	4				
σ^2 (Å ²)	0.01(1)	0.03(2)	0.02(1)				
(average first shell Pb-O distance = 2.53 Å)							

S_0^2 = amplitude reduction factor; E_0 = threshold energy; R = interatomic distance; N = coordination number; σ^2 = Debye-Waller factor (Å²). R-factor = $(\sum_i |y_{obs} - y_{calc}|) / (\sum_i y_{obs})$ (Roy and Gurman, 1999). BVS = bond valence sum for the first shell: $V_i = \sum_j S_{ij}$ with $S_{ij} = \exp\left(\frac{R_0 - R_{ij}}{b}\right)$; R_{ij} = distance between i and j atoms; R_0 and b values taken from Krivovichev and Brown (2001).

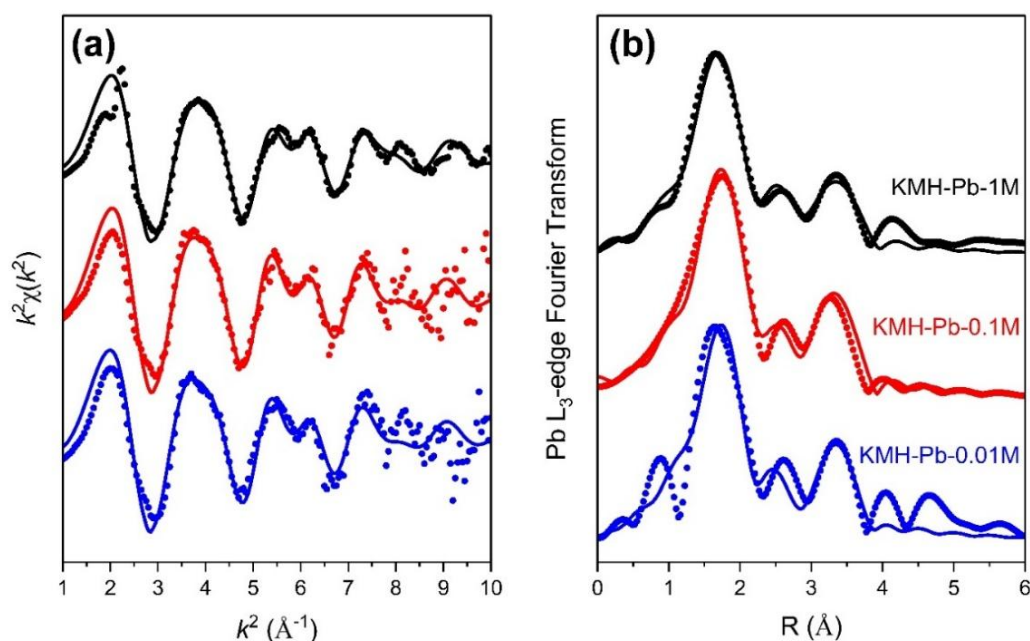


Figure 21. Pb L_3 -edge EXAFS (a) and Fourier transform (b) of the three Pb-treated samples. Experimental data are displayed by symbols and fit by solid lines. KMH-Pb-1M is reported in black, KMH-Pb-0.1M in red and KMH-Pb-0.01M in blue.

Table 10. Zn K-edge EXAFS analysis results for the KMH Zn-treated samples.

KMH-Zn-1M				KMH-Zn-0.1M			
S_0^2	0.9(1)			S_0^2	0.8(1)		
E_0	0.1(1.2)			E_0	0.2(1.4)		
R-factor	0.003			R-factor	0.004		
BVS	2.19			BVS	2.19		
Path	Zn-O	Zn-Mn	Zn-Mn	Path	Zn-O	Zn-Mn	Zn-Mn
R (Å)	2.00(1)	3.28(4)	3.42(2)	R (Å)	2.00(1)	3.28(4)	3.43(2)
N	5	2	2	N	5	3	2
σ^2 (Å ²)	0.010(2)	0.03(4)	0.005(2)	σ^2 (Å ²)	0.008(2)	0.014(8)	0.002(3)
KMH-Zn-0.01M							
S_0^2	0.8(1)						
E_0	0.03(1.97)						
R-factor	0.008						
BVS	2.25						
Path	Zn-O	Zn-Mn	Zn-Mn				
R (Å)	1.99(2)	3.25(5)	3.44(3)				
N	5	2	3				
σ^2 (Å ²)	0.007(3)	0.007(9)	0.003(4)				

S_0^2 = amplitude reduction factor; E_0 = threshold energy; R = interatomic distance; N = coordination number; σ^2 = Debye-Waller factor (Å²). R-factor = $(\sum_i |y_{obs} - y_{calc}|) / (\sum_i y_{obs})$ (Roy and Gurman, 1999). BVS = bond valence sum for the first shell: $V_i = \sum_j S_{ij}$ with $S_{ij} = \exp\left(\frac{R_0 - R_{ij}}{b}\right)$; R_{ij} = distance between i and j atoms; R_0 and b values taken from Brown and Altermatt (1985).

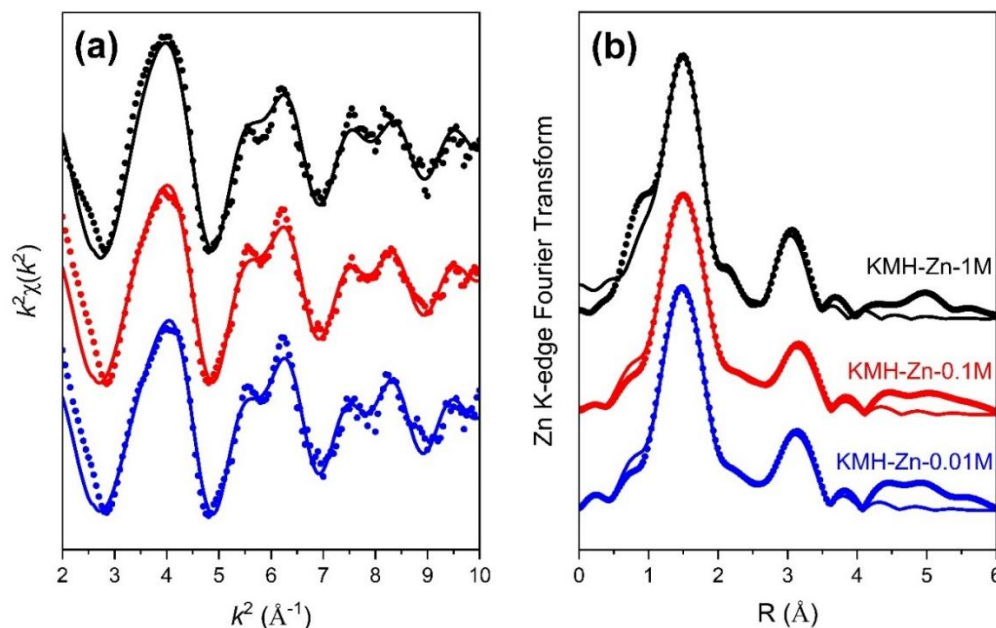


Figure 22. Zn K-edge EXAFS (a) and Fourier transform (b) of the three Zn-treated samples. Experimental data are displayed by symbols and fit by solid lines. KMH-Zn-1M is reported in black, KMH-Zn-0.1M in red and KMH-Zn-0.01M in blue.

7.6. Discussion

In this section, the discussion about the incorporation mechanisms of the three heavy metals in the cryptomelane structure is reported. First, the crystal structure and the chemical composition of the untreated KMH cryptomelane are introduced (7.7.1). Then, the effects of the heavy metal incorporation on the average structure, the local coordination environment and the ion exchange reactions are discussed in three consecutive sub-sections (7.7.2, 7.7.3 and 7.7.4), one for each heavy metal. A further paragraph (7.7.5) is dedicated to the final remarks.

7.7.1. Crystal Structure and Chemistry of the untreated KMH Cryptomelane

The KMH cryptomelane is monoclinic, space group $I2/m$. The unit cell parameters are in fair agreement with those found for a natural cryptomelane described by Post et al. (1982).

The K:Mn ratio measured by PIXE is about 0.17; the normalization on the basis of ΣM cations = 8 provided the potassium content, which is ~ 1.4 atom per formula unit. K was assigned to the tunnel site A ($2a$), in the special position (0, 0, 0). The latter site lies along the twofold axis of the monoclinic unit cell, coordinated by two set of four framework oxygen at 2.72(2) and 2.92(2) $\text{\AA}$ respectively.

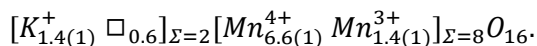
From FTIR analysis, the KMH cryptomelane resulted to be anhydrous, so A was considered occupied only by K^+ . The number of electrons in the A site found by XRD ($\sim 24 e^-$) is also

comparable with that brought by 1.4 *apfu* of K measured by PIXE ($\sim 26 e^-$), thus confirming the lack of water species within the tunnels.

The M1 and M2 framework sites are fully occupied by manganese in the two conventional oxidation states found in hollandites: Mn^{4+} and Mn^{3+} (e.g., Tumurugoti et al., 2021). Mn^{4+} and Mn^{3+} are considered disordered between M1 and M2. Both $M1O_6$ and $M2O_6$ octahedra resulted quite distorted (Table 7). The Mn-O distances in M1 ranges from 1.92(1) to 2.02(1) Å; those of M2 from 1.93(1) to 2.00 (3) Å. The bond angle variance is 176.01 deg² for M1 and 72.03 for M2. For comparison, the bond angle variances of the M1 and M2 octahedra for the natural cryptomelane studied by Post et al. (1982) were 35.5 and 35.7 deg², respectively, while the interatomic distances ranged between 1.88 and 1.95 for both octahedra. The average Mn-O distances are instead quite similar for the two cryptomelanes: $\langle M1-O \rangle = 1.96$ Å; $\langle M2-O \rangle = 1.95$ Å for KMH and $\langle M1-O \rangle = 1.92$ Å; $\langle M2-O \rangle = 1.92$ Å for the natural sample.

The large uncertainties inherent in the Rietveld refinements did not allow a detailed analysis of the octahedral distortion. Nevertheless, at least part of it can be attributed to a differential contraction of the crystal structure brought by the significant drop in temperature (from 600°C to room temperature) after the (high temperature) synthesis.

The $Mn^{4+}:Mn^{3+}$ ratio in the MO_6 octahedra was estimated to balance the chemical formula considering 1.4 positive charges brought by K^+ and 32 negative charges brought by O^{2-} . Since the Mn:O ratio is 1:2, for every K^+ , an Mn^{4+} reduces to Mn^{3+} . Therefore, the resulting chemical formula for the KMH cryptomelane is:



Having 1.4 *apfu* of potassium in A means that the site is occupied for approximately $\frac{2}{3}$. Nonetheless, if all the potassium was really placed in A, the distance between two adjacent sites (~ 2.87 Å) would be too short to allow the coexistence of two neighbouring K^+ ions, and the maximum occupancy of the site couldn't exceed $\frac{1}{2}$.

It was previously reported by many authors (e.g., Post and Burnham, 1986; Post and Bish, 1989; Tumurugoti et al., 2021) that tunnel cations can be slightly displaced from the expected position to minimize the electrostatic repulsion of neighbouring atoms or occupy satellite sites spread within the tunnel, thus increasing the total maximum occupancy of the tunnel itself. In particular, according to Post and Bish (1989), the displacement of a cation away from filled and toward vacant sites in adjacent unit cells can increase the total tunnel occupancy up to $\frac{2}{3}$, thus in good agreement with the occupancy calculated for the KMH cryptomelane. A homogeneous distribution of ~ 1.4 *apfu* of K along the tunnels axes would lead to K-K interatomic distances of about 3.8 Å, which is enough to avoid strong cationic repulsion phenomena. A displacement along the tunnel axis of the K^+ cations from the conventional A site position is then a plausible explanation that justifies the high potassium content in the KMH cryptomelane. Such a displacement could have been overlooked by the Rietveld refinement due to the poor degree of crystallinity of the powders and

the resulting broadening of the peak profiles, or due to the disordering brought by a not-so-homogeneous distribution of the atoms within the tunnels.

7.7.2. Incorporation Mechanisms of Thallium in Cryptomelane

Following the incorporation of thallium, the unit cell volume of cryptomelane increased from 277.06(4) Å³ to 280.24(5) Å³ for KMH-Tl-1M, 280.23(6) Å³ for KMH-Tl-0.1M and 277.68(3) Å³ for KMH-Tl-0.01M, corresponding to a relative change of +1.15(2); +1.14(2); +0.22(1) % (Table 2). These variations are consistent with the substitution of K⁺ (1.51 Å for ^{viii}K⁺) with the slightly larger cation Tl⁺ (1.59 Å for ^{viii}Tl⁺) (Shannon, 1976). The increase is indeed higher in the KMH-Tl-1M and KMH-Tl-0.1M, where the substitution is conspicuous, while it is lower in the KMH-Tl-0.01M, where the thallium concentration is significantly lower (Table 1).

In the XRD model, the electron density within the tunnels was attributed to two distinct sites, the conventional A site and the satellite A' site. A and A' lie on the tunnel axis at about 0.4 Å apart from each other to form an A'-A-A' row (Fig 24). Tl⁺ and K⁺ are considered disorderly distributed between the latter two tunnel site, that is to say along the A'-A-A' row.

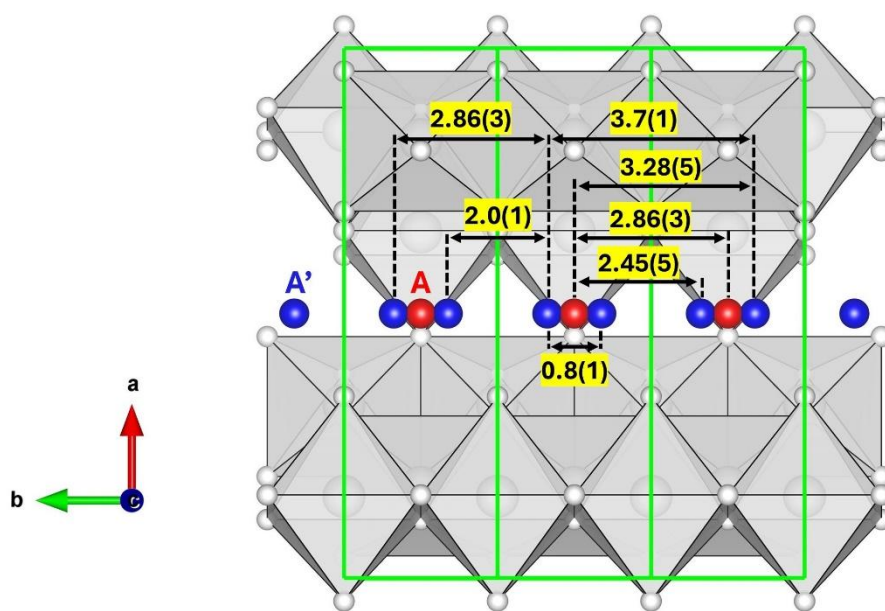
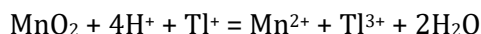


Figure 24. Distribution of cations along the tunnel of the KMH-Tl-1M sample. A and A' are painted in red and blue, respectively; the framework is reported in white; the green squares represent the unit cell boundaries. The distances between the different sites are reported in Å.

The presence of so close sites suggests a wide spatial distribution of cations and the occurrence of displacive disordering phenomena within the tunnels. Again, the distances between the A and A' sites (Fig. 24) suggest that at least 2/3 of the A'-A-A' rows are vacant, thus leading to a maximum tunnel atoms content of ~1.4 *apfu*. Nevertheless, the thallium contained in KMH-Tl-1M and KMH-

Tl-0.1M samples, measured by PIXE and normalized on the basis of ΣM cations = 8, stands at ~37 wt%, corresponding to ~1.3 *apfu*. In addition, the remaining potassium is about 0.4 *apfu*, leading to a total of ~1.7 *apfu* in the tunnel environment. The anomalously high occupancy of the tunnel environment is likely due to the contribution of the two impurities, detected by XRD in KMH-Tl-1M and KMH-Tl-0.1M, to the total amount of thallium. Indeed, the amorphous phase could have incorporated non negligible amounts of thallium during its formation, thus leading to an overestimation of the Tl content by PIXE. In addition, the KMH-Tl-1M samples contains small amounts of a Tl_2O_3 phase with the crystal structure of the mineral avicennite, apparently precipitated from the thallium solution during the ion exchange experiment, which might add a further contribution to the thallium content. The precipitation of avicennite was previously observed by Cruz-Hernández et al. (2019) during a sorption experiment involving birnessite powders and high concentrations of thallium. According to the latter authors, the oxidation of Tl(I) to Tl(III) is related to the sorption of Tl(I) over a vacant site of the layered structure of birnessite following the redox reaction:

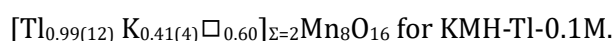
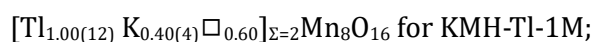


A similar reaction may have occurred during the ion exchange experiments in the 1M thallium solution involving the Mn(IV) cations of the hollandite framework. The vacant M sites on the surfaces of the cryptomelane particles may have triggered the redox reaction, leading to the formation of avicennite. The KMH-Tl-0.1M sample seems to be free of Tl_2O_3 . Nonetheless, weak peaks of small amounts of the latter compound could be hidden under the amorphous phase hump and the peaks of cryptomelane.

In conclusion, the interpretation of the thallium content given by PIXE resulted affected by the presence of two additional phases, whose contribution could not be evaluated.

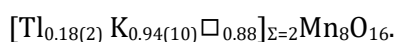
A measure of the amount of thallium incorporated by cryptomelane could be provided by number of electrons refined in the tunnel sites. Nevertheless, the number of electron of the A' site resulted to be quite unstable and the number of electrons calculated from the Rietveld Refinements was not considered completely reliable. As a consequence, the exact amount of thallium contained in the KMH-Tl-1M and KMH-Tl-0.1M samples couldn't be measured, but just estimated on the basis of some assumptions.

Assuming the filling of the tunnels at their maximum capacity ($\frac{2}{3}$ of the A'-A-A' rows occupied) and a $K^+ \rightarrow Tl^+$ exchange reaction (and then a stable $Mn^{4+}:Mn^{3+}$ ratio) the amount of incorporated thallium would be about 1 *apfu* for both cryptomelanes. The latter assumptions and the resulting logical implications lead to the following chemical formulae:



The PIXE results for the KMH-Tl-0.01M sample (which seems to be free from avicennite and amorphous phases) reported the incorporation of 0.18(2) *apfu* of thallium and the loss of ~0.3-0.5 *apfu* of K. As the amount of released potassium is not-negligibly higher than that of incorporated thallium, the Tl⁺:K⁺ ratio is not compatible with a K⁺ → Tl⁺ exchange reaction, thus implying a different reaction mechanism. It might be hypothesized that, at lower concentrations, the exchange reactions could involve H₂O, H₃O⁺, OH⁻ and H⁺. In particular, H⁺ ions bounded directly to the octahedral framework oxygens or H₃O⁺ placed within the tunnels may play an important role in the charge balancing (which in alternative would require the reduction of part of the Mn⁴⁺ to Mn³⁺). Unfortunately, the FTIR measurements were limited to the untreated and 1M-treated samples, so the latter hypothesis could not be verified. Future FTIR experiments will be planned to assess the hydration of the latter samples.

Anyway, for lack of evidence, the tunnel sites were considered anhydrous. The following chemical formula is then proposed for KMH-Tl-0.01M:



The significant level of disorder within the tunnels and the limits of XRD prevented a proper description of the thallium local environment, which was instead investigated in more detail by means of EXAFS.

The extent of the disorder was evidenced even by the latter technique, whose results showed high values of the amplitude reduction factors (*S*₀²) and Debye-Waller parameters (*σ*²).

The first shell of thallium was successfully modelled using three different Tl-O paths (each with N = 4) for all the Tl-treated samples. The shorter path resulted to be about 2.7 Å for all the samples, similarly to the A'-O distances, which are in the range of ~2.6-2.7 Å, but slightly shorter than the A-O distances, which are in the range of ~2.8-2.9 Å (Table 11). This fact supports the hypothesis of a systematic displacement of Tl along the tunnel axis from the conventional A site, which in turn justifies the high occupancy of the tunnel environment in terms of *apfu*.

The second path, which ranges from 2.9 to 3.0 Å for the three different Tl-treated samples, also resulted in fair agreement with different A-O and A'-O distances ranging between 2.8 and 3.1 Å. When longer (≥ 3 Å) Tl-O paths are considered, higher discrepancies arise between EXAFS and XRD results (Table 11).

In analogy with the first shell, the second shell of thallium was described employing three different Tl-Mn path, each with N = 4 and interatomic distances in the range of 3.6-4.3 Å. For the same reason of the first shell, probably the coordination environment is more complex than that described by the fits. Nonetheless, the EXAFS results are again in good agreement with those of XRD, which showed A-Mn and A'-Mn distances in the same range (Table 12). The clear presence of a manganese second shell, with interatomic distances comparable to those obtained by Rietveld refinements, confirm that most of the thallium is indeed contained within the tunnels, rather than adsorbed onto the surface of the particles or in the different impurities found by the XRD analysis.

Farther Tl-O and Tl-Mn were used in the EXAFS fits (Table 8) representing coordination shells beyond the second. Due to the high uncertainties in their interatomic distances, they cannot be effectively compared with the XRD results.

Table 11. Comparison between the A-O and A'-O distances obtained by XRD and Tl-O by EXAFS analysis. The interatomic distances are reported in Å.

KMH-Tl-1M		
XRD		EXAFS
A-O	A'-O	Tl-O
2.75(4) (x4)	2.56(4) (x2)	2.69(5) (x4)
2.84(4) (x4)	2.65(4) (x2)	2.94(5) (x4)
3.06(3) (x2)	2.98(5) (x2)	3.28(6) (x4)
3.93(2) (x2)	3.06(5) (x2)	
	3.08(3) (x2)	
	3.95(4) (x2)	
Average Tl-O distance		
A	A'	First shell
3.02	3.05	2.97
KMH-Tl-0.1M		
XRD		EXAFS
A-O	A'-O	Tl-O
2.89(3) (x4)	2.71(4) (x2)	2.73(3) (x4)
2.94(4) (x4)	2.76(4) (x2)	2.98(3) (x4)
3.25(2) (x2)	3.12(4) (x2)	3.28(3) (x4)
4.12(1) (x2)	3.17(4) (x2)	
	3.27(2) (x2)	
	4.14(2) (x2)	
Average Tl-O distance		
A	A'	First shell
3.17	3.20	3.00
KMH-Tl-0.01M		
XRD		EXAFS
A-O	A'-O	Tl-O
2.78(2) (x4)	2.60(4) (x2)	2.68(5) (x4)
2.90(2) (x4)	2.74(5) (x2)	2.94(5) (x4)
3.18(2) (x2)	2.98(6) (x2)	3.20(4) (x4)
3.88(1) (x2)	3.10(6) (x2)	
	3.20(2) (x2)	
	3.89(2) (x2)	
Average Tl-O distance		
A	A'	First shell
3.07	3.09	2.94

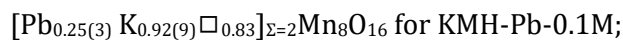
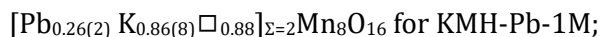
Table 12. Comparison between the A-M and A'-M distances obtained by XRD and Tl-Mn by EXAFS analysis. The interatomic distances are reported in Å.

KMH-Tl-1M		
XRD		EXAFS
A-M	A'-M	Tl-Mn
3.54(1) (x2)	3.56(1) (x2)	3.66(5) (x4)
3.65(1) (x2)	3.67 (1) (x2)	3.96(5) (x4)
4.11(1) (x4)	3.98(2) (x2)	4.26(5) (x4)
4.13(1) (x4)	4.01(1) (x2)	
	4.27(3) (x2)	
	4.29(3) (x2)	
Average Tl-O distance		
A-M	A'-M	Second shell
3.95	3.96	3.96
KMH-Tl-0.1M		
XRD		EXAFS
A-M	A'-M	Tl-Mn
3.55(1) (x2)	3.58(1) (x2)	3.67(5) (x3)
3.65(1) (x2)	3.67(1) (x2)	3.93(3) (x4)
4.03(1) (x4)	3.90(1) (x2)	4.18(3) (x4)
4.21(1) (x4)	4.08(1) (x2)	
	4.20(2) (x2)	
	4.31(2) (x2)	
Average Tl-O distance		
A-M	A'-M	Second shell
3.95	3.96	3.93
KMH-Tl-0.01M		
XRD		EXAFS
A-M	A'-M	Tl-Mn
3.54(1) (x2)	3.56(1) (x2)	3.62(4) (x4)
3.62(1) (x2)	3.63(1) (x2)	3.87(4) (x4)
4.06(1) (x4)	3.94(3) (x2)	4.07(4) (x4)
4.15(1) (x4)	4.04(3) (x2)	
	4.20(4) (x2)	
	4.29(4) (x2)	
Average Tl-O distance		
A-M	A'-M	Second shell
3.93	3.94	3.85

7.7.3. Incorporation Mechanisms of Lead in Cryptomelane

The KMH cryptomelane is able to incorporate good quantities of lead. The metal sorption amounts are 72(6), 69(8) and 41(6) mg/g for the samples treated with 1M, 0.1M and 0.01M solutions, respectively. The sorption amounts in the samples treated with 1M and 0.1M solutions are rather similar, thus suggesting that at such high concentrations the lead uptake reaches its maximum.

Formulae normalization obtained from PIXE data and based on ΣM cations = 8 yielded the following:



Considering the large uncertainties inherent in the PIXE measurements, the ratio between the incorporated lead and the released potassium is roughly 1:2 for KMH-Pb-1M and KMH-Pb-0.1M, thus suggesting an exchange reaction close to $2\text{K}^+ \rightarrow \text{Pb}^{2+}$. Since the *apfu* of released K^+ are twice those of incorporated Pb^{2+} , the number of vacancies in A increases after the ion exchanges (from 0.6 to 0.8-0.9 vacancies *pfu*). For this reason, the occupancy of the A site just exceeds $\frac{1}{2}$ for both KMH-Pb-1M and KMH-Pb-0.1M.

The sample treated with the 0.01M lead solution shows a Pb:K ratio lower than 1:2, leading to the same hypothesis issued for the KMH-Tl-0.01M sample (incorporation of H_3O^+ or H^+).

As a consequence of the treatment with the 1M, 0.1M lead solutions, the cell volume slightly decreased from 277.06(4) to 276.93(4) and 276.89(4) Å³, respectively, corresponding to a relative change of about -0.5%. This variation can be explained by the difference in the ionic radii between the original tunnel cation and the exchanged heavy metal. As Pb^{2+} has smaller ionic radii (1.29 for Pb^{2+}) than K^+ (1.51 Å for K^+), its occurrence within the tunnels replacing the original potassium led to a slight contraction of the octahedral framework and then to a general decrease in the unit cell volume (Shannon, 1976). In the KMH-Pb-0.01M, probably due to the lower Pb content, the variation resulted negligible, below the measurement uncertainty.

Due to its valence and small ionic radius, Pb^{2+} is expected to be displaced by the conventional A position (e.g., Post et al., 1982; Post and Burnham, 1986). Nonetheless, the presence of consistent amounts of potassium within the tunnels did not allow for the discrimination of the lead coordination environment by means of XRD. As a result, the electron density within the tunnels was modelled employing the conventional A site, which was considered occupied by both Pb^{2+} and K^+ . Important information on the local environment of lead was instead obtained by EXAFS analysis.

The first shell of the Pb-treated samples resulted characterized by two O atoms at about 2.3-2.4 Å and four further O atoms at ~2.6 Å for all the Pb-treated samples (Table 9). The Pb-O distances found by EXAFS are in good agreement with those reported for different lead minerals. For example, in minerals such as litharge [PbO] and blixite [$\text{Pb}_8\text{O}_5(\text{OH})_2\text{Cl}_4$] the Pb-O distances are approximately 2.3 Å (Boher et al., 1985; Krivovichev and Burns, 2006), while in the lead carbonate cerussite [PbCO_3] they are in the range 2.58-2.77 Å (Ye et al., 2012). Nevertheless, the Pb-O distances arrangements found by EXAFS are not compatible with Pb atoms placed in the conventional A site, which is instead surrounded by eight oxygens with Pb-O distances in the range of 2.8-2.9 Å. The reason of the discrepancies between EXAFS and XRD results (Table 13) involves

the different target of the two techniques. Indeed, eventual information provided by XRD on the local environment of specific elements inevitably arises from observations and considerations made on the average structure. In this particular case, due to the nature of the material, and then to the data quality, it was not possible to discriminate between the positions of Pb and K, nor to evaluate eventual displacement of lead from the conventional A position. On the opposite, since the X-ray absorption signal is inherently related to a specific scattering atom and its local coordination, even if they were marked by substantial limitations and large uncertainties, the EXAFS analyses provided a direct description of the average environment of Pb atoms only. In particular, two possible arrangements of Pb are compatible with the EXAFS results.

Table 13. Comparison between the A-O distances obtained by XRD and Pb-O by EXAFS analysis. The interatomic distances are reported in Å.

KMH-Pb-1M		KMH-Pb-0.1M		KMH-Pb-0.01M	
XRD (A site)	EXAFS (first shell)	XRD (A site)	EXAFS (first shell)	XRD (A site)	EXAFS (first shell)
2.80(3) (x4)	2.33(3) (x2)	2.78(3) (x4)	2.37(5) (x2)	2.80(3) (x4)	2.36(6) (x2)
2.85(3) (x4)	2.59(6) (x4)	2.87(2) (x4)	2.62(11) (x4)	2.84(3) (x4)	2.62(11) (x4)
Average Pb-O distance		Average Pb-O distance		Average Pb-O distance	
2.83	2.50	2.83	2.54	2.82	2.53

The first arrangement, depicted in Fig. 25a, involves a slight displacement of lead off the tunnel axis and toward the tunnel walls. Indeed, the two Pb-O paths employed to model the first shell (2.3-2.4 and ~2.6 Å) suggest a certain asymmetry of the Pb coordination environment, with the length of the shorter paths (2.3-2.4 Å), implying the approach of the lead atoms towards the oxygens of the octahedral framework. The large errors of S_0^2 , which is correlated with the coordination number (N), did not allow an unequivocal determination of the actual number of atoms in the first and second shell. Nevertheless, the bond valence sums (BVS), which are consistent with the predicted values for all the samples (Table 9), indicate that the so depicted first shell is a plausible environment for lead.

The lead displacement can be explained again considering the size of Pb^{2+} , which is too small to fit the large coordination polyhedron of the A site. A more peripheral environment, that is to say closer to the framework oxygens, may be more adequate for its size.

The asymmetry of the Pb coordination polyhedron can be also justified considering the effect of the stereoactive lone pair. In this scenario, the lone pair would be oriented toward the centre of the tunnel, in the opposite direction to the lead displacement, thus applying an electrostatic repulsion force against the oxygen atoms of the nearest wall.

This scenario already justifies all the EXAFS results. Nonetheless, as suggested by the large uncertainties on the path lengths and the high values of the Debye-Waller factors (Table 9), the

environment of lead could be even more complicated. In particular, a second arrangement of Pb atoms could be taken into account (Fig. 25b). This arrangement involves a displacement along the tunnel axis of the lead atoms from the conventional A site. Considering a shift of ~ 0.6 Å, Pb would be surrounded by four oxygen atoms of the octahedral framework at ~ 2.6 Å, in good agreement with the coordination number and the length of one of the paths used in the EXAFS analysis. The Pb atoms would then result at the top of a square pyramid with a O_4 basal plane perpendicular to the tunnel axis, in a coordination similar to that found in litharge (Boher et al., 1985). The Pb^{2+} lone pair activity would then be centred on the tunnel axis, in the opposite direction with respect to the O_4 basal plane.

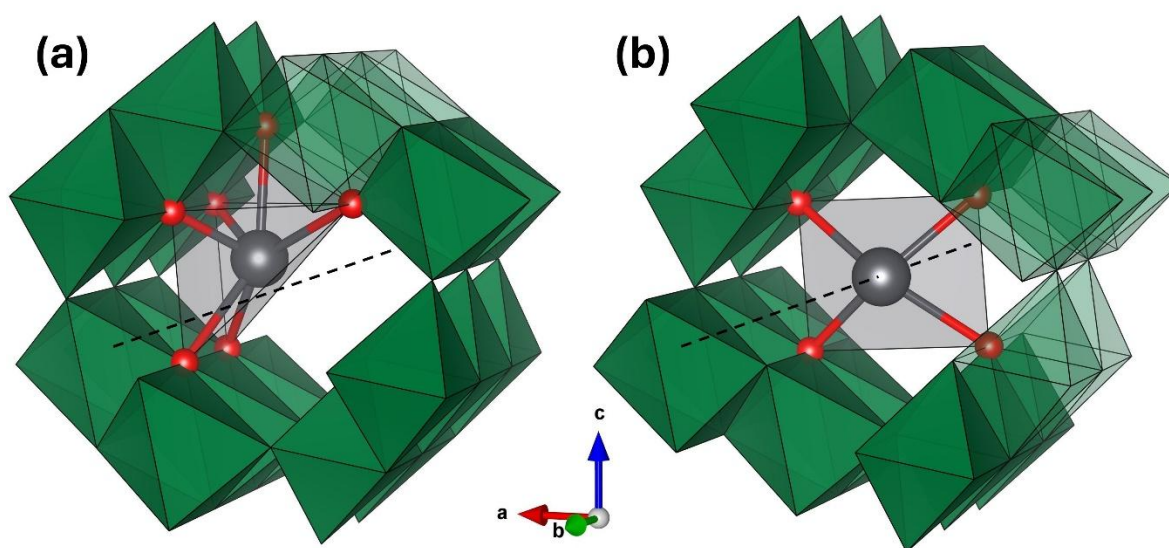


Figure 25. Possible arrangements of lead within the tunnel of the KMH Pb-treated samples: (a) Pb displaced off the tunnel axis toward the octahedral walls, and (b) Pb shifted along the tunnel axis.

The dotted black line represent the tunnel axis. Some of the MnO_6 octahedra (in green) are translucent to allow a better view of the Pb coordination polyhedra (in grey).

The latter coordination environment has been previously reported in literature for Pb contained in natural hollandite group minerals. Post et al. (1982) reported the case of a Pb-bearing hollandite where the tunnels were mainly occupied by barium and lead. While barium was located in the conventional A position, lead was displaced along the tunnel axis from A to be at about 2.65 Å from four framework oxygens. Post and Bish (1989) came with a similar result in their study on the crystal structure of coronadite [nominally $Pb(Mn^{4+}_6Mn^{3+}_2)O_{16}$], finding that lead was coordinated by four oxygen atoms (at ~ 2.61 Å) belonging to four different wall sides.

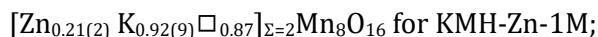
A combination of two different Pb arrangements was also reported by Mentre and Abraham (1996) for a synthetic $Pb_{1.32}V_{8.35}O_{16.7}$ hollandite. Specifically, the latter authors, following single-crystal X-ray diffraction measurements, were able to identify two different crystallographic sites hosting lead atoms. One was located near the conventional A site, shifted along the tunnel axis correspondingly to the second arrangement described above, and then to those reported by Post et al. (1982) and Post and Bish (1989). The second site was instead shifted from A toward one of

the edges of the square tunnel to become the top of a PbO₄ pyramid, less flat than that of the other coordination, with two Pb-O distances of 2.63(1) Å and other two of 2.83(1) Å. The latter coordination environment is close to that of the first arrangement described above which, despite being the result of a similar displacement, it nonetheless leads to a more complex coordination with a greater coordination number.

In conclusion, the first arrangement, with its more complex coordination encompassing both the Pb-O paths used in the fits, already explains all the EXAFS data. However, given the remarkable disorder highlighted by the EXAFS analysis and the findings of Mentre and Abraham (1996), a double coordination environment for lead is a valid option.

7.7.4. Incorporation Mechanisms of Zinc in Cryptomelane

The KMH cryptomelane incorporated good amounts of zinc. The Zn and K concentrations in the cryptomelane powders were normalized on the basis of ΣM cations = 8, giving a zinc content of 0.21(2), 0.19(2) and 0.16(2) *apfu* and a K content of 0.92(9), 0.94(9) and 0.95(9) for the samples treated with 1M, 0.1M and 0.01M solutions, respectively. The zinc contents found by PIXE correspond to a Zn sorption amount of 18(2), 17(2) and 14(2) mg/g for KMH-Zn-1M, KMH-Zn-0.1M and KMH-Zn-0.01M, respectively. The sorption amounts of zinc in the sample treated with 1M and 0.1M solutions are rather similar, thus suggesting that at such high concentrations the zinc loading reach its maximum for this particular cryptomelane. All said that, the chemical formulae for the different samples are reported as follows:



In the 1M and 0.1M treated samples the incorporated zinc/released potassium ratio is approximately 1:2, thus suggesting an exchange reaction $2\text{K}^+ \rightarrow \text{Zn}^{2+}$, which is in good agreement with that proposed by Cui et al. (2018) for the reversible intercalation of Zn in microspheres of synthetic cryptomelane in their work on aqueous zinc ion batteries. Such a reaction leads to an increase in the number of vacancies in A (from 0.6 to about 0.9 vacancies *pfu*). As a result, the occupancy of the A site just exceeds ½ for both KMH-Zn-1M and KMH-Zn-0.1M.

The KMH-Zn-0.01M shows an incorporated-zinc/ released-potassium ratio slightly lower than 1:2, thus suggesting the possible incorporation small amounts of H₃O⁺ or H⁺.

After the treatment with the 1M, 0.1M and 0.01M zinc solutions, the cell volume decreased to 276.75(4), 276.82(4) and 276.89(4) Å³, respectively, corresponding to relative changes ranging from about -0.06 to -0.11% (Table 2). These variations are in good agreement with the substitution

of K^+ (ionic radius of $^{VIII}K^+ = 1.51 \text{ \AA}$) with the rather smaller Zn^{2+} (ionic radius of $^{VIII}Zn^{2+} = 0.9 \text{ \AA}$) in the tunnel environment, which leads to a slight contraction of the octahedral framework and therefore in the unit cell volume (Shannon, 1976).

Since the coordination environment of the A site would be too wide for small, divalent cations, Zn^{2+} is not expected to be found in the latter, conventional position (Sinclair et al., 1980; Post and Burnham, 1986; Le et al., 2021). Nevertheless, no information in this regard could be obtained from the Rietveld refinements. Indeed, the coexistence of conspicuous amounts of potassium did not allow for the discrimination of the zinc coordination environment by means of XRD, and the electron density within the tunnels was modelled employing just the conventional A site, which was considered occupied by both Zn^{2+} and K^+ . The local environment of zinc was then investigated in detail by means of EXAFS.

The first shell of zinc was described using a single path with Zn-O distance of $\sim 2.0 \text{ \AA}$ and $N = 5$ for all the Zn-treated samples (Table 5). Such a coordination environment is quite consistent with the values predicted using the bond valence sum (BVS). The length of the Zn-O path is also in good agreement with the interatomic distances found for different zinc minerals. For example, in zincite $[ZnO]$ zinc atoms is in tetrahedral coordination with Zn-O distances of $2 \text{ \AA}$ (Kihara and Donnay, 1985), while in smithsonite $[ZnCO_3]$ it is found in octahedral coordination with Zn-O distances of $2.1 \text{ \AA}$ (Effenberger et al., 1981). The Zn-O distances found by EXAFS are significantly shorter than those considering the metal placed in the conventional A site, indicating that zinc is strongly displaced from the centre of the tunnels.

Le et al. (2021), in their work on the discharging behaviour of a synthetic hollandite in a zinc-ion battery, proposed a theoretical model based on the Density Functional Theory (DFT) showing the optimized structure of a hydration-free ideal $Zn_xMn_8O_{16}$ hollandite. From a thermodynamic perspective, for $x = 1$, the incorporated zinc resulted to prefer a site ($8h$, in a tetragonal $I4/m$ hollandite; $4i$ in a monoclinic $I2/m$ structure) located near the (100)-oriented tunnel edges and coordinated by five framework oxygens.

In the Zn-treated KMH samples, if we consider a shift of approximately $1.9 \text{ \AA}$ along the (100) direction, thus applying a displacement close to that predicted by Le et al. (2021), zinc would be coordinated by five framework oxygens forming a rectangular pyramid, with the oxygens placed at the five vertices and zinc at the centre of the rectangular base (Fig 26). In such an environment, the Zn-O distances would range from 1.93 to $2.12 \text{ \AA}$, with an average bond length of $2.07 \text{ \AA}$.

This scenario is in good agreement with the EXAFS observations. The discrepancies between the latter, strongly asymmetrical, arrangement of interatomic distances and the EXAFS results can be justified considering that the just discussed scenario does not involve any local distortion of the framework due to the presence of zinc. Such an approach of zinc to the tunnel walls, indeed, is expected to apply an electrostatic repulsion force against the framework manganese, thus producing a local rearrangement of the MnO_6 octahedra. The same theoretical model of Le et al. (2021) shows that the degree of distortion of the structure increases with the increasing zinc content (until the breakup of octahedral walls in proximity of the Zn ions, no less).

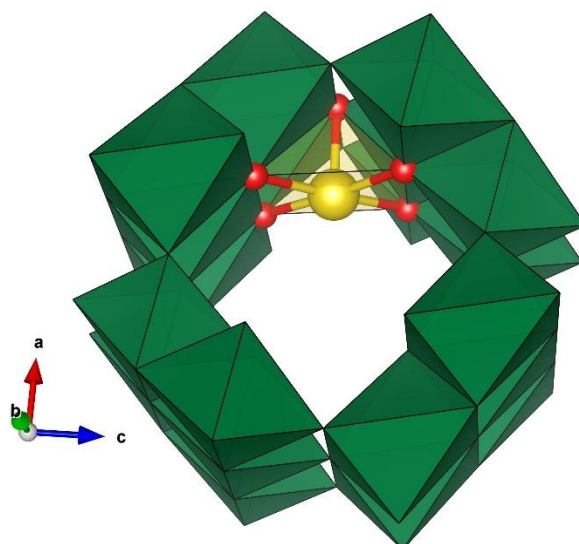


Figure 26. Local environment of zinc (in yellow), as suggested by EXAFS analysis.

The local deformation of the octahedral walls was indeed recorded by the EXAFS signal. Considering the marked displacement of Zn toward the tunnel walls, if the octahedral framework remained still and rigid, the Zn-Mn distances should proportionally decrease to theoretical values of 2.1-2.6 Å, which are evidently unrealistic. However, the EXAFS results show Mn-Zn distances in the range of 3.2-3.5 Å, which is a short but reasonable distances for cations such as Zn²⁺ and Mn^{3+/4+}.

7.7.5. Final remarks

The KMH cryptomelane demonstrated a high capacity for incorporating all three heavy metals, though with significant variations in sorption amounts and incorporation mechanisms.

At very high heavy metal concentrations (1M; 0.1M), the affinity showed by thallium for cryptomelane is greater than those of zinc and lead. In particular, the amount of incorporated thallium (in terms of *apfu*) is from four to five times greater than that of lead and zinc. The latter differences can be again explained by considering the similarities between K⁺ and Tl⁺, which are monovalent cations with a comparable size and the higher valence of Pb and Zn.

In the more diluted solutions (0.01M) the affinity of thallium, yet remaining the highest, is closer to that of the two other heavy metals, thus suggesting that the selectivity of the sorbent may decrease as the ion concentration in the exchanging solution decreases. In terms of moles, the amount of incorporated lead is comparable to that of zinc for all the concentrations and the much higher heavy metal sorption amount (*q_e*) (Table 14) in the Pb-treated samples is only due to the higher atomic weight of lead.

The EXAFS results highlighted the disordering of thallium and lead, showing high values of the amplitude reduction factors (*S₀²*) and Debye-Waller parameters (*σ²*). Conversely, the values of *S₀²*

and σ^2 for the Zn-treated samples, which fall within the normal range, suggest a more ordered distribution of zinc within the tunnels of the hollandite structure.

Table 14. Summary of the chemical formulae and the sorption amounts (q_e) of the whole sample set.

Sample	Chemical formula	q_e
KMH	$[\text{K}_{1.4(1)} \square_{0.6(1)}]_{\Sigma=2} \text{Mn}_8\text{O}_{16}$	–
KMH-Tl-1M	$[\text{Tl}_{1.00(12)} \text{K}_{0.40(4)} \square_{0.60(16)}]_{\Sigma=2} \text{Mn}_8\text{O}_{16}$	272(33) [†]
KMH-Tl-0.1M	$[\text{Tl}_{0.99(12)} \text{K}_{0.41(4)} \square_{0.60(16)}]_{\Sigma=2} \text{Mn}_8\text{O}_{16}$	270(33) [†]
KMH-Tl-0.01M	$[\text{Tl}_{0.18(2)} \text{K}_{0.94(10)} \square_{0.88(12)}]_{\Sigma=2} \text{Mn}_8\text{O}_{16}$	49(5)
KMH-Pb-1M	$[\text{Pb}_{0.26(2)} \text{K}_{0.86(8)} \square_{0.88(10)}]_{\Sigma=2} \text{Mn}_8\text{O}_{16}$	72(6)
KMH-Pb-0.1M	$[\text{Pb}_{0.25(3)} \text{K}_{0.92(9)} \square_{0.83(12)}]_{\Sigma=2} \text{Mn}_8\text{O}_{16}$	69(8)
KMH-Pb-0.01M	$[\text{Pb}_{0.15(2)} \text{K}_{0.95(10)} \square_{0.90(12)}]_{\Sigma=2} \text{Mn}_8\text{O}_{16}$	41(6)
KMH-Zn-1M	$[\text{Zn}_{0.21(2)} \text{K}_{0.92(9)} \square_{0.87(11)}]_{\Sigma=2} \text{Mn}_8\text{O}_{16}$	18(2)
KMH-Zn-0.1M	$[\text{Zn}_{0.19(2)} \text{K}_{0.94(9)} \square_{0.87(11)}]_{\Sigma=2} \text{Mn}_8\text{O}_{16}$	17(2)
KMH-Zn-0.01M	$[\text{Zn}_{0.16(2)} \text{K}_{0.95(9)} \square_{0.89(7)}]_{\Sigma=2} \text{Mn}_8\text{O}_{16}$	14(2)

q_e = sorption amount (mg/g) of heavy metals in KHM.
[†] Estimated assuming an exchange reaction $\text{K}^+ \rightarrow \text{Tl}^+$.

The positioning of the different metals within the tunnels resulted mainly determined by the ionic radii of the single metals. Tl^+ resulted placed at the centre of the tunnel, along the tunnel axis, slightly shifted from the conventional A site. Pb^{2+} show two possible concurrent arrangements where some cations might be located along the tunnel axis while others could be slightly displaced toward the tunnel walls. Zn^{2+} is instead strongly displaced towards the octahedral walls.

7.8. References

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8. Imbibition Experiments in Diluted Solutions

In the previous chapters, the results of a deep investigation on the incorporation mechanisms of thallium, lead and zinc within the crystal structure of microlite, elsmoreite and cryptomelane were presented. In the past experiments, to maximise the extent of the ion exchanges and their effects on the crystal structure of the three sorbents, highly concentrated solutions of heavy metals (in the range of 0.01-1 M) were employed.

Nonetheless, the latter concentrations are considered extremely high even for the most polluted environments. In mine drainage and industrial and urban wastewaters, the heavy metals, although still posing a severe risk to human health, usually occur in concentrations of several orders of magnitude lower than those used in the previous ion exchange experiments (see chapter 3). In the present chapter, the results of a batch of imbibition experiments conducted using diluted solutions of heavy metals are presented.

Imbibition experiments consist of the immersion of a sorbent material in a solution containing a single heavy metal for a predetermined amount of time. Every few minutes, an aliquot of solution was collected for chemical analysis to investigate the kinetic of the reactions. The experiments were aimed at exploring the behaviour of the three sorbent materials facing heavy metals concentrations closer to that usually reported for polluted waters. They have been called ‘imbibition experiments’ rather than ‘ion exchange experiments’ because at low concentrations another removal mechanism competes (and it improves the removal performance) with the ion exchange: the adsorption, which is the adhesion of the heavy metal ions to the surface of the sorbent particles (e.g., Arora, 2019; Chai et al., 2021).

The experiments and the chemical analysis presented in this chapter were performed at the Centro Ricerche Ecotec.

8.1. Imbibition Experiments and ICP-MS Analysis

Each imbibition experiment was conducted in 100 mL of a 10-20 mg/L heavy metal solution. The solutions were prepared by diluting 1-2 ml of a 1000 mg/L HMs ICP standard solution in a 100 mL volumetric flask using ultrapure water. Specifically, the utilized standard solutions were:

- Thallium ICP standard at 1000 mg/L, water with diluted nitric acid [HNO₃], provided by Ultra Scientific.
- Lead ICP standard at 1000 mg/L, Lead (II) nitrate [Pb(NO₃)₂] in 2-3% nitric acid [HNO₃] solution, provided by Sigma-Aldrich.
- Zinc ICP standard at 1000 mg/L, Zinc (II) nitrate [Zn(NO₃)₂] in 2-3% nitric acid [HNO₃] solution, provided by Sigma-Aldrich.

The amount of sorbent material powders used in a single experiment was 200 mg. The powders were immersed in the 100 mL heavy metal solution contained in a 150 mL borosilicate glass

beaker. The solution was kept under magnetic stirring at 1000 rpm for the whole duration of the experiment.

After 1, 5, 10, 15, 20, 25, 30, 45, 60 and 120 minutes, 1.5 mL of the reacting solution was collected and centrifugated at 4260 rpm for 1 min. After the centrifugation, about 1 mL of the separated solution was picked up using a plastic syringe with a stainless steel needle, filtered with a 0.22 μm mixed cellulose esters syringe and stored in a 1.5 mL plastic vial. The solid material precipitated after the centrifugation was readily reintroduced in the reacting solution.

Immediately after the end of the imbibition experiment, an aliquot of 0.5 mL of liquid was taken from every sample and diluted in a 20 mL volumetric flask employing a 2% nitric acid [HNO_3] solution (1:40 dilution) for ICP-MS analysis. An aliquot of 0.5 mL was also picked up before the start of the experiments (and diluted with 2% nitric acid following the same 1:40 ratio) to measure the precise initial concentration of the solution.

The results of the chemical analysis are reported in Table 1.

Table 1. Results of the ICP-MS chemical analysis.

t (min)	KTP microlite			NWP elsmoreite			KMH cryptomelane		
	Tl (mg/L)	Pb (mg/L)	Zn (mg/L)	Tl (mg/L)	Pb (mg/L)	Zn (mg/L)	Tl (mg/L)	Pb (mg/L)	Zn (mg/L)
0	23.15	12.13	9.60	11.52	12.19	9.49	11.25	13.12	9.33
1	5.32	3.00	0.06	0.01	5.05	8.96	0.02	0.03	0.03
5	4.19	0.06	0.16	0.01	1.93	8.55	0.01	0.02	0.01
10	3.54	0.05	0.26	0.01	0.03	8.63	0.01	0.02	0.00
15	3.23	0.02	0.26	0.01	0.01	8.57	0.01	0.02	0.02
20	3.02	0.03	0.20	0.01	0.02	8.42	0.01	0.02	0.01
25	2.85	0.02	0.25	0.00	0.01	8.55	0.01	0.01	0.01
30	2.68	0.02	0.34	0.00	0.02	8.50	0.01	0.02	0.02
45	2.43	0.02	0.40	0.00	0.01	8.48	0.01	0.01	0.02
60	2.31	0.02	0.47	0.00	0.02	8.45	0.00	0.01	0.02
120	2.09	0.02	0.33	0.01	0.02	8.30	0.00	0.01	0.03
% of heavy metal removed by the respective sorbent material [†] .									
1 min	77.00	75.25	99.33	99.94	58.57	5.61	99.84	99.80	99.72
10 min	84.71	99.56	97.34	99.95	99.74	9.03	99.93	99.88	99.98
120 min	90.98	99.87	96.61	99.95	99.87	12.56	99.96	99.89	99.63
[†] Assuming that the variation of the heavy metal concentrations were related to incorporation and adsorption phenomena. Note: Error % < 20 for Tl and Pb; < 10% for Zn.									

8.2. Discussion and Future Perspectives

The ICP-MS chemical analysis provided the concentrations of the residual solutions collected at fixed intervals of time after the beginning of the imbibition. Since there was no other component of the system, nor physical or chemical phenomena that could change the concentration of the heavy metals, every variation of concentration can be realistically attributed to the sorbent materials. In particular, the reduction of the heavy metal concentrations were all ascribed to the incorporation within the structural microporosities or to the adsorption onto the particles surface of the sorbents. Table 1 therefore results in a reasonable overview of the ability of the three sorbent materials to remove heavy metals from diluted solutions.

The KTP microlite showed good ability in removing all three heavy metals. The removal efficiency of thallium resulted lower (~91% of Tl removed after two hours) than that of lead and zinc (~99% of Pb and ~97% of Zn removed only ten minutes). This may be explained considering that the concentration of the Tl starting solution was about 20 mg/L, instead of 10 mg/L as in all other samples.

The NWP elsmoreite resulted very efficient in removing thallium, with 99.9% of Tl removed after just one minute of imbibition. It is slower but still efficient in the removal of lead, with 58% of Pb removed after 1 minute and 99.7% after 5 minutes. The elsmoreite resulted instead quite ineffective in the zinc clearing, with only ~13% of Zn subtracted from the solution after two hours. The KMH cryptomelane showed an impressive rapidity and efficiency in the removal of all the three heavy metals, with 99.7-99.8% of metal removed after only one minute.

In conclusion, microlite, elsmoreite and cryptomelane show great abilities in the removal of all the tested heavy metals (with the sole exception of elsmoreite for zinc) even in diluted solutions. Nevertheless, the experiments presented in this chapter are just a preliminary view on a very complex system that, outside the laboratory rooms, can be affected by different physical-chemical phenomena and complicated by countless variables.

For example, all the experiments have been conducted in ultrapure water, contaminated by a single, selected heavy metal. However, both polluted and unpolluted waters usually show a very complex chemistry, containing a wide range of anions and cations. The competition between different ions may (e.g., Srivastava et al., 2005) or may not (e.g., Benjamin and Leckie, 1981) affect the removal efficiency of a sorbent material for a particular heavy metal. Future experiments need to be addressed to evaluate the competition among the selected heavy metals and harmless ions commonly found in water environments (e.g., K^+ , Na^+ , Ca^{2+} , Mg^{2+} , Fe^{2+}).

Another important variable which was intentionally ruled out in course of the present work is the pH of the exchanging solution. As the concentrations of H^+ and OH^- ions can affect the removal performance of the sorbents, controlling the pH of the contaminated solution may thus lead to an improvement of the sorbents efficiency (e.g., Mu et al., 2015).

In addition to the chemical composition of the solutions, also that of the sorbent materials play an important role in the heavy metal ions removal. In the present work, the chemistry of the sorbents has been intentionally kept as simple as possible. Nonetheless, it has been shown that the doping

of the sorbent crystal structure with small amounts of different elements can modify the behaviour of the sorbent itself in relation to a specific ion (e.g., Mu et al., 2015). Since both pyrochlore and hollandite frameworks can accommodate a wide range of ions, tailoring the chemical composition of the sorbents opens a vast series of possibility to increase the efficiency and the selectivity of the sorbents. Further tuning of the physical-chemical variables (such as pH) could significantly enhance both the efficiency and selectivity of sorbents toward specific heavy metal targets.

Future experiments should take into consideration to work at a higher level of complexity, primarily to evaluate the effects of different thermodynamic conditions and competitor ions on the removal performance of the sorbents. Another opportunity for future experiments would be to use a combination of different sorbent materials for a selective removal of different heavy metals.

In conclusion, the points outlined above represent the initial steps of a more complex and lasting work that might lead to important results in the protection of the environment.

8.3. References

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9. Conclusions

The ability of synthetic analogues of microlite, elsmoreite and cryptomelane to incorporate thallium, lead and zinc and the mechanisms by which these elements are accommodated within their structures have been investigated. Microcrystalline powders of microlite (KTP) and elsmoreite (NWP) pyrochlores were obtained following hydrothermal procedures, while cryptomelane (KMH) was produced employing a new two-step high-temperature solid-state procedure. After a batch of ion exchange experiments, conducted using concentrated solutions of the three heavy metals, the ion exchange mechanisms and the effects of the heavy metal incorporation have been studied from two different perspectives:

- The average structure of both treated and untreated samples has been determined by means of XRD analysis.
- A thorough understanding of the local structure of the incorporated heavy metals was achieved by means of EXAFS analysis.

The structural investigations were followed by PIXE analysis, which provided the chemical composition of both treated and untreated samples, and FTIR measurements, which revealed the presence of water species in the two pyrochlores.

The picture emerging from such combination of structural and chemical analyses is that of an extremely chaotic tunnel environment, where the tunnel occupants are displaced from the conventional crystallographic positions and disordered around a constellation of satellite sites. Despite this, it was still possible to achieve a quite accurate overview of the coordination of the selected heavy metals, the structural response of the octahedral frameworks and the reorganization of the tunnel environment after the ion exchange reactions. Important considerations on the role of water species in the pyrochlore structure were also made, thus providing new information on an elusive but significant issue.

A separate chapter was dedicated to a series of preliminary imbibition experiments using diluted solutions of thallium, lead and zinc. ICP-MS analysis conducted on residual solutions revealed that the removal performances of microlite, elsmoreite and cryptomelane are excellent for low heavy metal concentrations.

As a whole, the work provides a good illustration of the ion exchange mechanisms in pyrochlore and hollandite structures, shedding new light on the possibility to employ the latter materials for future application in the remediation of polluted waters.

Acknowledgements

This thesis was financially supported by the program “PON Ricerca e Innovazione”, which was promoted by the Ministero dell'Università e della Ricerca (MUR) and co-financed by the European Structural and Investment Funds (ESIF), specifically the European Social Fund (ESF) and the European Regional Development Fund (ERDF).

A key partner in the project was the private company Ecotec Gestione Impianti Srl, which contributed by providing its facility labs (Centro Ricerche Ecotec, Zona Industriale Macchiareddu, Uta, Cagliari province, Italy) and the expertise of its research staff. In particular, I would like to acknowledge Mario Ragona, Carla Orrù, Arianna Casula, Riccardo Orrù and Lina Pusceddu for their precious help with the imbibition experiments and the ICP-MS analyses. I also extend a special thanks to Massimo Pisu for coordinating the collaboration with Ecotec.

Most of the structural analyses were conducted at ESRF, so I would like to thank the staff members of the BM08 and ID11 beamlines for the support during the lab shifts. They are Jacopo Orsilli, Alessandro Puri and James Ball. Special appreciation is extended to Francesco d'Acapito and Stefano Checchia for coordinating my work at ESRF and for the help provided in the planning of the experiments.

My biggest thanks go to Meriem Goudjil, who taught me the fundamentals of hydrothermal synthesis procedures and helped me with the ion exchange experiments, and Marta Morana, who provided a crucial aid with the Rietveld refinements and the revision of the thesis as co-supervisor. This project would not have been possible without them.

I'm very appreciative of Massimo Chiari for his support with the PIXE/PIGE analyses; Daniele Borrini for his assistance and full access to the petrology lab for synthesis and imbibition experiments; Laura Chelazzi (CRIST) and Laura Chiarantini (MEMA) for their aid with preliminary XRD characterizations and SEM imaging, respectively. I am also grateful to Prof. Bindi and Prof. Bonazzi for the useful advice and insights they provided, and for the contribution of their expertise to this work.

I am very grateful to Alice for all the time we spent chatting about minerals, for accompanying me to countless mineral fairs, and for helping me with the FTIR analyses.

I'd also like to extend my gratitude to my colleagues of the '*PhDs room*', who accompanied me throughout the whole PhD work, making my time spent at the University of Florence very enjoyable. They are, in random order, Gregorio, Rebecca, Alessia, Antonio, Gioia, Francesco, Federica, Martina, Sara, Diletta and several Francesche.

Finally, needed thanks are also due to Giovanni O. Lepore, who supervised this work.



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