



Assessment of Molybdenum and Antimony speciation in excavated rocks and soils from the Parisian basin using mineralogical and chemical analyses coupled to geochemical modelling

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1 **TITLE**

2 Assessment of Molybdenum and Antimony speciation in excavated rocks and soils from the Parisian
3 basin using mineralogical and chemical analyses coupled to geochemical modelling

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12 **HIGHLIGHTS**

13 Mo and Sb speciation in naturally contaminated excavated materials is characterized

14 Celestite plays a key role in Mo and Sb mobility in marly limestone samples

15 Associations with sulfides are not involved in Mo and Sb release at natural pH of the soils

16 Lime treatment changes Mo speciation and increases Mo mobility in tunnel excavation muck

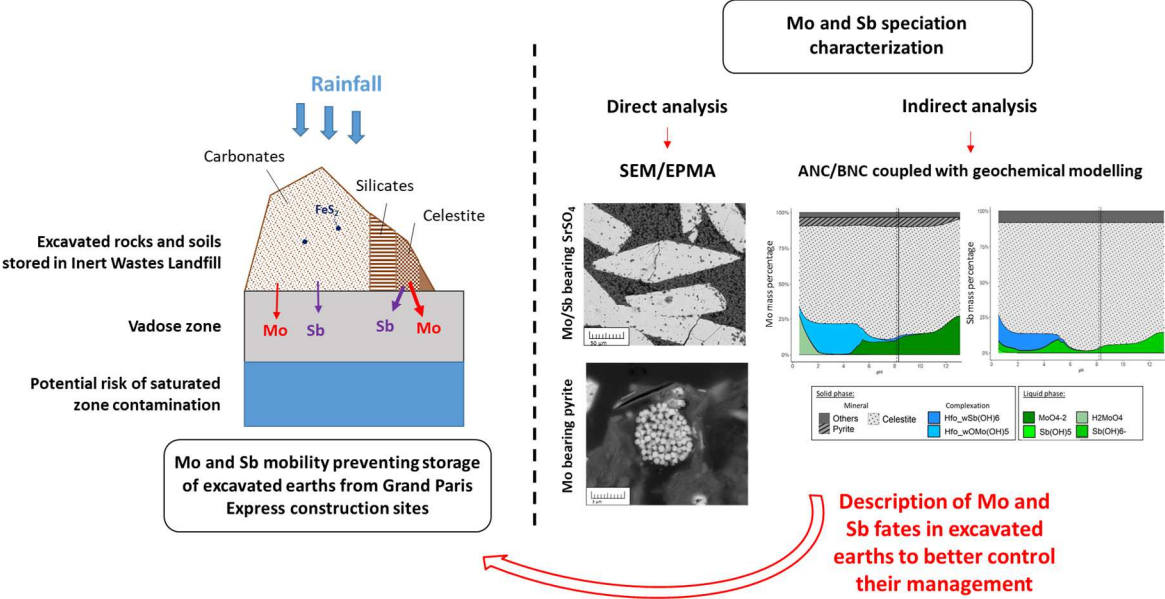
17 **KEYWORDS**

18 Molybdenum; Antimony; Excavated rocks and soils; Speciation; Geochemical Modelling

ABSTRACT

In the Parisian basin area, soils excavated from public works sites often reveal naturally occurring trace elements contaminations, especially in Molybdenum (Mo) and Antimony (Sb). More specifically, the relatively strong solubility of Mo and Sb in these excavated soils prevents them from being re-used or disposed of in inert waste type landfills according to the French regulation, which is based on leaching rather than total content. Furthermore, the observed total contents are in general relatively low making it difficult to determine correctly the speciation of the trace elements. Yet, this is a key information to estimate the potential environmental risks associated to Mo and/or Sb leaching.

Various direct and indirect methods of mineralogical and chemical characterizations were used in this study and coupled to geochemical modelling in the objective to determine the speciation and potential mobility of Mo and Sb in 4 samples of excavated rocks and soils from the Parisian basin. Three of them were raw materials, each one excavated in a single (but different) geological formation during classic earthworks. The fourth was a tunnel muck (a slurry) dug at the border between two geological formations and having undergone various treatments (e.g. liming) during the process of excavation. Studied samples all showed low total content of Mo and Sb. Mobility was particularly concerning for Mo in the carbonated sample (CS) and the tunnel muck (TM). Mo was found systematically carried by strontium sulfates (celestite, SrSO_4) in marly limestones samples. pH dependence leaching tests coupled to geochemical modelling confirmed celestite as a major sink of Mo, while also pointing out its influence on Sb speciation. In the calcareous sample, Mo and Sb mobility was mainly controlled by complexation onto iron oxides surfaces with high pH dependency. Furthermore, in this sample, correlations between Trace Elements (TE) and Sr concentrations were assumed to occur through incorporation in carbonates rather than through associations with celestite. Associations with iron sulfides were suggested to be responsible for a small fraction of total leachable Mo and only under basic conditions. Finally, geochemical modelling was used to describe accurately Mo and Sb speciations in the tunnel muck pointing out a more complex partitioning influenced by the treatment undergone during the excavation process. Results presented here suggested that Mo and Sb speciations show great similarities and vary significantly depending on the excavated material. It is also inferred that pH changes of materials especially expected for the alkaline tunnel muck could further increase TE mobility.



1. INTRODUCTION

Civil engineering works (road construction, tunnel digging, etc.) generate large volumes of excavated materials such as soils and rocks, which may reveal contaminations from anthropogenic or natural origins. In France, infrastructure and development projects generate each year over 110 million tons of excavated soils and rocks (ADEME, 2017). The Grand Paris Express Project (GPEP) is one of the major public works project in Europe with creation of 200 km of mainly underground train lines and almost 70 new train stations (SGP, 2019). As one of the main consequences of these works, a huge amount of soils and rocks will be excavated representing a 20% increase (40 million of tons) of solid waste production in the area (SGP, 2019). The bulk of these excavated soils is typically landfilled because, in accordance with the Waste Framework Directive (OJEU, 2008), these soils are considered as waste materials if they leave the excavation site. In this case, the demonstration of absence of contamination relies on reference to the inert-waste criteria of Annex II (OJEC, 2003) of the European Landfill Directive (OJEC, 1999).

Over the past decade, excavated soils reuse as secondary products for construction works (mainly as backfills materials) has been encouraged in accordance with the objective of 70% of reuse set by the European Commission (ADEME, 2017). However, although current national recommendations tend to frame the recycling of excavated soils coming from uncontaminated sites, a large amount is still systematically landfilled (BRGM, 2020), mainly because of the liabilities associated with their waste status. One obvious problem with this approach is that the inert-waste criteria were not set for natural soil materials but for waste materials (primarily construction and demolition; C&D waste). This systematical landfilling is mainly related to the lack of knowledge regarding the contaminant leaching behavior occurring in these soils. Indeed, historically, Trace Elements (TE) speciation studies have been carried out on more acute contaminations, often originated from anthropogenic activities (Halmi and Ahmad, 2014; He et al. 2012). Consequently, Molybdenum (Mo) and Antimony (Sb) speciation studies in natural soil and rock materials are scarce, mainly because of the low content of TE in these materials causing Detection Limit (DL) issues (Gourcy et al. 2011; Sterckeman et al., 2006).

Overall, Mo enrichment in rocks have mainly been recorded in shales and muds, while high concentrations in sandstones and carbonates are scarce (Smedley and Kinniburgh, 2017). Organic Matter (OM) plays an important role in Mo speciation through indirect (complexation favored by the presence of Fe-oxides associated with OM) and direct mechanisms (insertion of molybdate ions in organic sulfides macromolecules through covalent bonding) (Tribovillard et al. 2004). In areas where sulfate reduction occurs (*i.e.* strongly reducing conditions), Mo sulfides would form solid solutions in

pyrites, chalcopyrites or galena, rather than MoS_2 precipitation (Vorlicek et al. 2004 ; Harkness et al., 2017 ; Smedley and Kinniburgh, 2017). Further mobilization of Mo will then be linked with sulfides oxidation. In many cases, iron (Fe), aluminum (Al) and manganese (Mn) hydr-oxides are also inferred to control Mo mobility through sorption/desorption mechanisms (Smedley and Edmunds, 2002; Smedley et al. 2014). In such cases, water/rock interactions might cause high local concentrations in surface and groundwater since oxyanions retention at oxides surfaces strongly depends on pH and Eh conditions.

Natural Sb sources mainly come from specific environments such as hot springs, volcanic ore deposits or schists (Arai, 2010). It could be found either co-precipitated and associated with metal ores (pyrites, sulfosalts, oxides...) or as separate mineral ores (Roper et al. 2012; Wilson et al. 2010). A huge variety of primary mineral has been acknowledged with more than 200 species mostly sulfides and sulfosalts, among which stibnite (Sb_2S_3) is the main Sb ore (Wilson et al. 2010; Herath et al. 2017). Dissolution of such Sb sources often lead to enrichments, which could be mitigated by (co-)precipitation and/or adsorption phenomena, the latter being inferred as predominant when only low contamination occurs. Studies focused on Sb sorption on pure phases have shown that Mn, Al and Fe (hydr-)oxides might be the more important phases controlling Sb mobility in soils (Thanabalasingam and Pickering, 1990; Muller et al. 2002; Leuz et al. 2006b). As it has been seen for Mo, OM interactions should not be discarded when listing Sb retention factors although mechanisms are still unclear.

It is known that the geological characteristics of the Parisian basin often results in TE concentrations above the national geological background levels, in particular for Mo and more scarcely for Sb (Cabrerizo et al. 2020, Sterckeman et al., 2006). In a survey carried out in the northern Parisian basin (Sterckeman et al., 2006), Sb concentrations have been shown to be globally higher than the Upper Crust Continental (UCC) levels of $0.31 \text{ mg}\cdot\text{kg}^{-1}$ (Wedepohl, 1995). This enrichment was noticed in all geological layers studied but was more or less important depending on the parent materials composition. Hence, fluvial alluvial deposits and chalks from the later Cretaceous and Carboniferous limestones were inferred to be strongly concentrated in Sb (Sterckerman et al. 2006). As far as Mo is concerned, concentrations measured in sedimentary formations from the Parisian basin (Sterckeman et al. 2006) did not show an overall enrichment regarding UCC or regional geological background levels, which are commonly settled at $1.4 \text{ mg}\cdot\text{kg}^{-1}$ and between $0.04 \text{ mg}\cdot\text{kg}^{-1}$ and $1 \text{ mg}\cdot\text{kg}^{-1}$ respectively (Wedepohl, 1995; Gis Sol., 2011). However, enrichments have been noticed in particular geological layers such as the fluvial alluvial deposit, chalks from the later Cretaceous and limestones from the earlier Cretaceous, the Jurassic and the Carboniferous (Sterckeman et al. 2006). Mo and Sb enrichments all show correlations with fine silts and Al and Fe (hydr-)oxydes inferring that sand

fraction and carbonate minerals might act as a diluent for TE bearing phases. Such bearing phases could be mainly sulfides minerals (pyrites and chalcopyrites) for Mo (Cabrerizo et al. 2020). Finally, OM is also strongly correlated with Sb enrichment in the Parisian Basin while affinities are less clear in the case of Mo (Sterckeman et al. 2006; Gourcy et al. 2011). Except maybe for the topsoil layers, enrichments were not linked with anthropogenic activities. They might be originated from natural atmospheric fallout and/or alteration of the parent materials. In both cases, the high mobility of Mo and Sb allows them to percolate from the topsoil and fix in favoring environments (presence of OM, complexation at oxides surfaces...). This labile behavior is the critical parameter pointed out through evacuation of excavated soils and rocks in GPEP. Other studies involving a total number of close to 5900 leaching tests conducted on a series of excavated soil samples from the Parisian basin (unpublished) showed that Mo and Sb concentrations in the leachates were higher than the inert-waste criteria in 15% and 3.5% of cases respectively. These overall results hide high disparities between geological layers and are remarkable given the relatively low levels of TE total content recorded.

This paper reports in-depth investigations on Mo and Sb speciation in four excavated materials representative of TE release issues in GPEP: a calcareous soil with the highest Mo content, two marly limestones with lower but still significant Mo content and tunnel excavation muck. A combination of analytical tools and modelling approaches were used, which allowed to circumvent DL issues (total content in Sb and Mo are below $1 \text{ mg}\cdot\text{kg}^{-1}$ and below $11 \text{ mg}\cdot\text{kg}^{-1}$ respectively). Results were exploited and discussed to assess whether Mo and/or Sb mobility in these samples was controlled by particular interactions with identified mineral phases. The objective was to better understand the potential emissions from natural excavated soils for these TE to improve their conditions of management both in terms of reuse or landfilling.

2. MATERIALS AND METHODS

2.1. Samples

Three excavated rocks were collected by Bouygues Travaux Publics Company from construction sites in Paris area. The first one, hereafter referred to as calcareous sample (CS), was excavated during train station earthworks in Courbevoie (Hauts-de-Seine, France) in March 2018 and was mainly composed of carbonates from the Eocene period (Lutetien inferior, prof. 24 – 27 m). The two marly limestone samples (MLS-A and MLS-B) were both extracted in Vitry-sur-Seine (Val-de-Marne, France) in March and July 2018 respectively. MLS-A was also extracted during train station earthworks corresponding to Eocene (Lutetien superior, prof. 13 – 14 m) while MLS-B was originated from a deeper geological formation of the Paleocene period (Montien, prof. 14 – 23 m) and was excavated during diaphragm walls construction using trench cutters and/or mechanical augers. A fourth sample of tunnel muck (TM) was also studied. It was excavated by a slurry tunnel-boring machine under the city of Vitry-sur-Seine and exhibited several differences compared to the three other samples. First, the digging horizons were a mix between CS and MLS-A geological formations (prof. 30 – 40 m). Second, its sampling followed a process including various steps directly carried out in a slurry treatment plan settled in the construction site. The treatment was aimed to change slurries properties making them suitable for their evacuation. Hence, mucks were firstly scalped and sand fractions were removed. The residual fine fraction ($< 80 \mu\text{m}$) was limed (0.5 to 5 %wt of hydrated lime) to facilitate the following step of de-watering carried out with a filter press. The treatment led to the production of filtration cakes to which we will refer to as TM in the present study. Each of these steps might have an impact on the mineralogical assemblage of the sample, which makes Mo and Sb speciation study in TM more complicated than the simple mix between CS and MLS-A geological formations might first foreshadow. All samples were stored in closed plastic bags to avoid alteration due to humidity.

2.2. X-Ray Diffraction (XRD)

X-Ray Diffraction patterns were recorded in 2θ interval from 4 to 90° for each sample using a Bruker D8 Advance Da Vinci diffractometer equipped with a Cu $K\alpha$ radiation tube at a scanning speed of $0.03^\circ 2\theta.s^{-1}$. Samples were first dried (38°C) and then micronized ($20 \mu\text{m}$) in wet media using ethanol with a McCrone XRD micronizer (Retsch). The crystallized fractions were determined from their powder diffractogram while their clayey fractions were estimated from oriented aggregates mounts either standard, after glycolation or after a 4 h heating (490°C). Mineral identification and semi-quantitative determination of relative abundances of crystalline phases was performed using the software DIFFRAC.Suite. Quantitative analysis were realized with a refinement based on Rietveld

Method using the SIROQUANT™ V.4. software (Rietveld, 1969). It consists in describing completely the pattern including the background, the shape, the position and the intensities of the observed diffraction lines for the different phases with the use of structural models (Albinati and Willis, 2006). Then, models parameters are refined by least squares technique until obtaining a calculated diffractogram equivalent to the experimental diffractogram (Young R.A., 1993).

2.3. Total chemical analysis (TCA) and leaching tests

Major elements (Al, Ca, Fe, K, Mg, Mn, Na, P, Si and Ti) total content was analyzed by X-Ray Fluorescence Spectrometry. Total trace elements concentrations in solid samples were determined after calcination and a two steps mineralization by using hydrofluoric acid in presence of perchloric acid followed by hydrochloric acid. The resulting solutions were analyzed by ICP-MS (THERMO X Series II instrument) for TE total concentration determination (among which Mo and Sb) according to the standardized procedure NF EN ISO 17294-2 (AFNOR, 2016). Finally, Total Organic Carbon (TOC) was measured by dry combustion analysis according to NF ISO 10694 (AFNOR, 1995). TOC was analyzed after removal of carbonates by acidification using hydrochloric acid.

Standardized leaching tests were carried out in triplicate according to NF EN 12457-2 (AFNOR, 2002) in order to confirm TE mobility expected in our excavated materials. Samples were crushed (< 4 mm), dried (38 °C) and put in contact with water at a liquid/solid (L/S) ratio of 10 for 24 h in an end-to-end agitator. Supernatants were analyzed after centrifugation (30 min, 2000 g) and filtration (< 0.45 µm). Eluates composition were analyzed for their concentrations in 11 trace elements (among which Mo and Sb) by ICP-MS and 3 anions (Cl⁻, F⁻ and SO₄²⁻) by ionic chromatography (DIONEX). These parameters were chosen as they represent 14 out of the 17 regulated ones within the European Landfill Directive (OJEC, 1999).

2.4. Electron Probe MicroAnalysis (EPMA)

Polished sections of each soil sample have been prepared. They were carbon coated under secondary vacuum (thickness = 20 nm) using a CRESSINGTON 308Carbon (Cressington, Watford, UK). EPMA was carried out on Mo- and Sb-bearing phases pre-selected by SEM-EDS mapping. Polished sections were analyzed with an electron probe microanalyser CAMECA SXFive (CAMECA, Gennevilliers, France) equipped with five wavelength dispersive X-ray spectrometers (WDS) at ISTO (Orleans, France). The operating conditions were accelerating voltage HV = 15 kV and beam current BC = 20 - 40 nA. Ca K α , S K α and Mo L α were measured on PET, Fe K α on LiF and Si K α , Al K α and Mg K α , on TAP. Standards used for calibration were: Albite for Si, Al₂O₃ for Al, Andradite for Ca, BaSO₄ for S, Fe₂O₃ for Fe and Mo metal for Mo. The phi-rho-Z method X-Phi (Merlet, 1992; 1994) was used for quantitative calculation. Interferences were corrected for S (overlapping element Mo) and Mo (overlapping

element S). Unlike bulk spectroscopy, which might be limited by the low TE levels, this selective method could be used to get quantitative measurements of Mo and Sb presence on potential bearing phases selected beforehand on polished sections.. Since this study aims to investigate TE speciation in excavated materials, SEM/EPMA results presented here will only be focused on the identification of Mo/Sb bearing mineral phases.

2.5. pH dependence leaching test

pH dependence leaching test protocols were adapted from NF EN 14429 (AFNOR, 2015) and other references (Coussy et al. 2011; Drapeau, 2018). After preliminary drying (38 °C), solid was crushed (< 1mm) and a preliminary titration was performed to choose acid and basic concentrations needed to cover the whole pH range. Solutions of nitric acid (HNO₃) and sodium hydroxide (NaOH) were used with concentrations ranging from 0 to 1.9 mol·L⁻¹ and 0 to 0.50 mol·L⁻¹ respectively. At least 14 different concentrations were employed for each sample with four duplicates (or more) taken randomly in the series to ensure reproducibility of the method. A L/S ratio of 10 was used and batch agitation was performed with an end-to-end agitator (60 rpm, 72 h). Reaching of steady state was controlled in a preliminary study where different agitation times were performed and pH measurements after 72 hours did not lead to further change in pH values above 0.1 pH unit. A two cases scenario was carried out to see the influence of atmospheric gas phase on samples buffer capacity. In the first protocol, for MLS-A and CS, reaction bottles were regularly opened during the 72 h agitation ensuring renewal of gas phase whereas, in the second case (MLS-B and TM), bottles were kept closed during the whole experiment. Conductivity, pH and Eh were measured after solutions addition and at the end of agitation. Finally, samples were centrifuged (4500 rpm, 10 min) and supernatants were filtered (0.45 µm) with syringe filters. Major elements were analyzed by Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) with a Jobin Yvon Ultima 2 instrument (NF EN ISO 11885; AFNOR, 2009). TE and anions concentrations were analyzed as described in section 2.3. Standard deviations between duplicates were systematically below 15% for Mo and Sb concentrations in the leachates.

2.6. Geochemical modeling

2.6.1. General considerations

The geochemical model used was supported by the PHREEQ-C software (version 3.5.0.14000; Parkhurst and Appelo, 2013). Besides its ability to separate species between the gas, solid or liquid phases only based on mass equation law and thermodynamic data set associated with each species, the strength of PHREEQ-C comes to its adaptability to represent fairly laboratory experiments (especially through the keyword REACTION). A wide range of combinations can be used to describe a

240 solid sample (mineral phases' definition, solid solutions, sorption at surface sites...) which makes it
 241 interesting for solid wastes leaching behavior modelling. Geochemical modelling was therefore used
 242 to define mineral assemblages able to represent the behavior of each sample during pH dependence
 243 leaching tests and eventually link Mo and Sb concentrations evolution with selective mineral phase
 244 dissolution.

Name	Reaction	log _k (25°C)	Kinetic control
Mineral phases identified by XRD			
Calcite	$\text{CaCO}_3 = \text{Ca}^{+2} + \text{CO}_3^{2-}$	-8.48 ^a	No
Dolomite	$\text{CaMg}(\text{CO}_3)_2 = \text{Ca}^{+2} + \text{Mg}^{+2} + 2\text{CO}_3^{2-}$	-17.13 ^a	No
Aragonite	$\text{CaCO}_3 = \text{Ca}^{+2} + \text{CO}_3^{2-}$	-8.31 ^a	No
Quartz	$\text{SiO}_2 + 2\text{H}_2\text{O} = \text{H}_4\text{SiO}_4$	3.74 ^a	Yes ^e
Gypsum	$\text{CaSO}_4 \cdot 2\text{H}_2\text{O} = \text{Ca}^{2+} + \text{SO}_4^{2-} + 2\text{H}_2\text{O}$	-4.61 ^a	No
Celestite	$\text{SrSO}_4 = \text{SO}_4^{2-} + \text{Sr}^{2+}$	-6.63 ^a	Yes ^e
Illite (Fell)	$\text{K}_{0.85}\text{Fe}_{0.25}\text{Al}_{2.35}\text{Si}_{3.4}\text{O}_{10}(\text{OH})_2 + 8.4\text{H}^+ + 1.6\text{H}_2\text{O} = 0.85\text{K}^+ + 0.25\text{Fe}^{2+} + 2.35\text{Al}^{3+} + 3.4\text{H}_4\text{SiO}_4$	9.45 ^a	Yes ^e
Palygorskite	$\text{MgAlSi}_4\text{O}_{10}(\text{OH}) + 5\text{H}^+ + 5\text{H}_2\text{O} = \text{Mg}^{2+} + \text{Al}^{3+} + 4\text{H}_4\text{SiO}_4$	37.1 ^c	Yes ^e
Sepiolite	$\text{Mg}_4\text{Si}_6\text{O}_{15}(\text{OH})_2 \cdot 6\text{H}_2\text{O} + 8\text{H}^+ + \text{H}_2\text{O} = 4\text{Mg}^{2+} + 6\text{H}_4\text{SiO}_4$	31.42 ^b	Yes ^e
Microcline	$\text{K}(\text{AlSi}_3\text{O}_8) + 4\text{H}^+ + 4\text{H}_2\text{O} = \text{Al}^{3+} + \text{K}^+ + 3\text{H}_4\text{SiO}_4$	0.05 ^a	Yes ^e
Albite	$\text{NaAlSi}_3\text{O}_8 + 4\text{H}^+ + 4\text{H}_2\text{O} = \text{Al}^{3+} + \text{Na}^+ + 3\text{H}_4\text{SiO}_4$	2.74 ^a	Yes ^e
Ettringite	$\text{Ca}_6\text{Al}_2(\text{SO}_4)_3(\text{OH})_{12} \cdot 26\text{H}_2\text{O} + 12\text{H}^+ = 2\text{Al}^{3+} + 6\text{Ca}^{+2} + 3\text{SO}_4^{-2} + 38\text{H}_2\text{O}$	56.97 ^a	No
Talc	$\text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_2 + 6\text{H}^+ + 4\text{H}_2\text{O} = 3\text{Mg}^{2+} + 4\text{H}_4\text{SiO}_4$	24.92 ^a	No
Mineral phases added by deduction and/or identified by SEM/EPMA analysis			
Ferrihydrite	$\text{Fe}(\text{OH})_3 + 3\text{H}^+ = \text{Fe}^{3+} + 3\text{H}_2\text{O}$	1.19 ^a	No
Goethite	$\text{FeOOH} + 3\text{H}^+ = \text{Fe}^{3+} + 2\text{H}_2\text{O}$	0.39 ^a	Yes ^e
Pyrite	$\text{FeS}_2 + 2\text{H}^+ + 2\text{e}^- = \text{Fe}^{+2} + 2\text{HS}^-$	-15.79 ^a	Yes ^e
Mineral phases allowed to precipitate			
Strontianite	$\text{SrCO}_3 = \text{HCO}_3^{2-} + \text{Sr}^{2+}$	-9.27 ^a	No
CSH0.8	$\text{Ca}_{0.8}\text{SiO}_{2.8} \cdot 1.54\text{H}_2\text{O} + 1.6\text{H}^+ = 0.8\text{Ca}^{+2} + \text{H}_4\text{SiO}_4 + 0.34\text{H}_2\text{O}$	11.05 ^a	No
Gibbsite	$\text{Al}(\text{OH})_3 + 3\text{H}^+ = \text{Al}^{3+} + 3\text{H}_2\text{O}$	7.74 ^a	No
Brucite	$\text{Mg}(\text{OH})_2 + 2\text{H}^+ = \text{Mg}^{2+} + 2\text{H}_2\text{O}$	17.1 ^a	No
Powellite	$\text{CaMoO}_4 = \text{Ca}^{+2} + \text{MoO}_4^{-2}$	-7.9 ^a	No
$\text{Ca}(\text{Sb}(\text{OH})_6)_2$	$\text{Ca}(\text{Sb}(\text{OH})_6)_2 = \text{Ca}^{2+} + 2\text{Sb}(\text{OH})_6^-$	-12.55 ^d	No

245 Table 1: Mineral phases used to model pH dependence leaching tests with PHREEQ-C along with their
 246 dissolution reactions and the associated solubility constant at 25°C. ^aGiffaut et al. (2014); ^bSinger A.
 247 (1977); ^cBlanc et al. (2012); ^dCornelis et al. (2012); ^eMarty et al. (2015)

The geochemical modelling methodology was based on three main steps: (i) integration of the mineralogical assemblages of each excavated material based on XRD and EPMA results as input data, (ii) modelling of mineral assemblages and major elements behavior during pH dependence leaching tests and (iii) modelling of Mo and Sb behavior. A trials and errors approach has been used and step (ii) and (iii) were repeated until a satisfyingly match was found between experimental and modeling results. The goodness of the fit was evaluated through visual comparison and computation of the logarithm of the Root Mean Square Error ($RMSE_{log}$) to control the proportion of experimental data represented by modelling results within one order of magnitude (Dijkstra et al., 2009). The method of calculus and goodness-of-fit results for geochemical models discussed in this paper are given in Supplementary Information. Improvement or degradation of representation between each iteration were assessed according several hypotheses. These hypotheses are described below and they were mainly focused on solid phase and Mo/Sb speciation (from the initial mineral phase quantities to the way of taking into account Mo/Sb-bearing phases).

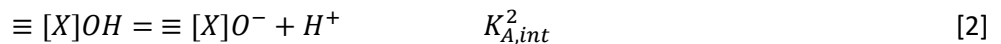
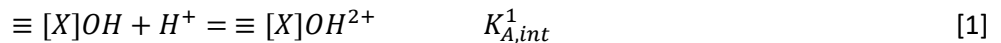
Initial simulations of pH dependence leaching tests were realized using quantities for each mineral phase as analyzed by XRD. Comparison with experimental data of general parameters (pH, Eh and conductivity) as long as major elements behavior over the pH range has led us to make adjustments through adaptation of mineral phases initial quantities and/or the addition of phases likely to precipitate during batch leaching tests. Table SI-1 presents mineral phases quantities used in geochemical modelling for each excavated material. All thermodynamic data used for solid phase modelling are summarized in Table 1. Most of them were extracted from Thermochimie v10a (Giffaut et al. 2014). This thermodynamic database contains a large set of major components representative of geological repository, which could be find in rocks and soils excavated from GPE construction sites. Occasional lacking mineral phases were added as reported in Table 1. Thermochimie can be found in a version in which activities of aqueous species are calculated through the Specific ion Interaction Theory (SIT) instead of the classic Debye-Hückel equation used in Thermoddem. In this study, SIT was used since it has been shown to be more suitable to represent systems with high ionic strength as obtained at extreme pH during pH dependence leaching tests (Trémosa et al. 2014; Grenthe et al. 1997).

In a context of pH dependence leaching tests modelling, time and pH influence on mineral phase's dissolution is of primary importance but often neglected. Our experimental results showed that major elements were far from being totally released even at the lowest pH (except for Ca and Mg) inferring incomplete dissolutions for most mineral phases. Thus, reaction rates were taken into account for dissolution and precipitation of initially present mineral phases (except for carbonated minerals and gypsum). Reaction rates used derived from the transition state theory (TST) for which

Marty et al. (2015) proposed complete kinetics parameters for a list of 15 mineral phases. All the parameters were used as computed by Marty et al. (2015) except for the mineral phase's reactive surface area (RSA) that we used as an optimization lever to describe the incomplete dissolution observed experimentally. Indeed, although values for RSA could be extracted from BET measurements for pure phases, large variation could occur for the same phase taken in a global mineral assemblage and measurement of independent RSA become difficult. Hence, by increasing or decreasing RSA (*i.e.* by accelerating or slowing dissolution rates), we attempted to represent major elements concentration maxima, which was often obtained at pH < 2 and could be linked to the maximum dissolution of the corresponding mineral phases).

2.6.2. Trace Elements modelling

Mo and Sb were uploaded in the geochemical model in two different ways: (i) exchangeable and (ii) in association with a mineral phase. The exchangeable fraction was established from standardized leaching test results and surface complexation models. Although several iron phases might coexist in mineral assemblages, no direct assessments were made to decipher the major oxide types in our samples. Hence, TE complexation at iron (hydr-)oxides surfaces was taken into account considering a generic reactive iron (hydr-)oxides whose behavior has been linked to goethite (FeOOH), given the fact that different iron (hydr-)oxides occurring in soils might react in a similar way. Thus, total moles of surface sites varied according to precipitation and/ or dissolution of goethite, which is convenient to qualitatively represent complexation at acidic pH where iron (hydr-)oxides are expected to (at least partially) dissolve. Iron (hydr-)oxides were introduced in the model through a goethite initial quantity settled at 25 %wt of total Fe in each sample. Surface reactive sites were defined according to the Generalized Two Layer Model (GTLM) (Dzombak and Morel, 1990). Such approach needs available data for protonation and deprotonation of each type of surfaces as given by Equations [1] and [2].



where $\equiv [X]OH$, $\equiv [X]O^-$ and $\equiv [X]OH^{2+}$ represent neutral, negatively and positively charged surfaces respectively; $[X]$ represents Fe atoms, $K_{A,int}^1$ and $K_{A,int}^2$ represent the intrinsic acidity constant of protonation and deprotonation respectively.

Proportions of available strong and weak surface sites were fixed at 0.005 and 0.2 mol per mol of reactive iron (hydr-)oxides respectively and specific surface area at 600 m².g⁻¹ (Dzombak and Morel, 1990). Thermodynamic data for complexation reactions with reactive iron (hydr-)oxides were

314 implemented from Dzombak and Morel (1990). Updated values were used for Mo complexation
315 according to Gustafsson (2003) recommendations, which have shown a good ability to describe
316 sorption impact on Mo speciation at $\text{pH} < 7$ (Dijkstra et al. 2009). Moreover, Sb complexation data
317 has been used as optimized by Cornelis et al. (2012). All complexations reactions and their
318 corresponding solubility constants used in our model are summarized in Table 2.

	Associated reactions	log_k
Hfo_s	Protonation / Deprotonation reactions	
	$\equiv \text{Hfo_sOH} + \text{H}^+ = \equiv \text{Hfo_sOH}_2^+$	7.00 ^a
	$\equiv \text{Hfo_sOH} = \equiv \text{Hfo_sO}^- + \text{H}^+$	-8.93 ^a
	Complexation reactions	
	$\equiv \text{Hfo_sOH} + \text{Ca}^{2+} = \equiv \text{Hfo_sOHCa}^{2+}$	4.97 ^a
	$\equiv \text{Hfo_sOH} + \text{Sr}^{2+} = \equiv \text{Hfo_sOHSr}^{2+}$	5.01 ^a
	$\equiv \text{Hfo_sOH} + \text{SO}_4^{2-} + \text{H}^+ = \equiv \text{Hfo_sSO}_4^- + \text{H}_2\text{O}$	7.78 ^a
	$\equiv \text{Hfo_sOH} + \text{SO}_4^{2-} = \equiv \text{Hfo_sOHSO}_4^{2-}$	0.79 ^a
	$\equiv \text{Hfo_sOH} + \text{MoO}_4^{2-} + 2\text{H}^+ + \text{H}_2\text{O} = \equiv \text{Hfo_sOMo(OH)}_5$	17.98 ^b
	$\equiv \text{Hfo_sOH} + \text{MoO}_4^{2-} = \equiv \text{Hfo_sOHMoO}_4^{2-}$	3.14 ^b
	$\equiv \text{Hfo_sOH} + \text{Sb(OH)}_6^- + \text{H}^+ = \equiv \text{Hfo_sOSb(OH)}_4 + 2\text{H}_2\text{O}$	10 ^c
Hfo_w	Protonation / Deprotonation reactions	
	$\equiv \text{Hfo_wOH} + \text{H}^+ = \equiv \text{Hfo_wOH}_2^+$	7.29 ^a
	$\equiv \text{Hfo_wOH} = \equiv \text{Hfo_wO}^- + \text{H}^+$	-8.93 ^a
	Complexation reactions	
	$\equiv \text{Hfo_wOH} + \text{Ca}^{2+} = \equiv \text{Hfo_wOCa}^+ + \text{H}^+$	-5.85 ^a
	$\equiv \text{Hfo_wOH} + \text{Mg}^{2+} = \equiv \text{Hfo_wOMg}^+ + \text{H}^+$	-4.6 ^a
	$\equiv \text{Hfo_wOH} + \text{Sr}^{2+} = \equiv \text{Hfo_wOSr}^+ + \text{H}^+$	-6.58 ^a
	$\equiv \text{Hfo_wOH} + \text{Sr}^{2+} + \text{H}_2\text{O} = \equiv \text{Hfo_wOSrOH} + 2\text{H}^+$	-17.6 ^a
	$\equiv \text{Hfo_wOH} + \text{SO}_4^{2-} + \text{H}^+ = \equiv \text{Hfo_wSO}_4^- + \text{H}_2\text{O}$	7.78 ^a
	$\equiv \text{Hfo_wOH} + \text{SO}_4^{2-} = \equiv \text{Hfo_wOHSO}_4^{2-}$	0.79 ^a
	$\equiv \text{Hfo_wOH} + \text{MoO}_4^{2-} + 2\text{H}^+ + \text{H}_2\text{O} = \equiv \text{Hfo_wOMo(OH)}_5$	17.98 ^b
	$\equiv \text{Hfo_wOH} + \text{MoO}_4^{2-} = \equiv \text{Hfo_wOHMoO}_4^{2-}$	3.14 ^b
	$\equiv \text{Hfo_wOH} + \text{Sb(OH)}_6^- + \text{H}^+ = \equiv \text{Hfo_wOSb(OH)}_4 + 2\text{H}_2\text{O}$	13.2 ^c
	$\equiv \text{Hfo_wOH} + \text{CO}_3^{2-} + \text{H}^+ = \equiv \text{Hfo_wCO}_3^- + \text{H}_2\text{O}$	12.56 ^d
	$\equiv \text{Hfo_wOH} + \text{CO}_3^{2-} + 2\text{H}^+ = \equiv \text{Hfo_wHCO}_3 + \text{H}_2\text{O}$	20.62 ^d

319 Table 2: Protonation/Deprotonation and complexation reactions with corresponding log(k) used in
320 sorption calculations at reactive iron (hydr)-oxides surfaces (Hfo_s and Hfo_w). ^a Dzombak and Morel
321 (1990); ^b Gustafsson (2003); ^c Cornelis et al. (2012); ^d Van Geen et al. (1994)

322 As it will be discussed in section 3, Mo and Sb were considered in association with several bearing
323 phases (namely celestite, pyrite, dolomite and ettringite). Mo and Sb were directly introduced in the
324 bearing mineral phases definition with unchanged solubility constants. Although quite simplistic,
325 such an approach has the ability to represent covariations between TE and major elements
326 concentrations resulting from mineral phase's dissolution based on a possible inclusion mechanism.
327 Table 3 sums up the quantity of each element incorporated in pyrite, celestite, dolomite and/or
328 ettringite to obtain the best description of experimental results. The remaining quantity of Mo and
329 Sb could be calculated from the difference between total amount of TE (total content analysis) and
330 the quantity of TE considered in the geochemical model. This quantity represents the non-leachable
331 fraction of Mo in pH dependence leaching tests conditions, which might be partly (but not only)
332 attributable to associations with silicate minerals.

Mineral	Element	MLS-A	MLS-B	CS	TM
Celestite	Mo (mg·g ⁻¹)	0.08	0.08	-	0.06
	Sb (mg·g ⁻¹)	0.007	0.005	-	0.004
	Sr (mg·g ⁻¹)	477	477	-	477
Dolomite	Mo (mg·g ⁻¹)	-	-	0.06	0.06
	Sb (mg·g ⁻¹)	-	-	0.002	0.002
	Sr (mg·g ⁻¹)	-	-	14.1	14.1
Ettringite	Mo (mg·g ⁻¹)	-	-	-	0.008
	Sb (mg·g ⁻¹)	-	-	-	0.001
Pyrite	Mo (mg·g ⁻¹)	8.0	8.0	8.0	8.0

Table 3: Mass of Mo, Sb and Sr introduced in celestite for MLS-A, MLS-B and TM, in dolomite for CS and TM, in ettringite for TM and in pyrite for all samples. Results are given in milligrams of element per gram of mineral phase.

3. RESULTS AND DISCUSSION

3.1. Samples characterization

3.1.1. Excavated soil characteristics

	MLS-A	MLS-B	CS	TM
Major elements atomic percentage				
Al	1.02 %	0.97 %	0.41 %	1.50 %
Ca	17.16 %	19.16 %	33.02 %	36.70 %
Fe	0.71 %	0.55 %	0.38 %	< 1.00 %
K	0.31 %	0.21 %	0.11 %	0.61 %
Mg	7.56 %	8.64 %	1.03 %	7.10 %
Sr	4.06 %	0.56 %	0.16 %	0.97 %
Na	0.54 %	0.59 %	< 0.15 %	< 0.50 %
P	0.03 %	< 0.02 %	< 0.02 %	0.01 %
Si	7.39 %	7.11 %	4.33 %	6.60 %
Ti	0.10 %	0.07 %	0.04 %	0.06 %
TOC	0.34 %	< 0.1 %	0.36 %	0.63 %
Total Content (mg·kg⁻¹)				
Mo	7.2	2	10.9	4.8
Sb	0.6	<0.5	0.4	<0.5
Se	1.4	<0.5	2.76	1.2

Table 4: Total content results in CS, MLS-A, MLS-B and TM for major and trace elements expressed in mass percentage and mg·kg⁻¹ of material respectively

TCA results are shown in Table 4. As expected, calcium (Ca) was the predominant element in all samples with 36.7 %wt, 33.0 %wt, 17.2 %wt and 19.2 %wt for TM, CS, MLS-A and MLS-B respectively. For CS, all other elements (except for silicon, Si) were close or below 1 %wt suggesting a mineral assemblage almost exclusively composed of calcium carbonates which was in agreement with XRD results (Table 5). Although carbonates were also dominant in MLS-A and MLS-B, two main differences have been outlined compared to CS. First, a lower content of carbonated minerals has been identified by XRD with 70 wt% and 73 wt% respectively, with, for both samples, dolomite (CaMg(CO₃)₂) as the dominant mineral consistently with the high magnesium (Mg) content observed in TCA. Second, a higher content of sulfate bearing minerals (gypsum, CaSO₄·2H₂O and especially celestite, SrSO₄) was shown in MLS-A and MLS-B compared to CS as long as a non-negligible Strontium (Sr) concentration in these samples. Celestite content was higher in MLS-A (8 %wt) than in MLS-B (1 %wt) and, as a balance, the proportion of silicate minerals (illite, sepiolite, plagioclase and feldspath) in MLS-B was higher (20 wt% versus 14 wt% in MLS-A). XRD and TCA confirmed that TM shared characteristics with CS and MLS-A. As such, carbonated minerals were the most represented (86 %wt) almost equally split between calcite and dolomite. The slightly higher Ca content could be a

consequence of lime addition in the slurry treatment plan before sampling. TM also showed a non-negligible amount of celestite (i.e. 3%). Finally, lime addition might have contributed to mineral phases precipitation such as ettringite ($\text{Ca}_6\text{Al}_2(\text{SO}_4)_3(\text{OH})_{12} \cdot 26\text{H}_2\text{O}$), which was not identified in CS or MLS-A. The pH increase following lime addition probably resulted in partial dissolution of silicate and sulfate minerals forming ideal conditions to ettringite precipitation by reaction with soluble Ca (Buttress et al. 2013).

	MLS-A	MLS-B	CS	TM
Calcite	9 ± 3 %	12 ± 2 %	82 ± 3 %	47 ± 2 %
Dolomite	61 ± 3 %	61 ± 5 %	4 ± 3 %	36 ± 2 %
Celestite	8 ± 3 %	1.0 ± 0.5 %	-	3 ± 2 %
Quartz	7 ± 3 %	4 ± 1 %	4 ± 3 %	3 ± 2 %
Sepiolite	6 ± 5 %	8 ± 2 %	-	tr
Palygorskite	4 ± 5 %	4 ± 1 %	2 ± 5 %	1 ± 3 %
Illite	4 ± 5 %	5 ± 1 %	tr	3 ± 3 %
Gypsum	1 ± 3 %	2 ± 1 %	2 ± 3 %	1.5 ± 2 %
Smectite	tr	-	tr	tr
Chlorite	tr	-	tr	tr
Plagioclase	-	2 ± 1 %	1 ± 3 %	-
Feldspath	-	1.0 ± 0.5 %	-	1 ± 2 %
Aragonite	-	-	5 ± 3 %	3 ± 2 %
Amphibole	-	-	1 ± 3 %	-
Kaolinite	-	-	tr	tr
Ettringite	-	-	-	1.5 ± 2 %
Talc	-	-	-	tr

Table 5: XRD results for CS, MLS-A, MLS-B and TM expressed in weight percentage of the total mineral assemblage. Hyphen marks are used for phases not identified while "tr" abbreviation is used when the phase was suggested to occur only in trace amounts.

Total Organic Carbon concentrations were low in all samples attesting a relative absence of organic matter in these geological formations. Furthermore, generic parameters for anion sorption onto humic and fulvic acids are still scarce (Milne et al. 2010) and reactive organic matter groups (mostly negatively charged) might not react extensively with anions. Hence, OM influence on Mo and Sb speciation has been neglected in the present study. It was confirmed that only low levels of TE concentrations occur. The highest concentrations for Mo and Sb were noticed in CS and MLS-A with 10.9 and 0.6 $\text{mg} \cdot \text{kg}^{-1}$ respectively. Total Mo content of 4.8 $\text{mg} \cdot \text{kg}^{-1}$ in TM was lower than both CS and MLS-A values, which was not consistent with the mix of CS and MLS-A geological formation represented in TM. This lower value might outline that a non-negligible Mo content was extracted during the slurry treatment process and more precisely during water recover after mucks pressing. High pH values induced by liming created conditions favorable to both oxyanions leaching and

potential bearing phase dissolution, thereby explaining such Mo impoverishment in TM. Finally, Sb was shown under the DL of $0.5 \text{ mg}\cdot\text{kg}^{-1}$ in MLS-B and TM.

Considering uncertainties of 2 to 3 %wt in XRD results, a good consistency between XRD and TCA was observed for Aluminum (Al), Ca, Mg, Potassium (K) and Si. Sr was also well retrieved as a celestite tracer for the two marly limestone samples and TM. Iron (Fe) was the only element for which XRD results led to underestimation of its total content in every samples. Such a result is not surprising since Fe is expected to be present mainly as iron oxy-(hydroxides), which could be ignored by XRD measurements given their poorly crystalized structures.

	DL	MLS-A	MLS-B	CS	TM
F ($\text{mg}\cdot\text{kg}^{-1}$ of DM)	1	10.7 ± 0.6	25 ± 2	9.0 ± 0.1	22 ± 1
Mo ($\text{mg}\cdot\text{kg}^{-1}$ of DM)	0.001	0.66 ± 0.07	0.30 ± 0.03	3.6 ± 0.1	3.8 ± 0.1
Sb ($\text{mg}\cdot\text{kg}^{-1}$ of DM)	0.001	0.006 ± 0.001	0.006 ± 0.001	0.009 ± 0.001	< 0.001
Se ($\text{mg}\cdot\text{kg}^{-1}$ of DM)	0.001	0.08 ± 0.01	0.030 ± 0.008	0.102 ± 0.002	0.011 ± 0.001
pH	-	7.8 ± 0.2	8.8 ± 0.1	8.8 ± 0.1	12.2 ± 0.1

Table 6: Leachates pH and concentrations obtained according to leaching tests at a L/S ratio of 10 (NF EN 12457-2). Values were calculated as the mean result obtained with triplicates while uncertainties are the corresponding standard deviation.

Molybdenum mobility was confirmed by the standardized leaching test NF 12457-2 results (Table 6). Mo release was above acceptation criteria in Inert Wastes Landfills (*i.e.* $0.5 \text{ mg}\cdot\text{kg}^{-1}$ of Dry Matter (DM)) for TM, CS and MLS-A. As far as the untreated excavated earths are concerned, the overrun was more important in the case of CS with $3.6 \pm 0.1 \text{ mg}\cdot\text{kg}^{-1}$ of DM against $0.66 \pm 0.07 \text{ mg}\cdot\text{kg}^{-1}$ of DM for MLS-A. Concentrations of Mo leached in TM were even higher (*i.e.* $3.8 \pm 0.1 \text{ mg}\cdot\text{kg}^{-1}$ of DM) and represented 80 %wt of total Mo in the sample. Mo leaching in MLS-B was not concerning but, for this sample as long as in TM, it was noticed that fluorides leaching concentrations were above acceptance criteria in inert-waste landfill (*i.e.* $10 \text{ mg}\cdot\text{kg}^{-1}$ of DM) with values of 25 ± 2 and $22 \pm 1 \text{ mg}\cdot\text{kg}^{-1}$ of DM respectively. Even though no particular mobility for Sb was shown in our sample, the close behavior expected for this element compared to Mo will help us to consolidate our observations.

3.1.2. Mo and Sb bearing phases

Given the similarities between all samples regarding their major mineral phases, only CS and MLS-A were investigated by SEM/EPMA assuming that main information could be obtained through these two samples. Associations between Sb and particular mineral phases were not detected because of the low total content of Sb occurring in all samples. Pyrite, although undetected by XRD, was shown

to be a systematic bearing phase for Mo in samples CS and MLS-A with Mo mass percentages (calculated as the mean value of seven measurements for each sample) equal to 0.8 ± 0.2 wt% and 1.0 ± 0.2 wt% respectively (Figure 1a and b). Such associations are direct consequences of Mo chalcophile behavior and probably consist in solid solutions Mo-Fe-S. (Smedley and Kinniburgh, 2017; Harkness et al. 2017). However, samples overall observations showed that the number of pyrite grains remained low so that Mo-FeS₂ associated might only represent a small fraction of total Mo. Unlike CS, MLS-A has shown other bearing phases for Mo. Indeed, 14 different measurements were performed on celestites spread all over the polished section (Figure 1c). Mo was systematically identified associated with those minerals with a mass percentage of 0.16 ± 0.08 wt%. These observations have been used to feed the geochemical modeling of pH dependence leaching tests.

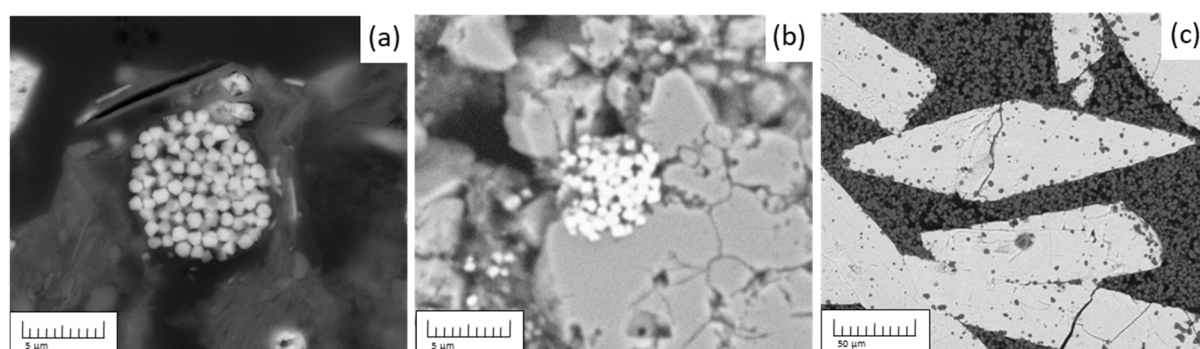


Figure 1: SEM images of Mo bearing pyrites in MLS-A (a) and CS (b) as long as Mo bearing celestites in MLS-A (c)

3.2. Geochemical modelling

3.2.1. General description

As a preliminary stage, models reliability was estimated based on pH evolutions as a function of the quantity of acid or base added. First, a natural batch pH (pH₀) has been determined for each sample, which corresponds to batches in which solids were in contact with water only. Measurements made after 72 h of agitation were 8.2, 9.1, 8.7 and 12.1 for MLS-A, MLS-B, CS and TM respectively. The alkaline nature of the untreated soils was already acknowledged through pH measurement during standardized leaching tests (Table 1). In the case of TM, pH value above 12 was the consequence of lime addition. Modeled values were close to experimental results with a maximum difference of 0.2 pH units, which could be explained by the low buffer capacity from pH₀ observed in all samples. Figure 2 shows experimental pH curves along with modeling results. A maximum acid neutralization capacity was observed at pH of 6.3, 5.1, 6.5 and 5.8 for MLS-A, MLS-B, CS and TM respectively, which was expected given the predominance of carbonates in all mineral phase's assemblages. Moreover, buffer plateau lengths for each sample, which represent the quantity of protons (H⁺) needed to

dissolve carbonate phases, were consistent with relative carbonates quantities determined by XRD and TCA. As such, CS have shown the most extended acid neutralization capacity (*ca.* 1.7 moles of $\text{H}^+\cdot\text{L}^{-1}$) followed by TM (*ca.* 1.6 moles of $\text{H}^+\cdot\text{L}^{-1}$), MLS-B (*ca.* 1.5 moles of $\text{H}^+\cdot\text{L}^{-1}$) and MLS-A (*ca.* 1.0 moles of $\text{H}^+\cdot\text{L}^{-1}$). Finally, one can note that CS and MLS-A showed higher experimental pH buffer values due to renewal of atmospheric gas phase as bottles were regularly opened during agitation.

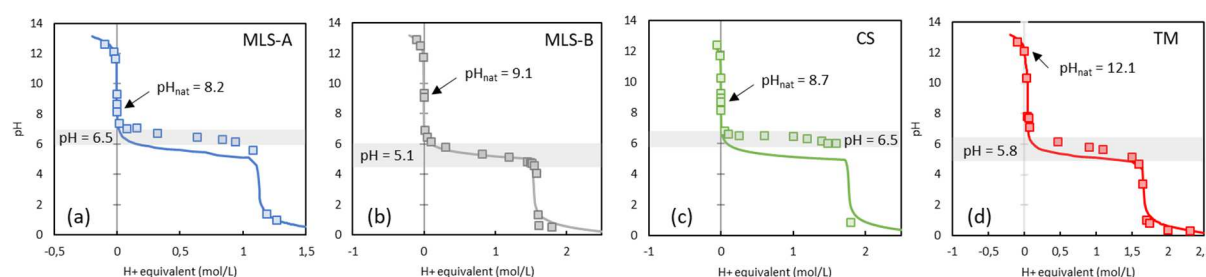


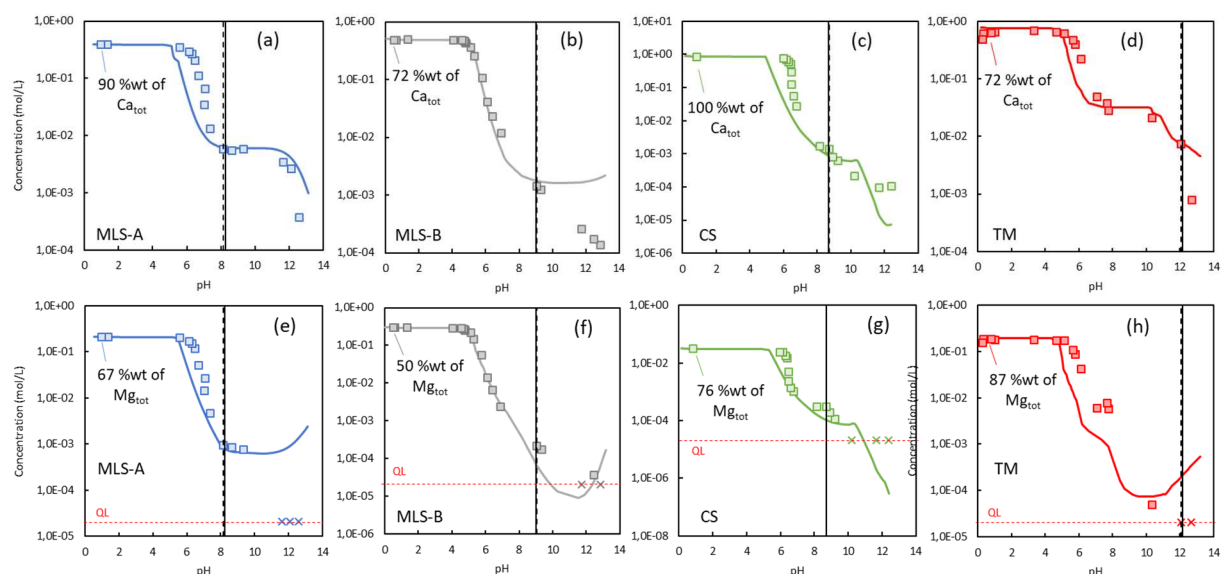
Figure 2: pH dependency curves for MLS-A (a), MLS-B (b), CS (c) and TM (d) as obtained during pH dependence leaching tests. Solid curves and marks represent modeled and experimental data respectively. Negative and positive values on the X-axis of pH dependency curves are defined for basic and acid batches respectively. Gray areas represent the carbonates buffer area with the retained value explicitly written in caption. Natural batch pH are also explicitly stated and represented by an empty mark.

3.2.2. Major elements

Beside the description of general parameters such as pH, major elements leaching concentrations during pH dependence leaching tests were used as tracers of mineral dissolution and/or precipitation. In the following sections, comparison between experimental and modelling results will be presented with particular attention paid on mineral phases susceptible to play a role in Mo and Sb speciation. For K and Si, results are presented in Supplementary Information.

3.2.2.1. Calcium and Magnesium

The modelled and experimental concentrations during pH dependence leaching tests for MLS-A, MLS-B, CS and TM are presented in Figure 3. In each sample, decrease of pH following addition of acid solutions have resulted in a rise of Ca and Mg concentrations until complete dissolution of carbonate minerals. In TM, a shift was observed between experimental and modelling results for Ca and Mg concentrations increase during carbonates dissolution. This could be a consequence of liming, which might trigger the precipitation of more soluble polymorph of calcite (aragonite, vaterite, hydrated calcite), either through the presence of impurities (Boynton, 1980) or through carbonation of C-S-H and/or ettringite (Auroy et al., 2018). Finally, in TM, Ca concentrations increase with the very first acid addition (pH = 10.4) was linked to ettringite dissolution.



459 *Figure 3: Experimental and modelling results of Ca and Mg concentrations as a function of pH during*
 460 *pH dependence leaching tests for MLS-A (a and e), MLS-B (b and f), CS (c and g) and TM (d and h).*
 461 *Marks and solid lines represent experimental and modelling data respectively, while cross marks*
 462 *represent value below the QL. Vertical dashed and solid lines represent the experimental and*
 463 *modelled natural batch pH respectively.*

464 At pH values above pH_0 (i.e. after NaOH addition), Ca and Mg concentrations measured in each
 465 sample were found to decrease. For Ca in MLS-A (Figure 3a), concentrations diminution was only
 466 observed at $pH > 11$ and a good fit was obtained by letting ettringite precipitate (Meima and
 467 Comans, 1998). In these sulfate-rich samples, the close behavior of Mg (Figure 3e) might be
 468 explained by the potential precipitation of a hydrotalcite-like (HT) mineral (Dou et al., 2017).
 469 Regarding TM, Ca concentrations decreased above pH_0 , which was explained by further precipitation
 470 of ettringite and hydrated silicate calcium (C-S-H). For MLS-B and CS (Figure 3b and c), the drop in Ca
 471 concentration was seen immediately after the first addition of base and could not be represented by
 472 ettringite precipitation, which was consistent with the much lower sulfates content compared
 473 to MLS-A. At $pH > 11$, Mg concentrations in MLS-B were reasonably well represented by dolomite
 474 equilibrium (Figure 3f). For CS, Mg concentrations below the Quantification Limit (QL) suggested the
 475 precipitation of at least one Mg bearing phase (Figure 3g). Brucite ($Mg(OH)_2$) was the only
 476 supersaturated mineral phase able to improve Mg concentration description without interfering with
 477 the rest of the system. Mg behavior at $pH > 10$ was already linked to brucite solubility in different
 478 context such as coal fly ash (Garavaglia and Caramuscio, 1994) or Municipal Solid Wastes incinerator
 479 residues (Dijkstra et al. 2006).

3.2.2.2. Strontium and Sulfates

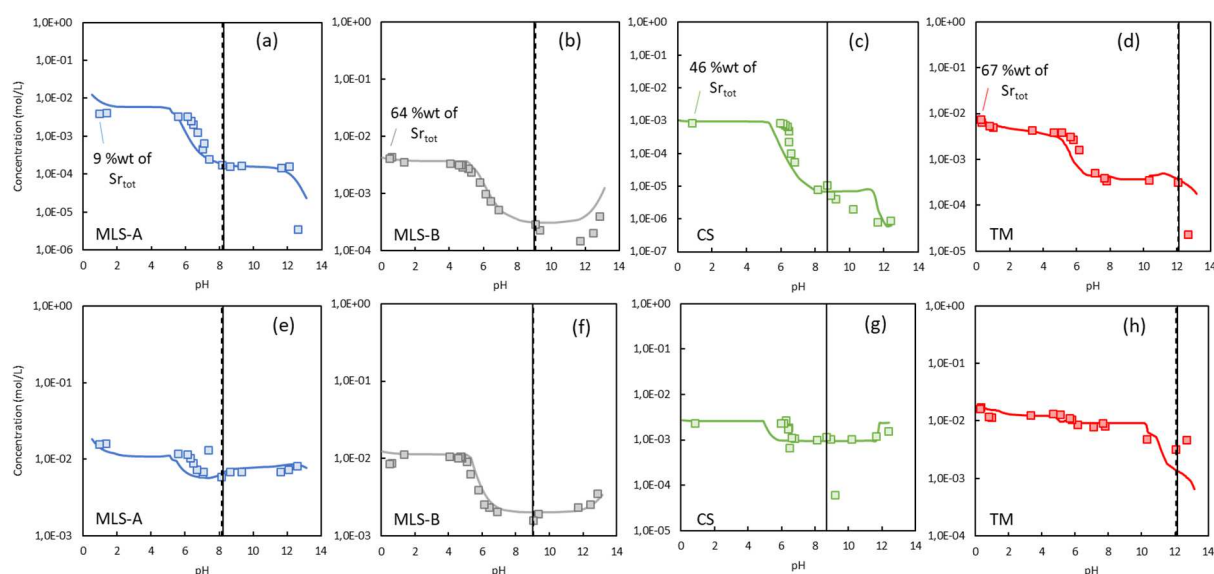


Figure 4: Experimental and modelling results of Sr and SO_4 concentrations as a function of pH during pH dependence leaching tests for MLS-A (a and e), MLS-B (b and f), CS (c and g) and TM (d and h). Marks and solid lines represent experimental and modelling data respectively. Vertical dashed and solid lines represent the experimental and modelled natural batch pH respectively

Figure 4 (a, b and d) show the good fit obtained between experimental and modelling data for Sr concentration as a function of pH in MLS-A, MLS-B and TM respectively. Legitimately considered as an exclusive tracer of celestite behavior, maximum Sr concentrations at $\text{pH} < 2$ gave us the proportion of actually dissolved celestite, which was approximatively 9 %wt, 63 %wt and 67 %wt for MLS-A, MLS-B and TM respectively. The same RSA of $0.04 \text{ m}^2 \cdot \text{g}^{-1}$ was fixed to represent the behavior of the natural celestite occurring in both marly limestone samples while a slightly lower value of $0.01 \text{ m}^2 \cdot \text{g}^{-1}$ was used for TM (Table SI-1). On the other side of the pH range, at pH values above 10, celestite dissolution inferred by modelling results was not experimentally correlated with an increase of Sr concentration, which could be explained by strontianite precipitation (Garavaglia and Caramuscio, 1994). SEM observations on solid residue for MLS-A after basic leaching test at $\text{pH} = 12.6$ (Figure 5) have shown a clearly altered celestite with a preferential dissolution at grains edges. Quantitative EPMA measurements inferred that in the attacked areas, grains were completely depleted in sulfates and Sr content was close to 60 %wt, which is the ratio expected in strontium carbonates. For CS, assuming the presence of celestite (not seen by XRD analysis for this sample) resulted in a two orders of magnitude overestimation of Sr concentration at $\text{pH} 0$. The higher proportion of carbonates in CS compared to MLS-A and MLS-B could have resulted in the incorporation of Sr as a solid solution in carbonated minerals (Lerouge et al. 2010), which was in better agreement with experimental results (Figure 4c).

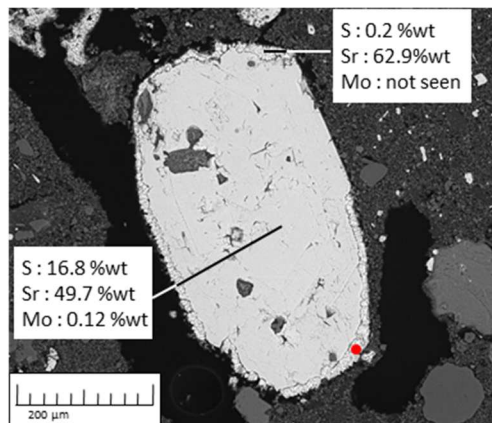


Figure 5: SEM images of partially dissolved celestite following basic leaching test at pH = 12.6 in MLS-A. EPMA measurements are presented in weight percentage for two points: one at the grain core and one at the edge. Results inferred the disappearance of both sulfates and Mo at celestite edges while grains core still showed typical composition for Mo-bearing SrSO₄.

Unlike strontium, sulfates (SO₄²⁻) concentrations can be impacted by the over- and undersaturation of several mineral phases so that it is often more difficult to discuss their evolutions. Celestite partial dissolution was shown to be responsible for at least a part of the rise in SO₄²⁻ concentrations at pH < 7 in MLS-A (Figure 4e). At high pH values, SO₄²⁻ was a part of both contradictory mechanisms of celestite dissolution and ettringite precipitation so that its concentration did not depict strong variations. Modelling results for sulfates concentrations in TM (Figure 4h) were in agreement with experimental data at pH values below 10. For higher pH, and consistently with what was observed for Sr, concentrations were underestimated either because precipitation of ettringite was too high or because celestite dissolution was underestimated. For MLS-B (Figure 4f), SO₄²⁻ concentrations were reasonably well described by celestite partial dissolution at pH values above pH₀. However, the rise of SO₄²⁻ concentration at pH < 7 could not be explained by celestite dissolution alone and it has been assumed that a part of SO₄²⁻ was trapped in carbonated minerals and especially in calcite as previously suggested by studies focused on alkaline fly ash leachates (Schramke J.A., 1992). The same assumption was made in the case of CS. Finally, even though pyrite (FeS₂) dissolution in carbonated systems was already recorded in both acid and basic areas during pH dependence leaching tests (Drapeau, 2018), no direct insights of pyrite oxidation was observed in the present study. Only basic conditions might lead to a partial dissolution as inferred by modelling results. In agreement with the low amount of iron sulfides noticed in our samples (below the XRD detection limit and only few grains observed by SEM), pyrite was only introduced in our model at trace levels so that its contribution on SO₄ behavior would be negligible.

3.2.2.3. Iron and Aluminum

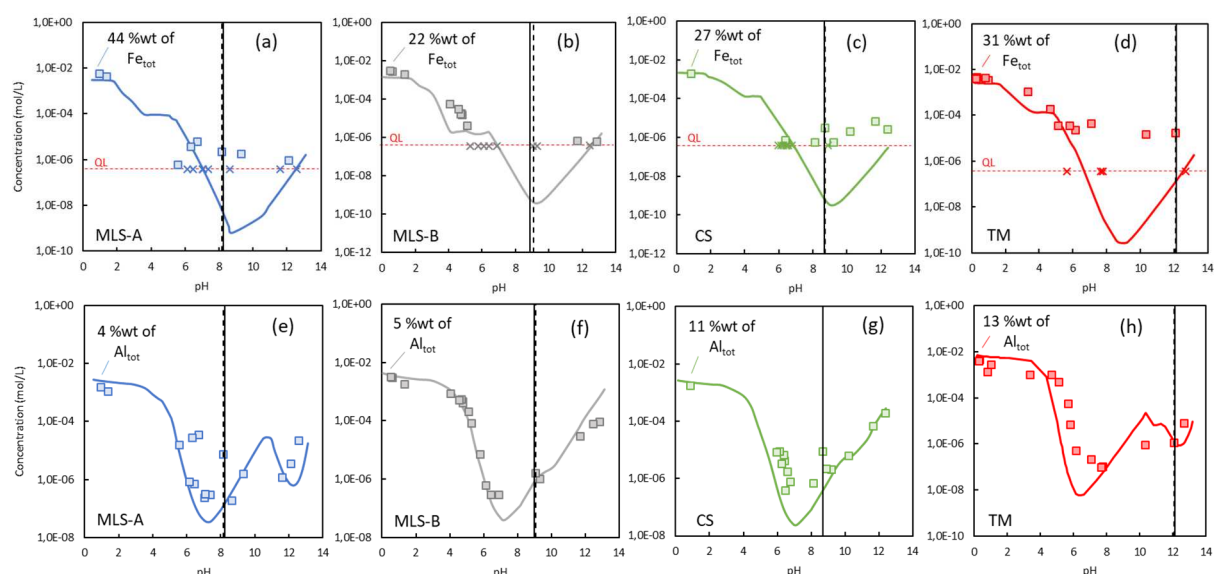


Figure 6: Experimental and modelling results of Fe and Al concentrations as a function of pH during pH dependence leaching tests for MLS-A (a and e), MLS-B (b and f), CS (c and g) and TM (d and h). Marks and solid lines represent experimental and modelling data respectively while cross marks represent value below the QL. Vertical dashed and solid lines represent the experimental and modelled natural batch pH respectively.

Fe behavior understanding is important since quantity of reactive surface sites for complexation phenomena would vary as iron oxides dissolve or precipitate. Experimental data have shown that Fe concentrations were often below or close to the QL of $0.2 \text{ mg} \cdot \text{kg}^{-1}$ (i.e. $4 \cdot 10^{-7} \text{ mol} \cdot \text{L}^{-1}$) at $\text{pH} > 5$, which could be explained by the oversaturation of iron (hydr-)oxides such as goethite and/or ferrihydrite for such slightly acidic to strongly alkaline conditions. However, this trend was less clear in CS and TM (Figure 6c and d), where Fe concentrations in solution were regularly above QL resulting in their underestimation by the geochemical model. One has to keep in mind that eluates were only filtrated at $0.45 \text{ } \mu\text{m}$, which limits but not prevents colloidal particles from being analyzed. Since our samples are almost completely depleted in OM, colloidal iron might rather occur as amorphous oxides either stable or being precursors for ferrihydrite precipitation (Van der Woude and De Bruyn, 1983). In all samples, at $\text{pH} < 5$, Fe concentrations increased sharply as dissolution of oxides became more and more important. For the most concentrated acid solution added in each sample, a maximum of Fe release was reached experimentally, which represented 25 wt%, 44 wt%, 21 wt% and 36 wt% of total Fe in CS, MLS-A, MLS-B and TM respectively. It pointed out the incomplete dissolution of both oxides and silicate minerals (Drapeau, 2018), which was well described by modelling results after modification of RSA for Fe-bearing phases. The best results were obtained by representing iron (hydr-)oxides with two different mineral forms: (i) goethite with a dissolution kinetically limited and

which was the seat of surface sites for complexation and (ii) amorphous ferrihydrite allowed to precipitate to control Fe leaching at pH > 5 but not considered for complexation reactions.

As Aluminum was concerned, at both ends of the pH range, incomplete dissolution of silicate phases (illite, albite, kaolinite...) initially present in the total assemblage resulted in a rise of Al concentration (Dijkstra et al. 2006). For pH values included between 5 and 10 approximatively, this rise was mitigated by gibbsite precipitation. All four samples therefore presented a V-shaped curve for Al concentrations as a function of pH (see Figure 6e, 6f, 6g and 6h). Inflections in the V-shaped curves were observed in MLS-A and TM between pH = 10 and 12, consistently with ettringite precipitation as pH increased and ettringite dissolution as pH decreased for MLS-A and TM respectively.

3.2.3. Trace elements

Experimental and modelling results for Mo and Sb concentrations during pH dependence leaching tests are given for each sample in Figure 7 and Figure 8 respectively. Each pH dependency curve is presented along with a surface area plot representing repartition of Mo or Sb between solid and liquid phases over the whole pH range. These results are expressed in weight percentage calculated from modelling data and total TE content measured by TCA.

3.2.3.1. Molybdenum

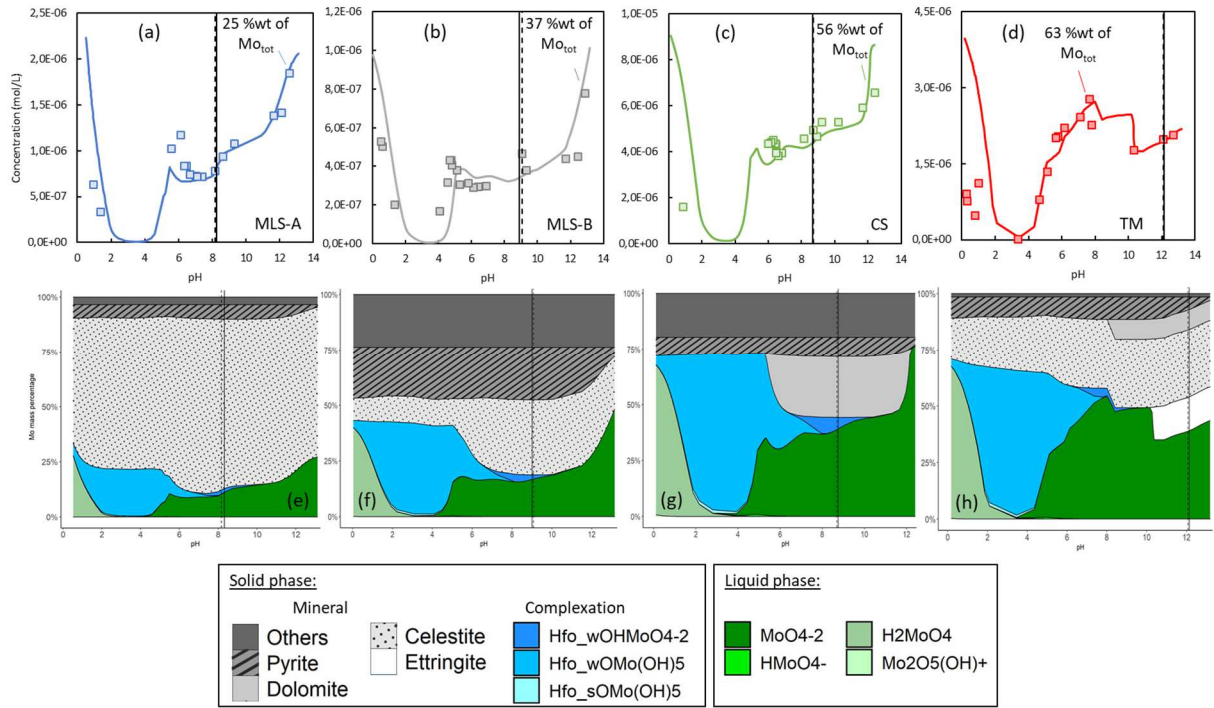


Figure 7: Experimental and modelling results of Mo concentrations as a function of pH during pH dependence leaching tests for MLS-A (a), MLS-B (b), CS (c) and TM (d). Marks and solid lines represent

experimental and modelling data respectively. Vertical dashed and solid lines represent the experimental and modelled natural batch pH respectively. For each pH dependency curve, a corresponding area plot representing Mo repartition between solid and liquid phase is given below. Mass balance has been made regarding the total Mo concentrations measured by total content analysis for each sample

Assuming 0.08 mg of Mo per gram of celestite in MLS-A and MLS-B allowed us to describe well Mo concentrations for pH > 5 (Figure 7a and b) directly confirming SEM/EPMA observations. For both samples, two leaching maxima were noticed in relation to celestite partial dissolution at pH = 6.2 and 12.5 for MLS-A and at pH = 5.5 and 12.5 for MLS-B. SEM/EPMA quantitative measurement on solid residue for MLS-A after basic neutralization capacity test (pH = 12.6) presented in Figure 5 have shown the attacked edges of celestite grains completely depleted in Mo. On the contrary, celestite core still presented a Mo content close to what was observed on the raw sample (*i.e.* 0.1 %wt). To our knowledge, no direct associations have been referenced between Mo and evaporitic salts like celestite (Smedley and Kinniburgh, 2017) even if evaporites have long been suspected to be a source of TE and especially oxyanions (Kohut and Dudas, 1993). As far as excavated earths are concerned, Tabelin et al. (2014) outlined significant associations between evaporitic salts (anhydrite, mirabilite, nahcolite...) and oxyanionic species (As, B and Se). Mechanisms of incorporation of these elements in trace amounts are related to ancient sedimentation in marine environment (Tabelin et al. 2018) which could be consistent with the Parisian basin enrichment scenario. Ong et al. (1997) inferred that in areas with high Mo contamination levels, the conditions recently created by saline agricultural evaporation ponds rather led to the precipitation of CaMoO_4 than Mo incorporation in evaporites. Hence, one can suggest that low Mo content (as occurring in our samples) could be of primary importance for the emergence of such associations.

Mo behavior at pH < 6 was similar in all samples. A drop of Mo concentrations was observed as complexation at oxides surfaces became more and more important until Mo was almost totally in solid form between pH = 2 and 4. The simultaneous kinetically limited dissolution of Mo-bearing phases and goethite at pH < 2 led to a final rise of Mo concentrations, mostly released in a doubly protonated form (H_2MoO_4). Other similarities could be seen in pyrite behavior for all samples, which systematically showed a partial dissolution at pH > 11 accounting for a relatively small fraction of total Mo release.

For CS (Figure 7c), Mo behavior revealed a strong pH dependency, showing leaching minimum and maximum at pH = 1 and 12.5 respectively. The first acid addition resulted in a small decrease of Mo concentration, as complexation at oxides surface sites was slowly favored. The subsequent dissolution of dolomite (modelled at pH = 6 and observed at pH = 6.8) triggered an increase of Mo concentration quickly compensated by the growing importance of complexation. In the basic area,

first NaOH addition led to a slight Mo concentration increase due to Mo desorption as oxides surface charges became more and more negative. The final Mo increase (pH > 10) was exaggerated by modelling results probably because of an overestimation of brucite precipitation (triggering dolomite dissolution and therefore Mo release). Our model failed to improve further Mo concentration description even considering time and pH dependencies for brucite precipitation (Dijkstra et al. 2006; Pokrovsky and Schott, 2004).

Consistently with the mix of CS and MLS-A geological formation represented in TM, both celestite and dolomite were considered to bear substantial quantities of Mo. Furthermore, lime addition disfavored complexation phenomena and created conditions (pH > 10) for celestite partial dissolution enhancing Mo mobility. Part of this labile Mo was removed during slurry treatment process resulting in the Mo impoverishment outlined in section 3.1.1. Nevertheless, non-negligible amounts of Mo could also have been incorporated in ettringite (Cornelis et al., 2008). Although not particularly favored by Mo large size (Zhang and Reardon, 2003), SO_4^{2-} replacement by Mo during ettringite precipitation might explain the Mo concentrations increase between pH = 10 and 7 (Figure 7d). For such pH values, both celestite and dolomite were oversaturated so that no particular impact on Mo concentrations were expected. On the other hand, ettringite was shown to dissolve quickly at pH < 10, which allowed us to describe Mo behavior assuming 0.008 mg of Mo per gram of ettringite. At pH values below 7, Mo release triggered by successive celestite and carbonates dissolutions were hidden by complexation at oxides surfaces.

3.2.3.2. Antimony

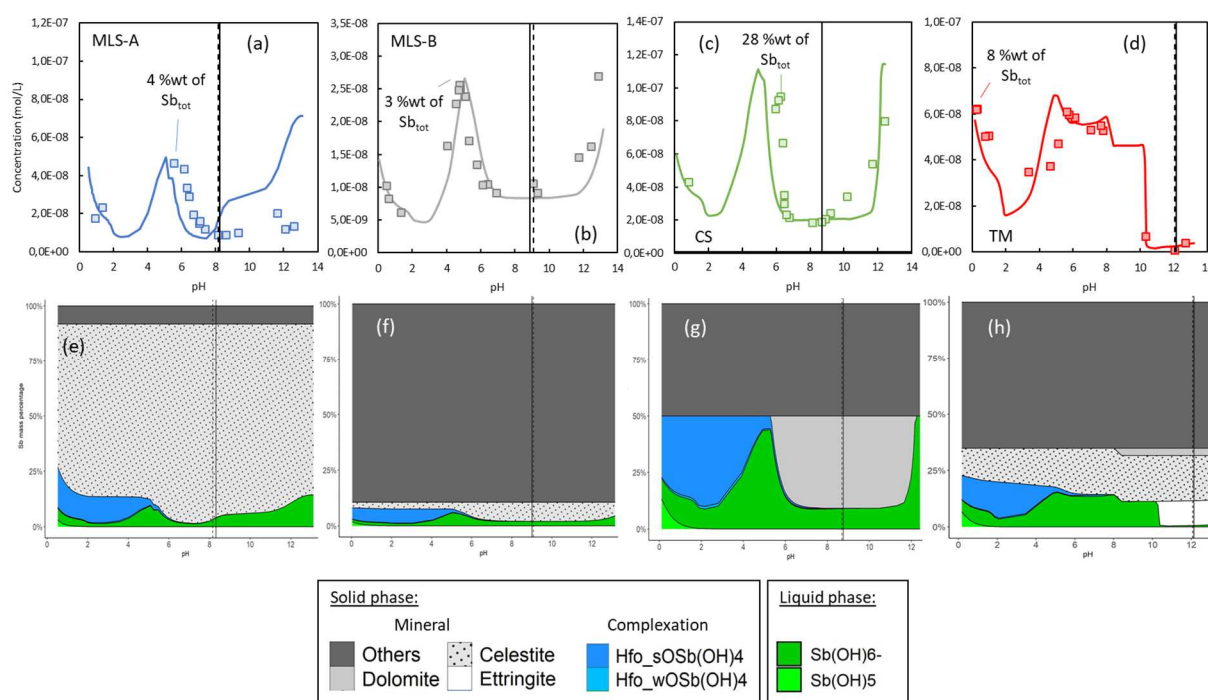


Figure 8: Experimental and modelling results of Sb concentrations as a function of pH during pH dependence leaching tests for MLS-A (a), MLS-B (b), CS (c) and TM (d). Marks and solid lines represent experimental and modelling data respectively. Vertical dashed and solid lines represent the experimental and modelled natural batch pH respectively. For each pH dependency curve, a corresponding area plot representing Sb repartition between solid and liquid phase is given below. Mass balance has been made regarding the total Sb concentrations as measured by total content analysis for each sample

For each sample, Sb concentrations presented similar features compared to Mo over the whole pH range (Figure 8). Repartition of Sb was not investigated by SEM/EPMA analysis because of DL issues, but modelling results strongly suggested that celestite associations were also the main factor affecting its mobility during pH dependence leaching tests in MLS-A and MLS-B. This was particularly clear for MLS-B (Figure 8b), where assuming 0.005 mg of Sb per gram of celestite was sufficient to describe Sb concentrations evolutions at pH > 4.5. At the end and after the carbonates buffer area (pH = 4.5 and below), Sb concentrations drop off in all samples because of the growing importance of complexation at these favoring pH conditions. Assumptions made regarding Sb complexation occurring through simple ligand exchange between reactive surface sites and $\text{Sb}(\text{OH})_6^-$ (Cornelis et al. 2012) satisfyingly described experimental observations. Sb seemed to be proportionally more retained than Mo at low pH. This might be due to its aqueous speciation in those pH and redox conditions, where a part of Sb was still under the $\text{Sb}(\text{OH})_6^-$ form directly concerned by complexation while the only Mo aqueous form at pH < 2 (H_2MoO_4) was not expected to be involved in complexation. One can note that surface plot presented for MLS-B and TM (Figure 8f and h) might largely

overestimate the non-leachable Sb proportion since it was computed by fixing a Sb total content equals to QL. Despite the slightly higher proportion of 0.007 mg of Sb per grams of celestite, the main difference between Sb behavior in MLS-A and MLS-B was seen at pH above pH_0 . Indeed, for MLS-A, the leaching maximum corresponding to celestite acidic partial dissolution ($pH = 6.2$) was not symmetrically retrieved at $pH > 12$, where Sb concentrations remained relatively low ($< 1.9 \cdot 10^{-8} \text{ mol} \cdot \text{L}^{-1}$). Sb concentrations were systematically under-saturated regarding calcium antimonate because of the low Sb total content. We suggest that Sb was incorporated in ettringite structure during pH dependence leaching tests at $pH > 10$ by replacement of SO_4^{2-} (Cornelis et al. 2008). Indeed, on one hand, ettringite was clearly shown to precipitate in MLS-A (see section 3.2.2.1) and, on the other hand, this behavior was not acknowledged in MLS-B or CS where no ettringite was formed. Figure 8e could be used to point out the importance of celestite on Sb overall speciation in MLS-A. Moreover, at pH_0 , Sb seemed to be mainly associated with unreactive mineral, consistently with its relatively low mobility compared to Mo.

Sb concentrations in CS (Figure 8c) during pH dependence leaching tests could be described by assuming a speciation close to what was stated for Mo. Indeed, considering a proportion of 0.002 mg of Sb per grams of dolomite, we managed to represent both acid and basic maximum leached concentrations, which were highly impacted by dolomite dissolution.

Finally, results for TM could be used to outline the main factor affecting Sb behavior (Figure 8d). Precipitated ettringite was suggested to control Sb release between $pH = 7$ and 13. The lowest Sb concentration in solution was seen at pH_0 because of ettringite initial presence and subsequent precipitation during experiment, which was likely to have a stabilizing effect. Representation of Sb complexation at oxides surfaces in TM was not as satisfactory as for other samples. Indeed complexation was first overestimated between $pH = 6$ and $pH = 8$ resulting in a drop of Sb concentrations inconsistent with experimental results. A second shift between modelling and experimental results occurred at acidic pH resulting in considering a too high proportion of Sb in the solid phase. Although some discrepancies persisted between modelling and experimental results in TM, it is interesting to point out that hypothesis made to describe CS and MLS-A major and trace elements speciation were also applicable to define this more complex material having undergone particular pretreatments (liming, filtration...). These conclusions might shed light to the fact that, upon contact with air in a storage scenario, Sb and in a lesser extent Mo mobility in tunnel mucks might be increased. Indeed, pH is expected to decrease following carbonation until an endpoint of 8 is reached (Dijkstra et al., 2019), which will trigger the release of TE incorporated in ettringite. Such conclusions consolidate the usefulness of geochemical modelling to help overcome issues in the management of excavated materials untreated or with particular treatments.

4. CONCLUSION

Excavated earths from Grand Paris Express construction sites often present high mobility regarding particular trace elements. This study was aiming to present a complete overview of Mo and Sb speciation in four different excavated rocks and soils through direct and indirect analysis coupled with geochemical modelling. Among the four samples, three were raw materials only representing one geological formation, while the fourth was a mix of two geological formations, which had been treated (liming, filtration...) in a slurry treatment plan before sampling for the present study. All samples were mainly carbonated and TE natural contamination only occurred through low levels. Total mineral assemblages were modelled assuming kinetically dependent dissolution for each mineral phases (excepted carbonates and gypsum). This approach could be determining to help us understand the global behavior of excavated earths and soils in different scenarii (e.g. reuse, storage...). Mo was seen in association with pyrite in all samples probably incorporated as a solid solution. The Mo associated with pyrite was suggested to be released only under basic conditions. Complexation at iron (hydr-)oxides surfaces was seen to control Mo and Sb at acidic pH and was satisfyingly described by the Generalized Two Layer Model. Mo and Sb associations with celestite were clearly identified in both marly limestones so that, in celestite-rich samples, celestite dissolution should be monitored to predict Mo and Sb long-term mobility. In the calcareous sample, an ambiguous behavior of Mo and Sb was noticed, where incorporation into carbonates was preferred to describe their speciation compared to celestite associations. Although only assumed from indirect characterization methods, it could partly explain the highest mobility attested in this sample where Mo exchangeable fraction would therefore be impacted by a large proportion of Mo associated with carbonates. Finally, hypothesis made for modelling both calcareous and marly limestone samples were extended to describe satisfyingly Mo and Sb behavior in the tunnel boring mucks, in which incorporation of both oxyanions during ettringite precipitation has mitigated their leaching at the natural pH of the mucks. In terms of environmental management of the excavated materials, the results presented here emphasize the importance of pH on TE leaching behavior especially for alkaline tunnel mucks, which would undergo a pH decrease upon contact with the air in a context of storage.

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