

REGULAR ARTICLE

Speciation, mobility and adsorption effects of various metals in sediments in an agricultural area surrounding an uranium ore deposit (Nisa, Portugal)

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ABSTRACT

The availability and mobility of metals in soil strongly depend on its sediments geochemical forms and, therefore, the sediments' particles composition evaluation is more meaningful than the estimation of total soil concentrations, particularly when risk and toxicity are under evaluation. The objective of the present study is to evaluate speciation, fractionation and mobility of the considered metals in sediment samples collected in the surrounding area of a very important unexploited uranium ore deposit located in the Alto Alentejo region of Portugal (Nisa). Sequential Extraction and analytical determinations using X-ray fluorescence technique of the tested materials allowed the determination of mobile fractions and the estimation of ionic speciation. Mobility factor for different elements was estimated, with some of them presenting high mobility rates for exchangeable ions and oxide fractions. The results evidence a high geochemical availability for U, Mo, Nb, Ca, Mn, and, in some particular cases for As, V and Cr. This availability is considerably lower for other elements such as Cu, Zn, Pb, Fe, Ba and Zr. Geochemically, regarding its form of occurrence, most of these metals are incorporated in the sediment matrixes as (oxide) secondary minerals and/or included in iron-exchangeable-oxyhydroxides precipitates. By contrast, binocular microscopy observations and Scanning Electron Microscopy analysis evidenced that U, As, Nb, Mo, and (but with less evidence) V and Cr, are adsorbed in iron-oxyhydroxides-clay minerals, being present as aggregates and as coatings at the surface of primary grains. It was possible to prospect that the majority of the more mobile metals, including uranium, probably occur as oxide or in secondary forms minerals being its origin related with weathering and dissolution of primary sources and subsequent transportation by local water courses in the dissolved fractions as hydrochemical solutes or included in colloids. Later, these metals precipitated as secondary forms and/or were adsorbed preferentially at the surface of the iron-oxyhydroxides-clay minerals precipitates.

Keywords: Adsorption-desorption; Geochemical availability; SEM; Sediment grain-coating; Sequential extraction

INTRODUCTION

The area under study is located near the village of Nisa, Portalegre district, in the Alto Alentejo province of Portugal (Fig. 1). In the region of Nisa a uranium-rich mineralized mass occurs (Faria & Mesquita, 1962; Ribeiro et al., 1965; Alves de Campos, 2002; Prazeres, 2011), which is considered one of the largest and most important unexploited uranium ore deposits ever discovered in Portugal. The area under study is used for grazing and agriculture proposes, and superficial water and groundwater are used for irrigation and as drinking water by cattle (Fig. 1).

Regarding generic baselines and toxicity standards, soils and sediments of the area surrounding the mineral deposit reveals anomalous concentrations in various metals such as uranium (U), molybdenum (Mo), niobium (Nb), zirconium (Zr), lead (Pb), iron (Fe), copper (Cu), manganese (Mn), chromium (Cr), vanadium (V), calcium (Ca), barium (Ba) and arsenic (As) (Barbosa, 2014; Ferreira et al., 2016).

Four sediment samples were considered for study (Am27, Am48, Am103 and Am218). These samples were collected in a local intermittent water stream that intersects the main mineralized area of the ore deposit. Their locations are presented in Fig. 1. Samples 48, 103 and 218 were collected

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in the riverbed. Sample 27, by its turn, was collected in a river side area where sedimentation has direct influence from intermittent drainage that is generated from a small ore waste dump in rainy periods.

The enrichment on uranium and other metals in the study area is related to a wide contact metamorphism aureole, mainly composed by hornfels and mottled schists. This metamorphic activity is related with the emplacement of granitic intrusions during the hercynian orogeny (Ferreira et al., 1987). In the Nisa region two main lithologies occur: one, in the northern sector, where the area of this study is located, essentially composed by metasediments (Ediacarian age shales and greywackes), and the other, in the southern sector, where mainly granitoids of the Nisa's Massif occur (Ribeiro et al., 1965; Solá, 2007).

One of the main objective of this work is to evaluate the availability and mobility of diverse metals in the environment and subsequently ascertain a possible ionic speciation of the different elements. To achieve such a goal, an adapted procedure of the sequential extraction (SE) process suggested by Tessier et al. (1979) was applied (Santos, 2017). Binocular microscopy (BM) observations were performed in order to understand the microscopic structure and grain mineralogy of the soil and sediment samples. Scanning Electron Microscopy (SEM) analyses were also performed for one of the original samples in order to achieve more information about the elements geochemical distribution in the grains, so a better understanding of the transportation and precipitation and/or adsorption processes that can be related with the metals detected in anomalous concentrations in the sediments can be achieved.

Evaluation of mobility and availability of metals in environment is very important, mainly to understand potential situations of contamination and subsequent adverse effects of toxicity (Sims, 1986; Pierzynski, 1994; Smith, 1999; Smith et al., 1999; Markich, 2002; Smith, 2007; Velimirović et al., 2011; Barbosa, 2014; Ferreira et al., 2016; Santos, 2017). The ability of a soil to provide and/or retain metals is one of the most important factors for such evaluation. Processes such as adsorption/desorption, precipitation/dissolution and complexation, influence the solubility of the metals in the environment, which leads to variation in mobility and availability (Sposito, 1986, Yuan & Lavkulich, 1997; McGrath & Semple, 2010).

The way metals are present in soil is defined by their intrinsic properties and soil characteristics, such as pH, mineralogy of clays, redox potential, ion exchange capacity, organic matter characteristics, temperature and microbial activity (Sims, 1986; Sposito, 1989; Pierzynski et al., 1994; Velimirović et al., 2011). The ion exchange capacity indicates the soil's ability to adsorb metals, however other aspects such as metal

selectivity, cation concentration, pH and ionic activity of the solution should also be considered (Ross, 1994).

Several authors suggest that the association of metals with the solid fraction in soils and sediments is largely due to adsorption processes (Sposito, 1986; Yuan & Lavkulich, 1997; McGrath & Semple, 2010; Velimirović et al., 2011), and this is the process that most influences the mobility and the availability of metals in soils (Ross, 1994; Alloway, 1990; Smith, 2007; McGrath & Semple, 2010). However, the role of precipitation reactions should not be neglected since these reactions play a role in controlling the concentration of metals in solution (Sims, 1986; Rodrigues et al., 2000).

The total concentration of trace elements present in the soil is subdivided according to three main fractions - the inert, reactive and available fractions (Fig. 2). The first



Fig 1. Location of Nisa village (Portugal); study area and sample location.

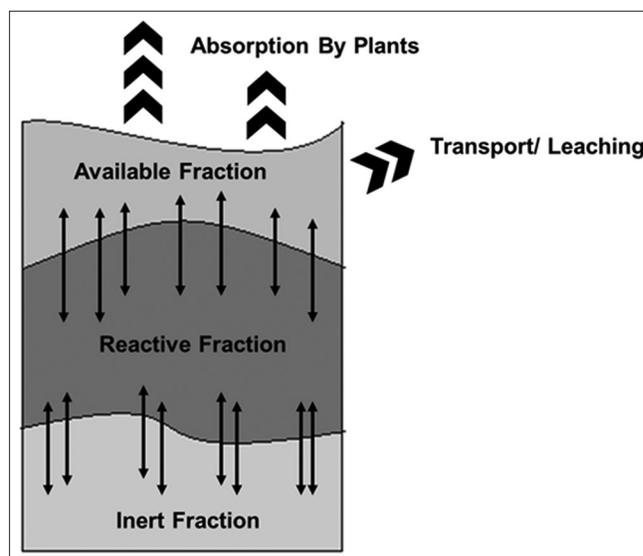


Fig 2. Representative scheme of the inert, reactive and available fractions in a soil with highlight for available fraction as the main source from soil of elements to processes related with other environmental compartments and biological phenomena. Adapted from Rodrigues et al. (2010)

two are in the solid phase of the soil while the inert fraction occurs in the soil solution (Rodrigues et al., 2010). In order to estimate fractionation, speciation and mobility of the elements within soils and sediments, it is important to know the distribution of the elements in the different fractions of the soil and also to understand how the main associated chemical processes occur. According to Rodrigues et al. (2010), the available fraction consists of free and complex ions combined with dissolved organic matter whereas reactive fraction can be formed by reactive precipitates, ions adsorbed by clays, organic matter, metal oxides, carbonates and organometallic complexes. These two fractions are in mutual equilibrium due to chemical processes such as precipitation/dissolution, adsorption/desorption, reduction/oxidation and microbiological processes. The inert fraction is associated to strong bonds between the trace elements and the crystalline matrix of the soil solid phase and is mainly influenced by erosion/fixation phenomena. According to these authors, the available fraction is the main source from soil of available elements to leaching and transport process and to plant absorption phenomena (Fig. 2).

In order to understand in what chemical form(s) the metals occur in this environment, the sequential extraction process was used. Its main objective is to selectively measure the distribution of metals in sediments and to determine the forms under which the elements occur in the different soil fractions (Shuman, 1982). This process also allows to correlate the chemical form extracted with the metal concentration and, therefore, it is possible to evaluate the remobilization potential.

To reach this objective, one of the most used methods is the one proposed by Tessier et al. (1979) in which extractors are used to separate metals bound to the exchangeable, carbonates, oxides, organic matter and residual fractions. Many relevant variations of Sequential Extraction methods and discussions from its applicability may be found in related literature (Tessier et al., 1979; Shuman, 1982; Ure et al., 1993; Arunachalam et al., 1996; Ma and Uren, 1998; Jardim, 1999; Ahnstrom and Parker, 1999; Sutherland et al., 2000; Rodrigues et al., 2010; Zimmerman and Weindorf, 2010; Suresh et al., 2014; Pandey et al., 2015).

MATERIALS AND METHODS

Sequential Extraction (SE)

In this work, 4 samples were studied (Am27, Am48, Am103 and Am218). Statistical results from a sample collection campaign previously carried on in this study area may be found in Ferreira et al. (2016). These authors

refer the existence of anomalous concentrations of some metals (U, Mo, Nb and As, Cr and V) with distinct spatial distribution behaviors. U, Mo and Nb are related to the metallogenetic process associated with the uranium-ore genesis. No evidence of contamination effects have been reported associated to the collected samples (Ferreira et al., 2016). The metal content increments are of natural origin and they are related to the geochemical anomaly resulting from the mineral deposit occurrence. For each sample, two distinct granulometric fractions, $\geq 1\text{mm}$ and $< 63\mu\text{m}$, were selected, in order to determine how the granulometric fraction is related with the availability of the metals.

The sequential extraction (SE) process has been applied to the four samples in order to evaluate availability, mobility and speciation of metals. In this study, the method suggested by Tessier et al. (1979) was considered. SE is a lengthy process and requires a varied amount of reagents suitable for the fraction to be extracted (Table 1).

The followed procedure consisted on the fractionation of the samples in 4 successive extractions: (i) exchangeable (F1); (ii) bound to carbonates (F2); (iii) bound to oxides (mainly Fe-Mn and Al oxides) (F3); (iv) bound to organic matter + residue (F4). To perform this process, 20g of dry material of each of the samples were weighed and then, for each sample, the extractions were performed as described as follows:

1. Exchangeable fraction (F1): 15 ml of MgCl_2 1 molL^{-1} (pH 7.0) were added, followed by agitation of the sample for 2 hours at room temperature.
2. Fraction bound to carbonates (F2): 30 ml of 1 molL^{-1} NaOAc (pH 5.0) was added, followed by agitation for 5 h at room temperature.
3. Fraction bound to oxides, mainly Fe, Al and Mn oxides (F3): This oxides fractionation was obtained from 40 ml of a reducing solution composed of ammonium oxalate (0.2 molL^{-1}), oxalic acid ($\text{C}_2\text{H}_2\text{O}_4$) (0.2 molL^{-1}) and ascorbic acid ($\text{C}_6\text{H}_8\text{O}_6$) (0.1 molL^{-1}). The mixture was stirred for 30 minutes in a water bath at 90 °C and in the absence of light, as some of the reagents may undergo changes with light.
4. Fraction bound to organic matter: for this fractionation 15 ml of 5% NaOCl (pH 8.5) was added, then it was stirred for 30 minutes in a water bath at 90 °C.

Table 1: Reagents used in the different sequential extraction fractions

Fraction	Reagents
Exchangeable	Magnesium chloride MgCl_2
Carbonates	Sodium acetate CH_3COONa
Oxides	Ammonium oxalate $(\text{NH}_4)_2\text{C}_2\text{O}_4$, Ascorbic acid $\text{C}_6\text{H}_8\text{O}_6$ Oxalic acid $\text{C}_2\text{H}_2\text{O}_4$
Organic matter + residue	Sodium hypochlorite NaClO

X-ray fluorescence (XRF) spectroscopy

Samples were air-dried in an oven at 60 °C for 2 days and afterward were gridded and separated in distinct granulometric fractions. Two fractions, with granulometry a) ≥ 1.0 -mm up to 5-6 mm, and b) $< 63\mu\text{m}$, were selected for XRF analyses (Beckhoff, 2006), that were performed on a XL3t 950 He GOLDD+, USA analyser. The equipment is fitted with an Ag anode target excitation source X-ray tube, that operates at voltages up to 50 kV and at beam currents up to 200 μA . Data was transferred via USB port, using ThermoScientific Niton data transfer (NDT) PC software. Overall measurement time for each sample was 360 seconds in a Helium environmental atmosphere. Each sample was measured 3 times and spectra up to 40 keV were quantified using a factory-installed algorithm (fundamental parameters calibration) for "soil" mode, yielding elemental concentrations in milligrams per liter (mg/l).

Binocular microscopy (BM) and scanning electron microscopy (SEM)

One of the four samples tested for SE was selected for evaluation of its qualitative mineralogy and macroscopic grain forms by means of binocular microscopy (BM).

This sample was also studied by SEM analysis, with the aim of detect the preferential spatial location of the more extractable metals (Argast & Tennis III, 2004; Beane, 2004). Before Scanning Electron Microscopy (SEM) observations, the grain samples were leached of their respective coatings. For this, hydrochloric acid (HCl) was used. For each sample, the grains (with and without coatings) and respective leaching materials resulting from the cleaning of the samples (filtrate residues) were observed. These analyses were carried out with the objective of ascertain, in more detail, the way how metals of higher mobility may be occurring. They were conducted in order to verify (1) whether these elements occur preferentially in the fine or granular matrix and (2) whether they are preferentially disposed in the primary lithic materials or in secondary geochemical phases.

Although the analyses were exploratory, qualitative, not systematic or quantitative, the results revealed to be interesting.

RESULTS AND DISCUSSION

XRF analysis and SE results

XRF analyses results are presented in Annex I. XRF analysis of the solid filtered fractions obtained by SE revealed different profiles regarding the behavior of different metals during the process. It was possible to conclude that:

- U, Mo and Nb have the same kind of behavior throughout the SE process. These elements undergo a small decrease in concentration during the first two fractions, with an abrupt drop in concentrations in the oxides fraction (Fig. 3).
- As, Cr, V, Cu, Zn, Pb and Fe have, in general, lighter variations in concentrations between different fractions throughout the SE process (Fig. 4). Results are not so conclusive like in case of U, Mo and Nb, although a certain tendency for more mobility in oxide fraction maybe observed. Slight unexpected increases in concentration values between the two last SE fractions are, in some cases, observed and are probably related with experimental procedure conditions, being a probable consequence of the insufficiency on the quantities of filtrates obtain in SE procedure. Irregularities derived from the granularity characteristics of these filtrates and its insufficient milling may also explain some irregular measurements that, in general, corresponds to higher standard deviations (Annex I). Significant outliers As, Cr, V are identified for the case of the sample 218, where the concentration of these elements is considerably higher. For this particular case, the presence of metals in higher concentrations influenced the extraction behavior, as for sample 218, As, Cr and V were extracted in the fractions of exchangeable ions and oxides (Fig. 4).
- Ba and Zr concentrations along de SE process do not suffer any remarkable differences, although a certain tendency for a slightly mobility in the oxide stage maybe observed (Fig. 5)

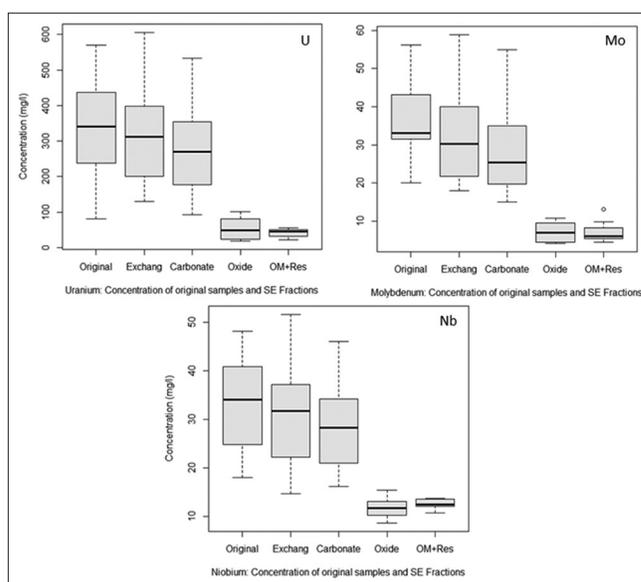


Fig 3. Uranium, Molybdenum and Niobium concentrations in original samples and in solid filtrates of the SE fractions.

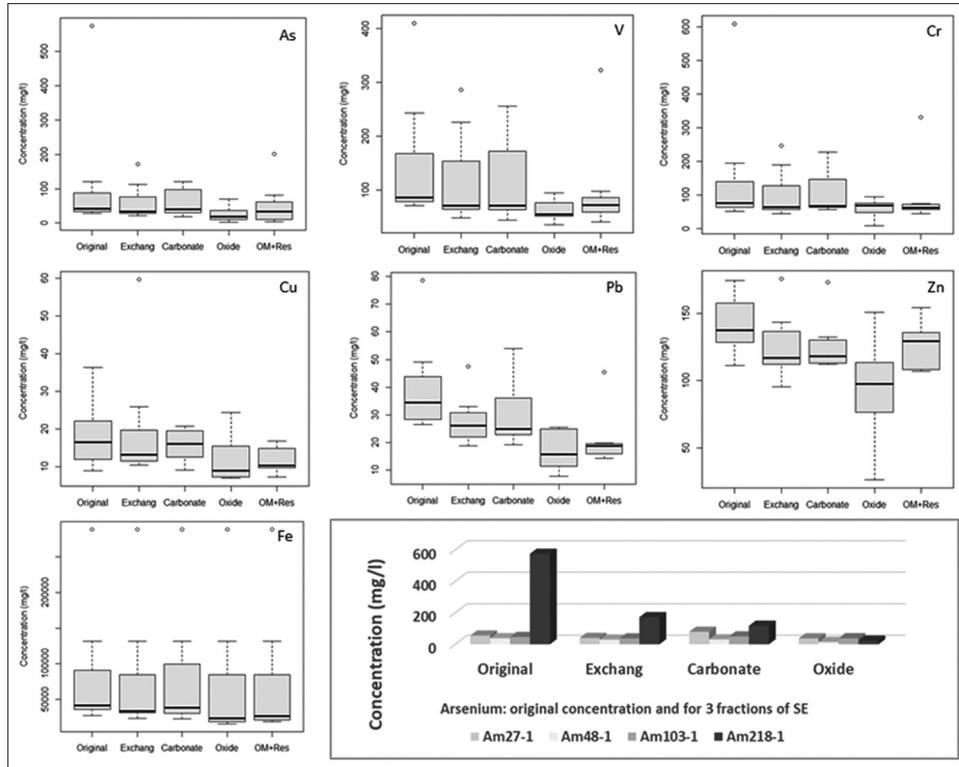


Fig 4. Arsenium, Vanadium, Cromium, Copper, Lead, Zinc and Iron concentrations in original samples and in solid filtrates of the SE fractions. Bottom right: arsenium outlier (read text).

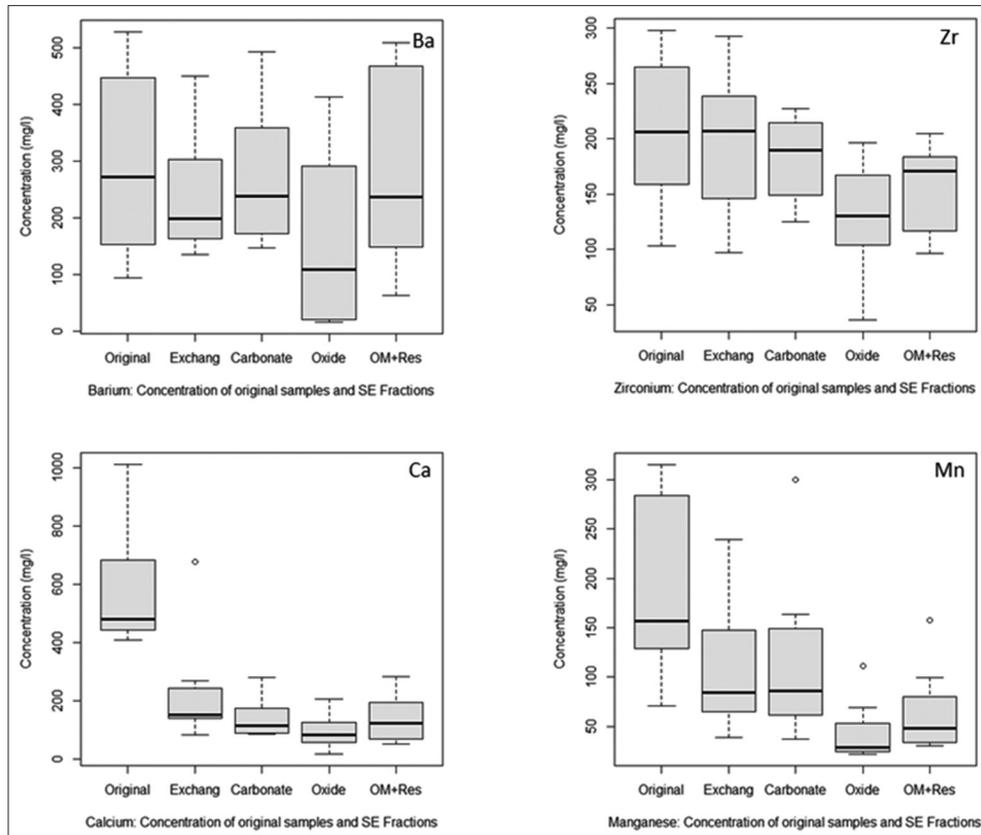


Fig 5. Barium, Zirconium, Calcium and Manganese concentrations in original samples and in solid filtrates of the SE fractions.

- Ca exhibits a great availability on the exchangeable ions fraction and also along the remaining SE fractions, which is according to its mobility profile, being also worth to evidence its higher extraction rates in the carbonate and oxides fractions (Fig. 5).
- Mn exhibits considerable availability being possible to be observed its higher extraction rates in the exchangeable ions and in the oxide fractions. This behavior reflects the usual form of occurrence of Mn in the soils and sediments as manganese-iron-oxide-hydroxide precipitate (Fig. 5).

According with SE results, in general, the highest mobility rates were detected for exchangeable ions and oxide fractions. The more available elements for potential environmental dispersion are: U, Mo, Nb, Ca, Mn, and, in some particular cases, As, V and Cr. The group U-Mo-Nb present a high mobility rate in the oxide fraction (Fig. 3). The group As-V-Cr present high mobility rates in the exchangeable ions and oxide fractions for the case that these elements are present in higher concentrations in the original samples (samples 218-1 and 218-7, Fig. 4). Sample 218 presents the higher total concentrations of As-V-Cr in its original form. Extreme to sever outliers are present as it can be verified in boxplots of Fig. 4. SE results also evidences highest mobility rates for these semi-metals. The differences between this sample with the other three (27-1, 48-1, 103-1) are well shown in bottom right graph presented in Fig. 4. This particular behavior is in accordance with

results achieved from previous campaign and described in Ferreira et al. (2016), were it was possible to verify an increasing of total concentrations of the association Cr-V-As (which is especially relevant for Cr), in samples collected further downstream of the river bed. According to the authors, the increase of Cr-V-As concentrations in sediments in more distal samples and accordingly with the river downstream direction is probably due to a higher transport capacity of this elements by circulation waters. In fact, in environmental oxidizing conditions, these elements usually occurs in ionic speciation forms that are mobile and may be transported in the dissolved solid fractions and as hydrochemical solutes. Also, these elements may have more ease in being combined with other constituents present in the finer-grain silty-clay granulometric fractions of sediments which can be more easily transported into longer distances by stream waters than coarser-grain sediments. So, comparisons of SE results for each fraction and according with the distinct classes of granulometric fractions ($\geq 1\text{mm}$, and, $<63\mu\text{m}$) were made. Fig. 6 shows the results of these comparisons for the cases of Arsenium and Vanadium. It is possible to verify that, in the case of V, for oxide fraction, concentrations in granulometric fractions $<63\mu\text{m}$ are tendentially higher than concentrations of coarser granulometric fractions $\geq 1\text{mm}$. For As, the tendency of higher concentrations in silty-clay fraction is present in carbonate fractions but only for the cases of samplings of lower concentrations. These facts evidence, first, a tendency of more availability and mobility

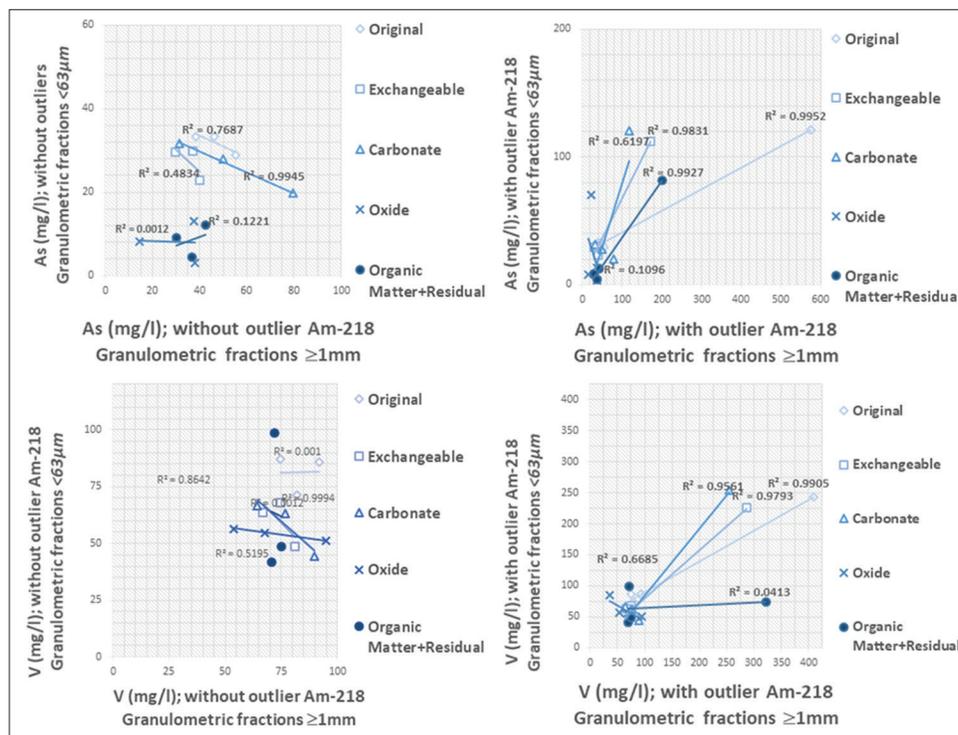


Fig 6. Sequential Extraction Results of Arsenium and Vanadium for all samples. $\geq 1\text{mm}$, and, $<63\mu\text{m}$.

of As and V in the silty-clayed fractions of the sediments, and, secondly, the possibility that transport was performed as hydrochemical solutes and/or as oxi-hydroxide ionic forms which facilitates transportation process along higher distances. It is important to refer that when outlier sample 218 is considered the graphic results tend to hide these particular tendencies for As and V.

The cases of Uranium and Molybdenum are presented in Fig. 7. In general, concentrations for each sample at each SE fraction do not present significant differences when distinct granulometric fractions are compared. For the case of U and Mo, no distinct behavior is detected related to the different granulometric fractions $\geq 1\text{mm}$ (samples with reference “1”), and, $<63\mu\text{m}$ (samples with reference “7”). Here, the tendencies are, on the opposite, close to positive linear regression, especially for the case of Uranium and Molybdenum which may mean that these two elements were mobilized in a different way, comparing with Arsenic and Vanadium.

For oxide fractions, and, organic matter + residuals, irregular behaviors give no chance of identifying any particular pattern in case of U, Mo and As. For oxide fractions, an inverse tendency is present in the case of V (Fig. 6). At lower concentrations, inverse tendency occurs in carbonate fractions for the case of As.

In order to determine the possible forms in which the elements occur in the environment, the data from SE procedure was crossed with information about the chemical elements (electronic configuration) and their ionic forms (their ionic rays and more stable states of valence). These data were adapted to the diagram proposed by Rose et al. (1979) that defines ionic speciation of different elements in natural environments. The results obtained for the present study suggest that U, Mo and Cr occur in the form of +6, and Nb, As and V occur in the form +5, that is to say that these elements may occur under oxidizing conditions. In such conditions, these elements tend to (re)precipitate after being leached and transported as solutes or in a colloidal form. This situation strongly suggests that these elements may have suffered leaching, transport and subsequent precipitation. As these elements are associated with exchangeable ions fractions in SE process, transport may have occurred in colloidal state and/or as hydrochemical solutes. As they show evidence of high-mobility rates in the oxide fractions, these elements may also be present in hydro-oxidizing forms and mineral secondary forms. It is also possible to conclude that the highest concentrations of U, Nb, Mo, As, V, and Cr are not associated to primary minerals structures but to secondary oxidizing mineralized states that are incorporating the studied samples matrixes. Zr most likely occurs in the form of +4, which in general

doesn't have great mobility in Nature and the remaining elements (Cu, Fe, Mn, Zn, Pb, Ba, Ca) occur in the form of +2, which is the most usual oxidation state in this type of environment.

BM and SEM analyses

Observations by BM and SEM analyses allowed the knowledge about the samples texture features, their mineralogical compositions and the understanding of which are the more probable geochemical forms of the more mobile metals – U, Mo, Nb, As, V and Cr – in the samples matrixes.

Fig. 8 shows some features, attained by BM observation, of grains $>1\text{-}2\text{ mm}$. It is possible, in all grains, to visualize a thin silty-clay-to-clay coating that most probably came from the finer granulometric fractions of the sample. Other interesting feature is the presence of iron-(manganese)-silty-clay aggregates of reddish colour that may be confused with grains of more quartzitic composition (that are also present) (Fig. 8, d). Regarding morphoscopy, the grains evidence a continental facies of low grade of maturation, the majority of the clasts

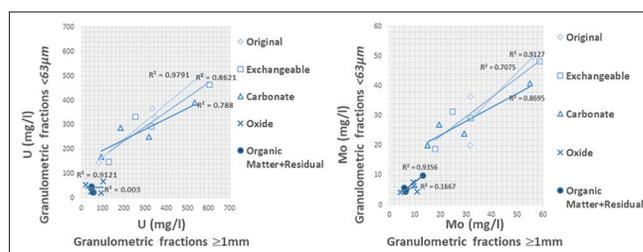


Fig 7. Sequential Extraction Results of Uranium and Molybdenum for all samples. Comparison between granulometric fractions $\geq 1\text{mm}$, and, $<63\mu\text{m}$.

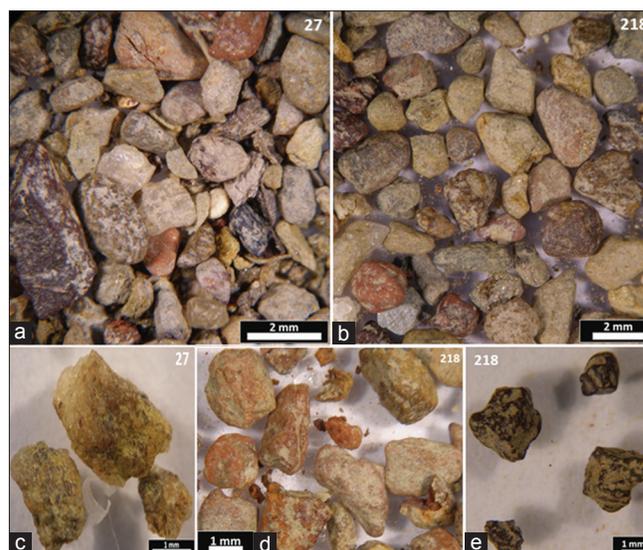


Fig 8. Binocular microscopy images of samples 27 (a and c) and 218 (b, d and e).

having the same constitution of the source rocks (Fig. 8, a) and b)). Intense alteration effects such as oxidation and caulinization of primary grains may be observed. Sericite crystallization is also observed in the remaining clasts of the source rocks. Various kinds of grains have been identified, namely granite, sericite-bearing granite, metasediments (with different types of clay mineral), and isolated or mineral aggregates of diverse minerals, mainly quartz, feldspar, biotite and muscovite. Coatings partially or totally cover the surfaces of these grains and aggregates. No grains of uranium primary minerals were found, but evidence of secondary mineral forms were observed.

Fig. 9 shows SEM images and the metal relative amounts along line for U, Mo, Nb, As, V, Cr and Mg of a) part of a grain with coatings, b) part of a grain after HCl leaching (without coatings) and c) the filtrate solid waste that resulted from the grain leaching with HCl. Fig. 10 presents the spectra for Al, Si, P, S, K, Ca, Fe, U of the respective analyzed samples. The results shown allow us to perceive the form of occurrence of the metals in the sample matrix, that is, it allow to verify if they are associated to the crystalline grain network or to the coating of the particles. For the highlighted elements U, Mo, Nb, As, V, Cr and Mg it is verified that the hydrochloric acid had an efficient leaching power and that these elements are almost totally or totally absent on the leached grain. They are also absent at the filtrate solid waste which is probably due to their remobilization and solubilisation, which probably have made difficult their retention by filtration. Comparing the results obtained from the original sample with the leached samples, there is a significant reduction in the concentrations of metals As, Nb, Mo and U and some reduction also in V and Cr. These results demonstrate the ease of leaching of these metals, which will probably have been remobilized for the liquid fraction, since they are not found again in the clean grains or in the solid waste matrix. These observations evidence and reinforce the previous conclusion about the fact that the more mobile metals may be precipitated in a secondary oxidizing state. Another interesting feature comes from the analysis shown in Fig. 10. The spectrum results are consistent with the presence of aluminium silicates, more specifically, clay minerals, that is, phyllosilicates with variable amounts of iron, magnesium or other alkaline earths metals, alkali metals, among other elements. It seems that the previous identified extractable metals U, Mo, Nb, As, V, Cr are related with the presence of these clay minerals, which, in turn, may be the main composition of the grain coatings. In such conditions it is plausible to prospect the possibility of the extractable metals being precipitated and attached to the surface of the clay minerals that forms the coating of the grains. This attachment may have occurred by true adsorption, or by

a weaker adsorption-like bonding, depending on the ionic radii values. In the case of the smaller ionic radii elements As and V, true adsorption may have occurred, whereas in the case of the bigger ionic radii elements U and Mo, weaker adsorption-like bonding could have occurred. This could explain the different patterns observed for U and Mo, on one side, and As and V, on the other. This way, U and Mo could have been more easily leached from the clay mineral host than As and V, and this could be the reason why these two elements are enriched in the downstream sediments, contrasting with the U and Mo behavior.

The most part of the grains are coated with clay minerals that include the metals and semi-metals present in higher concentrations. These are present in secondary mineral states and as oxi-hydroxide-precipitates that are adsorbed by the clay minerals being, therefore, detected in X-ray fluorescence in the grains of 1-2 mm mesh and in the materials of granulometry of silt and clay (< 93 µm) with no significant distinction.

CONCLUSIONS AND FINAL REMARKS

With this study it was possible to understand speciation of elements that are present in higher concentrations in soils and sediments surrounding this mineral deposit. Elements with high and less geochemical mobility degree were identified and some conclusions were possible to be made regarding its geo-environmental availability and transport process. The results evidence high geochemical availability of U, Mo, Nb, Ca, Mn, and, in some circumstances of As, Cr and V. Most of these metals have a high probability of being incorporated in the sediment matrix as precipitates, as oxides and/or mixed oxi-hydroxides, as secondary geochemical minerals and adsorbed on other mineral

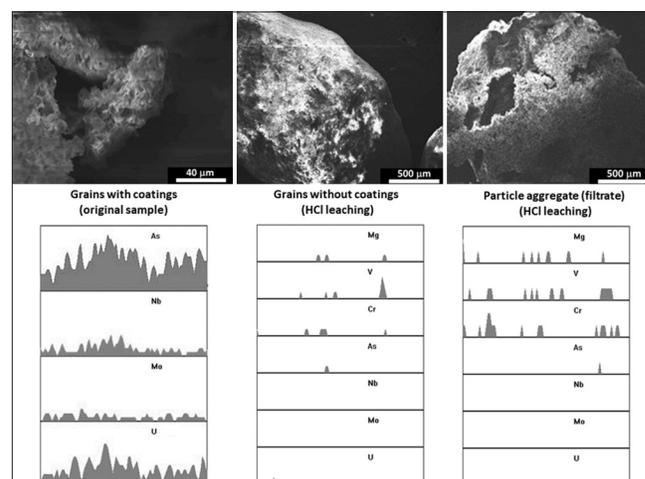


Fig 9. Metals semi-quantitative profile SEM analyses on grains and coatings.

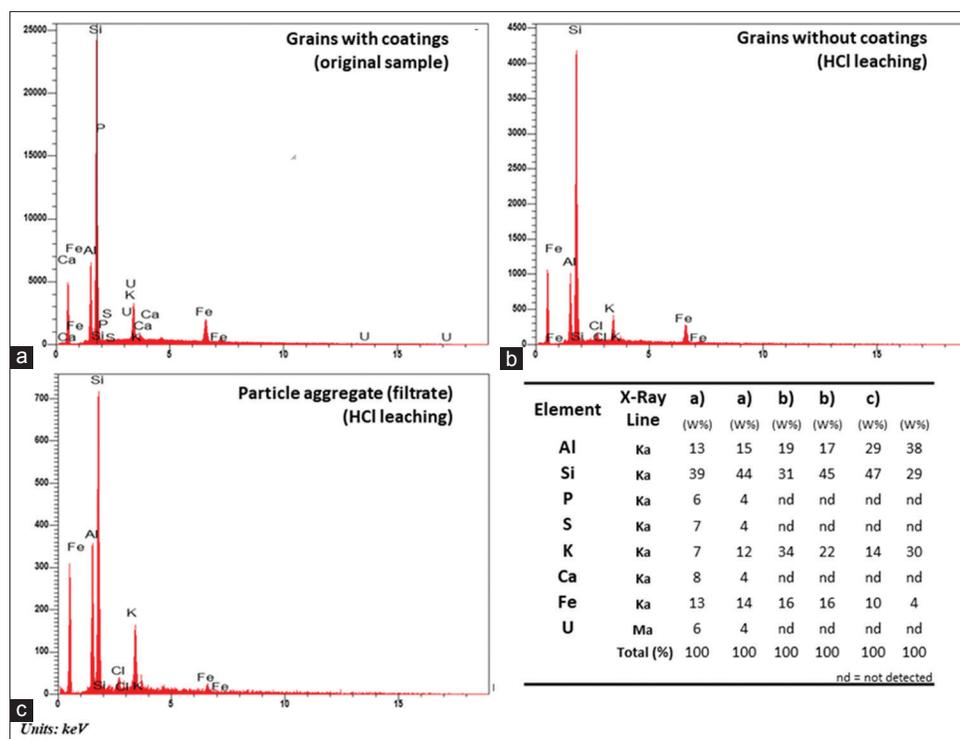


Fig 10. Spectrum of Al, Si, P, S, K, Ca, Fe, U of the analysed samples a) a part of a grain with coatings, b) a part of a grain after HCl leaching (without coatings) and c) the filtrate solid waste that results from the grain leaching with HCl.

phases. Combined BM and SEM observations evidence the presence of these elements adsorbed on the clay coatings of the primary rock and mineral grains. Depending on the ionic radii values, true adsorption of certain elements, like As and V, or weaker adsorption-like bonding of others of bigger ionic radii, like U and Mo, may explain the dual opposite behavior detected between the associations U-Mo-Nb and As-V-Cr. Despite (at least some of) these metals have been adsorbed, it should be expected a slow and difficult degree of release from the soils and sediments where they occur. In fact, desorption processes are not easy to occur in nature, since they depend on (sometimes very) drastic changes in environmental conditions, especially regarding pH and eH variations. Szecsody et al. (1998), for instance, have concluded, for the case of uranium, that desorption of this element is difficult. According with these authors, although U(IV) precipitates on surfaces, geochemical processes release uranium slowly to solution in cases where redox barrier effects are inhibited by oxidizing conditions. If, as suggested previously, uranium was not really adsorbed to the surface of the finer-grained minerals, these condition changes would not be necessary to justify the higher U (and Mo) contents in the coarser-grain samples, as no desorption process would occur.

Geo-availability of the mobile elements detected on SE tests may not be as high as might be expected. In this context, grain-coating is a phenomenon of importance

regarding storage, transport and retardation effects of metals and other chemical compounds in the environment, being its effects studied and reported by several authors (Reilly at al., 2009; Velimirović et al., 2011; Singleton at al., 2017).

To understand the behavior of metals in the soil there are diverse SE methods that can be used (Tessier et al., 1979; Ure at al., 1993; Ma & Uren, 1998; Ahnstrom & Parker, 1999; Zimmerman & Weindorf, 2010; Suresh et al., 2014) and therefore it is up to the researcher to determine the most appropriate procedure or even to adapt it to his case study, always taking into consideration factors such as type of soil, level of contamination, methods of comparison of results and limitations associated with the chosen SE method. In order to determine the metals concentrations in the soil and to analyze their speciation as good as possible, the researcher should not only rely on the results obtained by SE but should use other analytical techniques that complement the study of the elements present in the soil sample.

In the study area, agriculture and grazing are the main occupational activities, despite the mineralization and geochemical natural anomaly that is present. Water is used for irrigation and by cattle. Some of the streams of the local watershed intersect the area of the mineralized ore deposit and incorporate the more mobile naturally available

metals, that are, in this particular case, U, Mo, Nb, Ca, Mn, and, but with less incidence, As, Cr, and, V. Evidences of transport process along longer distances were possible to be identified for some of these metals, especially for As, Cr, and, V. Transport process could have been facilitated since these elements occur as hydrochemical solutes or in colloids, associated with silty-clay materials of the dissolved solid fractions. Afterward, re-precipitation process will include these metals in secondary mineral forms and/or as attached/adsorbed particles preferentially on the surface of the precipitates of iron-oxyhydroxides-clay minerals. Although the expected difficulties that may be associated to possible re-mobilization of these metals from the sediments, toxicity potential effects and risk derived from biogeochemical availability (Smith, 1999; Smith et al., 1999; McGrath & Semple, 2010; Velimirović et al., 2011) of U, Mo, Nb, Ca, Mn, As, Cr, and, V are questions of major concern in this area.

Determination of the concentrations of these metals in original collected samples and in SE solid and liquid fractions by quantitative methods, like ICP-MS (Inductively coupled plasma mass spectrometry), and, more detailed SEM analysis (with and without inducing leaching effects), are advisable to be developed in order to have a more accurate interpretation of the metal mobility and speciation phenomena and to achieve a more effective risk analysis. Distal sampling collection is also a way to pursue, in order to complement the present conclusions about transport process and its spatial effectiveness.

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Authors' Contributions

ACS, SB and NL conceived and planned the experiments, interpreted the results and wrote the manuscript. ACS, SB, MFP and NL carried out the experiments. FR, FL and JA provided critical feedback, helped the research and the manuscript review.

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Annex I. X-ray fluorescence results of some of the elements analysed according with Sequential Extraction fractions.

Sample	Fraction	ELEMENTS																											
		U		Mo		Zr		Pb		As		Zn		Cu		Fe		Mn		Cr		V		Nb		Ca		Ba	
		Avg	RSD	Avg	RSD	Avg	RSD	Avg	RSD	Avg	RSD	Avg	RSD	Avg	RSD	Avg	RSD	Avg	RSD	Avg	RSD	Avg	RSD	Avg	RSD	Avg	RSD	Avg	RSD
27-1	Original	570.5	3.6	56.1	4.2	206.8	8.1	49.2	10.7	55.3	4.7	171.8	5.7	15.5	14.2	45432	3.9	162.2	8.7	60.5	13.0	82.0	12.7	48.1	3.8	522.2	29.8	273.9	6.3
27-1	Exchangeable	605.3	7.5	58.8	3.6	194.7	6.7	47.5	10.8	40.2	28.8	175.6	5.1	13.6	29.3	36506	15.3	95.6	30.0	57.9	9.9	81.1	9.0	51.5	4.1	152.2	33.6	199.3	26.0
27-1	Carbonate	533.8	3.4	54.9	3.9	178.5	20.7	53.9	12.8	79.6	8.6	172.9	3.4	19.9	14.0	67049	22.6	135.4	27.0	68.7	8.0	89.6	22.0	46.1	1.9	52.1	32.4	279.1	11.7
27-1	Oxide	101.5	15.2	9.7	17.1	90.6	5.9	25.1	13.5	37.4	18.0	72.6	9.6	7.2	2.4	24161	12.3	24.1	2.6	44.6	34.3	53.7	8.8	12.1	1.5	38.8	0.0	18.8	1.4
27-1	OM+Res	45.9	35.6	6.3	31.3	170.0	9.6	45.5	12.7	42.4	28.6	154.1	15.2	10.3	13.1	20985	22.9	61.4	40.9	54.9	12.0	70.5	19.4	13.6	19.0	172.7	18.8	235.9	12.4
27-7	Original	504.1	0.4	49.8	1.7	285.7	11.0	36.3	1.3	28.9	4.2	143.2	1.2	9.1	3.6	27201	1.4	71.1	7.1	70.2	4.5	71.1	11.8	45.1	0.9	479.9	7.1	94.2	3.4
27-7	Exchangeable	463.9	8.2	48.1	10.6	234.2	11.2	33.0	4.5	22.7	17.1	129.7	2.8	10.5	7.8	23455	4.7	38.1	13.1	44.4	2.1	48.4	21.6	40.9	5.8	270.1	110.7	137.5	42.8
27-7	Carbonate	390.0	3.6	40.8	3.8	224.2	7.5	34.9	6.9	19.7	10.8	128.3	1.9	9.2	3.9	22550	1.1	37.5	25.8	66.0	59.7	44.4	9.7	37.2	1.7	107.8	16.2	174.0	22.0
27-7	Oxide	69.3	5.0	6.4	3.4	157.5	2.6	24.5	8.8	13.1	9.7	151.0	7.0	11.2	24.1	21796	3.7	38.6	24.3	68.6	46.1	56.5	4.3	14.2	5.7	74.5	11.3	195.2	13.7
27-7	OM+Res	41.0	22.9	4.6	24.4	129.4	10.2	19.9	16.5	12.1	13.1	129.7	18.9	10.5	2.0	18784	18.3	30.4	0.6	60.9	54.3	41.7	38.9	10.8	17.4	50.7	30.6	62.8	0.0
48-1	Original	348.9	4.2	34.4	1.8	205.4	7.1	26.4	10.8	38.6	19.6	111.4	13.7	17.7	46.9	36009	3.8	151.5	27.1	51.8	17.8	74.7	11.5	34.5	5.7	437.3	10.7	269.7	5.2
48-1	Exchangeable	331.7	3.7	31.8	2.8	219.8	8.4	28.6	42.9	29.7	19.5	111.7	5.5	13.2	7.4	31834	16.9	77.0	13.5	61.5	13.9	74.5	17.5	31.8	2.8	153.3	28.4	135.1	5.0
48-1	Carbonate	318.8	11.0	29.3	15.1	201.2	9.4	23.2	8.2	31.4	13.5	116.6	16.2	13.5	12.7	31342	8.9	77.2	8.9	68.2	20.2	64.1	17.8	31.1	12.6	122.4	29.5	147.6	10.4
48-1	Oxide	42.9	11.1	4.5	3.8	125.0	4.4	13.4	14.0	14.5	18.8	80.6	6.7	7.5	4.6	19289	10.1	25.4	1.2	74.9	3.6	67.8	17.2	10.3	4.6	97.8	19.5	21.3	3.0
48-1	OM+Res	55.1	12.4	6.6	14.2	175.9	1.9	19.5	25.0	30.1	7.2	107.0	8.3	9.2	0.6	32382	5.0	40.7	0.1	70.2	7.2	74.9	9.9	13.7	11.2	153.0	21.2	187.3	16.1
48-7	Original	330.9	0.9	31.4	2.2	244.3	3.0	30.6	6.0	33.2	1.1	136.0	3.6	12.8	24.1	36218	1.4	129.2	2.7	82.2	6.8	87.0	2.6	33.6	1.9	408.1	5.1	126.0	14.2
48-7	Exchangeable	293.5	7.9	29.1	4.2	243.1	3.3	26.8	3.4	29.5	2.6	112.3	1.6	11.4	0.0	29947	2.6	92.4	13.1	66.1	8.1	67.6	5.7	31.7	3.1	127.2	19.4	188.1	12.8
48-7	Carbonate	250.5	1.7	23.9	1.5	227.4	6.7	25.2	1.5	31.7	7.9	112.1	2.2	11.8	18.7	29850	2.2	59.0	19.2	60.3	10.8	66.5	5.3	27.8	4.1	87.3	26.4	168.9	9.1
48-7	Oxide	26.2	4.3	4.3	9.4	135.1	5.5	9.5	6.0	8.2	11.1	82.7	2.8	7.6	3.5	15729	3.4	25.1	2.8	75.7	6.2	54.7	3.4	10.2	1.3	76.6	25.2	118.9	3.3
48-7	OM+Res	22.8	9.7	5.1	17.3	191.4	2.7	14.2	4.3	9.0	9.6	109.0	4.0	10.3	3.4	21212	7.6	31.4	2.0	44.7	11.9	48.4	21.7	12.2	2.7	67.3	14.0	110.0	50.7
103-1	Original	333.1	7.5	31.7	8.9	194.3	14.0	78.6	12.1	46.4	10.7	121.0	10.5	22.7	12.9	49388	15.8	314.9	88.9	67.7	3.1	92.1	9.1	30.0	5.1	841.4	38.2	388.4	26.2
103-1	Exchangeable	254.2	12.7	24.7	4.2	170.8	3.2	18.9	15.6	37.2	19.0	96.3	11.0	13.2	28.7	34554	8.9	60.2	20.7	65.8	19.4	66.8	1.8	25.0	8.2	152.1	19.9	224.4	29.6
103-1	Carbonate	185.8	18.0	19.4	24.0	168.2	17.4	19.2	31.9	50.1	31.5	112.3	19.8	19.3	37.5	44286	25.0	94.8	40.6	66.5	29.8	76.9	36.7	21.8	21.5	86.8	26.5	303.6	41.5
103-1	Oxide	92.6	16.4	10.8	15.2	176.3	13.3	16.2	16.8	36.0	32.1	112.9	10.2	24.4	62.0	37033	10.9	69.2	28.2	70.4	6.3	94.8	11.1	15.5	10.1	155.1	31.1	413.2	14.4
103-1	OM+Res	53.2	20.4	5.9	16.3	171.9	3.9	18.4	8.5	36.9	36.4	107.4	18.3	16.9	38.4	36716	20.4	56.2	38.9	63.7	19.7	72.2	16.9	12.1	13.6	70.7	43.3	435.2	36.0
103-7	Original	368.2	3.1	36.6	5.1	297.9	0.8	26.5	0.7	33.3	3.7	136.8	3.7	11.4	0.0	36055	2.7	129.4	14.2	86.6	10.3	85.9	9.0	36.6	4.0	448.2	9.4	179.3	16.5
103-7	Exchangeable	333.8	5.1	31.3	4.7	292.9	14.9	25.4	2.7	29.7	8.7	121.8	2.1	11.9	0.0	33123	3.0	70.0	7.7	56.2	6.6	63.7	7.2	33.3	3.1	82.1	27.2	196.5	15.4
103-7	Carbonate	289.0	1.2	27.0	8.5	204.8	16.9	24.6	17.4	27.8	6.6	113.5	4.2	13.4	0.0	32771	6.5	65.1	4.9	50.9	19.3	63.0	17.6	28.7	7.8	146.1	56.8	198.1	52.5
103-7	Oxide	21.8	17.9	4.5	9.0	196.8	5.1	15.3	13.2	3.0	14.8	114.2	7.7	10.4	0.0	18713	9.7	31.9	1.6	51.3	12.1	51.0	20.2	12.1	11.4	93.0	98.8	240.5	11.5
103-7	OM+Res	24.8	8.1	7.2	204.5	3.3	15.3	10.8	4.5	25.7	129.3	0.8	13.6	36.9	20714	2.3	37.1	13.6	58.2	2.3	96.6	61.3	13.6	9.5	92.8	58.5	236.4	31.3	
218-1	Original	30.2	0.0	31.6	47.4	103.3	19.4	36.5	26.2	57.4	76.5	174.2	29.4	36.3	41.1	28880	36.6	283.4	17.7	608.2	96.9	409.2	54.4	18.1	32.6	48.2	22.7	527.8	32.5
218-1	Exchangeable	129.9	27.8	18.0	48.9	97.0	41.1	19.1	78.2	171.5	41.6	112.4	23.8	59.6	0.0	144799	11.2	239.3	34.0	246.1	15.3	286.1	21.2	14.7	38.0	213.6	24.2	381.8	39.1
218-1	Carbonate	93.4	0.0	15.0	20.5	125.2	20.6	22.5	73.1	117.2	21.1	119.4	30.5	20.9	37.8	164383	9.7	300.0	20.1	227.2	10.4	256.4	8.3	16.1	8.6	203.4	37.8	492.4	24.8
218-1	Oxide	19.1	18.3	9.4	15.8	36.6	12.8	7.9	33.0	22.3	30.2	26.7	29.0	7.1	4.1	23163	33.7	22.4	7.2	9.1	11.2	36.2	41.3	8.7	5.5	18.7	24.0	16.5	3.3
218-1	OM+Res	45.5	0.0	13.2	49.0	96.3	24.4	16.7	30.3	20.1	59.2	140.8	20.1	74.0	91.1	204754	46.1	157.5	48.6	331.4	56.8	322.2	34.2	12.1	15.4	283.8	38.2	508.4	27.6
218-7	Original	145.5	7.4	20.1	7.7	124.1	9.8	30.0	13.2	121.1	9.7	136.1	3.6	21.7	23.5	131972	9.1	284.8	15.4	194.2	7.4	243.4	14.1	19.7	2.5	1010.1	71.1	506.6	7.2
218-7	Exchangeable	147.8	16.8	18.7	9.2	121.3	9.9	24.9	19.1	112.2	1.8	143.5	7.5	26.0	0.0	119863	6.5	199.6	5.3	189.1	10.9	226.1	15.5	18.5	12.4	677.2	87.0	450.1	1.1
218-7	Carbonate	168.3	0.0	20.1	6.9	130.5	6.4	37.4	14.1	120.2	14.6	132.4	4.9	18.7	0.0	121632	7.5	163.7	26.1	223.2	1.6	254.3	6.3	20.2	4.0	281.0	12.8	415.0	19.3
218-7	Oxide	56.0	17.5	7.6	20.0	117.3	7.0	25.4	10.6	70.6	14.2	112.3	8.1	19.9	13.7	74662	7.2	110.9	9.3	94.6	29.1	85.1	21.8	11.5	11.5	206.9	0.0	342.9</	