

Distribution and origin of major and trace elements (particularly REE, U and Th) into labile and residual phases in an acid soil profile (Vosges Mountains, France).

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Abstract

A seven step sequential extraction procedure has been conducted on a podzolic soil profile from the Vosges Mountains in order to determine the ability of several elements to be released to the environment. Very little Si, K and Al were extractable (< 10% of the total soil concentration) but larger proportions (> 10% of the total soil concentration) of Ca, P, metals (Fe, Pb), REE and actinides (Th, U) could be leached. For each element, preferential binding sites can be recognized. High recovery of P and Ca in the acid soluble fraction (AS) suggests that phosphate minerals are highly involved in this step of the extraction. Organic matter appears to control the adsorption of Ca, Fe, Th, U and REE, even at depths in the soil profile where organic matter content is particularly low (0.5%). Weak acid leaching experiments (with HCl and acid acetic 0.001 N) were also performed in order to characterize the origin of the insoluble material in this soil profile. The leachable REE distributions indicate that a large part of the labile REE in the surface horizon has an atmospheric origin whereas at greater depth phosphate mineral (apatite) alteration is the main factor controlling REE release in the leachate. Our study further suggests that adsorbed material holding actinides and REE are not strictly the same. So, caution should be taken when using REE as analogues for actinides in soils systems.

Keywords: podzolic soil, sequential extraction, leaching experiments, rare earth elements, phosphate minerals, actinides, organic matter

1. Introduction

Physical and chemical weathering of rocks and minerals leads to soil formation. In order to determine accumulation and/or release rates of rock-forming elements during weathering it is necessary to establish the distribution and chemical binding of a given element. Heavy metals are particularly of environmental concern because of their potential toxicity and their importance as essential trace elements. The chemical form of the heavy metals strongly depends on pH or redox conditions as these will control or influence their adsorption-desorption, complexation or co-precipitation (Leleyter and Probst, 1999).

Soils exposed to anthropogenic activities may receive large quantities of heavy metals, the effects of which are now well documented (e.g. Chuan *et al.*, 1996; Steinmann and Stille, 1997; Sheppard *et al.*, 2000). However, this is not the case for remote areas, which are affected by the long range transboundary transport of heavy metals (De Vries *et al.*, 2002). Few studies have dealt with the distribution and the speciation of trace metals in non-contaminated soils, especially in forested soils far from any local pollution source and thus only affected by atmospheric deposition (Probst *et al.*, in press; Hernandez *et al.*, 2003). There is also a lack of data concerning the behaviour and speciation of Rare Earth Elements (REE); Land *et al.* (1999) show that REE from a spodosol from Sweden were bound to Mn and Fe oxides and also to organic compounds. The trivalent REE are of special interest because they may be fission products of actinides or act as analogues for other trivalent actinides produced by the nuclear industry (Krauskopf, 1986; Johannesson *et al.*, 1995; Aubert *et al.*, 2002a).

The purpose of this study is to determine the partitioning of several major and trace elements in an acidic forested podzolic soil profile, with particular focus on REE, Th and U. A sequential extraction procedure was used that allows determination of origin and behaviour

of particular elements in specific environments. There are a number of sequential extraction methods that have been used over the last few decades (e.g. Tessier *et al.*, 1979; Schuman, 1985; Ure *et al.*, 1995; Hall *et al.*, 1996a,b; Xiangdong *et al.*, 1995; Tan *et al.*, 1997) of which the selectivity and efficiency has been questioned (Sholkovitz, 1989; Xiao-Quan and Bin, 1993 ; Raksasataya *et al.*, 1996; Calmano *et al.*, 2001). A new extraction sequence (Leleyter and Probst, 1999), derived from Tessier *et al.* (1979) was used. In this method, selectivity, chemical product efficiencies, reproducibility and repeatability are rigorously tested. In addition, the results of the sequential extraction experiment were compared with those of two kinds of simple leaching experiments performed to distinguish between atmospheric deposition and mineral weathering of REE in this soil. This study aims to better understand the effect of both mineral strong acid input and natural organic acidity on element leaching in soils. For these batch experiments very dilute (0.001 M) HCl and acetic acid were used to match the natural pH range of the pore waters in this soil.

2. Material and methods

2.1 Site description

The Strengbach catchment (Fig. 1, from Aubert *et al.* (2001)) is located on the eastern part of the Vosges Mountains (North East of France). It covers an 80-ha forested area between 883 m at the outlet and 1146 m at the top of the catchment. This site has been thoroughly investigated since 1986 and many geochemical, mineralogical and biological studies have been undertaken (see the review of Probst *et al.*, 1990 and Aubert *et al.*, 2002b for more details).

The bedrock of the catchment is a fractured base-poor leucogranite (the Brézouard granite) that has been affected by hydrothermal fluids, which has resulted in reduction of plagioclase and biotite and accompanied by increasing muscovite, hematite, as well as hydrothermal clays (illite-vermiculite or illite-smectite) (Probst *et al.*, 2000).

At the top of the catchment, a banded gneiss lies in contact with the granite on which the 80 cm thick, sandy and stony soils, overlies a saprolite extending up to 10 m depth. These soils belong to the brown acidic to ochreous podzolic soil type.

2.2 Soil properties

An ochreous podzolic soil profile (Haplorthod, Soil Survey Staff, 1995) called HP (Fig. 2) is located on a rather steep slope under beech trees where the substratum has been less hydrothermally altered. The A horizon (about 20 cm thick) is enriched in organic matter and overlies a 50 cm thick B horizon. The lower part of this horizon corresponds to the illuvial level which reflects the migration of material from the top of the profile due to podzolisation processes and is enriched in organic material. The transition to saprolite begins at about 90 cm depth and ends at 120 cm. Coarse sand (0.2-2 mm) represents more than a half of the mineral fine fraction (<2 mm) (Fichter *et al.*, 1998a). This soil is described in more detail in Fichter *et al.* (1998a,b) and in Aubert *et al.* (2002a).

2.3 Sampling procedure

6 different horizons (A1, A2, B1, BFe, BC and C) were sampled between the surface and 150 cm depth (see Fig. 2) and stored in polyethylene bags. Samples were then air dried at room temperature and the < 2mm fraction separated by sieving using polyethylene sieves. Aliquots of this fraction were taken randomly for chemical analysis and for sequential extraction procedure and leaching experiments.

2.4 Analytical methods

The chemical compositions of the < 2mm soil samples were determined using ICP-AES (Jobin Yvon) for major elements and ICP-MS (Fisons VG-Plasma Quad) for trace elements after dissolution of samples in closed Savilex vessels containing a triacid (HCl,

HNO₃ and HF) mixture. The analytical precision determined by measuring two BE-N international reference standard during the experiment is < 10% for ICP-AES and < 5% for ICP-MS. For more details see also Aubert *et al.* (2001).

In order to determine the chemical constituents of the soil, which can be affected by changes in physico-chemical conditions, the fine fraction (< 2 mm) of each soil sample was submitted to a selective and efficient chemical extraction procedure. The selected method (Leleyter and Probst, 1999) is characterized by seven successive steps involving chemical reagents of diminishing pH (Table 1, from Leleyter and Probst, 1999). After each reaction, the residue is filtered, rinsed with deionised water and dried at 40°C before the next extraction. Filtrates were stored in Falcon™ tubes previously cleaned with diluted HNO₃. The efficiency of seven extracted fractions have been precisely tested with reference material by Leleyter and Probst (1999), which are outlined as follow: (1) elements dissolved by water (W), (2) exchangeable fraction (Exch), (3) acido-soluble fraction (AS), (4) elements bound to manganese oxides (Mn Ox), (5) elements bound to amorphous iron oxides (AFe Ox), (6) elements bound to crystalline iron oxides (CFe Ox) and (7) elements bound to organic matter (OM). The total quantity of elements leached during these seven steps forms the non-residual fraction of the sample. The chemical composition of the residual material was not analysed. The elemental content of the residue corresponds to the difference between the initial content in the soil sample and the total amount recovered in the seven leachates.

All the materials used during the extraction (polyethylene sieves, filtration apparatus, polypropylene flasks) were previously cleaned with diluted hydrochloric acid and then rinsed 2 times with bi-deionized water. All the reagents we used are from Prolabo™ and of Ultrapure quality. Blanks show no contamination problems. The leachates were analysed with ICP-AES for major elements and with ICP-MS for the trace elements. However, Mg and Na concentrations have not been measured because these elements are involved in the reagents in

step (2) and in step (3), respectively. The elements considered are therefore the major elements (Si, Al, K, Ca), P, Fe, the REE (Rare Earth Elements), Sr, Pb, Th and U.

Leaching experiments have also been conducted on three soil samples (HP1, HP4 and HP6) using acetic acid. Weathering solutions in the first centimetres of the soil horizons are often highly enriched in organic acids (humic acids) deriving from litter decomposition. Organic acids such as salicylic or citric acids are sometimes used to perform this kind of leaching experiment (Wickman, 1996). Numerous other studies (Mueller *et al.*, 1958; Barcelona *et al.*, 1980; Galloway *et al.*, 1982; McDowell and Likens, 1988) have shown that both acetic and formic acids are the most representative organic acids of low molecular weight in natural waters (rain water, throughfall, soil solutions, stream and lake waters). The acid concentration of 0.001 M corresponds to the most acid soil solutions in this area (Probst *et al.* 1990; Dambrine *et al.*, 1995). Extractions were conducted over 3 weeks, at room temperature, using 10 g of dry soil sample and 50 ml of acid solution in polypropylene flasks. The flask was shaken 3 times a day. The supernatant was collected after centrifugation and stored at 4°C prior to ICP-MS analysis. Parallel to this experiment and to mimic the mineral acidity which, is the main weathering factor in the deep horizons (Probst *et al.*, 1990; 1995a ; Dambrine *et al.*, 1995), we also performed the same procedure using 0.001 M HCl. At the end of the experiments, the pHs of the solutions ranged between 3.8 and 4.2.

Sr isotope ratios were determined on several leachates from the sequential extraction experiments in order to better constrain the origin of the components extracted during this procedure. These analyses were performed on a fully automatic VG Sector thermal ionisation mass spectrometer (TIMS). After leachate evaporation and dissolution of the residue in HCl 4N, Sr was separated in quartz column with cation exchange resin (AG 50W-X12, 200-400 mesh) and ammonium citrate and HCl as eluents. Sr was loaded with nitric acid on a W single filament using Ta₂O₅ as an activator. The ratio $^{86}\text{Sr}/^{87}\text{Sr} = 0.1194$ was used for fractionation correction. Typically, 100 ratios were collected to achieve adequate precision. During the

measuring period the NBS 987 Sr standard yielded $^{86}\text{Sr}/^{87}\text{Sr} = 0.710258 \pm 13$ (\pm sigma mean, $n = 9$)

3. Results

3.1 Mineralogical and chemical compositions of the soil samples

The mineralogical characteristics of the bedrock and the fine fraction (<2 mm) of the soil are given in Table 2 (data from Fichter, 1997; Probst *et al.*, 2000; Aubert *et al.*, 2002b). Quartz, clays (including micas), K-feldspars and plagioclase appear to be the most concentrated minerals in this soil and show little variation with depth.

The chemical composition of the bedrock and the 6 soil samples is reported in Table 3. The evolution of the major component and trace element concentrations throughout the whole profile is also represented in Fig. 2. The first 5 cm are strongly enriched in organic matter whereas deepest horizons are depleted. Most of the components measured show an increase of their contents with increasing depth. Al_2O_3 and Fe_2O_3 especially show an important accumulation between 70 and 150 cm depth, which can be related to podzolisation processes that allow the migration of Al and Fe from the surface (Duchaufour, 1995). Pb is enriched in the two upper horizons. Most of Pb in the surface layers probably originates from atmospheric deposition (Février, 2000; Quilici *et al.*, 2000) in this catchment where deposits of long range transport of atmospheric pollutants have been recorded over the last 15 years (Probst *et al.*, 1995b). This is also consistent with the dominant anthropogenic origin of Pb in shallow horizons from other acidic forested soils from north eastern France (Hernandez *et al.*, 2003b).

Table 4 gives the data concerning the total cation exchange capacity (CEC) and the respective exchangeable amount of the different cations from the different horizons determined at the INRA Laboratoire d'Analyse des Sols (Soil Analysis Laboratory) of Arras. The CEC is consistent with that found in other acidic forested soils from the northern part of

France (Hernandez *et al.*, 2003b). Ca appears to be the most exchangeable cation although it has a very low concentration.

3.2 Distribution of the elements on soil chemical phases: sequential extraction procedure

The portion of leached element in the different fractions was calculated on the basis of the total concentration of this element in the sample (determined by dissolving the sample using a tri-acid digestion method; HNO₃, HCl, HF).

3.2.1 Slightly extracted elements (<10 % of the original soil sample) (Fig. 3)

Silica (Fig. 3)

The full procedure conducted on a reference clay mineral by Leleyter and Probst (1999) showed no significant leaching of Si, indicating that silicate minerals are not attacked by the reagents. Silica is therefore the element that certifies the selectivity of the extraction method. For these 6 soil samples Si was not significantly extracted (less than 0.5 %) during the procedure. Thus, Si is almost entirely retained in the residual fraction of the soils.

Potassium (Fig. 3)

Potassium was only slightly extracted during the leaching experiments. The highest K concentration (1% of the total K in the sample) is attained in the exchangeable fraction. Thus, like Si, K is also associated to the residual phase of the soil, probably in illite, muscovite and orthoclase.

Strontium (Fig. 3)

Sr appears not to be very labile in this soil. Only the two deepest horizons contain a certain amount of leachable Sr (respectively 3.5 and 4 % of the total Sr in the sample) which is mainly associated with Mn oxides. In the shallowest layer, only 2.5 % of Sr is non-residual

essentially in the exchangeable form. The quantity of Sr bounded to organic matter is also very low (<1 %).

Aluminium (Fig. 3)

Only 2 to 9.5 % of Al is soluble in the soil profile. From the HP1 horizon (0-5 cm) to the HP4 horizon (45-70 cm, the most intensively Al leached horizon), Al appears to become increasingly leached with depth. In the 2 first horizons, Al is mainly associated with the exchangeable fraction and to amorphous Fe oxides. In the underlying horizons, most of the aluminium is carried by the acid-soluble fraction and the amorphous Fe oxides. In all horizons, Al bound to organic matter or to other oxides contributes to less than 1 % of the total Al content of the soil. The association of Al with iron oxides probably results from the podzolisation processes that allow Fe and Al to migrate to depth (Duchaufour, 1995).

3.2.2. Strongly extracted elements (>10 % of the original soil sample)

Calcium (Fig. 4)

10 % of Ca is leached in the deepest horizon, in contrast to 32% of Ca leached from the surface soil. In the latter, Ca in the exchangeable form represents 20 % of the total Ca in the soil whereas in the other layers, this fraction only contributes 3 to 8 % of the total Ca. These results are in good agreement with the Cation Exchange Capacity (CEC) measured in this soil (Table 4) indicating that in the upper horizon 30% of Ca is exchangeable whereas only 5 % of the total Ca is in this form in the five other layers. The acid-soluble fraction and also the reductible one (oxides) represents a maximum of 5 % of the total Ca. On the other hand, though organic matter content is very low in the deep soil, Ca bound to organic compounds represents almost one third of the Ca extracted from the HP5 and HP6 horizons.

Phosphate (Fig.4)

An important quantity (50 to 100 %) of phosphate is non residual in the different horizons of this soil particularly that associated to oxides. Nevertheless, the acid-soluble fraction contains about 10 % of the total phosphate in the soil, whatever the considered layer. In the deep horizons measurable quantities of phosphate are exchangeable in contrast to the surface horizons, where phosphate is not detected, probably as a result of vegetation uptake.

Iron (Fig. 4)

Iron is continuously leached from soils at the surface to 70 cm depth (HP4), but below this level the extracted Fe amount decreases. Most of the soluble Fe is bound to amorphous Fe oxides within the surface horizons whereas crystalline Fe oxides hold the major part of Fe in the saprolite. The deepest horizons (HP3, HP4 and HP5) enclose 7 to 8 % of the total Fe in the organic matter. Like Al, podzolisation processes are responsible for the migration of Fe in the oxidised form to 70 cm depth.

The Rare Earth Elements (REE) (Fig. 5)

Among the 14 elements that constitute the REE, only 9 could be significantly detected. 2 to 4 % of the REE are soluble in the shallowest horizon and between 4 to 15 % for the most leached horizon (HP4). The potential mobility of LREE (light REE, La to Nd) doubles with increasing depth whereas this potential mobility is 3 times higher for HREE (heavy REE, Ho to Yb) in deep horizons. Thus, as for Fe or Al, REEs are increasingly extracted from the top soil to the depth. In addition, the higher the concentration of REE in the samples (Tab. 3), the more leachable it is. In all the horizons, middle to heavy REE (Sm to Yb) are preferentially extracted compared to the LREE. At the soil surface, REE are preferentially associated with oxides (amorphous and crystalline Fe oxides) (Fig. 5). The quantity of REE bound to organic matter increases with depth mostly for the middle to heavy REE. The acid-soluble fraction contains a rather large amount of REE (mainly Dy, Gd, Er and Sm). The leachates of the

deepest horizons (HP3 to HP6) are preferentially REE enriched whereas the two upper horizon leachates are comparatively REE depleted, especially in HREE. REE concentrations in the two first extraction steps remain very low.

Uranium and Thorium (Fig. 6)

Both elements belong chemically to the actinide group. They are extracted together in the same proportion in the different extraction fractions. These two elements become more and more labile with depth. Most of the extracted Th and U are bound to Fe oxides especially at great depth. 5 to 10 % of U is associated to the acid-soluble fraction whereas the proportion of Th in this fraction is only about 5 %. Th seems to be more associated with organic matter in the surface layers than in the deepest horizons whereas the amount of U bound to organic matter is rather homogeneous in the whole profile.

Lead (Fig. 6)

Pb in the upper horizons seems to be largely non residual (50 to 60 % of the total Pb) and mainly associated with the exchangeable, acid-soluble and amorphous iron oxides fractions. Similar results have been found in acidic soils under spruce located in the Ardennes Massif (North of France) using the same extraction technique (Hernandez *et al.*, 2003a). The deeper horizons contain 10 to 20 % of non residual Pb, which is almost totally bound to Fe oxides. Pb associated to the organic matter represents a maximum of 5 % of the total Pb in the soil, which is not commonly reported in the literature (e.g. Steinnes *et al.*, 1989)

3.3 Leaching experiments using diluted acetic acid and HCl

REE concentrations measured in the leachates are reported in Table 5. In most of the leachates, middle to heavy REE contents are close to or below the detection limit of the ICP-MS. As a whole, HCl leaching seems to be more efficient than using acetic acid.

In Fig. 7 the REE distribution patterns of each soil sample have been compared with the patterns of the corresponding leachates. The distributions are normalized to the fresh granite (called HPT, internal reference). One can observe that the REE spectra of both HCl and acetic acid leachates are quite similar. Moreover, the REE distributions of the 3 leachates strongly resemble the original soil sample. In the case of the shallowest soil sample HP1, both leachates and original soil sample show a LREE depletion, a strong positive Eu anomaly and a progressive MREE to HREE enrichment. For the two others soil samples HP4 and HP6, the HREE enrichment in the leachates is less pronounced compared to that of the soil samples. No positive Eu anomaly is recognizable for the HP6 HCl leachate.

In a second step, the origin of the leachable REE of the soil solid phase was sought as discussed earlier for the percolating soil solutions (Aubert *et al.*, 2002a). Two major provenances can be defined from the REE patterns: 1) atmospheric deposition and 2) weathered residual minerals. This is shown in Fig. 8 where the REE spectra of the HCl soil leachates are compared to those of the most important REE carrying minerals in this soil (apatite and plagioclase) and to throughfall (taken as normalization reference which represents at the best the atmospheric component that reaches the soil surface). When normalized to the throughfall, the REE distribution of the HP1 HCl leachate is relatively flat (Fig. 8). This suggests that the surface horizon contains important quantities of REE derived from atmospheric deposition. The leachates of the deepest soil horizons (HP4 and above all HP6) show spectra with a MREE enrichment and a strong negative Eu anomaly typical of apatite REE distribution.

4. Discussion

General comments

Si and K are only weakly leached during the sequential extraction procedure. This means that the lattices of the most resistant silicate minerals, such as quartz or clay minerals, have

not experienced severe attack through this experiment and have been preserved. This reinforces the contention that this sequential extraction procedure is suitable for studying the different binding forms of adsorbed elements in soils as it has been previously established with the same method for sediments (Leleyter and Probst, 1999).

Overall, the results show that each element has its own preferential adsorption sites. Only small differences are recognized between the surface horizons and the deeper layers of this soil profile. Fe oxides represent the most important adsorption sites. This is particularly the case for P, the metals (Al, Fe, Pb) and the actinides (Th and U). These results are contrary to the finding of Kabata-Pendias and Pendias (1991) suggesting that Th and U are mostly carried by organic matter compounds. In our study, the elements that are strongly bound to organic matter are P and Ca, Fe and REE at great depth even though organic matter only represents less than 0.5% of the total fine earth over 1m depth. The explanation we suggest for these high contents of elements in the organic matter fraction is an earlier transport of weathered material together with the migration of pore waters down the profile. An increasing pH would probably have acted as a major factor leading to adsorption of elements (especially heavy metals) onto organic matter (e.g. Mc Bride *et al.*, 1997; Steinmann and Stille, 1997; Singh and Oste, 2001).

Several trace elements are also leached in the Acid-Soluble fraction. This fraction theoretically contains only material derived from the dissolution of the carbonates or easily weathered minerals (Leleyter, 1998; Leleyter *et al.*, 1999). A detailed check (cathodoluminescence) of the bedrock and the soils from the Strengbach catchment showed no trace of carbonate (Probst *et al.*, 2000) and because important Ca and P concentrations are leached from this fraction, it is suggested that phosphate minerals like apatite are dissolved during this step (Leleyter, pers. comm.). Additionally, Sr is not present in important quantity in this fraction, whereas apatite contains a significant proportion of Sr (Aubert *et al.*, 2001). No convincing explanation has been found to elucidate such a difference between the leached

proportion of Sr and those of P and Ca. We suggest the precipitation of insoluble Sr secondary minerals in the soil as the primary source. Insoluble phases incorporating Sr should also precipitate during sequential extractions as already observed for other elements (Calmano *et al.*, 2001) unless all the analytical precautions taken during the procedure were effective. However, a large quantity of P and Ca is also collected in the fraction bound to iron oxides, mostly amorphous iron oxides. This further suggests that dissolution of phosphate minerals would also occur during this step. In comparison the exchangeable fraction does not contain a large part of adsorbed elements. Only Ca (in the upper horizons), P (at greater depth) and Pb are significantly adsorbed in the exchangeable sites. Previous works from El Gh'Mari (1995) shows that superficial horizons of the soils contain smectite like clay minerals strongly suggesting that Ca (mainly of atmospheric origin (Probst *et al.*, 2000)) located in interlayer sites is easily exchangeable. Sr isotopes analyses performed on several leachates (the most Sr concentrated) from the Exch, AFe Ox and OM fractions from HP1 and HP5 samples indicate that the extracted material derives from at least two distinct sources (Fig. 9). Thus, Sr isotopic measurements are distributed between (1) a relatively low radiogenic end-member ($^{87}\text{Sr}/^{86}\text{Sr}$ around 0.714-0.715 for the HP5 amorphous Fe oxides fraction) and fairly Sr concentrated and (2) a more radiogenic end-member ($^{87}\text{Sr}/^{86}\text{Sr}$ around 0.735 for HP1 organic matter and HP5 exchangeable fractions) but significantly less Sr concentrated. Both Sr isotopic values are very similar to those measured in apatite (0.716; Aubert *et al.*, 2001) and plagioclase (0.742; Probst *et al.*, 2000) extracted from a fresh granite sample of this catchment. This similarity supports the assumption that material derived from phosphate minerals is leached during the 5th step of the sequential extraction procedure (AFe Ox fraction). But it is also apparent that material coming from the alteration of some plagioclase can contribute to the leachable pool, even in the fraction bound to organic matter.

Rare Earth Elements

In each soil horizon, middle REE (MREE) to heavy REE (HREE) are more labile than light REE (LREE) (Fig. 5). This is consistent with the previous work of Aubert *et al.* (2001) that shows severe MREE to HREE depletion in the upper horizons of the soils in this area. Using the same extraction technique for river sediments, Leleyter *et al.* (1999) found also the MREE to HREE of the Ill river (located in the Alsatian plain) sediments to be preferentially leached. In the particular case of the HP soil, REE distribution patterns normalized to the original fresh granite (Fig. 10) show REE depletion (especially MREE, except Eu that probably derives from unweathered orthoclase showing a positive Eu anomaly (Aubert *et al.*, 2001)) in surface horizons but also a progressive MREE to HREE accumulation in the deep layers (70 to 150 cm). On one hand, this explains why the sequential extraction is unable to extract a large amount of REE from the surface horizons, the latter being already intensively depleted. On the other hand, the migration and accumulation of surface leached REE is the reason why more REE from the deep horizons are extracted through the sequential extraction procedure. Thus, a large part of the extracted REE would originate from the leaching of REE from the surface horizon, and then adsorbed at greater depth onto organic matter due to progressive pH increase. Land *et al.* (1999) also report an important amount of REE being bound to organic substances in a spodosol from Sweden, although they observe a more important contribution in the surface horizons than in the deep horizons; the most important fraction carrying REE at greater depth being amorphous Fe-oxyhydroxides/Mn oxides. Concomitant to the increasing importance of REE bound to organic matter with increasing depth is the increasing contribution of REE linked to Fe oxides. Thus not only the organic matter is responsible for the accumulation of REE between 70 and 150 cm depth but also podzolisation processes that allow the migration of Fe and Al oxides (Duchaufour, 1995), which carry here a large amount of REE. No REE bound to Mn oxides were detected whereas Mn oxides are well known to carry a large amount of lanthanides (Walter *et al.*, 1995), particularly Ce (Rankin and Childs, 1976; Koppi *et al.*, 1996).

Analogy between Rare Earth Elements and actinides

The study of REE behaviour in natural environments and under laboratory experiments has increased in importance after the Chernobyl nuclear plant accident because some are fission derived radionuclides and can therefore be considered as good analogues for actinides (e.g. Wood, 1993; Read and Williams, 2001). Th and U are significantly more easily extracted than REE (especially with respect to LREE). As the whole REE and actinides seem to have more or less the same adsorption sites (highest recoveries in the AS, AFe Ox, CFe Ox and OM fractions), although there are differences. For example, Th behaviour is quite consistent with that of the REE regarding to AFe Ox and CFe Ox fractions (this latter being less concentrated, see Fig. 5 and Fig. 6), whereas the recovery rate of U is the same in both fractions. U behaviour is closer to that of REE in the OM fraction, with an increasing proportion of the extracted element with increasing depth. The opposite trend is observed for Th with the highest amount of Th bound to organic matter being recorded in the superficial horizon where organic matter content is maximal. In the Acid-Soluble fraction, U, Th and REE show the same behaviour with a maximum peak of recovery for HP3 and HP4 horizons. These results do confirm that REE can generally be used as analogues for actinides. But given the behaviour differences we identify between U and Th and as we show the REE group does not react homogeneously (HREE being more extracted than LREE), we suggest this analogy be used with caution.

5. Conclusions

Sequential extraction experiments show that Si, K, Al are weakly leached. These elements are presumed to be preserved in the crystalline lattice of the residual silicate minerals. Similarly, Sr recovery is small for all leachates and cannot be totally explained at the moment.

The exchangeable pool of the upper horizon encloses a large part (> 20%) of non residual Ca which can be related to important smectite-like clay content at the soil surface. Fe, Pb, Th, REE and also P appear to be mostly bound to Fe oxides, especially to the amorphous ones.

As a general rule, the availability of the largely extracted elements raises with increasing depth except for Pb and Ca, both elements being probably enriched in labile material at the soil surface through atmospheric deposits. At greater depth, although its very low content, organic matter appears to play a major role in the adsorption of Ca, Fe, U and REE. A progressive pH increase in this soil would probably enhance adsorption with organic ligands.

During the sequential extraction procedure, REE did not react as an homogeneous chemical group since HREE appear to be more leachable than LREE. Weak acid leaching experiments with HCl or acetic acid allow us to recognize atmospheric material at the top soil whereas REE originate progressively from alteration of phosphate minerals like apatite, with increasing depth.

Finally, we point out that caution is required when using REE as actinides analogues since LREE behaviour differs to that of the HREE and many differences have been shown between Th and U adsorption sites.

Acknowledgements

We would like to thank B. Kiefel, D. Million, R. Rouault and J. Samuel from the Centre de Géochimie de la Surface at Strasbourg for the technical assistance. The reviews by H.J. Percival and an anonymous referee greatly improved the manuscript. Special thanks are addressed to L.Warr for english corrections. D. Aubert benefited from a MRT grant. This work was supported by the Région Alsace within the framework of the IFARE (Institut Franco-Allemand de Recherche pour l'Environnement).

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Figure 10: REE distribution patterns of HP soil horizons normalized to the fresh granite

Table 1

Step	Fraction	Reagent	Time	pH	Temp
1	water soluble	H ₂ O	30 min	5.7	20°C
2	exchangeable	1M Mg(NO ₃) ₂	2 H	5.0	20°C
3	acido-soluble	1M NaOAc/HOAc	5 H	4.5	20°C
4	manganese oxides	0.1M NH ₂ OH HCl	30 min	3.5	20°C
5	amorphous iron oxides	0.2M (NH ₄) ₂ C ₂ O ₄ + 0.2M H ₂ C ₂ O ₄	4 H	3.0	20°C
6	crystalline iron oxides	0.2M (NH ₄) ₂ C ₂ O ₄ + 0.2M H ₂ C ₂ O ₄ + 0.1M C ₆ H ₈ O ₆	30 min	2.3	85°C
7	organic matter	35% H ₂ O ₂ /HNO ₃	5 H	2.0	85°C
		3.2M NH ₄ OAc	30 min	2.0	20°C

Table 2

Samples	Depth (cm)	Quartz (%)	K-feldspar (%)	Plagioclase (%)	Clays+Micas (%)	Apatite (%)
HP soil	0-20	39.5	18.9	14.7	23.3	0.15
	20-40	36.5	20.0	13.6	27.7	0.10
	40-60	35.1	17.8	12.5	27.4	0.05
	60-80	31.7	15.9	13.4	31.3	0.10
	80-100	28.6	14.4	14.3	34.8	0.15
	100-120	29.5	14.7	11.8	38.6	0.27
	120-140	27.3	13.9	13.1	40.8	0.33
	140-160	22.7	14.8	16.6	40.9	0.40
	160-180	23.3	17.9	19.1	34.6	0.28
	180-200	20.9	12.7	20.2	30.5	0.39
Fresh granite		36	18	33	9	0.5

Table 3

Sample	HP A1	HP A2	HP B1	HP BFe	HP BC	HP C	Fresh Granite*
Depth (cm)	0-5	5-20	20-45	45-70	70-100	100-150	-
pH (water)	4.2	4.4	4.8	4.9	5	5	-
% O..M.	15.3	5.2	2.5	1.9	0.6	0.5	-
SiO ₂	56.4	64.9	66.9	66.3	67	66.5	73.8
Al ₂ O ₃	12.8	16	17	17.1	17.5	18.2	14.1
MgO	0.26	0.33	0.35	0.35	0.56	0.58	0.24
CaO	0.12	0.12	0.13	0.18	0.29	0.26	0.37
Fe ₂ O ₃	1.3	1.7	2.3	2.4	2.7	2.7	1.1
Na ₂ O	1.5	1.9	2.2	2.2	2.1	2.3	3.7
K ₂ O	4	4.9	5.1	5.3	5.2	5.3	5.1
P ₂ O ₅	0.26	0.26	0.33	0.42	0.36	0.3	0.27
Sr (ppm)	42	48	60	48	54	53	45
REE (ppm)	59.3	67	82.5	64.7	103.5	82.2	88.4
Pb (ppm)	87	61	23	20	20	20	33.5
U (ppm)	3.2	3.6	4.9	4.4	5.8	7.6	9.3
Th (ppm)	5.9	7.2	9.6	8	11.8	9.4	12.6

* data from Probst et al. (2000)

Table 4

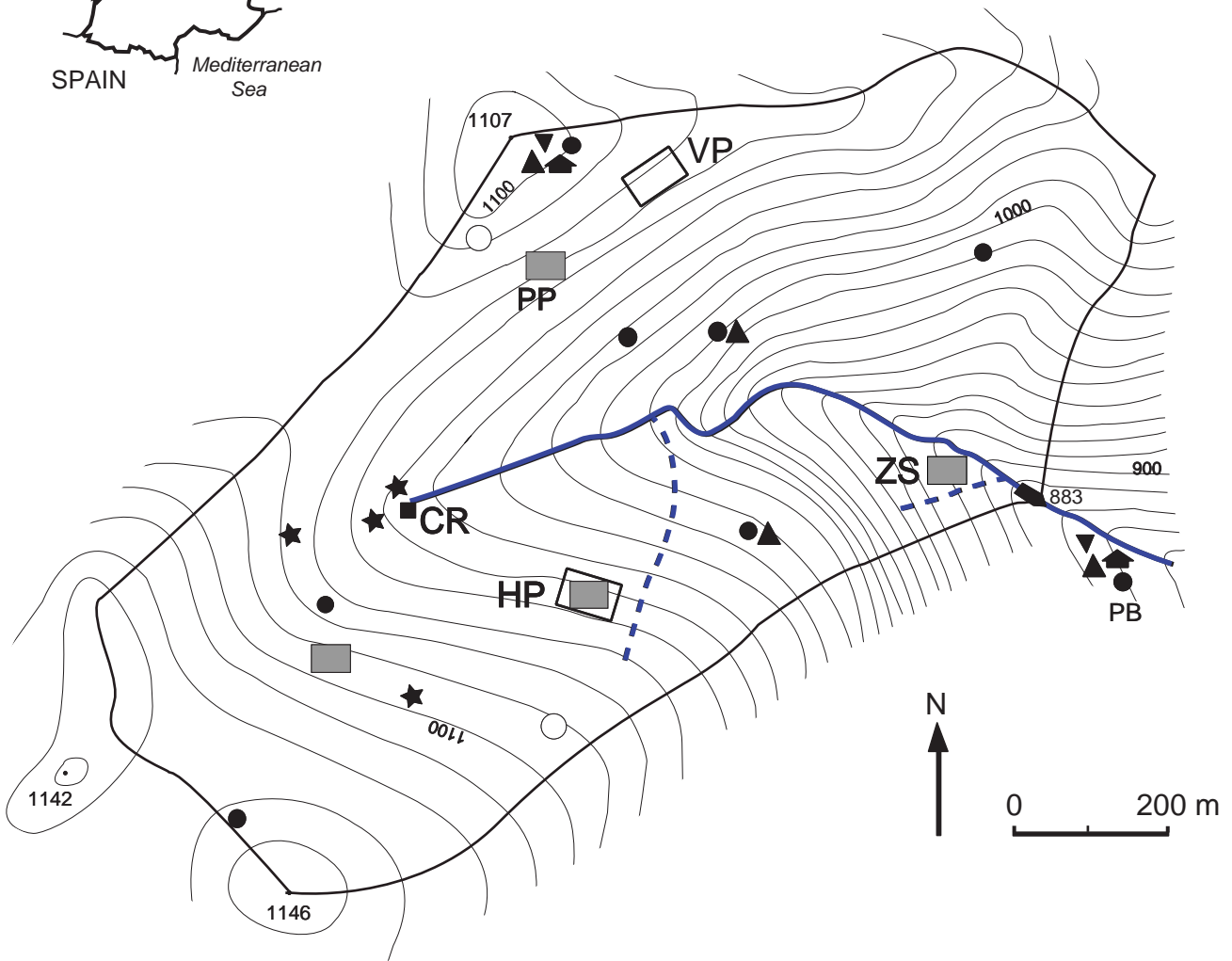
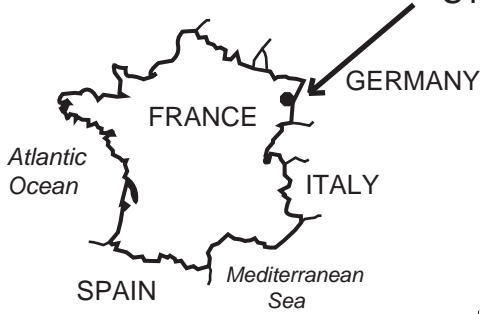
Sample	Depth (cm)	CEC (cmolc/kg)	Ca (cmolc/kg)	Mg (cmolc/kg)	K (cmolc/kg)	Na (cmolc/kg)	Si (g/100g)	Al (g/100g)	Fe (g/100g)
HP1	0-5	9.3	0.78	0.41	0.60	0.07	0.016	0.140	0.142
HP2	5-20	6.9	0.21	0.09	0.16	0.04	0.017	0.160	0.259
HP3	20-45	2.5	0.10	0.02	0.04	0.03	0.050	0.422	0.337
HP4	45-70	2.4	0.13	0.02	0.04	0.02	0.081	0.621	0.389
HP5	70-100	1.8	0.10	0.01	0.03	0.02	0.106	0.455	0.100
HP6	100-150	1.8	0.06	0.01	0.03	0.02	0.096	0.423	0.085

Table 5

Horizon	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
HP1 ac.	0.63	1.18	0.14	0.54	0.05	0.05	0.17	<dl	0.16	<dl	0.10	<dl	0.09	<dl
HP1 HCl	0.89	1.53	0.17	0.75	<dl	0.07	0.16	<dl	0.12	<dl	0.08	<dl	0.10	<dl
HP4 ac.	2.50	6.27	0.77	2.53	0.80	0.29	0.93	0.31	0.91	0.28	0.38	<dl	0.27	<dl
HP4 HCl	1.34	2.78	0.28	1.07	0.30	0.07	0.41	0.10	0.42	0.08	0.14	<dl	0.11	<dl
HP6 ac.	0.92	2.16	0.22	0.78	0.24	0.06	0.37	0.08	0.39	0.07	0.10	<dl	0.08	<dl
HP6 HCl	4.66	9.53	0.92	3.50	1.00	0.14	1.61	0.36	1.82	0.27	0.62	0.06	0.34	<dl

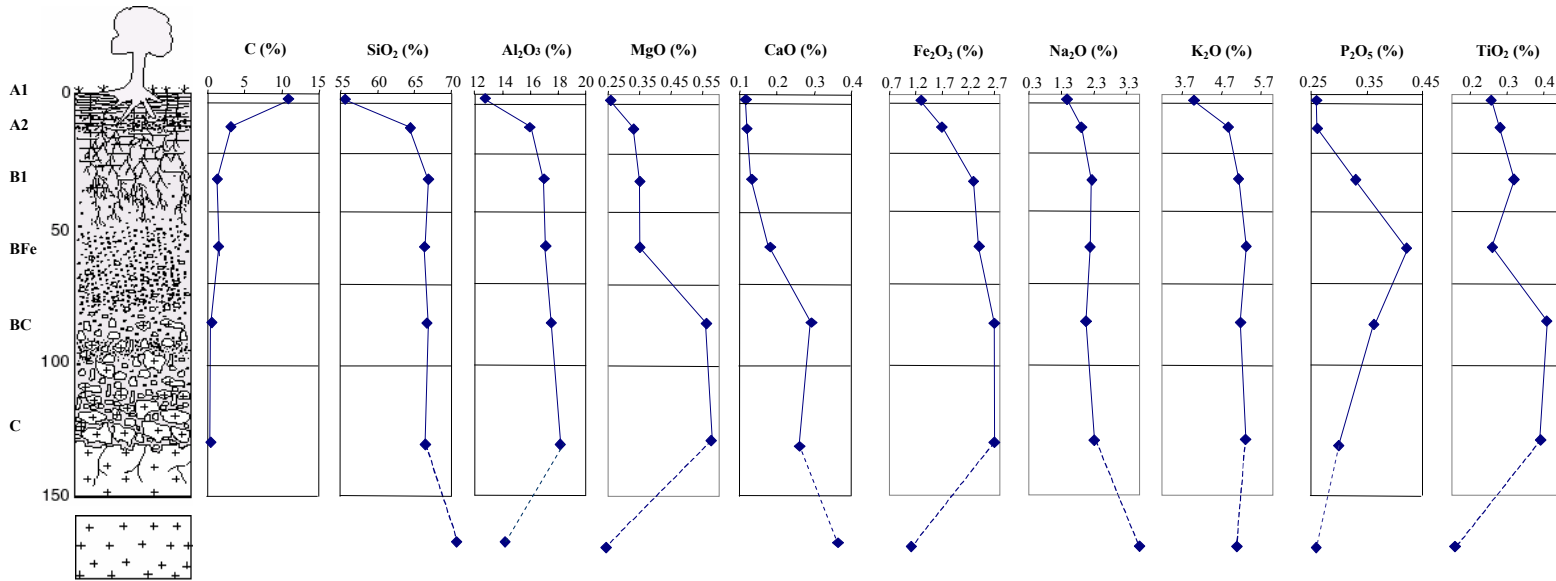
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STRENGBACH CATCHMENT



- | | |
|--|---------------------------------------|
| ★ SPRING | ▲ METEOROLOGICAL SHELTER |
| ■ SPRING COLLECTOR | ▲ PRECIPITATION COLLECTOR |
| ▭ WATER LEVEL RECORDER AND AUTOMATIC SAMPLER | ● RAIN GAUGE |
| ▼ PLUVIOGRAPH | ▭ THROUGHFALL AND SOIL SOLUTION SITES |
| — STREAM | ■ SOIL PROFILES |
| | ○ OUTCROPS |

Major elements



Trace elements

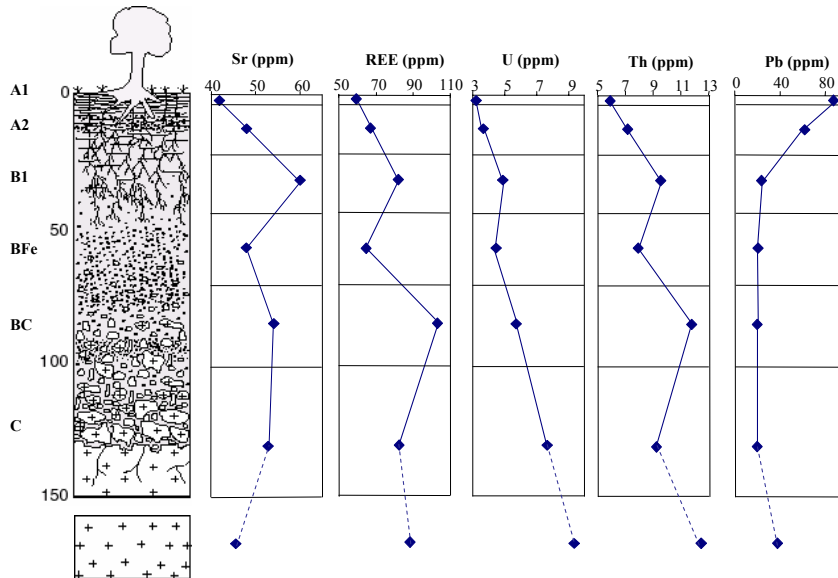


Figure 2, Aubert *et al.*

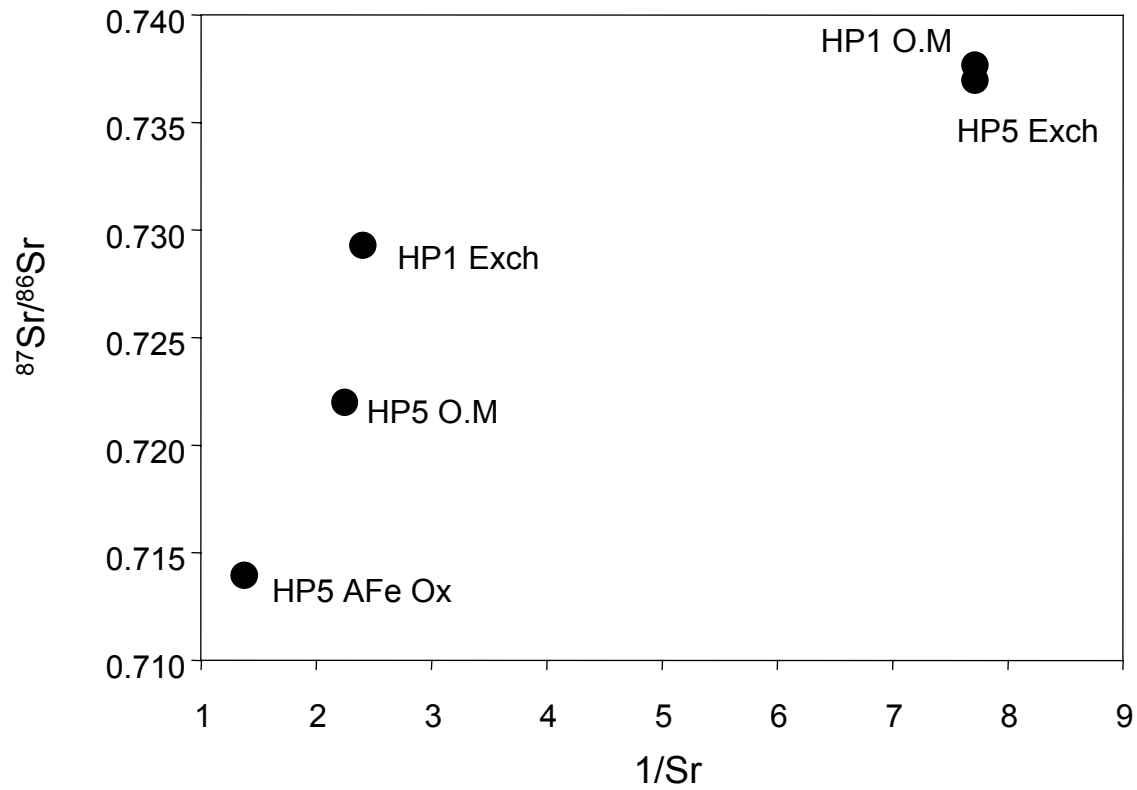


Figure 9, Aubert *et al.*

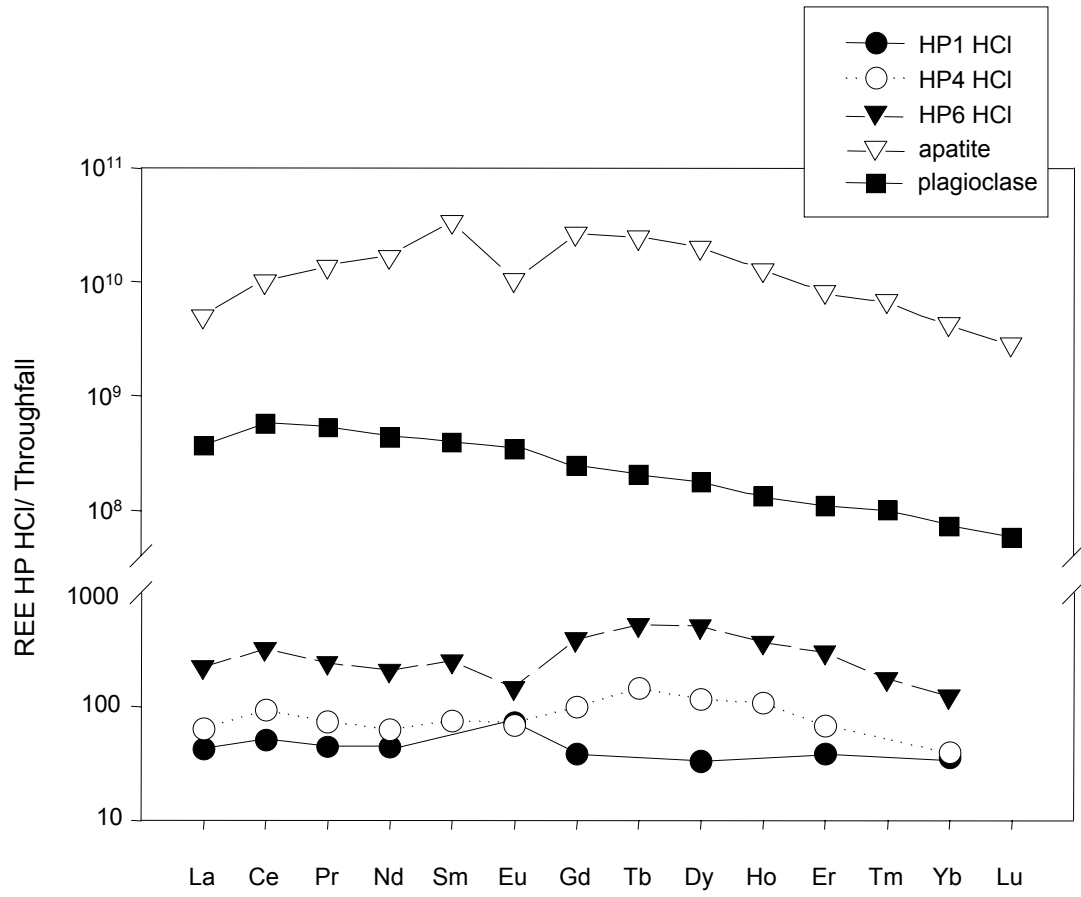


Figure 8, Aubert *et al.*

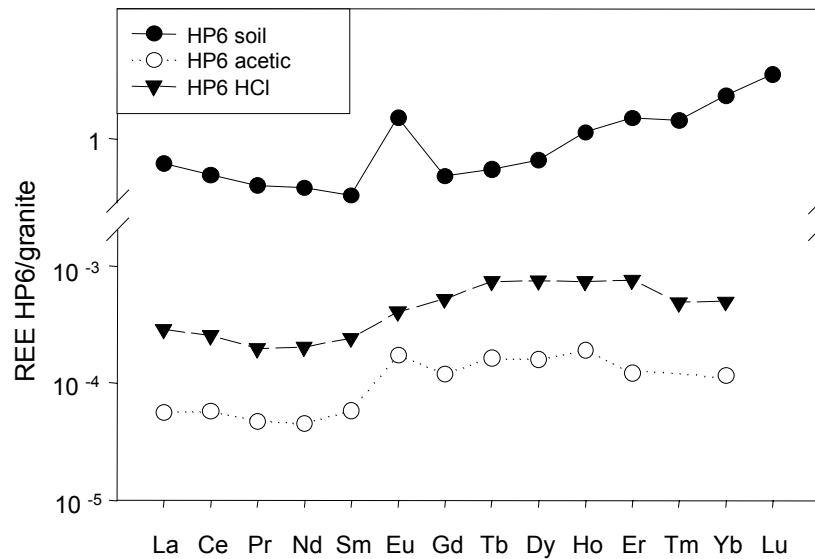
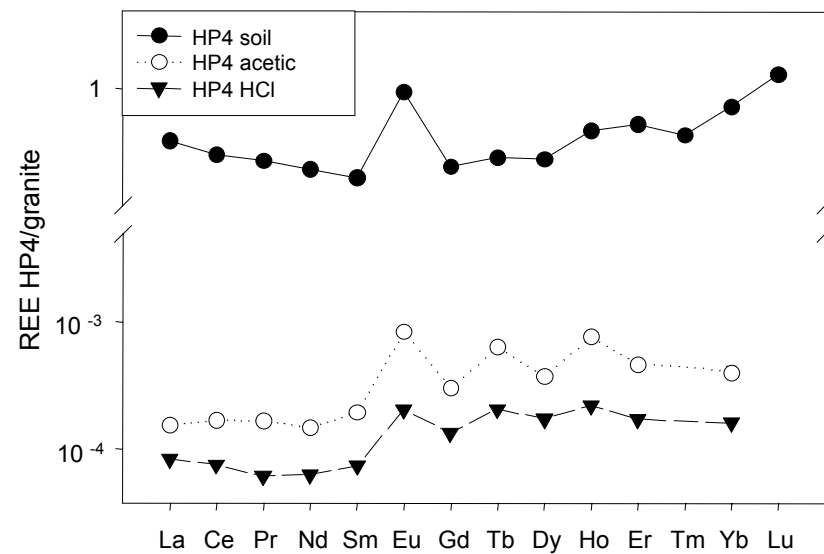
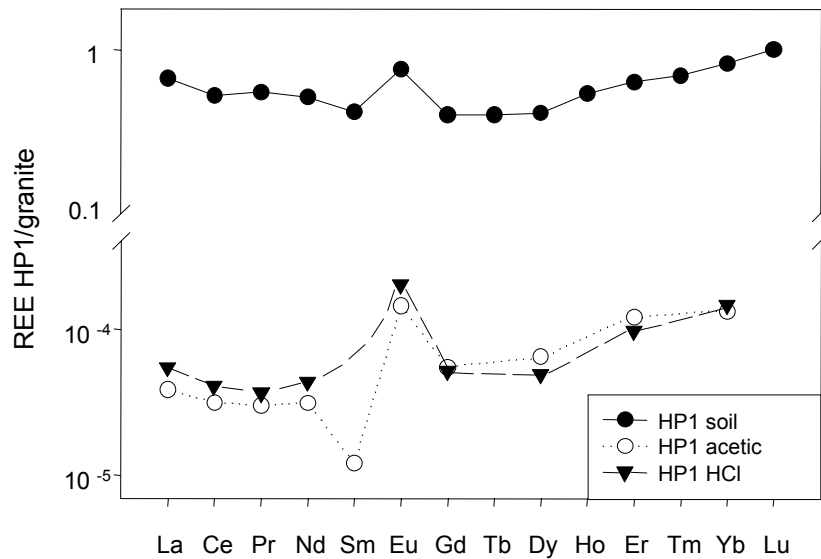


Figure 7, Aubert *et al.*

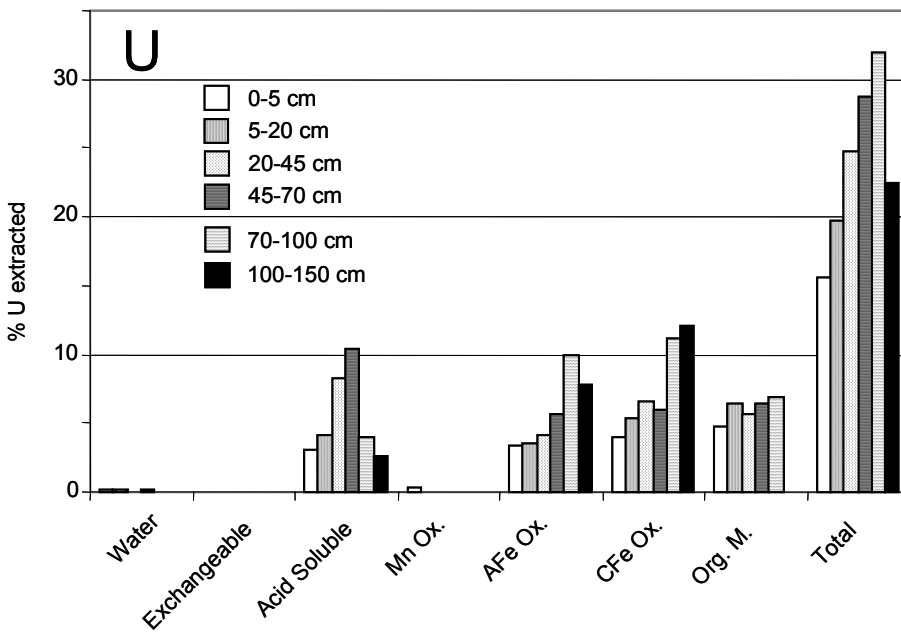
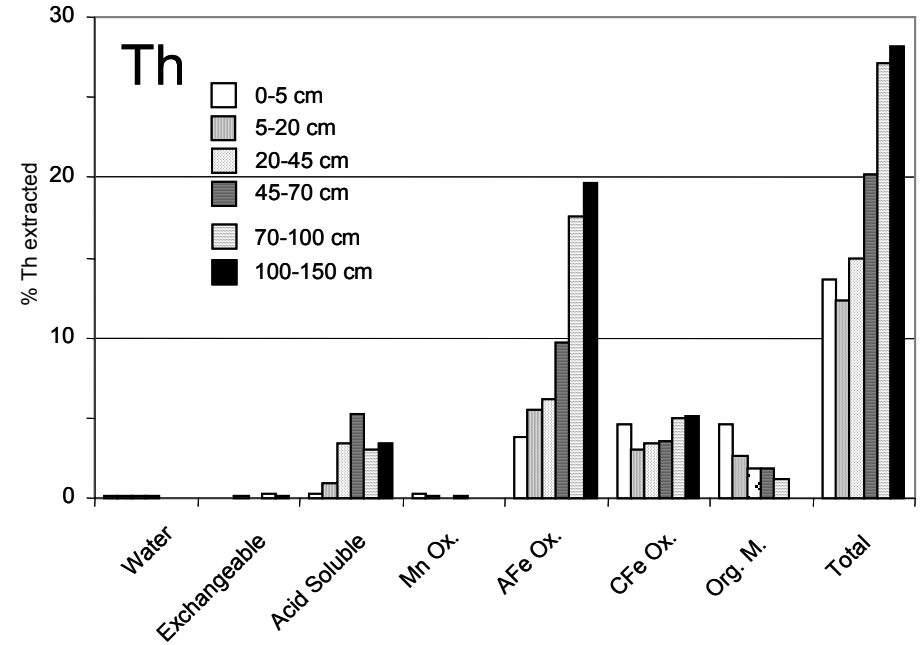
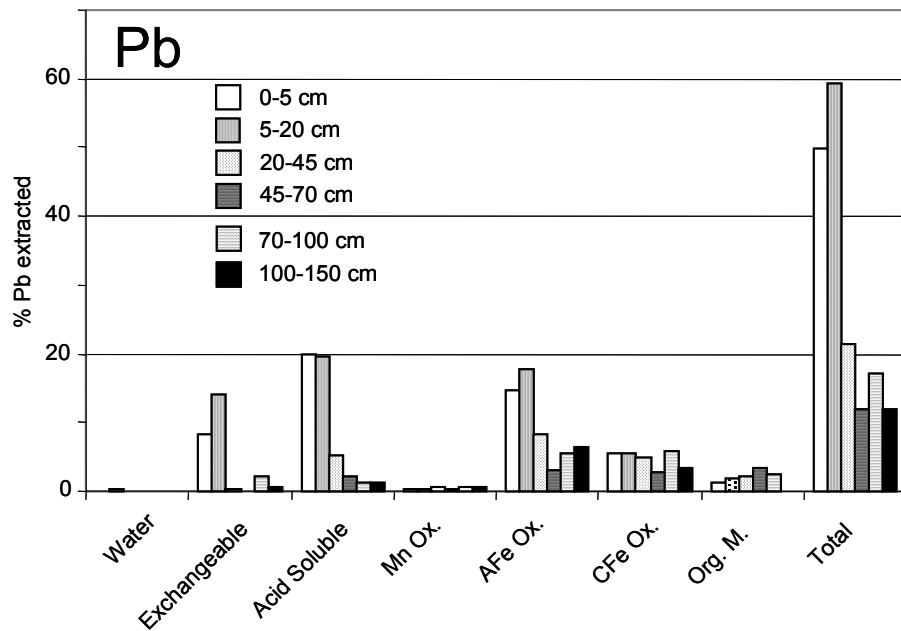


Figure 6, Aubert *et al.*

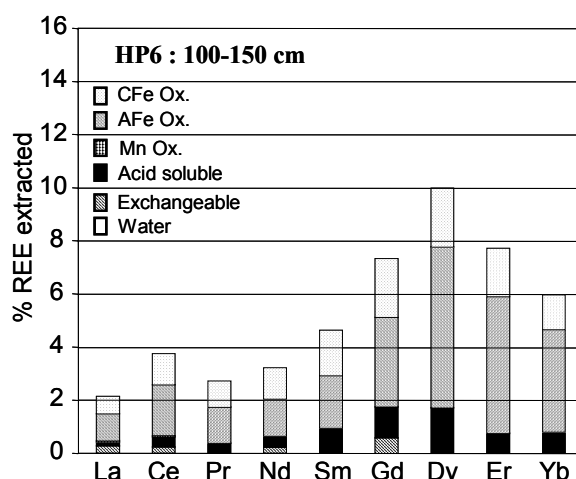
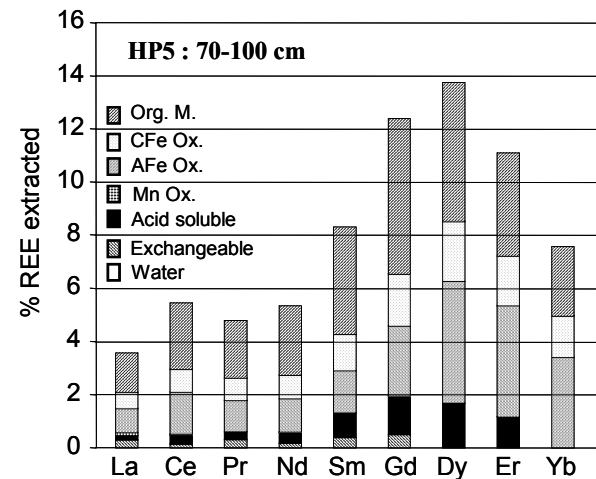
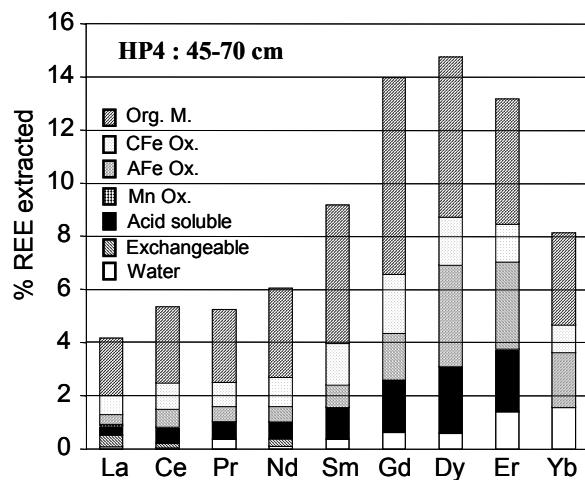
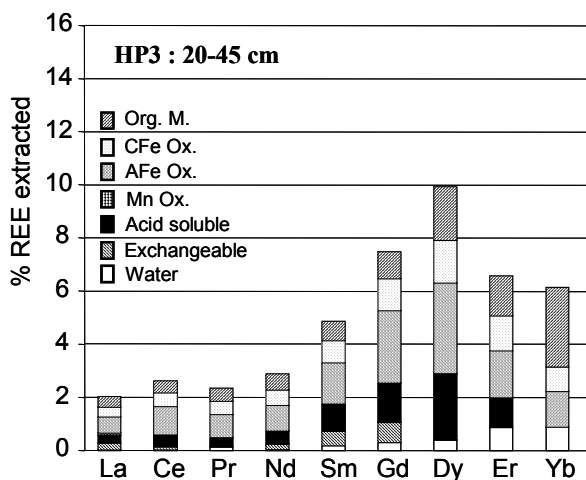
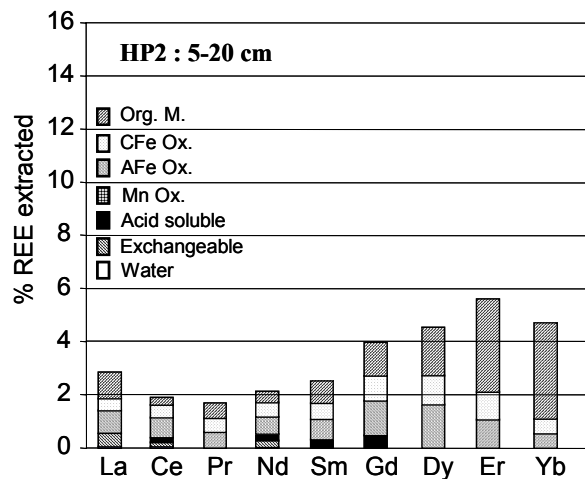
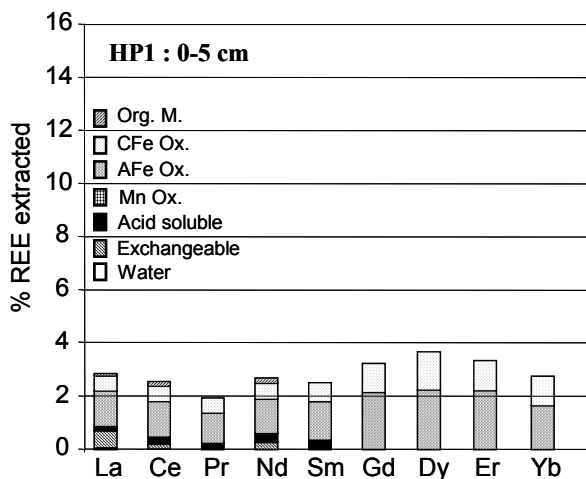


Figure 5, Aubert *et al.*

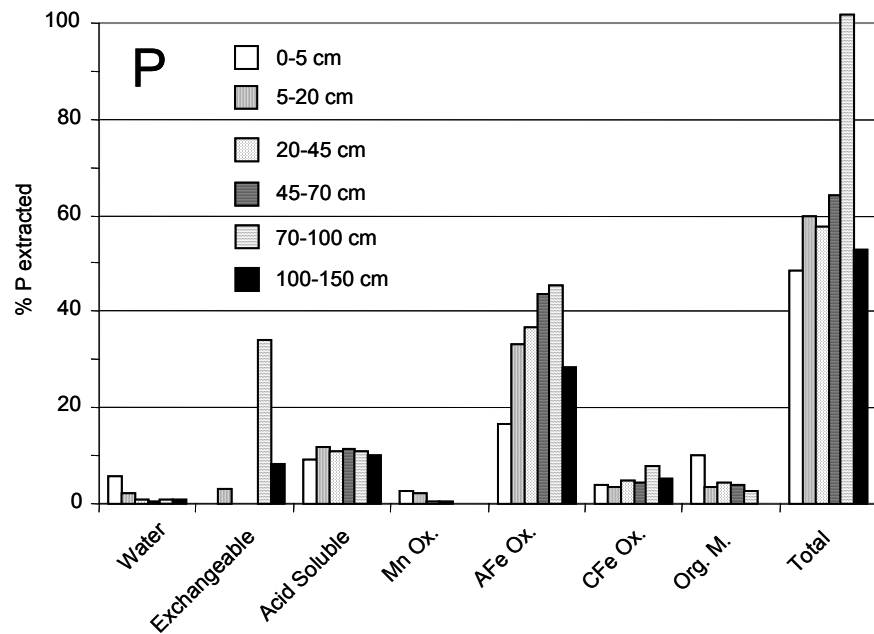
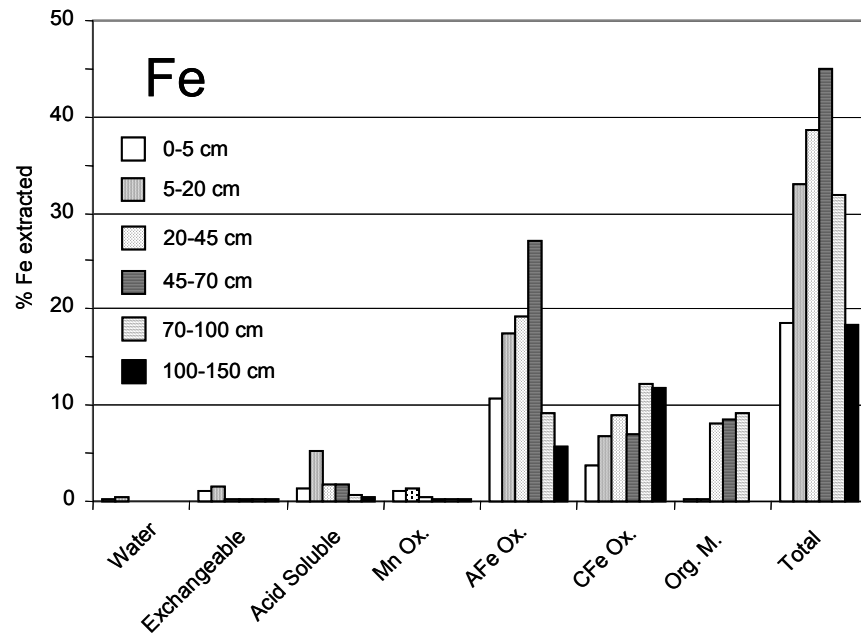
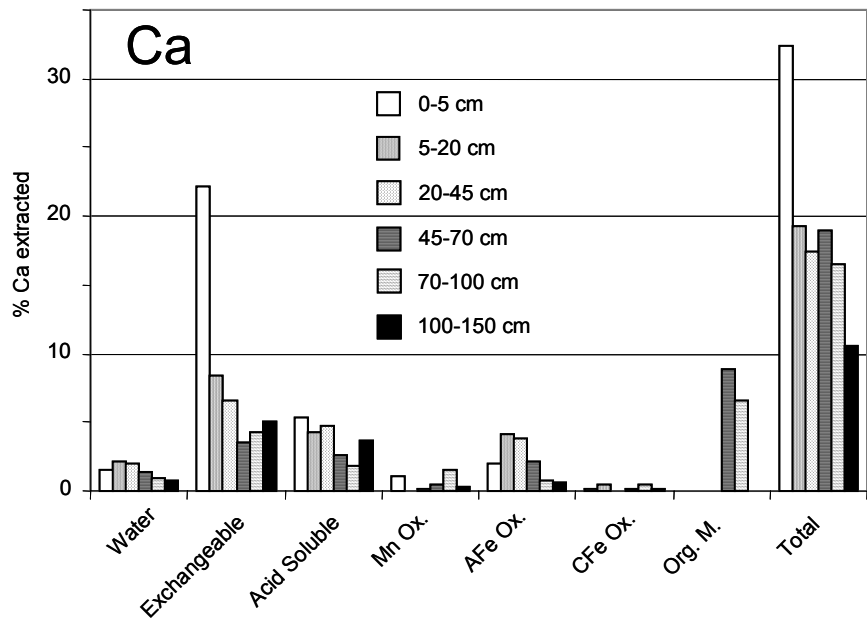


Figure 4, Aubert *et al.*

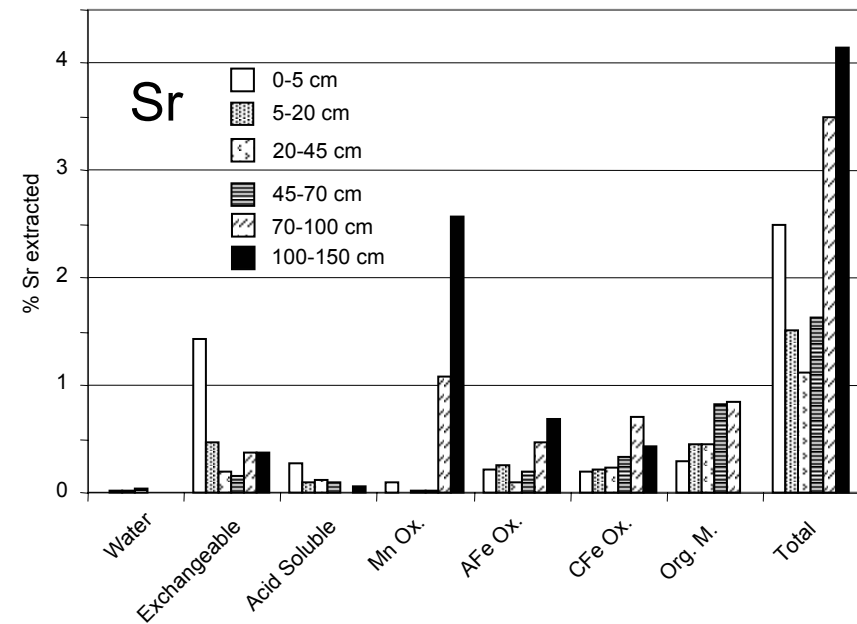
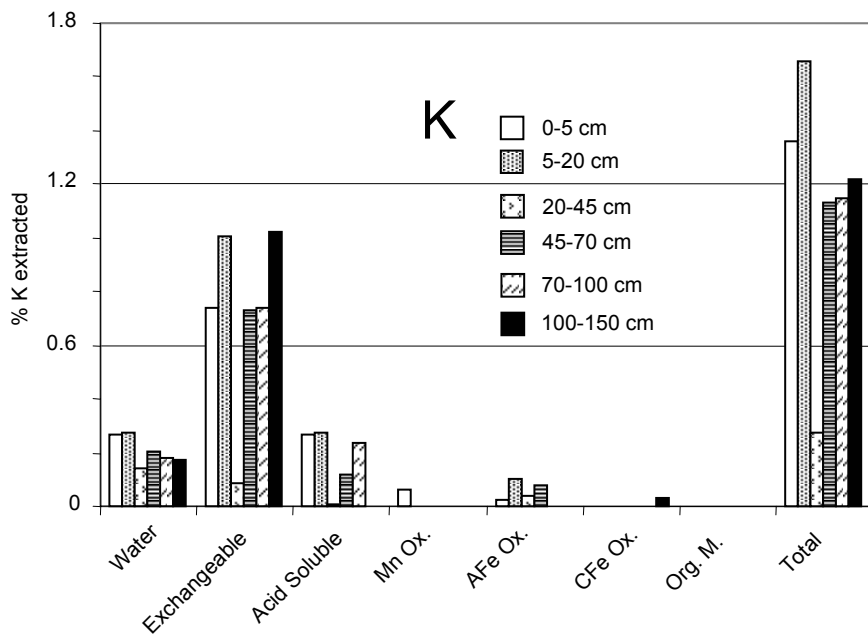
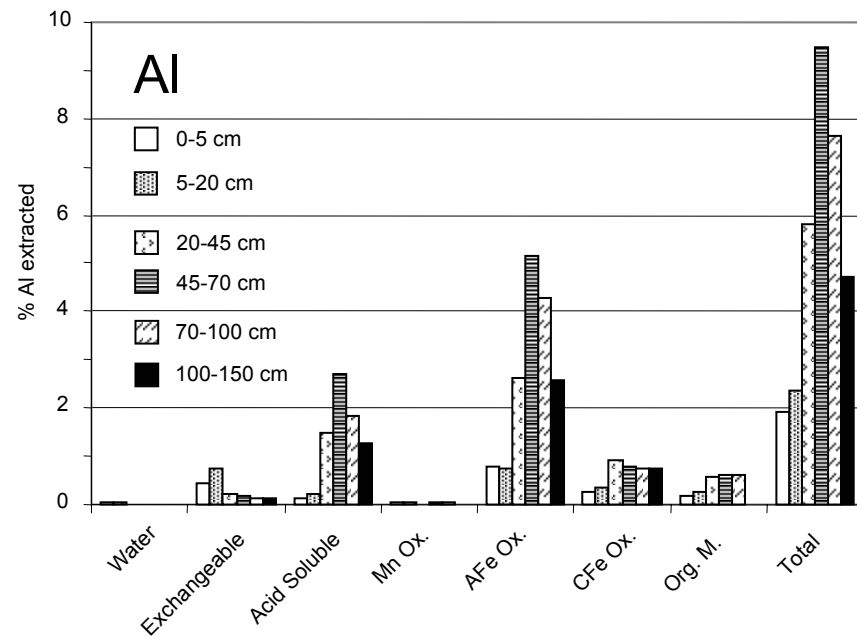
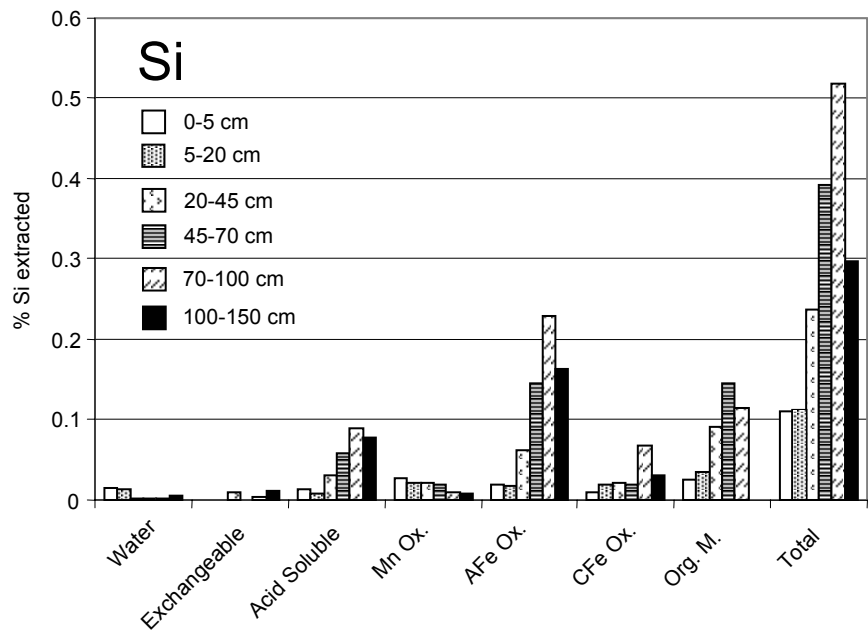


Figure 3, Aubert *et al.*

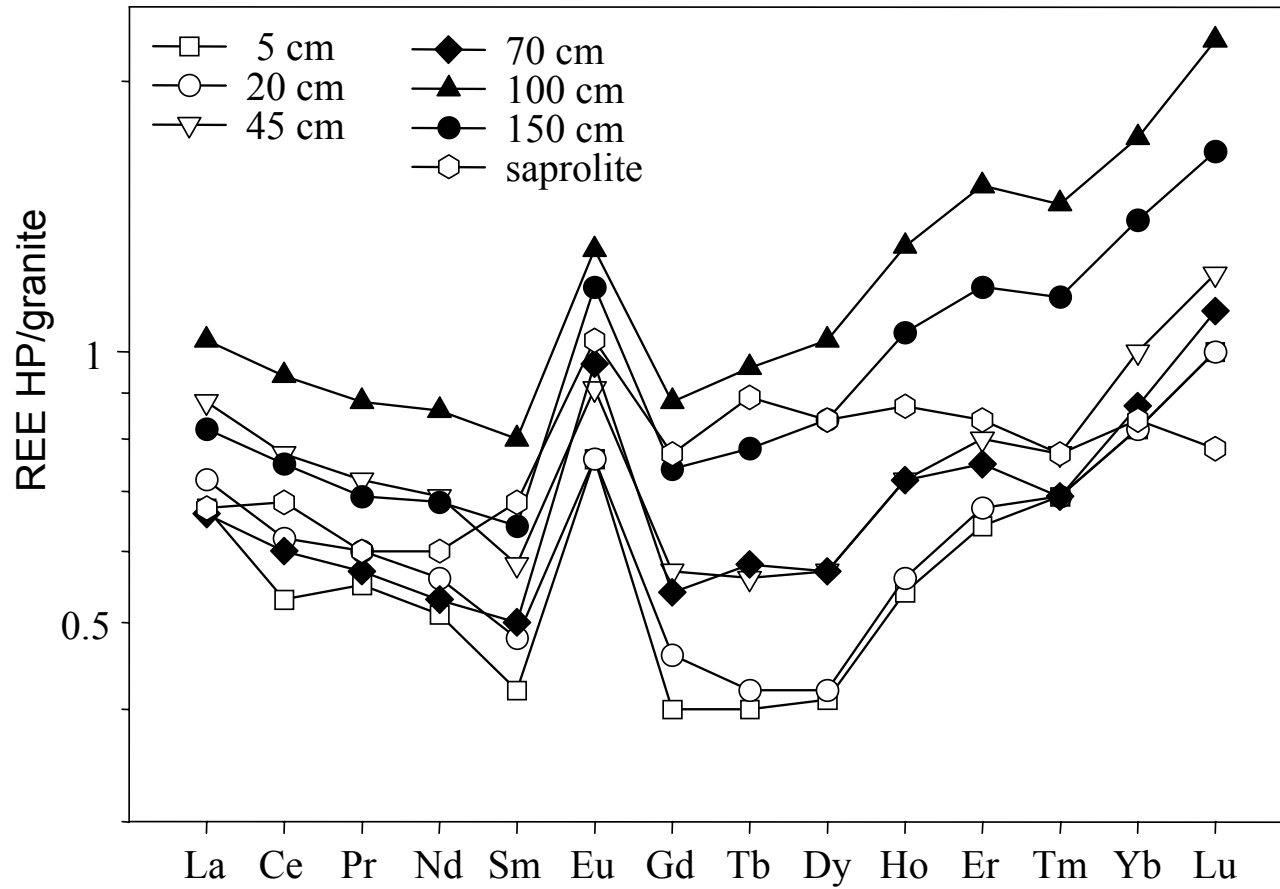


Figure 10, Aubert *et al.*