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Heavy metals speciation analysis as a tool for studying mine tailings weathering

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Abstract

A sequential extraction procedure derived from Tessier et al. (1979) was applied in the area west of Montevecchio to abandoned mine tailings which give rise to a neutralised drainage highly contaminated by heavy metals. The results were compared with mineralogical studies of the weathering processes. The proposed sequential extraction procedure confirms the general alteration modalities observed in the area through mineralogical studies: i.e., a relatively easy dissolution of Zn and Cd and strong immobilisation of Fe, Mn, Cu and Ni. The behaviour of Pb and Co is intermediate.

A generalization of a chemical approach to the comprehension of the weathering process is outlined, though an improvement of the methodology should include a more appropriate sequential extraction procedure capable of distinguishing siderite from iron oxyhydroxides, of leaching anglesite in a single step and of including calcium and magnesium among the analysed elements because of the role of their carbonates in buffering the drainage.

Keywords: tailings; pollution; heavy metals

1. Introduction

Environmental chemical contamination from mine- and smelter-wastes mainly occurs as heavy metal mobilization due to the weathering of solid inorganic materials under exogenic conditions.

So far the approach to the attenuation of the chemical impact from dismantled mines has been considered in terms of the spatial and temporal containment of contaminants. On the contrary, a relatively inexpensive and resolutive approach to be considered carefully in research, when economical reprocessing procedures cannot be applied, can only be the development of artificial or quasi-natural chemical and biological processes, capable of immobilizing contaminants.

The characterization of processes capable of immobilizing heavy metals from abandoned mine wastes in a quasi-natural process requires a good knowledge of the weathering processes occurring in the wastes from their deposition. These processes depend not only on the physics and chemistry of hydric bodies but also and mainly on the mineralogy of the ore body and host rocks, to such an extent that the effects of pollution are better described when each toxic element can be referred to specific mineralogical phases at least in a semi-quantitative way.

In these respects, the development of sequential extraction procedures (SEPs) is important because a SEP is more than a relatively simple tool in relating

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trace metals to mineralogical species. As a matter of fact it also gives detailed information about their mobilization and biological availability.

Different sequential extraction procedures have been applied to particulate (Tessier et al., 1979), river- (Håkansson et al., 1989), lake- (Helios Rybicka, 1992; Szefer et al., 1995) and sea-sediments (Karlsson et al., 1988) as well as stream-bed sediments, whether or not polluted by mine waste deposits (Cook et al., 1992). The main object of the present study is to consider the possibility and modes of application of a SEP to abandoned mine tailings directly. This arises from the conviction that SEP may be 'a useful means of studying qualitative metal associations, provided the data are interpreted with care' (from Tarutis et al., 1992).

2. The mine area west of Montevecchio (Sardinia)

The territory west of Montevecchio was chosen as an ideal site to test the efficiency of a SEP in speciating heavy metals from abandoned mine tailings. In this area lead and zinc mines had been operating since the mid-19th century; they were dismantled between 1968 and 1980. The ore body consists of galena and sphalerite veins in a gangue of quartz and carbonate minerals (siderite prevailing over ankerite, dolomite and calcite) with minor amounts of pyrite, chalcopyrite, barite, cerussite, anglesite, smithsonite and W-minerals.

After the mine shut down, several tailings were abandoned, giving rise to a neutralized mine drainage (NMD) rich in dissolved toxic metals contaminating all the streamlets in the area. No special attempt has ever been made to mitigate the impact of the pollution (Caboi et al., 1993, 1994).

The reasons to consider Montevecchio a target area for this kind of study can be summarized as follows: (a) the mining history of the area is well documented; (b) since the area is almost completely uninhabited other significant sources of pollution can be excluded; (c) a NMD makes the weathering process slower and the study of intermediate phases easier than in an acid environment; (d) notwithstanding the NMD, water in the streamlets is contaminated up to 100 ppm of Zn and 1 ppm of Cd and Pb (Fanfani, 1995); (e) the mineralogy of tailings is well known (Bertorino et al., 1995).

3. Sampling and analytical methods

The sampling was restricted to the area of the Sanna plant and downstream to the last containment dam on the Rio Piscinas. The Sanna plant was the largest at Montevecchio in the last years of mining activity. Not far from the plant a tailings pond was located in a narrow valley. Now the abandoned tailings are deeply cut by the uncontrolled flow of the Roia Cani stream and the surface is often covered by coarser materials. In Fig. 1 a sketch map of the area with the sampling points, the hydrographic network and the level of dissolved contaminants is shown.

Twenty samples were taken at the abandoned tailings pond close to the Sanna plant; nine of these were collected 10 cm below the top of the deposited material at different sites, while eleven were collected from the inner surface of an erosion wall at different depths from the top (down to 4 m) in the unsaturated zone. Yearly droughts of about four months cause the sediments to be dry to a depth of 3–4 m for quite a long time. Two samples are superficial samples from the deposited materials at the Rio Piscinas dam. This material has been removed from the Sanna pond by the rain-off along the Roia Cani streamlet.

All samples were analysed for grain-size using the Wentworth scale; the coarse materials were dry-sieved while the finer materials were wet-sieved.

A chemical characterization of the tailings materials was performed by analysing the soluble fraction resulting from a strong acid attack. A portion of 0.25 g of each sample, finely ground and dried at 105°C, was left for 12 h in contact with a concentrated mixture of high-purity HCl (5 ml) and HNO_3 (7.5 ml) in a Teflon container. Each container was then placed in a microwave digestion device for 25 min. After cooling, 2 ml 30% H_2O_2 were added and a new cycle of 17 min was started. The solution was filtered and brought to a volume of 25 ml with high-purity water. All elements were determined by ICP–OES and AAS. Carbonate contents were determined by developing CO_2 after digestion of the samples with concentrated HCl.

Since the SEP method was to take into account larger amounts (up to % levels) of some metals in the mine tailings than those in the sediments, some

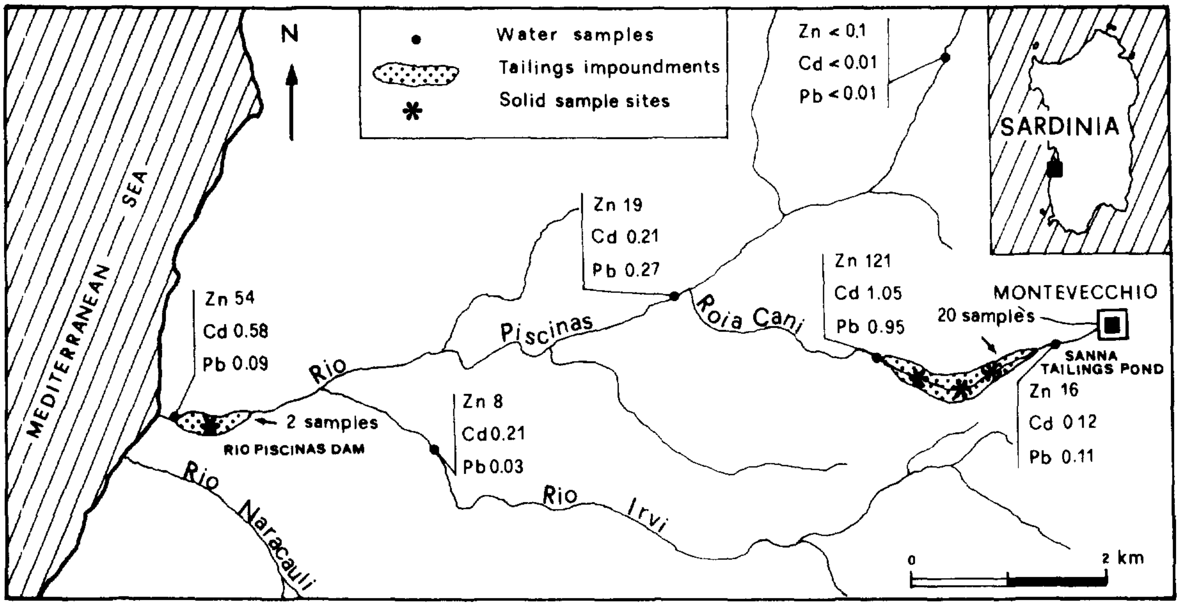

Fig. 1. Dissolved Zn, Cd and Pb contents (ppm) in the streams and solid sample sites west of Montevecchio.

operative conditions (sample quantity and digestion time) were modified as compared to previous methodologies (Mahan et al., 1987); e.g. because of the high iron content, the complete dissolution of the reducible fraction was not possible in one extraction and six repeated extractions were necessary at this stage. The sequential extraction method used is outlined as follows.

Soluble fraction: 1 g sample dried to 105°C + 40 ml demineralized water shaking for 2 h at room temperature.

Exchangeable fraction: residual fraction + 40 ml 1 *M* $MgCl_2$ (pH = 7) in a microwave oven (7′).

Carbonate fraction: residual fraction + 40 ml 1 *M* NaAc + HAc (pH = 5) in a microwave oven (10′).

Reducible fraction: (6 times) residual fraction + 40 ml 0.04 *M* NH_2OH–HCl in 25% HAc in a microwave oven (22′).

Organic fraction: residual fraction + 25 ml H_2O_2 (30%) + 15 ml 0.02 *M* HNO_3 (pH = 2) in a microwave oven (15′).

Sulphide fraction: residual fraction + 24 ml HNO3 + 16 ml HCl in a microwave oven (15′).

The analysis of the extracted fractions was limited to six surface samples (one of them from the Rio Piscinas dam) and three deep samples from the wall (depth: 180, 280 and 380 cm) and to the following elements: Fe, Mn, Zn, Pb, Cd, Cu, Ni, Co and S; they were determined by ICP–OES.

X-ray powder diffraction spectra were obtained on all total samples and their < 63 μm fractions using oriented, air-dried specimens. In several samples the analysis was extended to the residue after the last metal extraction; a few samples were investigated after each sequential extraction. X-ray analysis was performed on a Philips PW 1710 apparatus for powder diffraction analysis, using CuKα and FeKα radiation. A semi-quantitative estimation of the mineralogical content was performed by comparison with specific standards of known mineralogical mixtures.

Further mineral identification was performed by looking at images obtained with a Cambridge 250 MK3 Scanning Electron Microscope (SEM). Geochemical information on the minerals was obtained with the associated LINK AN 10/55S Energy Dispersive X-ray System (EDS).

4. Results

4.1. Grain-size analysis

Grain-size analysis indicates that the samples collected at a depth of more than 50 cm (D) exhibit a

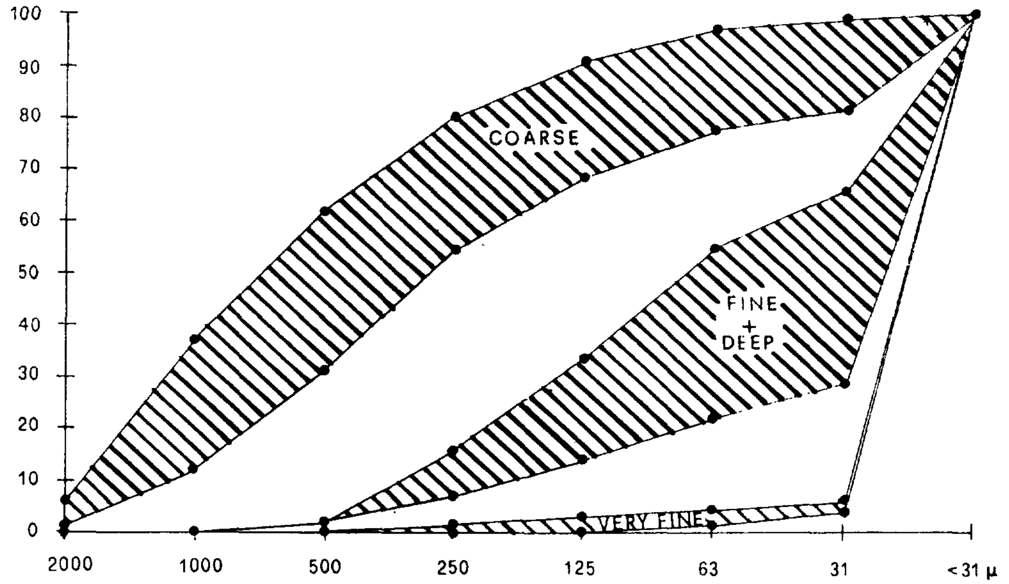

Fig. 2. Representative grain-size curves of tailings samples.

similar granular composition with prevalent fine particles (< 63 µm). Superficial samples, including the two uppermost samples collected along the wall, can be divided into three groups: a coarse one (C) with a prevalent grain-size of > 125 µm, a fine one (F) with grains so similar in size to the deep samples that distinction is impossible, and a very fine one (VF) essentially made up of grain-sizes of less than 31 µm.

The grain-size ranges of the three groups are shown in the cumulative curve diagram in Fig. 2.

4.2. Tailings chemical composition

Since the residue after the strong attack is free of heavy metals and rich only in Si and Al (as confirmed by several checks after an HF attack), each metal amount in the solubilized fraction represents

Table 1
Total average content ($\bar{X}$) in ppm with standard deviations (σ)

	Fe	Mn	Zn	Pb	Cd	Cu	Ni	Co	S	CO_3
Coarse material surface samples (C) ($n = 6$)										
($\bar{X}$)	83400	4190	16400	17200	150	700	21	13	6970	39500
σ	22800	670	14100	25200	120	1130	13	6	7870	14600
Fine material surface samples (F) ($n = 4$)										
($\bar{X}$)	125200	2450	21300	20900	140	570	43	19	11700	36500
σ	44500	2060	15600	32800	70	820	32	12	8400	36700
Very fine surface samples (VF) ($n = 3$, including both samples from the Rio Piscinas dam)										
($\bar{X}$)	70300	3200	16300	19000	120	520	37	19	5670	29900
σ	19700	860	5100	15300	10	360	4	3	1740	13700
Deep samples (D) ($n = 9$)										
($\bar{X}$)	78700	5200	8760	3100	80	80	28	21	4470	97100
σ	4700	500	1180	1260	10	30	5	4	860	14200

the total amount in the tailings. The analytical data are listed in Table 1 in the form of mean values for each group of samples as distinguished by grain-size (C, F, VF) and sampling depth (D).

In order to simplify the interpretation of mineralogical data, the contents of many other elements not listed in Table 1 were determined. The approximate content of Ca is 0.4%, that of K is 0.15%, and Mg is 0.03%. The Na and Sr contents are usually less than 0.01%, while the Ba content ranges from 0.1% to 0.5% in the deep samples (Chessa et al., 1995).

4.3. Elemental distribution at each extraction step

The results of the sequential extraction procedure are given in Table 2 as averaged elemental % amounts in each fraction with respect to the total amounts in the tailings. Indeed, when superficial and deep samples are considered as distinct, the share of individual fractions of elements is similar in the samples of each group.

4.4. X-ray diffraction

The mineralogical data from X-ray powder diffraction analyses are given in a semi-quantitative form in Table 3.

In this table secondary sulphate minerals such as gypsum, epsomite and hexahydrite are not reported; they are often present in the tailings samples as a result of wet–dry processes.

4.5. SEM and EDS analyses

The most common minerals in the ore body and in the gangue appear to be deeply weathered after they were deposited in the Sanna tailings pond. Galena is oxidized to anglesite and cerussite. After oxidation most of the iron-poor sphalerites are solubilized, while iron-rich sphalerites form alteration rims of Zn-rich iron oxyhydroxides (Fig. 3) as observed at Ingurtosu (Caboi et al., 1994; Bertorino et al., 1995). Pseudomorphous iron-oxides have grown on siderite grains and rare pyrite and chalcopyrite

Table 2
Distribution of metals and S in the leached fractions of the tailings as % of total amounts

	A	B	C	D	E
Surface samples (6)					
Fe	tr	tr	tr	64	36
Mn	1	1	9	86	3
Zn	4	3	18	38	37
Pb	tr	27	50	22	1
Cd	19	16	12	16	37
Cu	tr	1	14	34	51
Ni	2	3	23	57	14
Co	4	4	20	56	16
S	11	20	12	5	53
Deep samples (3)					
Fe	tr	tr	4	86	10
Mn	1	1	11	87	tr
Zn	1	3	20	52	24
Pb	tr	15	62	20	2
Cd	7	18	20	32	24
Cu	tr	2	1	71	26
Ni	2	tr	4	65	29
Co	4	1	26	46	23
S	11	3	4	8	74

A = soluble fraction, B = exchangeable fraction, C = fraction bound to easily soluble carbonates, D = fraction bound to reducible oxides, E = fraction bound to organic matter and sulphides.

Table 3
Mineralogical composition in tailings samples from XRD

	Quartz	Illite	Kaolinite	Siderite	Ankerite	Sphalerite	Cerussite	Anglesite
Coarse	xxx	xx	(x)	(x)	(x)	(x)	(x)	x
Fine	xxx	xx	(x)	x	(x)	(x)	(x)	(x)
Very fine	xxx	xx	(x)	xx	(x)	–	–	(x)
Deep	xxx	xxx	(x)	xx [a]	x	x [a]	(x)	–

[a] Increasing with depth.

(x) = trace; x = present; xx = abundant; xxx = predominant.

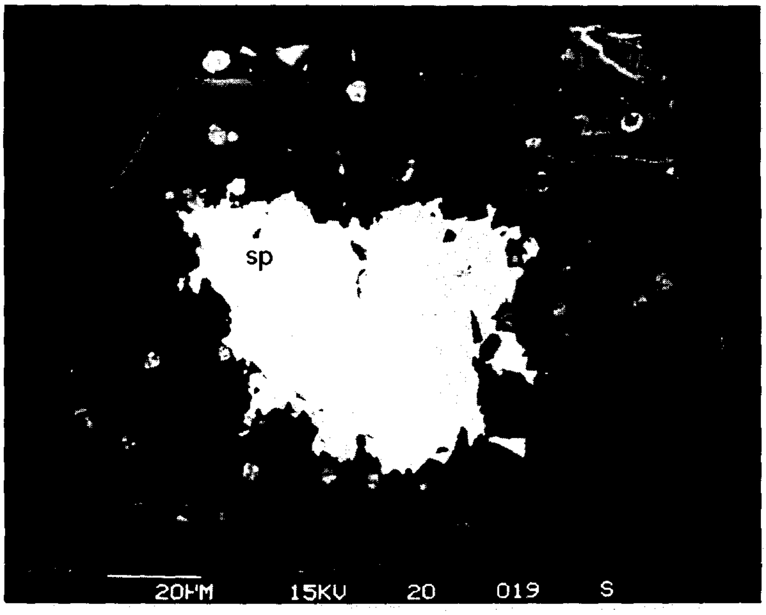

Fig. 3. Backscattered-electron image of an iron-rich sphalerite (*sp*) surrounded by an alteration rim of iron oxyhydroxides, with nodules of pyrite and chalcopyrite.

grains. Secondary Fe–Mg–Zn sulphates are commonly observed on the surfaces of weathered mineral grains.

5. Discussion

The top of the Sanna tailings pond consists of materials with different grain-size (Fig. 2), the size distribution of the material at the surface depending on the local situation, which may favour the accumulation of particles larger than those originally deposited with the tailings.

Grain-size does not affect total metal content in the material deposited at the top. Indeed the samples at the surface exhibit different metal amounts without any relationship with grain-size and sampling sites.

On the contrary the distribution of the material in the abandoned tailings is homogeneous in size from a depth of 50 cm down to the bottom of the pond. The amount of grains larger than 500 μm is negligible while 65 to 80% of the grains are smaller than 63 μm.

Metal content in the deep samples is rather constant and not correlated with sampling depth (only a slight increase of Pb is observed in the two deepest samples) indicating that materials and deposition modalities in the ponds have not changed with time and successive weathering has not affected individual levels differently at depths deeper than 50 cm.

In the deep samples, sulphur as sulphate or sulphide species is present at a percentage of 0.5%, Fe at 8% and CO_3 at 10%, while Ca and Mg amounts are less than 1% and 0.1% respectively. This suggests that iron-sulphides, though important in the weathering process, are quantitatively negligible, and siderite is the most abundant iron mineral.

An inspection of the results obtained by sequential extraction analysis shows the difficulties met in distinguishing the Pb and Fe phases. Indeed the distribution of Pb over the different leaching steps (including that of oxides) reveals that the selected procedure is not capable of dissolving Pb sulphate in a single step. The large amount of iron extracted at the oxide step indicates that siderite is extracted in a very small amount in the preceding step together with the more easily soluble carbonates.

Notwithstanding the large differences in the total metal amounts between superficial and deep samples

SEP results are reasonably comparable (Table 3). When you look at deep samples which are better representative of the deposited materials, Fe and Mn appear to be strongly immobilized, mainly in an oxide form. A similar behaviour is also shown by Cu and Ni, signifying that they are incorporated with strong linkages in the iron-oxide framework, besides in the sulphide lattice. Zinc, Cd and Co are much more mobile. They are only temporarily hosted in the oxidized rims of iron minerals, from which they are easily removed so that relatively high amounts of these elements are extracted in the early steps of the sequential procedure (the low content of Zn in the first step of the SEP has to be ascribed to the high solubility of Zn-sulphates). Pb is extracted prevalently in the exchangeable, carbonate and oxide fractions but, as stated above, this does not necessarily mean a real association with these phases. Probably part of the Pb is weakly adsorbed on Fe-oxide phases and in clay minerals (step B), while a larger part is in the form of sulphate (anglesite) (C + D step) and subordinately as carbonate (cerussite) (C step). Sulphur extraction shows a significant amount of the element extracted in the first stage, indicating the presence of easily soluble sulphates (Ca and Mg) in the dried tailings.

The general features derived from chemical studies are confirmed by X-ray and SEM investigations. The peculiarity of the contaminating drainage west of Montevecchio is strongly affected by the important role of iron-bearing carbonates. The prevalent presence of siderite among Fe-phases is confirmed by all diffraction spectra. Its presence increases in deep samples while in surface samples the relative amount of siderite is less, owing to its weathering into an oxide phase. Anglesite is the most abundant Pb mineral, while sphalerite is recognized often at a trace level only in some samples. As observed in the SEP analysis Zn has been largely removed from the primary sulphide and adsorbed on Fe-oxides or is completely leached. Cadmium content is too low to be identified in specific minerals.

6. Conclusions

The contamination hazard of soils and water by tailings wastes in abandoned mining areas can only be forecast with good approximation by detailed geochemical and mineralogical studies. These studies require specialised instruments and expert researchers capable of interpreting instrumental data.

The interpretation of weathering processes through chemical analyses has the following two advantages: (a) to avoid the use of typical mineralogical laboratory equipment, and (b) to study the behaviour of some trace elements that have an environmental impact but are difficult to detect with a mineralogical study since they do not form specific minerals.

A SEP has been chosen as the best approach to assess weathering processes since it allows single elements to be associated with certain phases and affords immediate information on the mobility of contaminants. This procedure has been tested in an area contaminated by Pb–Zn sulphide tailings in an approximately neutral environment. The following distribution of trace metals has been obtained in the following six sequential extraction steps:

(1) The heavy metal fraction leached by pure water essentially includes soluble sulphates; this fraction represents the final stage of the weathering of sulphide wastes and can be easily recognised only in arid climates.

(2) The exchangeable fraction includes the heavy metals temporarily hosted on the surfaces of clay minerals and iron oxides. This fraction is easily transferred into hydric bodies and soils.

(3) The carbonate fraction essentially includes trace metals associated with calcium and magnesium carbonates; Fe and minor elements are not extracted from siderite, while Pb is extensively extracted from anglesite in addition to cerussite. All the elements are transferred to the environment at a slightly acid pH.

(4) The reducible fraction is made up not only of iron oxyhydroxides from which trace metals in the lattice are removed in a reducing environment; indeed, most of the siderite and part of the anglesite are also leached at this stage owing to the relatively acid solution.

(5) The organic fraction is scarce and its metal content negligible.

(6) The sulphide fraction includes most contaminant elements which will be transferred to the environment only after a complex weathering process.

At the end of the SEP, the residue, that was essentially made up of Si and Al minerals, proved to be practically free from toxic metals.

Since with the proposed SEP it is not possible to distinguish siderite from iron oxyhydroxides and dissolve anglesite in a single step, the technique needs to be improved. However, a more efficient SEP, that will be developed in the near future, should not require a greater amount of analytical work than the present one. Indeed, if separation of anglesite from the carbonates and siderite from the oxyhydroxides requires at least an additional step, steps (1) and (2) of the present procedure could be combined and step (5) omitted. With a different leaching of the exchangeable fraction without a solution of $MgCl_2$ it could be possible to determine Mg content in the SEP. The sum of Ca and Mg content extracted from the carbonate fraction will provide a good estimation of the buffering capacity in the weathering process.

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