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FIELD EVIDENCES ON RELEASE/REMOVAL OF ARSENIC BY HYDROTALCITE-LIKE COMPOUNDS IN MINING WATERS. THE EXAMPLE OF BACCU LOCCI MINE (SARDINIA, ITALY)

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Abstract

Minerals belonging to the hydrotalcite group are assuming an increasing interest in environmental mineralogy. In fact, thanks to a high anionic exchange capacity, they can find applications in site-remediation as contaminant removers from polluted waters. The presence of hydrotalcite-like sulphates such as glaucocerinite, zincowoodwardite, hydrowoodwardite and woodwardite $[Me^{2+}_{1-x}Al_x(SO_4)_{x/2}(OH)_2 \cdot mH_2O]$ has been documented in a number of mining areas. They usually occur as fine-grained precipitates from mining waters or as porous crusts. While their role on removing cations such as Zn, Cu and Al from waters is immediately evident, the role they have in incorporating undesirable anions, other than $(SO_4)^{2-}$, is often disregarded. However, field evidences from a mine area in Sardinia (Italy) showed that these phases have a great capability to remove arsenic, probably as $(AsO_4)^{3-}$, from waters. The advantage of these hydrotalcites-like sulphates, in comparison with Fe-oxides-hydroxides (generally considered the most efficient arsenic removers, naturally occurring in mining areas), is to act as removers in waters at high pH values, when a reduced efficiency of Fe-oxides-hydroxides for arsenic sorption and a greater arsenic mobility account for an increased arsenic hazard.

Introduction

A group of related minerals such as glaucocerinite and its lower hydrated analogous zincowoodwardite $[Zn_{1-x}Al_x(SO_4)_{x/2}(OH)_2 \cdot mH_2O]$ as well as hydrowoodwardite and its lower hydrated analogous woodwardite $[Cu_{1-x}Al_x(SO_4)_{x/2}(OH)_2 \cdot mH_2O]$ are hydrated sulphates belonging to the hydrotalcite group (Witzke, 1999; Witzke and Raade, 2000). The general structure of hydrotalcites (also called "anionic clays" or "layered double hydroxides") is composed of a brucite-like octahedral sheet with an interstitial anionic layer. A key feature of this mineral group is the substitution of M^{3+} cations for M^{2+} cations within the brucite-like sheet $[(M^{2+}_{1-x} M^{3+}_x)(OH)_2]$. This makes the octahedral sheet positively charged, that is the reason for the presence of interstitial anionic groups, such as $(CO_3)^{2-}$ in hydrotalcite itself and $(SO_4)^{2-}$ in glaucocerinite and its related minerals, along with molecular water. Since the anionic groups are linked to the brucite-like layers by hydrogen bonding, they can easily exchange with solutions and this accounts for the high anionic exchange capacity of the hydrotalcite-like group of minerals. This property is the base of their use as catalysts or contaminant removers (Vaccari, 1998; Yang et al., 2005).

Glaucocerinite and its related minerals often occur as fine-grained precipitates with very poor or no crystallinity (Hawthorne, 2000), and for this reason they are difficult to be characterised,. Such hydrotalcite-like sulphates have been found associated at the abandoned Pb-As mine of Baccu Locci (Sardinia, Italy). The mine site is characterised by a diffuse, severe arsenic contamination which affects surface and ground waters, stream sediments and soils. Arsenopyrite is the main primary As-bearing mineral of the mineralization, whereas scorodite and ferrihydrite are the most important secondary phases responsible for As release to waters (Frau and Ardau, 2003, 2004). Glaucocerinite-like phases from Baccu Locci precipitate from waters interacting with waste-rock material derived from mine workings. The precipitates rarely exhibit a good degree of crystallinity and occasionally show high As content (up to 2.5 wt. %). Field observations indicate that these phases are rather sensitive to wet-dry seasonal cycles. They behave as a sink or as a source for As depending on climatic/geochemical conditions.

The aim of this study is the comprehension of the role of glaucocerinite-like minerals in removing As from aqueous environment. To clarify this role we also performed some experiments of As co-precipitation and adsorption by synthetic samples. The results of this study will certainly contribute to better understand the environmental importance of glaucocerinite and analogous phases at mine sites as contaminant removers and their possible application in site-remediation.

Field occurrences

Several streamlets, characterised by a torrential regime, drain the mining area of Baccu Locci. They all flow into the main stream of the area (Baccu Locci stream), which results affected by a considerable arsenic contamination (hundreds of $\mu g\ L^{-1}$). The Tr1 streamlet (as Tributary 1) represents one of them (Frau and Ardau, 2003). Before entering the mine area, water chemistry of Tr1 belongs to the low-metal Ca–Mg–HCO_3 type. As soon as it enters the mine area, interacting with mine wastes, its water chemistry becomes of high metal Ca–Mg–SO_4 type, with arsenic concentrations in the order of several tens of µg L^{-1}. All along the stretch where waste materials are placed, the phenomenon of an abundant precipitation of green-pale phases from the Tr1 waters is observed. The Tr1 streamlet is not the only one showing this peculiar precipitation phenomenon; another tributary of the Baccu Locci stream (named Tr2) is characterised by similar occurrences after its mixing with acid waters overflowing from mine adits. As a consequence of the torrential regime of these streamlets, the "permanence-time" of such precipitates *in loco* is seasonal-dependent, and usually quite short, ranging from weeks to months. Mechanical removal from the streambeds by water flowing and likely re-dissolution are the factors accounting for their disappearance. Shorter "permanence-times" are also possible in occasion of flooding events, which rapidly "clean" the streambeds from any occurrence. New phases would partially or completely replace the old ones as a function of rainfalls. However, the presence of the green-pale precipitates results quite continuous over the whole year.

Materials and Methods

A sampling campaign of the green-pale precipitates has been carried out with a monthly cadence on the Tr1 and Tr2 streamlets, and is still in progress. Nevertheless, in this paper we will only focus on the Tr1 samples, since Tr2 waters (and consequently Tr2 precipitates) do not contain significant amount of As.

After collection, precipitates were labelled and brought to the laboratory. Supernatant water was eliminated by centrifugation, and the recuperated solid materials were dried. A portion of each sample was used for mineralogical analyses by XRD and SEM-EDX. Another portion was solubilized in 10% v/v of HNO_3, and the solution analysed by ICP-AES to determine the chemical composition.

In laboratory we set up a method for the synthesis of glaucocerinite-like phases. This method consisted on mixing an aqueous Zn, Cu and Al sulphate solution (with established Al:Cu:Zn ratios) with a NaOH solution, inducing precipitation at pH 8.5. The first product resulted quite amorphous; to increase its crystallinity it was sufficient to prolong the aging time. Subsequently, an As-coprecipitated-hydrotalcite was obtained adding an aqueous Na_2HAsO_4 solution as "ingredient" during the synthesis. Finally, an As-adsorbed-hydrotalcite was obtained leaving a synthetic sample in contact with an aqueous Na_2HAsO_4 solution for an adequate time.

Results and Discussion

1. Natural precipitates

Mineralogical analyses performed by XRD on the natural green pale precipitates showed that these materials are rarely constituted by a single phase. They are quite often a mixture of different mineralogical phases (amorphous and/or crystalline), mainly woodwardite, intimately mixed with plumbojarosite. Chemical analyses of precipitates will be discussed later in this same paragraph. We just anticipate that, considering the predominance of Zn in the Me^{2+} position, these phases should be better defined as zincowoodwardite, which represents the Zn analogous of woodwardite, rather than woodwardite *sensu strictu* (marked by a predominance of Cu^{2+} in the Me^{2+} position). Zincowoodwardite is a relatively new phase (Witzke and Raade, 2000). The degree of structural order of these phases varies from completely or almost amorphous (when sampled during or just after precipitation) to poor crystalline (Fig. 1a); this weak degree of crystallinity, still sufficient to identify the phases, is usually reached within few weeks. Nevertheless, in the Baccu Locci mine, a well crystallised sample of woodwardite/zincowoodwardite has not been found yet.

Whereas zincowoodwardite is widely diffuse (both spatially and temporally) on the bed of the Tr1 streamlet, glaucocerinite is infrequent and limited to some spots along the streamlet course, usually where flow rate is minimised by some physical obstacle (like the presence of a dike) and, consequently, precipitation phenomena take place more slowly. Glaucocerinite, dissimilarly from zincowoodwardite, is always quite crystalline (Fig. 1b). Nevertheless, crystallite sizes are in the nano-scale range, so that they are not visible by SEM observations.

We are trying to understand whether glaucocerinite in the Baccu Locci system could represent an advanced aging stage of zincowoodwardite or whether the two phases have a distinct genesis. The main difference between the two phases is represented by the basal spacing that is ~ 10.88 Å in glaucocerinite and ~ 8.5 Å in zincowoodwardite, due to a different hydration. In dry atmosphere, for example, a synthetic glaucocerinite would tend to lose part of the interstitial water becoming zincowoodwardite (Witzke and Raade, 2000). But what happens in the field? Could the process be opposite? We found in the field some sort of layered crusts, characterised by levels of different colours, consistency and hydration. These distinct levels were the evidence of different precipitation events where the new phases arose in addition of the old ones instead of replacing them. Since the layers were extremely thin and intimately bound, we could not easily separate them. A rough separation was performed by centrifugation.

From XRD analyses, the oldest and more compacted levels resulted composed mostly of glaucocerinite, while the youngest ones of zincowoodwardite. This finding could support the hypothesis of glaucocerinite as an aged zincowoodwardite. However, at the moment, we could not exclude that the presence of levels of both phases within the same stratification is due to their alternate precipitation, caused by changes of some environmental factors (flow rate, temperature, water composition…) during their respective precipitation events.

Chemical analyses were performed to define the composition of precipitates. The main components (plus arsenic) for some selected samples are reported in Table 1.

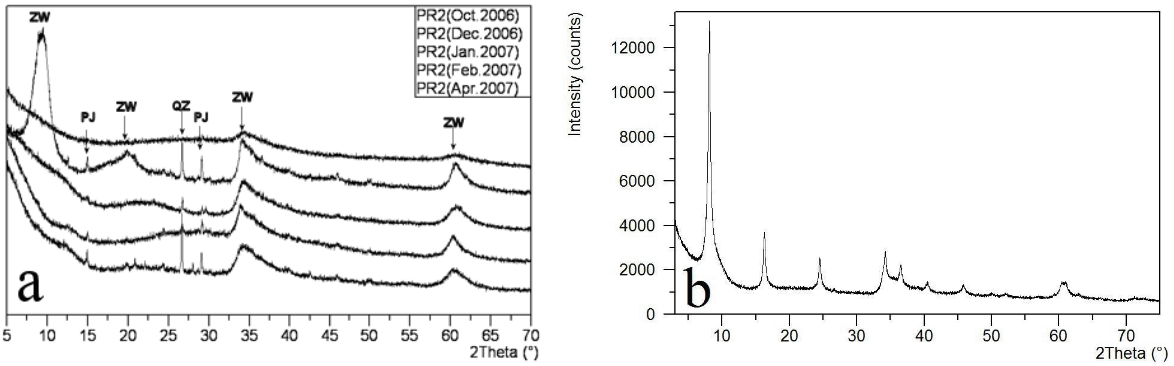

Figure 1. a) XRD patterns for zincowoodwardite-like phases with different degree of crystallinity; ZW=zincowoodwardite, PJ=plumbojarosite, QZ=quartz. b) XRD patterns for glaucocerinite (Pr2 sample: April 1999).

Table 1. Main chemical components (wt. %) in hydrotalcite-like precipitates from Baccu Locci mine. AA = almost amorphous; PC = poor crystalline; C = crystalline; ZW = zincowoodwardite; G = glaucocerinite; ? = uncertain identification.

sample	date	description	Al_2O_3	As_2O_5	CuO	SO_3	SiO_2	ZnO
Pr0	Dec. 2006	PC ZW	15	0.3	9.0	7.5	5.3	31
Pr1	Oct. 2006	AA ZW(?)	11	0.3	3.9	5.0	5.0	29
Pr1	Dec. 2006	PR ZW	12	0.4	4.7	7.8	5.7	33
Pr1	Feb. 2007	AA ZW(?)	8	1.5	2.5	2.1	2.6	34
Pr1bis	Dec. 2006	PR ZW	10	0.4	4.1	5.7	3.1	27
Pr1g	Feb. 2007	AA ZW(?)	9	1.1	2.5	3.2	2.0	32
Pr2	Apr. 1999	C G	12	2.5	7.3	8.7	1.6	31
Pr2	Nov. 1999	AA G (?)	10	4.1	6.5	7.0	nd	29
Pr2	Oct. 2006	AA ZW(?)	13	0.7	4.7	2.6	7.6	35
Pr2	Dec. 2006	AA ZW	10	1.1	6.2	7.0	1.6	24
Pr2	Jan. 2007	AA ZW(?)	11	1.6	3.5	2.2	3.9	34
Pr2	Feb. 2007	PC ZW	9	1.3	2.7	2.6	4,4	44

The chemical analyses were performed on 100 mg of each sample, dissolved in 10% v/v of HNO_3. Element concentrations in solution were referred to this weight, disregarding the possible amount of sample not dissolved by this chemical attack (like plumbojarosite). Therefore concentrations in Table 1 could be weakly substimated, and water content was impossible to be calculated.

These phases are mostly constituted by Zn, Al, Cu, Si and S that, except for Si, correspond to glaucocerinite-like main components. In the literature and mineralogical databases the value of Me^{2+}/Me^{3+} molar ratio in glaucocerinite has been fixed to 5/3 (from the first sample in Laurion, Greece; Raade et al., 1985), but this ratio is variable. Therefore, considering the more general formula for hydrowoodwardites ($Cu_{1-x}Al_x(SO_4)_{x/2}(OH)_2 \cdot mH_2O$) (Witzke, 1999) and for zincowoodwardites ($Zn_{1-x}Al_x(SO_4)_{x/2}(OH)_2 \cdot mH_2O$) (Witzke and Raade, 2000), we approximated the general formula of the precipitates to $(Cu+Zn)_{1-x}Al_x(SO_4)_{x/2}(OH)_2 \cdot mH_2O$) where x is the $M^{3+}/(M^{3+}+M^{2+})$ molar ratio, M^{2+} is the sum of Zn and Cu and Me^{3+} is Al. The $M^{3+}/(M^{3+}+M^{2+})$ molar ratio ranges from 0.23 to 0.38 and is in good agreement with bibliographic data referring to naturals and synthetic phases (Raade et al., 1985; Witzke, 1999; Witzke and Raade, 2000). The Cu/(Cu+Zn) molar ratio is moderately variable and ranges from 0.06 to 0.23. According with the general formula, the number of moles of $(SO_4)^{2-}$ should result equal to x/2. Nevertheless, if we compare $(SO_4)^{2-}$

calculated (fixing $x = M^{3+}/(M^{3+} + M^{2+})$) with observed $(SO_4)^{2-}$ values, we find mostly a deficit of $(SO_4)^{2-}$ in the samples. Since Tr1 waters contain a not negligible content of HCO_3^- in solution (Frau and Ardau, 2003), the presence of both $(SO_4)^{2-}$ and $(CO_3)^{2-}$ anions in the interstitial anionic layer could be hypothesised; a carbonate rich variety of hydrowoodwardite is known from the St. Christoph mine, Bärenhecke (Witzke, 1999). However, given the high Si concentrations detected, another option would be that $(SiO_4)^{4-}$ could partially substitute for $(SO_4)^{2-}$ in the interstitial anionic layer. In Figure 2a we reported the EDX spectrum of a precipitate (Pr1) from the Baccu Locci area, showing that Si and S could be, actually, associated at the phase. We calculated, for all the samples, the sum of (S + Si) in moles to see if it could reach the theoretical value of x/2. The calculated values are around the theoretical one. Others authors, who found significant amounts of Si in the chemical composition of similar phases, prefer to interpret its presence as a contamination by amorphous silica. The analyses of $(CO_3)^{2-}$ content on the Baccu Locci samples would likely clarify this point.

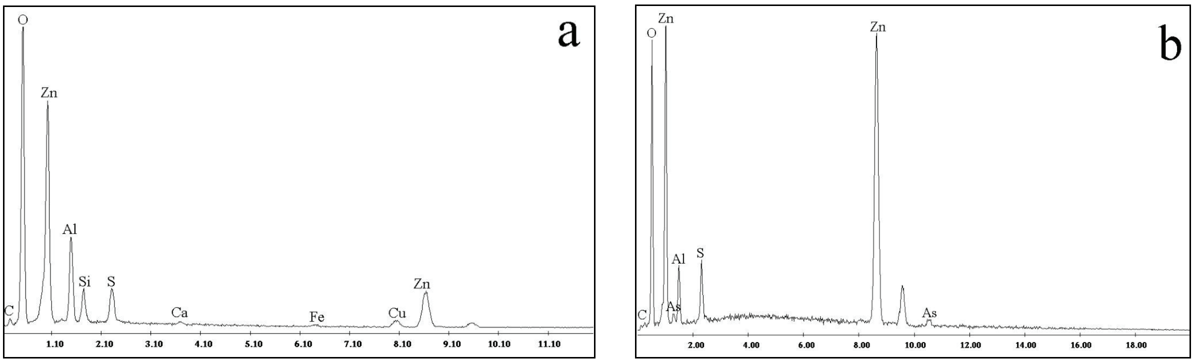

Figure 2. a) SEM-EDX spectrum of a hydrotalcite-like precipitate from the Baccu Locci mine (sample Pr1-Dec. 2006). b) SEM-EDX spectrum of a synthetic As-bearing-woodwardite.

In Table 1 we reported arsenic concentration in precipitates. Even if As can not be considered a main component, its content is always quite significant, often above 1 wt.% as As_2O_5 (ranging from 0.3 up to 4.1 wt.%). It occurs in both glaucocerinite and zincowoodwardite, leaving aside their degree of crystallinity. At the moment, we do not know whether arsenic is structural, present as oxyanion in substitution of $(SO_4)^{2-}$ in the interstitial anionic layer, or adsorbed onto specific surface sites of the brucite-like octahedral layer. Nevertheless, chemical analyses pointed out that its concentration does not significantly change during aging, supporting the idea that this element is quite strongly linked to the phase, and its removal from the solid phase to solution is only possible with the partial or total dissolution of the solid phase itself.

2. Synthetic precipitates

To clarify the role that hydrotalcite-like sulphates have in removing arsenic from solution we performed some experiments on synthetic samples. First stage of laboratory experiments was to obtain a reproducible method of synthesis. To simulate $M^{3+}/(M^{3+} + M^{2+})$ molar ratios in natural samples, we tried to synthesize a number of sulphates fixing x = 0.38 and x = 0.25 in aqueous solutions. We found that these ratios were respected in the relative solids, showing that $M^{3+}/(M^{3+} + M^{2+})$ depends on water composition variability. XRD analyses performed on synthetic samples showed that they are usually zincowoodwardite and, occasionally, glaucocerinite, confirming that, as observed in the field, the first phase is easiest to form.

A second step was to synthesize an As-coprecipitated-zincowoodwardite adding an aqueous Na_2HAsO_4 solution during precipitation. The amount of arsenic added to the solution corresponded to that necessary to obtain a synthetic sample with As concentration not dissimilar from natural samples. Chemical analyses on the synthetic sample showed that arsenic was contained in the solid in ~3.5 wt.%. SEM-EDX analyses confirmed the presence of As into the precipitate (Fig. 2b).

A third step was to synthesize an As-adsorbed-zincowoodwardite, leaving a synthetic zincowoodwardite in an aqueous Na_2HAsO_4 solution for an adequate time. Arsenic concentration drastically decreased in solution within 24 hours of experiment and weakly decreased for around 10 days. Chemical analyses showed that arsenic was contained in the solid in ~ 6 wt.%.

Conclusions

Results of this preliminary study pointed out that the occurrence of glaucocerinite-like compounds in the Baccu Locci system is cyclic and mostly depends on climatic/geochemical conditions. These mineral phases show a high capacity to remove arsenic from solution. Because of their role as arsenic removers in mine waters at circum-neutral pH values, they represent an important alternative to the most known Fe(III)-hydroxides, whose sorptive capacity for As(V) is notably reduced at near neutral pH values in comparison with acidic conditions (Pierce and Moore, 1982). However, due to their ephemeral nature, this role in the Baccu Locci system appears limited.

At the present time, we do not know how arsenic is bound to glaucocerinite-like phases. One hypothesis is that arsenic is structural, more precisely present as oxyanion (most probably as arsenate) in substitution of $(SO_4)^{2-}$ in the interstitial anionic layer; another hypothesis is that arsenic is adsorbed onto specific surface sites of the brucite-like octahedral layer. Co-precipitation and adsorption experiments left both options opened. Further studies have been planned to clarify this point. Since X-ray absorption spectroscopy (XAS) is one of the most suitable techniques to obtain detailed information on the chemical and structural state of an element at a molecular scale, natural and synthetic As-bearing samples will be used in XAS spectra acquisition to obtain detailed information on the local As environment in the hydrotacite-like structures. Clarification of this aspect will certainly contribute to better understand the environmental importance of glaucocerinite and analogous phases at mine sites.

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References

Frau F., Ardau C**.** (2003). Geochemical controls on arsenic distribution in the Baccu Locci stream catchment (Sardinia, Italy) affected by past mining. Applied Geochemistry 18, 1373-1386.

Frau F., Ardau C. (2004). Mineralogical controls on arsenic mobility in the Baccu Locci stream catchment (Sardinia, Italy) affected by past mining. Mineralogical Magazine 68(1), 15-30.

Hawthorne F.C., Krivovichev S.V., Burns P.C. (2000). The crystal chemistry of sulfate minerals. In: Sulfate Minerals (Alpers C.N., Jambor J.L., Nordstrom D.K. eds.), Reviews in Mineralogy and Geochemistry 40, 1-112.

Pierce M.L., Moore C.B. (1982). Adsorption of arsenite and arsenate on amorphous iron hydroxide. Water Research 16, 1247 –1253.

Raade G., Elliott C.J., Din V.K. (1985). New data on glaucocerinite. Mineralogical Magazine 49, 583-590.

Vaccari A. (1998). Preparation and catalytic properties of cationic and anionic clays. Catalysis Today 41, 53-71.

Witzke T. (1999). Hydrowoodwardite, a new mineral of the hydrotalcite group from Königswalde near Annaberg, Saxony/Germany and other localities. Neues Jahrbuch für Mineralogie 2, 75-86.

Witzke T., Raade G. (2000). Zincowoodwardite $[Zn_{1-x}Al_x(SO_4)_{x/2}(OH)_2\cdot(H_2O)_n]$, a new mineral of the hydrotalcite group. Neues Jahrbuch für Mineralogie 10, 455-465.

Yang L., Shahrivari Z., Liu P.K.T., Sahimi M., Tsotsis T.T. (2005). Removal of trace levels of arsenic and selenium from aqueous solutions by calcined and uncalcined layered double hydroxides. Industrial & Engineering Chemistry Research 44, 6804-6815.