Original paper

Pyromorphite formation from montmorillonite adsorbed lead

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Abstract. The reaction of Pb-adsorbed montmorillonite with aqueous solutions of PO_4 and Cl ions results in the decrease in phosphate concentration associated with the formation of a new phase – pyromorphite $Pb_5(PO_4)_3Cl$. Pyromorphite crystals range in size from hundreds of nm to several tens of μm, depending on the PO_4, K, and Ca concentrations in the reacting system. A strong ion-exchange effect of K^+ and Ca^{2+} cations on desorption of Pb^{2+} from Pb-adsorbed montmorillonite was observed. Also, a high concentration of cations leads to a rapid desorption of Pb and the formation of fine pyromorphite crystals. In contrast, low PO_4, K and Ca concentrations result in the formation of relatively large euhedral crystals. Final Pb concentrations are much lower in experimental sets than in control experiments with no phosphate present.

Key-words: sorption, desorption, immobilization, crystallization, apatite, smectite

1. Introduction

The addition of phosphate amendments to Pb-contaminated media has been investigated over the past few decades as a method of in-situ lead immobilization. This process aims to change Pb speciation from bioavailable (e.g. aqueous or sorbed) to unavailable for circulation (formation of Pb-phosphates with low solubilities). In this context, the formation of pyromorphite $Pb_5(PO_4)_3Cl$ is especially desirable because of its ease of formation under earth-surface conditions and its low solubility (log K_{sp} of -79.66;

Flis et al. 2010). Also, the formation of $Pb_5(PO_4)_3Cl$ is rapid, reaching steady-state conditions within minutes of the reaction starting. The addition of phosphates to contaminated media has been shown to be an effective method of Pb immobilization and reduction of its bioavailability (Ma et al. 1994; Cotter-Howells 1996; Hettiarachchi et al. 2000, 2001; Ryan et al. 2001; Basta, McGowen 2004; Raicevic et al. 2005; Manecki et al. 2006; Miretzky, Fernandez-Cirelli 2008). It is an effective means of immobilization of Pb in aqueous solutions as well as in contaminated soils (Ma et al. 1993, 1994, 1997). There are many easily available and easy-to-use phosphate sources which can be used for Pb sequestration (e.g., rock-phosphate, fertilizers, apatites; Melamed et al. 2002). Doubts have arisen as to the effectiveness of the application of PO_4 compounds in natural soil systems and as to the stability and bioavailability of Pb in pyromorphite due to microbial activity (Scheckel, Ryan 2002; Chappell, Scheckel 2007; Xie, Giammar 2007; Manecki, Maurice 2008; Debela et al. 2010). Owing to their diversity, the application of different PO_4 compounds introduces differing amounts of cations associated with PO_4 as well as differing proportions of the cations and PO_4 to Pb. Thus, an understanding the influence of these variables on the mechanisms and effectiveness of Pb sequestration would allow for the more efficient treatment of contaminated sites.

The solid speciation of Pb in soils can vary greatly depending on the soil type and its anthropogenic history. Most soil lead is associated with Pb-minerals and sorbed on organic matter, clay minerals and Fe, Mn, Al oxides (Sauvé et al. 2000). Therefore, studies of Pb immobilization must take into account its speciation. Most previous research has focused on the reactions between apatites and aqueous Pb (Manecki et al. 2000 and literature therein), i.e. between Pb minerals (anglesite, cerrusite, galena) and aqueous phosphates or apatites (Ruby et al. 1994; Zhang, Ryan 1998, 1999a, 1999b; Stack et al. 2004) and between phosphate-treated goethite and kaolinite and aqueous Pb (Manecki et al. 2006; Taylor et al. 2009). Zhang et al. (1997) suggested that it is possible, by pyromorphite formation, to stabilize Pb adsorbed on goethite. However, little is yet known about the mechanisms of sorbed-Pb immobilization by phosphate treatments.

This study focuses on the mechanisms of pyromorphite formation during the reactions between Pb-adsorbed montmorillonite and aqueous solutions with different concentrations of PO_4, K, and Ca. Montmorillonite is one of the most widespread phyllosilicate minerals in soils. It also has large cation adsorption capacity. Hence, it may play an important role in Pb transport and immobilization processes (Ranatunga et al. 2008). Montmorillonite surface- and Pb adsorption mechanism differ from those of Al and Fe oxides. Thus, the behavior and fate of Pb adsorbed on these phases may be different. This paper illustrates the mechanisms of pyromorphite formation during immobilization reactions between PO_4 and Pb-adsorbed montmorillonite.

2. Materials and methods

2.1. Materials

The source of montmorillonite used in the experiments was bentonite from Jelšový Potok, Slovakia. The clay-size fraction (< 2 μm) was separated from bentonite by a sedimentation procedure. The mineralogical composition was determined by X-ray

powder diffraction (XRD) in conjunction with standard cation-saturation procedures for the identification of expandable phyllosilicates (Moore, Reynolds 1997). The separated smectite concentrate consisted only of montmorillonite (Fig. 1). The XRD analysis showed no evidence of any other phases, confirming that the sedimentation process had effectively removed all mineral impurities from the initial sediment. The XRD analysis of the air-dried sample gave a very strong 001 diffraction peak at 14.9 Å which, in the glycol-treated sample, shifts to 17.0 Å. This indicates that Ca^{2+} is the predominant cation in the smectite interlayer positions (Moore, Reynolds 1997). Final identification was accomplished by drying the sample at 300ºC. This treatment shifted the 001 diffraction peak to 9.7 Å (Fig. 1), indicative of montmorillonite collapse. Results of the analysis of the initial montmorillonite composition obtained by wavelength dispersive X-ray fluorescence spectroscopy (Philips PW, 1410, Philips, Holland; Si, Al, Fe, Mg, Ca) and atomic absorption spectrometry (AAS; Na, K, Ti) are as follows (in wt%): SiO_2 – 67.25, Al_2O_3 – 21.85, Fe_2O_3 – 2.82, MgO – 3.64, CaO – 0.15, Na_2O – 0.24, K_2O – 0.15, TiO_2 – 0.12 and H_2O – 4.08. The cation exchange capacity (CEC) determined by sorption of hexadecyltrimethylammonium (HDTMA) bromide is 1.04 meq/g. To determine the amount of HDTMA bound by the mineral, C and N contents in the organo-smectite were measured
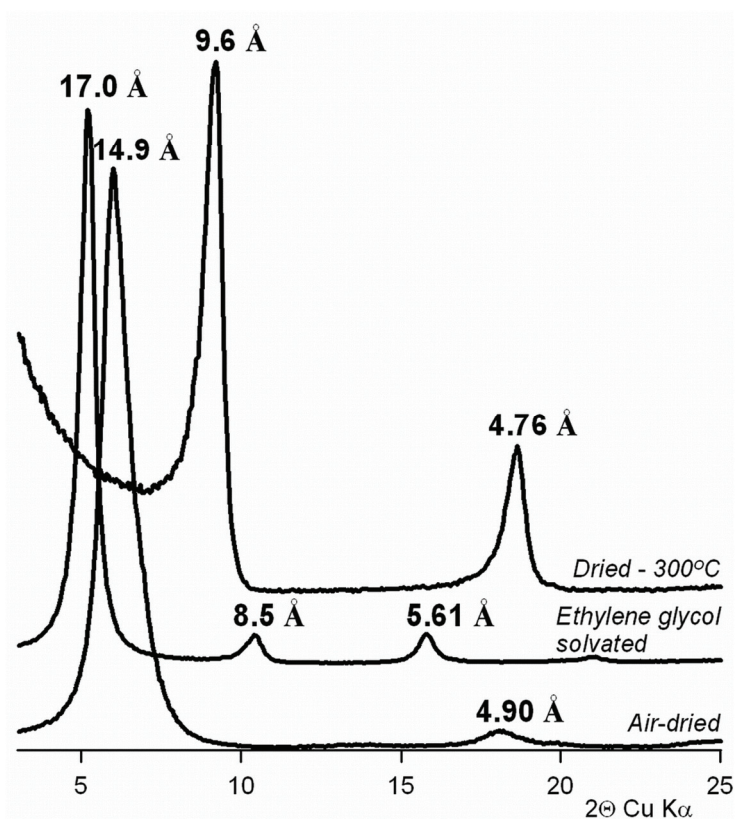

Fig. 1. Montmorillonite used in the study in the air-dried-, 300ºC dried- and ethylene glycol-solvated states.

using a Euro EA elemental analyzer (HEKAtech GmbH, Germany). The BET surface area measured on an ASAP 2405 automatic sorption analyzer from Micromeritics Inc. (Micromeritics, USA), using the N_2 adsorption method, was 715 m^2/g. The synthetic pyromorphite used as a reference material in the XRD study is described in our previous work (Flis et al. 2010).

2.2. Pb sorption

To prepare Pb-adsorbed montmorillonite, a suspension of 50 g/L montmorillonite was reacted with a 1 M $Pb(NO_3)_2$ solution in the presence of 0.01 M $Ca(NO_3)_2$ background electrolyte at an initial pH of 3.5. The pH of the solution was not adjusted and not maintained during the sorption process. The suspension was stirred for 24 hours using a mechanical stirrer and then left for a further 24 hours to reach equilibrium. Based on studies of the influence of time on the amount of metals adsorbed on montmorillonite, it was found that 24 h is a sufficient period for attaining the equilibrium state between Pb ions in the solution and adsorbed on smectite (Mozgawa et al. 2009). After equilibrium was reached, the Pb-adsorbed montmorillonite suspension was centrifuged and placed in dialysis tubes to remove all the ions remaining in the intergranular solution (Pb, Ca, NO_3). The tubes had a molecular weight cutoff of 1000 Da, allowing free passage of inorganic ions. The dialysis tubes were then placed in redistilled water, which was replaced every 24 hours, and its Pb concentration was measured. After 60 days, when the Pb concentration in the solution was less than 0.1 ppm, the Pb-montmorillonite suspension was freeze dried using an Alpha 1-2 LD (CHRIST, Germany) drier.

The amount of exchangeable lead was determined by a desorption experiment. 1 g of freeze dried Pb-adsorbed montmorillonite was mixed with 5 mL of 1 M CH_3COONH_4 solution (pH = 7). The suspension was shaken for 2 hours, than centrifuged and 4 mL of supernatant solution was sampled and replaced by the same volume of fresh 1 M CH_3COONH_4 solution. This process was repeated three times. The decanted solution was centrifuged, filtered using a 0.1 µm polycarbonate filter and the Pb concentration was measured by atomic absorption spectrometry (AAS). The determined amount of sorbed Pb was 0.35 ± 0.03 mmol Pb per g of montmorillonite (0.7 ± 0.06 meq Pb/g). The fact that the CEC of montmorillonite was equal to 1.04 meq/g indicates that the ion exchange sites of the montmorillonite were not fully exchanged with Pb ions.

2.3. Experiments

The purpose of the experiments was to investigate the mechanisms of the reaction between Pb-adsorbed montmorillonite and phosphate amendments during remediation by in-situ immobilization. In all experiments, 500 mg of montmorillonite was added to polypropylene bottles containing 500 ml of phosphate-additive solution. The pH of the suspensions was adjusted with 0.1 M HNO_3 or 0.1 M KOH to a pH of 5.0 ± 0.1. During the reactions, the pH was maintained and adjusted every day for two weeks. At the beginning of each reaction, the suspension was intensively shaken for 5 min and then stirred every day. 10 ml solution aliquots were taken for analysis after 1, 3, 7 and 14 days of reaction, centrifuged and filtered using a 0.1 µm polycarbonate filter. Concentrations of K, Pb

(AAS), Ca (ICP-OES), PO_4 (UV–Vis spectrophotometry) and pH were measured. At the end of each experiment, the suspensions were filtered through a 0.45 μm membrane, and the collected solids washed with redistilled water and acetone before air-drying for XRD and SEM-EDS analysis.

Two sets of experiments were conducted. In set 1, Pb-adsorbed montmorillonite was reacted with aqueous solutions containing K, PO_4 and Cl to simulate fertilizer phosphate amendments to a Pb-contaminated soil. In set 2, Pb-adsorbed montmorillonite was reacted with solutions containing Ca, K, PO_4 and Cl to simulate the apatite amendments commonly used in remediation procedures. The preliminary assumption was that all adsorbed Pb will be desorbed during the reactions and incorporated in precipitating pyromorphite $Pb_5(PO_4)_3Cl$. The stoichiometry of this reaction determined the concentrations of aqueous solutions used. For example, a 0.21 mM PO_4 (as KH_2PO_4) solution was used based on (a) the molar ratio Pb : PO_4 = 1.67 in pyromorphite, (b) the mass of Pb-adsorbed montmorillonite used in the experiments (500 mg in 500 ml of solution) and (c) the content of Pb adsorbed on the montmorillonite (0.35 mmol Pb/g). Each experimental set contained three series with different K : Pb : PO_4 (set 1) or K : Ca : Pb : PO_4 (set 2) proportions (Tables 1 and 2):

Series 1: 0.1 M K (KCl) or 0.1 M Ca ($CaCl_2$) concentrations and 0.21 mM PO_4 (KH_2PO_4) according to the stoichiometry of pyromorphite (PO_4 : Pb = 3 : 5).

Series 2: ten times greater concentration of PO_4 (KH_2PO_4) than in series 1 (PO_4 : Pb = 6 : 1); Ca ($CaCl_2$) concentration equal to the amount of adsorbed Pb; 2.11 mM K to reflect its content in the phosphate source (KH_2PO_4); 0.07 mM Cl (KCl) according to the stoichiometry of pyromorphite relative to the adsorbed Pb (Cl : Pb = 1 : 5).

Series 3: the amount of cations (K, Ca) equal to the amount of adsorbed Pb (0.35 mM g^{-1}); 0.21 mM PO_4 (KH_2PO_4) in stoichiometric proportions relative to the adsorbed Pb (PO_4 : Pb = 3 : 5).

TABLE 1

Assumed concentrations of K, Cl, and PO_4 in set 1.

	Experiment			Control		
Series 1 [mM]	K	PO_4	Cl	K	PO_4	Cl
	100.21	0.21	100.00	100.21	0	100.00
Molar ratio	Pb : K	Pb : PO_4	Pb : Cl	Pb : K		Pb : Cl
	1 : 286	5 : 3	1 : 286	1 : 286	-	1 : 286
Series 2 [mM]	K	PO_4	Cl	K	PO_4	Cl
	2.18	2.11	0.07	2.18	0	0.07
Molar ratio	Pb : K	Pb : PO_4	Pb : Cl	Pb : K		Pb : Cl
	1 : 6	1 : 6	5 : 1	1 : 6	-	5 : 1
Series 3 [mM]	K	PO_4	Cl	K	PO_4	Cl
	0.35	0.21	0.14	0.35	0	0.14
Molar ratio	Pb : K	Pb : PO_4	Pb : Cl	Pb : K		Pb : Cl
	1 : 1	5 : 3	2.5 : 1	1 : 1	-	2.5 : 1

TABLE 2

Assumed concentrations of Ca, K, Cl, and PO_4 in set 2.

	Experiment				Control			
Series 1	Ca	K	PO_4	Cl	Ca	K	PO_4	Cl
[mM]	100.00	0.21	0.21	200.00	100.00	0.21	0	200.00
Molar ratio	Pb : Ca	Pb : K	Pb : PO_4	Pb : Cl	Pb : Ca	Pb : K		Pb : Cl
	1 : 284	5 : 3	5 : 3	1 : 512	1 : 284	5 : 3	-	1 : 512
Series 2	Ca	K	PO_4	Cl	Ca	K	PO_4	Cl
[mM]	0.35	2.11	2.11	0.70	0.35	2.11	0	0.70
Molar ratio	Pb : Ca	Pb : K	Pb : PO_4	Pb : Cl	Pb : Ca	Pb : K		Pb : Cl
	1 : 1	1 : 6	1 : 6	1 : 2	1 : 1	1 : 6	-	1 : 2
Series 3	Ca	K	PO_4	Cl	Ca	K	PO_4	Cl
[mM]	0.35	0.21	0.21	0.70	0.35	0.21	0	0.70
Molar ratio	Pb : Ca	Pb : K	Pb : PO_4	Pb : Cl	Pb : Ca	Pb : K		Pb : Cl
	1 : 1	5 : 3	5 : 3	1 : 2	1 : 1	5 : 3	-	1 : 2

Along with the experimental sets, control samples were prepared. In the control samples, aqueous solutions of cations with concentrations consistent with those in the corresponding experimental samples were reacted with Pb-adsorbed montmorillonite in the absence of PO_4. An additional control experiment was carried out in which Pb-free montmorillonite was reacted with 0.21 mmol/L PO_4 solution at pH 5.0 (Fig. 2).
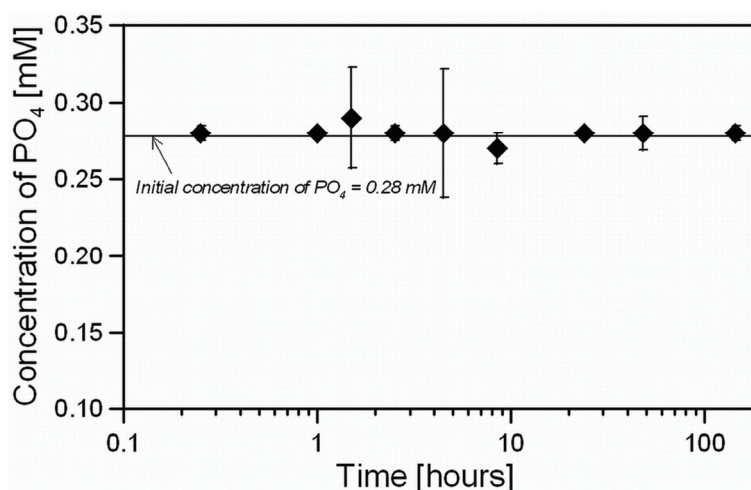

Fig. 2. Amount of phosphate sorbed by Ca-montmorillonite at 0.28 mM PO_4 initial concentration.

The reactions were considered to have reached equilibrium when concentrations of Pb and PO_4 in three consecutive solution samples were equal within two standard deviations of triplicate results (experimental error). The *t*-test was used to verify the absence of any trend

in the data from three consecutive analyses and the slope was not significantly different from zero at the 95% significance level.

2.4. Analytical Methods

Concentrations of Pb and K in aqueous solutions were determined using a Philips PU-9100x (Phillips, U.K.) atomic absorption spectrometer equipped with a flame head (FAA) and Ca-using inductively coupled plasma spectrometer (Perkin Elmer Plasm 40; PerkinElmer, USA). PO_4 concentrations were determined colourimetrically by the molybdenum blue method (Lenoble et al. 2003) using a Hitachi 1600 (Hitachi, Japan) spectrophotometer at 870 nm wavelength. The analytical detection limits for Pb, Ca and PO_4 were 5 μg/L and for K − 10 μg/L.

All solids were analyzed using an X-ray powder diffractometer (Philips PW 3020 X'Pert-APD Diffractometer system with graphite monochromator, Philips, Holland) using CuKα radiation, step scan mode with a step size of 0.02º 2Θ and a rate of 1 s per step. Air-dried uncoated samples were analyzed by electron microscopy using a variable pressure field-emission scanning electron microscope (FE-SEM, Zeiss Supra 35VP, Carl Zeiss, USA) equipped with an energy dispersive spectrometer (EDS) for elemental microanalysis.

3. Results and Discussion

The amount of Pb released from Pb-adsorbed montmorillonite to the solution in the control sets (without PO_4) is positively correlated with the initial concentration of K and Ca. Almost 100% of the sorbed Pb is exchanged by 0.1 M K and 0.17 M Ca+K in series 1 of both experimental sets and up to 50% of the sorbed Pb is desorbed in the other series (Tables 3 and 4). The molar ratios of adsorbed K and Ca to desorbed Pb indicate the ion exchange mechanism (Tables 3 and 4). The amount of Pb desorption in the experiments of set 2 (K and Ca present) is greater than in set 1 (only K present) because of the charge in desorbing cations. To preserve the charge balance in montmorillonite, one divalent Ca can replace one Pb from an ion-exchange site, whereas two monovalent K are necessary for the replacement of one Pb.

In the experimental series 2 of both sets, the presence of phosphates resulted in the reduction of Pb concentrations to about 0.001 mM (Tables 3 and 4). This means that 100% of the desorbed Pb was removed from the solution. In series 1 and 3, the reduction of the aqueous Pb with respect to a control sample was 80–85% and 20–60%, respectively. Pyromorphite $Pb_5(PO_4)_3Cl$ was the only reaction product detected in the experiments (Figs. 3 and 4). A decrease in PO_4 concentration was observed also. This and the lack of sorption of PO_4 on montmorillonite (Fig. 2) confirm that the drop in PO_4 and Pb concentrations is exclusively caused by precipitation of pyromorphite. Therefore, the molar ratio of the decrease in Pb concentration ($Pb_{removed}$ − the difference between Pb concentrations in control samples and experimental samples) to the decrease in PO_4 concentration ($PO_{4removed}$ − the difference between the initial and the final PO_4 concentrations in the experimental samples) should be consistent with the stoichiometry of pyromorphite $Pb_5(PO_4)_3Cl$ (5 : 3 = 1.67). However, the ratio varied in the series (Table 5). Only in series 1 of both sets are the ratios $Pb_{removed}$: $PO_{4removed}$ similar (within experimental error) to the expected 1.67. This

means that the amount of Pb desorbed from montmorillonite (as determined by controls) was sufficient to account for PO_4 loss in the experimental sample. In series 2 and 3, the ratios $Pb_{removed} : PO_{4removed}$ are < 1.67 indicating that PO_4 loss in the experimental samples was higher than calculated based on Pb desorption in controls and the stoichiometry of pyromorphite. Higher PO_4 loss suggests higher Pb desorption than in the control samples since pyromorphite formation is the only sink for phosphates. This is illustrated in Figures 5 and 6 which show the comparison between the amount of Pb desorbed from montmorillonite in the controls minus the final amount of Pb in the experimental samples and the amount of Pb necessary to form pyromorphite from the amount of PO_4 removed from the solution, (determined by the fall in PO_4 concentration and calculated from pyromorphite stoichiometry). It can be seen that only in series 1 is the amount of Pb desorbed in the control sample sufficient to account for PO_4 loss resulting from the precipitation of pyromorphite. In series 3, the concentration of Pb desorbed from the control equals the Pb concentration in the experimental sample even though pyromorphite formed (Figs 3 and 4).

TABLE 3

Initial and final concentrations in the experiments at various initial K and PO_4 concentrations (set 1)

		Experiment		Control	
		Initial	Equilibrium	Initial	Equilibrium
Series 1	K	120.0 ± 0.2	116.1 ± 0.7	117.6 ± 2.2	114.0 ± 2.7
[mM]	PO_4	0.240 ± 0.049	0.022 ± 0.015	–	–
	Pb	–	0.062 ± 0.013	–	0.405 ± 0.010
Ratio K/Pb [A]				$3.6 \pm 3.5 : 0.40 \pm 0.01$	
Series 2	K	1.767 ± 0.007	1.613 ± 0.002	1.785 ± 0.002	1.736 ± 0.002
[mM]	PO_4	2.508 ± 0.038	2.288 ± 0.056	–	–
	Pb	–	< 0.001	–	0.080 ± 0.002
Ratio K/Pb [A]				$0.06 \pm 0.00 : 0.08 \pm 0.00$	
Series 3	K	0.301 ± 0.001	0.221 ± 0.007	0.332 ± 0.029	0.276 ± 0.025
[mM]	PO_4	0.206 ± 0.002	0.083 ± 0.002	–	–
	Pb	–	0.024 ± 0.002	–	0.029 ± 0.003
Ratio K/Pb [A]				$0.05 \pm 0.04 : 0.03 \pm 0.00$	

The reported concentrations represent the mean $\pm$ the two standard deviation from triplicate experiments
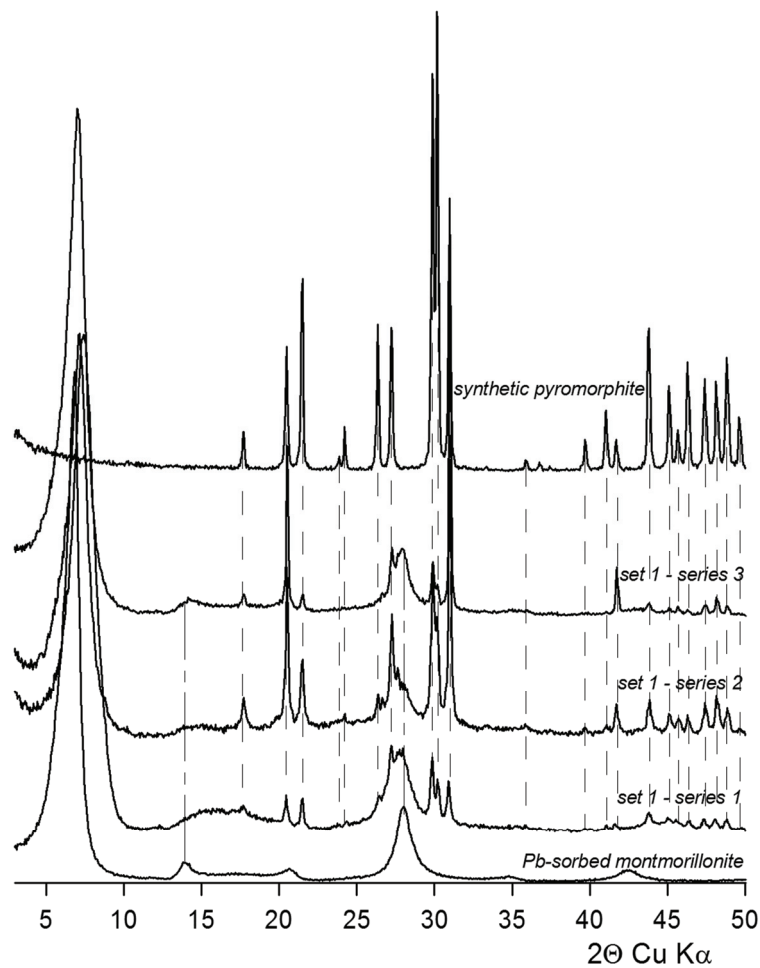
[A] Proportion of adsorbed K to desorbed Pb

Fig. 3. X-ray diffraction patterns for synthetic pyromorphite and Pb-adsorbed montmorillonite before and after reaction with the solutions containing Pb, PO_4, K, and Cl.

The discrepancy between the observed amounts of Pb desorption in the control samples and the PO_4 loss in the corresponding experimental samples can be explained by the following reaction mechanism. Cation exchange in the interlayer spaces of montmorillonite is the driving force of Pb desorption from the clay and its appearance in the solution. Therefore, increased aqueous K or Ca concentrations in the reaction system lead to a greater amount of desorbed Pb. Addition of PO_4 in the presence of Cl causes formation of pyromorphite. Due to the very low solubility of pyromorphite, almost all Pb present in the aqueous solutions is incorporated into this mineral. Pb disappears from the solution as a result and a new equilibrium for the reaction is established. If K or Ca is still present in the solution, it exchanges further with Pb from the interlayer spaces of the smectite. Released Pb reactes with PO_4 and a new equilibrium is established again. The approximate amount of Pb needed to form pyromorphite, determined by the drop in PO_4

concentration (calculated from pyromorphite stoichiometry) in the experimental series 1 and 2 is about 0.4 mM (Figs 5 and 6). This means that all Pb adsorbed on montmorillonite was desorbed and precipitated by PO_4 to form $Pb_5(PO_4)_3Cl$. Only in the experimental series 3 was only approximately 50% adsorbed Pb subsequently desorbed. The reaction between Pb and PO_4 explains the greater drop in K concentration in the experimental samples than in the controls (Fig. 7), as more Pb is replaced by K in the experimental samples.
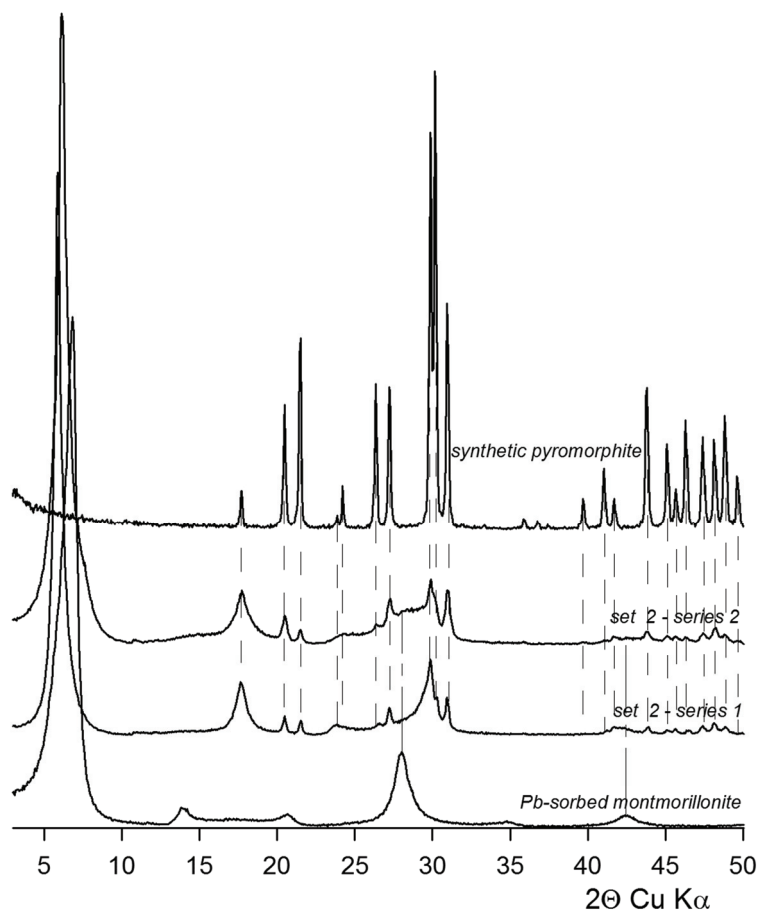

Fig. 4. X-ray diffraction patterns for synthetic pyromorphite and Pb-adsorbed montmorillonite before and after reaction with the solutions containing Pb, PO_4, Ca, K, and Cl.
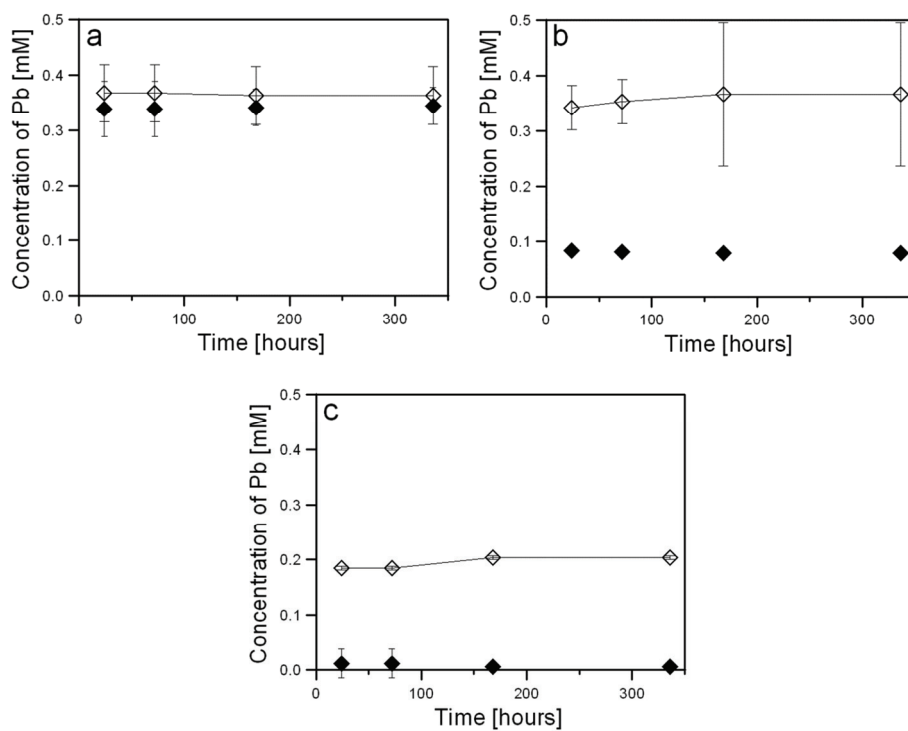
Fig. 5. Comparison of the amount of Pb removed from the solution in set 1 (filled diamonds) to the amount of Pb determined by the drop in PO_4 concentration (calculated from pyromorphite stoichiometry, open diamonds): a) series 1, b) series 2, c) series 3.
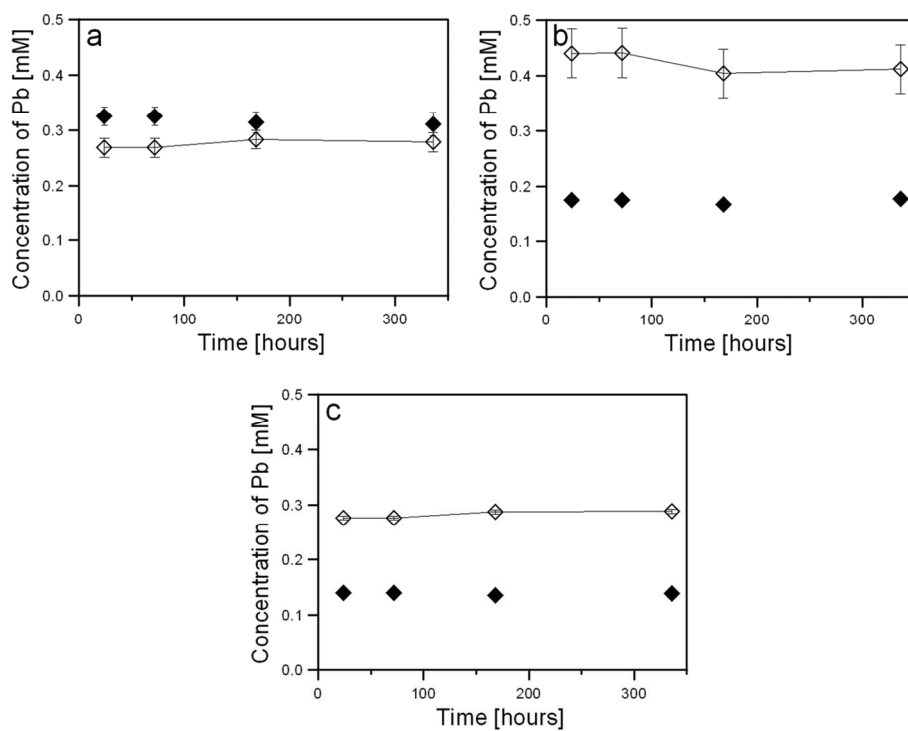
Fig. 6. Comparison of the amount of Pb removed from the solution in set 2 (filled diamonds) to the amount of Pb determined by the drop in PO_4 concentration (calculated from pyromorphite stoichiometry, open diamonds): a) series 1, b) series 2, c) series 3.
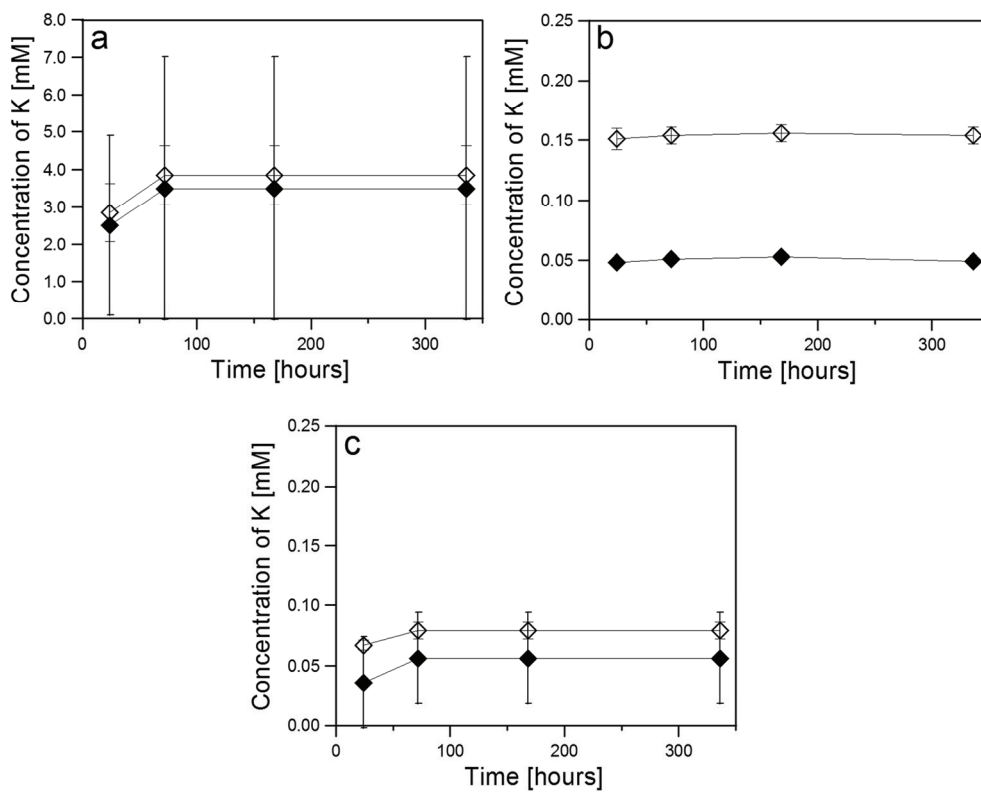
Fig. 7. Fall in concentration of K in experimental samples (open diamonds) and control samples (filled diamonds) for set 1: a) series 1, b) series 2, c) series 3.
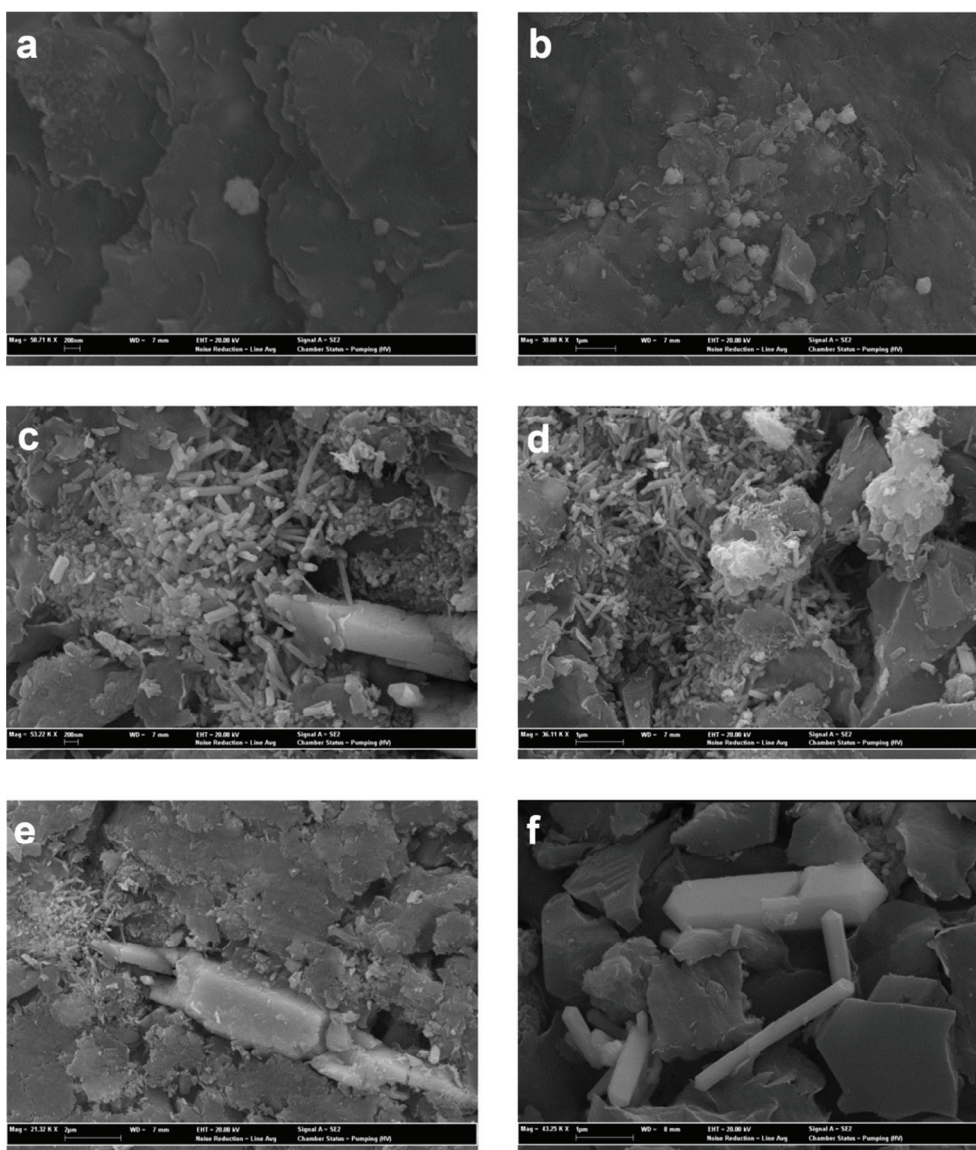
Fig. 8. SEM images of pyromorphite on the surface of montmorillonite: a-b) series 1, c-e) series 2, f) series 3.

The amount of Pb desorption from montmorillonite is controlled by two factors, namely, the aqueous concentration of desorbing cations and the activity of aqueous Pb. Pyromorphite formation shifts the equilibrium between the adsorbed and aqueous Pb, as the latter is being incorporated into the mineral structure. This, in turn, enables more desorption.

The reactions between phosphates and Pb desorbed from montmorillonite are rapid, as equilibrium is reached within 24 hours of the reaction. Cation exchange on

montmorillonite and crystallization of pyromorphite are simultaneous, suggesting that Pb desorption is controlling the precipitation of $Pb_5(PO_4)_3Cl$. However, the morphology of pyromorphite crystals and their size varied in each series. Pb-adsorbed montmorillonite reacted with the solutions of series 1 produced very small crystals without well defined faces (Figs 8a and 8b). These tended to form crystal aggregates rather than single crystals. Their morphology does not depend on the type of cation (K, Ca) in the initial solution. The sizes of the aggregates reached up to 500 nm, but were typically smaller. In some cases, they covered the surfaces of smectite plates. In series 2, it is apparent that two generations of pyromorphite crystals formed (Fig. 8c). The first are small crystals that form aggregates similar to the series 1 examples (Fig. 8c), but also some bigger crystals (Fig. 8d). The lengths of the first-generation crystals vary from 300 nm to 1 μm. Second generation crystals show well-defined morphologies with well-formed terminations at both ends that suggests homogenous formation (Fig. 8e). Their sizes vary from several to several tens of μm. In series 3, only one form of pyromorphite crystals formed (Fig. 8f). These crystals are euhedral and 0.5-3 μm long.

Although the formation of pyromorphite from Pb-adsorbed montmorillonite is quite rapid, the morphological variety of the crystals may suggest different reaction rates. The very fine crystals formed in the series 1 experiments suggest that Pb desorption is very fast with the desorbed Pb being immediately bonded to PO_4 and Cl to form pyromorphite. Because Pb was exchanged with K or Ca rapidly, a large amount of Pb in the solution led to the formation of many very small crystals. In the series where K and Ca concentrations were lower, Pb was released to the solution less rapidly and equilibrium of the reaction was established more slowly, allowing larger crystals to form.

4. Conclusions

Pb adsorbed on montmorillonite can be easily mobilized via cation exchange by K and Ca ions. The reaction of Pb-adsorbed montmorillonite with aqueous solutions containing PO_4 ions results in the formation of pyromorphite $Pb_5(PO_4)_3Cl$. Pb locked in the pyromorphite structure is no longer a hazard to the environment because of the very low solubility of the mineral (log K_{sp} = −79.66). The amount of adsorbed Pb that can be immobilized depends on the amount of phosphate available as well as on cations which can exchange with Pb in the interlayer spaces of the clay mineral or on its external surface. Pyromorphite precipitates homogenously in the solution but crystals generally cover the surface of the smectite. A high concentration of K and Ca cations leads to the formation of very fine crystals. This also causes a greater desorption of Pb. Conversely, low concentrations of cations result in the growth of larger crystals.

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