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Assessment of potential nutrient release from phosphate rock and dolostone for application in acid soils

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Abstract

The aim of this study was to evaluate the feasibility of using phosphate rock and dolostone as fertilizer and amendment, respectively, for application in tropical acid soils. The dissolution of different particle-size fractions by water and citric acid was studied. Laboratory column experiments were run following a completely randomized design, by using 0.063 – 0.25, 0.25 – 0.5, and 0.5 – 2 mm particle-size fractions of both rocks. Each rock particle-size was subjected to exhaustive dissolution with distilled water, citric acid solution at pH 4, and citric acid solution at pH 2, with the following extraction times: 1, 3, 5, 7, 12, 24, 72, 144, 240, and 360 h. The dissolution of both rocks depended on particle-size, leaching solution and extraction time. The dissolution rate of rock-forming minerals augmented as the specific surface area increased, corresponding to a decrease in particle-size. In all cases, the kinetics of release was characterized by two phases: *1*) a first stage of rapid release that lasted 24 h, which would ensure short-term nutrient release, and *2*) a second stage of slow release (after 24 h), representing the long-term nutrient release efficiency. Both rocks are suitable as slow release fertilizers in strongly acid soils and would ensure the replenishment of P, Ca, and Mg. A combination of fine and medium particle-size fractions should be used to ensure high nutrient release efficiency. Much work has to be done to assess the overall impact of considerable amounts of fresh rocks in soils.

Key words: citric acid, soil fertility, rock weathering, nutrient release

1. Introduction

Worldwide acid soils are mainly present into two belts: 1) humid northern temperate zones, which are mostly occupied by coniferous forest, and 2) humid tropics, which host savannah systems and tropical rainforests (FAO, 2016). Acid soils are deficient in plant nutrients such as phosphorus (P), nitrogen (N), potassium (K), calcium (Ca) and magnesium (Mg), while having increased availability of phytotoxic elements like aluminium (Al) and manganese (Mn) (van Straaten, 2002, 2006; Caires et al., 2005; van Raij, 2011; FAO, 2016). These deficient elements (with exception of N) are mostly derived from rocks and minerals (Chien et al., 2011).

Since soil acidification strongly reduces crop production, amelioration of acid soils is paramount for food security and agriculture sustainability. Application of fertilizers can satisfy the nutrient deficiency in acid soils (Chien et al., 2011), but the cost of fertilizers, particularly of P fertilizers, has increased substantially worldwide (van Straaten, 2002, 2006; Chien et al., 2011). Therefore, finding alternative local sources of plant nutrients which could supply P or other elements for sustainable crop production is a practical, low-cost, long-term strategy that addresses the need of poor farmers (Appleton, 2002; van Straaten, 2002, 2006; Zapata and Roy, 2004).

Apatites and calcareous rich rocks have been tested for their application in agricultural acid soils. For instance, it is known that the reactivity of apatites can be increased through grinding, and this increases P availability and produces similar yield responses and agronomic effects to those of triple superphosphate fertilizer (van Straaten, 2002, 2006; Szilas et al., 2008).

Thus the application of limestone, possibly with a certain amount of dolomite, can mitigate soil acidity, prevent Al and Mn toxicity (Álvarez et al., 2012; van Straaten, 2002, 2006, 2007), and provide Ca and Mg to the soil (Viadé et al., 2011). Consequently, food production and quality are enhanced (Maria and Yost, 2006). In addition, both apatitic and calcareous rocks may contain a wide range of minor chemical elements, some of which are beneficial for plant nutrition (IAEA, 2002; Szilas et al., 2007; van Straaten, 2006).

In Mozambique, acid soils cover ~70% of the country (Gouveia and Azevedo, 1949). Here, two important rock outcrops merit consideration: a metamorphic phosphate rock and a dolostone. Mineralogically, these two rocks are extremely relevant for mitigating acidity and replenishing P, Ca, and Mg. Their importance is even more significant considering that African Countries cannot afford to purchase expensive water soluble phosphatic fertilizers, but could exploit their own rock outcrops, with reduced and controlled environmental risks (Khasawneh and Doll, 1978; Appleton, 2002; van Straaten, 2006, 2007).

Phosphatic rocks and dolostones vary widely in their mineralogical and physicochemical properties. Consequently, their reactivity and agronomic potential also vary (IAEA, 2002; Szilas, 2002; Szilas et al., 2007, 2008). Thus it is prudent to evaluate their fertility value in terms of nutrient release to assess their possible use for crop production while minimizing fertilizer requirements (van Straaten, 2002; Zapata and Roy, 2004).

The dissolution rate of rocks tested for their possible use in agriculture mainly depends on their mineralogical composition as well as on the solubilizing acid and pH of the extracting solution (Goyne et al., 2006; Calvaruso et al., 2013). Low molecular weight organic acids (LMWOAs) are preferred to others, citric and oxalic acids being the most used (IAEA, 2002). In fact, citric acid originates in soil from the secretions of plant roots and soil microorganisms like fungi, lichens, and prokaryotes (Olsson and Wallander, 1998; Goyne et al., 2006; Joergensen and Wichern, 2008; Klugh-Stewart and Cumming, 2009; Goyne et al., 2010), and can simulate the weathering occurring in the rhizosphere (Turpault et al., 2009; Calvaruso et al., 2013).

For instance, when apatites are exposed to citrate and oxalate ligands, the release of P and Ca is the highest (Goyne et al., 2006, 2010). Instead, the dissolution of calcareous minerals such as calcite ($CaCO_3$) and dolomite [$CaMg(CO_3)_2$] depends on solution pH, pCO_2, temperature, and mineral properties such as crystallinity (Yasuda et al., 2013) as well as specific surface area (van Straaten, 2002, 2006, 2007). Dolomite dissolution rates are usually lower than those of calcite (Liu et al., 2005; Dewaide et al., 2014).

This study aims to investigate the feasibility of using a phosphate rock and a dolostone from local sources in Mozambique, ground to different grain sizes (0.063-0.25, 0.25-0.5, and 0.5-2 mm), as sources of P, Ca, and Mg or acid-neutralising agents. We assessed their effectiveness by testing their solubility in water and different concentrations of citric acid solutions in open-system columns under controlled conditions. We hypothesize that both rocks will provide substantive nutrient release in support of agronomic production and that finer particle size will facilitate enhanced solubility.

2. Materials and Methods

2.1. Sample preparation

Both studied rocks are from Mozambique. The phosphate rock was collected from the Nampula Province deposit in the Evate district, while dolostone was collected from the Mount Muambe deposit located in the Tete Province. Blocks of rocks were fragmented by using a grinding press; then the rock fragments were ground using an agate mortar. For both rocks, three size-fractions were obtained by dry sieving: 0.063-0.25, 0.25-0.5 and 0.5-2 mm.

2.2. General characterization

The mineralogical composition was determined on powdered rocks by x-ray diffraction with a Philips PW 1830 diffractometer, using the Fe-filtered Co Kα1 radiation (35 kV and 25 mA); the step size was 0.02° 2θ and the scanning speed was one second per step. A semi-quantitative estimation was obtained after the identification of the minerals on the basis of their characteristic peaks as reported by Dixon and Schulze (2002), and MINCRYST database (http://database.iem.ac.ru/mincryst, accessed on 22th June 2016).

The elemental analysis of both rocks was obtained using DP-6000 Delta Premium portable X-ray fluorescence (PXRF) spectrometer (Olympus, Waltham, MA, USA) according to Weindorf and Chakraborty (2016). The instrument features a Rh X-ray tube operated at 15–40 kV with quantification via ultra-high resolution (165 eV) silicon drift detector. The analysis was firstly conducted in "Soil Mode" (three beams of 30 s each), and secondly in "Geochem Mode" (two beams of 30 s each). Therefore, the contents of Al, Si, P, Mg, Ca, and S were validated using "Geochem Mode" readings, and the remaining elements were validated using "Soil Mode" (Weindorf and Chakraborty, 2016).

Total carbon concentration in dolostone was determined using CHNS-O analyser (EA1110, Carlo Erba Instruments, Milan, Italy). The fractions of phosphate rock were analysed for water soluble P, P extractable with neutral ammonium citrate (NAC-P), P extractable with 2% citric acid solution (citric-P), and P extractable with 2% formic acids solution (formic-P) as per Rajan et al. (1992). For each size- fraction of both rocks, 10 g of sample was added to 25 mL of distilled water, and the abrasion pH was measured after 6 min of solid – liquid contact (Romero et al., 1987). To measure the pH at 1.5 h, the suspension was stirred for 1 h on an oscillating table and left to rest for 30 min before repeating the pH measurement; in a similar way, pH was measured at 24 h (Pansu and Gautheyrou, 2006).

2.3. Leaching experiment

To assess the long-term dissolution (reactivity) of the different size-fractions of both rocks, two sets of column experiments were conducted using a completely randomized design. Samples of the three particle-size fractions (0.063 – 0.25, 0.25 – 0.5 and 0.5 – 2 mm) of both rocks were treated for 15 days with different leaching solutions (distilled water, citric acid solution at pH 4 and citric acid solution at pH 2); leachates were retrieved at the following extraction times: 1, 3, 5, 7, 12, 24, 72, 144, 240, and 360 h. Similarly, percolations without rock sample were conducted as controls. The experimental design consisted of three replicates for each fraction and leaching solutions.

The experiments were conducted in an isolated room at a temperature of 25 ± 1ºC. The leaching solutions were prepared 24 h prior to use by dissolving monohydrate citric acid crystals (AR manufactured by Carlo Erba Reagents) in distilled water. The citric acid solution at pH 4 (≈ 10^{-4} M) was considered representative of the soil solution conditions of acid soils from tropical environments, while the citric acid solution at pH 2 (≈ 10^{-1} M) was taken as an example of extreme acidity conditions that only rarely can occur in soil, even in the rhizosphere.

Each column (diameter x length of 30 x 400 mm) of 200 mL capacity was fitted with 0.3 g of fiberglass at the bottom to prevent rock fragments loss. Thus, 1.000 g of each rock size-fraction was put into the column, and 100 mL of leaching solution were added (solid:liquid ratio of 1:100, w:v). At each extraction time, the liquid was allowed to percolate at a constant rate (100 mL h^{-1}). Thus, 100 mL of fresh leaching solution was added to each column.

The elements measured in the leachate of both rocks were Ca, Mg, K, Na, Ba, Al, Fe, Mn, Zn, Cd, Ni, and Pb; only in those from phosphate rock fractions was P also determined. The analyses of leachates were carried out the same day they were collected. The cations were measured by an inductively coupled plasma optical emission spectrometer (Perkin Elmer Optima 8300) as described by Boss and Fredeen (1997), while a simple colorimetric method based on ascorbic acid reduction of the ammonium phosphomolybdate complex (Kuo, 1996) was used to measure P in the leachates.

2.4. Kinetic analysis

The Langmuir (1997) equation below was used to determine the release rate using the data obtained by the leaching experiment, assuming that the dissolution of minerals in phosphate rock and dolostone were controlled by surface reaction:

$$dC_{(t)}/dt = k;\ \text{Integrated rate law: } C = C_o + kt,$$

where $C_{(t)}$ (mol L^{-1}) is the concentration of released species in the bulk solution at the time t; C (mol L^{-1}) is the concentration of released species in the leachate after the release; C_o (mol L^{-1}) is the initial concentration of the species in bulk solution before the release starts; k (mol L^{-1} s^{-1}) is the rate constant.

2.5. Statistical analysis

R version 3.1.2 (2014-10-31) was used for statistical analysis. Single extraction data were analysed for analysis of variance (ANOVA) after a *boxcox* transformation (Meloun et al., 2005) of the data to perform parametric tests (Shapiro-Wilk normality test and Bartlett test of homogeneity of variances). A multiple comparison Tukey test (at 5% significance) was used to compare the means. Similarly, data obtained from the leaching experiments were analysed using parametric tests, but they revealed a non-normal distribution and heteroscedasticity. Therefore, summary statistics (mean, variance, standard error and deviation) were used whenever possible.

3. Results and discussion

3.1 Mineralogical and chemical composition of the two rocks

X-ray diffraction analysis showed that the phosphate rock was mainly made of fluoroapatite, while the dolostone was made of dolomite (Figs. 1 and 2, respectively). Both rocks contained traces of phyllosilicates. The major constituent elements of the phosphate rock were Ca and P, followed by Si, Al, Fe, K, Sr, and Ba; all the other elements were present in concentrations close to or <1000 mg kg^{-1} (Table I).

The rock P content was ~24%, equivalent to 55% of P_2O_5, which satisfies the European legislation in terms of total P content to be used for direct application to the soil, as it exceeds the threshold value of 25% of P_2O_5 (European Commission, 2000). The concentrations of trace elements were similar to those commonly reported for phosphate rocks (Adriano, 2013). The concentrations of As and Hg were moderately high, but they should not be problematic for the application of phosphate rock to soils at moderate rates.

The major elements in the dolostone were Ca, Mg, and C, followed by Si, P, Al, Fe, K, Mn, Ba, S, Sr, and Ti, with the other elements present in amounts <40 mg kg^{-1} (Table I). The richness in Ca, Mg, and C was ~ 29.4, 18.2, and 8.2%, respectively, equivalent to ~ 41, 30, and 41% of the respective oxides. The Ca:Mg molar ratio of 1:1 confirmed the mineralogical observation indicating that the main rock forming mineral was dolomite (Al-Awadi et al., 2009). This dolostone can be considered completely safe given its low concentration of potentially hazardous trace elements.

3.2. Phosphate rock

3.2.1. General properties

For the phosphate rock, the abrasion pH decreased significantly ($P < 0.05$) with contact time for all fractions, ranging from 9.36 for the finest fraction at 6 min of solid-liquid contact, to 7.81 for the coarsest fraction after 24 h (Table II). As expected, the finest fraction presented higher pH values ($P < 0.05$) compared with the other fractions. This was ascribed to the higher specific surface area of this fraction. Newly formed mineral surfaces like those obtained by grinding are able to release alkaline and alkaline-earth elements and adsorb H^+, so to induce an abrasion pH that lasts until other factors perturb the suspension (Grant, 1969; Romero et al., 1987).

The temporal decrease of abrasion pH was ascribed to the dissolution of atmospheric CO_2 (Grant, 1969) and possibly to surface passivation (Cuniglio et al., 2009).

Single extractions of P by water, NAC, 2% citric acid solution and 2% formic acid solution showed that the 2% formic acid solution was able to extract the highest ($P < 0.001$) amount of P (Table III). The increase of extractable P with the grinding for all the extractants except water indicates the highest reactivity of the finest fraction of this rock (Rajan et al., 1992). Therefore, taking 2% formic acid solution as the best predictor of agronomic effectiveness of phosphate rock (Rajan et al., 1992), the finest size fraction features high potential ($P < 0.001$) for a direct application in strongly acid soils (Ghani et al., 1994; Rajan et al., 1996; Zapata and Roy, 2004).

3.2.2. Long-term release in column experiments

(i) Cumulative releasing pattern of P, Ca, and Mg

The cumulative release of P, Ca, and Mg in water and in citric acid solutions at pH 4 and pH 2 from different particle sizes of phosphate rock was calculated for the different extraction times. Other elements such as K, Na, Ba, Al, Fe, Mn, Zn, Cd, Ni, and Pb were leached in concentrations always lower than 100 mmol kg^{-1}. The cumulative release of P, Ca and Mg showed an increasing trend for all leaching solutions (Fig. 3). The rate of release was relatively high in the first 24 h of leaching and decreased thereafter, indicating that most of the extractable nutrients were released within 24 h. For all nutrients and leaching solutions, the highest cumulative release was obtained for the finest fraction ($P < 0.01$), followed by the medium and, then, by the coarse fraction (Table IV).

The citric acid solution at pH 2 leached the highest amount of nutrients. For instance, at the end of the experiment, citric acid at pH 2 had leached from the finest fraction 27 and 86 times the amount of P obtained with the citric acid at pH 4 and water, respectively. The amounts of P and Ca extracted by the leaching experiment were higher than those extracted by single extraction in both water and 2% citric acid solution (Table V).

For Ca there was no difference between the coarse and medium size-fractions in water and citric acid solution at pH 4 and for all the extraction times. The same was true for Mg in the finest and medium size-fractions in the case of citric acid solution at pH 2 during the first 72 h of extraction; thereafter the medium size-fraction presented a slightly higher cumulative release than the finest size fraction.

(ii) Release kinetics of P and Ca

The release kinetics was determined for both P and Ca, the most important nutrients in the phosphate rock fractions. During the leaching period the release rate decreased sharply up to 24 h, to steadily decrease until reaching values close to zero (Fig. 4). The finest fraction showed a higher release rate than the other particle-size fractions, which did not differ significantly between them, indicating that the kinetics was controlled by superficial processes (Dorozhkin, 2012).

The citric acid solution at pH 2 showed the highest release rate, followed by citric acid solution at pH 4. The cumulative curves showed two leaching stages: 1) a rapid release during the first 24 h of leaching ascribed to the presence of easily dissolvable mineral surfaces probably activated during the grinding process, which could be taken as the short-term nutrient release efficiency (Truong and Fayard, 1995; Zapata and Roy, 2004; Gholizadeh et al., 2009), and 2) a slow release after 24 h of leaching, where the dissolution of the bulk mineral begins representing the medium- to long-term nutrient release efficiency, which is agronomically relevant.

Most of the solid had not dissolved when the near-zero release rate was reached, and therefore only the thin layer of superficial, very fine, poorly crystalline mineral material had dissolved. The amount of P and Ca extracted in this stage was similar among the particle-size fractions ($P < 0.01$) for citric acid at pH 2 (Table IV). The bulk mineral in the second stage was approaching the equilibrium by reaching the metastable conditions characterized by the persistence of apatite crystals with a passivated surface that reduces the reactivity of the mineral grain (Cuniglio et al., 2009). Because of this, mineral grains in contact with unsaturated solutions release lesser amounts of ions than expected from the mineral formula (Dorozhkin, 2012).

In our trial we demonstrated that the size of rock fragments and the leaching solution strength were the determinant factors for the release rates. The ideal (congruent) dissolution of fluoroapatite promoted by an organic acid is given below (adapted from Calvaruso et al., 2013):

$$Ca_5(PO_4)_3F + 6\ AH \leftrightarrows 5\ Ca^{2+} + 6A^- + 3\ H_2PO_4^- + F^-,$$

where A^- represents the organic anion

An appropriate supply of hydrogen ions (H^+) and the removal of the reaction products (Ca^{2+}, $H_2PO_4^-$, and F^-) are necessary for the reaction to proceed forward (Robarge, 1999). The open system used in this study (columns) ensured the removal of the reaction products through solution percolation, while the citric acid solutions supplied H^+ so the release could go forward. The mechanism of dissolution of fluoroapatite by LMWOAs such as citric acid is ascribed to the supply of H^+, the formation of surface complexes that weaken and break the bonds among metals and lattice oxygen (Goyne et al., 2006; Dorozhkin, 2002, 2012), and the complexation of metals (Ca, Fe, and Al) by carboxyl ligands (-COOH). All of these reactions entail the release of phosphorus ($H_2PO_4^-$) from the mineral (Goyne et al., 2006; Calvaruso et al., 2013).

The phosphate rock had a molar Ca/P ratio of ~ 1.2 (Table I). During the leaching in water and citric acid solution at pH 4, the molar Ca/P ratio in solution did not reach 0.5 (Fig. 5). The much lower Ca/P ratio in the leachates indicates the occurrence of an incongruent dissolution of fluoroapatite, since P was being released preferentially over Ca. With citric acid solution at pH 2, the fluoroapatite dissolution seemed to be incongruent too, even though between 24 and 72 h of leaching the Ca/P ratio reached values close to the Ca/P ratio in the initial solid phase. Yet, the finest size-fraction always displayed the highest Ca/P ratio.

According to Harouiya et al. (2007), Dorozhkin (2002, 2012), and Crundwell (2014, 2015, 2016), Ca-apatites in acid solutions dissolve by ionic detachment of Ca and orthophosphate ions from the solid toward the solution. In our case, the formation of a Ca-rich layer (self – inhibition model) in both water and citric acid solution at pH 4, probably was determinant in decreasing the dissolution rate of apatite in the second stage. Hence, the diffusion of Ca and orthophosphate ions occurred from the surface layer formed, so leading to incongruent dissolution (Dorozhkin, 2002, 2012).

The Ca rich layer was probably thicker in the second stage of leaching because of the major contact time between the unsaturated solutions and apatite crystals. Because of this, the dissolution of fluoroapatite in citric acid solution at pH 2 proceeded at a certain rate in first 72 h of extraction, and decreased thereafter due the lack of removal of the Ca rich layer formed during the longer periods of solid-solution contact.

The citrate anion (and others such as oxalic, formic, etc.) have higher affinity for Ca than orthophosphate (Goyne et al., 2006; Dorozhkin, 2002, 2012) and plays a considerable role in the dissolution of phosphate rock (Wei et al., 2011; Calvaruso et al., 2013). Therefore, the citric acid used in the leaching experiments may allow predicting the dissolution of phosphate rocks in acid soils. The LMWOAs produced in the soil rhizosphere by root exudates and microbial activity (Marschner et al., 2011; Wei et al., 2011) has the capability to solubilize phosphatic particles and increase the availability of P (Kpomblekou and Tabatabai, 2003; Li et al., 2011; Cocco et al., 2013; Gómez and Carpena, 2014; De Feudis et al., 2016).

The dissolution of phosphate rock fractions can be increased by the removal of reaction products, in the plant-soil system and, even more, in the rhizosphere. Thus, Ca uptake may increase rock particle solubilization and, consequently, the availability of P for plants and micrórganisms (Marschner et al., 2011; Panhwar et al., 2014).

3.3. Dolostone

3.3.1. General properties

Similar to phosphate rock, the abrasion pH of dolostone decreased significantly with contact time for all the particle-size fractions ranging from 9.57 at 6 min for the medium size fraction (0.25-0.5 mm) to 8.25 after 24 h for the coarse size fraction (Table II). There were no significant differences among the size fractions during the contact time. As in the case of the phosphate rock fractions, the temporal decrease of abrasion pH can be attributed to the dissolution of atmospheric CO_2.

3.3.2. Long-term release in column experiments

(i) Cumulative releasing pattern of Ca, Mg, and K

Ca and Mg were the major elements leached during the extraction period. Other elements such as Na, Ba, Zn, Cd, Ni, and Pb were present in concentrations close to or lower than 5 mmol kg^{-1}. Despite elements such as Fe, Mn, and Al being leached in concentrations lower than 30 mmol kg^{-1}, namely higher than K, here we discuss K together with Ca and Mg as plant macronutrients. The cumulative release of Ca, Mg, and K showed an increasing trend in all leaching solutions (Fig. 6). The release rate for Ca and Mg was relatively high in the first 24 h of leaching, and decreased thereafter. Among the particle-size fractions, the finest one showed the maximum cumulative release, followed by the medium size for Ca and Mg. As expected, the citric acid solution at pH 2 extracted substantively more nutrients than the other leaching solutions.

The cumulative pattern of K differed from other nutrients as the medium and coarse size-fractions showed a linear trend after 72 h of leaching for both citric acid solutions at pH 4 and 2. Interestingly, water dissolved more K from the finest and medium fractions than citric acid at pH 4 did; even more surprisingly, citric acid at pH 4 dissolved less K from the fine and medium fractions than from the coarsest fraction. We ascribed this behaviour to a mineral phase (probably calcium citrate) that precipitated upon dissolution of the fine and medium fractions and that prevents the release of K.

(ii) Release kinetics of Ca and Mg

The kinetics of release was assessed for both Ca and Mg as they were the most important nutrients in dolostone. During the leaching period the release rate decreased sharply up to 24 h, followed by a steady decrease until reaching values close to zero (Fig. 7). The finest size fraction showed a slightly higher release rate than the other fractions. There were no significant differences between the medium and coarse sizes. The citric acid solution at pH 2 showed much higher release rates than the other leaching solutions.

Two stages of release were evident for all leaching solutions: 1) a stage of fast release in the first 24 h, and 2) a stage of slow release after 24 h for all leaching solutions, probably due to the precipitation of calcium citrate during the long period of solid/liquid contact (Al-Khaldi et al., 2007). During this second stage, probably characterized by incongruent dissolution, the rates of the released Ca and Mg were higher for medium and coarse particle-size fractions ($P < 0.01$) in citric acid solution at pH 2, while there was not much difference among particle size fractions in water and citric acid solution at pH 4 (Fig. 7, Table VI).

The release rate of Ca was twice that of Mg in both water and citric acid solution at pH 4, and similar for both elements in citric acid solution at pH 2 because of the considerable amounts of Mg dissolved by this leaching solution. In water and citric acid solution at pH 4, Ca dissolved preferentially compared to Mg during most of the extraction time and the releasing was non-stoichiometric (Fig. 5). In citric acid solution at pH 2, after a short period of preferential release of Ca, the molar Ca/Mg ratio dropped to values close to 1, the Ca/Mg ratio in dissolved rock, because of the low pH (Pokrovsky et al., 2009). The ideal (congruent) dissolution of calcareous minerals due to an organic acid is given below (adapted from Pansu and Gautheyrou, 2006):

$$CaCO_3 + 2AH \leftrightarrows Ca^{2+} + 2A^- + H_2O + CO_2 \text{ (fast reaction)}$$

$$MgCO_3 + 2AH \leftrightarrows Mg^{2+} + 2A^- + H_2O + CO_2 \text{ (slow reaction),}$$

where A^- represents the organic anion

The dissolution rate of dolomite is generally slower than that of calcite and in acid solution is affected by the transport rate of the reactants, surface reaction, and transport rate of products away from the surface (Yasuda et al., 2013). The same as in the phosphate rock, the open system of columns used in this study ensured the removal of products and the supply of H^+ by citric acid solutions, so favouring the dissolution of dolostone. This explanation is in accordance with the sharp decrease of Ca/Mg ratio in the first 24 h of leaching, which was due to the increase of Mg release.

In citric acid solution at pH 2, the steady decrease of Ca/Mg ratio after 24 h of leaching was ascribed to higher dissolution of the remaining carbonates (enriched in Mg). The higher affinity of the citrate anion for Ca over Mg (Dorozhkin, 2002, 2012) and the leaching of the reaction products were the driving force of dolostone dissolution. The high citrate concentration in citrate solution at pH 2 favored the complexation of Mg, rendering the dissolution congruent in the later periods of leaching. Thus, this type of rock can be used for pH correction and Ca plus Mg replenishment for plant uptake, while mitigating Al toxicity (Conyers et al., 1996; Conyers, 2003; Viadé et al., 2011; Bothe, 2015; da Costa and Crusciol, 2016; Tiritan et al., 2016).

The LMWOAs such as citric acid promote dolostone dissolution by complexing both Ca and Mg from the rock surface (Manahan, 2000; Zimdahl, 2015) resulting in an increase of nutrients (Panhwar et al., 2014; da Costa and Crusciol, 2016). Based on leaching curves, the dolostone will have a much higher impact in strongly acid soils, even though the slower release rate of dolomite within the dolostone will ensure the long-term efficiency of nutrient release.

4. Conclusions

The leaching experiments run in an open-system (columns) under controlled conditions showed that the nutrient release from phosphate rock and dolostone fraction was mainly a function of particle-size, strength of the leaching solution, and time. Increased concentrations of citric acid solution resulted in a greater dissolution. The application of the tested rocks fractions to strongly acid soils from tropical areas is suitable as they behave like slow release fertilizers that are able to replenish the soil with P, Ca, and Mg with the benefit of liming.

Application of the coarse size fraction (0.5 – 2 mm) of both rocks demands less energy inputs for crushing and grinding than other sizes; however the reactivity of this size fraction is low, and its application to the soil would be much less effective than finer size-fractions. The application of both fine and medium grained materials might represent a good balancing to ensure a short and medium-term release of nutrients and alkalizing species. Managing the rhizosphere activities to promote the production of LMWOAs will be a good strategy to improve nutrient release by these rocks fractions in acid soils. Much work has to be done to transfer these lab results to the field, in particular on the overall impact of considerable amounts of fresh rocks added to tropical soils.

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Table I
Elemental analysis and corresponding composition in oxides of the phosphate rock and dolostone from Mozambique used for the trials. Numbers in parentheses are the standard deviations (n=3)

Phosphate rock				Dolostone			
Element	mg kg^{-1}	Oxide	mmol kg^{-1}	Element	mg kg^{-1}	Oxide	mmol kg^{-1}
Si	20,161 (240)	SiO_2	718.0 (8.6)	Si	12,942 (242)	SiO_2	460.9 (8.6)
C	< LOD [a)]	CO_3	< LOD	C	82,122 (3250)	CO_3	6843 (271)
Al	7684 (485)	Al_2O_3	142.8 (9.0)	Al	2439 (1241)	Al_2O_3	45.3 (23.1)
Fe	7378 (63)	Fe_2O_3	66.1 (0.6)	Fe	1411 (19)	Fe_2O_3	12.6 (0.2)
P	239,666 (690)	P_2O_5	3866 (11)	P	2801 (160)	P_2O_5	45.2 (2.6)
Ca	362,923 (5,277)	CaO	9073 (132)	Ca	293,958 (1751)	CaO	7349 (44)
Mg	<LOD	MgO	<LOD	Mg	181,719 (4508)	MgO	7478 (186)
K	3275 (123)	K_2O	42.0 (1.6)	K	695 (67)	K_2O	8.9 (0.9)
S	<LOD	SO_2	<LOD	S	315 (31)	SO_2	9.8 (1.0)
Ba	2004 (112)	BaO	14.6 (0.8)	Ba	332 (56)	BaO	2.4 (0.4)
Sr	2572 (39)	SrO	29.4 (0.5)	Sr	285 (4)	SrO	3.3 (0.1)
Cl	1254 (171)	ClO_2	35.4 (4.8)	Cl	<LOD	ClO_2	<LOD
Ti	1228 (22)	TiO_2	25.7 (0.5)	Ti	114 (8)	TiO_2	2.4 (0.2)
Mn	498 (11)	MnO_2	9.1 (0.2)	Mn	448 (8)	MnO_2	8.2 (0.2)

[a)] LOD - Limit of detection

Table II

Abrasion pH at different contact times of different particle size fractions of phosphate rock and dolostone from Mozambique. Numbers in parentheses are the standard deviations (n=3).

Contact time (hours)	Particle size			ANOVA [a]		
	0.063 – 0.25 mm	0.25 – 0.5 mm	0.5 – 2 mm	Contact time	Rock size	Contact time x Rock size
Phosphate rock						
0.1	9.36 (0.01) aA [b]	8.63 (0.23) bA	8.66 (0.02) bA	***	***	**
1.5	8.24 (0.07) aB	7.79 (0.01) bB	7.69 (0.01) bB			
24	8.23 (0.08) aB	7.98 (0.03) bB	7.81 (0.03) bB			
Dolostone						
0.1	9.36 (0.04) aA	9.57 (0.14) aA	9.50 (0.11) aA	***	*	**
1.5	8.73 (0.10) aB	8.81 (0.05) aB	8.66 (0.03) aB			
24	8.29 (0.03) aC	8.27 (0.03) aC	8.25 (0.03) aC			

[a] * Significant at the 0.05 probability level; ** Significant at the 0.01 probability level; *** Significant at the 0.001 probability level.

[b] Means with different lowercase or uppercase letters (for rock size fraction or contact time, respectively) significantly differed per Tukey multiple mean comparison test at the 95% level of significance.

Table III

Reactivity of the different particle-size fractions of phosphate rock from Mozambique in water, neutral ammonium citrate (NAC), 2% citric acid solution and 2% formic acid solution. Numbers in parentheses are the standard deviation (n=3). The values are express as the percentage of P_2O_5 extracted from the rock fractions

Particle size	Extractant				ANOVA [a]
	Water	NAC	2% citric acid	2% formic acid	
0.063 – 0.25 mm	0.14 (0.01) d A [b]	1.90 (0.42) c A	8.74 (0.04) b A	13.34 (1.33) a A	***
0.25 – 0.5 mm	0.11 (0.01) d A	0.63 (0.13) c B	5.34 (0.26) b B	7.19 (0.26) a B	
0.5 – 2 mm	0.08 (0.00) c A	0.37 (0.25) b B	4.35 (0.37) a B	5.42 (0.63) a C	

[a] *** Significant at the 0.001 probability level.

[b] Means with different lowercase and uppercase letters (for extractants or particle size fraction, respectively) significantly differ per Tukey multiple mean comparison test at 95% of significance.

Table IV

Cumulative amounts of P, Ca and Mg (mmol kg^{-1}) released in water, citric acid solution at pH 4 and citric acid solution at pH 2 during the extraction time between 24 and 360 h by the different particle-size fractions of phosphate rock from Mozambique. Numbers in parentheses are the standard deviation (n=3).

		Particle size			ANOVA a)		
Element	Leaching solution	0.063 - 0.25 mm	0.25 - 0.5 mm	0.5 – 2 mm	Rock size fraction	Leaching solution	Rock size fraction x Leaching solution
P	Water	11.8 (3.1) aA b)	6. 7 (0.5) bA	7.7 (0.6) bA			
	Citric acid at pH 4	67.6 (2.3) aB	49.3 (5.9) bB	61.6 (4.9) aB	***	***	**
	Citric acid at pH 2	1874.7 (23.8) aC	1826 (35) aC	1702 (118) aC			
Ca	Water	4.9 (1.6) aA	2 (0.6) bA	1.1 (0.1) bA			
	Citric acid at pH 4	16.3 (0.8) aB	4.8 (0.3) bB	8.2 (0.8) cB	***	***	**
	Citric acid at pH 2	1367 (95) aC	1244 (124) aC	1308 (212) aC			
Mg	Water	1.7 (0.7) aA	0.9 (0.43) bA	0.6 (0.1) bA			
	Citric acid at pH 4	0.8 (0.2) aB	0.6 (0.2) aA	1.2 (0.0) aB	***	***	**
	Citric acid at pH 2	14.2 (1.3) aC	27.4 (2.4) bB	25.0 (5.4) bC			

a) ** Significant at the 0.01 probability level; *** Significant at the 0.001 probability level.

b) Means with different lowercase or uppercase letters (for rock size fraction or leaching solution, respectively) significantly differed per Tukey multiple mean comparison test at 95% of significance.

Table V

Amounts of P and Ca (mmol kg^{-1}) released in water and 2% citric acid solution during the leaching and single extraction by the different size fractions of phosphate rock from Mozambique. Numbers in parentheses are the standard deviation (n=3)

Element	Extractant	Type of extraction	Particle size			ANOVA [a]
			0.063 – 0.25 mm	0.25 – 0.5 mm	0.5 – 2 mm	
P	Water	Single	19.7 (1.5) a A [b]	15.0 (1.7) b A	11.0 (0.0) c A	**
		Leaching	62.7 (4.6) a B	35.3 (3.2) b B	30.7 (2.1) b B	
	2% Citric acid	Single	1231 (5) a A	751.7 (36.1) b A	613.0 (52.0) b B	
		Leaching	5375 (135) a B	4590 (197) a B	3492 (296) b B	
Ca	Water	Single	1.0 (0.0) a A	1.0 (0.0) a A	1.0 (0.0) a A	**
		Leaching	16.7 (2.5) a B	9.0 (0.0) b B	7.7 (1.5) b B	
	2% Citric acid	Single	485.3 (18.5) a A	219.3 (17.4) b A	165.7 (4.6) b A	
		Leaching	4328 (263) a B	3094 (192) b B	2285 (320) b B	
Ca:P	Water	Single	0.05 (0.03) a A	0.07 (0.01) a A	0.09 (0.01) a A	**
		Leaching	0.27 (0.06) a B	0.25 (0.02) a B	0.25 (0.03) a B	
	2% Citric acid	Single	0.39 (0.02) a A	0.29 (0.01) a A	0.26 (0.02) a A	
		Leaching	0.81 (0.05) a B	0.67 (0.02) a B	0.65 (0.05) a B	

[a] ** Significant at the 0.01 probability level.

[b] Means with different lowercase and uppercase letters (for particle size fraction or type of extraction, respectively) significantly differed per Tukey multiple mean comparison test at 95% of significance.

Table VI
Cumulative amounts of Ca, Mg and K (mmol kg^{-1}) released in water, citric acid solution at pH 4 and citric acid solution at pH 2 during the extraction time between 24 and 360 h by the different particle-size fractions of dolostone from Mozambique. Numbers in parentheses are the standard deviation (n=3)

Element	Leaching solution	Particle size			ANOVA [a]
		0.063 – 0.25 mm	0.25 – 0.5 mm	0.5 – 2 mm	
Ca	Water	57.7 (0.7) a A [b]	37.9 (4.3) b A	26.9 (1.6) c A	
	Citric acid at pH 4	73.2 (16.0) a A	55.8 (1.2) a A	56.3 (4.6) a B	**
	Citric acid at pH 2	643.0 (413.1) a B	1747 (293) b C	1600 (64) b C	
Mg	Water	26.5 (0.4) a A	23.6 (3.6) a A	13.7 (2.6) b A	
	Citric acid at pH 4	37.1 (9.0) a B	30.8 (2.2) a A	27.4 (1.7) a B	**
	Citric acid at pH 2	579.9 (327.0) a C	1913 (261) b B	1782 (59) b C	
K	Water	0.6 (0.1) a A	0.7 (0.3) a A	0.4 (0.2) b A	
	Citric acid at pH 4	0.0 (0.0) a B	0.1 (0.0) a B	0.5 (0.1) b A	**
	Citric acid at pH 2	0.8 (0.1) a C	4.9 (0.5) b C	3.6 (0.5) b B	

[a] ** Significant at the 0.01 probability level.

[b] Means with different lowercase and uppercase letters (for rock size fraction or contact time, respectively) significantly differed per Tukey multiple mean comparison test at 95% of significance.

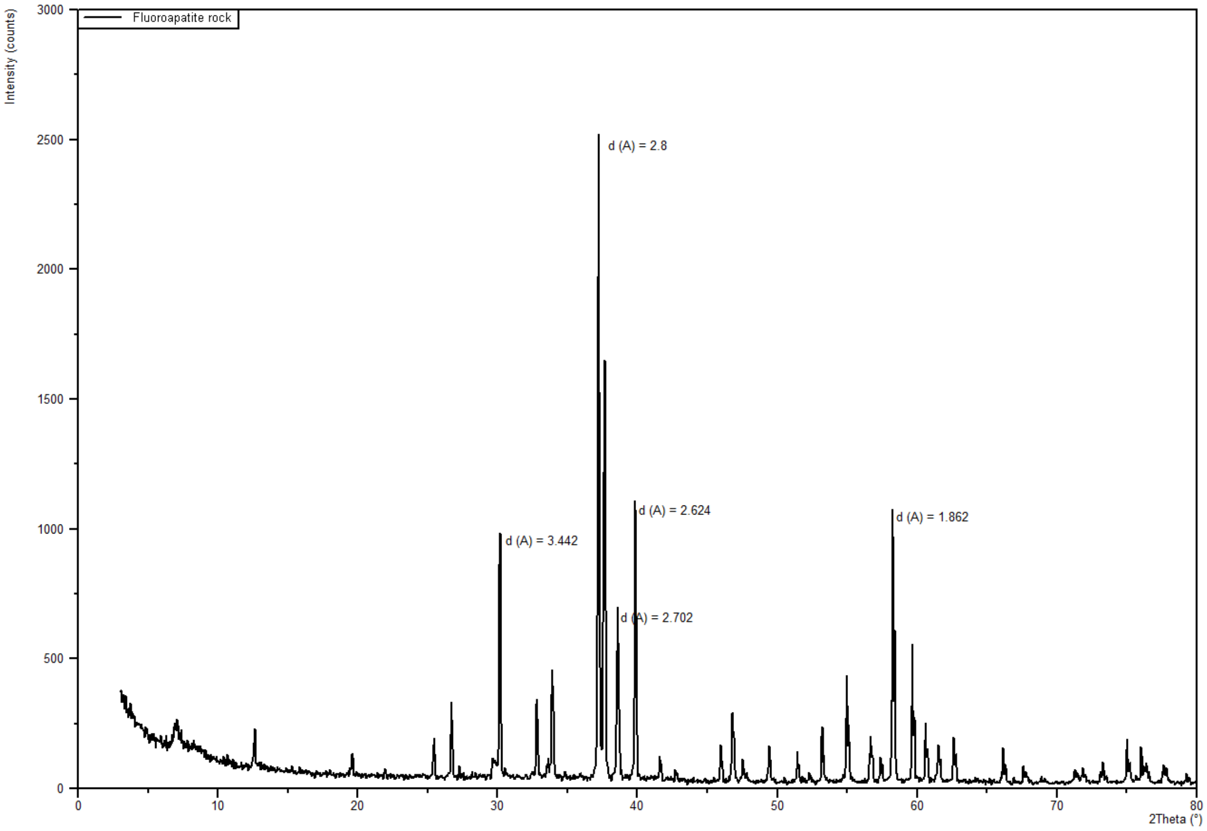

Fig. 1 X-Ray diffractogram of the phosphate rock from Mozambique, indicating a composition mostly made of fluoroapatite with traces of phyllosilicates. Beam: Co Kα1 radiation.

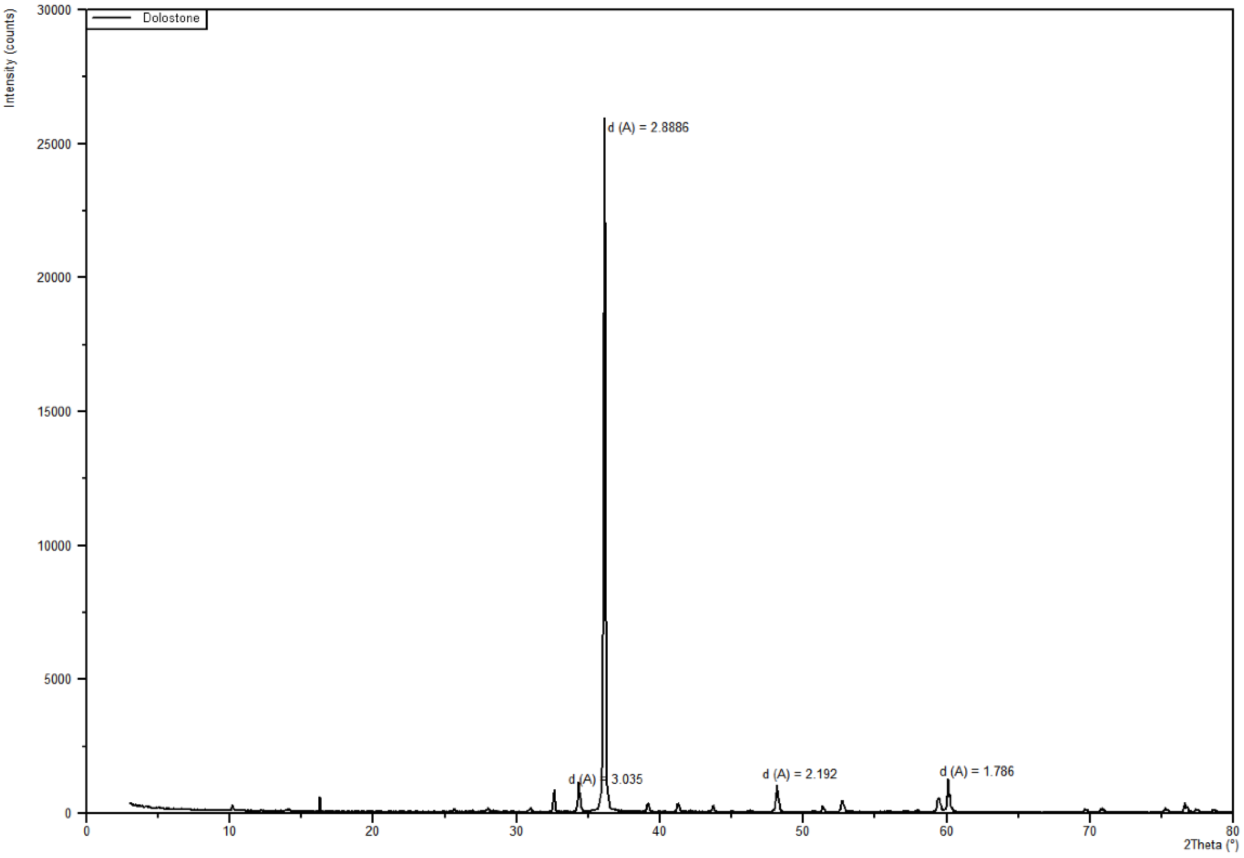

Fig. 2 X-Ray diffractogram of dolostone from Mozambique, indicating a composition mostly made of dolomite with traces of phyllosilicates. Beam: Co Kα1 radiation.

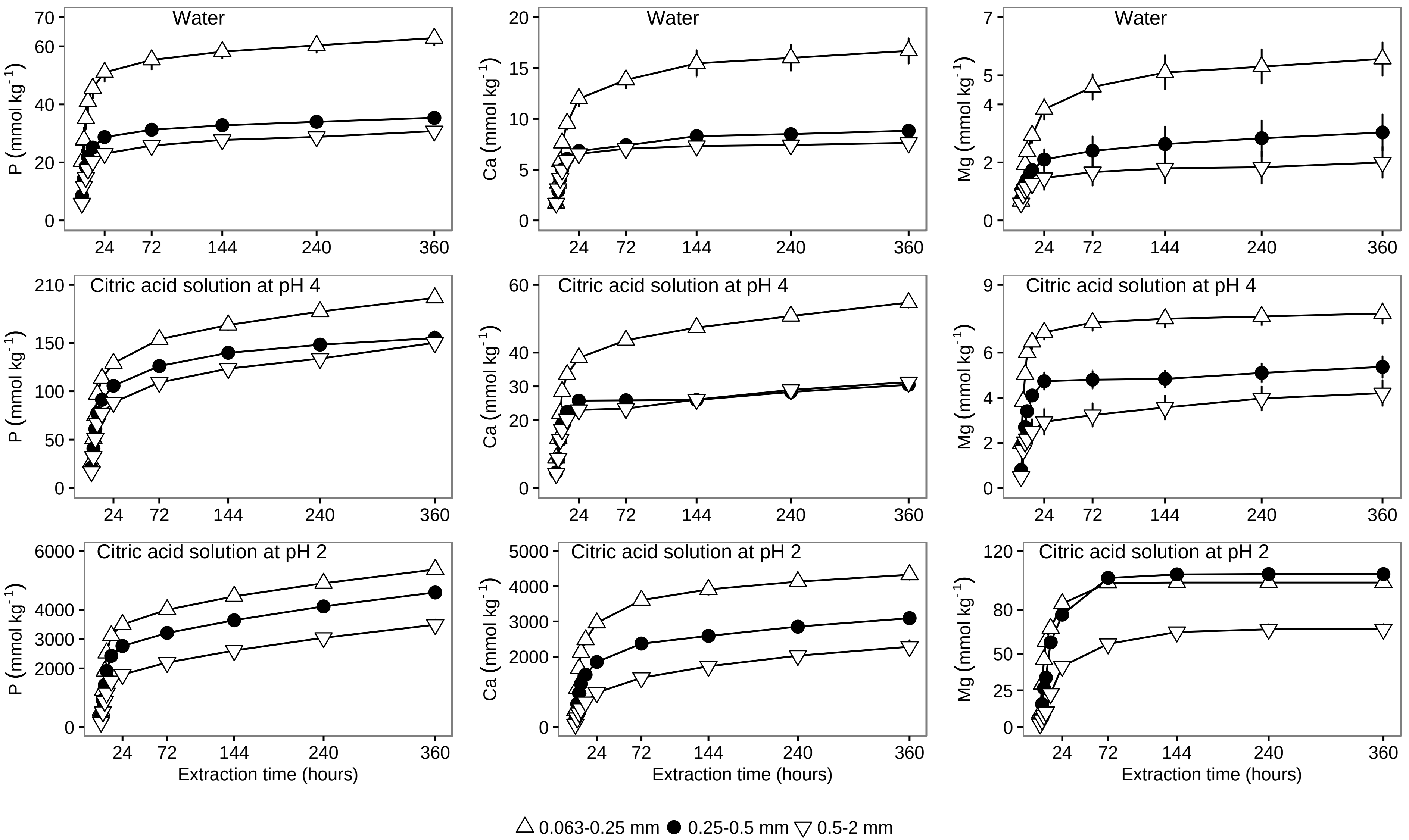

Fig. 3 Cumulative release of P, Ca and Mg (mmol kg^{-1}) freed in water, citric acid solution at pH 4 and citric acid solution at pH 2 during the extraction time of 360 h by the different particle-size fractions of phosphate rock from Mozambique. The whiskers indicate the error bars and represent the 95% confidence interval from triplicate leachate samples.

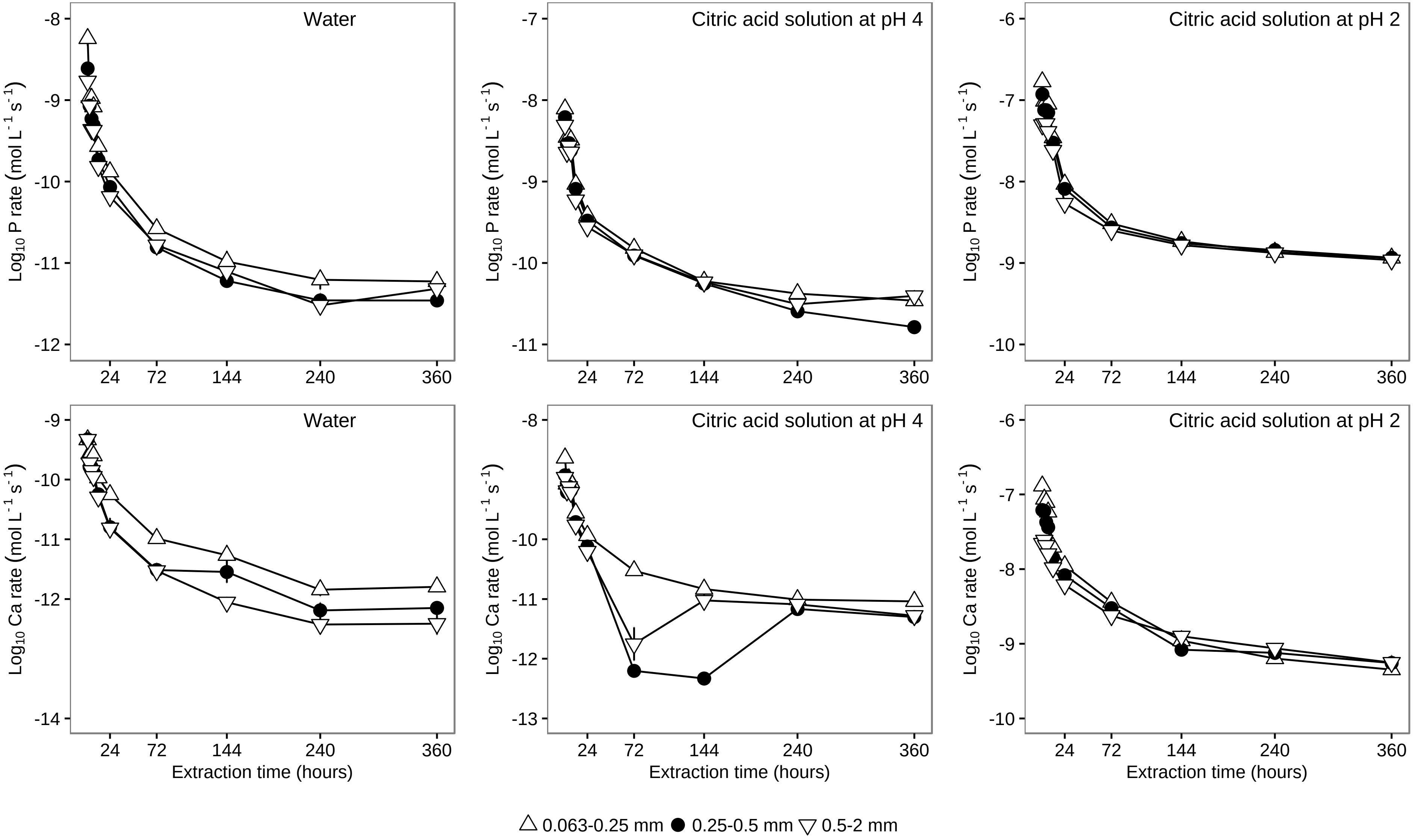

Fig. 4 Logarithms of releasing rate (R) of P and Ca (mol L^{-1} s^{-1}) for water, citric acid solution at pH 4 and citric acid solution at pH 2 during the extraction time of 360 h by the different particle-size fractions of phosphate rock from Mozambique. The whiskers indicate the error bars and represent the 95% confidence interval from triplicate leachate samples.

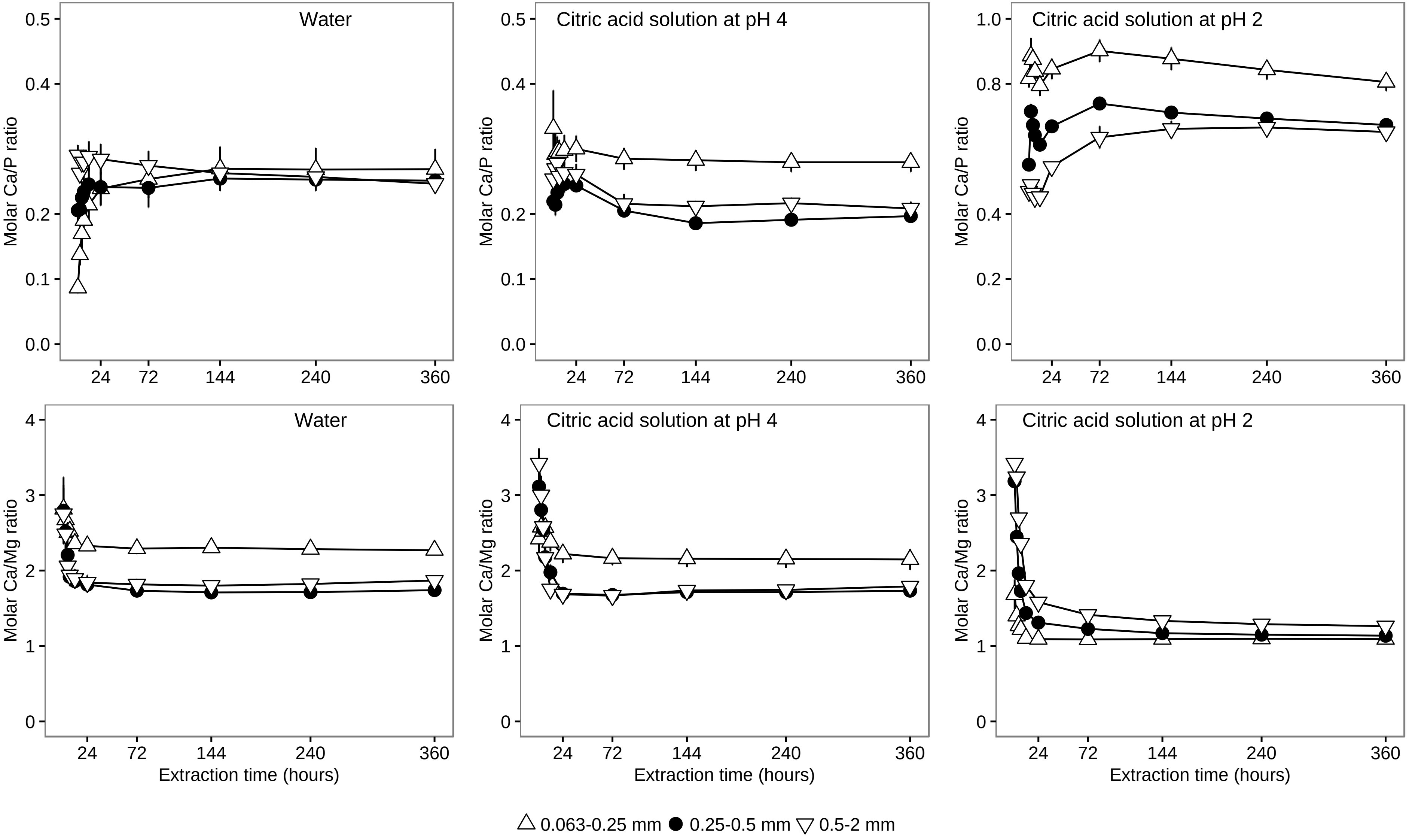

Fig. 5 Molar Ca:P and Ca:Mg ratios for water, citric acid solution at pH 4 and citric acid solution at pH 2 during the extraction time of 360 h for the different particle-size fractions of phosphate rock and dolostone from Mozambique. The whiskers indicate the error bars and represent the 95% confidence interval from triplicate leachate samples.

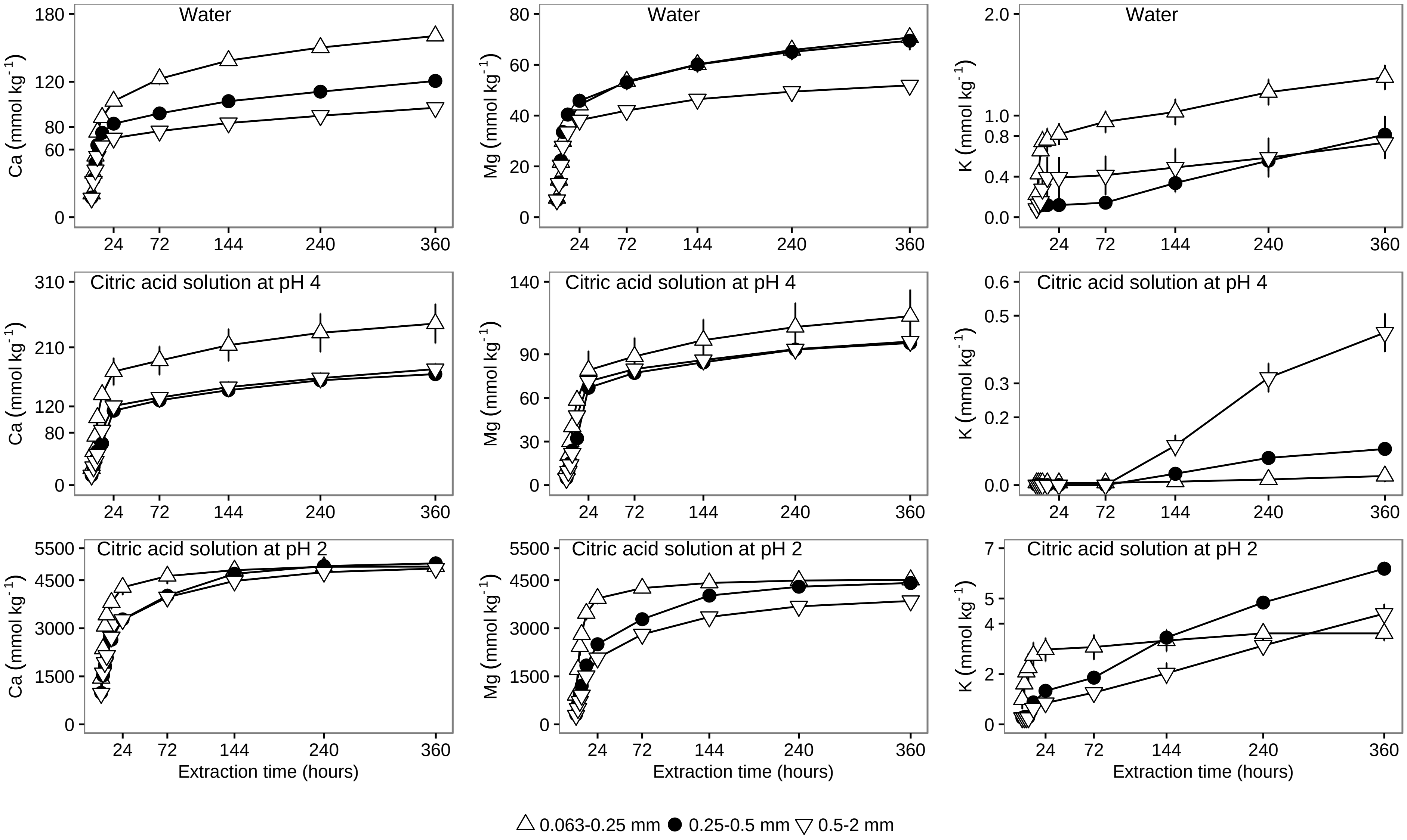

Fig. 6 Cumulative release of soluble Ca, Mg and K (mmol kg^{-1}) freed in water, citric acid solution at pH 4 and citric acid solution at pH 2 during the leaching period of 360 h from the different particle-size fractions of dolostone from Mozambique. The whiskers indicate the error bars and represent the 95% confidence interval from triplicate leachate samples.

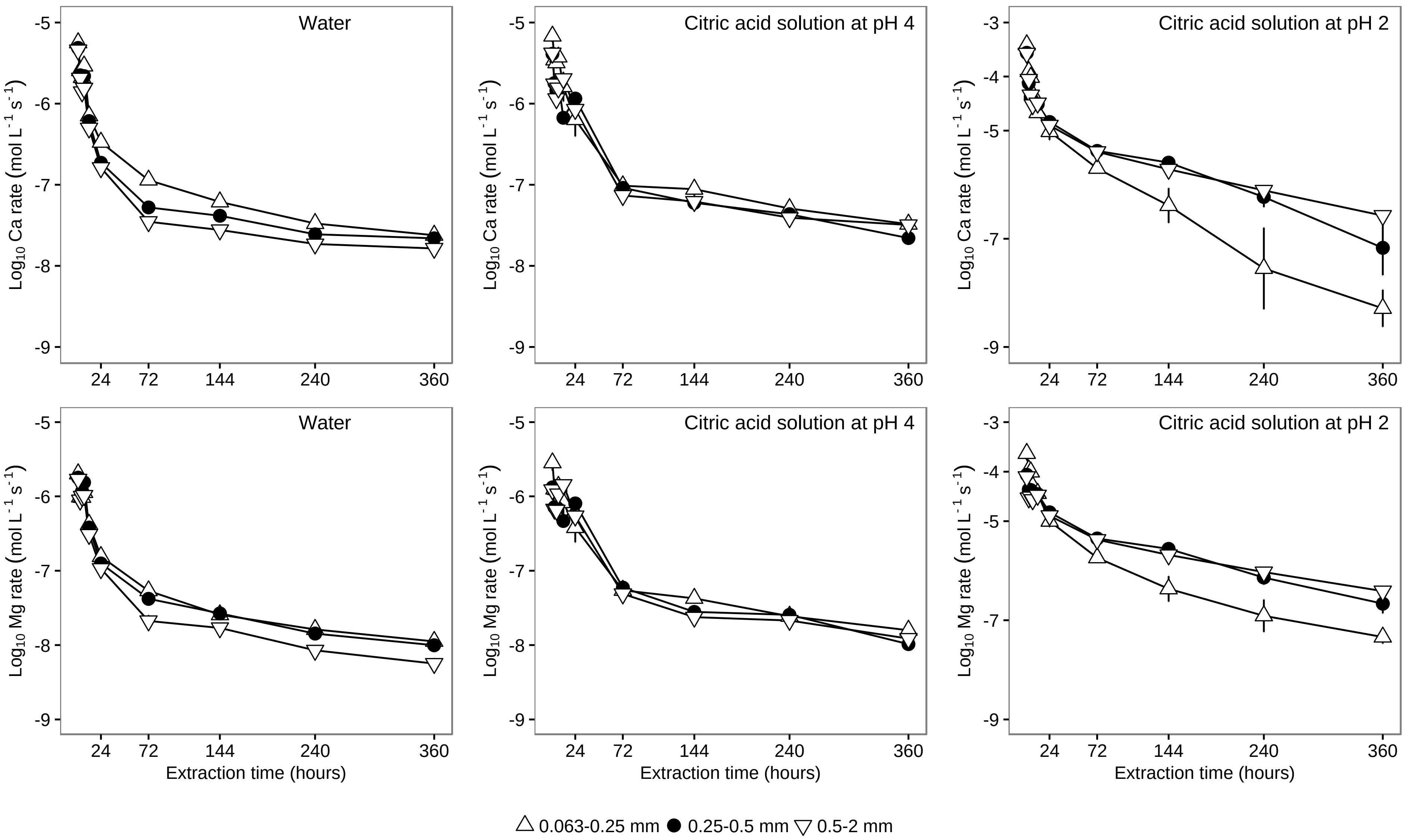

Fig. 7 Logarithms of releasing rate (R) of Ca and Mg (mol L^{-1} s^{-1}) for water, citric acid solution at pH 4 and citric acid solution at pH 2 during the extraction time of 360 h for the different particle-size fractions of dolostone from Mozambique. The whiskers indicate the error bars and represent the 95% confidence interval from triplicate leachate samples.