Common Ion Effects In Zeoponic Substrates: Dissolution And Cation Exchange Variations Due to Additions of Calcite, Dolomite and Wollastonite

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ABSTRACT

A clinoptilolite-rich tuff-hydroxyapatite mixture (zeoponic substrate) has the potential to serve as a synthetic soil-additive for plant growth. Essential plant macro-nutrients such as calcium, phosphorous, magnesium, ammonium and potassium are released into solution via dissolution of the hydroxyapatite and cation exchange on zeolite charged sites. Plant growth experiments resulting in low yield for wheat have been attributed to a Ca deficiency caused by a high degree of cation exchange by the zeolite. Batch-equilibration experiments were performed in order to determine if the Ca deficiency can be remedied by the addition of a second Ca-bearing, soluble, mineral such as calcite, dolomite or wollastonite. Variations in the amount of calcite, dolomite or wollastonite resulted in systematic changes in the concentrations of Ca and P. The addition of calcite, dolomite or wollastonite to the zeoponic substrate resulted in an exponential decrease in the phosphorous concentration in solution. The exponential rate of decay was greatest for calcite (5.60 wt.% $^{-1}$), intermediate for wollastonite (2.85 wt.% $^{-1}$) and least for dolomite (1.58 wt.% $^{-1}$). Additions of the three minerals resulted in linear increases in the calcium concentration in solution. The rate of increase was greatest for calcite (3.64), intermediate for wollastonite (2.41) and least for dolomite (0.61). The observed changes in P and Ca concentration are consistent with the solubilities of calcite, dolomite and wollastonite and with changes expected from a common ion effect with Ca.

Keywords: zeolite, zeoponics, common-ion effect, clinoptilolite, hydroxyapatite

1. Introduction

An important aspect of a regenerative life support system at a Lunar or Martian outpost will be the ability to utilize plants to produce food and convert carbon dioxide into oxygen. Plant growth systems will most likely utilize the local regolith, in combination with synthetic soil-additives to provide essential plant nutrients as well as a solid support substrate [1,2]. A zeolite-hydroxyapatite mixture (zeoponic substrate) has the potential to serve as a synthetic soil-additive for plant growth during long duration space missions [1,3,4]. The zeoponic substrate can provide slow release fertilization of essential plant nutrients through dissolution and ion-exchange reactions [5].

Lai and Eberl [6] first reported an increase in P released from phosphate rock by the addition of clinoptilolite-rich tuff. Chemical equilibria among clinoptilolite-rich tuff, hydroxyapatite and water will be dominated by the dissolution of hydroxyapatite and subsequent ion exchange between Ca^{2+} and K^+ or NH_4^+ on exchange sites in the clinoptilolite-rich tuff. According to Allen et al. [5] these reactions can be represented as:

$Ca_5(PO_4)_3OH + 3H_2O \Leftrightarrow 5Ca^{2+} + 3HPO_4^{2-} + 4OH^-$ and

$$(K^+)_x - Cp - (NH_4^+)_y + Ca^{2+} \Leftrightarrow Ca^{2+} - Cp + (K^+)_x + (NH_4^+)_y$$

where Cp = clinoptilolite and x,y = 2,0; 1,1; or 0,2. The first reaction represents a simplified dissolution of hydroxyapatite ignoring the trace micronutrients present. The second reaction represents the exchange of K^+ or NH_4^+ by Ca^{2+} in clinoptilolite-rich tuff which results in the removal of Ca^{2+} from solution and the shifting of both reactions to the right.

The zeoponic substrate material investigated in this study was developed by the National Aeronautics and Space Administration (NASA) and is composed of mixtures of synthetic nutrient-substituted hydroxyapatite [7] and naturally-occurring Wyoming clinoptilolite that has been exchanged with NH_4 or K [8]. Plant growth experiments on dwarf wheat (Triticum aestivum L. cv. 'Super Dwarf') in this zeoponic substrate indicate a positive correlation between percent of zeoponic material in the substrate and dry-matter production [9] however the dry-matter production was less than that in controls (potting mix plus K-exchanged clinoptilolite watered with Hoagland nutrient solution.). Poor seed production has been noted in the wheat grown in zeoponic substrate. Goins et al. [10] noted that dwarf wheat (Triticum aestivum L. cv. 'USU-Super Dwarf') grown in zeoponic substrates (K-exchanged and NH_4-exchanged clinoptilolite-rich tuff and synthetic hydroxyapatite) produced excessive seedless tillers compared to wheat produced by fertilization via a nutrient solution. Gruener et al. [9] also reported poor seed production and suggested that the low yield may have been attributed to high NH_4^+ in solution causing NH_4-induced Ca deficiency and/or high P concentrations, which may have inhibited the uptake of other essential plant nutrients. A NH_4-induced Ca deficiency was also proposed by Steinberg et al. [11] to explain excess seedless tillers of wheat (Triticum aestivum L. cv. 'USU-Apogee') grown in a zeoponic substrate (2:2:1:0.55 mixture (by weight) of K-exchanged clinoptilolite-rich tuff, NH_4-exchanged clinoptilolite-rich tuff coated with ferrihydrite, synthetic hydroxyapatite, dolomite) compared to wheat grown in a recirculating hydroponic system. Henderson et al. [12] successfully increased wheat (Triticum aestivum L. cv. 'USU-Apogee') dry-matter and seed production, in zeoponic plant growth experiments by adding nitrifying bacteria (to covert NH_4-N to NO_3-N), dolomite (to lower apatite dissolution) and ferrihydrite (to sequester P). However, even with increased yields, plant tissue concentrations of Ca ranged from 0.13 to 0.2 wt % (day 30 samples) which were lower than the expected levels of 0.2 to 0.55 wt. % reported in field-grown wheat [13]. Batch equilibrium solution studies of the same zeoponic substrates used in the above mentioned plant growth experiments [14] indicated that K, N, P and Mg are present in solution at plant-sufficient levels, however Ca may be deficient. In this case the low Ca^{2+} in solution was attributed to the high degree of Ca^{2+} exchanged onto extraframework sites in the clinoptilolite-rich tuff.

The positive plant growth results reported by Henderson et al. [12] due to addition of dolomite to the zeoponic substrate led us to propose the hypothesis that another Ca-bearing mineral with higher solubility than dolomite, and containing no harmful ions, could be used to increase the bioavailablity of Ca^{2+} in zeoponic substrates. The goal of this study was to determine, by a series of batch-equilibration experiments, if Ca^{2+} can be increased in solution by adding a second Ca-bearing mineral: calcite, dolomite, or wollastonite to the zeoponic substrate. The published solubility products for these minerals are listed in

Table 1. Because calcite, dolomite and wollastonite are all much more soluble than hydroxyapatite, the addition of one of them to the hydroxyapatite plus clinoptilolite-rich tuff mixture should result in higher concentrations of Ca^{2+} in solution. Additionally, the dissolution of hydroxyapatite should be inhibited because its solubility is diminished by the presence of one of its own ions in solution (i.e. Ca^{2+}) from the added Ca-bearing mineral by what is called the common-ion effect [e.g.23]. The addition of calcite ($CaCO_3$) and wollastonite ($CaSiO_3$) should increase the concentration of Ca^{2+} in solution and should also lower the amount of P in solution due to the common ion effect on hydroxyapatite dissolution. The addition of dolomite ($CaMg(CO_3)_2$) should increase the concentrations of Ca^{2+} and Mg^{2+} in solution. The net change in the dissolution of hydroxyapatite due to the addition of dolomite will be a sum of the off-setting effects of Ca's common-ion effect and Mg's propensity to increase the solubility of the hydroxyapatite. The increased concentration of Ca^{2+} (and Mg^{2+} for dolomite) in solution may result in increased cation exchange in the clinoptilolite-rich tuff resulting in increased K^+ or NH_4^+ in solution.

2. Experimental

2.1. Materials

Starting materials consisted of clinoptilolite-rich tuff mined from the Green River Formation in Sweetwater County, Wyoming, a synthetic hydroxyapatite developed at NASA's Johnson Space Center Advanced Life Support Laboratory [7], calcite from Montana (D. J. Minerals M-61), dolomite (Baker Grandol Regular # 4) and wollastonite from the NYCO Minerals Inc. Lewis mine, northeastern Adirondacks, New York [24,25]. All materials were sieved and the 0.5 to 1.0 mm sieve fraction was used.

The composition of the natural clinoptilolite-rich tuff is shown in Table 2. Based on a 72 oxygen per formula unit the clinoptilolite-rich tuff has the formula $(Na_{3.55}\,K_{0.87}\,Ca_{0.63}\,Mg_{0.11}\,Fe_{0.03}\,Ti_{0.01}\,Al_{0.21})\,Al_6\,(Al_{0.66}\,Si_{3.34})\,Si_{26}\,O_{72}\cdot 24\,H_2O$. Sodium is the dominant extraframework cation with subsidiary amounts of K and Ca and trace amounts of Mg, Fe, and Ti. The clinoptilolite-rich tuff has a cation exchange capacity of 199 $\mathrm{cmol_c\,kg^{-1}}$ [9] determined by a CsCl method described by Ming and Dixon [26]. The clinoptilolite-rich tuff was exchanged into K^+-exchanged clinoptilolite-rich tuff and NH_4^+-exchanged clinoptilolite-rich tuff using the method of [5]. The nutrient substituted synthetic hydroxyapatite (Table 2) was synthesized using the method of Golden and Ming [7]. In addition to the major components Ca and P it contains the plant nutrients Mg, S, K, Cu, Fe, Mn, Zn, B, and Cl. The compositions of calcite, dolomite and wollastonite (Table 3) were determined using a Cameca SX100 Electron Probe Micro Analyzer (EPMA) operated at 15 kV and a beam current of 10 nanoamps using well characterized silicate and carbonate standards. . The calcite is close to pure, containing trace amounts of Fe and Mn. The dolomite is non- stoichiometric, having the formula $Ca_{1.17} Mg_{0.82} (CO_3)_2$. The wollastonite is stoichiometric and pure, containing trace amounts of Fe and Mn, which is common [27].

2.2. Experimental Methods

The effects of adding calcite, dolomite or wollastonite on hydroxyapatite dissolution and ion-exchange was determined by combining varying amounts of calcite, dolomite or wollastonite to K^+-exchanged clinoptilolite-rich tuff, NH_4^+-exchanged clinoptilolite-rich tuff, hydroxyapatite and 100 ml of de-ionized water in a 125 ml Erlenmeyer flask. The clinoptilolite-rich tuff to hydroxyapatite ratio was held constant at 4:1 and the K^+ to NH_4^+ ratio was held constant at 1:1. The amount of the third mineral (calcite, dolomite or wollastonite) was varied at 0, 5, 10, 15, 20, 25 and 50-weight %. For example, a sample with 20-weight % calcite consisted of 0.500 g of calcite, 0.000 g of dolomite, 0.000 g of wollastonite, 0.800 g of K^+-exchanged clinoptilolite-rich tuff, 0.800 g of NH_4^+-exchanged clinoptilolite-rich tuff and 0.400 g of hydroxyapatite. In each case the total solid was 2.5 grams resulting in a constant fluid-solid ratio of 40 mL g^{-1}. Each flask was capped with a foam stopper to allow free exchange with atmospheric CO_2 and was placed in an environmentally controlled orbital shaker set at 90 rpm and 25° C. Samples were removed at 500 hours and were filtered through a #42 Whatman filter. Each treatment was replicated three times. Concentrations of P, NH_4, K, Mg and Ca as well as pH and electrical conductivity were measured. Potassium, Mg and Ca concentrations were determined by atomic absorption spectrometry (AAS). Phosphorous was determined using a ascorbic-acid, molybdophosphate-blue colorimetric method [28]. Ammonium was measured by ion-selective electrode. Electrical conductivity and pH were measured using conventional probes. Ionic strength was calculated from measured conductivity using the empirical relationship of Griffin and Jurinak [29] where ionic strength (mol L^{-1}) = 0.0127 Electrical Conductivity (ds m^{-1}). Least squares linear regression of ionic concentration data was performed using the software program DeltaGraph Pro ver. 3.0 (SPSS Inc. Chicago, IL). Equilibrium estimates of hydroxyapatite dissolution over the observed range of pH were performed using the chemical speciation program Visual MINTEQ [30], a Windows version of MINTEQA2 ver 4.0 [17].

3. Results

The measured solution pH, ionic strength, and P, NH_4, K, Mg and Ca concentrations after 500 hours of shaking time for samples containing various amounts of calcite, dolomite or wollastonite are shown in Table 4. The pH ranged from 8.0 to 8.5 and varied systematically with the amount added calcite, dolomite or wollastonite. A control sample containing no additional Ca-bearing mineral had a pH of 8.0. Addition of calcite, dolomite or wollastonite systematically raised the pH to 8.5, 8.2 or 8.4, respectively.

3.1. Phosphorous

Phosphorous in solution is a result of the dissolution of hydroxyapatite. The addition of calcite, dolomite or wollastonite should inhibit the dissolution of hydroxyapatite and result in lower solution P concentrations due to the common ion effect. The measured solution P concentration as a function of wt. % of added calcite, dolomite or wollastonite is listed in Table 4 and shown graphically in Figure 1. P concentration in solution decreases systematically with added calcite, dolomite and wollastonite from a maximum of 15.05 mg L^{-1} with no added mineral to a minimum of 1.49 mg L^{-1} for 50 wt. % added calcite. The reduction in P represents reduced dissolution of hydroxyapatite due to the common ion effect of additional Ca in solution. For all of the weight percents studied (5, 10, 15, 20, 25, 50) the addition of calcite resulted in the largest reduction of P concentration. The addition of dolomite had the least effect and wollastonite had an intermediate effect. This relationship is consistent with the solubilities of calcite, dolomite and wollastonite (Table 1). A linear least squares regression of the P concentration in solution data indicates that the relationship between P concentration in solution and wt. % of added calcite, dolomite or wollastonite can be modeled by an exponential function (Figure 1) of the form:

$$[P]=[P_0]* e^{-kx}$$

$[P]$= P concentration in solution

$[P_0]$ = P concentration in solution (15.045 mg L^{-1}) with 0.0 wt. % of added calcite, dolomite or wollastonite

k = rate of decrease (wt. $\%^{-1}$)

x = wt. % of added calcite, dolomite or wollastonite (in decimal form)

The values of k are 5.60 wt. $\%^{-1}$ for calcite ($R^2 = 0.991$), 2.85 wt. $\%^{-1}$ for wollastonite ($R^2 = 0.995$), and 1.58 wt. $\%^{-1}$ for dolomite ($R^2 = 0.987$). The order of the k values (calcite > wollastonite > dolomite) can be correlated with the solubility products for these three minerals (see below).

3.2. Calcium

Equilibrium Ca^{2+} concentrations in solution will be the result of the dissolution of hydroxyapatite and calcite, dolomite or wollastonite and of the cation exchange of Ca^{2+} with K^+ and NH_4^+ on extraframework sites in clinoptilolite-rich tuff. Because calcite, dolomite and wollastonite are all much more soluble than hydroxyapatite, their addition to the hydroxyapatite plus clinoptilolite-rich tuff mixture should result in higher concentrations of Ca^{2+} in solution. Calcium concentrations in solution as a function of wt. % of added calcite, dolomite or wollastonite are shown in Fig. 2. Calcium concentrations in solution increase systematically from a value of 0.51 mg L^{-1} for the hydroxyapatite only system after added calcite, dolomite and wollastonite. Similar to the P data, calcite has the greatest effect and dolomite the least effect on the change in Ca^{2+} concentration in solution and is consistent with the solubilities of calcite, dolomite and wollastonite (Table 1). A linear least squares regression of the Ca^{2+} concentration in solution data indicates that the relationship between Ca^{2+} concentration in solution and wt. % of added calcite, dolomite or wollastonite can be modeled by a linear function (Figure 2) of the form:

$[Ca] = mx + [Ca_0]$

$[Ca]$ = Ca^{2+} concentration in solution

$[Ca_0]$ = Ca^{2+} concentration in solution (0.51 mg L^{-1}) with 0.0 wt. % of added calcite, dolomite or wollastonite

m = rate of increase (mg L^{-1} wt. $\%^{-1}$)

x = wt. % of added calcite, dolomite or wollastonite (in decimal form)

The values of m are 3.64 mg L^{-1} wt. $\%^{-1}$ for calcite ($R^2 = 0.984$), 2.41 mg L^{-1} wt. $\%^{-1}$ for wollastonite ($R^2 = 0.967$), and 0.61 mg L^{-1} wt. $\%^{-1}$ for dolomite ($R^2 = 0.967$). The order of the m values (calcite > wollastonite > dolomite) can be correlated with the solubility products for these three minerals (see below).

3.3. Magnesium

Magnesium in solution is a result of the dissolution of hydroxyapatite which contains 2.25 wt. % Mg (Table 2) and, when present, the dissolution of dolomite which contains 17.66 wt. % Mg (Table 3). Cation exchange of Mg^{2+} with K^+ and NH_4^+ in the clinoptilolite-rich tuff would be expected to be minimal due to the high selectivity of K^+ and NH_4^+ over Mg^{2+} in clinoptilolite-rich tuff. According to Ames [31] the ion selectivity order for clinoptilolite-rich tuff cations is $Cs^+ > Rb^+ > K^+ > NH_4^+ > Ba^{2+} > Sr^{2+} > Na^+ > Ca^{2+} > Fe^{3+} > Al^{3+} > Mg^{2+} > Li^+$. The addition of calcite or wollastonite to the clinoptilolite-rich tuff and hydroxyapatite mixture should result in reduced dissolution of hydroxyapatite due to the common ion effect and consequently reduced solution Mg concentrations. The overall effect of adding dolomite on solution Mg concentrations will be the sum of two competing effects: 1) reduced hydroxyapatite dissolution due to the common ion effect and 2) Mg released into solution from the dissolution of dolomite. Krauskopf and Bird [23] point out that the presence of ions in solution (e.g., Mg^{2+}) not present in a salt (e.g., hydroxyapatite), will tend to make the salt more soluble. In this case the salt in question, hydroxyapatite, does contain a small amount (2.25 wt. %) of Mg and it is unclear if the Mg^{2+} in solution due to dolomite dissolution will have any effect on hydroxyapatite dissolution that will be discernable from the common ion effect due to Ca.

The measured solution Mg concentration as a function of wt. % of added calcite, dolomite or wollastonite is listed in Table 4 and shown graphically in Figure 3. Magnesium concentrations in solution increase systematically with added dolomite from a value of 1.33 mg L^{-1} for the hydroxyapatite only system. A linear least squares regression of the Mg concentration in solution data indicates that the relationship between Mg concentration in solution and wt. % added dolomite can be modeled by a linear function (Figure 3) of the form:

$[Mg] = mx + [Mg_0]$

[Mg]= Mg concentration in solution

$[Mg_0]$ = Mg concentration in solution (1.33 mg L^{-1}) with 0.0 wt. % of added calcite, dolomite or wollastonite

m = rate of increase (mg L^{-1} wt. $\%^{-1}$)

x = wt. % of added dolomite (in decimal form)

The value of m is 1.61 mg L^{-1} wt. $\%^{-1}$ for dolomite ($R^2 = 0.985$). Both calcite and wollastonite do not show a strong correlation between Mg concentration in solution and wt. % added calcite or wollastonite. There is a weak negative correlation with wt. % added wollastonite (m = -0.394 mg L^{-1} wt. $\%^{-1}$, R^2 = 0.688) that can be explained by reduced hydroxyapatite dissolution due to the common ion effect. There is an unanticipated weak positive correlation between Mg concentration in solution and wt. % added calcite (m = 0.535 mg L^{-1} wt. $\%^{-1}$, $R^2 = 0.805$). The mechanism for this correlation is unknown.

3.4. Potassium

Potassium in solution is a result of cation exchange between K^+ on extraframework exchange sites in the clinoptilolite-rich tuff and Ca^{2+} in solution. Because the origin of the Ca^{2+} in solution (dissolution of hydroxyapatite vs. dissolution of calcite, dolomite or wollastonite) is inconsequential on cation exchange equilibria there should be no net effect on solution K^+ concentrations due to the addition of calcite, dolomite or wollastonite. A possible exception could occur if the total sample contained only a small amount of clinoptilolite-rich tuff. Potassium concentrations in solution as a function of wt. % of added calcite, dolomite or wollastonite are shown in Fig. 4. With the exception of the 50 wt. % samples, K concentration in solution does not change with wt. % added calcite, dolomite or wollastonite.

3.5. Ammonium

The effect on solution NH_4^+ concentrations with the addition of calcite, dolomite or wollastonite should be similar to the effect expected for K^+. Ammonium concentrations in solution as a function of wt. % of added calcite, dolomite or wollastonite are shown in Fig. 5. With the exception of the 50 wt. % samples, NH_4^+ concentration in solution does not change with wt. % added calcite, dolomite or wollastonite.

3.5. Discussion

The addition of calcite, dolomite and wollastonite to mixtures of clinoptilolite-rich tuff and hydroxyapatite changes the concentrations of P and Ca^{2+} in solution in a continuous and systematic fashion that is consistent with changes expected due to the common ion effect. The response of P and Ca^{2+} in solution to the addition of calcite, dolomite or wollastonite is greatest for calcite, intermediate for wollastonite and the least for dolomite. This response can be correlated with the solubilities of these minerals. Plotted in Figure 6 are the estimated rate coefficients (described above) for P and Ca with additional calcite, wollastonite or dolomite (k = rate of decrease for P, m = rate of increase for Ca) versus the solubility products for these minerals from Table 1. There is a linear correlation between the rate coefficient and solubility product. Both P and Ca have a linear least squares correlation coefficient (r^2) greater than 0.97. Albeit the correlation is based on only three data points, those three data points represent a reduction of data from 57 experiments.

The range of P concentrations in solution observed in this study (1.49 to 15.05 mg L^{-1}) is greater than the soil solution concentrations of 0.19 to 0.31 mg L^{-1} reported by Tisdale et al. [32] to be adequate for a variety of crops. The decrease in dissolution of hydroxyapatite, as reflected by the decrease in P concentration, with addition of calcite, dolomite and wollastonite cannot be attributed to solely to pH. The variation in pH in all the samples studied is from

8 to 8.5 (Table 4). Using the chemical equilibrium speciation program Visual Minteq, the expected range of total P in solution in equilibrium with hydroxyapatite and atmospheric CO_2 is from 0.33 (pH = 8) to 0.19 (pH = 8.5) mg L^{-1}. The variation in P concentration as a function of pH observed in this study is an order of magnitude greater (13.6 to 1.5 mg L^{-1}) than predicted by Visual Minteq (Figure 7a). The trend in Ca concentrations in solution observed in this study is opposite to the trend expected due to a change in pH (Figure 7b). Average Ca in solution data for pH 8 in this study is 0.55 mg L^{-1} increasing to a value of 2.5 mg L^{-1} for pH 8.5. Total Ca in solution predicted by Visual Minteq for this same pH region decreases from 0.7 mg L^{-1} (pH = 8) to 0.4 mg L^{-1} (pH = 8.5).

Calcium concentrations in solution range from a minimum value of 0.51 mg L^{-1} (hydroxyapatite only system) to a maximum value of 2.47 mg L^{-1} (50 wt % added calcite) (Table 2). These values are comparable to Ca concentrations reported by Allen et al. (1993) of 0.52 to 3.45 mg L^{-1} for mixtures of K- and NH_4-exchanged clinoptilolite-rich tuff and naturally occurring phosphate rock. These values are low compared to Lindsay's [33, Table 1.1] selected average soil solution concentration of 339.5 mg L^{-1} (adjusted to a fluid:solid ratio of 40) and to the concentration of a Hoagland nutrient solution (approximately 200 mg L^{-1}) [34] or to the half-strength Hoagland nutrient solution used as a control in NASA's zeoponic plant growth experiments [9,11,12]. The Ca concentrations reported here are also low compared to the minimum required for good corn yields (14.8 mg L^{-1}) or to the range of 8.02 to 44.9 mg L^{-1} for a typical soil solution, both reported by Tisdale et al. [32]. The Ca concentrations in solution measured in this study are within the "Just adequate" range of 0.24 to 40 mg L^{-1} reported by Jones [35] in his guide to hydroponic plant growth systems.

In a study of P removal by wollastonite (using wollastonite mined from the same locality as this study) Brooks et al. [36] reported reduced levels of P in solution over time when 5 and 10 mg L^{-1} phosphate solutions were exposed to wollastonite (20:1 solution to wollastonite ratio) and attributed the mechanism to either adsorption of P on the wollastonite surfaces or precipitation of calcium phosphates of high solubility. The reduced P concentrations in solution with the addition of calcite, dolomite and wollastonite reported in this study are not consistent with either mechanism proposed by Brooks et al. [36] because an adsorption of P on the wollastonite (or calcite or dolomite) surfaces would not co-vary with the increase in Ca^{2+} concentrations in solution reported here. A reduction on P concentrations in solution due to the precipitation of calcium phosphates as proposed by Brooks et al. [36] would be expected to co-vary with reduced Ca^{2+} concentrations in solution, opposite to the trend reported in this study.

The response of the concentrations of Mg^{2+} in solution with the addition of a second Ca-bearing mineral varies for calcite, dolomite and wollastonite. Magnesium concentrations in solution increase systematically with added dolomite are reduced slightly with added wollastonite and increase slightly with added calcite. Except for the 50 weight percent samples, the higher concentrations in Ca in solution with added calcite, dolomite or wollastonite do not result in significant changes in solution K^+ or NH_4^+ concentrations. The samples with 50 weight percent calcite, dolomite or wollastonite have the lowest concentrations of K^+ and NH_4^+ in solution, possibly due to the smaller amount of K- and NH_4-exchanged clinoptilolite-rich tuff in these sample.

5. Conclusions

Plant growth studies using zeoponic substrates have resulted in poor seed production in wheat, which has been attributed to Ca deficiency and/or high P concentrations [9]. The results of this study indicate that the addition of calcite, dolomite or wollastonite to a zeoponic substrate results in increased Ca^{2+} and reduced P in solution. These experiments suggest that the addition of a second Ca-bearing mineral is a viable remedy to the problem of poor seed production in wheat. Zeoponic substrates containing calcite, dolomite or wollastonite can provide essential plant nutrients and a solid support substrate for plant growth during long duration space missions.

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Table 1: Published Solubility Products for Apatite, Calcite, Dolomite and Wollastonite.

Mineral	Solubility Product (-log Ksp)	Reference
Apatite	58.3	[15]
Apatite (synthetic)	58 ± 1	[16]
Apatite (natural)	70	[16]
Hydroxyapatite	44.2	[17]
Calcite	8.35	[18]
Calcite	8.33 to 8.48	[19]
Calcite	8.48	[17]
Dolomite	17.2 ± 0.2	[20]
Dolomite	16.7	[21]
Dolomite (ordered)	17.09	[22]
Dolomite (disordered)	16.54	[22]
Dolomite	17.0	[17]
Wollastonite	12.996	[17]

Table 2. Composition of Clinoptilolite (Cp) and Hydroxyapatite (Ap) used in experiments.

Cp		Ap	
oxide	wt. %	oxide	wt. %
SiO_2	70.36	CaO	46.8
Al_2O_3	13.99	P_2O_5	39.61
Na_2O	4.39	Fe_2O_3	1.21
K_2O	1.64	MgO	2.25
CaO	1.42	SiO_2	0.59
MgO	0.18	SO_3	2.07
FeO	0.1	OH	3.61
MnO	0.01		
TiO_2	0.02		
Cr_2O_3	0.01		
P_2O_5	0.01		
SO_2	0.02		

element	µg/mg	element	µg/mg
Ni	<18.5		
Co	0.8	Na	23.74
Sr	421	K	18.26
Cs	2	Mn	330
Rb	81.6	Cu	28.9
Zr	206.3	Zn	282
Ba	906	Sr	140
As	1.6		

Table 3: Mean composition of Wol, Cal and Dol used in experiments. Numbers in parentheses represent one standard deviation.(n = # of analyses)

	Wol		Cal		Dol	
n	25		28		25	
MgO	0.00	(0.00)	0.00	(0.00)	17.66	(0.12)
Al2O3	0.03	(0.02)				
SiO2	51.23	(0.14)				
CaO	48.37	(0.19)	55.72	(0.05)	35.03	(0.15)
MnO	0.19	(0.03)	0.25	(0.04)	0.02	(0.03)
FeO	0.49	(0.07)	0.09	(0.03)	0.31	(0.08)
CO2			43.94	(0.01)	46.98	(0.02)
Total	100.32	(0.23)	100.0	(0.00)	100.0	(0.00)
			Moles per 6 oxygen			
Mg	0.00	(0.00)	0.00	(0.00)	0.82	(0.01)
Al	0.00	(0.00)				
Si	1.98	(0.00)				
Ca	2.01	(0.01)	1.99	(0.00)	1.17	(0.01)
Mn	0.01	(0.00)	0.01	(0.00)	0.00	(0.00)
Fe	0.02	(0.00)	0.00	(0.00)	0.01	(0.00)
C			2.00	(0.00)	2.00	(0.00)

Table 4: pH, Ionic Strength (I.S.), and concentrations of P, Ca, Mg, K and NH_4 as a function of wt% calcite, dolomite or wollastonite. Values represent average of three replicates. Numbers in parentheses represent one standard deviation.

wt %	wt %	wt %	pH		I.S.		P		Ca		Mg		K		NH_4	
Cal	Dol	Wol			mmol L^{-1}		mg L^{-1}		mg L^{-1}		mg L^{-1}		mg L^{-1}		mg L^{-1}	
0	0	0	8.0	(0.01)	3.91	(0.01)	15.05	(0.19)	0.51	(0.04)	1.33	(0.01)	23.6	(0.53)	36.3	(0.23)
5			8.2	(0.01)	3.92	(0.02)	10.24	(0.59)	0.65	(0.06)	1.31	(0.09)	25.3	(0.40)	37.3	(0.26)
10			8.2	(0.04)	3.97	(0.04)	8.48	(0.41)	0.82	(0.11)	1.34	(0.08)	25.9	(1.55)	38.6	(0.18)
15			8.3	(0.04)	3.96	(0.10)	6.73	(0.87)	0.93	(0.13)	1.41	(0.14)	24.5	(1.05)	37.9	(1.78)
20			8.3	(0.08)	4.00	(0.07)	5.00	(0.44)	1.16	(0.05)	1.47	(0.03)	25.6	(1.34)	38.5	(0.48)
25			8.4	(0.01)	4.06	(0.06)	3.89	(0.35)	1.32	(0.02)	1.54	(0.04)	26.7	(1.32)	39.4	(0.91)
50			8.5	(0.01)	3.75	(0.02)	1.49	(0.09)	2.47	(0.09)	1.56	(0.03)	26.1	(0.94)	36.5	(0.48)
	5		8.0	(0.00)	3.98	(0.08)	13.93	(0.21)	0.53	(0.08)	1.48	(0.09)	25.8	(0.25)	38.7	(0.40)
	10		8.0	(0.02)	3.83	(0.07)	12.44	(0.66)	0.59	(0.06)	1.51	(0.14)	25.6	(0.66)	37.5	(0.90)
	15		8.1	(0.02)	3.84	(0.03)	11.96	(0.26)	0.62	(0.03)	1.61	(0.05)	24.8	(0.42)	38.2	(0.49)
	20		8.1	(0.02)	3.75	(0.08)	11.53	(0.28)	0.65	(0.04)	1.64	(0.02)	24.0	(0.68)	37.9	(0.38)
	25		8.2	(0.03)	3.69	(0.05)	9.87	(0.26)	0.68	(0.03)	1.75	(0.09)	24.8	(1.14)	37.5	(0.23)
	50		8.2	(0.04)	3.31	(0.03)	6.72	(0.29)	0.79	(0.03)	2.11	(0.10)	23.1	(0.15)	33.3	(0.00)
		5	8.1	(0.03)	3.98	(0.13)	13.01	(0.77)	0.73	(0.09)	1.27	(0.17)	25.4	(0.84)	39.2	(1.01)
		10	8.1	(0.02)	3.99	(0.04)	11.14	(0.27)	0.89	(0.01)	1.35	(0.04)	25.9	(0.39)	39.0	(0.15)
		15	8.2	(0.04)	3.80	(0.03)	9.42	(0.53)	0.93	(0.02)	1.30	(0.01)	25.4	(0.74)	39.6	(0.92)
		20	8.3	(0.01)	3.67	(0.04)	8.37	(0.53)	0.96	(0.14)	1.18	(0.05)	24.5	(1.03)	39.8	(0.72)
		25	8.3	(0.02)	3.69	(0.04)	7.36	(0.21)	1.10	(0.09)	1.24	(0.08)	24.6	(1.32)	39.0	(1.02)
		50	8.4	(0.01)	3.36	(0.06)	4.22	(0.08)	1.68	(0.18)	1.14	(0.03)	24.0	(0.96)	35.4	(0.51)

Figure 1: Solution P concentration as a function of weight percent of added calcite (Cal), dolomite (Dol) or wollastonite (Wol). Error bars represent ± 1 σ. Derived curves are of the form $[P]=[P_0]* e^{-kx}$ where the values of k are 5.60 for Cal ($R^2 = 0.991$), 2.85 for Wol ($R^2 = 0.995$), and 1.58 for Dol ($R^2 = 0.987$).

Fig. 2: Solution Ca Concentration as a Function of Weight Percent Calcite (Cal), Dolomite (Dol) or Wollastonite (Wol). Error bars represent ± 1 σ. Derived curves are of the form $[Ca]= mx + [Ca_0]$ where the values of m are 3.64 for Cal ($R^2 = 0.984$), 2.41 for Wol ($R^2 = 0.967$), and 0.61 for Dol ($R^2 = 0.967$).

Fig. 3: Solution Mg Concentration as a Function of Weight Percent Calcite (Cal), Dolomite (Dol) or Wollastonite (Wol). Error bars represent ± 1 σ. Derived curves are of the form $[Mg]= mx + [Mg_0]$ where the values of m are 0.535 for Cal ($R^2 = 0.805$), -0.394 for Wol ($R^2 = 0.688$), and 1.61 for Dol ($R^2 = 0.985$).

Fig. 4: Solution K Concentration as a Function of Weight Percent Calcite (Cal), Dolomite (Dol) or Wollastonite (Wol). Error bars represent ± 1 σ.

Fig. 5: Solution NH_4 Concentration as a Function of Weight Percent Calcite (Cal), Dolomite (Dol) or Wollastonite (Wol). Error bars represent ± 1 σ.

Fig. 6: Rate coefficients with additional Calcite, Wollastonite or Dolomite, (rate of decrease for P (from Fig. 1), rate of increase for Ca (from Fig. 2)) versus the solubility products of Calcite ($-\log K_{sp} = 8.4$, midpoint of range in [19]), Wollastonite ($-\log K_{sp} = 13$, from [17]), and Dolomite ($-\log K_{sp} = 17$, from [17]).

Fig. 7: Variation in P (7a) and Ca (7b) concentrations observed in this study as a function of pH compared with values predicted by Visual Minteq for a solution in equilibrium with Ap and atmospheric CO_2. Circles represent data from this study. Diamonds represent values predicted by Visual Minteq.

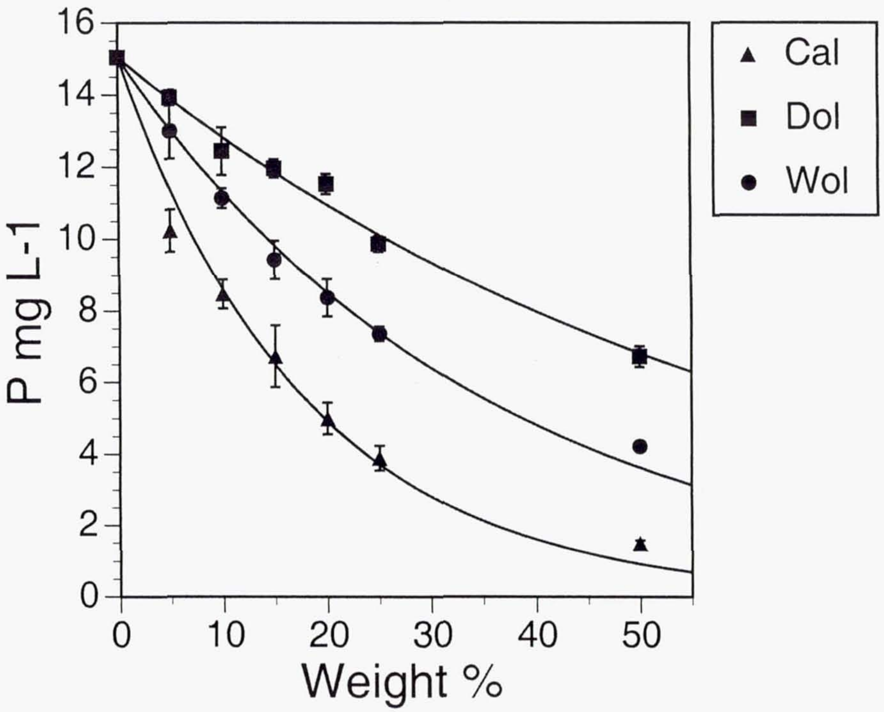

FIG. 1

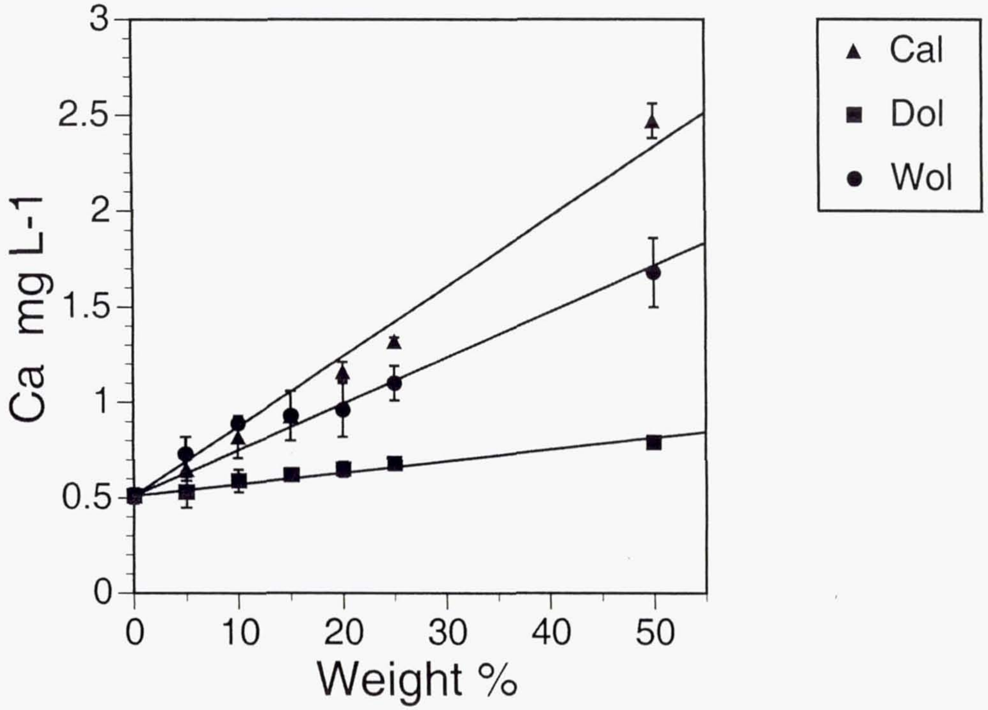

FIG. 2

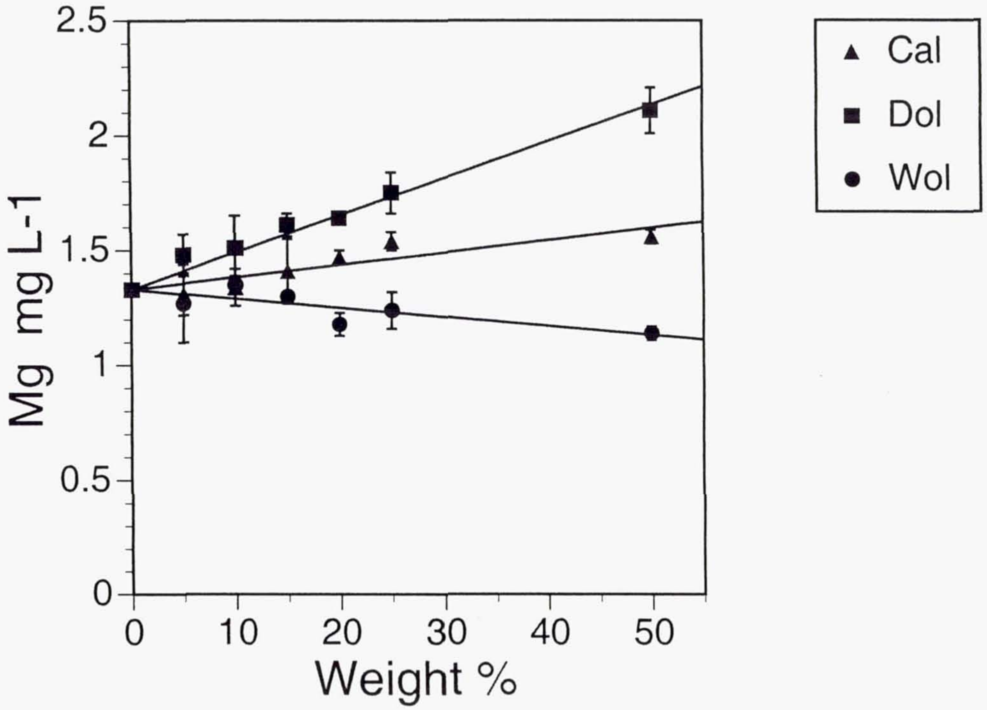

FIG. 3

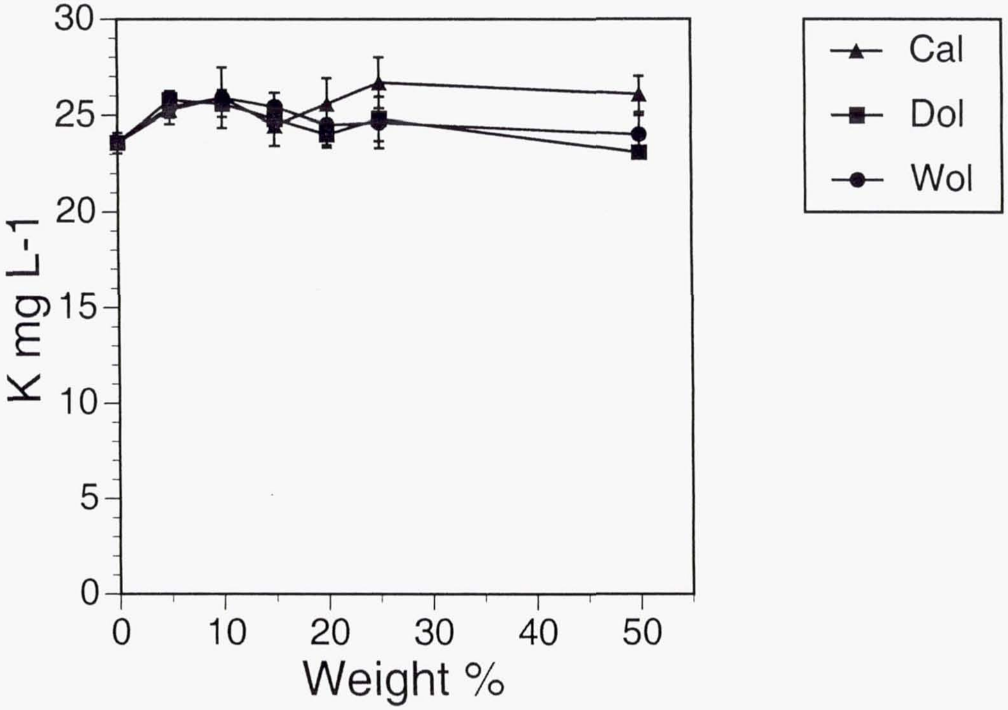

FIG. 4

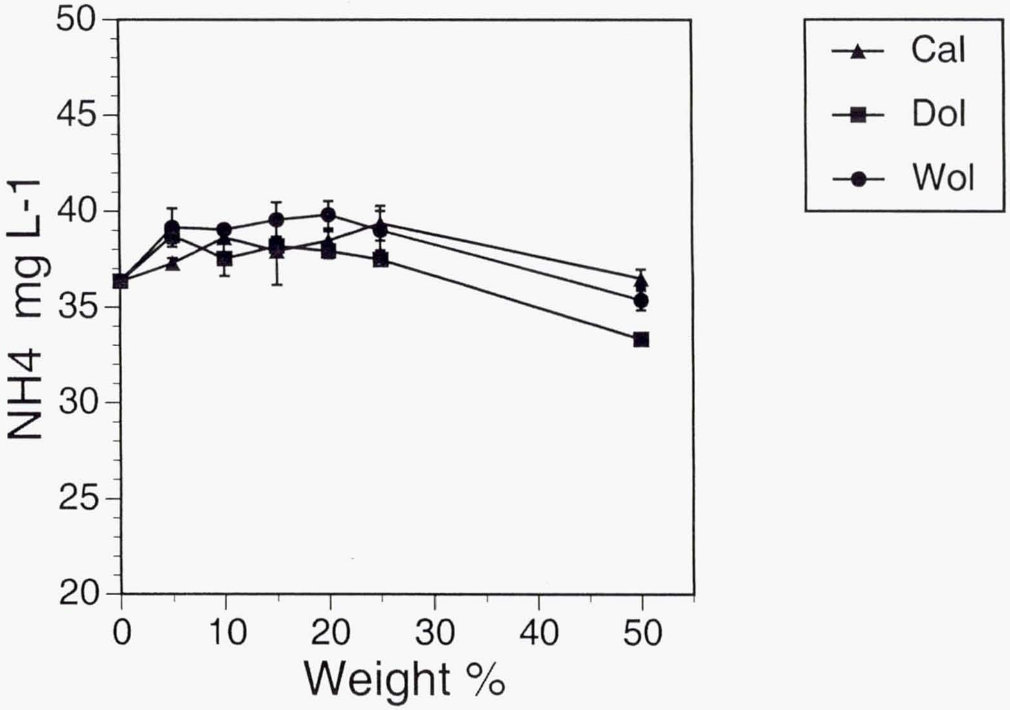

FIG. 5

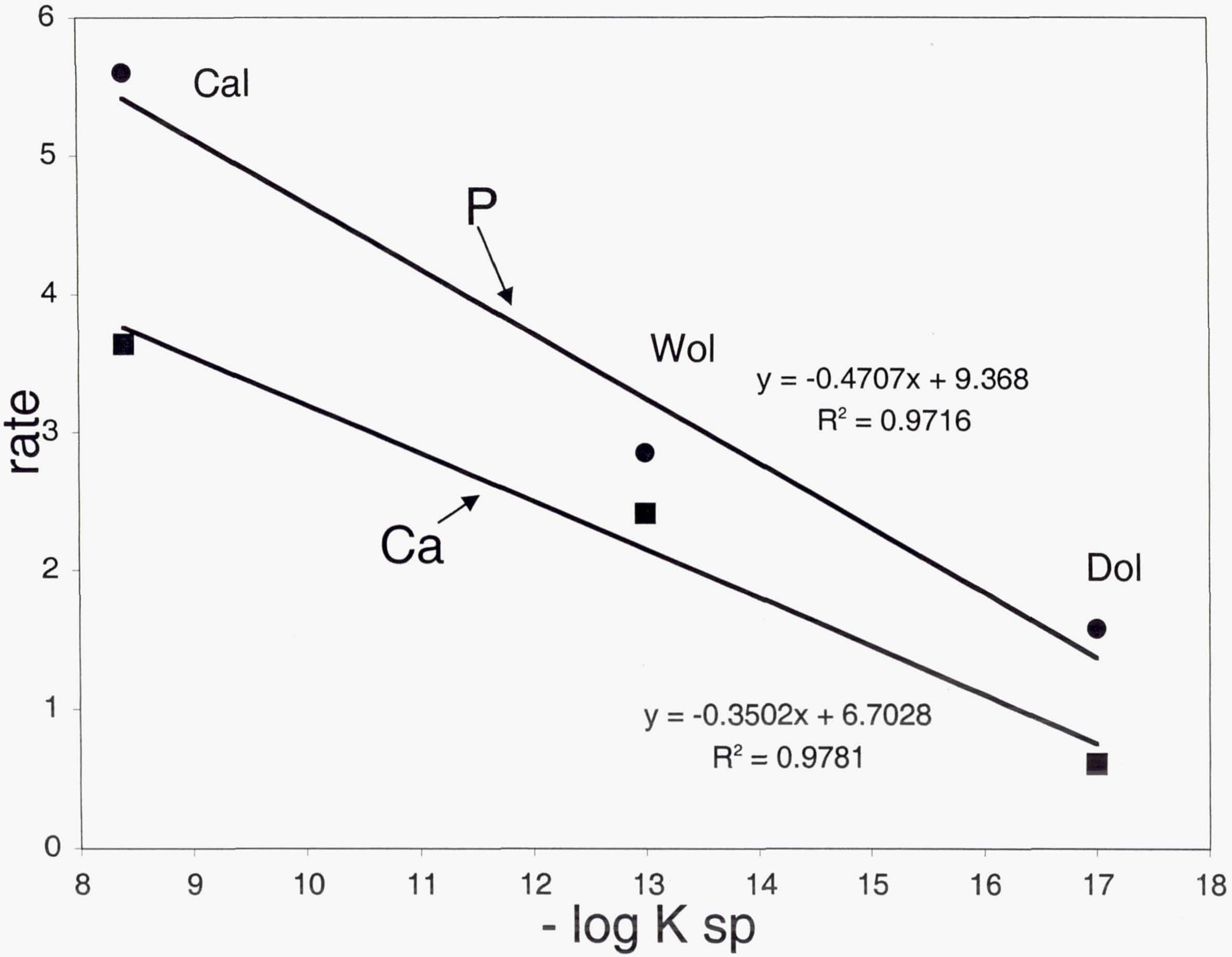
6
5
4
3
2
1
0
rate
8
9
10
11
12
13
14
15
16
17
18
- log K sp
Cal
P
Wol
Dol
Ca
y = -0.4707x + 9.368
R² = 0.9716
y = -0.3502x + 6.7028
R² = 0.9781

FIG.

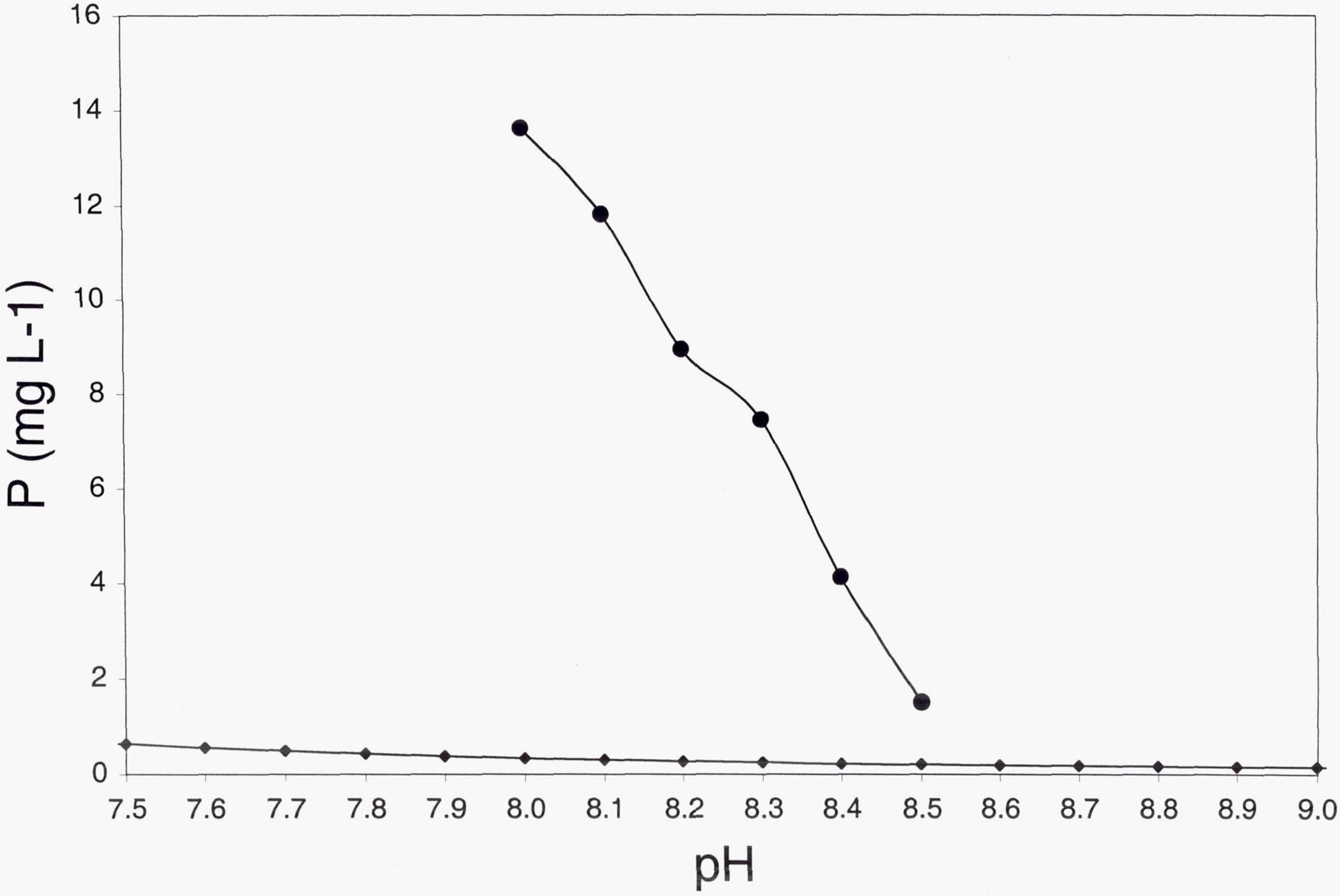
16
14
12
10
8
6
4
2
0
P (mg L-1)
7.5
7.6
7.7
7.8
7.9
8.0
8.1
8.2
8.3
8.4
8.5
8.6
8.7
8.8
8.9
9.0
pH

FIG. 7A

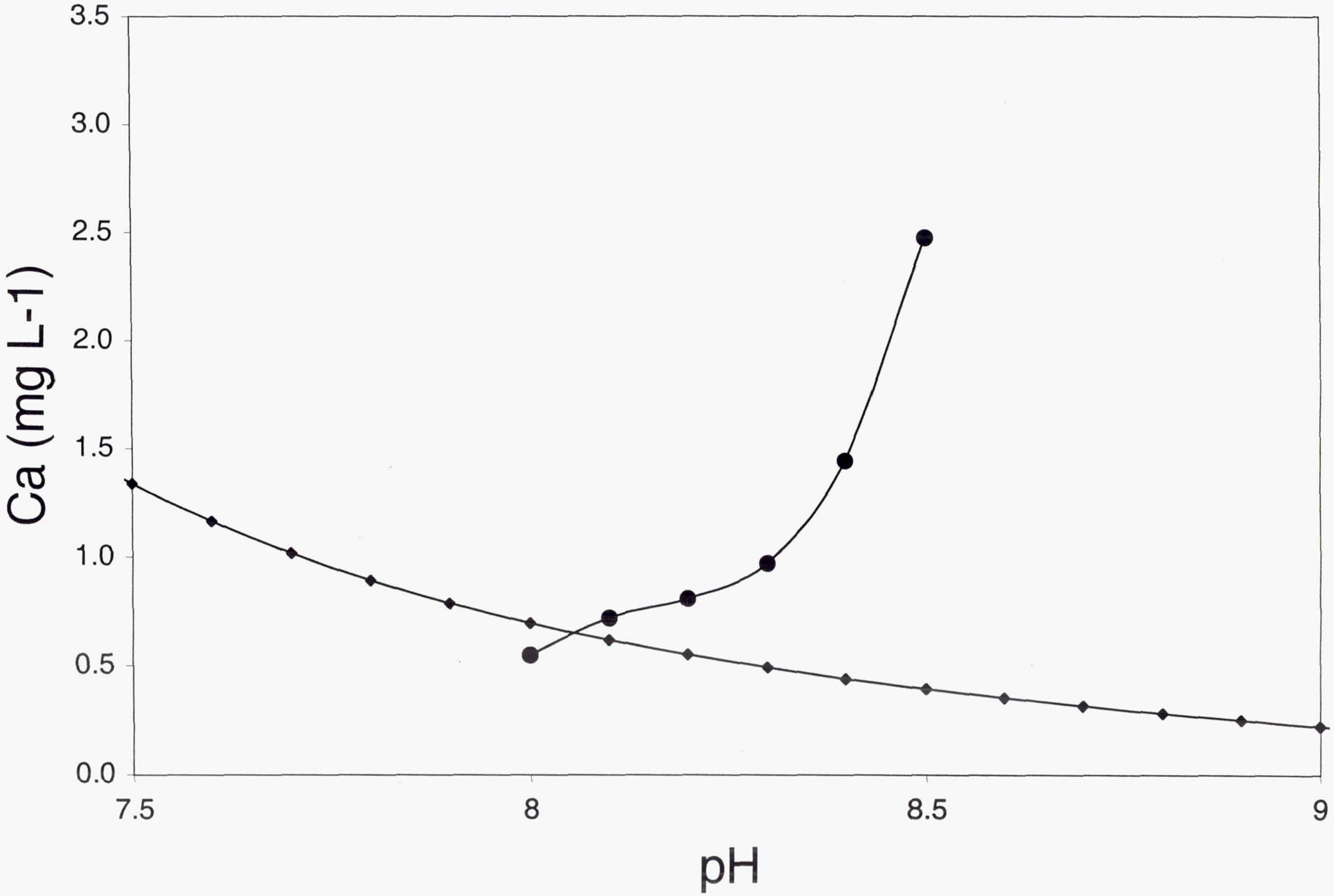

FIG. 7B