

## The influence of the amount and the origin of calcium carbonates on the isotopically exchangeable phosphate in calcareous soils

BY O. TALIBUDEEN AND P. ARAMBARRI

*Rothamsted Experimental Station, Harpenden, Herts.*

(Received 25 May 1963)

Large variations in the physical properties of limestones are reported in the literature. North (1930) quoted an eightfold increase in the crushing strength of materials going from the Chalk to the Carboniferous; the density of the limestones correspondingly increased from 2.0 to 2.5. Love & Whittaker (1954) measured by krypton adsorption the total surface areas (internal 'reactive' and 'unreactive' surface + external geometric surface) of dolomitic and 'high calcium' limestones, and of massive calcite. They found that total surface areas ranged from 0.008 to 12.85 m.<sup>2</sup>/g. from the coarsest fraction of the massive calcite to the finest fraction of a 'high calcium' limestone.

The surface reactivity of carbonates in some soils and limestones has been investigated. Boisshot, Coppenet & Hebert (1950) found that the 100–160  $\mu$  and < 75  $\mu$  fractions of a powdered marble adsorbed 0.7 and 1.6  $\mu$  moles of orthophosphate ion per g. from a  $1.4 \times 10^{-5}$  M phosphate solution, indicating a larger reactive surface on smaller particles. They also measured the phosphate adsorbed by the coarser size fractions of a calcareous soil with mean diameters from 87.5 to 1500  $\mu$ . Assuming that phosphate ions were adsorbed on the external surfaces of spherical particles, they calculated, from the CaCO<sub>3</sub> content of each size fraction, that  $0.28 \pm 0.05$   $\mu$  mole of orthophosphate ions were adsorbed per cm.<sup>2</sup> of surface of the CaCO<sub>3</sub> in the soil. Mattingly & Close (1962) found that differences in phosphate uptake between (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>- and NaNO<sub>3</sub>-treated soils were greater with Saxmundham Chalky Boulder Clays than with Rothamsted Clay. This may partly be caused by the CaCO<sub>3</sub> in the Saxmundham soil being more reactive.

In calcareous soils, chlorosis because of deficiencies of iron (Drouineau, 1942; Hagin, 1952) and other trace elements, especially manganese and zinc (Leeper, 1952), have been related to the surface reactivity of the CaCO<sub>3</sub> in the finer fractions of the soil. Methods using ammonium oxalate or oxalic acid (Drouineau, 1942; Boisshot & Hebert, 1947; Yaalon, 1957) do not measure the true surface area of the CaCO<sub>3</sub> in the soil; similar methods have been described for determining the surface reactivity

of limestones (Love & Whittaker, 1954; Elphick, 1954).

We now report an investigation of the phosphate status of soils containing different amounts of carbonates derived from underlying parent material of varying origin. An isotopic exchange method described previously (Talibudeen, 1958) was used to define the distribution of the native and added phosphate, and a method using <sup>45</sup>Ca was developed to measure the surface reactivity of the carbonate.

### MATERIALS

Soils from six arable sites containing carbonates derived from different parent materials were studied. Within each site, varying amounts of carbonates had been incorporated into the selected soils during cultivation. Single samples from five other sites with different calcareous parent materials were also chosen, four of which had between 27 and 35% CaCO<sub>3</sub>. Particulars of all the soils are in Table 1.

### EXPERIMENTAL

#### (1) Evaluation of residual phosphate by isotopic exchange method

The 'labile' phosphate was determined in all the soils by an 'isotopic exchange' procedure using <sup>32</sup>P and it was fractionated into components exchanging at different rates (Talibudeen, 1958; Arambarrri & Talibudeen, 1959). The isotopic exchangeability of the labile phosphate was defined by  $P_r/P_s$ , the ratio of the rapidly exchanging fraction,  $P_r$ , to the total labile phosphate,  $P_s$ . The first-order rate constant for the slowly exchanging labile phosphate was also calculated from the isotopic exchange data by the equation

$$R_{\text{slow}} = \frac{0.693}{t_{\frac{1}{2}}} \times \frac{P_{\text{slow}} \times P_{\text{solution}}}{P_{\text{slow}} + P_{\text{solution}}}$$

where  $P_{\text{solution}}$  is the equilibrium phosphate concentration in solution,  $P_{\text{slow}}$  is the slowly exchanging isotopically labile phosphate, and  $t_{\frac{1}{2}}$  is its half-time of exchange.

(2) *Recovery of phosphate added in laboratory incubations*

Soils, except those from site D, were treated with a solution containing 10 mg P as monocalcium phosphate, whose volume was such that the soil moisture content was about 25%. This is equivalent to a concentration of  $1.3 \times 10^{-2}$  M  $H_2PO_4$  ions per litre. The soils were incubated at 25° C. for 1, 2 and 6 months at this moisture content; after incubation they were subsampled and air-dried. The phosphate distribution in the air-dried soils was measured as before.

Previous work (Boischoit *et al.* 1950; Cole, Olsen & Scott, 1953) suggests that, at phosphate concentrations greater than  $10^{-3}$  M, dicalcium phosphate is precipitated in suspensions of calcium carbonate after a very rapid initial surface reaction. Analogous to the reaction of oxalate ions with calcium carbonate (Elphick, 1954), the amount of dicalcium phosphate precipitated is proportional to the initial surface reaction, and both surface reaction and precipitation depend on the porosity of the carbonate. The surface distribution of the added phosphate on the calcareous fraction was therefore measured by the isotopic exchangeability index,  $P_r/P_s$ , and by the percentage recovered after 6 months in the isotopically labile phosphate. The rate of exchange of the 'slow' fraction,  $R_{slow}$ , was calculated as before and compared with that of the untreated soil.

(3) *Evaluation of the total surface area of the calcium carbonate in the soil using  $^{45}Ca$* 

Isotopic exchange with  $^{45}Ca$  has been used to measure the exchangeable calcium in non-calcareous soils and clays (Rosenquist, 1954) and in apatite in bone and calcite crystals (Falkenheim, Underwood & Hodge, 1951; Dawson, 1955; Newman, 1959). Measurements on non-calcareous soils show that calcium ions in exchangeable positions in the soil exchange isotopically within a few minutes.

Little change in the specific activity of the equilibrating solution is observed after 1 hr. even in montmorillonitic soils. By contrast, isotopic exchange of ionic calcium in sparingly soluble calcium compounds like phosphates and carbonates is made up of a rapid initial exchange process, ( $t_{\frac{1}{2}} \sim$  a few minutes) and a slower exchange reaction ( $t_{\frac{1}{2}} \sim$  a few hours) similar in nature to that with the limestone: oxalic acid reaction rates (Elphick, 1954). The initial rapid exchange process involves the exchangeable calcium in the soil and the external surface of the carbonate fraction. The slower isotopic exchange is caused by the internal reactive surfaces in the calcium carbonate being slowly accessible to calcium ions. The method described below was used to measure the reactive surface of the calcium carbonate fractions in soils E-I.

*Pre-treatment of soil.* Two portions of calcareous soil were used such that each would yield approximately 10 g. of a residue after calcium carbonate was removed by acid. One portion was immersed in 50 ml. M- $CaCl_2$ ; small amounts of N-HCl, and, finally, 0.1 N-HCl, were added gradually over a week with intermittent stirring to the suspension, until its equilibrium pH was between 4 and 5 after shaking overnight. The soil was then washed free of chloride with water and then 95% alcohol, air-dried and weighed to check the complete solution of the carbonate. The ionic ratio of  $Ca^{2+}:H^+$  in the soil solution during acid treatment was  $> 10^4$ , so the soil remained fully calcium-saturated as its calcareous fraction dissolved.

*Isotopic exchange procedure.* The original soil and its acid-treated counterpart were weighed out so that each portion had approximately the same weight of the acid-treated residue. This ensured that the error in estimating the 'exchangeable' calcium was the same in both samples. Known volumes of 0.01 M- $CaCl_2$  were then added to the untreated and acid-treated soils to give a soil:solution ratio of 1:10, shaken overnight, and labelled with high specific activity  $^{45}Ca$  ( $2\mu C./100$  ml. of solution). The

Table 1. *Description of soils*

| Site | Parent material                | County            | No. of soils | CaCO <sub>3</sub> in soil (%) | Specific surface (m. <sup>2</sup> /g. of CaCO <sub>3</sub> )* | pH in 0.02-M-KCl | Total P, mg./100 g. soil (HClO <sub>4</sub> digestion) |
|------|--------------------------------|-------------------|--------------|-------------------------------|---|------------------|--|
| A    | Upper/Middle Chalk             | Herts. and Bucks. | 6            | 7-81                          | 38.1  | 7.4-8.1          | 110-188  |
| B    | Great Oolite                   | Glos.             | 6            | < 0.2-26                      | —   | 7.8-8.0          | 133-220  |
| C    | Magnesian limestone (A)        | Yorks.            | 6            | 0.7-36                        | —   | 7.7-8.0          | 52-63  |
| D    | Magnesian limestone (B)        | Yorks.            | 1            | 36                            | 35.8  | 8.0              | 90   |
| E    | Lower Lias                     | Somerset          | 6            | 0.8-30                        | —   | 7.6-7.8          | 61-99  |
| F    | Lake Marl                      | Cambs.            | 1            | 52                            | 51.0  | 7.8              | 67   |
| G    | Chalk Marl                     | Bucks.            | 1            | 34                            | 38.1  | 7.6              | 126  |
| H    | Portland limestone             | Bucks.            | 1            | 27                            | 32.7  | 7.7              | 533  |
| I    | Coral Rag and Coralline Oolite | Cambs.            | 1            | 35                            | 20.3  | 7.8              | 164  |

\* This work.

suspensions were shaken continuously and the  $^{45}\text{Ca}$  concentration in 0.5 ml. aliquots of the solution measured, with a scintillation counter, after intervals ranging from  $\frac{1}{4}$  to 24 hr. With almost all the soils, acid-treated or untreated, isotopic equilibrium was reached in reaction periods not exceeding 10 hr.; mostly, equilibrium was attained within an hour. The exchangeable calcium in the soil was calculated from the  $^{45}\text{Ca}$  activity in solution after 10–12 hr. exchange by the isotopic dilution law

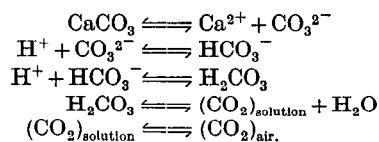
$$\begin{aligned} & \text{Isotopically exchangeable Ca}^{2+} \text{ in soil} \\ &= \frac{1 - [^{45}\text{Ca in solution}]}{[^{45}\text{Ca in solution}]} \times (\text{total Ca in solution}). \end{aligned}$$

Isotopically exchangeable calcium values from duplicate measurements did not differ by more than 5%. The isotopically exchangeable calcium per g. of calcium carbonate is given by difference.

The specific surface of the calcium carbonate in the soil can then be calculated on the basis that there is one calcium atom per  $20 \text{ \AA}^2$  on the rhombohedral cleavage faces of calcite crystals.

## RESULTS AND DISCUSSION

Differences in the reactivity of phosphates in calcareous soils can be attributed primarily to the formation of basic calcium phosphates ranging in composition from octo-calcium phosphate to apatite. Such reactivity is directly related to the rate of solution of calcium ions from the soil carbonate by the following equilibria



Assuming that none of these processes is rate-controlling, the rate of solution of calcium ions is proportional to the total surface of the carbonate. Within each group of soils, the index  $P_r/P_e$ , representing the proportion of rapidly exchanging sites, decreases with increasing carbonate content

(Table 2); this implies that  $P_r/P_e$  is inversely proportional to the total surface of the  $\text{CaCO}_3$  in the soil if the particle size distribution of the carbonate is not affected by  $\text{CaCO}_3$  content. Between groups, the decrease of the isotopic exchangeability index per unit weight of calcium carbonate in the soil varies by a factor of 4. This demonstrates the extent to which carbonates of varying origin in soils differ in their ability to retain and redistribute added soluble phosphates.

These differences, between groups of soils containing calcareous materials of different origin, can also be seen when relating the equilibrium phosphate concentration in 0.02M-KCl, as the 'intensity' factor, to the isotopically exchangeable phosphate ' $P_e$ ', the 'quantity' factor (Fig. 1). The 'capacity' of the soil to release phosphate ions, i.e. the slope of the line relating 'intensity' to 'quantity', is approximately constant within a group, despite large variations in carbonate content: but it differs between groups.

The three relationships studied (i.e.  $P_r/P_e$ :%  $\text{CaCO}_3$  in the soil, the intensity:quantity relationship, and the influence of the specific surface of the  $\text{CaCO}_3$  on  $R_{\text{slow}}$ ,  $P_r/P_e$  and the recovery of added phosphate) do not always agree. Thus the 'intensity:quantity' relationship (Fig. 1) suggests that the magnesian limestone soils in group C should isotopically exchange phosphate more rapidly than soils from group A, B and E (Cretaceous Chalk, Great Oolite, and Lower Lias). Table 2 shows that this is to some extent true for soils from groups A and B, but soils from group E exchange phosphate much more rapidly than the magnesian limestone soils.

For groups of soils containing carbonates from the Upper and Middle Chalk, enough observations on the rate of isotopic exchange were made with each soil to enable the rate constant for the slowly exchanging fraction to be calculated. This rate constant  $R_{\text{slow}}$  shows little systematic change with carbonate content especially on incubation after addition of phosphate in the laboratory (Table 3). It can thus be regarded as being specific for and

Table 2. Linear regression coefficients for the influence of carbonate contents of varying origin on the isotopic exchangeability index,  $P_r/P_e$ , and the recovery after 6 months' incubation in the isotopically exchangeable phosphate of 10 mg. P added per 100 g. soil

| Series no. | Origin of soil carbonate | Regression coefficients per g. $\text{CaCO}_3$ for |  |
|------------|--------------------------|--|--|
|            |                          | $P_r/P_e$ on carbonate content $\times 10^2$       | % recovery of added P on carbonate content |
| A          | Upper/Middle chalk       | $-0.295 \pm 0.072$                                 | $0.826 \pm 0.304$                          |
| B          | Oolitic limestone        | $-0.309 \pm 0.166$                                 | $2.376 \pm 0.854$                          |
| C          | Magnesian limestone      | $-0.519 \pm 0.074$                                 | $0.532 \pm 0.240$                          |
| E          | Lower Lias               | $-1.123 \pm 0.365$                                 | —  |

reflecting the physics and chemistry of the surfaces of the calcium carbonate in the soil. When this group of soils was treated with phosphate and incubated for 6 months in the laboratory, the rate constants were approximately doubled and could therefore be measured more precisely. Measurements of the rate constant of isotopic exchange, equilibrating the soils 1, 2 and 6 months after phosphate was added in the laboratory, showed that the soils reached equilibrium after 2 months. Table 3 shows that

variations in this rate constant between the soils with phosphate added in the laboratory is much smaller than between the untreated soils.

These observations suggest that the rate constant of the 'slow' exchange reaction will differentiate between the surface reactivity of calcium carbonates in the soil of different geological origins especially on reaching equilibrium 2 months after adding phosphate. Fig. 2 shows that the specific rate constant for the 'slow' exchange in soils D, F, G, H and I

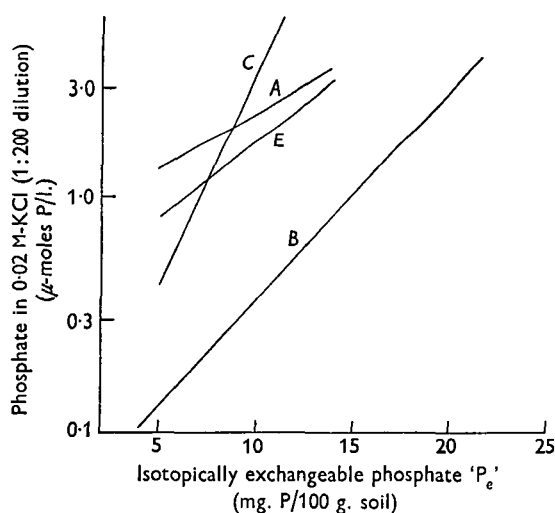


Fig. 1. The influence of the nature of carbonates in soils on the relation between the equilibrium phosphate concentration in 0.02M-KCl ('intensity') and the isotopically exchangeable phosphate ('quantity'). (Values of  $b$  for A. Upper Middle Chalk  $0.060 \pm 0.027$ ; B. Great Oolite  $0.080 \pm 0.010$ ; C. Magnesian limestone  $0.159 \pm 0.023$ ; E. Lower Lias  $0.068 \pm 0.015$ .)

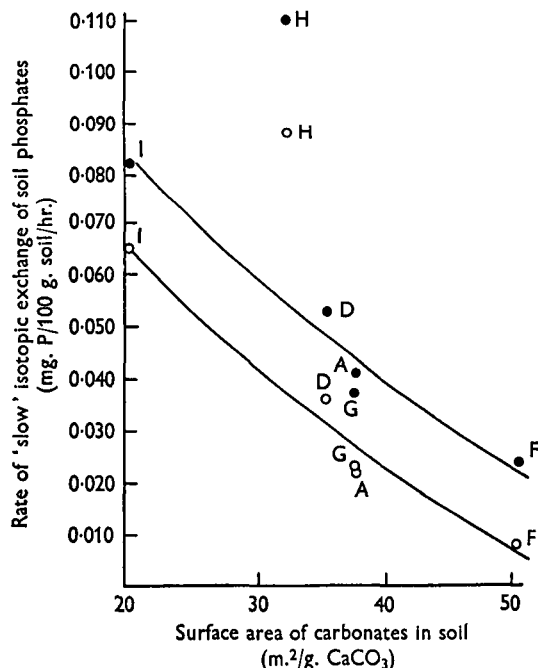


Fig. 2. The influence of the specific surface of carbonates of different geological origin in soils on the first-order rate constant of the 'slow' isotopically exchangeable soil phosphate. (○—○, untreated soil; ●—●, soil after incubating 6 months with 10 mg. P as mono-calcium-phosphate per 100 g. soil).

Table 3. The influence of phosphate treatment, after 6 months' equilibration at 20° C. and field capacity, on the rate of isotopic exchange of the 'slow' isotopically exchangeable soil phosphate

| Soil no. | CaCO <sub>3</sub> in soil (%) | Total P (mg./100 g. soil) | Rate of exchange of 'slow' fraction (mg.P/100 g. soil/hr.) |                        |
|----------|-------------------------------|---------------------------|--|------------------------|
|          |                               |                           | Untreated soil   | Phosphate-treated soil |
| A1       | 7.4                           | 122                       | 0.025  | 0.048                  |
| A2       | 23.2                          | 191                       | 0.039  | 0.046                  |
| A3       | 39.7                          | 110                       | 0.013  | 0.038                  |
| A4       | 40.6                          | 128                       | 0.010  | 0.034                  |
| A5       | 55.8                          | 188                       | 0.024  | 0.040                  |
| A6       | 80.1                          | 119                       | 0.020  | 0.040                  |
| Mean     |                               |                           | $0.0220 \pm 0.0094$  | $0.0410 \pm 0.0047$    |

and one soil from group A, with and without added phosphate, decreases approximately linearly with larger values of the specific surface of the  $\text{CaCO}_3$  in the soil. The specific surface of the  $\text{CaCO}_3$  in these soils was also inversely related to (i) the index  $P_r/P_e$ , and (ii) the recovery of phosphate added in the laboratory.

The simple relationship between the 'slow' rate of isotopic exchange and the specific surface of the calcium carbonate in the soil (Fig. 2) can be modified by the exchange adsorption of cations and of anions, because this would affect the surface chemistry of the calcium carbonate. Douglas & Walker (1950) showed that the negative electro-kinetic potential of Iceland spar is changed to increasingly positive values by small concentrations ( $\sim 10^{-3}\text{M}$ ) of cations in the series  $\text{Ca}^{2+} > \text{Ba}^{2+} > \text{Mg}^{2+} > \text{Na}^+$ , and to increasingly negative values by the anionic series  $(\text{PO}_3)^{6-} > (\text{CO}_3)^{2-}$  or  $(\text{HCO}_3)^- > \text{OH}^- > \text{Cl}^-$ . Jurinak & Bauer (1956) found that Zn ions, at equilibrium concentrations of  $\text{Zn} \sim 10^{-6}\text{M}$ , are adsorbed more strongly on dolomites than on calcite. The soil solution contains cationic Al, Fe, Mn and Zn in addition to phosphate anions in concentrations  $< 10^{-5}\text{M}$ ; these could influence considerably the surface chemistry of calcium carbonate in the soil. Thus the 'Portland limestone' soil (soil 'H', Table 1) departs considerably from the simple relationship shown in Fig. 2; it has a total phosphate content of 533 mg. P per 100 g. soil (more than 4 times the average phosphate content of the other five soils) and it exchanges phosphate isotopically much more rapidly than predicted by the ' $R_{\text{slow}}$ : surface area' relationship.

The surface areas of carbonates in soils measured by the  $^{45}\text{Ca}$ -exchange method (Table 1) suggest that the average diameter of  $\text{CaCO}_3$  crystallites in these soils is  $< 0.1\mu$ .

## SUMMARY

The kinetics of the isotopic exchange of phosphate ions in soils with and without phosphate added in the laboratory were examined in relation to the amount and origin of the  $\text{CaCO}_3$  they contained. The isotopic exchange index, ' $P_r/P_e$ ', and the recovery of added phosphate were inversely proportional to carbonate content in soils containing carbonates of similar geological origin; soils from the Lower Lias showed the biggest change in  $P_r/P_e$  with carbonate content.

In soils from the Cretaceous Chalk, the first-order rate of isotopic exchange of the 'slow' phosphate fraction was constant. It increased to a larger but constant value in the soils incubated for 6 months after adding phosphate in the laboratory. This rate constant is therefore specific to the calcium phosphates in a group of soils derived from the same calcareous parent material and with similar phosphate manuring.

A method using  $^{45}\text{Ca}$  as a radio-tracer was developed and used for measuring the specific surface of  $\text{CaCO}_3$  in soil.

The 'slow' rate constants for calcareous soils derived from different parent materials but containing similar amounts of  $\text{CaCO}_3$  were inversely proportional to the specific surfaces of their  $\text{CaCO}_3$ . The ' $P_r/P_e$ ' index and the recovery of 10 mg. P added as  $\text{Ca}(\text{H}_2\text{PO}_4)_2/100$  g. soil were also inversely related to the specific surfaces of the  $\text{CaCO}_3$ .

We thank B. W. Avery and others in the Soil Survey of England and Wales for soil samples, Margaret Chater for analytical help and J. H. A. Dunwoody for statistical analyses. One of us (P. A.) received a grant from the Ramsay Memorial Fellowships Trust from 1957-59.

## REFERENCES

- ARAMBARRI, P. & TALIBUDEEN, O. (1959). *Plant & Soil*, **11**, 343.
- BOISCHOT, P., COPPENET, M. & HEBERT, J. (1950). *Plant & Soil*, **2**, 311.
- BOISCHOT, P. & HEBERT, J. (1947). *Ann. Agron.* **17**, 521.
- COLE, C. V., OLSEN, S. R. & SCOTT, C. O. (1953). *Soil Sci. Soc. Amer. Proc.* **17**, 352.
- DAWSON, K. B. (1955). *Biochem. J.* **60**, 389.
- DOUGLAS, H. W. & WALKER, R. A. (1950). *Trans. Faraday Soc.* **46**, 559.
- DROUINEAU, G. (1942). *Ann. Agron.* **12**, 441.
- ELPHICK, B. L. (1954). *N.Z. J. Sci. Tech.* **36A**, 137.
- FALKENHEIM, M., UNDERWOOD, E. & HODGE, H. (1951). *J. Biol. Chem.* **188**, 805.
- HAGIN, J. (1952). *Bull. Res. Council. Israel*, **2**, 138.
- JURINAK, J. J. & BAUER, N. (1956). *Soil Sci. Soc. Amer. Proc.* **20**, 466.
- LEEPER, G. W. (1952). *Ann. Rev. Plant Physiol.* **3**, 1.
- LOVE, K. S. & WHITTAKER, C. W. (1954). *J. Agric. Fd Chem.* **2**, 1268.
- MATTINGLY, G. E. G. & CLOSE, B. (1962). *Rep. Rothamst. Exp. Sta. for 1961*, p. 53.
- NEWMAN, A. C. D. (1959). *Rep. Rothamst. Exp. Sta. for 1958*, p. 50.
- NORTH, F. J. (1930). *Limestones, their Origins, Distribution and Uses*. London: Thomas Murby.
- ROSENQUIST, I. T. (1954). *Proc. 2nd Radioisotope Conference, Oxford*, vol. 1, 412. London: Butterworths.
- TALIBUDEEN, O. (1958). *J. Soil Sci.* **9**, 120.
- YAALON, D. H. (1957). *Plant & Soil*, **8**, 275.