

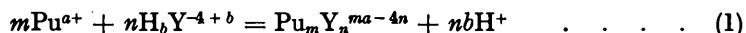
331. *The Nature and Stability of the Complex Ions formed by Ter-, Quadri-, and Sexavalent Plutonium Ions with Ethylenediaminetetraacetic Acid. Part I. pH Titrations and Ion-exchange Studies.*

By J. K. FOREMAN and T. D. SMITH.

Potentiometric pH titrations and cation-exchange studies have shown that plutonium(III), plutonium(IV), and plutonyl ions form 1 : 1 chelates with ethylenediaminetetraacetic acid (edta). In the first two cases complexes containing two atoms of plutonium to one molecule of edta are also formed. The stability constants for the 1 : 1 complexes of the three ions have been determined by a cation-exchange technique; the values of $\log K$ are: plutonium(III), 18.12; plutonium(IV), 17.66; plutonyl, 16.39.

The value for the plutonium(IV) chelate relates to a hydrolysed species of the ion.

THE properties of complex ions formed by the reaction of metal ions with chelating agents of the amino-carboxylic acid type in general, and ethylenediaminetetraacetic acid (edta) in particular, have been studied by a variety of techniques, notably potentiometric pH titration,^{1,2,3} oxidation-reduction titration,⁴ polarography,^{3,5} electrode-potential measurements,^{6,7} spectrophotometry,^{8,9,10} reaction rate kinetics,^{11,12} and methods based on solubility, solvent extraction, etc.^{13,14} The nature of the component ions and the stability of the resulting complex largely determined the most appropriate method of examination. The tetrabasic edta being denoted as H_4Y , its general reaction with plutonium ions over the pH range in which chelation can occur may be written



and the stability constant of the chelate is then given by

$$K_c = [Pu_mY_n^{ma-4n}]/[Pu^{a+}]^m[Y^{4-}]^n \quad . \quad . \quad . \quad (2)$$

The evaluation of the term $[Y^{4-}]$ requires a knowledge of the ionisation constants of edta; these have been determined by a number of workers.^{1, 15, 16}

This paper is concerned with the assignment of values to m , n , and K_c for the edta chelates of the ions of ter-, quadri- and sexavalent plutonium. The formulæ of the complexes were derived from potentiometric pH titration of the hydrogen ions liberated on chelation according to equation (1).

The stability constants of the edta chelates of plutonium(III) and plutonium(IV) are likely to be high as judged purely from ionic charge density considerations and, in the case of plutonium(III), from the reported³ high stabilities of the corresponding complexes of the formally analogous rare-earth metal ions. Hence, unless a competitive complex-forming technique of the type described by Schwarzenbach and Freitag² is employed, these stability constants cannot be accurately evaluated from pH titration curves by the

¹ Schwarzenbach and Ackermann, *Helv. Chim. Acta*, 1947, **30**, 1798.

² Schwarzenbach and Freitag, *ibid.*, 1951, **34**, 1503.

³ Wheelwright, Spedding, and Schwarzenbach, *J. Amer. Chem. Soc.*, 1953, **75**, 4196.

⁴ Schwarzenbach and Heller, *Helv. Chim. Acta*, 1951, **34**, 576.

⁵ Kolthoff and Auerbach, *J. Amer. Chem. Soc.*, 1952, **74**, 1452.

⁶ Bjerrum and Nielsen, *Acta Chem. Scand.*, 1948, **2**, 297.

⁷ MacNevin and Krieger, *J. Amer. Chem. Soc.*, 1955, **77**, 6149.

⁸ Plumb, Martell, and Bersworth, *J. Phys. Colloid Chem.*, 1950, **54**, 1208.

⁹ Martell and Plumb, *J. Phys. Chem.*, 1952, **56**, 993.

¹⁰ Hughes and Martell, *ibid.*, 1953, **57**, 694.

¹¹ Jones and Long, *ibid.*, 1952, **56**, 25.

¹² Cook and Long, *J. Amer. Chem. Soc.*, 1951, **73**, 4119.

¹³ Irving and Williams, Proc. Internat. Analyt. Congress, Oxford, 1952, p. 257.

¹⁴ Irving and Williams, *Nature*, 1948, **162**, 764.

¹⁵ Carini and Martell, *J. Amer. Chem. Soc.*, 1952, **74**, 5745.

¹⁶ Cabell, Atomic Energy Research Establishment Report A.E.R.E. C/R.813.

familiar Bjerrum¹⁷ method. Accordingly, they have been determined by the cation-exchange procedure developed initially by Schubert,^{18,19,20} which can be applied both when the resulting complex is a cation and is itself adsorbed by the cation-exchange resin,^{21,22} and when the complex is neutral or anionic and does not undergo exchange. In the latter instance, provided the cation concentration is negligible compared with that of the chelating agent, the simple equation derived by Schubert may be applied in the form :

$$\log (\lambda_0/\lambda - 1) = \log K_c + x \log [Y^{4-}] \dots \dots \dots (3)$$

where λ_0 and λ are the ion-exchange distribution coefficients respectively in the absence and the presence of a large excess of edta, and x is the number of edta ions bound per atom of plutonium. It will be shown from the pH titration curves that, for any excess of edta over plutonium, $x = 1$; hence the edta chelates of the three plutonium ions under consideration are anionic and equation (3) may be used to evaluate K_c .

EXPERIMENTAL

pH Titrations.—The technique employed was essentially similar to that of Cabell¹⁶ for studying the reactions of uranyl and thorium ions with complexones. The titration apparatus comprised a 200 ml. beaker fitted with a rubber bung carrying the electrodes (glass and saturated calomel), a burette, stirrer, and inlet and outlet tubes for passage of nitrogen. The titrations were carried out by mixing solutions of plutonium and the dipotassium salt of edta in the required stoichiometric proportions in constant ionic strength of 0.1N-potassium chloride and titrating against 0.05N-potassium hydroxide with use of an Electronic Instruments Direct Recording pH meter, all operations being performed in an atmosphere of nitrogen and at room temperature ($20^\circ \pm 0.5^\circ$). The edta used in preparing the dipotassium salt was purified by Blaedel and Knight's method.²³

Plutonium(III) solutions were prepared by dissolving the metal in 5N-hydrochloric acid. To remove the free hydrochloric acid without hydrolysing the plutonium trichloride the required volume was introduced into the titration vessel and evaporated to dryness in a current of nitrogen before addition of the chelating agent. Plutonium(IV) solutions were made by dissolving the hydroxide in 8N-nitric acid. Removal of excess of nitric acid in a stream of nitrogen led to erratic results, and consequently all titration curves were corrected for this free acidity which was determined by titration with sodium hydroxide after precipitation of the plutonium as ferrocyanide. Plutonium(VI) solutions were prepared by anodic oxidation of plutonium(IV) in dilute nitric acid, and their pH was adjusted to that of the dipotassium edta solution before titration. All plutonium(VI) solutions used were shown chromatographically²⁴ to contain less than 1% of plutonium(IV).

Ion-exchange Studies.—The pH dependence of the term $[Y^{4-}]$ introduces a similar dependence in the extent of chelate formation, and in order to carry out determinations over a wide range of $[Y^{4-}]$ values it is necessary to select a pH at which reasonable values of λ_0 and λ [equation (3)] are obtained over this range. Preliminary experiments indicated that pH 3.30 fulfilled this requirement. Strict control of pH throughout the experiments is essential; the use of buffer solutions for this purpose was not favoured since it introduced a (possibly unknown) correction for the competitive complex-formation by the weak acid anion of the buffer. Instead, unbuffered media were used and extreme care taken to condition the resin to pH 3.30 before use.

All solutions were made up in 0.1N-potassium chloride solution and were about $10^{-7}M$ in plutonium. The concentration range of chelating agent studied was $10^{-6}M$ to $10^{-4}M$. 20 ml. of each solution were shaken mechanically for 12 hr. with 0.2 g. of 60–80-mesh Amberlite IR 120 cation-exchange resin conditioned with 0.1N-potassium chloride at pH 3.30, and the plutonium concentration in the solution was determined before and after equilibration by α -particle

¹⁷ Bjerrum, "Metal Ammine Formation in Aqueous Solution," P. Haase and Son, Copenhagen, 1941.

¹⁸ Schubert, *J. Phys. Colloid Chem.*, 1948, **52**, 340.

¹⁹ Schubert and Richter, *ibid.*, p. 352.

²⁰ Schubert and Richter, *J. Amer. Chem. Soc.*, 1948, **70**, 4259.

²¹ Fronaeus, *Acta Chem Scand.*, 1951, **5**, 389.

²² Carleson and Irving, *J.*, 1954, 4390.

²³ Blaedel and Knight, *Analyt. Chem.*, 1954, **26**, 741.

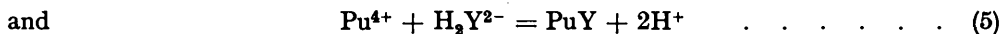
²⁴ Cowan and Foreman, *Chem. and Ind.*, 1954, 1583.

counting. Temperature variations were less than $\pm 0.2^\circ$ and occasional checks failed to reveal changes of greater than 0.01 pH unit.

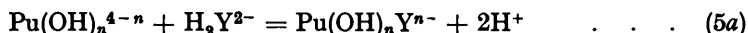
The plutonium(III) solutions were made up in the presence of 0.003M-hydroxylamine hydrochloride and passed through a silver reductor immediately before use as a precaution against the oxidation of plutonium(III) to plutonium(IV) which is thermodynamically possible at pH 3.30.²⁵ In the case of plutonium(IV) a direct determination at this pH of λ_0 in the absence of edta is impossible owing to hydrolysis of the Pu^{4+} ion;²⁶ λ_0 was therefore calculated by solving equation (3) from pairs of edta concentrations. To minimise effects due to the hydrolysis of the Pu^{4+} ion in the chelation studies the plutonium(IV) was added to the edta-containing solution in a very small volume (0.01 ml.) of 1N-nitric acid, and any small pH adjustment made subsequently.

RESULTS AND DISCUSSION

pH Titrations.—(a) *Plutonium (III) and plutonium(IV).* Figs. 1 and 2 show the titration curves for plutonium(III) and plutonium(IV); in each, the mole ratio of edta to plutonium was varied from 0.5 to 4. The curves for both ions are very similar and in no case did any precipitation occur up to the highest pH values recorded. Curves C, D, and E demonstrate that the only inflexion which occurs is at pH 4 approximately where two moles of alkali per mole of plutonium have been added, which corresponds to the formation of 1 : 1 chelates according to the equations

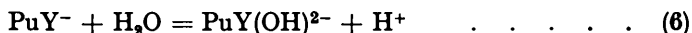


The latter equation should more strictly be represented as



to allow for the hydrolysis of the plutonium(IV) ion.

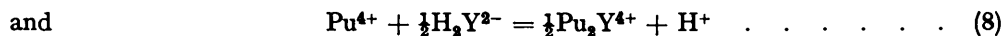
The inflexion is complete at about pH 5, though clearly the chelates can exist, at least partially, at considerably lower pH values, the lower limit for complex formation being governed directly by the stability of the appropriate complexes. Above pH 5 the titration curves rise less steeply than predicted theoretically, and this is presumably due to the liberation of further quantities of hydrogen ion by hydrolysis of the complexes. This can be most simply represented in stages such as



and similarly for plutonium(IV).

The addition of a second ligand through the partially dissociated species of edta does not occur when excess of chelating agent is present. At the higher pH values the curves are adequately represented by the third neutralisation of the excess of edta, except that the neutralisation point is shifted to larger titres by the hydrolysis of the complex. However, the addition of Y^{4-} ions to the complex at high pH cannot be ruled out since no hydrogen ion is involved and the titration curve would be unaffected.

The absence of precipitation in the titration of the solution containing a twofold excess of plutonium to edta (Curve B, Figs. 1 and 2) indicates the formation of stable complexes. These complexes are of the type Pu_2Y , since titrations carried out with larger excesses of plutonium to edta yielded hydroxide precipitates. Formation of stable complexes according the equations [which neglect hydrolysis of plutonium(IV)]



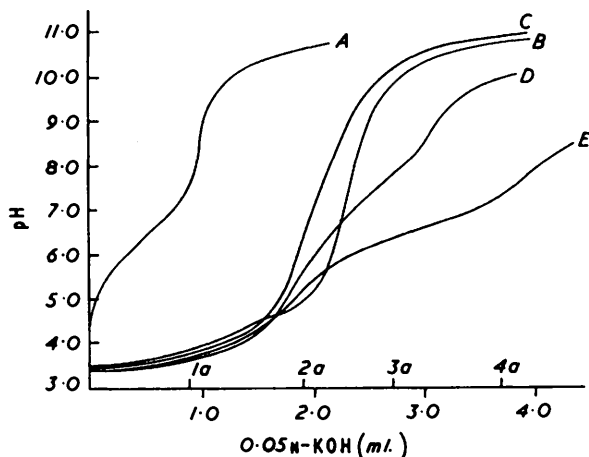
should lead to inflexions at the addition of one mole of alkali per mole of plutonium, and it must be assumed that hydrolysis of the complexes to $\text{Pu}_2\text{Y}(\text{OH})_2$ and $\text{Pu}_2\text{Y}(\text{OH})_2^{2+}$ occurs

²⁵ "The Transuranium Elements" (Ed. Seaborg, Katz, and Manning), National Nuclear Energy Series, IV-14B, Part 1, McGraw-Hill, London, 1949, p. 253.

²⁶ Kraus and Nelson, *J. Amer. Chem. Soc.*, 1950, **72**, 3901.

at low pH in order to account for the observed inflexion at two moles of alkali per mole of plutonium. The existence of Pu_2Y -type complexes for plutonium(III) and plutonium(IV) accords with Cabell's observation¹⁶ of the formation of similar complexes of thorium and uranium(VI), the latter being unstable. Schwarzenbach, Ackermann, and Ruckstuhl²⁷ have noted similar species, and measured the relevant equilibrium constants, between calcium and magnesium ions and 1 : 3- and 1 : 4-diaminocyclohexane- $\text{NNN}'\text{N}'$ -tetra-acetic acid.

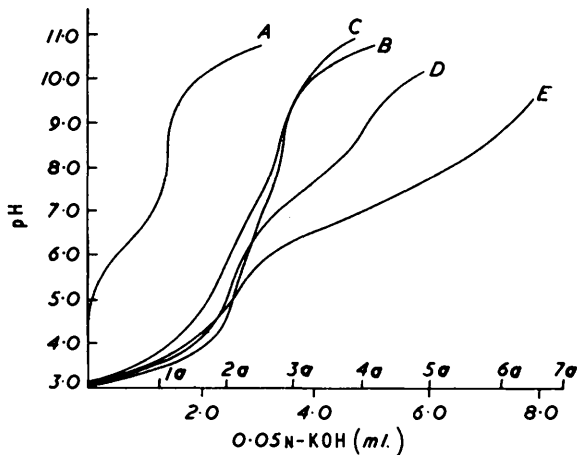
FIG. 1. pH Titration of the plutonium(III)-edta system.



Ratio $\text{Pu} : \text{H}_2\text{Y}^{2-}$ A, 0 : 1; B, 1 : 0.5; C, 1 : 1; D, 1 : 2; E, 1 : 4.

The numerals followed by *a* in this and other Figures give the number of equivalents of alkali per mole of plutonium.

FIG. 2. pH Titrations of the plutonium(IV)-edta system (key as in Fig. 1).



Above a pH of about 3.5 the edta complexes of plutonium(III) are thermodynamically unstable with respect to those of plutonium(IV), since then plutonium(III) is oxidised by water to plutonium(IV).²⁵ Uncomplexed plutonium(III) becomes oxidised to plutonium(IV) and can undergo exchange with complexed plutonium(III) ions. The extent of this interconversion will depend upon the rate of exchange between free and complexed plutonium ions, and upon the concentration of free plutonium ions. The former quantity may not be negligible since the complexes are essentially ionic, but the latter is extremely

²⁷ Schwarzenbach, Ackermann, and Ruckstuhl, *Helv. Chim. Acta*, 1949, **32**, 1175.

small and ever decreasing above pH 3.5 on account of the high stability of the complexes. In addition, it is probable that the plutonium(IV) content of the uncomplexed plutonium at such pH values would be appreciably colloidal as a result of hydrolysis.²⁶ Thus the overall interconversion process is likely to be a slow one, and this is qualitatively verified by the colour differences in solutions of the plutonium(III) and plutonium(IV) chelates on completion of the potentiometric titrations.

Plutonium(VI). The titration curves for the plutonium(VI)-edta system are reproduced in Fig. 3. In these titrations no precipitation occurred up to the maximum pH values studied, indicating the presence of a stable 1:1 complex. In the case of the uranyl ion Cabell¹⁶ finds a complex UO_2HY^+ which is unstable, precipitation occurring in the region of pH 8. This difference may be attributed to the much reduced tendency for the plutonyl than for the uranyl ion to undergo hydrolysis.

There appear to be no stable plutonyl-edta chelates containing more than one molar equivalent of plutonium to edta, since titrations performed with solutions containing an excess of plutonium yielded indefinite curves and a plutonate precipitate at pH 10 approximately.

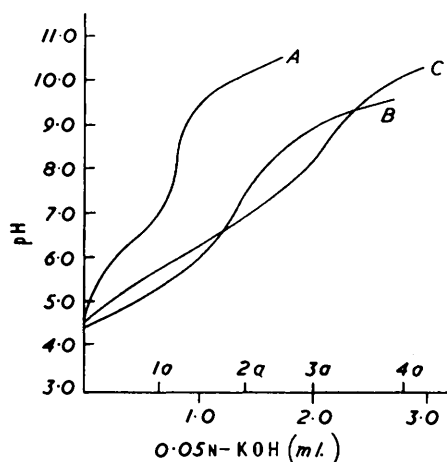


FIG. 3. pH Titrations of the plutonium(VI)-edta system.

Ratio Pu(VI) : H_4Y^{4-} ... A, 0 : 1; B, 1 : 1; C, 1 : 2.

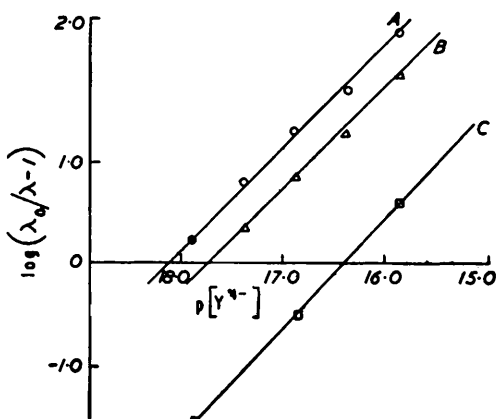


FIG. 4.

A, Pu(III)-edta. B, Pu(IV)-edta. C, Pu(VI)-edta.

Ion-exchange results. The plots of $\log(\lambda_0/\lambda - 1)$ against $\log[Y^{4-}]$ are shown in Fig. 4. It is evident from the slopes that the complexes are of the 1:1 type in each instance, and the $\log K_c$ values are 18.12, 17.66, and 16.39, respectively, for plutonium-(III), -(IV), and -(VI). It is unlikely that these values are in error by more than $\pm 3\%$ except in the case of plutonium(IV), where the calculated values for λ_0 showed an overall spread of about 10% and the total error in $\log K_c$ could be $\pm 5\%$.

The Stability Constants.—In attempting to correlate the measured stability constants for the plutonium chelates of edta with those reported for other elements it must be remembered that the stability constant is not itself a fundamental quantity, but is related to the entropy and enthalpy of the system. For thermodynamic stability constants the relation assumes the familiar form

$$-RT \ln K_a = \Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad \dots \quad (9)$$

For chelates of high stability the entropy term becomes predominant, as demonstrated by Carini and Martell²⁸ and by Charles.²⁹ Of the factors contributing to the increase in

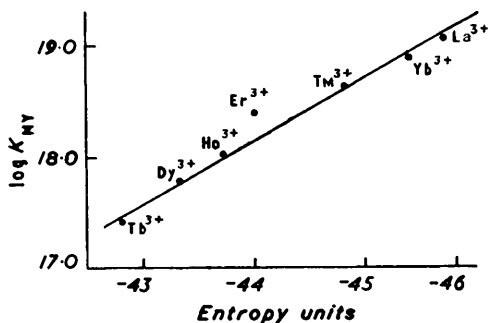
²⁸ Carini and Martell, *J. Amer. Chem. Soc.*, 1954, **76**, 2153.

²⁹ Charles, *ibid.*, p. 5854.

entropy on chelate formation the most important is the increase in the number of particles in the system arising from the release of water molecules from the hydrated cation to the bulk solution. This entropy increase, shown to be 16.7 e.u. per water molecule,³⁰ can therefore be considerable in the formation of edta chelates assuming that one water molecule is released for each bond formed by the ligand, though it is partially offset by the entropy decrease, calculated by Cobble³¹ to be 14 e.u. for each ring formed. Where similar elements form chelates of high stability with a particular ligand the value of the partial molal entropy of the ions concerned should provide a relative guide to the stability constants of the chelates. The rare-earth elements, and possibly the actinides, are probably the only series of ions having the required degree of similarity in charge and radius necessary to maintain the entropy and enthalpy changes on chelate formation sufficiently constant to test this approach. Fig. 5 shows the plot of $\log K$ for the edta chelates against partial molal entropy of the lanthanide ions above gadolinium, where the chelates are considered³ to be isostructural. The graph is reasonably linear in view of experimental errors involved in determination of the stability constants and some uncertainty regarding the values of the ionic radii used in evaluating the partial molal entropies.³

Apart from the value reported above for plutonium(III), no data are available for the edta chelates of the actinide elements. However, from the similarity in charge and

FIG. 5. Stability constant-entropy relation for reaction $M^{3+} + Y^{4-} \rightleftharpoons MY^{1-}$



entropy between elements in the two series it seems unlikely that the $\log K$ values for the edta chelates of the actinides will be much displaced from those of the corresponding lanthanides, and the experimental value for plutonium(III) supports this view. Whilst such correlations hold strictly only for thermodynamic stability constants, it is apparent from the work of Martell and Carini²⁸ that errors introduced in using concentration stability constants are small provided that these are determined at fairly low ionic strength.

The partial molal entropy of the Pu^{4+} ion (-87 e.u.)³² is more negative than the values for Fe^{3+} (-70.1 e.u.)³² and Cr^{3+} (-73.5 e.u.)³² both of which form very stable complexes with edta, e.g., $\log K = 25.0$ for the iron(III) complex. This, together with the analogous case of thorium ($\log K = 23.2$),³³ suggests that the $\log K$ value of 17.7 for plutonium(IV) is anomalously low. However, at pH 3.30, at which the determinations were performed, hydrolytic effects will be such that the concentration of Pu^{4+} will be negligible and the major species present will be the first hydrolysis product $Pu(OH)^{3+}$. The experimental conditions are, in fact, sufficient to permit further hydrolysis to the irreversible stages of the mechanism, but it would appear from the experimental results that the presence of the chelating agent, together with the hydrolysis-minimising method of introducing the plutonium(IV) into the system, has largely prevented this. Whilst the partial molal entropy of the ion $Pu(OH)^{3+}$ is not recorded, this property is very similar for the ions U^{3+} and $U(OH)^{3+}$,³² and the value for Pu^{3+} being taken as a first approximation for that of

³⁰ Latimer, "Oxidation Potentials," 2nd Ed., Prentice-Hall, New York, 1952, p. 39.

³¹ Cobble, *J. Chem. Phys.*, 1953, **21**, 1451.

³² *Op. cit.*, ref. 30, p. 298.

³³ Schwarzenbach, *Analyst*, 1955, **80**, 713.

$\text{Pu}(\text{OH})^{3+}$, the similar observed stability constants for the edta chelates of plutonium(III) and plutonium(IV) at pH 3.30 may be understood.

Experimental confirmation that at pH 3.30 the plutonium(IV) chelate should be formulated as a negatively charged species, say $\text{PuY}(\text{OH})^-$, rather than PuY , is forthcoming from the appreciable adsorption of the chelate at this pH on the anion-exchange resin Amberlite IRA-400. This behaviour is consistent with the hydrolysis of the Pu^{4+} ion, rather than formation of the complex PuY and its subsequent hydrolysis, since from the pH titration curves the latter effect is negligible at pH 3.30. Again, spectrophotometric examination of the plutonium(IV)-edta system in 1N-nitric acid indicates a log K of about 24.2 for the unhydrolysed Pu^{4+} ion chelate.³⁴

The relatively high stability of the plutonyl chelate of edta contrasts markedly with that of the uranyl ion which forms only a very weak complex. Hydrolysis and polymerisation of the uranyl ion³⁵ at low pH to give ions of charge density too low for stable chelate formation account for this difference.

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WINDSCALE WORKS, SELLAFIELD, CUMBERLAND.

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³⁴ Foreman and Smith, Part II, following paper.

³⁵ Sutton, *J.*, 1949, S 275.
