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TB11: Speculation on Recovery of Rubidium–86 from Clays

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SPECULATION ON RECOVERY OF
RUBIDIUM–86 FROM CLAYS

Harold W. Gausman and David C. Frost

Pilot investigations on the retention of \( \text{NH}_4^+ \) by soils indicated that the dominant clay mineral in a Merrimac sandy loam soil did not collapse from 14 Å to 10 Å on saturation with K\(^+\).\(^2\)^ Following a suggestion by Walsh and Murdock that organic matter could occupy space between 2:1 lattice-type clay minerals, a concurring premise was advanced that aside from possible interstratification with mica-vermiculitic materials, interlayer materials were present in the clay of the Merrimac soil.\(^4\) It was speculated that the interlayer organic matter might interfere with the collapse of the clay mineral and \( \text{NH}_4^+ \) or K\(^+\) fixation would be correspondingly decreased. Hanway et al. in 1955 indicated ample evidence for a reciprocity between K\(^+\) and \( \text{NH}_4^+ \) in fixation by clay minerals.\(^5\) Lattice distortions of organic-clay complexes have also been investigated by Weiss and Brunton et al.\(^6\)

Clay fractions were obtained by sedimentation from Merrimac sandy loam and Suffield clay loam soils using Stoke’s law.\(^7\) Water was evaporated from resulting clay suspensions at temperatures of 100° C. Clays of both soils were identified as predominantly vermiculite or interstratified vermiculite.\(^3\) Nine to one ratios of washed, fine-sea sand to respective clays were prepared. Twenty-five g. samples were mixed with 20 ml. of deionized water to form a slurry. Excessive amounts of finely-ground, potato-plant tissue (0.23 g.) and \( \text{NH}_4\text{Cl} \) (1.2 g.) were added to some slurries, stirred frequently, and allowed to equilibrate 24 hours. \( \text{Rb}^{86} \) was then added, 10uc/ml, followed by stirring intermittently for one hour, then incubation for 50 hours at room temperature. Control slurries consisted of those which received no imposed treatment and those which received only \( \text{Rb}^{86} \). Procedures of Dharival and Stevenson for the determination of fixed \( \text{NH}_4^+ \) were used to partition \( \text{Rb}^{86} \) into

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1 Professor of Soil Chemistry and Research Graduate Assistant, respectively.
three fractions: first, water soluble; secondly, “adsorbed” fraction—sim­mered on hot plate for six hours with 1 N KOH; and thirdly, “fixed” or interlattice—treated with HF solution for 12 to 16 hours with occasional stirring. Radioassays were made at the 5% error rate on two aliquots of respective filtrates from duplicate samples.

Results shown in table 1 indicate that the clay minerals from both soils generally responded the same to treatment. In the water-soluble fraction, pretreatment with NH$_4^+$ as NH$_4$Cl apparently partially satu­rated the exchange sites and resulted in the largest recovery of Rb$^{86}$. The addition of plant material to the Suffield clay but not the Merrimac clay slurries resulted in a higher percentage of recovery of water soluble Rb$^{86}$ compared with those which received no treatment with plant ma­terial prior to the addition of Rb$^{86}$. Theoretically, amorphous coatings of plant material may have blocked some exchange sites on the Suffield clay which could have been occupied by Rb$^{86}$; or conversely, it might be argued that pretreatment with plant material could have increased the cation exchange capacity. With the Merrimac soil, the recovery of “adsorbed” Rb$^{86}$ was highest for the sedimented clay minerals when plant material was added prior to Rb$^{86}$ which would tend to substantiate the theory of increased cation exchange. In refutation, however, re­coveries of “adsorbed” Rb$^{86}$ from the Suffield clay were essentially alike for no pretreatment and for pretreatment with plant material. Most significantly, the addition of plant material appeared to reduce the inter­lattice amounts of Rb$^{86}$ in the filtrate of the fraction treated with HF solution. As noted, for example, in table 1, the Suffield clay had an Rb$^{86}$ recovery rate of 14.8% when plant material was added; whereas, the rate was 29.2% when only Rb$^{86}$ was used. The same trend occurred with the Merrimac clay. The lowest recovery of “fixed” Rb$^{86}$ was pres­ent when clays were pretreated with NH$_4$Cl. Ammonium ions might be expected to collapse the lattice structure of the clays thus blocking the entry of Rb$^{86}$. It also seems apparent that the Merrimac clay “fixed” more Rb$^{86}$, 46.9%, than the Suffield clay, 29.2%. This might indicate that the interstratification of their minerals differed and the lattice struc­ture of the Merrimac clay was collapsed to a greater extent by Rb$^{86}$ than the Suffield clay. From a practical viewpoint, one might, there­fore, expect the Merrimac clay to fix more NH$_4^+$ than the Suffield clay.

Since the valences of NH$_4^+$ and Rb$^{86}$ are alike and their ionic radii are essentially the same, 1.4 to 1.5 Angstroms, it might be assumed that Rb$^{86}$ could be used to evaluate the retention of NH$_4^+$ and K$^+$ by clay minerals or soils. Thence it is interesting to speculate and con-

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elude analogously that pretreatment of clay slurries with plant material resulted in interlayer organic matter which would restrict the entrance or interlattice "fixation" of these ions, since the interlayer amounts of Rb\textsuperscript{86} appeared to be reduced. To appropriately substantiate this premise, however, considerations need to be given to effects of Rb\textsuperscript{86} on lattice expansion and collapse of clays and to correlation studies of Rb\textsuperscript{86} recovery data with X-ray diffraction patterns.


<table>
<thead>
<tr>
<th>Treatment</th>
<th>Fractionation for recovery of Rb\textsuperscript{86}</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>water-soluble</td>
<td>&quot;adsorbed&quot; \textsuperscript{1}</td>
</tr>
<tr>
<td>Suffield clay, plant material, Rb\textsuperscript{86}</td>
<td>17.1</td>
<td>68.1</td>
</tr>
<tr>
<td>Suffield clay, NH\textsubscript{4}Cl, Rb\textsuperscript{86}</td>
<td>73.4</td>
<td>16.3</td>
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<tr>
<td>Suffield clay, Rb\textsuperscript{86}</td>
<td>3.2</td>
<td>67.6</td>
</tr>
<tr>
<td>Merrimac clay, plant material, Rb\textsuperscript{86}</td>
<td>17.9</td>
<td>58.8</td>
</tr>
<tr>
<td>Merrimac clay, NH\textsubscript{4}Cl, Rb\textsuperscript{86}</td>
<td>51.0</td>
<td>35.9</td>
</tr>
<tr>
<td>Merrimac clay, Rb\textsuperscript{86}</td>
<td>12.9</td>
<td>40.2</td>
</tr>
</tbody>
</table>

1 KOH treatment on steam bath 6 hours.
2 HF treatment 12 to 16 hours.