Solid State Phosphorus N.M.R. Spectroscopy of Minerals and Soils

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Summary A study of ^{31}P n.m.r. spectra of a few chosen minerals and one soil has been made using solid state n.m.r. procedures and the observations show that this procedure will be a valuable additional method for the study of phosphorus in environmental materials of unknown structure.

The understanding of the chemistry of minerals and clays has benefited greatly from the structural data provided by *X*-ray diffraction studies. This approach depends upon the presence of ordered lattices. Some minerals and soils do not have long range order and it is therefore necessary to find an alternative study of their solid state properties. Recently n.m.r. spectroscopy has been shown to be adaptable to the study of solid materials, whether crystalline or not. The experimental use of nuclear resonances depended upon the development of the simultaneous use of cross polarization (CP) and magic angle spinning (MAS) procedures. The method and the theory of its application have been given[1] and have already been applied to organic minerals such as coal[2] and to some silicates.[3] This paper is an extension of the method to phosphate-containing minerals.

The CP MAS n.m.r. ^{31}P spectra were measured at 121·48 MHz in 10 mm n.m.r. tubes packed with *ca.* 1 g of material, using a Bruker CXP-300 spectrometer. The spectrometer was operated for us by Dr. H. Forster of the Bruker laboratory at Rheinstetten-Fo. The spinning rate used was 3·4 kHz. Contact time was 15 ms with 10 s repetition time. For all but the soil sample excellent signal-to-noise was obtained with ten scans. The soil sample was accumulated over 5,200 scans and the broad line in the spectrum, Figure, is possibly an artefact. A spectrum of a single chemical phosphate species has a central line and, since the spinning is slow compared to the shift anisotropy, side-bands which in principle allow determination of the shift tensors from their relative intensities.[4] The combination of chemical shift and side-band intensities permits discussion of the nature of the chemical species.[5] The table lists the compounds studied and, together with the Figure, gives details of the spectroscopic observations. The line widths are not of great significance without detailed studies at different spinning rates.

The materials which we have examined are listed in the Table. Three were chosen that represent known, very different states of the phosphate anion. In $AlPO_4$ the

Table. ^{31}P Chemical shifts in some materials and a soil.

Compound	Shift (p.p.m.)	Side-bands	Comment (width/Hz)
$NH_4H_2PO_4$	zero[a]	weak	Symmetrical line (150)
$AlPO_4$	$-30·3$	intermediate	Not symmetrical line ? (800)
$Ca_5(PO_4)_3OH$(hydroxyapatite)	$+2·61$	strong[b]	„ „ „ ? (650)
$CaAl_3(PO_4)_2(OH)_2(H_2O)$ (crandallite)	$-1·81$	weak	„ „ „ ? (150)
Soil[c]	$+1·75$	weak	„ „ „ ? (600)

[a] Origin of all spectra. [b] The intensity of the side-bands is noticeably different in this sample (ref. 4). [c] The details of this soil can be obtained from Drs Giles and Posner, see text.

phosphate is surrounded by four aluminium ions at the tetrahedral corners, the whole structure being one of linked P and Al tetrahedra much as in quartz, compare SiO_2 with $AlPO_4$. The second known structure is that of hydroxyapatite,[6] formally $Ca_5(OH)(PO_4)_3$, in which the phosphate is co-ordinated to calcium (and hydrogen) ions with much longer metal–oxygen bonds than in $AlPO_4$. This mineral is related to bone, of course. The third material of known structure is $NH_4(H_2PO_4)$[7] which is used here also as a reference standard in the n.m.r. experiment. Here the phosphate is surrounded by several H-bonds. The mineral crandallite has the formula $CaAl_3(PO_4)_2(OH)_5(H_2O)$ and is of known structure[8] in which the phosphate anion is bound to three aluminium ions but is also extensively bound *via* H-bonds. The soil sample was one from the Department of Soil Science and Plant Nutrition, University of Western Australia. The soil gave a pH of 5·9 in an aqueous suspension and contained 580 p.p.m. of phosphorus. Further details are available from the above address.

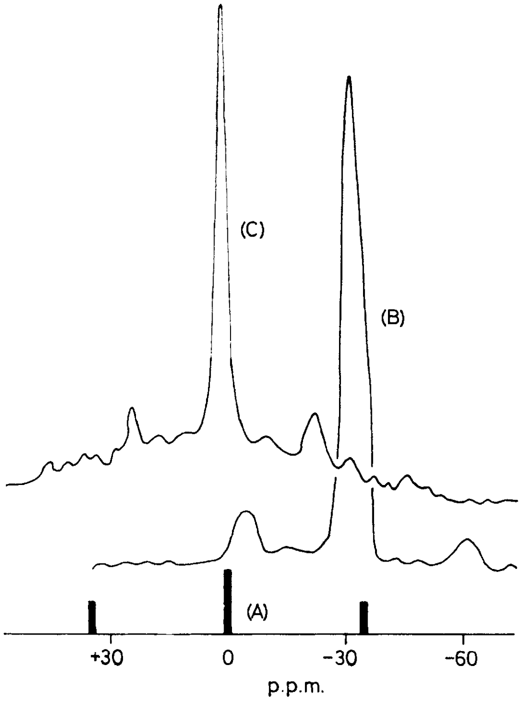

FIGURE. The ^{31}P spectra of (A) the standard $NH_4{\cdot}H_2PO_4$ shown as a set of bars since it was used as a reference (shift of central line equals zero), (B) $AlPO_4$, and (C) the soil sample.

The phosphorus in soil is largely as phosphate but since soil contains a variety of cations and especially H^+, Ca^{2+}, and Al^{3+} the co-ordination of the phosphate in the soil is ill-defined. Solid state n.m.r. studies of the ^{31}P nucleus in solids then open the prospect of uncovering the nature of bound phosphate in the soil. In the light of these considerations we decided to examine the ^{31}P spectrum of a soil in comparison with minerals of known structure containing phosphate bound in different geometries to H^+, Ca^{2+}, and Al^{3+}. Each spectrum has a central line and side-bands at characteristic particular chemical shift positions (Figure, Table). The central line characterises the phosphate in the normal manner through secondary shift influences and the side-bands characterise the chemical shift anisotropy. The data show that $AlPO_4$, in which PO_4^{3-} is a tetrahedral site of four Al^{3+}, has a totally different chemical shift from all the other compounds in which phosphate is undoubtedly in an environment of very different symmetry and H-bonding. We can state that there is no site equivalent to that in $AlPO_4$ for phosphate in soil. The soil phosphate is quite closely related to hydroxyapatite but rather different from crandallite and $NH_4(H_2PO_4)$ insofar as chemical shift is concerned but hydroxyapatite has a very different shift anisotropy possibly arising from its deprotonation state.[5] Further discussion of mineral and soil phosphate will require very detailed study of a large number of samples but we hope that it is clear that the parameters of the spectra do act as fingerprints of the chemical state of phosphate in these complex materials.

We are grateful to Dr. H. Forster (Bruker, Rheinstetten-Fo) for considerable help and to Dr. C. M. Dobson (Oxford) for much discussion.

(*Received, 9th July* 1981; *Com.* 800.)

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