

**Direct evidence for the availability of reactive, water soluble phosphorus  
on the early Earth. H-Phosphinic acid from the Nantan meteorite.**

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**SUPPLEMENTARY MATERIAL**

## SM1. Materials and Methods

### SM1.1 General

Solvents were pre-dried, THF, toluene and pentane were pre-dried over sodium wire and dichloromethane was pre-dried over calcium chloride before being distilled under a dinitrogen atmosphere and degassed before use. THF was distilled over sodium-benzophenone, toluene over sodium metal, pentane over lithium aluminium hydride and dichloromethane over calcium hydride. Drying columns containing molecular sieves (Å4) and phosphorus pentoxide were used to dry all di-nitrogen gas which itself was vent-gas from a liquid di-nitrogen Dewar.  $^1\text{H}$ ,  $^{13}\text{C}\{^1\text{H}\}$  and  $^{31}\text{P}\{^1\text{H}\}$ -NMR spectra were recorded on a Bruker DPX300 spectrometer (operating frequency 300.1 MHz for  $^1\text{H}$  and 75.48 MHz for  $^{13}\text{C}$ ) or Bruker DRX500 spectrometer (operating frequency 500.13 MHz for  $^1\text{H}$ ) or Bruker ARX250 spectrometer (operating frequency 101.26 MHz for  $^{31}\text{P}$ ) unless noted otherwise. All spectra were recorded at 300 K unless stated otherwise, chemical shifts ( $\delta$ ) are given in parts per million (ppm) downfield of tetramethylsilane (TMS) at zero ppm for  $^1\text{H}$  resonances using  $\text{CHCl}_3$   $\delta$  7.24 ppm as an internal standard.  $^{13}\text{C}\{^1\text{H}\}$  spectra were referenced to the centre triplet peak of deuterated chloroform ( $\delta$  77.16 ppm). Coupling constants  $J$  are given in Hertz (Hz). Multiplicities are reported as singlet (s), doublet (d), triplet (t), quartet (q) and some combination of these, broad (br) or multiplet (m). Infrared spectra were recorded using a MIDAC FT-IR spectrometer (4000-600  $\text{cm}^{-1}$ ) as KBr discs or nujol mulls, recorded in wavenumbers ( $\text{cm}^{-1}$ ) and referenced to the polystyrene vibration at 1601  $\text{cm}^{-1}$ . Only principal absorptions are reported.

Our sample of Nantan meteorite (28 g) was purchased from British Jurassic Fossils and elemental compositional data collected *via* ICP shows it to be comparable to known compositional data for this particular meteorite. Specifically, a sample was dissolved in aqua regia over a period of six days to afford a total dissolved material of 2.5664 g in 250 cm<sup>3</sup> (10.2656 g L<sup>-1</sup>). This was then analysed by ICP-OES to afford the following concentrations; Fe (6350 ppm); Ni (375 ppm); P (18 ppm); Ga (2 ppm).

### **SM2 Anaerobic modification of Fe<sub>n</sub>P with water**

In a di-nitrogen glovebox, Fe<sub>n</sub>P (0.5g), was loaded into a Schlenk tube equipped with a magnetic follower. The tube was transferred to a vacuum Schlenk line where 20 cm<sup>3</sup> of deionised water, degassed by 3-freeze-pump-thaw cycles, was transferred by cannula. The phosphide suspension was stirred for 5 days at 298K. The phosphide solids were then removed by filtration and aqueous sodium sulfide solution (1.0M) added to the filtered solution which was allowed to stand overnight. The resulting FeS suspension was removed by centrifuge and the supernatant solution pipetted into a round bottomed flask and reduced to dryness on a rotary evaporator. The dried materials were taken up in D<sub>2</sub>O (0.5 cm<sup>3</sup>) for analysis by <sup>31</sup>P-NMR. The principle product observed is H-phosphonic acid (Fig. SM2.1). When instead of degassed water, degassed H<sub>2</sub>SO<sub>4</sub> (0.1 M) is used at 298K for 5 days, the product mixture is slightly different (Fig. SM2.1) with the major product being H-phosphonic acid ( $\delta$ 4.4;  $^1J_{\text{PH}} = 565$  Hz) with minor components including orthophosphate at  $\delta$ 6.9 ppm, pyrophosphate at  $\delta$ -2.9 ppm. hypophosphate at  $\delta$ 15.0 ppm. Each component has been identified by sequential addition of authentic samples.

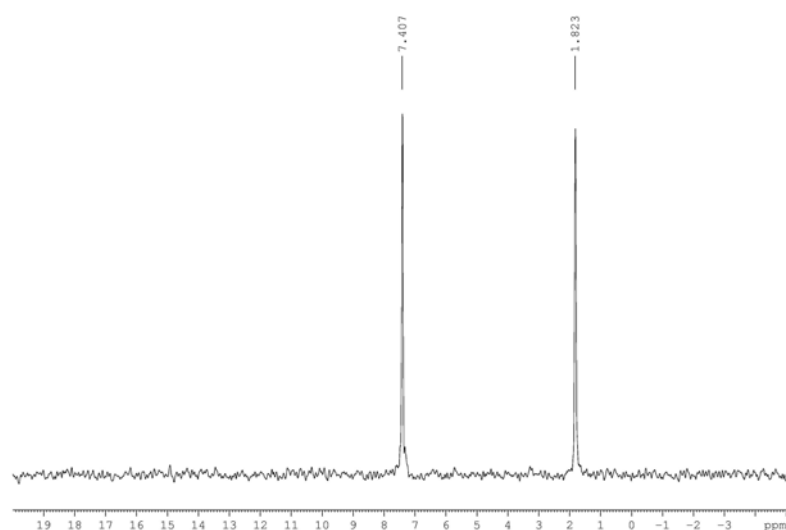


Fig. SM2.1  $^{31}\text{P}$ -NMR spectrum of non-acid treated  $\text{Fe}_3\text{P}$  ( $\text{D}_2\text{O}$  solvent, 300K, 101.3MHz).

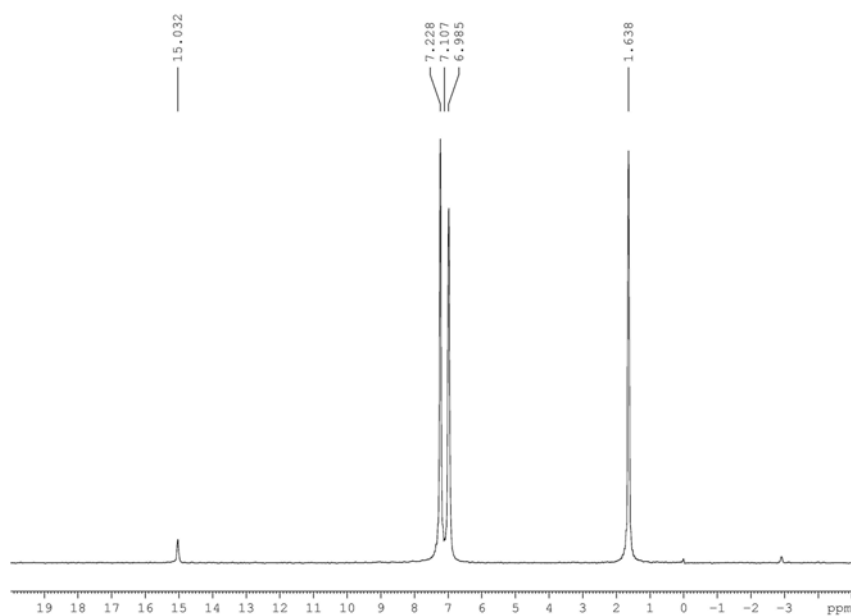
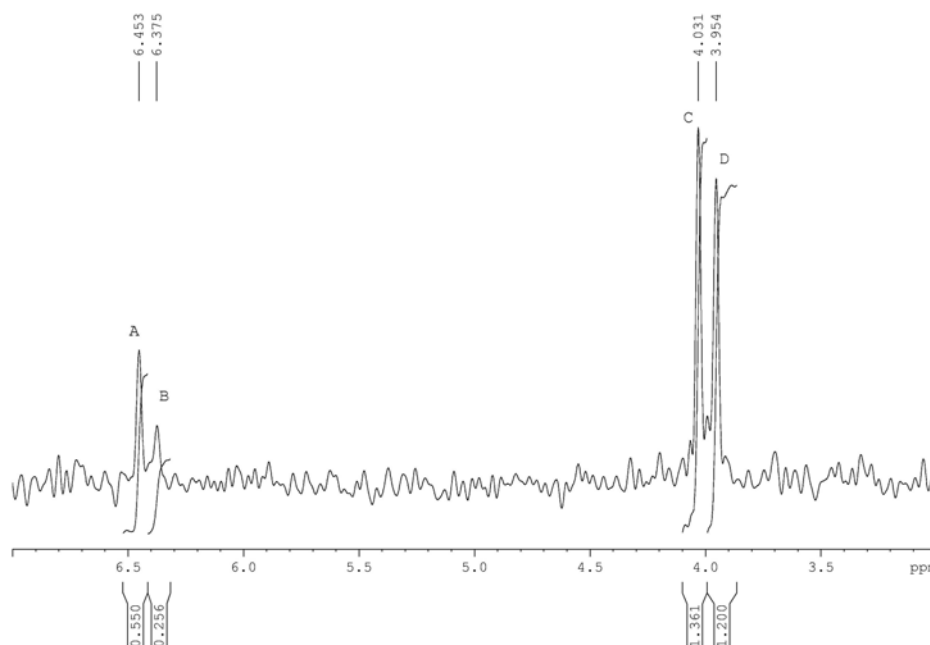


Fig. SM2.2  $^{31}\text{P}$ -NMR spectrum of acid treated  $\text{Fe}_3\text{P}$  ( $\text{D}_2\text{O}$  solvent, 300K, 101.3MHz).

### SM3 Anaerobic modification of Fe<sub>3</sub>P with <sup>18</sup>O-water

In a di-nitrogen glovebox, Fe<sub>3</sub>P (0.1g), was loaded into a screw topped glass vial and H<sub>2</sub><sup>18</sup>O added (1.0 cm<sup>3</sup> of 98.5%:1.0%:0.5% <sup>18</sup>O:<sup>17</sup>O:<sup>16</sup>O-Cambridge Isotope Laboratories). The mixture was allowed to stand at room temperature with occasional agitation for 8 weeks. A control sample using degassed deionised water (1.0 cm<sup>3</sup>) was similarly treated. The phosphide solids were then removed by filtration and excess aqueous sodium sulfide solution (1.0M) added to the filtered solution which was allowed to stand overnight. The resulting FeS suspension was removed by centrifugation and the supernatant solution pipetted into a round bottomed flask and reduced to dryness on a rotary evaporator. The dried materials were taken up in D<sub>2</sub>O (0.5 cm<sup>3</sup>) for analysis by <sup>31</sup>P-NMR. The assignment of the peaks to each isotopomer was achieved by two successive additions of a D<sub>2</sub>O solution of the control sample where products have only <sup>16</sup>O atoms.



*Fig. SM3.1  $^{31}\text{P}\{^1\text{H}\}$ -NMR spectrum of product mixture from  $\text{Fe}_3\text{P}$  and  $^{18}\text{O}$ -water ( $\text{D}_2\text{O}$  solvent, 300K, 101.3MHz).*

#### **SM4 Anaerobic modification of $\text{Fe}_n\text{P}$ with water in the presence of UV radiation**

A glass photochemical reaction chamber was specially designed for irradiating solids at 77K (Fig.SM4.1). The chamber is cylindrical with a round bottom and is fitted with a flange at the top to allow introduction of a quartz tube containing the low pressure mercury lamp. There are two side arms ending with Young's vacuum fittings to allow attachment to a vacuum line. The chamber was cleaned with concentrated acid, rinsed with copious amounts of water, then deionised water and acetone before being dried in an oven. The hot chamber was then transferred to a di-nitrogen glovebox,  $\text{Fe}_3\text{P}$  (0.5 g), was loaded into the chamber and it was sealed using the lamp insert. The chamber was then transferred to a vacuum line. On the second side arm was attached a Schlenk tube containing deionised water (20  $\text{cm}^3$ ), degassed by 3-freeze-pump-thaw cycles. The chamber was evacuated and cooled by liquid nitrogen (77 K). Under continuous pumping the tap connecting the chamber to the water was opened and water evaporated and re-condensed in the chamber as ice on the walls of the chamber and on the iron phosphide. The UV lamp, a low pressure mercury vapour arc tube with emissions at 254 nm; *ca.* 500mW and 185 nm; *ca.* 40mW, was lit for 3 hours during continued condensation of water. After this period the chamber was re-pressurised with di-nitrogen gas and allowed to warm to room temperature. The contents were filtered and the solution treated with sodium sulfide as before prior to evaporation and dissolution in  $\text{D}_2\text{O}$  (0.5  $\text{cm}^3$ ) for  $^{31}\text{P}$ -NMR analysis.



*Fig. SM4.1 Reactor used in conjunction with a low pressure mercury arc lamp for photochemical studies on iron phosphides and meteoritic material. The frosted glass walls help the dispersion of solid powders on to the walls of the vessel to optimise irradiation area.*

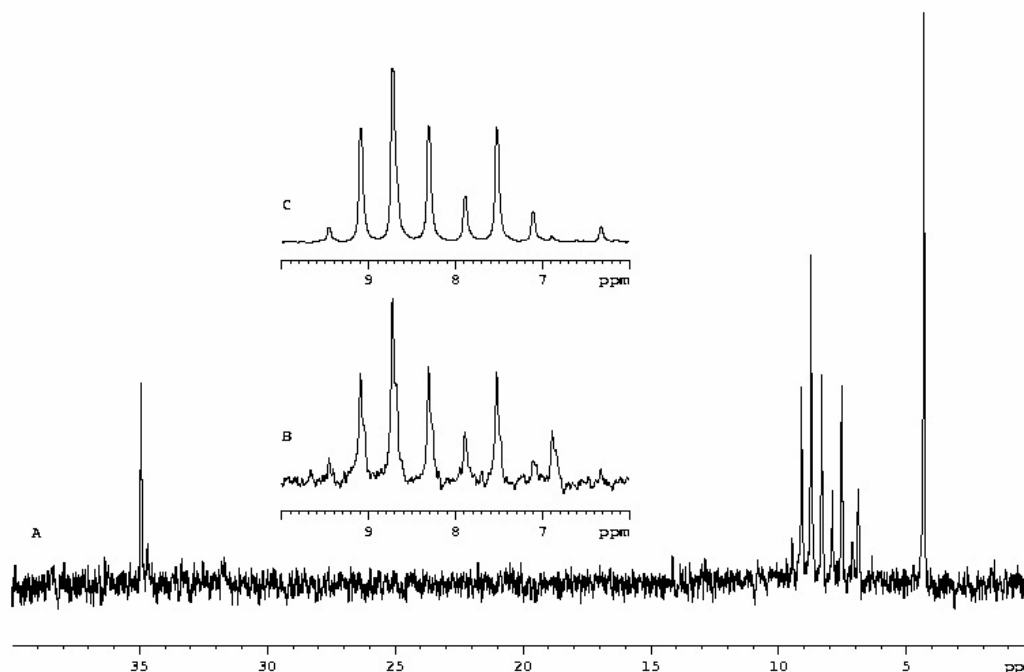


Fig. SM4.2  $^{31}\text{P}\{^1\text{H}\}$ -NMR spectrum of product mixture from  $\text{Fe}_3\text{P}$  and water under UV radiation ( $\text{D}_2\text{O}$  solvent, 300K, 101.3MHz). **A** full spectrum. **B** expansion of  $\delta 5$ -10ppm region. **C** Same region with added aliquot of authentic H-phosphinic acid.

#### SM5 Anaerobic modification of Nantan with water in the presence of UV radiation

The chamber described above (SM4) was cleaned with concentrated acid, rinsed with copious amounts of water, then deionised water and acetone before being dried in an oven. The hot chamber was then transferred to a di-nitrogen glovebox, the meteorite was loaded into the chamber and it was sealed using the lamp insert. The chamber was then transferred to a vacuum line. On the second side arm was attached a Schlenk tube containing 20 cm<sup>3</sup> of deionised water, degassed by 3-freeze-pump-thaw cycles. The chamber was evacuated and cooled by liquid nitrogen. Under continuous pumping the tap connecting the chamber to the water was opened and water evaporated and re-condensed in the chamber as ice on the



walls of the chamber and on the meteorite. The UV lamp was lit for 3 hours during continued condensation of water. After this period the chamber was re-pressurised with di-nitrogen gas and allowed to warm to room temperature. The contents were filtered and the solution treated with sodium sulfide as before prior to evaporation of volatiles and dissolution of the product mixture in  $\text{D}_2\text{O}$  ( $0.5 \text{ cm}^3$ ) for  $^{31}\text{P}$ -NMR analysis. Solution concentration of phosphorus in the sample NMR was estimated by comparison of the signal strength with a known solution containing of a mixture of  $\text{Na}_2\text{HPO}_4$ ,  $\text{H}_3\text{PO}_3$ ,  $\text{Na}_4\text{P}_2\text{O}_7$ ,  $\text{NaH}_2\text{PO}_2$  at pH 7.5 with each component being set at a stock concentration of 1.0 mM. Of this stock solution, an aliquot of  $0.225 \text{ cm}^3$  was added to  $0.15 \text{ cm}^3$   $\text{D}_2\text{O}$ , concentration overall of 0.6 mM. It was observed that the signal to noise levels of this mixture after 24,576 scans (101MHz; 300K) was comparable to those observed for the Nantan mixture under the same operating conditions. This is approximately equivalent to  $0.3 \text{ }\mu\text{moles}$  of phosphorus in  $0.5 \text{ cm}^3$  of  $\text{D}_2\text{O}$  or *ca.* 9.3 ppm phosphorus. More accurate solution concentration measurements are on-going and will form part of our full paper.

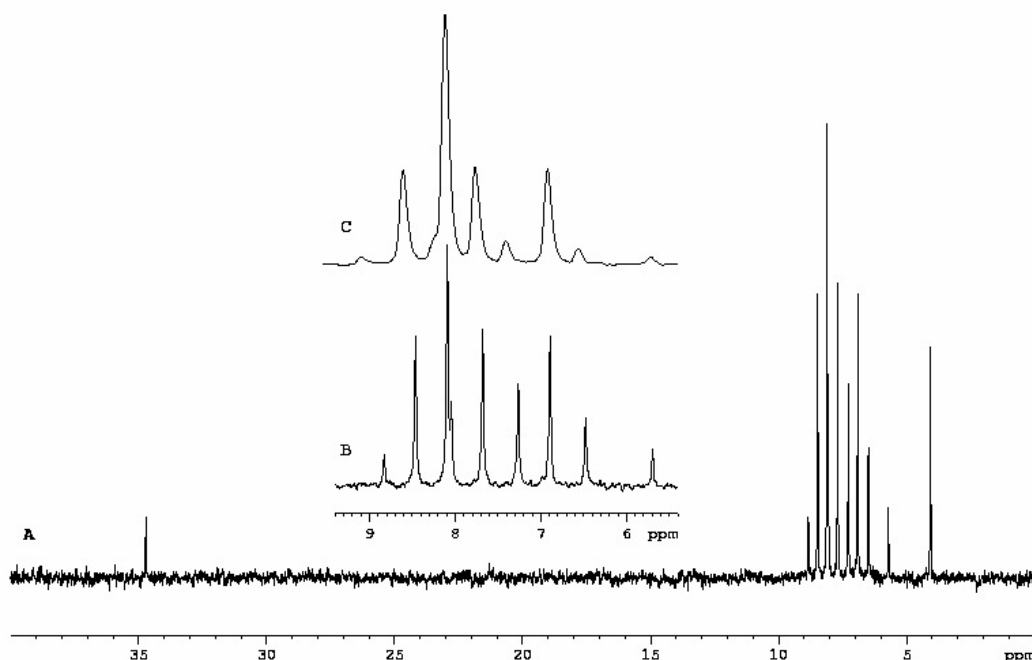
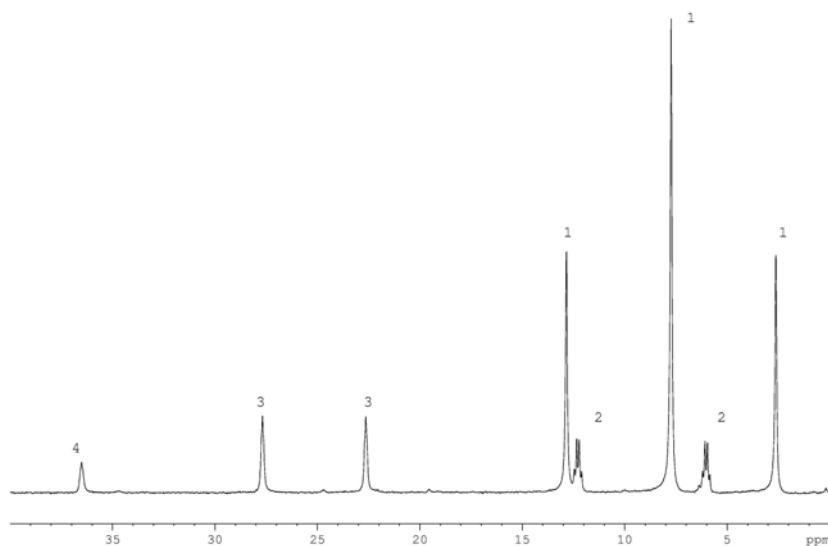


Fig. SM5.1  $^{31}\text{P}\{^1\text{H}\}$ -NMR spectrum of product mixture from Nantan meteorite and water under UV radiation ( $\text{D}_2\text{O}$  solvent, 300K, 101.3MHz). **A** full spectrum. **B** expansion of  $\delta$ 5-10ppm region. **C** Comparison against authentic H-phosphinic acid in  $\text{D}_2\text{O}$  in the presence of catalytic HCl illustrating H/D exchange.

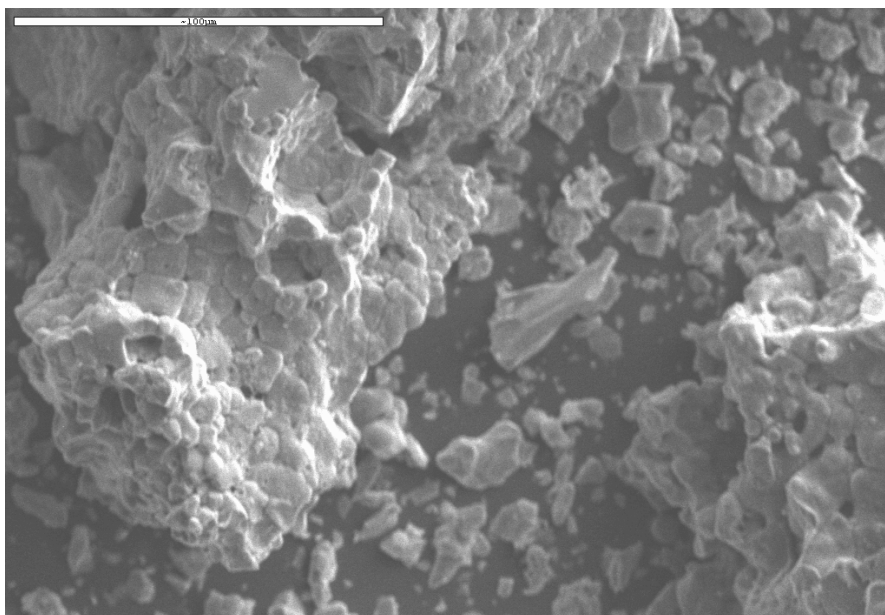
#### SM6 Reaction of H-phosphinic acid salts with alcohols in the presence of UV radiation

The following is a representative synthetic protocol for photochemical reactions between  $\text{NaH}_2\text{PO}_2$  and alcohols either pure or aqueous. A stirred solution of  $\text{NaH}_2\text{PO}_2$  (0.08g) in 40  $\text{cm}^3$  MeOH (0.022M) was degassed for 15 mins *in situ* by bubbling through nitrogen. The nitrogen exit was sealed and the solution photolysed for 16 hrs using a low pressure mercury lamp. The resulting solution was reduced to dryness on a rotary evaporator and the residues taken up in  $\text{D}_2\text{O}$  (0.5  $\text{cm}^3$ ) for analysis by  $^{31}\text{P}$ -NMR spectroscopic analysis.

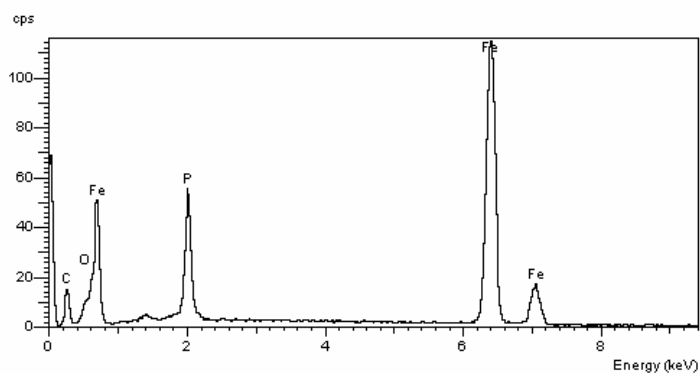


*Fig. SM6.1  $^{31}\text{P}$ -NMR spectrum of product mixture from  $\text{NaH}_2\text{PO}_2$  and methanol under UV. ( $\text{D}_2\text{O}$  solvent, 300K, 101.3MHz). 1 =  $\text{NaH}_2\text{PO}_2$  starting material; 2 =  $\text{NaOHPO}(\text{OMe})$ ; 3 =  $\text{NaOHPO}(\text{CH}_2\text{OH})$ ; 4 = unknown.*

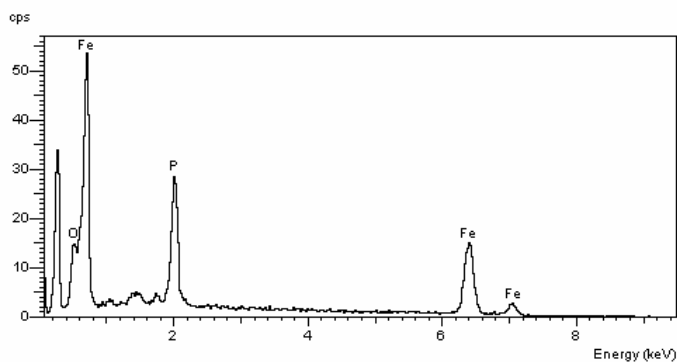
#### SM7 SEM and EDX analysis on $\text{Fe}_3\text{P}$



SEM analysis of  $\text{Fe}_3\text{P}$  above shows a rather inhomogeneous mixture of small ( $1\ \mu\text{m}$ ) fragments alongside irregular shaped grains which appear fused into large composites of  $<100\ \mu\text{m}$  dimensions.



EDX analysis of  $\text{Fe}_3\text{P}$  at 30kV accelerating voltage.



EDX analysis of  $\text{Fe}_3\text{P}$  at 20kV accelerating voltage.

### SM8 XPS analysis on Fe<sub>n</sub>P

Full details will be released in the full paper

