

A QUANTITATIVE NMR ANALYSIS OF PHOSPHORUS IN CARBONACEOUS AND ORDINARY CHONDRITES. M. A. Pasek, V. D. Smith, and D. S. Lauretta, Lunar and Planetary Laboratory 1629 E University Boulevard, Tucson AZ, 85721 USA (mpasek@lpl.arizona.edu).

Introduction: Phosphorus is important in a number of biochemical molecules, from DNA to ATP. Early life may have depended on meteorites as a primary source of phosphorus as simple dissolution of crustal apatite may not produce the necessary concentration of phosphate. Phosphorus is found in several mineral phases in meteorites. Apatite and other Ca- and Mg-phosphate minerals tend to be the dominant phosphorus reservoir in stony meteorites, whereas in more iron-rich or reduced meteorites, the phosphide minerals schreibersite, $(\text{Fe, Ni})_3\text{P}$, and perryite, $(\text{Ni, Fe})_5(\text{Si, P})_2$ are dominant. However, in CM chondrites that have experienced significant aqueous alteration, phosphorus has been detected in more exotic molecules. A series of phosphonic acids including methyl-, ethyl-, propyl- and butyl- phosphonic acids were observed by GC-MS in Murchison [1]. Phosphorian sulfides are in Murchison and Murray [2].

NMR spectrometry is capable of detecting multiple substances with one experiment, is non-destructive, and potentially quantitative, as discussed below. Despite these advantages, NMR spectrometry is infrequently applied to meteoritic studies due in large part to a lack of applicability to many compounds and the relatively high limit of detection requirements. Carbon-13 solid-state NMR has been applied to macromolecular carbon in Murchison [3]. P-31 NMR has many advantages over aqueous carbon-13 NMR spectrometry. P-31 is the only isotope of phosphorus, and P-31 gives a signal approximately twice as strong as C-13. These two factors together with the relative abundances of carbon and phosphorus imply that phosphorus should give a signal approximately $20\times$ as strong as carbon in a given sample.

Preparation of Quantitative standard. We are developing techniques to quantify NMR spectrometry. Differences in molecular structure influence signal strengths, as do molecular composition and solution effects. In order to eliminate some of these factors in our quantitative approach to composition, we prepared a series of mixtures of two compounds, phosphoric acid (H_3PO_4) and methylphosphonic acid ($\text{CH}_3\text{PO}_3\text{H}_2$). We then compared the peak heights and peak areas observed in the NMR spectrum to the known concentrations of each compound. The lower limit of detection in these experiments was established as 0.0001 M.

Concentrations of 0.1 M and above are subject to significant solution effects, and thus can not be used in quantitative analysis as peak height and area do not vary linearly with concentration. Fortunately, based

on the known abundances of phosphates in meteorites and the small mass used in each experiment, the probability of exceeding this limit during experimentation was very low. Peak area can be used to quantify a concentration, and the standard deviation in our results is 19%. Peak height is less useful as a quantitative tool, with a standard deviation of 24%. We determine empirically that concentration can be correlated to a function of peak height and peak area, with a standard deviation of 3%.

Using these standards and the derived empirical relationship, the amount of water-soluble phosphorus in meteorites can be determined using NMR. We added a set amount of methylphosphonic acid (in this case 0.01 M) to each extract and compared the resulting peak to the orthophosphate peak to elucidate the abundance of water-soluble phosphate in each extract.

NMR studies of meteorites. Samples of several meteorites with masses between 0.3 to 1 g were crushed and extracted over the course of 24 hours with a 1:1 solution of 0.5 M NaOH and 0.1 M EDTA at room temperature, as outlined in soil science extractions [4]. The resulting fluid was filtered, evaporated down, and subsequently dissolved in a 0.01 M solution of methylphosphonic acid in D_2O .

A Varian 300 four-nucleus probe NMR spectrometer was used for all NMR experiments. Each solution was examined at 121.443 MHz for 20 minutes to 16 hours, depending on the desired signal to noise ratio. Four meteorite samples were examined: Murchison (CM2), Allende (CV3), Gold Basin (L4), and NWA 502 (CO3). Of these, Murchison and NWA 502 yielded significant orthophosphate peaks (Fig 1 A & B). Analysis of our samples by C-13 NMR failed to yield any peaks, as opposed to several peaks observed through P-31 NMR analyses. Molecule-peak correlation was accomplished through comparison of each peak with a series of spectra taken of various phosphorus compounds.

In addition, a sample of Murchison was extracted using a mixture of water and reagent alcohol, and the subsequent extract was analyzed by NMR. A peak corresponding to ethylphosphonic acid was detected (Fig 2).

Discussion: The concentration of water-soluble phosphate in Murchison is $1.8 \pm 0.1 \times 10^{-5}$ moles/g, approximately half of the total phosphorus in the meteorite. The abundance of water-soluble orthophosphate in Murchison suggests that aqueous alteration processes have generated new soluble phosphorus

compounds from the starting mineral assemblage, further supported by the presence of ethylphosphonic acid. The lack of any discernable phosphorus peak in either Allende or Gold Basin indicates that water-soluble phosphate is present at less than 5×10^{-7} moles/g (our detection limit). Allende is the most equilibrated of the CV chondrites [5], so thermal heating may have changed the accessible forms of phosphorus in these meteorites. The lack of a peak in Gold Basin suggests that soluble orthophosphate is lost during weathering, similar to the loss of other volatiles during this process [6]. In addition, a lack of a phosphorus peaks in these samples indicates that the observed peak in Murchison is not merely the result of dissolution of a phosphate mineral, as both of these meteorites contain apatite and other phosphate minerals [7]. The presence of a phosphate peak in NWA 502, a CO 3.3 chondrite, merits further discussion. Water-soluble orthophosphate is less common in this chondrite than in Murchison, and occurs at an abundance of $2.0 \pm 0.1 \times 10^{-6}$ moles/g. NWA 502 is pristine, experiencing little in the way of heating, terrestrial weathering, or aqueous alteration. These results indicates that even primitive meteorites have water-soluble phosphate. Thus processes such as weathering or heating can decrease the amount of water-soluble phosphorus available, whereas aqueous alteration can increase its concentration.

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References: [1] Cooper G.W. et al. (1992) *GCA* 56, 4109-4115. [2] Nazarov M.A. et al. (1998) *Geokhimiya* 5, 475-484. [3] Cody G.D. et al. (2002) *GCA* 66, 1851-1865. [4] Cade-Menun B.J. et al. (2002) *J Environ Qual* 31, 457-465. [5] Guimon R.K. et al. (1995) *MAPS* 30, 704-714. [6] Lauretta D.S. et al (2002) *LPS XXXIII*, 1602. [7] Rubin A.E. (1997) *MAPS* 32, 733-734.

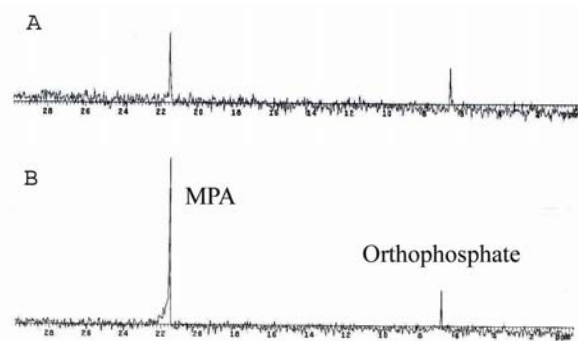


Figure 1A & B. NMR spectra of Murchison (A) and NWA 502 (B). The left peak is the standard, methylphosphonic acid or MPA (0.01 M in D_2O). The right peak is orthophosphate extracted from each meteorite. The x-axis is ppm, or deviation in terms of frequency from the standard, 85% H_3PO_4 , at 0 ppm to 30 ppm. The height of each peak is dependent on the strength of the signal received from the compound.

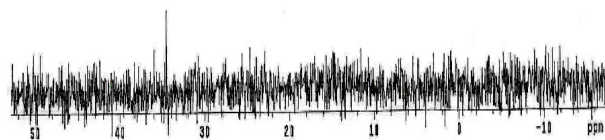


Figure 2. NMR spectrum of the water and alcohol extract of Murchison. The main peak occurs at 34.5 ppm, the same location as ethylphosphonic acid. The x-axis is in ppm, and ranges from -20 to 55 ppm.