

Phosphate as an Indicator of pH in Raman Spectra of Brines. B. C. Abney¹ and M. E. Elwood Madden²,
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Introduction: Raman spectroscopy can be used to determine the chemistry of geomaterials, including brines on Earth, or on other planets. Raman uses a laser to excite the sample, then a spectrometer collects the Raman shifted light. Raman bands within the spectra can be used to determine the molecular composition of the sample. Raman can detect trace amounts of organic matter and determine, based on distribution/concentration factors, if these organic molecule accumulations are biosignatures or simply background abiotic noise [1]. Raman instruments can be used to search for signs of transient flowing water on the Martian surface, such as hydrated salts or the detection of liquid water absorptions, including recurring slope lineae (RSL) [2]. Raman can also be used to measure ion concentrations in solution by studying their peak height ratios, either in modern surface water or within ancient fluid inclusions, which can help us understand the geochemical conditions on Mars millions or even billions of years ago [3].

While exploring Gale Crater, an ancient Martian lake, the Curiosity rover recently detected nitrogen, organic carbon compounds, phosphate minerals, as well as sulfur and iron-bearing minerals in various redox states within the sedimentary strata. This coupled with evidence of relatively stable climate conditions suggests the chemical/physical conditions essential for life existed on Mars 3.1-3.8 Ga ago [4]. However, pH is also an important factor to consider when trying to determine if Mars was habitable in the past or shows signs of biological potential for the future. Here we aim to document changes in Raman spectra of anions as a function of pH by examining peak intensities and peak positions observed under a range of pH conditions. Changes in the spectra represent changes in the overall aqueous chemistry of the solution which can affect habitability and biogeochemical processes. This study focuses primarily on phosphate anions (PO_4^{3-}) as phosphate minerals have already been detected on Mars [4]. Phosphate creates the structural backbone of genetic molecules and is a fundamental nutrient required for life on Earth as P is essential to formation of DNA and RNA [5].

Methods: We created aqueous solutions of sulfate, carbonate, phosphate, chloride, and chlorate anions over a range of pH conditions by mixing anion standards with buffer solutions of known pH in 1:1 mixtures. We used both HCl (pH ~0-5) and NaOH (pH ~8-13) solutions to fix the pH and measured the pH of a separate aliquot of each solution using an Orion pH electrode. For the phosphate brines we also conducted a titration

experiment by adding drops of HCl at a rate of 2 ml/minute to an initial 40 ml of 1 mol/kg NaH_2PO_4 brine and took sub samples along the way to fill in the pH gaps from the initial experiments. For the Raman analyses we placed 1 ml of each sample into a small well on a ceramic painter's plate and used a Renishaw InVia High Resolution Raman Spectrometer to collect spectral data with a 532 nm laser and a 1200 1/cm grating. We collected data from 400-2700 wavenumbers (cm^{-1}) and accumulated 10s of data 10 times, allowing the Raman to collect 100s of data for increased accuracy.

Results/Discussion: The Raman spectra for the carbonate, sulfate and phosphate brines vary considerably with pH, while the chloride and chlorate brines recorded only minor or no changes with pH. The phosphate brines produced major changes in peak positions and peak intensities as pH changed, making them a promising indicator of pH in Raman spectra. We found 6 major phosphate peaks corresponding to different vibrational frequencies for phosphate that change with pH (Figure 1a, 1b).

The $\nu_1\text{PO}_4$ peak at 890 cm^{-1} represents a symmetric stretching $\text{P}(\text{OH})_3$ bond that can be used to help determine pH [6]. This peak has a high intensity at pH 1.06-5.56, but the peak position shifts to slightly higher wavenumbers in the pH 1.06 sample. At pH 6-7, the peak intensity decreases, while at $\text{pH} \geq 7$, not only is there a significant decrease in intensity but the center of the peak also shifts towards lower wavenumbers and broadens (Figure 1a). These shifts in peak position are likely due to the different phosphate species present over the pH range contributing to this $\nu_1\text{PO}_4$ peak. H_3PO_4 is expected to be the dominant species in the 1.06 pH sample which could explain the shift towards higher wavenumbers, while H_2PO_4^- is the dominant species for samples with a pH between 2-7. HPO_4^{2-} is dominant in the samples with a $\text{pH} \geq 7$ which could explain the broadening peak/shift towards lower wavenumbers (Figure 2). The $\nu_2\text{PO}_4$ peak at 1174 cm^{-1} represents a stretching $\text{P}=\text{O}$ bond [6] that decreases in intensity as pH increases, disappearing completely at pH 5 or more (Figure 1a). This peak likely comes from H_3PO_4 as this species is dominant in very acidic brines and decreases in concentration as pH increases, with no significant concentration expected at $\text{pH} \geq 4$ (Figure 2).

The $\nu_3\text{PO}_4$ peak has intensity of ~0.4 in the pH 2.78-5.56 samples, while the pH 1.06 sample has an intensity of 0.2 and the peak position is shifted towards lower wavenumbers (Figure 1a). At $\text{pH} \geq 6$ the intensity also decreases, but the peak shifts towards higher wavenumbers. This pattern in the direction of peak shift

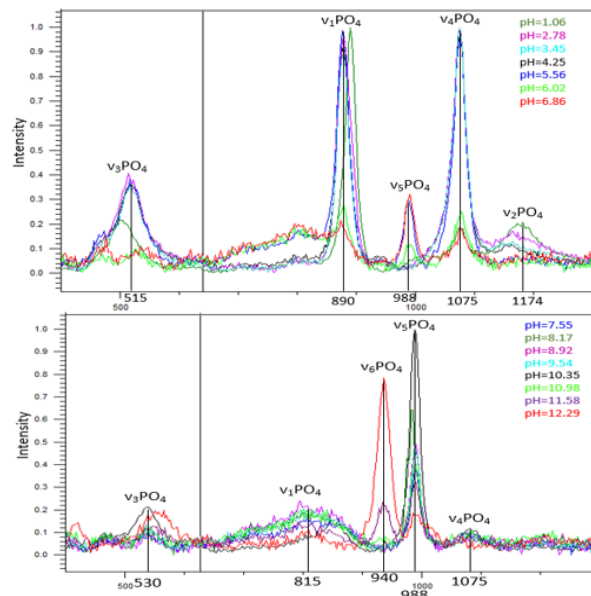
for the $\nu_3\text{PO}_4$ peak with pH is opposite to the behavior observed in the $\nu_1\text{PO}_4$ peak. Combining observations between the ν_1 and ν_3 peaks suggests highly acidic pH causes the $\nu_3\text{PO}_4$ peak to shift towards lower wavenumbers and the $\nu_1\text{PO}_4$ peak to shift towards higher wavenumbers while neutral to highly alkaline pH conditions cause the $\nu_3\text{PO}_4$ peak to shift towards higher wavenumbers and the $\nu_1\text{PO}_4$ peak to shift towards lower wavenumbers. Both peaks correspond to symmetric $\text{P}(\text{OH})_3$ bond structures [6]. However, the bonds for the $\nu_1\text{PO}_4$ peak are being stretched while the bonds for the $\nu_3\text{PO}_4$ peak are being bent. Furthermore, the phosphate speciation diagram (Figure 2) suggests the species being observed at this peak for the lower pH's (Figure 1a) corresponds to the H_2PO_4^- species while the higher pH's (Figure 1b) likely correspond to HPO_4^{2-} species. Typically, adding H^+ to a system causes an increase in intensity and a shift towards lower energy due to the stretching of the donor molecule as observed here [7].

The $\nu_4\text{PO}_4$ peak at 1075 cm^{-1} represents the asymmetric stretching of $\text{P}(\text{OH})_3$ [6]. The $\nu_4\text{PO}_4$ peak has similar intensity at pH between 2.78–5.56, but lower intensity at pH 1.06 and $\text{pH} \geq 6$ (Figure 1a, 1b). This suggests this peak is due to H_2PO_4^- as it is the most common phosphate species at pH 3–6 (Figure 2). This shows the $\nu_4\text{PO}_4$ peak height can be greatly reduced under highly acidic or neutral to alkaline conditions. Using this observation in conjuncture with the other peaks can help determine the pH range. In this case, the lack of a $\nu_2\text{PO}_4$ peak at 1174 cm^{-1} hints at neutral to alkaline waters but when analyzing this sample alone it may be hard to notice a missing peak and use that as evidence to justify higher pH (Figure 1b).

However, the $\nu_5\text{PO}_4$ peak at 988 cm^{-1} corresponds to a symmetrical stretching $\text{P}=\text{O}$ bond and only appears in samples with a $\text{pH} > 5$ [6]. This peak shows the highest intensity around pH 10.35 and peak intensity decreases at both higher and lower pH conditions (Figure 1a, 1b). The speciation diagram indicates this peak is likely due to HPO_4^{2-} as this species dominates at pH 9–10 (Figure 2). Additionally, to narrow down whether a solution containing phosphate has a neutral or alkaline pH one can look for a $\nu_6\text{PO}_4$ peak around 940 cm^{-1} which corresponds to an asymmetric stretching $\text{P}(\text{OH})_2$ bond structure [6] and only appears in the samples with a $\text{pH} > 10$ (Figure 1b). The $\nu_6\text{PO}_4$ peak also increases in intensity as pH increases, suggesting it is indicative of PO_4^{3-} species (Figure 2).

Conclusion: It is evident that pH has a major effect on peak height intensity and peak position of Raman spectra of phosphate anions. By analyzing how pH affects the different peaks of chemically possible Martian brines in a lab, it is possible to cross reference this information with future Raman data to help determine the relative pH and composition of past brines on Mars. This information could also help us

understand the brines beneath the Martian surface, which is essential to the future habitability of Mars as



we plan to terraform the red planet.

Figure 1a) Raman spectra for NaH_2PO_4 mixed with HCl/NaOH for $\text{pH} < 7$. 1b) for $\text{pH} > 7$.

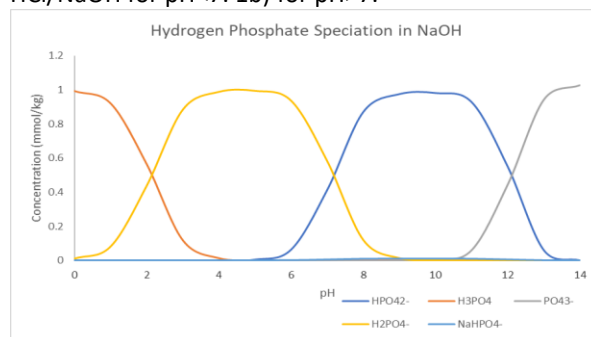


Figure 2) Phosphate speciation predicted by Geochemist's Workbench.

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