

PHOSPHATE STABILITY IN DIAGENETIC FLUIDS CONSTRAINS THE ACIDIC ALTERATION MODEL FOR LOWER MT. SHARP SEDIMENTARY ROCKS IN GALE CRATER, MARS

J.A. Berger¹, M.E. Schmidt², M.R.M. Izawa², R. Gellert³, D.W. Ming⁴, E.B. Rampe⁴, S.J. VanBommel³, A.C. McAdam⁵. ¹University of Western Ontario, London, CAN, jeffberger@cpsx.uwo.ca; ²Brock University, St. Catharines, CAN; ³University of Guelph, Guelph, CAN; ⁴NASA JSC, Houston, USA; ⁵NASA Goddard, MD, USA.

Introduction: The Mars rover *Curiosity* has encountered silica-enriched bedrock (as strata and as veins and associated halos of alteration) in the largely basaltic Murray Fm. of Mt. Sharp in Gale Crater. Alpha Particle X-ray Spectrometer (APXS) investigations of the Murray Fm. revealed decreasing Mg, Ca, Mn, Fe, and Al, and higher S, as silica increased (Fig. 1) [1]. A positive correlation between SiO₂ and TiO₂ (up to 74.4 and 1.7 wt %, respectively) suggests that these two insoluble elements were retained while acidic fluids leached more soluble elements. Other evidence also supports a silica-retaining, acidic alteration model for the Murray Fm., including low trace element abundances consistent with leaching, and the presence of opaline silica and jarosite determined by CheMin [2,3].

Phosphate stability is a key component of this model because PO₄³⁻ is typically soluble in acidic water and is likely a mobile ion in diagenetic fluids (pH < 5). However, the Murray rocks are not leached of P; they have variable P₂O₅ (Fig. 1) ranging from average Mars (0.9 wt%) up to the highest values in Gale Crater (2.5 wt%). Here we evaluate APXS measurements of Murray Fm. bedrock and veins with respect to phosphate stability in acidic fluids as a test of the acidic alteration model for the Lower Mt. Sharp rocks.

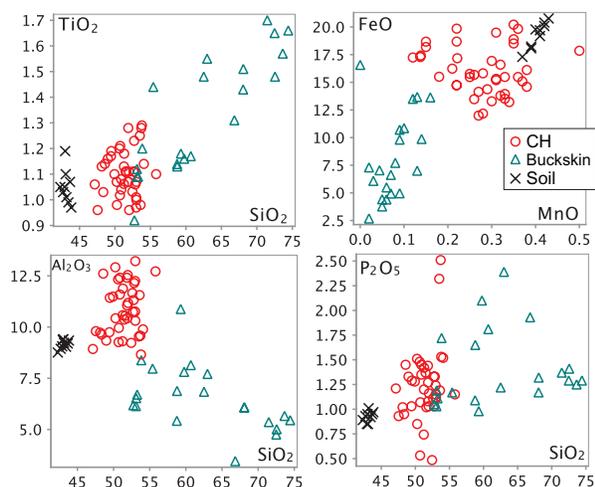


Fig. 1: Chemical trends (wt %) indicating acidic alteration of the Murray Fm. bedrock. The classes Confidence Hills (CH; high in Al₂O₃ and relatively unaltered) and Buckskin (higher in silica and low in Al₂O₃) are shown relative to avg. Mars (soil).

Methods: Phosphate stability was calculated with Geochemist's Workbench using the LLNL thermodynamic database. Water compositions were (a) a neutral basaltic aquifer [4] and (b) acidic water from oxidizing, Fe³⁺- and SO₄²⁻-rich mine drainage [5] to model low and high ionic strength (*I*) fluids, respectively. Modeled phosphate activities were low (10⁻⁶) and high (10⁻³). We assume that the high *I* model follows the Debye-Huckel relationship; we acknowledge that this introduces error that is not evaluated here.

Results: With low *I* and low sulfate content, phosphate forms aqueous complexes at low pH and apatite at pH > 4 (Fig 2a). With higher *I* and sulfate, phosphate is stable as a crystalline Fe-phosphate (strengite) at high Eh over most of the pH range, while crystalline Al-phosphate (berlinite) is stable at lower Eh and pH > 5 (Fig 2b). Lower phosphate activity increases the aqueous stability field to higher pH (dashed line).

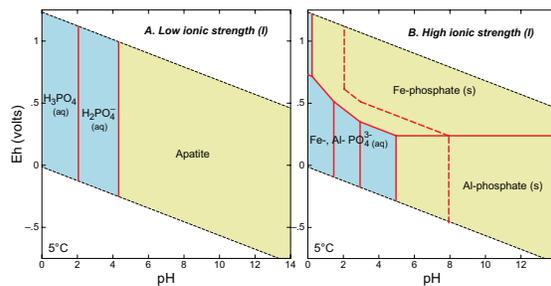


Fig. 2: Phosphate phase diagrams as a function of Eh and pH for water with (a) low *I* and (b) high *I* and high sulfate. The dashed line indicates the larger aqueous stability field at lower PO₄³⁻ activity.

Discussion: Eh, pH, and fluid composition control phosphate stability and have implications for acidic alteration models for the Murray Fm. in Gale Crater. Solid phosphate phases are stable under most circum-neutral and alkaline pH conditions, and PO₄³⁻ is soluble when pH < 5. Variable P abundances and inferred P mobility in the Murray Fm. is consistent with acidic alteration. In the case of dilute, lower *I* solutions (Fig. 2a), acidic solutions capable of leaching Fe, Mn, and Zn ions would also efficiently leach PO₄³⁻ from the bedrock. Conversely, fluids with more dissolved cations (higher *I*) would scavenge PO₄³⁻ (aq.) and precipitate insoluble Fe-phosphates (Fig. 2b). Low abundances of soluble cations with high SiO₂ and variable PO₄³⁻ in the Buckskin and Confidence Hills classes (Fig. 1) leads to two possible interpretations for P mobility:

1. *Dissolution and reprecipitation of secondary phosphates.* Dissolution of primary igneous apatite in basaltic sediments by low pH (< 5) fluids (Fig. 2a) may have initially mobilized PO_4^{3-} in solution. Acidic fluids carrying dissolved PO_4^{3-} would precipitate insoluble secondary Fe-phosphates along alteration fronts or other localized areas where ionic strength was high and abundant Fe ions were available (Fig. 2b). Although they are not modeled here, amorphous ferrous and/or ferric phosphates may also form; these have higher solubility than crystalline phosphates, but follow similar trends with respect to pH, Eh, and composition [6].

2. *Immobilized detrital apatite.* If the Murray Fm. sediment was basaltic with detrital apatite, it is possible that PO_4^{3-} was never extensively released in solution, despite the acidic leaching of other soluble ions. This could occur if apatite-bearing sediment interacted with a low pH, high I fluid with abundant dissolved Fe, forming in-situ Fe-phosphate or Fe-phosphate armour on apatite grains, rendering it immobile [e.g., 7]. The elevated P abundances in this scenario would be caused by passive enrichment via leaching of other soluble elements.

Both models demonstrate that P_2O_5 can be elevated in apatite-bearing sedimentary rocks that were altered (and leached) by acidic fluids. However, evidence from a vein cluster named Garden City in the Murray Fm. (sols 930-948) suggests that the dissolution and reprecipitation processes of *model 1* may dominate. The Garden City veins are ~50 m south of the Pahrump outcrop in the Murray Fm. Most are ~1-6 cm thick, and stand out in relief a few cm above the bedrock (Fig. 3a). Dark material in the veins is composed primarily of Ca (18.1 wt. %), Si (14.5 wt. %), and Fe (11.4 wt.%) with notable enrichments in Mn (~1 wt %) and Ge (650 ppm) (Fig. 3b) [8,9]. White Ca-sulfate formed in a later fluid event, fracturing and entraining the dark material in the pre-existing veins. The Garden City target Kern Peak (KP), interpreted to be bedrock adjacent to the veins within an alteration halo, has low Ca, high Fe and Ge, and the 2nd highest P_2O_5 measured in Gale. The Ge-rich vein-forming fluid was likely acidic because, at low temperature, Ge will only complex with F, a process only stable at a pH < 2.5 [10]. The veins are a micro-environment, demonstrating mobile Ca, Fe, Mn, and PO_4^{3-} ions that were concentrated and precipitated in the vein vicinity. The targets around the Garden City veins illustrate the mobility and concentration of P where precipitation of Fe, Mn, and Ca occurred, supporting the model of Fig. 2b where high I can locally concentrate phosphate phases. While this is evidence that *model 1* may have dominated, immobilization of detrital apatite (*model 2*) could also have occurred, i.e., the two models are not mutually exclusive.

Conclusion: High P_2O_5 in Murray Fm. rocks does not preclude acidic diagenetic fluids in the formation; instead, it may indicate low pH and high ionic strength fluids. However, we acknowledge that multiple geochemical conditions were likely involved; acidic alteration is not the only plausible model (e.g., precipitation of silica cement).

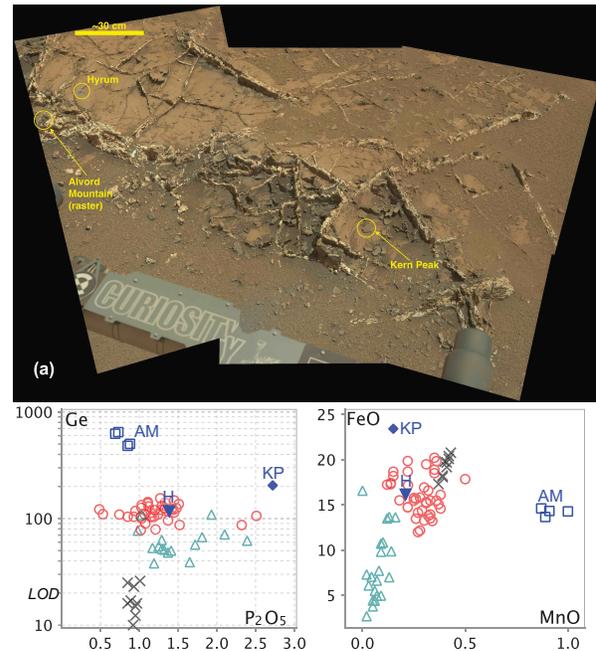


Fig. 3: (a) MastCam mosaic of the Garden City vein cluster and (b) enrichments (oxides in wt %; Ge in ppm) in the veins (bold blue symbols) relative to Murray Fm. bedrock and average Mars (symbols as in Fig. 1). Alvard Mountain (AM) is the dark vein material, Hyrum (H) is unaltered bedrock, and Kern Peak (KP) is altered bedrock next to the vein.

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References: [1] Gellert et al., 2015, AGU abstract #P43B-2120. [2] Yen et al., 2015, AGU abstract #P51E-02. [3] Morris et al., 2015, AGU abstract #P53F-04. [4] Wood and Low, 1986, *GSA Bulletin*, v. 97, no.12. [5] Ferris et al., 2004, *Chemical Geology*, 212, 291-300. [6] Tu et al., 2014, *Am. Mineralogist*, 99, 1206. [7] Johnson and Halberg, 2005, *Science of the Total Environment* 338, 3– 14 [8] Berger et al., 2015, Goldschmidt Conf. abstract #270. [9] VanBommel et al., this conf. [10] Golovnev et al., 2003, *Russian Journal of Gen. Chem.*, 73, 9.