

MANGANESE – PHOSPHORUS SUBSTANCES, PRESENT AND PAST, IN THE GROKEN/AYTON ROCK (GLEN TORRIDON, GALE CRATER, MARS). A.H. Treiman¹, T. Bristow², N. Lanza³, M.T. Thorpe⁴, Yen, A.⁵, E. Rampe⁴, R.T. Downs⁶, G.W. Downs⁶, E. Swanner⁷, D.W. Ming⁴, R.V. Morris⁴, and the CheMin MSL team. ¹Lunar and Planetary Institute / USRA, 3600 Bay Area Blvd., Houston, TX 77058 (treiman@lpi.usra.edu). ²NASA Ames Research Center, CA. ³Los Alamos National Laboratory, NM. ⁴ARES, NASA Johnson Space Center, Houston TX. ⁵Jet Propulsion Laboratory, Pasadena, CA. ⁶University of Arizona, Tucson, AZ. ⁷Iowa State University, Ames, IA.

Introduction: In Glen Torridon (GT), the Curiosity rover analyzed the adjacent drill sample Groken and rock sample Ayton [1] - mudstones with dark diagenetic nodules rich in P and Mn [2,3]. The nodules are important indicators of diagenetic processes and conditions; their P & Mn are of potential astrobiological significance. X-ray diffraction data from the CheMin instrument [4] shows that the P and Mn are in X-ray amorphous material that makes up ~50 wt% of the rock. Bulk chemistry from APXS shows, however, that the molar ratio P/Mn = 2 for these (and other) samples [5]. The small integral ratio suggests that the P and Mn were originally in a stoichiometric crystalline phase. Based on this stoichiometry, possible original P-Mn minerals include laeite and strunzite, which can occur on Earth in moderately oxidizing, acidic to neutral aqueous environments. The rocks' current P-Mn-rich amorphous component could have formed by oxidation of early laeite-strunzite, forming dark-toned X-ray amorphous or nanophase Fe-Mn oxides and/or phosphate.

Data: The CheMin instrument is a transmission X-ray diffractometer (XRD) that provides limited X-ray fluorescence (XRF) data [4]. Drilled rock powders are moved by vibration in sample cells, and thousands of short-duration patterns XRD (minor frames) are summed to make a full XRD pattern. Each minor frame gives diffraction & fluorescence for the few grains in the X-ray beam at that instant. The full pattern for Groken [6] shows diffractions from plagioclase, pyroxenes, bassanite, anhydrite, hematite, Fe-rich carbonate, Fe-Mg smectite, a phyllosilicate that diffracts at 9.22 Å [6,7], and amorphous material.

The APXS instrument analyzes elemental compositions by XRF, induced by α and γ radiation from a solid source [8]. Figure 1 shows P₂O₅ and MnO abundances for rocks and drill fines in GT. The analyses near 1% P₂O₅ and 0.3% MnO represent typical GT rocks [9]. Several samples including Groken are relatively enriched, with molar P/Mn consistently near 2. The composition of the Groken nodules, calculated by deconvolution of a raster analysis [5], includes ~18% P₂O₅, ~8% MnO and ~12% 'FeO.' Several analyses from near GT show similar enrichments, notably the Jones_Marsh vein (7.6% P₂O₅ and 4.0% MnO).

Mn & P Today - Amorphous: It had been proposed that Groken's P and Mn were in a mineral of the jahnsite

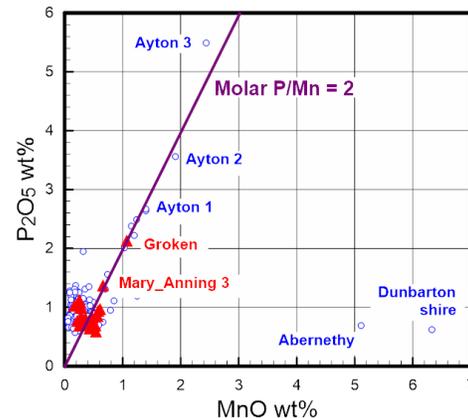


Figure 1. MnO and P₂O₅ abundances, by APXS [9], in rocks of the GT area (blue) and drill fines (red), with some site names. Several analyses show correlated enrichments in P and Mn in a molar ratio of 2 (purple line).

group (with a strong diffraction at 9.22Å) [10], but both elements are concentrated in the rock's amorphous material. The 9.22Å diffraction is assigned to a serpentine-talc interstratification [7], leaving no crystal diffractions assignable to a phosphate. Thus, Groken's P must reside in the amorphous component. XRD and XRF of Groken's CheMin minor frames show that Mn is not correlated with the 9.22Å peak height, but with abundances of phyllosilicate and amorphous material. Because phyllosilicates typically contain little Mn, we also assign Mn to the amorphous component. These assignments are consistent with the Mn-Mg correlation in ChemCam LIBS shot-to-shot data [11].

Mn-P Minerals in the Past: Groken's P and Mn reside in amorphous material, which does not explain why Groken (and others) have molar P/Mn≈2 (Fig. 1). This low integral ratio, if not coincidental, it implies that Groken contained a phase with molar P/Mn≈2, most likely crystalline but possibly amorphous to XRD.

Not Jahnsite. The P-Mn phase cannot have been a mineral of the jahnsite group [10]. Its structure allows extensive substitution for Mn²⁺ in several sites [12]; it seems incredible that we would encounter only those varieties with P/Mn=2. Also, jahnsite is not stable under the conditions of GT sedimentation and diagenesis [13].

Separation of Mn and Fe. To form a mineral with molar P/Mn=2, conditions must prevent significant substitution of other elements for P and Mn. The major substituent for P is As, which has not been detected in

GT rocks. Fe^{2+} can substitute for Mn^{2+} , and Fe is abundant in GT rocks, including Groken. We see three mechanisms that could separate Mn and Fe: crystal chemistry, and oxidation state.

Fe^{2+} and Mn^{2+} have slightly different sizes (effective radii) in mineral, and so can be partitioned among cation sites. Such strong partitioning occurs among sites in beusite-Ca (Table 1). Fe^{2+} and Mn^{2+} can substitute freely in and among many minerals (e.g., olivine, carbonates), but could be strongly partitioned among some phases. For instance, Fe^{2+} could be so strongly partitioned into clay minerals so that contemporaneous phosphates would contain little Fe. The simplest mechanism is oxidation – Fe^{3+} is significantly smaller than Fe^{2+} and can be partitioned effectively away from Mn^{2+} into different crystallographic sites and minerals.

Thus, we sought phosphate minerals with molar P/Mn=2, and with all iron as Fe^{3+} in sites unsuitable for Mn^{2+} , see Table 1. Most in the Table are manganous ferric phosphates with differing crystal structures and hydrations. If Fe^{2+} were available, it could substitute for Mn^{2+} (e.g., ferrolaueite, ferrostrunzite), so Fe^{2+} must be unavailable, i.e., conditions were oxidizing and/or Fe^{2+} is sequestered in a different phase (e.g., clay). Of the minerals in Table 1, laueite (and its polymorphs) and strunzite seem most likely because they are known to form in low-temperature aqueous settings. Stability relations (Fig. 2) suggest formation at oxidizing and near-neutral conditions [14]. Minerals with Al^{3+} in place of Fe^{3+} are possible (e.g., kastningite), but not considered further.

From Past to Present: What might have happened to transform original putative laueite-strunzite to the current amorphous material? Stability relations (Fig. 2) show that oxidation or increasing pH could transform laueite-strunzite into Fe-Mn oxides & hydroxides, many of which are dark-toned and amorphous to X-rays.

Implications: These inferred events are consistent with progressive oxidation or de-acidification: from a

Table 1. Selected Mn-Fe-P Minerals with Molar P/Mn = 2

Minerals	Formula	Setting
Laueite, Stewartite, Pseudolaueite	$\text{Mn}^{2+}\text{Fe}^{3+}_2(\text{PO}_4)_2(\text{OH})_2 \cdot 8\text{H}_2\text{O}$	P F L W V(?)
Strunzite	$\text{Mn}^{2+}\text{Fe}^{3+}_2(\text{PO}_4)_2(\text{OH})_2 \cdot 6\text{H}_2\text{O}$	P F L W
Earlshannonite	$\text{Mn}^{2+}\text{Fe}^{3+}_2(\text{PO}_4)_2(\text{OH})_2 \cdot 4\text{H}_2\text{O}$	P
Wilhemvierlingite	$\text{CaMn}^{2+}\text{Fe}^{3+}(\text{PO}_4)_2(\text{OH}) \cdot 2\text{H}_2\text{O}$	P
Beusite-Ca	$\text{CaFe}^{2+}\text{Mn}^{2+}(\text{PO}_4)_2$	P I
Kastningite, Mangangordonite	$\text{Mn}^{2+}\text{Al}_2(\text{PO}_4)_2(\text{OH})_2 \cdot 8\text{H}_2\text{O}$	P W
Kayrobertsonite	$\text{Mn}^{2+}\text{Al}_2(\text{PO}_4)_2(\text{OH})_2 \cdot 6\text{H}_2\text{O}$	P
Fairfieldite	$\text{Ca}_2\text{Mn}^{2+}(\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$	P

Geological settings of mineral formation, from the literature: P, pegmatite; F, Fe-Mn nodule; L, lake sediments; W, weathering; V, rock varnish; I, iron meteorites.

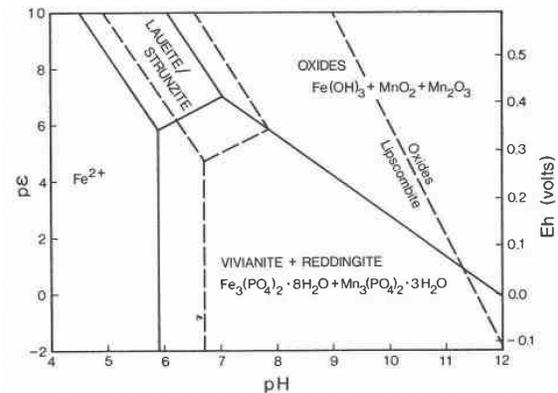


Figure 2. Predicted stability of Mn-Fe-P minerals in aqueous solution, 25°C, dissolved PO_4^{3-} and Fe activities of 10^{-6} and 10^{-4} . Dissolved Mn activities are 10^{-2} (solid lines) and 10^{-4} (broken lines). No carbonate or sulfate. Figure 3 of [14].

precursor containing PO_4^{3-} , Fe^{2+} and/or Mn^{2+} (possibly vivianite [15]); to formation of Fe^{3+} - Mn^{2+} phosphate(s); and then, if the phosphates were crystalline, to X-ray-amorphous phosphate(s) and/or oxy-hydroxides (Fig. 2). This oxidation could be consistent with GT's geological setting, perhaps from redox stratification [16,17] in a lake that progressively shallowed (as by drying up), or by alteration by waters that interacted with the atmosphere [18] (e.g., related to the eroded surface at the top of the GT group).

These inferences constrain but do not define the origin of the Groken/Ayton nodules. It remains unknown why this rock is so rich in Mn and P, nor how and why Mn-P enrichment is distributed in Gale Crater rocks. The abundance of P in Groken/Ayton etc. is significant for astrobiology, as P is commonly the limiting factor for biological productivity. And evidence for changing oxidation states of both Fe and Mn suggests that either redox couple could have been available as a biological energy source.

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