On the occurrence of jahnsite/whiteite phases on Mars: A thermodynamic study

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ABSTRACT

Jahnsites/whiteites are a large family of phosphate hydrate minerals of relevance to terrestrial and martian mineralogy. It was recently hypothesized as being present in Gale Crater sediments from XRD analyses performed by the CheMin analyzer aboard the Curiosity rover. However, the conditions of formation and thermodynamic properties of these compounds are essentially unknown. In this work, we have optimized the ThermAP predictive thermodynamic approach to the analysis of these phases, allowing us to estimate for the first time the standard formation enthalpy (ΔHf), Gibbs free energy (ΔGf), and entropy (Sf) of 15 jahnsite/whiteite end-member compositions, as well as of related phases such as segellerite and alluaudites. These estimations were then used to feed speciation/phase diagram calculation tools to evaluate the relative ease of formation and stability of these hydrated minerals, including considering present martian conditions. Selected laboratory experiments confirmed calculation outcomes. All of our data suggest that the formation of jahnsites is an unlikely process, and point instead to the formation of other simpler phosphate compounds. The stability domain, as calculated here, also raises serious questions about the possible presence of jahnsites on Mars as in Gale Crater, which appears rather improbable.

Keywords: Jahnsite, whiteite, thermochemistry, phase diagram, ThermAP, PHREEQC, stability, Curiosity rover, CheMin, precipitation, dehydration

INTRODUCTION

The terms jahnsite and whiteite, as approved by the IMA Commission on New Minerals and Mineral Names, refer to a supergroup of phosphate hydrous compounds, initially described in 1974 from the analysis of the sample CaMnMgFe3(PO4)(OH)2·8H2O (Moore and Ito 1974). These minerals share the general formula XM1M2M3(PO4)(OH)2·8H2O in which X, M1, and M2 represent mostly divalent cations and where M3 is a trivalent cation in octahedral coordination, dominantly Fe3+ for jahnsites—named after Richard H. Jahns—and Al3+ for whiteites—named after John S. White.

The monoclinic symmetry, space group P21/a, was assessed for all samples analyzed. The structure may accommodate a variety of substituting cations, hence the occurrence of several end-member compositions (often involving manganese) (Grey et al. 2020) and possibly solid solutions. Among reported substituting elements are Ca2+, Mn2+, Na+, in X sites, Mg2+, Mn2+, Fe2+, or Fe3+ in M1 sites and Mg2+, Mn2+, Fe3+(Fe3+) or Zn2+ in M2 sites. While M1 and M2 involve divalent cations again in sixfold octahedral coordination, X ions are located in eightfold cages formed by adjacent phosphate O atoms. As a general observed trend, although exceptions may occur, the cations radii tend to follow an increasing tendency in the order M3 < M2 < M1 < X (Kampf et al. 2019). The crystal structure (Fig. 1) of several end-member compositions has been explored in detail from the analysis of specimens from different terrestrial origins: Table 1 reports the main members of the jahnsite and whiteite subgroups known to date, along with typical localities where they were observed. Additional information on localities containing jahnsites or whiteites may be found, for example, in the MinDat.org online database, respectively with references no. 53039 and 29343. Although these compounds do not represent a high volumetric proportion of phosphate minerals on Earth (Treiman et al. 2021), they were nonetheless observed punctually at distinct places on several continents.

In spite of the above, the conditions of formation of jahnsites/whiteites remain highly unclear. No reports have been made available, to the best of our knowledge, neither on the preparation of pure jahnsite/whiteite synthetic analogs in view of systematic crystallization or dissolution studies, nor on the exploration of their thermodynamic properties (e.g., via calorimetry approaches), which remain essentially unknown. Only a single report addressed the thermal decomposition of one jahnsite-(CaMnMn) and one whiteite-(CaMnMg) specimen, pointing to a degradation pattern until complete dehydration/dehydroxylation (Grice et al. 1990). For the jahnsite-(CaMnMn) compound, the authors mentioned an alluaudite-like X-ray diffraction (XRD) pattern without further details. Unveiling the energetics of jahnsites (in iron-rich contexts) and whiteites (aluminum-rich) vs. their chemical composition would allow understanding further their conditions of formation and exploring their related stability fields depending on local environmental constraints (past or present), not only on Earth but also in other contexts such as the surface of Mars.

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