IS TRIDYMITE A WITNESS OF EXPLOSIVE VOLCANISM IN EARLY MARS?
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Introduction: Tridymite is a silica polymorph (SiO_2) that crystallizes at high temperature (870-1470°C) and low pressure (< 4kbar) in a stable hexagonal form. Its presence in terrestrial settings is usually associated with silicic volcanic environments. A variety of metastable polymorphs occasionally enable tridymite to be found at temperatures outside of its stability field. Monoclinic tridymite is a rare metastable form that forms by displacive transformation from hexagonal tridymite during fast cooling [1], but has only been found in five locations on Earth (e.g., [2]). Surprisingly, monoclinic tridymite was detected in a lacustrine mudstone in Gale crater on Mars by the *Curiosity* rover [3]. The formation mechanism of the martian monoclinic tridymite remain controversial, with studies suggesting silicic volcanism [3], in-situ hydrothermal alteration [4], or low-temperature processes. We will review the formation of hexagonal and monoclinic tridymite in natural settings and evaluate the most plausible pathway(s) enabling the formation of monoclinic tridymite in Gale crater.

Methods: Using X-ray diffraction (XRD), the CheMin instrument onboard the *Curiosity* rover detected a large amount of monoclinic tridymite (15 %) within the Buckskin mudstone, along with plagioclase (19%), minor sanidine (4%), magnetite (3%), cristobalite (3%), and anhydrite (1%), along with a significant amount of a Si-rich amorphous material (44%) containing opal-CT and opal-A and/or Si-rich glass [2,4]. The XRD pattern of monoclinic tridymite is distinct from any opaline silica ($SiO_2.nH_2O$) form despite often confusing nomenclature in the literature discussing the stackings of disordered tridymite (Fig. 1; [5]).

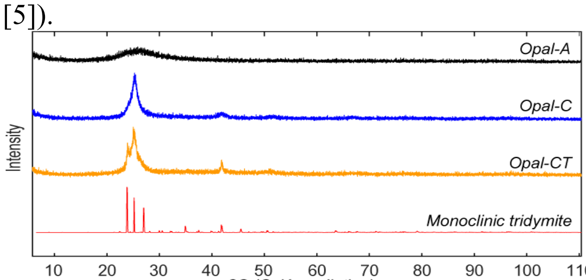

Fig. 1. Diffraction pattern of various forms of opaline silica versus monoclinic tridymite (red line; RUFF database).

The Alpha Particle X-ray Spectrometer (APXS) also onboard *Curiosity* measured the composition of the Buckskin mudstone, revealing a SiO_2-rich (SiO_2 ~ 74 wt.%) and Al_2O_3-depleted (Al_2O_3 ~ 5.5 wt.%) rock [2,6].

Geological Context: The Gale impact basin contains strata displaying fluvial sandstones in the Bradbury formation leading to lacustrine mudstones and sandstones in the Murray formation, with the lake deposits continuing hundreds of meters higher in the stratigraphy [6]. The >1 m-thick Buckskin mudstone layer [7] is part of the Pahrump Hills member of the Murray, interpreted to form from river-generated hypopycnal plumes entering the lake [8]. The composition and mineralogy of Buckskin is radically distinct from any other materials analyzed within Gale crater. The 10 m of Murray formation immediately above Buckskin was not observed on the rover traverse.

Natural Tridymite Formation: In terrestrial settings, meteorites, and lunar basalts, monoclinic tridymite is formed after hexagonal tridymite crystallizes within a magma or impact melt [2]. Hexagonal tridymite forms from impact melt, hydrothermal or fumarole alteration, magmatic melt, or vapor (Fig.2). Reviewing the mineral assemblages of each setting, impact structures presenting tridymite recurrently display quartz paramorphs after hexagonal tridymite due to slow cooling that enables reconstructive transformation to quartz, or due to the occurrence of impurities like Na in the melt that favor transformation to quartz (e.g., Chesapeake Bay, USA [2]). Tridymite from impact melts is usually <<5% [2]. Within geothermal environments, in addition to tridymite, the large range of temperature enable fluids to weather primary and secondary minerals from the basement to a wide range of minerals including phyllosilicates and zeolites as observed at Mount Rainier, USA [9]. Magmatic settings can crystallize large amounts of tridymite (< 45%), cristobalite, and/or feldspar within differentiated melts, with or without the occurrence of quartz depending on the cooling rate of the melt, as observed in an ordinary chondrite [10]. If vapor crystallization occurs in various settings, vapor at the vent of a volcano can crystallize up to 30% of tridymite along with cristobalite, and/or feldspar as observed at the Soufriere Hills volcano [11].

Tridymite Formation in Gale Crater: The formation model of tridymite from Gale crater must explain (i) the large amount of tridymite found in Buckskin, (ii) the mineral assemblage of Buckskin, (iii) the absence of quartz as it was not observed in the large Buckskin vicinity, (iv) the chemical composition of the Buckskin mudstone, and (v) the geological context of Gale crater and the Murray formation.

The low amount of tridymite in terrestrial impact settings and the occurrence of quartz pseudomorphs after tridymite do not support an impact-melt origin. The large range of minerals and the mineralogical zoning related to hydrothermal alteration of the basement does not correspond to the limited mineralogy observed in or around the Buckskin mudstone. Note that no zeolite or high-T phyllosilicate is observed in Buckskin or its vicinity. If *in situ*, hydrothermal alteration would leave patchy features as identified in Gusev crater [12], which was not observed in Buckskin vicinity. The geological context of a paleo-lake, the laminated structures of sedimentary rocks, and the mineral assemblage observed in Gale support a low-temperature system [6]. The two scenarios left are magmatic or vapor crystallization at the vent of a volcano. According to rhyolite-MELTS [13] models from [14] that explain the crystallization of detrital feldspar and pyroxene in the Bradbury formation, tridymite simultaneously crystallizes within rhyolitic melts with plagioclase An_{40} that has a composition matching that of Buckskin. The absence of volcanic features in Buckskin vicinity support a detrital origin. Vapor crystallization at the vent may produce a large amount of tridymite, along with cristobalite and feldspar, which after an eruption would be released into the ash plume. However, direct deposition of ashes would lead to a deposit with higher Al_2O_3 and thicker laminations than the Buckskin mudstone. Instead, ashfall deposition in the upper reaches of the watershed followed by transport into the lake, with some dilution of authigenic SiO_2, is more consistent with Buckskin's sedimentary structure and composition.

Proposed Model: The abrupt change of mineralogy and composition between Buckskin and the 10 m above and below Buckskin [6] supports a limited supply of silica-rich sediment, which can be explained by the erosion of a loose deposit like ashfall. As observed within the Tecocomulco lake, Mexico analog [15], tridymite, cristobalite, and feldspar, either magmatic or vapor crystallized at the vent, were likely erupted from an explosive volcano that could be located thousands of km away (Apolinaris Patera?; Fig.2).

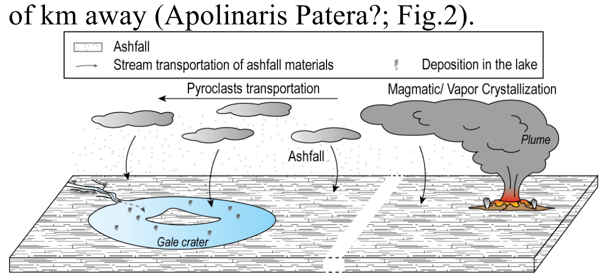

Fig. 2. Sketch of the proposed model for the formation and deposition of tridymite in Gale crater

Deposition within the lake and watershed would lead to the dissolution of rhyolitic glass that would precipitate opaline silica, diluting the concentration of oxides while enhancing SiO_2 concentration. A thinly laminated Si-rich mudstone layer consistent with Buckskin would then form. If true, explosive volcanism on Mars might not be restricted to basaltic systems.

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