DETECTION OF SIDERITE (FeCO₃) IN GLEN TORRIDON SAMPLES BY THE MARS SCIENCE LABORATORY ROVER.

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Introduction: Siderite ($FeCO_3$) has been detected in Gale Crater for the first time by the Mars Science Laboratory (MSL) *Curiosity* and is seen in multiple samples in the Glen Torridon (GT) region. The identification of siderite is based on evolved gas analysis (EGA) data from the Sample Analysis at Mars (SAM) instrument and X-ray diffraction (XRD) data from the Chemistry and Mineralogy (CheMin) instrument.

Curiosity descended off of the Vera Rubin ridge (VRR) into the Glen Torridon region on Sol 2300. Glen Torridon is of particular interest because a strong clay mineral signature had been detected by orbital instruments [1]. To date, four drilled samples have been collected at two different drill locations: Kilmarie and Aberlady from adjacent blocks at the base of the south side of VRR in the Jura member and Glen Etive 1 and 2 on the same block in the Knockfarril member.
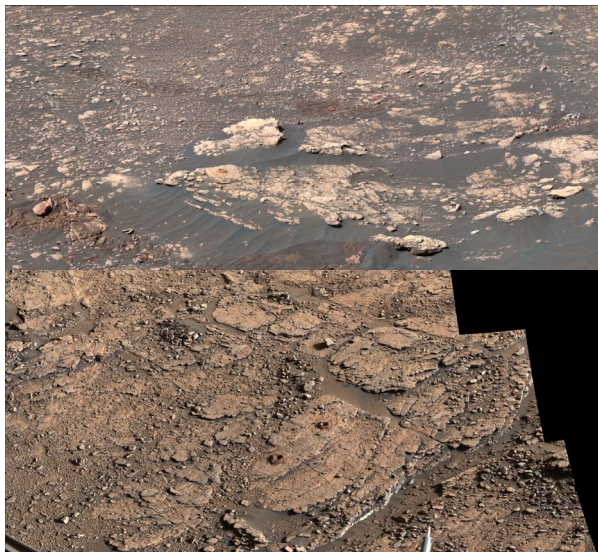

Figure 1 – images of Kilmarie/Aberlady (top) and Glen Etive drill sites (bottom). Image credit: NASA/JPL-Caltech/MSSS

Methods: The SAM and CheMin instruments analyzed drilled rock powders from the samples mentioned above. The SAM instrument has many modes of operation, with this detection using the EGA mode where samples are heated to ~850 °C and evolved gases are moved by a helium carrier gas into a mass spectrometer [2]. CheMin operates in transmission mode (CoKα) from 5-52 °2θ with ~0.35° angular resolution, resulting in a detection limit of ~1 wt.% for crystalline

phases [3]. Mineral and amorphous abundances are derived from Rietveld refinement and full pattern fitting using FULLPAT [e.g. 4, 5].

Lab work was conducted to investigate the low temperature limit for siderite decomposition. Synthesis followed the methods described in Nassar et al. [6], with the sample heated at 140 °C for 1.5 hrs. Instead of drying the products at 60 °C to remove liquid, the sample was frozen and then freeze-dried. The synthesized sample was verified as siderite by XRD using a Rigaku MiniFlex 6G. The sample was also analyzed by the CheMin IV instrument, an engineering model that produces comparable data to the CheMin flight instrument. EGA data was obtained by running the sample in duplicate in an instrument configured to run under SAM-like conditions [7].

Results: *XRD.* The CheMin XRD pattern of Kilmarie shows compelling evidence for the presence of siderite (Fig. 2). Siderite improves the fit to the peaks at 28.8, 37.4, and 49.6 °2θ, representing the (012), (104), and (113) planes in the siderite crystal lattice, respectively. Rietveld refinement and FULLPAT analysis of the Kilmarie pattern demonstrates siderite composes ~2.2 wt.% of the bulk sample and ~7.9 wt.% of the crystalline fraction. Other minerals, including fluorapatite and thenardite, have I100 peaks in similar positions as the I100 peak of siderite at 37.4 °2θ, but siderite provides the best fit to the data.
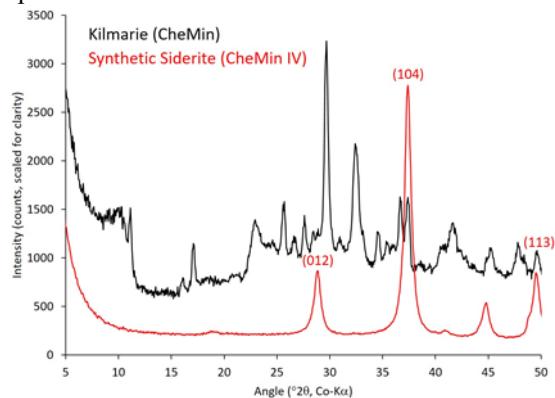

Figure 2 - XRD pattern of Kilmarie (black) and synthetic siderite (red) showing matching peaks.

Siderite is near the detection limit of CheMin (~1 wt.%) in other samples in Glen Torridon and VRR. Siderite and fluorapatite provide equally good fits to

the Rock Hall sample on VRR [8]. Abundances of ~1 wt.% improve the fits of Aberlady and Glen Etive 1. The lack of a peak at 37.4 °2θ in Glen Etive 2, however, indicates siderite is below detection limits in that sample. The CheMin team continues to refine the patterns of Aberlady and Glen Etive 1 to constrain siderite abundances in those samples.

EGA. The SAM instrument detected a CO_2 release peaking between 250-400 °C in the Kilmarie sample and between 250-425 °C in the Glen Etive 1 and 2 samples (SAM did not analyze the Aberlady sample). Siderite decomposition typically peaks around 450-500 °C, higher than what was detected by SAM in these samples. However, as shown in figure 3, siderite synthesized under moderate hydrothermal conditions (140 °C) can decompose at temperatures as low as ~325 °C, likely due to small crystallite size [9] (Fig. 3). Therefore, the CO_2 release detected by SAM in Glen Torridon samples is consistent with siderite decomposition. Furthermore, the carbon isotopic composition, measured by both the mass spectrometer and Tunable Laser Spectrometer (TLS) on SAM are consistent with carbonate as the CO_2 source.
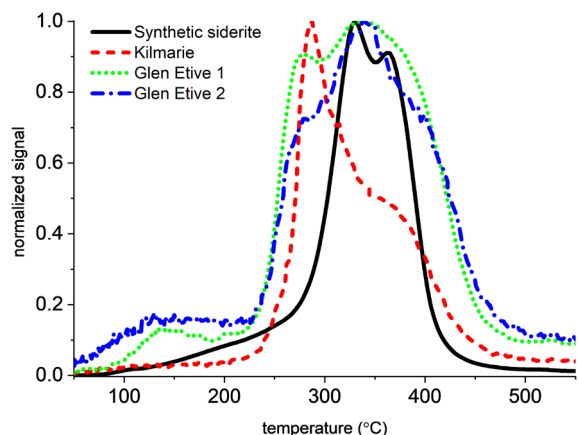

Figure 3 – CO2 release vs. temperature for GT samples and synthetic siderite.

The other line of evidence that points to siderite is the overall abundance of CO_2 detected (Table 1). Other potential sources of CO_2 include combustion of either martian or terrestrial organics, decarboxylation, or decomposition of oxalates. Combustion is not likely because there is no detectable oxygen released from this sample, and 100% efficiency of O_2 removal during combustion is not expected based on many lab runs. Decarboxylation or oxalate decomposition are consistent with the temperature of CO_2 release, but the overall abundance seen would be much higher than expected for organics or oxalates [10].

Siderite Heterogeneity. Due to a drill feed anomaly, the MSL rover no longer uses the sample handling pathway that portioned a known volume of sample.

Delivered sample mass is now calculated by taking CheMin mineral abundances, which do not depend on delivered sample mass, and SAM molar abundances and calculating the delivered mass. For most samples, there are two or more volatile-releasing minerals detected by both SAM and CheMin (including phyllosilicates, sulfates, akaganeite, etc), allowing for multiple sample mass estimates for the same SAM analysis. For the Kilmarie and Glen Etive samples, the sample mass estimates based on siderite do not agree with estimates based on other minerals. This could be caused by different mineral abundances in the samples delivered to SAM and CheMin, which were from the same drill hole, demonstrating that the detected siderite is heterogeneously distributed in the sediment.

Table 1 – FeCO₃ in GT samples based on SAM data

Sample	FeCO$_3$ upper limit (wt%) based on CO$_2$
Kilmarie (2 runs)	1.79 ± 0.91
Glen Etive 1 (2 runs)	1.28 ± 0.48
Glen Etive 2 (1 run)	0.26 ± 0.26

Implications: Siderite forms in fluids with low water:rock ratios, the presence of Fe(II), and low sulfur abundances [11, 12]. Siderite heterogeneity could indicate authigenic formation in particular locations in the Murray formation or that detrital siderite that was uniformly distributed initially but was heterogeneously altered post-burial and lithification. The proximity of the Kilmarie sample to the VRR, a topographic feature likely caused by diagenesis, would be consistent with either case.

Conclusions: The detection of siderite in Gale Crater was the first detection of a carbonate mineral on Mars by XRD. The detection was corroborated by a large CO_2 release at temperatures consistent with decomposition of siderite, and C isotopes consistent with martian carbonates. The presence of siderite implies periods of fluid flow in relatively neutral pH and low sulfur abundances, important constraints on past environmental conditions (and habitability) of Gale Crater.

References: [1] Milliken R. E. et al. (2010) *GRL, 37.* [2] Mahaffy P. R. et al. (2012) *Space Science Reviews*, 1-78. [3] Blake D. F. et al. (2012) *Space Science Reviews*, 170, 341-399. [4] Rietveld H. (1969) *JAC, 2*, 65-71. [5] Chipera S. J. and D. L. Bish (2002) *JAC, 35*, 744-749. [6] Nassar M. Y. et al. (2016) *RSC Advances, 6*, 20001-20013 [7] Archer P. D., Jr. et al. (2014) *JGR: Planets*, 2013JE004493 [8] Rampe E. B. et al. (submitted) *JGR*. [9] Archer P. D., Jr. et al. (2013) *Planetary Science, 2*, 1-21. [10] Benner S. A. et al. (2000) *PNAS, 97*, 2425-2430. [11] Garrels R.M. and C.L. Christ (1965). [12] Matsumoto R. et al. (1981) *Sedimentology, 28*, 239-259.