STOICHIOMETRIC MODELING OF MINERAL ABUNDANCES FROM LIBS IN Al-RICH LIGHT-TONED FLOAT ROCKS IN JEZERO CRATER.

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Introduction: The Mars 2020 *Perseverance* rover has detected light-toned float (LTF) rocks in the crater floor and at the Jezero western fan, with recent long-distance observations showing that they are also present on the crater rim [1]. More than 4,000 candidate LTFs have been identified in Mastcam-Z images as boulders, gravel, and pebble grain size.

The SuperCam instrument [2,3] determined using LIBS that these rocks consist almost exclusively of aluminum and silicon oxides (median 34 and 48 wt%, respectively). SuperCam visible/near-infrared (VISIR) reflectance spectra have provided data for the same Al-rich points measured by LIBS. In previous work, the Infrared (IR) spectra were modeled to find the most likely mineral phases to explain the spectra [4,5].

In this work, stoichiometric modeling has been applied to the Major-element Oxide Composition (MOC) values supplied by SuperCam-LIBS of all the points that are Al-rich on the LTFs considered in previous works [1,4,5], except for targets Ikatan Bay and Lake Clark (extensive coatings), AEGIS 0910A (strong mixing coefficient for hydrated silica [6]), and Trayfoot Mountain (> 10 m away). The respective MOC totals are consistently below 100 wt. %, thus the presence of elements not included in the quantification models, including volatiles such as carbon, hydrogen or sulfur, must be considered. As the LIBS spectra of the analyzed spots did not show carbon above the detection limit and background of the atmospheric CO_2, carbonates were ruled out for these targets. By contrast, a significant hydrogen signal was seen in most of the analyzed points. The IR modeling suggests the presence of sulfates in many of the points although the LIBS spectra did not show clear signals of sulfur due to the high limit of detection (e.g., > 10 wt% SO_3) for this element. Thus, hydrated minerals (kaolinite and metakaolinite), hydroxylated compounds (Al-smectite), sulfate minerals, zeolites, spinel, cordierite and Fe-hydroxide (for some cases also Al-hydroxide), suggested by the IR model, were considered candidates in the different analyzed rasters of the 15 Al-rich LTF rock targets considered in this work (sols 554-924).

Stoichiometric Modeling Method: The starting point to construct the model is the set of minerals proposed during the IR modeling of the LTF rocks [4,5]. As the IR model showed, not all the minerals are present in all the targets, thus, the stoichiometric modeling considers that each element could be in the form of different minerals. To perform the calculations with the stoichiometric modeling, the MOC values (wt. % units) were transformed to the scale of mol/kg for each element (in the oxide form).

To reduce the possible mineral phases, some constraints were applied based on elemental compositions and the IR model. First, igneous minerals are not favored, due to the dearth of many elements typically found in igneous rocks, e.g., Fe, Mg, Ca, Na, and generally also K. Considered next:

- Only 4/15 Al-rich LTF rock targets are compatible with kaolinite ($Al_2O_3.2SiO_2.2H_2O$) because the other 11 LTF rocks obtain calculated %Total values higher than 100% when this di-hydrated mineral was considered in the model; for those 11 rocks, metakaolinite ($Al_2O_3.2SiO_2.H_2O$) gave values close to 100%.
- Illite ($K_2O.4Al_2O_3.10SiO_2.H_2O$) was considered the most likely Al-smectite as the SiO_2 (wt%) vs Al_2O_3 (wt%) plot shows a straight line that goes over the illite composition (see Fig. 2 in [5]).
- Spinel in the form of ($(Mg_x,Fe_{1-x})O.(Al_y,Cr_{1-y})_2O_3$) was considered for all the targets, except for Elk Mountain and Coral Bay. Spinel is suggested by the IR spectra [4,5].
- The CaO abundances (median < 1 wt% but a few up to 8 wt%) show a positive correlation with the deficit (difference to 100 %) in the sum of the wt % of the tabulated major element abundances. This might

Table 1. Mineral Abundances (% units) of the different phases proposed by the best stoichiometric model, for all the Al-rich, Light-toned Float Rocks observed at the Delta Front, Upper fan and margin Unit (until sol 1100) campaigns of the Mars2020 mission. The Total average is 100.01±0.32

	Rock Target	Sol	TiO_2	Illite	Cordierite	Anorthite	Zeolite Mesolite	$CaSO_4$	$MgSO_4$	Spinel	$Fe(OH)_3$	$Al(OH)_3$	(Meta) Kaolinite	Anhydrous SiO_2	TOTAL
Delta Front	Barrier_Range	554	0.53	7.56		2.40	3.56	0.30		4.78	0.17		77.88	3.15	100.33
	Dolgoi_Island	657	1.11	9.46				2.77	4.44	9.16	2.18		60.43	9.96	99.52
	Unga_Island	676	0.91	8.03			23.28	0.86	0.90	2.92	0.83	11.43	50.70		99.86
	Chignik	680	1.26	7.19		1.59	24.59	7.83	3.81		2.02		30.17	21.60	100.06
	Ouzinkie	691	0.74	4.76	9.02			1.57	2.16	1.68	1.42		69.97	8.32	99.66
	AEGIS_0701A	701	1.6			15.23		7.64		7.46	0.34		50.53	17.21	100.00
	Dean_Mountain	702	1.08	8.91		0.52	9.35	1.61	2.19	3.03	0.65		49.75	23.22	100.32
Delta Top	Skeleton_Gulch	775	1.13	3.43		2.16	7.81	0.17		6.01	1.23		70.76	7.54	100.24
	Rainbow_Curve	777	1.01	7.78	5.75	1.92		2.53	4.67	5.30	2.74		47.90	20.76	100.37
	Finch_Lake_782 #1-6	782	1.11	6.52		2.89	30.29	1.89	1.33	6.27	2.91		40.46	6.90	100.57
	Finch_Lake_782 #7-10	782	0.65	6.08		1.11	14.64	4.46	3.48	3.27	0.42	6.94	59.02		100.07
	The Dove #4-5	881	1.05	3.31	7.06			1.04	3.66	4.25	5.25		74.00		99.60
	AEGIS 0912A	912	0.88	3.98	13.37	1.67		1.66	4.22	2.20	7.20	5.98	58.46		99.64
Margin Unit	Elk Mountain	895	0.44	1.55	20.14			2.12	5.50		3.13		54.91	12.00	99.78
	Coral Bay #6-9	924	0.95	1.42	15.51			1.55	2.97		10.19		52.50	15.08	100.17

suggest that most of the Ca is bonded to an element that was not quantified, like sulfur, being particularly true for points with the highest CaO values.

- As suggested by the IR model, Mg-sulfate would be present with anhydrite (Ca-sulfate).

- For half of the targets, zeolite improved the IR model [4,5]. Analcime, chabazite and mesolite were considered as zeolite candidates for the calculations.

- The IR model also suggests the presence of cordierite ($(Mg_xFe_{1-x})O.2Al_2O_3.5SiO_2$) for nearly half of the targets [4,5].

- The Fe- and Al-hydroxides were assumed to be $Fe(OH)_3$ and $Al(OH)_3$ respectively.

Results and Discussion: Different combinations of the given minerals were tested to reach a calculated %Total value as close as possible to 100%. For each combination of minerals in the 15 Al-rich targets, the average %Total was calculated, together with its standard deviation. The best combination is showed in Table 1, with an average calculated Total value of 100.01±0.32.

Kaolinite or metakaolinite proportion ranges from 30% to 78%, and is the only mineral consistently > 10%, being present in all the targets. Also $Fe(OH)_3$ and anhydrite (with Mg-sulfate for most of the targets) it is present in all 15 Al-rich LTF rocks. Excess SiO_2 was modeled as anhydrous silica. When there is no excess silica (4 samples), $Al(OH)_3$ is required to explain the excess of aluminum. Only The Dove target has no excess of neither SiO_2 nor Al_2O_3.

Illite is present in all the targets, except for AEGIS 0701A, the only target that had no potassium above the LIBS detection limit; however, not all of the K_2O is as illite. Among the three zeolites tested, mesolite ($((K_2O)(Na_2O)].2CaO.3Al_2O_3.9SiO_2.8H_2O$) always gave the lowest standard deviation.

Spinel ($((MgO)_{0.51}.(FeO)_{0.49}].[(Al_2O_3)_{0.92}.(Cr_2O_3)_{0.08})$) was present above 1.5% in all targets except for Elk Mountain, Chignik and Coral Bay, with the highest abundance (9.2%) in Dolgoi Island, as predicted by the IR model [4,5]. Anorthite was required to explain the Ca-rich rocks. Cordierite was modeled in the rocks with relatively lower Al_2O_3 that showed this mineral in the IR model [4,5].

Conclusion: The stoichiometric modeling estimates the relative proportions of different minerals. The list of minerals is consistent with that proposed by the IR modeling and strongly support the proposed origin of these rocks as intensely aqueously altered and subsequently heated, causing dehydration and potentially converting some material to spinel [1,5]. To date (Sol ~1100), no outcrop of these light-toned float rocks has been found.

As seen in Table 1, targets from the Delta Front campaign do not require the presence of cordierite to explain the overall composition, except for Ouzinkie. In contrast, targets from the Upper fan campaign require the presence of all the minerals.

The two targets that seem the most unique are from the Margin Unit campaign, for which anorthite, zeolite, spinel and $Al(OH)_3$ are not required. We will continue searching for these Al-rich LTF rocks as the mission moves to the crater rim where long-distance SuperCam RMI images have detected such LTF boulders.

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