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ENVIRONMENTAL FACTORS INFLUENCING SODIUM PERCHLORATE PRECIPITATION ON MARS. I. Población¹, F. Alberquilla¹, J. Aramendia¹, L. Coloma¹, J. Huidobro¹, I. Martínez-Arkarazo¹, K. Castro¹, G. Arana¹, C. García-Florentino^{1,2}, E. Cloutis³, A.M. Ollila⁴, Z.U. Wolf⁴, J.A. Manrique⁵, J. R. Johnson⁶, M. Veneranda⁵, G. López-Reyes⁵, T. Fornaro², A. Alberini², F. Rull⁵, L. García-Gomez⁷, T. Delgado⁷, J. Laserna⁷, J. Martínez-Frías⁸, S.K. Sharma⁹, S.M. Clegg³, J.M. Madariaga¹, T.S.J. Gabriel¹⁰, A. Cousin¹¹, O. Gasnault¹¹, S. Maurice¹¹ and R.C. Wiens¹² and the SuperCam team. ¹Univ. Basque Country UPV/EHU, 48940 Leioa, Spain (iratxe.poblacion@ehu.eus); ²INAF-Astrophysical Observatory of Arcetri, Largo E. Fermi 5, 50125 Florence, Italy; ³Univ. Winnipeg, Manitoba, Canada; ⁴Los Alamos National Laboratory, Los Alamos, NM 87545, USA; ⁵ERICA, U. Valladolid, Spain; ⁶John Hopkins University Applied Physics Laboratory, USA; ⁷UMALASERLAB, Univ. Málaga, Spain; ⁸Institute of Geociencias (IGEO, CSIC-UCM), Madrid, Spain; ⁹Univ. Hawaii, Honolulu, HI, USA; ¹⁰U.S. Geological Survey, Astrogeology Science Center, Flagstaff, AZ, USA; ¹¹IRAP, CNRS, CNES, 31400 Toulouse, France; ¹²Purdue Univ., West Lafayette, IN, USA.

Introduction: The Phoenix spacecraft successfully landed on the northern plains of Mars on 25 May 2008. Its mission was to confirm the presence of substantial ice deposits beneath the planet's surface, initially identified by the 2002 Odyssey mission [1,2]. The spacecraft was equipped with a Wet Chemistry Laboratory (WCL), which enabled the analysis of solution concentrations of various ions, including calcium, magnesium, potassium, ammonium, sodium, hydrogen, chloride, bromide, and iodide, using ion-selective electrodes (ISEs). Among these, a Hofmeister anion ISE, initially designated for nitrate detection, was adapted to detect perchlorate. The findings indicated that each soil sample tested leached 0.4–0.6% of total chlorine by mass, with perchlorate (ClO_4^-) being the dominant soluble chlorine compound detected, followed by chloride (Cl^-) and minor oxichlorides [3]. A more detailed examination of the WCL data suggested that approximately 60% of the parent perchlorate molecules belonged to calcium perchlorate, with the remaining 40% being magnesium perchlorate [4]. Furthermore, a reevaluation of data from the Viking lander indicates the presence of 0.1% perchlorate at landing sites 1 (The Plains of Gold) and 2 (Utopia Planitia) [4]. Kounaves et al. (2014) [5] additionally identified perchlorate at a concentration of 0.67 ± 0.1 ppm in the sawdust portion of Martian meteorite EETA79001, thereby excluding the possibility of terrestrial contamination due to its specific quantity and location.

In addition, the SuperCam instrument onboard the Perseverance rover, observed a narrow peak at approximately 954 cm^{-1} in the abraded patches of both Guillaumes (sol 166, Máz formation) and Bellegarde (sol 188, Máz formation) feldspatic targets. The results of Raman spectroscopy and laser-induced breakdown spectroscopy (LIBS) indicated the presence of anhydrous sodium perchlorate and identified that its presence was mostly accompanied by magnesium

sulfate and chloride-rich calcium phosphate, mixed with a clinopyroxene-rich igneous substrate [6].

In light of the possible significance of these compounds in Mars surface exploration, the primary objective of this study is to enhance our comprehension of the possible pathways of sodium perchlorate formation in feldspar matrices, as well as its competitiveness against the formation of other metal-perchlorate in igneous rocks, by laboratory simulation experiments.

Materials and methods: Two albites, one with low potassium content and the other with medium K content, were used for the experiments. The semi-quantitative elemental concentrations (Wt%) are summarized in Table 1.

Table 1. Semi-quantitative concentrations (Wt%) of the elements present in the Sample 1 and Sample 2.

Wt (%)	Na	Al	Si	S	K	Ca	Fe
Sample 1	10.7	18.2	68.6	0.1	0.9	1.2	0.08
Sample 2	0.9	55.5	34.6	0.3	6.6	0.9	0.7
Wt (%)	Ti	Sr	Zr	Cr	Mn	Cu	Rb
Sample 1	0.02	0.2	0.05	-	-	-	-
Sample 2	0.1	0.04	-	0.03	0.1	0.01	0.02

Albite dissolution was performed at 298 K with stirring, using a ratio of 0.1 g albite in 100 ml ultrapure water solution. The pH of the solution was adjusted to 2 with dilute HNO_3 and the change in pH was monitored with a pH meter. The beakers were sealed with paraffin and kept under stirring for 10 days. At the end of the procedure, the solution was subjected to vacuum filtration and the enriched sodium extract obtained was quantified by inductively coupled plasma mass spectrometry (ICP-MS). After determining the free

sodium concentration, different mixtures of $\text{Sr}(\text{ClO}_4)_2$:extract were prepared with concentrations of 1:1 Na, 1:2 Na and 2:1 Na (molar ratio). $\text{Sr}(\text{ClO}_4)_2$ was selected to add ClO_4^- because it is the most soluble of the perchlorates. After ten days of stirring, the sample was precipitated using an infrared lamp and analyzed by Raman spectroscopy.

Results and discussion: The results of Raman spectroscopy demonstrated compositional differences depending on the sodium perchlorate ratio. Figure 1 illustrates the major compounds obtained by means of Raman spectroscopy in the precipitation process.

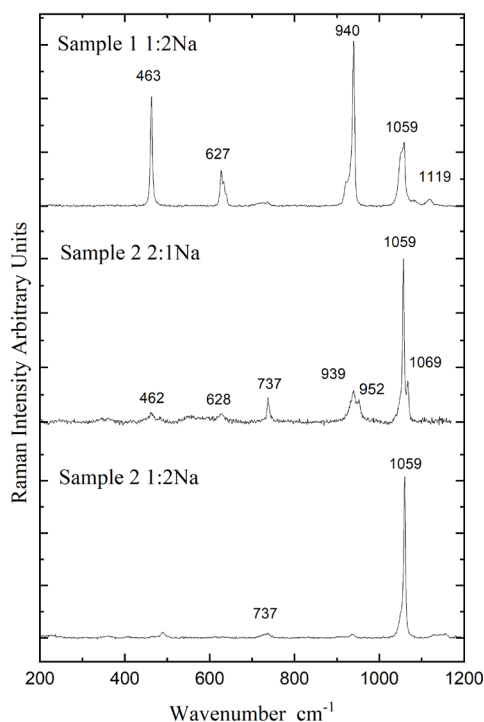


Figure 1. Raman spectra of Sample 1 (with 1:2 Na ratio, with KClO_4 and $\text{Sr}(\text{NO}_3)_2$) and Sample 2 (with 2:1 Na ratio, with NaClO_4 , $\text{Ca}(\text{ClO}_4)_2$ and $\text{Sr}(\text{NO}_3)_2$, and 1:2 Na ratio, with $\text{Sr}(\text{NO}_3)_2$).

Sample 1 is the solid precipitated from extracts with $\text{ClO}_4^- = 1:2 \text{ Na}$, where the extract contains both Na^+ and K^+ ions, exhibited a clear tendency towards the precipitation of potassium perchlorate with its main bands appearing at 463 (strong, s), 627 (medium, m), 940 (very strong, vs), and 1119 (very weak, vw) cm^{-1} and strontium nitrate at 1059 (s) cm^{-1} as a side product.

Sample 2 is the precipitate obtained from extracts with $\text{ClO}_4^- = 2:1 \text{ Na}$, exhibiting a greater compositional heterogeneity with the presence of both calcium perchlorate [bands at 462 (weak, w), 628 (w), and 939 (m) cm^{-1}], and sodium perchlorate with the main band at 952 (m) cm^{-1} and its secondary bands overlapping with those of calcium perchlorate, was ascertained

together with the side strontium nitrate [bands at 737 (m) and 1059 (vs) cm^{-1}].

Sample 2 $\text{ClO}_4^- = 1:2 \text{ Na}$, was obtained precipitating the extract with the highest amount of Na^+ . However, the precipitate showed almost the exclusive presence of the side strontium nitrate.

The continuous appearance of nitrate compounds and strontium is due to the use of external HNO_3 and $\text{Sr}(\text{ClO}_4)_2$ in the experiments. The observation of strontium nitrate is due to its lower solubility product, which makes it the first nitrate to precipitate, followed by potassium nitrate, and finally sodium nitrate. These compounds are not considered to understand the environmental condition to form sodium perchlorate.

The formation of insoluble perchlorate phases follows the order first potassium perchlorate, then by calcium (and magnesium) perchlorate, and lastly the most soluble phase is sodium perchlorate.

These results indicate that the precipitation of sodium perchlorate on the surface of Mars occurred over millions of years after the release of K^+ and Ca^{2+} and the precipitation of magnesium sulfate, the other less soluble phases to sodium perchlorate. If in rock targets similar to Guillaume and Bellegarde, ions like K^+ , Ca^{2+} and Mg^{2+} were released when the perchlorate-rich fluids get in contact with the rock, the corresponding K^+ , Ca^{2+} and Mg^{2+} perchlorate would be formed and not the sodium one. Thus, in the case of Guillaume and Bellegarde, the formation of the detected sodium perchlorate took place when a second perchlorate-rich fluid arrived after the precipitation of magnesium sulfate in a previous event (thousands of years ago) with a sulfate-rich fluid.

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