

OXYGEN AND CARBON ISOTOPE SYSTEMATICS IN CO₂-H₂O-(Ca,Mg,Na)ClO₄ BRINE SYSTEM BELOW 0 °C: IMPLICATIONS FOR OXYGEN ISOTOPE COMPOSITION OF WATER AND CARBON SEQUESTRATION ON MARS. M. I. El-Shenawy¹ and P. B. Niles², ¹USRA, NASA Johnson Space Center, Houston, TX 77058 (mohammed.i.elshenawy@nasa.gov), ²NASA Johnson Space Center, Houston, TX 77058.

Introduction: Perchlorates have been detected on Mars at locations across the surface including Phoenix landing site at 68°N, Gale Crater at 4.5°S, and two Viking landing sites at 22.5°N and 48.3°N [1-3]. This wide occurrence of perchlorates (~ 6.5 % of the Martian surface area) suggests the possible widespread existence of perchlorate brines on Mars at temperatures down to 198 K [4,5]. Evidence of liquid water on Mars was inferred from the spectral analysis of modern flow structures on surface (RSLs) and the radar imaging of subsurface large water body, which are potentially associated with the occurrence of Mg, Ca, Na - perchlorates [6,7].

Under modern Martian climatic conditions, cryogenic perchlorate brines would allow oxygen isotope exchange between H₂O and atmospheric CO₂. As a result, the oxygen isotope reservoir in water (minor oxygen reservoir) would be closely related to the reservoir in atmospheric CO₂ (major oxygen reservoir). The relation between the oxygen isotope composition in both oxygen reservoirs, oxygen isotope fractionation between CO₂ and water ($1000 \ln^{18}\alpha_{\text{CO}_2\text{-H}_2\text{O}}$), would be governed by ambient temperature [e.g., 8]. This relation has not been defined at temperatures below 273.15 K. This relationship is crucial to better understand the oxygen isotope composition of Martian surface water and the history of aqueous processes on Mars. In addition, cryogenic perchlorate brines could potentially have a high solubility of atmospheric CO₂ [e.g., 5], trapping carbon either in the form of dissolved inorganic carbon (DIC) or carbonates (i.e., carbon sequestration). The latter would result from the combination of CO₂ and cations (Mg, Ca, Na) in brines.

In this study, we attempt to determine the oxygen isotope fractionation ($\ln^{18}\alpha_{\text{CO}_2\text{-H}_2\text{O}}$ – temperature relation) and to investigate the solubility of CO₂ in perchlorate brines between +30 and -33 °C.

Methods: Na, Ca, Mg-perchlorate solutions of eutectic concentration (i.e., 9.25, 4 and 3.4 mol.kg⁻¹, respectively) were prepared in a dry glove box under continuous nitrogen gas flow at room temperature. To prepare these solutions, 18 MΩ deionized water was boiled to release any dissolved CO₂, and was measured for its oxygen isotope composition ($\delta^{18}\text{O}_{\text{H}_2\text{O}}$) against the international water standards (i.e., VSMOW and SLAP). Then dried anhydrous perchlorate salts were dissolved in this carbon free-water. The solutions were poured into 20 mL vials sealed with aluminum seal and septum. Meanwhile, Exetainer® vials (10 ml) were

automatically flushed and filled with a 0.4 % CO₂ and 99.6 % He mixture for 10 mins using the Gas Bench II system to assure that similar volume of CO₂-He mixture were added to the vials and no other gases were in the vials. Carbon and oxygen isotope compositions ($\delta^{13}\text{C}_{\text{CO}_2}$ and $\delta^{18}\text{O}_{\text{CO}_2}$) of the starting CO₂ gas in the mixture were -4 ‰ relative to VPDB and +26.12 ‰ relative to VSMOW, respectively. All vials containing solution and gas mixture were stored at either 30, 4, -15 or -33 °C, depending on the target experimental temperature for a day to establish the thermal equilibria.

Subsequently, 0.4 mL of the perchlorate solution was drawn with a 1 mL syringe through the septum of the solution vial and injected into the Exetainer® vial containing the gas mixture. Then the Exetainer® vial was aged for a certain time at the storage temperature until the measurement of oxygen isotope composition of the CO₂ in the headspace was performed. The $\delta^{13}\text{C}_{\text{CO}_2}$ and $\delta^{18}\text{O}_{\text{CO}_2}$ were measured using the Gas Bench II system coupled with a Finnigan MAT 253 continuous flow isotope ratio mass spectrometer (CF-IRMS) at JSC.

Results and Discussion:

Determination of oxygen isotope fractionation between CO₂ and water ($1000 \ln^{18}\alpha_{\text{CO}_2\text{-H}_2\text{O}}$) in brines.

The $^{18}\alpha_{\text{CO}_2\text{-H}_2\text{O}}$ values were determined by the following expression:

$$1000 \ln^{18}\alpha_{\text{CO}_2\text{-H}_2\text{O}} = 1000 * \ln [(1000 + \delta^{18}\text{O}_{\text{CO}_2}) / (1000 + \delta^{18}\text{O}_{\text{H}_2\text{O}})]$$

The $1000 \ln^{18}\alpha_{\text{CO}_2\text{-H}_2\text{O}}$ values increase exponentially with time from the initial $1000 \ln^{18}\alpha_{\text{CO}_2\text{-H}_2\text{O}}$ value at aging time zero and then level off at a certain time-invariant $1000 \ln^{18}\alpha_{\text{CO}_2\text{-H}_2\text{O}}$ value (Fig. 1). In general, this time-invariant $1000 \ln^{18}\alpha_{\text{CO}_2\text{-H}_2\text{O}}$ value decreases with increasing temperature. Furthermore, it also depends on the cation in the perchlorate brines within a certain temperature (i.e., the time-invariant $1000 \ln^{18}\alpha_{\text{CO}_2\text{-H}_2\text{O}}$ value in Na > Ca > Mg) (Fig. 1). The latter observation is explained by the salt isotope effect which has been reported by other researchers [e.g., 9]. However, the time-invariant $1000 \ln^{18}\alpha_{\text{CO}_2\text{-H}_2\text{O}}$ value in NaClO₄ brines is statistically indistinguishable from that determined in pure water at a same temperature (i.e., +30 and +4 °C). In this study, the time-invariant $1000 \ln^{18}\alpha_{\text{CO}_2\text{-H}_2\text{O}}$ values determined in pure water and NaClO₄ brines at +30 and +4 °C are in a good agree-

ment with the previously reported $1000 \ln^{18}\alpha_{\text{CO}_2\text{-H}_2\text{O}}$ value at isotopic equilibrium in Bottinga and Craig [8]. This suggested that our CO_2 -brine system has reached isotopic equilibrium and can be used to calibrate the $\ln^{18}\alpha_{\text{CO}_2\text{-H}_2\text{O}}$ – temperature relation at below 0°C . At present time, our calibration of this relation is: $1000 \ln^{18}\alpha_{\text{CO}_2\text{-H}_2\text{O}} = 17.24 (1000/T) - 17.80$; and it is based upon the $1000 \ln^{18}\alpha_{\text{CO}_2\text{-H}_2\text{O}}$ values obtained from three temperatures (i.e., $+30$, $+4$ and -15°C) because the experiments at -33°C are still ongoing.

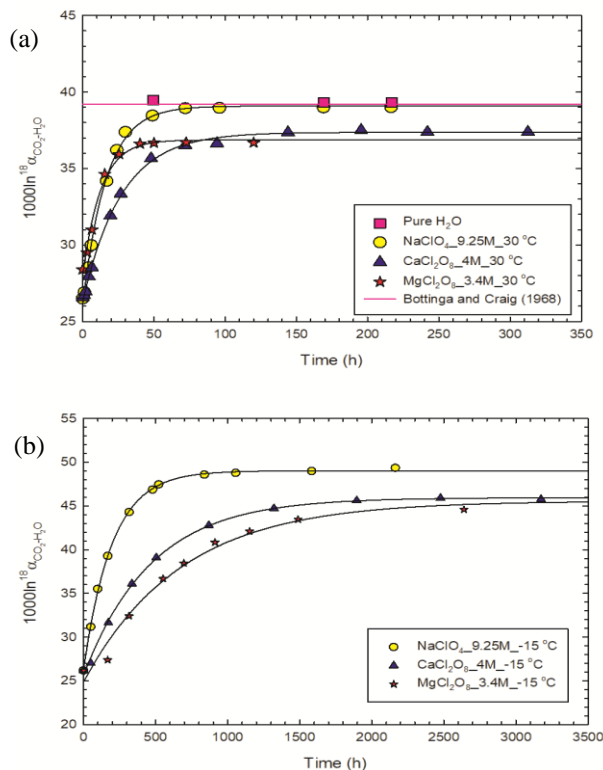


Fig. 1: $1000 \ln^{18}\alpha_{\text{CO}_2\text{-H}_2\text{O}}$ evolution versus time in CO_2 – perchlorate brines. (a) at 30°C and (b) at -15°C . Full data will be presented in the poster due to the page limitation.

Carbon isotope systematics in CO_2 - perchlorate brines.

The $\delta^{13}\text{C}_{\text{CO}_2}$ value of CO_2 in the headspace above the perchlorate brines quickly (compared to the $1000 \ln^{18}\alpha_{\text{CO}_2\text{-H}_2\text{O}}$) evolved from the starting $\delta^{13}\text{C}_{\text{CO}_2}$ at zero time to a lower constant value which decreases with decreasing temperature (Fig. 2). At all temperatures, the CO_2 above the MgCl_2O_8 brines possess the lowest $\delta^{13}\text{C}_{\text{CO}_2}$ value. The decrease in the $\delta^{13}\text{C}_{\text{CO}_2}$ value was also associated with a decrease in the CO_2 fraction in the headspace suggesting that CO_2 was trapped in the brines. If there was a CO_2 leakage out of the Exetainer® vial, the $\delta^{13}\text{C}_{\text{CO}_2}$ value would be higher than the starting CO_2 at zero time because the ^{12}C in CO_2 escapes first enriching the remaining CO_2 fraction

in ^{13}C . We interpret the decrease in the $\delta^{13}\text{C}_{\text{CO}_2}$ value as an indication to the carbonate precipitation in the brines, especially in the MgCl_2O_8 brines.

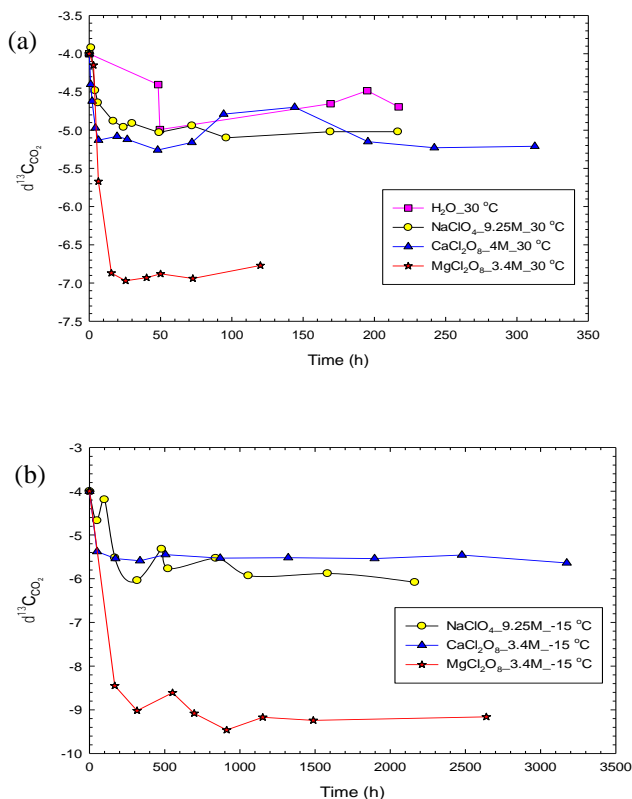


Fig. 2: The $\delta^{13}\text{C}_{\text{CO}_2}$ evolution versus time in CO_2 – perchlorate brines. (a) at 30°C and (b) at -15°C . Full data will be presented in the poster due to the page limitation.

Conclusions: Based upon our $1000 \ln^{18}\alpha_{\text{CO}_2\text{-H}_2\text{O}}$ – temperature calibration, the $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ on Mars surface (average temperature = -63°C and the $\delta^{18}\text{O}_{\text{CO}_2}$ of Mars atmosphere = $48 \pm 5\text{‰}$) would be $-16 \pm 5\text{‰}$ VSMOW which is consistent with low temperature equilibrium with the Martian silicate crust. The potential carbonate precipitation inferred from the $\delta^{13}\text{C}_{\text{CO}_2}$ in our experiments suggests that carbon sequestration on Mars may have occurred via large subsurface carbonate deposition in subglacial salt lakes [e.g., 7]. This would preferentially remove the ^{13}C driving the remaining atmospheric CO_2 to lower $\delta^{13}\text{C}$ values. This could reduce ^{13}C enrichment from atmospheric loss [10].

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