



Cite this: *RSC Adv.*, 2017, 7, 46866

Water uptake and hygroscopicity of perchlorates and implications for the existence of liquid water in some hyperarid environments

Wenjun Gu,^{ac} Yongjie Li,^b Mingjin Tang,  ^{*,a} Xiaohong Jia,^{ac} Xiang Ding,^a Xinhui Bi^a and Xinming Wang^{ad}

The existence of liquid water is a prerequisite for habitability. Deliquescence of perchlorates under subsaturated conditions has been proposed to explain the occurrence of liquid water in some hyperarid environments on the earth and on the Mars. However, the amount of liquid water associated with perchlorates under different conditions is not well understood yet. In this work, we have measured deliquescence relative humidity (DRH) of three perchlorates at different temperatures from 278 to 303 K. DRH decreases from $(42.8 \pm 0.6)\%$ at 278 K to $(40.5 \pm 0.5)\%$ at 303 K for $\text{Mg}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$, and from $(18.5 \pm 0.5)\%$ at 278 K to $(15.5 \pm 0.5)\%$ at 303 K for $\text{Ca}(\text{ClO}_4)_2 \cdot 4\text{H}_2\text{O}$; in contrast, deliquescence of KClO_4 did not occur even when RH (relative humidity) was increased to 95%. In addition, we have determined the amount of water taken up by $\text{Ca}(\text{ClO}_4)_2 \cdot 4\text{H}_2\text{O}$ and $\text{Mg}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ as a function of RH (0–90%) and temperatures (278–298 K). It is found that when both salts are deliquesced, more water ($\sim 10\%$ on average) is associated with $\text{Mg}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ than $\text{Ca}(\text{ClO}_4)_2 \cdot 4\text{H}_2\text{O}$ on the per mole ClO_4^- base. Overall, this work would significantly improve our knowledge in hygroscopicity of perchlorates, and thus may provide fundamental insights into the hydrologic cycles in some hyperarid regions on the earth and on the Mars.

Received 29th July 2017
Accepted 27th September 2017

DOI: 10.1039/c7ra08366a

rsc.li/rsc-advances

1 Introduction

As we currently understand, liquid water is a prerequisite for the occurrence of life. In hyperarid environments on the earth such as the Atacama Desert in Chile, pure liquid water is not stable due to extremely low water vapor concentrations in the atmosphere.^{1–3} Deliquescence of soluble minerals, such as chlorates and perchlorates, could lead to the formation of stable aqueous solution (and thus liquid water) in these hyperarid regions.^{2,4–6} Deliquescence is the phenomenon that under subsaturated conditions a soluble component takes up water vapor and forms a stable aqueous solution.⁷ Indeed, perchlorates have been found in soils in many arid and/or semi-arid regions on the earth, including the Antarctic Dry Valleys, Southwest US, and the Atacama Desert.^{8–12} Perchlorates may be formed photochemically from chlorides and emitted by anthropogenic activities,^{8,11,13–15} but their sources are not entirely clear.

The deliquescence of perchlorates is also relevant for the Martian environment. One important question in research of the Mars is whether liquid water exists or existed on the Mars. Evidence which supports the existence of liquid water on the Mars is mounting,^{16–18} though pure liquid water is not stable on the Mars due to its extremely dry and cold environment as well as low atmospheric pressure. It has been proposed that the presence of perchlorates in Martian soil, which have been detected at a number of sites on the Mars,^{19,20} can lower the freezing temperature of liquid water and form stable aqueous solutions by absorbing water vapor from the atmosphere even under subsaturated conditions.^{21–25}

Several laboratory and theoretical studies have investigated the deliquescence and efflorescence of perchlorates at different temperatures.^{22,23,25–28} For example, a laboratory study by Zorzano *et al.*²³ found that sodium perchlorate could absorb water vapor and form aqueous solutions under Martian conditions at temperatures as low as 225 K. The deliquescence relative humidity (DRH) decreases from 64% at 223 K to 42% at 273 K for $\text{Mg}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$, and decreases from 64% at 228 K to 51% at 273 K for $\text{NaClO}_4 \cdot \text{H}_2\text{O}$.²⁵ The DRH of calcium perchlorate varies between 5% and 55% for the temperature range of 223–273 K,²² probably because the hydration state of calcium perchlorate changes at different temperatures. It has not been clearly stated in the two original studies^{22,25} whether the RH was respected to liquid water or ice, though RH with respect to liquid water is

^aState Key Laboratory of Organic Geochemistry, Guangdong Key Laboratory of Environmental Protection and Resources Utilization, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, Guangzhou 510640, China. E-mail: mingjintang@gig.ac.cn

^bDepartment of Civil and Environmental Engineering, Faculty of Science and Technology, University of Macau, Avenida da Universidade, Taipa, Macau, China

^cUniversity of Chinese Academy of Sciences, Beijing 100049, China

^dCenter for Excellence in Regional Atmospheric Environment, Institute of Urban Environment, Chinese Academy of Sciences, Xiamen 361021, China



commonly used for DRH.⁷ In another study using a Raman scattering lidar,²⁶ $\text{Mg}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ was found to deliquesce when the temperature is only ~ 4 K higher than the frost point. Phase transition of chloride–perchlorate binary mixtures and the salt analog, which closely replicates the composition and relative concentrations of common cations and anions found at the Phoenix landing site on Mars, has also been explored.^{29,30} While previous studies support the possible occurrence of liquid water in some hyperarid regions on the earth (as well as on the Mars) from a fundamental point of view, a better understanding of hydrologic cycles in these hyperarid environments requires quantitative knowledge of water partitioning between the gas phase and perchlorates under different conditions. However, to our knowledge such information is not available yet.

In this work we have quantitatively measured the amount of water associated with $\text{Ca}(\text{ClO}_4)_2 \cdot 4\text{H}_2\text{O}$, $\text{Mg}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ and KClO_4 in equilibrium with water vapor as a function of RH (0–90%) at different temperatures (278–298 K). In addition, we have also determined the DRH of $\text{Ca}(\text{ClO}_4)_2 \cdot 4\text{H}_2\text{O}$ and $\text{Mg}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ as a function of temperature (278–303 K) in a very accurate manner. Our results provide quantitative knowledge of deliquescence properties of perchlorates, and thus may help better understand the hydrologic cycles in some hyperarid environments on the earth and on the Mars.

2 Experimental section

The interaction of perchlorates with water vapor under subsaturated conditions was investigated using a commercial vapor sorption analyzer (model no. Q5000SA; manufacturer: TA Instruments, New Castle, DE, USA). The instrument has been detailed in our previous study,³¹ and here we only briefly describe experimental procedures that are important for this study. High purity N_2 was used in this work unless otherwise stated.

2.1 Vapor sorption analyzer

The schematic diagram of the vapor sorption analyzer used in this work is shown in Fig. 7 in the Appendix. The principle of this instrument lies on accurate and precise measurements of the absolute mass of the sample under investigation at well controlled temperature and RH. A humidity chamber was used to control the temperature and RH under which the sample was exposed to water vapor. RH was regulated by mixing a dry N_2 flow with a humidified N_2 flow, both controlled using mass flow controllers (MFC), and the total flow delivered into the humidity chamber was set to 200 mL min^{-1} . Temperature (278–353 K) and RH (0–98%) to which perchlorates were exposed could be programmed and were monitored in real time as well. Temperature stability of ± 0.1 K and RH stability of $\pm 1\%$ could be achieved. In this work all the experiments were conducted under isothermal conditions, *i.e.* during each experiments temperature was kept constant while RH was varied.

Two semispherical metalized quartz crucibles, connected to a high-precision balance *via* hang-down wires, were located in

the humidity chamber. These crucibles, each with a volume of $180 \mu\text{L}$, were provided by the instrument manufacturer. One crucible contained perchlorate powder and the other one was empty, and therefore water uptake by the empty crucible could be simultaneously measured and subtracted. The balance used to measure sample mass has a dynamic range of 0–100 mg, a stated sensitivity of $<0.1 \mu\text{g}$, and a weighing accuracy of $\pm 0.1 \mu\text{g}$. The baseline drift in mass measurement was found to be $<5 \mu\text{g}$ within 24 h at 20% RH and 298 K when no sample was used for the sample crucible. A small N_2 flow (10 mL min^{-1}) was used to purge the balance continuously in order to prevent moisture condensation. In this work the initial mass of perchlorate samples was typically in the range of 1–5 mg, and in each experiments fresh perchlorate samples were used. Since only data under equilibrium were used, the amount of sample should not impact our results; however, it affected the time to reach the equilibrium (*i.e.* it took longer to reach the equilibrium if the initial mass of the sample was larger).

2.2 Water uptake measurements

In the first type of experiments, the amounts of water associated with perchlorates were determined as a function of RH at different temperatures. The following experimental procedures were used: (i) temperature was set to a given value; (2) after the temperature was stabilized, the sample was dried at 0% RH (the actual RH was measured to be $<5\%$ under “dry” conditions) until the mass change was $<0.05\%$ within 30 min; (3) RH was increased stepwise to 90% with an increment of 10% per step, and at each RH the sample was equilibrated with water vapor until its mass became stable (*i.e.* the sample mass change was $<0.1\%$ within 30 min); (4) the sample was dried again at 0% RH until its mass change was $<0.1\%$ within 30 min.

Fig. 1 shows the dataset for a typical experiment designed to measure the amount of water taken up by $\text{Ca}(\text{ClO}_4)_2 \cdot 4\text{H}_2\text{O}$ as

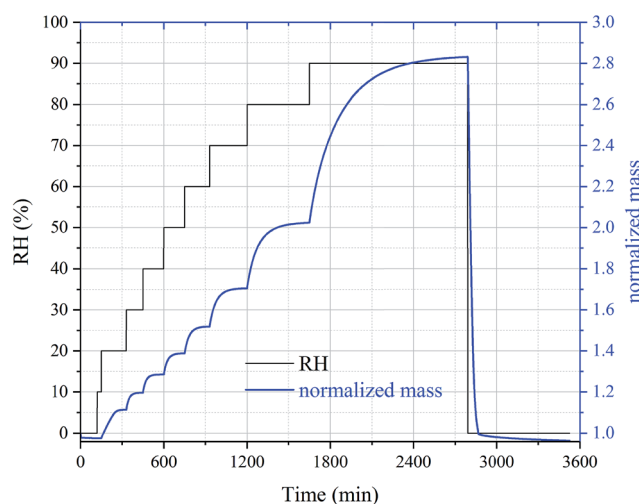


Fig. 1 Time series of RH and normalized sample mass in a typical experiment designed to measure mass hygroscopic growth factors of perchlorates. In the experiment shown in this figure, $\text{Ca}(\text{ClO}_4)_2 \cdot 4\text{H}_2\text{O}$ was used and the temperature was set to 298 K.



a function of RH at 298 K. Significant increase in sample mass was observed when RH was increased from 10% to 20%, suggesting that the deliquescence of $\text{Ca}(\text{ClO}_4)_2 \cdot 4\text{H}_2\text{O}$ occurred at a RH between 10% and 20% at 298 K. Further increase in RH caused additional increase in sample mass. After RH was returned to 0%, the sample mass was equal to the initial value within the experimental uncertainty, suggesting that after the humidification–dehumidification process, the sample had the same hydration state as the unprocessed one. The data shown in Fig. 1 could be used to derive the amounts of water taken up by $\text{Ca}(\text{ClO}_4)_2 \cdot 4\text{H}_2\text{O}$ as a function of RH.

2.3 DRH determination

Accurate DRH values were measured in the second set of experiments as a function of temperature for perchlorates, and the following experimental procedures were used: (1) temperature was set to a given value; (2) after the temperature was stabilized, the sample was dried at 0% RH until the mass change was $<0.05\%$ within 30 min; (3) RH was then increased to a value which was at least 5% lower than the expected DRH (which could be roughly estimated from experiments described in Section 2.2) and kept at this level for 60 min; (4) RH was increased stepwise with an increment of 1% per step until a significant increase in sample mass occurred, and at each RH the sample was equilibrated with the environment for 30 min. DRH is equal to the RH at which a significant increase in sample mass was observed (*i.e.* the mass increase was significant compared to the noise level and baseline drift).

Fig. 2 shows the time series of sample mass and RH in an experiment to measure DRH of $\text{Ca}(\text{ClO}_4)_2 \cdot 4\text{H}_2\text{O}$ at 298 K. As shown in Fig. 2, a slow and small decrease in sample mass was observed when RH was increased from 0% to 16%, suggesting that gradual loss of residual water, which may be adsorbed by

the powdered $\text{Ca}(\text{ClO}_4)_2 \cdot 4\text{H}_2\text{O}$ sample, occurred before it was deliquesced. When RH was increased from 16% to 17% (shaded region in Fig. 2), a significant increase in sample mass was observed, suggesting that the DRH of $\text{Ca}(\text{ClO}_4)_2 \cdot 4\text{H}_2\text{O}$ was measured to be $(16.5 \pm 0.5)\%$ (strictly speaking, between 16% and 17%). Fig. 2 also reveals that when RH was above the DRH, further increase in RH would lead to quicker increase in sample mass, as expected.

3 Results and discussion

In this work we have studied water uptake by $\text{Ca}(\text{ClO}_4)_2 \cdot 4\text{H}_2\text{O}$, $\text{Mg}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ and KClO_4 , because previous studies suggested^{22,32–35} that they are the most stable forms of $\text{Ca}(\text{ClO}_4)_2$, $\text{Mg}(\text{ClO}_4)_2$ and KClO_4 for the temperature range (278–303 K) covered by our work. $\text{Ca}(\text{ClO}_4)_2 \cdot 4\text{H}_2\text{O}$, $\text{Mg}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ and KClO_4 were provided by Aldrich with stated purity of $>99\%$. All the chemicals were used as received without any pretreatment.

3.1 DRH of perchlorates

DRH values were determined as a function of temperature from 278 to 303 K for $\text{Ca}(\text{ClO}_4)_2 \cdot 4\text{H}_2\text{O}$ and $\text{Mg}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$, and the results are summarized in Table 1. The DRH of $\text{Mg}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ was found to slightly decrease with increasing temperature, from $(42.8 \pm 0.6)\%$ at 278 K to $(40.5 \pm 0.5)\%$ at 303 K. DRH of $\text{Mg}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ was measured to be 42% at 273 K by a previous study by Gough *et al.*,²⁵ and it increased to 64% when temperature decreased to 223 K. The DRH measured at 273 K by Gough *et al.*²⁵ is in good agreement with that measured at 278 K in our work. In addition, our measured DRH values and their dependence on temperature are also consistent with those calculated using a thermodynamic model²⁵ for temperature in the range of 278–303 K. The thermodynamic model used by Gough *et al.*²⁵ and Nuding *et al.*²² was developed by Chevrier *et al.*²⁴ In brief, this thermodynamic model, in which the Pitzer ion interaction model³⁶ was used to calculate activities of water and different ions, calculated the stability diagram of perchlorates as a function of solute concentration and temperature.²⁴

For comparison, DRH of $\text{Ca}(\text{ClO}_4)_2 \cdot 4\text{H}_2\text{O}$ is much lower than that of $\text{Mg}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ at the same temperature. In addition, a weak negative dependence of DRH on temperature was also observed for $\text{Ca}(\text{ClO}_4)_2 \cdot 4\text{H}_2\text{O}$, with DRH increasing from (15.5

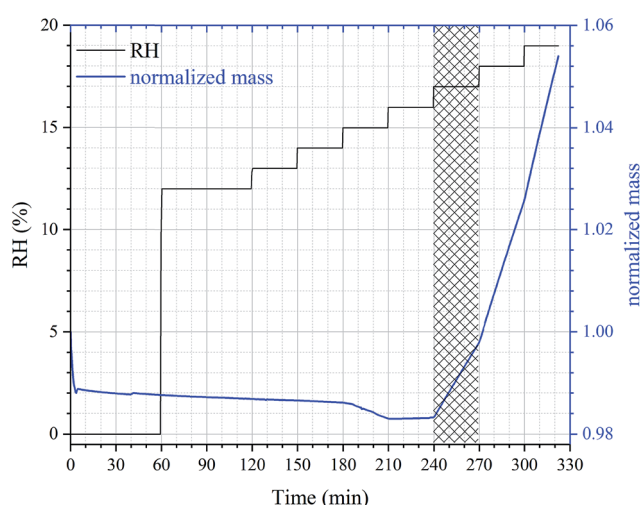


Fig. 2 Time series of RH and normalized sample mass in a typical experiment designed to measure DRH of perchlorates. In the experiment shown in this figure, $\text{Ca}(\text{ClO}_4)_2 \cdot 4\text{H}_2\text{O}$ was used and the temperature was set to 298 K. The shadowed region shows the RH at which a significant increase in sample mass was first observed due to deliquescence of $\text{Ca}(\text{ClO}_4)_2 \cdot 4\text{H}_2\text{O}$.

Table 1 Deliquescence relative humidities (DRH) of $\text{Ca}(\text{ClO}_4)_2 \cdot 4\text{H}_2\text{O}$ and $\text{Mg}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ at different temperatures (278–303 K). All the measurements were repeated three times, and the stated errors ($\pm 1\sigma$) are statistical only

T (K)	DRH (%)	DRH (%)
	$\text{Ca}(\text{ClO}_4)_2 \cdot 4\text{H}_2\text{O}$	$\text{Mg}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$
278	18.5 ± 0.5	42.8 ± 0.6
283	17.5 ± 0.5	42.2 ± 0.6
288	17.5 ± 0.5	41.5 ± 0.5
293	16.5 ± 0.5	41.2 ± 0.6
298	16.5 ± 0.5	40.5 ± 0.5
303	16.5 ± 0.5	40.5 ± 0.5



$\pm 0.5\%$) to $(18.5 \pm 0.5)\%$ when temperature decreases from 303 to 278 K. The DRH of calcium perchlorate was measured to be $(10 \pm 4)\%$ at 273 K and $(55 \pm 4)\%$ at 223 K by Nuding *et al.*,²² and the large variation in DRH at different temperatures was suggested to result from the formation of different hydrates at different temperatures. Our measured DRH ($\sim 18.5\%$) at 278 K is slightly higher than that measured at 273 K ($\sim 10\%$) by Nuding *et al.*²² Furthermore, it appears that compared to DRH measured by Nuding *et al.*,²² our reported values agree better with those predicted by their thermodynamic model.

It is suggested that the dependence of DRH on temperature can be approximated by the Clausius–Clapeyron equation:^{37–39}

$$\ln[\text{DRH}(T)] = \ln[\text{DRH}(298)] + \frac{A\Delta H_s}{R} \left(\frac{1}{T} - \frac{1}{298} \right) \quad (1)$$

where $\text{DRH}(T)$ and $\text{DRH}(298)$ is the DRH at the temperature of T and 298 K, A is a dimensionless constant dependent on the solubility of the salt in water, R is gas constant ($\text{J mol}^{-1} \text{K}^{-1}$), and ΔH_s is the enthalpy of solution (J mol^{-1}). Eqn (1) implies that plotting $\ln(\text{DRH})$ versus $1/T$ would generate a straight line, with its slope equal to $A\Delta H_s/R$. This is confirmed by the data shown in Fig. 3, and the slopes are found to be $587 \pm 96 \text{ K}$ for $\text{Ca}(\text{ClO}_4)_2 \cdot 4\text{H}_2\text{O}$ and $198 \pm 18 \text{ K}$ for $\text{Mg}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$, respectively.

The interaction of water vapor with KClO_4 was also explored at 278 and 298 K. As shown in Fig. 4, KClO_4 did not take up significant amount of water even when RH was increased from 0% to 95%. This observation suggests that the DRH of KClO_4 is above 95% for the temperature range (278–303 K) covered in our work. This is qualitatively consistent with the low solubility of KClO_4 in water ($\sim 2.1 \text{ g KClO}_4$ in 100 g water) at 298 K reported by Willard and Smith.⁴⁰

3.2 Mass hygroscopic growth factors of perchlorates

We have further measured the mass hygroscopic growth factors (defined as the ratio of sample mass at a given RH to that at 0% RH) as a function of RH at three different temperatures (278,

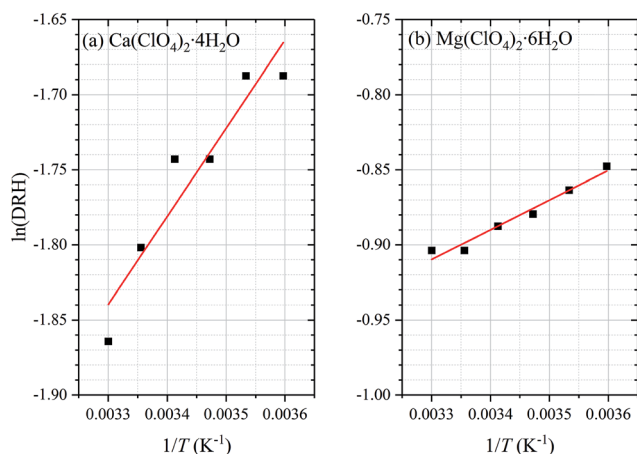


Fig. 3 Dependence of deliquescence relative humidities (DRH) of (a) $\text{Ca}(\text{ClO}_4)_2 \cdot 4\text{H}_2\text{O}$ and (b) $\text{Mg}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ on temperature in the range of 278–303 K. As suggested by eqn (1), plotting $\ln(\text{DRH})$ versus $1/T$ would generate a straight line, and the two red lines represent the fitted linear lines.

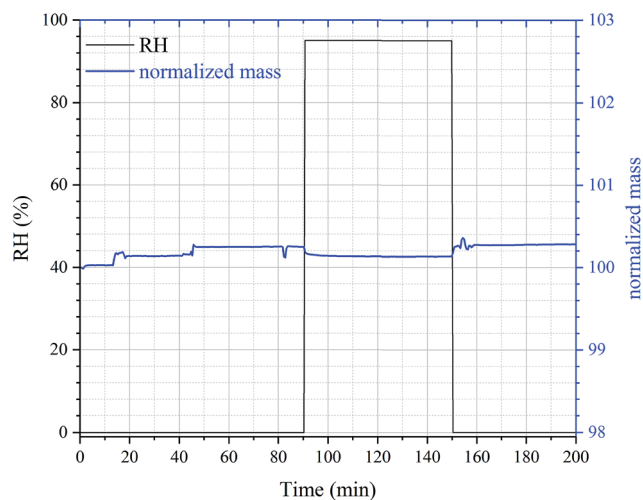


Fig. 4 Time series of RH and normalized sample mass in an experiment designed to measure the mass hygroscopic growth factors of KClO_4 at 278 K. No significant change in sample mass was observed when RH was increased from 0% to 95%, suggesting that the DRH of KClO_4 was $>95\%$. Additional experiments were carried out at 298 K, and the DRH of KClO_4 was also found to be $>95\%$ at 298 K.

288 and 298 K). The results are compiled in Table 2. To our knowledge, the amount of water associated with $\text{Ca}(\text{ClO}_4)_2 \cdot 4\text{H}_2\text{O}$ under well controlled conditions has never been reported, and quantitative information for $\text{Mg}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ is also very limited.

As shown in Table 2 and Fig. 5, $\text{Ca}(\text{ClO}_4)_2 \cdot 4\text{H}_2\text{O}$ undergoes deliquescence when RH was increased from 10% to 20%, and deliquescence occurred for $\text{Mg}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ when RH was increased from 40% to 50%. This is consistent with their measured DRH values (see Section 3.1). After deliquesced, both $\text{Ca}(\text{ClO}_4)_2 \cdot 4\text{H}_2\text{O}$ and $\text{Mg}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ could take up significant amount of water under subsaturated conditions. For example, due to absorption of water vapor from the gas phase at 298 K, the mass of $\text{Ca}(\text{ClO}_4)_2 \cdot 4\text{H}_2\text{O}$ was increased by $\sim 44\%$ at 50% RH, $\sim 77\%$ at 70% RH, and $\sim 190\%$ at 90% RH, respectively, compared to the initial mass at 0% RH. It is also observed that at a given RH, decrease in temperature will increase the amounts of water associated with deliquesced $\text{Ca}(\text{ClO}_4)_2 \cdot 4\text{H}_2\text{O}$ and $\text{Mg}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$. Toner *et al.*⁴¹ showed that from a thermodynamic point of view, for a given solute concentration, decrease in temperature would lead to decrease in water activity; in other words, for the same water activity (*i.e.* at a given RH), decrease in temperature would cause decrease in solute concentration, and thus increase in mass ratio of water to solute ratio and increase in mass growth factors. Therefore, our experimental measurement is consistent with theoretical prediction by Toner *et al.*⁴¹

Water to solute ratio (WSR), defined as the molar ratio of H_2O to ClO_4^- , can be calculated from the measured mass hygroscopic growth factors, and the results are displayed in Fig. 6. Note that RH in Fig. 6 is plotted on the scale of 0–1 instead of 0–100%. Aqueous water in the solution formed due to deliquescence of $\text{Mg}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ or $\text{Ca}(\text{ClO}_4)_2 \cdot 4\text{H}_2\text{O}$ comes from two sources: (i) water absorbed from the gas phase and (ii)



Table 2 Mass hygroscopic growth factors (defined as the ratio of the sample mass at a given RH to that at 0% RH) of $\text{Ca}(\text{ClO}_4)_2 \cdot 4\text{H}_2\text{O}$ and $\text{Mg}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ as a function of RH at 278, 288 and 298 K. Measurements at 298 K were repeated three times to ensure the reproducibility, and the shown errors ($\pm 1\sigma$) are statistical only. Only one measurement was carried out for each of other conditions, because the reproducibility at 298 K was very good and duration of each individual measurement was rather long at 278 and 288 K (typically 4–7 days)

RH (%)	$\text{Ca}(\text{ClO}_4)_2 \cdot 4\text{H}_2\text{O}$			$\text{Mg}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$		
	298 K	288 K	278 K	298 K	288 K	278 K
0	1.0000 \pm 0.0001	1.0000	1.0000	1.0000 \pm 0.0001	1.0000	1.0000
10	0.9998 \pm 0.0002	0.9998	0.9997	0.9996 \pm 0.0001	0.9995	0.9996
20	1.1573 \pm 0.0326	1.1988	1.2122	0.9991 \pm 0.0003	0.9991	0.9993
30	1.2434 \pm 0.0355	1.2872	1.3021	0.9988 \pm 0.0003	0.9988	0.9990
40	1.3352 \pm 0.0377	1.3830	1.4001	0.9990 \pm 0.0009	0.9985	0.9988
50	1.4419 \pm 0.0406	1.4942	1.5148	1.4407 \pm 0.0070	1.4473	1.4631
60	1.5778 \pm 0.0436	1.6364	1.6585	1.5788 \pm 0.0074	1.5868	1.6085
70	1.7714 \pm 0.0463	1.8392	1.8664	1.7767 \pm 0.0081	1.7902	1.8132
80	2.1004 \pm 0.0499	2.1895	2.2325	2.1184 \pm 0.0094	2.1401	2.1852
90	2.9241 \pm 0.0349	3.0777	3.2687	2.9876 \pm 0.0132	3.0677	3.2277

water released by $\text{Mg}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ or $\text{Ca}(\text{ClO}_4)_2 \cdot 4\text{H}_2\text{O}$ once dissolved. It can be concluded that after both salts were deliquesced (for RH at 50% and above), more water ($\sim 10\%$ on average) was associated with $\text{Mg}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ than $\text{Ca}(\text{ClO}_4)_2 \cdot 4\text{H}_2\text{O}$ on the per mole ClO_4^- base. A recent thermodynamic model study⁴² suggests that for a given perchlorate concentration in molality (mol kg^{-1}), water activity of $\text{Mg}(\text{ClO}_4)_2$ solution is slightly larger than that for $\text{Ca}(\text{ClO}_4)_2$. Since water activity decreases with solute concentration, this implies that for a given water activity, the molality concentration is smaller for $\text{Mg}(\text{ClO}_4)_2$. In other words, the theoretical work by Toner *et al.*⁴² also suggested that at a given RH more water is associated with $\text{Mg}(\text{ClO}_4)_2$ than $\text{Ca}(\text{ClO}_4)_2$ on the per mole ClO_4^- base.

As shown in Fig. 6, the dependence of WSR on RH at 298 K for both $\text{Ca}(\text{ClO}_4)_2 \cdot 4\text{H}_2\text{O}$ and $\text{Mg}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ can be fitted using the following polynomial equation:⁴³

$$\text{WSR} = k_0 + k_1RH + k_2RH^2 + k_3RH^3 + k_4RH^4 \quad (2)$$

It is further found that the WSR data at 288 and 278 K can also be fitted using eqn (2), and the polynomial coefficients obtained are summarized in Table 3 for both salts at three different temperatures.

At 20% RH $\text{Ca}(\text{ClO}_4)_2 \cdot 4\text{H}_2\text{O}$ was deliquesced to form a solution with WSR of ~ 3.82 , which should be slightly larger than that for saturated solution (a saturated solution should be formed at the RH equal to DRH, which was determined to be $\sim 16.5\%$ at 298 K). Similarly, when RH increased from 40% to 50%, $\text{Mg}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ underwent deliquescence and formed a solution with $n(\text{H}_2\text{O})/n(\text{ClO}_4^-)$ of ~ 7.26 , which should also be slightly larger than that for saturated solution. The solubility was determined to be 188.6 g per 100 g H_2O for anhydrous $\text{Ca}(\text{ClO}_4)_2$ and 99.6 g per 100 g H_2O for anhydrous $\text{Mg}(\text{ClO}_4)_2$ at

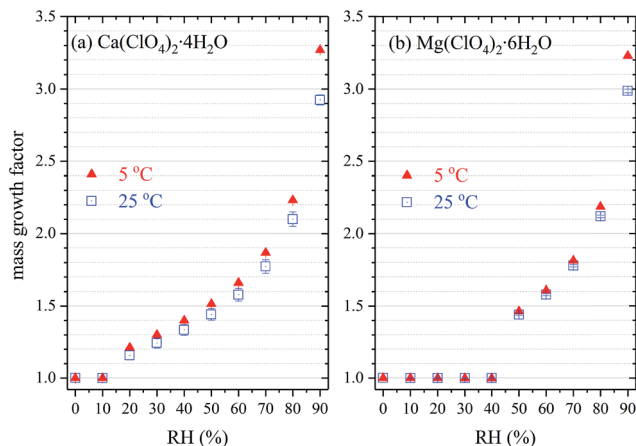


Fig. 5 Mass hygroscopic growth factors of (a) $\text{Ca}(\text{ClO}_4)_2 \cdot 4\text{H}_2\text{O}$ and (b) $\text{Mg}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ as a function of RH at 278 (triangles) and 298 K (squares). Measurements were also carried out at 288 K, and the results are not displayed in this figure for better readability (but included in Table 2).

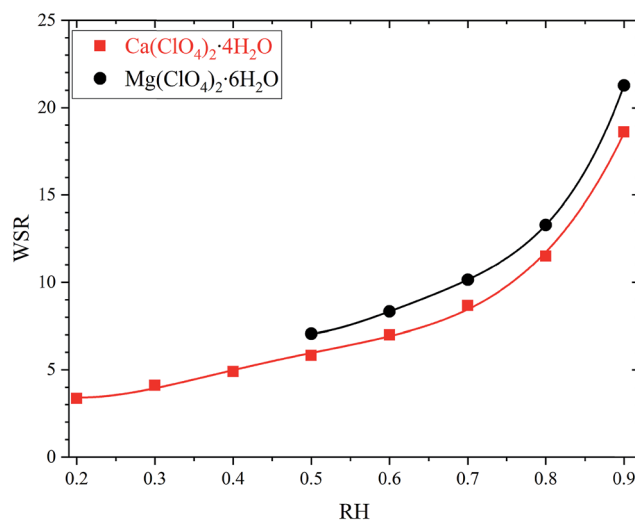


Fig. 6 Water to solute ratio (WSR), defined as the molar ratios of H_2O to ClO_4^- , as a function of RH for $\text{Ca}(\text{ClO}_4)_2 \cdot 4\text{H}_2\text{O}$ and $\text{Mg}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ after deliquescence at 298 K. The two curves show the polynomial fittings to the experimental data, as described by eqn (2).



Table 3 Polynomial coefficients obtained when using eqn (2) to fit the WSR data measured in this work as a function of RH for $\text{Ca}(\text{ClO}_4)_2 \cdot 4\text{H}_2\text{O}$ and $\text{Mg}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ at three different temperatures. Note that in this work WSR is defined as the molar ratio of H_2O to ClO_4^- in deliquesced salts

T (K)	k_0	k_1	k_2	k_3	k_4	Valid RH range
$\text{Ca}(\text{ClO}_4)_2 \cdot 4\text{H}_2\text{O}$						
298	8.982	-68.613	280.385	-431.422	241.907	0.2–0.9
288	10.027	-76.214	309.064	-474.868	265.622	0.2–0.9
278	12.644	-102.880	406.286	-619.776	341.669	0.2–0.9
$\text{Mg}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$						
298	174.765	-1103.441	2676.955	-2855.798	1147.936	0.5–0.9
288	207.530	-1309.148	3157.012	-3349.155	1336.810	0.5–0.9
278	228.714	-1455.690	3534.575	-3775.969	1515.893	0.5–0.9

298 K,⁴⁰ corresponding to WSR of 3.52 for saturated $\text{Ca}(\text{ClO}_4)_2$ solution and 6.22 for saturated $\text{Mg}(\text{ClO}_4)_2$ solution. Therefore, our measured WSR values are consistent with those derived from solubility measurements. Zhang and Chan *et al.*²⁷ utilized an electrodynamic balance coupled with Raman spectroscopy to determine water to solute molar ratios as a function of RH at room temperature. Comparison of our results at 298 K with those presented graphically by Zhang and Chan²⁷ suggests a reasonably good agreement.

4 Conclusions and implications

The deliquescence behaviors of perchlorates under subsaturated conditions are suggested to be the reason why liquid water can exist in some hyperarid regions on the earth. In this study we have measured the DRH of $\text{Ca}(\text{ClO}_4)_2 \cdot 4\text{H}_2\text{O}$, $\text{Mg}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ and KClO_4 in the temperature range of 278–303 K. While the DRH of KClO_4 is above 95%, $\text{Ca}(\text{ClO}_4)_2 \cdot 4\text{H}_2\text{O}$ and $\text{Mg}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ are found to deliquesce at much lower RH. More specifically, the DRH of $\text{Mg}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ decreases from $(42.8 \pm 0.6)\%$ at 278 K to $(40.5 \pm 0.5)\%$ at 303 K, and it decreases from $(18.5 \pm 0.5)\%$ at 278 K to $(15.5 \pm 0.5)\%$ at 303 K for $\text{Ca}(\text{ClO}_4)_2 \cdot 4\text{H}_2\text{O}$, both exhibiting a slightly negative dependence on temperature. Therefore, our work confirms that liquid water can exist as perchlorate solutions at temperatures relevant for the earth even when RH is much lower than 100%.

More importantly, we have quantitatively measured the amount of water associated with $\text{Ca}(\text{ClO}_4)_2 \cdot 4\text{H}_2\text{O}$ and $\text{Mg}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ as a function of RH at 278–298 K. It is found that when both salts are deliquesced, under the same condition more water ($\sim 10\%$ on average) is associated with $\text{Mg}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ than $\text{Ca}(\text{ClO}_4)_2 \cdot 4\text{H}_2\text{O}$ on the per mole ClO_4^- base. Our work would significantly improve our knowledge in hygroscopic properties of perchlorates, and therefore could help us better understand the hydrological cycles in some hyperarid environments on the earth, such as the Atacama Desert in Chile.

Most of the time the Mars is extremely cold with typical temperature at 200–220 K; however, the temperature around the Martian equator in the summer can reach >280 K,²¹ overlapping with the temperature range our current work covers. Therefore, our work may also be relevant for the possible existence of liquid water on the Mars. In addition, experiments at Martian

relevant temperatures are difficult and thermodynamic models are widely used for prediction and interpretation;^{9,24,25} as a result, the comprehensive and systematical dataset obtained at 278–303 K for $\text{Mg}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$, $\text{Ca}(\text{ClO}_4)_2 \cdot 4\text{H}_2\text{O}$ and KClO_4 in our work could be used to constrain and verify these thermodynamic models. We are also developing a new instrument which would be able to measure hygroscopicity of perchlorates at much lower temperatures.

Conflicts of interest

There are no conflicts to declare.

Appendix

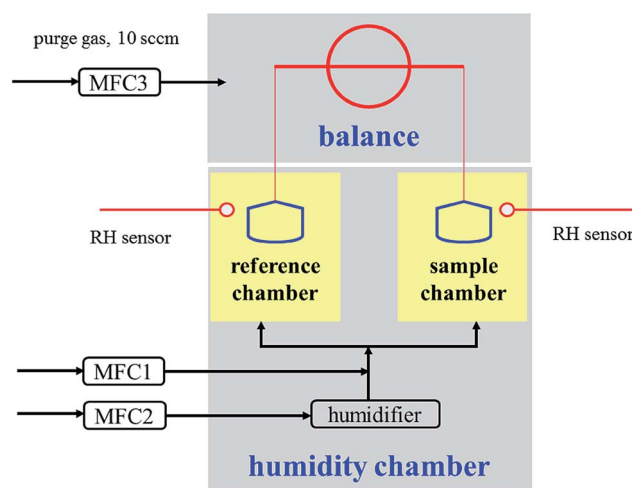


Fig. 7 Schematic diagram of the vapor sorption analyzer used in this work. MFC1, MFC2 and MFC3 were mass flow controllers.

Acknowledgements

This work is financially supported by Chinese National Science Foundation (grant No. 91644106 and 41675120), the Chinese Academy of Sciences international collaborative project (grant No. 132744KYSB20160036), the Science and Technology



Development Fund of Macau (136/2016/A3), and State Key Laboratory of Organic Geochemistry (grant No. SKLO-GA201603A). Mingjin Tang would like to thank the CAS Pioneer Hundred Talents program for providing a starting grant. This is contribution No. IS-2443 from GIGCAS.

References

- 1 R. Navarro-Gonzalez, F. A. Rainey, P. Molina, D. R. Bagaley, B. J. Hollen, J. de la Rosa, A. M. Small, R. C. Quinn, F. J. Grunthaler, L. Czaceres, B. Gomez-Silva and C. P. McKay, *Science*, 2003, **302**, 1018–1021.
- 2 A. F. Davila, B. Gómez-Silva, A. de los Rios, C. Ascaso, H. Olivares, C. P. McKay and J. Wierzchos, *J. Geophys. Res.: Biogeosci.*, 2008, **113**, G01028, DOI: 10.101029/02007jg000561.
- 3 C. P. McKay, E. I. Friedmann, B. Gomez-Silva, L. Caceres-Villanueva, D. T. Andersen and R. Landheim, *Astrobiology*, 2003, **3**, 393–406.
- 4 J. Levy, A. Fountain, W. B. Lyons and K. Welch, *Antarct. Sci.*, 2015, **27**, 163–171.
- 5 R. V. Gough, V. F. Chevrier and M. A. Tolbert, *Planet. Space Sci.*, 2016, **131**, 79–87.
- 6 A. F. Davila, I. Hawes, C. Ascaso and J. Wierzchos, *Environ. Microbiol. Rep.*, 2013, **5**, 583–587.
- 7 S. T. Martin, *Chem. Rev.*, 2000, **100**, 3403–3453.
- 8 D. C. Catling, M. W. Claire, K. J. Zahnle, R. C. Quinn, B. C. Clark, M. H. Hecht and S. Kounaves, *J. Geophys. Res.: Planets*, 2010, **115**, E00E11, DOI: 10.1029/2009je003425.
- 9 S. P. Kounaves, S. T. Stroble, R. M. Anderson, Q. Moore, D. C. Catling, S. Douglas, C. P. McKay, D. W. Ming, P. H. Smith, L. K. Tamppari and A. P. Zent, *Environ. Sci. Technol.*, 2010, **44**, 2360–2364.
- 10 B. Rao, T. A. Anderson, G. J. Orris, K. A. Rainwater, S. Rajagopalan, R. M. Sandvig, B. R. Scanlon, D. A. Stonestrom, M. A. Walvoord and W. A. Jackson, *Environ. Sci. Technol.*, 2007, **41**, 4522–4528.
- 11 D. R. Parker, *Environ. Chem.*, 2009, **6**, 10–27.
- 12 P. K. DasGupta, J. V. Dyke, A. B. Kirk and W. A. Jackson, *Environ. Sci. Technol.*, 2006, **40**, 6608–6614.
- 13 B. L. Carrier and S. P. Kounaves, *Geophys. Res. Lett.*, 2015, **42**, 3739–3745.
- 14 S. P. Kounaves, B. L. Carrier, G. D. O'Neil, S. T. Stroble and M. W. Claire, *Icarus*, 2014, **229**, 206–213.
- 15 S. P. Kounaves, N. A. Chaniotakis, V. F. Chevrier, B. L. Carrier, K. E. Folds, V. M. Hansen, K. M. McElhoney, G. D. O'Neil and A. W. Weber, *Icarus*, 2014, **232**, 226–231.
- 16 A. S. McEwen, L. Ojha, C. M. Dundas, S. S. Mattson, S. Byrne, J. J. Wray, S. C. Cull, S. L. Murchie, N. Thomas and V. C. Gulick, *Science*, 2011, **333**, 740–743.
- 17 A. S. McEwen, C. M. Dundas, S. S. Mattson, A. D. Toigo, L. Ojha, J. J. Wray, M. Chojnacki, S. Byrne, S. L. Murchie and N. Thomas, *Nat. Geosci.*, 2014, **7**, 53–58.
- 18 L. Ojha, M. B. Wilhelm, S. L. Murchie, A. S. McEwen, J. J. Wray, J. Hanley, M. Masse and M. Chojnacki, *Nat. Geosci.*, 2015, **8**, 829–832.
- 19 L. A. Leshin, P. R. Mahaffy, C. R. Webster, M. Cabane, P. Coll, P. G. Conrad, P. D. Archer, S. K. Atreya, A. E. Brunner, A. Buch, J. L. Eigenbrode, G. J. Flesch, H. B. Franz, C. Freissinet, D. P. Glavin, A. C. McAdam, K. E. Miller, D. W. Ming, R. V. Morris, R. Navarro-Gonzalez, P. B. Niles, T. Owen, R. O. Pepin, S. Squyres, A. Steele, J. C. Stern, R. E. Summons, D. Y. Sumner, B. Sutter, C. Szopa, S. Teinturier, M. G. Trainer, J. J. Wray, J. P. Grotzinger and M. S. L. S. Team, *Science*, 2013, **341**, 1238937, DOI: 10.1231126/science.1238937.
- 20 D. W. Ming, P. D. Archer, D. P. Glavin, J. L. Eigenbrode, H. B. Franz, B. Sutter, A. E. Brunner, J. C. Stern, C. Freissinet, A. C. McAdam, P. R. Mahaffy, M. Cabane, P. Coll, J. L. Campbell, S. K. Atreya, P. B. Niles, J. F. Bell, D. L. Bish, W. B. Brinckerhoff, A. Buch, P. G. Conrad, D. J. Des Marais, B. L. Ehlmann, A. G. Fairen, K. Farley, G. J. Flesch, P. Francois, R. Gellert, J. A. Grant, J. P. Grotzinger, S. Gupta, K. E. Herkenhoff, J. A. Hurowitz, L. A. Leshin, K. W. Lewis, S. M. McLennan, K. E. Miller, J. Moersch, R. V. Morris, R. Navarro-Gonzalez, A. A. Pavlov, G. M. Perrett, I. Pradler, S. W. Squyres, R. E. Summons, A. Steele, E. M. Stolper, D. Y. Sumner, C. Szopa, S. Teinturier, M. G. Trainer, A. H. Treiman, D. T. Vaniman, A. R. Vasavada, C. R. Webster, J. J. Wray, R. A. Yingst and M. S. L. S. Team, *Science*, 2014, **343**, 1245267, DOI: 10.1241126/science.1245267.
- 21 F. J. Martin-Torres, M.-P. Zorzano, P. Valentin-Serrano, A.-M. Harri, M. Genzer, O. Kempainen, E. G. Rivera-Valentin, I. Jun, J. Wray, M. Bo Madsen, W. Goetz, A. S. McEwen, C. Hardgrove, N. Renno, V. F. Chevrier, M. Mischna, R. Navarro-Gonzalez, J. Martinez-Frias, P. Conrad, T. McConnochie, C. Cockell, G. Berger, A. R. Vasavada, D. Sumner and D. Vaniman, *Nat. Geosci.*, 2015, **8**, 357–361.
- 22 D. L. Nuding, E. G. Rivera-Valentin, R. D. Davis, R. V. Gough, V. F. Chevrier and M. A. Tolbert, *Icarus*, 2014, **243**, 420–428.
- 23 M. P. Zorzano, E. Mateo-Marti, O. Prieto-Ballesteros, S. Osuna and N. Renno, *Geophys. Res. Lett.*, 2009, **36**, L20201, DOI: 10.21029/22009gl040315.
- 24 V. F. Chevrier, J. Hanley and T. S. Altheide, *Geophys. Res. Lett.*, 2009, **36**, L10202, DOI: 10.11029/12009gl037497.
- 25 R. V. Gough, V. F. Chevrier, K. J. Baustian, M. E. Wise and M. A. Tolbert, *Earth Planet. Sci. Lett.*, 2011, **312**, 371–377.
- 26 G. Nikolakakos and J. A. Whiteway, *Geophys. Res. Lett.*, 2015, **42**, 7899–7906.
- 27 Y. H. Zhang and C. K. Chan, *J. Phys. Chem. A*, 2003, **107**, 5956–5962.
- 28 E. Fischer, G. M. Martinez and N. O. Renno, *Astrobiology*, 2016, **16**, 937–948.
- 29 R. V. Gough, V. F. Chevrier and M. A. Tolbert, *Earth Planet. Sci. Lett.*, 2014, **393**, 73–82.
- 30 D. L. Nuding, R. D. Davis, R. V. Gough and M. A. Tolbert, *J. Geophys. Res.: Planets*, 2015, **120**, 588–598.
- 31 W. J. Gu, Y. J. Li, J. X. Zhu, X. H. Jia, Q. H. Lin, G. H. Zhang, X. Ding, W. Song, X. H. Bi, X. M. Wang and M. J. Tang, *Atmos. Meas. Tech.*, 2017, DOI: 10.5194/amt-2017-5156.
- 32 O. N. Pestova, L. A. Myund, M. K. Khripun and A. V. Prigaro, *Russ. J. Appl. Chem.*, 2005, **78**, 409–413.



- 33 T. A. Dobrynina, N. A. Akhapkina and V. Y. Rosolovskii, *Russ. J. Inorg. Chem.*, 1984, **29**, 1818–1822.
- 34 K. Robertson and D. Bish, *J. Geophys. Res.: Planets*, 2011, **116**, E07006, DOI: 10.1029/2010je003754.
- 35 D. J. Devlin and P. J. Herley, *Thermochim. Acta*, 1986, **104**, 159–178.
- 36 K. S. Pitzer, *Activity Coefficients in Electrolyte Solutions*, CRC Press, Boca Raton, Florida, USA, 1991.
- 37 A. S. Wexler and J. H. Seinfeld, *Atmos. Environ.*, 1991, **25**, 2731–2748.
- 38 J. H. Seinfeld and S. N. Pandis, *Atmospheric Chemistry and Physics: From Air Pollution to Climate Change*, Wiley Interscience, New York, 2006.
- 39 G. Zeng, J. Kelley, J. D. Kish and Y. Liu, *J. Phys. Chem. A*, 2014, **118**, 583–591.
- 40 H. H. Willard and G. F. Smith, *J. Am. Chem. Soc.*, 1923, **45**, 286–297.
- 41 J. D. Toner and D. C. Catling, *Geochim. Cosmochim. Acta*, 2016, **181**, 164–174.
- 42 J. D. Toner, D. C. Catling and B. Light, *Geochim. Cosmochim. Acta*, 2015, **166**, 327–343.
- 43 Y. Liu and A. Laskin, *J. Phys. Chem. A*, 2009, **113**, 1531–1538.

