THERMODYNAMIC PROPERTIES OF OXIDIZED FORMS OF CHLORIDE AND APPLICATIONS TO THE PHOENIX SURFACE CHEMISTRY. V. F. Chevrier[1], J. Hanley[1], [1]Arkansas Center for Space and Planetary Sciences, 202 Old Museum Building, University of Arkansas, Fayetteville, AR 72701, vchevrie@uark.edu.

Introduction: the recent discovery of perchlorates (ClO_4^-) by Phoenix triggered a high interest for this rare ion on the surface of the Earth [1]. Indeeed perchlorate solutions have very low eutectic favoring potential liquid water on the surface [2]. The mechanisms by which such a highly oxidized ion formed remain largely unknown. Two major pathways are possible: atmospheric oxidation of aerosols [3], potentially through UV or reaction of strong oxidants like H_2O_2 with chlorides in liquid or solid form. A major problem for these models is the lack of thermodynamic data. Indeed, between chloride (oxidation state -1) and perchlorate (oxidation state +7) three other ions exist: hypochlorite ClO^- (+1), chlorite ClO_2^- (+3) and chlorate ClO_3^- (+5). These ions may be present (and undetected) at the Phoenix landing site as intermediate species of the processes leading to perchlorates.

Therefore, we started a detailed investigation of the thermodynamic properties of the intermediate oxidation states of chloride. Using literature data we determine the thermodynamic parameters controlling their stability, focusing on sodium and magnesium as being the most relevant to the Phoenix chemistry [2,4].

Results and discussion: Table 1 summarizes preliminary data gathered for Na-species from stability diagrams (Fig. 1). All except the chlorate have one or several hydrates, the highest being hypochlorite. We observe a general decrease of eutectic temperature with increasing oxidation of Cl, perchlorate presenting the lowest value.

Table 1. Eutectic conditions determined for the oxidized species of Na. Perchlorates are indicated for comparison.

Specie	Hydrates	Eutectic T	Eutectic C
NaClO	5 and 2.5	257 K	19 wt%
$NaClO_2$	3	n.d.	n.d.
$NaClO_3$	-	250 K	39 wt%
$NaClO_4$	2,1	236 K	52 wt%

For $Mg(ClO_x)_2$, the situation is even more complicated since we have only found data for the chlorate (Fig. 2). The measured eutectic is much higher than for perchlorate (255 against 206 K), but interestingly $Mg(ClO_3)_2$ presents similar hydration states than $Mg(ClO_4)_2$: 6, 4 and 2 H_2O.

These preliminary results show the need for thermodynamic data of aqueous equilibrium and water vapor equilibrium [5]. Using these data we will extract the Pitzer parameters used in the thermodynamic models of perchlorate formation and stability through evaporation and freezing [4].

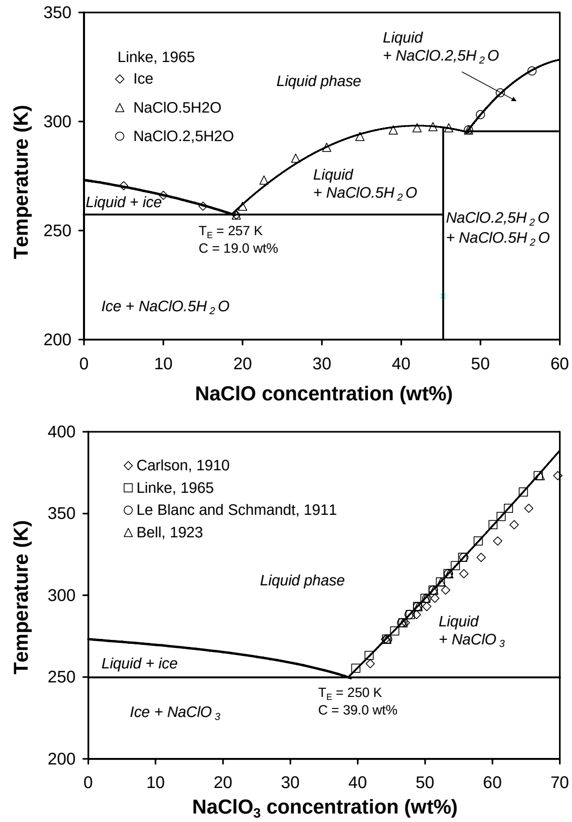

Figure 1. Thermodynamics stability diagrams of sodium hypochorite (top) and chlorate (bottom).

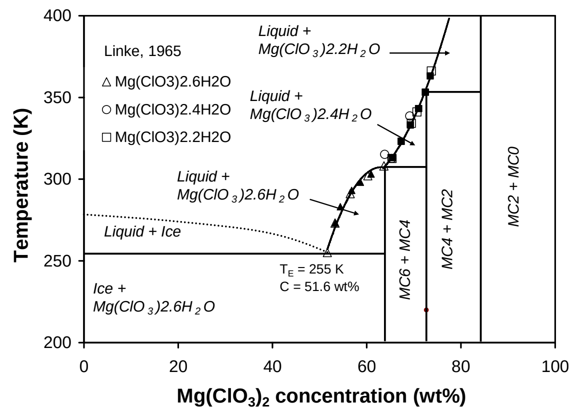

Figure 2. Partial thermodynamic stability diagram of magnesium chlorate. The ice – liquid dotted line needs to be determined.

References: [1] Hecht M. H. et al. (2009) *LPSC* XL. [2] Chevrier V. et al. (2009) *Geophys. Res. Lett.* 36. [3] Catling D. C. et al. (2009) *LPSC* XL. [4] Marion G. M. et al. (2009) *LPSC* XL. [5] Besley L. M., G. A. Bottomley (1969) *J. Chem. thermodynamics* 1, 13-19.