Aqueous fluid composition in CI chondritic materials: Chemical equilibrium assessments in closed systems

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ABSTRACT

Solids of nearly solar composition have interacted with aqueous fluids on carbonaceous asteroids, icy moons, and trans-Neptunian objects. These processes altered mineralogy of accreted materials together with compositions of aqueous and gaseous phases. We evaluated chemistry of aqueous solutions coexisted with CI-type chondritic solids through calculations of chemical equilibria in closed water–rock–gas systems at different compositions of initial fluids, water/rock mass ratios (0.1–1000), temperatures (<350 °C), and pressures (<2 kbars). The calculations show that fluid compositions are mainly affected by solubilities of solids, the speciation of chlorine in initial water–rock mixtures, and the occurrence of Na-bearing secondary minerals such as saponite. The major species in modeled alkaline solutions are Na+, Cl–, CO3²⁻, HCO₃⁻, K+, OH⁻, H₂, and CO₂. Aqueous species of Mg, Fe, Ca, Mn, Al, Ni, Cr, S, and P are not abundant in these fluids owing to low solubility of corresponding solids. Typical NaCl type alkaline fluids coexist with saponite-bearing mineralogy that usually present in aqueously altered chondrites. A common occurrence of these fluids is consistent with the composition of grains emitted from Enceladus. Na-rich fluids with abundant CO₃²⁻, HCO₃⁻, and OH⁻ anions coexist with secondary mineralogy depleted in Na. The Na₂CO₃ and NaHCO₃ type fluids could form via accretion of cometary ices. NaOH type fluids form in reduced environments and may locally occur on parent bodies of CR carbonaceous chondrites. Supposed melting of accreted HCl-bearing ices leads to early acidic fluids enriched in Mg, Fe and other metals, consistent with signs of low-pH alteration in chondrites. Neutralization of these solutions leads to alkaline Na-rich fluids. Sulfate species have negligible concentrations in closed systems, which remain reduced, especially at elevated pressures created by forming H₂ gas. Hydrogen, CO₂, and H₂O dominate in the gaseous phase, though the abundance of methane cannot be fairly estimated.

Keywords: Aqueous environments, Mineralogy, Asteroids, Composition, Satellites, Composition, Meteorites

1. Introduction

Solids of about solar composition have reacted with aqueous fluids throughout history of numerous bodies in the Solar System. Signs of these interactions are seen in the phase, chemical and isotopic compositions of carbonaceous chondrites, micrometeorites, and interplanetary dust particles (e.g., Zolensky and McSween, 1988; Brearley and Jones, 1998; Clayton and Mayeda, 1999; Brearley, 2006a, 2006b; Krot et al., 2006; Zolensky et al., 2008), reflectance spectra of carbonaceous asteroids (e.g., Rivkin et al., 2002; Milliken and Rivkin, 2009) and Europa (McCord et al., 1999; Carlson et al., 2009), in the exosphere of Europa (Brown, 2001; Johnson et al., 2002), solid emissions from Enceladus (Porco et al., 2006; Postberg et al., 2009, 2011), and cometary dust (Lisse et al., 2006; Zolensky et al., 2006; Bridges et al., 2008; Berger et al., 2011). Cryovolcanic surface features on icy moons also imply melting of ices and water–rock interactions. Aqueous processes were likely in large icy bodies such as Ganymede, Titan, and trans-Neptunian objects that underwent complete or partial water–rock differentiation (Hussmann et al., 2006; Schubert et al., 2010).

Despite likely similarity of initial rocky materials on these bodies, conditions of alteration vary in temperature, pressure, water to rock ratio (W/R), redox conditions, fluid movements, and gas escape. The duration of water–rock reactions varies from seconds (after collisions) and several Myr in ²⁶Al-powered objects to billions of years in bodies heated by tides (e.g., Europa) and/or decay of long-lived radionuclides (e.g., Ceres, Titan, Triton, Eris, Sedna). The diversity of alteration conditions should affect the composition and chemical evolution of fluids and degree of fluid–rock equilibration.

The composition of fluids interacted with primitive Solar System materials could be assessed from a few nearly direct observations and diverse indirect data. The occurrence of NaCl-rich fluid inclusions in halite and sylvinite (chemical formulas are depicted in Table 1) in Monahans 1998 and Zag ordinary chondrite breccias reveal the composition of asteroidal solutions (Zolensky et al., 1999, 2000). Halite and sylvinite could also be present in carbonaceous...
chondrites (Barber, 1981), though the occurrence has not been confirmed in recent works. However, the composition of icy grains emitted from Enceladus (Postberg et al., 2009) and aqueous leaches from carbonaceous chondrites (Fanale et al., 2001; Izawa et al., 2010) indicate occurrences of Na and Cl in fluids on corresponding parent bodies.

The mineralogy of CI and CM chondrites and corresponding aqueous leaches imply sulfate-bearing solutions. Despite some terrestrial remobilization of chondritic sulfates (Gounelle and Zolensky, 2001), the large amounts of sulfates in CI samples, corresponding O and S isotopic data (Airieau et al., 2005; Bullock et al., 2010), and data on the Tagish Lake meteorite fall (Izawa et al., 2010) suggest mainly extraterrestrial origin of sulfates. The detections of diverse organic species in aqueous leaches of CI chondrites (Waite et al., 2009, 2011) indicate the occurrence of dissolved organic compounds in corresponding fluids. The presence of CO2 in pristine solutions. These models could constrain fluid chemistry on reduced and alkali fluids coexisted with partially altered metal and serpentine-rich phyllosilicates (e.g., Weisberg et al., 1993; Weisberg and Huber, 2007). The mineralogy of CV3 chondrites implies different stages of aqueous alteration at low W/R ratios and subsequent thermal processing that affected many specimens (Alexander et al., 1989; Krot et al., 1998; Zolensky et al., 2008). Several H3 ordinary chondrites also reveal minor aqueous transformations characterized by oxidation of kamacite, alteration of silicate glasses, formation of fayalite, a mobility of alkalis, Al, and Si in peripheral zones of chondrules, and formation of altered matrices enriched in halogens, alkalis, and Al (Alexander et al., 1989; Hutchison et al., 1998; Grossman et al., 2000, 2002; Krot et al., 2011). The mobility of Al and the occurrence of secondary silica may indicate acidic pH of initial solutions. However, the occurrence of saponite and carbonates indicate neutralization of early fluids.

In addition to the mentioned salts, mineralogy of aqueously altered chondrites provides wealth of indirect information on chemistry of aqueous alteration. Although CI carbonaceous chondrites are the most compositionally similar to the solar photosphere (Lodders, 2003), other meteorites (CM, CR, CV3, H3) provide additional insights. Alteration in CI chondrites led to almost complete replacement of initial mineralogy by serpentine, saponite, magnetite, pyrrhotite, pentlandite, carbonates, Ca-phosphates, and sulfates (Zolensky et al., 1988; Zolensky et al., 1993; Brearley and Jones, 1998) at temperature ~50–150 °C and W/R mass ratios ~1 (Zolensky et al., 1993; Clayton and Mayeda, 1999). In many CM chondrites, alteration typically occurred at temperatures at or below ~20–35 °C at lower W/R ratios than in CI samples (e.g., Clayton and Mayeda, 1999; Guo and Eiler, 2007), and major secondary phases are cronstedite, serpentine, tochilinite, pentlandite, pyrrhotite, and carbonates (e.g., Brearley and Jones, 1998). CM chondrites reveal different stages of aqueous processes and indicate coupled evolution of mineralogy and fluid composition (e.g., Tomeoka and Buseck, 1985; Zolensky et al., 1993; Browning et al., 1996; Rubin et al., 2007). Early acidic fluids in CM chondrites could have evolved to alkaline solutions (Brearley, 2006b). The mineralogy of CR chondrites indicates alteration by reduced and alkaline fluids coexisted with partially altered metal and serpentine-rich phyllosilicates (e.g., Weisberg et al., 1993; Weisberg and Huber, 2007). The mineralogy of CV3 chondrites imply different stages of aqueous alteration at low W/R ratios and subsequent thermal processing that affected many specimens (Alexander et al., 1989; Krot et al., 1998; Zolensky et al., 2008). Several H3 ordinary chondrites also reveal minor aqueous transformations characterized by oxidation of kamacite, alteration of silicate glasses, formation of fayalite, a mobility of alkalis, Al, and Si in peripheral zones of chondrules, and formation of altered matrices enriched in halogens, alkalis, and Al (Alexander et al., 1989; Hutchison et al., 1998; Grossman et al., 2000, 2002; Krot et al., 2011). The mobility of Al and the occurrence of secondary silica may indicate acidic pH of initial solutions. However, the occurrence of saponite and carbonates indicate neutralization of early fluids.

The occurrence of inorganic C species (HCO3 and CO2) in extraterrestrial fluids is evidenced from the common presence of carbonates in altered chondrites from diverse groups (Brearley and Jones, 1998) and from the detection of alkali carbonates and/or bicarbonates in Enceladus’ solid emissions (Postberg et al., 2009). The detections of diverse organic species in aqueous leaches of CI and CM chondrites (Seibert, 2002) and in Enceladus’ emissions (Waite et al., 2009, 2011) indicate the occurrence of dissolved organic compounds in corresponding fluids. The presence of CO2 in endogenic surface features on Europa also implies C-bearing oceanic water (Hansen and McCord, 2008), though aqueous speciation cannot be evaluated from these data because of radiolytic oxidation of organic compounds at the moon’s surface.

Table 1

<table>
<thead>
<tr>
<th>Name</th>
<th>Chemical formula</th>
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<tbody>
<tr>
<td>Alahamite</td>
<td>MnS</td>
</tr>
<tr>
<td>Amesite</td>
<td>Mg6Al2Si4O16(OH)6</td>
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<tr>
<td>Andradite</td>
<td>Ca2Fe3Si2O12</td>
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<tr>
<td>Calcite</td>
<td>CaCO3</td>
</tr>
<tr>
<td>Ca–Mg–Fe pyroxene</td>
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<td>Chromite</td>
<td>FeCr2O4</td>
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<tr>
<td>Chrysolite</td>
<td>Mg2Si3O10(OH)4</td>
</tr>
<tr>
<td>Cronstedtite</td>
<td>Fe3+(Fe3+)Si2(Fe3+)O4(OH)4</td>
</tr>
<tr>
<td>Dolomite</td>
<td>CaMg(CO3)2</td>
</tr>
<tr>
<td>Eskolaithe</td>
<td>Ca2CO3</td>
</tr>
<tr>
<td>Goethite</td>
<td>Fe(OH)</td>
</tr>
<tr>
<td>Greenalite</td>
<td>Fe2Si2O5(OH)4</td>
</tr>
<tr>
<td>Halite</td>
<td>NaCl</td>
</tr>
<tr>
<td>Magnesite</td>
<td>MgCO3</td>
</tr>
<tr>
<td>Magnetite</td>
<td>Fe2O4</td>
</tr>
<tr>
<td>Mg–Fe chloride</td>
<td>(Mg,Fe)SiO4</td>
</tr>
<tr>
<td>Na–K phlogopite</td>
<td>(Na,K)Mg(SiAl)O10(OH)2</td>
</tr>
<tr>
<td>Na–K saponite</td>
<td>(Na,K)Mg2Si32Al2O10(OH)12</td>
</tr>
<tr>
<td>Millerite</td>
<td>NiS</td>
</tr>
<tr>
<td>Olivine</td>
<td>(Mg,Fe)SiO4</td>
</tr>
<tr>
<td>Pentlandite</td>
<td>(FeNi)S</td>
</tr>
<tr>
<td>Pyrene</td>
<td>Fe2S</td>
</tr>
<tr>
<td>Pyrrhotite</td>
<td>Fe3S3</td>
</tr>
<tr>
<td>Quartz</td>
<td>SiO2</td>
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<tr>
<td>Rhodochrosite</td>
<td>MnCO3</td>
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<tr>
<td>Rhodonite</td>
<td>Mg2Si3O6</td>
</tr>
<tr>
<td>Serpentine</td>
<td>(Mg,Fe)Si2O3(OH)3</td>
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<tr>
<td>Sylvite</td>
<td>KCl</td>
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<tr>
<td>Talc</td>
<td>Mg2Si2O5(OH)2</td>
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<td>Tephroite</td>
<td>Mn2SiO4</td>
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<tr>
<td>Tochilinite</td>
<td>Mn2SiO4</td>
</tr>
<tr>
<td>Trolite</td>
<td>Fe3S3</td>
</tr>
<tr>
<td>Whitlockite</td>
<td>Ca2(PO4)2</td>
</tr>
</tbody>
</table>

Note: The formulas correspond to those used in equilibrium calculations. The formula of whitlockite is simplified.
2. The modeling approach

Chemical equilibria were calculated in closed O–H–C–Cl–S–Mg–Fe–Ca–Na–K–Mn–Si–Al–Ni–Co–Cr–P water–rock gas systems. Closed systems are used because of strong signs of isochronal alteration in chondritic samples (e.g., Bland et al., 2009). The initial rock was represented by either H2O-free (Table 2) or H2O- and chlorine-free bulk compositions of Cl chondrites (Lodders, 2003). The use of the H2O-free rock composition stands on the assertion about accretion of anhydrous crystalline and amorphous species together with water ice and other condensed volatiles. The use of the H2O–Cl free rock composition is based on the supposed accretion of HCl hydrate(s) with ices (Zolotov and Mironenko, 2007). Initial fluids were pure water, the HCl solution that signified melted ices with HCl hydrates, and a fluid formed through melting of a simulated cometary ice (Table 2). The concentration of HCl in solution corresponds to the solar mole ratio HCl/H2 = 1.0 (Lodders, 2003) and the H2O/H2 = 10^{3.3} ratio in the low-T solar nebula after condensation of oxides and silicates. The composition of melted volatile-rich ice reflects mole ratios CO/H2O = 0.1, CO2/H2O = 0.05, CH3OH/H2O = 0.02, H2S/H2O = 0.01 that roughly characterize cometary volatiles (Bockéele–Morvan et al., 2004). The simulated cometary melts also contained 0.044 mole HCl per kg of H2O, as in the HCl solution model. We explored interactions of the H2O-free rock with pure water and interactions of the H2O–Cl free rock with HCl-bearing fluids. Calculations were performed for T = 0–350 °C, P = 0.0001–2000 bars, and W/R mass ratio of 0.1–1000. The pressure range covers the conditions within asteroids and the dwarf planet Ceres (<2 kbars), Enceladus (<0.5 kbars), and the ocean–rock interface on Europa (~1.5 kbars).

Chemical equilibria were calculated with the GEOCHEQ code and database (Mironenko et al., 2008) previously used in (Zolotov et al., 2006; Zolotov, 2007, etc.). The input parameters are elemental compositions of initial rocks and aqueous fluids, temperature, pressure, and thermodynamic properties of solids, aqueous species, and gases which may form in the system. The specified database for this work included 123 one-component solids, 21 non-ideal and ideal solid solutions, and non-ideal gas (H2O, H2, CO2, CO, CH4, H2S, SO2) and aqueous solutions (98 species). Thermodynamic data for aqueous species were mainly from Shock et al. (1989, 1997). Properties of gaseous and solid species were mostly from Holland and Powell (1998) and Helgeson et al. (1978). The database included major primary and secondary minerals observed in chondritic materials (Fe–Mg–Ca silicates, Fe–Ni-rich metal, tropilite, pyrrhotite, magnetite, serpentine, saponite, chlorite, Ni sulfides, carbonates, phosphates, etc.). However, tochilinite, cronstedtite, and pentlandite were not included because of the lack of reliable thermodynamic data. Activity coefficients of aqueous and gas species were calculated using the Debye–Hückel and Peng and Robinson (1976) models, respectively. A regular solution model is used for Mg–Fe olivine, Ca–Fe–Mg pyroxenes, and Fe–Mg chlorite, while many solutions were ideal (Na–K–Ca–Mg saponite, Mg–Fe serpentine, K–Na phlogopite, Mg–Fe talc, Fe–Ni–Co–Cr metal, etc.). Data sources are described in more details in (Zolotov et al., 2006). The calculated values are concentrations and activities of dissolved species in aqueous solution, molar amounts and volumes of solids, compositions of solid solutions, and amounts, concentrations and fugacities of gases.

Initial calculations have shown low abundances of the chlorite solid solution, consistent with observations in chondrites (except for some CR specimens). However, the formation of chlorite and saponite appears competitive and some saponite-free low-T mineral assemblages with chlorides did not look reliable. We suppressed formation of chlorites in specified runs. In some cases, we observed formation of K–Na phlogopite at temperatures as low as 50 °C. Such low temperatures are not consistent with the absence of phlogopite in aqueously altered chondrites that avoided high-temperature dehydration. Therefore, we suppressed formation of phlogopite in some runs.

Many organic molecules do not equilibrate at chosen temperatures (Section 4.1) so only a few organic species were considered. Soluble compounds were represented by one-C species (formic acid, formate, methanol, and formaldehyde) that may equilibrate at T = 200–300 °C (Seewald et al., 2006) and pyrene (a polycyclic aromatic hydrocarbon, C16H10) as a proxy for condensed organic species. Formation of methane was suppressed in nominal calculations because of low efficiency of corresponding redox reactions. However, methane could have occurred in chondritic fluids (Guo and Eiler, 2007) because of the initial accretion of CH4 hydrates and/or aqueous alteration of organic matter (hydrogenation and/or hydrolytic disproportionation, Price and DeWitt, 2001). To reflect this, complete equilibria in the C system with methane were calculated for specified cases. Default calculations refer to suppressed methane and unsuppressed chlorite and phlogopite solid solutions.

3. Results

3.1. Effects of water/rock ratio

The composition of fluids calculated as a function of W/R ratio characterizes either different bulk water + rock compositions or degree of aqueous alteration at a fixed bulk composition. In the latter case, lowering W/R ratio along with alteration progress corresponds to the increasing mass of rocks involved in alteration (Helgeson, 1979). The decreasing local W/R ratio approaches bulk W/R ratio upon complete equilibration. Low W/R ratios (<1–10) could characterize both bulk compositions of aqueous environments in the Solar System beyond Mars and advanced stages of alteration.

Fig. 1 illustrates effects of W/R mass ratio on equilibrium compositions of water–rock systems in which Cl-type rocks reacts with either pure water or HCl solution. The formation of chlorites and phlogopite is suppressed. The compositions rich in Na+ and Cl− (Table 3) form at W/R ≤ 2–10 which are expected in hydrous asteroids and icy moons. Other solutes (K+, NaCl, KCl, Ca2+, etc.) are
increasingly abundant only at $W/R < 1$ (Section A1 and Fig. A1 in Appendix A). Complete consumption of these aqueous solutions at lowering $W/R$ ratio leads to precipitation of NaCl-rich salt assemblages (Section A2 and Fig. A2 in Appendix A). Aqueous fluids do not form at $W/R \leq 0.13$ because all initial water consumes through formation of phyllosilicates and oxidized phases such as magnetite. Oxidation of reduced solids (e.g., Fe–Ni metal) by water is accompanied by dissociation of $\text{H}_2\text{O}$ followed by $\text{O}$ consumption in newly-formed minerals and release of $\text{H}_2$.

$$3\text{Fe (in metal)} + 4\text{H}_2\text{O}(l) \rightarrow \text{Fe}_3\text{O}_4 \text{ (magnetite)} + 4\text{H}_2 \text{ (gas)}.$$ (1)

The amount of $\text{H}_2$ increases as more mass of reduced solids become available for oxidation with decreasing $W/R$ ratio. Hydrogen dominates in the gaseous phase over aqueous solutions at $W/R \leq 0.4$ and over altered solution-free rocks (Section A3 and Fig. A3 in Appendix A).

The compositions of aqueous solutions calculated at high $W/R$ ratios are strongly affected by the composition of initial solution. If pure water interacts with CI-type solids (Fig. 1a and b), the anionic composition of diluted Na+-beating solutions is dominated by $\text{HCO}_3^-$/$\text{CO}_3^{2-}$, $\text{OH}^-$, and $\text{Na}^+$. The decrease in $W/R$ ratio may illustrate evolution of diluted Na bicarbonate solutions toward more saline NaCl-rich compositions. The increase in concentrations of $\text{Cl}^-$ and $\text{Na}^+$ with lowering $W/R$ ratio reflects accumulation in solution, though the concentration of $\text{Na}^+$ is influenced by the incorporation in increasingly Na-rich saponite.

If chlorine is supplied with initial HCl fluids (Fig. 1c and d), early alteration solutions at elevated $W/R$ ratios are acidic. The rock cannot provide enough $\text{Na}^+$ to balance $\text{Cl}^-$ so other cations (Mg, Fe, Ca, Mn, etc.) get leached. The decrease in $W/R$ ratio may illustrate neutralization of solution as alteration progresses. With lowering $W/R$ ratios, precipitation of minerals occurs at sequentially higher $\text{pH}$: Fe-rich serpentine ($\text{pH} = 6.3$), Mg-rich saponite ($\text{pH} = 7$), rhodochrosite ($\text{pH} = 8.6$), and calcite ($\text{pH} = 8.9$) (at $25^\circ\text{C}$; Fig. 1c). The precipitation of these solids decreases concentrations of $\text{Fe}^{2+}$, $\text{Mg}^{2+}$, $\text{Mn}^{2+}$, and $\text{Ca}^{2+}$ in solution. The evolution of acidic,

![Fig. 1. The effect of $W/R$ ratio on the composition and pH of aqueous solutions equilibrated with CI-type solids. The conditions are specified on each plot. The pressures correspond to that of water gas-liquid saturation. Formation of Mg–Fe chlorites and Na–K phlogopite is suppressed. Major minerals in equilibrium with solution are Mg–Fe serpentine, saponite (occurs at $W/R < 250$; Na-rich saponite at $W/R \leq 100$, Ca–Mg–Na–K saponite at $W/R = 100–250$), pyrrhotite, magnetite, amesite, and calcite (a); saponite (Na-rich saponite at $W/R < 30$, Ca–Mg saponite at higher $W/R$ ratios), chrysotile, magnetite, pyrrhotite, calcite, and amesite (b); serpentine (Mg-rich serpentine at $W/R \leq 80$, Fe-rich serpentine at $W/R = 80–400$), saponite (Na-rich saponite at $W/R \leq 8$, Mg–Ca saponite at $W/R = 8–207$), pyrrhotite, magnetite ($W/R < 30$), calcite ($W/R < 23$), and amesite ($W/R < 350$) (c); saponite (Na-rich saponite at $W/R \leq 5$, Mg–Ca saponite at $W/R = 5–300$), serpentine (Mg-rich serpentine at $W/R \leq 75$, Fe-rich serpentine at $W/R = 75–400$), pyrrhotite, magnetite ($W/R < 150$), calcite ($W/R < 20$), and amesite ($W/R \leq 400$) (d). In all plots, other phases are whitlockite, millerite, chromite, rhodochrosite ($W/R < 40$ and $<25$ in (c and d), respectively), and pyrene. Aqueous solution exists at $W/R \leq 0.13$. The gaseous phase mainly consists of $\text{H}_2$ and $\text{H}_2\text{O}$, as illustrated in Fig. A3. For (a and b), concentrations of other elements at $W/R < 2$ are shown in Fig. A1.]
Fe-, Mg-rich solutions toward alkaline NaCl-rich fluids is accompanied by increase of the Mg/Fe ratio in serpentine and the (Na + K)/(Mg + Ca) ratio in saponite.

Low-T calculations performed with unsuppressed chlorite result in strongly alkaline Na-rich fluids equilibrated with chlorite-bearing and serpentine-rich assemblages without Na-saponite (Fig. 2). Concentrations of major anions (CO$_3^{2-}$ and OH$^-$) in these fluids are mainly affected by the redox-dependent partition of C between carbonate and condensed organic species.

### 3.2. Effects of temperature

Elevated temperatures correspond to lower concentrations of CO$_3^{2-}$ in solution and higher abundances of H$_2$, CO, CH$_4$, CH$_2$OH, HS$^-$, H$_2$S, SiO$_2$, NaCl, and KCl, which reflect changes in relative stabilities of solutes, solubilities of solids, and pH (Section 4.2). The concentration of K$^+$ also increases with temperature, if phlogopite does not form (Fig. 3). NaCl-rich solutions coexist with saponite-bearing solids in a wide range of temperatures. For T–P conditions of water gas–liquid saturation and W/R ≤ 2–10, similar NaCl-rich solution compositions are obtained for initial fluids presented by pure water (Figs. 1b and 3) and HCl solution (Fig. 1d and Table 3).

If the formation of chlorites is allowed, low-T Na-rich (Na > Cl) fluids coexist with mineralogy dominated by serpentine and chlorite (Figs. 2, 4 and 5). However, NaCl-rich solutions form at higher temperatures in equilibrium with Na-rich saponite, Mg-rich serpentine and minor chlorites (Figs. 4 and 5).

### 3.3. Effects of pressure

In the presence of aqueous phase, the lowest possible pressure corresponds to the partial pressure of water vapor (p$_{H_2O}$) over that phase. For aqueous solutions, the p$_{H_2O}$ values are lower than pressures at gas–liquid saturation for pure water (p$_{H_2O}$sat). Here we use the T-dependent p$_{H_2O}$sat as a reference. Specified pressures above the reference values imply a presence of other gaseous species in addition to H$_2$O vapor.

The modeled high-P systems are characterized by the H$_2$-rich gaseous phase (Fig. 4a) or absence of the gaseous phase. High-P aqueous solutions are enriched in reduced aqueous species (H$_2$, formate, methanol, HS$^-$, and CO) (Figs. 5–7). Organic solutes (formate, methanol) could be more abundant than HCO$_3^-$ and CO$_2$ in high-P–T environments. Elevated pressures and corresponding high fugacities (f) of H$_2$ also affect speciation of solids. The following phase substitutions are observed with increasing fH$_2$: pyrrhotite → trolite, magnetite → Fe-rich olivine, and Ni sulfide → Ni-rich metal. Condensed organic species become more stable and abundant at the expense of dissolved C in fluid phase.

A major effect of pressure and H$_2$ is observed on the occurrence of saponite. Both high-P and low-T conditions stabilize Fe-bearing serpentine and correspond to higher serpentine/saponite ratios, lower Na concentrations in saponite, and higher Na abundances in solution. If chlorites are allowed to form, they also tend to form instead of saponite at high-P and low-T conditions (Figs. 2b, 4 and 5, and 6b). At the pressure of 2000 bars, minor saponite occurs only at T > 230 °C and has a minor effect on Na$^+$ content in solution (Fig. 7a).

Fig. 7b illustrates a hypothetical case of complete high-P equilibration when formation of methane is allowed. Condensed organic species are unstable and CH$_4$ is the most abundant component in the aqueous and gaseous phases, which forms at the pressure as

### Table 3

Concentrations (mole/kg H$_2$O) of major aqueous solutes in equilibrium with Cl-type materials at W/R = 1 and total pressure of water liquid–gas saturation.

<table>
<thead>
<tr>
<th>Species</th>
<th>25 °C, 0.032 bars</th>
<th>150 °C, 4.75 bars</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>A</td>
<td>B</td>
</tr>
<tr>
<td>Na$^+$</td>
<td>5.1 × 10$^{-2}$</td>
<td>7.4 × 10$^{-2}$</td>
</tr>
<tr>
<td>Cl$^-$</td>
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<td>7.5 × 10$^{-2}$</td>
</tr>
<tr>
<td>K$^+$</td>
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<tr>
<td>CO$_3^{2-}$</td>
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<td>NaCl</td>
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<td>OH$^-$</td>
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<td>CaCl$^+$</td>
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<td>Mg$^{2+}$</td>
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<tr>
<td>MgCl$^+$</td>
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<td>6.8 × 10$^{-7}$</td>
</tr>
<tr>
<td>Mg$^{2+}$</td>
<td>4.3 × 10$^{-8}$</td>
<td>2.3 × 10$^{-8}$</td>
</tr>
<tr>
<td>Mn$^{2+}$</td>
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<td>3.7 × 10$^{-8}$</td>
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<tr>
<td>Mn$^{2+}$</td>
<td>2.4 × 10$^{-6}$</td>
<td>1.2 × 10$^{-6}$</td>
</tr>
<tr>
<td>MnOH$^-$</td>
<td>4.3 × 10$^{-8}$</td>
<td>1.7 × 10$^{-7}$</td>
</tr>
<tr>
<td>MnO$^+$</td>
<td>4.4 × 10$^{-9}$</td>
<td>4.5 × 10$^{-9}$</td>
</tr>
<tr>
<td>Co$^{2+}$</td>
<td>8.5 × 10$^{-8}$</td>
<td>8.5 × 10$^{-8}$</td>
</tr>
<tr>
<td>H$_2$O</td>
<td>4.6 × 10$^{-6}$</td>
<td>4.6 × 10$^{-6}$</td>
</tr>
<tr>
<td>pH</td>
<td>10.5</td>
<td>10.1</td>
</tr>
</tbody>
</table>

Notes: (A) The Cl-type rock interacts with pure water (Fig. 1a and b); (B) The Cl-type rock without chlorine interacts with HCl solution (Fig. 1c and d). The formation of chlorites and phlogopite is suppressed.
high as 2000 bars. Na\(^+\) and Cl\(^-\) dominate in low-T aqueous phase, and high-T solution is dominated by Na\(^+\) and HCO\(_3^-\). The composition of the high-T system reflects partial oxidation of CH\(_4\) to HCO\(_3^-\) and CO\(_2\), which becomes more abundant as temperature increases.

### 3.4. Alteration by melted cometary fluids

The calculated alteration by cometary fluids results in the formation of C-rich solutions in equilibrium with abundant Mg and Fe carbonates and minor Na minerals. The major solutes are Na\(^+\), HCO\(_3^-\), Cl\(^-\), CO\(_2\), and CH\(_4\), if its formation is allowed (Fig. 8). The high abundance of C solutes mainly reflects the C-rich composition of cometary melts. The major portion of Na\(^+\) to aqueous phase to balance abundant HCO\(_3^-\) results in low abundances (or lack) of Na-saponite. High-T solutions are characterized by elevated concentrations of HCO\(_3^-\) and CO\(_2\), reflecting lesser stability of organic species with respect to oxidation. The elevated concentrations of dissolved CO\(_2\) account for relatively low alkaline pH, which does not favor the stability of serpentine and calcite, and corresponds to the elevated HCO\(_3^-\)/CO\(_2\) ratio. CO\(_2\) is also a major component of the gaseous phase (Fig. A3e).

The speciation of the aqueous and gaseous phases depends on whether methane formation is allowed. In methane-free models, the majority of C is in condensed organic species, which are more stable at low temperatures (Fig. 8a and b). If formation of methane is not suppressed, condensed organic species are unstable and fluids are C-rich (Fig. 8c and d). At relatively low-T–P conditions (Fig. 8c), the NaHCO\(_3\) solution coexists with Na-poor solids (Mg-clorites, Mg–Fe carbonates, etc.), and methane is the major species in the gaseous phase (Fig. A3f). At higher pressures (Fig. 8d), methane is the major solute in the CH\(_4\)–CO\(_2\)–Na\(^+\)–HCO\(_3^-\) fluids coexisted with abundant Mg-saponite and carbonates. The high-P gaseous phase is dominated by CH\(_4\), especially at lower temperature. Note that applicability of this end-member model to natural systems is equivocal and requires discussion about kinetics of organic reactions.

### 4. Discussion

#### 4.1. Applicability of the models

The presented models have both conceptual and explicit limitations that affect their applicability to natural systems. The assumed complete chemical equilibration between aqueous, gaseous and solid species may not be achieved in Solar System bodies at T \(\leq 350\) °C. In chondrites, the common survival of initial solids reflects short duration of alteration and consumption of small amounts of fluids. Initial mineral grains have different grain sizes and alter with different rates, so the composition of reactive portions of natural systems differs from their bulk composition. Therefore, our results are more applicable for alteration of sub-\(\mu\)m-size materials that compose chondritic matrices.

The closed system models are applicable to aqueous environments where fluids and gases do not migrate. The strong evidence for isochemical aqueous alteration in chondrites at the scale above \(\sim 100\) \(\mu\)m indicates closed system conditions, consistent with the low permeability of matrices (10\(^{-19}\)–10\(^{-17}\) m\(^2\)) (Bland et al., 2009). The low abundance of chondrules in CI chondrites together with the models for chondrule formation in the inner solar nebula (e.g., Morris and Desch, 2010) imply a dominance of fine-grained low-permeability materials accreted on icy bodies at and beyond Jupiter. Sealing of asteroids and moons by ice may limit motion.
and escape of gases, but common carbonaceous asteroids may not sustain internal overpressure above \(10^2\) bars (Grimm and McSween, 1989; Wilson et al., 1999). However, the closed system models are not applicable for major shifts of redox and acid–base equilibria, which could be caused by destruction of icy shells, gas escape, and fluid motions.

Although the equilibrium thermodynamic approach ignores kinetic factors of mineral precipitation, compositions of oversaturated solutions could be evaluated by suppressing formation of minerals that may not precipitate due to kinetic reasons. Such an approach allowed us to address effects of oversaturation of low-\(T\) fluids with respect to chlorites and phlogopite (Figs. 1 and 3).
The presented models also ignore adsorption of ions on mineral/organic surfaces, which affects speciation of low-T fluids. For example, adsorption of K on smectites and organic colloids in terrestrial sediments and soils result in lower K⁺ concentration in the aqueous phase compared to the values calculated from solubility equilibria (e.g., Harder, 1967; Du et al., 2004). Therefore, the modeled low-T concentrations of K in solutions are upper limits.

The equilibration in low-T systems is limited by low rates of redox reactions, especially among C- and S-bearing species. The majority of chondritic organic C remains in the insoluble polymer equilibria (e.g., Harder, 1967; Du et al., 2004). Therefore, the modeled low-T concentrations of K in solutions are upper limits.

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Fig. 5. The effect of temperature on the composition and pH of aqueous solutions equilibrated with CI-type solids at W/R = 1 and the pressure of 10 bars above that of water saturation. Formation of chlorites and phlogopite is allowed. Major minerals are serpentine (less abundant and Mg-rich at T > 130 °C), Na-rich saponite (forms at T > 130 °C and becomes as abundant as serpentine at T > 230 °C), and chlorite (becomes unbalanced and Mg-rich at T > 140 °C), troilite (T < 80 °C), pyrrhotite (T > 80 °C), magnetite (forms at T < 70 °C and is abundant at T = 150 °C), and pyrene. Minor phases are andradite (T < 130 °C), Ca-Mg-Fe pyroxene (T > 130 °C), millerite, Ni-rich metal (at T < 70 °C and T ≤ 320 °C), Na-K phlogopite (T > 110 °C becomes Na-rich at higher T), whitlockite, alabandite (T < 100 °C), rhodochrosite (T > 100 °C), chromite (T > 290 °C), and eskolaite (T > 290 °C). The low-T gaseous phase (T < 200 °C) is dominated by H₂, while H₂O is the major gas at higher temperatures. The amounts of gas and liquid phases are shown in Fig. A4b. Concentrations of other elements are described in Appendix A.

Fig. 6. The effect of pressure on the composition and pH of aqueous solutions equilibrated with CI-type solids at 25 °C at W/R = 1. In (a), formation of chlorites is suppressed and Na-rich saponite is abundant at P < 0.2 bars; amesite is a minor phase. In (b), Mg-Fe chlorite occurs within the shown pressure range. Other minerals in (a and b) are abundant Mg-rich serpentine, pyrrhotite (P < 2 bars), troilite (>2 bars), pyrene, magnetite (<4 bars), calcite (<0.1 bars), andradite (<0.1 bars), millerite (<20 bars), whitlockite, chromite, rhodochrosite (<0.1 bars), Mn sulfide (<0.08 bars), and Ni-rich metal (>5 bars). The gas composition and amounts of fluid and gaseous phases are shown in Figs. A3c and A4c. Concentrations of other elements in aqueous solution are described in Appendix A.
that is only partially affected by asteroidal aqueous processes (Septon, 2002; Cody and Alexander, 2005; Alexander et al., 2007). Carbonaceous chondrites provide no evidence of synthesis of hydrocarbons from H2, CO and/or CO2 (Alexander et al., 2007). Carbon species do not equilibrate in hydrothermal experiments (expect one C species like CO2, HCO3−, and formate, Seewald et al., 2006; McCollom and Seewald, 2007). Therefore, the calculated low-T equilibria that imply organic–inorganic and organic–organic reactions may not represent natural environments. In particular, the calculated equilibria with unsuppressed methane (Figs. 7b, 8c and d) do not represent low-T–P environments existed on asteroids and small icy bodies during geologically short periods. However, these end-member calculations show a potential for hydrogenation of condensed organic compounds at low-T and high-P conditions in large bodies such as at Titan. The models with unsuppressed methane also give insights about speciation of fluids that contained melted methane hydrate, which could have accreted on some bodies in the outer Solar System.

Although redox reactions between sulfide and sulfate solutes are inhibited below ~100–200 °C (Ohimoto and Lasaga, 1982), the presented closed system calculations correspond to reduced conditions at which sulfides overwhelmingly dominate. These results roughly reproduce sulfide mineralogy of carbonaceous chondrites, and the speciation and abundance of S in the fluid phase appear evaluated fairly.

Equilibrium models with non-ideal gaseous and aqueous solutions are highly applicable for gas–liquid partitioning. Likewise, acid–base interactions in solution are fast and corresponding pH values are reliable estimates. A notable exception is fluids with high ionic strength (at W/R < 0.4 in Figs. 1 and 2) where the Debye–Hückel model does not work properly. Nevertheless, the composition of concentrated fluids could be roughly estimated by extrapolation to low W/R values (Figs. 1, 2 and A1) or by using the Pitzer model for activity coefficients (Section A2 in Appendix A and Fig. A2).

The evaluated compositions of fluids depend on inventory of solid phases in the database and accuracy of their thermodynamic properties. The applicability of the results is limited by the lack of key but poorly characterized minerals (tachiolinite, cronstedtite, pentlandite) in the database. The use of other solids as a proxy for minerals (e.g., millerite for pentlandite, rhodonite for Mn-bearing pyroxenes) also limits the applicability of models. The thermodynamic data used for some solids (e.g., saponite) are uncertain so the conclusions on their stability are not robust. The formation of Fe–Mg chlorite and Fe-bearing serpentine rather than saponite in some low-T and high-P runs (Figs. 2, 4 and 5, and 6b) may reflect quality of thermodynamic data. The use of ideal solid solution models for key minerals is another source of uncertainty that may affect compositions of aqueous solution and corresponding phases (saponite, serpentine, etc.). The use of high-T mixing parameters for other multi-component solids (chlorite, olivine, pyroxenes) in low-T models also causes uncertainty. Therefore, the calculated compositions of solid solutions reveal tendencies rather than concrete mole fractions of end-members, especially at lower temperatures.

4.2. Factors affecting the composition, pH, oxidation state, and compositional evolution of fluids

The amount of aqueous phase (Section A3 in Appendix A) mainly affects concentrations of elements that are preferentially partitioned to the aqueous solution: Cl and Na in alkaline fluids, and many other elements in diluted and acidic solutions (Fig. 1). Consumption of solutions causes proportional increases in concentrations of these elements until corresponding solids precipitate. Chlorine completely partitions to solution, except for the brines equilibrated with precipitated chlorides (Fig. A2). To maintain electroneutrality, Cl− is mainly compensated by Na+ in alkaline solutions (Figs. 1a, b, 3, and 4) and by Mg, Fe, Na, Ca, Mn, and K in acidic fluids (Fig. 1c and d). Without abundant Na-bearing secondary phyllosilicates, copious Na+ in solution is compensated by a variety of anions (HCO3−, CO32−, OH−, Cl−, HCOO−) depending on P–T–W/R conditions. In turn, abundant anions (e.g., from cometary melts) cause a major partition of Na to the aqueous phase. Despite...
the high abundance of Fe, Mg, and Ca in CI-type solids, these elements are minor constituents of aqueous solutions because of low solubility of corresponding solids in alkaline conditions, though a notable increase in concentrations of the elements is observed in fluids at $W/R = 0.13–1$ (Section A1 in Appendix A).

Although this increase implies an elevated elemental mobility, the low amount of aqueous solution and a low permeability of altered materials (Bland et al., 2009) would limit lateral transport.

Temperature affects aqueous chemistry through $T$-dependent dissociation of water, and solute-solute and solubility equilibria. The increase in concentration of dissolved $H_2$ with temperature (Figs. 3–5 and 7) reflects oxidation of $Fe^0$, $Fe^{2+}$, $Ni^0$, $P^{3+}$, and $C$ in accreted solids and organic compounds by water (e.g., Eq. (1)). The changes in C speciation (e.g., Figs. 3–5) imply the $pH$- and $T$-dependent $CO_2^2 \rightarrow HCO_3^- \rightarrow CO_2$ conversion, the reduction of oxidized C species to formate, methanol, and CO at elevated $pH_2$, and a supply of C from condensed organic species. Elevated aqueous concentrations of $HS^-, H_2S$, and $SiO_2$ reflect increasing solubilities of sulfides, some silicates, and silica phases with temperature. The increased association of ions with temperature accounts for elevated abundances of neutral solutes ($NaCl$, $KCl$) and a decrease in concentrations of $Na^+$, $K^+$ and $Cl^-$ ions notable at $T > 250^\circ C$.

Solution $pH$ is affected by dissociation of water to $H^+$ and $OH^-$, and the acid–base balance of anions and cations influenced by solubilities of solids. At the $P$–$T$ conditions of water saturation, dissociation of pure water has a maximum at $250^\circ C$ (lowest neutral $pH$) which shifts to higher temperature as pressure increases (Fig. 8). The calculated $pH$ in CI-type systems is higher than the $pH$ of pure water but shows the temperature dependence similar to that in pure water. The ultramafic composition of the CI-type rocks accounts for alkaline $pH$, as previously modeled by Zolensky et al. (1989) and Rosenberg et al. (2001). In our models, alkaline fluids always dominate at low $W/R$ ratios ($\leq 10$), which also...
correspond to advanced stages of alteration regardless of a presence of HCl in initial fluids (Fig. 1). Elevated concentrations of Na⁺ are associated with strongly alkaline pH, and alteration progress typically corresponds to increasing pH, except some concentrated fluids (Figs. 1 and 2). Exceptionally high pH in OH-rich solutions is achieved if Na⁺ is not balanced by Cl⁻ and C-bearing anions (Fig. 2b, 5, 6, and 7a). Reduced conditions favor formation of high-pH fluids because of suppressed oxidation of organics to C-bearing anions and the formation of ferrous phyllosilicates instead of Na-bearing saponite. Although the modeled high-P reduction of carbonate species to condensed organics (Fig. 6) may not be efficient (Section 4.1), the calculations reveal a possibility of OH⁻-rich solutions to occur in H₂-rich environments. In turn, interactions with melted ices rich in C oxides account for more oxidized and less alkaline fluids (Fig. 8). High-T oxidation of organic species to CO₂ also results in lower pHs.

Although this work is not aimed at modeling alteration pro-
gress, some insights could be acquired. In early alteration fluids, concentrations of solutes increase due to dissolution of solid and amorphous phases until corresponding secondary phases precipi-
tate. If Cl accretes in putative low-solubility solids, diluted Na-bicarbonate solutions may evolve to NaCl type solutions equilibrated with saponite-bearing mineralogy (Fig. 1a). In a case of Cl accretion in low-solubility solids (e.g., metal chlorides), likely early fluids are NaCl type solutions. If Cl was accreted in HCl hy-
drate(s) (Zolotov and Mironenko, 2007), early Mg-, Fe-rich acidic fluids evolve to NaCl type solutions upon dissolution of initial minerals, neutralization of solution, and precipitation of serpentine, saponite, and carbonates (Fig. 1c; Zolotov and Mironenko, 2008). Early-formed Fe-rich serpentine and Mg-rich saponite could be replaced by Mg-serpentine and Na-saponite. These scenarios for early fluids do not strongly affect subsequent alteration pathways.

Isothermal alteration in low T–P environments (Figs. 1a and c and 2a) is accompanied by increases in saponite/serpentine and saponite/chlorite ratios. Na content in saponite, and Mg/Fe ratio in serpentine. Similar compositional changes in serpentine group minerals are observed in CM2 chondrites (e.g., Tomeoka and Busseck, 1985; Zolensky et al., 1993; Browning et al., 1996). If gas does not escape, pressure build up by the H₂-rich gas favors formation of high-pH fluids because of suppressed oxidation of organics to C-bearing anions and the formation of ferrous phyllosilicates instead of Na-bearing saponite. Although the modeled high-P reduction of carbonate species to condensed organics (Fig. 6) may not be efficient (Section 4.1), the calculations reveal a possibility of OH⁻-rich solutions to occur in H₂-rich environments. In turn, interactions with melted ices rich in C oxides account for more oxidized and less alkaline fluids (Fig. 8). High-T oxidation of organic species to CO₂ also results in lower pHs.

Table 4

<table>
<thead>
<tr>
<th>Major ions</th>
<th>Conditions and localities of occurrence</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na⁺, Cl⁻, HCO₃⁻, CO₃²⁻, K⁺</td>
<td>Abundant Na-bearing saponite in secondary mineralogy; low W/R ratios (&lt;10); occurs on early and/or today’s Enceladus; evidenced from fluid inclusions in chondritic halite; possibly the most common fluid on icy moons and early asteroids.</td>
</tr>
<tr>
<td>Na⁺, CO₂⁻, Cl⁻, K⁺</td>
<td>No abundant Na-saponite in secondary mineralogy; moderately alkaline low-T (&lt;100 °C) environments rich in inorganic C; could occur on bodies which accreted cometary ices.</td>
</tr>
<tr>
<td>Na⁺, HCO₃⁻, Cl⁻, K⁺, CO₃²⁻</td>
<td>No abundant Na-saponite in secondary mineralogy; sodium, predominantly high-T (&gt;100 °C) environments rich in inorganic C; could occur on bodies which accreted cometary ices.</td>
</tr>
<tr>
<td>Na⁺, OH⁻, Cl⁻, NaOH, K⁺, CO₃²⁻</td>
<td>Abundant Na-saponite in secondary mineralogy; strongly alkaline low-T environments deficient in inorganic C; elevated temperatures at reduced high-P environments; could have occurred locally on parent bodies of CR chondrites.</td>
</tr>
<tr>
<td>Cl⁻, Mg²⁺, Fe²⁺, Na⁺, Ca²⁺, Mn²⁺</td>
<td>Acidic conditions caused by melting of HCl-bearing ices; no abundant secondary mineralogy; possible occurrence at very early low-T stages of alteration on parent bodies of CM chondrites and other bodies.</td>
</tr>
<tr>
<td>Mg²⁺, Na⁺, SO₄²⁻, Cl⁻</td>
<td>Formation through oxidation of sulfide sulfur; the oxidation could be facilitated by escape of reduced gases and elevated temperature; occurred on parent bodies of CI/CN carbonate chondrites and, possibly, on Europa.</td>
</tr>
</tbody>
</table>

Note: The first line in the second column shows the most abundant solutes.
Fig. 9. The modeled Na/K ratio in fluids formed through aqueous alteration of CI-type solids. The curves show equilibrium compositions calculated for W/R = 1, where initial solution is present by pure water. (1) At pressure of water saturation when saponite is not present in low-T mineralogy (Fig. 4). (2) At pressure of water saturation with suppressed formation of chlorites (Fig. 3a). (3) At pressure of water saturation with suppressed formation of chlorites and K-Na phlogopite (Fig. 3b). (4) Modeled Enceladus’ fluids at P > 100 bars and 10% C reacted at moderately oxidized open system conditions (Zolotov, 2007). Note that the W/R ratio has a little effect on the Na/K ratio (Fig. 1a and b). The upper dotted lines show the range of Na/K ratios in icy grains emitted from Enceladus’ (Postberg et al., 2009). The lower dotted lines correspond to the exosphere of Europa that may characterize the moon’s subsurface ice and an ocean (Cipriani et al., 2009). These data may indicate lower temperature of aqueous processes on Enceladus than on Europa.

The Na,HCO\textsubscript{3} and Na,HCO\textsubscript{3} types of alkaline fluids coexist with secondary mineralogy deficient in Na-bearing secondary minerals such as saponite. These fluids have higher salinity and pH than solutions equilibrated with abundant Na-bearing saponite. Abundant CO\textsubscript{2}\textsuperscript{-} and HCO\textsubscript{3}\textsuperscript{-} species could form through accretion of carbon oxides in ices and/or oxidation of organic species in low-\textsuperscript{12} and/or high-T environments. The deficit or lack of Na-saponite reflects a major partition of Na\textsuperscript{+} to solution needed to balance CO\textsubscript{2}\textsuperscript{-} and/or HCO\textsubscript{3}\textsuperscript{-} ions. The Na,HCO\textsubscript{3} type fluids with pH of ~10 coexist with serpentine and some chlorite at T < 100 °C (Figs. 2a, 4, and 6b). The Na,HCO\textsubscript{3} type with pH 6–9 occurs at higher temperatures and/or elevated amounts of accreted carbon oxides (Figs. 7b and 8). In high-T (~200 °C) cometary systems, the Na,HCO\textsubscript{3} type fluids could be rich in dissolved CO\textsubscript{2}, H\textsubscript{2} and/or CH\textsubscript{4} (Fig. 8). Although the Na\textsuperscript{+} and HCO\textsubscript{3}\textsuperscript{-} may dominate in some early diluted fluids (Fig. 1a and b), a rapid release of Cl\textsuperscript{-} from accreted chlorides or hydrates makes this case unlikely.

The extremely alkaline NaOH type fluids are depleted in inorganic C and coexist with saponite-less solids (Figs. 2b, 5, 6, and 7a). The deficiency of inorganic C solutes may result from limited accretion of C oxides and/or suppressed oxidation of organic species at high-\textsuperscript{12} and/or low-T conditions. The usual presence of Na-bearing secondary phases and carbonates in altered chondrites imply a rare occurrence of these solutions. However, OH–rich solutions could have occurred locally on parent bodies of some CR chondrites, which are characterized by chlorite-serpentinite assemblages, depletion in Na and K relatively to CI chondrites, and overall reduced mineralogy (Weisberg et al., 1993; Weisberg and Huber, 2007). The OH–rich solutions could have coexisted with chlorites in vicinity of feldspars that supply AI. The presence of only partially altered metal in CR chondrites suggests high-\textsuperscript{12} conditions that also suppress oxidation of organic species. The preservation of metal may reflect a formation of the Fe(OH)\textsubscript{2} protective layer at high pHs (Chizmadia et al., 2008). Note that the common presence of Ca carbonates in CR chondrites implies the occurrence of HCO\textsubscript{3}\textsuperscript{-} and CO\textsubscript{3}\textsuperscript{2-} in corresponding solutions.

The acidic Mg–Fe–Cl solution type may characterize early stages of alteration by HCl-bearing solutions. These fluids are also enriched in Na, Ca, Mn, K, Ni, Co, Al, Cr, and P. A possible formation mechanism involves accretion of HCl hydrate(s) together with ice followed by dissolution of solids and amorphous materials until a NaCl-rich alkaline fluid is formed (Fig. 1c; Zolotov and Mironenko, 2008). The occurrence of early acidic fluids is consistent with local mineralogy of CM2 chondrites (Brearley, 2006b) and sags of local (<1 mm) Al mobility in H3 ordinary chondrites (Grossman et al., 2000, 2002). Note that in outer Solar System bodies HCl could be neutralized in ammonia-rich solutions at temperatures ~160–180 K before major water–rock interactions.

The MgSO\textsubscript{4}–NaCl type fluids form at strongly oxidizing conditions that may require escape of reduced gases (H\textsubscript{2}, CH\textsubscript{4}) and elevated temperature. The presence of sulfates in CI and CM carbonaceous chondrites and on the surface of Europa implies precipitation from sulfate-bearing solutions formed by oxidation of sulfides. A possible open system formation of these solutions were considered elsewhere (e.g., Bourcier and Zolensky, 1992; Rosenberg et al., 2001).

5. Conclusions

The calculations of chemical equilibria in closed aqueous systems with CI-type materials is a first-order approach to understand compositions of aqueous, solid, and gaseous phases on early carbonaceous asteroids and icy bodies in the outer Solar System. Although these models do not take into account kinetically-controlled dissolution of solids, low-T inhibition of redox reactions, adsorption of ions, flows of gases and fluids, and gas escape that could occur in natural systems, they still provide reasonable estimates of concentrations of solutes and solution pH. Calculations of redox equilibria provide initial insights into end-member cases and directions of chemical processes. However, equilibrium calculations in low-T systems do not provide reliable estimates for many coexisted organic and inorganic C species.

In addition to solubilities of solids, the modeled solution chemistry is affected by the speciation of chlorine in initial water–rock assemblages, and the occurrence and composition of saponite, which mainly controls the solid-aqueous partition of Na. Despite the dominance of Mg, Fe, Si, Ca, and S in CI-type systems, major species in typical aqueous solutions are Na\textsuperscript{+}, Cl\textsuperscript{-}, HCO\textsubscript{3}\textsuperscript{-}, CO\textsubscript{3}\textsuperscript{2-}, K\textsuperscript{+}, OH\textsuperscript{-}, H\textsubscript{2}O and CO\textsubscript{2}. Sulfate species do not form in closed systems which remain reduced, especially at elevated pressures created by forming H\textsubscript{2}O gas.

Other elements are not abundant in fluids owing to low solubilities of corresponding solids (phyllosilicates, magnetite, sulfides, phosphates, etc.) in common alkaline fluids. However in typical alkaline solutions, concentrations of aqueous species of Ca, Mg, Fe, Mn, Ni, and Co increase with lowering the W/R mass ratio below unity. Such an increase could illustrate alteration progress at advanced stages of water–rock interaction.

Putative accretion and melting of HCl-bearing ices creates early acidic fluids rich in CI, Mg, Fe, Na, Ca, Mn, Al, Cr, Ni, Co, and P, consistent with chemical and mineralogical evidence for low-pH processes in some chondrites. After neutralization of these fluids, the initial speciation of Cl does not have major effects on evolution of fluids and solids.

Elevated temperatures correspond to higher concentrations of HS\textsuperscript{-}, SiO\textsubscript{2}, NaCl, COOH\textsuperscript{-}, H\textsubscript{2}O, and C species (CO\textsubscript{2}, COOH\textsuperscript{-}). The high concentrations of these C species reflect oxidation of organic
species. Elevated pressure corresponds to reduced H₂-rich environments. The high-P conditions result in lower concentration of oxidized species in aqueous solution and stabilize reduced solids and condensed organic matter.

The NaCl-rich alkaline fluids with subordinate amounts of HCO₃⁻, CO₃²⁻, and K⁺ form in a wide range of conditions in equilibrium with saponite-bearing mineralogy and could be the most common solutions on early asteroids and icy moons. These and previous equilibrium models for NaCl type solutions are consistent with the composition of icy grains emitted from Enceladus (Postberg et al., 2009, 2011). The high Na/K ratio in these grains indicates low-T (<=0 °C) aqueous processes in history of Enceladus, while the low Na/K ratio in the exosphere of Europa is consistent with hydrothermal processes.

If Na-bearing secondary minerals (e.g., saponite) are absent from secondary mineralogy, the electroneutrality of strongly alkaline Na-rich fluids is achieved by elevated contents of C anions (HCO₃⁻, CO₃²⁻, and COOH⁻) and/or OH⁻. Alteration by fluids rich in C oxides leads to fairly oxidized and moderately alkaline Na carbonate/bicarbonate solutions coexisted with carbonate-rich mineralogy. These solutions could form via accretion of cometary ices with C oxides or through a major oxidation of organic species. Although the mineralogy of some CR chondrites is consistent with strongly alkaline and reduced fluids, the common presence of Na-bearing secondary phases and carbonates in altered chondrites implies uncommon occurrences of NaOH-rich fluids.

Acknowledgments

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Appendix A

A.1. Aqueous concentrations of Ca, Mg, Fe, Mn, Ni, Co, Cr, Al, P, and S

This section describes aqueous chemistry of low abundant elements in alkaline solutions based on calculations presented in Figs. 1a, b, 2–6, and 7a.

The calculated aqueous concentrations of Ca, Mg, Fe, Mn, Ni, Co, Cr, Al, P, and S do not change strongly at W/R = 1–1000. However, Ca, Mg, Fe, Mn, Ni, and Co are increasingly abundant in NaCl-rich fluids at W/R < 1 (Fig. A1). The elevated Ca content agrees with results of Petaev and Mironenko (1997). The increase is accounted for by increasing stabilities of chloride, hydroxyl, oxide, and silicate aqueous complexes of metals and corresponding increases in solubilities of solids. Aqueous concentrations of Ca, Mg, Fe, Ni, and Co are slightly lower at 25 °C than at 150 °C (see also Table 3). In contrast, Cr, P, Al, and S are typically less abundant in aqueous solutions at W/R < 1. The concentration of Cr (mainly in CrO₂³⁻; 10⁻¹³ at 25 °C and 10⁻¹⁰ at 150 °C) decreases by one order of magnitude as the W/R ratio decreases from 1 to 0.2. The concentration of P (mainly in HPO₄²⁻) decreases from 10⁻¹⁵ to 10⁻²⁰ at 25 °C and from 10⁻¹³ to 10⁻¹⁰ at 150 °C.

Strongly alkaline low-T solutions (Fig. 2) are depleted in Ca and Mg (<10⁻⁵, <10⁻⁶ mole/kg H₂O, respectively) and these elements do not become more abundant at W/R < 1. Metal cations and positively charged complexes are not abundant. However, these solutions are rich in anions (H₂FeO₂⁻, MnO₂²⁻, HS⁻), which become more abundant as pH increases at lower W/R ratios and reach concentrations of 10⁻²–10⁻³ mole/kg H₂O at W/R = 0.2 in NaOH type solutions. Other elements also occur in anions, AlO₂⁻, ~10⁻⁷; NiO₂⁻, 10⁻⁸; CoO₂⁻, 10⁻⁸, CrO₂⁻, 10⁻¹⁰; HPO₄²⁻, 10⁻¹².

The following description covers aqueous abundances of elements at W/R = 1. At P = pH₂Osat, the molality of Ca species

Fig. A1. Concentrations of low abundant species in NaCl-rich aqueous solutions formed through alteration of CI-type solids at pressure of water saturation. Other species are shown in Fig. 1a and b.
changes from ~10 ppm at T < 100°C to ~1 ppm at 300–350°C (e.g., Fig. 4) in accord with the increasing Ca content in saponite (Fig. 4d) and decreasing solubility of calcite with temperature. At high-P conditions, Ca concentration (0.1–50 ppm) is controlled by saponite, andradite, and Ca-bearing pyroxene (Figs. 5, 6, and 7a).

At P = pH2O Sat, the molality of Mg species (mainly Mg2+, MgCO3, and MgOH−) decreases with temperature from ~3 ppm at 0°C to ~10 ppm at 350°C and reflects changing solubilities of phyllosilicates and Mg content in them (e.g., Fig. 4). The increase in pressure at 25°C (Fig. 6) corresponds to lowering Mg molality from 0.1 ppm to 0.1 ppm at increasing pH. At P = pH2O Sat + 10 bars (Fig. 5), an increase in Mg concentration (0.1 ppm at 0°C and 7 ppm at 350°C) is affected by the solubility of Mg-bearing pyroxene. At 2000 bars (Fig. 7a), Mg concentration (3 ppm at 0°C and 20 ppm at 350°C) reflects the solubility of Mg-bearing pyroxene and high-T formation of olivine from serpentine.

At P = pH2O Sat, the concentration of Fe (mainly HFeO2−) irregularly increases from 0.1 to 1 ppm at T ≤ 50°C to a few ppm at 350°C. This corresponds to decreasing Fe content in phyllosilicates (Fig. 4e and f) and reflects increasing solubilities of magnetite and pyrrhotite with temperature. Increasing P corresponds to higher Fe concentrations in solution and reflects replacements of magnetite, pyrrhotite, and andradite (if it forms) by troilite, Fe-olivine, and Fe-bearing alloy. At 2000 bars (Fig. 7a), the concentration (~10−3) reflects the occurrence of Fe-bearing pyroxene and metal alloy stable in a wide temperature range.

The concentration of Mn (mainly in MnO, MnO2−, MnOH−, and Mn2+) is controlled by solubilities of Mn carbonate, silicates, and sulfide. In the presence of rhodochrosite (T < 150–180°C), the modeled Mn molality (0.01–0.6 ppm) increases with temperature. High-P equilibria show the same pattern, though at 2000 bars the equilibria are two orders of magnitude higher, reflecting equilibration with tephroite. At P = pH2O Sat + 10 bars, alabandite forms at T < 100°C and accounts for Mn concentration of 3–50 ppm. Rhodonite forms at higher temperatures in a wide range of pressures and its decreasing solubility accounts for the concentration drop to 10−8 at 350°C. Pressure increase at 25°C (Fig. 6) corresponds to the increase in Mn concentration from 0.1 ppm to 10 ppm and reflects the formation of MnS. Tephroite, rhodonite and alabandite are not modeled as components of olivine, pyroxene, and troilite, respectively. Pure Mn silicates and MnS are not present in chondrites that avoided metamorphism, so these estimates are tentative.

The abundance of Ni species (mainly NiO and NiO2−) strongly increases with temperature, reflecting solubilities of millerite and Ni-rich alloy. At T ≤ 100°C, Ni concentration varies with pressure (10−14 at P = pH2O Sat, 10−10 at P = pH2O Sat + 10 bars, and 10−12 at 2000 bars). At 300–350°C, the concentration is 10–100 ppm. Pressure increase at 25°C (Fig. 6) corresponds to the increase in Ni concentration from 10−13 to 10−10 at 4 bars and reflects the increasing solubility of NiS, which becomes less abundant. At P > 4 bars, decreasing Ni concentration reflects the increasing stability of Ni-rich alloy.

The modeled concentration of Co (CoO and CoO2−) is not reliable because it is only affected by the solubility of Co-bearing metal alloy with estimated thermodynamic properties. At P = pH2O Sat, the molality of Co drops from 10−7 at 0°C to 10−9 at 350°C. At 25°C, pressure increase (Fig. 6) corresponds to lowering Co concentrations in solution (from 10−8 to 10−13 at 100 bars) and in increasingly abundant metal alloy. At P = pH2O Sat + 10 bars (Fig. 5), Co concentration increases from 10−12 at 0°C to 10−9 at 300°C. At 2000 bars (Fig. 7a), Co concentration increases from 10−13 at 0°C to 10−10 at 350°C.

The concentration of Al (mainly in AlO2−) is controlled by solubilities of saponite, chlorite, and amesite. The concentration increases from 10−8 at 0°C to 10−6 at 350°C in saponite-rich systems without chlorites (Fig. 3) and from 10−11 to 10−6 in the presence of low-T chlorites (Fig. 4). Aluminon is more abundant in solutions with elevated alkaline pH. The increase in pH with pressure at 25°C corresponds to increasing Al content from 10−7 to 10−5 in the chlorite-free system (Fig. 6a) and from 10−10 to 3 × 10−9 in the chlorite-rich system (Fig. 6b). These values are tentative because of uncertain thermodynamic properties of saponite.

In the presence of chromite, molality of Cr (mainly in CrO2−) increases from 10−13–10−14 at 0°C to 10−9 at 290°C and then decreases, if eskolaites forms at higher temperature. At elevated pressures (Fig. 6), the same pattern is observed at higher concentrations and reflects the elevated pH of Na+–rich solutions. At 2000 bars, the concentrations are two orders of magnitude higher.
The evaluated low concentration of phosphorus (mainly PO$_3^{2-}$ and HPO$_2^{-}$/CO$_4^{4-}$) in alkaline solutions is controlled by the solubility of whitlockite. At $P = p_{H2Osat}$, P concentration increases from 10$^{-14}$ at 0°C to 10$^{-12}$ at 50°C and does not change much at higher temperatures. At 25°C and $P < 100$ bars (Fig. 6), the concentration is 10$^{-13}$ to 10$^{-9}$ at $T > 200°C$, were P$^{3+}$ species ($\text{HPO}_2^-$) becomes abundant.

The modeled S species are presented by HS$^-$ and some H$_2$S coexisted with troilite, pyrrhotite, and Ni and Mn sulfides. The elevated solubilities of sulfides at high-$T$ and high-$f_{H2}$ conditions account for elevated concentrations of sulfide S (up to 0.1 molal at 350°C). At $P = p_{H2Osat}$, S concentration increases from 10 ppm at 0°C to 10$^{-2}$ at 350°C. At 25°C, the concentration increases with pressure (from 10$^{-4}$ to $5 \times 10^{-3}$ at 20 bars) due to lower stability of pyrrhotite and millerite relative to troilite at elevated $f_{H2}$. The NaOH type solutions are enriched in HS$^-$ (Fig. 5). The decrease in S concentration at $P > 20$ bars results from the increasing stability of troilite at increasingly more reducing conditions. At $P = p_{H2Osat} + 10$ bars, S concentration ($\sim 10^{-3}$ at 0°C and 10$^{-2}$ at 350°C) is affected by solubilities of troilite and alabandite at lower temperatures, and pyrrhotite and millerite at higher temperature. At 2000 bars (Fig. 7a), the concentration increases from 10$^{-4}$ to 10$^{-9}$ at $T > 200°C$, were P$^{3+}$ species (HPO$_2^-$) becomes abundant.

A.2. Freezing and evaporation of NaCl type fluids

Fig. A2 illustrates evaporation and freezing of a typical NaCl-rich alkaline solution calculated with equilibrium models. The calculations were performed with the FREZCHEM code (Marion et al., 2010) that is based on the Pitzer model for activity of solutes and water activity. Evaporation and freezing result in precipitation of NaCl or NaCl$_2$H$_2$O, respectively. Less abundant precipitates are KCl, and Na carbonates and bicarbonates, whereas Ca and Mg carbonates form in trace amounts. These results are consistent with other freezing models (e.g., Zolotov, 2007) and with the composition of icy grains emitted from Enceladus.

A.3. Factors affecting the amount and partition of alteration fluids

In addition to bulk W/R ratio, the amounts of aqueous and gaseous phases depend on degree of alteration, temperature, and...
pressure. Water is consumed by competitive hydration and oxidation reactions. Hydration is mainly accounted for by the formation of serpentine, saponite, and chlorites (and cronstedtite and tochilinite, which are not modeled). Oxidation of Fe, Ni, P, C, and S from kamacite, schreibersite, organic species, and sulfides consumes oxygen from water and releases H₂ and/or CH₄, as illustrated by Eq. (1) for Fe-metal. Low-solubility H₂ and CH₄ mainly partition into the gaseous phase (Fig. A3). Temperature has a complex effect on the amount of fluid and reflects preferable low-T hydration, high-T oxidation and dehydration, and liquid–gas partition of water (Fig. A4a and b). The effect of pressure includes low-P partition of water and dissolved gases to the gaseous phase and high-P dissociation of water accompanied the formation of H₂-rich gas (Figs. A3c and d and A4c).

References


