AQUEOUS ALTERATION AND HYDROGEN GENERATION ON PARENT BODIES OF UNEQUILIBRATED ORDINARY CHONDrites: THERMODYNAMIC MODELING FOR THE SEMARKONA COMPOSITION. M. Yu. Zolotov1, M. V. Mironenko1, and E. L. Shock1,2. 1Department of Geological Sciences, 2Department of Chemistry and Biochemistry, Arizona State University, Tempe, Arizona 85287, 3Vernadsky Institute of Geochemistry and Analytical Chem., Russian Academy of Sciences, Kosygin Str. 19, Moscow, Russia. E-mails: eshock@asu.edu, mironenko@geokhi.ru, zolotov@asu.edu.

Introduction: Ordinary chondrites are the most abundant class of meteorites that could represent rocky parts of solar system bodies. However, even the most primitive un-equilibrated ordinary chondrites (UOC) reveal signs of mild alteration that affected the matrix and peripheral zones of chondrules. Major chemical changes include oxidation of kamacite, alteration of glass, removal of alkalis, Al, and Si from chondrules, and formation of phases enriched in halogens, alkalis, and hydrogen [1,2]. Secondary mineralogical changes include formation of magnetite, ferrous olivine, fayalite, pentlandite, awaruite, smectites, phosphates, carbonates, and carbides [1,4-10]. Aqueous alteration is consistent with the oxygen isotope data for magnetite [11].

The presence of secondary magnetite, Ni-rich metal alloys, and ferrous silicates in UOC implies that H2O was the oxidizing agent. However, oxidation by H2O means that H2 is produced in each oxidative pathway. In turn, production of H2, and its redistribution and possible escape should have affected total pressure [12], as well as the oxidation state of gas, aqueous and mineral phases in the parent body.

Here we use equilibrium thermodynamic modeling to explore water-rock reactions in UOC. The chemical composition of gas, aqueous, and mineral phases is considered.

Model: The composition of Semarkona (LL3.0) [13] is selected to exemplify UOC. Semarkona is one of the best-studied chondrites that reveal clear signs of aqueous alteration [2,3,5,6,8-11]. The calculations are performed with our new codes [14] in the 17-component system O-H-Mg-Fe-Ca-Si-Al-C-P-S-Cr-Na-K-Cl-Mn-Co-Ni that also includes 117 new codes [14] in the 17-component system O-H-Mg-Fe-Ca-Si-Al-C-P-S-Cr-Na-K-Cl-Mn-Co-Ni that also includes 117.

Results: Chemical equilibration in the rock-water system leads to the formation of gas, aqueous solution and secondary minerals. An aqueous solution forms at WWR > 0.15-0.2. H2 is the dominant gas except at P < ~2 bar when H2O(g) is abundant. Progress of alteration reactions causes water consumption through oxidation and hydration, and a decrease in WWR among altered parts of the rock. Formation of H2 and changes in volumes affect P, unless it is externally fixed. Generally, lower WWR and high P represent relatively reduced conditions.

Mineralogy: The composition unaltered chondrite corresponds to the following normative mineralogy (in mole/kg): metallic alloy (Fe0.9103Ni0.0652Cr0.0216Co0.0283), 3.227; troilite, 0.5920; forsterite, 0.9531; pyroxene (Di, 0.33085; En, 2.1669); feldspar (An, 0.05665; Ab, 0.33, Mc, 0.0226); albundite, 0.0526; schreibersite, 0.0360; lawrencite, 3.005·10-3; and graphite, 0.5055. The following minerals are observed in the calculated assemblages: Fe-depleted metal alloys, magnete, pyrrhotite, hornblende, olivine of different compositions (FeO-MgO), enstatite-diopside, diopside-hedenbergite, rodonite, andradite, saponite, chlorite, serpentine, whitlockite and halite.

Ni-Co-rich metal is among the major secondary phases, especially at low WWR (<0.1) and P > ~2-30 bar (depending on WWR). The Fe/(Co+Ni) ratio decreases with increasing WWR and decreasing P. Small amounts of Co and Co-Ni metals form in the presence of aqueous solution at WWR > ~0.2, and the Co/Ni ratio decreases as P increases.

Magnetite is typically present in low-P, relatively oxidizing conditions (low fH2) and at moderate WWR. At high WWR, ferrous serpentines and chlorites form instead of magnetite, which only forms at P < ~5 bar. At low WWR, iron is mainly present as metal. However, at P > ~30 bar, a small amount of magnetite can be associated with pure fayalite that forms in a limited range of WWR (around 0.1). At lower WWR, forsteritic olivine (Fo95-Fo0) is stable and ferrous hydrosilicates become abundant at higher WWR.

Secondary Ca-Mg-Fe pyroxenes are mostly represented by diopside-hedenbergite in which Fe/(Mg+Fe) ratio reaches 0.34 at elevated WWR and P. In the absence of an aqueous solution (WWR < ~0.2), much lower Fe contents are typical. Andradite is a minor phase that often associates with magnetite at low P and high WWR conditions in the presence of a solution.

Saponites are present in all calculated assemblages and become abundant at moderate WWR (~0.02-0.2) where solution is absent and at lower P. Typical saponites are Na-rich with K content of ~8 mol %. Mg-rich saponite are only abundant at WWR < 0.05. Compared to smectites, serpentines and chlorites are more common at elevated WWR and P. Although Mg-rich phases are abundant at WWR = ~0.05-0.2 without solution and at low P, increases in WWR and P causes increases in the Fe/(Mg+Fe) ratio to 0.3 and 0.8 in serpentine and chlorite, respectively. Chlorites are about 10 times less abundant than serpentines.

Ni sulfide (here exemplified by NiS) forms at WWR > ~0.2 in the presence of solution at P < ~20-30 bar. Formation
of Ni sulfide corresponds to a decrease in Ni/Co ratio in secondary metal alloys. Pyrrhotite and Mn silicate (exemplified by rhodonite) form at mildly oxidizing conditions at elevated WRR (~0.1) and P < ~20-30 bar. Otherwise, primary troilite and alabandite remain stable in secondary assemblages.

Chromite and whitlockite are present in all calculated secondary assemblages, indicating a strong drive for oxidation of Cr and P in asteroids.

Although graphite remains stable, relatively high CO$_2$ activity (~10$^{-8}$) is observed in the solutions. This implies that carbonates could deposit once the solution is consumed. Formation of Fe$_2$C is not observed.

Halite forms at WRR < 0.2 from concentrated solutions and always present in “dry” secondary assemblages. This is the only Cl-bearing mineral formed.

**Solution chemistry and the pH:** All solutions are rich in Na and have alkaline pH. At P < ~2 bar and/or concentrated (WRR ~ 0.15-0.2) solutions, Cl-Na-K-bearing species (Cl', Na', NaCl(aq), K', CaCl$_2$(aq), KCl) dominate at pH 8-10. At higher P and WRR, Na', OH', NaOH(aq), NaH$_2$SiO$_3$(aq), HS', K', and KOH are the most abundant solutes at pH 11-12.

H$_2$ production and fate. Since water is the only oxidizing agent, H$_2$ is produced in all oxidation pathways: (1) Fe-rich metal to magnetite, ferrous silicates (olivine, hedenbergite, serpentine and chlorite), Ni sulfide and chromite; (2) schreibersite to whitlockite; (3) troilite to pyrrhotite, and (4) alabandite to rhodonite. Iron phosphides, Cr$^6+$ and Fe$^6+$ are unstable with respect to the oxidation that generates H$_2$ even at small (~0.05) WWR. Oxidation of Fe and Mn sulfides, and Ni$^2+$ requires more oxidizing conditions that correspond to low P and/or H$_2$O-rich environments. The calculations show that H$_2$ is produced until consumption of either H$_2$O or the reduced mineral reactants. The maximum amount of H$_2$ can be produced if a bulk water-chondrite balance is close to the stoichiometry of the Fe$^6+$ oxidation reactions that yield Fe$^2+$ and magnetite. More H$_2$ is produced if magnetite forms. However, formation of OH-bearing minerals (e.g., smectites) may confine the amount of H$_2$ released.

Although H$_2$ is preferentially concentrated in the gas phase, the H$_2$(gas)/H$_2$(aq) ratio decreases as P increases, e.g. due to progress of oxidation reactions. The activity of H$_2$(aq) is ~10$^{-4}$ of H$_2$, which is close to total P at high pressures. The H$_2$(g)/H$_2$O(g) ratio also increases with P and alteration progress because of water condensation (mostly from 1.01 bar to ~5 bar), water consumption through oxidation and hydration, and H$_2$ production.

Increases in the volume of solids and H$_2$ production contribute into the increase in P above that of water saturation. In addition, total P depends on the initial porosity. Our results show that low initial porosity would lead to explosive destructions of asteroids (at ~10$^2$ bars [12]) even at low degrees of alteration progress, as can be seen in Fig. 1a in [14]. Note that production of H$_2$ and total P are limited by the amount of incorporated water ice.

**Alteration Scenario and Discussion:** Here we summarize our results of a possible alteration scenario (see also [14]). Following the melting of ice, aqueous alteration in UOC started with interaction of water with mineral surfaces. This first stage was characterized by low pressure (equal to that of water saturation) and a dilute solution (because of locally high WRR) that mostly contained Na, Cl, OH, HS', K, and H$_2$(aq). Magnetite, Fe-Mg serpentine, pyrrhotite, Ni-sulfide, chromite, and whitlockite formed. Further alteration caused consumption of water though hydration and H$_2$ production, and increases in the volume of solids, H$_2$, and in total P (if gas was unable to migrate). Smectites formed at the expense of serpentinite. An increase in total P caused condensation of H$_2$O and dilution of solution for a while; then the solution became saline, Cl-rich, and halite precipitates.

Once the solution was consumed, further equilibration in a close system caused interaction of original (metal-rich) mineral assemblages with secondary products of oxidation and hydration. Magnetite, serpentine, and chlorite were partially converted to olivine (including pure fayalite) and metal, while smectites remained abundant. In other words, even in an isothermal regime, early-formed oxidized minerals could be converted to more reduced secondary minerals, and early-formed hydrous silicates can dehydrate. These conversions decreased the volume of solids, P$_2$O$_5$ and P. Note that reduction and dehydration at high degrees of alteration progress were only possible at low ice/ratio and low porosities, which were typical for ordinary chondrites.

Comparison of model results with observations [1-10] could be used to evaluate conditions of alteration. In brief, enrichments of altered solids in Na, K, and Cl, the presence of smectites among secondary minerals in UOC, along with unaltered grains and cores of chondrules, are consistent with a low amount of incorporated ice (WWR ~ 10$^{-2}$-10$^{-3}$), and only partial re-equilibration after consumption of solution. Our models show that high-pH solutions rich in Na, OH', Cl, HS', and H$_2$(aq) were typical for parent bodies of UOC and may characterize ocean-forming fluids on large bodies.

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