AQUEOUS ALTERATION AND HYDROGEN GENERATION ON PARENT BODIES OF UNEQUIVOLUTED 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 unequilibrated 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 halogenics, 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 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]. Secondary Ca-Mg-Fe pyroxenes are mostly represented by diopside-hedenbergite in which Fe/(Mg+Fe) ratio reaches 0.43 at elevated WRR and P. In the absence of an aqueous solution (WRR < ~0.2), much lower Fe contents are typical. Andradite is a minor phase that often associates with magnetite at low P and high WRR conditions. Magnetite is typically present in low-P, relatively oxidizing conditions (low fH₂) and at moderate WRR. At high WRR, ferrous serpentine-chlorite forms instead of magnetite, which only forms at P < 5 bar. At low WRR, 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 WRR (around 0.1). At lower WRR, forsteritic olivine (Fo₉₀₋₁₀₀) is stable and ferrous hydrosilicates become abundant at higher WRR.

Results: Chemical equilibration in the rock-water system leads to the formation of gas, aqueous solution and secondary minerals. An aqueous solution forms at WRR > 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 (Fe₆₀₋₉₁,Cr₀.₂₋₀.₅,Mn₀.₀₂₋₀.₀₃), 3.227; troilite, 0.5920; forsterite, 0.9531; pyroxene (Di, 0.33085; En, 2.16699); feldspar (An, 0.05665; Ab, 0.33, Mc, 0.0226); alabandite, 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, magnetite, pyrrhotite, chromite, olivine of different compositions (Fe₉₀₋₁₀₀), 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 WRR (<0.1) and P > ~2-30 bar (depending on WRR). The Fe/(Co+Ni) ratio decreases with increasing WRR and decreasing P. Small amounts of Co and Co-Ni metals form in the presence of aqueous solution at WRR > ~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 WRR. At high WRR, ferrous serpentine-chlorite forms instead of magnetite, which only forms at P < ~5 bar. At low WRR, 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 WRR (around 0.1). At lower WRR, forsteritic olivine (Fo₉₀₋₁₀₀) is stable and ferrous hydrosilicates become abundant at higher WRR.

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

Saponites are present in all calculated assemblages and become abundant at moderate WRR (~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 saponites are only abundant at WRR < 0.05. Compared to smectites, serpentine-chlorite and chlorites are more common at elevated WRR and P. Although Mg-rich phases are abundant at WRR ~ 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 serpentine.

Ni sulfide (here exemplified by NiS) forms at WRR > ~0.2 in the presence of solution at P < 20-30 bar. Formation

The amount of incorporated water ice.

The hydration, and $H_2O$ to ~5 bar), water consumption through oxidation and the reduced mineral reactants. The maximum amount of $H_2O$ alabandite to rhodonite. Iron phosphides, $Cr_2$ serpentine and chlorite), Ni sulfide and chromite; (2) metal to magnetite, ferrous silicates (olivine, hedenbergite, may confine the amount of $H_2O$.

However, formation of OH-bearing minerals (e.g., smectites) show that $H_2O$ is produced until consumption of either $H_2O$ and/or $H_2O$-rich environments. The calculations show that $H_2O$ is produced until consumption of either $H_2O$ or the reduced mineral reactants. The maximum amount of $H_2O$ can be produced if a bulk water-chondrite balance is close to high-pH solutions rich in Na, OH, 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, $H_2O$ and $P$. Note that reduction and dehydration at high degrees of alteration progress were only possible at low ice/rock ratios 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 ($WWR \sim 10^{-2}-10^{-3}$), and only partial re-equilibration after consumption of solution. Our models shows that high-pH solutions rich in Na, OH, Cl, $HSO_4$ and $H_2O$ were typical for parent bodies of UOC and may characterize ocean-forming fluids on large bodies.

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