

AQUEOUS ALTERATION AND HYDROGEN GENERATION ON PARENT BODIES OF UNEQUILIBRATED ORDINARY CHONDRITES: THERMODYNAMIC MODELING FOR THE SEMARKONA COMPOSITION. M. Yu. Zolotov¹, M. V. Mironenko³, and E. L. Shock^{1,2}, 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 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 minerals, 21 mineral solid solutions, a non-ideal gas solution (7 gases) and a non-ideal aqueous solution (194 species). The composition of unaltered Semarkona was estimated by decreasing the O abundance so that Fe, Ni, Co, Cr and Mn were in the metal/sulfide form and P was in Fe₃P.

We explored how the water/rock mass ratio (*WRR*), total pressure (*P*), and alteration progress affect the composition of the gas-aqueous-mineral system, amount of H₂ produced, and its partitioning among phases. We also explored how *P* may change with alteration progress (also see [14]). Formation of CH₄ was suppressed because of inhibition of its formation at low temperatures and pressures, consistent with the presence of carbides, aromatic hydrocarbons, and carbonates in UOC. Initial modeling was performed for 100°C.

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 *WRR* among altered parts of the rock. Formation

of H₂ and changes in volumes affect *P*, unless it is externally fixed. Generally, lower *WRR* and high *P* represent relatively reduced conditions.

Mineralogy. The composition unaltered chondrite corresponds to the following normative mineralogy (in mole/kg): metallic alloy (Fe_{0.9103}Ni_{0.0652}Cr_{0.0216}Co_{0.0028}), 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); 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 (Fo₁₀₀-Fo₀), enstatite-diopside, diopside-hedenbergite, rhodonite, 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 *f*H₂) and at moderate *WRR*. At high *WRR*, ferrous serpentines and chlorites form 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 (Fo₉₃₋₁₀₀) 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, serpentines 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 *WRR* 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 *WRR* > ~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 ($> \sim 0.1$) and $P < \sim 20$ -30 bar. Otherwise, primary troilite and alabandite remain stable in secondary assemblages.

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

Although graphite remains stable, relatively high CO_3^{2-} activity ($\sim 10^{-4}$) is observed in the solutions. This implies that carbonates could deposit once the solution is consumed. Formation of Fe_3C 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 $P < \sim 2$ bar and/or concentrated ($WRR \sim 0.15$ -0.2) solutions, Cl-Na-K-bearing species (Cl⁻, Na⁺, NaCl(aq), K⁺, CaCl₂(aq), KCl) dominate at pH 8-10. At higher P and WRR , Na⁺, OH⁻, NaOH(aq), NaHSiO₃(aq), HS⁻, K⁺, and KOH are the most abundant solutes at pH 11-12.

H₂ production and fate. Since water is the only oxidizing agent, H₂ 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, Cr⁰ and Fe⁰ are unstable with respect to the oxidation that generates H₂ even at small ($> \sim 0.05$) WRR . Oxidation of Fe and Mn sulfides, and Ni⁰ requires more oxidizing conditions that correspond to low P and/or H₂O-rich environments. The calculations show that H₂ is produced until consumption of either H₂O or the reduced mineral reactants. The maximum amount of H₂ can be produced if a bulk water-chondrite balance is close to the stoichiometry of the Fe⁰ oxidation reactions that yield Fe²⁺ and magnetite. More H₂ is produced if magnetite forms. However, formation of OH-bearing minerals (e.g., smectites) may confine the amount of H₂ released.

Although H₂ is preferentially concentrated in the gas phase, the H₂(gas)/H₂(aq) ratio decreases as P increases, e.g. due to progress of oxidation reactions. The activity of H₂(aq) is $\sim 10^{-4}$ of $f\text{H}_2$, which is close to total P at high pressures. The H₂(g)/H₂O(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 H₂ production.

Increases in the volume of solids and H₂ 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 $\sim 10^2$ bars [12]) even at low degrees of alteration progress, as can be seen in Fig. 1a in [14]. Note that production of H₂ 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 H₂(aq). Magnetite, Fe-Mg serpentine, pyrrhotite, Ni-sulfide, chromite, and whitlockite formed. Further alteration caused consumption of water through hydration and H₂ production, and increases in the volume of solids, $f\text{H}_2$, and in total P (if gas was unable to migrate). Smectites formed at the expense of serpentine. An increase in total P caused condensation of H₂O 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, $f\text{H}_2$ 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 ($WRR \sim 10^{-2}$ - 10^{-4}), and only partial re-equilibration after consumption of solution. Our models shows that high-pH solutions rich in Na, OH⁻, Cl, HS⁻ and H₂(aq) were typical for parent bodies of UOC and may characterize ocean-forming fluids on large bodies.

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