

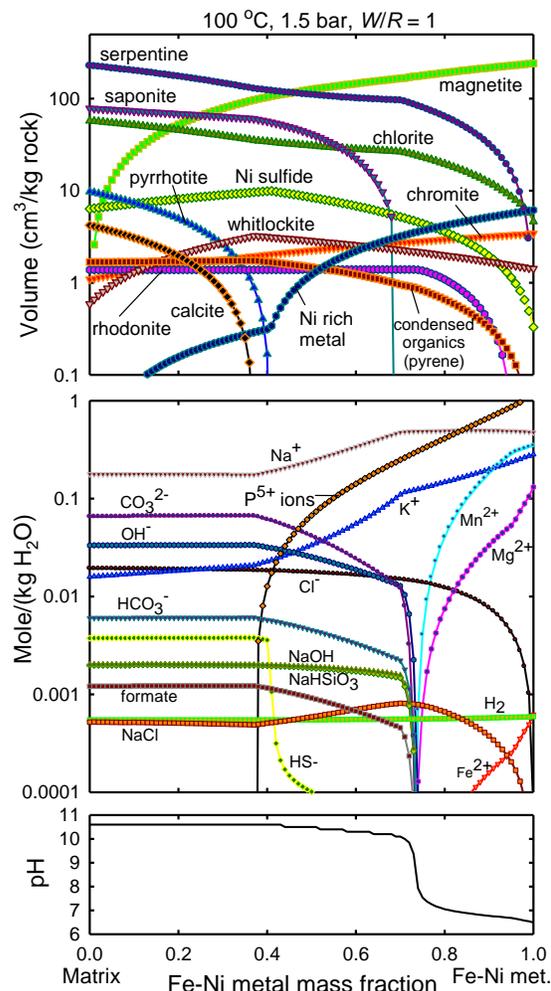
MICROCHEMICAL ENVIRONMENTS OF AQUEOUS ALTERATION IN CR CHONDRITES: CHEMICAL EQUILIBRIUM MODELS. M. Yu. Zolotov¹, A. Morlok², and G. Libourel³. ¹School of Earth and Space Exploration, Arizona State University, Tempe, Arizona 85287-1404, e-mail: zolotov@asu.edu; ²Wilhelm-Klemm-Strasse 10, 48149 Münster, Germany; ³Géozur, UNS-CNRS, OCA, 250 rue Albert Einstein, 06560 Valbonne, France.

Introduction: The CR carbonaceous chondrites reveal signs of uneven aqueous alteration on parent bodies [1-4]. Some CR samples are among the least aqueously altered carbonaceous chondrites [4] while others show nearly complete alteration. The alteration occurred below ~ 300 °C and led to the formation of serpentine, saponite, magnetite, pyrrhotite, pentlandite, carbonates, and phosphates. The distinct alteration mineralogy of fine-grained matrix (serpentine, saponite, magnetite, pyrrhotite, pentlandite, and calcite), Fe-Ni metal (magnetite, Fe- and Fe-Ni sulfides, Ni rich metal, and phosphates), and chondrule silicate phases (e.g. chlorite) implies alteration in microchemical environments. Petrochemical studies of CR chondrites indicate fluid mixing and/or aqueous diffusion of species at the Fe-Ni metal-matrix and other interfaces (mesostasis-matrix, Fe-Ni metal-mesostasis) [5]. These data imply that S from matrix is supplied to alteration rims around Fe-Ni metal grains. The alteration of Fe-Ni metal grains delivers Fe, Ni, P, Cr, Ti, and Mn to the surroundings [5]. The chemical exchange of local fluids is reflected in the mineralogical zoning of rims around Fe-Ni metal grains [6].

Here, we have used equilibrium chemical thermodynamic methods to evaluate microenvironments (secondary mineralogy, solution chemistry and pH) during alteration of CR's matrix and Fe-Ni metal, and developed initial models for the matrix-metal interface.

Approach: The mineralogy and chemistry of aqueous alteration were evaluated through calculations of chemical equilibria in the rock-water-gas type system O-H-C-Cl-S-Mg-Ca-Si-Al-Na-K-Cr-Mn-Fe-Co-Ni-P. The unaltered rock was signified by the composition of CR's Ni-Fe metal [5], water-free matrix [7], or their mixtures. Water was represented by either pure water or aqueous solution formed through alteration of the matrix. Equilibria were calculated for $T = 0-300$ °C and $P < 100$ bars above P of water-gas saturation, which is considered to be a minimal P during aqueous alteration. Formation of methane was suppressed because of low reaction rates at chosen T and P [8]. Water-soluble organic species were represented by one C species that may equilibrate: formate, methanol, and formaldehyde [8]. Condensed organic species were exemplified by pyrene ($C_{16}H_{10}$), which may not equilibrate with other species. Therefore, the models for the organic-inorganic equilibration were tentative. Calcula-

Fig. 1. The equilibrium secondary mineralogy and aqueous chemistry that correspond to aqueous alteration of CR's matrix and Fe-Ni metal end members and their mixtures. The model gives insights into chemical gradients at matrix-metal interfaces.



tions were performed with GEOCHEQ codes [9] which were previously applied for chondrites [e.g. 10].

Alteration progress (A_p) of a chosen rock was modeled by calculations of equilibria at a series of water/rock (W/R) mass ratios at a specified bulk W/R mass ratio, $A_p = [\text{bulk } W/R]/[W/R]$. The common presence of unaltered phases in CR chondrites indicates incomplete alteration at low bulk W/R ratios [3-5]. We used the bulk (accreted) W/R mass ratio of 0.1 to interpret runs at variable W/R ratios in terms of alteration progress.

Matrix alteration: The computed secondary mineralogy mainly consists of serpentine and saponite and lesser amounts of chlorite, as can be seen at the left-hand side of Fig. 1. These phyllosilicates form in most of the modeled conditions. Pyrrhotite and NiS (a proxy for pentlandite) form in a wide range of T s at mildly oxidizing conditions corresponding to early stages of alteration and/or fluid pressures < 20–50 bars above that of water-gas saturation. At higher T s, these sulfides form at higher P s. Troilite and Ni rich metal, which are not common in CR matrices, form at higher P s and at advanced stages of alteration. Magnetite occasionally forms at earlier stages and lower P s; it occurs in a wide range of P s at higher T s. Cronstedtite, which has not been reported in CR chondrites, forms at low T s (< ~100 °C) and at P s of water saturation. Minor phases are calcite, whitlockite, chromite, and organics.

Alteration fluids are strongly alkaline (pH depends on T and P) and the most abundant solutes are Na^+ , Cl^- , OH^- , CO_3^{2-} , HCO_3^- , K^+ , and H_2 . Low- T and early alteration fluids are $\text{Na-CO}_3^{2-}/\text{HCO}_3^-$ or NaOH type solutions while high- T and advanced alteration fluids are NaCl type fluids rich in H_2 . NaOH fluids form in carbonate-deficient reduced high- P systems [cf. 10]. Advanced alteration fluids coexist with H_2 rich gas formed via oxidation of elements (Fe, P, Ni, Cr, etc.) by water.

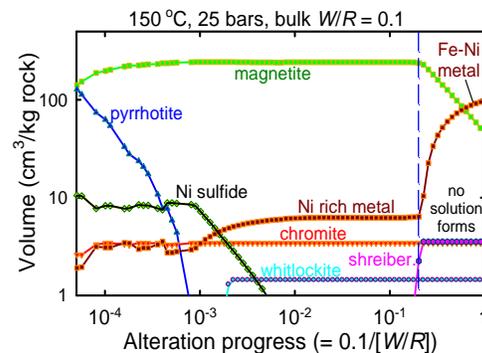
If the bulk W/R mass ratio in the matrix is below 0.16 ± 0.4 , water solution completely converts to hydrated and/or oxidized phases, salts, and H_2 rich gas. Partially altered matrices observed in some CR chondrites imply bulk W/R ratios below these values.

Fe-Ni metal alteration: The computed alteration products of Fe-Ni metal (Figs. 1 and 2) are dominated by magnetite. Magnetite, Ca-phosphate (whitlockite), and chromite form in all of the considered conditions. Pyrrhotite, NiS, Ni rich metal, and FeS, mainly form at conditions described above for matrices. Schreibersite is stabilized at high- P conditions and/or at advanced H_2 -rich stages of alteration. Solutions are rich in Na^+ and P^{5+} -bearing ions (PO_4^{3-} , HPO_4^{2-} , and H_2PO_4^-) and have a pH of 4 ± 0.5 units lower than in matrix fluids. The solutions are more abundant in Mn^{2+} , Mg^{2+} , and Fe^{2+} ions than matrix fluids. Metal oxidation by water forms abundant H_2 that separates to the gas phase. The solution is fully consumed at a bulk W/R mass ratio of ~0.5 and a portion of metal remains unaltered at lower W/R ratios.

Abundant H_2 rich gas may divert the aqueous solution from metal grains and account for the patchy alteration of matrix. Alteration in CR chondrites seems to take place on a scale of only a few 100s of μm , which would confirm a localized, patched alteration [4–6].

Matrix-metal interfaces: The modeled alteration of matrix-metal mixtures demonstrates strong compositional and pH gradients which are reflected in the com-

Fig. 2. An exemplary mineralogy of aqueous alteration of Fe-Ni metal by matrix-equilibrated solution at a bulk W/R mass ratio of 0.1. Early stages of alteration correspond to larger masses of aqueous solution reacted with smaller masses of metal. An addition of even a small amount of Fe^{2+} from altering metal to the S-bearing fluid causes precipitation of low-solubility Fe and Ni sulfides observed in sulfide-magnetite alteration rims at matrix-metal interfaces. The solution fully consumes at $Ap \geq 0.2$.



position of alteration minerals (Fig. 1). The alteration of matrix-equilibrated fluids with Fe-Ni metal (Fig. 2) leads to formation of abundant Fe and Ni sulfides at elevated W/R ratios which could represent the early stages of metal alteration. These stages correspond to formation of the observed multilayer sulfides-magnetite mineralogy of outer alteration rims around metal grains in Al Rais CR2 and GRO 95577 CR1.

Conclusions: The models show formation of chemically distinct solid-liquid-gas type environments through aqueous alteration of matrix and Fe-Ni metal. This diversity implies compositional, pH, and redox gradients at metal-matrix interfaces, diffusion of aqueous species, and precipitation of diverse minerals in local fluid mixing zones. These models reproduce observed local alteration mineralogies in a series of CR2 to CR1 chondrites [4, 5]. Further comparison with CR's chemistry and mineralogy will be presented in [6].

References: [1] Weisberg M. K. et al. (1993) *Geochim. Cosm. Acta*, 57, 1567–1586. [2] Krot A. N. et al. (2002) *Meteorit. Planet. Sci.*, 37, 1451–1490. [3] Brearley A. J. (2006) In: *Meteorites and the Early Solar System II*, U. of Ariz. Press, Tucson, 587–624. [4] Abreu N., Brearley, A. (2010) *Geochim. Cosm. Acta*, 74, 1146–1171. [5] Morlok A., Libourel G. (2013) *Geochim. Cosm. Acta*, 103, 76–103. [6] Morlok A. et al. (2015) in prep. [7] Zolensky M. E. et al. (1993) *Geochim. Cosm. Acta*, 57, 3123–3148. [8] Seewald J. et al. (2006) *Geochim. Cosm. Acta*, 70, 446–460. [9] Mironenko M. V. et al. (2008) *GEOCHEM. M.* In: *Vestnik Otdelenia Nauk o Zemle RAN*, 1(26). [10] Zolotov M. Yu. (2012) *Icarus*, 220, 713–729.