

**THERMODYNAMIC MODELS FOR AQUEOUS ALTERATION COUPLED WITH VOLUME AND PRESSURE CHANGES IN ASTEROIDS.** M. V. Mironenko<sup>1</sup> and M. Yu. Zolotov<sup>2</sup>, <sup>1</sup>Vernadsky Institute of Geochemistry and Analytical Chemistry, Russian Academy of Sciences, 19 Kosygin str., Moscow 119991, Russia, <sup>2</sup>Department of Geological Sciences, Arizona State University, Tempe, Arizona 85287. E-mails: zolotov@asu.edu, mironenko@geokhi.ru.

**Introduction:** All major classes of chondrites show signs of alteration on their parent bodies (asteroids) [1-3]. The prevalence of oxidation and hydration in alteration pathways implies that water was the major reactant [1-6]. Sublimation and melting of water ice, generation of gases, formation of aqueous solutions, alteration of primary minerals and glasses and formation of secondary solids in interior parts of asteroids was likely to be driven by heat from the radioactive decay of short-lived radionuclides [2-4]. Progress of alteration reactions should have affected masses and volumes of solids, and aqueous and gas phases. In turn, pressure evolution should have been controlled by changes in volumes and temperatures, escape processes [7], and production/consumption of gases.

Despite the usual lack of chemical equilibration among solid phases in aqueously altered chondrites, some mineral assemblages (e.g., in matrix) reveal such equilibration [2,6]. In fact, application of equilibrium chemical calculations to aqueous alteration shows promising results in reproducing secondary mineralogy of chondrites [6, 8-13]. Broad-scale oxidation and hydration along with formation of alkaline reduced fluids have been modeled for CM carbonaceous chondrites [8-12]. Formation of Na- and Cl-rich solutions [13], and the likely production of reduced gases (H<sub>2</sub>, CH<sub>4</sub>, CO) have been noticed [6,9-14]. Even with these achievements, effects of progress of water-rock reactions on volumes of phases and pressure remain to be explored.

We developed new codes that allow us to model how pressure ( $P$ ), volumes ( $V$ ), and compositions of solid, gas, and aqueous phases are affected by temperature ( $T$ ), alteration progress, initial rock composition, amount of incorporated ice and initial porosity of an asteroid. Non-idealities in gas, aqueous, and solid solutions are taken into account. Here we describe the model and show case study calculations for the composition of Semarkona (see also [15]).

**Models:** The codes were developed on the basis of the GEOCHEQ program [16] that is used to calculate chemical equilibria in closed or partially open multicomponent systems with ideal gas, aqueous, and one-component solid phases over wide ranges of  $T$ - $P$  conditions: 0-500°C, 1b - 5kb. The program includes the CHEMEQ code to compute equilibria by the free energy minimization method and a database with thermodynamic properties of gas, solid and aqueous species mainly from SUPCRT92 [17] and [18,19]. For this project, we updated data for solids, included several meteoritic minerals, and created two databases to calculate activities of components of gas and solid solutions. The CHEMEQ code was enhanced to consider non-ideality of

gases, formation of solid solutions, and reaction progress with use of kinetic data, and to calculate equilibria at a specified  $V$  of the system.

The Peng-Robinson equation of state [20] is used to calculate compressibilities of non-ideal gas mixtures and fugacities of the gas species at various  $T$  and  $P$ . Binary interactions among H<sub>2</sub>, H<sub>2</sub>O, CH<sub>4</sub>, CO<sub>2</sub>, and CO are considered.

For solid solutions, a sub-regular mixture model with complete configurational disorder (zero approximation) is used to calculate excess free energies of mixing. The following solutions are taken into account: Fe-Ni-Co-Cr metal alloy, Fe-Mg olivine, twelve Mg-Fe-Ca orthopyroxenes and clinopyroxenes, Mg-Fe serpentine (chrysotile-greenalite), Na-K-Mg-Ca saponite, Fe-Mg chlorite (daphnite-clinochlore), Mg-Fe mica (phlogopite-annite), tremolite-ferroactinolite, Mg-Fe talc, and OH-Cl apatite. The metal, serpentine, saponite, talc and amphiboles are considered as ideal solutions. For other minerals, Margules binary mixing parameters are used from published data.

Aqueous alteration can be modeled in isobaric, isochoric or in mixed regimes at constant or variable temperature. The isobaric regime could represent conditions when  $P$  is controlled outside the modeled system. For example, escape processes [7] or chemical equilibria in hot zones can govern  $P$  in a porous asteroidal media. In isobaric calculations,  $V$  of phases and that of the whole system are dependent parameters.

The isochoric regime could be typical for warm zones (or whole asteroidal interiors) that are sealed by recondensed ice. In these conditions,  $P$  depends on  $T$ ,  $V$  of phases and chemical production/consumption of gases. In our isochoric models, total  $V$  of the system is an input parameter that is calculated from a specified ice/rock ratio and an original porosity of the asteroid. Total  $P$  and the equilibrium composition are computed iteratively. This is done by a series of equilibrium calculations in isobaric-isothermal systems at various  $P$  until the calculated  $V$  of the system (gas+solution+solids) becomes equal to the specified volume. In isochoric models,  $V$  of aqueous solution at various  $T$  and  $P$  is calculated with the Hill equation of state for water [21] and partial molar volumes of aqueous species computed with the revised Helgeson-Kirkham-Flowers (HKF) model [22], which incorporates equation-of-state parameters obtained from analysis of experimental data [18,19]. Note that  $P$  in asteroids is limited by the internal strength of rocks and can not exceed  $\sim 10^2$  bars for asteroids of typical sizes [7].

Progress of alteration reactions is modeled by specifying the amounts of solid phases that are allowed to react during

each time step. Either relative rates of chemical reaction (for example, mineral dissolution) or real kinetic constants are taken into account. Effects of chemical affinity on rates of mineral dissolution, which becomes important when a reaction approaches equilibrium, can be easily considered since affinities are calculated at each time step. Reaction progress can be calculated in isothermal, isobaric and isochoric regimes, and at changing  $T$ - $P$ - $V$  conditions as well.

Major input data for alteration modeling are as follow: masses and elemental/mineral compositions of rock and water (ice, solution),  $T$ , thermodynamic properties of all species that are available in a database,  $P$  or porosity, and kinetic parameters for reactions. Output results include amounts and  $V$  of all phases, concentrations and activities of components of gas, aqueous and solid phases, ionic strength and pH of aqueous solution, and total  $V$  or  $P$ . In reaction progress models, amounts of non-reacted solids are also among the output data.

#### Alteration progress for the Semarkona composition:

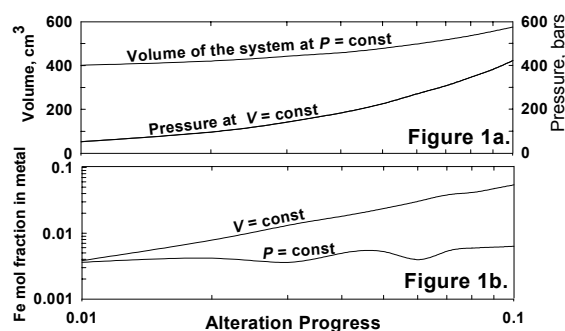
We modeled alteration progress for a 17-component O-H-Mg-Fe-Ca-Si-Al-C-P-S-Cr-Na-K-Cl-Mn-Co-Ni closed system exemplified by the composition of the Semarkona (LL3.0) ordinary chondrite. To simulate its composition before alteration, the amount of O in the bulk composition [23] was decreased slightly to preclude association of Fe, Ni, Co, Mn and P with O. The normative mineralogy of an unaltered chondrite was represented by the Fe-Ni-Co-Cr metal alloy, troilite, enstatite-rich pyroxene, forsterite, Ca-Na-K feldspar, alabandite, schreibersite, graphite, and lawrencite.

For comparison, alteration progress was modeled in isochoric and isobaric regimes at 100°C and a bulk ice/rock mass ratio of 0.01. In the first case, bulk  $V$  (401 cm<sup>3</sup>) of the system is constant and defined by the volumes of the rock, ice, and original porosity of 30%. In the second case, gas is permitted to expand at constant  $P$  (51.7 bar). For simplification, dissolution rates for all solids were assumed as equal. Formation of CH<sub>4</sub> was suppressed, as argued in [15].

Both scenarios of the alteration progress show that H<sub>2</sub>O is consumed through oxidation, which is accompanied by H<sub>2</sub> generation, and hydration. The H<sub>2</sub>O/H<sub>2</sub> ratio decreases and the solution eventually disappears. At early stages, hydrous silicates (serpentine, saponite, chlorite) and magnetite form. However, reaction progress causes decreases in the water/rock ratio and secondary minerals become more reduced.

Alteration progress at constant volume leads to more reducing conditions caused by higher fugacities of H<sub>2</sub> than in isobaric system where the gas phase expands. This is illustrated in Fig. 1, which shows how  $P$ ,  $V$  and Fe content in secondary Ni-Co rich metal change with reaction progress. Reducing environments in isochoric systems cause elevated Fe<sup>0</sup> content in alloys.

It should be noticed that depending on the temperature, ice/rock ratios, porosities, and extent of reaction progress, different mineral assemblages could be obtained (including



formation of ferrous olivine and pyroxenes, magnetite and clays). Comparison of equilibrium compositions obtained in different scenarios (see [15]) with mineralogy of chondrites could be used to qualify physical-chemical processes on specific parent bodies.

These new advances in model development will enable new research projects aimed to explore coupling of physical and inorganic/organic chemical processes on early solar system bodies, quantify reduction and oxidation pathways, examine high-pressure aqueous reactions and estimate compositions of primordial oceans on large bodies, investigate consequences of H<sub>2</sub> escape, and evaluate parameters of alteration that may cause explosions of asteroids.

**Acknowledgments:** We thank Everett Shock for helpful discussions. This work is supported by NASA grants from Origins, Exobiology, and Outer Planets Research programs.

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