

AQUEOUS ALTERATION ON THE RYUGU PARENT BODY CONSTRAINED BY CHEMICAL EQUILIBRIUM MODELS. M. Yu. Zolotov¹, T. Nakamura², M. E. Zolensky³, H. Yurimoto⁴, T. Noguchi⁵, R. Okazaki⁶, H. Yabuta⁷, H. Naraoka⁸, K. Sakamoto⁹, S. Tachibana^{9,10}, S. Watanabe¹¹, Y. Tsuda⁹. ¹Arizona State University, Tempe, Arizona 85287-1404, USA, e-mail: zolotov@asu.edu; ²Tohoku University, Sendai 980-8578, Japan; ³NASA Johnson Space Center, Houston TX 77058, USA; ⁴Hokkaido University, Sapporo 060-0810, Japan; ⁵Kyoto University, Kyoto 606-8502, Japan; ⁶Kyushu University, Fukuoka 812-8581, Japan; ⁷Hiroshima University, Higashi-Hiroshima 739-8526, Japan; ⁸Kyushu University, Fukuoka 812-8581, Japan; ⁹ISAS/JAXA, Sagami-hara 252-5210, Japan; ¹⁰The University of Tokyo, Tokyo 113-0033, Japan; ¹¹Nagoya University, Nagoya 464-8601, Japan.

Introduction: The composition of solid samples returned from the asteroid 162173 Ryugu by Hayabusa2 indicates aqueous alteration of rocks that formed a parent body of Ryugu [1, 2]. As on parent bodies of carbonaceous chondrites [3-5], Ryugu materials could have went through (1) accretion of anhydrous and reduced rocky grains together with water-rich ices, (2) melting of ices in the body's interior through release of radiogenic heat [6], and (3) aqueous alteration of rocky and organic materials that produced secondary minerals, salt- and organic-bearing water solutions, gases, and altered organic matter. Although the bulk chemical composition and major mineralogy (phyllosilicates, magnetite, pyrrhotite, carbonates, phosphates, etc.) of Ryugu [1, 2] are similar to those of CI carbonaceous chondrites [3-5, 7], the lack of sulfates and a deficiency of oxygen in the returned samples suggest a distinct alteration pathway.

Chondritic materials [3-5] do not indicate complete chemical equilibration though low-temperature parent body processes. However, calculations of chemical equilibria in modeling rock-water-gas type systems [e.g., 8, 9], could assess deviations of chondritic materials from equilibrium conditions and constrain partitioning of chemical elements between solid, aqueous, and gas phase for different stages of alteration. Here we constrained speciation of solid, aqueous, and gaseous phases during aqueous alteration on the Ryugu parent body through chemical equilibrium calculations.

Models: Chemical equilibria are calculated in the H-C-O-Si-Mg-Fe-Ca-Al-Na-K-Mn-Ni-Co-Cr-S-P-Cl solid-water-gas type system at $T = 40$ °C at the pressure (P) at water saturation and at higher P . The chosen temperature reflects that of carbonate formation in Ryugu samples [10]. The bulk composition of the system is assembled from supposedly accreted rocky and icy ingredients that are mixed in different proportions.

The bulk composition of modeled rock reflects that of Ryugu samples [1, 2] with modified contents of C, H, and O. Abundances of Si, Mg, Fe, Ca, Al, Na, K, Mn, Ni, Co, Cr, S, and P correspond to the composition of CI chondrites [8]. The rock's C (2/3 of total abundance of 4.6 wt% in Ryugu samples [10]) and H are assumed to be present in the insoluble organic matter (IOM, [11]) with the composition $C_{100}H_{80}O_{20}S_3$. The modeled rock has no Cl. The oxygen content is calculated from abundances of elements that could have accreted in silicates

(Si, Mg, Ca, Al, Na, K, and 85 % Cr) and from the amount of IOM.

The initial composition of the water-rich ingredient corresponds to H_2O - CO_2 -HCl mixtures used as analogs of accreted ices. Our nominal ice composition, $H_2O + 8 \times 10^{-2} CO_2 + 8 \times 10^{-4} HCl$ in moles, represents a simplified cometary ice [12], agrees with the composition of fluid inclusions in Ryugu pyrrhotite [1, 13] and reflects the current views on sources of inorganic C and Cl in carbonaceous chondrites [14-16].

The fraction of chemically active IOM is varied in the models to reflect only a partial alteration of IOM in chondrites that did not experience a severe thermal metamorphism [11]. Formation of methane is suppressed because it does not equilibrate in low-temperature C-O-H systems [17]. Formation of light hydrocarbons and some solids that do not form at low T - P conditions is suppressed as well (e.g., graphite, cohenite). High molecular weight organic compounds in equilibrium models are represented by pyrene, $C_{16}H_{10}$. Details of equilibrium calculations, data sources, and codes are described elsewhere [9, 18].

Results and Discussion: The calculated secondary mineralogy in a majority of models demonstrate the dominance of minerals that form through hydration (saponite, serpentine), oxidation (saponite, serpentine, magnetite, pyrrhotite, Ni-sulfide, chromite, phosphate) and carbonation (dolomite, magnesite, calcite) of accreted anhydrous and reduced materials. Lower ice/rock ratios in starting compositions correspond to less altered and more reduced equilibrium mineral assemblages with olivine, pyroxenes, Al/Na/K-bearing silicates, troilite, Fe-phosphide, and Fe-Ni metal that could remain unaltered or form through alteration at H_2O -poor, H_2 -rich conditions. The consistency of calculated mineral assemblages with the composition of most and least altered fragments in Ryugu samples [1, 2] implies a major effect of original ice content. The agreement also indicates at least partial inorganic chemical equilibration during parent body alteration.

End-member models for both inert and 100 % reactive IOM are not fully consistent with the observed mineralogy. An inert organic case corresponds to more reduced phase composition in which coexistence of Fe-rich metal with calcite is inconsistent with mineralogy of least altered fragments [1, 2]. A completely chemically active IOM case does not allow stability of some

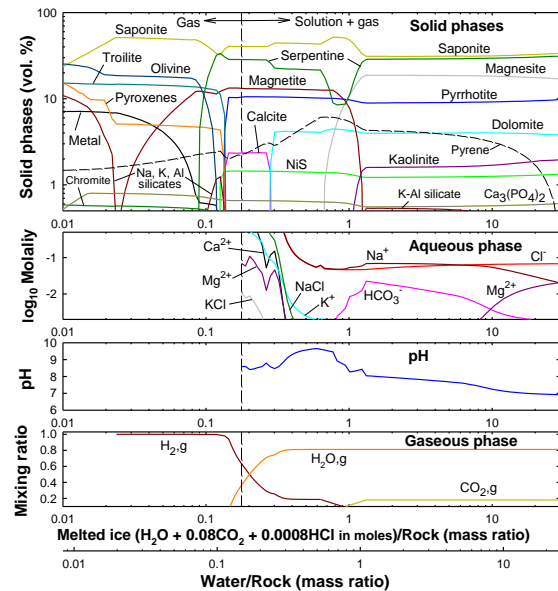
reduced phases (e.g., Fe phosphide) in H₂O-poor environments and suggests a major formation of pyrene at elevated ice/rock ratios. The latter model disagrees with a mild chemical transpiration of IOM during low-*T* alteration on parent bodies of chondrites [11].

Models with ~10–20 % of chemically active organic matter are better consistent with the observed mineralogy of less- and more-altered fragments (Fig. 1). At the initial water/rock mass ratio (*W/R*) of ~0.06–0.15 modeled mineralogy essentially reproduces that of the least altered fragments [1, 2]. Results for *W/R* ≈ 0.15–0.3 match the less altered lithology. The modeled high Na concentrations both in the fluid and saponite at lower *W/R* ratios agree with the composition of the least- and less-altered lithology [1, 2]. Results for *W/R* ≈ 0.3–0.9 agree with the major strongly-altered lithology [1, 2] that could have equilibrated with Na⁺-Cl⁻-HCO₃⁻ type fluid at *pH* > 8.5. If the latter *W/R* ratio is referred to a fully equilibrated composition, the ratio of ~0.3–0.9 constrains the amount of ice accreted on the Ryugu parent body.

The decreasing *W/R* ratio (Fig. 1) could also be interpreted in terms of alteration progress when the ratio represents only a chemically active part of the system. Higher *W/R* ratio characterizes early alteration when a small amount of rock interacts with the whole mass of water. In such an interpretation, the modeling at variable *W/R* ratio suggests evolution of Mg²⁺-Na⁺-Cl⁻ type solution and an H₂O-CO₂ gas phase toward a more reduced and Na-Cl type alkaline brine that coexists with a H₂-rich gas phase. The modeled increase in the Mg/Fe ratio in serpentine at lower *W/R* ratios could reflect compositional changes in the mineral composition with an involvement of more silicates into the alteration. Though, some other minor early minerals (silica, kaolinite) could alter at later stages and may not be present in a final lithology. This may explain the lack of such minerals in Ryugu samples.

No strongly oxidized phases (sulfates, ferrihydrite, etc.) are observed in these and preceding [e.g. 8, 9, 18, 19] equilibrium models for chondritic water-rock systems. Formation of such phases likely requires a presence of strong radiolytically-produced oxidants such as O₂, H₂O₂ and/or H₂SO₄ in accreted ices or ice-bearing rocky particles [19, 20]. The apparent lack of sulfates and ferrihydrite in Ryugu samples [1, 2, 10] implies the lack or deficiency (a minor Ca sulfate is reported [1]) of strong oxidants in materials that formed the parent body. This phenomenon makes Ryugu materials unique among carbonaceous chondrites in the meteorite collection and suggests an explicit formation conditions, possibly at larger heliocentric distances than parent bodies of known chondrites. Although sulfates are common in chondrite falls, a likelihood of terrestrial oxidation of chondrites [e.g. 21] needs to be considered when Ryugu is compared with chondrites.

Fig. 1. Modeled equilibrium speciation of the water-rock-gas type system during aqueous alteration on the Ryugu parent body at 40 °C, 0.074 bar, and 10 % of chemically active organic matter.



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