Modeling of aqueous alteration in the parent body of the asteroid Ryugu

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The mineralogy, petrology and chemical properties of the samples collected from the asteroid 162173 Ryugu by the Hayabusa2 spacecraft show that the samples correspond to CI meteorites not affected by terrestrial weathering (e.g., [1-3]). The parent body of Ryugu were formed by accretion of minerals, organics, and ice, and aqueous alteration occurred by reaction of melted ice with the minerals and organics [1]. The major lithology of the Ryugu samples consists mostly of hydrous phyllosilicates (serpentine and saponite), carbonates, FeS and magnetite which precipitated from liquid (melted ice) during the aqueous alteration. Least- and less-altered lithologies, where some anhydrous minerals, such as olivine, remained unaltered or partially altered, were also observed [1]. Model chemical equilibrium of the aqueous alteration was calculated in an appropriate condition (*e.g.*, 40°C based on oxygen isotope equilibrium [2] and ice of H₂O + 0.08 CO₂ based on CO₂-bearing fluid inclusion[1]) as a function of the initial water/rock ratio (in mass), *W/R*, and found that the mineral assemblages are almost consistent with the least-altered, less-altered and altered major lithologies at *W/R* of 0.06 to 0.1, 0.1 to 0.2, and 0.2 to 0.9, respectively [1]. The order of precipitation of minerals in the major lithology was also estimated from the included and enclosed relations among these minerals [4].

We understood the outline of the aqueous alteration by the Ryugu sample initial analysis as mentioned above. However, we still do not know how the aqueous alteration occurred and ceased; for example, how liquid was present, and precipitation occurred from the liquid. Therefore, in this study, we performed a modeling of the aqueous alteration by reference to the minerals and their assemblages and the chemical composition of the Ryugu samples.

In the present model, we made the following assumptions to simplify the problem; (1) the system Mg-Fe-Si-Ca-O-S-C-H is taken into consideration with the bulk chemical composition of CI [5] that is unchanged during the alteration except for O (oxidation or reduction permitted). (2) The starting material is composed of anhydrous minerals, amorphous silicate, organics, and CO₂-H₂O ice. Olivine, metallic Fe, and FeS are considered for the anhydrous minerals. We adopted Mg# (Mg/(Mg+Fe) in mole) of 0.99 for olivine, which was observed in least- and less-altered lithologies [6]. Material similar to GEMS (glass embedded with metal and sulfide) is considered for amorphous silicate based on the observation in the least-altered lithology [1]. This GEMS-like material (GLM) is assumed to have the mean GEMS composition of [7]. We consider relatively oxidized GLM, where only nanoFeS particles (without nanoFe) are embedded in FeO-bearing amorphous silicate. Thus, the Mg# of the amorphous silicate becomes 0.612 to maintain the mean GEMS composition. The density of GLM is assumed to be 3 g/cm³. (3) We consider only IOM as organics. The chemical composition of IOM is adopted from [8] and its density is assumed to be 1.3 g/cm^3 . IOM is not changed by the alteration. (4) The ice CO₂/H₂O ratio is 0.08 as proposed by [1]. The ice melts to form CO₂bearing water. The temperature is 40°C proposed by [2] and the pressure is less than \sim 50 bar for a 50-km-radius parent body [1]. In these conditions, the melted ice is a liquid state (not fluid) and the densities of H_2O and CO_2 are almost constant (1 g/cm³ [9]) and 1.04 g/cm³ [10], respectively). (5) The aqueously altered products are serpentine, saponite, FeS, magnetite, and dolomite. The Mg#'s of serpentine and saponite are 0.85 based on the Ryugu sample analysis [1]. Dolomite is only considered as a carbonate although other carbonates (magnesite and calcite) are present in the Ryugu samples. (6) GLM stats to react with liquid to form serpentine and saponite first, and simultaneously the same proportion of Fe as that of altered GLM becomes magnetite. If the GLM is completely altered, olivine starts to react with liquid. (7) GLMs and the phyllosilicates (serpentine and saponite) have nano-sized pores (nanopores) based on the TEM observation of the Ryugu samples [1]. Any other pores are not present in the initial state, but the space that used be as ice acts as micron-sized pores (micropores). (8) The water/rock ratio, W/R, is defined as the mass ratio of water (or ice) to whole of the other materials including IOM.

The amounts of the formula weights of the phases (minerals, IOM and liquid) were calculated to have elemental balance among the chemical compositions of the phases and the bulk chemical compositions, and their volumes were obtained from the densities of the phases. This calculation is similar to the CIPW norm calculation, and chemical equilibrium was not considered. We made calculation for a case where the initial IOM volume is 10% with respect to solid phases and the porosities of the nanopores in both GLM and phyllosilicates are 40%.

In the initial state, the modes of olivine, Fe, FeS (nanoFeS in GLM not included), GLM with nanopores, and IOM are calculated to be 17.2, 2.5, 4.9, 67.4, and 8.1 vol.%, respectively, to have the elementary balance (Fig.1 at W/R = 0). We changed the initial water/rock ratio (in mass), W/R, as a parameter. The final mineral assemblages after the complete reaction with liquid were calculated with different W/R. Changes in the volumes of the phases are shown in Fig. 1. In the range of W/R = 0 to 0.10 (Stage-1 in Fig. 1), mainly saponite and minor amounts of serpentine and magnetite form from GLM and Fe, and H₂O in liquid

is completely consumed. CO₂ in liquid is also completely consumed to form dolomite, and therefore no liquid remains in this stage after the aqueous alteration. GLM and Fe are completely consumed at W/R = 0.10. With further increase in W/R, olivine starts to react with water, and serpentine forms by consuming some saponite together with olivine to accommodate their Mg/Si ratios (W/R = 0.10 to 0.12, Stage-2 in Fig. 1). Olivine is completely consumed at W/R = 0.12, and no liquid remains in this stage too. In W/R > 0.12, some liquid remains after complete reaction with GLM, Fe and olivine, and the volumes of magnetite, saponite, serpentine, and FeS are constant (W/R = 0.12 to 0.19, Stage-3 in Fig. 1). The volume of dolomite increases by consuming CO₂ in liquid, and no CO₂ remains in liquid in this stage. In W/R > 0.19 (Stage-4 in Fig. 1), some CO₂ remains in liquid because [C] > 2[Ca] and the volume of dolomite is constant. Stage-1, Stage-2 and Stages-3 and -4 roughly correspond the least-altered, less-altered, and altered major lithologies, respectively, in terms of their mineral assemblages. The modes of dolomite, magnetite, saponite with nanopores, serpentine with nanopore, FeS, and IOM in Stage-4 are 2.0, 4.3, 31.3, 48.1, 8.1, and 6.2 vol.%, respectively. These are similar to those of the main lithology [1]. The relation of W/R and stages are also roughly consistent with the chemical equilibrium calculation of [1]. The boundary between Stages-2 and -3 (W/R = 0.12) corresponds to W/R = 0.18 in [1]. This difference is derived from the rough calculation in the present model. The broad similarities suggest that the present model roughly reflects the equilibrium although the model itself does not consider equilibrium.

As a next step, we calculated the proportions of liquid filling pores. The total volume of the bulk material consisting of minerals, IOM, and pores (nanopore in GLM and/or phyllosilicates and micropore after ice) increases by the aqueous alteration from the initial volume (minerals, IOM, nanopore in GLM, and ice) by $\sim 10 - 20\%$. Because such volume increase would not occur for asteroids, we assumed that the initial bulk volume maintains constant by collapsing some of micropores. Liquid (if present) occupies the remaining pores. Fig. 2 shows the liquid proportion filling pores, f, and the total porosity including liquid, ϕ , as a function of W/R for the initial state before aqueous alteration. As we assumed liquid preferentially fills nanopores due to capillarity, with increasing W/R, f(nanopore) increases first, and then f(micropore) increases after f(nanopore) reaches 100 %. For the final state after aqueous alteration (Fig. 3), similar behavior of f's can be seen, but f(nanopore) and f(micropore) are 0 % in Stages-1, and -2. These results showed that liquid partially occupies only nanopores if W/R is small, and even if W/R is large, macropores are not fully filled with liquid, suggesting that pores are not fully filled with liquid during aqueous alteration. The bulk density of Ryugu samples was determined to be 1.79 g/cm³, indicating the porosity of 31 % if we compared with the grain density of CI meteorites [1]. If the porosity has not changed from the end of aqueous alteration to present, ϕ of 31 % corresponds to W/R of 0.19 (Fig. 3), where 100 % of nanopores and 61 % of micropores are filled with liquid, respectively, before the alteration (Fig. 2), and 55 % of nanopores and 0 % of micropores are filled with liquid, respectively, after the alteration (Fig. 3). These suggest that aqueous alteration in the Ryugu parent body should occur through dissolution and reprecipitation in conditions where not so much water present.



Figure 1. The volumes of phases after aqueous alteration at different water/rock ratio, W/R.

Figure 2. Liquid proportion filling pores and porosity before aqueous alteration.

Figure 3. Liquid proportion filling pores and porosity after aqueous alteration.

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