Electronic Annex –Supplement

for

Isotopic responses of Mg to two types of dissolution-reprecipitation processes for the growth of the double-carbonate mineral norsethite

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Calculation of the amount of surface Mg

The amount of Mg in the surface of norsethite can be roughly calculated by the unit cell parameters of norsethite (Effenberger and Zemann, 1985) and the SSA value. Assuming one norsethite crystal consists of n^3 unit cells of norsethite, the surface area (S) of this crystal can be expressed as:

$$S = 2n*ab*\sin(\pi/3) + 2n*bc + 2n*ac \tag{1}$$

where the a, b, c represent the lattice parameters.

The weight (m) of the norsethite crystal can be expressed as:

$$m = M*n^3/N_A \tag{2}$$

where M and N_A stand for the molar mass of norsethite [$BaMg(CO_3)_2$] and Avogadro constant, respectively. Then the SSA of the norsethite crystal can be expressed as:

$$SSA = S/m \tag{3}$$

We take the experiments at 50℃ as an example. Based on the measured SSA value (39.660 m_2/g at t = 120 min), one norsethite crystal consists of approximately 8×10^6 unit cells on average and the calculated total amount of Mg at the surface accounts for less than 2.92% of the total Mg in norsethite crystal.

Magnesium diffusion in carbonate

The Mg diffusion in the mineral can be expressed as:

$$C_x = C_s + (C_b - C_s)erf[x/(2*(Dt)^{1/2})] \tag{4}$$
$$D_x/D_{25} = (m_x/m_{25})^\beta \tag{5}$$

where C_x is the concentration of solid which has the distance of x from the surface, C_s is the concentration at the surface, C_b is the bulk concentration, t is the diffusion time,

and D is the diffusion coefficient in equation (4). The D_{25} in equation (5) refers to the

^{25}Mg diffusion coefficient adopted from Fisler and Cygan(1999) for calcite, while D_x

and m_x stand for the diffusion coefficient for ^{26}Mg or ^{24}Mg and corresponding atomic

mass. The β is defined by Jambon (1980). We take the experiments at 50°C as an

example. For simplifying the calculation, two assumptions are made. One is that the

Mg isotope composition of the norsethite surface is equal to that of solutions. The other

one is that the isotope composition of the solution remains constant, which would to

the overestimate of the solid isotope composition because the diffusion would lead to

the decreasing ^{26}Mg in solution. The calculation results are plotted as Appendix Fig. S8.

Mass transfer correction

The mass transfer correction was conducted by assuming the equilibrium

fractionation between the extra precipitated Mg and aqueous Mg, because our results

showed that there was continuous Mg exchange between the solid and solution phase

during the whole reaction process. Therefore, the δ^{26}Mg value of extra precipitated Mg

(δ^{26}Mg$_{extra}$) can be calculated by:

$$\delta^{26}Mg_{extra} = \delta^{26}Mg_{soln} + \Delta^{26}Mg_{equilibrium} \tag{6}$$

where the equilibrium fractionation factor (Δ^{26}Mg$_{equilibrium}$) was determined by our

theoretical calculation results. Moreover, since the Mg concentration began to decrease

after 1 days of reaction (Fig. S7C). The Mg concentrations obtained after 2 hours of

reaction were set as the initial values. The proportion of extra Mg precipitation (F) can

be calculated by:

$$F = ([Mg]_{2h} - [Mg])/[Mg]_{2h} \qquad (7)$$

where the $[Mg]_{2h}$ and $[Mg]$ represent the Mg concentration of aqueous solution after 2

hours and a longer time of reaction. Then the corrected $\delta^{26}Mg$ values of solid phases

($\delta^{26}Mg_{correct}$) could be obtained by:

$$\delta^{26}Mg_{correct} = (1 + F)*\delta^{26}Mg_{solid} - F*\delta^{26}Mg_{extra} \qquad (8)$$

The corrected Mg isotope results were listed in Table. S7 and plotted as Fig. S9.

The difference between the measured and corrected Mg isotope data are insignificant

(Fig. S9).
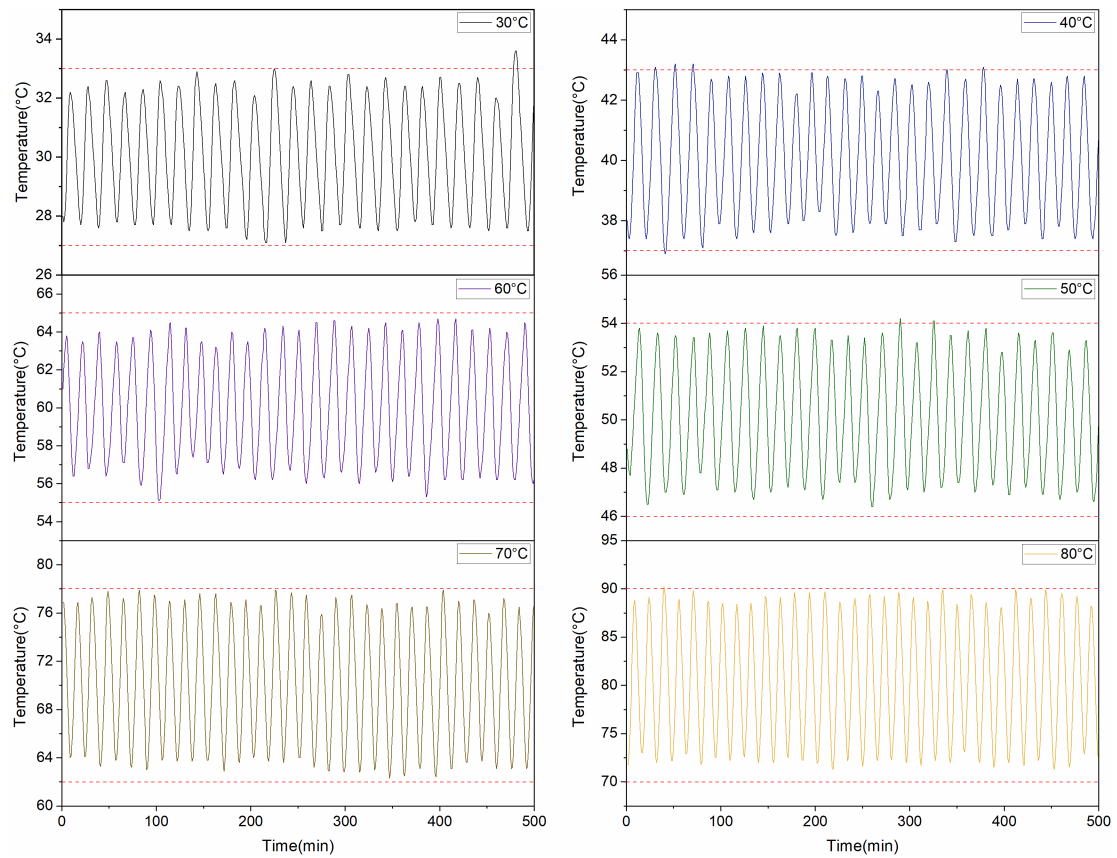
Fig. S1. The plots show the temperature variability of hotplate.
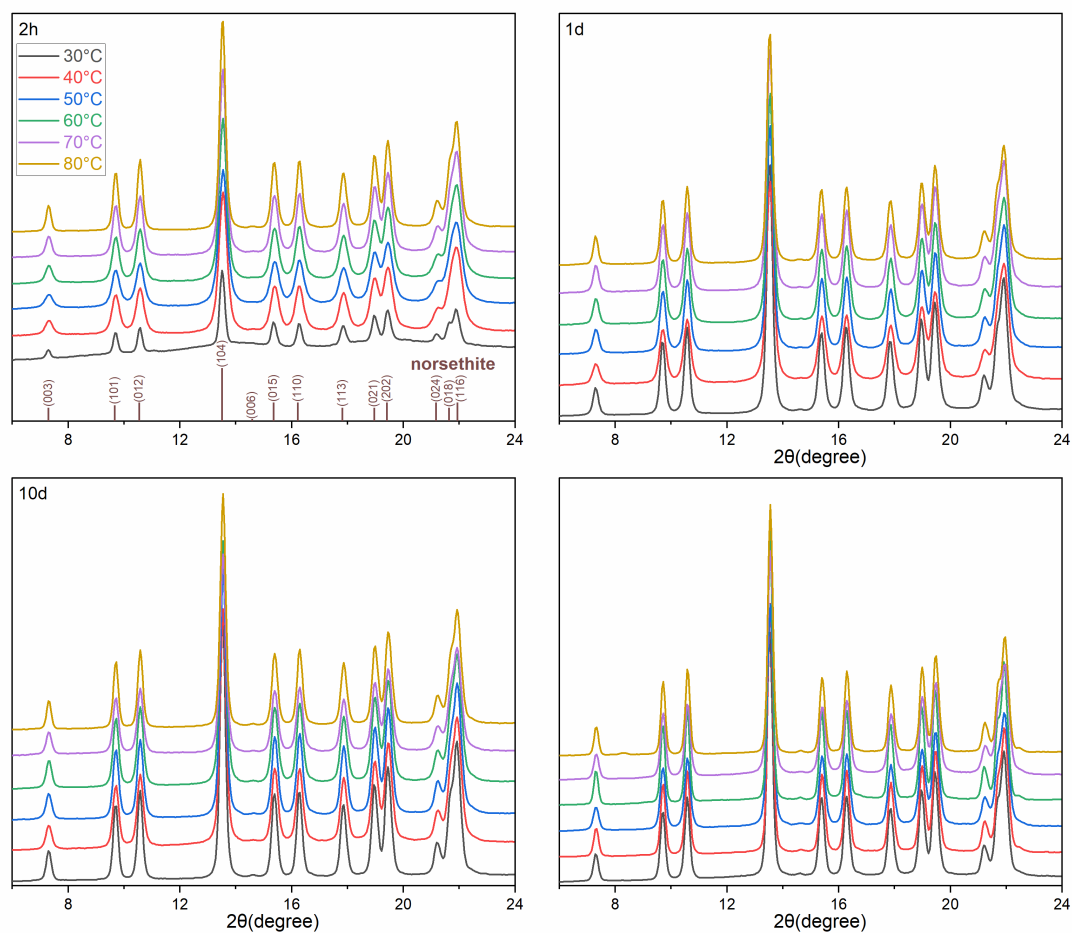
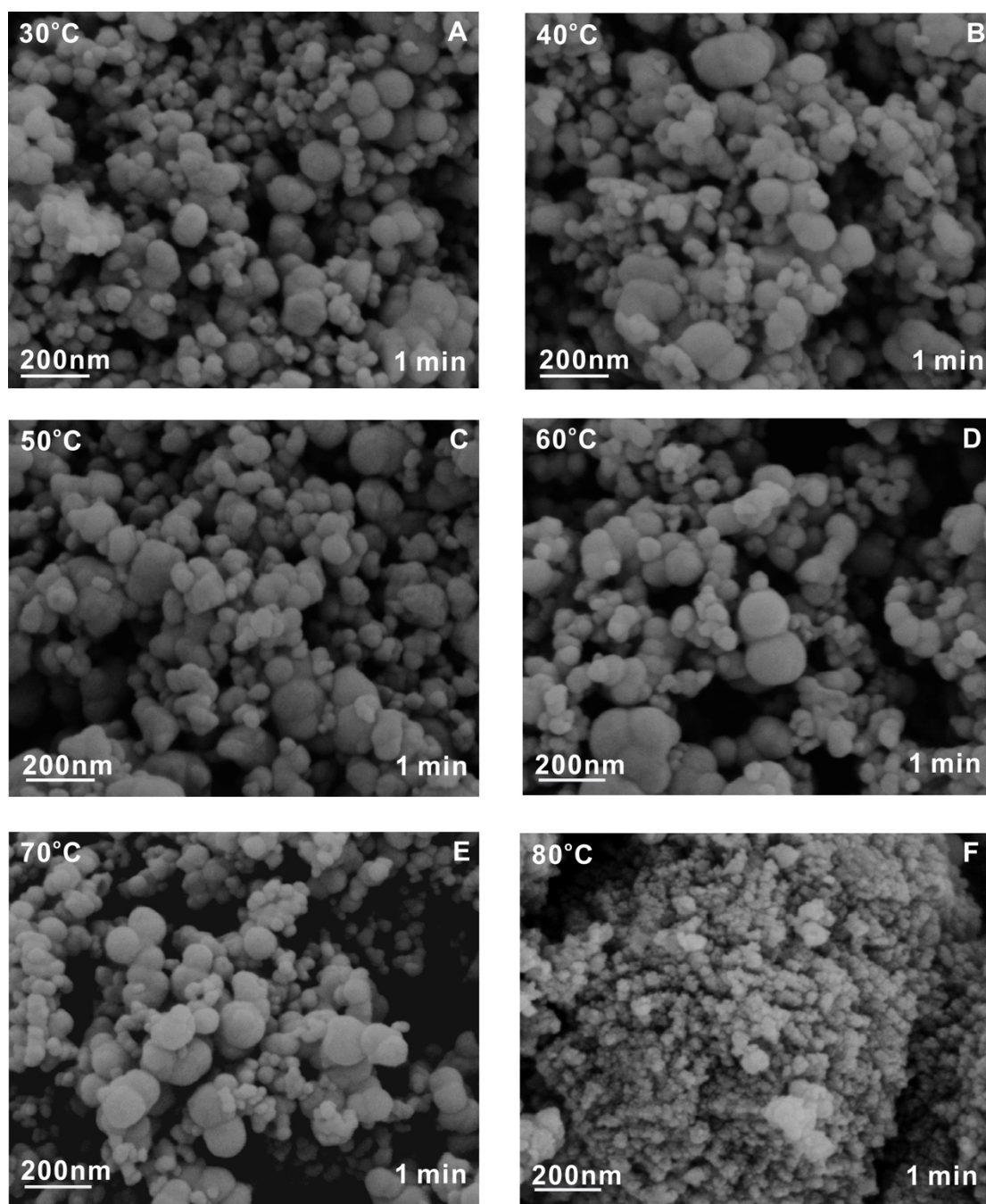**Fig. S2.** XRD patterns of solid products for experiment set I.

Fig. S3. SEM images of the solid products after 1 minute of reaction. For details of experiments, see TableS1.
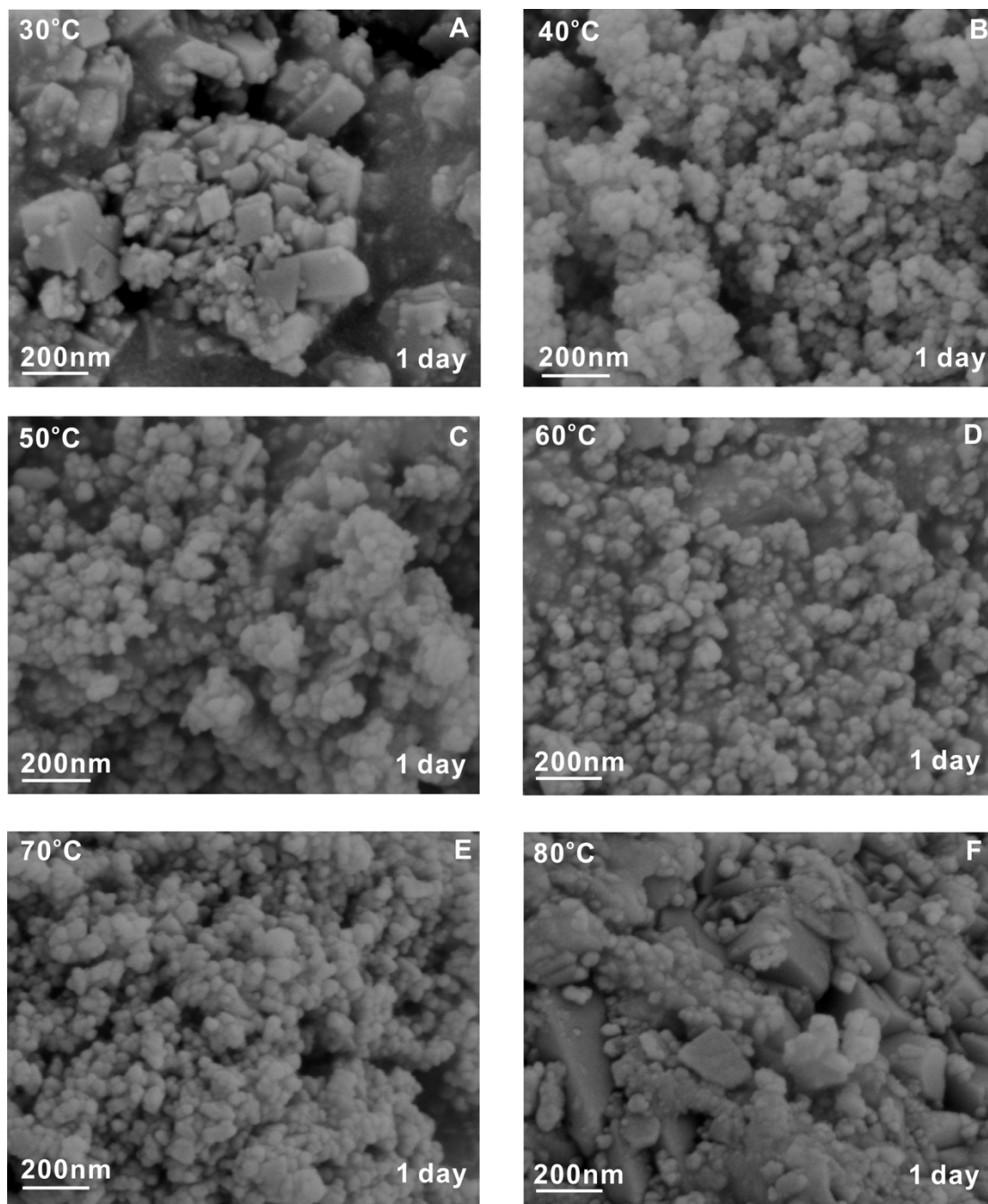
Fig. S4. SEM images of the solid products after 1 day of reaction. For details of experiments, see TableS1.
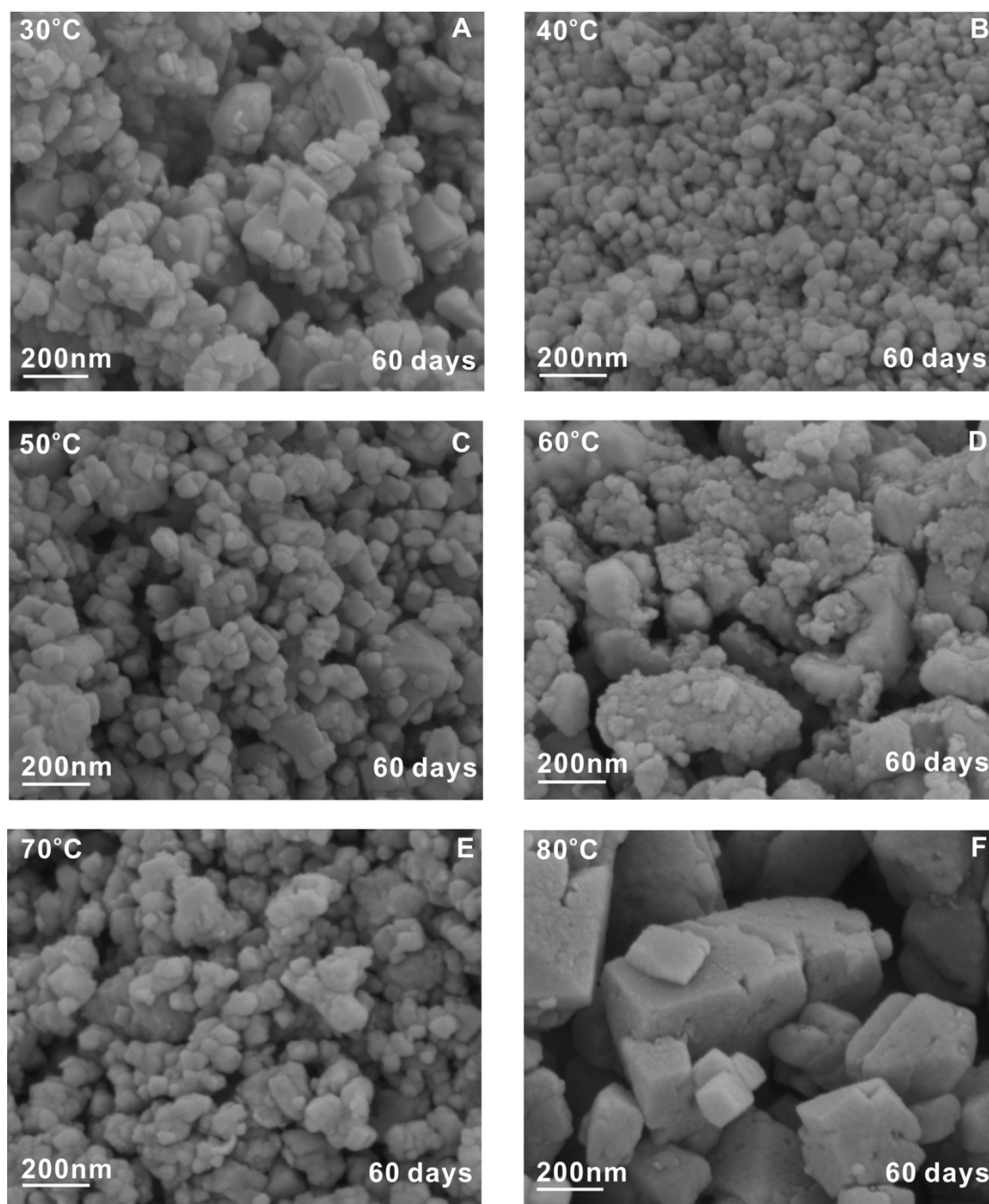
Fig. S5. SEM images of the solid products after 60 days of reaction. For details of experiments, see TableS1.
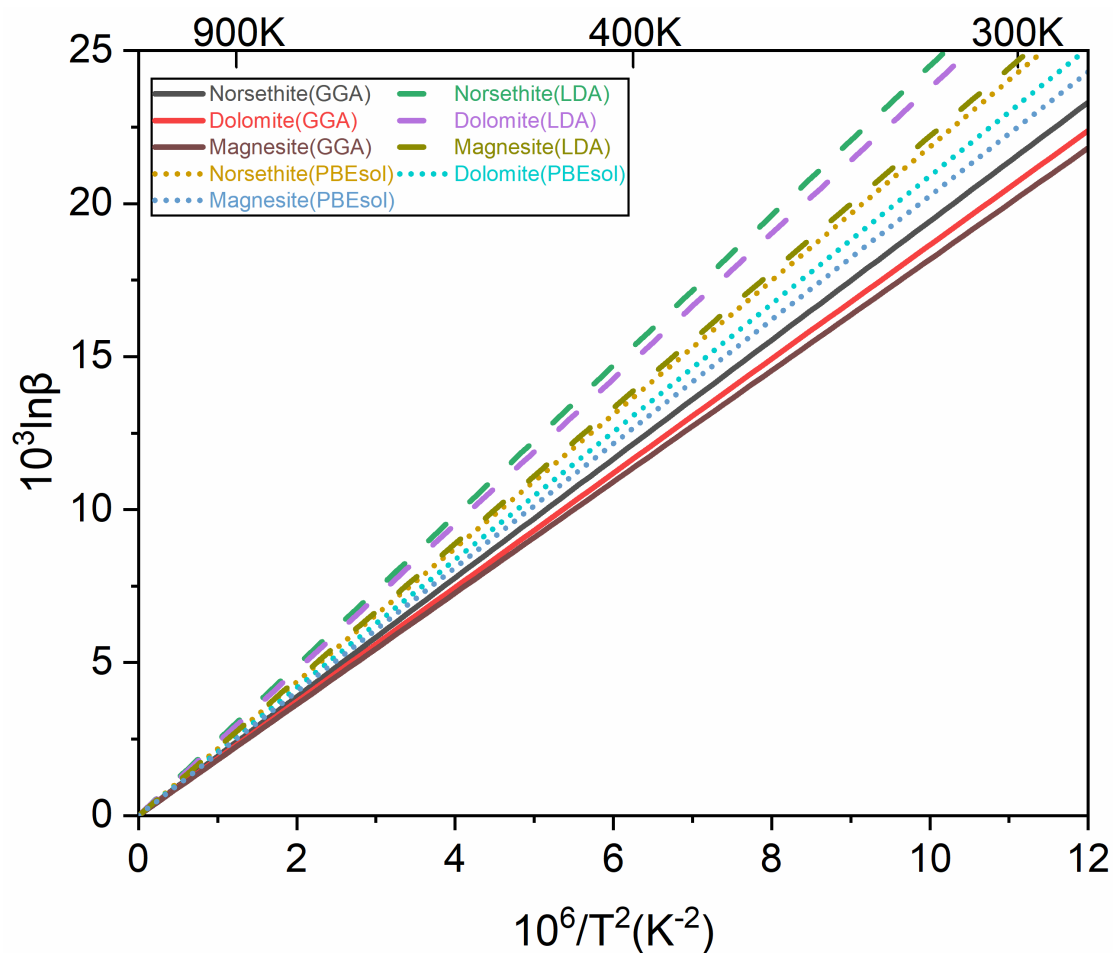
Fig. S6. Theoretical temperature dependence of Mg isotope β-factor for norsethite and dolomite.
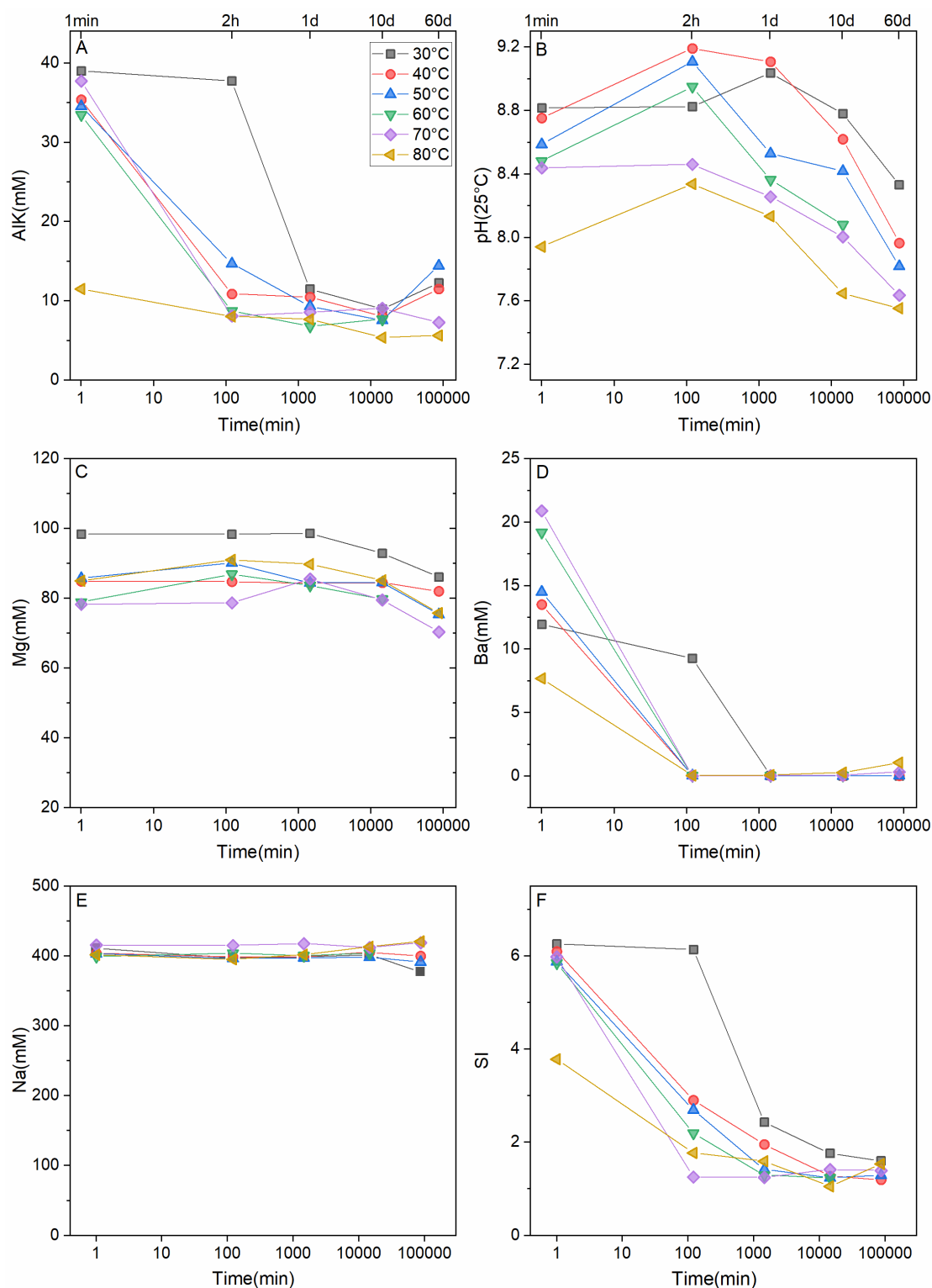
Fig. S7. The evolution of solution chemistry with reaction time for experiments set I. (A) Alkalinity versus reaction time. (B) pH (measured at 25°C) versus reaction time. (C) Mg concentration versus reaction time. (D) Ba concentration versus reaction time. (E) Na concentration versus reaction time. (F) Saturation Index(SI) of norsethite versus reaction time.
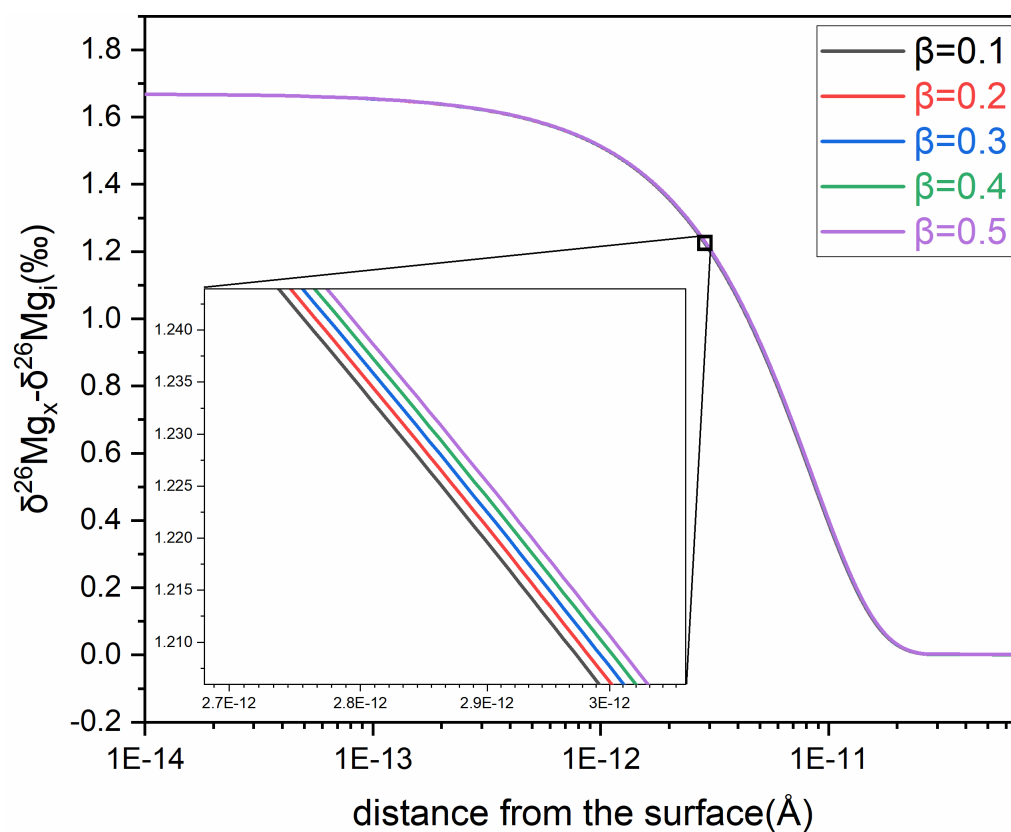
Fig. S8. The diffusion modeling results for the experiments at 50°C. The X axis represents the distance mineral surface. The Y axis stands for the difference between the $\delta^{26}Mg$ value of the initial mineral and the $\delta^{26}Mg$ value of mineral which has the distance of x from the surface.

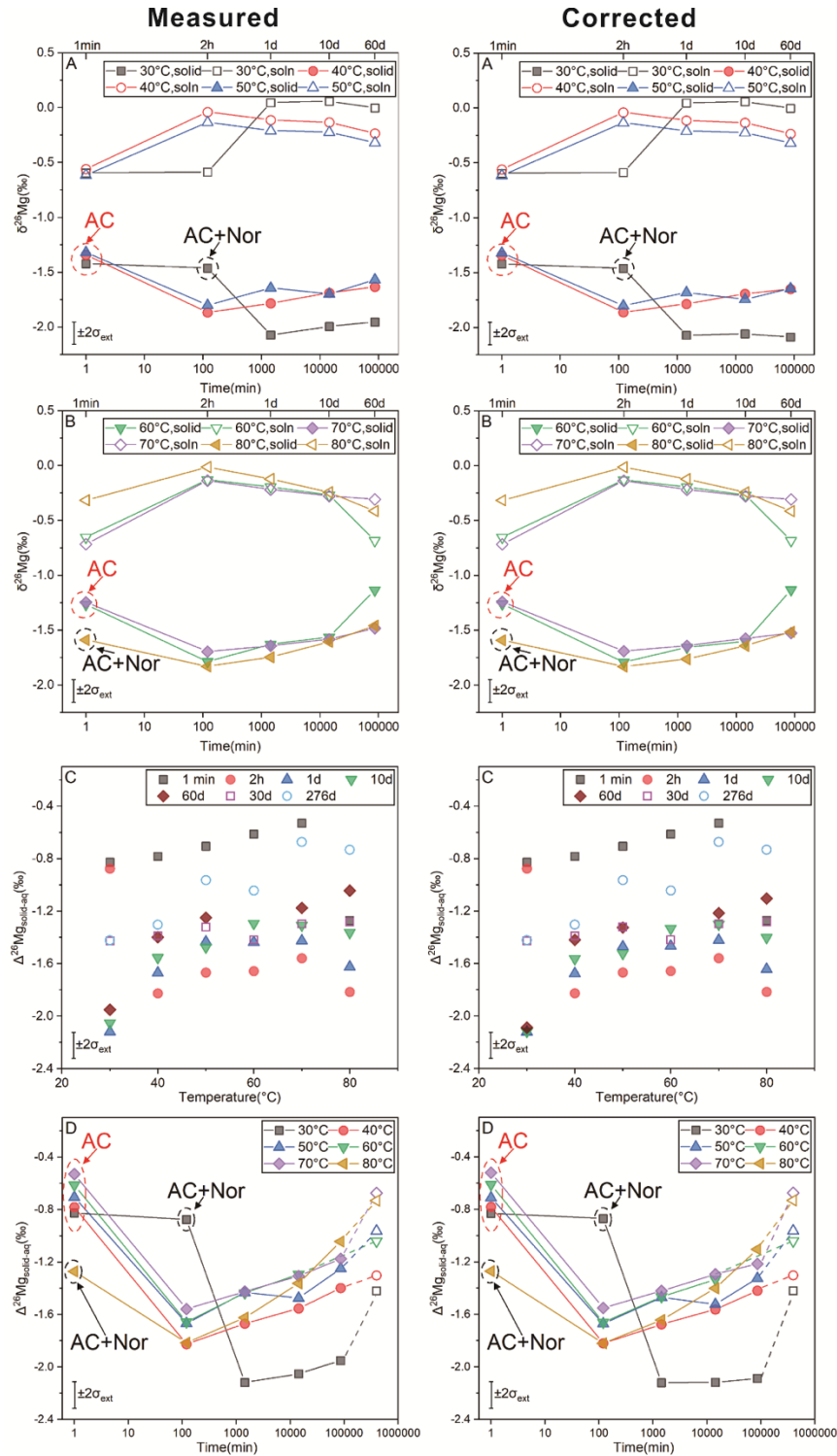**Fig. S9.** The measured (left column) and corrected (right column) $\delta^{26}Mg$ values and $\Delta^{26}Mg$ values in experiments (A) $\delta^{26}Mg$ values of solid and aqueous phases versus reaction time for experiments at 30 to 50°C. (B) $\delta^{26}Mg$ values of solid and aqueous phases versus reaction time for experiments at 60 to 80°C. (C) $\Delta^{26}Mg_{solid-aq}$ versus reaction temperature at different reaction time. (D) $\Delta^{26}Mg_{solid-aq}$ versus reaction time at different temperature. The solid dots represent the data for experiments Set I, while the hollow dots represent the data for experiments Set II in (C) and (D). AC: amorphous carbonate, Nor : norsethite.