

Stabilities of Some Silicate Minerals under Approximate Venusian Surface Conditions

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Stability field diagrams have been constructed for forsterite, enstatite, wollastonite, and their precursors and reaction products under 90 atm CO₂ at 427°C, approximating the environment on Venus. The compounds were also studied experimentally under similar conditions. The results show that forsterite and enstatite are stable but that wollastonite is not. Periclase and magnesite undergo reaction, the former to magnesite and the latter to synthetic forsterite. Calcite is stable.

Introduction

The question of mineral stability at elevated temperatures and pressures is of interest not only for terrestrial applications but also for environmental considerations of other planets in the solar system. Thermodynamic calculations can give some indication of the compounds which might be expected, assuming equilibrium between the mineral and the gas phase above it. Such calculations for mineral stabilities are somewhat restricted in their applicability to natural systems, and O'Connor (1) has discussed some of these limitations. Nevertheless, when the limitations and hazards are recognized, mineral stability field diagrams can yield very useful information concerning natural processes. The present communication presents a study of some magnesium and calcium silicate systems under an approximate Venusian atmosphere of high pressure CO₂ 427°C. Thermodynamic calculations and an experimental study have been carried out. The experimental study shows that equilibrium is attained in times short on a geologic scale.

Experimental Procedures

The cylindrical test chamber was of steel with nickel-plated internal surfaces. It was 25 cm i.d. by 84 cm long (43 liters vol), mounted vertically in an insulation nest. At the experimental temperature of 427 ± 3°C, the composition of the

atmosphere in the chamber consisted of 90 atm CO₂, 2 atm N₂, 1 atm O₂, and approximately 5 mg liter⁻¹ of water, approximating the Venusian surface environment (2).

The minerals and related precursors and reaction products were contained in a series of stainless steel trays supported as a vertical assembly from the underside of the chamber lid. The naturally occurring minerals were crushed and spread in a thin layer on the trays. Precursors and reaction products of the minerals were mixed with SiO₂ prior to spreading on other trays. After loading, the sample tray assembly was immediately sealed in the test chamber, and the chamber brought to operating conditions. The chamber was held at the experimental conditions for four days, after which time it was allowed to cool over several hours, depressurized, opened, and small portions of the samples were removed for powder X ray diffraction studies. After sampling, the test chamber was immediately resealed and brought back to experimental conditions. This cycle was repeated four times for a total exposure time of approximately 20 days.

In the first series of tests of the magnesium minerals, forsterite, enstatite, periclase, and magnesite were studied. The magnesite was obtained commercially as hydromagnesite and converted to magnesite in the laboratory. However, the diffraction studies of the blank

(before exposure to test conditions) showed that the material picked up water and reverted to hydromagnesite during handling prior to insertion in the test chamber.

In a second series of tests, wollastonite and calcite were subjected to the same test sequence as indicated above for the magnesium minerals.

Results

Stability Field Diagrams

The equilibrium constant K is obtained from

$$\Delta F^\circ = -2.303 RT \log K,$$

where ΔF° at the desired temperature is calculated by usual methods from tabulated values of enthalpy and entropy taken from standard references such as the U.S. Bureau of Mines Bulletins and the JANAF Tables.

Figure 1 shows the stability fields for some minerals in the MgO-SiO₂ system in terms of the equilibrium constant which is here equal to $P_{\text{H}_2\text{O}}$ or P_{CO_2} (in atm) at 427°C. This figure is constructed from consideration of the following

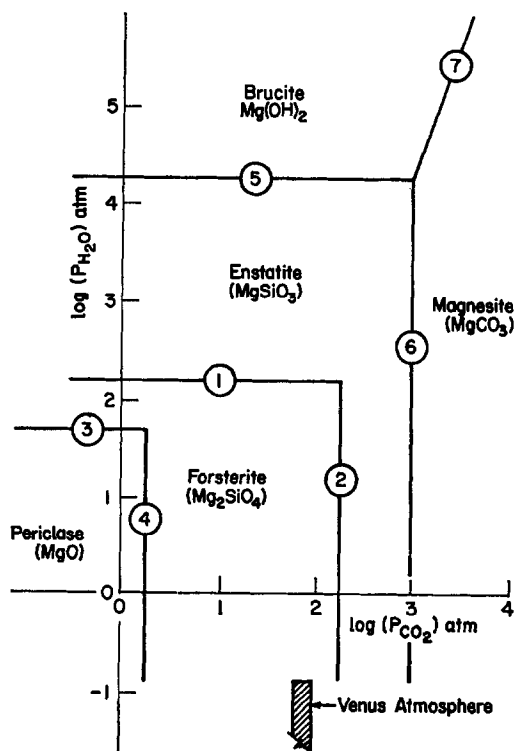
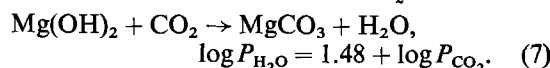
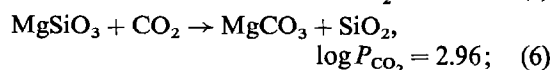
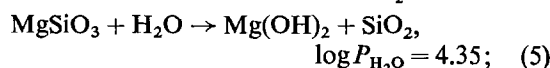
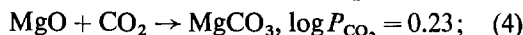
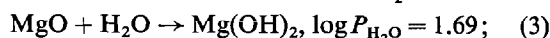
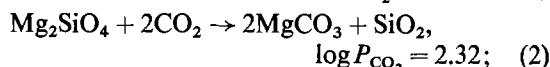
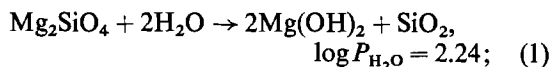


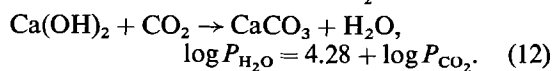
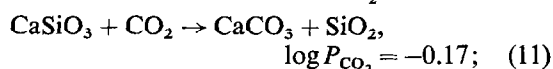
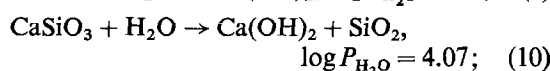
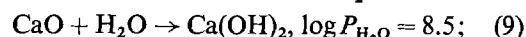
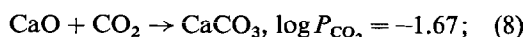
FIG. 1. Stability fields for some minerals in the MgO-SiO₂ system in terms of P_{CO_2} and $P_{\text{H}_2\text{O}}$ at 700°K (Numbered phase boundary lines correspond to reactions given in the text).

reactions (with the calculated equilibrium constant given after each reaction):



It should be noted that the range of atmospheric composition lies within the forsterite field, indicating that the weathering processes on Venus will not alter any forsterite that may be on the surface. Weathering processes should lead to the formation of forsterite from magnesium minerals present, e.g., MgO plus SiO₂.

Calculation of the stability fields of the calcium phases has been carried out in the same way as for the magnesium phases. Figure 2 shows the stability fields for some minerals in the CaO-SiO₂ system in terms of P_{CO_2} or $P_{\text{H}_2\text{O}}$ at 427°C. The reactions studied and equilibrium constants are:



The experimental values of the partial pressure of CO₂ over CaCO₃ (3) indicate that the stability line on the $\log P_{\text{CO}_2}$ axis probably lies closer to -4 rather than -1.67 as shown on the figure. However, Fig. 2 is self-consistent, and the stability fields are correct relative to each other. Figure 2 shows that wollastonite is expected to weather to CaCO₃ and SiO₂ and that the latter products should be the stable final phase. It should be noted that the range of atmospheric composition lies within the CaO + SiO₂ field, indicating that the weathering process on Venus will lead to the formation and stability of CaO plus SiO₂.

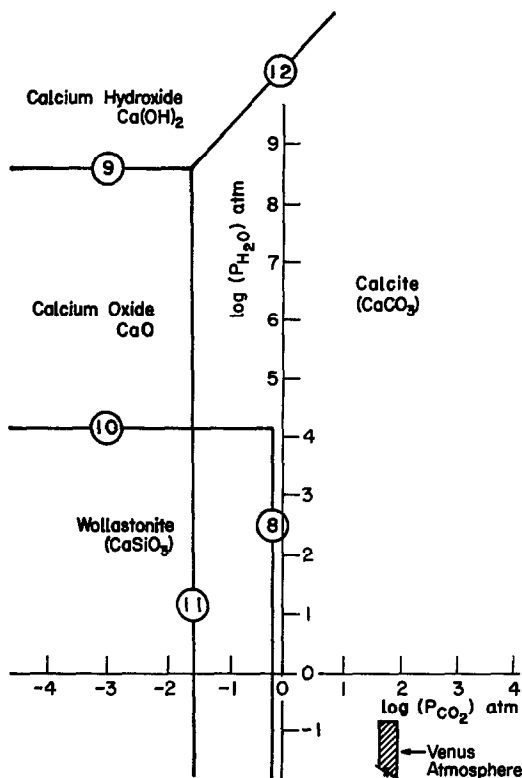


FIG. 2. Stability fields for some minerals in the CaO-SiO₂ system in terms of P_{CO_2} and $P_{\text{H}_2\text{O}}$ at 700°K (Numbered phase boundary lines correspond to reactions given in the text).

Experimental

All powder diffraction patterns were compared with the "ASTM Diffraction Reference File" (4). Assignments for the formation of new compounds were made when several lines not present in the blank (before exposure) pattern were matched with a product of reaction.

Figure 1 shows that, under the experimental conditions of the present investigation, forsterite is a stable phase. After four weeks of exposure at pressure and temperature, the results of X ray diffraction indicated that natural forsterite (source unknown) had not undergone any change.

The blank diffraction showed that magnesium carbonate starting material was a mixture of magnesite and hydromagnesite (see Experimental Procedures). At the end of the first week of exposure, it was predominantly magnesite. Figure 1 shows that this is to be expected since brucite is stable only above $\log P_{\text{H}_2\text{O}} > 4$. By the end of the third week of exposure, reaction of MgCO_3 (+SiO₂) began with the appearance of two strong diffraction lines of synthetic forsterite

as well as some of its weaker lines. From Fig. 1, weathering of MgCO_3 to forsterite is expected.

By the third week, periclase was converted to magnesite and forsterite. This reaction probably occurs in a stepwise fashion, the first step being the formation of magnesite, the diffraction lines appearing at the end of the second week of exposure. At the end of the third week, forsterite lines appear, probably due to the conversion of the first product, magnesite.

California enstatite remained virtually unchanged for the full four weeks of exposure. Two very weak lines appear from which it is not possible to make identification. From Fig. 1, it is to be expected that enstatite remains stable under the experimental conditions imposed.

As early as the end of the first week of exposure, decomposition of wollastonite (Obendalshausen, Kaiserstuhl, Germany) to CaCO₃ and SiO₂ is apparent. This result is expected from the calculated stability fields depicted in Fig. 2.

From Fig. 2, it is also expected that calcite is a stable phase under the imposed experimental conditions. After four weeks of exposure, no changes were observed in the diffraction pattern of calcite.

Conclusion

If reliable thermodynamic data are available, stability field diagrams for relatively complex chemical systems may be calculated with a considerable degree of confidence. These diagrams then may be used to predict the range of stability for a compound, including naturally occurring minerals, in a heterogeneous system when the amount of gas phase reactant is varied. The results reported here have both terrestrial and planetary implications which are useful in geological predictions of the stable phase assemblages in the near surface and surface environment. The present study has experimentally confirmed that equilibrium is attained in times short on a geologic scale, for the minerals studied here analytically, under conditions approximating the Venus environment.

References

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