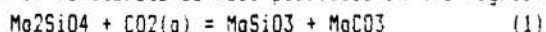


STABILITY OF MAGNESIUM- AND MANGANESE-BEARING CARBONATES ON THE SURFACE OF VENUS. M. Yu. Izotov, Vernadsky Institute, USSR Academy of Sciences, Moscow, USSR.

Investigation of carbonate stability on the surface of Venus is important for the understanding of the geochemical cycle of carbon in the atmosphere-lithosphere system. Calcite  $\text{CaCO}_3$  which has been earlier considered as a major soil component for the buffering of atmospheric  $\text{CO}_2(\text{g})$  content [1-5] now is found to be unstable thermodynamically [6,7] and kinetically [8] in relation to high  $\text{SO}_2(\text{g})$  content in the atmosphere. Dolomite  $\text{CaMg}(\text{CO}_3)_2$  also is unstable in relation to  $\text{SO}_2(\text{g})$  [6,7]. The evaluation of magnesite  $\text{MgCO}_3$  and rhodochrosite  $\text{MnCO}_3$  stability in the system:  $\text{H-O-S-Cl-F-Mg-Fe-Mn-Si}$  at the T,P-range of Venus surface is presented in this report.

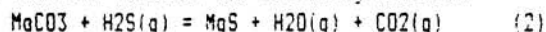
The thermodynamic estimations show that the chemical weathering of magnesian olivines ( $\text{Fo} > 50$ ) should result in forsterite formation [9] which probably could react with  $\text{CO}_2(\text{g})$  and sulfur-bearing gases at the conditions differing from that at the mean planetary radius. According to [5] and our data the formation of magnesite as a product of carbonation of forsterite is well plausible at the highlands in accord with the reaction:



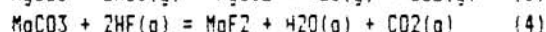
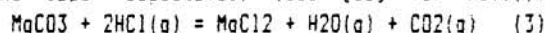
Unfortunately the instrumental uncertainties in determination of thermodynamic properties of the compounds in (1) (e.g. clinoenstatite) do not allow the accurate estimations of hypsometric level of equilibrium in (1). This elevation of the beginning of forsterite carbonation is variable within an interval of several kilometers (Fig. 1).

The stability estimation for forsterite and magnesite in relation to  $\text{SO}_2(\text{g})$  seems to be highly depended on uncertainties of redox conditions (see Fig. 1.A). If we assume that those conditions are governed by redox capability of measured atmospheric gases (e.g.  $\text{CO}_2$ ,  $\text{CO}$ ,  $\text{H}_2\text{O}$ ) (see [10]) it seems more likely to expect carbonation of forsterite (see eq. 1) rather than its sulfatization at the highland conditions (see Fig. 1.B and [9]). The calculations of equilibrium mineral assemblages made by the free energy minimization method in the system  $\text{C-O-S-Fe-Mg-Si}$  show that above the hypsometric level of equilibrium for the reaction (1) (i.e. above 6054.4 or 6058.1 km) the chemical weathering of typical olivine solid solutions in basalts ( $\text{Fo} > 50$ ) could result in magnesite formation in assemblage with enstatite and pyrite (see Table 1 in [9]).

Mixing ratios of reduced sulfur-bearing atmospheric gases:  $\text{COS}$ ,  $\text{H}_2\text{S}$  and  $\text{S}_2$  (<2-3ppm, 3ppm, 0.02ppm (see [11] for ref.)) are found to be not high enough for the niningerite  $\text{MgS}$  formation as a result of chemical weathering of rhodochrosite. For instance, at 740K and 95.2 bar the following reaction



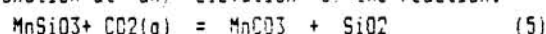
could proceed only if  $\text{H}_2\text{S}(\text{g})$  mixing ratio exceeds 0.03-0.14 at the mixing ratios for  $\text{H}_2\text{O}(\text{g})$  and  $\text{CO}_2(\text{g})$ : 20-100ppm and 0.965 respectively (see [11] for ref.). At the conditions of Venus' surface magnesite also should not react with  $\text{HCl}(\text{g})$  and  $\text{HF}(\text{g})$  if the mixing ratios of these gases near the surface are in accordance with spectroscopic measurements (0.4ppm and 5ppb respectively (see [11] for ref.)). The following reactions



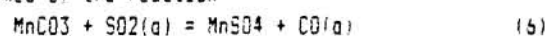
could proceed if  $\text{HCl}(\text{g})$  mixing ratio exceeds 900-2100ppm at 740K (95.2 bar), 1100-2500ppm at 675K (55.2 bar); and  $\text{HF}(\text{g})$  mixing ratio exceeds 0.12-0.27ppm at 740K, 0.05-0.11ppm at 675K at the mentioned above mixing ratios for  $\text{H}_2\text{O}(\text{g})$  and  $\text{CO}_2(\text{g})$ .

An aeolian transportation of magnesite particles to the lowlands and interaction with enstatite could result in forsterite formation and the release of  $\text{CO}_2$  in the atmosphere as it has been suggested in [5]. If magnesite is isolated from enstatite it should be stable on the lowlands. If to take into account the relatively low rate of the solid-solid type interaction of magnesite and enstatite the accumulation of magnesite on the lowlands is not excluded.

According to the thermodynamic calculations rhodochrosite could be formed as a result of rhodonite  $\text{MnSiO}_3$  (rather than tephroite  $\text{Mn}_2\text{SiO}_4$ ) carbonation at any elevation by the reaction:



Equilibrium partial pressures of carbon dioxide for this reaction is 60.9 bar at the temperature of 740K and 16.3 bar at 675K. Rhodochrosite is suggested to form as a by-product of chemical weathering (oxidation or sulfidization) of Mn-bearing olivines and pyroxenes from basalts (see [9]) resulted in  $\text{MnSiO}_3$  formation.  $\text{MnCO}_3$  appeared to be a single carbonate which is thermodynamically stable in respect of  $\text{SO}_2$  at any hypsometric level. Manganese sulfate  $\text{MnSO}_4$  could be formed by the reaction

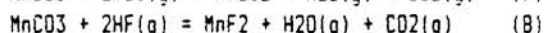
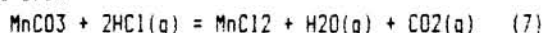


at 740K only if  $\text{SO}_2$  mixing ratio will be more than 0.023, and more than 570ppm at 675K: ( $\text{CO}$  mixing ratio: 17 ppm). Manganese carbonate is also stable in relation to  $\text{HCl}(\text{g})$  and  $\text{HF}(\text{g})$ . Reaction (7) could proceed if

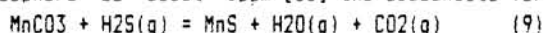
## STABILITY OF CARBONATES

M. Yu. Zolotov

HCl(g) mixing ratio exceeds 8-17ppm at 740K, 6-13ppm at 675K. Reaction (8) could proceed if HF(g) mixing ratio exceeds 5-10ppm at 740K and 3-7ppm at 675K



If the H<sub>2</sub>S(g) content in the atmosphere is about 3ppm [11] the alabandite formation should not be excluded



That reaction could proceed if H<sub>2</sub>S(g) mixing ratio exceeds 0.02-0.11ppm at 740K and 0.03-0.15ppm at 675K.

The scale of the contemporary carbonation seems not to be essential. Magnesite formation is evidently severely limited by low olivine content in basalts (usually < 10%) as well as by subordinate role of areas where the forsterite carbonation could take place: only 2.3% of total surface area is situated above 6054.4 km. That is taking into account the unstability of calcite and dolomite only a few vol. percents of carbonates (magnesite or/and rhodochrosite) could be expected on the surface as products of the present weathering of basalts.

The carbonation as well as other chemical processes on the surface-atmosphere interface are also limited by the low resurfacing rate [14]. For instance, the total mass of CO<sub>2</sub> in the atmosphere (4.7E+23 g) theoretically could be consumed by magnesite formation within the 10 km thick layer of fresh basalts covering the total surface of the planet. Hence the local contemporary carbonation is evidently considered as a largely subordinate factor of the changes of the total mass of atmospheric CO<sub>2</sub>. In this case the possibility of some buffering of atmospheric CO<sub>2</sub> by carbonate-silicate equilibria as have been proposed previously [1-3,5] now is considered as unreal.

REFERENCES: 1. Urey H. C. (1951) *Geochim. Cosm. Acta*, 1, p. 209. 2. Mueller R.F. (1964) *Icarus* 3, p.295. 3. Lewis Y.S. (1970) *EPSL* 10, p.73. 4. Khodakovskiy I.L. et al. (1979) *Icarus* 39, p.352. 5. Nozette S., Lewis J.S. (1982) *Science* 216, p.181. 6. Zolotov M.Yu. (1985) *LPSC XVI*, p.942. 7. Volkov V.P., Zolotov M.Yu., Khodakovskiy I.L. (1986) in *Phys. and Chem. of Terrest. Planet.*, ed. S. Saxena, Springer, p.136. 8. Fegley B.J., Prinn R.G. (1989) *Nature* 337, p.55. 9. Zolotov M.Yu. *Chemical weathering...* this vol. 10. - Redox conditions... this vol. 11. Von Zahn U. et al. (1983) in *Venus*, ed. D. Hunten, Ariz. Univ. Press, p.299. 12. Kiseleva I.A. et al (1979) *Geokhimiya* No12, p.1811. 13. Robie R.A., Hemingway B.S., Fisher J.R. (1978) *Geol. Surv. Bull.* 1452, Wash. 14. Arvidson R.E. et al. (1990) *Geoph. Res. Lett.* 17, p.1385. 15. Seiff A. et al. (1985) *Adv. Space Res.* 5, No 11, p.3.

Fig. 1. Phase relations in the system Mg-Si-C-O-S as a function of temperature, oxygen (A) and carbon monoxide (B) partial pressures for the conditions of Venus' surface. The mixing ratios for CO<sub>2</sub> (0.965) and SO<sub>2</sub> (150 ppm) were used from [11]. 1 - (solid equilibrium lines) for clinoenstatite enthalpy of formation at the temperature 298.15K (-1545.2 kJ/mol) taken from [12]; 2 - (dotted lines) for the clinoenstatite enthalpy of formation at 298.15K (-1547.8 kJ/mol) taken from [13]. The Venus' atmospheric conditions (CO mixing ratio: (17-20 ppm) are shown on the right of plot B. P-T-h atmospheric profile is from [15]. Fo - forsterite Mg<sub>2</sub>SiO<sub>4</sub>; En - clinoenstatite MgSiO<sub>3</sub>; Mag - magnesite; Ms - magnesium sulfate MgSO<sub>4</sub>.

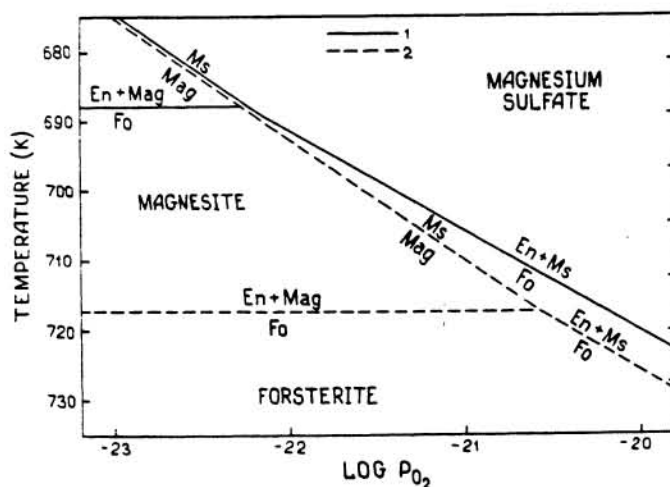


FIG. 1A

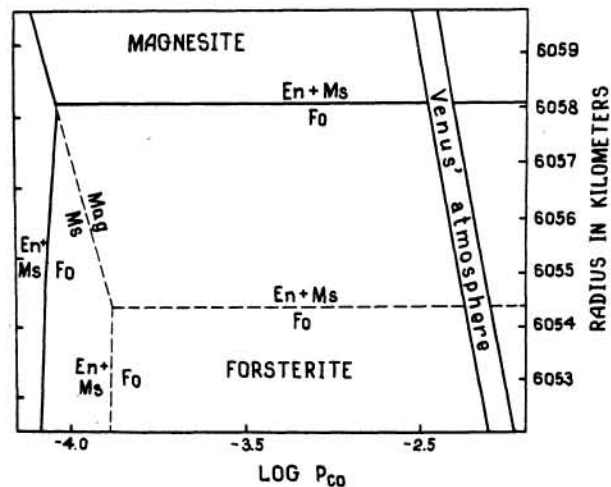


FIG. 1B