

# Disappearance of the liquid-liquid miscibility gap in the system CaO-MgO-SiO<sub>2</sub> at high pressure.

P. Hudon  
D.R. Baker  
A.D. Pelton  
P. Wu

Department of Earth and Planetary Sciences, McGill University,  
3450 University Street, Montreal, Quebec, H3A 2A7, Canada  
Centre for Research in Computational Thermochemistry, Ecole  
Polytechnique de Montreal, P.O. Box 6079, Station A,  
Montreal, QC, H3C 3A7, Canada

## Introduction

The system CaO-MgO-SiO<sub>2</sub> has been extensively studied in the past because it includes the phases forsterite, enstatite, and diopside which are major constituents of peridotitic and basaltic rocks. The presence of a liquid-liquid miscibility gap in the silica-rich portion of this ternary has been known since Greig's study (1927). Experimental work has been performed recently along the CaO-SiO<sub>2</sub> (Tewhey and Hess, 1979; Hageman *et al.*, 1986) and the MgO-SiO<sub>2</sub> binaries (Hageman and Oonk, 1986) in order to constrain this miscibility gap. All these investigations have been performed at atmospheric pressure and no attempt has been made to explore the effect of pressure on the miscibility gap in this system. The present study reports preliminary results related to the disappearance of the liquid-liquid miscibility gaps in the CaO-SiO<sub>2</sub> and MgO-SiO<sub>2</sub> binaries at high pressure.

## Methods

Starting materials were CaO + SiO<sub>2</sub> and MgO + SiO<sub>2</sub> oxide mixtures which were loaded into molybdenum capsules. Experiments of 12 to 60 min duration were performed in a 1.91-cm piston-cylinder apparatus using the high-temperature assembly and techniques of Hudon *et al.* (1994). Prior to each run, all the assembly components except the lead foil, salt, and base plug were fired to 300°C for 1 hour to eliminate adsorbed water. Temperatures were measured with W<sub>97</sub>Re<sub>3</sub>-W<sub>75</sub>Re<sub>25</sub> (type D) thermocouples or by W<sub>95</sub>Re<sub>5</sub>-W<sub>74</sub>Re<sub>26</sub> (type C) thermocouples. No pressure correction was applied to the emf of the thermocouples. Electron probe microanalysis of the quenched liquids was performed with an accelerating voltage of 15 keV, a 20-nA beam current, a 10-μm spot size, and a counting times of 20 s. The data were reduced with ZAF corrections using synthetic enstatite and diopside as standards.

## Result

In the CaO-SiO<sub>2</sub> binary, a small liquid-liquid miscibility gap appears to be present at 1 GPa. The gap extends from 80.5 to 96.0 mol% SiO<sub>2</sub> at a monotectic temperature of 1835°C ± 14°C with a consolute point at 1893°C ± 56°C and 89.6 mol% SiO<sub>2</sub>. In the MgO-SiO<sub>2</sub> system, a wider liquid immiscibility field is present at 1 GPa. The two immiscible liquids extend from 68.0 to 97.8 mol% SiO<sub>2</sub> at a monotectic temperature of 1854 ± 21°C with a consolute point at 1997 ± 48°C and 86.5 mol% SiO<sub>2</sub>.

## Discussion

The liquid phases were modelled in the MgO-SiO<sub>2</sub> system (Wu *et al.*, 1993) and the CaO-SiO<sub>2</sub> system (Ericksson *et al.*, 1994) at 1 bar with the modified quasichemical model of Pelton and Blander (1986). The phase diagrams measured in this study at 1 GPa were similarly modelled to yield parameters of the quasichemical model for the liquid:

CaO-SiO<sub>2</sub> binary

$$\omega = -63176 - 38074 Y_{\text{SiO}_2} - 90148 Y_{\text{SiO}_2}^2 + 439893 Y_{\text{SiO}_2}^3 \text{ J mol}^{-1} \quad (1)$$

$$\eta = -19.456 Y_{\text{SiO}_2} + 133.888 Y_{\text{SiO}_2}^2 \text{ J mol}^{-1} \text{ K}^{-1}, \quad (2)$$

MgO-SiO<sub>2</sub> binary

$$\omega = -62760 - 70710 Y_{\text{SiO}_2} + 41840 Y_{\text{SiO}_2}^2 \text{ J mol}^{-1} \quad (3)$$

$$\eta = -25.104 Y_{\text{SiO}_2} + 154.808 Y_{\text{SiO}_2}^2 \text{ J mol}^{-1} \text{ K}^{-1}, \quad (4)$$

where  $\omega$  and  $\eta$  are enthalpy and excess entropy parameters, and  $Y_{\text{SiO}_2}$  is the equivalent fraction of SiO<sub>2</sub>. (See Pelton and Blander, 1986). This model reproduces the measured miscibility boundaries as well as liquidus curves of the binary phase diagrams at 1 GPa. The parameters of Eqs. (1-4) differ very little from those obtained for the liquid at 1 bar. That is, pressure has only a small effect upon the component activities in the liquids, and hence has only a small effect on the topology of

the miscibility gap. When the calculated 1 bar and 1 GPa binaries are compared, the shapes of the miscibility gaps are very similar. At atmospheric pressure the differences between the melting temperatures of SiO<sub>2</sub> and the monotectic temperatures of the CaO–SiO<sub>2</sub> and MgO–SiO<sub>2</sub> binaries are 34°C (compared to 51°C at 1 GPa) and 36°C (compared to 21°C at 1 GPa) respectively. The consolute temperatures are also raised at high pressures but not as much as the monotectic temperatures. The decrease of the area of the gaps at high pressures is related mainly to the increase in the monotectic temperatures which follows closely the increased melting temperature of SiO<sub>2</sub> at high pressures.

From the thermodynamic model, using the melting curve of SiO<sub>2</sub> silica with pressure of Zhang *et al.* (1993), the disappearance of the liquid–liquid miscibility gaps in the CaO–SiO<sub>2</sub> and MgO–SiO<sub>2</sub> binaries is calculated to occur at 1.2 GPa and 1.5 GPa respectively. Pressure thus has the same effect on silicate melts as do alkalis which cause the elimination of immiscibility effects.

## References

- Eriksson, G., Wu, P., Blander, M. and Pelton, A.D. (1994) *Canad. Metall. Quart.*, **33**, 13–21.
- Greig, J.W. (1927) *Amer. J. Sci.*, **13**, 1–44, 133–54.
- Hageman, V.B.M. and Oonk, H.A.J. (1986) *Phys. Chem. Glasses*, **27**, 194–8.
- Hageman, V.B.M., van den Berg, G.J.K., Janssen, H.J. and Qonk, H.A.J. (1986) *Phys. Chem. Glasses*, **27**, 100–6.
- Hudon, P., Baker, D.R. and Toft, P.B. (1994) *Amer. Mineral.*, **79**, 145–7.
- Pelton, A.D. and Blander, M. (1986) *Metall. Trans. B*, **17B**, 805–15.
- Tewhey, J.D. and Hess, P.C. (1979) *Phys. Chem. Glasses*, **20**, 41–53.
- Wu, P., Eriksson, G., Pelton, A.D. and Blander, M. (1993) *J. Iron Steel Inst. Jpn.*, **33**, 26–35.
- Zhang, J., Liebermann, R.C., Gasparik, T. and Herzberg, C.T. (1993) *J. Geophys. Res.*, **98**, B11, 19785–93.