

EQUILIBRIA BEARING ON THE BEHAVIOR OF TITANATE PHASES DURING CRYSTALLIZATION OF IRON SILICATE MELTS UNDER STRONGLY REDUCING CONDITIONS, B. R. Lipin and A. Muan, Geosciences Dept., The Pennsylvania State University, University Park, Pa. 16802.

Phases in which titanium is present as a major constituent (for instance ilmenite, spinel, armalcolite) are relatively abundant in lunar rocks from the mare regions, and serve as potential indicators of crystallization sequences and thermal history of these rocks. The interrelations among the various titanate phases under carefully controlled laboratory conditions have been delineated previously for a number of oxide combinations (e.g.  $\text{MgO-Al}_2\text{O}_3\text{-TiO}_2$  (1),  $\text{MgO-Cr}_2\text{O}_3\text{-TiO}_2$  (1),  $\text{FeO-Al}_2\text{O}_3\text{-TiO}_2$  (2) and  $\text{FeO-Cr}_2\text{O}_3\text{-TiO}_2$  (3)). The present work deals with equilibria among titanates in the presence of a liquid phase in relatively simple model systems where the various parameters can be carefully controlled. The studies reported herein represent the initial part of an investigation of liquidus-solidus relations in the system  $\text{CaAl}_2\text{Si}_2\text{O}_8\text{-CaMgSi}_2\text{O}_6\text{-FeO-TiO}_2$  under strongly reducing conditions, and is concerned specifically with phase relations in the composition volume  $\text{CaAl}_2\text{Si}_2\text{O}_8\text{-Fe}_2\text{TiO}_4\text{-FeTi}_2\text{O}_5$  of the above system. Within this composition volume occur under equilibrium conditions the main titanate phases of lunar rocks (ilmenite, ulvospinel and pseudobrookite), as well as hercynite, in equilibrium with a silicate liquid, with or without the presence of anorthite as a crystalline phase, depending on the composition of the mixtures. The interrelations among the various titanate phases and hercynite under these conditions is the main subject of this study.

Oxide mixtures of desired compositions were prereacted and prereduced in  $\text{CO}_2/\text{CO}$  atmospheres and subsequently placed in iron crucibles and sealed into silica glass capsules for equilibration under conditions approximating those prevailing on the lunar surface. Following equilibrations, the samples were quenched rapidly to room temperature and the phases identified by microscopy, x-ray diffraction and electron microprobe analysis.

Phase relations at liquidus temperatures in the system  $\text{CaAl}_2\text{Si}_2\text{O}_8\text{-Fe}_2\text{TiO}_4\text{-FeTi}_2\text{O}_5$  are characterized by three piercing points with temperatures and phase assemblages as follows: at  $1300 \pm 5^\circ\text{C}$  ilmenite, ulvospinel, ferropseudobrookite and liquid are present together in equilibrium. Another piercing point at  $1260 \pm 5^\circ\text{C}$  is characterized by the coexistence of ulvospinel, ferropseudobrookite, hercynite and liquid. Finally, at  $1270 \pm 5^\circ\text{C}$  hercynite, ferropseudobrookite and anorthite are the crystalline phases in equilibrium with liquid.

Relations more closely approaching those of lunar rocks are obtained by adding  $\text{CaMgSi}_2\text{O}_6$  to the system. Preliminary data on the bounding system  $\text{CaMgSi}_2\text{O}_6\text{-FeO-TiO}_2$  have established the coexistence of olivine and/or clinopyroxene in equilibrium with one or more of the titanate phases ilmenite, ulvospinel, or pseudobrookite within this model system at temperatures in the range of approximately  $1250\text{-}1300^\circ\text{C}$ . These liquidus temperatures are lowered to approximately  $1150\text{-}1200^\circ\text{C}$  in the system  $\text{CaAl}_2\text{Si}_2\text{O}_8\text{-CaMgSi}_2\text{O}_6\text{-FeO-TiO}_2$ , where one or more of the phases olivine, clinopyroxene, and anorthite

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coexist with liquid and one or more of the titanate phases ilmenite, ulvospinel and pseudobrookite. The sequences of appearance of the various titanate phases depend on the partitioning of cations between the liquid and the crystalline phases, and on the effect of cation combinations on the stability interrelations among the various titanates. The latter relations have been determined for a number of ionic combinations. Addition of  $\text{Al}^{3+}$  or  $\text{Cr}^{3+}$  to ilmenite decreases the stability of the latter phase relative to the phase assemblage spinel plus pseudobrookite at temperatures above the lower stability limit of pseudobrookite.

REFERENCES

1. Muan, A., Hauck, J., Osborn, E. F. and Schairer, J. F. (1971), Equilibrium relations among phases occurring in lunar rocks. Proc. Second Lunar Sci. Conf., Geochim. Cosmochim. Acta Suppl. 2, Vol. I, pp. 497-505. The M.I.T. Press.
2. Muan, A., Hauck, J. and Löfwall, T. (1972), Equilibrium studies with a bearing on lunar rocks. Proc. Third Lunar Sci. Conf., Geochim. Cosmochim. Acta Suppl. 3, Vol. I, pp. 185-196. The M.I.T. Press.
3. Shuart, S. and Muan, A., unpublished data.