revealed significant damage to the mica lattice resulting in dislocation and additional mosaic structures.

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Corrections to the system anorthite–åkermanite–diopside by means of Gibb's free energy analyses of the systems anorthite–åkermanite and anorthite–diopside

THE ternary system anorthite–åkermanite–diopside located in the petrologically significant four component system $CaO–MgO–Al_2O_3–SiO_2$ shows some troublesome abnormalities in the trends of the isofracts and isotherms in the anorthite primary field (de Wys and Foster, 1958). In addition an analysis of the effective molecular weights of the anorthite components in solution for the system anorthite–åkermanite (de Wys and Kapadia, 1971) compared to that of the anorthite components in solution for the system anorthite–diopside (Adams and Cohen, 1966) revealed an untenable combination of anionic group structures to exist in the primary field of anorthite. This anionic group structure conflict is also emphasized by the results of the freezing point lowering analysis of the system anorthite–åkermanite (de Wys, 1960) resulting in a van't Hoff factor of 2 for the anorthite molecule in solution. It was felt that a reanalysis of the anorthite region of the above-mentioned binary system might resolve the above-mentioned anomalies.

Thermodynamic discussion and results. Gibb's thermodynamic potentials, such as $G = H - TS$ where H represents the enthalpy and S the entropy, are very applicable for the evaluation of the liquidus curves of binary phase diagrams. The method consists of evaluating the free energy of the various liquid compositions of the phase
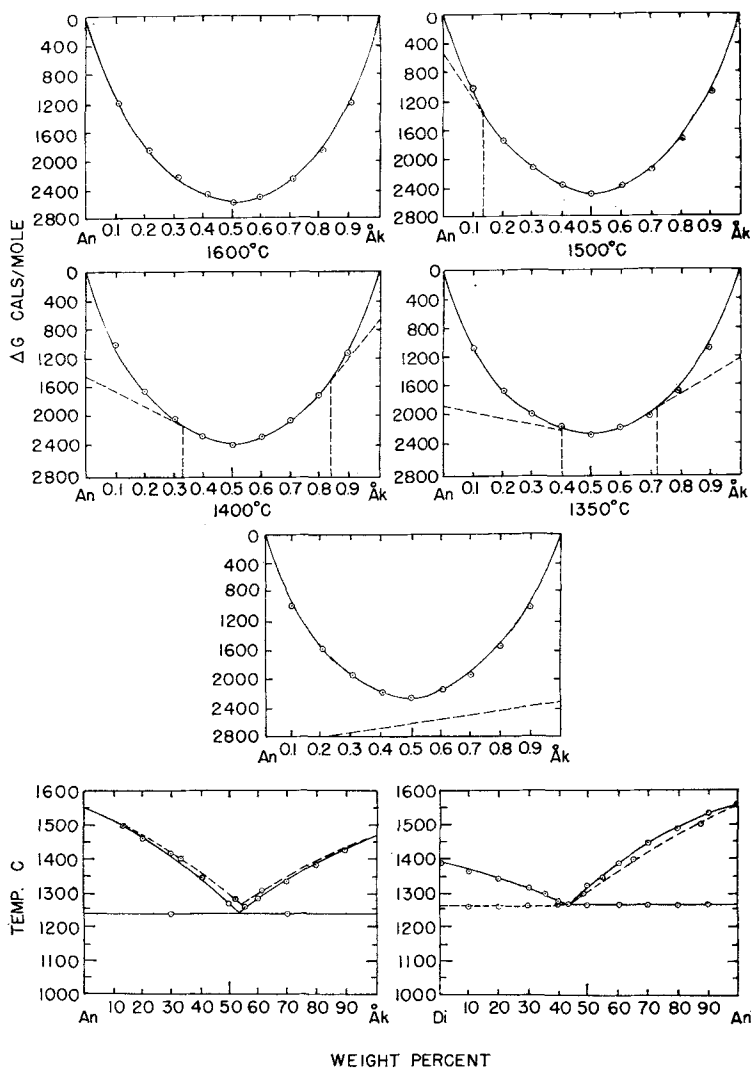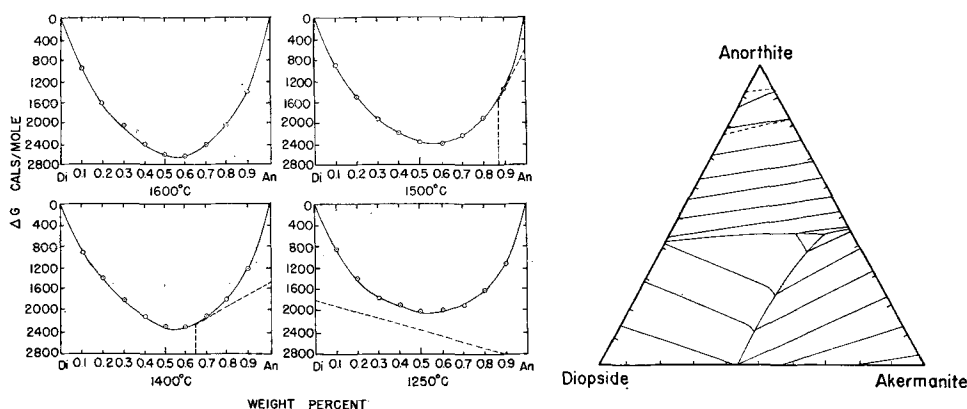
FIG. 1. Free energies of liquid and solid phases of the system anorthite–åkermanite. The dashed lines (free energies of the solid) intersecting the solid lines (free energies of the liquid phases) indicate at the points of tangency the liquidus point at the indicated temperatures. The results are indicated by the binary phase diagrams anorthite–åkermanite and diopside–anorthite.

equilibrium system at various temperatures by means of the standard thermodynamic relationship: $\Delta G = RT(N \ln N + (1-N)\ln(1-N))$ where N is the mole fraction of the solute. In order to determine the ΔG value of the solid component at the same temperature one may use the relationships: $\Delta G = \Delta H_f - T_{mp}\,\Delta S = 0$ at T_{mp} (melting point temperature) therefore $T_{mp}\,\Delta S = \Delta H$ at T_{mp} and $\Delta S = \Delta H_f / T_{mp}$.

Therefore at temperatures different from T_{mp} one may obtain a reasonable approximation of ΔG by means of $\Delta G = \Delta H_f - T\,\Delta H_f/T_{mp}$ which results in $\Delta G = \Delta H_f(1 - T/T_{mp})$ where $\Delta H_f =$ enthalpy change of fusion, which is approximately 17·7 Kcal. mole^{-1} and 20·5 Kcal. mole^{-1} for anorthite and åkermanite respectively.

The delineation of the liquidus curve is accomplished by determining the temperatures and liquid composition where the solid component and the particular liquid composition possesses the identical values of ΔG.

FIGS. 2 and 3: FIG. 2 (left). Free energies of the liquid and solid phase for the system diopside–anorthite. The modified binary system diopside–anorthite based on the free energy calculation is shown in fig. 1. FIG. 3 (right). Equilibrium diagram for the system diopside–anorthite–åkermanite shows the proposed corrections to the 1480 °C and 1520 °C isotherms.

Figs. 1 and 2 indicate the free energies of the liquid and solid phases for the systems anorthite–åkermanite and anorthite–diopside. The results of the above analyses are projected on the respective experimental binary phase diagrams. The deduced liquidus geometry shows good agreement with the experimental one for the system anorthite–åkermanite, especially, as one would expect from the use of the above equations, in the dilute composition regions. A significant deviation, is evident, however, in the dilute composition region of the anorthite primary field of the anorthite–diopside system. This observation suggests that a slight but significant change in the liquidus slope of the anorthite primary field for the latter system should be made.

It is of interest to note that when such a suggested change is projected on the ternary system anorthite–åkermanite–diopside the previously indicated high-temperature isotherm anomalies cease to exist (fig. 3). In all likelihood the isofract anomalies would also disappear.

It is significant to observe that the newly suggested slope of the anorthite primary field liquidus would provide an effective molecular weight of 0·5 An, which is in full agreement with the previously calculated effective molecular weights of the anorthite

components in solution for both anorthite–åkermanite (de Wys and Kapadia, 1971) and anorthite–forsterite (Adams and Cohen, 1966).

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Additional data concerning the stability of åkermanite

ÅKERMANITE was initially alleged to decompose into diopside when held at and below 1325 °C (Osborn and Schairer, 1941). Experimental data by others (de Wys and Foster, 1955, 1956) revealed, however, that åkermanite was stable down to at least 1000 °C. Later Harker and Tuttle (1956) indicated that at various pressures in a water
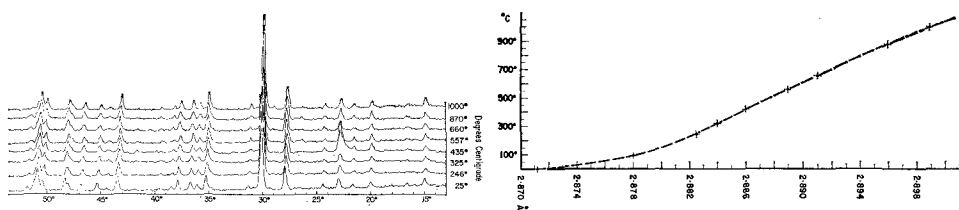
FIGS. 1 and 2: FIG. 1 (*left*). X-ray diffraction patterns of åkermanite at various temperatures. Abscissae are degrees 2θ for Cu-$K\alpha$ radiation. FIG. 2 (*right*). Diagram showing the shift in d_{211} of åkermanite with temperature.

vapour atmosphere åkermanite was stable to 700 °C, below which it decomposed by a univariant reaction such as: $Ca_2MgSi_2O_7 \rightleftharpoons CaSiO_3 + CaMgSiO_4$. The present author has attempted to investigate the stability limits of åkermanite below 1000 °C in an anhydrous atmosphere.

Pure microcrystalline åkermanite was mounted in a high-temperature furnace attached to an X-ray goniometer and diffraction patterns obtained at first at 25 °C followed by one at 1000 °C. The temperature of the sample was then slowly dropped to various temperatures, as indicated by fig. 1, and diffraction patterns obtained after