SHORT COMMUNICATIONS

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Rapidly quenched $KAlSi_3O_8$-$NaAlSi_3O_8$ glasses

THE microstructure of the decomposition in minerals has been related (McConnell, 1975) to their cooling history with special reference to spinodal decomposition in alkali feldspars (McConnell, 1969). Transmission electron microscopy (TEM) of potassium-rich alumino-silicate single crystals from a rapidly cooled igneous rock, pantellerite, exhibited spinodal textures on the order of 100 Å suggesting that decomposition by a spinodal mode may occur in the $KAlSi_3O_8$-$NaAlSi_3O_8$ system (McConnell, 1969, 1971).

Christie (1968) originally suggested that the alkali feldspars may exsolve by a spinodal mechanism and indeed spinodal decomposition may be the operative mechanism in natural exsolution (Fletcher and McCallister, 1974; Champness and Lorimer, 1976; Willaime *et al.*, 1976). In order to examine the kinetic path (or paths) by which unmixing of a supersaturated solution is accomplished, as well as the structural and morphological form of the product phases, the earliest regime of decomposition must be detected. A natural $KAlSi_3O_8$-$NaAlSi_3O_8$ composition was, therefore, rapidly quenched and examined by TEM during *in situ* annealing.

Experimental. The $KAlSi_3O_8$-$NaAlSi_3O_8$ mixtures were made from natural orthoclase* and albite* sintered in an electrically heated muffle furnace at 1050 °C in air. The samples were subsequently melted in the same furnace at 1200 °C and quenched into water.

An Applied Research Laboratory XSM Electron Microprobe was used for all element analyses. $CaAl_2Si_2O_8$ and $NaAlSi_3O_8$ standards were used for CaO and Na_2O determinations, while $KAlSi_3O_8$ was used to determine the Al_2O_3 content of the end-member feldspars and kyanite was used as a secondary standard. In addition, pure SiO_2 was used as a secondary standard for the silica determinations. The Bence and Albee (1968) probe data reduction technique was used.

The quenched sample was ion-beam thinned on a Commonwealth Scientific IMMI-5 Ion-thinner. The TEM and electron diffraction were carried out on a Phillips EM300 Electron Microscope.

Results. The $KAlSi_3O_8$-$NaAlSi_3O_8$ mixtures made from natural crystalline orthoclase and albite were analysed as $(K_{0.79}Na_{0.20})AlSi_3O_8$ and $(Na_{0.96}Ca_{0.02})AlSi_3O_8$. A 1:1 mixture of these two end-member components yielded an average bulk composition of ≈ 39.7 mole % $KAlSi_3O_8$, ≈ 59.2 % $NaAlSi_3O_8$, and ≈ 1.1 % $CaAl_2Si_2O_8$. After melting and water quenching the samples were found to be amorphous to X-rays and one quenched sample was subseqently examined by TEM.

The as-quenched sample exhibited a modulated spinodal structure with an average spacing of 50-70 Å (fig. 1*a*). This as-quenched sample yielded diffuse rings during electron diffraction indicating that it was amorphous (fig. 1*b*).[1]

The sample was aged in the heating holder of the electron microscope at 400 °C for about 1 minute and small spherical precipitates began to appear. The corresponding SAD patterns were streaked indicating periodic composition or lattice modulations. Problems were encountered with the thermocouple but the final ageing temperature achieved was between 800-850 °C. After ageing at this temperature for about 15 minutes well-formed lath-shaped crystals appeared (fig. 1*c*). The corresponding SAD patterns were poor due to continued thermal drift of the sample and, therefore, fig. 1*d* is a composite of two simultaneous SAD patterns. The lath-shaped crystals are identified as K-rich $(Na,K)AlSi_3O_8$ crystals with their long dimension parallel to (001). The SAD is a [110] projection and although it is not clear in the micrograph (fig. 1*c*), except perhaps in the region between the extensions of the lath-shaped crystal, the matrix phase is still modulated.

Conclusions. Spinodal decomposition may be operative in $KAlSi_3O_8$-$NaAlSi_3O_8$ quenched glasses. Although quenching metallic melts into

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[1] Decomposition under the electron beam was considered negligible since similar decomposition wavelength *vs.* temperature calibrations derived from small-angle neutron scattering and TEM analyses on quenched Al_2O_3-SiO_2 glasses revealed that temperatures > 50 °C were never reached during either ion-thinning or TEM (Jantzen, 1978). Secondly, concentration of the electron beam in one position for up to 10 minutes produced no change in microstructure.

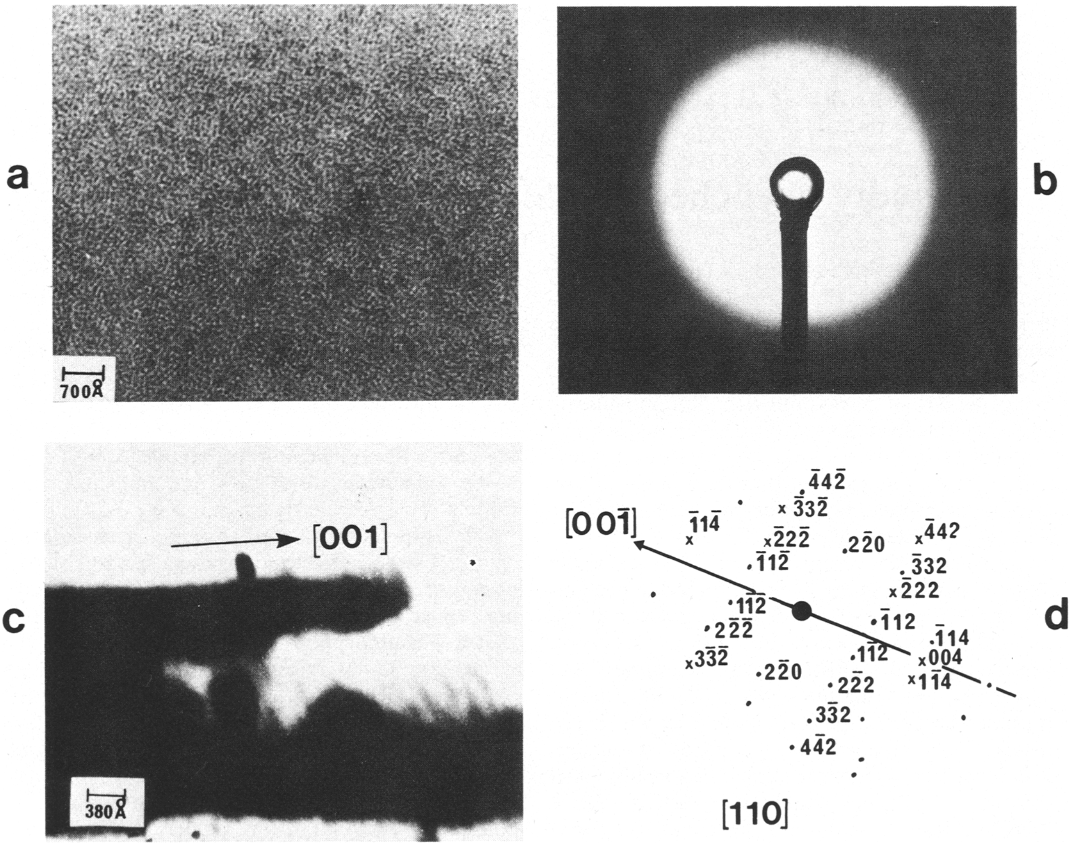

FIG. 1. Rapidly quenched $KAlSi_3O_8$–$NaAlSi_3O_8$. (*a*) Micrographs of the as-quenched structure. (*b*) SAD of the as-quenched sample. (*c*) Lath-shaped crystal after heating at 850 °C for ≈ 15 minutes. Blurring is due to thermal drift of the sample during heating (*d*) Corresponding SAD is a [110] of K-rich $(K,Na)AlSi_3O_8$. The [110] is a composite of two SAD patterns of the same crystal in the same orientation. The reflections taken from the different micrographs are marked with x's and dots, respectively.

water or other solutions yields quench rates of the order of 5×10^4 to 1×10^5 °C/sec. (Olsen and Hultgren, 1950), the quenched-in microstructure observed suggests that a more rapid quench is necessary to prevent decomposition during quenching. Quenching the samples into water precluded the use of small angle X-ray scattering techniques, used to delineate decomposition by a spinodal mode, because of the formation of quench bubbles. Roller quenching would yield higher quench rates, ≈ 10^6 °C/sec. However, at the solution temperature of ≈ 1550 °C, which is ≈ 400 °C above the melting point of the $(Na,K)AlSi_3O_8$ composition, the melt was found to be too viscous to be poured between stainless steel rollers. Laser splat quenching at 10^6–10^7 °C/sec. (Jantzen *et al.*, 1980) was also attempted on this material after presintering at 1050 °C. Vapourization of the sample in the laser beam was severe and no quenched samples were obtained.

The observation of a $KAlSi_3O_8$-rich lath-shaped crystal in a modulated glassy matrix at ≈ 850 °C may be significant since this temperature lies in the stable one-phase crystalline region above the predicted coherent solvi at the bulk composition examined. It is suggested that the $KAlSi_3O_8$–$NaAlSi_3O_8$ system may, therefore, have a metastable liquid plus crystals field above a stable miscibility gap similar to the amorphous SiO_2–Al_2O_3 system in which a metastable liquid plus crystals field exists above a metastable miscibility gap but in a stable two-phase crystalline field (Jantzen and Herman, 1979). Some supportive evidence comes from gel preparations where a similar phenomena, i.e. crystallization of a K-rich composition in a gel matrix, occurs at temperatures and compositions corresponding to a stable one-phase crystalline field (Smith and Parsons, 1974; Parsons, 1978).

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Zinc- and manganese-bearing chromites and associated grossular from Zimbabwe

ZINC-RICH chromites have been reported from relatively few localities, and some of these have been discredited in the light of modern analytical techniques. Moore (1977), for example, showed by detailed electron microprobe analysis of Donath's original samples that the supposed zinc-rich (up to 2.6%) chromites from the Helgeland area, Norway (Donath, 1931) contain only up to 0.3% ZnO. Moore suggested, therefore, that the Outokumpu deposit of Finland might be a unique location for zinc-rich chromites, and emphasized that a very unusual geochemical environment must have been necessary for their formation.

We report here the occurrence of chromites with up to 4.3% ZnO in a 'nephrite' sample (BM 1961, 404) from the Mashaba Chromite Mine, Rhodesia, during a routine investigation of the amphibole. The mine, in Archaean Basement rocks, is in a small serpentine body, part of the predominantly ultramafic Mashaba layered complex. The complex is thought to have been formed by multiple intrusion, with the oldest, most ultramafic pulse at the top (Wilson, 1968). The serpentines appear to have been derived almost entirely from the dunites, peridotites, and harzburgites by the action of hydrothermal solutions after consolidation. The 'nephrites', however, occur 'as masses enclosed in . . . aplite which appear to have been derived from original xenoliths of serpentinised dunite by interaction with the intruding granitic magma' (Wilson, 1968).

X-ray scanning photographs obtained with the microprobe (fig. 1) show the distribution of some elements in the chromite and the presence of a fringing reaction mineral which is an unusual chromium- and manganese-bearing grossular. The chromites are markedly zoned, and the irregular and diffuse boundaries between areas of different composition suggest that the zoning is a secondary, metasomatic, feature rather than a primary one.

The traverse (fig. 2) shows that magnesium has been replaced by Mn^{2+}, Fe^{2+}, and Zn^{2+}. Each of the 23 points represents a nine-element analysis performed on a Cambridge Instruments wavelength-dispersive Microscan 9 microprobe. From the diagram it can be seen that Mn replacement has penetrated a greater distance into the crystal than Zn replacement, implying different rates of diffusion.

This type of zoning is in marked contrast to that of the Outokumpu chromites, where sharp-bounded, sometimes oscillatory, primary zoning