A comparison of gel and glass starting materials for phase equilibrium studies

G. M. BIGGAR AND M. J. O'HARA

Grant Institute of Geology, University of Edinburgh, West Mains Road, Edinburgh 9

SUMMARY. A method of preparing compositions suitable for phase equilibrium studies in systems containing $CaO-MgO-Al_2O_3-SiO_2-Fe-O_2-Na_2O$ employing a gelling technique is described. The subsolidus assemblages obtained from the recrystallization of some of these gels and from the re-crystallization of devitrified glasses of the same composition are compared. It is not yet clear whether either starting material has any advantage as the gels may retain early formed metastable phases and the glasses may fail to nucleate stable phases.

THE provision of homogeneous bulk compositions of the maximum purity is a pre-requisite for accurate determinations of phase equilibria in silicate systems. As the samples taken for experiments are often small (40 mg) or extremely small (5 mg) in high-pressure experiments, it is necessary for the bulk preparation to be homogeneous on a scale such that sampling errors will be avoided. Two methods have been adopted in the past to obtain this order of homogeneity, the first involves weighing of the oxides or carbonates, mixing, melting several times with intermediate quenching, crushing, and grinding, to yield a homogeneous glass, and the second involves titrating nitrate solutions, precipitating gelatinous hydroxides with ammonia, evaporating down and calcining to remove nitrates. Known briefly as glassing and gelling techniques respectively it is not yet clear if either has a particular advantage and no comparative work has been published.

The techniques used to make gel compositions are described and the first results using these gels to determine phase equilibria have shown that some subsolidus 'equilibria' are not the same as the 'equilibria' observed in glass starting materials. The problems of obtaining equilibrium from both types of starting material are con-sidered, although no universal preference for one form or the other can yet be advo-cated.

Preparation of gel compositions. The method of preparation adopted differs from that of Hamilton and Henderson, 1968. Compositions in systems containing CaO, MgO, Al_2O_3, SiO_2, $Fe-O_2$, Na_2O were prepared by mixing the required weights of standard solutions of calcium, magnesium, aluminium, sodium, and ferric nitrates. Sufficient ethanol was added to ensure complete miscibility with the required weight of tetraethyl orthosilicate (TEOS) used as a source of silica. The mixture was gelled by the addition of concentrated ammonia, which precipitates first the iron and alu-minium hydroxides followed by magnesium hydroxide as gelatinous products in which the calcium, sodium, and silica (TEOS) are distributed. Slow additions of ammonia were not satisfactory as clots of iron and aluminium hydroxides formed that

were not broken up by mechanical agitation but a rapid addition of excess ammonia produced a thick gel and prevented differentiation. The TEOS was hydrolyzed over sixteen hours by the excess ammonia. The method was not suitable in the absence of iron and magnesium and aluminium and the problem of sodium and calcium silicate gels is not dealt with in this paper. After drying gels were roasted at 900 °C and ground to give a fine-grained, partially crystalline product.

The nitrate solutions of magnesium and aluminium were prepared at concentrations safely below the solubility of the nitrates at room temperature. Calcium and ferric nitrates were prepared at similar concentrations for convenience and sodium nitrate solution was prepared dilute because the soda additions required for the particular series of compositions were small.

TABLE I. *Materials used*

Material	Quality	Final solution strengths (approx.)	
		% HNO_3	% oxide
$CaCO_3$	AnalaR, powder dried at 450 °C	2	8
Mg	Spectrographically pure crystals	5	8
Al	99·99 %, dust	20	4
Fe	99·995 %, 'sponge' ex desiccator	20	9
Na_2CO_3	AnalaR, powder dried at 450 °C	1	1

Details of the starting materials and solution strengths appear in table I. In each case the starting material and some de-ionized water were cooled in an ice bath and a capillary drip feed of 45% AnalaR nitric acid added. After violent reactions had ceased some solutions, notably iron and aluminium, required digestion at 70 to 90 °C for 48 hours to achieve complete solution. The solutions were made up in volumetric flasks although it was found more convenient to weigh the standard solutions and make up the mixtures on a weight basis. Burettes were used and the readings noted as a second check on the weighings.

A 10-gm batch of each composition was made by weighing solutions into a 500 ml polythene container with an air-tight lid, the volumes added being noted. Ethanol (40 ml) was added followed by a weighed quantity of TEOS and after thorough mixing an excess of 0·88 NH_4OH was added and a thick gel formed. The airtight lid was quickly fitted and the gel left at least overnight to achieve complete hydrolysis of the TEOS.

The gel was transferred to a 250-ml glass beaker using mixed ethanol–water wash liquid, and dried for 2–4 days at 75 °C. The dry gel was slowly heated to 200 °C, driving off much of the ammonium nitrate, and then heated for two hours at 300 °C, and a further two hours at 500 °C. After transfer of the gel to a Palau basin the removal of volatiles and nitrates was completed in two hours at 900 °C and the yield weighed. The sample was ground for 10 min in an amalgamator and transferred to a platinum crucible and heated in air at a temperature below the beginning of melting for up to 48 hours to produce a partially crystalline product. The crystalline assemblage over much of the compositional range studied frequently contained metastable pyroxene, melilite, and monticellite phases.

For iron-free compositions a recovery of 9·97–10·01 gm was regarded as acceptable. The metal nitrate solutions each yielded 9·97–10·01 gm of the oxide when treated in the manner described. Gels containing iron have yields dependent on the oxidation state of the iron. The yield of SiO_2 from TEOS was determined from each batch, values of 99·5–99·7 % of the

theoretical value being recorded. A correction factor was used in calculating the required addition of TEOS.

Each sample made up was thought to contain the desired amount of each component to the nearest 0·1 % of total charge. One sample was analysed by Dr. E. L. P. Mercy with the following result (values in parentheses are those to which the gel had been made) CaO 19·22 % (19·36 %), MgO 12·80 % (12·76 %), Al_2O_3 6·08 % (5·87 %), SiO_2 61·81 % (62·01 %), Na_2O less than 80 ppm (nil), Fe less than 130 ppm (nil). In view of the uncertainties of silicate analysis this measure of agreement was taken as satisfactory. Soda was determined on six nominally soda-free samples by M. J. Saunders and the values ranged from 150 to 290 ppm. This soda content could be reduced by using P.T.F.E. instead of glass beakers.

The nature of gels and glasses. To provide glass samples for comparison portions of some gels were totally fused, quenched to a glass, and subsequently devitrified at temperatures approximately the same as the original gels had been crystallized. Although of the same chemical composition the gels and glasses were, sometimes, distinct with respect to phases present and texture, and a general description of each type of material is necessary.

The gels, in the composition ranges studied to date, started to crystallize at about 900 °C and X-ray diffraction patterns had a few broad peaks identifiable, in the limited cases studied, as melilite and diopside. At 1150 °C the gels were a mass of minute crystals rarely larger than 1 μ and the X-ray diffraction pattern was more intense but the peaks still ragged or broad. At increasing temperatures the crystals grew but were less than 10 μ even when the gel was held for 30 days at temperatures just below its beginning of melting provided this was lower than about 1300 °C. With compositions that melted at increasingly higher temperatures crystal sizes in the subsolidus increased gradually to 20 μ. Some gels that melt close to 1490 °C developed very coarse textures with crystals as large as 50 μ just below the solidus.

Devitrified glasses commonly contained fibrous or strained crystal fragments, often very large, 50 μ, and composed of a predominant phase with inclusions that were sometimes identifiable as other phases and that were sometimes thought to be glass that had failed to crystallize. The rapid crystallization that occurs when glasses are devitrified commonly yields a metastable range of solid solutions and a limited number of phases. For these reasons the devitrified glasses are commonly recrystallized for long periods at high temperatures. At temperatures below 1300 °C prolonged crystallization resulted in the loss of some of the strained texture and many of the inclusions but the large crystals were preserved although presumably recrystallized and crystals of other phases grew. Compositions that recrystallized at higher temperatures up to 1490 °C lost much or all of the texture derived from the devitrification process and the products were indistinguishable from those derived from the gel. Both gel and glass tend to lose inherited structures and textures at high temperature.

Proof that equilibrium existed in a particular charge and was preserved during quenching can never be absolute and textural differences do not represent disequilibrium provided the phases present are identical. Unfortunately several discrepancies in subsolidus assemblages have become apparent between recent results using gels and published work in which glasses were used and an investigation of gel and glass charges was initiated.

The results are from a scattered variety of compositions in the system CaO–MgO–Al_2O_3–SiO_2 (CMAS). Samples of gel and glass were maintained in platinum capsules as two of a bunch of twelve capsules for periods of 27–30 days unless otherwise mentioned and were thus subject to the same conditions of time and temperature. Differences in the results must be ascribed to the inherited features of the gel and devitrified glass starting materials. All X-ray results were obtained with Cu-$K\alpha$ radiation.

The molar composition

$$3CaO.2{\cdot}75MgO.Al_2O_3.5SiO_2.$$

An X-ray diffraction study was made of a gel and a devitrified glass of this composition. The gel was prepared by heating at 1150 °C for one day. Charges of this were subsequently crystal-lized for at least 27 days at 1199 °C and 1224 °C. A further charge was melted at 1400 °C, quenched, and the resulting glass devitrified at 1150 °C for half an hour. This devitrified glass was also recrystallized for at least 27 days at 1199 °C and 1224 °C. In all charges a diopside solid solution was the predominant phase but a constant feature of the diffraction patterns was the variation of the diopside peaks from charges derived from gel and glass starting materials and this is most strikingly illustrated for the peaks between 36·0° and 34·9° 2θ (fig. 1).

Crystallization of phases other than diopside is adequately illustrated in fig. 2. The gel at 1150 °C (fig. 2A) contains abundant melilite (peaks at 36·4°, 37·3°, 37·6°) but at 1199 °C some of the melilite has recrystallized and a spinel peak at 36·8° is clear. At 1224 °C the spinel peak pre-dominates (although there is also a melilite peak at 36·8° it is of approximately the same intensity as the melilite peak at 37·6° and subtraction of this still leaves an intense spinel peak).

FIG. 1. Diopside diffraction peaks from charges of the composition

$$3CaO.2{\cdot}75MgO.Al_2O_3.5SiO_2$$

maintained at 1224 °C for 28 days. The starting materials used were: A, devitrified glass, and B, gel.

The assemblage is diopside, melilite, spinel, and a trace of forsterite (identified from other parts of the diffraction pattern). Relative to the results at 1224 °C it appears that the crystallization of spinel is not complete at 1199 °C and there must be speculation as to whether the result at 1224 °C represents perfect equilibrium. The composition was found to melt at 1230 °C$\pm$1·5 and 1224 °C represents the maximum practical temperature of crystallization.

The crystallization of the glass (fig. 2B) shows little change other than an increase in resolution with increasing temperature and in the final assemblage at 1224 °C
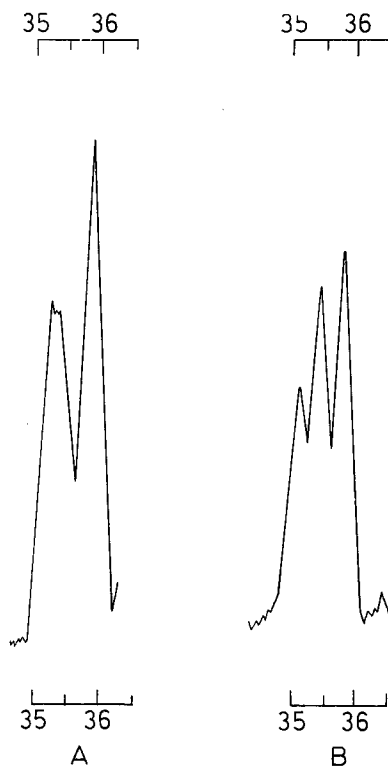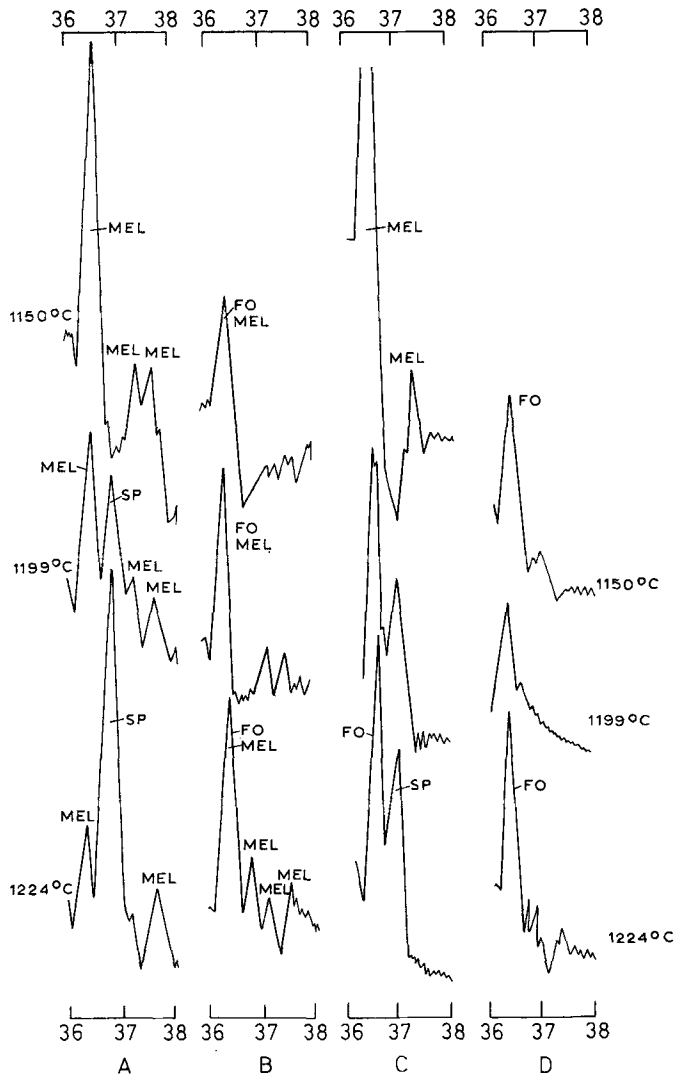
FIG. 2. Partial diffraction patterns to illustrate the crystallization behaviour of gels and devitrified glasses of the same composition. Different crystalline assemblages result after 28 days at 1224 °C. The starting materials used were: A, gel of composition $3CaO.2·75MgO.Al_2O_3.5SiO_2$; B, devitrified glass of the same composition; C, gel of composition $3CaO.3MgO.Al_2O_3.6SiO_2$; and D, devitrified glass of the same composition.

forsterite and melilite are present and although there is a small peak at 36·8° in the spinel position its intensity is just that expected for melilite. The final assemblage is diopside, forsterite, and melilite and other parts of the diffraction pattern indicate that anorthite may be present in trace amounts.

The molar composition $3CaO.3MgO.Al_2O_3.6SiO_2$. Gel and devitrified glass starting materials were prepared as indicated for the previous composition and diopside was present in all subsolidus charges. The crystallization of the gel is illustrated in fig. 2C and is an example of a phenomenon that occurs frequently during gel crystallization in which a phase, in this case melilite, is initially abundant or predominant at 1150 °C but completely reacts at higher crystallization temperatures. Melilite may be present at 1199 °C but the final assemblage at 1224 °C is diopside (not illustrated), anorthite (not illustrated), forsterite with a peak at 36·4°, and spinel with a peak at 36·8°.

Devitrified glass of the same composition changed little with temperature but the final assemblage was devoid of spinel, containing diopside, anorthite, and forsterite.

In the cases of both the above compositions there is evidence (O'Hara and Biggar, in press) that the gel results represent equilibrium but it is sufficient for this paper that demonstrably different subsolidus assemblages are obtained from different starting materials without entering into arguments about stabilities.

The molar composition $CaMgSi_2O_6$ 9·0, $CaAl_2SiO_6$ 1·0. Crystallized gel and devitrified glass charges prepared as previously and maintained at 1224 °C gave diffraction patterns with differences in the angular positions and in the intensities of the pyroxene peaks. Melilite was detected in the diffraction patterns of charges derived from gel starting materials, but was absent from the diffraction pattern of charges derived from devitrified glass although an optical examination revealed the presence of a trace of melilite.

The molar composition diopside 9·5, *alumina* 0·5. Gel and devitrified glass charges of this composition maintained at 1224 °C contained melilite although it was present in different amounts and as for the previous composition the relative positions and intensities of the pyroxene peaks were different.

These observations imply that the amount of, and the composition of, the diopsidic pyroxene solid solution differs in charges of the same composition. The extent of the stability range of diopside solid solutions in the system $CaO-MgO-Al_2O_3-SiO_2$ is a considerable problem (O'Hara and Schairer, 1963; Hytönen and Schairer, 1961; Sakata, 1957) and the differences noted above merely add to this problem and imply that equilibrium is not obtainable in 30 days.

Compositions on the diopside–pyrope join. Gel and devitrified glass starting materials were prepared as previously for the molar composition diopside 9·0, pyrope 1·0. After 28 days at 1224 °C both starting materials had recrystallized to anorthite, forsterite, and a diopside. The value of $\Delta(2\theta_{310}-2\theta_{221})$ for the diopside from the glass charge was 0·56, identical with the value reported by O'Hara and Schairer, and the value from the gel charge was 0·54.

A gel starting material of molar composition diopside 7·5, pyrope 2·5 recrystallized to anorthite, forsterite, enstatite, and a diopside for which $\Delta(2\theta_{310}-2\theta_{221})$ was 0·54 at 1203 °C and 0·58 at 1232 °C. Compositions that should contain the same pyroxene at equilibrium were reported by O'Hara and Schairer, 1961, to have values in excess of 0·80° at 1050° and a value of 0·61° at 1235 °C. Either the gel or glass results (at

1232 °C and 1235 °C, respectively) may represent the equilibrium diopside or both may be approaching equilibrium from different sides. As the temperature of crystallization cannot be increased because melting commences at 1238° periods in excess of 30 days would be required in future studies. The results, nevertheless, indicate a fair measure of agreement between gel and glass starting materials. Similar studies on the *join diopside–enstatite* at crystallization temperatures of 1367 °C confirm in all details the work of Boyd and Schairer, 1964.

Monticellite solid solutions. Gels with compositions in the range of monticellite solid solutions from pure monticellite up to 20 mol. % forsterite failed to equilibrate after 15 days at 1474 °C and traces of periclase were present in all charges. In an attempt to glass these gels at 1720 °C the product was periclase plus a devitrified matrix composed essentially of a monticellite solid solution. Through part of the range of compositions studied this devitrified material when subsequently held at 1477 °C gave products different from those obtained from gels. The gels gave monticellite solid solution, merwinite, and periclase and the devitrified glass gave monticellite solid solution and periclase. In this case it is tempting to describe the merwinite as a phase formed early during the crystallization of the gel and one that had failed to react completely. There is also the possibility that the devitrified glass failed to nucleate merwinite.

Discussion. The advantage of gels appears to lie in their small crystal size as the maximum diffusion path to release an ion metastably held in a lattice is often less than 10 μ, but they have the disadvantage that during preparation and crystallization many phases nucleate metastably and fail to react or be resorbed. In the composition ranges studied to date, the phases that commonly form metastably are diopside, melilite, monticellite, merwinite, and anorthite and cases are known where each of these is totally lost from the final assemblage. Devitrified glasses form large crystals, which may be capable of retaining ions metastably and with a small excess of free energy, and if ions are so held they may not be available in sufficient numbers to nucleate another phase.

Other cases will undoubtedly be found in which the gel yields more phases than the glass and criteria to test which of the assemblages is stable may not always be obtainable. It is of some interest to speculate on cases where glass may devitrify to a metastable range of solid solution that will not undergo further reaction to nucleate stable phases or will do so very slowly. The diopsidic pyroxene problem has been mentioned and garnet solid solution would seem to be a possible case but it is likely that each join or system will behave uniquely, although the presence of particular components, for example alumina, may influence the measure of agreement obtained from different starting materials.

Because glasses have been used for sixty years and the results widely accepted there will be a certain prejudice in favour of such results. In view of the problems of reaction rates in the subsolidus, even 5 °C below the solidus, the gels (and their results where different) provide an alternative and it is too early yet to condemn either form of starting material. Intimate physical mixtures of gels and glasses may yet be used combined with runs of extreme duration. The increased purity of chemicals over the last

sixty years reduces the amount of 'fortuitous' liquid below the solidus of the major components and perhaps increases the problems of obtaining equilibrium.

The majority of gel and glass results, at least in the system $CaO-MgO-Al_2O_3-SiO_2$, agree well (only differences have been described in this paper) with respect to the number of phases present. There are, however, many cases in which solid solution compositions have not been investigated and it is these that may prove to differ.

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