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The preparation of starting mixes for mineral syntheses by a freeze-dry technique

TONY A. FINNERTY,[1] G. A. WAYCHUNAS AND WARREN M. THOMAS

Department of Geology, University of California
Los Angeles, California 90024

Abstract

A technique to improve the homogeneity and reactivity of starting materials for mineral syntheses has been developed. Aqueous solutions of any major and many minor elements of geologic importance are mixed in the correct proportions and frozen by spraying as fine droplets into stirred liquid nitrogen. The resulting material is dried under vacuum and subsequently fired into an intimately-mixed oxide powder.

Synthetic forsterite was crystallized from freeze-dried mixes at 800°C under hydrothermal conditions in 10 percent of the time required when a mix prepared by the gel technique is used. Homogeneous ferroan periclases (magnesiowüstites) were formed from freeze-dried mixtures at 1000°C in 25 percent of the time required when using mechanically-mixed ground-oxide starting materials. Low structural states in albite were achieved by hydrothermal crystallization as quickly from freeze-dried mixtures as from gel mixtures.

The compatibility of water-soluble compounds of Na, K, Ca, Mg, Al, Si, Fe, Mn, Co, Ni, Zn, Ge, Sr and Ba has been investigated, and the freeze-dry method has been successfully applied to feldspar, olivine, pyroxene, and oxide mineral syntheses.

Introduction

In many types of experimental mineralogic or petrologic investigations it is desirable to start with materials of the highest possible homogeneity. Uniformity in composition is especially important in order-disorder studies, in which the phenomena measured can be due to compositional variations on a scale of several unit cells. Homogeneity is particularly difficult to achieve in preparation of trace-element doped mixtures. Techniques commonly used in silicate mix preparation have been reviewed by Edgar (1973). All have disadvantages, either in achieving effective dispersal of minor components, in possible loss of volatile components such as Na during high-temperature decomposition, or in possible minor-element contamination during grinding. A technique based on rapid freezing of aqueous solutions, followed by removal of water by sublimation under vacuum, was applied by Schnettler *et al.* (1967) to silica-free solutions of salts. A similar approach is applicable to silicate systems. The silica component is mixed as an aqueous colloidal suspension that has been stabilized against the precipitation or gellation that usually results upon addition of electrolytes. The freeze-dry technique described here has several important advantages over other methods.

(1) Mixing of all elements in aqueous solution ensures initial homogenous distribution. Inasmuch as freezing of the solution is instantaneous, relative to diffusion processes, and because only solid-state diffusion can operate in the mix during subsequent freeze-drying, the initial homogeneity is retained in the freeze-dried solid.

(2) With the use of organic anions, the mixes may be fired at temperatures sufficiently low to prevent loss of volatile elements such as Na, and to minimize recrystallization.

(3) No mechanical attrition of the mix is required at any stage, eliminating contamination from the apparatus used for grinding.

The method

An aqueous sol of silica, such as ammonia-stabilized Ludox AS (E. I. duPont de Nemours Company), is diluted to approximately 1 molar in SiO_2. The small concentration of Na^+ present is reduced to less than 0.02 wt % relative to SiO_2 by exchange with

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[1] Now at Geophysical Laboratory, 2801 Upton Street, Washington, D. C. 20008.

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NH_4^+ in an exchange column, and the silica content determined gravimetrically.

Aqueous solutions of the desired elements at concentrations up to about 1.0 molar are prepared by dissolving the appropriate salts of carboxylic acids in distilled water, or the metals, oxides, or hydroxides in solutions of the carboxylic acids. The specific organic anions used should meet several requirements. First, all cations must form soluble salts with the particular anions. Second, the decomposition temperatures of the selected salts must be lower than their respective melting points, so that partial melting, with loss of homogeneity, does not accompany firing. In addition, for ease of handling, the salts should not be deliquescent and preferably not hygroscopic, and of low toxicity. Commercially available reagent-grade salts of formic, acetic, propionic, oxalic, and citric acids have been used successfully.

Aqueous mixtures containing combinations of these salts are stable for at least one month, with the exception of those containing both Al and the oxalate anion, which form a precipitate of aluminum oxalate in about 48 hours, and those containing both Ca and the citrate anion, which form a precipitate of calcium citrate in about 12 hours. Salts of Fe^{3+} do not freeze-dry properly, and Fe^{2+} salts must be used. Solutions of Fe^{2+} slowly oxidize, and become useless in about one month.

The aqueous solution is frozen rapidly by squirting through a fine capillary tube from a pressurized vessel into continuously stirred liquid nitrogen. A suitable vessel may be constructed from a 500 ml polyethylene wash bottle reinforced with strong tape, by fitting a hose to the lid through which compressed air or nitrogen at 1.2 to 2.0 atm pressure may be introduced, and by fitting a hose and glass capillary to the spout through which solution may be squirted. After excess liquid nitrogen has been allowed to vaporize, the frozen droplets are placed in a laboratory freeze-drier and water is removed by vacuum sublimation.

The organic anions are decomposed in air at relatively low temperatures, *e.g.* 600°C, to give an intimate mixture of oxides. The firing must be done in air, otherwise graphite may form, requiring higher temperatures (around 1000°C) for removal. The final low-density powder, in which the shape of the initial frozen droplets is retained, may be lightly crushed to increase the packing density when loading capsule charges, or compressed into pellets for one-atmosphere furnace synthesis work.

Results

Initial syntheses with the freeze-dry technique used the salts of a variety of organic acids, and resulted in the successful syntheses of forsterite, enstatite, albite, plagioclase, magnetite, wüstite, and ferroan periclase (magnesiowüstite). Forsterite and enstatite mixes were prepared from Ludox and magnesium citrate solution. Trace amounts (5 to 3200 ppm by weight relative to dry oxide) of several elements were added before freeze-drying, using formate solutions of Mn, Co, Ni, Zn, Sr, and Ba, and an oxide solution of Ge. The freeze-dried products were fired at 1000°C in air for one hour. Repeated neutron-activation analysis of 100 mg aliquots showed the resultant powders to be homogenous on a capsule-load scale with respect to trace elements.

Successful syntheses of pure albite and plagioclase containing 10 and 15 mole percent anorthite were obtained from mixes prepared with sodium oxalate, calcium formate, and aluminum formylacetate. Electron microprobe analysis of the individual 1 to 5 μm feldspar grains indicated grain-to-grain compositional homogeneity, and scanning electron photomicrographs showed well-developed crystallinity. The albite, crystallized from nonstoichiometric mixes of the type described by Martin (1969) under experimental conditions similar to his, yielded comparable values of $\Delta 2\Theta(131-1\bar{3}1)$ indicating attainment of low structural states.

Ferroan periclase mixes (2, 5, and 10 mole percent Wu) were prepared from iron and magnesium citrate solutions. Solubilities of the cations were enhanced by addition of NH_4OH. After firing the freeze-dried mixtures at 1000°C for one hour to remove NH_3 and the organic anions, the $MgFe_2O_4$ regions were so small within the MgO crystallites that superparamagnetic spectral features were obtained in Mössbauer analyses of these products. Individual $MgFe_2O_4$ particles were estimated to be on the order of 100A in diameter, consistent with the data of Collins *et al.* (1967) and Gonser *et al.* (1968). Mixes prepared by grinding of Fe_2O_3 and MgO under acetone for one hour in an agate mortar and heat-treated in the same fashion did not show superparamagnetic effects, even at lowest Fe_2O_3 concentration levels, suggesting mixing on a much coarser scale. In comparison, Schnettler *et al.* (1967) observed particle size of less than 200A in Al_2O_3 formed by calcining freeze-dried $Al_2(SO_4)_3$ for two hours at 1000°C.

The rate of formation of ferroan periclase from

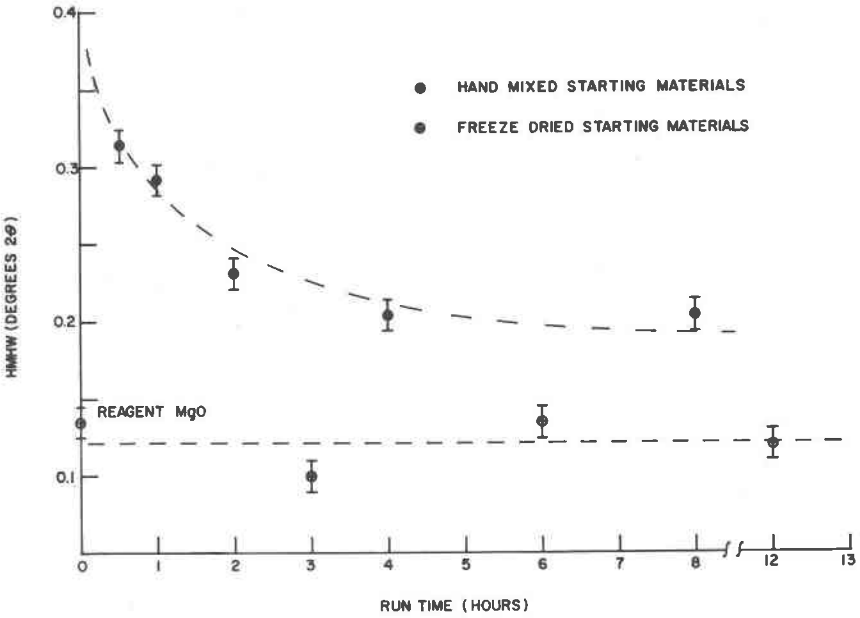

Fig. 1. Half-maximum half-width (HMHW) of 422 reflection (Cu$K\alpha$ radiation) for synthetic ferroan periclase composition ($Fe_{0.2}Mg_{0.8}$) as a function of run duration. The datum at zero run time shows HMHW for unfired reagent-grade MgO (periclase).

oxide mixtures of Fe and Mg in proportion 1:4 was studied at 1000°C and $f(O_2) = 10^{-11}$ atm. The width of the 422 X-ray powder diffraction line was much narrower, for equivalent heat-treatment durations, for products derived from freeze-dried mixtures than for those made by mechanical grinding of reagent-grade Fe_2O_3 + MgO for 30 minutes under acetone (Fig. 1), despite similar grain sizes. Only regrinding and a second heat treatment under identical conditions produced line widths (and hence inferred homogeneity) comparable to those observed for products of freeze-dried mixtures. Microscopic inspection showed color inhomogeneities in products obtained from all mechanically-ground mixes, whereas those prepared from freeze-dried mixes were uniformly colored.

A freeze-dried fired mixture of composition Mg_2SiO_4 was crystallized to pure forsterite in the presence of water at 900°C and 250 bars in less than one day. The crystallized product was characterized by grain size of less than 1 μm to 5 μm and sharply defined powder X-ray diffraction peaks. No other phases were detected by powder X-ray diffraction or optical examination. In contrast, mixes of the same composition, but formed by the gel technique, require up to two weeks at 800°C and 1400 bars in the presence of water before the unstable reaction products, enstatite and periclase, give way to forsterite (A. L. Boettcher, University of California, Los Angeles, personal communication, 1976).

Conclusions

The freeze-dry method results in homogeneous mixtures for silicate and oxide compositions. These mixtures appear to crystallize to stable crystalline phases more rapidly than those made by conventional techniques, although one must always be aware of possible formation of metastable phases from high-energy starting mixes. Contamination from grinding may be entirely avoided by using the freeze-dry method.

The techniques listed above have been developed for each new composition as the need in the laboratory arose. A systematic search for a compatible solution chemistry for all cations of geologic interest, for use on a routine basis, has been initiated. Preliminary results indicate that solution chemistry based on mixed salts of formic and citric acids may be satisfactory.

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