

pling errors. The method is rapid and has proved very useful in quickly evaluating the rock phosphate potentialities of an area economically. Several thousand samples were studied by this method.

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GEL PREPARATION OF STARTING MATERIALS IN
IRON-CONTAINING SILICATE SYSTEMS

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ABSTRACT

A solution of ferric benzoate in N,N-dimethylformamide may be used as a source of iron in the gel method of preparing starting materials in the system MgO-SiO₂-Fe-O.

INTRODUCTION

Recently Luth and Ingamells (1965) published an excellent summary of the "gel" method of preparing starting materials for phase equilibrium and thermodynamic studies on silicate systems at high temperatures and

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pressures. First described by Roy (1956), the method consists of mixing ethanolic solutions of metal nitrates, together with silica in the form of tetraethylorthosilicate or ludox (duPont sodium-stabilized silica sol). An excess of water is added, causing the silica to form a gel in a period of a few hours or days. The gel is then dessicated and fired at a high temperature to give a finely-divided, homogeneous and reactive mixture of oxides of precisely known composition.

In their discussion, however, Luth and Ingamells did not include iron oxide, which presents a special problem. An ethanolic solution of ferric nitrate will hydrolyze upon standing, forming a precipitate of basic salts of iron. The amount of nitric acid which must be added to prevent hydrolysis is prohibitive; the resulting ethanol-concentrated nitric acid mixture is potentially explosive.

METHOD

It seemed desirable to find another method of preparing iron-containing gels which would avoid these problems. Required was a ferric (or ferrous) salt which can be fired to give pure iron oxide, and a volatile solvent in which the salt would dissolve and not hydrolyze. The solution must be completely miscible with the ethanolic nitrate solutions of the other metal ions, and must not prevent the formation of a gel by the hydrolysis of tetraethylorthosilicate or ludox. The system decided upon was a solution of ferric benzoate, nominally $\text{Fe}(\text{C}_7\text{H}_5\text{O}_2)_3$ but evidently a mixture of basic salts, in *N, N*-dimethylformamide, $\text{HCON}(\text{CH}_3)_2$. Ferric benzoate is quite soluble in dimethylformamide, at least to the extent of giving 45 mg Fe_2O_3 per ml. The solution which forms is stable indefinitely. The only drawback is that ferric benzoate is available commercially only at rather high cost. Fortunately, however, it is a simple matter to prepare quite pure ferric benzoate by simple precipitation from aqueous solutions.

A number of starting materials have been prepared for thermodynamic studies of the system $\text{MgO}-\text{SiO}_2-\text{Fe}-\text{O}$. The procedure used was essentially that of Luth and Ingamells, but differed from it as follows:

PREPARATION OF FERRIC BENZOATE

Fifty grams of ammonium benzoate are dissolved in 800 ml distilled water. To this solution is added a solution of 50 g ferric nitrate nonahydrate and 1 ml concentrated nitric acid in 80 ml water. The resulting light brown precipitate is filtered by suction and washed once with water. Extensive washing is not necessary, since all by-products are volatile, and will be eliminated when the gel is ignited. After washing, the ferric benzoate is dried at 50°C.

PREPARATION AND STANDARDIZATION OF THE IRON STOCK SOLUTION

The desired amount of ferric benzoate is dissolved in reagent-grade dimethylformamide. For our purposes, a concentration which yielded about 40–45 mg Fe_2O_3 per ml seemed to be optimum. The resulting dark brown solution is filtered through two Whatman No. 42 filter papers until it passes through easily. Standardization is accomplished by igniting a known volume of the solution to Fe_2O_3 and weighing. This is most easily done by adsorbing the solution on ashless filter paper in a crucible, burning off most of the organic material with a bunsen burner, and then igniting in a muffle furnace at 900–950°C.

PREPARATION AND STANDARDIZATION OF OTHER STOCK SOLUTIONS

Tetraethylorthosilicate is used as a source of silica when a sodium-free system is desired. It can be used neat, or as an alcoholic solution. However it is used, it should be standardized in the same way. Standardization is accomplished by precipitation of the silica with aqueous ammonia in the presence of ethanol, evaporating to dryness and firing to constant weight on a Fisher burner.

Magnesium nitrate in absolute ethanol is a convenient source of magnesia; it is best standardized by titration with EDTA.

PREPARATION OF THE GEL MIXTURE

The gel is prepared by pipetting the proper amount of each solution into a crystallizing dish and adding a ten-fold excess of water and 2 or 3 drops of concentrated ammonia. The mixture is placed in a drying oven at 50°C until the tetraethylorthosilicate hydrolyzes and a gel forms. This usually takes 3 to 5 days. If a gel does not form in that time, 10 to 15 drops of 1:40 ammonia may be added to accelerate the process. During the period the mixture is in the oven, the crystallizing dish should be covered with a watch glass to prevent contamination of the mixture and possible evaporation of tetraethylorthosilicate. For mixtures which contain less than 2–3% tetraethylorthosilicate, evaporation of dimethylformamide may result in precipitation of ferric benzoate before gelling occurs. This can be avoided by sealing the crystallization dish closed.

The gel is then desiccated and fired as described by Luth and Ingamells.

One batch of starting material was analyzed for iron, using methods described by Presnall (1966). No ferrous ion was found by titration; virtually all of the iron present in the starting material occurs as ferric ion. A triplicate analysis for total iron gave 59.0 ± 1.1 percent Fe_2O_3 , for a starting material made up to contain 58.98 ± 0.35 percent Fe_2O_3 . No analysis was made for MgO and SiO_2 .

Further indirect confirmation of the accuracy of the gel technique came from weight-loss studies of magnesium iron silicate melts in platinum containers. For samples weighing about 100 mg, the actual loss in weight due to reduction of Fe_2O_3 to FeO and Fe (the latter dissolves in the platinum) agreed within ± 2 mg with a value calculated from an analysis of the final ferric: ferrous ratio of the silicate and the assumed composition of the starting material. In a few cases where agreement was not obtained, there was reason to suspect the accuracy of the iron analysis.

The X-ray diffraction pattern of the starting material is that of ferric oxide, and shows no lines for silica or magnesia, which evidently are not present in a very crystalline form. The Mössbauer spectrum of the material consists of the six-line pattern characteristic of ferric oxide.

No attempt was made to prepare gels yielding ferric oxide and silica together with the oxides of calcium, aluminum, sodium or potassium. It appears to be difficult, if not impossible, to prepare gels yielding only Fe_2O_3 and SiO_2 . The problem is to find a solvent system which will keep the ferric benzoate in solution until the gel has time to form.

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PUMPELLYITE OF DEUTERIC ORIGIN

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ABSTRACT

Pumpellyite occurs as radiating crystals in cavities in altered syenite from the Prospect Intrusion near Sydney, New South Wales, with a variety of other minerals. Optically positive and negative pumpellyite coexist, and the optical properties show no correlation with mineral association. The cavity-filling minerals grew at low temperature and confining pressure.