

## Use of aluminum-amalgam in mineral synthesis at low temperatures and 1 atmosphere total pressure

(Received 19 February 1971)

SOLUTIONS to problems of mineral genesis have traditionally been approached from three general directions. Firstly field studies have revealed certain regularities in mineral parageneses, which in turn give some insight into pressure-temperature conditions within the earth. Eskola's mineral facies technique is the pre-eminent example of this approach. Secondly, experimental studies have in many cases been successful in determining the physiochemical conditions of crystallization of mineral phases. Bowen's work was most influential in this regard. Finally, theoretical (and particularly thermodynamic) methods have been used to delimit mineral stability fields. Garrels' contributions to this approach are well known.

The most difficult of these methods to apply to the study of mineral formation at the earth's surface is undoubtedly the experimental one. Many of the reactions that proceed in surficial deposits are so slow as to render impractical their duplication in the laboratory. This is particularly true of reactions to form those aluminosilicates that are known to be authigenic in the zone of weathering. Generally, in order to synthesise such phases in the laboratory, experimental conditions must be changed appreciably from those that exist at the earth's surface. The most common change is to increase temperature, though doing this makes any application of the results to an interpretation of the earth's surface questionable.

The most common synthesis technique in low temperature, low pressure geochemistry is the aging of silicon and aluminum containing gels, that are often of too great a compositional complexity to permit the ready analysis of results in terms of Gibb's Phase Rule. Thus even for the chemically simple system  $Al_2O_3-H_2O$  there is still no generally accepted phase diagram for earth-surface conditions. Consequently deposits containing gibbsite, boehmite and other phases in this system cannot yet be interpreted unambiguously in terms of conditions of formation. A similar statement could be made concerning virtually all mineral phases that form at the earth's surface and ultimately is the reason why the study of soil genesis is not yet on the same plane of physico-chemical rigor that, for example, igneous and metamorphic petrogenesis are.

The situation would be more hopeful if more direct methods of mineral synthesis were available to the low temperature geochemist. In fact one method has been available at least since 1870 (Chesworth, 1971) though it has been ignored by workers in this field. This employs aluminum amalgam to give aluminum hydroxide by reaction with water. The well known passivity of aluminum is caused by a deposit of hydroxides on the outer surface of the metal and amalgamation with mercury serves to remove this impediment. As an amalgam the aluminum displays its true electropositive character and reacts immediately with cold water. Use of such amalgams is new to geochemistry and is potentially a powerful aid to

solving problems of mineral genesis at low temperatures and pressures. Some illustrative results of the application of this technique are presented here.

### PREPARATION OF THE AMALGAM

The most direct way is to grind aluminum pellets or wire in mercury. This is not a particularly easy method to control or standardize, and ideally it should be performed in an inert atmosphere to prevent the amalgamated aluminum from reacting immediately.

A much more convenient method is to immerse aluminum wire in a dilute (0.1M) solution of mercuric chloride in water for 10 min. Aluminum displaces mercury from the solution and the mercury deposits on the surface of the wire. More aluminum from the wire gradually diffuses into the outer coating of mercury to form the amalgam used in the subsequent experiments. Within 10 min no visible reaction of the aluminum with the water of the solution takes place so that initially the outer coating is quite probably pure or nearly pure mercury. Only later, after a longer period of diffusion does the aluminum concentration in the mercury build up to a level where obvious reaction takes place.

After 10 min the aluminum wire, plated with mercury, is removed from the mercuric chloride solution and washed with distilled water. It is then ready to be placed in a reaction vessel with whatever reaction medium is required.

### SYNTHESIS OF ALUMINUM HYDROXIDES

Aluminum occurs in nature as hydroxide ( $Al(OH)_3$ ) and oxyhydroxide ( $AlOOH$ ) forms, each of which exists in a number of polymorphs. The generally held opinion is that the true hydroxide is the stable form at the surface of the earth (Marshall, 1964, p. 147 and Garrels and Christ, 1965, p. 10), though Kittrick (1969) provides an opposed view.

In the laboratory aluminum amalgam was immersed in several media and a variety of hydroxy forms of aluminum were made. Constant temperatures were maintained by means of a water bath. Experimental results are shown in Table 1 which also includes earlier results from Chesworth (1971). The initial precipitate was predominantly amorphous though even within 3 hr minute anisotropic crystals could be recognized with the polarizing microscope.

It will be noticed that some of the runs were made by reacting the amalgam with the aqueous vapour in equilibrium with reaction solutions. This was an attempt to show that an oxyhydroxide will precipitate in preference to a hydroxide if the chemical potential of water is lowered sufficiently. Experimentally it was accomplished by confining the amalgam to an open glass vial which was placed in a flask containing the reaction solution.

It is noteworthy that diaspore is the only oxyhydroxide

phase that has not been synthesized at 1 atmosphere pressure. This is not surprising since Ervin and Osborn (1951) and Kennedy (1959) indicate that diaspore does not have a low pressure synthesis field.

### CONCLUSION

The amalgamation technique of mineral synthesis reported here promises to be a useful aid to the study of mineral formation under the low temperatures and pres-

Table 1. Conditions and results of synthesis experiments using aluminum-amalgam. Total pressure in all cases is 1 atmosphere. All phases were determined by X-ray diffraction

Reacting Medium	Duration	Temp. (°C)	Products
1 Distilled water	89 hr	25	Bayerite
2 Distilled water	18 hr	51	Bayerite + Pseudoboehmite
3 Distilled water	1 hr	99	Pseudoboehmite
4 Vapour in equilibrium with 0.5M NaCl solution	672 hr	25	Bayerite + Pseudoboehmite
5 Vapour in equilibrium with 0.1M Na <sub>2</sub> CO <sub>3</sub> solution	120 hr	44	Boehmite
6 2M NaOH solution	408 hr	30	Boehmite + Nordstrandite
7 Conc. NH <sub>4</sub> OH	48 hr	30	Nordstrandite
8 Conc. NH <sub>4</sub> OH	672 hr	40	Gibbsite
9 0.1M Na <sub>2</sub> CO <sub>3</sub> solution	792 hr	25	Bayerite
10 0.5M Na <sub>2</sub> CO <sub>3</sub> solution	190 hr	25	Bayerite + Dawsonite
11 1M Na <sub>2</sub> CO <sub>3</sub> solution	354 hr	25	Dawsonite
12 Na <sub>2</sub> SiO <sub>3</sub> solution	10 weeks	30	Faujasite
13 Ethyl orthosilicate	3 months	25	Amorphous + less than 1% of anisotropic material.

### SYNTHESIS OF A BASIC ALUMINO-CARBONATE

Dawsonite (NaAlCO<sub>3</sub>(OH)<sub>2</sub>) occurs in a variety of earth surface of near surface deposits. For example, it is found in saline soils of the Olduvai gorge, in deposits of the Sydney Basin, and in the Green River formation of Colorado (Hay, 1963; Loughnan and See, 1967; Goldberry and Loughnan, 1970; Smith and Milton, 1966).

An aluminum amalgam was used to form dawsonite by reaction with sodium carbonate solution at 25°C and 1 atmosphere total pressure. Initial results would indicate that a concentration of at least 0.5 M Na<sub>2</sub>CO<sub>3</sub> is required before dawsonite will form at this temperature.

### SYNTHESIS OF AN ALUMINO-SILICATE

The principal aluminosilicates that form at or near the earth's surface are the clay minerals and zeolites. Other authigenic species have been found (including feldspars) but these two remain volumetrically the most important.

Two reaction media were tried in an attempt to make an aluminosilicate. First, aluminum amalgam was immersed in ethyl orthosilicate, and secondly a charge of amalgam was placed in a 1M solution of sodium metasilicate. Both experiments were maintained at 25°C and 1 atmosphere total pressure.

A white precipitate accumulated in the ethyl orthosilicate but even after a period of 3 months it was amorphous to X-rays. It did, however, after this length of time contain a small percentage of grains that examination by optical microscopy revealed to be anisotropic and thus presumably crystalline. It has not however been possible to determine so far what this species is.

The sodium metasilicate solution also produced an amorphous precipitate to begin with but within 10 weeks this aged to a form of faujasite.

sure that prevail at the surface of the earth. It promises to extend further the techniques of experimental petrology to such deposits of the zone of weathering as soils and other sediments. Such techniques have already proved their usefulness to the understanding of mineral genesis in zones of igneous and metamorphic petrogenesis.

*Acknowledgments*—For help in the laboratory I would like to thank George Patton and Katharine LaHay.

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