PHASE EQUILIBRIUM STUDIES BEARING ON GENETIC LINKS BETWEEN ALKALINE AND SUBALKALINE MAGMAS, WITH SPECIAL REFERENCE TO THE LIMESTONE ASSIMILATION HYPOTHESIS

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ABSTRACT

The limestone assimilation hypothesis for forming alkaline, magmas from subakaline magmas is based on circumstantial petrological evidence. It requires (1) desilication, (2) alkali transfer by CO_2 and H_2O. Experimental results indicate that limestone assimilation causes crystallization, and that the thermal barrier between granitic and feldspathoidal liquids persists in the presence of H_2O and CO_2 to high pressures. Desilication of SiO_2–oversaturated magmas remains an unlikely process. Results in silicate-salt-volatile systems suggest that alkali transfer is only effective from liquids already enriched in alkalis. In general, experimental studies have failed to validate proposed genetic links between alkaline and subalkaline magmas through assimilation.

INTRODUCTION

In 1910, Daly concluded that alkaline igneous rocks must be derived from subalkaline magma, and he proposed that the process involved was limestone assimilation. From the very beginning, the idea has been avidly supported by ardent advocates and vigorously contested by sceptical adversaries. Although the development of petrology has been noted for its controversies, there are few that have lasted for so long. The two opposing views persist into the sixth decade. Schuiling (1964*b*) considered the limestone theory to be "the only theory which really has been demonstrated in the field with a degree of certainty, scarcely ever achieved by petrological observation." On the other hand, Turner & Verhoogen (1960, p. 396) concluded that "Several decades of investigation have failed to confirm the efficacy of limestone assimilation as a significant factor in the development of nepheline-syenite magma." The fact that 50 years of field study and detailed petrology have not resolved this conflict makes it reasonable to conclude that the petrological evidence is circumstantial, and not definitive. This is one of the problems of petrological evidence in general.

In a chapter contributed to Sørensen's (1970) book on alkaline rocks, Wyllie traced certain aspects of his controversy through successive time periods, and Table I summarizes the history of the experimental approach to the problem. The selected time periods of 25, 20, and 15 years do appear to represent rather distinct stages. The first period, 1910–1935, is the period during which the stimulating hypothesis was launched, and petrologists took sides in full battle array. The second period, 1936–1955, was one during which the lines of attack and defense became deeply entrenched, and experimental studies of silicate systems revealed thermal barriers on the liquidi of silicate systems, rearing their ugly humps between subalkaline and alkaline liquids. During the third period, 1956–1970, the widespread discovery of carbonatites disrupted the field evidence for limestone assimilation, and additional experimental data made it even more difficult to support the hypothesis. Daly had great hopes that experimental studies would provide a physico-chemical basis for his theory, but the following outline of experimental data suggests that limestone assimilation is not a significant process in the generation of feldspathoidal magmas. However, negative experimental evidence does not prove that a postulated process can not occur under natural conditions perhaps not achieved in the laboratory.

TABLE 1. OUTLINE HISTORY OF THE EXPERIMENTAL APPROACH TO THE PROBLEM OF LIMESTONE SYNTEXIS

PERIOD	EXPERIMENTAL APPROACHES
1910–1935	Pleas for experimental support Dry silicate systems Dry fusion of igneous rock-sediment mixtures
1936–1955	Thermal barrier established on feldspar join between liquids over- and under- saturated with respect to SiO_2 Silicate–H_2O systems
1955–1970	Silicate–CO_2 systems CaO–CO_2–H_2O and the nature of carbonites Silicate–carbonate systems : liquidus studies Silicate–carbonate systems : subsolidus reactions

THE LIMESTONE ASSIMILATION HYPOTHESIS

Daly maintained that the majority of feldspathoidal rock types are produced from a parent subalkaline magma, which may range in composition from basaltic to granitic, by the following processes :

(1) Desilication of the subalkaline magma by reaction with partly dissociated carbonate,

(2) Gravitative differentiation of the desilicated magma, fluxed by the limestone or dolomite,

(3) Upward transfer of alkalies by resurgent or juvenile CO_2.

These processes have been discussed in detail by Daly (1910, 1933) and Shand (1930).

With the later realization that many of the limestones associated with alkaline rocks were carbonatites, petrologists such as von Eckermann (1948), Holmes (1950), and Dawson (1966, 1967) reversed the limestone assimilation hypothesis and developed schemes whereby the assimilation of sialic crustal material by a carbonatite magma could produce a series of alkaline rocks. Schuiling (1964*a*) used the term sial-syntexis for this type of reaction and claimed that there was no physico-chemical distinction between the sial-syntexis and limestone-syntexis theories.

EARLY EXPERIMENTAL STUDIES

Perhaps the clearest exposition of experimentally-based views opposing the limestone assimilation hypothesis during the period 1910–1935 is the paper by Bowen in 1922 on the behavior of inclusions in igneous magmas. He used as models the paths of crystallization known for liquids in simple silicate systems at 1 atmosphere pressure. He demonstrated that because addition of sedimentary inclusions to a basaltic magma adds nothing that is not already present, the same crystalline phases appear, slightly modified in composition. He added that if enough material is dissolved, which requires an adequate supply of heat from some source, then the path of crystallization might be extended sufficiently for new phases to appear. An example is melilite in the system CaO–MgO–SiO_2 when CaO is added. However, Bowen considered it questionable that enough heat could be available to produce this effect.

An ambitious experimental approach aimed directly at the limestone assimilation hypothesis arose from the interest of Stanfield (1923) in the origin of the okaite and associated rocks at St. Joseph du Lac, Québec. He advanced field and chemical evidence to support his conclusion that the okaite had originated by assimilation of Grenville limestone by a magma of unknown type (possibly peridotite), and he suggested that, in general, rock magmas which yield melilite and monticellite on crystallization have dissolved considerable amounts of limestone.

Stanfield (1928) conducted a series of fusion experiments in which ten different igneous rocks were made to assimilate materials representing pure sediments. The igneous rocks varied in composition from granite to peridotite, and the sedimentary materials were calcite, kaolin, and glass sand. The igneous rocks and calcite were mixed in various proportions, and the mixtures were fused in 57 different experiments at temperatures ranging from 1,270°C to 1,470°C. Most of the products of the experimental assimilation of calcite contained glass, indicating that melting had occurred, and all products were characterized by the presence of melilites. No feldspathoids were produced. These experiments thus support the hypothesis that melilitic rocks can be derived from subalkaline magmas by limestone assimilation, provided that sufficient heat is available, but they provide no evidence for the hypothesis that feldspathoidal magmas or rocks can be produced in the same way. Stanfield concluded tentatively that 10 or 15 percent may be the limit of foreign rock matter which can be assimilated by natural magmas.

The Thermal Barrier between Granitic and Feldspathoidal Liquids

In 1928, Bowen predicted the existence of a thermal barrier on the feldspar join of the system $CaAlSi_2O_8$(An)–$NaAlSiO_4$(Ne)–$KAlSiO_4$(Ks)–SiO_2(Qz), except where the field for leucite extends across it, consequent upon the incongruent melting of orthoclase (figure 63, p. 244). The significance of the system Ne-Ks-Qz for theories of origin of granitic, syenitic, and feldspathoidal magmas was discussed by Bowen in 1937. A preliminary phase diagram published in 1935 by Schairer & Bowen was confirmed and revised by Schairer in 1950. The temperature maximum on the feldspar join through this system constitutes a real thermal barrier which can be crossed during equilibrium or fractional crystallization only if leucite appears during the course of crystallization. It is readily shown (see Wyllie 1970) that desilication of a granitic magma consisting of liquid coexisting with feldspar and quartz crystals, even if the temperature is maintained constant, causes crystallization of the liquid and precipitation of the feldspars that lie on the thermal barrier. The liquid composition changes only slightly. If the desilication is caused by limestone assimilation, the liquid is enriched in CaO, and the feldspar precipitated is enriched in the anorthite component, but the liquid portion of the magma is not likely to change composition greatly in the direction of desilication.

The experimental results obtained much later by Yoder & Tilley (1962) confirm that there exists a similar thermal barrier in basaltic liquids between saturated liquids, and liquids capable of precipitating feldspathoids. These barriers persist to pressures corresponding to conditions within the earth's mantle.

The dry experiments at low and high pressures thus provide no support for the limestone assimilation hypothesis; on the contrary, they weigh against it. The effect of volatiles was considered most important in the limestone syntexis hypothesis, and Shand (1943) suggested that perhaps dissolved H_2O and the CO_2 released from the limestone affected the liquidus so that the feldspar thermal barrier was suppressed. Bowen & Tuttle demonstrated the effect of H_2O under pressure on the melting relationships of the feldspar join Ab-Or in 1950, but it was two decades after Shand's suggestion before sufficient experimental data became available to show that the feldspar barrier persisted in the presence of H_2O under pressure (Fudali 1963 ; Hamilton & MacKenzie 1965 ; Morse 1969), and that the effect of CO_2 on the liquidus relationships in granitic systems was rather small (Wyllie & Tuttle 1959). From the available experimental data in systems containing H_2O or CO_2, we are confident that CO_2 at pressures corresponding to conditions within the earth's crust (to 10 kbars) will not significantly affect the thermal barrier between silica-saturated and feldspathoidal liquids.

Tilley (1958) considered possible ways for silicate liquids to by-pass the thermal barrier, and he suggested that the incongruent melting relationship of aegirine might make this possible. Reactions involving minerals certainly seem more promising than the effects of volatile components. It proves easier to silicate and undersaturated liquid than vice versa. (*cf.* Bailey & Schairer 1966; Luth 1967).

Dehydration and Crystallization of Silica–saturated Magmas by the Addition of CO_2

Daly's (1910) early pleas for experimental work to dispel the mystery of the effects of *les agents minéraliseurs* in petrogenesis were not answered until more than forty years later by systematic studies of the effect of H_2O under pressure on melting relationships in silicate systems. Daly was considering mainly CO_2 and its relevance to the generation of alkaline rocks, and in 1959 Wyllie & Tuttle published qualitative data on the effects of CO_2 on the melting relationships in feldspathic and granitic systems. The application of these results to a situation where a magma came into contact with a limestone and produced CO_2 by dissociation was discussed by Wyllie & Tuttle (1960*a*), and illustrated by Wyllie (1970). Addition of CO_2 to a H_2O-undersaturated magma with temperature and pressure maintained constant would produce a separate gas phase, cause extraction of H_2O from the liquid, and force the liquid to crystallize. If sufficient CO_2 were added, which is most unlikely in a magma chamber, crystallization would be completed at constant temperature and pressure. It seems likely that near the margins of a granitic body, and in dykes emplaced in limestones, dehydration and rapid crystallization of the magma could occur in this way. This would offset any tendency of the assimilation process to yield a desilicated magma.

Gas Transfer of Alkalis

Daly (1910) proposed that resurgent or juvenile CO_2 would dissolve alkalis from the subalkaline magma undergoing desilication, and transport these upwards within the magma chamber. Shand (1930) elaborated upon the nature and mechanism of this process of gaseous transfer. He proposed that reaction between limestone and albite components in the magma would produce Na_2CO_3 and Na_2SiO_3 molecules, and that these light and very soluble salts must tend to rise towards the top of the magma chamber with the gaseous phase, generating alkaline magmas at sites removed from the position where assimilation was occurring.

The available experimental data suggest that CO_2 is only slightly soluble in granitic magmas, and that probably very little solid material dissolves in a CO_2-rich vapor phase coexisting with a granitic magma. Under these conditions, it does not seem likely that CO_2 would be a very effective transport agent. However, the results of Morey & Fleischer (1940) in the system K_2O–SiO_2–CO_2–H_2O indicate that the solubility is greater in a more alkaline system. Koster van Gross & Wyllie (1966, 1968*a*) studied the phase fields intersected by the composition join $NaAlSi_3O_8$–Na_2CO_3–H_2O, and discovered a compositional range characterized by the coexistence of three fluid phases : a silicate liquid containing dissolved Na_2CO_3 and H_2O, a carbonate liquid containing dissolved H_2O and very little silicate, and an aqueous phase containing dissolved CO_2 and other components. If similar phases persist in bulk compositions closer to natural rock systems, then there are many processes possible involving the separation of alkali-rich fluid phases, with their subsequent upward migration and concentration. For this to occur, however, it appears that the liquid must have excess alkali present compared to the feldspar composition. Experimental data in other silicate-salt-H_2O systems such as $NaAlSi_3O_8$–$NaCl$–H_2O and $NaAlSi_3O_8$–NaF–H_2O (Koster van Groos & Wyllie 1968*b*, 1969) seem consistent with this conclusion. Therefore, there is experimental evidence that gas or fluid transfer of alkalis could be effective in alkaline magmas ; but this does not help the limestone syntexis hypothesis to convert subalkaline basaltic or granitic magmas into feldspathoidal magmas.

The application of experimental data to a problem such as the limestone syntexis hypothesis is at present limited to the consideration of equilibrium or fractional processes of crystallization or separation of a gas phase. In nature, however, we have to consider also the effects produced by the existence of regional and local temperature gradients, and chemical potential gradients. Under appropriate conditions, material may migrate through large distances, producing chemical changes not readily predicted from the available equilibrium phase diagrams.

Regional metasomatism, or migration of silica and alkalis through a pervasive pore fluid in a section of the crust, is another process involving gaseous or fluid transfer of material in such a way that feldspathoidal rocks could be produced (Gittins 1961). This process is distinct, however, from that required by the limestone syntexis hypothesis. Possibly, transfer of material by diffusion through a gaseous phase, or even a liquid phase, rather than by physical migration of the gas phase with dissolved material, could contribute towards the formation of feldspathoidal rocks. Relatively low diffusion rates through the liquid suggest that this process would not be very effective.

SOME LIMESTONES PROVE TO BE CARBONATITES: SYSTEM $CaO–CO_2–H_2O$

Field interpretations during the period 1936–1955 (see Table 1) produced revised versions of the familiar arguments on both sides of the controversy, but increasing attention was being paid to carbonatites. Many petrologists became convinced that these rocks were of igneous lineage, and had nothing to do with limestones. Carbonatites pose a dual problem : what is the physical and chemical nature of a carbonatite during emplacement, and what is its source? Many field workers concluded that carbonatites were emplaced in a liquid or plastic state. Doubts concerning the feasibility of a magmatic carbonatite persisted because the available experimental data indicated that carbonate liquids (excluding alkali carbonate liquids (excluding alkali carbonates) could exist only at high temperatures, whereas the field evidence demanded relatively low temperatures of emplacement (*cf*. Garson & Campbell Smith 1958, p. 111).

Wyllie & Tuttle (1960*b*) demonstrated that melts in the system $CaO–CO_2–H_2O$ precipitate calcite at temperatures down to 640°C at pressures up to at least 4 kbars. These results have since been revised, and extended to 40 kbars by Wyllie & Boettcher (1969). The liquids involved, with compositions close to the join $CaCO_3–Ca(OH)_2$, were referred to as "synthetic carbonatite magmas", with the full realization that natural carbonatite magmas would contain many additional components. These results were considered to provide experimental verification for the existence of carbonatite magmas, when the field evidence was consistent with such an interpretation. Re-examination of the lists compiled by Daly of alkaline complexes associated with limestone reveals that many of the limestones are carbonatites. Consequently, according to Heinrich (1966, p. 286), most investigators of alkalic-carbonatite complexes have rejected the limestone syntexis hypothesis.

Silicate—Carbonate Systems : Liquidus Studies

The problem of the source of the carbonatite magmas remains. There are many hypothesis for the origin of carbonatites, and the relevant experimental data, field, petrographic, and chemical results have been reviewed in two books on carbonatites by Tuttle & Gittins (1966) and Heinrich (1966), and in a volume containing the results of a symposium on kimberlites and carbonatites (Naidu 1966). The hypothesis may be considered in two main groups : (1) carbonatite is a residual magma derived from a carbonated alkali peridotite magma by one or more of several processes ; (2) a primary carbonatite magma is generated in the mantle, and reacts with crustal material to produce alkaline magmas and rocks. One experimental approach to the relationship between carbonatites and alkaline magmas is to determine the melting relationships in silicate-carbonate systems. The study of systems involving feldspars, silica phases, and carbonates also has specific application to the hypothesis of limestone-syntexis and sial-syntexis.

Watkinson (1965) determined the phase fields intersected by parts of three composition joins : $CaCO_3$–$Ca(OH)_2$–$NaAlSi_3O_8$, $CaCO_3$–$Ca(OH)_2$–$KAlSi_3O_8$, and $CaCO_3$–$Ca(OH)_2$–$NaAlSiO_4$, in the presence of 25 weight per cent H_2O at 1 kbar pressure. Each of these joins is a triangular slice through a six-component system, and geometrical representation of the results is difficult. The results applicable to the limestone assimilation hypothesis have been reviewed and illustrated by Watkinson & Wyllie (1964, 1969) ; and Wyllie (1970) also considered the melting relationships in the system CaO–SiO_2–CO_2 as a model for the more complex system. The application of the nepheline join to the development of residual carbonatite magmas from nephelinite magmas is discussed by Watkinson elsewhere in this symposium volume.

Results for the two feldspar joins follow similar patterns. At the feldspathic end, solidus temperatures in the presence of H_2O under pressure are moderate, and at the synthetic carbonatite end they are even lower. In the central portions, however, solidus temperatures are higher than at either end of the system. Experimental work in the systems CaO–

SiO_2–CO_2–H_2O (Wyllie & Haas 1965) and CaO–MgO–SiO_2–H_2O (Franz & Wyllie, 1966) indicates that the high melting temperatures are related to a thermal barrier corresponding to the melting of dicalcium silicate, and probably to other similar barriers in the complex systems. The feldspathic liquids are separated from the carbonatite liquids by the thermal barrier(s).

The results for the albite join provide a model for the assimilation of limestone by a feldspathic (syenitic) magma. If limestone is dissolved in such a magma with the temperature and pressure being maintained constant, this would cause the following sequence of changes : (1) precipitation of plagioclase feldspar, (2) precipitation of wollastonite alongside plagioclase, (3) reaction of plagioclase leaving wollastonite, (4) the precipitation of nepheline in small quantities through a narrow composition interval, (5) complete crystallization of the silicate liquid leaving wollastonite, nepheline, and vapor, (6) subsolidus decarbonation reactions could then produce a series of silica-undersaturated assemblages. Assimilation of about 20 weight per cent of limestone is required to produce liquids capable of precipitating nepheline, and this would require a large amount of heat; even under equilibrium conditions with temperatures maintained at a high level, the amount of liquid remaining at this stage is very small. In magmas, the heat required for the solution of limestone is usually considered to be provided for the most part by crystallization of the magma. Another factor that would tend to make the magma crystallize, even if the temperature were to remain high, is the dehydration effect described above when CO_2 is added to a magma. Thus, a feldspathoidal magma can be produced from a syenitic magma by limestone assimilation, but apparently this requires a combination of favorable circumstances. The same changes would *not* occur in a granitic liquid represented by albite-quartz mixtures, because the join albite-H_2O is a thermal barrier separating silica-saturated liquids from silica-undersaturated liquids.

The carbonate ends of the phase diagrams indicate the kinds of reactions that might be expected from sial-syntexis by a carbonatite magma. Less than 5 weight per cent of albite dissolves in the synthetic carbonatite magma, with depression of liquidus temperatures, before primary silicate phases appear and the liquidus temperatures rise sharply. Continued addition of albite causes precipitation of silicate minerals such as calciochondrodite, melilite, dicalcium silicate, and spurrite along with calcite. It appears that the composition of a carbonatite magma (cafemic variety) assimilating feldspathic or granitic material is limited to low silica contents by the thermal barrier for the orthosilicate ratio of 1:2 for SiO_2: cafemic oxides. There is no evidence in these experiments to suggest that this kind of process could produce either alkaline silicate magmas, or feldspathoidal rocks by precipitation. However, the actual composition of carbonatite magmas in the earth's crust remains unknown, and thus the experimental results, although suggestive, are not definitive.

SILICATE—CARBONATE SYSTEMS : SUBSOLIDUS REACTIONS

It is well established that subsolidus decarbonation and desilication reactions between feldspars and carbonates yield feldspathoids. A whole series of such reactions awaits investigation in the feldspar-carbonate joins discussed above, within the central subsolidus portions between the silicate and carbonatite liquids. Schuiling (1964*a*) described experiments at 1,000°C at 1 atmosphere, supposedly involving the reaction of calcite or dolomite with feldspars to yield feldspathoids, but which actually involved reactions with CaO because the carbonates would be dissociated at this temperature. Philpotts *et al.* (1967) described an experiment at 900°C and 0.72 kbar in which they reacted microcline and dolomite in the presence of excess H_2O to form diopside and kalsilite. This result they compared with kalsilite-bearing assemblages in a sedimentary xenolith within the alkaline gabbro of Brome Mountain. Schuiling & Philpotts *et al.* accepted these subsolidus reactions as evidence supporting the limestone syntexis hypothesis.

There is a distinction to be drawn between the formation of an undersilicated alkalic magma, and the formation of an undersilicated alkalic rock from a magma that is forced to crystallize as syntexis proceeds. The formation of alkalic, silica-undersaturated rocks in localized reaction zones at limestone contacts with subalkaline igneous rocks is to be expected, and continued subsolidus reaction between contiguous limestone and igneous rock could possibly yield more feldspathoids. It is not a valid extrapolation to relate these subsolidus reactions to magmatic processes.

SUMMARY

If we consider the effects of limestone assimilation in a granite magma, the available experimental data suggest strongly that the dominant effect is to cause it to crystallize, with little change in composition of the liquid portion of the magma.

(1) Solution of limestone causes crystallization in order to provide heat for the solution.

(2) Addition of CO_2, even under isothermal conditions, causes dehydration and at least partial crystallization of the magma.

(3) If the magma is desilicated in some way at constant temperature, it is forced to crystallize with the precipitation of feldspar, and insignificant change occurs in the degree of silica-saturation of the liquid portion of the magma.

Other conclusions unfavorable to the limestone-syntexis hypothesis based on experimental data include :

(4) Gaseous transfer of alkalis may be effective with alkaline magmas, but the process does not look promising for subalkaline magmas under normal magmatic conditions as a method for producing undersaturated, alkaline magmas.

(5) Even for a syenitic magma, it takes about 20 weight per cent of dissolved limestone to produce small amounts of liquid (even if the temperature is maintained constant) capable of precipitating feldspathoids.

(6) Sial-syntexis by carbonatite magmas does not appear to yield alkaline magmas.

Feldspathoidal rocks may be produced locally, at contacts between limestone and a magma, but the process appears to be more closely related to subsolidus decarbonation reactions than to processes involving significant changes in magma composition with respect to silica or alkalis. Petrological evidence by its circumstantial nature is often unsatisfactory, compared to experimental evidence which may demonstrate that a postulated process can occur. However, negative experimental data are not proof that a specific process cannot occur under natural conditions, different from those achieved in the laboratory. We consider the experimental evidence against the limestone assimilation hypothesis as strongly suggestive, but it is not definitive.

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