

intrusions of a stratiform nature, i.e., "stacked saucers" or the stromoconoliths of TOMKEIEFF (1961), whereas, miascitic massifs, especially those with carbonatites, are noteworthy examples of "piercement (vertical) tectonics".

The restriction of major alkalic provinces to cratonic areas was noted by BACKLUND (1932) who described this symbiosis as the epeirodiatresis relationship, i.e., the perforation of stable crustal areas. The close spatial and temporal relationships of most African carbonatites to rift valleys has now been documented in detail (see, e.g., BAILEY, 1964). Similar relationships are found in the U.S.S.R. and have been recently recognized for many other carbonatitic provinces; e.g., Ontario—the Moose River magnetic lineament; India—the Narbada Valley.

PECORA's (1956) summary lists 32 carbonatite localities; that by HEINRICH (1958) records 60; in my new monograph about 320 are described or listed. Of some 35 major alkalic rock localities in the United States 13 are known to have carbonatites. The total volume of carbonatites for the world is exceedingly small; they form an average of 10% or less of their host alkalic complexes and alkalic rocks constitute no more than 1% of all igneous rocks. As an order of magnitude it is estimated that the total world area of exposed carbonatite is 200 sq. miles.

THE MYTH OF THE RING-DIKE-CONE-SHEET COMPLEX

While it is true that some of those carbonatites that have been studied in greatest detail (Magnet Cove, Arkansas; Iron Hill, Colorado; Chilwa Island, Malawi; Alnö, Sweden) occur in composite intrusions that approximate to varying degrees of perfection the classic concept of a ring-dike-cone-sheet complex, it is now evident that this type of intrusive manifestation is representative of but one of the many diverse depth-levels in which carbonatites were developed and are now exposed. In truth, carbonatites, like other "normal" igneous rocks range from volcanic through subvolcanic and hypabyssal to plutonic. The ideal concentric ring massifs with their centrifugal progression from alkalic ultramafic to felsic alkalic rocks, their central stock of carbonatite and their spokes of radial dikes represent just one of the diverse manifestations, probably the mesozone type. Both downward and upward the patterns of the complexes become more irregular.

FENITIZATION

The process of fenitization, i.e., the production of a metasomatic alkalic syenite from such a wall rock as granite gneiss, for example, has been delineated in detail with respect to both compositional and mineralogical transformations for a number of complexes (e.g., Alnö, Sweden; Fen, Norway; Spitskop, South Africa). Widespread observations on more shallow carbonatites have shown that

at least three intergrading varieties of metasomatic products may be formed: (1) "Typical" fenite, i.e., aegirine–potash feldspar rocks; (2) rock consisting chiefly of riebeckite and albite; (3) rocks consisting almost entirely of hematitic potash feldspar (orthoclasis, perthosite, sanidinite, etc.).

Less commonly there is evidence that certain nepheline syenites (ultrafenites) and some ijolites may be of metasomatic origin.

RELATIONS TO KIMBERLITES

The genetic links between carbonatites and kimberlites have been reinforced in a number of ways. Not only are kimberlites present as integral parts of carbonatitic complexes and as inhabitants of alkalic–carbonatitic provinces, but experimental studies by WYLLIE (1964) have demonstrated that residual lime-rich carbonatitic fluids can result from the fractional crystallization of alkalic peridotitic magmas. The discovery of extrusive hypohyaline peridotites (meimechites), compositionally the equivalents of kimberlites, at Igwisi, Tanzania (SAMPSON, 1956) and in the Meimecha–Kotui region of Siberia (KRUTOYARSKY, 1958) point to the reality of kimberlitic magmas and their ability, albeit rare, to penetrate even to super-crustal levels.

CARBONATITES AND VULCANISM

Of extraordinary interest to carbonatite studies are the volcanoes of eastern Africa. Dissected Napak in Uganda, with its carbonatitic core (Lokupoi), shows best of all the close relationship between carbonatites and volcanoes of the Mount Elgon type—volcanoes of highly explosive character that spew out extraordinary amounts of pyroclastic debris, much of it of nephelinitic composition. Kerimasi on the Eastern Rift has slope beds of "limestone" that carry inclusions of more coarsely crystalline carbonate rock, *possibly* a unique example of an extrusive carbonatite with xenoliths of intrusive carbonatite (WILLIAMS, 1959).

The epitome of carbonatitic vulcanism is, of course, displayed by Oldoinyo Lengai in Tanzania, which, in 1960, erupted soda-rich and essentially silica-free lava as both pahoehoe and aa (DAWSON, 1962b). Soda carbonate ash had been produced in earlier eruptions. The lava consists of 1–2 mm phenocrysts of a new Ca–Na–K carbonate species in a microcrystalline matrix of thermonatrite. Calcitic pyroclastics are widespread around Chasweta and Mwambuto centers in Zambia (BAILEY, 1960).

CARBONATITES: NIL-SILICATE IGNEOUS ROCKS

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SUMMARY

This paper is a review of the more important facts, ideas, and discoveries in the study of carbonatites during the last decade. All evidence is shown to affirm the igneous nature of these carbonate rocks.

INTRODUCTION

Rocks called carbonatites have become increasingly important to geologists in the last decade for both economic and scientific reasons. They are not only major potential sources of niobium, rare earths, thorium and other elements and minerals, but their study has opened an entire new field of igneous petrology, that of the nature and origin of non- or nil-silicate igneous rocks, simultaneously providing collateral information on such related subjects as the tectonic behavior of cratons, on the origin of kimberlites, the transition from magmatic to hydrothermal processes, and the significance of carbon-dioxide in vulcanism.

At the University of Michigan a 5-year study of carbonatites has been climaxed by the recent publication of a general monograph *The Geology of Carbonatites* (HEINRICH, 1966). The purpose of this article is to present, in summary form, some of the more important new facts, ideas and discoveries in the overall study of carbonatites that have accumulated since the last two major summaries, those of PECORA (1956) and HEINRICH (1958).

HISTORY

HÖGBOM (1892, 1909) has long been credited as the originator of the idea of igneous carbonate rocks. However, during an examination of the newly discovered carbonatite in India, Dr. G. R. Udas brought to my attention the work of BOSE (1884) whose investigations in the Lower Narbada Valley of west-central India predate Högbom by about a decade. Bose found masses "of yellowish, altered calcareo-siliceous rocks" forming the crest of basalt-covered ridges. He noted

(1) that these rocks were more resistant than the basalts to weathering and erosion, (2) that they were not bedded, (3) that they contained no fossils, (4) that they were "fine-grained but crystalline", (5) that they were markedly calcareous with local "nests and patches of a trappian-looking substance, the igneous origin of which is manifest under the microscope" (BOSE, 1884, p.59), (6) that the outcrop distribution was linear and straight and (7) that locally associated were "highly altered and intensely hardened shaly and siliceous rocks" (p.59). He concluded (p.60) that "there can be very little doubt that... the rocks under notice have been severed and forced up from the infra-trappian beds by intrusive rocks. They have been most effectually baked, being rendered quite crystalline... and... portions of them would appear to have been converted into a trappian substance". These rocks are the ones verified by SUKHESWALA and UDAS (1963) as the first carbonatite discovered in India. Certainly credit must be given to Bose, not only for being the first to recognize a carbonatite but also for suggesting at the same time its origin in the remobilization of limestone.

Similarly, another long-forgotten piece of work is that of STUTZER (1907) who apparently originated the idea that a carbonatite magma could be originated as the ultimate differentiation product of a parent alkalic-subsilic magma. Based on his work at Alnö, he wrote: "Es müssen daher die Kalksteine von Alnö als magmatisch entstandene Kalksteine angesehen werden, die wahrscheinlich nur durch extreme Differenzierung eines mit Gasen reich geschwängerten Nephelinsyenit magmas entstanden sind. Wie kam das Calciumkarbonat ins Magma? War es ursprünglich in demselben vorhanden oder hat der Nephelinsyenit bereits präexistierende Kalksteinmassen durchbrochen, losgerissen, aufgeschmolzen und wieder auskristallisiert? In kilometerweiter Entfernung von Alnö finden wir heute keinen Kalkstein anstehen. Überall finden wir nur Gneis. Auch die Annahme einer höher gelegenen, jetzt wegerodierten Kalksteinmasse hat keine Wissenschaftlichkeit für sich (STUTZER, 1907, p.393).

ALKALIC CARBONATITIC COMPLEXES

One of the newly emergent relationships in carbonatite occurrences emphasizes the dichotomy between alkalic rocks of agpaitic character and those of miascitic character. Carbonatites and carbonate of magmatic derivation are essentially restricted to miascitic complexes. The two types differ rather sharply in bulk composition and therefore contrast in mineralogy. Volatile elements that characterize agpaitic massifs are F, Cl and H₂O, whereas abundant H₂O and CO₂ typify the miascitic complexes. The reason for this schismatic nature is uncertain. A few dominantly miascitic intrusions have late dike differentiates of agpaitic composition (e.g., Magnet Cove); the reverse is not known. Many major agpaitic occurrences (southern Greenland; Kola Peninsula) are represented by

MINERALOGY AND GEOCHEMISTRY

About 170 minerals, exclusive of supergene species, are now known from carbonatites, thus ranking them close to pegmatites in the variety of their constituents. It has now been established that the usual sequence of the carbonate minerals (oldest to youngest) is: calcite, dolomite, ankerite, siderite and rhodochrosite, RE carbonates. This sequence, which also has been experimentally verified, may now be regarded as the fundamental mineralogical "reaction series" for carbonatites. The early calcites are notably enriched in Sr and Ba (Quon and Heinrich, 1965), and those from a few deposits contain exsolved blebs or lamellae of dolomite (carbonate "perthites"—VAN DER VEEN, 1965).

Pyrochlore, one of the most characteristic of carbonatite constituents, has been shown by VAN DER VEEN (1963) to be subject to manifold compositional variations and to complex transformations:

(1) Ca-Na pyrochlores may be altered as the result of solution removal of A ions (Ca, Na), accompanied by hydration, in some instances with substitution of hydronium ions (H_3O^+) in the A position. The alteration can apparently be low-temperature hypogene or supergene.

(2) Ca-Na pyrochlores may be subject to hydrothermal alteration with consequent replacement of Ca-Na with Ba, Sr, Ba-Sr, or K-Sr. This may be accompanied by hydration.

(3) Metamictization of strongly radioactivity (high U + some Th) pyrochlores (betafites) may occur.

(4) Exsolution of Ti and Fe may occur and yield inclusions of ilmenite and rutile in both Ca-Na and Sr pyrochlores.

(5) Pyrochlore may be replaced with fersmite.

(6) Pyrochlore may be replaced with columbite.

A particularly diagnostic group of minor elements characterizes carbonatites: Ti, Nb, Zr, RE, P, F, Ba, Sr, Th. In addition high ratios of Nb/Ta, Zr/Hf, Th/U, $\Sigma CeRE/\Sigma YRE$ are typical. Another powerful tool for identifying igneous carbonate rocks is their $^{87}Sr/^{86}Sr$ ratios which for carbonatites are distinctly lower than those of sedimentary carbonate rocks and identical with those of their associated alkalic silicate rocks (POWELL, 1965).

One of the most unusual of the newly discovered features of some U.S.S.R. and Colorado alkalic rocks and associated carbonatites is the presence, in the primary vacuoles of pyrogenic minerals, of complex hydrocarbon gases including methane and higher polymers (PETERSILIE, 1964; HEINRICH and ANDERSON, 1965). That they are magmatic is heretical but the only construction that fits their occurrence, distribution and isotopic composition.

ECONOMIC GEOLOGY

Carbonatites and their associated rocks are major sources or potential sources for a long list of elements and minerals. Noteworthy are:

Nb:	Iron Hill, Colo., (U.S.A.); Oka, Que. (Canada); Araxá (Brazil); Fen (Norway).
CeRE:	Mountain Pass., Calif. (U.S.A.).
Th:	Iron Hill, Colo. (U.S.A.).
Phosphate:	Sukulu Hills (Uganda); Phalaborwa (South Africa).
Cu:	Phalaborwa (South Africa).
Fe:	Mount Essale (Angola); Kaiserstuhl (Germany).
Ti:	Magnet Cove, Ark. (U.S.A.).
Zr:	Phalaborwa (South Africa).
Al:	Baikalia (U.S.S.R.).
Barite:	Mountain Pass, Calif. (U.S.A.); Magnet Cove, Ark. (U.S.A.)
Fluorite:	Okorusu, (South West Africa); Amba Dongar (India)
Vermiculite:	Dorowa (Rhodesia).

SUMMARY OF RECENT ADVANCES

Investigations of the last decade have established that, although carbonatites are very rare igneous rocks, they display most of the characteristics of their more common cousins:

- (1) Both intrusive and extrusive carbonatites occur.
 - (2) Extrusive carbonatites are represented by both flows and pyroclastics.
 - (3) Intrusive carbonatites have been emplaced over a considerable depth range.
 - (4) Intrusive carbonatite bodies are dikes, sills, sheets, pipes, stocks and more irregular bodies; batholiths are not represented.
 - (5) The intrusion of carbonatites has been accompanied by metasomatism of their wall rocks: sedimentary, metamorphic or comagmatic alkalic igneous rocks.
 - (6) Many carbonatite bodies, even some small dikes are structurally and petrologically diverse, multistage composites.
 - (7) Extensive deuterian and autohydrothermal changes have affected many carbonatites.
 - (8) Some carbonatites display endomorphic compositional modification resulting from syntaxis.
 - (9) Many contain xenoliths, which may be flow-oriented, armored by reaction rims or partly assimilated.
 - (10) Texturally, some are granitoid; others show well-defined primary foliation. Some are porphyritic; either with silicate or carbonate species appearing as phenocrysts.
- Studies by ROEDDER (1965) on vacuoles show that the distribution, amount

and genetic significance of juvenile CO₂ in mafic and ultramafic rocks have been severely underestimated. His results suggest that carbonatitic-alkalic complexes are not unique because they contain "abnormal" amount of CO₂ or carbonate and are derived from a mantle fraction of atypical composition but rather that they represent the end products of a special tectonic environment in which "normal" amounts of CO₂ have been extraordinarily concentrated.

The limestone-syntaxis hypothesis is now clearly inadequate, both from field and experimental evidence, to account for most occurrences of undersaturated rocks. That foidal rocks can be formed in reaction zones between limestones and silica-saturated igneous rocks has been demonstrated, but what is germane here is that neither experimental results nor modern interpretations of the geology of carbonatitic alkalic complexes offer any evidence that limestone assimilation can produce any significant amount of alkalic subsilicic magma (WATKINSON and WYLLIE, 1964).

Although a magmatic derivation for carbonatites is now widely accepted, an interesting argument has developed with respect to the relations of carbonatites to their consanguineous alkalic rocks. The more widely held viewpoint is that carbonatitic magmas are secondary, being the youngest fractional differentiate of an alkalic mafic (nephelinic) or alkalic ultramafic (kimberlitic) parent (KING, 1965). The opposing idea (DAWSON, 1964) suggests that the initial fluid is carbonatitic and that the associated silicate rocks are formed as the result of varying degrees of replacement of wall rocks by this fluid. In some cases such metasomatic rocks are remobilized and intruded rheomorphically.

Powerful support for the magmatic origin of carbonatites has resulted from the successful laboratory synthesis of simplified carbonatitic fluids (see, e.g., WYLLIE and TUTTLE, 1960, 1962). These results indicate that mobile carbonatite magmas can exist at temperatures between 683–450°C and at pressures from 1,000 to 10 bar, environments that are in accord with those deduced from geological data.

In conclusion, all lines of evidence strongly affirm the igneous nature of carbonatites and indicate their derivation as secondary magmas from alkalic-mafic or alkalic-ultramafic, upper-mantle material under a regimen based on a long period of continental crustal stability providing for the concentration of normal amounts of juvenile CO₂ in the mantle followed by explosive penetration of the crust accompanying major crustal fracturing.

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