EVOLUTION AND INVOLUTION OF CARBONATITE THOUGHTS

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DOI: 10.2138/gselements.17.5.303

During my doctoral studies, in the late 1980s, I realised that the Italian kamafugites (kalsilite melilitites) had to be related to carbonatite magmatism. I started a detailed study of the kamafugitic sites, and I explored remote areas deep in Italy's Apennine mountains. When I found the Polino carbonatite, I put a few drops of acid on it, and the rock reacted. I have a vivid memory of my heart beating faster. I had found it! My fellow geologists were somewhat sceptical, but the late Professor Giorgio Marinelli (1922–1993) encouraged me and predicted many new carbonatite discoveries. He was right. Overcoming my Latin temperament, I focused on the concept that carbonatites, however unusual as rocks, cannot be dismissed as simple geological oddities but require detailed and comprehensive study. I am fond of all the history that marked my latest 40 years of life, and it reminds me of the many friends and mentors that I have had, especially when I was a young researcher. Sadly, some of them are no longer with us. I am so grateful to them, and I consider it a life-changing experience to have met them.

CARBONATITES: BACKGROUND

The "carbonatite saga" parallels the Plutonist vs. Neptunist *querelle* of the 18th and 19th centuries concerning the pyrogenic versus chemical origins of igneous rocks. In the mid-19th century, minerals in alkaline rocks attracted mineralogists, who considered them fascinating examples of rocks containing minerals that combined calcium silicates and carbonates. These minerals occur in skarns, which are thermally metamorphosed rocks formed at contacts between silicate magma and limestone. Skarns may contain perfectly faceted crystals and, despite their marginal importance and volume, monopolised European mineralogical studies. On this basis, the concept of magma–limestone interactions was applied to carbonatitic and alkaline igneous rocks, which have as essential minerals both calcium silicates and carbonates, like skarns. At the beginning of the 20th century, the concept of sedimentary limestone melting (often referred to as "syntaxis") directed scientific attention to the problematic interpretation of alkaline rocks and carbonatite genesis. People argued at length whether carbonatites and related alkaline rocks were igneous or the reaction products between silicate igneous melt with sedimentary limestone. Following a century of discussion, this story now has a surprising finale that overturns the assimilation concept.

PIONEERING AGE: 1900–1950

Reginald Daly (1871–1957) initiated the discussion on the genesis of alkaline igneous rocks. His proposition was based on three main concepts: (1) that sub-alkaline igneous bodies intrude sedimentary limestones; (2) that limestone assimilation leads to the formation of minerals with CO_2 as an essential component (e.g., calcite and cancrinite); (3) that the residual limestone-contaminated melt could migrate towards the top of the magma chamber and separate from the rest of the sub-alkaline liquid. The process would deplete the liquid in silica and so lead to the subsequent crystallisation of feldspathoids (e.g., sodalite, haüyne, leucite, nepheline, kalsilite) instead of feldspars.

Limestone assimilation became a fashionable model. Most distinguished geologists of the day discussed the role of limestone in the origin of feldspathoidal rocks. For example, Alfred Rittmann (1893–1980) proposed that Mount Vesuvius volcano leucitites form by dolomitic limestone assimilation into a trachytic magma. Not everyone agreed: Whitman Cross (1854–1949) rejected Daly's model based on the geological observation that the melilite-bearing rocks of Hawaii (USA) formed in the absence of limestones and sub-alkaline rocks.

The person often credited with the first compelling hypothesis that these limestones are, in fact, igneous was Waldemar Brøgger (1851–1940). Although Brøgger was initially a proponent of Daly's assimilation model, he changed his mind after studying the Norway's Fen alkaline complex. He advanced the idea that limestones associated with alkaline silicate rocks are not sedimentary. Instead, he proposed them to be igneous rocks that he referred to as carbonatites. This was a radical idea that was strongly opposed. James Shand (1882–1957), one of the most famous alkaline rock petrologists of the time, did not believe in the igneous origin of carbonatites. Norman Bowen (1887–1956) suggested that carbonatites are non-igneous metasomatic and hydrothermal rocks. Likewise, William Pecora (1913–1972) concluded that carbonatites formed by carbonate solutions derived from alkaline magmas. Nevertheless, the field evidence overwhelmingly supported the idea that carbonatites were igneous, and an increasing number of "limestones" were recognised as igneous carbonatites.

THE CARBONATITE GOLDEN AGE: 1960–2000

The most intense effort in studying carbonatites took place between 1950 and 2000. Based on experimental petrology, an increasing number of Russian and US scientists became supporters of the carbonatite magmatic origin. Field observations of carbonatites on Alnö Island (Sweden) by Harry von Eckermann (1886–1969) supported the seminal experimental work of Peter Wyllie and his co-authors, leading to the conclusion that wollastonite and calcite can crystallise in a magmatic environment. Numerous geological, mineralogical, petrographic, geochemical, and isotope studies confirmed the magmatic genesis of carbonatites and their associated alkaline rocks, such as melilitites and foidites. Many experimental studies have suggested that carbonatites can be generated in several different ways, including by primary mantle melting, differentiation of carbonatite from silicate melts, liquid immiscibility, and crystal fractionation. Beginning in the late 1970s, a new generation of scientists demonstrated that carbonatitic liquids are largely immiscible at crustal pressures and form conjugate pairs, with silicate liquids starting from CO_2-rich, mafic-alkaline parental melts. The thermobarometric geochemical work of Russian petrologists on melt inclusions in carbonatite-hosted minerals was particularly important in demonstrating the igneous genesis of alkaline silicate and carbonatites rocks.

Mantle metasomatism plays a considerable role in the evolution of carbonatites, and for many years it was believed that metasomatism involved solely the lithosphere. In recent decades, based on the study of mantle xenoliths and inclusions in diamonds, the idea of deep mantle metasomatism has developed. Carbonatite specialists from Europe, Russia, North America, Brazil, and China met at the Euro-Carb workshops, which were held in Italy, the Canary Islands, and the Kola Peninsula in 2002 and 2003. These meetings started an international discussion that is ongoing and have promoted new ideas about the economic potential of European carbonatites (e.g., Stoppa et al. 2016).

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THE IMPORTANCE OF THE EXTRUSIVE CARBONATITES: THE CASE HISTORY OF ITALY

A completely new insight into the origins of carbonatites came from observations of extrusive carbonatite volcanism, including the 1960 eruption of Oldoinyo Lengai (Tanzania), the discovery of tear-drop lapilli-stone at Kaiserstuhl (Germany), and the carbonatitic tuffs and bombs found at Fort Portal and Katwe-Kikorongo (both in Uganda). These studies corroborated the decades-earlier intuition of David Bailey (1931–2012) concerning the existence of extrusive carbonatites at Rufunsa (Zambia). Extrusive carbonatites preserve astonishing evidence of rapid cooling from high-temperature carbonatite liquids, as well as having high-pressure aragonite inclusions. Studies of volcanic carbonatites have revealed a new type of alkaline carbonatite consisting of sodium- and potassium-rich calcium carbonates. The rapid transformation of these ephemeral phases to form Ca-carbonatites led to the generalisation that initially all extrusive carbonatites were alkaline. Supporting evidence now includes the existence of wide alkali-rich fenite aureoles around most carbonatite intrusions and alkali-carbonate inclusions in extrusive carbonatite minerals.

Although carbonatites are now accepted as igneous, the role played by mantle and crustal silicate material reaction and contamination was somewhat forgotten or ignored, overshadowed by the new enthusiasm that all carbonatites are igneous. Calcite carbonatite rocks were often erroneously interpreted as forming from melts of equivalent composition, and any oxide or silicate crystals were inferred as having crystallised from the carbonatite magma itself, without clear evidence. The unexpected discovery of extrusive carbonatites in Italy, within the Quaternary extensional intermountain belt, opened a new front of discussion. These rocks are very primitive silica-rich carbonatites with high Cr–Ni contents, mantle nodules, and high incompatible element contents. As deduced by the presence of abundant mantle debris, the magmas were initially propelled, at the mantle level, by violent CO_2 release with sufficient force to bring the magma and xenoliths to the surface at high speeds. This produces a fluidised mantle-rock breccia immersed in an immiscible mixture of mafic alkaline silicate and carbonatite droplets. Passing through the lithosphere, specific concentric-shelled lapilli are formed in the conduit by the attachment of melt droplets to mantle xenolith fragments. These silica-rich carbonatites are important for their primitive character (high-Mg content and abundant mantle debris), because most experimental work indicates that melting of carbonated peridotite produces magnesian carbonatite melts with silica. The so-called "Italian silicocarbonatites", with their primitive compositions, are invariably associated with potassic undersaturated rocks called kamafugites, while the geochemical and isotopic equilibrium between the two rock types indicates genesis by immiscibility at crustal levels. Notably, Italian carbonatites contain monticellite and wollastonite as mantle debris and carbonatite-liquid low-pressure reaction minerals. This is consistent with experimental work showing assimilation of silicate rock by carbonatite magma.

A more recent discovery is that Italian late-stage carbonatites are strongly enriched in fluorite, baryte, light rare earth element phases, Nb, V, and Sc (FIG. 1) (Stoppa et al. 2019). The discovery of carbonatites in Italy initiated vigorous discussion about their geodynamic context. Strong opinions arose from those who consider that Italian alkaline magmatism is related to subduction, because carbonatites are typically associated with intracontinental rifting but only rarely with intraplate oceanic islands. However, most of the papers about Italian carbonatites attribute this magmatism to upwelling of mantle asthenosphere and stretching of the lithosphere that is related to the Tyrrhenian opening, possibly controlled by a mantle plume of deep origin. Some authors have invoked Reginald Daly's petrogenetic theory for these rocks; others oppose that view.

FIGURE 1 A group of students led by Prof. Francesco Stoppa (G. d'Annunzio University of Chieta, Italy) look at carbonatite exposed at the Pianciano quarry (Italy). The white materials are pseudo-dykes and crypto-domes of fluorine-rich calciocarbonatite that intruded plastically deformed grey-blue and light-brown fluorspar ore. PHOTO CREDIT: GIANLUIGI ROSTELLI 2019.

A FINAL SURPRISE

Recent studies have proffered the idea that carbonatites can react with silicates (accidental mantle and crustal debris or felsic country rocks) to produce a suite of calcium silicate minerals that include diopside, wollastonite, monticellite, and andradite: assemblages that are typically found in skarns. However, whilst these minerals often appear to be phenocrysts that crystallised directly from the carbonatite melt, it seems more likely that the carbonatite melt was instead a diffusive medium in which SiO_2 derived from the silicate rocks was transported into the carbonatite system and sequestered in the skarn-like mineral assemblage. In this model, carbonatite rocks are hybrid rocks that result from a traditional magmatic crystallisation of carbonate minerals and from contamination by silicate material. This model now better explains field and thin-section observations and reverses Daly's hypothesis based on reactions proposed by Rittman. It explains the specific crystal chemistry of the carbonatite minerals and their textural relationship, which are entirely different from those of skarns. The reactions that form the carbonatite-hosted skarn assemblages follow the same thermodynamics that govern the formation of true skarns hosted in sedimentary carbonate rocks. However, there is a fundamental difference: the liquid magma is carbonatitic, not siliceous. Essentially, this is not a skarn per se, but rather an "antiskarn".

Sometimes there are circular thoughts in science, which reconcile old theories with new ones but that acknowledge observations developed over a century. In the end, one of the processes concomitant to the formation of calc-silicate assemblages in carbonatites is a metasomatic antiskarn reaction, which is precisely the opposite of what was proposed a century ago by Daly.

REFERENCES

Stoppa F and 6 coauthors (2019) Italian carbonatite system: from mantle to ore-deposit. Ore Geology Reviews 114: 103041, doi: 10.1016/j.oregeorev.2019.103041

Stoppa F, Pirajno F, Schiazza M, Vladykin NV (2016) State of the art: Italian carbonatites and their potential for critical-metal deposits. Gondwana Research 37: 152-171, doi: 10.1016/j.gr.2016.07.001