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Carbonatite genesis: A reexamination of the role of intrusion-related pneumatolytic skarn processes in limestone melting

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ABSTRACT

The unusual elemental enrichment typical of many carbonatites and their stable and radiogenic isotope signatures—which are unlike those of sedimentary limestones—forced researchers to abandon limestone melting theories in the early 1960s and to support mantle-related models of carbonatite genesis. However, the fluid compositions [$\text{CO}_2/(\text{H}_2\text{O} + \text{CO}_2) = 0.05$] required to melt limestone near its eutectic in the $\text{CaO-MgO-CO}_2\text{-H}_2\text{O}$ system (600–675 °C) are virtually identical to those found in infiltrative magmatic-hydrothermal, skarn-forming systems; therefore, carbonates within such systems would melt via volatile fluxing. Skarn-related decarbonation reactions produce the CO_2 required to form the carbonic acid (H_2CO_3) in the infiltrative H_2O -rich fluid essential to carbonate melting. In addition to H_2O , other fluxes (HF , HCl , H_3PO_4) and related salts derived from fluid-phase saturation of silicate intrusions could further depress the carbonate-melting eutectic temperatures, as well as enhance mass transfer of mineralizing elements into a forming skarn system and any low-viscosity carbonate melts produced within the skarn. The isotopic signatures of the resultant carbonate melts should reflect the elemental mass transfer of constituents from the intrusion, as well as Rayleigh decarbonation and elemental mixing processes typical of contact-metamorphic (pneumatolytic) processes. Many intrusions exsolving volatiles into limestone during final stages of solidification should produce some carbonate melt. Only carbonatites with enrichments in F, P, Sr, Nb, U, Th, and rare-earth elements, have been considered intrusive melts, whereas the solidified products of other melts may have been erroneously considered hydrothermal veins.

INTRODUCTION

The petrogenesis of carbonatites has been controversial, since they were first postulated to be carbonate magmas. This fact is now well established on the basis of empirical evidence from active volcanoes, such as Oldoinyo Lengai (East Africa), and from experimental studies. Many of W. C. Brögger's contemporaries (cf. Daly, 1933) thought that carbonate magmas resulted from simple limestone or marble melting and/or from syntaxis (assimilation) of limestone (Pecora, 1956). However, since the mid-1960s, carbonate magmas have generally been considered mantle-derived magmas (Wyllie, 1989) largely because carbonatites are enriched in F, P, Sr, Nb, rare-earth elements (REEs), U, and Th, among other possible elements, and have stable and radiogenic isotope signatures that are quite different from limestones. Heinrich (1966) summarized the various primary magmatic hypotheses on carbonatite genesis, which are still being debated. However, he also described a "secondary" magmatic hypothesis in which the "carbonatitic fluid is a secondary magma formed as the ultimate fractionation during the differentiation of an alkalic magma contaminated by limestone." One of the problems with the primary magmatic hypotheses is how to generate excess amounts of CO_2 by partial melting or differentiation, which theoretically can only be achieved in mantle magmas (Wyllie, 1989). Excess CO_2 is not a problem in the secondary mag-

matic scenario, but the elemental and isotopic compositions of carbonatites did not appear compatible with limestone melting (cf. Tuttle and Gittins, 1966). The purpose of this paper is to show that there is a genetic relationship and, therefore, a possible continuum between magmatic-hydrothermal skarn systems and *some* carbonatite systems, as depicted in Figure 1; this is based on the existing, well-established experimental constraints on skarn reactions, carbonate melting, and carbonate solubility. Furthermore, the trace element and isotopic compositions of carbonatites may be explained by decarbonation and fluid-exchange reactions in the magmatic-hydrothermal system that generated the crustal carbonate melt.

LIMESTONE MELTING CONDITIONS: VOLATILE FLUXING

The importance of water in carbonate melting was first documented by Paterson (1958) and Wyllie and Tuttle (1959a, 1959b). Subsequently, Wyllie and Tuttle (1960) then described detailed crystal-melt-volatile phase relationships in the system $\text{CaCO}_3\text{-H}_2\text{O-CO}_2$, which turn out to be critical to much of the subsequent discussion. Wyllie and Tuttle (1960) stated:

"In the presence of water vapour at a pressure of 1,000 bars, calcite begins to melt at 740 °C. . . . Temperatures of this order are probably attained quite frequently at limestone contacts with igneous rocks, and one might expect partial melting to occur during contact metamorphism. The process leads also to decarbonation, providing free CO_2 within the rock. Under

these conditions, a higher temperature would be required to initiate melting. If the materials evolved by the igneous magma are rich in H_2O and poor in CO_2 , the CO_2 could possibly be swept away from the contact aureole by continued efflux of volatiles from the magma. If this should occur, then partial melting of a contact limestone seems not unlikely."

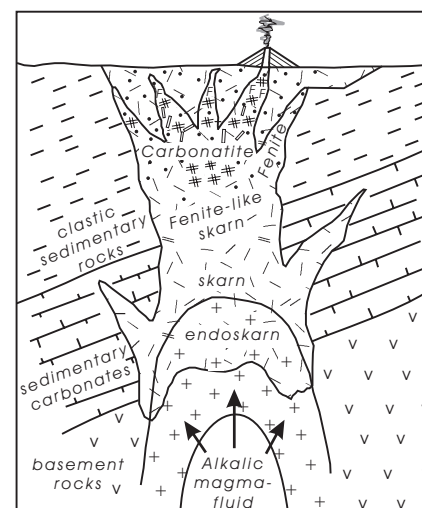


Figure 1. Schematic diagram of hypothetical relationships between intrusion and limestone that produced skarns, fenite-like skarns, fenites, and "distal" carbonatitic magmas at upper-crustal levels via simple volatile fluxing (no scale) (modified from Lentz, 1998). Cross-hatch pattern—carbonates, double-line pattern—apatites, F—fluorite.

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To my knowledge, only Schuiling (1961) presented a volatile-fluxing model for carbonatites. It is important to note that the minimum melting temperature (calcite-portlandite-melt-fluid eutectic) in this system coexists with a mixed H₂O-CO₂ fluid of ~5% CO₂, i.e. $X(\text{CO}_2) = 0.05$ at temperatures as low as 640 °C at 400 MPa (4 kbar) to 675 °C at 100 MPa (1 kbar) (Wyllie and Tuttle, 1960). It is evident that the mixture of small amounts of CO₂ in the H₂O-rich fluid forms H₂CO₃ that significantly enhances melting and/or fractional crystallization in this simple carbonate system. To melt calcite at the eutectic in this system, ~13 wt% H₂O and ~0.65 wt% CO₂ [$X(\text{CO}_2) = 0.05$] are required (Wyllie and Tuttle, 1960). Fanelli et al. (1986) added MgO to this simple carbonate system (CaO-MgO-H₂O-CO₂), which depressed the eutectic temperature even lower—i.e., to ~600 °C. It is interesting that phase equilibria studies of the Oka carbonatite revealed that the magma was water rich (Treiman and Essene, 1984). However, numerous other fluxing agents and components have been investigated in carbonatite genesis (Wyllie, 1989), although in analogy to silicate magma systems, many more fluxes must be considered.

INTRUSION-RELATED PNEUMATOLYTIC PROCESSES IN SKARN SYSTEMS

In contrast to normal metamorphic decarbonation reactions in siliceous carbonate rocks (CO₂ rich), infiltrative magmatic-hydrothermal (pneumatolytic) skarn systems are water rich, according to well known phase relationships (Bowman, 1998a, 1998b). The role of silicate magma pneumatolytic skarn formation in sedimentary carbonate rocks is well understood, particularly because of its metallogenic significance (see Einaudi et al., 1981). The vapor-saturated solidus of the granite minimum melting-temperature composition and the carbonate eutectics are illustrated in Figures 2 and 3. These diagrams show that a silicate magmatic fluid evolving during contact-metasomatism has the composition necessary to melt a carbonate at its eutectic to produce a carbonatite melt. The type of skarn reactions depends on the protolith carbonate composition, as well as temperature, pressure, and additional solute components involved (see Bowman, 1998a). The diversity and complexity of infiltrative skarn reactions increase with increasing contact-metasomatic temperatures, such as those characteristic of the relatively high temperature, subalkalic to peralkalic, anorogenic (A-type) felsic magmatic systems (Eby, 1992); these intrusions are most commonly associated with typical carbonatites and fenites.

It is well known that supercritical to subcritical vapor saturation of a silicate magma yields considerable volatiles, mainly water, but also HCl, HF, H₃PO₄ (hard acids), and other complex fluxes, salts, and solutes (Wyllie and Tuttle, 1961,

1964; Burnham, 1997). These volatiles contain metals depending on the ligands available, particularly hard acids for high-field-strength elements, like U, Th, Nb, and REEs (Keppler and Wyllie, 1991; Candela and Piccoli, 1995). The proportion of dissolved volatiles in a saturated subalkalic magma is typically on the order of 3 wt%, i.e., on the order of 30 vol% of a melt at 800 °C and 1 kbar, considering that the volatile has a density of ~0.25 g/cm³ (Burnham, 1997). However, the H₂O, HF, H₃PO₄, HCl, and related salt contents may be considerably higher and more complex in peralkalic melts (Kogarko, 1990), enhancing the possibility of mineralization (Sørensen, 1992).

Infiltrative Decarbonation Processes: End-Member Models

There are two end-member infiltrative decarbonation processes that can influence limestone melting in contact metasomatic systems: (1) the simple decarbonation reaction of carbonates, particularly the destabilization of dolomite due to infiltration of water (Fig. 2) and (2) the complex skarn-related (calc-silicate-forming) decarbonation reactions during which dissolved components in the infiltrating fluid react with the host sedimentary carbonates to produce skarns (Fig. 3).

The simple decarbonation reaction of dolomite → periclase, calcite, and CO₂ with influx of H₂O into the limestone system (Fig. 2) intersects the fluid-phase composition (near V₂; Fig. 2) required for the lowest-temperature partial melting (fluxing) of calcite-dolomite (L₂) in the simple MgO-CaO-H₂O-CO₂ system (Fanelli et al., 1986). This type of simple decarbonation reaction, calcite → CaO + Ca(OH)₂ (lime + port-

landite) (very high temperature and water-rich) and/or dolomite to periclase + brucite (intermediate temperature and water contents) should be relatively common during high-temperature, contact-metasomatic infiltration reactions because silicate magmas must evolve any dissolved fluids into their host environment during solidification. Infiltrative, metasomatic, prograde skarns proximal to the intrusion are formed at the highest temperatures and water-rock ratios and have the lowest proportion of CO₂ [$X(\text{CO}_2) < 0.1$].

The wollastonite-forming reaction is well defined in *P-T-X(CO₂)* space and therefore useful for illustrating skarn-related, calcite-melting reactions (Fig. 3). Magmatic H₂O containing dissolved silica will react with sedimentary calcite to form wollastonite and generate CO₂ that will mix with infiltrating H₂O from the intrusion. The increasing component of CO₂ in the water would approach the proportion necessary to partially melt (V₁, Fig. 3) a pure calcitic limestone (near L₁) undergoing skarn formation to wollastonite. Silica is a common dissolved constituent in the magmatic fluids that cause calc-silicate-forming (skarn) decarbonation reactions in calcitic and/or dolomitic sedimentary rocks.

The mass transfer of silica from subalkalic, quartz-saturated intrusive melts is considerable as well (~2.5 g SiO₂ per 1 kg H₂O at 800 °C and 1 kbar; see Holland and Malinin, 1979) and is directly involved in calc-silicate-forming decarbonation exoskarn reactions. Silica mass transfer also occurs from quartz-undersaturated peralkalic melt systems, although to a lesser degree. In the scenario with 2.5 g SiO₂ per 1 kg H₂O involved in the infiltrative skarn reaction, the proportion of CO₂ generated is approximately

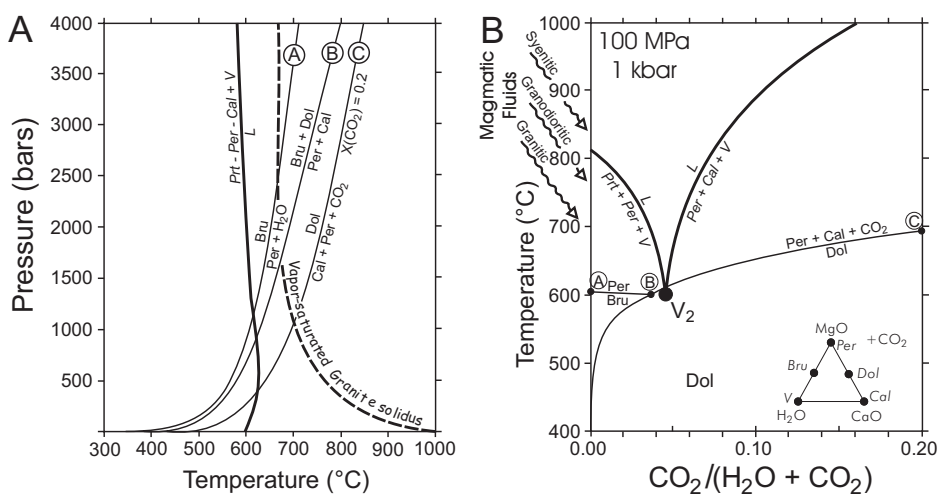


Figure 2. (A) Pressure vs. temperature diagram (B) temperature vs. $X(\text{CO}_2)$ diagram illustrating decarbonation reaction dolomite → periclase (or brucite) + calcite + CO₂ [at a $X(\text{CO}_2) = 0.05$ in A] relative to portlandite-calcite-periclase-vapor-liquid (melt) eutectic (MgO-CaO-CO₂-H₂O system; Fanelli et al., 1986), and the vapor-saturated granite solidus. Dol—dolomite, Per—periclase, Bru—brucite, Cal—calcite, Prt—portlandite, V—vapor (fluid), and L—liquid (melt). L₂ is melt eutectic composition in equilibrium with vapor (fluid) V₂. Inset shows phase relationships in CaO-MgO-CO₂-H₂O system.

$X(\text{CO}_2) = 0.03$ at the wollastonite-forming front at temperatures between the infiltrative magmatic fluid temperature and that of the skarn front. Calcite would melt if the wollastonite skarn formed at infiltrative temperatures in excess of 675 °C at 1 kbar pressure, which is not unreasonable; the proportion of CO_2 would be exactly that of the eutectic or cotectic calcite-melting curve at a point along the fluid-mixing zone or even at the skarn front. There are numerous other skarn reactions and phases, which are common metasomatic products in exoskarn systems, as well as within high-temperature reaction zones of endoskarns and/or hybridized magmas. Phenocrysts in carbonatites, their xenoliths, and associated alkalic rocks (e.g., forsterite, melilite, monticellite, vesuvianite, spurrite, tilleyite, titanite) are also very common in pyrometasomatic endoskarn and exoskarn systems (see Burnham, 1959; Zharikov, 1991), as well as in the products of assimilation (syntexis) of limestone by intrusive igneous magmas (see Lentz, 1998) so may be skarn-related xenocrysts. Other more complex skarn reactions are much easier to envisage as affecting carbonate melting because calcite is a product in those skarn reactions.

Carbonate Solubility Considerations

The noteworthy fact that few prograde infiltrative skarns have carbonates left in the proximal to distal reaction zones suggests that at least some of the carbonate is removed via reaction with the infiltrating fluid. To explain the absence of these carbonates from the skarn assemblage, it has been generally thought that they are dissolved from the sequence via “acidic” magmatic volatiles. However, most high-temperature mag-

matic fluids have near-neutral pHs (Burnham, 1997) together with the retrograde solubility of carbonates in the supercritical region limits the carbonate dissolution capacity in magmatic H_2O at high temperature. In the simple calcite- CO_2 - H_2O system, H_2O and CO_2 are completely miscible above the critical point of water. Carbonic acid (H_2CO_3) is produced in the H_2O - CO_2 solution proportional to the concentration of CO_2 on the H_2O -rich side of the solution according to Henry's law behavior. The proportion of carbonic acid generally increases with increasing temperature above 100 °C and is on the order of 10% of the CO_2 content of the fluid—i.e., if $X(\text{CO}_2) = 0.1$, then $X(\text{H}_2\text{CO}_3) \approx 0.01$ at the high temperatures under consideration (>600 °C). The solubility maxima of calcite in this simple system is at an $X(\text{CO}_2)$ value between 0.02 and 0.05 and is related to the formation of partially dissociated carbonic acid; the solubility maxima decreases with increasing temperature, but is prograde with increasing pressure (Sharp and Kennedy, 1965; Fein and Walther, 1987) even in saline solutions (Fein and Walther, 1989). For example, at 200 MPa (2 kbar), 600 °C, and $X(\text{CO}_2) = 0.02$, the molality of Ca is $1.6 \cdot 10^{-4}$ (Fein and Walther, 1987), which is the same as the molality of dissolved CaCO_3 [~ 0.09 wt% (CaCO_3)_{aq}]. It is evident that the limited solubility of carbonates in high-temperature, neutral-pH orthomagmatic fluids is problematic with respect to the absence of carbonates within many infiltrative skarns.

The absence of “excess” carbonates in the inner zones of infiltrative skarns could be explained by the mobilization of very low viscosity carbonate melts generated via volatile fluxing within the skarn-reaction zone. Removal

of carbonate melts could generate permeability and even cause a further reduction in volume (mass-balance) of some skarn zones.

ISOTOPIC RELATIONSHIPS

As stated by Tuttle and Gittins (1966), the isotopic data were thought to be inconsistent with sedimentary limestone as a source for carbonatites such that these hypotheses were not entertained subsequently. Unfortunately, the isotopic fractionation relationships for the stable isotopes and the mixing relationships for stable and radiogenic isotopes were poorly understood during the pivotal period of carbonatite evaluation.

Mobilization of carbonate melts from an evolving skarn system, however, would produce a spectrum of heavy to light stable isotopic signatures analogous to many skarn-related, calcite “vein” systems (Shimazaki et al., 1986) as a function of their stage in the skarn-related, limestone melting process and the types and extent of decarbonation reactions and fluid exchange at the time of mobilization from the skarn system. In metasomatic skarn systems, infiltrative metasomatic Rayleigh decarbonation equilibria, CO_2 evolution, and H_2O mixing relationships produce the entire spectrum of $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values in calc-silicates (skarn residue) and resultant straight mixing lines in remobilized carbonates that span from the isotopically heavy limestone-marble to the light values typical of the igneous spectrum (Nabelek, 1991; Bowman, 1998b). In carbonatites, these same covariant stable isotopic values and trends observed in skarn carbonates were generally attributed to Rayleigh crystallization processes, as well as to very low temperature hydrothermal and/or meteoric exchange processes (Deines, 1989).

Bell and Blenkinsop (1989), Kwon et al. (1989), and Barker (1996) have shown that most carbonatites have dominantly mantle like signatures for Sr, Pb, and Nd isotopes, although these researchers acknowledged a degree of “crustal” contamination, i.e., more radiogenic Sr and Pb in particular, beyond the upper-mantle evolutionary curves. The minimal capacity of carbonatite magmas to be contaminated by silicate crustal components (solids), especially Sr and Nd, which are very high in carbonatites, is problematic (see Barker, 1996).

The alternative model presented here involves hydrothermal partitioning of large amounts of Sr, Nd, and Pb from the silicate magma into a low-Sr (610 ppm), low-Nd (4.7 ppm), and low-Pb (9 ppm) limestone (Turekian and Wedepohl, 1961). The abundances and isotopic signatures of Sr, Pb, and particularly Nd will be dominated by those of the silicate magma, which is typically a mantle-derived alkalic magma. The low Sr abundance and high $^{87}\text{Sr}/^{86}\text{Sr}$ signature of limestone combined with the Sr-rich magmatic fluid having the low primitive $^{87}\text{Sr}/^{86}\text{Sr}$ signature of alkalic magma forms the limestone-skarn-related car-

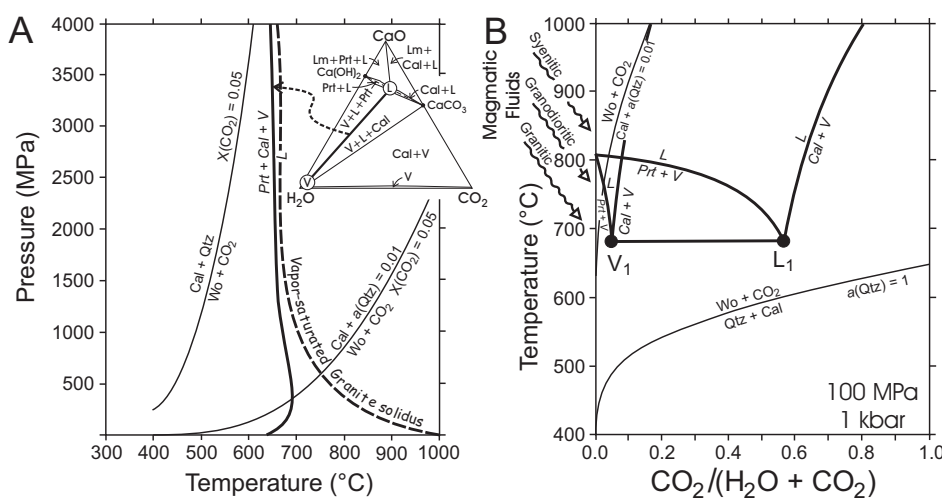


Figure 3. (A) Pressure vs. temperature diagram (B) Temperature vs. $X(\text{CO}_2)$ diagram illustrating calcite + quartz \rightarrow wollastonite + CO_2 decarbonation reaction [at an $X(\text{CO}_2) = 0.05$ in A] and a quartz activity [$a(\text{Qtz})$] of 1 and 0.01 (in solution) relative to portlandite-calcite-vapor-liquid (melt) eutectic ($\text{CaO}-\text{CO}_2-\text{H}_2\text{O}$ system; Wyllie and Tuttle, 1960), and the vapor-saturated granite solidus. Cal—calcite, Prt—portlandite, Qtz—quartz, V—vapor (fluid), and L—liquid (melt). L₁ is the melt eutectic composition in equilibrium with vapor and fluid V₁. Inset shows phase relationships in $\text{CaO}-\text{CO}_2-\text{H}_2\text{O}$ system.

bonatite through a simple mixing relationship that is directly analogous to isotopic fluid-rock mixing. It is interesting that Lentz (1998) pointed out (1) a coincident secular appearance and increase in abundance of limestones and carbonatites since the Early Proterozoic and (2) the fact that the Sr isotopic signatures of carbonatites (Bell and Blenkinsop, 1989; Barker, 1996) consistently falls between the mantle evolutionary curve and the synsedimentary limestone Sr evolutionary curve (Veiser, 1989). The two observations are compatible with the volatile fluxing and syntectic hypothesis.

CONCLUSIONS

If these volatile fluxing and limestone syntectic relationships are correct, then an entire spectrum of carbonatite melts and associated mineralization could be generated from the diverse array of intrusion-related, skarn systems. Only carbonate bodies enriched in F, P, REE, Nb, etc. would have been traditionally considered carbonatites—i.e., those associated with alkalic igneous rocks (see Lentz, 1998); others are usually interpreted as hydrothermal veins or pseudocarbonatites. Therefore, these carbonate-melt-generating processes should be entirely re-examined in light of skarn reaction equilibria in order to elucidate the origin of various carbonate bodies (carbonatites, pseudocarbonatites, and carbonate vein systems; see Lentz, 1998). It is possible that there are a spectrum of crustal to mantle sources for carbonatites; the challenge will be discriminating between them.

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