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Carbonatite magmas: natural examples and the phase relations they define

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ABSTRACT — As the picture of carbonatite magmatism continues to improve, so the bimodal distribution of calcio- and magnesio-carbonatites becomes more apparent. Calcite carbonatites are much more abundant: some of these may be differentiated from silicate parent magmas. But carbonatite volcanism requires that calciocarbonatite can be sourced in the mantle, without involvement of silicate melts. Phase relations in the Ca-Mg carbonate system impose the requirement for separate sources for calcitic and dolomitic carbonatites. Dolomite is the expected product of incipient mantle melting. Calciocarbonatite may arise from melting of a higher level CaCO₃ rich stockwork metasome, in which higher pressure polymorphs, possibly including aragonite, might be the controlling influence on the melt composition.

RIASSUNTO. — Con il miglioramento delle notizie sul magmatismo carbonatitico, diviene più evidente la distribuzione bimodale delle calcio- e magnesio-carbonatiti. Le calcite-carbonatiti sono molto più abbondanti: alcune delle quali potrebbero essere differenziate a partire da magmi silicatici. Ma il vulcanismo carbonatitico richiede che le calciocarbonatiti possano avere come sorgente il mantello senza il coinvolgimento di fusi silicatici. Le relazioni di fase nel sistema Ca-Mg carbonato impone sorgenti separate per le carbonatiti calciche e magnesiache. La dolomite è ritenuta il prodotto della fusione incipiente di mantello. Le calciocarbonatiti possono derivare dalla fusione di un'area metasomatizzata con più alti tenori di arricchimento in CaCO₃, in cui i polimorfi di più alta pressione,

possibilmente includendo l'aragonite, potrebbero controllare la composizione del magma.

KEY WORDS: *bimodality; phenocrysts; melts; metasome; mantle.*

INTRODUCTION

In recent years more instances of carbonatite volcanics have come to light, and there has been increasing recognition of its special information content (Bailey, 1993; Church, 1995). Already over 40 examples are known (Woolley, this vol.), and of these, 2 are dolomitic, with the rest calcitic. Among their important features, fine grained («volcanic») carbonatites carry evidence of crystal-melt conditions, with phase relations that can provide insights into carbonatite magmatism.

PHASE RELATIONS

Fine grained calcite carbonatites provide convincing evidence for natural calcic melts, many with high temperature indicators, and some carrying mantle debris. High Ti magnetite, quite distinct from that in coarse carbonatite, is a typical accessory, and encompasses the composition ranges found in silicate volcanics (Bailey and Kearns, 2002).

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Monocrystalline calcite phenocrysts (tabular on 0001) are typical, suggesting that this is the high temperature habit. Mg, Fe, Mn are very low in the calcite crystals, which have high Sr: hence, most of the Mg and Fe in the whole rock analyses is in oxides and silicates. «Dry» calcite carbonatite melts would require temperatures in the range 1000-1500°C., consistent with the intrinsic high temperature evidence in natural examples. Some lowering of melt temperature by fluxing components, such as Fe, P, and F, must be expected, but there is no evidence of massive devolatilisation from fine grained calcite carbonatite.

Pure dolomitic melt eruptions are rare,

possibly because pressure quenching (above the dissociation P) accompanied by gas-solid entrainment from depth, impose stringent eruption conditions. Some samples are essentially porphyritic dolomite melts, and here too the dolomite crystals are tabular, as distinct from the characteristic rhomb habit of lower temperature dolomite. High Mn and Sr, with negligible Fe is the normal dolomite composition: also distinctive is magnesiochromite as the only cognate spinel, coupled with an absence of cognate apatite.

Related to these are eruptions largely composed of dolomite plus phlogopite, with kimberlite affinities.

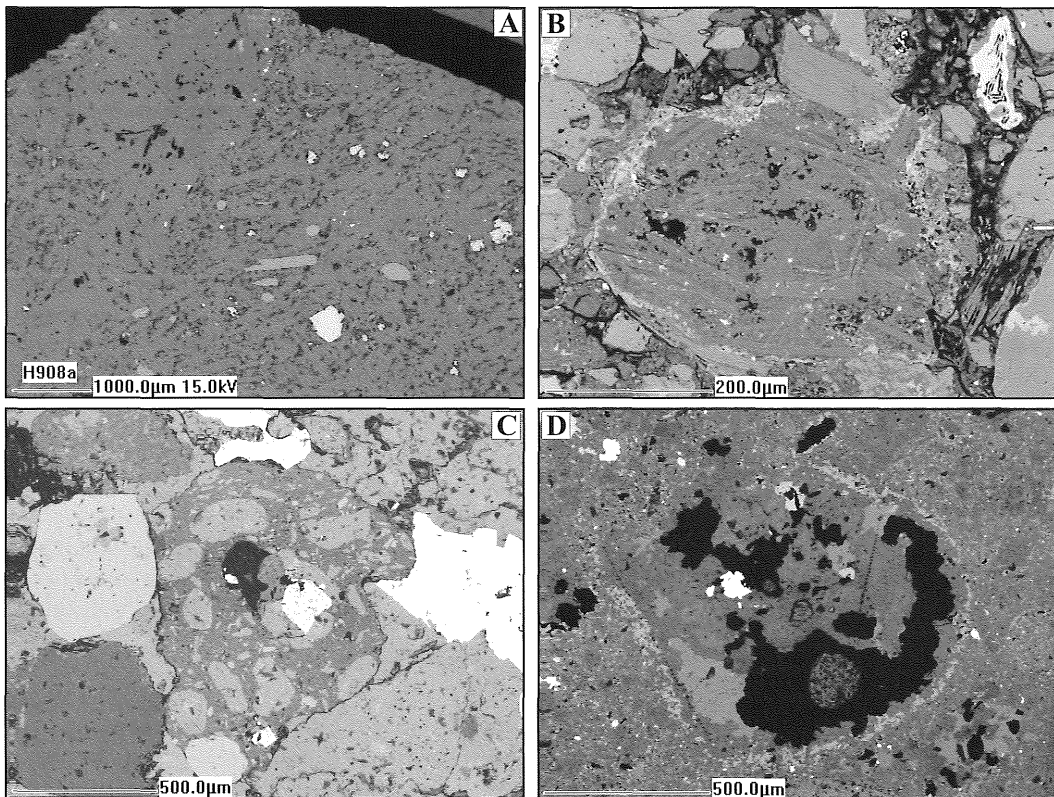


Fig. 1 – BSE images of some fine grained carbonatites. A) Sample H908. Calcite phenocrysts in calcite carbonatite. B) Sample S12. Dolomite phenocrysts in dolomite carbonatite lapillus. C) Sample S37. Calcite phenocrysts in a dolomite carbonatite lapillus. D) Sample H861. Dolomite lapillus with coarse calcite in core

PROBLEMATIC MG – CA CARBONATITE LAPILLI

Some primary dolomite eruptions have dolomite lapilli with calcite cores, which also carry magnesiochromite. In most cases the core (with some discrete anhedral dolomite) is coarser grained than the dolomite rim (Fig. 1, H861), and in others the calcite core is fine grained, with intergrown K feldspar, grading towards the dolomite rim.

In the Kaluwe layered fragmental complex (Zambia), there are mixed eruptions containing fine grained lapilli displaying a range of phase assemblages, including calcite phyric calcite carbonatite (as in, Bailey and Kearns, 2002, Fig. 1, H908), calcite phyric dolomite, aphyric dolomite, aphyric dolomite + calcite, and dolomite phyric dolomite, representing different melt compositions of uncertain relationship. Examples of these are shown in Fig. 1, and are under renewed study (Bailey and Kearns, in prep.). Some of these lapilli types were described previously (Ngwenya and Bailey, 1991), and the calcite phyric dolomite lapilli (Fig. 1, S37) in particular, defy explanation in terms of classic experiments on calcite–dolomite, because the crystal and matrix compositions lie at opposite sides of the phase diagrams (Fig. 2). At any given temperature, crystals and liquid can be in equilibrium only on the same solid solution loop.

A few examples are reported of high level intrusions with dolomite rhombs in a calcite matrix. These might appear to be porphyritic melts, but dolomite in calcite melt presents the same enigma as the calcite phyric dolomite lapilli mentioned above: phenocryst and melt compositions would be required to lie on different, and opposite, solid solution loops (Fig. 2).

FUNDAMENTAL GAP IN CARBONATITE
COMPOSITION DISTRIBUTIONS

Volcanic carbonatites are 95% calcitic, with 5% dolomitic, and as yet intermediate compositions have not been reported as an

eruption event. This is a dramatic illustration of a similar distribution noted for intrusive carbonatite analyses (Bailey, 1993). This latter distribution is almost certainly skewed, because many dolomitic carbonatites in intrusive complexes are replacements of earlier calciocarbonatites, indeed Barker (1993) has argued that virtually all have this origin. There is no doubt that many are not magmatic, which implies that the intrusive composition frequency may be of similar form to the volcanic, i.e. predominantly calcitic, with a much lower proportion of igneous dolomites than that derived simply from tables of analyses.

In his classic review, written when carbonatite magmatism was widely questioned, Campbell Smith (1956) proposed that carbonatite cone sheets were perhaps the best evidence for carbonate melt emplacement. Within the present knowledge of the volcanism, the cone sheets can be seen as an integral part of the magmatic story. What may be lost from view is that where cone sheet complexes have been studied in detail (von Eckermann, 1966; Garson, 1966) the same compositional dichotomy emerges: most of the cone sheets are either calcitic or dolomitic carbonatites, and furthermore these two types originate from different focal depths.

Hence, evidence for the compositional gap (and the need for explanations) grows rather than diminishes. Separation of calcic and silicate melts by fractionation/immiscibility may contribute to the greater abundance of calciocarbonatites, but many calcic volcanics have no associated silicate eruptions, and many carry mantle debris, so separate generation in the mantle source cannot be ignored. This becomes even more evident when other possible, and proposed courses of magma generation are viewed in terms of the carbonate phase diagram (Fig. 2). There it may be seen that the liquidus/solidus boundaries are defined by two solid solution loops which meet at a temperature minimum between calcite and dolomite. This relationship means that in the absence of source composition constraints, the observed bimodal distribution of carbonatites

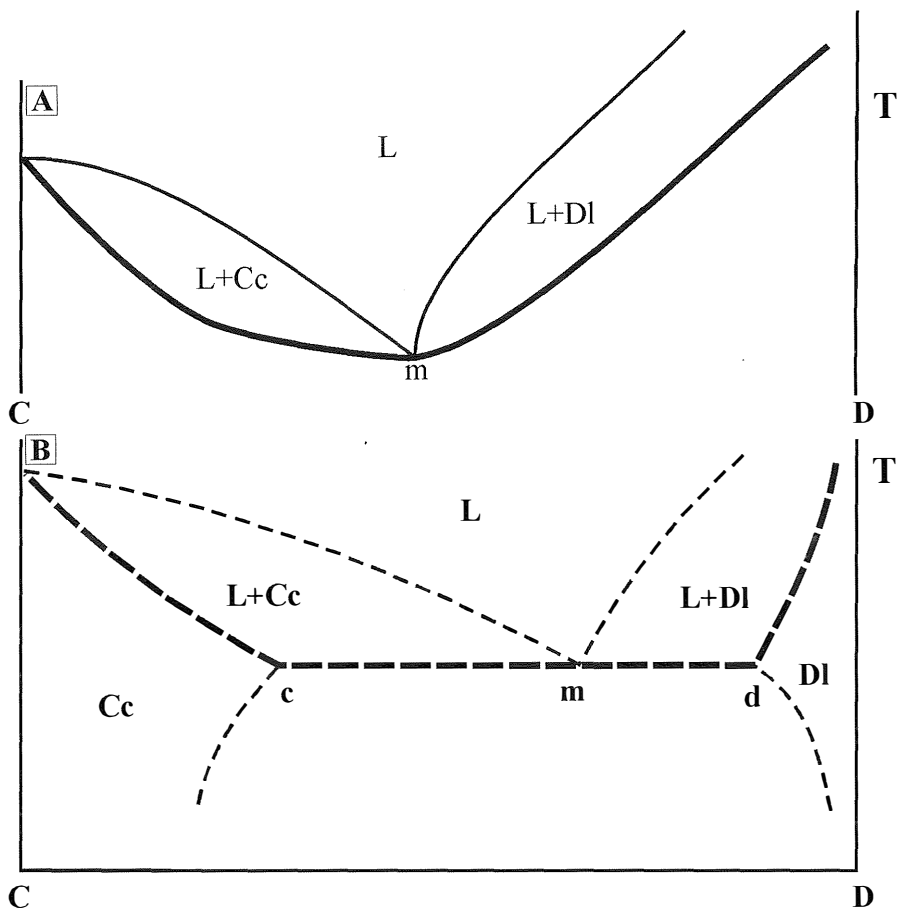


Fig. 2 – Schematic phase diagrams for $\text{CaCO}_3\text{--CaMg}(\text{CO}_3)_2$ (C–D) to facilitate text discussion of natural carbonatites and experiments (see Goldsmith (1983) for actual diagrams covering pressures from 6–30 kb). T indicates temperature axis.

A). Solid solution loops where the solidus (heavy line) is above the solvus.
 B). Illustrating the proposed case where addition of volatiles (e.g. H_2O , Wyllie, 1989) may lower the solidus to intersect the solvus. In both cases 'm' is the liquidus minimum; L, liquid; Cc, calcite solid solution; Dl, dolomite solid solution. Most carbonatites have carbonate bulk compositions clustering near C or D, with a marked gap in frequency between.

If initial carbonatite melt compositions could lie anywhere between C and D, then the natural frequency distribution of the final rocks (from cumulates/residual liquids/liquids + crystals) would be the opposite of that observed because the frequency maximum would be in the range around 'm'. Calciocarbonatites with low Mg, near C, (which are in the majority) cannot be cumulates from melts ranging towards D because these would precipitate solid solutions with compositions defined by the solidus between C–D. Given these phase relations, only calciocarbonatite melts could generate calcitic igneous rocks.

If carbonatites were produced by melting of carbonate solid sources (with compositions that could lie anywhere between C and D) then again the maximum composition frequency would be in the range around 'm'. Only a calcite rich source could provide calciocarbonatite magma.

Similar constraints would apply to dolomite carbonatites in the crust. In the mantle some melts with dolomite contents as low as 20 Wt. % may be possible as a result of wallrock reaction (Dalton and Wood, 1993) but as yet, none of positive mantle origin have been identified.

could not result from crystallisation nor melting of source compositions between calcite and dolomite. Calcitic or dolomitic melts can form only from sources of similar composition.

MANTLE SOURCE CONTROLS

Some high temperature melts coming direct from the mantle lack associated silicate volcanics (Bailey, 1993; Woolley, this vol.), and must represent low volume extracts. Dolomite may be the incipient deep mantle melt but experiments are so far unable to provide for calcite carbonatite by melting of carbonated peridotite-wehrlite (Dalton and Wood, 1993): as calcic melts are the most abundant, and dolomites are the only other type reported, alternative hypotheses are needed. A possibility is that calcite carbonatite may be from a higher level pervasive (or stockwork) carbonate metasome. The beginning-of-melting carbonate assemblage could be aragonite-dolomite, with aragonite dominant, whence only minor amounts of melt with significant Mg could be liberated, by a new flux of volatiles.

Calcite carbonatite is also the most common variety in plutons, most of which are reported as showing little or no sign of high T at the present intrusion level. Consequently, final emplacement as a calcite crystal mush is widely favoured: this is sometimes coupled with the suggestion that the mush is a cumulate from a different carbonate parent composition. As pointed out in the caption for Fig. 2, this is not explicable in terms of the Ca-Mg carbonate phase diagram. High temperature calcite carbonatite is the common volcanic magma type indicating that some calcite intrusions form simply from the solidification of mantle melts that were slowed (or ponded) during ascent through the crust.

When the bimodal distribution was first noted (Bailey, 1993) it was concluded that:

«A compositional gap exists between calcio- and magnesio-carbonatites, which is not explicable in terms of fractionation (based on present experimental data). The compositional

gap may reflect primary differences in sources, or in melt generation mechanisms. This remains a crucial area for further research.»

The final sentence still applies.

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