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CARBONATITE METASOMATISM, THE KEY TO UNLOCKING THE CARBONATITE-PHOSCORITE-ULTRAMAFIC ROCK PARADOX

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Abstract

One of the features of carbonatite-phoscorite complexes that has received comparatively little attention is that many of them are surrounded by large bodies of ultramafic rocks. Although it is generally assumed that all the rocks are of igneous origin, there is disagreement over whether the carbonatites and phoscorites are genetically related to the ultramafic rocks. This is despite the fact that in complexes where they have been dated, these three suites of rocks are identical in age. A major challenge for any igneous hypothesis is the paradox posed by the observation that the ultramafic and carbonatitic magmas are the products of very high and very low degrees of partial melting of the mantle, respectively. We resolve this paradox by proposing a hypothesis, in which the ultramafic rocks are metasomatic in origin. According to this hypothesis, a carbonatitic magma, generated by partial melting of carbonated mantle, acts as the agent of metasomatism. The interaction of this magma with quartz-rich rocks, including granites and gneisses, transforms them into ultramafic rocks. This is made possible by the extremely low viscosity of the magma that allows it to pervasively infiltrate the wall rocks. As a result, Mg, Ca and other components are transferred to the host, leading to the crystallisation of minerals such as olivine, clinopyroxene and biotite, and the loss of CO_2 from the system. Because of its low viscosity, the carbonatitic magma

is emplaced as numerous intrusions, ranging in width from the micron to the metre scale, that progressively transform the host rocks into ultramafic rocks. As this metasomatism proceeds, the Na concentration of the magma gradually increases and eventually becomes high enough to permit large scale assimilation of Si (and Al) and the generation of an alkaline silicate magma that is emplaced at the margins of complexes, forming ijolites. The metasomatism and assimilation are envisaged as a front that moves progressively from the conduit to the limits of the complex, producing an outward zonation from dunite through clinopyroxenite to ijolite or from clinopyroxenite to ijolite directly. Whether the zonation is fully developed or dominated by a single zone, e.g., dunite or clinopyroxenite, depends on the initial composition of the carbonatitic magma and/or the degree of progress of the metasomatic reaction. The processes described above constitute the “silicate stage” of carbonatite-phoscorite-ultramafic rock complex development and are marked by the complete consumption of the carbonatitic magma. During the waning stages of the formation of these complexes, metasomatism by new batches of carbonatitic magma is restricted to remnants of reactive wall rocks adjacent to the magma conduit. Consequently, the magma is only partially consumed. This results in a residual liquid that is enriched in phosphate and iron and crystallises phoscorite. We refer to this as the “phoscorite stage” of carbonatite-phoscorite-ultramafic rock complex development. The final, “carbonatite stage”, is marked by the cessation of metasomatic activity and the crystallisation of carbonatites from batches of magma that are unaffected by interaction with the wall rocks and are compositionally identical to those that initiated the “silicate stage”. This model explains the spatial association of the different rock types, in which the complexes are zoned outwards from a core of carbonatite, through a zone enriched in phoscorite, into a broad halo of ultramafic/ultrabasic rocks. In so doing, the model accounts for the many features of these complexes that have not been adequately explained in previous genetic models.

Introduction

A feature of many carbonatite complexes is a close association of the carbonatites with large bodies of ultramafic rocks and phoscorites. For example, the Phalaborwa complex (South Africa) comprises a relatively small body of carbonatite and adjacent phoscorite surrounded by a large elliptical (in plan) body of clinopyroxenite (Eriksson, 1989). At Serra Negra (Brazil), there are two small centres of carbonatite (one of them contains phoscorite) surrounded by a large circular (in plan) mass of dunite (Grasso, 2007). Finally, the Kovdor complex (Russia) contains a small intrusion of carbonatite and accompanying phoscorite in a sea of ultramafic rocks, including peridotite, clinopyroxenite and ijolite (Mikhailova et al., 2016, Kalashnikov et al., 2017). In some complexes, there is a roughly concentric zonation of the ultramafic rocks. For example, at Kovdor the peridotite (core) passes outward into a zone of clinopyroxenite and, in turn, a zone dominated by Na-Fe-rich basic to ultrabasic rocks, mainly ijolite. In the Phalaborwa complex, the clinopyroxenites are surrounded by a thin rim of feldspathic (microcline) pyroxenite. This spatial association of carbonatites, phoscorites and ultramafic rocks suggests that they are genetically related. The challenge is to explain this relationship, assuming, as discussed below, that the carbonatitic and ultramafic magmas originated in the mantle.

Carbonatitic magmas originating from direct melting of carbonated mantle are the products of extremely low degrees of partial melting (<0.5%; Dalton and Presnall, 1998), whereas ultramafic magmas are generated at very high degrees of partial melting; picritic and komatiitic magmas require 20-50 % of partial melting (Herzberg, 1992, Mole et al., 2014, Zhao et al., 2021). This presents a major problem for any igneous hypothesis that uses the spatial association between carbonatites and ultramafic rocks in carbonatite-phoscorite-ultramafic rock complexes to argue that the two suites of rocks are genetically related. The problem is compounded by the fact that no amount of partial melting of the mantle can produce a magma with the composition of dunite. Consequently, the dunites in these complexes are considered to be cumulate rocks produced by fractional crystallisation of mafic to ultramafic magmas. However, the lack of rocks that would have crystallised from the residual magmas of such fractional crystallisation precludes this explanation for dunite-rich carbonatite complexes, such as Serra Negra.

An important feature of carbonatite-phoscorite-ultramafic rock complexes is that the ultramafic rocks commonly contain significant proportions of apatite, magnetite and phlogopite (Eriksson, 1989, Brod et al., 2000, Verhulst et al., 2000), which is unusual for ultramafic rocks originating from fractional crystallisation, but would be consistent with a genetic link to carbonatites and phoscorites; most researchers agree that phoscorites are genetically related to carbonatites, but are divided over whether they fractionally crystallised or crystallised from a liquid that had separated immiscibly from a parental carbonatitic magma (Krasnova et al., 2004). A genetic link between carbonatites/phoscorites and ultramafic rocks in some complexes, e.g., Phalaborwa and Kovdor, is also consistent with the observation that their ages are identical within the analytical uncertainty (Wu et al., 2011, Wu et al., 2013). In summary, the available evidence indicates that the carbonatites and phoscorites in complexes, such as those mentioned above, are genetically related to the large masses of ultramafic rocks that surround them.

In this paper, we use examples of carbonatite complexes containing phoscorite and high proportions of ultramafic rocks to propose a model that explains the spatial and temporal association of these three rock types. The model involves the metasomatism of quartz-rich rocks by mantle-derived magnesio- and calcio-carbonatitic magmas to produce dunite and/or clinopyroxenite. As a result of this alteration, the magma is progressively depleted in Mg and Ca, and enriched in P, Si and Fe, producing a residual magma that crystallises phoscorite. The end stage of the process is the complete replacement of the country rocks and continued emplacement of carbonatites that are unaffected by further interaction with their host.

It is important to emphasise that this paper presents an idea that needs to be thoroughly tested both experimentally and by further field observations. To this end, we have initiated an experimental study to evaluate the feasibility of our hypothesis and encourage researchers working on these complexes to rigorously test the model in their ongoing investigations of the genesis of the carbonatite-phoscorite-ultramafic rock association.

Carbonatitic magma origin and evolution

The key to understanding the association between carbonatites, phoscorites and ultramafic rocks lies in identifying the processes that control the nature, origin and evolution of carbonatitic magmas. Three models have been proposed for the genesis of these magmas, namely, partial melting of carbonated mantle to yield a carbonatite magma directly, extreme fractional crystallisation of a mantle-derived carbonate-rich silicate magma or exsolution from such a magma of an immiscible carbonate melt (Bell and Rukhlov, 2004). In the case of carbonatite-phoscorite-ultramafic rock complexes, only the last two models can be invoked in a purely igneous explanation of the carbonatite-phoscorite-ultramafic rock association, because of the widely differing degrees of partial melting required for the genesis of carbonatitic and ultramafic magmas. We will show, however, that direct melting of the mantle to produce a carbonatitic magma provides a plausible and indeed superior explanation for this association by involving a metasomatic origin for the ultramafic rocks.

As might be expected from the Mg-rich nature of the mantle, carbonatitic magmas are initially dolomitic in composition (Hammouda and Keshav, 2015). Such magmas invariably interact with orthopyroxene in the overlying mantle to form forsterite, leading to magmas that are more calcitic in composition; at constant silica activity, conversion of orthopyroxene to forsterite depletes the magma in Mg via the reaction:

$$MgSiO_3 \text{ (orthopyroxene)} + CaMg(CO_3)_2 \text{ (melt)} = Mg_2SiO_4 \text{ (olivine)} + CaCO_3 \text{ (melt)} + CO_2 \qquad (1)$$

Although this reaction may partly explain the preponderance of calcite carbonatite in the Earth's crust, it should be noted that ongoing passage of carbonatitic magma through the mantle to the crust will inevitably armour the conduits, leading to the later emplacement of magmas that are dolomitic in composition.

Magma ascent

Molecular dynamic simulations of the properties of calcio-carbonatitic magmas, in particular their density and low viscosity, have shown that in narrow conduits, e.g., 1-2 m in diameter, these magmas can ascend at rates between 20 and 65 m/s (Genge et al., 1995). The implication of this is that a carbonatitic liquid generated in the mantle could reach the surface of the Earth in less than an hour. In reality, however, the conduits need to be created and the ascent of the magma is likely to take considerably longer. We propose that this ascent results from fluid overpressures created by the production of CO_2 during metasomatism of the wall rocks by the magma. These overpressures lead to fracturing of the wall rocks, pressure release and a rapid rise of magma that is followed by a period of quiescence during which there is renewed build-up of fluid pressure due to the ongoing metasomatism (Fig. 1). This episodic build-up of CO_2 and percussive fracturing of the wall rocks controls the rate of magma ascent (see also Walter et al. (2021)).

The nature of carbonatite intrusions

There is a tendency to consider large carbonatitic intrusive centres as comprising a single intrusion or a small number of separate intrusions. Although this may be the case for granitic plutons, we think it likely that most carbonatite intrusions are composed almost entirely of very large numbers of narrow veins, dykes and plugs ranging from millimetres to several metres in diameter. In the extreme, a carbonatitic intrusive centre would comprise a stockwork of veins and dykes in which all the intervening space has been taken up by carbonate minerals and the contacts between the individual veins and dykes are eliminated. The reason for this contrast in the behaviour of granitic and carbonatitic magmas is the enormous difference in their viscosity. Whereas the viscosity of silicate and, particularly granitic magmas, is very high, e.g., 10^5 to 10^6 Pa·S for peralkaline granitic magma at 700 ^{o}C (Siegel et al., 2018), the viscosity of carbonatitic magmas is extremely low, similar to that of water, i.e., 10^{-2} to 10^{-3} Pa·S, (Genge et al., 1995). As a result, carbonatitic magmas should behave like aqueous liquids and be readily injected into extremely narrow fractures (and even along grain boundaries). In contrast, granitic magmas need to create their own space either by opening up large fractures and intruding them as dykes or, in some cases, by stoping the overlying and adjacent wall rocks, creating hundreds of metre- to kilometre-scale intrusions in the process.

A major consequence of the emplacement of carbonatites as narrow veins and dykes to form large intrusive centres is that nearly the entire volume of the magma has the opportunity to interact with the wall rock. As a result, the potential for metasomatic exchange between the magma and the wall rock is enormous.

Carbonatitic magma-wall rock interaction

As discussed above, we propose that carbonatites are emplaced as stockworks of dykelets, dykes and small plugs. This, and the extremely low viscosity of the magma allow for its pervasive interaction with the wall rocks and their metasomatic replacement by a process analogous to the hydrothermal process of fenitisation. Thus, for example, a magnesio-carbonatitic magma could alter the wall rocks by replacing K-feldspar with phlogopite through the transfer of Mg and OH to them, which would result in an increase in the $CaCO_3$ content of the magma and a loss of CO_2 from the system. Evidence for this process is provided by observations made by the authors of the St Honoré carbonatite, Québec, showing that K-feldspar in the wall rock syenite was altered to phlogopite and the carbonatite adjacent to the phlogopitised syenite is calcitic. Figure 2a illustrates the onset of phlogopitisation of syenite by magnesio-carbonatitic magma injected along narrow fractures in the syenite. In Figure 2b, the syenite has been brecciated by the magma and altered almost entirely to phlogopite. We interpret this process to have occurred via the reaction:

$$KAlSi_3O_8\ (\text{K-feldspar}) + 3CaMg(CO_3)_2\ (\text{magma}) + H_2O = KMg_3(Si_3Al)O_{10}(OH)_2\ (\text{phlogopite}) + 3CaCO_3\ (\text{magma}) + 3CO_2 \qquad (2)$$

which is illustrated in Figure 3. For this reaction to proceed, a thermodynamic driver is required, and an obvious driver is the overpressure fracture-induced loss of CO_2 invoked for the percussion model of carbonatite emplacement discussed above. A feature of this model is the resulting fragmentation, support for which is provided by the ubiquitous occurrence of variably sized phlogopitised fragments of syenite in the carbonatite at St Honoré (Fig. 2b).

Although the example presented above refers to the metasomatic replacement of syenite by phlogopite, the nature of the metasomatic rock will vary considerably with the composition of the wall rock. For example, interaction of a magnesio-carbonatitic magma with quartzite could produce a rock consisting entirely of clinopyroxene via the reaction:

$$MgCa(CO_3)_2 \text{ (magma)} + 2SiO_2 \text{ (quartz)} = CaMgSi_2O_6 \text{ (diopside)} + 2CO_2 \qquad (3)$$

In principle, the interaction with quartzite could also lead to the formation of a rock consisting entirely of olivine either by reacting earlier formed diopside with new batches of magma (this is suggested by inclusions of diopside and calcite in forsterite of the ultramafic rocks at Kovdor; see below) or directly, via the reactions:

$$3MgCa(CO_3)_2 \text{ (magma)} + CaMgSi_2O_6 \text{ (diopside)} = 2Mg_2SiO_4 \text{ (olivine)} + 4CaCO_3 \text{ (magma)} + 2CO_2 \qquad (4)$$

$$2MgCa(CO_3)_2 \text{ (magma)} + SiO_2 \text{ (quartz)} = Mg_2SiO_4 \text{ (olivine)} + 2CaCO_3 \text{ (magma)} + 2CO_2 \qquad (5)$$

The latter reaction, however, would require initial metastable crystallisation of olivine because it cannot form in equilibrium with quartz (enstatite is the stable magnesium silicate phase in contact with quartz, whereas olivine is the stable magnesium silicate phase in carbonatite magma; see Reaction 1).

If, instead of quartzite, the wall rock is a K-feldspar-rich granite, the resulting metasomatic alteration by a magnesio-carbonatitic magma (Reactions 2 to 5) might lead to the formation of phlogopitic peridotite or phlogopitic clinopyroxenite. Such ultramafic rocks are common in many complexes hosting carbonatites, for example, those of the Kola Alkaline Province (e.g., the Kovdor) in Russia (Verhulst et al., 2000), the complexes of the Alto Paranaiba Alkaline Province (e.g., Serra Negra, Salitre, Tapira, Catalão) in Brazil (Brod et al., 2000), the Gardiner complex in Greenland (Nielsen et al., 1997), and the Phalaborwa complex in South Africa (Eriksson, 1989). The possibility that these ultramafic rocks may be metasomatic is discussed in more detail below.

The carbonatite-phoscorite-ultramafic rock association

Although, there are over 500 carbonatite complexes, a relatively small number of them, located mainly in the Kola Peninsula (Russia) and Alto Paranaiba belt (Brazil), contain large proportions of ultramafic rocks. For the purpose of this paper, we review the geology/geochemistry of four of these complexes, which were selected because they contain phoscorites and either have been very well studied and/or contain a single type of ultramafic rock. These are the adjacent Serra Negra and Salitre I complexes (Brazil), the Phalaborwa complex (South Africa) and the Kovdor complex (Russia).

Serra Negra comprises two small (~1 km in diameter) carbonatite centres, one of which contains phoscorite, in an ellipsoidal body of dunite (10 km x 8 km in plan; Fig. 4a), whereas the Salitre I complex comprises a 3 km wide centre of carbonatite-phoscorite ring dykes in a 8 km x 5 km elliptical (in plan; Fig. 4b) body of clinopyroxenite that is characterised by elevated proportions of apatite and perovskite (Grasso, 2007, Barbosa et al., 2012). Such clinopyroxenites are referred to as bebedourites by Brazilian geologists (Barbosa et al., 2012). The carbonatite in the Serra Negra complex is mainly a magnesio-carbonatite that grades outwards in both centres into a breccia comprising variably phlogopitised fragments of dunite and clinopyroxenite cemented by carbonatite (Grasso, 2007). Calcio-carbonatite is present in the northern of the two carbonatite centres and locally contains decimetre-wide layers of phoscorite. Over 70 % of the Serra Negra complex is composed of dunite (Fig. 4a) containing small proportions of magnetite, phlogopite and interstitial calcite. The carbonatites of the Salitre I complex form ring- and, locally, radial-dykes of both magnesio- and calcio-carbonatite containing subordinate olivine, phlogopite and magnetite, and minor proportions of pyrochlore and sulphide minerals (pyrite, pyrrhotite and chalcopyrite). These dykes cut concentric dykes of phoscorite containing olivine, phlogopite, magnetite and apatite and minor pyrochlore, pyrrhotite and chalcopyrite (Barbosa et al., 2020). The clinopyroxenites typically contain less than 50 modal % clinopyroxene, with the balance comprising variable proportions of apatite, magnetite, phlogopite, perovskite, melanite, carbonate and olivine (Barbosa et al., 2012).

Researchers, who have worked on Serra Negra, Salitre I and other similar complexes in the Alto Paranaiba Alkaline Igneous Province (~85 Ma; Gibson et al., 1995), consider the ultramafic parts of the complexes to be the products of partial melting of a metasomatised subcontinental lithospheric mantle associated with the Trindade Mantle Plume (Gibson et al., 1995, Brod et al., 2000, Barbosa et al., 2012). According to their interpretation, the parental magma was a phlogopite picrite (common as late dykes in the Alto Paranaiba complexes) from which the carbonatites evolved through liquid immiscibility or fractional crystallisation.

Another interesting example of the carbonatite-phoscorite-ultramafic rock association is the Paleo-Proterozoic Phalaborwa complex (South Africa). This complex contains a relatively small central core of carbonatite-phoscorite (1.3 km x 0.8 km in plan) in a much larger body of clinopyroxenite (6.5 km x 2.5 km in plan; Fig. 5a). The carbonatite/phoscorite core (Loolekop) consists of an outer zone of phoscorite, which grades progressively inwards through larger irregular blocks and lenses of calcio-carbonatite into a massive magnetite-rich calcio-carbonatite that is referred to as “banded” carbonatite (Eriksson, 1989). The phoscorite comprises roughly equal proportions of apatite, magnetite, calcite and silicate minerals (olivine and/or phlogopite), except locally, where olivine is the dominant mineral. There were two stages of carbonatite emplacement, an early “banded” carbonatite stage, which was coeval with emplacement of the phoscorite, and a later “transgressive” stage. The “banded” carbonatite consists dominantly of calcite containing up to 7.5 wt.% $MgCO_3$ and fine layers of magnetite. There are also minor proportions of apatite and olivine; the latter was partly replaced by phlogopite, monazite or clinohumite. The “transgressive” carbonatite occurs as dykes that cut both the phoscorite and the “banded” carbonatite. As is the case for the “banded” carbonatite, the “transgressive“ carbonatite consists mainly of calcite, however, the calcite is richer in Mg, containing up to 14 wt. % $MgCO_3$, and there is subordinate dolomite. The magnetite content is similar to that of the “banded” carbonatite, but rather than concentrating in layers, the magnetite occurs primarily as blebs and idiomorphic crystals ranging up to several tens of cm in diameter. Apatite is more abundant in the “transgressive“ carbonatite than in the “banded” carbonatite and typically occurs as finely disseminated grains; olivine is rarely observed. Clinopyroxenites comprise ~70 % of the Phalaborwa complex (Fig. 5a). These rocks may be composed almost exclusively of clinopyroxene or consist dominantly of phlogopite, subordinate apatite and less than 25 volume % clinopyroxene. The textural relationships are extremely complex, and include sharp and gradational contacts, layering and inclusions of one compositional type of clinopyroxenite in another. These relationships led Eriksson (1989) to conclude that the clinopyroxene, phlogopite and apatite co-crystallised. The outmost part of the Phalaborwa complex comprises a 100-500 m wide semi-continuous rim of feldspathic pyroxenite containing K-feldspar and apatite.

The origin of the Phalaborwa complex is poorly understood and there is considerable disagreement over whether the carbonatites/phoscorites are genetically related to the spatially associated ultramafic rocks. Decrée et al. (2020), on the basis of the higher initial $^{87}Sr/^{86}Sr$ ratios of the clinopyroxenites compared to the carbonatites/phoscorites, concluded that these two rock suites had different mantle sources and, therefore, are not genetically related. The same conclusion was reached by Giebel et al. (2019), based on the large differences in the mica chemistry of the carbonatites/phoscorites and clinopyroxenites. However, Wu et al. (2011), because the ages of the carbonatites/phoscorites and clinopyroxenites are identical within the analytical uncertainty (2060 ± 4 to 2062 ± 2 Ma), suggested that the carbonatites/phoscorites and ultramafic rocks are genetically related, observing that although the parental magma for the clinopyroxenite is unknown, the carbonatites "can be regarded as differentiates" of this magma. This interpretation is consistent with their observation that the εNd and εHf values of the carbonatites, phoscorites and clinopyroxenites are very similar. Significantly, the similar εNd and εHf values of the three rock units are consistent with the metasomatic model discussed below. Importantly, this model might also explain the higher initial $^{87}Sr/^{86}Sr$ ratios of the clinopyroxenites, assuming, as seems reasonable, that the quartzo-felspathic gneisses hosting the complex had a much higher initial $^{87}Sr/^{86}Sr$ ratio than the carbonatite magma (such gneisses have high Rb contents, including ^{87}Rb, which decays to ^{87}Sr, and low Sr contents).

Our final example of the carbonatite-phoscorite-ultramafic rock association is the Late Devonian Kovdor complex in Russia, which is arguably the most studied of any carbonatite-phoscorite complex. Like Serra Negra, Salitre I and Phalaborwa, the Kovdor carbonatites and phoscorites form a relatively small centre (600 m x 1300 m in plan) in a large body of ultramafic rocks (7.5 km x 9 km in plan, Fig. 5b), although unlike these other complexes, the carbonatite-phoscorite centre is located near the edge of the complex (south-west). In addition to this centre, there are numerous separate calcio-carbonatite and phoscorite dykes, particularly in the south-west part of the complex. The entire complex is surrounded by a wide halo of fenitised Archean gneisses. The carbonatites and phoscorites of the centre occur as swarms of dykes with the phoscorite dykes being more numerous towards its edge (Krasnova et al., 2004, Mikhailova et al., 2016). There is also a temporal progression from early phoscorite dykes to later carbonatite dykes, although both rock units evolved synchronously, i.e., early phoscorites and carbonatites were succeeded by compositionally more evolved phoscorites and carbonatites (Krasnova et al., 2004). The early phoscorite dykes are composed of olivine, apatite, magnetite and calcite, and evolved to an assemblage of tetraferriphlogopite, apatite, magnetite and dolomite, whereas the carbonatite dykes evolved from calcio-carbonatite to magnesio-carbonatite. Ultramafic rocks in the complex are distributed zonally outwards from a core of olivine-rich peridotite through clinopyroxenite to a rim of ijolite. The peridotite is essentially a dunite containing minor proportions of magnetite and calcite and is interpreted to have been variably altered to diopside, phlogopite and apatite (Mikhailova et al., 2016). Significantly (see above), the forsterite in these rocks contains inclusions of diopside and calcite (Mikhailova et al., 2018). This zone passes gradationally into the clinopyroxenite zone, which contains variable proportions of phlogopite, melilite, monticellite and hydroxyapatite that some have interpreted to represent a metasomatic interface between the peridotite and ijolite zones (e.g., Mikhailova et al., 2016). Others, e.g., Verhulst et al (2000) have interpreted the clinopyroxenites to be igneous. The ijolite zone consists of variable proportions of nepheline, diopside and melilite and locally contains several percent of calcite (as inclusions in nepheline and diopside).

Most of the research on the Kovdor complex has focused on the relationships between the carbonatites and phoscorites. Some studies, however, have also considered the relationship between the carbonatites/phoscorites and the ultramafic rocks that dominate the complex. These latter studies, e.g., Veksler et al. (1998) and Verhulst et al. (2000), have concluded that the carbonatites and phoscorites are the end-products of the fractional crystallisation of a carbonated mela-nephelinite magma that initially crystallised to form cumulate dunites, peridotites and pyroxenites, and evolved to crystallise melilitolites, melteigites, ijolites and urtites (some, e.g., Mikhailova et al. (2016), consider the clinopyroxenites to be metasomatic; see above). Support for the hypothesis that the ultramafic rocks and carbonatites/phoscorites are genetically related is provided by the fact that the peridotites, ijolites and clinopyroxenites have initial $^{87}Sr/^{86}Sr$ ratios and εNd values that are indistinguishable from those of the carbonatites/phoscorites (Verhulst et al., 2000), although the ranges for the two sets of isotope data are relatively wide. Further support for this hypothesis is provided by the fact that, within the analytical uncertainty, the carbonatites/phoscorites and ultramafic rocks are identical in age (~380 Ma; Wu et al., 2013). Because of the relatively wide ranges in the initial $^{87}Sr/^{86}Sr$ ratios and εNd values, Verhulst et al. (2000) concluded that the parental magma(s) was either derived from a heterogeneous mantle or there were two sources for the magma, namely, a depleted mantle and a mantle plume. The ijolites have much lower εNd values than the other ultramafic rocks, but the reason for this has not been explained.

The close spatial and temporal association of the phoscorites and the carbonatites at Kovdor has been the subject of considerable discussion, and there is a general agreement that these two rock types are genetically related. There is a consensus that these units represent a magmatic system that evolved in-situ to produce a phoscorite-dominated outer part and a carbonatite-dominated core, with the mineralogy of both rock units recording the evolving composition of the magma(s). Whether this evolution was the result of side-wall crystallisation of a single batch of magma, as proposed by Mikhailova et al. (2016), or fractional crystallisation of multiple batches of magma, as proposed by Krasnova et al. (2004), is unresolved for researchers working on the Kovdor complex, nor has the possibility been excluded that the two rock units formed as a result of liquid immiscibility (Krasnova et al., 2004).

In summary, carbonatites and phoscorites frequently occur in large complexes dominated by ultramafic rocks. These latter rocks may be exclusively dunites or clinopyroxenites, or comprise a variety of ultramafic rocks including dunite, peridotite, clinopyroxenite and alkaline ultrabasic rocks, such as ijolite. Commonly, the carbonatite/phoscorite centres, which may occur anywhere in a complex, are zoned from an outer phoscoritic part to a core of carbonatite. In some cases, the surrounding ultramafic rocks are also zonally distributed. For example, at Kovdor, they are zoned from a core of dunite through clinopyroxenite to ijolite, and at Phalaborwa, from clinopyroxenite to feldspathic (K-feldspar) clinopyroxenite. The ultramafic rocks are also conspicuous for the common occurrence of domains that are strongly enriched in phlogopite (glimmerite). All the complexes are surrounded by a halo of fenitisation.

The genesis of carbonatite-phoscorite-ultramafic rock complexes is very poorly understood and, although most researchers consider them to be igneous in origin, there is disagreement over whether the carbonatites/phoscorites and the ultramafic rocks are genetically related. Those who argue for this genetic relationship are either forced to speculate on the nature of the parental magma (Nielsen et al., 1997, Veksler et al., 1998, Brod et al., 2000) or have to admit that evidence linking the ultramafic rocks to a magma type parental to carbonatite-phoscorite-ultramafic rock complexes simply does not exist (Wu et al., 2011). For example, Nielsen et al. (1997) proposed that the parental magma for the Gardiner complex, Greenland, was an olivine melilitite or mela-nephelinite (based on melt inclusion compositions and phase equilibria). Veksler et al. (1998) used similar types of information to conclude that the parental magma for Kovdor was a mela-nephelinite. In both cases, however, rocks with these compositions have not been observed in the corresponding complexes. Brod et al. (2000) used the occurrence of compositionally primitive phlogopite picrite dykes in the complexes of the Alto Paranaiba Province to conclude that the parental magma for these complexes had the composition of a phlogopite picrite. Whether, as the authors propose, the carbonatites and associated silicate rocks were related to this parental magma by a combination of fractional crystallisation and liquid immiscibility, however, is unclear.

A major reason that the relationship between carbonatites/phoscorites and the spatially associated ultramafic rocks is poorly understood is that the carbonatites commonly have Sr isotopic signatures that differ from those of the ultramafic rocks (the isotopic signature of the phoscorites may be similar to or different from those of the carbonatites). In order to reconcile these differences, researchers postulating a genetic link between the carbonatites/phoscorites and the ultramafic rocks have attributed the differences to the melting of heterogeneous carbonated mantle (see above). This, however, does not address the requirement of an extremely low degree of partial melting to produce the carbonatites and a very high degree of partial melting to generate the temporally related ultramafic rocks. To avoid this problem, researchers favouring a genetic link between them have been forced to propose that the carbonatites formed by fractional crystallisation of a silicate melt or liquid immiscibility (see above). However, there is no evidence to support either of these hypotheses for carbonatites associated with ultramafic rocks. In the absence of such evidence, the simplest, most plausible explanation (Occam’s razor) is one involving the generation of the carbonatitic magmas by direct partial melting of the mantle. Similarly, although the carbonatites and phoscorites are spatially and temporally associated, there is no convincing evidence to support either of the prevailing hypotheses linking them genetically, i.e., fractional crystallisation and liquid immiscibility.

The model

As discussed above, none of the genetic models that have been proposed for carbonatite-phoscorite-ultramafic rock complexes are able to explain the close spatial and temporal relationships of the three compositionally distinct rock units that comprise these complexes. In the paragraphs that follow, we develop a carbonatite magma-wall rock interaction model for the genesis of carbonatite-phoscorite-ultramafic rock complexes that explains these relationships.

The starting point for our model is the generation of magnesio-carbonatitic magmas by extremely low degrees of partial melting (<0.5%; Dalton and Presnall, 1998) of a carbonated subcontinental lithospheric mantle. These magmas, which are dolomitic in composition, rise through the mantle and, on reaching the solidus ledge, at a depth between 70 and 35 km, react metasomatically with enstatite to form diopside, forsterite and CO_2 (Lee and Wyllie, 2000, Hammouda and Keshav, 2015). If this reaction goes to completion, the magmas are entirely consumed. However, once the wall rocks are armoured by forsterite and diopside, the reaction terminates, and subsequent batches of the magma are able to rise above this ledge (Fig. 6). The upwards motion of the magma and the introduction of new batches of magma is facilitated by the production of CO_2, its accumulation, and overpressures that fracture the wall rock. Because of the relatively ductile nature of the lithospheric mantle, the lateral brittle deformation is very limited and most of the fractures are vertical and radial/concentric. Consequently, the magma proceeds upwards as a pipe (conduit), and it does so in a series of steps due to the reaction-mediated episodic build-up and fracture-related release of pressure (Fig. 1).

In the crust, the carbonatitic magma continues to react metasomatically with the wall rocks but the nature of this reaction differs from that in the mantle because of the much greater importance of silicic rocks. Whereas armouring in the mantle involves the reaction of the magma with enstatite, in the crust a variety of other minerals, particularly quartz, are involved in this reaction.

Nonetheless, the outcome is similar. As in the mantle, the reactions produce CO_2, which creates the overpressures needed to continue fracturing the rock and facilitate the introduction of new batches of magma.

In the lower crust, the fractures are also dominantly vertical and radial/concentric, and consequently, the carbonatitic magma is emplaced as a pipe. At a depth of ~15 km, corresponding to the ductile-brittle transition, lateral fractures gradually become more important, and the magma is consequently emplaced both laterally and vertically causing the pipe to become funnel-shaped (Fig. 6). The resultant increase of lateral fracturing permits a high degree of magma-wall rock interaction. In the centre of the stress field, the fractures are wide but small in number and, with increasing distance from the conduit, decrease in size but increase in number due to the propagation of sets of new fractures from the tips of earlier fractures (Fig. 6). Because of the extremely low viscosity of this magma (comparable to that of water; see above), the alteration is pervasive in the same way that it is for hydrothermal fluids. Thus, if access to unaltered wall rock is unlimited, all of the carbonatitic liquid is consumed, and there is complete replacement of the rock by secondary minerals.

The metasomatism begins with the transfer of MgO and CaO from the magma to form clinopyroxene, olivine or wollastonite, depending on the MgO/CaO ratio. With progressive magma/rock interaction, the early formed mineral gives way to other minerals to reduce the chemical potential gradients for MgO, CaO and SiO_2. If the MgO/CaO ratio is low, i.e., the magma is a calcio-carbonatitic, wollastonite will be the first mineral to form followed by diopside (excess quartz in the wall rock precludes further reaction). However, if the MgO/CaO ratio in the magma is high, forsterite will be the first mineral to form and then diopside. At an intermediate MgO/CaO ratio, the most common scenario, the only mineral to crystallise is diopside. The ratio for which this is the case, depends on the MgO/CaO chemical potential ratio rather than the mole ratio of these components in the magma, but the MgO/CaO mole ratio is likely to be close to unity (a dolomitic composition).

During the early stages of magma/rock interaction, repeated batches of new magma react with unaltered wall rock along the pathways propagated by the fracturing mechanism described above and illustrated in Figure 6. Magma/rock interaction, therefore, progresses outwards from the conduit as a front, producing a zonation, which, as discussed above, may vary from olivine proximal to the conduit to clinopyroxene distal from it (Fig. 7), or clinopyroxene and even wollastonite proximal to the conduit. At an advanced stage of alteration, new batches of magma will interact with progressively higher proportions of wall rock that has been previously altered (excess of carbonatitic magma, Reaction 4), whereas interaction of the magma with olivine will produce no further change. The extent to which the latter alteration proceeds will depend on the magma availability and particularly, the ability of the magma to penetrate the rock; the stress that leads to brittle failure in a tectonosilicate like quartz, may produce a ductile response in a chain silicate like diopside. Consequently, because of the lack of fracturing, the magma may be directed preferentially towards unaltered rock, precluding further alteration of the clinopyroxenite.

The preceding paragraphs explain the domination of many carbonatite-phoscorite-ultramafic rock complexes by clinopyroxenite (e.g., Phalaborwa and Salitre I) or dunite (e.g., Serra Negra) or clinopyroxene and dunite (e.g., Kovdor). If the wall rocks contain K-feldspar, the formation of clinopyroxene and/or olivine is accompanied by the metasomatic replacement of K-feldspar by phlogopite, owing to the high proportion of H_2O dissolved in the carbonatite magma; MgO and H_2O in the magma react with the K-feldspar to form phlogopite (Reaction 2). This explains the abundance of phlogopite in the Phalaborwa clinopyroxenites and the common occurrence of phlogopitites in many of the complexes containing ultramafic rocks, e.g., Kovdor, Phalaborwa, Araxá (Traversa et al., 2001) and Catalão I (Cordeiro et al., 2010).

With progress of the metasomatism, the Na concentration of the magma gradually increases and, in some complexes (e.g., Kovdor), becomes high enough to permit large scale assimilation of silica-rich minerals and the generation of an alkaline silicate magma. Depending on the composition of the assimilated minerals, this magma is also variably enriched in Fe and Al, leading to the crystallisation of ijolites. The evolution of the carbonatitic magma eventually leads to its saturation with an aqueous phase that alters the rocks adjacent to the complex to fenite (Fig. 7).

In summary, the metasomatic interaction of a magnesio-carbonatitic magma with quartzo-feldspathic rocks leads to a monomineralic (olivine or clinopyroxene) or mineralogically zoned body of rock, and ultimately, in some complexes, to an intrusive alkaline silicate zone of rocks (ijolite) at the outer margin of the complex and dykes (mainly ring dykes) in the other zones (Fig. 7). We refer to the metasomatism and assimilation described above as the “Silicate stage” of carbonatite complex development (Fig. 8). A major feature of this stage is the complete consumption of the carbonatitic magma (i.e., the consumption of the cationic components to produce the silicate minerals and magma, and the loss of CO_2), and the creation of a large aureole of ultramafic/ultrabasic rocks with a carbonatitic magma signature recorded by high concentrations of elements like P and minerals such as apatite and calcite.

During the subsequent stages of metasomatism, the proportion of reactive wall rock remaining near the conduit becomes progressively smaller, and eventually alteration ceases, leaving behind a residual carbonatitic magma that is enriched in components that were not transferred to the wall rock, namely, Si, P and Fe. In our model, this residual magma evolves by crystallising calcite, thereby further enriching the magma in the above components. Subsequent crystallisation of apatite, magnetite and olivine (or phlogopite) leads to the formation of phoscorite. We refer to this stage as the “Phoscorite stage” in the development of a carbonatite complex (Fig. 8). In contrast to the “Silicate stage”, the phoscorite stage is marked by partial consumption of the carbonatitic magma because the last remnants of reactive wall rock adjacent to the conduit are insufficient to completely consume the magma. The result is the generation of a Si-P-Fe-rich magma, which crystallises to form phoscorites and ensures the occurrence of these unusual rocks adjacent to the magma conduits that are preserved as carbonatites (Fig. 8). Significantly, however, carbonatite complexes free of ultramafic rocks but showing evidence of wall rock alteration, e.g., the replacement of feldspar by phlogopite, commonly contain layers of apatite-rich segregations with magnetite and phlogopite, e.g., St Honoré. According to our model, these segregations would represent very small aliquots of phoscoritic liquid that are swept up by subsequent batches of carbonatitic magma.

The final stage in the formation of a carbonatite-phoscorite-ultramafic rock complex is the “Carbonatite stage”, during which metasomatism by new batches of magma ceases because of the lack of reactive wall rocks, and progressively more Mg-rich carbonatite crystallises (from red to yellow in Figure 8). The youngest carbonatitic magma batches preserve their original mantle composition.

The model presented in the preceding paragraphs provides a convincing explanation for the spatial and temporal evolution of carbonatite complexes. In this evolution, there is an outward and upward progression from dunite through clinopyroxenite to ijolite or from clinopyroxenite to ijolite directly, and an inward evolution to phoscorite and carbonatite (Fig. 8). Whether all units of these evolutionary sequences are preserved in a single complex depends on the initial composition of the magma, the extent of alteration and the level of erosion. In a deeply eroded, fully developed system, all units are present in a map of the complex (Fig. 8-1). This would be the case for Kovdor. If, however, the complex is less deeply eroded, the dunite would be absent as is the case at Phalaborwa (Fig. 8-2). At still shallower levels of erosion, only the ijolites are present and even the phoscorites are absent (Fig. 8-3) as exemplified by Oka (Gold, 1963). The highest erosional levels (Fig. 8-4) are characterised by carbonatites that are directly in contact with fenites, e.g., the Amba Dongar carbonatite in India (Williams-Jones and Palmer, 2002).

In summary, carbonatitic complexes are the result of large numbers of injections of carbonatitic magma in narrow fractures. Interaction of this magma with the wall rocks involves the transfer of components (especially MgO and CaO) from the magma to the rock and the loss of CO_2 from the system. This results in the formation of ultramafic metasomatic rocks dominated by olivine and/or clinopyroxene (diopside) depending on the MgO/CaO ratio of the magma. With progress of the reaction, there is gradual enrichment of the magma in Na and Fe and assimilation of Si (and Al) from the wall rocks that culminates in the magma having a Si (Al) content sufficiently high to crystallise alkaline ultrabasic rocks containing aegirine and nepheline (ijolite). Each of the magma batches forming these ultramafic/ultrabasic rocks eventually saturates with an aqueous phase, which leads to the development of the fenite aureole. In this “silicate stage” of the development of carbonatite-phoscorite-ultramafic rock complexes, virtually all of the carbonatite magma is consumed. This is followed by a “phoscorite stage”, during which the remnants of the reactive wall rock are altered, leaving behind a residual magma that is enriched in Si, Al, Fe and P, and crystallises apatite, magnetite and a silicate mineral (olivine or phlogopite). The formation of a carbonatite-phoscorite-ultramafic rock complex terminates with the cessation of carbonatitemediated alteration and the emplacement of carbonatites that retain their original mantle composition.

This model solves the paradox of the association of carbonatites and phoscorites with ultramafic rocks by providing a convincing explanation for their genetic relationship. It also explains how carbonatites and phoscorites are genetically related. Most importantly, the model explains why some carbonatite complexes are dominated by ultramafic rocks, why phoscorites do not occur in complexes without accompanying ultramafic rocks, why glimmerites are common in carbonatite complexes, why some complexes are composed exclusively of carbonatite, why many carbonatites display a fine layering representing an alternation from carbonate-rich to apatite-magnetite-phlogopite-dominated assemblages and, finally, why in most complexes there is an evolution from calcio-carbonatite to magnesio-carbonatite.

Concluding remarks

The idea that the ultramafic rocks in carbonatite-phoscorite-ultramafic rock complexes are the products of metasomatic reactions involving carbonatitic magmas is not new. Indeed, it was first proposed over seventy years ago by von Eckermann (1948) and Holmes (1950), and taken up by Russell (1954), who used it to explain the origin of the ultramafic rocks of the Phalaborwa complex, proposing that the carbonatitic magmas reacted with granites in the area to produce "Olivine-Biotite-Pyroxene" rocks and CO_2. The idea was subsequently used by Dawson (1962) to explain the relationships between the carbonatites and silicate rocks at Oldonyo Lengai. As far as we can establish, the last mention of this metasomatic hypothesis for the origin of ultramafic rocks in carbonatite-phoscorite complexes was that of Dawson and Powell (1969), who by then appeared to favour a fractional crystallisation model for relating the carbonatites and ultrabasic rocks at

Oldonyo Lengai. The hypothesis that carbonatitic magmas can be metasomatising agents was recently revived by Anenburg and Mavrogenes (2018) in an experimental study designed to explain the origin of apatite veins with diopside selvages in the Nolans Bore REE deposit (Australia). They showed that a phosphorus-rich carbonatitic magma in contact with granite will crystallise calcite and react with the granite to produce diopside, forsterite or wollastonite depending on the MgO/(MgO+CaO) ratio of the magma. Accordingly, they proposed that the apatite veins at Nolans Bore represent the residues of an apatite cumulate, from which the carbonatite magma escaped, and that the diopside records its interaction with the host granite. This envisages an evolution for the Nolans Bore deposit that in many ways resembles the evolution of carbonatite-phoscorite-ultramafic rock complexes.

The principal contribution of this study has been the recognition that hydrothermal fluids are not the only agents of metasomatism. Because their viscosity is similar to that of water, carbonatitic magmas are able to infiltrate rocks on the same scale (sub-millimetre to micron) and, therefore, are able to interact with them pervasively in the same way as hydrothermal fluids. The combination of an extremely low viscosity magma and high chemical potential gradients for Mg, Ca and Si (Fe and Na) results in the complete transformation of quartzo-feldspathic rocks into ultramafic rocks, such as biotitites (glimmerites), clinopyroxenites and peridotites/dunites. Thus, the key to understanding the origin of carbonatite-phoscorite-ultramafic rock complexes is the realisation that the evolution of the carbonatitic magmas is controlled by the intensity of alteration, which may lead either to their complete consumption (unlimited access to reactive rocks), partial consumption with the production of phoscorites (limited access to reactive rocks) or no consumption of the magmas and the crystallisation of unevolved carbonatites (no access to reactive rocks).

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Figure captions

Figure 1. An illustration of the progressive (left to right) percussive emplacement of carbonatitic magma. Metasomatic interaction of the magma with the wall rocks (cross-hatched) leads to the production of CO_2 bubbles (black dots) that accumulate at the top of the intrusion. The resulting overpressure leads to fracturing of the rock, pressure release and the emplacement of magma (red) into the newly formed fractures (subvertical black lines). The process is episodic, with periods of quiescence alternating with periods of catastrophic failure.

Figure 2. Photographs showing (a) – incipient metasomatic replacement of syenite (pink) by biotite (black) along fractures due to the transfer of Mg and OH from the carbonatitic magma (white) and (b) – brecciated syenite that has undergone intense biotitisation (black) by carbonatitic magma (white), leaving behind small fragments of partially altered syenite

(pink). The photographs are of drill core from the St Honoré carbonatite complex (Québec, Canada).

Figure 3. A photomicrograph showing perthite that has been replaced by biotite due to the interaction of magnesio-carbonatitic magma with syenite. The replacement proceeded via Reaction 2 (see text). The calcite is interpreted to have crystallised from the magma after its interaction with the syenite. The photomicrograph is of a thin section cut from a sample from the Niobec mine, Québec, Canada (St Honoré carbonatite).

Figure 4. Maps of (a) – the Serra Negra and (b) – Salitre I carbonatitic complexes (Brazil) showing the distribution of carbonatites, phoscorites and ultramafic rocks, modified after Grasso (2010) and Barbosa et al. (2012), respectively.

Figure 5. Maps of (a) – the Phalaborwa carbonatitic complex (South Africa) and (b) – the Kovdor carbonatitic complex (Russia) showing the distribution of carbonatites, phoscorites and ultramafic rocks, modified after Eriksson (1989) and Kalashnikov et al. (2017), respectively.

Figure 6. A schematic diagram illustrating the percussive emplacement of carbonatitic magma from the solidus ledge (see text) through the mantle and the brittle-ductile transition in the crust. Also shown is the fracture network above the brittle-ductile transition (LHS) and the zones of metasomatic alteration (RHS) that accompanied interaction of the carbonatitic magma with crustal rocks (the rock types corresponding to each of the colours are indicated in the legends of Figures 4 and 5). The closely spaced horizontal lines indicate the distribution of fenite.

Figure 7. Cross-sections (a) and plan views (b) showing the progressive fracturing and development of the metasomatic front that gives rise to the zonation of silicate rocks in a carbonatitic complex generated by a carbonatitic magma with a high MgO/CaO ratio; the olivine zone would be absent, if the MgO/CaO ratio of the magma had been significantly lower (the rock types corresponding to each of the colours are indicated in the legends of Figures 4 and 5). Also shown are concentric and radial intrusions of ijolite. The closely spaced horizontal lines indicate the distribution of fenite.

Figure 8. Stages in the development of a carbonatite-phoscorite-ultramafic rock complex (silicate stage → phoscorite stage → carbonatite stage) using the scenario depicted in Figure 7. Also shown are plan views of a carbonatite complex at four erosional levels (1-4). For the significance of the various colours, readers are referred to the legends in Figures 4 and 5, except yellow, which refers to late “transgressive” magnesio-carbonatite. The closely spaced horizontal lines show the distribution of fenite.

Figure 1

Vasyukova, O. V., and Williams-Jones, A. E., 2022, Carbonatite metasomatism, the key to unlocking the carbonatite-phoscorite-ultramafic rock paradox: Chemical Geology, v. 602, p. 120888.

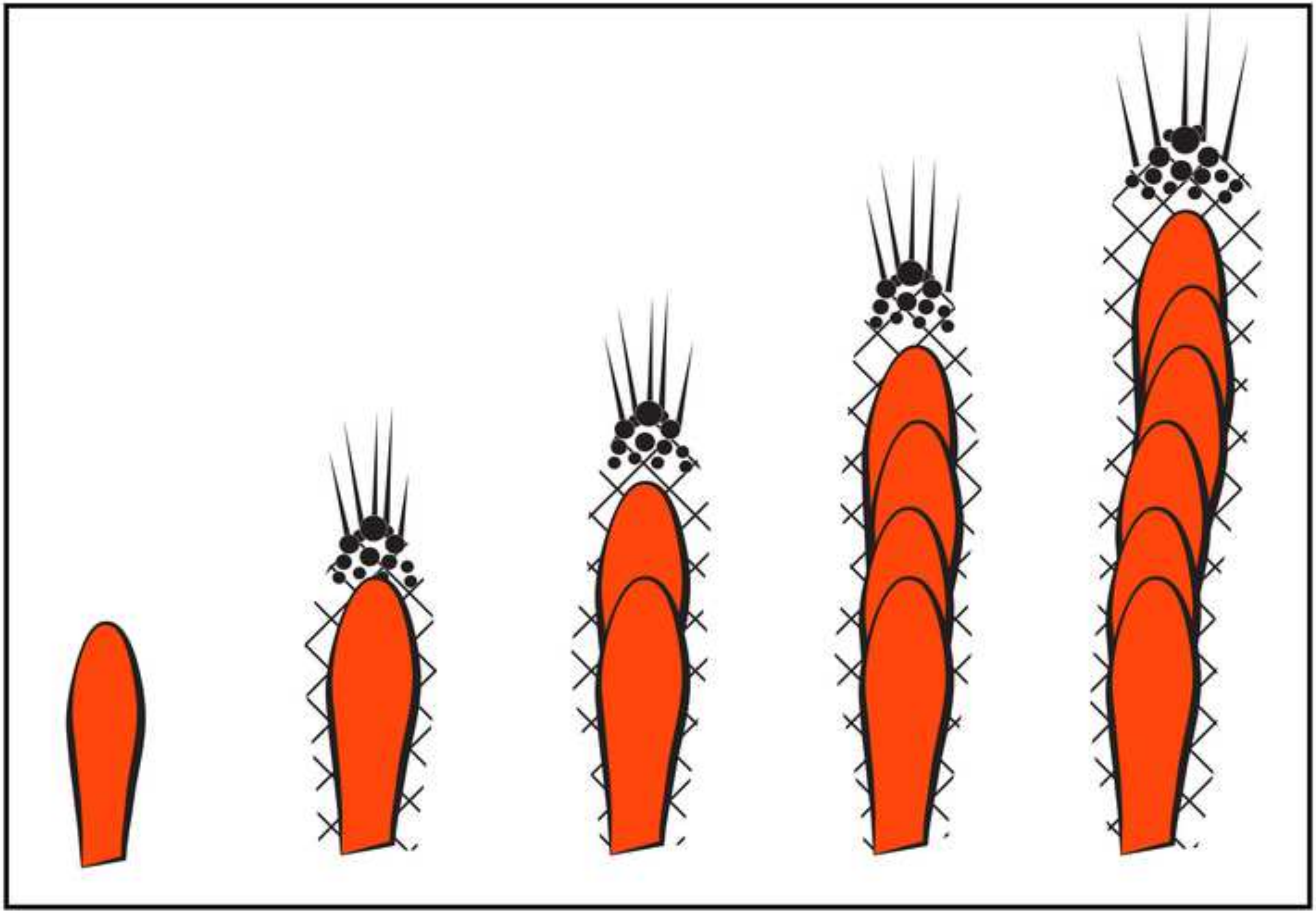


Figure 2

Vasyukova, O. V., and Williams-Jones, A. E., 2022, Carbonatite metasomatism, the key to unlocking the carbonatite-phoscorite-ultramafic rock paradox: Chemical Geology, v. 602, p. 120888.

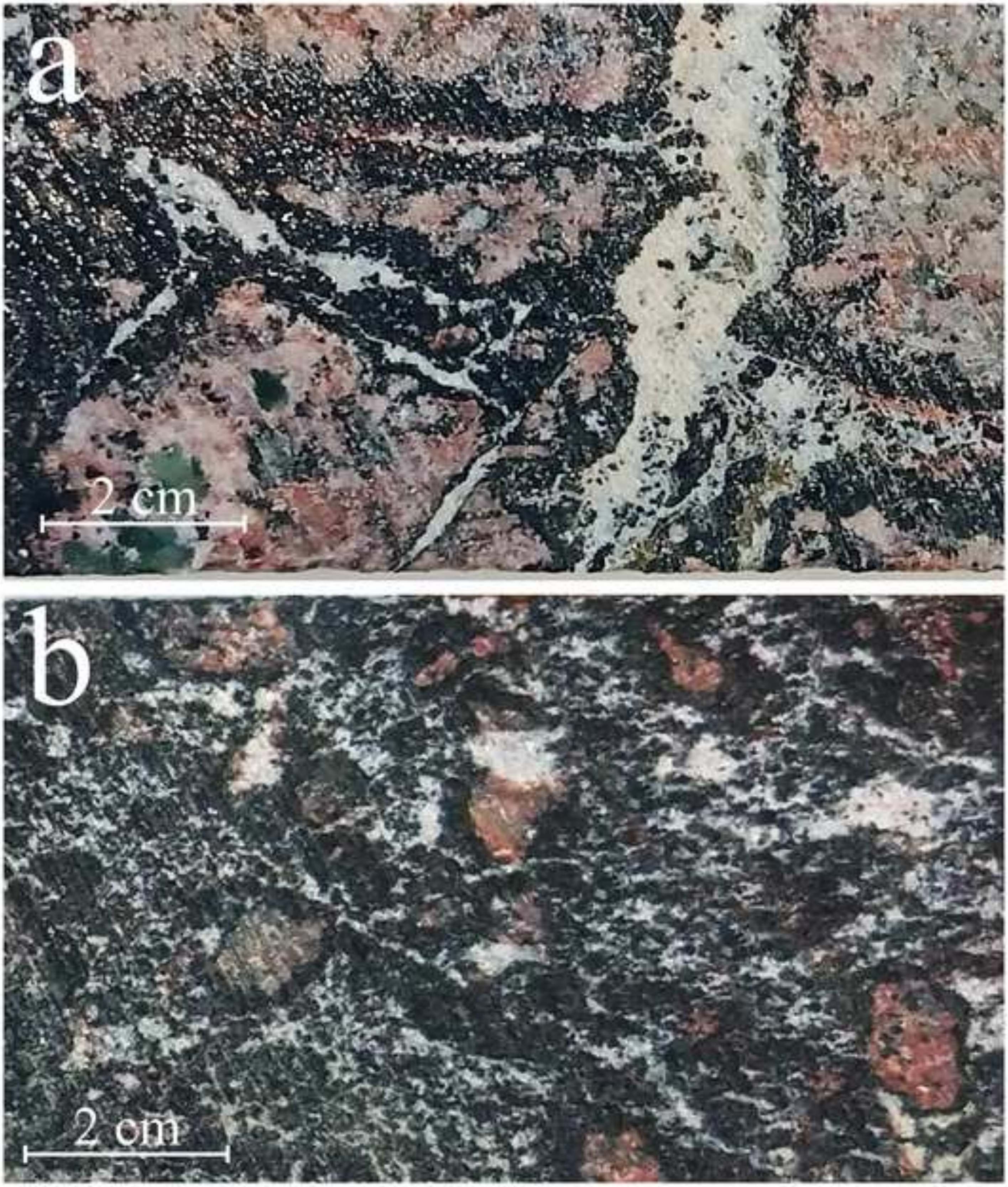


Figure 3

Vasyukova, O. V., and Williams-Jones, A. E., 2022, Carbonatite metasomatism, the key to unlocking the carbonatite-phoscorite-ultramafic rock paradox: Chemical Geology, v. 602, p. 120888.

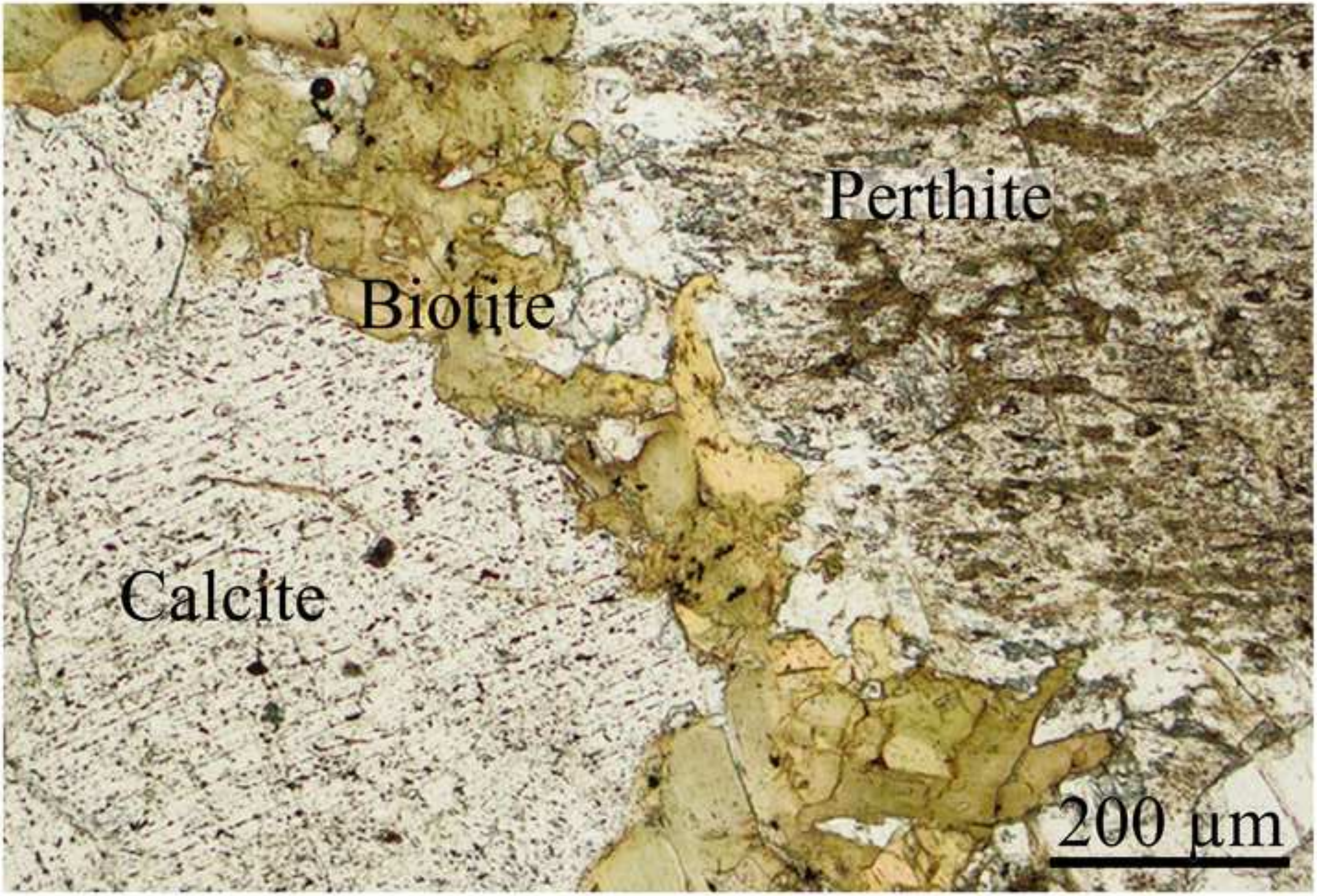


Figure 4

Vasyukova, O. V., and Williams-Jones, A. E., 2022, Carbonatite metasomatism, the key to unlocking the carbonatite-phoscorite-ultramafic rock paradox: Chemical Geology, v. 602, p. 120888.

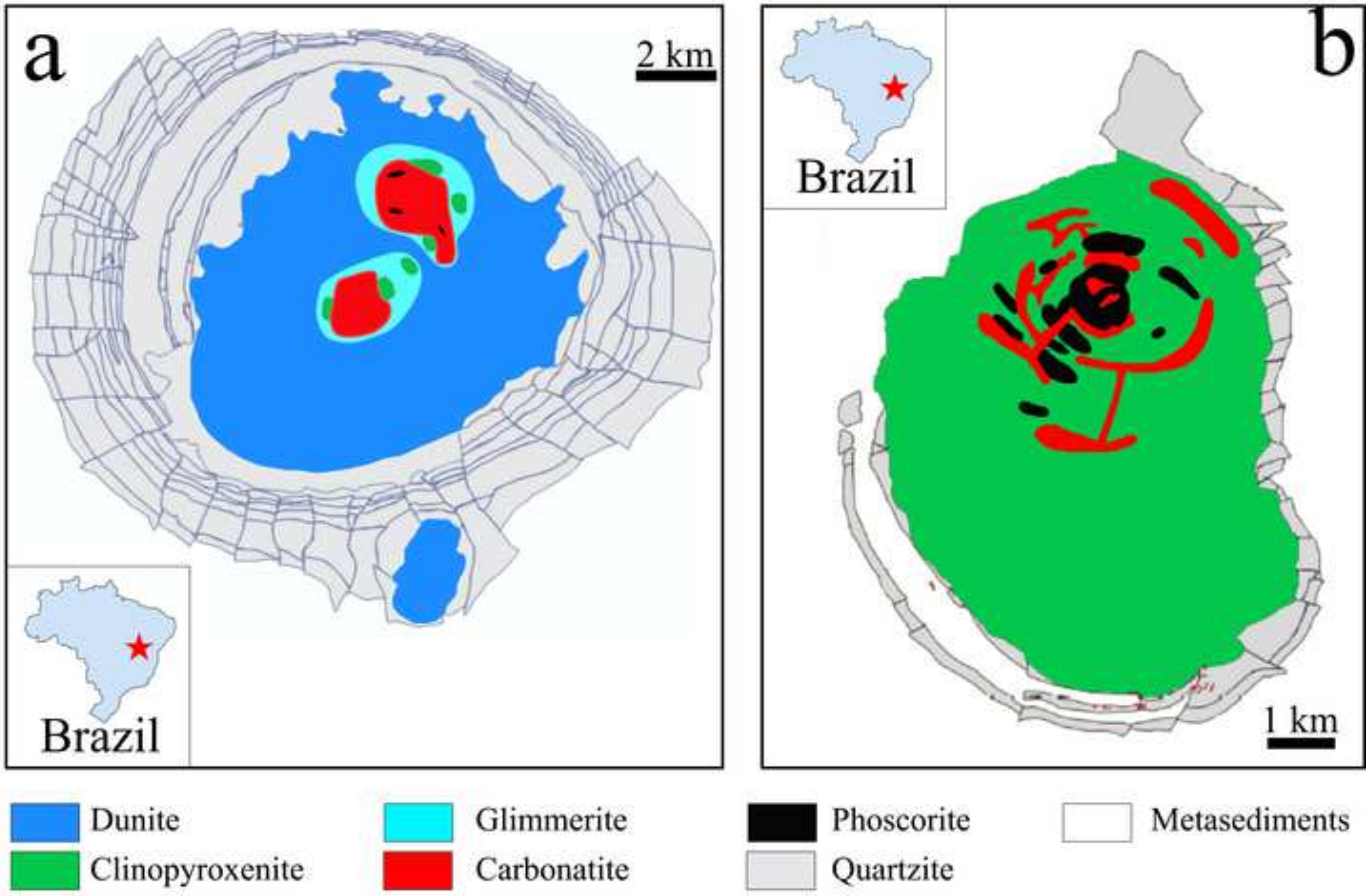


Figure 5

Vasyukova, O. V., and Williams-Jones, A. E., 2022, Carbonatite metasomatism, the key to unlocking the carbonatite-phoscorite-ultramafic rock paradox: Chemical Geology, v. 602, p. 120888.

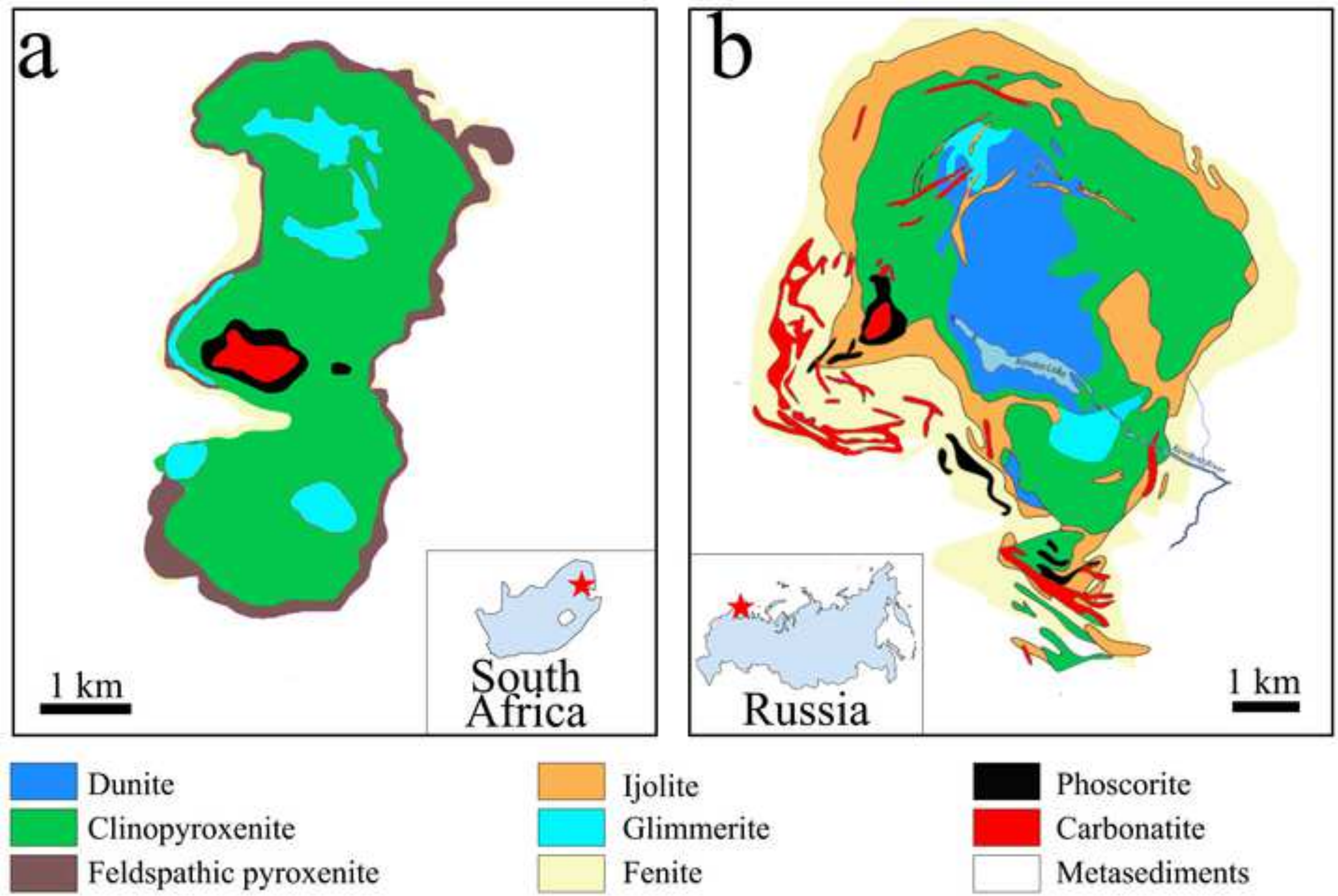
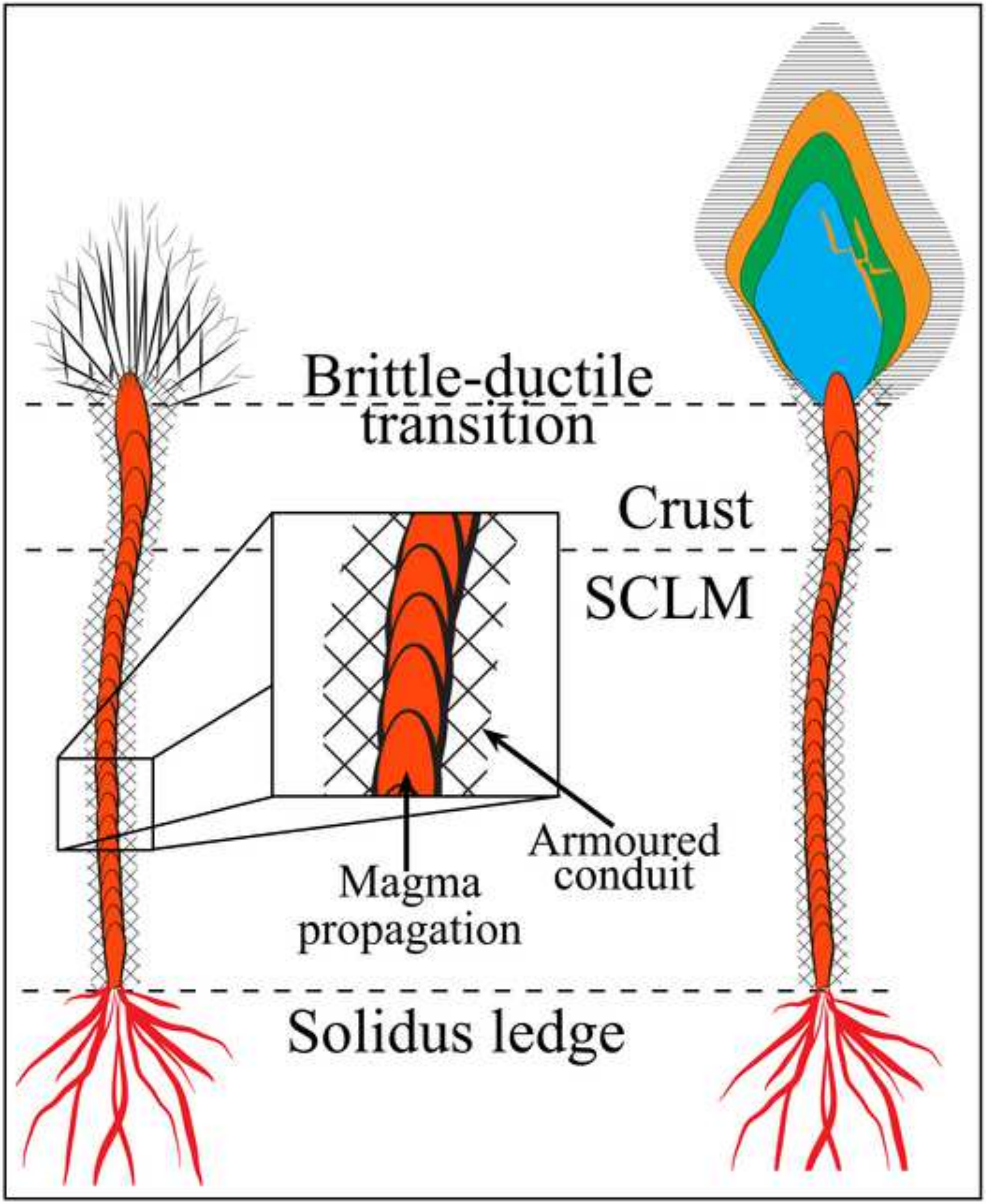


Figure 6

Vasyukova, O. V., and Williams-Jones, A. E., 2022, Carbonatite metasomatism, the key to unlocking the carbonatite-phoscorite-ultramafic rock paradox: Chemical Geology, v. 602, p. 120888.



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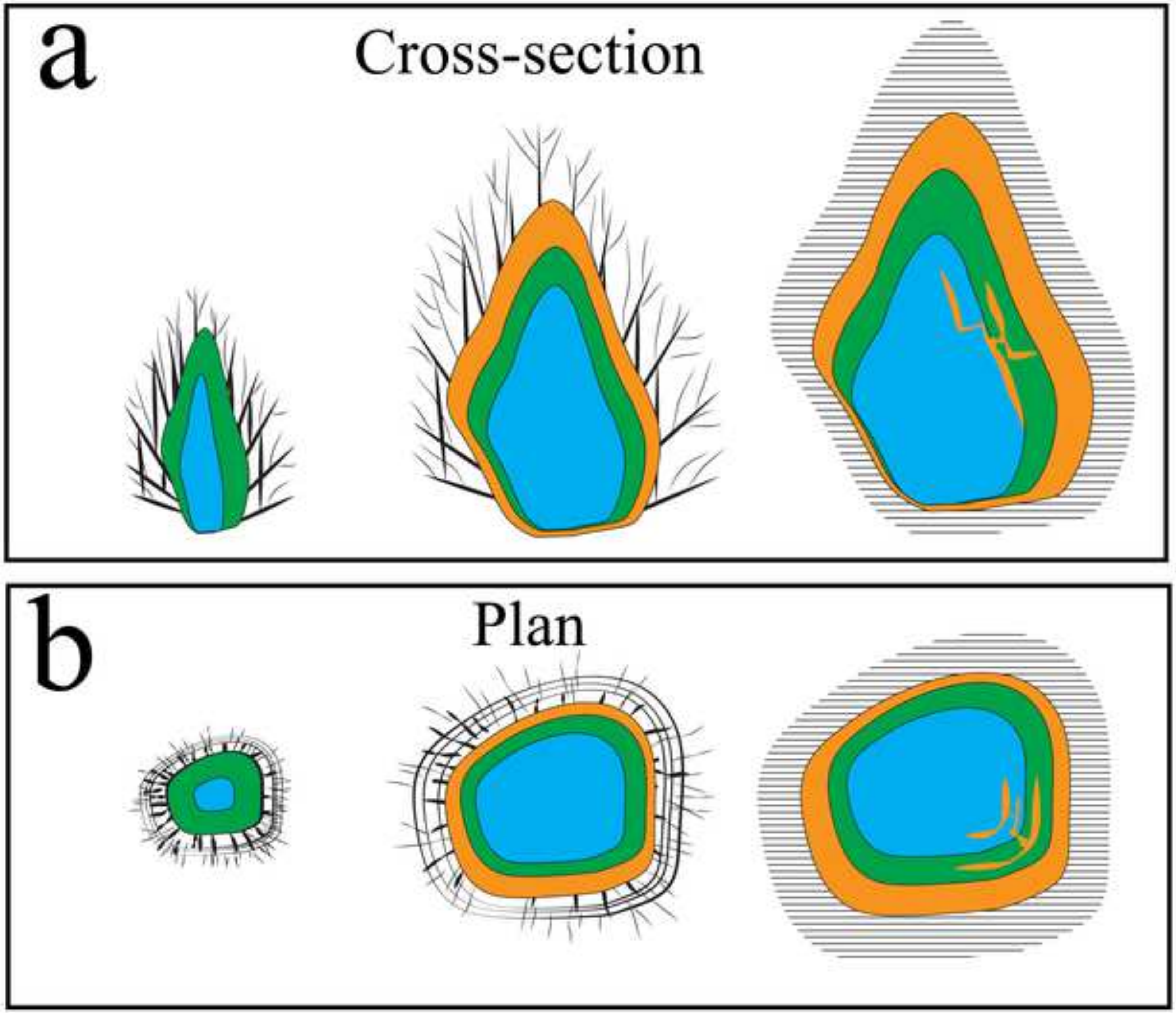

Figure 8

Vasyukova, O. V., and Williams-Jones, A. E., 2022, Carbonatite metasomatism, the key to unlocking the carbonatite-phoscorite-ultramafic rock paradox: Chemical Geology, v. 602, p. 120888.