Corundum occurrence

by

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From Weed (1899) on sapphire exploration techniques at Yogo, Montana

"…the course of the fissure can be traced by a grassy depression in the bare limestone surface, which is dotted with badger and gopher heapings. One of the heapings yielded several hundred carats of gems and was the direct cause of the discovery of the dike…"

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Declaration

This thesis contains no material which has been accepted for the award of any other degree or diploma in any tertiary institution, and to the best of my knowledge and belief, contains no material previously published or written by another person, except where due reference is made in the text of the thesis.

Signed

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Abstract

Corundum consists of Al_2O_3, has a high hardness (9) and high specific gravity (~4). Corundum's hardness and chromophoric lattice substitutions make it a valuable gemstone in the form of sapphire and ruby and is important as an abrasive in the form of emery. Corundum occurs in a wide variety of igneous and metamorphic rocks and is commonly found in detrital deposits due to its hardness.

In metamorphic rocks, corundum is found in metamorphosed laterites, partially melted pelitic rocks, high-Mg and high-Al schists, Si-poor hornfels within the aureole of igneous intrusions and metamorphosed marbles. In metamorphic rocks the presence of corundum reflects a silica undersaturated-alumina rich paragenesis.

Corundum, as an accessory mineral in igneous rocks, is found in monzonite, syenite and nepheline syenite, ultramafic dikes and other pegmatitic dikes. The presence of corundum as an accessory mineral in igneous rocks is an indication of silica undersaturation in parent magma or a post-intrusive desilicification process.

A major source of gem quality corundum is detrital deposits sourced from alkali basalt terrains. The formation of alkali basalt hosted corundum involves two stages: the formation of corundum and the subsequent incorporation and expulsion via intraplate basaltic volcanism related to rifting. The genesis of the corundum xenocrysts has been debated and no single model is able to satisfactorily explain the genesis of poly-modal gem fields. For alkali basalt hosted corundum, the favourable model for sapphire formation is the plutonic crystallisation at lower crustal/upper mantle depths from a highly aluminous volatile and trace element rich alkaline parental magma. Alkali basalt hosted rubies are likely to form from the metamorphic recrystallisation of mafic rocks in the upper mantle.

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Chapter 1 Introduction

Corundum (essentially pure Al_2O_3), due to its high hardness and variety of colours is an important mineral in industrial uses (emery as an abrasive) and as a valuable gemstone (sapphire and ruby). Corundum occurs in a wide variety of metamorphic and igneous rocks, where its presence indicates a silica-undersaturated and alumina-rich paragenesis. Due to its hardness, corundum is also found in alluvial deposits. Corundum occurs throughout the world in a variety of geological settings, although a majority of the commercial production of gem corundum is from the alkali basalt fields of Eastern Australia and SE Asia. These gemstones are sourced in alluvial, eluvial and residual soils.

The aim of this paper is to document the many corundum occurrences in all types of rocks and discuss the genetic processes associated with the more important field of alkali basalt related corundum.

1.1 Properties of corundum

Corundum (α-Al_2O_3) belongs to the trigonal crystallographic system. β-Al_2O_3 (hexagonal) and γ-Al_2O_3 (cubic) are synthetic polymorphs that, along with heating, convert to α-Al_2O_3 and therefore not found in nature (Deer et al., 1992).

The physical properties of corundum include an extreme hardness (9/10 on Moh's Scale), high specific gravity (3.98-4.02), a distinctive basal parting {0001} and is insoluble in all acids.

1.1.1 Rubies and sapphires

Ruby and sapphire is the gem variety of corundum. Substitution in the lattice of aluminium with Fe^{2+} or Ti^{2+} is responsible for the variety of blue hues exhibited in sapphires whilst Cr^{3+} causes the red tint of rubies. Substitution of Fe^{3+} into the lattice produces a yellow tint and combinations of these impurities are responsible for the other colours known in gem corundum (eg. green, purple and black). It is important to note that only red gem corundum is referred to as ruby whilst yellow, green and blue corundum is known as sapphire. Synthetic gems can be produced by the Verneuil process, with chromium or ferric ion being added for colour.

Star sapphires occur when titanium impurities in corundum crystallise as rutile needles in three directions at 120º and perpendicular to the *z*-axis. This affect can be created synthetically.

1.1.2 Emery

Emery is a rock consisting of a mixture of finely granular corundum and either haematite or magnetite. It is useful for grinding and polishing purposes. Corundum for abrasive purposes can now be created in large quantities artificially from bauxite.

1.2 Corundum Occurrence

Guo (1993) divided corundum occurrence into three main types with 7 groups on the basis of the host rock (ignoring detrital grains). This is summarised in table 1.2.

Table 1 - Major occurrence of corundum in different rock types (Modified from Guo, 1993). Entries in bold are covered in this paper

Occurrence classification	Group	Sub group	Occurrence (Guo 1993)	Occurrence (this paper)
Metamorphic	1	1.1	Si-poor hornfels within the aureole of igneous intrusions (Evans, 1964; **Smith, 1965**; Ferguson and Al-Ameen, 1985)	**Riesco, Stuwe et al., (2004); Grant and Frost (1990)**
Metamorphic		1.2	Various types of gneisses, schists and granulites in metamorphic terrains as porphryroblasts (e.g., **Clabaugh, 1952**; **Wells, 1956**; Cooray and Kumarapelli, 1960; Lawrence et al., 1987) or as corundum rich bands within normal metasediments (**Coetzee, 1940; Golani, 1989**)	**Grant and Frost (1990); (Kerrich et al., 1987); (Mercier et al., 1999) and** **Feenstra (1985, 1996)**
Metamorphic		1.3	Al-rich xenoliths enclosed in mafic and granitic intrusive rocks (Thomas, 1922; Hall and Nel, 1926; Read, 1931; Murdoch and Webb, 1942)	

Metamorphic	2	2.1	Marbles interbedded with other metasediments (**Okrusch et al**., 1976; Guberlin, 1982; Bender, 1983; Keller, 1983; Bowersox, 1985)	**Pecher et al., (2002); Garnier, Giuliani et al., (2002)**
Metamorphic		2.2	Skarns developed between limestones and granitic intrusion (Silva and Siriwandena, 1988)	
Accessory phase in igneous rocks	3		Syenites, nepheline syenites and associated pegmatites (e.g. Du Toit, 1918; **Wells, 1956**; Carlson, 1957; Kerr, 1977)	
Accessory phase in igneous rocks	4		Plagioclase pegmatite (Sokolov, 1931; Tomlinson, 1939; Rose, 1957; Solesbury, 1967; Petrussenko, 1981; Atkinson and Kothavala, 1983), oligoclase pegmatite (Lawson, 1904; Oftedal, 1963) and albitite veins (Larsen, 1928)	**Simonet et al., (2003)**
Accessory phase in igneous rocks	5		Altered igneous rocks in association with mineralisation (Schwartz, 1982; Steefel and Atkinson, 1984; Wojdak and Sinclair, 1984)	
Accessory phase in igneous rocks	6		Alkremite xenoliths (Exley et al., 1983) and ecologitic xenoliths in kimberlites (Sobolov et al., 1968; Dawson, 1980; Kornprobst et al., 1982; Hill and Haggerty, 1989)	
Discrete crystals or simple intergrowths in mafic\ultramafic dikes and basaltic rocks	7	7.1	Ultramafic dike as discrete crystals (**Claubaugh, 1952**; **Brownlow and Komorowski, 1988**; **Meyer and Mitchell, 1988**)	
Discrete crystals or simple intergrowths in mafic\ultramafic dikes and basaltic rocks		7.2	Basaltic rocks as large discrete crystals or simple intergrowths with other phases (McNevin; 1972, Stephenson, 1976; **Upton et al., 1983**)	**Guo (1993, 1996); Sutherland et al., (1996, 1998ab, 2002); Garnier (2005); Saminpanya (2003); Aspen (1990); Khin Zaw et al.,(2002); Limutrakun (2001); Yui (2002); Sutthirat et al., (2001)**

1.3 Trace element geochemistry of corundum

Trace element geochemistry can be used to distinguish between natural and synthetic corundum, differentiate rubies from different localities and to classify corundum derived from basaltic terrains into a metamorphic suite and a basaltic suite in conjunction with mineral inclusions. Recent studies have also attempted to classify basaltic and non-basaltic terrain corundum on the basis of trace element distribution (Saminpanya et al., 2003) as well as the further classification of corundum from alkali basaltic terrain into discrete groups.

Transition group elements (V, Ni, Fe, Mn, Cr and Ti) substitute in the structure of corundum and some of them are known to cause body colour: Cr is responsible for red in ruby, Ti and Fe for the blue of sapphire and V, Cr, Ti and Fe for colour change sapphire (purple-red colour under incandescent light, blue-green colour under fluorescent light) (Scmetzer and Bank, 1980). Gallium also substitutes into the corundum structure having the same charge and similar ionic radius to Al.

Chapter 2 Corundum hosted in metamorphic rocks

The presence of corundum in a metamorphic rock is an indication of silica undersaturation and is typically formed in metamorphosed laterites (Coetzee, 1940; Gall, 1992), in partially melted pelitic rocks (Harris, 1981; Grant and Frost, 1990), in high-Mg and High-Al schists (Kerrich et al., 1987; Schumacher and Robinson, 1987), in Si-poor hornfels within the aureole of igneous intrusions (Smith, 1965), and in marbles interbedded with metasediments (Okrusch et al., 1976; Fraser et al., 2001).

2.1.1 On corundum + quartz assemblages

Rare occurrences of a corundum + quartz assemblage have been reported (Bottrill, 1998; Harlov and Milke, 2002; Mouri et al., 2003). This assemblage, generally corundum + quartz + aluminosilicate (commonly sillimanite or rarer kyanite), is found to occur in relatively Al_2O_3-SiO_2-rich, high-grade metamorphic rocks either as an assemblage of grains isolated from each other or in direct contact (Santosh, 1987; Waters, 1991). This latter texture suggests that corundum + quartz could form a stable assemblage (Guiraud et al., 1996) although this contradicts current thermodynamic databases which indicate that a corundum + quartz assemblage is not stable over P-T represented by crustal and upper mantle rocks (Gottschalk, 1997; Holland and Powell, 1998). Thermodynamic data suggests that corundum + quartz is a metastable assemblage and should react to form either sillimanite or kyanite until either of the constituents is consumed.

Harlov & Milke (2002) demonstrate experimentally that the corundum + quartz assemblage can persist with very little (atmospheric) H_2O present in either the kyanite or sillimanite stability fields. However, when 2% H_2O is present, the assemblage rapidly nucleates and grows kyanite. This reaction is considered self-promoting and therefore rapidly completing, explaining the rarity of the quartz + corundum assemblage in nature, as either quartz or corundum should have been used up in the formation of kyanite or sillimanite. Mouri et al. (2003) surmise three possible mechanisms by which corundum and quartz could come into contact during metamorphism:

1. Corundum and quartz are formed in different locations and brought into contact by deformation.

2. Corundum could be one of the restitic minerals in Al-rich rocks and comes into arbitrary contact with quartz from the leucosome.

3. Corundum forms as an exsolution product in spinel in the presence of quartz inclusions.

The third mechanism is supported by Waters (1991) with a suggested reaction:

$FeAl_2O_4 + 0.5O_2 \Rightarrow 3Al_2O_3 + Fe_3O_4$

Spinel corundum magnetite

2.2 Occurrences

2.2.1 Metamorphosed bauxites (laterites)

Several occurrences of corundum in metamorphosed laterites have been documented. The two major types of corundum bearing metamorphosed laterites are documented by Feenstra (1985, 1996) who describes corundum bearing metabauxites (emeries) that occur on the islands on Naxos and Paros in Greece and by Golani (1989) and Coetzee (1940) who both describe separate sillimanite-corundum assemblages in paleosols in Meghalaya, India and Namaqualand, South Africa, respectively.

The emery deposits of Naxos and Paros (Feenstra, 1996) are described as the product of the dehydration of diasporite-bearing metabauxites of karstic origin. The emery, a fine grained mixture of corundum +/- diaspore, occurs as lenses up to 8m thick within certain metacarbonate units. Feenstra suggests the Jurassic metabauxites followed a P-T-t path within the stability field of diaspore during an early Alpine high-pressure metamorphic event and that the dehydration into emery occurred later during a medium-pressure Barrovian-type phase. This later event produced greenschist-grade rocks regionally, but reached upper amphibolite grade with associated migmatitization on Naxos and Paros. This higher level of metamorphism coincides with a greater level of dehydration and hence corundum becomes more dominant closer to the migmatite zone.

The sillimanite-corundum rocks of Meghalaya (Golani, 1989) are described as the product of high grade isochemical metamorphism of a Precambrian low-iron, high-alumina paleosol. The individual massive sillimanite-corundum bodies assume lensoid to irregular shapes commonly 1-5m thick (up to 20m thick locally due to stacking from isoclinal folding) within a quartz-sillimanite schist. The assemblage has a bulk rock chemistry low in Fe, Ca and Mg which is explained by the protolith being a high alumina-low iron paleosol geochemically similar to that of the 'white bauxites' of Queensland. The paleosol has experienced granulite facies metamorphism with only the loss of refractories (isochemical metamorphism). A similar sillimanite-corundum-ilmenite rock occurs in Namaqualand. Coetzee explains that the petrography; ilmenite enclosed by corundum aggregates, indicates a relict pisolitic texture, albeit with a reduction of volume due to water expulsion.

2.2.2 Partially melted pelitic rocks

The occurrence of corundum bearing assemblages has been reported in partially melted pelitic rocks (Grant and Frost, 1990; Frost, 1991). This is because pelitic precursors that were not rich in quartz, melting and melt loss may lead to a complete exhaustion of quartz and ultimately to the formation of silica-undersaturated paragenesis including corundum (Grant, 1985).

Grant and Frost (1990) describe a corundum occurrence within partially melted amphibolite facies pelites at Morton Pass, Wyoming. Evidence for partial melting (segregation of leucocratic material, oikocrystic K-feldspar) is present with the heat source being successive igneous intrusions from the Laramie Anorthosite Complex. Grant and Frost calculate the minimum temperature across the aureole to be 650ºC to 800ºC with a pressure of 3±0.5 kb.

The corundum occurrence exists as crystals within aggregates of sillimanite up to 20cm across within xenoliths in the intrusive complex. The corundum formation is due to desilicification of the restite as partial melting took place. The restite became highly aluminous and corundum was formed. Grant and Frost indicate that the sequence of phases to crystallise out of an Al_2O_3 rich liquid in the mullite (a complex aluminosilicate) stability field is: mullite – corundum – spinel – cordierite, which compares favourably with the observed mineralogy as the corundum and sillimanite appear to be pseudomorphs after mullite.

2.2.3 Silica poor hornfels with the aureole of igneous intrusions

The occurrence of corundum in silica poor hornfels within the aureole of igneous intrusions has been documented (Smith, 1965; Riesco et al., 2004).

Riesco et al. (2004) discuss an occurrence of corundum in a low pressure metamorphic aureole around the Susqueda igneous complex, Spain. The rocks in the aureole had previously experienced a regional cordierite-andalusite grade metamorphic event that caused localised depletion of silica by the segregation of quartz veins. Intrusion and subsequent migmatisation produced silica-undersaturated melting of these rocks.

The corundum bearing rock is a hornfels that occurs as halos around quartz veins. The corundum is present as a euhedral phase with sillimanite, spinel, cordierite and biotite and makes up 2% of the hornfels. The peak metamorphic conditions calculated are above 725ºC at 3kbar.

Grant and Frost (1990) also describe an occurrence of corundum in a metamorphic aureole. The corundum bearing assemblage appears within in pelites close to the contact with the intrusive anorthosite-monzogabbro complex. The corundum occurs as swarms within a matrix of k-feldspar-cordierite-spinel. This is representative of a corundum bearing hornfels.

2.2.4 High-Mg and high-Al schists

Kerrich et al. (1987) discuss the occurrence of corundum within ultramafic schists of the Harare greenstone belt at O'Briens in Zimbabwe. Chlorite, corundum and chromium muscovite form essentially monomineralic lens-shaped domains in an association 1km in length and 50m in width within volcanic schists. Individual lenses of corundum have dimensions of ~16m in width by 50m in length with the corundum forming anhedral grains 5-50cm in diameter. Regionally the volcanic rocks are characterised by greenschist facies mineral assemblages and it is not clear if the corundum association developed pre- or syn- to this low grade event.

Kerrich et al. (1987) interpret the replacement textures, geochemical and isotopic evidence and suggest that these rocks have developed as part of a progressive metasomatic alteration of ultramafic rocks (komatiitic lavas) by high temperature, low pH hydrothermal solutions, carrying LIL elements: originally chloritite was formed during intense hydrothermal leaching of the ultramafic rocks, then due to silica undersaturation of the fluid led to reaction of chlorite to corundum.

For this occurrence however, Schreyer (1988) proposes a different intermediate product and that the formation of corundum is a breakdown product of alunite. This breakdown reaction releases two-thirds of the bound oxygen which Schreyer explains may have had considerable isotopic effects on the Kerrich et al. data.

Mercier et al., (1999) describe the occurrence of gem corundum (ruby) within rootless ultramafic bodies of the Mangari area in SE Kenya. The corundum occurs as discrete crystals (up to 10x4cm) in two mineralogical settings:

1) In lenses (plagioclaise+kyanite or sapphirine+chlorite+spinel) within the contact zone between the ultramafics and the surrounding country rocks (metasedimentary sequence dominated by sillimanite-graphitic gneisses).

2) In veins within the ultramafic bodies (zoisite+plagioclaise) or forming at their margins (plagioclaise+K-feldspar+kyanite).

The ultramafic bodies have experienced granulite facies conditions of ~700-750ºC and 8-10.5kbar and consist of mainly serpentinised dunite with localised anthophyllite schists, garnet-metapyroxenites and graphitic gneisses. In contrast, the surrounding metasedimentary sequence has only undergone amphibolite facies conditions of 650ºC and less than 7kbar. The corundum is considered to be related to the ultramafics which have been tectonically emplaced within the surrounding metasediments.

In the case of the lenticular corundum bearing mineralogy (1) the hydration of sapphirine to form corundum + chlorite + spinel is postulated. In the case of the vein related corundum (2), the hydration and desilification of anorthite to produce zoisite + corundum, is postulated, with the active removal of aqueous silica explaining the lack of quartz at the reaction site.

2.2.5 Marble hosted corundum

Marble-hosted deposits are the most important sources of high-quality rubies in Southeast Asia (Hughes, 1997). Primary deposits occur in Tajikstan, Afganistan, Pakistan, Azad

Kashmir, Nepal, Myanmar, North Vietnam and South China. All the deposits are hosted by metamorphosed platform sedimentary series that are intruded by granites or pegmatites (Giuliani et al., 2003). The source of the chemical elements composing ruby is always in debate for ruby hosted in marbles. The most common genetic model for the formation of this corundum is the regional metamorphism of limestones and shales. Another possible model is the mixing of metamorphic and magmatic fluids (Kammerling et al., 1994).

Pecher et al., (2002) describe the Nangimali ruby deposit, Azad Kashmir, Pakistan. The deposit outcrops in folded high-grade metamorphic gneisses capped by a metasedimentary sequence of marbles and amphibolites. The ruby mineralisation is hosted by marbles over an area of 1.8 x 0.5km.

The ore body consists of several grey carbonate-bearing bands (from 1cm to 6m), parallel to bedding and associated micro-scale shear-zones, parallel or sub-parallel to the regional foliation. The corundum-bearing bands pinch and swell and are irregular in length. The shear-zone mineralogy consists of pyrite ± phlogopite ± rutile ± margarite ± ruby ± pargasite and carbonate. The ruby crystals are up to 5cm long and 1cm wide with colour varying from pinkish-red to deep-red.

Pecher et al., (2002), through a mass-balance calculation, determined that the marbles were aluminous enough to supply a hydrothermal system with enough aluminium to deposit ruby. The marbles are also considered the source of chromium and vanadium in the ruby structure. The source of the mineralising fluids was also studied and through carbon and oxygen isotopic signatures and it was determined that the fluids are metamorphic and the CO_2 was derived from the decarbonation of marbles ($\delta^{18}O$=23.6 to 27.6‰ rel. to SMOW and $\delta^{13}C$= -1.9 to 2.6‰ rel. to PDB). The Giuliani et al., (2003) study of fluid inclusions in marble hosted rubies confirmed that marbles are the source of aluminium and that aluminium can be easily transported in CO_2-rich fluid at high pressures and temperatures.

Chapter 3 Corundum as an accessory mineral in igneous rocks

As an accessory mineral in igneous rocks, corundum occurs in pegmatites and other rocks associated with nepheline syenite (Deer et al., 1992; Clabaugh, 1952), rare monzonite (Simonet, 2004) and as the result of desilification of felsic igneous rocks by more mafic material (Deer et al., 1992, Wells, 1956).

3.1 Occurrences

3.1.1 Monzonite

Simonet (2004) documents a rare igneous-hosted sapphire deposit in the Mozambique Belt at Dusi in central Kenya. The deposit is the largest primary sapphire deposit in the world and yields blue and yellow sapphires from a 4-5m thick monzonite dike that extends N-S over at least several kilometres. The Pb/U age of zircons (579+/-6Ma) indicates the crystallisation of the monzonite coincides with a major shearing event characterised by large-scale N-S trending shears and "straightening" zones, accompanied by granitoid intrusions (the Barsaloian event, Key et al., 1989).

The dike consists of a fresh and unfractured leucocratic monzonite showing scattered black mica crystals in a coarse feldspathic matrix. The corundum is either scattered in veins or locally concentrated as euhedral, barrel shaped crystals. The dike is hosted unconformably on one side by biotite-hornblende gneisses with an unknown contact on the other side. The petrology of the dike reveals the dike consists of mainly microcline, plagioclase, corundum and biotite with minor zircon and magnetite. Corundum and feldspar in some cases are altered to muscovite and sericite.

It is interesting to note the composition of these corundums contains significant amounts of Fe (FeO = 0.95-1.13%) and small amounts of Ti (TiO_2 < 0.04%). The chemical composition of these sapphires is close to that of basaltic corundum xenocrysts. However inclusions of Nb-Ta-Ti oxides are absent in the Dusi sapphires which may provide a clue to the diversity of corundum from alkali basaltic terrain.

3.1.2 Syenites, nepheline syenites and associated pegmatites

Wells (1956) describes the occurrence of corundum (up to gem quality) that has developed along the contact of a syenite intrusion into limestone at World's End Drop, Sri Lanka. Corundum is also found in alluvial deposits in the area.

A syenite intrusion is separated from limestone by a continuous zone of phlogopite up to 20mm thick. The corundum bearing rock occurs within the syenite in nodular zones adjacent to the phlogopite boundary in areas of the intrusion where there is a greater abundance of diopside-scapolite inclusions. The nodular zones are up to 1m in thickness and are composed of feldspar, corundum (including blue and blue-green sapphires up to 1cm in length), spinel, sillimanite and phlogopite.

The diopside-scapolite inclusions are limestone xenoliths that have had volatile CO_2 removed and replaced by silica. This local removal of silica increased to proportion of alumina in the magma causing the localised formation of aluminous minerals, including corundum. It is important to note that the magma need not be highly aluminous initially to crystallise corundum in this manner.

3.1.3 Ultramafic dike as discrete crystals

Clabaugh (1952) describes a sapphire bearing Tertiary lamprophyre dike that intrudes Mississippian limestone and shale at Yogo, Montana.

The vertical dipping biotite-pyroxene dike has dimensions of up to 7km in length and a width of up to 6m (average 2m) and contains poorly distributed altered limestone inclusions ranging from granule to boulder size. Meyer and Mitchell (1988) further classify the dike as an ouachtite. The corundum is distributed evenly throughout the dike with barren zones appearing only when the dike pinches down in size and is jammed with limestone fragments. The gem corundum occurs mainly as sapphires with minor ruby with the largest sapphire found at this deposit weighing 19 carats (85g). The corundum exhibits a reaction rim (with magma) of spinel and individual crystals exhibits etching consistent with magmatic corrosion.

Meyer and Mitchell note that the distribution, reaction rim and the evidence of magmatic corrosion indicate a xenocrystic origin for the sapphires and postulate an unknown basement rock as the source. Brownlow and Komorowski (1988) further propose a genesis model based on the similarities between this sapphire deposit and the sapphire-bearing alkali basalts of Australia and Thailand: 1) The formation of sapphire through the magmatic differentiation of an aluminium-rich melt formed from partial melting of mantle rock, 2) Injection of sapphire bearing melt into the crust where reaction rims and magmatic corrosion occur on now unstable sapphires, 3) explosive injection of dike rock into current position due to splitting of remaining liquid into a silicate melt phase and a gas phase.

Chapter 4 Corundum associated with alkali basalts

Corundum is found in certain alkali basalt fields and their associated alluvial deposits. This occurrence is significant due to the large number of associated economic gem corundum deposits (sapphire and lesser ruby). Corundum is considered a xenocryst phase of the associated basaltic rocks but controversy exists over the origin of the corundum-bearing xenocrysts and their relationship with alkaline basaltic volcanism. One critical issue is whether mantle-derived magmas at depth can evolve to compositions peraluminous enough to crystallise significant amounts of corundum without contamination of an Al-rich crustal rock (Upton et al., 1999). Oxygen isotopes, fluid/melt inclusions, mineral inclusions and other methods have been used to tie down the origin of the basalt-derived corundum.

4.1.1 Occurrence

Corundum in alkaline basaltic terrains is commonly observed as alluvial placer deposits or much less commonly as in situ megacrysts.

The weathering and erosion of basaltic lavas, pyroclastics, plugs and diatremes has created economic deposits of gem-quality sapphire in eastern Australia, eastern China, Thailand, Vietnam, Cambodia, Kenya and Nigeria (Guo, 1996). Lesser deposits exist in Madagascar and Europe (Sutherland, 1998).

Although rare, corundum xenocrysts have been reported in situ in basaltic rocks: MacNevin (1972), Stephenson (1976) and Vichit (1978) have reported occurrences of corundum or corundum-composite megacrysts in basalts. Guo et al. (1992) reported the occurrence of alkali basalt breaking down to form alluvial material containing gem-quality corundum. Other evidence associating alluvial corundum with corundum from basaltic terrains includes corundum colour, trace element patterns, crystal habits and corrosion textures (Guo 1993).

4.1.2 Corundum in basalt, xenocryst or phenocryst?

Contrary to some literature corundum is designated as a xenocryst phase in basaltic rocks due to petrological evidence that suggests that corundum cannot crystallise from basaltic magmas (Green et al., 1978, Liu and Presnall, 2000). Also Guo (1996) explains that the presence of low Ca feldspar inclusions in sapphires suggest the magma was more evolved and felsic.

Oxygen isotope evidence (Garnier et al., 2005; Khin Zaw et al., 2002) indicates corundum is not in isotope equilibrium with its host basalt and therefore a xenocryst.

4.2 Trace element geochemistry

Sutherland et al. (1998b) were able to classify corundums derived from basaltic terrains into a metamorphic suite and a basaltic (magmatic) suite on the basis of their trace element contents, mineral inclusions and absorption spectra. It was determined these different types represented different underlying sources tapped by basaltic eruptions. The metamorphic suites were characterised by high Cr/low Ga chemistry with Ga_2O_3 contents <0.01 wt% and Cr_2O_3/Ga_2O_3 ratios above 3. The basaltic (BGY suite) suites were characterised by higher Ga_2O_3 (up to 0.04 wt%) and Cr_2O_3/Ga_2O_3 ratios below 1.

Schwarz et al. (2000) determined that the most useful trace element tool for separating corundum of magmatic and metamorphic origin are correlation diagrams that plot Cr_2O_3/Ga_2O_3 against Fe_2O_3/Cr_2O_3 or Fe_2O_3/TiO_2. Magmatic corundum show higher Ga/Cr than metamorphic corundum, apart from some Ga rich metasomatic corundum which can distinguished by Fe_2O_3/Cr_2O_3 ratios of between 20-110.

Sutherland et al. (2002) further used trace element distribution, absorption spectra and geochronology and to characterise the corundum occurrence in the Tumbarumba Basalt field. It was determined that the corundum could be divided into six groups:

1. BGY sapphires with a Fe^{2+}-Fe^{3+} transition (low Cr/Ga, moderate to high Fe)

2. BGY sapphires without a Fe^{2+}-Fe^{3+} transition (low Cr/Ga, moderate to high Fe)

3. BGY related trapiche-like corundum (moderate Cr/Ga, moderate to high Fe)

4. Blue, green, pink diffuse zoned (higher Cr/Ga, moderate Fe)

5. Blue, light blue, white colour zoned (higher Cr/Ga, moderate Fe)

6. Dark pink, purple, red (extreme Cr/Ga, low to moderate Fe)

The BGY and trapiche-like sapphires are considered magmatic, the intermediate sapphires magmatic-metasomatic and the pink to red corundums metamorphic in origin. This, importantly, classified the Tumbarumba corundums as a polygenetic suite and further research indicates that other gem provinces are also likely to have polygenetic origins.

Saminpanya et al., (2003) assembled trace element data of corundum from different genetic environments in an attempt to classify corundum occurrence and link corundum xenocrysts from alkali basaltic terrain with a parent rock. This is summarised in Figure 1. Figure 1A exhibits the differentiation of basalt hosted rubies and sapphires in Thailand using Fe/Ti vs Cr/Ga discrimination. Figure 1B contains corundum analysis from 8 different geological environments (1 – Al-rich diorite, 2 - Al-rich pelite, 3 – ultramafic, 4 – syenitic, 5 – pelitic, 6 – Al,Mg-rich pelitic, 7 – metabauxite, 8 – calcareous).

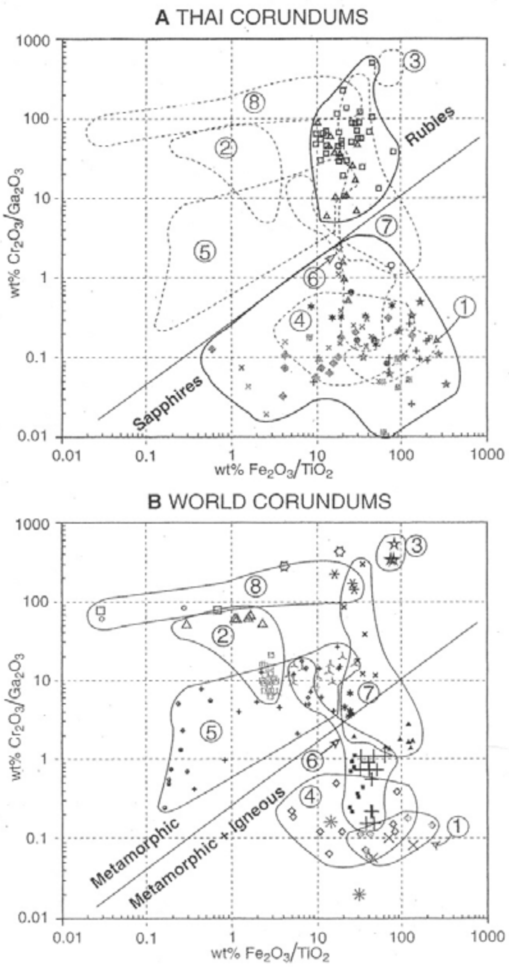

Figure 1 – Trace element analysis of Thai sapphires and rubies (A) compared with worldwide corundum occurrence (B) from different terrains (Saminpanya et al., 2003)

4.3 Oxygen Isotopes

Oxygen isotopes are useful to determine the origin of corundum because of the distinct O-isotope values of mantle and crustal rocks (Yui et al., 2003).

Garnier et al., (2005) assembled O-isotope data of corundum and their host rocks from a wide variety of environments (Appendix 1) to produce Figure 2:

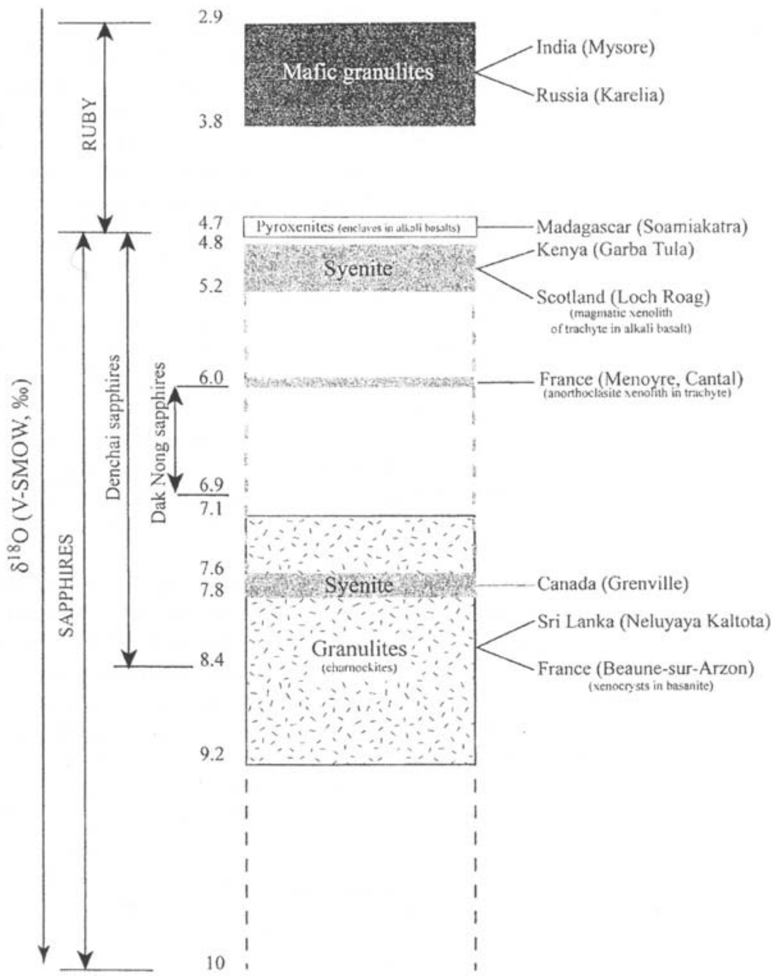

Figure 2 – O-isotope values for corundum and some corundum host rocks (Garnier et al., 2005)

This can be used as a tool to deduce the likely source of corundum in alkali basalt terrain, especially to differentiate between syenitic (magmatic) and granulitic (metamorphic) origins.

4.4 Tectonic controls

Corundum xenocrysts are known only in basalts erupted through continental crust, and appear to be associated with alkalic basaltic provinces in continental regions which have undergone extensional rifting at some time (Guo, 1996). This is the case in eastern Australia, SE Asia and eastern China and it is inferred that the generation of corundum bearing rocks takes place in rifting environments.

4.5 Genesis models

With corundum being unable to crystallise out of basaltic magmas, current understanding of the topic calls for a two stage process. The first stage involves the magmatic/metamorphic **generation** of corundum at crustal/mantle depths followed by a second stage of alkaline intraplate basaltic **incorporation and transport** of the xenocrysts. This implies that the generation of corundum has to occur at levels higher than the magma generation.

It is noted that many of the models suggest origins for either sapphire generation or ruby generation. More recently papers have been published which attempt to constrain the origins of the multi-modal gem suites (eg. Sutherland et al., 2002; Saminpanya et al., 2003).

The currently postulated models for metamorphic/magmatic generation of corundum can be divided into three groups (after Khin Zaw et al., 2002):

4.5.1 Plutonic crystallisation at high pressures

a. Plutonic crystallisation from highly evolved alkaline melts derived by the crystallization of intraplate (nephelinite, basinite etc.) magmas at mantle and lower crustal pressures (Irving, 1986)

b. Plutonic crystallisation from syenitic melts that are the result of high temperature crystallization of anhydrous trachytic magmas at deep crustal level or the upper mantle (Aspen et al., 1990)

c. Plutonic crystallisation from primary alkaline melts which are produced by low to moderate degrees (6-14 wt%) of partial melting of amphibole-metasomatised mantle, or alternatively partial melting of a lower crustal amphibole bearing assemblage (e.g. amphibole pyroxenite; Sutherland et al., 1998).

d. Plutonic crystallisation from syenitic melts originating from partial melting of a metasomatised mantle, but with aluminous character developed by the loss of alkalis and carbonatitic fractions (Upton et al., 1999).

e. Plutonic crystallisation from a fractionated partial melt from a metasomatised mantle interacting with a lower-crustal Al-rich rock (Khin Zaw et al., 2002).

f. Plutonic crystallisation in a deep magma chamber, at the lower continental lithosphere and upper mantle boundary, in evolved melts issued from the fractionation of alkali basaltic magmas contaminated with lower crustal fluids (Garnier et al., 2005).

The plutonic crystallization models of corundum genesis are very similar in that they require a highly aluminous volatile and trace element rich alkaline parental magma. They only differ in how such a magmatic melt composition was produced.

4.5.2 Corundum generation by magma mixing at mid crustal levels

Guo et al., (1996) suggests that at mid-crustal depth the interaction between a host pegmatite body and intruding carbonatitic magma causes Al-rich phases to crystallise in the hybrid zone, including corundum. Subsequent episodes of basaltic magmatism may have carried fragments of corundum-bearing wall rocks rapidly to the surface.

4.5.3 Corundum generation by metamorphic recrystallisation

The generation of corundum by metamorphic recrystallisation of aluminous lower crustal rocks has also been documented.

a. Metamorphic corundum is formed due to the recrystallisation of Al-rich Si-poor host rocks by ocean floor subduction (Levinson and Cook, 1994).

b. Suitthirat et al., (2001) proposed that high-pressure metamorphism of Al-rich mafic rocks also crystallised corundum (ruby only).

c. The model proposed by Oakes et al., (1996) suggested that corundum was derived by the reworking of clay-altered volcaniclastic host rocks.

Chapter 5 Discussion of models

The plutonic crystallisation of corundum is the favoured model of the formation BGY zoned sapphires. Although controversy exists over the exact source rock of the sapphires, it is now generally accepted that the corundum crystallised at either lower crustal or upper mantle depths in a highly aluminous volatile and trace element rich parental magma. Many of the models are concerned with the conditions of crystallisation and lack a genetic link with the associated intraplate basaltic volcanism. There are two models that attempt to link both **generation and transport** of BGY corundum in alkali basalts which will now be discussed.

5.1 Sutherland et al., (1998a) - Advancing thermal plume-partial melting model

This model is based on the generation of BGY sapphires and **ignores the formation of the metamorphic type sapphires**. The model is based on evidence from inclusion and intergrowth mineralogy, petrological observations and tectonic setting. The model indicates that the corundum is formed by partial melting of amphibole-bearing mantle during an advancing thermal plume and transported to the surface during a period of volcanism. A thermodynamic modelling program (MELTS) was used to test to potential of crystallising corundum from partial melting of amphibole-bearing mantle assemblages.

5.1.1 Evidence

5.1.1.1 Europium in zircons

It is already known that normal peridotitic mantle melts to produce basaltic alkaline magmas that may evolve into felsic magmas capable of crystallising corundum (Irving 1986). “However inconsistent Eu depletions found in zircons associated with corundum are a problem, as Eu should partition into plagioclase preferentially” (Sutherland et al., 1998). From mineral inclusion overlap it is clear that corundum and zircon crystallise in similar melts. Sutherland proposes that corundum crystallisation is thus better explained by felsic melts unrelated to extended plagioclase crystallisation, such as phonolites and trachytes (outside the plagioclase crystallisation environment) or an evolved melt derived from an enriched mantle.

5.1.1.2 Hafnium in zircons and Nb-Ta oxide mineral inclusions

Relative Hafnium enrichment (10000-28000ppm) in corundum related zircons indicate either an extreme fractionation process to concentrate Hf or that their melts come from sources already enriched in Hf. As the corundum bearing basalts exhibit normal Hf-Th-Ta levels, Sutherland indicates that the corundum crystallisation is linked to melting of mantle sources that incorporates additional components. This would also explain the presence of Nb-Ta oxides (commonly columbite, ilmenorutile and uranopyrochlore) as this process will also lead to enrichment of Nb and Ta.

5.1.1.3 MELTS modelling

The MELTS modelling program calculates equilibrium mineral compositions and their proportions during crystallisation, using a large thermodynamic database, and is useful for discussing mantle minimum melt compositions (Falloon et al., 1996).

Sutherland et al. selected mantle-lower crust xenolith assemblages (amphibole-bearing pyroxenites to amphibolites) from within regions of known basaltic sapphire fields. The MELTS modelling indicated that after initial melting and segregation many of the amphibole-mantle assemblages (originally only up to 15wt% Al_2O_3) produced residual liquids that started to crystallise corundum (up to 5wt%) above 720ºC. Also noteworthy were the compositions of the other minerals to crystallise out of the theoretical melt: sanidine, anorthoclase and garnet. The compositions of these minerals typified the compositions of the same minerals that are known to occur in corundum bearing xenoliths or as inclusions in corundum.

5.1.2 Model

The model is based on relationship between corundum producing basalt fields in East Australia and the temporal lithospheric migration over an asthenospheric “hot spot” plume that originated during the Coral Sea rifting (Sutherland et al., 1996).

Sutherland's model is summarised in Figure 3.

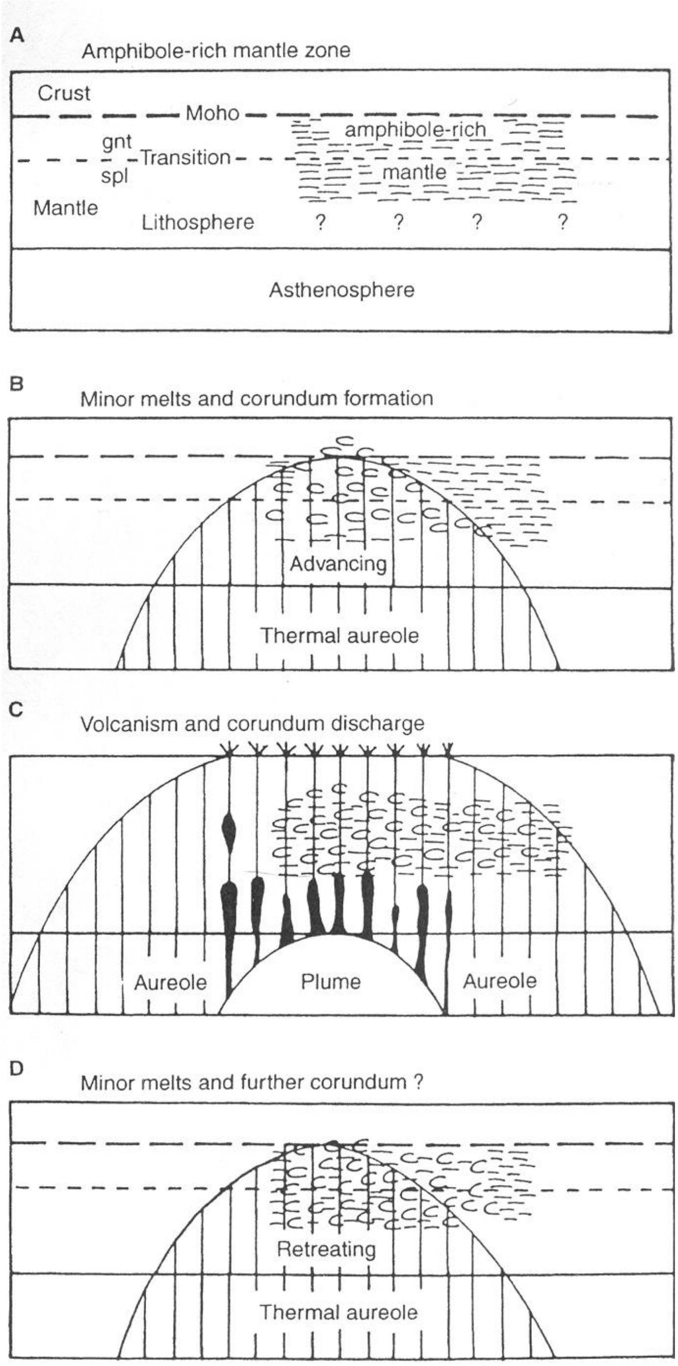

Figure 3 – Partial melting model (Sutherland et al., 1996)

The model begins with a partly amphibole-rich mantle in the path of an encroaching mantle plume (**A**). The encroaching plume produces a thermal aureole, that produces partial melting on the mantle, and where amphibole is present, initial melting will generate volatile-rich felsic melts that can fractionate and crystallise zircon and corundum (**B**). As the plume passes below the region, greater degrees of partial melting produce the alkali basalt magmas that transport the earlier crystallised corundum (**C**). As the plume migrates away and the temperature decreases, more crystallisation of corundum and zircon can take place awaiting further plume activity to carry it to the surface (**D**).

5.1.2.1 Model discussion

Further work by Sutherland (2002) in the polygenetic corundum gem field of Tumbarumba, Australia indicates that this model is only partly responsible for corundum genesis. It is proposed that interactions between basaltic melts and an amphibole-rich mantle, serpentinite bodies and metamorphic sourced corundum are responsible for Tumbarumba-type corundum occurrence.

5.2 Guo et al., (1996) - Generation of corundum by magma mixing

Guo et al. propose that generation of corundum is a result of the interaction between a host pegmatite body and an intruding carbonatitic magma at mid-crustal depths. This causes an Al-rich phase to crystallise triggering corundum crystallization at mid-crustal depth. Evidence taken from mineral inclusion geochemistry and feldspar exsolution textures are the basis of this genetic model.

5.2.1 Evidence

5.2.1.1 Nb-Ta oxide inclusions

Analysis of Nb-Ta oxide inclusions in corundum reveal that they encompass a narrow range of compositions, suggesting a common petrogenesis. Columbite inclusions exhibit high TiO_2, low Ta_2O_5 and a low MgO which is a similar composition found in columbites from carbonatite-related intrusions. The uranopyrochlore is rich in U, Nb and Ti and is also representative of pyrochlore from carbonatites and related alkaline rocks.

5.2.1.2 Zircon inclusion morphology and geochemistry

The zircons generally have a short prismatic habit with the {110} prism being more developed than the {100} prism. The growth of {110} zircons is favoured in a melt containing U, Th, REE's, alkalis and H_2O and are thought to be the result of low temperature crystallisation in a peralkaline and hyperaluminous melt.

The zircons contain high levels of Hf, U, Th, Y and REEs which is consistent with the crystallisation of zircon from highly evolved silicic melts, which have undergone extensive fractional crystallisation (Guo 1996).

5.2.1.3 Feldspar exsolution temperatures

Guo identified a probable perthitic intergrowth of albite and k-feldspar as an inclusion in corundum. The low Ca content of the inclusion is consistent with the source rock of the corundum being evolved and felsic.

It was also determined that the perthitic feldspars equilibrated at a temperature of around 400ºC or lower. This implies that the corundum must have been formed at around 400ºC at the time of entrainment which places it at mid-crustal levels (10-20km).

5.2.1.4 Bimodal genetic distribution of mineral inclusions

A range of other inclusions were studied (eg. Sulphides, phosphates and spinels) and Guo et al., (1996) divided the mineral inclusions into two groups based on their genetic implications:

1) An evolved felsic suite (syenite or alkaline granite) typified by feldspar, zircon, uraninite, ilmenorutile and sulphide, and

2) A carbonatitic suite typified by Ti-columbite and uranopyrochlore.

5.2.2 Model

Given the bimodal mineral inclusion distribution, the model is based on the mixing and/or interaction between an alkaline granite or syenite pegmatite composition (magma or rock) and a carbonatitic magma. The setting is constrained to intracontinental rifting regimes where carbonatite magmas occur and to mid-crustal levels as indicated by the feldspar exsolution textures. Guo's model involves two stages of magmatism and is summarised in figure 4. The model begins with an early melting event due to the upwelling of an asthenospheric mantle and the formation of mafic magmas which intrude the lower crust/upper mantle.

The cooling intrusions at the crust/mantle boundary provide a heat source to produce granitoid magmas. Partial melting of carbonate-bearing peridotite produces carbonatite magma which intrudes into mid-crustal levels and hybridises with the granitoids **(1)**. The hybridisation results in rapid crystallisation of corundum due to an increase in CO_2 (from the carbonatite) markedly reducing the solubility of Al_2O_3 in the magma **(2)**.

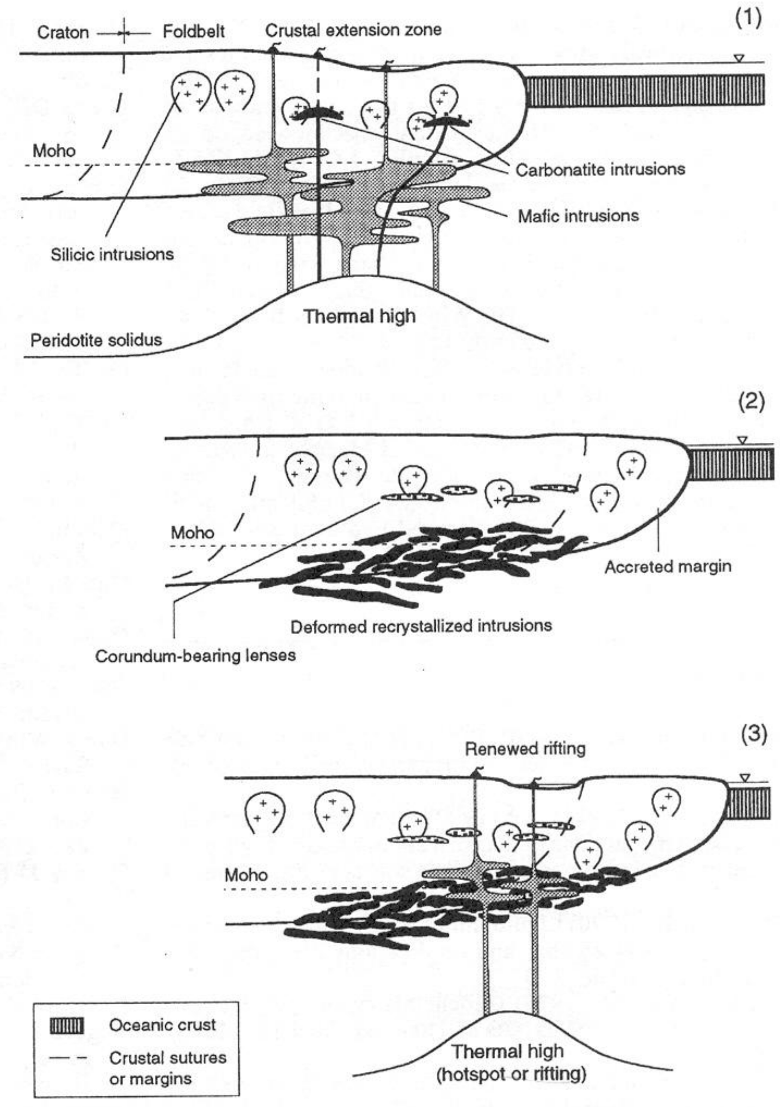

Figure 4 – Carbonatite magma-mixing model (Guo et al., 1996)

A later upwelling event triggers further mantle melting which produces alkali and volatile rich mafic magmas which rise rapidly to the surface. The magma may entrain rock from the corundum bearing hybrid zone in a similar fashion to the entrainment of mantle xenoliths **(3)**.

5.2.2.1 Model discussion

According to Guo et al., the origin of the Nb-Ta oxide inclusions in corundum is due to the addition of a carbonatitic component. Sutherland et al., (1998a) argue that although the minerals do have a limited overlap with the carbonatite compositional field, they more closely match the same minerals found in a more silicic paragenesis (enriched granitic pegmatite). Saminpanya et al., (2003) indicates that although the carbonatite involvement can produce corundum (eg. Carbonatite magma intruding gneiss to form a corundum-bearing fenite) and explains the Nb-Ta oxides, the likelihood that it produces large quantities is very low. Other sources of Nb-Ta oxides are granitic pegmatites and peralkaline granite.

Sutherland et al. (2002) suggests that carbonatite model is unlikely for several other reasons:

1. Lack of mineral inclusions that suggest carbonatitic input (eg. Carbonate)

2. Lack of silicic melts associated with eastern Australian gem fields

3. Presence of corundum-bearing xenoliths in basalts of syenitic character

4. Oxygen isotopes that suggest magmatic crystallisation in a deep chamber at 800ºC, which is too deep for Guo's model.

5.3 Sutthirat et al., Metamorphic recrystallisation (2001)

This model examines the formation of Thai rubies only and is based on mineral inclusion data. It is suggested that the origin of an observed clinopyroxene-corundum assemblage is the metamorphic recrystallisation of mafic rocks within the upper mantle.

A corundum+clinopyroxene xenocryst was found in-situ in alkali basalt. It was found that the compositions of the minerals in the xenocryst and that of locally sourced alluvial rubies were very similar, supporting the idea of a common genesis. Furthermore, compositions of mineral inclusions found in Thai rubies (clinopyroxene, garnet and sapphirine), indicate a mafic source rock. Clinopyroxene crystal morphology suggests that it did not crystallise from magma. Thermodynamic calculations applied to the corundum+pyroxene assemblages give crystallisation temperatures of between ~800ºC and 1150ºC at pressures of between ~10 and 25 kbar, probably within the upper mantle. Based on thermodynamic stability at the calculated T-P regime, the source rock of the ruby is suggested to be a corundum-garnet-pyriclasite or a corundum-garnet-pyroxenite.

5.4 Saminpanya et al., Metasomatised syenitic gneiss (2003)

This model examines the formation Thai rubies and sapphires and is based on trace element geochemistry comparisons with corundum bearing rocks (Chapter 4.5) and mineral inclusions. It is inferred that although ruby and sapphire occur in the same deposits, their origin is different. It is suggested that the origin of Thai sapphires is the metasomatism of a syenitic gneiss by a highly evolved magma such as a carbonatite and the origin of Thai rubies is the metamorphic recrystallisation of a mafic metamorphic rock.

Sapphires: The basis of this model is the similarity in trace element chemistry between the Thai sapphires with that of nepheline-corundum syenitic gneisses from other locations. The author suggests that the origin of the Thai sapphires is result of metasomatism of a Thai paragneiss by emanations from a felsic magma (enriched in Ga and incompatible elements) or a carbonatite (rich in Nb-Ta) at deep levels in Thailand. The suggested paragneiss would be altered to a nepheline-corundum syenitic gneiss, which is supported by a nepheline inclusion found in corundum by the author and examples of nepheline-corundum assemblages found in syenitic rocks.

Rubies: The ruby did not fall distinctly into a discrete genetic field on the basis of trace element discrimination. On the basis of the ruby inclusion suite which includes garnet, sapphirine and pyroxene, and the high Ga/Cr ratio, the author suggests that the origin of rubies is the metamorphic recrystallisation of a mafic metamorphic rock (Ga is enriched in felsic and intermediate rocks, Cr is enriched in ultramafic and mafic rocks).

Chapter 6 Conclusion

Corundum occurs in many types of metamorphic rocks where its presence generally represents a silica undersaturated-alumina rich paragenesis. Examples of this are the segregation of quartz to produce alumina rich zones and dehydration of alunite to produce corundum. Calculated minimum temperatures and pressures for the formation of corundum are ~650ºC to 800ºC with a pressure range between ~3 and 7kbar and much higher for ruby (~800ºC and 1150ºC at pressures of between ~10 and 25 kbar). For corundum to persist, the assemblages must be transported to the surface reasonably quickly, to avoid retrograde decomposition.

Nepheline syenite and associated pegmatites commonly host corundum as an accessory mineral. Other rare occurrences, such as the formation of corundum due to a felsic rock intruding, and becoming desilicified, by a basic rock have also been reported. The presence of corundum in an igneous rock suggests silica undersaturation or a desilicification process.

The genesis of economically important, alkali basalt hosted gem corundum is widely debated. It is certain that the corundum megacrysts found in and associated with these basalt fields cannot crystallise from a basaltic melt, and therefore the corundum is designated as a xenocryst phase. Thus, it is agreed that the formation of alkali basalt hosted corundum involves two stages: the formation of corundum and the subsequent incorporation and expulsion via intraplate basaltic volcanism. Models for the formation of the corundum xenocrysts fall into three groups: 1) plutonic crystallisation at lower crustal/upper mantle depths from a highly aluminous volatile and trace element rich alkaline parental magma; 2) magma mixing at mid-crustal levels involving a carbonatite phase and a highly fractionated felsic phase; 3) metamorphic crystallisation at upper mantle depths. Further work indicates that in poly-modal gem fields, although rubies and sapphires occur together, they are most likely formed in through different processes and more complicated hybrid models are required.

The plutonic crystallisation models are favoured for the genesis of sapphire, although the origin of Nb-Ta oxide inclusions may need a better explanation, as the introduction of a carbonatitic phase (Guo et al., 1996) through magma-mixing is improbable. For ruby genesis, mineral inclusion and trace element evidence strongly suggest the metamorphic recrystallisation of mafic rocks at mantle depths as the best genetic model.

A summary of this data is in Table 2.

Table 2 - Summary of corundum occurrences discussed in this paper

Location	Occurrence type	Host rock	Associated minerals	Genesis	Author(s)
Naxos Is and Paros Is, Greece	Metamorphosed bauxite (laterite)	Marble	Diaspore, biotite, staurolite, sillimanite	Dehydration of diaspore to corundum	Feenstra (1985, 1996)
Meghalaya, India	Metamorphosed bauxite (laterite)	Quartz-sillimanite schist	Sillimanite	Dehydration to corundum	Golani (1989)
Namaqualand, South Africa	Metamorphosed bauxite (laterite)	Sillimanite schist	Sillimanite, ilmenite	Dehydration to corundum	Coetzee (1940)
Morton Pass, Wyoming, USA	Partially melted pelitic rocks	Amphibolite facies pelite	K-feldspar, cordierite, spinel	Desilicification by partial melting	Grant and Frost (1990)
Susqueda Complex, Catalonia, Spain	Si-poor hornfels in the aureole of an igneous intrusion	Micaschist	Sillimanite, spinel, cordierite, biotite	Desilification by partial melting and segregation of quartz veins	Riesco (2004)
Morton Pass, Wyoming, USA	Si-poor hornfels in the aureole of an igneous intrusion	Amphibolite facies pelite	k-feldspar-cordierite-spinel	Desilification by partial melting	Grant and Frost (1990)
O'Briens, Zimbabwe	High Mg and Al schists	Volcanic schists	Chlorite, Cr muscovite	Desilification by low-pH/high T fluids or an alunite breakdown reaction	Kerrich (1987) Schreyer (1988)
Mangari, Kenya	High Mg and Al schists	Sillimanite-graphitic gneiss	plagioclaise+kyanite or sapphirine+chlorite+spinel	Hydration of sapphirine to produce corundum	Mercier (1999)
Mangari, Kenya	High Mg and Al	Serpentinised	zoisite+plagioclaise	Hydration and desilification of	Mercier (1999)

	schists	dunite		anorthite to produce zoisite + corundum	
Nangimali ruby deposit, Azad Kashmir, Pakistan	Marble hosted corundum	Marble	Pyrite, phlogopite, rutile, margarite	Marble sourced alumina enriched by metasomatism	Pecher (2002)
Dusi, Kenya	Accessory mineral in igneous rock	Monzonite	microcline, plagioclase, corundum and biotite	Plutonic growth	Simonet (2004)
World's End Drop, Sri Lanka	Accessory mineral in igneous rock	Syenite	Feldspar, spinel, sillimanite and phlogopite	Desilification of magma by carbonate	Wells (1956)
Yogo, Montana, USA	Accessory mineral in igneous rock	Ouachtite	Biotite, pyroxene	Plutonic growth	Clabaugh (1952) Meyer (1988) Brownlow (1988)
SE Asia, China, Cambodia, Eastern Australia, Kenya Nigeria, Madagascar and Europe	Sapphires associated with alkali basalts	Alkali basalt - lavas, pyroclastics, plugs and diatremes	Spinel, zircon, Nb-Ta oxides (inclusions)	See chapters 4 & 5	Guo (1993, 1996); Sutherland (1996, 1998ab , 2002); Garnier (2005); Saminpanya (2003); etc.
SE Asia, China, Cambodia, Eastern Australia, Kenya Nigeria, Madagascar and Europe	Rubies associated with alkali basalts	Alkali basalt - lavas, pyroclastics, plugs and diatremes	Spinel, zircon, Nb-Ta oxides, clinopyroxene (inclusions), garnet, sapphirine	See chapters 4 & 5	Guo (1993, 1996); Sutherland (1996, 1998ab , 2002); Garnier (2005); Saminpanya (2003); etc.

Appendix

O-isotope data for figure 1 (Chapter 4.3). From Garnier et al., (2005).

Country	Mine	Corundum	Host rock	Sample number	$\delta^{18}O$ (‰, V-SMOW)	Reference
Vietnam	Dak Nong	basalt	tholeiitic basalt	V75d	5.7±0.1 (n = 3)	this work
		basalt	alkali basalt	V75b	5.0±0.2 (n = 3)	"
		basalt	alkali basalt	V75f	5.2±0.1 (n = 3)	"
		dark blue	placer	V76a	6.0	"
		dark blue	placer	DN-1	6.4	"
		blue	placer	V76b	6.7	"
		green-yellowish	placer	V76c	6.9	"
		yellow	placer	V76d	6.9	"
Sri Lanka	Neluyaya Kaltota	pinkish	gneiss (granulite)	KCl-3	7.1	this work
France	Velay Beaune sur Arzon	light blue	placer in a basanite	V1	8.7	this work
		lilac	(granulitic complex)	V2	9.2	"
		colourless	"	V3	8.0	"
	Mont Coupet	brown to light blue	colluvium and alluvium from a basanite	–	5.9±1.1	Gaillou (2003)
	Mont Dore Sioulot	blue to green	placer in volcanic fields	–	6.0±0.2	Gaillou (2003)
	Cantal Menoyre	light blue	anorthoclasite xenolith in trachyte	–	5.9±0.6	Gaillou (2003)
India	Mysore	red	gneiss (granulite)	MYHM96	3.8	this work
		red	"	RNDUD002	3.5	"
Russia	Karelia	pink	gneiss (granulite)	Karelia 1	3.0	this work
		pink	"	Karelia 2	2.9	"
Madagascar	Soamiakatra	red	pyroxenite xenolith in alkali basalt	RNANTA	4.7	this work
Kenya	Garba Tula	yellow-green	syenite	GT-1	5.2	this work
Thailand	Denchai	dark blue	placer in alkali basalt	BK-MS	4.7–5.5 (n = 7)	Yui *et al.* (2003)
		blue	"		4.9–8.4 (n = 5)	"
		blue-green-yellow	"		5.1–5.9 (n = 4)	"
Canada	Grenville Province	corundum	syenite	S1	7.6	Kerrich *et al.* (1987)
		"	"	S2	7.8	
		"	"	S3	7.6	"
Scotland	Loch Roag	Colourless to brown	trachyte xenoliths in alkali basalts	LR core	4.8	Upton *et al.* (1999)
		"	"	LR rim	5.25	"
		"	"	LR-250	4.65	"
		"	"	LR-299	4.8	"

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