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Gems and chemistry of Heat Treatment of Geuda

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WHAT ARE GEMS?

Gems may be described as those specimens of minerals or organic materials used for personal adornment that possess beauty, rarity, and durability. Organic materials used as gems include pearl, coral, amber, and jet. Gems are devided into two classifications:

i) diamonds and

ii) colored stones.

In its broadcast sense, the term **"colored stones"** is used in the jewelry trade to refer to all gem minerals and organic gem materials, but not diamonds. In a narrower sense, pearls are also eliminated from this classification and treated separately; Diamond is considered separately for several reasons:

i) In its finer qualities it is usually nearly colorless, whereas the finer qualities in the major varieties of the other gem minerals are coloures;

ii) its physical and optical properties are sufficiently different from other gems to make its beauty and use totally distinctive;

iii) unlike good-quality coloured stones, diamonds have been consistently available in both quantity and quality to permit standardization in general marketing procedures and pricing.

The subsequent competition in sales has demanded a specialization that has not been required of individual coloured-stone speices. In other words, competitive diamond marketing is a fultime occupation. The sources of rough, the cutting techniques and marketing are totally foreign to those of coloured stones, and thus it has rarely been practical to attempt to combine the two other than at the retail sales level.

FACTORS THAT AFFECT THE VALUE OF GEMSTONES.

The basic factors that contribute to the value of a gemstone are;

a) BEAUTY (color, luster, perfection of cutting, etc.),

b) DURABILITY,

c) RARITY,

It is interesting to note that a gem material or potential gem material may sometimes be too rate to be in demand. Unless it is common enough to be known to consumers, too little demand exists for it to achieve sufficient status to bring high prices.

d) Demand

The fourth factor having a bearing on the value of gemstones is DEMAND, or VOGUE. There are times when some of the less important gemstones enjoy great demand and other times when they are in ralative eclipse.

From time to time, fashion dictates the use of very large stones or numerous small stones massed in settings. Factors such as these have a bearing on value at that time.

e) Tradition

One of the important factors affecting the demand and value of gemstones is TRADITION. It might be said that tradition, as applied to gems, is the sum of all the efforts throughout the centuries to interest and educate the public in the use of gems for ornamentation, symbolism, and as a medium of exchange. Such efforts include promotions on the part of jewellers, publicized purchases and use of gems by royalty and wealthy individuals, the symbolic use of gems in various churches and other developments in which gems play a part. All of these activities have, over a period of time, created an acknowledgement by the public of the importance of gems.

f) Portability

Another factor contributing to the importance of gems is PORTABILITY. This applies to any fine gemstone because it represents a high concentration of value in a small object, permitting the owner to transport great wealth on his person. This is what gives gemstones a universal security value, perhaps greater than any other commodity. This is the factor that has influenced royalty and many wealthy families to invest a certain amount of their funds in jewels. When everything else fails, even their government, they can take or send their gems out of the country and realize a return on them quickly.

d) DEMAND (or VOGUE),

e) TRADITION, and

f) PORTABILITY.

a) Beauty

Unless a gem material possesses BEAUTY, it can be considered a gemstone.

A transparent coloured stone, such as ruby, depends for its beauty on several factors; namely, the quality and depth of colour, the degree of transparency, and fashioning. The beauty of an opaque stone depends mainly on colour and, to a lesser extent, on fashioning.

It is not necessary that a specimen display its maximum beauty in order to be valuable. For example, a fine-quality rough specimen of ruby with highly abraded surfaces might be very unattractive to the layman but have great potential beauty that could be revealed by proper fashioning. Thus, to qualify as a gem or gem mineral, a specimen must display beauty or posses potential beauty that can be revealed by fashioning.

b) Durability

Another essential quality for a gem is DURABILITY. To be of use as a personal ornament, however, a stone must withstand ordinary wear well enough to retain its beauty for a reasonable period.

One outstanding characteristic of gems is chemical and structural STABILITY. Unlike some metals that oxidize and slowly disintegrate, or some fabrics and woods that decompose, gems will withstand for centuries conditions that quickly destroy most other materials. In this sense thay are exceptionally durable.

c) Rarity

The third factor contributing to the value of a gemstone is RARITY. Rarity frequently plays a very important role in determining the value of a gemstone, since, obviously, the rather the material in great demand as a gemstone, the higher its value. In sizes over 2 carats, the finest qualities of ruby and emerald are more valuable per carat than colourless diamonds of comparable quality.

THE CLASSIFICATION OF GEMSTONES

Of approximately two thousand minerals that have been identified, only about ninety have varieties that produce specimens possessing the requisite beauty and durability to be considered gemstones. Of this ninety, only about twenty are particularly important to the jeweller.

Since most gemstones are minerals, the classification method used in gemology is the same one applied by mineralogists to the various minerals, with minor adjustments. Each mineral that produces gemstones is considered a gem SPECIES. A gem species is characterized by a definite chemical composition and usually a characteristic crystal structure; therefore, each species possesses characteristic properties. Most species, however, include a number of different types of material with variations that are usually based on color, transparency or phenomena; each of these is called a VARIETY. For example, ruby and sapphire are both varieties of the gem species corundum. Ruby is the red variety and sapphire is the name applied to blue and all other colors. Since both are corundum, ruby and sapphire have the same basic chemical composition, the same crystal structure, and the same properties. They differ only in color. Rubies and sapphires also occur in "asteriated" or "star" varieties.

Sri Lanka in relation to its surface area, is the most dense gem-bearing country in the world. No other country in the world exept perhaps Bras.. has such a wide variety of gem stones as Sri Lanka (Table 1 and Figure 1).

In addition to the commonly found gem stones, one also finds associated with the gem gravels, minerals such as taaffeite, Sinhalite, Olivine, Ekanite etc. which may be useful as index minerals. These are the potential of valuable elements generally found in the gem gravels such as gold, thorium, uranium, inobium, tantalum, have rarely been considered.

Corrundum is one of the fairly common minerals in Sri Lanka and also in the earth's crust. It is found in many different kinds of rocks and in many places on the earth's surface, but only under the rare occurrence of nearly ideal conditions is transparent material formed. With the exception of black star sapphire, only the transparent to translucent varieties are classed as gemstones.

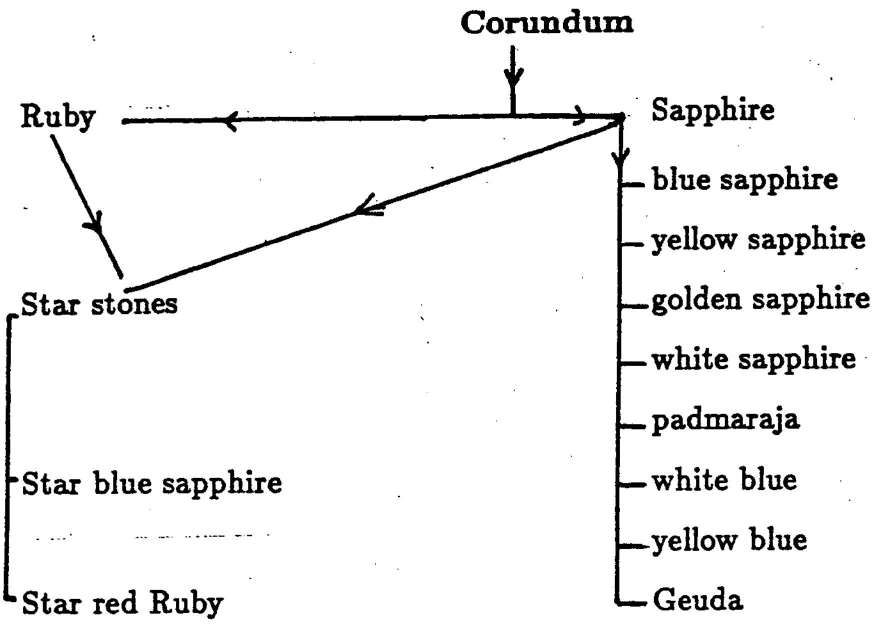
Corrundum was formed under a wide variety of geological conditions. In almost any mineral, crystals suitable for gem use occur only under usually good conditions.

Conditions conducive to ideal crystal growth seem even more rare during the formation of corrundum than of most other gem minerals, for it is among the most widely occurring but least commonly transparent minerals. The right conditions seem to occur most frequently in the contact metamorphism of certain limestones that recrystallize into marble. In the process, the necessary impurities in the limestone, mainly aluminium oxide, are concentrated under conditions that permit them to crystallize as corrundum.

Corrundum also occurs in a variety of aluminium rich igneous rocks. There are some pegmatite dikes (Fig.2) bearing a higher than ordinary percentage of aluminium in which gem quality material was formed. Also it is occasionally found in very basic igneous rocks.

Corrundum is next to Diamond, in the grade of hardness. Many gems obtained from Illama show round or oval shapes due to rolling in river beds and streams. But often corundum gives a crystal form due to its hardness.

Some Characteristics of Corundum



Chemical Composition : AL_2O_3

The colour caused by chromium oxide in the red; titanium and iron oxide in the blue, iron oxide in the yellow, clrromium and iron oxide in the orange, iron and titanium oxide in the green and chromium, titanium and iron oxide in the purple.

Crystallographic Character :

Hexagonee system - usually occurs in a double pyramid with twelve inclined faces

Hardness : (Diamond has 10)

Specific Gravity : Ruby : 3,95 to 4,05 Normal 4,00

Sapphire : 3,95 to 4,03 Normal 3,99

Characteristic Inclusions :

Needlelike rutile crystals

- zircon crystals
- spinel crystals

- mica crystals
- hematitc slabs
- garnet grains
- liquid and gas filled inclusions

Degree of Transparency : Transparent to opaque

Retractive Index : 1,762 - 1,770

Table 1 : Gems in Sri Lanka

Mineral	Chemical formula	Variety
Silicates		
Feldspar		Orthoclase
		Moonstone
Olivine	(Mg, Fe_2) $[Sio_4]$	
Garnet	Mg_3Al_2 $[SiO_4]_3$	Pyrope
	Fe_3Al_2 $[SiO_4]_3$	Almandine
	$Ca_3Al_2[SiO_4]_3$	Grossularite
	$Mn_3Al_2[SiO_4]_3$	Spessartite
Zircon	$Zr[SiO_4]$	
Titanite (sphene)	$CaTi[O/SiO_4]$	
Andalusite	$Al_2[O/SiO_4]$	
Sillimanite (Fibrolite)	Al_2 $[SiO_5]$	
Topaz	$Al_2[F_2/SiO_4]$	
Kornerupine	$Mg_4Al_6[(O,OH)_2/BO_4/(SiO_4)_4]$	
Danburite	$CaB_2(SiO_4)_2$	
Epidote	$Ca_2(Fe,Al)Al_2[O/OH/SiO_4[Si_2O_7]$	
Ekanite	K $(Ca,Na)_2$ $Th[Si_8O_{20}]$	
Beryl	$Al_2Be_3[Si_6O_{18}]$	Aquamarine
Cordierite (Iolite)	$Mg_2Al_3[Al$ $Si_5O_{18}]$	
Tourmaline	(Na,Ca) $(Li,Mg,Fe,Al)_9$ $B_3Si_6(O,OH)_{31}$	Schrol
Axinite	$Ca_2(Mn,Fe)$ Al Al $[BO_3OH/Si_4O_{12}]$	Uwait
Pyroxene	$LiAl[Si_2O_6]$	Spodumene
	$Mg_2[Si_2O_6]$	Enstatite
	$(Fe, Mg)_2[Si_2O_5]$	Hypersthens
	$CaMg$ $(SiO_3)_2$	Diopside
Scapolite	$(Na,Ca)_8[(Cl_2,SO_4,CO_3)_{1-2}$ $(AL_{1-2}Si_{3-2}O_8)_6]$	
Haloids		
Fluorite	CaF_2	

Sulphides		
Chalcopyrite	$Cu\ Fe\ S_2$	
Marcasite	$Fe\ S_2$	
Pyrites	$Fe\ S_2$	
Oxides		
Quartz	SiO_2	Rock crystal, Amethyst Rose-quartz, Smoky-quartz, Brown-quartz, Citrine
Quartz with inclusions		Quartz - Cat's eye Quartz - Tiger's eye
Quartz (Cryptocrystalline)		Chalcedony, Jasper, Agate
Chrysoberyl	$BeAl_2O_4$	Chrysoberyl Cat's eye
Spinel	$MgAl_2O_4$	Ceylonite
Taaffeote	Al_4MgBeO_8	
Corundum	Al_2O_3	Ruby, Star-ruby, Sapphire, Star sapphire, Yellow sapphire, Pink sapphire, Padmaraga
Rutile	TiO_2	
Carbonates		
Calcite	$CaCO_3$	
Phosphates		
Apatite	$Ca(F,Cl)Ca_4(PO_4)_3$	
Monazite	$Ce(PO_4)$	
Borates		
Sinhalite	$Mg\ Al(BO_4)$	
Tungsten		
Scheelite	$CaWO_4$	

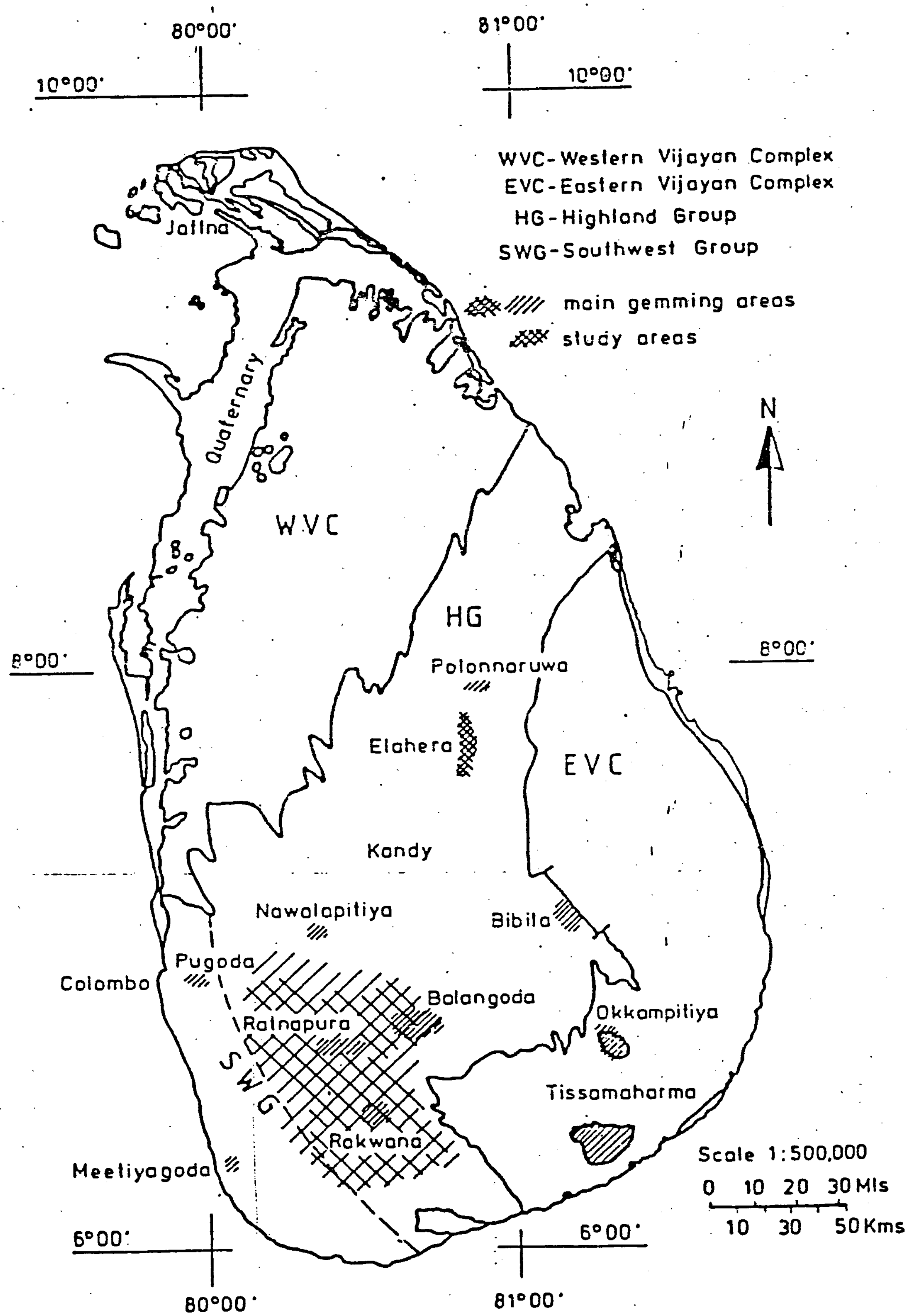

80°00'
81°00'
10°00'
10°00'
WVC-Western Vijayan Complex
EVC-Eastern Vijayan Complex
HG-Highland Group
SWG-Southwest Group
main gemming areas
study areas
Jaffna
Quaternary
N
WVC
HG
8°00'
8°00'
Polonnaruwa
Elahera
EVC
Kandy
Nawalapitiya
Bibila
Pugoda
Colombo
Balangoda
Ratnapura
Okkampitiya
SWG
Tissamaharma
Rakwana
Scale 1:500,000
0 10 20 30 Mls
10 30 50 Kms
Meetiyagoda
6°00'
6°00'
80°00'
81°00'

Figure 1

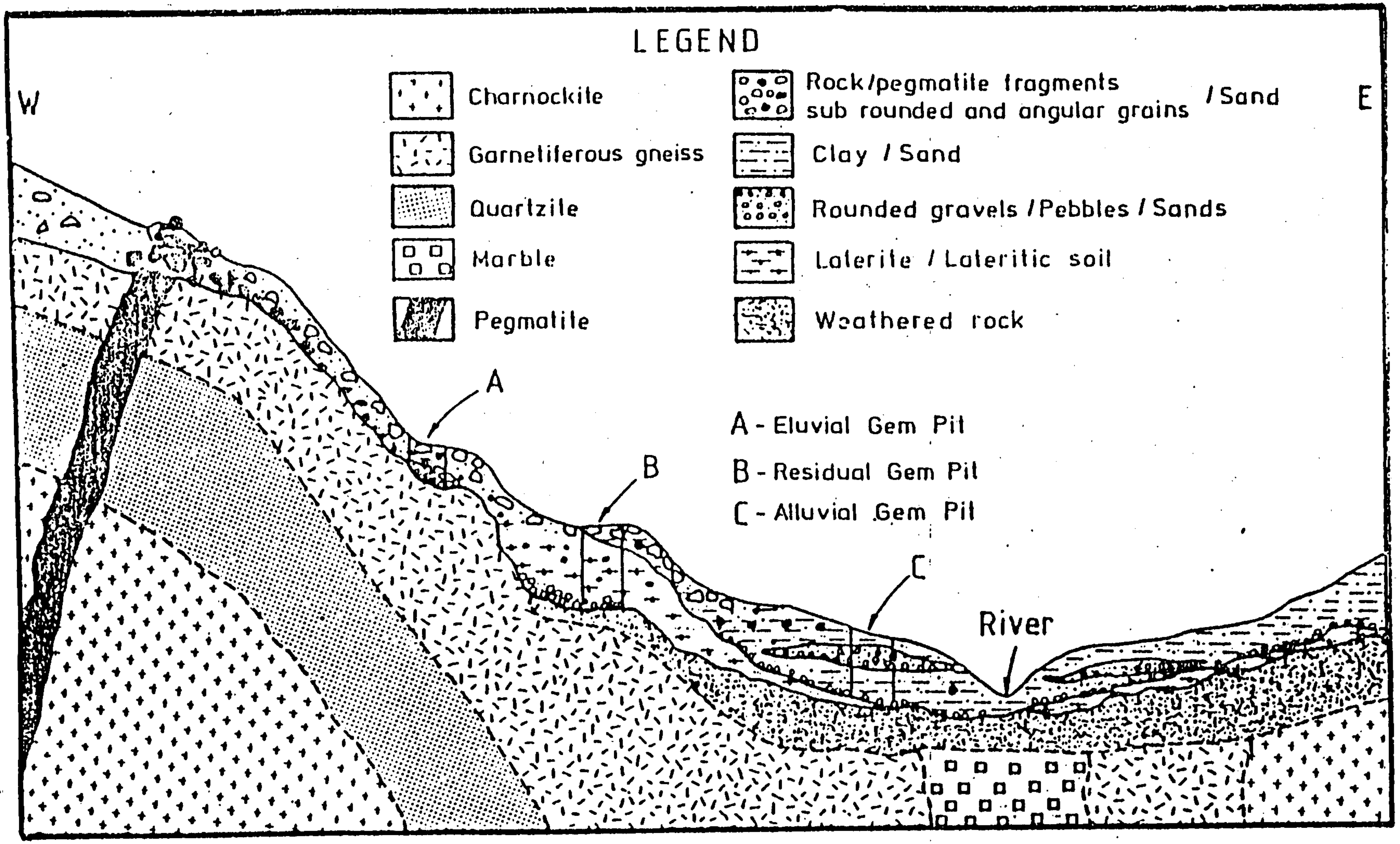

LEGEND
W
E
Charnockite
Garnetiferous gneiss
Quartzite
Marble
Pegmatite
Rock/pegmatite fragments sub rounded and angular grains / Sand
Clay / Sand
Rounded gravels / Pebbles / Sands
Laterite / Lateritic soil
Weathered rock
A
B
C
A - Eluvial Gem Pit
B - Residual Gem Pit
C - Alluvial Gem Pit
River

Figure 2

Chemistry of colour of blue sapphires and heat treatment

A characteristic feature of the transition elements is the wide variety of colours exhibited by these compounds. The colour of a compound is due to its absorption of visible light. As you know the visible light (white light) which the human eye can see is composed of several types of colours. A common demonstration of this is the rainbow where sunlight gets dispersed by tiny droplets of water giving the characteristic colours from violet to red. Transtion metals have d orbitals and transitions between different d orbitals can occur with absorption of light in the visible region. The colour of a compound that is absorbing light in the visible region is the complement of the absorbed light. For example an aqueous solution containing Ti^{3+} is violet in colour which is due to the absorption of most of the green and yellow light and the transmission of blue and some red. In simple terms, coloured compounds absorb some colours of visible light and the transmitted colour is what the human eye sees as the colour of a particular compound.

The beautiful colours of gems are due to the presence of traces of transition elements in them. Most gems are mixed oxide crystals (silicates, aluminosilicates, borosilicates, alumina, silica). These aluminosilicates and pure oxides like corundum (aluminium oxide) are white. However in the presence of traces of transition elements such as iron, titanium, and chronium, these compounds exhibit brilliant colours. Some examples are given in table 1.

Blue sapphires contain small amounts of iron and titanium as impurity ions. Their combined percentage concentration is generally less than 1%. It has been found that both iron and titanium are necessary for a sapphire to exhibit the blue colour. However some synthetic corrundum samples with Ti^{3+} incorporated into it also show the characteristic blue colour. The oxidation states of iron and titanium in blue sapphire are not well established. It is quite possible that all four possible oxidation states, i.e. Fe^{2+}, Fe^{3+}, Ti^{4+}, Ti^{3+} may be present and their relative concentrations are important factors in determining colour.

Scientists have explained the origin of blue colour as due to the absorption of visible light by the ion-pair Fe^{2+}/Ti^{4+}. An electron transfer arising from this light absorption results in Fe^{3+}/Ti^{3+}. The question of the origin of colour of blue sapphire is not fully established.

Chemistry of geuda heat treatment

The white sapphire popularly known as geuda has the same basic structure of corundum as the blue sapphire. However these stones appear as white, pale blue or colourless stones with silkiness. The stone is not clear and various non-uniform inclusions are generally present.

The geuda stones until 1970 were generally discarded as valueless stones. Then the Thai gem merchants started buying the geuda stones on a large scale. The Thai gem traders having masterminded the technique of geuda heat treatment to convert them to valuable blue sapphire, were buying these geuda to be exported to Thailand. The Thais used empty tar barrels lined with bricks to heat geuda stones. A burner using LP gas and oxygen was generally employed for heating geuda placed in an alumina crucible. The exact details of the heat treatment remained a close secret among the Thai gem traders. However, since then several Sri Lankans have mastered this technique and heat treatment is done fairly extensively in Sri Lanka. The furnaces used in Sri Lanka are made in Sri Lanka. There are many varieties available. Out of these the Lakmini furnace manufactured by Ceylon Ceramics Limited is most popular.

The geuda heat treatment requires heating geuda stones placed in an alumina crucible to a temperature of around 1850^{0}c initially. The stones are next maintained at a temperature of about 1700 - 1800^{0}c for several hours. The exact temperature and the duration of heating depends on the type of geuda to be heated. Another important requirement is that the stones should be heated in a reducing atmosphere. The carbon monoxide formed in the combustion of LP gas with oxygen provides the reducing atmosphere necessary. However higher temperatures generally require more oxidizing conditions and this can cause the appearance of white colour again. Thus carefully controlled conditions are absolutely essential for a successful heat treatment.

What happens during heat treatment? Several things may happen.

Since the geuda stones are normally heated in a reducing atmosphere some Fe^{3+} can be converted to Fe^{2+}. Now with both Fe^{2+} and Ti^{4+} present, Fe^{2+} - Ti^{4+} interaction becomes possible. This is called a charge-transfer transition which results in blue colour (Note that the presence of Fe^{3+} can impart only a pale yellow colour while Ti^{4+} does not give any colour). If the iron concentration is high relative to titanium, after reduction, a yellow or a green (due to Fe^{2+}) sapphire may result. If the titanium content is higher, then asterism or the formation of a white star like appearance may result. This may also cause silkiness to reappear. In this process atmospheric oxygen converts Ti^{3+} to Ti^{4+} which appears as TiO_2.

$$2Ti_2O_3 + O_2 \longrightarrow 4TiO_2$$

TiO_2 separates as needles, silkiness or star like structures. These features are not desirable in the geuda heat treatment since a clear blue coloured stone is the ultimate goal. Such features can be removed by reheating the stones above 1600^{o}c and cooling rapidly so as to prevent entry of oxygen.

Another possibility regarding the chemical reactions which occur during heat treatment is as follows. Under reducing condition $Ti^{3}+$ is produced by the following reactions.

$$O^{2-} \longrightarrow 1/2O_2 + 2e$$

$$Fe^{3+} + e \longrightarrow Fe^{2+}$$

$$Ti^{4+} + e \longrightarrow Ti^{3+}$$

$$Fe^{2+} + Ti^{4+} \longrightarrow Ti^{3+} + Fe^{3+}$$

The last reaction usually goes in the opposite direction. However at elevated temperatures and strongly reducing conditions, it may well be possible. Thus basic research into what exactly takes place during heat treatment is quite important.

The Institute of Fundamental Studies has initiated a research programme to study such scientific aspects such as original of the colour of blue sapphire and the chemistry of the heat treatment process.

Heat treatment of other gems

Heat treatments of most gems have been practiced for a very long time Red agate and carnelian that have been heat treated to enhance colour are reported to have been found in Tutankhamen's tomb (about 1300 BC). During this century Wild made a scientific study on the effect of heat on a variety of gems in 1932. Heat treatment is widely practiced by gem producing countries and exporting countries in order to enhance colour and improve clarity. The deep blue (almost black) Australian sapphires can be lightened by heating under oxidizing conditions. Table 2 gives some examples for such processes.

Table 1. Colouring ions in gems

Gem	Basic Structure	Transition Metal ions
Emerald	Beryllium alumino silicate	Cr^{3+}
Blue sapphire	Corundum (aluminium oxide)	Fe^{3+}, Ti^{4+}
Ruby	Corrundum	Cr^{3+}
Alexandrite, cats eye	Beryl (Beo Al_2O_3)	Fe^{3+}, Cr^{3+}

Table 2 - Major changes on heating gemstones

Type of gem	Change upon heating
Beryl, agnamarine	green to blue, yellow to colourless, orange to pink
Corrundum, ruby	purple to brown to red pink to orange
Quartz, amethyst	colourless, yellow-brown, green or milky
Carnelian	Yellow, brown or red
Topaz	Yellow, brown, blue to colourless
Tourmaline	Blue or blue green green, red to pale red or colourless
Zircon	Brown to reddish, green to blue or yellow