A CHEMICAL STUDY OF THE NELLORE BERYL AND THE CAUSE OF ITS COLOURATION

By N Jayaraman

Introduction —A detailed investigation of the mode of occurrence and distribution of beryl in the mica-pegmatites of Nellore is described by Swaminathan[1] He has also published in the same paper the results of analyses of two samples of beryl

The present work was undertaken with a view to study the colouration of this beryl and also to investigate its exact chemical constitution

It was found that the Nellore beryls could be classified under five different categories according to colour and composition Specimens of beryl were noticed having the following colours, viz , (1) clear rich blue, (2) pale-blue, (3) light apple-green, (4) pale greenish-blue to greenish-yellow and (5) colourless

Stability of colour of beryls on heating —It was found that samples of blue, pale blue or colourless beryls did not show any change in colour on heating, while the green or greenish-yellow samples were converted into blue varieties on continued heating at a temperature of 500°C A similar change in colour of green beryls on heating has been noticed previously by Kurbatov and Kargin[2]

The samples of green beryl obtained from Nellore were kept in an electric furnace, the temperature of which was slowly raised The colour change was first noticed after about an hour's heating at a temperature of 450°C The change into blue colour was complete on heating at 500° for five hours Even continued heating for 12 hours at 350° did not produce any change in colour, and heating for a similarly long period even at 400°C showed only a rather incipient colour-change As for the general change in colour, the two types, viz., the green variety and greenish-yellow variety behaved differently The green variety showed a uniform pale blue colour after it was heated while the greenish-yellow variety assumed a pale dirty blue colour The colour change in the greenish-yellow specimen was slower than in the green specimen The experiment to study change in colour on heating had to be conducted carefully If the specimens were introduced suddenly into the furnace which was already hot, or the temperature of the furnace was raised suddenly, the specimens splitted into small pieces making the observations difficult It was therefore necessary to keep the specimens in the furnace first and then gradually to raise the temperature to the desired point An examination of the greenish-yellow specimen under a microscope indicated that the yellow colour was due to the presence of ferric oxide in a dispersed state or as very thin films in the body of the mineral

Chemical analysis—Finely powdered samples of these beryls were subjected to chemical analysis, the method of procedure being as follows Fusion with Na_2CO_3 was carried out as usual and silica determined with the usual precautions The filtrate after removal of silica was used for estimating aluminium, beryllium and iron by precipitation in the third group as hydroxides The precipitate was filtered off and washed well with ammonium nitrate solution It was then ignited and weighed as the mixed oxides The filtrate from the third group precipitation was tested for magnesium and calcium

The mixed oxides of aluminium, beryllium and iron were fused with Na_2CO_3 and the cooled melt taken up in dilute hydrochloric acid This acid solution was nearly neutralised with Na_2CO_3 10 grams of sodium bicarbonate was then added and the solution boiled for a minute or two Then the solution was cooled quickly and the precipitated aluminium and iron hydroxides filtered off and washed three or four times with hot 10 per cent. solution of sodium bicarbonate The precipitates of iron and aluminium were again dissolved in hydrochloric acid and the precipitation by sodium bicarbonate was repeated once again Iron was determined in the precipitate and alumina was obtained by difference.

The joint filtrates from the two precipitations were acidified with nitric acid, and beryllium was precipitated as hydroxide with ammonia in the presence of ammonium chloride The beryllium hydroxide thus obtained was washed well with a dilute solution of ammonium acetate, ignited and weighed as BeO.

FeO was determined in a separate sample by the hydrofluoric-sulphuric acid method. Rare earths were examined for by precipitating as oxalates after fusing the third group mixed oxides with potassium bisulphate and taking the cooled melt in dilute sulphuric acid. The alkali was determined by a Lawrence Smith fusion followed by a cobaltinitrite separation. As potassium was absent, the total alkali chloride obtained was taken to be sodium chloride.

TABLE I

The Chemical composition of samples of Beryl per cent

Specimens	Rich blue		Pale blue		Apple green		Greenish yellow		Colourless
	1	1*a*	2	2*a*	3	3*a*	4	4*a*	5
SiO_2	66.69		66.89		66.35		66.21		66.48
Al_2O_3	17.57		17.66		18.37		18.34		18.62
BeO	12.58		12.73		12.29		12.26		12.55
Fe_2O_3	1.25	1.37	1.09	1.20	0.43	1.75	0.73	1.79	0.17
FeO	0.35	0.27	0.34	0.21	1.16	0.19	1.24	0.12	0.39
Na_2O	0.63		0.42		0.29		0.26		0.35
H_2O	0.82		0.73		0.88		0.89		1.58
Total	99.89		99.86		100.07		99.93		100.14
Specific gravity	2.7192		2.7153		2.7061		2.7088		2.6993

Figures under columns 1*a*, 2*a*, 3*a* and 4*a* reveal the amount of ferric and ferrous iron in specimens 1, 2, 3 and 4 respectively after heating for 5 hours at a temperature of 500°C.

None of the specimens contained either TiO_2, Cr_2O_3 or MnO. CaO, MgO, and rare earths are not present in any significant quantity. It can be deduced therefore, that iron is almost entirely responsible for the colouration of these beryls. A glance at analyses Nos. 1 and 2 shows that the blue beryls are rich in Fe_2O_3 and it was noticed that the intensity of the blue colour was more or less proportional to the Fe_2O_3 content of the specimens. Analyses Nos. 3 and 4 show that the green beryls are rich in FeO and that the Fe_2O_3 content is smaller than in specimens 1 and 2. In specimens 3 and 4 the intensity of the green colour appeared to be proportional to the FeO content of the specimens. The slightly larger Fe_2O_3 content of specimen No 4 is perhaps due to the alteration of the beryl and consequent oxidation of the ferrous iron. It is interesting to note that the colourless beryl No 5 contains only a very low percentage of iron but more of water than the other four specimens. The composition of this colourless beryl agrees well with the formula $6(BeO\ FeO\ Na_2O)\ 2(Al_2O_3\ Fe_2O_3)\ 12SiO_2.H_2O$ and is similar to the water-clear beryl and aquamarine samples analysed by Jacob[1]. The other four specimens also are of more or less the same composition corresponding to the formula $6(BeO\ FeO\ Na_2O)\ 2\ (Al_2O_3, Fe_2O_3)\ 12SiO_2\ \frac{1}{2}H_2O$, but the iron content varies significantly.

Analyses 1*a*, 2*a*, 3*a* and 4*a* give the iron content, both ferrous and ferric, of the beryls after heating for 5 hours at 500° C. Analyses 1*a* and 2*a* show that the state of oxidation is not altered very much by heating and that only part of the ferrous iron is oxidised to the ferric state. On the other hand, analyses 3*a* and 4*a* show that a large portion of the ferrous iron of the specimens Nos. 3 and 4 is converted into ferric iron. This change takes place without the elimination of iron from the crystal element as ferric oxide. Even after heating the iron forms part of the crystal and is probably present in solid solution as in the case of the blue varieties.

It can therefore be concluded that the state of oxidation of the iron in the beryl is responsible for the particular colouration noted. The presence of ferric iron causes both blue and yellow colours while ferrous iron causes the green colour.

The exact mechanism of the change of ferrous iron to ferric state is rather difficult to visualise, as it involves the oxidation of iron inside the body of the crystal The entry of oxygen from outside appears to be improbable as the crystal packing would not allow it The mechanism of oxidation of ferrous to ferric iron must be of internal origin and this is facilitated by heating the crystal

Summary—1. Greenish and greenish-yellow beryls are completely converted into blue modifications on heating them for a period of 5 hours at 500°C

2 A complete chemical analysis shows that these beryls hold no colouring material except iron and this is present either in the ferric or in the ferrous condition

3 It is found that the intensity of colour of these beryls is proportional to iron content

4 Blue varieties are rich in ferric iron and the green varieties are rich in ferrous iron

5 In the green varieties most of the ferrous iron is converted into the ferric state on heating

6 The composition of the colourless beryl corresponds to the formula $6(BeO\ Na_2O\ FeO)\ 2(Al_2O_3\ Fe_2O_3)\ 12SiO_2\ H_2O$, while the compositions of the blue and green varieties agree with the formula $6(BeO\ Na_2O\ FeO)\ 2(Al_2O_3 . Fe_2O_3) . 12SiO_2\ \frac{1}{2}H_2O$

7 It is concluded that the state of oxidation of the iron present in the beryl is responsible for the particular colouration of the specimen

8 Ferric iron causes both blue and yellow colours in these beryls, while ferrous iron is responsible for the production of green colour

9 The exact mechanism of the conversion of colour namely, green to blue noticed on heating the specimens, involving oxidation of ferrous to ferric iron cannot be clearly understood It is probably due to an obscure internal phenomenon.

The author wishes to express his grateful thanks to Dr K R Krishnaswami, D Sc , F I C , for his kind and helpful criticism during the course of this work

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