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ORIGINAL PAPER

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Characterization of beryl (aquamarine variety) by Mössbauer spectroscopy

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Abstract The Mössbauer spectra of several blue beryls have been obtained in the temperature range of 4.2–500 K. A common feature observed in all room-temperature spectra is the presence of an asymmetric Fe^{2+} doublet ($\Delta E_Q \sim 2.7 \text{ mm s}^{-1}$, $\delta \sim 1.1 \text{ mm s}^{-1}$), with a very broad low-velocity peak. This asymmetry seems to be related to a relaxation process involving ferrous ions and water molecules in the structural channels, as suggested by Price et al. (1976). Surprisingly, the spectrum at 500 K also shows a broad, but symmetrical, doublet, with a clear splitting of the lines indicating the presence of at least two Fe^{2+} components. The room-temperature spectrum obtained after the 500 K run shows the same features as prior to the heating. At 4.2 K the spectrum of a deep blue beryl was well fitted with four symmetrical doublets, one of which could be related to Fe^{2+} in the structural channels. Ferrous ion was also found to occupy the octahedral and tetrahedral sites, whereas ferric ion is most probably located in the octahedral site. A meaningful fit of the room-temperature spectrum, as well as an explanation for the temperature dependence of the Mössbauer spectra, are discussed. Finally, it is believed that the color in beryl will be dictated by the relative proportions of Fe^{3+} in the octahedral sites and of Fe^{2+} in the channels.

Keywords Beryl · Mössbauer spectroscopy

Introduction

Beryl (ideally $\text{Be}_3\text{Al}_2\text{Si}_6\text{O}_{18}$) is a ring silicate with hexagonal structure in which the Al ions are octahedrally coordinated to six oxygens, and both Si and Be are tetrahedrally coordinated to four oxygen atoms (Fig. 1). The staggered arrangement of six $(\text{SiO}_4)^{4-}$ tetrahedra gives rise to relatively open wide channels that run along the crystallographic *c* axis. In natural beryl it is usually found that these channels are partially filled with water, alkali metals, transition metal ions, and other impurities (Wood and Nassau 1968; Aurisicchio et al. 1988). The iron content in most natural beryls is less than 1%, but some deep blue specimens may have up to 3%.

It has been proposed that the iron atoms can occupy all three crystallographic sites described above, but the replacement of Be^{2+} or Si^{4+} (ionic radius 0.35 and 0.42 Å, respectively) by Fe^{2+} , which has an ionic radius of 0.74 Å, is considered to be unlikely. The existence of iron ions in the channels and the occurrence of an intervalence charge transfer between ferrous and ferric atoms located either in the crystallographic sites or in the channels was proposed by some authors (Wood and Nassau 1968; Parkin et al. 1977; Goldman et al. 1978; Isotani et al. 1989).

The blue and green colors of beryl have been attributed to the presence of iron in the structure, and therefore Mössbauer spectroscopy has been used as a potential tool along with optical spectroscopy to find a correlation between color and the location of the iron atoms. Unfortunately, because of the complexity of the spectra, some questionable conclusions have been put forward.

As far as known, there is only one paper in the literature dealing specifically with the Mössbauer spectrum (MS) of beryl (Price et al. 1976). These authors collected the spectra at several different temperatures and for different samples, and their main conclusions were that the ferrous atoms are located in both octahedral and

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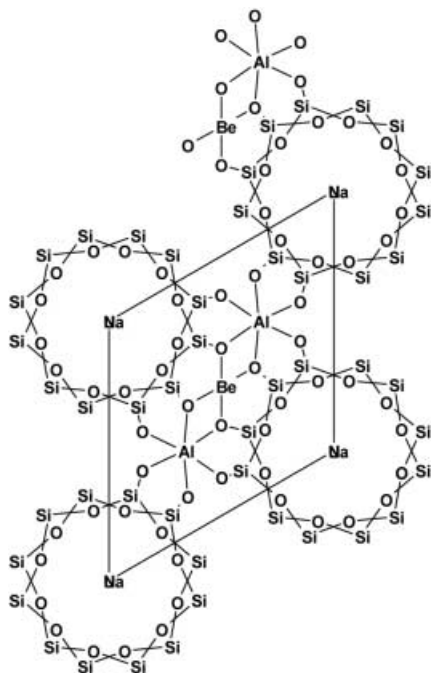


Fig. 1 Schematic representing the structure of beryl projected on the basal plane (0 0 0 1)

tetrahedral sites, whereas the ferric ions are probably in the octahedral sites. An intriguing observation was that the low-velocity line of one doublet, which is symmetric at 4.2 K, broadens as the temperature increases, and at 77 K the shape of the doublet is clearly very asymmetric. A relaxation effect was proposed as a possible cause for this behavior, but no conclusive proof was offered. A representation based on our own data of the 295-K (room temperature, RT) spectrum is shown in Fig. 2A, from which it can be seen that the ferrous doublet is present in larger proportion. The small doublet with the high- and low-velocity peaks at approximately 1.5 mm s^{-1} and 0.1 mm s^{-1} , respectively, originates from Fe^{2+} in the tetrahedral sites.

The room-temperature MS of a blue beryl showing a quite broad central envelope near zero velocity and a relatively sharp peak close to 2.5 mm s^{-1} (similar to Fig. 2B) was obtained by Parkin et al. (1977). The presence of both Fe^{2+} and Fe^{3+} was a confirmation, according to these authors, for a charge-transfer mechanism between Fe cations in the octahedral sites that have faces bridged by Si atoms. For this sample, the MS suggests the predominance of Fe^{3+} . The MS of a sodium-rich blue beryl is similar to that shown in Fig. 2B, but no asymmetry in the peak depths is apparent from the spectrum (Sanders and Doff 1991).

Goldman et al. (1978) reported another type of RT spectrum for a deep blue beryl (similar to Fig. 2C). The asymmetry of the doublet is clearly visible, and, according to these authors, the high-velocity peak is associated to a Fe^{2+} doublet, whereas a very small absorption near 1.5 mm s^{-1} is associated with the presence of iron in the structural channels. The broad absorption

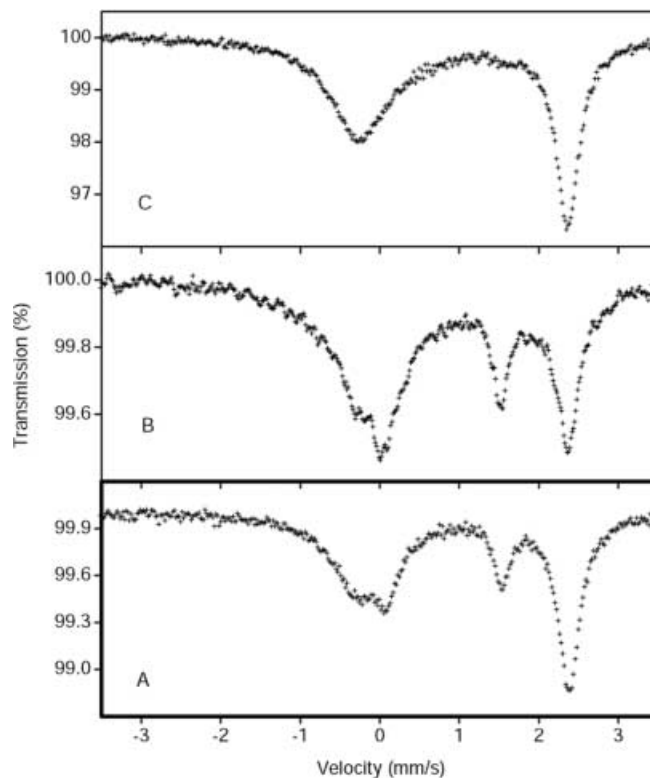


Fig. 2 Typical room-temperature Mössbauer spectra of beryl. **A** Light blue. **B** Bluish green. **C** Deep blue

near the center of the spectrum was attributed to the presence of Fe^{3+} in more than one crystallographic site.

Almost all of the above-cited papers did not show an adequate fit for the RT spectrum, the reasons for this shortcoming being related to the very broad low-velocity line and the strong asymmetry, features that are common to all spectra. In an attempt to obtain a better understanding of this strange behavior, in the present work MS at different temperatures have been collected for several deep, light and greenish blue beryls.

Experimental

Five beryl samples of the aquamarine variety were collected in pegmatites near the city of Pedra Azul, northeast of Minas Gerais State, Brazil. The crystals showed a prismatic shape with basal pinacoid and size usually less than 5 cm in length. The color varies from dark blue to greenish blue. The crystals are in most cases limpid, well finished, terminated, transparent, and commonly of gemmological quality.

MS were collected with a spectrometer using a constant-acceleration drive with triangular reference signal. Velocity calibration was achieved from the MS of a standard α -Fe foil at RT, and the isomer shifts are quoted relative to α -Fe. Due to the low iron content, which implies long acquisition times, only one 4.2 K spectrum was obtained for a deep blue beryl. RT and 80-K spectra were collected for all samples, and a few MS at intermediate temperatures were recorded as well. In some cases, a closed-cycle system was used, and the signals due to the Be and Al windows were subtracted from the spectra. It is relevant to mention that for some samples MS were collected for 7 days' duration, and even

after this extremely long counting time the statistics of the data were not sufficient to allow a reliable quantitative analysis.

The fitting procedures for the various spectra depended on the sample and temperature of measurement and will be specified hereafter.

Results

Deep blue beryl (RBLF)

The MS of sample RBLF (deep blue beryl) at a few selected temperatures are shown in Fig. 3, and the numerical results for the fits are listed in Table 1. At 4.2 K three symmetric doublets can be resolved, the most intense one having parameters typical for octahedral Fe^{2+} ($\Delta E_Q = 2.74 \text{ mm s}^{-1}$ and $\delta = 1.28 \text{ mm s}^{-1}$). The line width for this ferrous component is 0.32 mm s^{-1} . There is

no evidence for the presence of another Fe^{2+} doublet with similar parameters. The hyperfine parameters for the doublet accounting for about 10% of the spectral area indicative for octahedral Fe^{3+} ($\Delta E_Q = 0.68 \text{ mm s}^{-1}$ and $\delta = 0.53 \text{ mm s}^{-1}$). The values of the isomer shift (0.91 mm s^{-1}) and quadrupole splitting (1.73 mm s^{-1}) for the third doublet are typical of ferrous ions in tetrahedral coordination (McCammon 1995).

The 14-K spectrum shows basically the same features as discussed above, but the Fe^{2+} doublet is slightly asymmetric, with area ratio of 1:1.1 and line width of 0.35 mm s^{-1} . At 30 K the overall shape of the spectrum is significantly different from the previous ones, and an asymmetry in the line intensities of the main Fe^{2+} doublet is evident. Several attempts were made to properly fit the data, and the best results for all spectra collected between 30 K and RT were obtained with the following strategy. In cases where the doublet is

Fig. 3 Mössbauer spectra of sample RBLF (deep blue beryl) at some selected temperatures. Crosses represent the experimental data; full lines represent the fitted subspectra and their sum

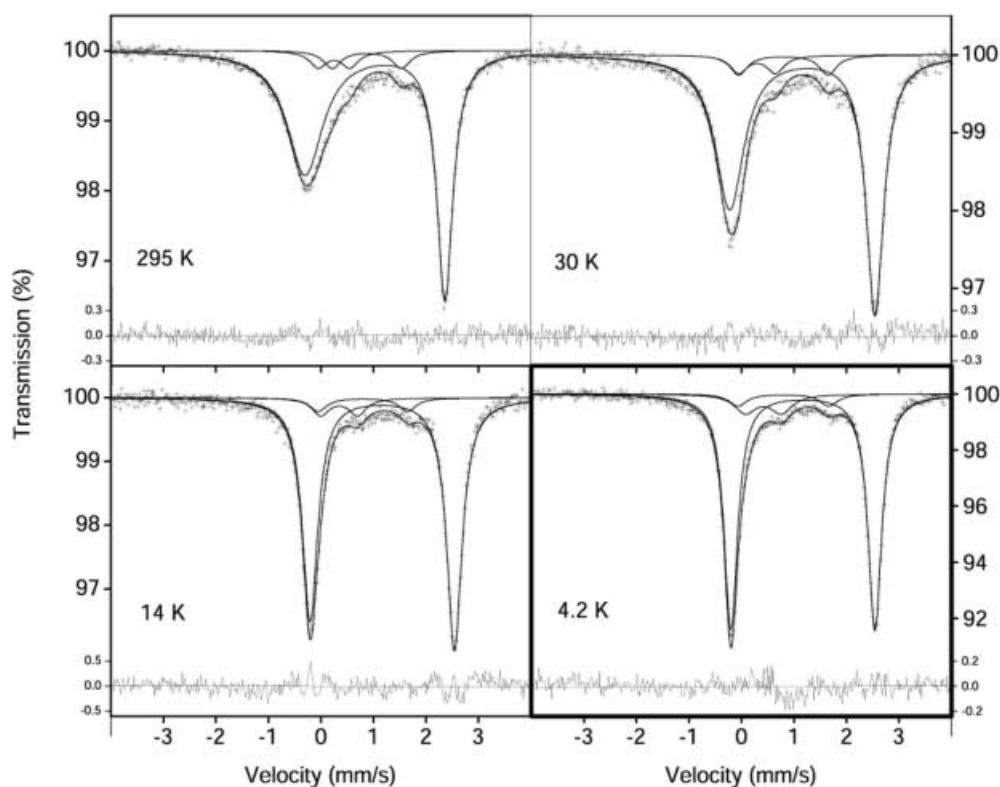


Table 1 Mössbauer parameters obtained for sample RBLF at some selected temperatures. The quadrupole splittings (ΔE_Q), isomer shifts (δ), line widths (W) are in mm s^{-1} , whereas the relative areas (S) are given in %. χ^2 is the reduced chi-squared

$T(\text{K})$	ΔE_Q	δ	W_1	W_2	I_1/I_2	S	ΔE_Q	δ	W	S	ΔE_Q	δ	W	S	χ^2
295	2.66	1.14	0.83	0.37	0.88	88	1.32	0.98	0.40^c	6	0.60^c	0.36^c	0.40^c	6	1.4
4.2	2.74	1.28	0.32	—	1.0^c	84	1.73	0.91	0.40^c	6	0.68	0.42	0.40^c	10	1.7
14	2.75	1.28	0.35	—	1.12	87	1.70^c	0.91^c	0.40^c	6	0.70^c	0.46^c	0.40^c	7	1.5
30	2.77	1.27	0.65	0.40	1.02	87	1.70^c	0.91^c	0.40^c	7	0.70^c	0.46^c	0.40^c	6	1.3
80	2.66	1.28	1.57	0.51	0.71	93	1.70^c	0.91^c	0.40^c	6	0.70^c	0.46^c	0.40^c	2	3.4
295 ^a	2.61	1.18	1.04	0.50	0.77	94	1.17	1.02	0.40^c	4	0.60^c	0.36^c	0.40^c	2	1.5
500 ^b	2.78	1.01	0.44	—	1.00	39	2.18	1.02	0.44	36	1.75	1.14	0.44	10	2.1

^a Results refer to the spectrum taken after the 500 K measurement

^b There is an additional doublet due to Fe^{3+} accounting for 15% of the spectral area

^c These parameters were fixed in the fit

relatively well defined the quadrupole splitting and isomer shift were not fixed; one width parameter (fixed at 0.40 mm s^{-1}) and fixed area ratios (1:1) were forced for the two minor components. Two independent widths and adjustable area ratios were used for the major Fe^{2+} doublet in an attempt to account for the strong asymmetry. In this way, reasonable fits, as far as reproducing the experimental MS is concerned, were obtained. In addition, the derived hyperfine parameters are also in line with the low-temperature measurements. The asymmetry in the low-velocity line increases with the temperature, and at 295 K a broad envelope is observed. This asymmetry is not caused by preferred orientation, since the spectrum collected under the magic angle did not show any difference in the line intensities. It is also not caused by the superposition of a ferric doublet because the amount of Fe^{3+} is relatively small. It is interesting to note that the quadrupole splitting for the major Fe^{2+} doublet only changes from 2.74 mm s^{-1} at 4.2 K to 2.66 mm s^{-1} at 295 K, indicating a relatively strong deformation of the axial symmetry of the involved crystallographic site (Bancroft 1973).

A surprising result not reported in the earlier literature was obtained for the spectrum collected at 500 K (Fig. 4). The broad central envelope close to -0.3 mm s^{-1} has vanished, and two relatively sharp doublets have emerged. The spectrum could be well fitted with four doublets, and the numerical results are listed in Table 1. The two minor components discussed above are still present, but two Fe^{2+} doublets with almost the same isomer shift are clearly seen. At first it was thought that perhaps some transformation occurred due to the heating, but the RT spectrum obtained after this 500-K run is almost the same as the one obtained before this experiment (Figs. 2 and 3). This cycle of RT and 500-K measurements was repeated three times, and the effect was found to be reproducible. This finding is a conclusive proof that a reversible process is taking place, but before further discussion it is preferred to present the MS of the other samples considered in this study.

Light blue beryl (RBIP)

The shape of the RT spectrum of this sample is similar to that of RBLF, but there are two important differences: there is no evidence of Fe^{3+} , and the middle doublet is present in higher proportion (Fig. 5). A fit based on the same methodology as described above again produces a reasonable agreement with the experimental data, and the derived hyperfine parameters are listed in Table 2. The parameters for the most intense doublet are representative for Fe^{2+} , and the middle doublet has the same parameters as those obtained for sample RBLF. At 80 K the asymmetry in line width of the ferrous doublet is still present, but at 14 K it has almost vanished (Fig. 5). Although statistically the MS taken with the absorber at 500 K is of poor quality, it is nevertheless obvious that the symmetric shape is

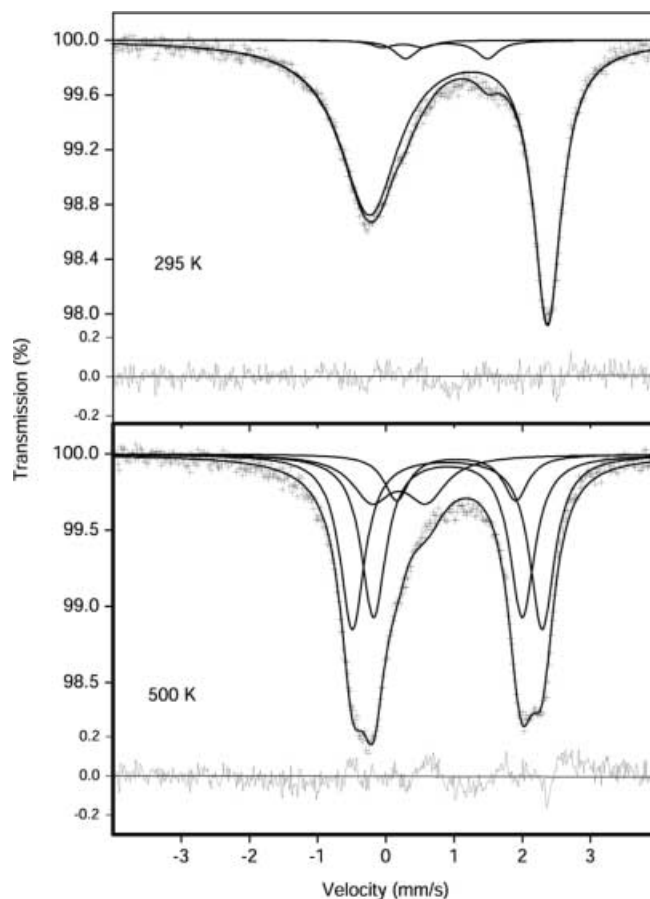


Fig. 4 Mössbauer spectrum of sample RBLF at 500 K showing the split of the high-velocity lines. The 295 K spectrum was taken after the 500 K measurement. *Crosses* represent the experimental data; *full lines* represent the fitted subspectra and their sum; the *bottom line* represents the residual of the fits

restored, similarly to what is observed for sample RBLF. The spectrum recorded after cooling the absorber back to RT is again identical to that shown in Fig. 5, and therefore the same conclusion about the reversibility of the underlying phenomena remains valid for RBLF.

Greenish blue (RBBA) and bluish green (R101) beryls

The MS shown in Fig. 6 for sample R101 (those for sample RBBA are very similar) are quite different from the MS of samples RBLF and RBIP. A fit with two symmetric and one asymmetric doublets was attempted, yielding reasonable results in spite of the poor statistics of the experimental data. However, the weak shoulder near 1 mm s^{-1} could not be accounted for. The parameters derived from the three-doublet fits are listed in Table 2. The inner and outer doublets are due to ferric and ferrous atoms, respectively, whereas the doublet with $\Delta E_Q = 1.33 \text{ mm s}^{-1}$ at RT seems to be similar to the weak ferrous doublet resolved from the MS of samples RBLF and RBIP (see Table 1). It is relevant to mention at this point that the relative areas for the ferric

Fig. 5 Mössbauer spectra of sample RBIP (light blue beryl) at some selected temperatures. *Crosses* represent the experimental data; *full lines* represent the fitted subspectra and their sum; the *bottom line* represents the residual of the fits

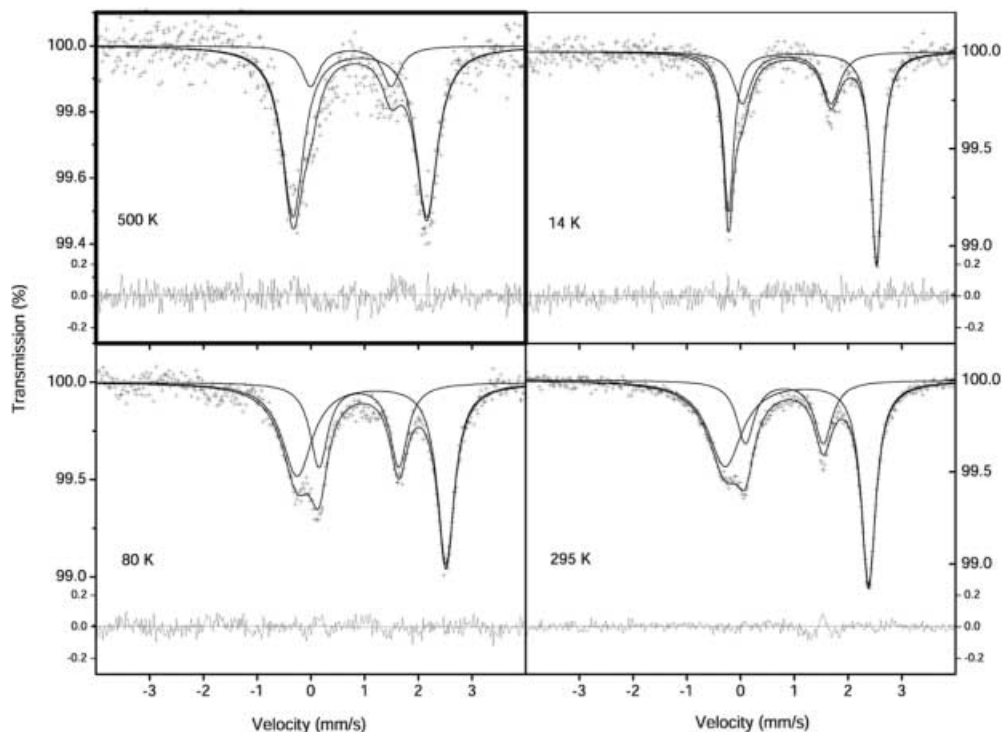


Table 2 Mössbauer parameters obtained for samples R101, RB01, and RBIP at some selected temperatures. The quadrupole splittings (ΔE_Q), isomer shifts (δ), line widths (W) are in mm s^{-1} , whereas the relative areas (S) are given in %. χ^2 is the reduced chi-squared

Sample	$T(\text{K})$	ΔE_Q	δ	W_1	W_2	I_1/I_2	S	ΔE_Q	δ	W	S	ΔE_Q	δ	W	S	χ^2
R101	295	2.68	1.12	0.96	0.61	0.70 ^a	49	1.33	0.98	0.40 ^a	18	0.61	0.36 ^a	0.40 ^a	33	1.0
	80	2.81	1.16	0.74	0.64	0.82	43	1.60	0.94	0.40 ^a	24	0.46	0.46 ^a	0.40 ^a	33	1.6
RB01	295	2.54	1.20	1.22	0.40	0.49	73	1.48	0.90	0.40 ^a	27	–	–	–	–	0.6
	80	2.55	1.36	1.27	0.53	0.53	70	1.58	0.96	0.40 ^a	30	–	–	–	–	1.3
	14	2.74	1.30	0.27	–	1.38	51	1.58	1.03	0.43	49	–	–	–	–	1.3
RBIP	295	2.67	1.16	0.77	0.33	1.01	73	1.45	0.93	0.40 ^a	27	–	–	–	–	1.1
	80	2.77	1.24	0.69	0.39	1.09	67	1.49	1.01	0.40 ^a	33	–	–	–	–	1.3
	14	2.76	1.26	0.23	0.25	1.42	69	1.65	0.97	0.40 ^a	31	–	–	–	–	1.1
	500	2.49	1.02	0.49	–	1.00	84	1.5	0.85	0.40 ^a	16	–	–	–	–	1.4

^aThese parameters were fixed in the fit

component obtained from the MS collected at both temperatures and for both samples are close to 30%. Hence, the different shape of these spectra compared to those discussed before is certainly related to the presence of this component in higher proportion.

Several unsuccessful attempts were made to fit the spectra shown in Fig. 6 with model-independent quadrupole splitting distributions. The existence of superimposed components, associated with poor statistics, made it difficult to properly estimate the quadrupole intervals for each subspectrum (Vandenberghé et al. 1994).

Greenish blue (RB01)

The spectra of this sample are different from those discussed so far, as can be seen in Fig. 7. The absorptions

at RT near zero velocity and 2 mm s^{-1} have approximately the same intensity, and there is no apparent Fe^{3+} shoulder near the central peak. A two-doublet fit, with parameters as listed in Table 2, is considered to be acceptable. No Fe^{3+} is detected for this sample. At 80 K the shape of the spectrum is similar, but, at 14 K the lines are sharper and the two doublets have evolved to a more symmetrical pattern.

Discussion

Interpretation of the Mössbauer spectra

The two crucial points for which no conclusive answers have been found so far are the site preference of iron in the beryl structure and the reason for the strong

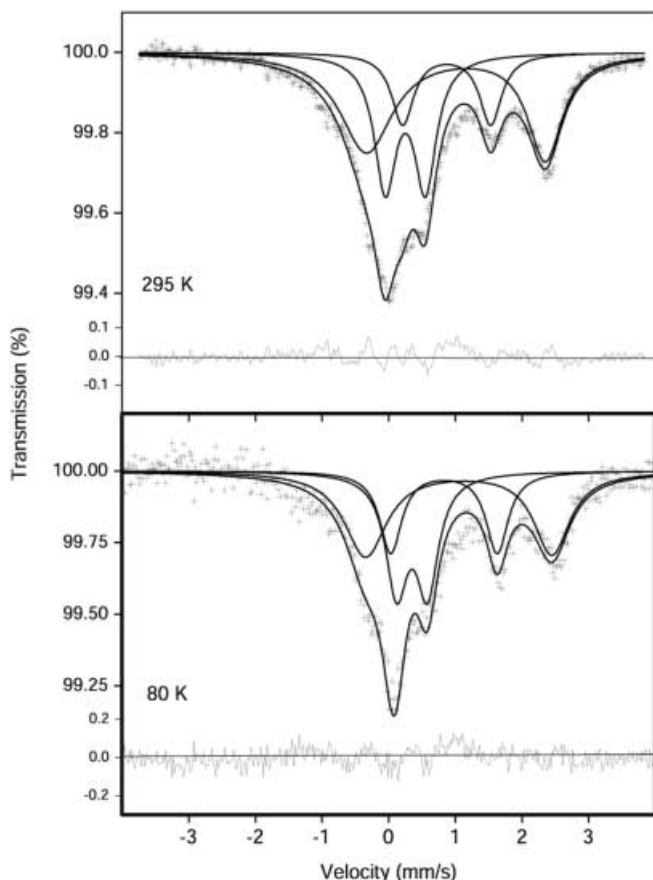


Fig. 6 Mössbauer spectra of sample R101 (bluish green beryl) at room temperature and 80 K. *Crosses* represent the experimental data; *full lines* represent the fitted subspectra and their sum; the *bottom line* represents the residual of the fits

asymmetry in the RT spectrum. Although the fitting procedure that was applied to analyze the spectra might be questioned at some points, it is believed that it is at least a fair approximation and that some important conclusions can be drawn from the results.

The first part of the discussion will be focused on the doublet with the quadrupole splitting in the range 2.5 to 2.8 mm s⁻¹ (14 to 500 K), for which the following observations are thought to be relevant:

- This doublet is present in the MS of all samples considered in this work and also in all spectra reported in the literature (Price et al. 1976; Parkin et al. 1977; Goldman et al. 1978; Sanders and Doff 1991). It is strongly asymmetric, with the low-velocity absorption being broader than the high-velocity one.
- The asymmetry remains down to 30 K, but at 14 K (and 4.2 K) a narrow, symmetrical doublet is observed.
- Both the isomer shift and quadrupole splitting are typical for Fe²⁺ in octahedral coordination.
- The quadrupole splitting changes from 2.74 mm s⁻¹ at 4.2 K to 2.66 mm s⁻¹ at 295 K, suggesting that there is a relatively strong deformation of the axial symmetry of the involved crystallographic sites (Bancroft 1973).

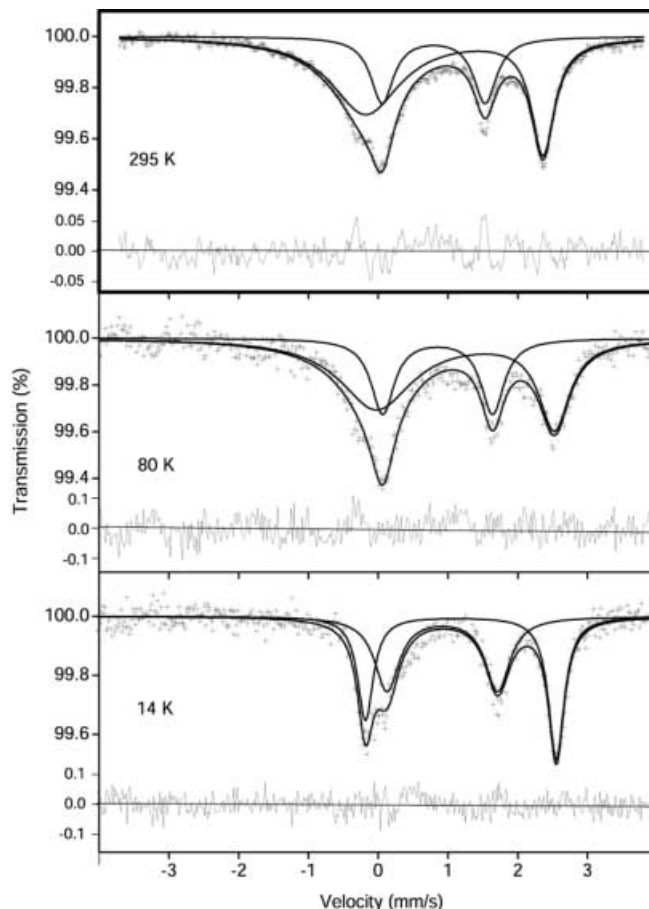


Fig. 7 Mössbauer spectra of sample RB01 (greenish blue beryl) at room temperature, 80, and 14 K. *Crosses* represent the experimental data; *full lines* represent the fitted subspectra and their sum; the *bottom line* represents the residual of the fits

- At 500 K two well-resolved symmetrical doublets with $\Delta E_Q = 2.78$ and 2.18 mm s⁻¹ and with the same isomer shift (1.01 mm s⁻¹) emerged instead of the broad doublet. Their hyperfine parameters are again very typical for Fe²⁺. The RT spectrum taken after this 500-K run shows the same broad and asymmetric doublet as before warming up, which means that no irreversible structural changes have occurred upon heating at this temperature.

The fact that two doublets with similar hyperfine parameters are clearly observed at 500 K implies that the Fe²⁺ atoms must be located in two crystallographic sites with similar symmetry. Based on the fact that there is only one type of octahedral site with the same nearest or next-nearest neighbors in the beryl structure, it seems reasonable to propose that some of the Fe²⁺ species are located in the channel sites. However, an explanation remains to be found for the unusual temperature dependence of the Mössbauer spectrum. The diameter of the structural channels is approximately 2.8 Å in the plane of the Si₆O₁₈ rings and 5.1 Å between two rings, which is large enough to accommodate a variety of species such as CO₂, H₂O, Na⁺, Li⁺, Cs⁺,

Fe^{2+} , methane, etc. (Wood and Nassau 1968). It has also been established that there are two different types of water molecules: one with the H–H vector parallel (type I) and the other with the vector perpendicular (type II) to the c axis (Wood and Nassau 1968). Currently, it is accepted that the above-mentioned cations are only coordinated by two type II water molecules, one below and one above in the channel (Aines and Rossman 1984). These latter authors performed a detailed infrared spectroscopic study of the influence of the temperature upon the behavior of water in the beryl structure, and a summary of their findings is given below:

- The channel ions are located in the center of the rings, i.e., at the most narrow spaces along the channels.
- Upon heating above 160 °C, the water molecules become unbound and there is a partition of both types of water into a gas-like state; the cations have thus more freedom to move inside the channels.
- After cooling down both types of water are again observed, indicating a reversible process.
- A hopping between types I and II occurs at low temperatures (below RT), whereas a random motion of the water molecules occurs at high temperatures.

At RT the time scale of the bonded state (τ_b) is between that of infrared spectroscopy and NMR (Charoy et al. 1996). Thus, τ_b is of the order of the nuclear Larmor precession time ($\tau_L \sim 10^{-8}$ s). It is well known that when $\tau_b \sim \tau_L$ the Mössbauer spectrum is usually complicated with broad lines, and therefore this kind of “relaxation” could explain the RT spectrum of sample RBLF. This spectrum, and those at lower temperatures, indeed exhibit features similar to those observed, e.g., in the MS of ankerite (a Fe^{2+} -containing carbonate), for which the existence of electronic relaxation has been proven (De Grave 1986). It can be expected that at 500 K $\tau_b \gg \tau_L$, so that a static average interaction will be experienced during the Mössbauer event, and hence a well-defined spectrum appears. On the other hand, at 4.2 K the water molecules are tightly bound to the iron species and a single, sharp doublet is observed. It is also important to mention that the iron atoms residing in the channels are subjected to different interactions, depending on the other constituents in the channels, and this certainly will cause a distribution of the hyperfine parameters.

As mentioned before, Fe^{2+} is also present in the octahedral sites and therefore the fitting procedure that was used is not entirely correct because only one ferrous doublet was included in the fits to account for the component with $\Delta E_Q \sim 2.5$ mm. The paramagnetic Mössbauer spectrum of Fe^{2+} at a given octahedral site in a silicate is commonly a symmetric doublet (Bancroft 1973; Coey 1984; McCammon 1995) and thus it seems reasonable to assume that also in beryl the octahedral doublet would be symmetric, as indeed was found for the RBLF spectrum recorded at 500 K (see Fig. 3). To refine the analyses of the MS recorded at 4.2 and 295 K

for RBLF (the statistical quality of all other spectra is insufficient for a detailed refinement), four quadrupole doublets were introduced, however, with some constraints. From the 500 K measurement (Fig. 4; Table 1), it was found that the area ratio of the two major doublets is close to 1.1. It is expected that this ratio does not vary significantly with temperature. Therefore, the 4.2-K spectrum was fitted with four symmetric components with fixed area ratio for the channel and octahedral Fe^{2+} doublets. The resulting calculated line shapes are shown in Fig. 8 and the numerical values are listed in Table 3. The fit is excellent, with the chi-square being 30% lower than the value obtained for the three-doublet fit. The quadrupole splittings and isomer shifts for the channel and octahedral irons are nearly equal, in agreement with the 500-K measurement. The 295-K spectrum was fitted with three symmetric and one asymmetric doublet (with fixed area ratio for the channel and octahedral Fe^{2+} doublets); the latter is to account for the “relaxed” component of the channel iron. Again, the fit is quite good and the hyperfine parameters are also in line with the 4.2 and 500 K measurements,

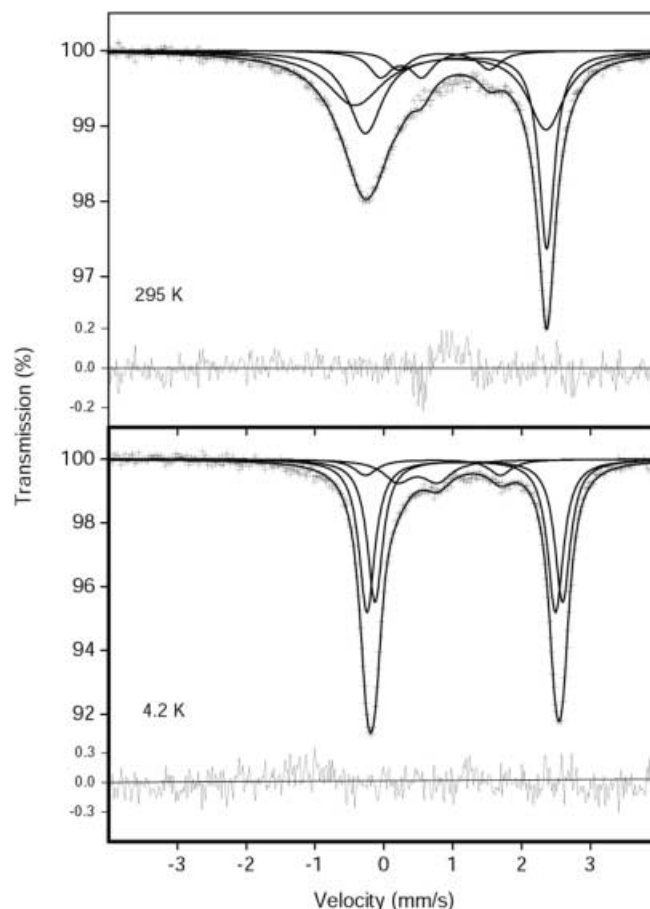


Fig. 8 Mössbauer spectra of sample RBLF (deep blue beryl) at room temperature and 4.2 K. This figure is to be compared with Fig. 3, where only three doublets were used in the fit. *Crosses* represent the experimental data; *full lines* represent the fitted subspectra and their sum; the *bottom line* represents the residual of the fits

Table 3 Mössbauer parameters obtained for sample RBLF at RT and 4.2 K. The quadrupole splittings (ΔE_Q) and isomer shifts (δ) are in mm s^{-1} , whereas the relative areas (S) are given in %. χ^2 is the reduced chi-squared

$T(\text{K})$	ΔE_Q	δ	S	ΔE_Q	δ	S	ΔE_Q	δ	S	ΔE_Q	δ	S	χ^2
295	2.79	1.08	45	2.62	1.15	41	1.32	0.98	6	0.60 ^a	0.36 ^a	8	1.4
4.2	2.82	1.29	43	2.61	1.29	39	1.43	1.10	7	1.1	0.37	11	1.2

^a These parameters were fixed in the fit

although a relatively broad doublet emerged for the octahedral Fe^{2+} .

The doublet with $\Delta E_Q \sim 1.5 \text{ mm s}^{-1}$ is present in higher proportions in samples RBIP, R101, and RB01. The quadrupole splitting does not change drastically with temperature, again indicating a strongly distorted coordination. The nature of this coordination remains puzzling. On the basis of the isomer-shift values, one would be inclined to attribute the doublet to Fe^{2+} in a tetrahedral site, as suggested earlier by Price et al. (1976). However, it is considered to be unlikely that ferrous ions would substitute on the Si or Be sites. The doublet seems to be present at all temperatures with, for a given sample, more or less invariable relative proportion. This latter finding could be a reason to dismiss the assignment of the doublet to Fe species involved in some kind of charge-transfer process, as proposed by Parkin et al. (1977) and Goldman et al. (1978). However, the possibility cannot be excluded that in beryl such a process does take place, provided that its relaxation time down to 4.2 K remains much shorter than the characteristic measuring time of the Mössbauer effect.

The hyperfine parameters of the remaining doublet ($\Delta E_Q \sim 0.6 \text{ mm s}^{-1}$ and $\delta \sim 0.35 \text{ mm s}^{-1}$ at RT) are typical for Fe^{3+} in an octahedral coordination. It is clearly observed only in samples R101 and RBBA, which have approximately 30% of this component, and most likely the doublet originates from Fe^{3+} replacing Al in the octahedral sites.

Correlation with the color of beryl

The first systematic work focusing on the color of beryl was reported by Wood and Nassau (1968), and since that time several other papers dealing with the subject have been published (Price et al. 1976; Parkin et al. 1977; Goldman et al. 1978; Blak et al. 1982; Aines and Rossman 1984; Sanders and Doff 1991; Mathew et al. 1998; Pulz et al. 1998; Nassau 1999). The majority of these papers are based on the optical spectra (UV–VIS and infrared spectroscopy), but so far no agreement about the origin of the variety in colors has been reached. The present study shows that the amount of Fe^{3+} increases from about 10% in the deep blue beryl (sample RBLF) to about 30% in the greenish blue samples (R101 and RBBA). It was suggested that Fe^{2+} – Fe^{3+} charge transfer causes blue color (Parkin et al. 1977; Goldman et al. 1978). If this were the case, then samples R101 and RBBA should show a deep blue color

because they are the samples with the highest amounts of octahedral Fe^{3+} and tetrahedral Fe^{2+} . If it can be accepted that ferric ion in the octahedral site causes a yellow color and that Fe^{2+} in the channel sites causes the blue color (Nassau 1999), then the different colors of the present beryl samples can be explained: the color will be dictated by the relative proportions of Fe^{3+} in the octahedral sites and of Fe^{2+} in the channels. Thus, deep blue samples have little Fe^{3+} , whereas greener samples have more Fe^{3+} or less channel Fe^{2+} . This reasoning can also elucidate the experimental observation that heating of green beryl causes a change in its color to blue. Some authors have proposed that heating results in the reduction of Fe^{3+} to Fe^{2+} (Blak et al. 1982; Goldman et al. 1978). As octahedral Fe^{2+} produces no intense color, the green will disappear and the blue will be enhanced by this reduction.

Conclusions

The strong asymmetry in the RT Mössbauer spectrum of beryl was shown to be caused by a relaxation process involving ferrous ions and water molecules in the structural channels, in support of an idea first proposed by Price et al. (1976). In all investigated samples it was also found that Fe^{2+} is present, replacing Al in the octahedral site and Be in the tetrahedral site, whereas Fe^{3+} is most probably replacing Al in the octahedral site. The color of beryl seems to be dictated by the relative proportions of Fe^{3+} in the octahedral sites and of Fe^{2+} in the channels. Thus, deep blue samples have little Fe^{3+} , whereas greener samples have more Fe^{3+} or less channel Fe^{2+} .

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References

- Aines RD, Rossman GR (1984) The high-temperature behavior of water and carbon dioxide in cordierite and beryl. *Am Mineral* 69: 319–327
- Aurisicchio C, Fioravanti G, Grubessi O, Zanazzi PF (1988) Reappraisal of the crystal chemistry of beryl. *Am Mineral* 73: 826–837
- Bancroft GM (1973) Mössbauer spectroscopy. J Wiley, New York
- Blak AR, Isotani S, Watanabe S (1982) Optical absorption and electron spin resonance in blue and green natural beryl. *Phys Chem Miner* 8: 161–166

- Charoy B, De Donato P, Barres O, Pinto-Coelho C (1996) Channel occupancy in an alkali-poor beryl from Serra Branca (Goias, Brazil): spectroscopic characterization. *Am Mineral* 81: 395–403
- Coey JMD (1984) Silicate minerals. In: Long GJ (ed.) *Chemical applications of Mössbauer spectroscopy*, vol. 1, Plenum, New York, pp 443–509
- De Grave E (1986) ^{57}Fe Mössbauer effect in ankerite: study of the electronic relaxation. *Solid State Commun* 60: 541–544
- Goldman DS, Rossman GR, Parkin KM (1978) Channel constituents in beryl. *Phys Chem Miner* 3: 225–235
- Isotani S, Furtado WW, Antonini R, Dias OL (1989) Line-shape and thermal analysis of the Fe^{2+} band in Brazilian green beryl. *Am Mineral* 74: 432–438
- Mathew G, Karantah RV, Gundu Rao TK, Deshpande RS (1998) Maxixe-type colour centre in natural colourless beryl from Orissa, India: an ESR and OA investigation. *J Gemmol* 26: 238–251
- McCammon C (1995) Mössbauer spectroscopy of minerals. In: Ahrens TJ (ed.) *Mineral physics and crystallography*, vol. 2: a handbook of physical constants, pp 332–347
- Nassau K (1999) *Gemstone enhancement: history, science, and state of the art*. St. Edmundsbury Press Ltd., Manchester
- Parkin KM, Loeffler BM, Burns RG (1977) Mössbauer spectra of kyanite, aquamarine and cordierite showing intervalence charge transfer. *Phys Chem Miner* 1: 301–311
- Price DC, Vance ER, Smith G, Edgar A, Dickson BL (1976) Mössbauer effect studies of beryl. *J Phys* 37(C)6: 811–817
- Pulz GM, D'el-Rey Silva LJH, Barros Neto LS, Brum TMM, Juchem PL, Santos CA, Pereira VP, Silva JJ (1998) The chemical signature of emeralds from the Campos Verdes Santa Terezinha Mining District, Goias, Brazil. *J Gemmol* 26: 252–261
- Sanders IS, Doff DH (1991) A blue sodic beryl from southeast Ireland. *Mineral Mag* 55: 167–172
- Vandenberghre RE, De Grave E, de Bakker PMA (1994) On the methodology of the analysis of Mossbauer spectra. *Hyperfine Interac* 83: 29–49
- Wood DL, Nassau K (1968) The characterization of beryl and emerald by visible and infrared absorption spectroscopy. *Am Mineral* 53: 777–806