Emeralds are again being mined in the historic district of the Ural Mountains. Physical, chemical, spectroscopic, and microscopic characteristics of stones from the recent production are presented and compared with data on older samples as well as those reported in the literature. Chemical analysis and visible and infrared spectroscopy provide information on crystal chemistry and color-causing trace elements that is useful both to characterize these stones and to separate them from their synthetic counterparts. A variety of mineral inclusions as well as liquid, two-phase, and three-phase inclusions were seen with magnification. All of the data are critically evaluated with respect to the confirmation of unknown samples as Uralian.

Historically, the most important emeralds came from the famous mining districts of Muzo and Chivor, in Colombia, and from the Ural Mountains of Russia (figure 1). Emeralds were discovered in Russia in 1830, near the Takovaya River, about 90 km northeast of Sverdlovsk (formerly Ekaterinburg), on the east side of the Ural Mountains (Bauer, 1896). Significant amounts were produced through the 19th and into the early 20th century. For the last several decades, however, emeralds from this source were only occasionally available—either historic stones or stones that resulted from the limited mining that continues in the region.

Today, though, there appear to be large quantities of Russian emeralds entering the trade, many of very fine color (figure 2). Faceted stones as large as 57 ct have been reported (figure 3). Soviet colleagues (e.g., V. Balitsky, pers. comm., 1991) have told the authors that these emeralds are from a mine called Malysheva, situated in the old Takovaya River mining area. Apparently, the Malysheva mine has been exploited in recent decades for beryllium, with emerald as a byproduct. Not until 1990, however, when a joint venture called Emural was formed between the Soviet government and a Panamanian company (that includes two Israeli partners) to cut and market the emeralds, did significant quantities of Russian emeralds appear in the market (see, e.g., "New Joint Venture to Market Soviet Emerald," 1990; "USSR Supplies Rough Emerald to Israel," 1991; B. Harel, pers. comm., 1991).

Although a small number of Russian emeralds have been included in modern research into the diagnostic properties of natural and synthetic emeralds (e.g., Schrauder, 1983; Stockton, 1984; Schwarz, 1987), no general summary of physical, chemical, and gemological characteristics of Uralian emeralds has been published since the appearance of the detailed study of inclusions in gemstones by Gübelin (1953). Relatively recent papers in...
Russian published by Lokhova et al. [1977], Zher-nakov (1980), Granadchikova et al. [1983], and Gromov et al. [1990], which might fill this gap, are generally not accessible to non-Russian-speaking gemologists.

The authors selected 100 fashioned samples from a parcel of more than 1,000 Russian emeralds that had recently entered the marketplace. On the basis of his decade-long study of known samples from the Takovaya River mining area, the senior author concluded that the properties of these new samples were identical to those of older emeralds known to have come from this general mining district. To characterize this new production for the gemological community, the authors conducted a comprehensive gemological, spectroscopic, and chemical study of these 100 stones.

THE HISTORIC RUSSIAN DEPOSITS:
LOCATION AND OCCURRENCE
A detailed geologic description of the Takovaya River mining area and the emerald-bearing rocks, as well as an account of the historic development of mining activities in the area, was published by Fersmann [1929] and summarized in part by Sinkankas [1981]. In general, the mining area consists of two emerald-bearing belts. The main belt runs approximately north-south over a distance of more than 20 km; at its southern end it intersects a second belt, about 8 km long, that runs northwest-southeast. Historically, the most important mines in the main belt were (from north to south) the Mariinsky, Troitzky, Lubinsky, and Stretiensky mines; and, in the smaller belt (from northwest to southeast), the Ostrowsky, Krasnobolotsky, and Chitny mines (as illustrated in Sinkankas, 1981).

The emeralds occur in Paleozoic metamorphic rocks trapped between the acidic rocks of a granite massif to the west (granites, albitites, pegmatites, and kaolinites) and ultrabasic rocks (peridotites, serpentinites, dunites, pyroxenites, and gabbros) to the east. The metamorphic rocks of the emerald-bearing central contact zone include talc, mica, chlorite, and actinolite schists. This zone follows the granite/ultrabasite contact for about 25 km. As summarized by Sinkankas [1981], emerald mineralization resulted when elements such as beryllium from the silica-rich granites to the west and chromium from the basic rocks to the east were brought together during the process of metamorphism.

On the basis of his interpretation of more than 200 geologic profiles, Fersmann [1929] concluded that the emerald deposits consist of four dominant rock types:
1. Pegmatites or pegmatitic rocks, including albitite and kaolinite (white, up to 2 m thick)
2. Emerald-bearing biotite schists (black, 1.5 m thick)
3. Chlorite-actinolite schists (green, 1 m thick)
4. Talc schists (blue and yellow, more than 3 m thick)
According to Fersmann, emeralds are found only in the biotite and actinolite schists, but Zhernakov (1980) mentioned emeralds from talc schists as well. Fersmann also reported that dark green emeralds are confined to the biotite schists that are in contact with massive pegmatite bodies, and light green material is found in the biotite schists that are in contact with smaller pegmatites and/or in the albite feldspar itself. Zhernakov main-

![Image](image1.png)

Figure 2. Some of the emeralds that have emerged recently from the Ural Mountains are of very fine color, as evidenced by these 2-3 ct cabochons and faceted stones.

![Image](image2.png)

Figure 3. This 37-ct emerald is reportedly from the new production in the Ural Mountains. Photo courtesy of B. Harel, Hargem.

![Image](image3.png)

Figure 4. Some of the emeralds that have emerged recently from the Ural Mountains are of very fine color, as evidenced by these 2-3 ct cabochons and faceted stones.

MATERIALS AND METHODS
The present study is based on the examination of about 120 Uralian samples, 100 from the recent production and 20 older specimens that have all of the characteristics associated with Uralian stones. Included among these older stones are data from three faceted samples that were made available by a private collector who had obtained them as Uralian emeralds after they were removed from period jewelry; these stones are designated samples X, Y, and Z in this study. Also available were two reportedly Russian emeralds that had been in the possession of an Idar-Oberstein gem-dealing family for more than 50 years.

From a large parcel of more recently produced Russian emeralds (available since the end of 1989) that contained cut samples between 0.5 and 8.0 ct,
**TABLE 1.** Physical and chemical properties of Uralian emeralds.

<table>
<thead>
<tr>
<th>Sample</th>
<th>X</th>
<th>Y</th>
<th>Z</th>
<th>5A</th>
<th>5E</th>
<th>5B</th>
<th>3L</th>
<th>3B</th>
<th>3E</th>
<th>5C</th>
<th>5D</th>
<th>5F</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Fac. square</td>
<td>Fac. round</td>
<td>Fac. oval</td>
<td>Cab. oval</td>
<td>Fac. emerald cut</td>
<td>Fac. oval</td>
<td>Fac. emerald cut</td>
<td>Fac. oval</td>
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<td>Fac. oval</td>
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<td>Fac. oval</td>
</tr>
<tr>
<td></td>
<td>X</td>
<td>Y</td>
<td>Z</td>
<td>5A</td>
<td>5E</td>
<td>5B</td>
<td>3L</td>
<td>3B</td>
<td>3E</td>
<td>5C</td>
<td>5D</td>
<td>5F</td>
</tr>
<tr>
<td></td>
<td>8.0 x</td>
<td>7.3</td>
<td>7.9 x</td>
<td>8.7 x</td>
<td>8.6 x</td>
<td>5.4 x</td>
<td>8.3 x</td>
<td>7.3 x</td>
<td>6.8 x</td>
<td>7.7 x</td>
<td>8.4 x</td>
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<td></td>
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<td>7.3</td>
<td>7.9</td>
<td>8.7</td>
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<td>5.4</td>
<td>8.3</td>
<td>7.3</td>
<td>6.8</td>
<td>7.7</td>
<td>8.4</td>
<td>6.6</td>
</tr>
</tbody>
</table>

**Color:**

- Light green
- Light green
- Light green
- Light green
- Light green
- Light green
- Medium green
- Light green
- Light green
- Light green
- Very intense green
- Medium green
- Light green

**Refractive indices:**

- $n_0 = 1.582$
- $n_0 = 1.576$
- $\Delta n = 0.006$
- $n_0 = 1.589$
- $n_0 = 1.585$
- $n_0 = 1.580$
- $\Delta n = 0.006$
- $n_0 = 1.580$
- $n_0 = 1.584$
- $n_0 = 1.580$
- $\Delta n = 0.006$
- $n_0 = 1.589$
- $\Delta n = 0.006$
- $n_0 = 1.589$
- $\Delta n = 0.006$

**Density (g/cm³):**

- 2.72
- 2.72
- 2.72
- 2.72
- 2.72
- 2.72
- 2.72
- 2.72
- 2.72
- 2.72
- 2.72
- 2.72
- 2.72
- 2.72
- 2.72

**Number of analyses:**

- 3
- 3
- 2
- 5
- 20
- 20
- 20
- 20
- 20
- 20
- 20
- 20
- 20
- 15
- 24
- 24

**Microprobe analyses**

- SiO$_2$
- Al$_2$O$_3$
- Cr$_2$O$_3$
- V$_2$O$_5$
- FeO
- MnO
- MgO
- K$_2$O
- Na$_2$O
- Total

- 84.99
- 84.35
- 84.46
- 85.44
- 85.65
- 84.99
- 85.17
- 85.57
- 85.65
- 85.30
- 84.75
- 85.10
- 85.25
- 85.25

**Cations calculated**

- Si
- Al
- Cr
- V
- Fe
- Mn
- Mg
- K
- Na

<table>
<thead>
<tr>
<th>0.007</th>
<th>0.007</th>
<th>0.004</th>
<th>0.009</th>
<th>0.003</th>
<th>0.008</th>
<th>0.005</th>
<th>0.002</th>
<th>0.005</th>
<th>0.000</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.864</td>
<td>1.802</td>
<td>1.339</td>
<td>1.548</td>
<td>1.198</td>
<td>0.970</td>
<td>1.198</td>
<td>1.948</td>
<td>1.304</td>
<td>1.022</td>
</tr>
</tbody>
</table>

**Sum of alkalies and transition metal oxides**

| 1.05 | 1.67 | 1.98 | 0.87 | 1.16 | 1.51 | 1.52 | 1.63 | 1.64 | 1.81 | 1.85 | 1.90 | 2.05 | 2.12 |

**Notes:**

- *Stones in mm; cab = cabochon; fac. = faceted.
- *Almost colorless; selected as the stone with the highest color among hundreds of stones.
- *Total from ref. 10.
- *Na = not analyzed.

We selected about 100 cabochon-cut and faceted samples for examination. The stones were chosen to cover the complete quality range from extremely clean samples to very heavily included stones, as well as the complete color range from very light green, almost colorless, beryls (sample 5B) to very intense green emeralds (sample 1B; also, see figure 2). After microscopic examination and determination of refractive indices, 30 samples from this group of 100 were selected for spectroscopic investigation; 13 of these 30 were also subjected to chemical analysis (see table 1).

Refractive indices were obtained by a standard gemological refractometer, and densities were determined hydrostatically.

Microprobe analyses of the older samples X, Y, and Z were performed by K. Schmetzer in 1987 on an ARL SEMQ instrument with an operating voltage of 20 kV and a beam current of 10 nA; values were calculated by the MAGIC IV correction program provided by the manufacturer. The 13 samples of the new production of Uralian emeralds were analyzed by H.-J. Bernardt in 1991 with a Cameca Camebax electron microprobe using an acceleration voltage of 15 kV and a beam current of 15 nA; for the calculation of values, the correction procedure described by Pouchou and Pichoir [1984] was applied. For the examination of chemical zoning within the samples, 15–25 point analyses were performed at uniform distances across the table facets of the faceted samples and across the bases of the cabochons.

In recent gemological papers, crystal chemistry and isomorphic replacement schemes of emer-
RESULTS
Visual Appearance. The older stones examined by the senior author were light green to medium green. The few rough samples available were dark green and revealed a typical prismatic habit with residual mica crystals bound to the prism faces. Microprobe analyses of some mica platelets taken from two of the emerald crystals confirmed the micas as members of the phlogopite-biotite series with iron contents in the range of 4 to 8 wt. % FeO.

Most of the stones of the new production also appeared to be light to medium green (figure 4; table 1). Visually, these samples resembled light to medium green material from Colombia, specifically Chivor, or from Nigeria [Lind et al., 1986]. On the basis of the stones seen on the market to date, it appears that a relatively small percentage of samples from the new production are a very intense green, comparable to that of the finest Colombian emeralds [sample 1B, table 1].

In the parcels examined, we saw very few light green, almost colorless [sample 5B, table 1] or light yellowish green [sample 5A, table 1] stones. Undoubtedly, most such material either was not cut or was sorted out before the stones were brought to market.

For the most part, both the older and newer stones revealed weak pleochroism of yellowish green parallel to the c-axis and bluish green perpendicular to the c-axis.

Physical Properties. On the gemological refractometer, the shadow edges for \( n_w \) and \( n_p \) of most of the stones examined were found to be slightly broader and less distinct than are usually seen for well-polished emeralds. These results indicate a distinct chemical zoning across the table facets or (for the cabochons) flat bases of the stones examined, which was confirmed by microprobe analysis. The refractive indices were found to range from 1.581 to 1.590 for \( n_w \) and from 1.575 to 1.582 for \( n_p \), with a birefringence of 0.006 to 0.008 (table
Densities measured ranged between 2.71 and 2.75 g/cm³. These values are within the range reported for Uralian emeralds, as well as for emeralds from other sources (Sinkans et al., 1981; Schrader, 1983; Granadchilzova et al., 1983; Schwarz, 1987; Gromov et al., 1990).

Chemical Properties. The microprobe analyses also showed a distinct chemical zoning in all of the stones, which was clearly indicated by the 268 point analyses of the 13 stones from the new production. For example, the Cr₂O₃ content in sample 3B ranges from 0.11 to 0.22 and in sample 3L, from 0.05 to 0.14. This chemical zoning is responsible for the weak color zoning observed with the microscope in many of the stones.

All samples revealed significant amounts of sodium and magnesium, which were also indicated by qualitative analyses using the energy-dispersive system of the electron microprobe. However, the presence of distinct sodium and magnesium peaks in the energy-dispersive spectrum of an emerald of unknown origin is useful only to confirm that the sample is natural; it is not sufficient to indicate locality of origin.

The iron and chromium contents of the light green to medium green samples are characteristic for Uralian stones (Lokhova et al., 1977; Sinkans, 1981; Franz, 1982; Schrader, 1983). The average chromium content in the very intense green emerald (sample 1B), however, is distinctly higher than that of its paler counterparts.

Note that electron paramagnetic resonance data on Uralian emeralds published by Lokhova et al. (1977) indicate that this material contains between 0.05 and 0.15 wt.% Fe³⁺. Lokhova et al. also determined contents of manganese and titanium in the range of 0.004 to 0.016 wt.% Mn and 0 to 0.016 wt.% Ti. Schrader (1983) determined low concentrations of nickel (approximately 0.002 wt.% Ni) in two Russian emeralds he analyzed.

Spectroscopic Data. Absorption spectroscopy in the near-infrared, visible, and ultraviolet ranges revealed the same type of absorption spectra for all samples examined. In the visible area, a typical emerald spectrum with chromium absorption bands was found (figure 5). In addition, strong absorption bands of divalent iron with a maximum at 12,200 cm⁻¹ (820 nm) were observed in the spectrum perpendicular to the c-axis, whereas the generally known absorption maximum of divalent iron at 12,000 cm⁻¹ (833 nm) in the spectrum parallel to the c-axis was only of low intensity. Absorption bands of trivalent iron observed in some stones at 23,500 and 27,000 cm⁻¹ (426 and 370 nm) were weak or extremely weak if present at all.

In the yellowish green samples—e.g., sample 5A—an additional absorption is superimposed on the chromium-iron emerald spectrum described above. This additional absorption consists of an absorption maximum in the ultraviolet range with a low-energy tail that extends into the visible area, causing an almost continuously increasing absorption from green to violet. This additional absorption is responsible for the shift in color from a bluish to a yellowish green.

The spectra obtained were consistent with the nonpolarized spectrum of a Uralian emerald presented by Lokhova et al. (1977), as well as with polarized spectra of natural Russian emeralds from the Ural mountains published by Granadchilzova et al. (1983) and Gromov et al. (1990). The presence of two types of iron absorption bands in the near infrared, in some cases in combination with weak absorption bands of trivalent iron in the bluish violet and ultraviolet range, is useful to characterize these samples as natural emeralds (Schmetzer, 1988).

The infrared spectra of three samples in the range of water-stretching vibrations (3500–3800 cm⁻¹) revealed the presence of three absorption bands.
maxima: at 3694 cm$^{-1}$ (band A), at 3592 cm$^{-1}$ (band B), and at 3655 cm$^{-1}$ (band C). This infrared spectrum is typical for medium alkali-bearing natural emeralds, as described comprehensively by Schmetzer (1989) and by Schmetzer and Kiefert (1990).

Microscopic Properties. Some of the “older” Uralian stones available for microscopic examination were heavily included. Most of the samples we examined (more than 70%) from the more recent production were of typical cabochon quality and were cut accordingly; they also revealed a high concentration of healing fractures and mineral inclusions. The remainder of the samples from the newer production, however, were high-clarity, faceted stones.

All of the Uralian stones examined showed a number of inclusions that are useful to confirm that the samples are natural. However, a natural emerald of unknown origin can be characterized as Uralian on the basis of its microscopic properties only in exceptional cases, because most of the microscopic features observed in the Uralian emeralds have also been seen, if rarely, in emeralds from other localities.

Growth Structures. Growth structures parallel to prism faces were frequently observed (figure 6). In general, the first-order hexagonal prism m (1010) is the dominant prism face, and the second-order hexagonal prism a (1120) is subordinate if present at all. Occasionally, the growth structures parallel to the prism faces are also confined to a weak color zoning. Rarely, a mosaic-like growth structure consisting of frequently alternating growth planes parallel to the first-order and second-order hexagonal prism faces is seen. In some cases, growth structures were also present parallel to the basal pinacoid c (0001) that are occasionally confined to a growth zoning parallel to the first-order hexagonal dipyramid p (1012). Similar growth structures have been observed in emeralds from other localities (Kiefert and Schmetzer, in press).

Solid Inclusions. Different forms of birefringent mineral inclusions were frequently present: densely clustered and/or irregularly distributed small brown crystals; rounded platelets or tabular crystals (figure 7); and, occasionally, needle-like mineral inclusions or elongated tabular crystals (figure 8). In one stone, we found two columnar developed crystals with prismatic cross-sections (figure 9). Several crystalline inclusions exposed at the surfaces of the faceted emeralds were examined by electron microprobe. Qualitative investigations of all types of mineral inclusions mentioned above (figures 7-9) using the energy dispersive systems of the microprobes, indicated that the crystals consist mainly of Mg, Al, Si, and K, with variable amounts of Fe also detected. Quantitative analyses (table 2) revealed a chemical composition typical for phlogopite or for intermediate members of the biotite-phlogopite solid-solution series. In general,
Figure 7. Frequently present in the Russian specimens examined were rounded platelets of a birefringent mineral that was subsequently identified as phlogopite. Under polarized light, these inclusions show a vivid display of interference colors. Immersion, crossed polarizers, magnified 85x.

Figure 8. Larger, elongated tabular crystals, also subsequently identified as phlogopite, were occasionally seen in the Russian specimens. Immersion, crossed polarizers, magnified 60x.

Iron-poor phlogopites appear virtually colorless in the gem microscope (figures 7 and 8), and crystals of the biotite-phlogopite series with higher iron contents take on a brown hue (figure 9). The chemical data for these brown micas are similar to the data reported by Fersmann (1929) for a “biotite” schist rock (table 2) from one of the historic Uralian emerald mines.

Actinolite needles, which are mentioned occasionally in the literature as inclusions in Uralian emeralds (Gubelin, 1973; Gubelin and Koivula, 1986), were neither seen nor revealed by electron microprobe analysis in either the older or the more recent samples.

Liquid and Two-Phase Inclusions. The crystals examined contained several types of liquid and two-phase inclusions. The most noteworthy were found in the form of thin, flat cavities oriented on planes parallel to the basal pinacoid (figure 10). When the stones were examined perpendicular to the c-axis, these planes appeared as small lines at right angles to the c-axis. In general, extremely thin channel-like structures running parallel to

<table>
<thead>
<tr>
<th>Oxide</th>
<th>Phlogopites, almost colorless</th>
<th>Biotite-phlogopite, brown</th>
<th>&quot;Dolich&quot; microcline, Muscovite mineral</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>42.05-42.13</td>
<td>41.37</td>
<td>41.37</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>12.08-12.15</td>
<td>12.86</td>
<td>12.70</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>0.08-0.15</td>
<td>0.17</td>
<td>0.12</td>
</tr>
<tr>
<td>MgO</td>
<td>3.98-4.53</td>
<td>4.15</td>
<td>4.15</td>
</tr>
<tr>
<td>FeO</td>
<td>n.a.</td>
<td>0.03</td>
<td>0.15</td>
</tr>
<tr>
<td>MnO</td>
<td>24.11-25.88</td>
<td>20.79</td>
<td>0.20</td>
</tr>
<tr>
<td>MgO</td>
<td>3.98-4.53</td>
<td>4.15</td>
<td>4.15</td>
</tr>
<tr>
<td>K₂O</td>
<td>8.55-9.54</td>
<td>8.70</td>
<td>8.70</td>
</tr>
</tbody>
</table>

All determined by microprobe analysis.

Delemined by wet chemical analysis, as published in Fersmann (1929).

As determined by microprobe analysis.

Note: no analyzed.
Figure 10. When some of the Russian material was examined perpendicular to the c-axis (running vertically in this photo), primary liquid and two-phase inclusions were observed in a characteristic orientation on planes parallel to the basal pinacoid, confined to channel-like structures oriented parallel to the c-axis (i.e., perpendicular to the cavity). Immersion, magnified 25×.

the c-axis, that is, perpendicular to the flat cavities, are confined to these planes. A view in a direction parallel to the c-axis reveals that these thin, flat cavities consist of liquid (figure 11) and/or two-phase inclusions (figure 12). Tilting the crystal slowly, so that the angle between the c-axis of the crystal and the microscope axis is increased, causes total internal reflection of the gaseous components of the two-phase inclusions, which are transparent when viewed exactly parallel to the c-axis (again, see figure 12).

Less frequently, we also observed channel-like growth tubes parallel to the c-axis and elongated fluid inclusions trapped on growth planes parallel to prism faces.

Undoubtedly, the phlogopite and biotite-phlogopite inclusions, the growth channels parallel to the c-axis, and the liquid and two-phase inclusions oriented parallel to the basal pinacoid or to prism faces are primary inclusions; that is, they were trapped during crystal growth. We do not know the exact growth mechanism of the channel-like structures, with liquid and two-phase inclusions, that are confined to planes parallel to the basal pinacoid. However, we regard these inclusions (figures 10-12) and the different forms of mica (figures 7-9) to be the most typical and diagnostic inclusions in Uralian emeralds.

Numerous partly healed fractures were observed irregularly traversing most of the crystals. Although for the most part these healing "feathers" consisted of liquid inclusions, occasionally two- and even three-phase inclusions were observed in larger cavities of these feathers. These secondary (or pseudosecondary) inclusions were trapped after the host crystal had formed. However, we also observed some isolated cavities with multiphase fillings in these healing fractures (figure 13) that we could not establish as primary or secondary on the basis of their microscopic appearance. These isolated inclusions frequently form flat, more-or-less elongated cavities with the same orientation described above for the primary liquid and two-phase inclusions.

A typical two-phase inclusion consists of a cavity with a liquid filling that contains an additional gaseous phase. Most of the three-phase inclusions consist of two immiscible liquids and one gaseous component, but in one sample we observed a solid/liquid/gas three-phase inclusion (figure 13). Extremely rare are healing fractures in which larger birefringent mineral inclusions (as yet unidentified) are trapped with smaller liquid and/or gaseous components.

According to a recent paper by Gromov et al. (1990), the multiphase inclusions in Uralian emeralds were determined to consist of halite crystals, liquid CO₂, a saline aqueous solution, and a gaseous component.

DISCUSSION

Crystal Chemistry and Cause of Color. Although the general chemical formula of beryl, \( \text{Be}_3\text{Al}_2\text{Si}_6\text{O}_{18} \), looks quite simple, natural beryl in general contains major amounts of impurities. A great number of isomorphous substitution schemes are discussed in the literature (see Shatskiy et al., 1981; Aurisicchio et al., 1988), but only some of these schemes are generally accepted:

1. Substitution of Al³⁺ in octahedral sites of the beryl structure by trivalent transition metal ions or by divalent transition metal ions or
magnesium, with alkali metal ions entering vacant channel sites in the beryl structure for charge compensation.

$\text{Al}^{3+} \text{ (octahedral)} + \text{Mg}^{2+}, \text{Fe}^{3+}, \text{Mn}^{3+} \text{ (octahedral)}$ or $\text{Al}^{3+} \text{ (octahedral)} \rightarrow \text{Mg}^{2+}, \text{Fe}^{2+}, \text{Mn}^{2+} \text{ (octahedral)} + \text{Li}^{+}, \text{Na}^{+}, \text{K}^{+}, \text{Cs}^{+} \text{ (channel)}$

$\text{Be}^{2+} \text{ (tetrahedral)} \rightarrow \text{Fe}^{2+} \text{ (tetrahedral)}$ or $\text{Be}^{2+} \text{ (tetrahedral)} \rightarrow \text{Li}^{+} \text{ (tetrahedral)} + \text{Li}^{+}, \text{Na}^{+}, \text{K}^{+}, \text{Cs}^{+} \text{ (channel)}$

In both substitution types, octahedral and tetrahedral, the alkali ions in channel sites are bound to water molecules, however, free water molecules—that is, which are not bound to alkali ions—are also present in channel sites of the beryl structure (Schmetzer, 1989, Schmetzer and Kiefert, 1990).

Infrared spectroscopy established the presence of both alkali-bonded and non-alkali-bonded water molecules in channel sites of the beryl structure for the Uralian specimens examined. Specifically, the I.R. spectra revealed absorption bands B and C, at 3592 and 3655 cm$^{-1}$, which are assigned to alkali-bonded water molecules, and band A, at 3694 cm$^{-1}$, which is assigned to alkali-free water molecules.

Unfortunately, the standard electron microprobe cannot measure lithium, beryllium, oxygen, and water contents. However, the presence of small amounts of lithium was established by Vlasov and Kuzakova (1960), Franz (1982), and Aurisicchio et al. (1988), and may not be neglected.

The visible-range absorption spectra (figure 5) revealed the presence of strong absorption bands that are generally assigned to trivalent chromium ($\text{Cr}^{3+}$) in octahedral sites. Since the absorption bands at 23,500 and 27,000 cm$^{-1}$ (426 and 370 nm), due to trivalent iron ($\text{Fe}^{3+}$) in octahedral sites, are weak or absent, most of the iron in the samples examined is assumed to be divalent (see also, Ledkova et al., 1977) and replacement of $\text{Al}^{3+}$ by $\text{Fe}^{3+}$ is limited if present at all.

According to Solntsev et al. (1984, 1985), near-infrared absorption maxima at 24,100 cm$^{-1}$ (7820 nm) (perpendicular to the c-axis) and 12,000 cm$^{-1}$ (833 nm) (parallel to the c-axis) can be assigned, respectively, to (1) $\text{Fe}^{2+}$ replacing $\text{Be}^{2+}$ in tetrahedral sites, and (2) $\text{Fe}^{2+}$ replacing $\text{Al}^{3+}$ in octahedral sites. Thus, most of the iron in Uralian emeralds is bound as $\text{Fe}^{2+}$, primarily in tetrahedral sites with lesser amounts in octahedral sites, and with only minor amounts of $\text{Fe}^{3+}$ present. The absorption bands of divalent iron in the infrared do not affect the visible area of the absorption spectra of Uralian emeralds. Nor does the absorption band of $\text{Fe}^{3+}$ in the bluish violet region—usually weak or extremely weak, if present at all—fluence the color of the samples. In general, the low concentrations of other transition metal elements present—including $\text{Mn}$, $\text{Ti}$, and $\text{V}$ as well as the low nickel concentrations (approximately 0.002 wt.% Ni) found by Schrader (1983)—also do not influence the color of the samples.

Consequently, for most natural emerald, the

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Figure 11. Although these are not unique to emeralds from the Urals, this material often contains primary liquid inclusions trapped on planes parallel to the basal pinacoid, as is shown in this view parallel to the c-axis. Immersion, magnified 65X.

Figure 12. Some of the crystals examined contained several types of liquid and two-phase inclusions. In a number of instances, as shown here, they occurred trapped on a plane parallel to the basal pinacoid. Immersion, view parallel to the c-axis, magnified 60X.
Three-phase (liquid/solid/gas) inclusions are observed less frequently in Russian emeralds than in their Colombian counterparts, but they do occur. This photomicrograph illustrates one type of three-phase inclusion we saw. It is interesting to note that it lacks the characteristic jagged outline often associated with Colombian stones. Immersion, magnified 70×.

The bluish green color of Uralian emeralds is mainly due to chromium, and the intensity of the coloration is caused by the average chromium content of the individual crystal (table 1). The color in yellowish green samples is caused by a chromium spectrum superimposed by the absorption spectrum of naturally radiation-induced color centers, most probably confined to iron ions, that contribute a yellow component. For some time, the authors have been familiar with this absorption in natural untreated yellow beryl, natural untreated yellowish green emerald, and irradiated yellow or irradiated bluish green Maxixe-type beryl (Rink et al., 1990).

Complex aspects of crystal chemistry determined for the Uralian stones in the study are discussed in box A. Such data are useful in understanding modes of isomorphic replacement and in pursuing methods of determining emerald origin (locality as well as natural vs. synthetic). For example, as stated earlier, the sodium (Na) and magnesium (Mg) contents of the Uralian emeralds clearly establish their natural origin. Moreover, the variation in physical properties, especially the variation in refractive index, is explained as a function of chemical composition. For beryl, it is generally established that increasing amounts of alkalis as well as increasing amounts of transition metal oxides cause an increase in refractive index (Cerny and Hawthorne, 1976; Deer et al., 1986). Although the exact water and carbon dioxide contents of the samples, which also influence the optical properties of beryl (Lebedov and Kaikukin, 1984), are unknown, a direct relationship between increasing amounts of impurities and increasing refractive indices is confirmed by the results of this investigation. In figure 14, the refractive indices of the 13 new and three older samples are plotted as a function of the sum of sodium (and potassium) and transition metal oxides (vanadium, chromium, iron, and manganese). With increasing impurities, increases in birefringence and density are also observed (table 1).

Diagnostic Features of Uralian emeralds. Most of the data presented in this article confirm the natural origin of the samples and demonstrate the applicability of modern analytic techniques to supplement conventional microscopic examination. In the present case, however, optical microscopy is the most appropriate technique to prove the natural origin of the samples and provide some indication of locality of origin.

Phlogopite crystals are typically seen as inclusions in gem-quality Russian emeralds, which are known to originate from phlogopite-bearing host rocks (Zhentalov, 1980). In earlier papers (e.g., Fersmann, 1929), these micas are often described as biotites, but microprobe analyses (table 2) strongly indicate iron contents typical for phlogopite or members of the biotite-phlogopite solid-solution series rather than for pure biotite. However, neither phlogopite nor biotite is unique to Uralian emeralds, and either may be found in natural emeralds from various other deposits.

In the gemological literature, biotite flakes, actinolite rods, and tourmalinite crystals have been mentioned as characteristic mineral inclusions in Uralian emeralds (Gübelin, 1953, 1973). Gübelin and Koivula, 1986). Zhentalov (1980) noted, in addition to phlogopite and actinolite inclusions, the presence of rutile in emeralds from both phlogopite and actinolite schists, and of talc, tremolite, and chrome in emeralds from talc schists.

Another type of inclusion previously regarded as characteristic for Uralian emeralds (Gübelin,
Using the information available from chemical and spectroscopic investigations of the Uralian material in this study as well as the generally established schemes for an isomorphic replacement in beryl, the crystal chemistry is summarized as follows.

The 268 point analyses performed on 13 samples by electron microprobe clearly indicate that, as the number of magnesium ions increases, the number of trivalent ions in octahedral sites decreases, one for one. That is, if we neglect the small amounts of iron (Fe^{2+} and Fe^{3+}) that may be present in octahedral aluminum sites, the sum content of Al^{3+} + Cr^{3+} + V^{3+} is inversely related to the magnesium (Mg^{2+}) content (figure A-1). A similar inverse relationship is established for the sum of Al^{3+} + Cr^{3+} + V^{3+} and the sum of monovalent alkalis (Na^{+} + K^{+}; figure A-2). A direct relationship, however, is established between magnesium (Mg^{2+}) and the sum of Na^{+} + K^{+} (i.e., as Mg^{2+} content increases, so does Na^{+} + K^{+}; figure A-3). From these diagrams, the following substitutional scheme is established:

\[(\text{Al}^{3+} + \text{Cr}^{3+} + \text{V}^{3+})_{\text{oct}} - (\text{Mg}^{2+})_{\text{oct}} + (\text{Na}^{+} + \text{K}^{+})_{\text{channel}}\]

For 12 of the samples, the sum of monovalent alkali (Na^{+} + K^{+}) ions exceeds the sum of Mg ions for only one stone (sample 3C) does Mg content exceed the sum of alkalis (point analyses shaded in figures A-2, and A-3). These results can be explained by the presence of small amounts of lithium, which is assumed

A. to replace Be^{2+} in tetrahedral sites in 12 samples; or

B. to enter empty channel sites for charge compensation (in one sample)

Thus, for those 12 samples in which Na^{+} + K^{+} exceeds Mg content—that is, for which the expression \((\text{Na}^{+} + \text{K}^{+}) - \text{Mg}^{2+}\) is positive—the following substitutions are established:

- octahedral: \((\text{Al}^{3+} + \text{Cr}^{3+} + \text{V}^{3+})_{\text{oct}} - (\text{Mg}^{2+})_{\text{oct}} + (\text{Na}^{+} + \text{K}^{+})_{\text{channel}}\)
- tetrahedral: \((\text{Li}^{+})_{\text{tet}} + (\text{Na}^{+} + \text{K}^{+})_{\text{channel}}\)

For sample 3C, in which Mg content exceeds Na^{+} + K^{+}, the expression \((\text{Na}^{+} + \text{K}^{+}) - \text{Mg}^{2+}\) is negative—two octahedral substitution schemes are established:

- octahedral: \((\text{Al}^{3+} + \text{Cr}^{3+} + \text{V}^{3+})_{\text{oct}} + (\text{Na}^{+} + \text{K}^{+})_{\text{channel}}\)
- octahedral: \((\text{Li}^{+})_{\text{tet}} + (\text{Na}^{+} + \text{K}^{+})_{\text{channel}}\)

In summary, in all the samples we examined, an octahedral substitution is dominant; and in 12 of the 13 samples, a subordinate tetrahedral substitution is also established.
1953) was also observed in the samples examined for this study; thin cavities of liquid or two-phase inclusions oriented with their flat planes parallel to the basal faces of the emeralds (figures 10–12). Although like Göbel in the authors found this type of inclusion to be most typical of Russian emeralds, identical inclusions have been observed by the senior author in some emeralds from a distinct source in Africa (probably the Gravelotte mining district in the Transvaal, South Africa) and illustrated by Schwarz (1987) for a sample from Socot56, Bahia, Brazil. Consequently, this type of inclusion cannot be regarded as unique for Uralian emeralds, but may be characteristic of samples that originate from a group of genetically related emerald deposits (Schwarz, 1987).

Our examination established the presence of multiphase inclusions in emeralds from this mining area and confirmed the findings of Gromov et al. (1990). They mentioned all five types of multiphase inclusions in Uralian emeralds that we also observed in our samples: [1] primary two-phase, aqueous solution and gas (the most common); [2] primary and pseudosecondary three-phase — aqueous solution, gas, and liquid carbon dioxide (rarely seen); [3] primary and pseudosecondary three-phase — aqueous solution, gas, and a small halite crystal (rare, figure 13); [4] pseudosecondary and secondary aqueous solution with a small gas component (the most common of the nonprimary inclusions); and [5] extremely rare pseudosecondary inclusions consisting of small aqueous solution and/or gas phases with larger crystal inclusions.

Gromov et al. (1990) also mentioned as extremely rare two types of two- and three-phase inclusions with a dominant gaseous component and subordinate liquid and solid phases, which we have not yet observed. However, inasmuch as three-phase inclusions are known to occur in emeralds from other localities (e.g., Thurm, 1972; Yu, 1974; Graindorge, 1974; Schrader, 1985, 1986), they do not help prove the geographic source of an emerald.

In summary, we determined that the Uralian stones reveal a number of interesting properties and diagnostic features. However, it must be emphasized that, at present, we know of no single property that would allow one to designate stones of unknown origin unequivocally as Uralian emeralds. Only by using a combination of physical, chemical, spectroscopic, and microscopic features can one suggest that an unknown sample probably originates from the Tolkowaya area near Sverdlovsk, USSR.

Figure 14. This graph of refractive index versus impurities reveals that an increase in impurities correlates directly to an increase in refractive indices ($n_1$, $n_2$, and $n_3$).

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