# GEMS & EMOLOGY

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Figure 44. Phenakite with beryl in mica (left) and yellow phenakite (right). Photos by Mikhail Popov; fields of view 5 cm.

ppmw, Rb 10-64 ppmw, and Cs 310-3220 ppmw. The amount of total alkali content including Li, Na, K, Rb, and Cs ranged from 1296 to 6033 ppmw. As alkali ions (mainly for Na) were associated with "type II" water molecules in structural channels (D.L. Wood and K. Nassau, "The characterization of beryl and emerald by visible and infrared absorption spectroscopy," American Mineralogist, Vol. 53, No. 5, 1968, pp. 777-800), the relatively low Na content was in agreement with the low peak intensity of "type II" H<sub>2</sub>O revealed by Raman and IR spectroscopy. The low concentration of alkali content and lack of "type II" water in our aquamarine samples were similar to that in aquamarine from Italy and Vietnam (R. Bocchio et al., "Aquamarine from the Masino-Bregaglia Massif, Central Alps, Italy," Fall 2009 G&G, pp. 204-207; L.T.-T. Huong et al., "Aquamarine from the Thuong Xuan District, Thanh Hoa Province, Vietnam," Spring 2011 G&G, pp. 42-48). The chromophore Fe, responsible for blue color, was the richest among all transition elements between 1350 and 5080 ppmw; the samples showed the typical iron absorption at 375, 425, 620, and 820 nm in UV-Vis-NIR spectra. Transition elements V and Mn were present at 1-33 ppmw and 17-56 ppmw, respectively, and the bluish white fluorescence mentioned above may originate from Mn<sup>2+</sup> or VO<sub>4</sub>

centers (M. Gaft et al., *Modern Luminescence Spectroscopy of Minerals and Materials*, 2005, Springer Berlin, pp. 97–99). Chemical and spectral characteristic suggested the Pakistani samples were low-alkali aquamarine colored by Fe ions rather than irradiation (i.e., Maxixe beryl).

#### Yang Hu and Ren Lu Gemmological Institute China University of Geosciences, Wuhan

**Color origin of phenakites from the Ural emerald mines.** Phenakite ( $Be_2SiO_4$ ) was first discovered at Russia's Ural emerald mines, and was chemically identified in 1833. The mineral is widely distributed in beryllium deposits, but crystals of gem quality or large size are rare. At the Ural mines, however, there are large transparent crystals that can be used in jewelry. Jewelry-grade phenakite is generally colorless or yellowish brown (figure 44; see M.P. Popov et al., "Features of phenakite mineralization from the Ural emerald mines," *Bulletin of the Ural Branch of the RMS*, No. 13, 2016, pp. 105–111). The main mineral inclusions are chlorite, talc, phlogopite, actinolite, and ilmenite; fluid inclusions with a gas-liquid composition also occur.

The color origin of phenakite using optical absorption spectroscopy has not been studied in detail. Many authors agree that the coloration is associated with electron-hole centers (see A.S. Marfunin, Spectroscopy, Luminescence and Radiation Centers in Minerals, 1975, Nedra, Moscow). This is indicated by the disappearance of color when phenakite is exposed to either ultraviolet radiation or high temperatures. According to one theory of absorption, this is related to the oxygen vacancies that have captured electrons (again, see Marfunin, 1975). Other researchers believe that the absorption features are associated with bridging electronic centers such as Al-O-Al, which are formed by isomorphous replacement of silicon by aluminum ions in the crystal lattice, in amounts up to 0.5% (see A.N. Platonov, Nature of Coloring of Minerals, 1976, Naukova Dumka, Kiev).

To determine the color origin of yellow-brown phenakites, we obtained optical absorption spectra of colorless and yellow-brown phenakite from the Mariinsky deposit. These spectra were collected in the 185–700 nm wavelength range, at room temperature, on a specialized Shimadzu UV-3600 spectrophotometer. A broad absorption band was noted in the 225–325 nm range of the yellow-brown phenakite spectrum, with a maximum at 268 nm. Absorption in the ultraviolet range of the optical spectrum was not detected in transparent colorless phenakites (figure 45).

To study electron-hole centers and to reveal color centers in phenakite, crystals were examined using electron paramagnetic resonance (EPR). EPR is an informative method for studying dissymmetry of crystals, the role of the symmetry elements of the spatial group, and the distribution of impurity ions and point defects in the bulk of the crystal. Dissymmetry of crystals, as a result of the uneven distribution of point defects in the process of crystal growth, is a widespread phenomenon (see G.R. Bulka et al., "Dissymmetrization of crystals: Theory and experiment," *Physics and Chemistry of Minerals*, Vol. 6, 1980, pp. 283– 293; R.A. Khasanov et al., "Derivation of the conditions for equivalent positions in crystals: The dissymmetrization of barite by electron spin resonance," *Crystallography Reports*, Vol. 57, No. 5, 2012, pp. 751–757; J.M. Hughes et al.,



Figure 45. Absorption spectra of colorless phenakites (blue trace) and yellow-brown phenakites (black trace).

"Dissymmetrization in tourmaline: the atomic arrangement of sectorally zoned triclinic Ni-bearing dravite," The Canadian Mineralogist, Vol. 49, 2011, pp. 29–40). We used an Adani CMS8400 spectrometer (frequency v=9, 4 GHz) at room temperature to perform EPR on our samples. During an experiment on the EPR spectra of the impurity radical [PO<sub>4</sub>]<sup>4-</sup> phenakite of deposits in Volynskii (see A.I. Novozhilov et al., "Electron paramagnetic resonance in irradiated phenakite Be2SiO4," Journal of Structural Chemistry, Vol. 11, 1970, pp. 393–396), we found a difference in intensity of the lines of three magnetically nonequivalent centers for the impurity radical. The paramagnetic center  $[PO_{4}]^{4-}$  was only detected in the yellow-brown crystals (figure 46), and active centers were absent in colorless specimens. From this we concluded that the origin of the yellow-brown color of phenakite is associated with a paramagnetic complex [PO<sub>4</sub>]<sup>4-</sup>that produces absorption bands

Figure 46. Phosphorus ions replace silicon ions in a tetrahedral structure to form a  $[PO_4]^{4-}$  complex in yellow-brown phenakites. This complex is paramagnetic and gives several signals in the range of 320–340 mT. Splitting of the hyperfine structure of the signal occurs; lines 1, 2, and 3 appear and indicate the existence of the  $[PO_4]^{4-}$  radical. When the crystal rotates along its c-axis, it changes the intensity of these lines.



in the ultraviolet region, which in turn leads to the formation of this color in the mineral.

These results can be used in gemological identification of phenakites from the Ural emerald mines.

This study was performed in the context of the Russian Government Program of Competitive Growth of Kazan Federal University, "Paleogeodynamics and evolution of structural-material complexes in the formation of the continental-type crust ...," theme no. 0393-2016-0019.

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**Freshwater natural pearls from the Concho River, Texas.** Throughout history, natural pearls have been found in many species of freshwater mollusk in North American lakes and rivers. They are most abundant within the Mississippi River drainage basin, which provides the perfect habitat for these animals because of the large watershed areas with their underlying limestone substrata (J.L. Sweaney and J.R. Latendresse, "Freshwater pearls of North America," Fall 1984 *G&G*, pp. 125–140). Lesser-known sources of natural freshwater pearls are the Colorado River and Brazos River and their tributaries in the state of Texas. However, the best samples are sometimes found in a species named Tampico Pearlymussel (*Cyrtonaias tampicoensis*) that inhabits the Concho River in West Texas.

The mollusk is distributed from northeastern Mexico into the Concho, Colorado, and Brazos Rivers of central Texas and has been collected by licensed harvesters. Mussel harvesting is restricted to hand collection only, and there is a legal minimum shell size requirement. In addition, several areas in Texas have been designated mussel sanctuaries in order to provide protection and species conservation (R.G. Howells, "The Tampico pearlymussel (Cyrtonaias tampicoensis), shades of the Old West," http://www.conchologistsofamerica.org/articles/1996/thetampico-pearlymussel.html). Pearlers find mussels by wading into water that is three to four feet deep and feeling for the shells with their toes. Rattlesnakes on the banks and water moccasins and snapping turtles in the murky water (J. Morthland, "Irregular radiance: The rare beauty of Conch River pearls," Texas Highways, April 2015) pose risks to these adventurers searching for gems.

GIA's New York laboratory recently received nine loose pearls from Stone Group Laboratories (Jefferson City, Missouri) for a joint study. The pearls ranged in size from 2.95  $\times$  2.45 mm to 14.76  $\times$  13.55  $\times$  13.13 mm. Reportedly recovered from Tampico pearlymussel shells taken from the Concho River, they exhibited colors ranging from purplish pink to orangy pink. Some of the samples also possessed varying degrees of a brownish hue (figure 47). Most of t