In colored gems, minor and trace chemical components commonly determine the difference between a common mineral specimen and a gemstone. Also, these components are often responsible for the color, and may provide a "fingerprint" for determining the provenance of the gemstone. The minor elements that are incorporated will depend on local geologic conditions such as temperature, redox conditions, and, particularly, chemistry.

**COLOR IN GEMSTONES**

Metal ions from the first row of transition elements in the periodic table, especially Ti, V, Cr, Mn, Fe, and Cu, are the most important causes of color in oxide and silicate gemstones. V$^{3+}$, Cr$^{3+}$, Mn$^{3+}$, and Cu$^{2+}$ can produce strong coloration when present at concentrations of tenths of a weight percent. Color comes from electronic transitions involving only the electrons in the d-orbitals (referred to as ligand-field transitions or crystal-field transitions). When present by themselves, Fe$^{2+}$, Fe$^{3+}$, and Mn$^{2+}$ typically require higher concentrations to cause significant color. Intervalance charge transfer (IVCT) interactions, which involve an exchange of an electron between two cations with different valences (for example, between Fe$^{2+}$ and Fe$^{3+}$ or between Fe$^{2+}$ and Ti$^{4+}$) are a major source of color in gems and require only a small amount of the interacting couple to produce intense color. In some systems, charge transfer from oxygen to the metal ion also contributes to the color.

**Garnets**

Good examples of the compositional dependence of color are provided by the garnet group. When grossular garnet, Ca$_3$Al$_2$(SiO$_4$)$_3$, is composed of just the end member components, it is colorless. Ca$^{2+}$, Al$^{3+}$, Si$^{4+}$, and O$^{2-}$ ions do not absorb light in the range of the visible spectrum. However, low concentrations of minor elements can dramatically modify the color. Small amounts of V$^{3+}$ with some Cr$^{3+}$ turn grossular into the green tsavorite variety (Fig. 1A). Spectacular examples of these garnets occur in marble seams in graphitic gneisses of the Mozambique belt in northeastern Tanzania and southeastern Kenya. There, metamorphic fluids were able to mobilize traces of vanadium and chromium from the host rock and incorporate them in the grossular garnet. The unusual beauty of these garnets was recognized after their discovery in 1967 and they were given the trade name tsavorite, in honor of the nearby Tsavo National Park in Kenya (Bancroft 1984).

Green color can also occur in andradite garnet, Ca$_3$Fe$_3$(SiO$_4$)$_3$. Andradite is pale yellow-green when it has exactly the end member composition, but commonly, minor amounts of Ti$^{4+}$ coupled with Fe$^{2+}$ turn andradite to brown or black. A beautiful green variety of andradite occurs when minor amounts of Cr$^{3+}$ enter the garnet (Mattice 1998). These stones, known as the variety demantoid, are highly valued (Fig. 1B).
PROVENANCE OF GEMS

Over time, gems from certain localities have been recognized as having greater beauty, and thus greater value. Even as new sources of gems are located, gems from the classic localities may still be perceived to have a higher value than more recently discovered stones of similar color and quality. The geographical origin of gems, in a general sense, is becoming an important commercial factor. More value is ascribed to particular deposits of gems compared to others with similar geology.

One question that must be addressed is what can be done with a faceted stone to determine its locality of origin. The need to avoid visually destructive analytical methods restricts the use of many standard geochemical methods and presents demanding analytical challenges. A variety of tools are now available, including minimally or nondestructive chemical analysis for major and trace elements, luminescence, and isotopic analysis. Other avenues of investigation, such as inclusions and growth features, are discussed in Fritsch and Rondeau (2009 this issue) and Devouard and Notari (2009 this issue).

**Minor and Trace Elements**

Minor and trace elements are often different or incorporated differently in gems of the same species but from different localities. Thus, they may provide a readily available tool for determining the locality of origin of gems. The following examples illustrate this concept.

Tourmaline

Most gem tourmalines owe their color to Fe$^{2+}$ (most blue tourmalines), Fe$^{2+}$ plus Fe$^{2+}$–Ti$^{4+}$ IVCT (green), Mn$^{3+}$ (pink), Mn$^{3+}$–Ti$^{4+}$ IVCT (yellow), or a combination of these factors (Fig. 3). At a few localities, such as in Kenya and Tanzania, G$^{4+}$ and V$^{3+}$ are the minor components responsible for the color.

In 1988, a new find of gem-quality elbaite with unusually saturated shades of green and blue was made in the Brazilian state of Paraíba. The unusual blue color comes from the copper content, which can range up to 1.7 wt% CuO (Rossman et al. 1991). The stones became an instant success in the commercial market (Fig. 4, inset). Later, tourmalines were found in Nigeria and Mozambique that also contained copper and had blue colors approaching those of the tourmaline gems from Paraíba. The question was raised about the possibility of distinguishing the provenance of copper-containing tourmalines once they had been faceted and entered the market.

Quantitative laser ablation–inductively coupled plasma–mass spectrometry (LA–ICP–MS) analysis can be used to differentiate tourmalines from the various localities by comparing concentrations or proportions of selected minor and trace elements such as Cu, Mn, Ga, Pb, Be, Mg, and Bi. For example, the Brazilian stones generally have more Mg, Zn, Bi, and Sb, while the Nigerian stones generally contain elevated levels of Ga and Pb (Abduryim et al. 2006). By comparing the relative proportions of Bi, Pb, and Ga in such tourmalines, one can, in most cases, distinguish between the three main geographical provenances (Fig. 4). However, there is still a small overlap between the compositions of tourmalines from Mozambique and Brazil (Krzemnicki 2007).

Corundum

For many years, rubies from the Mogok region of Burma were considered the finest in the world and commanded a high price (Hughes 1997). Beginning in the early 1990s, rubies from a different source in Burma appeared in markets in Bangkok. The Mông-Hsu rubies generally are unsaleable as mined. They usually must be heated, often to high temperatures, to remove a naturally occurring dark blue color that arises from a combination of Fe$^{2+}$–Ti$^{4+}$ and Fe$^{2+}$–Fe$^{3+}$ IVCT in the core of the stones. Heating oxidizes the Fe$^{2+}$ to Fe$^{3+}$, which disrupts the IVCT couple. Furthermore, the heating of rubies from Mông-Hsu introduces flux into cracks in the stones (Peretti et al. 1995; Emmett 1999). Although beautiful, the rubies from Mông-Hsu are generally valued less than rubies from Mogok because they have been treated to enhance their appearance (Drucker 1999).

Thus it would be useful to be able to distinguish rubies from different localities. Apart from specific microscopic features, it has been shown that rubies from the Mogok and Mông-Hsu localities can be differentiated on the basis of their Ti/V ratio (Mühlmeister et al. 1998; Mittermayer et al. 2008) as determined using X-ray fluorescence (XRF) or LA–ICP–MS. In other examples, key elements, such as V, Ti, Ga, and Fe, have been used to separate rubies from Vietnam/Burma versus Thailand or Tanzania. For a more general distinction of ruby localities, the ratios of Fe, Ga, and Cr have proven useful (Rankin et al. 2003; Peretti 2008; Schwarz et al. 2008). Likewise, the source of blue sapphires can be determined using the trace element ratios.
of Zn, Sn, Ba, Ta, and Pb as determined by LA–ICP–MS analysis of element concentrations down to levels approaching ppb (Guillong and Günther 2001; Rankin et al. 2003; Abduриим and Kitawaki 2006a).

Isotopic Methods
The provenance of gems has always been important to some degree. However, now that provenance has increased in importance for commercial reasons, the tools to determine origin have been refined. Chemical composition, inclusions, growth features, luminescence, and trace elements may all have a role in the determination of provenance. While stable isotopes have proven highly useful in geochemistry for studying the geological history of rocks and minerals, they have, to date, found little practical application in the determination of the provenance of gemstones. In principle, isotopes should provide information about the origin of gems, but the cost, time required, and destructive nature of these tests have, until now, prevented isotopic methods from gaining wide application in gemology. A few examples demonstrate the utility of isotopic methods when applied to gem minerals.

Emerald
Emerald is a green variety of beryl, Be₃Al₂Si₆O₁₈, that contains Cr³⁺ and, occasionally, some V⁵⁺ as the chromophore. It forms from hydrothermal fluids. The isotopic composition of these fluids varies with locality (Giuliani et al. 1998; Zwaan et al. 2004). In an elegant study, Giuliani et al. (2000) used the isotopic composition of oxygen in emerald to trace international trade routes since antiquity (Fig. 5).

Corundum
Because both ruby and sapphire occupy an important place in the gem market, the origin of corundum gems is a matter of interest. In addition to the use of chemical element ratios, as discussed above, to distinguish among localities, certain classes of corundum show large isotopic differences between different localities (Yui et al. 2003; Giuliani et al. 2005). Oxygen isotopes in carbonate-hosted corundum show wide variations, whereas oxygen isotopes in mantle-derived corundum vary much less. Because of the time required for isotope analysis, its expense, and the destructive nature of the technique, the approach has not gained wide use in commercial gem laboratories, but holds much promise for the future. As is the case with many analytical methods, the overlapping ranges of oxygen isotope ratios, especially for the classical or commercially important deposits such as Mogok, Kashmir, Sri Lanka, and Madagascar, mean that no single analytical method will provide the answers to all problems of provenance.

SYNTHETIC CRYSTALS
Many of the same analytical methods used to differentiate the geographic or geologic source of a gem can also be applied to distinguish synthetic from natural stones. Such distinctions will become increasingly important as the quality of synthetic materials rises to nearly match that of their natural counterparts.

Synthetic Amethyst
Hydrogen is an important trace element in many natural minerals. It is a common charge-balancing cation (in the form of an OH group). Its mode of incorporation can vary depending on the geologic conditions of formation of the host crystal. The intensity and shape of absorption bands in the OH region of the electromagnetic spectrum provide a test for synthetic amethyst. A band at 3595 cm⁻¹ is present in the infrared spectrum of all natural amethysts but only rarely in synthetic ones. If present in synthetic amethyst, its full width at half maximum (FWHM) is about 7 cm⁻¹, whereas it is about 3 cm⁻¹ in all natural samples. This absorption band difference provides a method to separate natural from synthetic amethysts (Karampelas et al. 2005).

Synthetic Ruby
Minor and trace components commonly found in nature can be lacking in some synthetic gems. Such differences can be detected by some of the same testing methods previ-
REFERENCES


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TREATED NATURAL GEMS

Many of the tests to determine the geological or geographic origin of a stone can also be used to find out if a stone has been subjected to laboratory processes to change its color or other properties. As an example, consider the corundum gems, which are commonly heated to clarify and modify their color. A recent development is the diffusion of beryllium, at the level of 10 ppm or less, into the stones to change their color to extents that range from subtle to dramatic. This treatment was initially difficult to detect, but now a variety of analytical methods have been developed. Laser-induced breakdown spectroscopy (LIBS), LA–ICP–MS, and secondary ion mass spectrometry (SIMS) now make it possible to detect these low levels of beryllium in treated stones (Krzemnicki et al. 2004; Abduriyim and Kitawaki 2006a, b).

CONCLUSIONS

The examples cited illustrate just a few of the methods, both common and sophisticated, that are employed to determine the origin of gem materials. In many cases, rigorous tests prove to be too expensive compared to the value of the item tested, or currently are too destructive for routine use. In several instances, the geochemical reasons for some of the observed differences are not fully understood. In other cases, suitable tests are still lacking.