SEPARATING NATURAL AND SYNTHETIC RUBIES ON THE BASIS OF TRACE-ELEMENT CHEMISTRY

By Sam Muhlmeister, Emmanuel Fritsch, James E. Shigley, Bertrand Devouard, and Brendan M. Laurs

Natural and synthetic gem rubies can be separated on the basis of their trace-element chemistry as determined by energy-dispersive X-ray fluorescence (EDXRF) spectrometry. This method is especially important for rubies that do not have diagnostic inclusions or growth features, since such stones are difficult to identify using traditional gem testing methods. The results of this study indicate that the presence of nickel, molybdenum, lanthanum, tungsten, platinum, lead, or bismuth proves synthetic origin, but these elements were not detectable in most of the synthetic rubies tested. Alternatively, the concentrations of titanium, vanadium, iron, and gallium—considered together, as a trace-element "signature"—provide a means for separating nearly all synthetic from natural rubies. EDXRF can also help identify the geologic environment in which a ruby formed, and thus imply a geographic origin.

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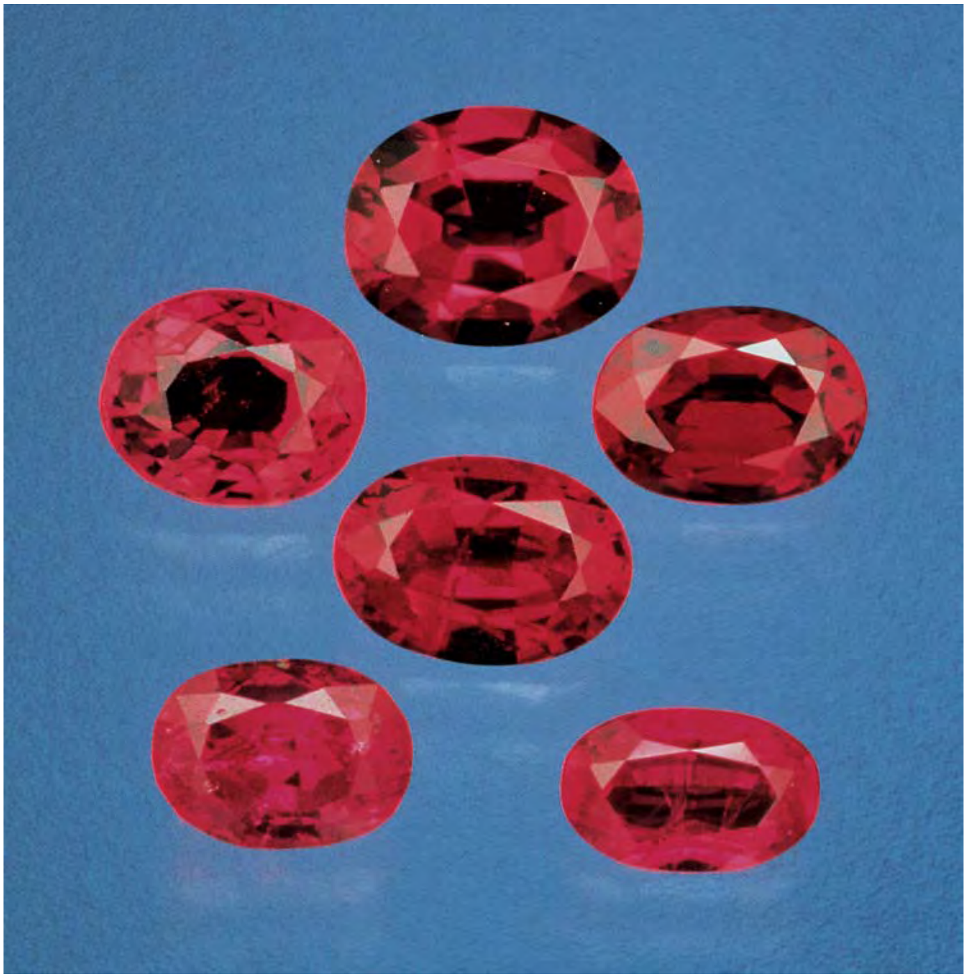
Correct gem identification is crucial to the gem and jewelry trade. However, accurate information on a gem's origin rarely accompanies a stone from the mine, or follows a synthetic through the trade after it leaves its place of manufacture. Today, natural and synthetic rubies from a variety of sources are seen routinely (figure 1). Usually, careful visual observation and measurement of gemological properties are sufficient to make important distinctions (Schmetzer, 1986a; Hughes, 1997). In some cases, however, traditional gemological methods are not adequate; this is particularly true of rubies that are free of internal characteristics or that contain inclusions and growth features that are ambiguous as to their origin (Hänni, 1993; Smith and Bosshart, 1993; Smith, 1996). The consequences of a misidentification can be in the tens of thousands, and even hundreds of thousands, of dollars.

Ruby is a gem variety of corundum (Al_2O_3) that is colored red by trivalent chromium (Cr^{3+}). Besides Cr, most rubies contain other elements in trace amounts that were incorporated during their growth, whether in nature or in the laboratory. For the purpose of this article, we consider trace elements to be those elements other than aluminum, oxygen, and chromium. These trace elements (such as vanadium [V] and iron [Fe]) substitute for Al^{3+} in the corundum crystal structure, or they may be present as various mineral inclusions (such as zirconium [Zr] in zircon) or as constituents in fractures. The particular assemblage of trace elements (i.e., which ones are present and their concentrations) provides a distinctive chemical signature for many gem materials. Since the trade places little emphasis on establishing the manufacturer of synthetic products, this article will focus on how trace-element chemistry, as determined by EDXRF, can be used for the basic identification of natural versus synthetic rubies. It will also explore how EDXRF can

Figure 1. These six natural and synthetic rubies are typical of material that might be submitted to a gemological laboratory for identification. From top to bottom and left to right: 1.29 ct Kashan flux-grown synthetic ruby, 1.10 ct natural ruby, 0.93 ct Czochralski-pulled synthetic ruby, 0.95 ct Ramaura synthetic ruby, 1.05 ct natural ruby from Tanzania, and 0.57 ct Swarovski flame-fusion synthetic ruby with flux-induced fingerprints. The 1.10 ct natural ruby was reported to have come from Mogok, but trace-element chemistry indicated that the stone was from a basalt-hosted deposit (such as Thailand); microscopy also indicated a basaltic origin. Photo © GIA and Tino Hammid.



help determine the geologic origin of a natural ruby, which is useful for identifying the country of origin.

BACKGROUND

Previous research has indicated the potential of trace-element chemistry for separating natural from synthetic rubies (Hänni and Stern, 1982; Stern and Hänni, 1982; Kuhlmann, 1983; Schrader and Henn, 1986; Tang et al., 1989; Muhlmeister and Devouard, 1991; Yu and Mok, 1993; Acharya et al., 1997), and also for differentiating rubies from different localities (Harder, 1969; Kuhlmann, 1983; Tang et al., 1988, 1989; Delé-Dubois et al., 1993; Osipowicz et al., 1995; Sanchez et al., 1997). The two most common analytical techniques for determining ruby chemistry are electron microprobe and EDXRF. Other methods include wavelength dispersive X-ray fluorescence spectrometry, neutron activation analysis, proton-induced X-ray emission (PIXE) analysis, and optical emission spectroscopy. Most of these methods involve instrumentation that is not readily available to gemological laboratories, or use techniques that may damage the sample. EDXRF, however, is nondestructive and has become standard equipment in many gemological laboratories.

Qualitative EDXRF analyses have shown that synthetic rubies contain relatively few trace elements, and that the presence of molybdenum (Mo) indicates a flux origin; natural rubies, on the other hand, show a greater number of trace elements, and Myanmar rubies show relatively low Fe and high V (Muhlmeister and Devouard, 1991; Yu and Mok, 1993). Analyses by electron microprobe (Delé-Dubois et al., 1993) and PIXE (Tang et al., 1988, 1989; Sun, 1992; Osipowicz et al., 1995) have revealed the same trends for Myanmar rubies, and have indicated that Thai stones show high Fe and low V; these studies have also shown significant variations in trace elements in rubies from the same deposit. PIXE analyses of rubies from several deposits have detected numerous trace elements, including silicon (Si), sulfur (S), chlorine, potassium

Figure 2. The discovery of new gem localities presents constant challenges for the gemologist. These two rubies (2.59 ct total weight) are from Mong Hsu, Myanmar, which first became known only in the early 1990s. Photo © Tino Hammid.

(K), calcium (Ca), titanium (Ti), V, Cr, manganese (Mn), Fe, and gallium (Ga); in contrast, with the exception of Cr, synthetic stones from Chatham, Inamori, and Seiko showed no significant trace elements, Kashan synthetic rubies showed some Ti, and Knischka and Ramaura synthetics contained Fe (Tang et al., 1989). Using optical emission spectroscopy, Kuhlmann (1983) reported the following trace elements (besides Cr) at levels >0.001 wt.% in these synthetics: Chatham and Verneuil—Fe, Si, Mo, beryllium (Be); Knischka—Fe, Si, Be, copper (Cu); Kashan—Si, Ti, Fe, Cu, Mn, Be. In natural rubies, the following (besides Cr) were detected at levels >0.001 wt.%: Mogok, Myanmar—V, Fe, Ti, Si, tin (Sn), Mn, Be; Jegdalek, Afghanistan—Si, Fe, Be; Umba Valley, Tanzania—Fe, Si, Ti, Cr, V, Mn; Morogoro, Tanzania—Ti, Si, Cr, Fe, V; Tsavo Park, Kenya—Cr, Fe, Si, Ti, V; Rajasthan, India—Fe, Si, Ti, Sn, Cu, V, Mn, Be.

In recent years, a number of new synthetic ruby products have entered the market, including those grown by the flux method (Smith and Bosshart, 1993; Henn and Bank, 1993; Henn, 1994; Hänni et al., 1994); by the hydrothermal method (Peretti and Smith, 1993); and by the Czochralski technique with natural ruby as the feed material, marketed as "recrystallized" (Kammerling et al., 1995b,c; Nassau, 1995). Other synthetic materials that have caused identification problems for the contemporary gemologist include flame-fusion synthetic rubies with flux-induced "fingerprints" (Koivula, 1983; Schmetzer and Schupp, 1994; Kammerling et al., 1995a) and Czochralski-pulled synthetic rubies that are inclusion-free (Kammerling and Koivula, 1994).

Natural rubies can also present identification problems. Heat treatment can significantly alter the appearance of the inclusions in natural ruby (Gübelin and Koivula, 1986; Themelis, 1992; Hughes, 1997). Fluid inclusions commonly rupture when heated, creating fractures that can be subsequently filled by the fluid or partially repaired on cooling (Gübelin and Koivula, 1986). These secondary fingerprints—common in heat-treated rubies from Mong Hsu, Myanmar, for example—are similar to the white, high-relief fingerprint-like inclusions commonly seen in flux synthetics (Laughter, 1993; Smith and Surdez, 1994; Peretti et al., 1995).

In addition, the locality of a natural ruby can have a significant impact on its market value (figure 2). Although the importance of "country of origin" in helping establish a natural ruby's value is a topic of ongoing debate (Liddicoat, 1990; Hughes, 1990a), it is nonetheless a significant consideration in some trading circles, especially for larger stones.

GEOLOGIC ORIGINS OF GEM-QUALITY RUBIES

Rubies are mined from both primary deposits (the host rock where the ruby formed) and secondary deposits (i.e., alluvial—stream transported, or eluvial—weathered in place) [Simonet, 1997]. Because of its durability and relatively high specific gravity, ruby is readily concentrated into secondary deposits; the processes of weathering and alluvial transport tend to destroy all but the best material, so these deposits can be quite valuable. In general, primary deposits are economically important only if the ruby is concentrated in distinct mineable areas, such as layers within marble.

The conditions under which ruby forms are important to gemologists, because the chemical composition, inclusions, and growth features visible in fashioned stones are influenced by the composition, pressure, and temperature of the ruby-forming environment (see, e.g., Peretti et al., 1996). The trace elements in a ruby are incorporated into the crystal structure, or are present as mineral inclusions (table 1) or as constituents in fractures. Therefore, the geologic environment influences the assemblage of trace elements present. Corundum (Al_2O_3) crystallizes only in silica-deficient environments because, in the presence of Si, the Al is used to form more common minerals such as kyanite,

TABLE 1. Geology and mineralogy of gem-quality ruby deposits.

Deposit type	Geology	Typical associated minerals	Typical mineral inclusions	Localities[a]
Basalt-hosted	Xenocrysts in alkali basalt (alluvial and eluvial deposits)	Sapphire, clinopyroxene, zircon, Fe-rich spinel, garnet; sometimes sapphirine	Pyrrhotite (commonly altered to goethite), apatite; sometimes spinel, almandine garnet	Australia—Barrington (Sutherland, 1996a,b; Sutherland and Coenraads, 1996; Webb, 1997; Sutherland et al., 1998) Cambodia—Pailin (Jobbins and Berrangé, 1981; Sutherland et al., 1998) Thailand—Chanthaburi, at Bo Rai–Bo Waen (Charaljavanaphet, 1951; Gübelin, 1971; Keller, 1982; Vichit, 1987; Coenraads et al., 1995) Vietnam—southern, at Dak Nong (Kane et al., 1991; Poirot, 1997)
Marble-hosted	Calcite or dolomite marble, commonly interlayered with schists and gneisses; may or may not be cut by granite intrusions (primary and alluvial deposits)	Calcite, dolomite, spinel, pargasite, phlogopite, rutile, Cr-muscovite, chlorite, tremolite, tourmaline, apatite, sphene, anorthite, margarite, pyrrhotite, pyrite, ilmenite, graphite, fluorite	Calcite, dolomite, rutile, apatite, pyrite, phlogopite, boehmite; sometimes spinel, zircon, margarite, graphite, pyrrhotite	Afghanistan—Jegdalek (Hughes, 1994; Bowersox and Chamberlin, 1995) China—Aliao Mountains, Yunnan Province (Keller and Fuquan, 1986; ICA Gembureau, 1991) India—southern (Viswanatha, 1982) Myanmar—Mogok (Iyer, 1953; Keller, 1983; Gübelin and Koivula, 1986; Kammerling et al., 1994) Myanmar—Mong Hsu (Peretti and Mouawad, 1994; Smith and Surdez, 1994; Peretti et al., 1995) Nepal—Taplejung district (Harding and Scarratt, 1986; Smith et al., 1997) Pakistan—Hunza (Bank and Okrusch, 1976; Okrusch et al., 1976; Gübelin, 1982; Hunstiger, 1990b) Pakistan—Kashmir ("Kashmir Yields Ruby, Tourmaline," 1992; Kane, 1997) Russia—Ural Mountains (Kissin, 1994) Tanzania—Morogoro (Hänni and Schmetzer, 1991) Tajikistan—eastern Pamir Mtns. (Henn et al., 1990b; Smith, 1998) Vietnam—northern, at Luc Yen (Henn and Bank, 1990; Henn, 1991; Kane et al., 1991; Delé-Dubois et al., 1993; Poirot, 1997)
Metasomatic	Desilicated pegmatite cutting ultramafic rock or marble (primary, eluvial, and alluvial deposits)	Plagioclase, vermiculite, phlogopite, muscovite, tourmaline (highly variable)	Rutile, boehmite; sometimes apatite, zircon, spinel, vermiculite, muscovite, pyrrhotite, graphite (highly variable)	India—southern (Viswanatha, 1982; Menon et al., 1994) Kenya—Mangari (Pohl et al., 1977; Pohl and Horkel, 1980; Bridges, 1982; Hunstiger, 1990b; Levitski and Sims, 1997) Tanzania—Umba (Solesbury, 1967; Zwaan, 1974; Hänni, 1987) Vietnam—central, at Quy Chau (Kane et al., 1991; Poirot, 1997)
Metasomatic	Desilicated aluminous schist/gneiss adjacent to ultramafic rock (primary, eluvial, and alluvial deposits)	Plagioclase, amphibole, epidote, tourmaline, micas, sillimanite, kyanite (highly variable)	Rutile, plagioclase, apatite, zircon, graphite, sillimanite, amphibole, ilmenite (highly variable)	India—southern (Viswanatha, 1982; Hunstiger, 1990a) Kenya—Mangari (Pohl et al., 1977; Pohl and Horkel, 1980; Hunstiger, 1990b; Key and Ochieng, 1991; Levitski and Sims, 1997) Malawi—Chimwadzulu Hill (Rutland, 1969; Henn et al., 1990a) Sri Lanka—Ratnapura, Elahera (Dahanayake and Ranasinghe, 1981, 1985; Munasinghe and Dissanayake, 1981; Dahanayake, 1985; Rupasinghe and Dissanayake, 1985; Gunawardene and Rupasinghe, 1986)

[a] *Although there are known deposit types in the countries listed, there may also be deposits (e.g., alluvial) that have not yet been characterized. Consequently, we do not know the specific geologic environment for all of the rubies obtained for this study.*

feldspars, and micas. The scarcity of gem corundum—especially ruby—results from this requirement for Si-depleted conditions in the presence of the appropriate chromophore(s) (i.e., Cr for ruby and Fe and Ti for blue sapphire), under the appropriate temperature and pressure conditions. The mechanisms by which gem corundum forms are still debated by geologists (see, e.g., Levinson and Cook,

Figure 3. This specimen (4.6 cm high) from Jegdalek, Afghanistan, shows a ruby embedded in calcite marble, along with traces of associated minerals. Courtesy of H. Obodda; photo © Jeffrey Scovil.

1994). With the exception of a few occurrences, gem-quality ruby has been found in three types of primary deposits (again, see table 1): basalt-hosted, marble-hosted, and metasomatic. (The latter two form by different metamorphic processes, as explained below.)

Basalt-Hosted Deposits. Some of the world's largest ruby deposits, past and present, are secondary deposits associated with alkali basalts (e.g., Cambodia and Thailand). However, the formation conditions of this type of corundum are the least understood. The occurrence of corundum in basalt is similar to that of diamond in kimberlite: The ruby and sapphire crystals (xenocrysts) are transported in molten rock from lower levels of the earth's crust (or upper mantle) to the surface. During transport from depths of 15–40 km (Levinson and Cook, 1994), the corundum is partially resorbed, as shown by the rounded edges and surface etch patterns typically seen on basalt-hosted corundum (Coenraads, 1992).

From evidence revealed by trace elements, mineral inclusions, fluid inclusions, and associated mineral assemblages observed in rare corundum-bearing assemblages (as xenoliths), geologists have suggested that both metamorphic- and igneous-formed rubies may be present in a given basalt-hosted deposit (see, e.g., Sutherland and Coenraads, 1996; Sutherland et al., 1998). The metamorphic rubies in such deposits may be derived from regional metamorphism of aluminous rocks (such as shales, laterites, and bauxites) that were subducted to great depths (Levinson and Cook, 1994). Two models have been proposed for the igneous origin of gem corundum: (1) from magma mixing at mid-crustal levels (Guo et al., 1996a,b), or (2) from the pegmatite-like crystallization of silica-poor magma in the deep crust or upper mantle (Coenraads et al., 1995). Regardless of the specific origin, the mineral inclusions and associated minerals suggest that the corundum formed in an environment containing Fe, S, and geochemically incompatible elements (Coenraads, 1992). This geochemical (or trace-element) "signature" is consistent with the relatively enriched Fe content that is characteristically shown by basalt-hosted rubies (see Results section, below).

Marble-Hosted Deposits. Some of the world's finest rubies form in marble-hosted deposits, such as those in Myanmar. These deposits are commonly thought to have formed as a result of the regional metamorphism of limestone by heat and pressure (see, e.g., Okrusch et al., 1976). At some localities, the close association of granitic intrusions with the ruby-bearing marble has led some researchers to consider them "metasomatic" (e.g., Mogok; Iyer, 1953); that is, chemical interaction between the marble and fluids associated with the intrusions caused ruby mineralization. Therefore, marble-hosted ruby deposits may form from regional metamorphism or contact metasomatism, or from a combination of the two (Konovalenko, 1990).

Depending on the composition of the original limestone, ruby-bearing marbles may be composed of calcite ($CaCO_3$) and/or dolomite [$CaMg(CO_3)_2$]. Ruby and associated minerals, such as spinel and micas (again, see table 1), form in layers that are irregularly distributed within the marble (figure 3). These ruby-bearing assemblages are thought to represent impure horizons within the original limestone, where Al-rich clays or sediments (such as bauxite) were deposited (see, e.g., Platen, 1988; Okrusch et al., 1976). The composition of the associated minerals (table 1) indicates that these impure layers contain traces of Si, S, K, Ti, V, Cr, and, in general, are low in Fe. Rubies from certain marble-type deposits (such as Mogok) are prized for their "pure" red color (i.e., absence of brown modifying hues), which is supposedly due to their lack of iron; this is consistent with the low iron content of their marble host rocks.

Metasomatic Deposits. Metasomatism is a metamorphic process whereby chemical components are exchanged in the presence of fluids. One important mechanism is "desilication," in which Si is mobilized (i.e., removed from the rock), leaving Al behind to form corundum. Metasomatic deposits of gem ruby can be divided into two groups: (1) desilicated pegmatites intruding silica-poor rocks such as serpentinite (as, e.g., at Umba, Tanzania: Solesbury, 1967) or marble (as at Quy Chau, Vietnam; Poirot, 1997); and (2) desilicated schists and gneisses that have been altered by metasomatic fluids in the presence of ultramafic (low Si; high Mg, Fe) rock (e.g., Malawi: Rutland, 1969; again, see table 1). As stated above, the ruby deposits at Mogok may also be metasomatic; if so, they would constitute a third type of metasomatic deposit—marble that has been altered by pegmatite-derived fluids.

The trace-element chemistry of rubies formed in metasomatic deposits is variable because of the different rock types and the particular local geochemical conditions under which these rubies formed (see, e.g., Kuhlmann, 1983). For example, rubies from different metasomatic deposits at Mangari, Kenya, show different characteristics: At the John Saul mine, "pure" red ruby coloration is common; at the Penny Lane deposit, the ruby is "darker" (Bridges, 1982; Levitski and Sims, 1997). These color variations most likely result from the variable composition of the host rocks; that is, at John Saul, the host rocks contain lower concentrations of Fe than at Penny Lane. Other metasomatic-type ruby localities with variable host rocks are in India (see, e.g., Viswanatha, 1982) and Sri Lanka (see, e.g., Dahanayake and Ranasinghe, 1985; Rupasinghe and Dissanayake, 1985).

MANUFACTURE OF SYNTHETIC RUBY

Synthetic rubies were introduced to the gem market in 1885. Originally sold as natural rubies from a fictitious mine near Geneva, and hence named "Geneva ruby," they were later proved to be synthetic (Nassau and Crowningshield, 1969; Nassau, 1980, 1995). The producer of these early synthetic rubies was never disclosed. The first scientific paper describing ruby synthesis using the flame-fusion process was published by Auguste Verneuil in 1904, two years after his first success. The flame-fusion process used today to grow rubies is largely unchanged from the one Verneuil introduced at the turn of the century (Nassau and Crowningshield, 1969; Nassau, 1980; Hughes, 1990b). Although flame-fusion material is still the most common synthetic corundum used in jewelry, other techniques are commercially available (figure 4; table 2).

Figure 4. Synthetic rubies were first manufactured more than 100 years ago. Today, several types are available in the gem marketplace. Here, a Chatham flux-grown synthetic ruby is set in 14k gold. Ring courtesy of Chatham Created Gems, photo © Tino Hammid.

Ruby manufacturing methods can be divided into two general categories: melt and solution. Melt-grown synthetic rubies—including flame-fusion, Czochralski, and floating zone—are produced by melting and crystallizing aluminum oxide powder to which traces of Cr and (possibly) various trace elements have been added. With the Czochralski and floating-zone methods, crystallization typically takes place in an iridium crucible; with flame-fusion, crystallization occurs on a rotating boule, without a container. The chemistry of melt-grown synthetic rubies is usually relatively "pure"—that is, they contain detectable amounts of relatively few elements—in comparison to other synthetic rubies, because the melt generally contains few additives.

Solution-grown synthetic rubies are crystallized from a solution in which aluminum and trace elements are dissolved. There are two types of growth solutions: flux and hydrothermal. A variety of chemical fluxes are used (again, see table 2), and the solutions are contained within a metal crucible, usually platinum. Hydrothermal synthetic rubies are grown from a water-rich solution enclosed in a pressurized autoclave. These synthetic rubies may contain trace elements originating from the flux or the hydrothermal solution, and possibly from the crucible or autoclave.

MATERIALS AND METHODS

Materials. For this study, we examined 121 natural and 162 synthetic rubies, most of which were faceted. These samples were chosen to represent the known commercially available sources of gem-quality material. The stones ranged from 0.14 to 52.06 ct, with most samples between 0.50 and 3.00 ct. The majority were transparent, but some were translucent; many had eye-visible inclusions. The samples were provided by individuals who had reliable information on the country of origin, although in some cases the specific deposit was not known. Note that some corundums with Lechleitner synthetic ruby overgrowth were included in this study, although they are not true synthetic rubies (Schmetzer, 1986b; Schmetzer and Bank, 1987). Red diffusion-treated corundum and "recrystallized" synthetic ruby were also analyzed.

At least seven representative samples were obtained for most localities and manufacturers, although the actual number varied from one to 31 for each type. Due to the limited number of samples from some deposits or manufacturers, and the possible future compositional variations of these rubies, the results of this study should only be considered an indication of the chemistry from these sources. Also, the trace-element data in this study are valid only for rubies, and do not necessarily apply to corundum of other colors (including pink). The fol-

TABLE 2. Manufacturing methods and possible sources of trace elements in synthetic rubies.

Manufacturing method/ manufacturer[a]	Growth material	References
Melt	**Feed**	
Czochralski-pulled	Alumina and Cr_2O_3	Rubin and Van Uitert, 1966; Nassau, 1980
Flame-fusion	Alumina and Cr_2O_3	Verneuil, 1904; Nassau, 1980; Yaverbaum, 1980
Floating zone	Alumina and Cr_2O_3	Nassau, 1980; Sloan and McGhie, 1988
Induced fingerprint	(Flame-fusion synthetic rubies with induced "fingerprints" by any of various fluxes)	Koivula, 1983; Schmetzer and Schupp, 1994; Kammerling et al., 1995a
Solution—Flux	**Fluxes**	
Chatham	Li_2O-MoO_3-PbF_2 and/or PbO	Schmetzer, 1986b
Douros	PbF_2 or PbO_4	Smith and Bosshart, 1993; Hänni et al., 1994
Kashan	Na_3AlF_6	Henn and Schrader, 1985; Schmetzer, 1986b; Weldon, 1994
Knischka	Li_2O-WO_3-PbF_2, PbO, $Na_2W_2O_7$, and Ta_2O_5	Knischka and Gübelin, 1980; Schmetzer, 1986b, 1987; Galia, 1987; Brown and Kelly, 1989
Lechleitner	Flux overgrowth (using Li_2O-MoO_3-PbF_2 and/or PbO flux) on natural corundum	Schmetzer, 1986b; Schmetzer and Bank, 1987
Ramaura	Bi_2O_3-PbF_2, also rare-earth dopant[b] added to flux as well as La_2O_3[c]	Kane, 1983; Schmetzer, 1986b
Solution—Hydrothermal	**Solution**	
Tairus (Russia)	Alumina or aluminum hydrates partially dissolved in an aqueous medium with Cr compounds such as $Na_2Cr_2O_7$	Nassau, 1980; Yaverbaum, 1980; Peretti and Smith, 1993; Peretti et al., 1997; Qi and Lin, 1998

[a] *The following containers are typically used during manufacture: Melt—iridium crucible (except no container is used for flame-fusion), Flux—platinum crucible, Hydrothermal—metal autoclave containing Fe, Ni, and Cu, possibly lined with silver, gold, or platinum.*

[b] *Produces a yellow fluorescence, which is usually absent in faceted material (Kane, 1983).*

[c] *Promotes the growth of facetable crystals.*

lowing were not included in the study samples: material from localities not known to provide crystals suitable for faceting, synthetic rubies grown for experimental purposes only, and phenomenal rubies (e.g., star rubies). Although it is possible to obtain analyses of larger mounted stones with EDXRF, we did not include mounted samples.

Methods. We used a TN Spectrace 5000 EDXRF spectrometer for the chemical analyses. This instrument can detect the elements sodium (atomic number 11) through uranium (atomic number 92), using an X-ray tube voltage of up to 50 kV and a current of 0.01 mA to 0.35 mA. Two sets of analytical conditions were used to maximize sensitivity: for sodium (atomic number 11) through sulfur (atomic number 16)—a voltage of 15 kV, current of 0.15 mA, no filter, and a count time of 200 seconds; for chlorine (atomic number 17) through bromine (atomic number 35)—a voltage of 25 kV, current of 0.25 mA, 0.127 mm aluminum filter, and a count time of 200 seconds. Each sample was run once under the two separate instrument conditions, in order to generate one analysis.

We used the spectra derived from these procedures to obtain "semi-quantitative" data for the elements Al, Ca, Ti, V, Cr, Mn, Fe, and Ga using the Fundamental Parameters (FP) method of Criss and Birks (1968; see also Jenkins, 1980). (Oxygen was assumed present in stoichiometric proportions, and Fe is reported as FeO [i.e., +2 oxidation state]). In addition, the presence of heavier elements (e.g., Zr, Ni, Cu, Mo, lanthanum [La], tungsten [W], and lead [Pb]) was noted from the spectra, but these elements were not analyzed quantitatively. The samples were analyzed for Si; however, because of peak overlap with Al, results for Si were unreliable and are not reported in this study.

The following standards were used for calibration and to check the instrument's performance: colorless Czochralski-pulled synthetic corundum for Al; tsavorite garnet for Al and Ca; and almandine garnet for Al, Mn, and Fe. The compositions of the standards were quantitatively determined at the California Institute of Technology by Paul Carpenter using an electron microprobe.

We used a 3 mm diameter X-ray beam collimator to limit the beam size to about 20 mm^2. (However, the actual area analyzed varied depending on the size of the sample; on most, it was less than 20 mm^2.) This area was analyzed to a depth of approximately 0.1 mm. Whenever possible, we oriented each sample to avoid prominent color zoning or conspicuous mineral inclusions. We usually analyzed the table facet; for some samples, we analyzed the pavilion. We did not include analyses if we suspected that the presence of diffraction peaks caused erroneous quantitative results.

Both the accuracy and the sensitivity of the analyses are affected by the size of the area analyzed, because this determines the number of counts obtained for a given element. Table 3 illustrates the differences in detection limits for rubies of three different sizes. In general, the detection limits decreased with increasing sample size. Above approximately 1 ct, there were only minor improvements in the detection limits.

The concentrations of each element in the sample are calculated from the counting statistics and the FP algorithm, and they are expressed as weight percent oxides. The number of counts determined for each element had to be normalized to 100% to compensate for the different sample sizes. Because the concentrations reported are not directly calculated from the peak counts, our analyses are considered semi-quantitative. For comparison purposes, we had five natural rubies from our study analyzed by Dr. W. B. Stern of the University of Basel using his EDXRF. Dr. Stern's results for these samples were very similar to our own. Based on multiple analyses of three of the samples used in this study, we found the repeatability of the trace-element data to be generally within 10%–20%.

RESULTS

Qualitative Results. *Synthetic Rubies.* The following elements were detected in all of the synthetic

TABLE 3. Variation in EDXRF detection limits according to sample size.[a]

Oxide (wt.%)	0.20 ct	0.65 ct	1.27 ct
Al_2O_3	0.15	0.13	0.06
Cr_2O_3	0.007	0.003	0.002
CaO	0.044	0.013	0.017
TiO_2	0.012	0.006	0.005
V_2O_3	0.009	0.004	0.003
MnO	0.011	0.005	0.003
FeO	0.005	0.002	0.001
Ga_2O_3	0.006	0.002	0.001

[a] *Calculated after Jenkins, 1980.*

ruby growth types (but not all samples) we examined: Ca, Ti, Cr, Mn, and Fe. Ga and V were also detected in the products of all specific manufacturers except the one Inamori sample we examined. The greatest variety of trace elements was detected in the flux-grown synthetics. In addition to the elements noted above, the Chatham flux synthetic rubies had Mo (six out of 21 samples), the Douros contained Pb (seven out of 15), and the Knischka samples showed W (five out of 14). La was seen only in Ramaura flux-grown synthetic rubies (12 out of 31), as previously reported by Schmetzer (1986b); Pt was also detected in one Ramaura synthetic ruby, Pb in four, and Bi (bismuth) in three. All of the flame-fusion synthetic rubies with flux-induced fingerprints revealed traces of Mo or Zr; otherwise, the melt-grown synthetics contained no trace elements other than those mentioned above. Traces of Ni were detected in 15 samples, and Cu in six samples, of the Tairus hydrothermal synthetic rubies (as previously reported by Peretti and Smith, 1993; Peretti et al., 1997; and Qi and Lin, 1998). One Tairus sample also contained cobalt, which we did not detect in any of the other synthetic or natural samples.

Natural Rubies. Traces of Ca, Ti, V, Cr, Mn, Fe, and Ga were noted in rubies from all of the localities we analyzed. Zr was detected in seven of the eight rubies analyzed from India, all of which contained numerous zircon inclusions. Cu was detected in one sample from Mong Hsu, Myanmar.

Semi-Quantitative Results. In addition to Al, the following elements were analyzed semi-quantitatively: Ca, Ti, V, Cr, Mn, Fe, and Ga. The natural rubies we examined typically contained a greater variety and higher quantity of these elements than the synthetics (tables 4 and 5; figures 5–8), which is consistent with the results reported by Kuhlmann (1983) and Tang et al. (1989).

Synthetic Rubies. Compared to many natural rubies, most of the synthetic samples contained little V and Ga (table 5; figures 5 and 6). In general, the melt-grown synthetic rubies contained the lowest concentrations of the elements listed above, especially Fe (figure 7; see also Box A). Two of the 10 flame-fusion samples had relatively high Ti (nearly 0.05 wt.% TiO_2; figure 8); one of these also contained relatively high V (nearly 0.02 wt.% V_2O_3), and the other contained the highest Cr level measured on the synthetics in this study (2.41 wt.% Cr_2O_3), with the exception of the red diffusion-treated corundum (see Box B). All the other synthetic rubies had Cr contents that ranged from about 0.07 to 1.70 wt.% Cr_2O_3, without any discernable trends. The floating-zone synthetic rubies were the only

TABLE 4. Summary of natural ruby chemistry.[a]

	Basalt-hosted		Marble-hosted					Metasomatic	
Oxide (wt.%)	Cambodia (1)[b]	Thailand (15)	Afghanistan (15)	Mogok, Myanmar (19)	Mong Hsu, Myanmar (11)	Nepal (3)	Southern Yunnan (2)	Kenya (8)	Umba Valley, Tanzania (4)
Al_2O_3	99.09	98.91–99.25 (99.06)	96.39–99.66 (98.31)	98.73–99.67 (99.27)	96.83–99.25 (98.69)	99.51–99.60 (99.57)	98.48–99.28 (98.88)	95.13–99.63 (98.22)	97.94–98.23 (98.11)
Cr_2O_3	0.417	0.237–0.732 (0.419)	0.205–0.575 (0.350)	0.255–1.02 (0.562)	0.576–1.19 (0.887)	0.190–0.347 (0.260)	0.608–1.29 (0.950)	0.222–1.70 (0.675)	0.246–0.571 (0.372)
CaO	0.018	bdl–0.036 (0.023)	bdl–3.11 (0.784)	bdl–0.065 (0.029)	bdl–0.063 (0.030)	bdl–0.044 (0.025)	0.064–0.072 (0.068)	0.028–0.193 (0.068)	bdl–0.033 (0.023)
TiO_2	0.021	0.008–0.033 (0.020)	0.009–0.091 (0.045)	0.015–0.047 (0.026)	0.019–0.207 (0.078)	0.059–0.096 (0.080)	0.007–0.024 (0.016)	0.020–0.042 (0.033)	bdl–0.017 (0.009)
V_2O_3	0.004	bdl–0.007 (0.004)	bdl–0.016 (0.009)	0.028–0.171 (0.066)	0.024–0.104 (0.048)	0.014–0.024 (0.017)	0.017–0.022 (0.020)	0.003–0.048 (0.018)	0.002–0.006 (0.004)
MnO	0.003	0.003–0.008 (0.005)	bdl–0.005 (bdl)	bdl–0.013 (0.004)	bdl–0.012 (0.006)	bdl	0.005–0.014 (0.010)	bdl–0.009 (0.005)	0.003–0.007 (0.006)
FeO	0.439	0.299–0.722 (0.468)	0.009–0.133 (0.070)	0.006–0.080 (0.028)	bdl–0.022 (0.010)	0.012–0.038 (0.029)	0.012–0.072 (0.042)	0.005–0.040 (0.020)	1.21–1.67 (1.46)
Ga_2O_3	0.006	0.004–0.009 (0.005)	bdl–0.011 (0.006)	bdl–0.026 (0.012)	bdl–0.014 (0.009)	0.009–0.025 (0.018)	0.008–0.008 (0.008)	0.012–0.048 (0.033)	0.008–0.023 (0.014)

[a] *Values shown are normalized wt.%. Minimum and maximum values are given, along with the average (in parentheses below each range). bdl = below detection limits (varies according to size of sample; see table 3).* [b] *Number of samples in parentheses.*

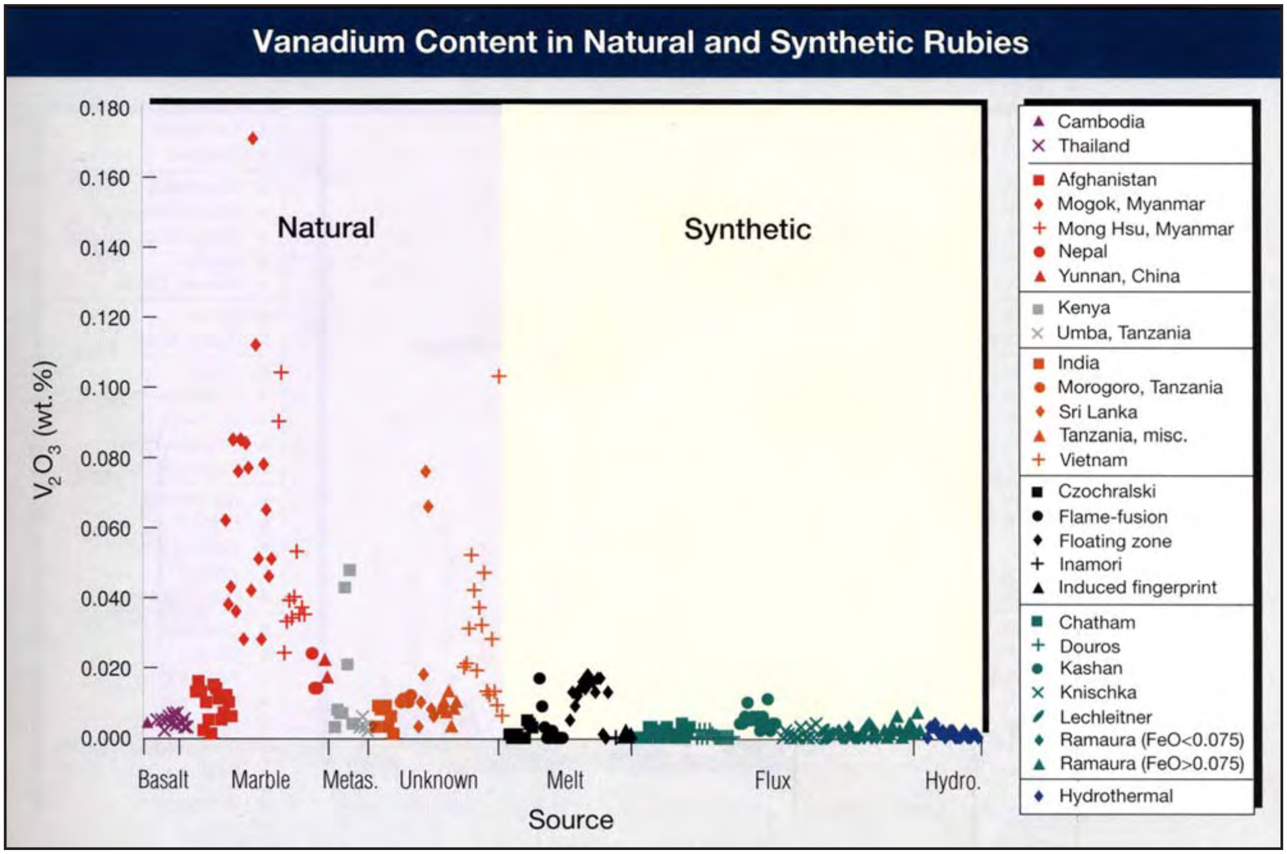


Figure 5. Most synthetic rubies contain little vanadium compared to natural rubies. In general, rubies from marble-hosted deposits contained the highest V content, although those from Afghanistan showed atypically low V. (Note that the Czochralski samples in these graphs are all produced by Union Carbide, as distinct from the Inamori Czochralski-pulled sample that was also analyzed.)

Unknown deposit type				
India (8)	Morogoro, Tanzania (5)	Sri Lanka (7)	Tanzania, misc. (7)	Vietnam (16)
98.80–99.36 (99.10)	98.35–98.69 (98.52)	97.95–99.63 (99.14)	98.69–99.44 (99.08)	97.31–99.49 (98.70)
0.192–0.518 (0.358)	1.10–1.51 (1.30)	0.182–1.00 (0.327)	0.448–1.16 (0.713)	0.344–2.38 (1.01)
bdl–0.025 (bdl)	0.027–0.046 (0.035)	bdl–0.072 (0.024)	0.017–0.100 (0.052)	0.007–0.153 (0.062)
0.013–0.024 (0.017)	0.023–0.038 (0.032)	0.017–0.170 (0.083)	0.021–0.046 (0.031)	0.011–0.268 (0.071)
bdl–0.009 (0.006)	0.010–0.012 (0.011)	0.003–0.076 (0.027)	0.003–0.013 (0.008)	0.006–0.103 (0.030)
bdl–0.004 (0.002)	0.007–0.014 (0.010)	bdl–0.010 (0.003)	bdl–0.009 (0.004)	0.002–0.027 (0.011)
0.184–0.947 (0.502)	0.043–0.137 (0.093)	0.032–0.494 (0.178)	0.003–0.175 (0.098)	0.015–0.482 (0.103)
0.004–0.008 (0.007)	0.004–0.010 (0.007)	0.004–0.024 (0.011)	0.008–0.020 (0.013)	0.005–0.034 (0.014)

synthetic samples with a relatively high average V content (0.012 wt.% V_2O_3).

Variable trace-element contents were measured in the flux-grown synthetic rubies. The Chatham samples contained insignificant amounts of most trace elements, except for 0.024 wt.% Ga_2O_3 in one sample. The Douros synthetics contained elevated Fe (0.055–0.241 wt.% FeO), and the highest concentration of Ga of all the natural and synthetic rubies tested for this study (0.051–0.079 wt.% Ga_2O_3). The Kashan synthetic rubies showed very low Fe, and they had the most Ti of all the synthetics analyzed (0.042–0.174 wt.% TiO_2). One Knischka sample also contained elevated Ti (0.159 wt.% TiO_2), and another showed high Ga (0.071 wt.% Ga_2O_3). The Knischka synthetic rubies contained about the same amount of Fe as the Douros samples, with the exception of one Knischka sample that contained 1.15 wt.% FeO; this anomalous sample contained the greatest amount of Fe of all the synthetics analyzed. Ramaura synthetic rubies typically contained some Ga (up to 0.017 wt.% Ga_2O_3) and Fe

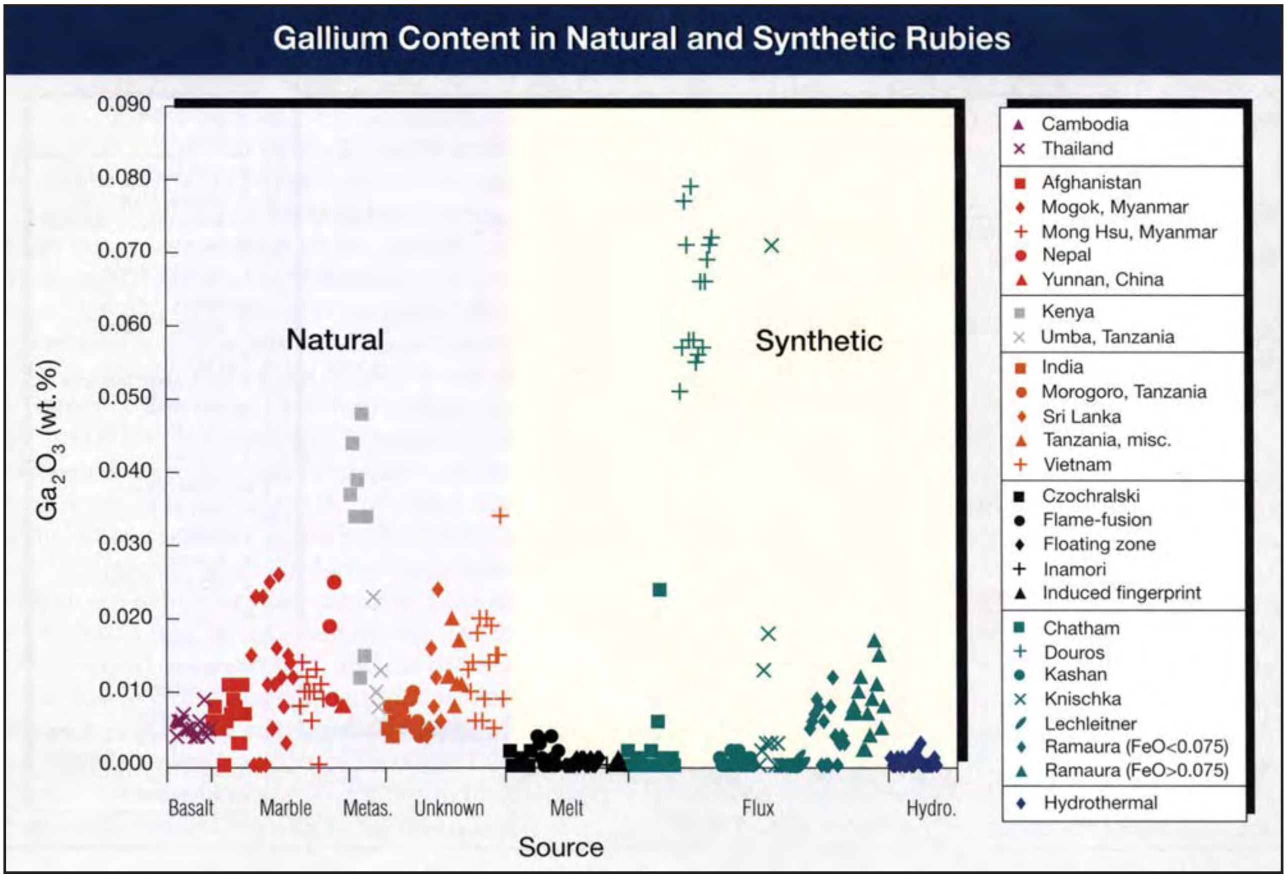


Figure 6. Gallium is another key trace element for separating natural from synthetic rubies. While fewer than one-seventh of the natural stones contained less than 0.005 wt.% Ga_2O_3, more than three-quarters of the synthetic samples did. However, Douros synthetic rubies (and one Knischka sample) were exceptions to this, with more than 0.050 wt.% Ga_2O_3.

TABLE 5. Summary of synthetic ruby chemistry.[a]

	Melt					Flux		
Oxide (wt.%)	Czochralski: Union Carbide (10)[e]	Flame-fusion (10)	Floating zone (16)	Czochralski: Inamori (1)[b]	Induced fingerprint flame-fusion (4)	Chatham (21)	Douros (15)	Kashan (15)
Al_2O_3	98.67–99.34 (98.86)	97.47–99.80 (99.15)	99.08–99.59 (99.40)	99.37	98.25–99.40 (98.84)	98.22–99.53 (98.98)	98.06–99.79 (99.32)	99.32–99.77 (99.57)
Cr_2O_3	0.634–1.28 (1.08)	0.184–2.41 (0.788)	0.366–0.869 (0.521)	0.595	0.583–1.71 (1.12)	0.444–1.66 (0.956)	0.067–1.50 (0.484)	0.121–0.506 (0.291)
CaO	bdl–0.020 (bdl)	bdl–0.056 (0.034)	bdl–0.035 (0.024)	0.022	bdl–0.028 (0.018)	bdl–0.089 (0.040)	bdl–0.022 bdl	bdl–0.067 (0.023)
TiO_2	bdl–0.007 (0.002)	bdl–0.044 (0.013)	bdl–0.011 (bdl)	bdl	bdl–0.017 (0.009)	bdl–0.027 (0.009)	0.005–0.034 (0.013)	0.042–0.174 (0.096)
V_2O_3	bdl–0.005 bdl	bdl–0.017 (0.003)	bdl–0.018 (0.012)	bdl	bdl	bdl–0.004 (0.001)	bdl	bdl–0.011 (0.005)
MnO	0.004–0.010 (0.007)	bdl–0.014 (0.005)	bdl–0.005 (0.003)	0.007	0.003–0.014 (0.007)	bdl–0.010 (0.006)	bdl–0.009 (0.004)	bdl–0.015 (0.003)
FeO	0.001–0.005 (0.003)	0.002–0.019 (0.007)	bdl–0.038 (0.006)	0.005	0.002–0.008 (0.005)	0.004–0.018 (0.010)	0.055–0.241 (0.085)	0.001–0.016 (0.007)
Ga_2O_3	bdl–0.002 (0.001)	bdl–0.004 (0.002)	bdl–0.001 bdl	bdl	bdl–0.001 bdl	bdl–0.024 (0.002)	0.051–0.079 (0.064)	bdl–0.002 (0.001)

[a] *Values are normalized wt.%. Minimum and maximum values are given, along with the average (in parentheses below each range). bdl= below detection limits (varies according to size of sample; see table 3).* [b] *Number of samples in parentheses.*

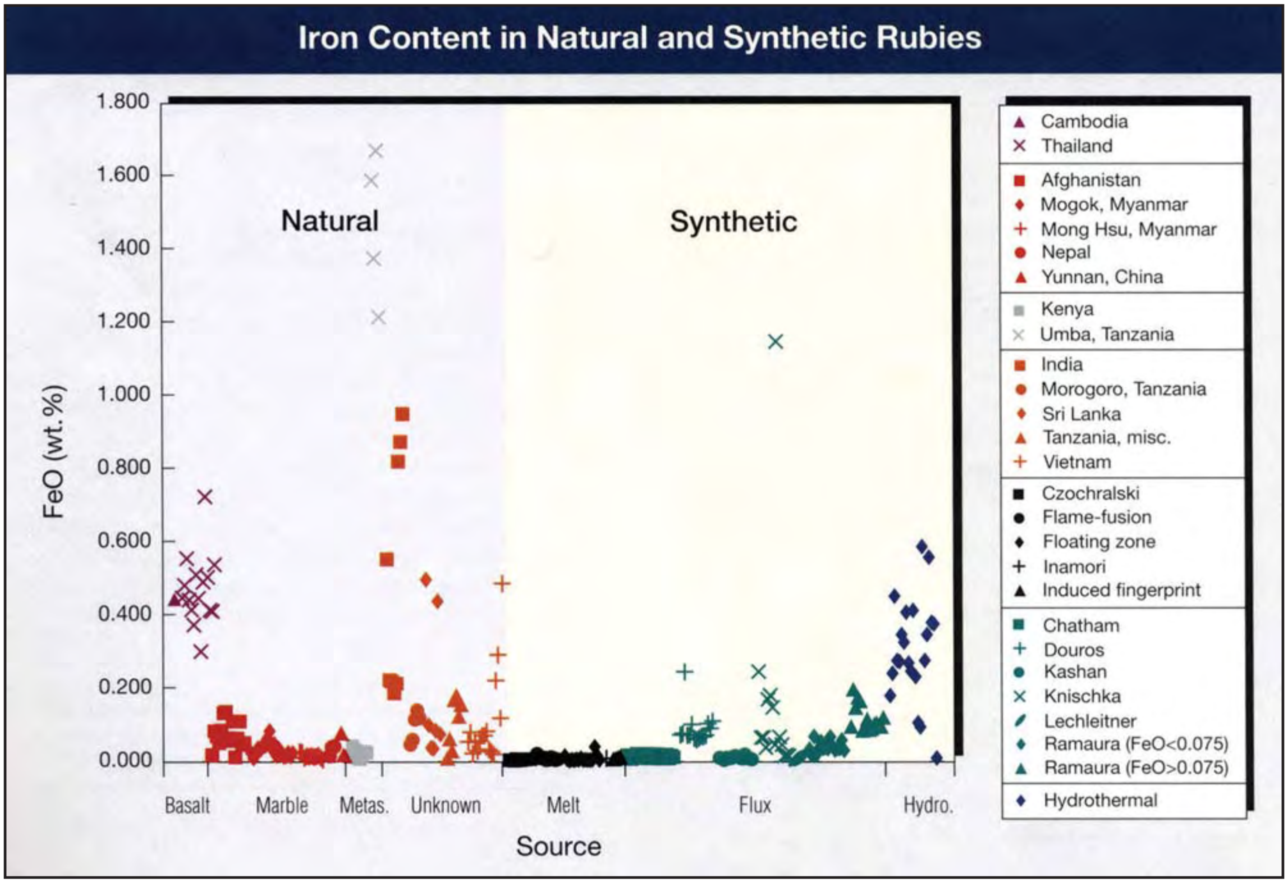


Figure 7. Iron is also useful for separating natural from synthetic rubies, especially when used in conjunction with vanadium. Only one of the melt-grown synthetic rubies and approximately half of the flux-grown synthetic rubies displayed an FeO content greater than 0.02 wt.%, while three-quarters of the natural stones did. Hydrothermal synthetic rubies had the highest overall Fe contents of the synthetics we analyzed.

(0.014–0.192 wt.% FeO), with those Ramaura synthetic rubies marketed as "Thai tone" richer in Fe than those marketed as "Burma tone."

The Tairus hydrothermal synthetic rubies contained relatively high Fe (up to 0.584 wt.% FeO) and traces of Ti (up to 0.034 wt.% TiO_2).

Natural Rubies. In general, there was greater variability in the trace-element chemistry of the natural rubies than of the synthetics, but there were also some distinct trends according to geologic occurrence. Basalt-hosted rubies were the most consistent: Samples from Thailand and Cambodia showed relatively high Fe (0.299–0.722 wt.% FeO) and low V (up to 0.007 wt.% V_2O_3). Marble-hosted rubies showed the opposite trend: low Fe (up to 0.133 wt.% FeO) and high V (typically 0.02–0.09 wt.% V_2O_3), with the exception of Afghan rubies, which showed low V contents (less than 0.02 wt.% V_2O_3). The Afghan rubies contained the highest levels of Ca measured in this study (up to 3.11 wt.% CaO). Rubies from Myanmar contained the most V measured in this study (up to 0.171 wt.% V_2O_3). Some

Flux (cont'd)				Hydrothermal
Knischka (14)	Lechleitner (4)	Ramaura[c] (FeO < 0.075) (15)	Ramaura[d] (FeO > 0.075) (15)	Tairus (21)
97.81–99.51 (98.97)	98.34–99.55 (99.00)	98.45–99.77 (99.23)	98.17–99.66 (99.01)	97.95–99.89 (98.51)
0.266–1.15 (0.690)	0.413–1.57 (0.933)	0.171–1.45 (0.688)	0.128–1.65 (0.822)	0.084–1.74 (1.12)
bdl–0.104 (0.034)	bdl–0.046 (0.031)	bdl–0.061 (0.033)	bdl–0.065 (0.039)	bdl–0.054 (0.030)
bdl–0.159 (0.023)	0.011–0.044 (0.026)	bdl–0.012 bdl	bdl–0.010 bdl	0.007–0.034 (0.023)
bdl–0.004 bdl	bdl	bdl–0.004 bdl	bdl–0.007 bdl	bdl–0.004 bdl
bdl–0.013 (0.006)	0.003–0.015 (0.008)	0.002–0.014 (0.006)	bdl–0.011 (0.005)	BDL–0.015 (0.008)
0.012–1.15 (0.159)	0.004–0.008 (0.006)	0.014–0.065 (0.037)	0.079–0.192 (0.112)	0.006–0.584 (0.302)
bdl–0.071 (0.008)	bdl–0.001 bdl	bdl–0.012 (0.005)	0.002–0.017 (0.008)	bdl–0.003 (0.001)

[c] *Includes all "Burma tone" samples.*
[d] *Includes all "Thai tone" samples.*

BOX A: Trace-element Chemistry of “Recrystallized” or “Reconstructed” Ruby

In late 1994 and early 1995, the trade was introduced to “recrystallized” Czochralski-pulled synthetic ruby by TrueGem of Las Vegas, Nevada, and Argos Scientific of Temecula, California (Kammerling et al., 1995b,c). “Reconstructed” rubies of South African origin have also been reported (Brown, 1996). TrueGem sells its synthetic ruby product under the trademarked name “TrueRuby.” In its promotional material, TrueGem has claimed that its process “enhances the clarity of ruby and sapphire to perfection, while retaining nature’s elemental formula for the finest colored stones ever mined.” In this process, natural ruby is reportedly used as feed material, rather than the alumina used by most corundum manufacturers. The final step in the growth process is Czochralski pulling.

We analyzed four TrueGem synthetic rubies (see, e.g., figure A-1, table A-1). These samples showed a composition that is different from any of the natural rubies we analyzed: Cr is high, and the absence of V combined with low Fe precludes natural origin. The trace-element chemistry of this material is similar to that of the melt-grown synthetic rubies we examined, except for the enriched Cr contents. This result contradicts the manufacturer’s claim that this ruby product retains “nature’s elemental formula.” In agreement with the arguments of others (e.g., Nassau, 1995), the GIA Gem Trade Laboratory calls this material synthetic ruby on its reports (T. Moses, pers. comm., 1998).

Figure A-1. The trace-element chemistry of “TrueRuby” most closely resembles that of melt-grown synthetic ruby. These samples of TrueGem’s “recrystallized” (synthetic) ruby weigh 0.45 ct (rounds) and 0.65 ct (oval). Photo by Maha DeMaggio.

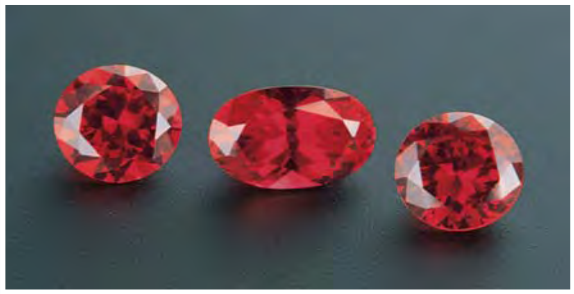


TABLE A-1. Trace-element chemistry of TrueGem “recrystallized” rubies.

Oxide	Specimen number				Average
(wt.%)	2852	2854	4325	4326	
Al_2O_3	98.21	98.60	98.26	98.22	98.32
Cr_2O_3	1.69	1.32	1.71	1.71	1.61
CaO	0.018	0.039	0.017	0.032	0.027
TiO_2	bdl	0.011	bdl	0.007	0.005
V_2O_3	bdl	bdl	bdl	bdl	bdl
MnO	0.010	0.016	0.005	0.004	0.009
FeO	0.008	0.014	0.007	0.009	0.010
Ga_2O_3	0.002	0.003	0.003	0.003	0.003

Mong Hsu samples contained up to 0.207 wt.% TiO_2 (high Ti was also reported by Smith and Surdez [1994] and Peretti et al. [1995]).

The rubies from metasomatic deposits showed wide variations in composition. Samples from Umba in Tanzania had the greatest Fe measured in this study (1.21–1.67 wt.% FeO), combined with low V and Ti. Rubies from Kenya, however, showed low Fe and the most Ga (0.12–0.48 wt.% Ga_2O_3) measured in the natural samples.

DISCUSSION

Chemical Variations in Synthetic and Natural Rubies. *Synthetic Rubies.* Verneuil’s original flame-fusion process required that the feed powder used be free of Fe, since Fe caused the boule to turn brown (Verneuil, 1904; Nassau, 1980). Today’s melt-grown products are still essentially Fe-free, and they typically contain none or very small amounts of other elements besides Cr. Flux-grown synthetic rubies revealed the most trace elements, which is consistent with the variety of fluxes used to manufacture these synthetics (again, see table 2). Li, F, Na, Al, Mo, Ta (tantalum), W, Pb, or Bi may be present in the flux in which these rubies were grown or treated (for synthetic rubies with “induced fingerprints”) [Schmetzer, 1986a,b, 1987; Schmetzer and Schupp, 1994; Kammerling et al., 1995a]. Lanthanum has been used experimentally to help grow crystals with rhombohedral rather than flat, tabular habits

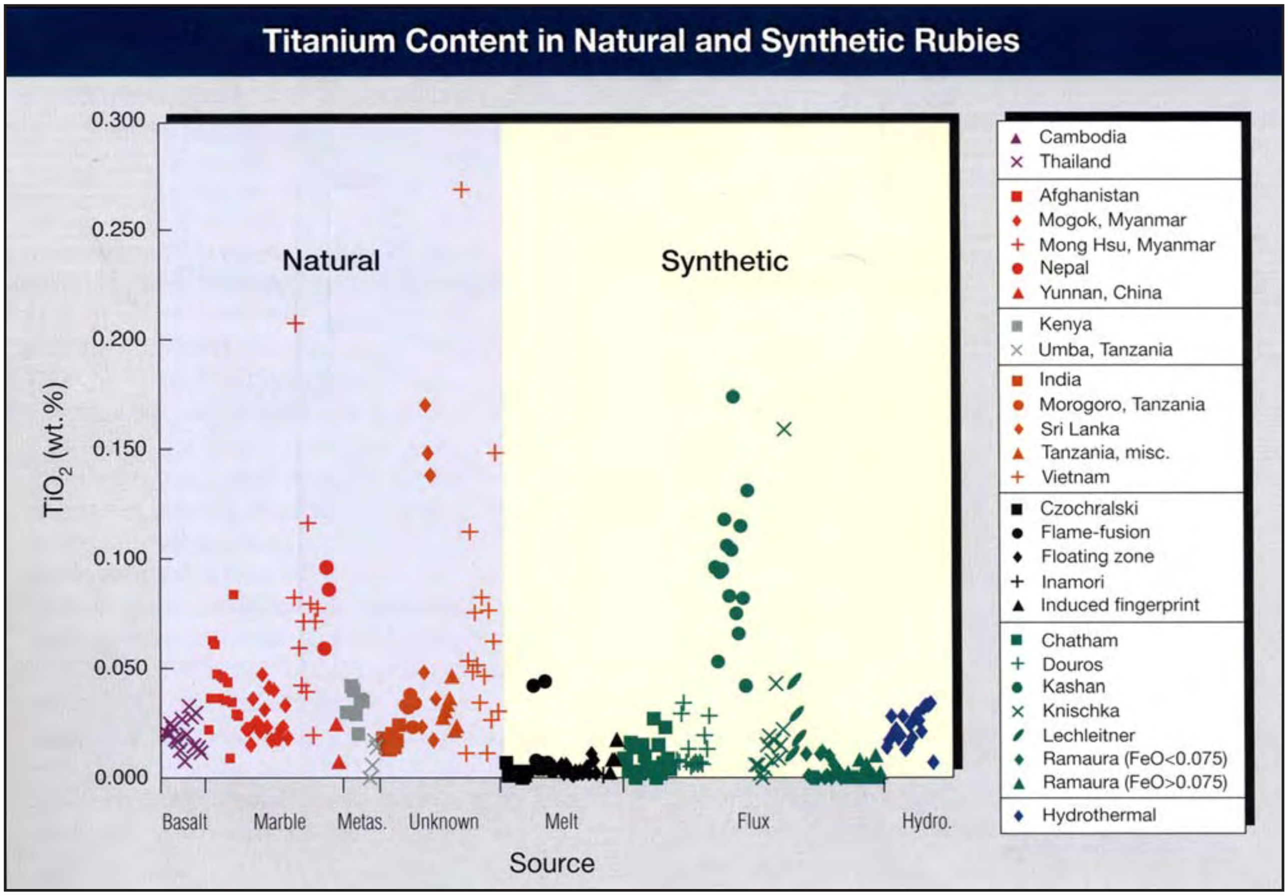


Figure 8. Natural rubies contain, on average, more titanium than synthetic rubies, but there was significant overlap in this study. Therefore, Ti alone is not useful for separating most natural from synthetic rubies. Among the synthetic rubies we analyzed, the Kashan samples had the highest Ti contents, while melt-grown and some flux-grown synthetics had the lowest.

(Chase, 1966), which significantly increases cutting yield from the rough. Because their charges and atomic radii are different from Al^{3+}, some of the elements detected (e.g., Mo, La, W, Pt, Pb, and Bi) do not readily enter the corundum structure. It is interesting to note, therefore, that the samples in which these elements were detected had no flux inclusions visible with 63↔ magnification. In the Tairus hydrothermal samples, the Fe, Ni, and Cu that we detected were probably derived from the autoclave in which they were grown (see, e.g., Peretti and Smith, 1993).

Natural Rubies. Some of the elements detected in the natural rubies (i.e., Ca and Zr) do not readily substitute for Al^{3+} in the corundum crystal structure, and were probably present in mineral inclusions. The Afghan rubies, in particular, contained abundant inclusions, and these samples showed elevated amounts of Ca. Zr was detected in those Indian samples that contained abundant zircon inclusions. The other trace elements measured in the natural samples (Fe, V, Ti, and Ga) can substitute for Al^{3+}, and their abundance reflects the geologic environment of formation (see below).

Distinguishing Natural from Synthetic Ruby. According to this study, the presence of Mo, La, W, Pt, Pb or Bi proves that a ruby is synthetic. Ni and Cu suggest synthetic origin; however, both of these elements could be present in sulfide inclusions within natural rubies, and Cu has been detected in natural rubies (Kuhlmann, 1983; Osipowicz et al., 1995; Sanchez et al., 1997).

Although no single trace element proves natural origin, trace-element assemblages can provide the distinction for nearly all samples. Many of the synthetic rubies contained low amounts of Fe (<0.02 wt.% FeO), whereas most of the natural stones had more than 0.02 wt.% FeO (again, see figure 7 and table 4). Tairus hydrothermal synthetic rubies contained elevated Fe, but the common presence of Ni

BOX B: TRACE-ELEMENT CHEMISTRY OF RED DIFFUSION-TREATED CORUNDUM

In the diffusion-treatment process, faceted pale-colored to colorless corundum is embedded in a powder that consists of aluminum oxide and color-causing trace elements, within an alumina crucible. Prolonged heating of the crucible to high temperatures (usually 1600°–1850°C) causes the chemicals to diffuse into a thin outer layer of treated color over the entire surface of the stone. Blue diffusion-treated corundum first appeared in the late 1970s, although it did not become widely available until 1989 (Kane et al., 1990). Red diffusion-treated corundum was introduced in the early 1990s (McClure et al., 1993; figure B-1).

Although diffusion treatment initially caused a great deal of concern in the jewelry trade, it is relatively easy to identify with standard gemological techniques. When observed in immersion with diffused transmitted light, diffusion-treated corundum displays uneven or patchy coloration, color concentration along facet junctions, and a high relief when compared to natural or synthetic stones. Other identifying features include spherical voids in the diffusion layer, dense concentrations of very small white inclusions just under the surface, and anomalous refractive index readings—including different readings from different facets and some R.I. values over the limit of the refractometer (McClure et al., 1993).

In the event, however, that a deeper diffusion layer is achieved, perhaps making some of these identifying features less obvious, we decided to include red diffusion-treated corundum in this study to determine the effectiveness of EDXRF analysis in making this separation. Because the color of a diffusion-treated stone is present only in a thin surface layer, this layer has to be significantly darker than a similarly colored natural or synthetic ruby to achieve an equivalent depth of color. Thus, the layer of diffused color must have a high Cr concentration. To document this characteristic, we analyzed 23 samples from a number of sources using EDXRF (table B-1). The analyses revealed high to extremely high Cr contents (2.72–13.16 wt.% Cr_2O_3). In fact, the diffusion-treated sample with the least amount of Cr contained even more of this element than any of the other samples analyzed for this study; the next-highest Cr content (2.41 wt.% Cr_2O_3) was measured in a flame-fusion synthetic ruby. The enriched Cr concentrations measured in diffusion-treated corundum probably cause the anomalously high R.I. readings that are commonly measured on this material (see, e.g., McClure et al., 1993).

Figure B-1. EDXRF analyses of red diffusion-treated corundums such as this 2.55 ct stone showed that this material had a higher Cr content than any of the other samples examined for this study.

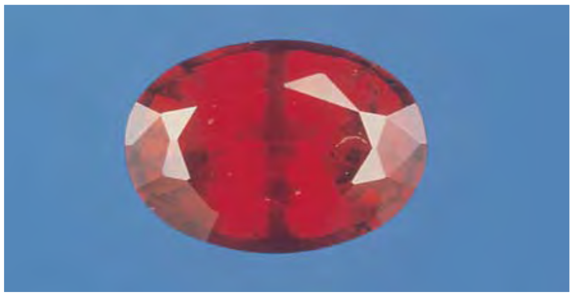
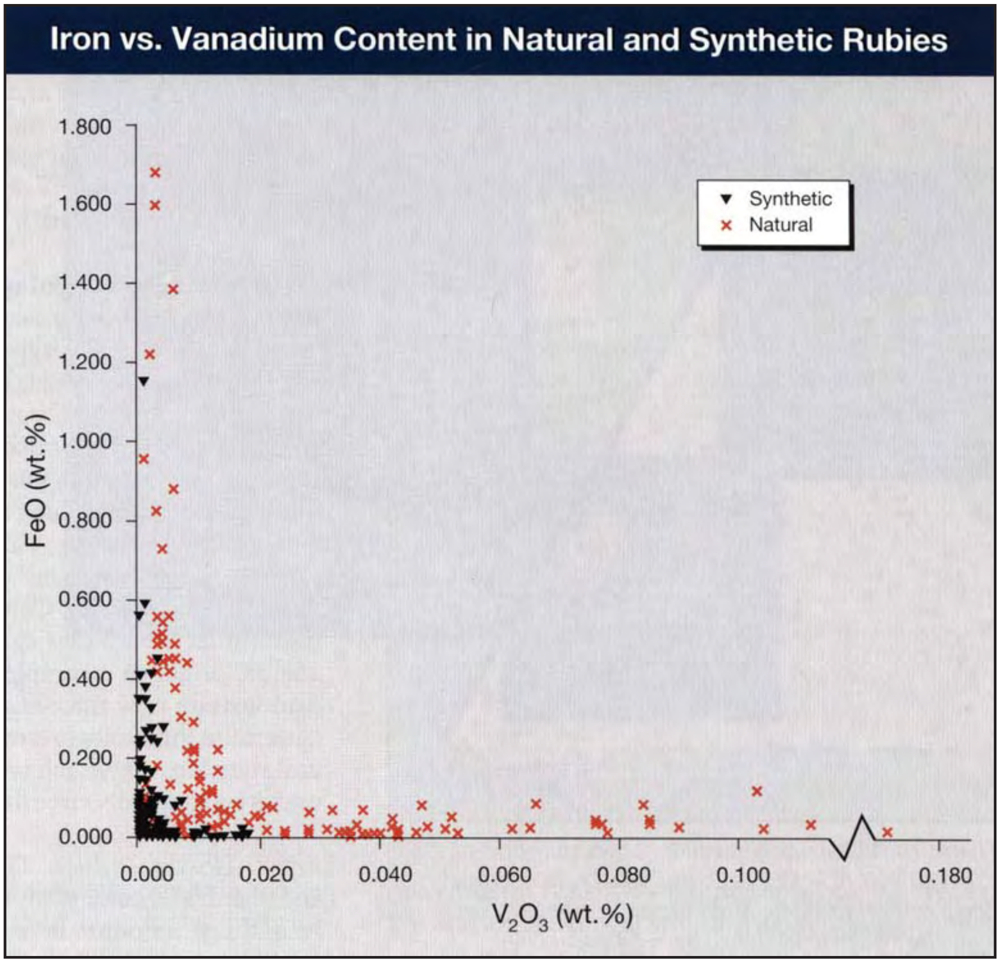


TABLE B-1. Trace-element chemistry of red diffusion treated corundum.

Oxide (wt.%)	Min.	Max.	Average[a]	Std. Dev.[b]
Al_2O_3	85.85	96.92	92.30	3.06
Cr_2O_3	2.72	13.16	7.13	2.81
CaO	0.011	0.283	0.087	0.087
TiO_2	0.004	0.478	0.215	0.149
V_2O_3	bdl	0.010	0.002	0.003
MnO	bdl	0.035	0.006	0.011
FeO	0.077	0.501	0.188	0.153
Ga_2O_3	bdl	0.023	0.011	0.005

[a] *Average of 23 samples.*
[b] *By definition, about two-thirds of the analyses will fall within one standard deviation of the average.*

Figure 9. *This graph of FeO content vs. V_2O_3 content illustrates the usefulness of these elements in making the separation between natural and synthetic rubies, even though there is some overlap between these populations. Most of the synthetic samples cluster near the origin of the diagram (due to their lower Fe and V contents), while the natural samples plot further from the origin and also display greater variations in their contents of Fe or V.*



and Cu, combined with a lack of V and Ga, identifies them as synthetic.

Relatively high concentrations of V were measured in the natural rubies. Few of the synthetic rubies we examined contained detectable amounts of V, which is consistent with the findings of Kuhlmann (1983) and Tang et al. (1989). However, a low V content is not proof of synthetic origin, since several of the natural rubies we analyzed contained relatively low V (again, see figure 5). Nevertheless, many synthetics, especially melt products, can be identified by their relative lack of both Fe and V (figure 9). In contrast to the synthetics, natural rubies contained a broad range of Fe and V contents. Therefore, with the exception of one anomalous (Knischka) sample, the data for synthetics are clustered below 0.60 wt.% FeO, and 0.02 wt.% V_2O_3, toward the corner of the graph in figure 9.

Although most synthetics contained very little Ga—and in many cases, none—a few samples (i.e., Ramaura, Knischka, and Chatham) showed Ga contents similar to those recorded in natural samples (again, see figure 6). Douros synthetic rubies have a consistently high Ga content, which is unique among both synthetic and natural rubies. In our analyses, a concentration above 0.050 wt.% Ga_2O_3 with some Fe, little or no Ti, and no V strongly indicates Douros as the source. When Ga is plotted together with V and Fe in a triangular diagram (figure 10), further distinctions can be made. The triangular V-Fe-Ga diagram shows a ratio of these three elements, rather than their actual concentrations. Many of the synthetics plot near the edges of the triangle. These samples are distributed fairly evenly between the V and Fe apexes (i.e., little or no Ga, variable Fe/V ratio), or extend halfway from Fe to the Ga apex (i.e., little or no V, variable Fe/Ga ratio with Fe>Ga). The natural samples, by contrast, are distributed throughout much of the triangle. Within the triangle, the considerable overlap in the region between the Fe and V apexes is due mostly to the Ga-enriched composition of the Douros synthetic rubies.

Synthetic rubies generally contain less Ti than

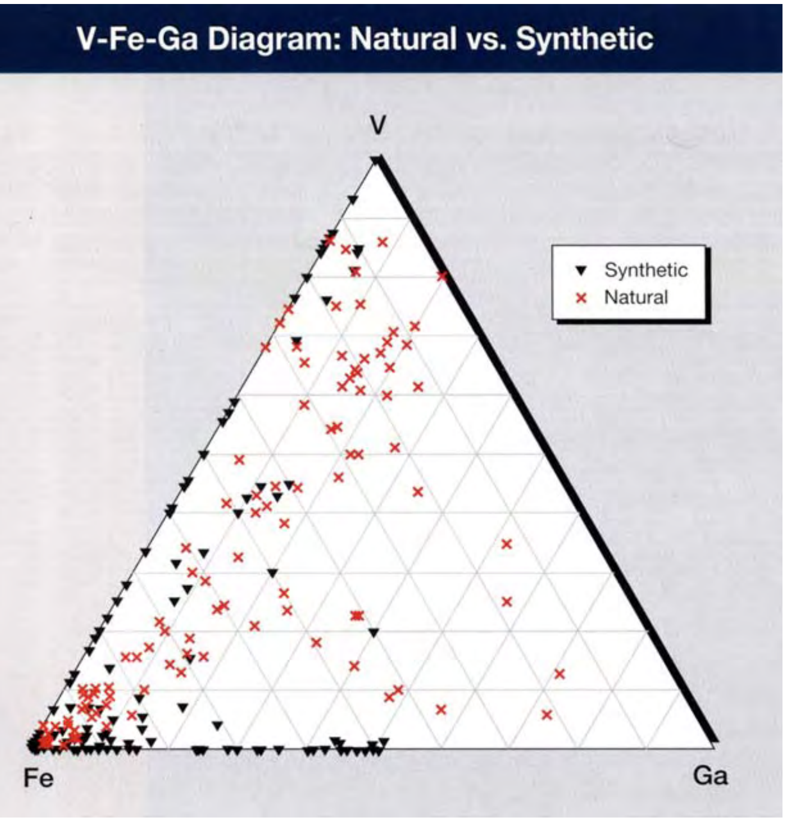


Figure 10. This triangular plot shows the ratio of the contents of V_2O_3, FeO, and Ga_2O_3 in natural and synthetic rubies. Most of the synthetics plot near the Fe apex or along the V-Fe and Fe-Ga edges, reflecting the low V and Ga contents. Natural stones plot throughout the area of the triangle, which is consistent with their more complex trace-element chemistry.

do natural rubies (again, see figure 8), although there is a large overlap between the natural stones and the flux and hydrothermal synthetics. Therefore, we did not find Ti alone useful for separating natural from synthetic rubies. Kashan synthetic rubies have a high Ti content (>0.042 wt.% TiO_2; table 4), but low V, Fe, and Ga concentrations. This distinctive chemistry makes it easy to identify most Kashan rubies by EDXRF.

We did not find Cr to be useful for separating natural from synthetic rubies. However, red diffusion-treated corundum consistently shows high to extremely high concentrations of Cr, which is diagnostic (see Box B).

Even if abundant chemical evidence is available, it is important to combine chemical data with standard gemological observations when making a ruby identification. For example, one flame-fusion synthetic contained 0.017 wt.% V_2O_3, as well as a significant amount of Ti and some Fe. Attempting to determine this ruby's origin based on trace-element chemistry alone would lead one to erroneously conclude that the sample was natural, yet curved striae were clearly visible with a microscope.

Determining the Geologic Origin of a Natural Ruby. Using EDXRF trace-element data, we could often determine the type of geologic deposit in which a stone originated, but not its specific locality (table 4). However, optical microscopy, growth structure analysis, and laser Raman microspectroscopy studies have provided useful data on the internal features that are present in rubies from various localities (see, e.g., Gübelin, 1974; Gübelin and Koivula, 1986; Delé-Dubois et al., 1993; Peretti et al., 1995; Smith, 1996). Combining EDXRF data with these other techniques can help establish the geographic origin of a sample. Our purpose here is to demonstrate how trace-element chemistry can help determine the geologic environment in which a natural ruby formed, which is one step toward identifying its geographic source (figure 11).

Basalt-Hosted Rubies. The rubies from Thailand and Cambodia contained relatively high contents of Fe and low amounts of V. Although the formation conditions of basalt-hosted rubies are not well known, the compositions of associated minerals and mineral inclusions are consistent with the Fe-rich compositional trends measured in this study. In a triangular plot of V-Fe-Ga, the basalt-hosted rubies form a tight cluster at the Fe apex (i.e., high Fe, little or no Ga or V; figure 12).

Marble-Hosted Rubies. A low Fe content characterized the rubies from Afghanistan, Myanmar, Nepal, and China (southern Yunnan), and is consistent with the Fe-deficient geochemistry of the host marbles. With the exception of Afghanistan, the marble-hosted rubies contained high amounts of V (table 4, figure 5). Elevated V contents are consistent with the fact that this element, like Cr, is concentrated into clays during weathering and the formation of residual bauxites (Wedepohl, 1978), which are thought to account for the aluminous layers in ruby-bearing marbles (see, e.g., Okrusch et al., 1976). Most of the marble-hosted rubies plot in a diagnostic area within figure 12, toward the V apex (i.e., V>Fe and V>Ga). Afghan rubies are an exception, however; because they contain relatively low V compared to Fe, some samples plot near the Fe apex.

Figure 11. In some gem markets, the geographic origin is an important consideration toward its value. EDXRF analysis can help establish the geologic origin in many cases. Shown here (clockwise from the left) are: a crystal from Mogok, Myanmar (Hixon ruby, 196.1 ct; specimen courtesy of the Los Angeles County Museum of Natural History, photo © Harold a & Erica Van Pelt), a 2.98 ct step cut from Thailand (photo © Tino Hammid), a round brilliant from Myanmar (stone courtesy of Amba Gem Corp., New York; photo © Tino Hammid), and an 8.33 ct oval brilliant from Sri Lanka (photo courtesy of ICA/Bart Curren).

Metasomatic Rubies. As one would expect from the variable composition of their host rocks, metasomatic rubies have widely varying trace-element chemistries. This was apparent in our samples. Rubies from Kenya plotted over a wide area of the V-Fe-Ga diagram (figure 12). Two of the analyses overlapped with the field of marble-hosted rubies, while the remainder of the samples plotted in a distinctive area closer to the Ga apex (i.e., Ga>Fe and Ga>V). Because of their enriched Fe content, the Umba rubies plotted within the field for basalt-hosted rubies. Overall, the variable composition of rubies from metasomatic deposits makes separation by trace elements alone ambiguous. However, if such data are combined with gemological observations (e.g., the presence of carbonate inclusions in marble-hosted rubies), then a more meaningful distinction between deposit types could be made.

CONCLUSION

Trace-element chemistry as provided by EDXRF spectrometry is effective for separating natural and synthetic rubies. It can also help determine the deposit type of a natural ruby. Because of the chemistry of the laboratory growth environment, certain trace elements are diagnostic of a synthetic product. Ni, Cu, Mo, La, W, Pt, Pb, and Bi were found only in synthetic rubies. When present, Mo, La, W, Pt, Pb, and Bi are diagnostic of flux synthetic rubies, and Ni and Cu are indicative of (Tairus) hydrothermal synthetic rubies. In those cases where these elements are not detected, the concentrations of Ti, V, Fe, and Ga provide a means for separating nearly all natural stones from synthetic rubies. Generally, the natural stones in our study contained higher concentrations of these four elements than the synthetics.

However, it is important that a sample's entire trace-element signature be considered when attempting this separation. For example, the presence of significant amounts of V should not be considered proof of natural origin, since some melt-grown synthetic rubies contained V in amounts similar to those typically seen in natural stones. Furthermore, trace-element chemistry should be used in conjunction with traditional gemological methods, because a few synthetic rubies had trace-element assemblages that suggested a natural origin.

Trace-element chemistry can also help determine the geologic origin of a sample, although for these distinctions, too, EDXRF should be used in conjunction with traditional methods such as microscopy. Rubies from basalt-hosted deposits typically contained little V and moderate to high Fe. The opposite trends were seen in rubies from mar-

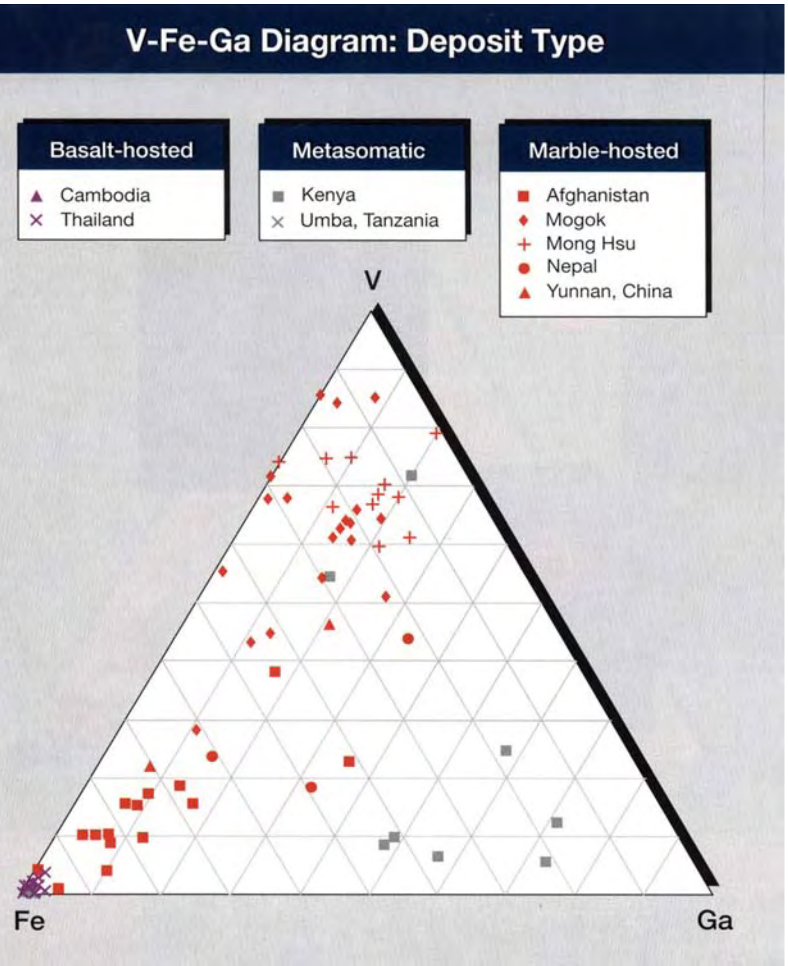


Figure 12. Natural rubies from different deposit types are plotted on this V-Fe-Ga diagram. All of the rubies from basalt-hosted deposits plot near the Fe apex, due to their high-Fe, low-V contents. Most of the marble-hosted rubies plot closer to the center of the diagram, toward the V apex; however, due to their low V contents, the marble-hosted Afghan rubies plot closer to the Fe apex. Metasomatic rubies are less systematic due to their variable growth environment: Some plotted near the Fe apex (Umba), whereas others showed a wide distribution (Kenya).

ble-hosted deposits. Rubies from metasomatic deposits, however, displayed a wide variety of trace-element chemistries, so it may be difficult to establish origin for some of these stones. Combining trace-element chemistry with traditional gemological methods, such as microscopy, will strengthen the means for determining the geographic origin of rubies.

Difficulties with separating natural from synthetic rubies using traditional gemological techniques will, in all likelihood, persist in the future, as producers continue to improve the quality of their product or possibly change the trace-element contents. As rubies from new localities, new manufacturers, or new processes are introduced to the market, they will have to be characterized to keep this database current. It should be recognized that although trace-element chemistry can correctly separate nearly all natural and synthetic rubies, it does not substitute for careful gemological measurements and observations. Rather, chemical analysis provides a useful supplement to standard gemological techniques for ruby identification.

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