A wide number of genetic models have been proposed for volcanically-transported ruby and sapphire deposits around the world. In this contribution we compare the trace element chemistry, mineral and melt inclusions, and oxygen isotope ratios in blue to reddish-violet sapphires from Yogo Gulch, Montana, USA with rubies from the Chantaburi-Trat region of Thailand and the Pailin region of Cambodia. The similarities between Thai/Cambodian rubies and Yogo sapphires suggest a common origin for gem corundum from both deposits. Specifically, we advance a model whereby sapphires and rubies formed through a peritectic melting reaction when the lamprophyre or basalts that transported the gem corundum to the surface partially melted Al-rich lower crustal rocks. Furthermore, we suggest the protolith of the rubies and sapphires was an anorthosite or, in the case of Thai/Cambodian rubies, an anorthosite subjected to higher pressures and converted into a garnet-clinopyroxenite. In this model the rubies and sapphires are rightfully considered to be xenocrysts in their host basalts or lamprophyre; however, in this scenario they are not “accidental” xenocrysts but their formation is intimately and directly linked to the magmas that transported them to the surface. The similarities in these gem corundum deposits suggests that the partial melting, non-accidental xenocryst model may be more
wide-reaching and globally important than previously realized. Importantly, in both cases the gem corundum has an ostensibly “metamorphic” trace element signature, whereas the presence of silicate melt (or magma) inclusions shows they ought to be considered to be “magmatic” rubies and sapphires. This discrepancy suggests that existing trace element discriminant diagrams intended to separate “metamorphic” from “magmatic” gem corundum ought to be used with caution.

Keywords: sapphire, ruby, Yogo Gulch, melt inclusions, corundum, gemology

Introduction:

Volcanically-hosted gem corundum deposits are widespread across the western Pacific margin (eastern Australia, southeast Asia, China, eastern Russia). There are also examples in northeast Russia, France, Slovakia, Africa, Scotland, and North and South America (see references in Giuliani et al. 2014; Hughes, 2014; Hughes et al. 2017). They mostly produce sapphires with minor ruby. However, the southeastern Asian nations of Thailand and Cambodia are important major historic producers of rubies [gem-quality corundum (α-Al₂O₃) colored red by Cr³⁺] derived from basalts. While gem production in these areas has declined significantly in recent years, these two countries were major suppliers of gem corundum (especially ruby) during the 20th century. Rubies are found here in alluvial deposits in a region spanning the southern border between Thailand and Cambodia. In Thailand, the gems fields are found in the Chanthaburi-Trat area, while in Cambodia the gem-bearing deposits are in the Pailin region. In both cases, it is generally accepted that the rubies were transported to the surface by young Cenozoic alkali basalt volcanism (<3 Ma, Barr and MacDonald, 1981; Sutthirat et al. 1994). Yet, it is also accepted that the rubies are xenocrysts within the basalts and were transported from somewhere deep within the Earth. Genetic models for Thai/Cambodian rubies generally suggest they formed through high pressure metamorphism of (ultra)mafic rocks (Sutthirat et al. 2001; Saminpanya and Sutherland 2011). These gemfields have also produced a significant quantity of blue sapphires (gem-quality corundum colored by
Fe and Ti), which have distinct inclusion suites and trace element chemistry patterns indicating a
different origin than the rubies. The Thai and Cambodian gem fields are generally very similar to other
alluvial sapphire deposits associated with alkali basalt fields across the western Pacific margin. The main
difference is the generally higher proportion of rubies found in Thailand and Cambodia relative to other
major producers of gem corundum like Australia, which produce predominantly blue, green, and yellow
sapphires (Graham et al. 2008). This study focuses only on Thai/Cambodian rubies, whereas sapphires
from that region are not discussed. While many studies of ruby deposits focus on either the Chathaburi-
Trat area in Thailand or the Pailin region in Cambodia, it is widely recognized that both gem-producing
regions are essentially one single deposit straddling the border between the two countries. The rubies
found in both countries are generally indistinguishable in terms of their trace element chemistry and
inclusions suites, so in the rest of this contribution we will refer to these rubies simply as
Thai/Cambodian rubies without distinguishing between the two.

Nearly on the other side of the world in Montana, USA is the Yogo Gulch sapphire deposit. Yogo
sapphires are found in a primary deposit and are embedded in a lamprophyre dike. Similar to
Thai/Cambodian rubies, Yogo sapphires were transported to the surface from somewhere deep within
the Earth by this lamprophyre and they are considered to be xenocrysts in the dike. The Yogo
lamprophyre is properly classified as a ouachitite and has been dated at 48.2 Ma (Gauthier 1995). Yogo
sapphires are revered for their cornflower blue color, although a small proportion of sapphires are
enriched in Cr and veer into the domain of violet sapphires to the rare red Yogo rubies.

What exactly do these seemingly disparate deposits of gem corundum have in common?
Besides the fact that Thai/Cambodian rubies and Yogo sapphires were transported to the surface by
relatively recent Cenozoic volcanism, on the surface there doesn’t appear to be much linking them.
Thai/Cambodian rubies are generally considered to have a “metamorphic” origin based on their trace
element chemistry and inclusion suites (Sutthirat et al. 2001; Sutherland et al. 2002, 2003, 2008;
Saminpanya and Sutherland 2011). Yogo sapphires also have “metamorphic” trace element chemistry; however, Palke et al. (2016) noted the presence of Na- and Ca-rich glassy melt inclusions in Yogo sapphires, which suggest a magmatic origin instead. Based on their analysis, it was proposed that these sapphires formed through partial melting of an anorthite-plagioclase-rich protolith such as a troctolite or anorthosite when the Yogo lamprophyre intruded and temporarily pooled at the base of the crust. Importantly, melt inclusions have been reported in Thai/Cambodian rubies (Gübelin and Koivula 2008) which also suggests a magmatic origin for this deposit. The similar mineralogical and gemological properties of gem corundum from Yogo Gulch and Thailand/Cambodia was also recognized by Hughes et al. (2017) who suggested that these sapphires and rubies may have a similar origin. Hughes et al. (2017) noted similarities in their inclusion suites and the morphology of rough crystals. This study will analyze melt inclusions and trace element compositions of Thai/Cambodian rubies in order to test the hypothesis that they have a common genetic origin involving partial melting of an Al-rich protolith when basaltic or lamphyric magma intruded into or near the base of the crust. While this model has been proposed already for sapphires from Montana (Palke et al. 2016, 2017), its likely involvement in two seemingly unrelated deposits formed during different geological events suggests that this may be a more wide-reaching model for ruby and sapphire genesis than previously realized.

Analytical Methods:

Electron Probe MicroAnalysis

Electron Probe MicroAnalysis (EPMA) was performed at Caltech on a JEOL JXA-8200 with an accelerating voltage of 15 kV and a defocused beam of 10 μm and 10 nA to avoid alkali migration. When possible, melt inclusions were analyzed in several clean spots on a single inclusion with a reduced beam current of 5 nA or 2.5 nA. In all cases, repeat analyses with lower current gave identical results suggesting that alkali migration is not a problem for these glasses even with conditions of 10 μm and 10
nA. Standards include rhyolite glass VG-568 (Si), TiO$_2$ (Ti), anorthite (Al, Ca), fayalite (Fe), olivine (Mg), albite (Na), and microcline (K) with basaltic glass VG-2 used as a secondary standard. Errors are generally <2% for major elements and <10% for minor elements.

**Raman Spectroscopy**

Mineral inclusions were identified using Raman spectroscopy at the Gemological Institute of America (GIA) in Carlsbad, CA collected with a Renishaw inVia Raman microscope system. The Raman spectra of the inclusions were excited by a Stellar-REN Modu Ar-ion laser at 514 nm and collected at a nominal resolution of 3 cm$^{-1}$ in the 2000–200 cm$^{-1}$ range. Each spectrum of the inclusions was accumulated three times for 10 s each at 20× or 50× magnification. Confocal optics allowed inclusions beneath the surface to be analyzed without having to polish through the inclusion and without significant interference from the host corundum.

**LA-ICP-MS analysis**

LA–ICP–MS sapphire analyses were performed at GIA Carlsbad, CA on a Thermo Scientific iCap-Q ICP–MS with plasma rf power of 1400 W coupled with a New Wave Research UP-213 laser ablation unit with a frequency-quintupled Nd:YAG laser (213 nm wavelength with 4 ns pulse width). A laser spot-size of 55 µm was used with a fluence of 10±1 J/cm$^2$ and 15 Hz repetition rate. NIST 610 and 612 glasses were used for standardization using $^{27}$Al as an internal standard. Isotopes measured are $^{24}$Mg, $^{47}$Ti, $^{51}$V, $^{52}$Cr, $^{57}$Fe, $^{71}$Ga. Additional LA–ICP–MS core and rim analyses were performed on seven blue Yogo sapphires and two reddish-violet Yogo sapphires using a New Wave Excimer laser ablation system at the Queensland University of Technology following a modified procedure from Wong et al. (2017). A laser spot-size of 100 µm was used with a fluence of 2.5 (J/cm$^2$) and 7 Hz repetition rate. Data were processed using the software package, Iolite (Paton et al. 2011), based on the calculation style of Longerich et al. (1996), using the same reference materials and internal standards as mentioned above. Detection limits are reported in **Table 2** and relative standard deviations are generally <5% for all isotopes.
Oxygen Isotope Measurements

Oxygen isotopic measurements of the same seven blue Yogo sapphires and two reddish-violet Yogo sapphires were carried out with the Sensitive High Resolution Ion Microprobe – Stable Isotopes (SHRIMP-SI) at the Research School of Earth Sciences, Australian National University. Yogo sapphire crystals were mounted in conventional 1-inch epoxy mounts and ground to expose cross sections of the crystals, then polished to 1 micron diamond paste. The polished mounts were cleaned and coated with 30nm of gold, then loaded into a steel holder. SHRIMP-SI measurements were performed with a Cs+ primary beam of ~ 2 nA, 15 keV, focused to sputter an area of ~ 20 x 30 μm. Negative secondary ions were extracted and accelerated through a total of 10 kV, and 16O− and 18O− were measured simultaneously on Faraday cups. The electrometers measuring 16O− and 18O− were set to 10^11 Ω (50V range) and 10^11 Ω (5V range), respectively. Charge neutralization of the sample surface was achieved using a focused oblique-incidence, high energy electron gun. Electrons were delivered to the target surface with an energy of ~ -1.8 keV. Analyses were corrected for isotopically fractionated electron-induced secondary ion emission (Ickert et al., 2008). For the oxygen isotope measurements presented here the collector slit widths were set at 400 μm for 16O− and 300 μm for 18O−. Typical count rates on 16O− were ~ 1.6 – 2.0 × 10^9 cps, and on 18O− about 3.3 – 4.0 × 10^6 cps. Each analysis took about 6 min and consisted of 120 s of presputtering, ~ 100 s of automated steering of secondary ions, ~ 5 s of automated centering of the secondary ions in the collector slits with magnet control, and 120 s of data collection, which consisted of 1 set of 6 scans, 20 s each, with each scan comprising ten 2 s integrations. Isotopic ratios have been corrected for instrumental mass fractionation by applying a correction factor calculated from the analyses of a synthetic corundum reference material with known 18O/16O ratio (δ18O = -6.1 ± 0.3‰). Background counts were subtracted from the total counts (16O and 18O mass positions) prior to ratio calculation. The corrected 18O/16O ratios are then expressed in standard δ18O notation in
permil (‰) relative to VSMOW. The internal precision of δ¹⁸O of individual measurements was typically
0.1–0.3 ‰ (2SE). The reproducibility of δ¹⁸O was ca. 0.2 ‰ (1SD).

Oxygen isotope compositions of the synthetic corundum reference material were measured by
laser fluorination (LF) at GNS Science, New Zealand (Analyst: Dr. Jannine Cooper). Oxygen was extracted
from sample powders for isotope analyses using a CO₂-laser and BrF₅ (Sharp, 1990). Samples and
standards were heated overnight to 150°C prior to loading into the vacuum extraction line. These were
then evacuated for approximately 6 hours. Blank BrF₅ runs were done until yield was less than 0.2 moles
oxygen. Oxygen yields were recorded and CO₂ gas analysed on a Geo20-20 mass spectrometer. Samples
were normalized to the international quartz standard NBS-28 using a value of +9.6 ‰. Values for NBS-28
analysed with the samples had values that varied by less than 0.15 ‰. Five analyses gave an average
δ¹⁸O value of -6.1 ± 0.3‰ for the synthetic corundum reference material.

Sample Description

Sapphires and rubies analyzed here were from the collections of Nathan Renfro of the
Gemological Institute of America and from Will Heierman of Earth’s Treasures, or from the Gemological
Institute of America’s reference collection which was collected in the field by Vincent Pardieu of the
Gemological Institute of America. Synthetic ruby standards were purchased from Aussie Sapphire
Lapidary Warehouse. All samples analyzed were small (usually <5 mm), gem quality, transparent rubies
and sapphires. Samples analyzed in this study include 14 rubies from Pailin, Cambodia, 10 rubies from
Chantaburi-Trat, Thailand, and 44 sapphires from Yogo Gulch, Montana, USA. Samples from Yogo Gulch
were generally flat, tabular hexagonal prisms while those from Thailand and Cambodia tended to be
rounded to angular fragments not showing any crystal faces. Note, the color of the sapphires from Yogo
Gulch generally ranged from light, cornflower blue to violet to reddish-violet to (rarely) red. The latter
variety ought to bear the moniker “ruby”; however, the color of these samples seems to vary
continuously from blue to violet to red with concomitant continuous variations in chemistry. Given that there are no clear-cut boundaries for the boundary between reddish-violet sapphire and ruby, we have opted to simply not use the term “ruby” for gem corundum from Yogo. Instead, we will refer to (blue) sapphires and reddish-violet sapphires from Yogo. This is a reasonable solution since the color of this gem corundum is not the focus of this manuscript. We generally placed three LA-ICP-MS spots on each sample but some samples had more than three spots. See Supplementary Table S1 for the full analyses.

Results and Discussion:

Trace Element Chemistry

The trace element chemistry measured by LA–ICP–MS analysis is summarized in Table 1 with full results in Table S1 in the data depository. Plots of the full analyses are shown in Figures 1–4. In these plots the Thai and Cambodian rubies were grouped together for simplicity as they have overlapping trace element signatures. These plots show, in general, the broadly similar trace element chemistry of Thai/Cambodian rubies and Yogo sapphires. In summary, Thai rubies have an average of 150 ppm Mg, 148 ppm Ti, 2986 ppm Fe, and 26 ppm Ga, Cambodian rubies have an average of 129 ppm Mg, 136 ppm Ti, 2957 ppm Fe, and 24 ppm Ga, while Yogo sapphires have an average of 128 ppm Mg, 215 ppm Ti, 3219 ppm Fe, and 47 ppm Ga. The concentration of Cr is much more variable than the other trace elements here ranging from 450-7761 ppm in Thai rubies (median = 2410 ppm), 955-2856 ppm in Cambodian rubies (median = 2123 ppm), and 2-12590 ppm in Yogo sapphires (median = 286). However, note that Cr-rich Yogo samples were deliberately oversampled here for the sake of comparison with Thai/Cambodian rubies. Table 1 also provides several elemental ratios used to separate “magmatic” from “metamorphic” sapphires such as Ga/Mg, Ga*/Al (= 10,000×Ga/Al), Cr/Ga, and Fe/Ti. Overall, the chemistry of gem corundum from these two deposits is largely similar relative to other worldwide gem corundum deposits (e.g. Peucat et al. 2007) with high values of Mg, relatively high Fe, and relatively low
values of Ga. Nonetheless, Figure 4a–b clearly shows that sapphires and rubies from these deposits can be confidently separated based on their relative concentrations of Mg, Ga, and Ti. The most obvious distinction is the overall higher concentrations of Ga in Yogo sapphires and higher concentrations of Mg relative to Ti in Thai/Cambodian rubies (Figure 4b). The latter relationship is important as the co-substitution of Mg$^{2+}$ and Ti$^{4+}$ for two Al$^{3+}$ cations is likely the most important mechanism for incorporation of both Mg and Ti in ruby and sapphire. Both of these relationships are also apparent in Figures 1–2.

Figures 1–3 also show trace element data in relation to various discriminant diagrams developed by researchers (Sutherland et al. 1998; Peucat et al. 2007) to differentiate between “magmatic” and “metamorphic” sapphires and rubies. Thai/Cambodian rubies and Yogo sapphires generally show an affinity for the “metamorphic” fields in these diagrams. The main difference in trace element chemistry is in the Cr content (Figure 3). This is, of course, related to the fact that only rubies (red Cr-bearing gem corundum) were analyzed from Thailand and Cambodia while a range of colored gem corundum from blue to reddish-violet was analyzed from the Yogo Gulch deposit. This is illustrated most clearly in Figure 3, which plots Fe/Ti against Cr/Ga and shows a continuous variation in Cr/Ga values for Yogo sapphires from values close to those of Thai/Cambodian rubies down to very low Cr/Ga values. Note that Yogo sapphires cross over into the “magmatic” domain defined in Figure 3. It is frequently assumed that Cr-enrichment in gem corundum is indicative of a metamorphic genesis rather than a magmatic origin. However, the continuous and seamless variation from ostensibly “magmatic” blue to “metamorphic” reddish-violet sapphires from Yogo Gulch suggests that Cr-enrichment is not diagnostic of a metamorphic origin. In fact, the presence of silicate melt inclusions in blue sapphires and reddish-violet sapphires from Yogo and rubies from Thailand and Cambodia suggests that they all ought to be considered as magmatic rubies and sapphires irrespective of their Cr concentrations.
One of the most commonly used trace element discriminants to distinguish between magmatic and metamorphic gem corundum is the overall Ga concentrations and the Ga/Mg ratio. In general, gem corundum with low values of Ga (<100 ppm) and Ga/Mg < 3 are considered to have a “metamorphic” origin and high Ga (>100 ppm) and Ga/Mg > 3 is considered to suggest a “magmatic” origin. The 100×Mg–10×Ti–Fe ternary is also used where higher Mg values indicate a metamorphic origin and higher Fe values a magmatic origin. Nonetheless, the gem corundum studied here is generally classified as “metamorphic” except for a small proportion of analyses plotting in the magmatic field in the Cr/Ga vs. Fe/Ti diagram (Figure 3). As proposed above, the silicate melt inclusions in these rubies and sapphires suggest that it is reasonable to consider them to have a magmatic origin. It seems, then, that the problem of differentiating between magmatic and metamorphic sapphires through trace element chemistry ought to be revisited.

Finally, one discriminant plot that is becoming more widely accepted is the FeO+TiO$_2$+Ga$_2$O$_3$ vs. FeO-MgO-V$_2$O$_3$-Cr$_2$O$_3$ plot of Giuliani et al. (2015). Thai/Cambodian rubies and Yogo sapphires generally lie in the “ruby in mafic-ultramafics” field in this plot (Figure 4c). This is generally consistent with our model considering that basic rocks such as anorthosites are commonly genetically similar to mafic-ultramafics. The usefulness of this discriminant diagram may lie in its classification based on the likely composition of the protolith to the gem corundum and its avoidance of attempting to determine magmatic vs. metamorphic origin from trace elements. Note, however, that many Yogo sapphires and some Thai/Cambodian rubies also lie in the “corundum in metasomatite” field which clearly would not be an accurate classification.

**Melt Inclusions**

Glassy melt inclusions are found frequently in Thai and Cambodian rubies (Gübelin and Koivula 2008). They are identified by their negative-crystal morphology imposed on the inclusion by the
corundum crystal lattice and by the presence of a spherical contraction bubble (Figure 5a). Glassy melt inclusions are generally 25–100 µm in size. Also observed are larger light-colored, opaque inclusions that have a negative-crystal morphology defined by the corundum crystal lattice. These inclusions generally range from 200–500 µm in size and have a “sugary” appearance suggesting they are polycrystalline aggregates (Figure 5b). The negative-crystal morphology of these larger inclusions suggests that they are also melt inclusions that recrystallized after entrainment in the corundum.

Melt inclusions are observed in blue sapphires from Yogo Gulch, MT as reported previously by Palke et al. (2016). Glassy melt inclusions in Yogo sapphires are <50 µm and are generally smaller than in the Thai and Cambodian rubies. Nonetheless, these inclusions are also typified by their negative crystal morphology and contraction bubble (Figure 5c). Larger negative-crystal-shaped, light-colored, opaque inclusions are seen in Yogo sapphires as well and are also interpreted to represent recrystallized melt inclusions (Figure 5d). Gübelin and Koivula (2008) and Palke et al. (2016) reported the presence of multiphase analcime and calcite inclusions in Yogo sapphires. The inclusions identified by Palke et al. (2016) were negative-crystal shaped, light-colored inclusions that were interpreted to be recrystallized melt inclusions as described above. Palke et al. (2016) further suggested that these larger recrystallized melt inclusions may simply be larger, recrystallized versions of the smaller glassy silicate melt inclusions. However, further consideration of the mineralogical composition of these analcime/calcite melt inclusions suggests that it is unlikely that they have the same bulk composition as the smaller silicate glass inclusions. Palke et al. (2017) suggested that these larger, recrystallized melt inclusions and the smaller glassy melt inclusions actually represent immiscible silicate and carbonatite melts produced during the partial melting event that produced the corundum. Similar bimodal melt inclusion suites have been noted in peritectic garnet produced during partial melting events (Ferrero et al. 2016). The larger recrystallized melt inclusions in Thai/Cambodian rubies may also indicate that rubies crystallized in the...
presence of immiscible silicate and carbonatite melts during a partial melting event although further work is required to analyze the mineralogy of these inclusions.

While the rarity of Cr-rich gem corundum from Yogo Gulch, MT made it difficult to make microscopic observations on a statistically large population of reddish-violet sapphires, one glassy melt inclusion was observed in a deep red Yogo ruby. This sample was prepared for EPMA measurements on the glassy melt inclusion in addition to melt inclusions in one ruby from Thailand and Cambodia each. The results of these analyses are shown in Table 2 in addition to the results from Palke et al. (2016) for blue sapphires from Yogo Gulch, MT. The melt inclusions in all cases are broadly similar in composition with SiO$_2$ ranging from 53.4 to 60.5 wt.%, Al$_2$O$_3$ from 20.6 to 24.0 wt.%, and are moderately enriched in CaO and Na$_2$O from 4.9 to 6.2 wt.% and 4.3 to 5.2 wt.%, respectively. In general, melt inclusions have relatively low concentrations of TiO$_2$ (0.1–0.4 wt.%), MgO and FeO$_{tot}$ (0.4–1.9 wt.% each), and K$_2$O (0.1–1.7 wt.%), with the exception of the Cambodian ruby with 3.1 wt.% K$_2$O. The higher CaO content of these melt inclusions makes them distinct from the low-CaO syenitic or phonolitic melt inclusions measured in classical blue-green-yellow basalt-related sapphires (Izokh et al. 2010; Baldwin et al. 2017).

Dissolved volatile concentrations can be measured as the difference in oxide totals from 100 wt.% (Table 2). For blue Yogo sapphires average volatile content in the melt inclusions are 9.0 wt%, the melt inclusions in the Yogo ruby, Thai ruby, and Cambodian ruby studied here have 6.7, 6.3, and 7.5 wt.% dissolved volatiles, consistently lower than for the Yogo blue sapphires. Overall, the melt inclusions in Yogo sapphires and the preliminary sampling of Yogo, Thai, and Cambodian rubies studied here have broadly similar compositions.

Mineral Inclusions

The most common mineral inclusions in Yogo sapphires are plagioclase feldspar, garnet, and blocky to columnar rutile (i.e. not needle-like or “silky” rutile). Less frequently, apatite, phlogopite, and
zircon have been reported (Gübelin and Koivula 2008; Palke et al. 2016). Analcime and/or calcite
inclusions are reported in Yogo sapphires; however, as described above these are likely multiphase
inclusions that represent recrystallized melt inclusions and are not primary analcime and/or calcite
inclusions.

In this study the most commonly observed mineral inclusion in Thai and Cambodian rubies is
clinopyroxene with occasional identification of garnet inclusions. Plagioclase feldspar has also been
identified as an inclusion in Thai/Cambodian rubies (Sutherland et al. 1998; Hughes et al. 2017);
however, the absence of plagioclase inclusions in this study suggests they are less common than
clinopyroxene and garnet inclusions. More rarely, but perhaps more importantly for the genetic model
that will be outlined below, sapphirine has been reported as an inclusion in Thai rubies (Koivula and
Fryer, 1987; Sutthirat et al. 2001; Saminpanya and Sutherland, 2011; Khamloet et al. 2014).

Oxygen isotopes

Previous $\delta^{18}$O measurements for ruby from Cambodia gave a range of 2.4 to 4.9 ‰ (Giuliani et
al. 2005) while Yui et al. (2006) reported $\delta^{18}$O values of 1.3 to 4.2 ‰ for rubies from Thailand.
Furthermore, Giuliani et al. (2005) measured $\delta^{18}$O values of 5.4 to 6.8 ‰ for Yogo sapphires. Additional
oxygen isotope data was collected on a small suite of blue to reddish-violet Yogo sapphires in this study
and the results are shown in Figure 6. This new data significantly increases the range of $\delta^{18}$O values for
Yogo sapphires to 4.5-7.7 ‰. Note also that the two reddish-violet sapphires analyzed here have a lower
range of $\delta^{18}$O from 4.5 to 5.4 ‰ while the blue to violetish-blue sapphires range from 5.7 to 7.7 ‰. LA-
ICP-MS data were also collected on these samples with the ablation pits placed as close as possible to
the spots analyzed by SHRIMP for a comparison between trace element and oxygen isotope data. The
full results of our oxygen isotope analyses and the additional accompanying LA-ICP-MS data are
contained in Table S2 in the data depository. $\delta^{18}$O of the Yogo sapphires show a generally negative
correlation with Cr and Mg, and positive correlation with Ga (Figure 6). However, note that the sample size analyzed here is relatively small and the nature of the correlation (linear correlation or otherwise) cannot be determined. Core to rim measurements were made on several samples. The sapphires analyzed are generally homogeneous in their oxygen isotope compositions from core to rim which has been noted before in other cases (e.g. Yui, et al. 2003; Sutherland, et al. 2017).

The Genetic Model

Palke et al. (2016) argued that the Na- and Ca-rich melt inclusions in Yogo sapphires suggest corundum formation during partial melting of hydrated and carbonated lower crustal anorthosites or troctolites by local intrusion of the lamprophyre that eventually transported the sapphires to the surface. Anorthite-plagioclase-rich rocks such as anorthosites are likely candidates as they are sufficiently Al-rich to form corundum during partial melting and Ca-rich enough to explain the relatively high CaO concentrations in the glassy melt inclusions. Anorthosites or similar rocks are also reasonable protoliths as they are relatively rare in the Earth (e.g. Ashwal 1993). Given the rarity of sapphire and ruby deposits, it is almost necessary that the rocks producing them are similarly rare. This conclusion rested largely on the similarity between globular, light-color structures (leucocratic ocelli) composed of analcime and calcite in the Yogo lamprophyre and the analcime- and calcite-bearing inclusions in sapphires, which were interpreted to be crystallized melt inclusions. It was argued that the leucocratic ocelli and the melt inclusions had a common origin through partial melting of a precursor, hydrated and carbonated anorthosite (although as argued above these likely represent a carbonatite melt that was immiscible in the silicate melt represented by the smaller glassy melt inclusions). Palke et al. (2016) also modeled this process using the MELTS package and suggested specifically that corundum can grow during such a process through an incongruent melting reaction of another Al-rich mineral such as kyanite.
The similarity in trace element chemistry and melt inclusion compositions for Thai/Cambodian rubies and Yogo sapphires suggests these gem corundum deposits may have been produced through similar geological processes (i.e. corundum formation through partial melting of an anorthosite, although note our discussion of nomenclatural issues for anorthosites below). One argument against this hypothesis is that the inclusion suites in the gem corundum vary between the two deposits. Garnets and melt inclusions occur in both cases but Yogo sapphires commonly have plagioclase and rutile with rare apatite and zircon inclusions while Thai/Cambodian rubies host dominantly clinopyroxene with less common garnet, plagioclase, and sapphirine inclusions. On face value this appears to discredit the hypothesis of a common origin. However, taking a simple approach and considering the melting relations in the forsterite-anorthite-quartz ternary (at 2.0 GPa, Liu and Presnall 1990) suggests a way forward. In this diagram (Figure 7) there exists a field for corundum (Co) near the anorthite apex. A super-liquidus melt with its bulk composition in this corundum field will crystallize corundum at the liquidus. However, this corundum will incongruently react with the liquid upon further cooling to crystallize anorthite. Note that in this system corundum will not persist as a sub-solidus mineral in the case of equilibrium crystallization. Alternatively, if we start to melt a solid rock with the same bulk composition in this corundum field, we would see corundum start to crystallize through an incongruent melting reaction once the liquid reached the corundum field.

We can illustrate how one might produce two different inclusion suites by slightly altering the bulk composition. We take two different hypothetical protoliths with overall similar bulk compositions lying in the corundum field of the An-Fo-Qz ternary at 2.0 GPa (Figure 7), but with one being more enriched in a forsterite component and the other being more enriched in a quartz component (i.e. one more mafic and one more felsic). Note that both compositions roughly represent an anorthosite protolith. The more felsic anorthosite was chosen to be composed of dominantly anorthite and equal components of quartz and enstatite at subsolidus conditions. The first melt occurs at point E which also

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has nearly equal amounts of an enstatite and quartz component. Therefore, after the melting has consumed all the enstatite and quartz, the liquid will leave point E on a projection toward the anorthite apex (blue path, Figure 7). Once the liquid reaches the boundary between anorthite and corundum, the leftover anorthite will melt incongruently to produce corundum. If the corundum produced in this way could be preserved, the dominant mineral inclusion in corundum would be anorthite. The more mafic protolith was chosen to be composed of dominantly anorthite with minor enstatite and only a small amount of quartz at subsolidus conditions. In this case, the first liquid is also at E but quartz will be consumed quickly and the liquid will evolve along the enstatite-anorthite join (red path, Figure 7). When the liquid meets the anorthite-enstatite-sapphirine point, sapphirine will crystallize. At this point enstatite will fully melt and the liquid will evolve along the sapphirine-anorthite join. As in the case above, once the liquid reaches the boundary with corundum, anorthite will melt incongruently to produce corundum. In this scenario, coexisting sapphirine could become included in the resulting corundum in addition to anorthite. In fact, a recent study by Karmakar et al. (2017) provides some petrological evidence that this is a plausible scenario. In that study, Karmakar et al. (2017) interpreted corundum coexisting with sapphirine to have been formed during incongruent melting of a hydrated anorthosite.

Obviously this simplified three component model cannot fully explain all of the observations for gem corundum from these deposits. For one thing, the relatively Na$_2$O-enriched melt inclusions suggest that Na$_2$O was likely an important component in sapphire and ruby genesis. Additionally, the presence of clinopyroxene and garnet inclusions is obviously not accounted for in the simple forsterite-anorthite-quartz ternary. Furthermore, the volatile-enriched melt inclusions also suggest that H$_2$O and/or CO$_2$ were essential components in the processes that formed sapphire and ruby and their involvement will undoubtedly alter the phase diagram shown in the An-Fo-Qz ternary in Figure 7. Nonetheless, this simple system can qualitatively show how significantly different inclusion suites in gem corundum might
be generated through the same geological process (partial melting of an anorthosite) due only to relatively small differences in bulk composition.

In fact, this model may also help explain differences in trace element chemistry between these two deposits. For instance, it could be argued that a more mafic protolith should have been involved in Thailand and Cambodia in order to supply Cr for the rubies produced there. The relatively rare occurrence of ruby and violet sapphires in Yogo Gulch, then, suggests that the protolith there was predominantly more felsic but perhaps with some more mafic enclaves that locally supplied Cr to the gem corundum. A more mafic protolith for the reddish-violet sapphires from Yogo is also supported by their lower $\delta^{18}$O (from 4.5 to 5.4 ‰). The overall lower Ga content of rubies from Thailand and Cambodia also suggests a more mafic protolith as Shaw (1957) has shown that ratios of Ga*/Al (=$10,000\times\text{Ga}/\text{Al}$) are lower for “basic igneous” rocks (0.6–1.7) than for “granitic and alkalic” igneous rocks (0.9–4.5). Finally, the higher average concentration of Mg in Thai/Cambodian rubies is also consistent with the involvement of a more mafic protolith. Notably, trace element vs. oxygen isotope ratio patterns also corroborate this narrative with higher Mg and Cr and lower Ga evidently correlated with the lower $\delta^{18}$O in Figures 6b–d.

One problem with this model is the lower frequency of plagioclase inclusions in rubies from Thailand and Cambodia than for Yogo sapphires. If Thai/Cambodian rubies were derived from the partial melting of an anorthosite (i.e. a plagioclase-dominant igneous rock) one would expect to find plagioclase as a common inclusion. One possible explanation may be that the Thai and Cambodian rubies originated at higher pressures deeper within the Earth. In this case, it may be possible that Thai and Cambodian rubies originated from partially melting a rock that was initially an anorthosite, but which was subducted and buried deep within the Earth to pressures at which plagioclase feldspar was less stable and largely replaced by other phases such as clinopyroxene and garnet. In fact, Kornprobst et al. (1990), Morishita et al. (2001), and Gysi et al. (2011) have described corundum-bearing garnet clinopyroxenites in
peridotite bodies and have interpreted these to represent original plagioclase-rich gabbros that were
subsequently buried and converted to garnet clinopyroxenites at high pressures. Note that in all cases
sapphirine was found as a minor constituent as well (although not necessarily in direct contact with
corundum). Additionally, Raheim and Green (1974) used experimental petrology to show that an
originally gabbroic anorthosite protolith corresponding to some lunar highland basalts could be
converted to an assemblage of garnet + clinopyroxene + kyanite + quartz at high pressures of around 2.0
GPa. Raheim and Green (1974) also showed that in this system corundum would be produced as a
supersolidus phase from this assemblage through an incongruent melting reaction but would not exist
below the solidus. It is likely, then, that the Thai and Cambodian rubies were derived from a high-
pressure clinopyroxenite that was, in turn, derived from a similar (but possibly more mafic) anorthositic
protolith as sapphires from Yogo Gulch. In our model, we suggest that the protolith involved in sapphire
and/or ruby formation was initially an anorthosite emplaced near the base of the continental crust
during ancient (Yogo, Palke et al. 2016) or more modern subduction events (Thailand/Cambodia). In this
case, a higher pressure of formation for Thai and Cambodian rubies agrees well with estimates of crustal
thickness in the region of the ruby mines in Thailand (50–60 km, Promprated et al. 2003) compared to
estimates for crustal thickness in central Montana (around 40 km, Mahan et al. 2012; Purevsuren 2014).

A note on nomenclature

We suggested above an origin for Yogo sapphires and Thai/Cambodian rubies from partial
melting of anorthosites. Strictly speaking, using the accepted nomenclature of Streckeisen (1976),
anorthosites are igneous rocks composed of >90 % plagioclase. Other plagioclase-rich plutonic rocks
include leucotroctolites and leucogabbros (>65 % plagioclase with the remainder as mafic minerals).
Ashwal (1993) further subdivided leucogabbros and leucotroctolites into varieties with >77.5 %
plagioclase being labelled “gabbroic anorthosites” and “troctolitic anorthosites” and from 65-77.5 %
plagioclase as “anorthositic gabbros” and “anorthositic troctolites”. Note that the hypothetical protoliths from Figure 7 would not strictly be considered as “anorthosites” but rather gabbroic or troctolitic anorthosites according to Ashwal (1993). However, as a matter of convenience and clarity, the term “anorthosite” is used somewhat loosely here to denote plagioclase-dominant rocks including gabbroic or troctolitic anorthosites and possibly even anorthositic troctolites or gabbros.

What do the oxygen isotope data say?

Palke et al. (2016) noted that the range in δ¹⁸O values for Yogo sapphires (new data here extends it to 4.5 to 7.7 ‰) is within the range given by Kempton and Harmon (1992) of 5.4 to 13.5 ‰ for lower crustal xenoliths. Similarly, δ¹⁸O values for plagioclase from mantle-related anorthosites range from 5.8 to 7.6 ‰ or 7.7 to 12.1 ‰ (Taylor 1968) for plagioclase from Proterozoic anorthosites from Quebec which are assumed to have involved some degree of crustal assimilation (Peck and Valley 2000). These ranges seem to be at odds with the lower range of δ¹⁸O values from 1.3 to 4.9 ‰ for Thai/Cambodian rubies. However, it should be noted that little is actually known about oxygen isotope fractionation factors between corundum and a silicate melt or other buffering fluids/minerals. Assuming an anorthositic protolith was involved in the formation of Thai/Cambodian rubies but that it was metamorphosed into a clinopyroxenite, as a first approximation we can use the calculated mineral-water fractionation factors of Zheng (1991) and Zheng (1993) to derive a fractionation of 4.2 ‰ between diopside and corundum at 850 °C with corundum being isotopically lighter [temperature of 850 °C chosen to correspond to formation conditions as suggested by Palke et al. (2016)]. In this case, even the very lowest δ¹⁸O value of 1.3 ‰ for Thai ruby would be in equilibrium with diopside with δ¹⁸O of 5.5 ‰, which is right at the lower range for lower crustal xenoliths given by Kempton and Harmon (1992) and anorthosites from Taylor (1968). It should be noted, however, that clinopyroxene from a high-pressure metamorphosed anorthosite is likely to be quite Al-rich involving a significant Ca-Tschermak...
(CaTS) component (CaAl$_2$SiO$_6$) and so the use of a fractionation factor between diopside and corundum is a very rough approximation.

**Implications:**

Gem corundum as xenocrysts but not “accidental” xenocrysts

One of the more important conclusions from this work is that these sapphires and rubies are considered xenocrysts in their volcanic hosts, but they are not “accidental” xenocrysts as their formation is directly related to the interaction between the transporting mafic magmas and Al-rich (but corundum free) lower crustal protoliths. If the sapphires and rubies were, in fact, “accidentally” entrained, this would require a significant portion of the Earth’s lower crust or upper mantle to be corundum-bearing in areas hosting large basalt-related sapphire and ruby deposits (e.g. eastern Australia and southeast Asia).

On the other hand, in the partial melting model, the preexistence of corundum is not necessary as basalts can generate corundum by partially melting Al-rich rocks as they pass through the lithosphere. This model suggests that not all xenocrysts necessarily represent faithful records of the formations that magmas pass through on their journey to the Earth’s surface. In fact, it is known that other peraluminous minerals such as garnet also often grow during incongruent melting reactions when crustal rocks are partially melted (Cesare et al. 2011). Given the close association between gem corundum deposits and hot, mantle-derived volcanics, this partial melting model is intuitively appealing and ought to be considered as a possible origin of other volcanically-associated sapphire and ruby deposits, even those that are obviously distinct from the Yogo and Thai/Cambodian gem corundum (e.g. the eastern Australian blue-green-yellow [BGY] suite of alkali basalt-related sapphires).
Comparison to eastern Australian rubies

For eastern Australian alluvial sapphires and rubies, the distinction of ‘magmatic’ and
‘metamorphic’ sources through trace elemental ratios have already been questioned, due to the finding
of a continuous spectrum of trace elemental compositions by Wong et al. (2017). Eastern Australian
sapphires are generally associated with a ‘magmatic’ origin, whereas rubies have been associated with a
‘metamorphic’ source. Similarities between Thai/Cambodian rubies and eastern Australian rubies
suggest that Australian alkali basalt-related rubies may have been formed by magmatic processes as
well. The occurrence of Al-rich diopside and sapphirine mineral inclusions in eastern Australian rubies
are similar to those observed in Thai/Cambodian rubies. Rubies found from the Cudgegong-Macquarie
River system in New South Wales also contain high-Al clinopyroxene inclusions (Sutherland et al. 2003)
similar to the Thai/Cambodian rubies and may also fit into the anorthosite partial melting model.
Additionally, feldspatic melt inclusions are found in Australian pink to lavender sapphires from
Barrington Tops (Zaw et al. 2006) suggesting a magmatic origin. Trace element chemistry of pink
sapphires and rubies from Table 2 of Zaw et al. (2006) shows them to be very similar to the
Thai/Cambodian rubies and Yogo sapphires and rubies studied here (averages for Barrington corundum:
Ti = 140 ppm, Fe = 4292 ppm, Cr = 744 ppm, V = 51 ppm, Ga = 30 ppm; Zaw et al. 2006), suggesting a
similar origin as well. Furthermore, Sutherland and Coenraads (1996) described an alkali basalt related
ruby-sapphire-sapphirine-spinel xenolith from the Barrington volcanic province in New South Wales,
Australia. Sapphirine-spinel thermometry suggested a temperature of formation from 780–940 °C for
this assemblage, similar to temperature estimates for formation of the Yogo sapphires and in line with
an origin through low-degree partial melting. The results of Sutherland and Coenraads (1996) show that
sapphirine-ruby assemblages can be consistent with temperatures that are likely to be near-solidus and
are, hence, consistent with a partial melting scenario.
Of particular note is the range in oxygen isotope composition of eastern Australian rubies, 3.6 to 5.9‰ (Giuliani et al. 2005; Zaw et al. 2006; Graham et al. 2008; Sutherland et al. 2009, 2017), which is transitional between those observed in the reddish-violet Yogo sapphires from this study (4.5 to 5.4‰) and Thai/Cambodian rubies (1.3 to 4.9‰). This transition in oxygen isotope compositions shows that basalt-related rubies appear to have a continuous spectrum of $\delta^{18}$O values. While we suggest that Cr-rich gem corundum from these deposits may have a common origin, as argued above, variations in the range of $\delta^{18}$O values for a specific deposit may be related to variations in the extent of the “mafic” character of the protolith with more mafic compositions producing corundum with lower $\delta^{18}$O value. Note that Yogo sapphires and eastern Australian sapphires extend this continuous spectrum of $\delta^{18}$O values further (5.5 to 7.7‰ and 4.6 to 6.5‰ respectively), suggesting that more felsic compositions having higher $\delta^{18}$O values. However, further work on rubies from other deposits is warranted to support this hypothesis. Specifically, further analysis of mineral and melt inclusions in eastern Australian rubies could support this claim.

Can trace elements separate magmatic and metamorphic gem corundum?

The rubies and sapphires studied here add to the list of gem corundum with questionable predictions for geological origin (metamorphic or magmatic) based on trace element chemistry (Izokh et al. 2010; Uher et al. 2012; Sutherland et al. 2015, 2017; Palke et al. 2016, 2017; Baldwin et al. 2017; Wong et al. 2017). The reason for this discrepancy is likely because the original discriminant diagrams were produced with groups of sapphires and rubies that were too narrow to completely represent the full suite of metamorphic and magmatic gem corundum. For instance, while Peucat et al. (2007) reported trace element data for Yogo sapphires, they did not consider them to be magmatic sapphires. If Yogo sapphires had been classified as magmatic at the time, their discriminant diagrams would have looked very different. The same can be said for the alluvial Montana sapphire deposits which significantly overlap both metamorphic and magmatic fields from Peucat et al. (2007) but which have
melt inclusions and should be classified as magmatic. It was previously thought that only the blue-green-yellow (BGY) suite of sapphires from alkali basalts were magmatic, but it is clear now that the magmatic group of sapphires needs to be expanded. As it stands, it seems that none of the existing trace element defined discriminant diagrams can accurately separate magmatic and metamorphic sapphires and rubies and it is suggested that these discriminant schemes are used with great caution, if at all.

Finally, several previous studies have identified bimodal or polymodal assemblages of magmatic/metamorphic/metasomatic gem corundum in many basalt-related gem fields (i.e. Sutherland et al. 2002, 2008; Yui et al. 2006; Zaw et al. 2006; Peucat et al. 2007; Graham et al. 2008; Saminpanya and Sutherland 2011). These assignments are generally based on trace element chemistry and mineral inclusions. However, given the discussion above, the criteria generally used to discriminate magmatic and metamorphic gem corundum are not robust enough to produce reliable genetic separations. In fact, the observations described show that the mineralogical and chemical properties of so-called “metamorphic” volcanically-associated sapphires and rubies can also be consistent with a magmatic origin. This leaves open the possibility that volcanically-associated “metamorphic” gem corundum from other deposits may, in fact, be magmatic. Taken a step further, this calls into question the suitability of the bimodal (metamorphic/magmatic) or polymodal (metamorphic/magmatic/metasomatic) genetic hypothesis of volcanically-associated gem corundum deposits in general. It may be that all volcanically-associated gem corundum is magmatic and their variations in trace element chemistry, oxygen isotopes, and inclusions are simply caused by differences in the protolith from which the rubies and sapphires were derived.

Acknowledgements:
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References Cited:


Figure Captions:

Figure 1: Trace element chemistry of Yogo sapphires and Thai/Cambodian rubies plotting Ga/Mg against Fe. The “metamorphic” and “magmatic” discriminant fields are taken from Peucat et al. (2007)

Figure 2: Trace element chemistry of Yogo sapphires and Thai/Cambodian rubies in the Mg×100-Ti×10-Fe ternary. The “metamorphic” and “magmatic” discriminant fields are taken from Peucat et al. (2007)

Figure 3: Trace element chemistry of Yogo sapphires and Thai/Cambodian rubies plotting Cr/Ga against Fe/Ti. The “metamorphic” and “magmatic” discriminant fields are taken from Sutherland et al. (1998)

Figure 4: Trace element chemistry of Yogo sapphires and Thai/Cambodian rubies plotting (a) Ga against Mg and (b) Ti against Mg and (c) the FeO-MgO-V2O3 vs. FeO+TiO2+Ga2O3 plot of Giuliani et al. (2015).

Figure 5: Photomicrographs of (a) a glassy melt inclusion from a Thai ruby, (b) a recrystallized melt inclusions from a Thai ruby, (c) a glassy melt inclusion from a Yogo sapphire, and (d) a recrystallized melt inclusion from a Yogo sapphire

Figure 6: Oxygen isotope compositions and trace elemental compositions of seven Yogo sapphires (in blue) and two reddish-violet Yogo sapphires (in red). The data for the trace element and oxygen isotope comparisons were from pairs of spots placed as close as possible to each other in an attempt to sample
nearly the same volume. (a) shows 2 core and rim spots only, and (b–d) contains core and rim spots of all nine Yogo samples, and additional core to rim traverses (5 spots) in four sapphires and one ruby.

Figure 7: Melting relations in the quartz (Qz) – anorthite (An) – forsterite (Fo) ternary at 2.0 GPa from Liu and Presnall (1990). Bulk compositions for two hypothetical protoliths for Thai/Cambodian rubies and Yogo sapphires are marked by the red and blue circles. Dashed red and blue lines show the evolution of the two hypothetical protoliths during partial melting and demonstrate that corundum can be formed through a peritectic melting reaction in this system. Red and blue stars mark the appearance of corundum during partial melting.
Table 1: Trace element chemistry of rubies from Thailand and Cambodia and rubies and sapphires from Yogo Gulch, Montana, USA

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<th>V ppmw</th>
<th>Cr ppmw</th>
<th>Fe ppmw</th>
<th>Ga ppmw</th>
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<th>Ga*/Al</th>
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Detection Limits

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1. Averages are shown at the top of each row and the range is shown below in parentheses. Analyses are for 14 rubies from Pailin, Cambodia, 10 rubies from Chantaburi-Trat, Thailand, and 44 rubies and sapphires from Yogo Gulch, Montana, USA.
2. Ga*/Al = Ga×10,000/Al
Table 2: Compositions of the melt inclusions (MI’s) from blue sapphires and one reddish-violet sapphire from Yogo Gulch, MT, USA, one ruby from Thailand, and one ruby from Cambodia.

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<th>wt%</th>
<th>Yogo blue sapphire MIs remelted(^a)</th>
<th>Yogo reddish-violet sapphire MI(^b)</th>
<th>Thai ruby MI(^b)</th>
<th>Cambodian ruby MI(^b)</th>
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\(^a\)Four averaged melt inclusions from Palke et al. (2016)
\(^b\)One melt inclusion each for reddish-violet Yogo sapphire and Thai and Cambodian ruby
Figure 1
Figure 2

Always consult and cite the final, published document. See http://www.minsocam.org or GeoscienceWorld
Figure 3
Figure 4a
Figure 4b
Figure 4c
Figure 5
Figure 6
Figure 7