minerals

Editorial

Editorial for Special Issue "Mineralogy and Geochemistry of Ruby"

Frederick L. Sutherland [1,*] and Khin Zaw [2]

1. Mineralogy and Petrology, Geosciences, Australian Museum, 1 William Street, Sydney, NSW 2010, Australia
2. CODES—Centre of Ore Deposit and Earth Sciences, University of Tasmania, Hobart, TAS 7001, Australia; khin.zaw@utas.edu.au

* Correspondence: linsutherland1@gmail.com

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1. Introduction

Ruby as a natural gemstone has an early history in which its colorful properties [1] were much valued in ornamental and symbolic jewelry by potentates and other persons of power and prestige [2,3]. This appreciation has extended into latter times and more so into the more general populace. It is an important gem for scientific study [4] and for exploration quests to find new ruby deposits [5,6]. This Special Issue brings together seven papers representing a diversity of scientific teams that have studied ruby and its allied mineral associates from a wide range of global deposits across various genetic settings. The papers cover a significant component of previous ruby literature within their pages, and with use of cutting-edge analytical results in most studies, the Special Issue offers a substantial advance towards a fuller understanding of ruby genesis. Not every aspect of ruby and known ruby deposit is referenced within the Special Issue contents due to the limited number of papers. It is hoped, however, that the Issue will stimulate further research into perceived gaps.

The seven separate papers represent 34 individual authors from 16 different institutions in 14 cities and 9 countries. The total number of countries that rubies were described or sourced from exceeded 33 and involved more than 70 separate areas.

2. The Special Issue

The centerpiece of the Special Issue is a major review of ruby and its range of genetic expressions in its deposits by Giuliani et al. [7]. This not only provides a solid foundation on the mineralogy and geochemistry involved in this gem varietal, but also presents an encompassing survey of its global deposits through historic and geological time. From this supporting synthesis, the satellite papers present their own particular points of interest that carry the ruby theme into new research territory [8–13]. Research into gem corundum, however, is a continuing process, and new aspects are already appearing since publication of the papers in the Special Issue. For example, a recent study into the chromophore trace elements that determine the spectrum of colors seen in gem corundum shows that their combined individual effects can now be quantified in their contributions to the observed final color [14]. In the case of ruby, not only do Cr^{3+}, Fe^{3+} and V^{3+} substitutions in the structure give the characteristic colors, but the Cr^{3+} and Fe^{3+} can also introduce charge compensation by a trapped hole that can add subsidiary orange and yellow, respectively, into the resultant color.

2.1. Ruby Review

This large review by Giuliani et al. [7] runs to 83 printed pages, lists 270 cited references and includes 61 mostly color illustrative figures. The figures include many photos of rubies from different areas discussed throughout the text, field distribution maps of ruby deposits, field settings of ruby in deposits and a summary diagram of relative recorded ruby productions from different countries in the early 21st century. There are line drawings of ruby crystallographic features, graphs of different ruby spectra, photomicrographs of ruby-bearing host assemblages and internal fluid and mineral inclusions within rubies. A host of geochemical variation diagrams plot comparative ruby suites and their variously attempted classification boundaries. Other geochemical diagrams relate data to physical genetic parameters, such as pressure, temperature and oxidation states and associated mineral stability fields. Summary figures model ruby deposit genesis within lithospheric sections. One figure uses an innovative design to illustrate the geological history of economic ruby deposits. This spiral Earth-time diagram captures the irregular punctuated succession of the main ruby episodes, starting with Greenland deposits at around 2.7 Ga, then a major period of ruby formation linked to the Kuugan and East African orogenic events from ~650 to 500 Ma and finishing with a profusion of Cenozoic deposits mostly associated with Himalayan orogenic events from 55 to 5 Ma.

The review surveys a great variety of ruby deposits across the continents and includes newer exploration regions, such as Greenland. Ruby deposits in India, however, lack direct description and need further examples, such as a recent study on a rare peraluminous ensemble in which ruby and sapphire associate with spinel and sapphirine in a highly calcic anorthosite-layered complex in Tamil Nadu, India [15]. Overall, a feature of the review is an application of an enhanced ruby classification based on the surveyed deposits. A simplified outline of the classification is given in a final figure in the Conclusions. Three environments of host rocks for rubies are categorized. Magmatic-metamorphic assemblages (Type I) are subdivided into alkali basalts (IA) and kimberlite (IB) hosts. Metamorphic rocks (Type II) are subdivided into Metamorphic, sensu stricto, hosts (Type IIA), which subdivide into mafic-ultramafic (IIA1) and marble (IIA2) types, and Metasomatic hosts (Type IIB), which then subdivide into plumasite-metasomatic (IIB1) and shear zone, fault and fold structural metasomatic (IIB2) types. A Sedimentary, detrital, category (Type III) includes alkali basalt and kimberlite sources (IIIA) and metamorphic (IIIB) sources [7].

Three tables are included in the review [7]. Table 1 presents selected representative major/minor electron microprobe analyses (EMPA) of the rubies used in the classification of the global deposits. Table 2 provides laser ablation-inductively coupled plasma-mass spectrometry (LA-ICP-MS) analyses of trace element contents in selected rubies related to the classification of their deposits. Table 3 sets out representative typological ruby localities that exemplify the different categories established for the new and enhanced classification for global ruby deposits.

Finally, photographic images scattered through the text depict hands cupping ruby crystals, fingers indicating ruby within outcrops, miners working at mine sites and locals selling gemstones at source. These visuals remind readers of the human interactions involved in extracting ruby from its natural environment [7].

2.2. Myanmar Ruby Studies

Two studies focus on ruby from Myanmar, in particular from the Mogok area, a historic and still-active venue for top quality ruby [16]. The Mogok gem tract includes marbles that commonly host these ruby deposits, while suites of igneous intrusive rocks in the area [17] also formed some contact zone ruby-bearing skarn deposits.

A Swiss-based research team, Myint Myat Phyo et al. [9], presented new detailed U–Pb dating on gem-quality ruby (and spinel) by using zircon and zirconolite inclusions in these rubies and within the host and adjacent lithological units within the Mogok gemstone-tract. The use of zirconolite is a first for such dating in ruby. Besides the age-dating results, accompanying rare earth elements (REE) data on the mineral inclusions help to characterize the genetic origin of the ruby and assist its profiling for geographic typing of Mogok area rubies. Two variants of laser ablation-inductively coupled mass spectrometry (LA-ICP-MS) methods were used in the analytical determinations. One [18] was the 'Time of Flight' method (LA-ICP-TOF-MS) and the other was a 'Sector Field' method (LA-ICP-SF-MS). The single detector 'SF' method has 15× higher sensitivity than the 'TOF' method and was more adapt at analyzing between transitions in highly zoned zircons. The 'TOF' method was ideal for monitoring elemental variations when switching between grains and was used for detailed elemental and isotopic determinations in small and more complex zircons and zirconolite crystals.

In the study, 109 zircon and 14 zirconolite grains were analyzed from ruby and spinel crystals. Analyses were made of core and rim zones where well defined. Zircon cores ranged from 94 to 26 Ma and rims from 30 to 22 Ma. The youngest ages were concordant for both ruby at 22.3 ± 0.4 Ma and spinel at 22.9 ± 0.7 Ma. Accessory zircon and zirconolite grains in the host marble gave similar age spreads from 95 to 17 Ma to the inclusion range, but the youngest concordant rim ages at 17.01 ± 0.4 Ma were slightly younger. Accessory zircon in ruby-bearing garnet-orthopyroxene gneiss gave Jurassic to Cretaceous core values and a young concordant rim age of 32.0 ± 0.03 Ma, while zircon in a biotite-garnet gneiss gave core ages up to ~985 Ma, with young rims giving concordant ages at 26.1 ± 1.2 Ma. All the age ranges related to this study are plotted up in a summary figure along with the age data available from previous Mogok gem tract studies. This shows the substantive increase in dating now available from the present study for ruby inheritance and growth recorded for the Mogok tract than in previous age dating within the 200–15 Ma age range [9].

The REE data on zircons and zirconolite in this study were analyzed from core zones. The zircons in the rubies show enrichments in HREE, associated with very low to below detection LREE, and show subdued to absent Ce and Eu anomalies. The accessory zircon grains in the marble host and proximal gneissic rocks show more pronounced REE contents and Ce and Eu anomalies. The new data form a firmer base to specify inclusion signatures in Mogok tract ruby and allied rock suites. These low LREE/higher REE profiles reported for the included zircon in ruby in this study find reinforcement in a previous study [19]. Those zircon inclusions showed similar notably low LREE and more enriched HREE but were recorded in Mogok ruby with a different locality and ruby age.

A further Mogok ruby study by Vertriest and Palke [13] targeted the identity and genetic implications of opaque sulfide inclusions in the marble-hosted rubies. The authors then compared the Mogok inclusion features against those of opaque sulfide inclusions in Mozambique rubies, which formed in a very different host lithology and genetic growth processes. The aim of the study was to identify the mineralogy of the two inclusion suites and to consider any potential effects on ruby chromophore coloration and fluorescence and any signaled differences in their genetic formation. The Mogok rubies formed in carbonate platforms contaminated with organic materials and evaporated salt deposits which underwent metamorphic events and fluid interchanges. The Montepuez rubies formed in less clearly understood peak metamorphic processes associated with amphibole formation. These differences were expected to show up in the opaque sulphide suites.

The studied rubies came from the documented field collections in the Gemological Institute of America and were prepared for photomicrography in the Bangkok laboratory. Back-scattered electron (BSE) images and electron microprobe analyses (EMPA) on the inclusions were gathered at the Analytical Facility at CalTech, Pasadena, California. Sulfide inclusions were found in 85% of Mogok samples and 40% of Montepuez rubies. Two figures each of Mogok and Montepuez photomicrographs and BSE images of the inclusions provide instructive viewing of the opaque sulphide inclusion phases. Mogok inclusions are mostly single phases, whereas Montepuez inclusions have more complex phases and show exsolution features. The tabled EMPA data identified pyrrhotite, sphalerite and one pyrrhotite-pyrite composite among Mogok inclusions, while complex Montpuez inclusions contained chalcopyrite, pentlandite and pyrrhotite with some exsolved Fe–Ni sulfides. An important outcome in this new study over previous studies is better identifications. An earlier suggested predominance of pyrite for Mogok sulfide inclusions had misidentified the phase, which is now identified as pyrrhotite. Similarly, claimed chalcopyrite in Montepuez rubies has proved to be largely Fe–Ni–Cu sulfides [13].

In a wide-ranging discussion, the authors debate the complexities involved in unravelling the precise geneses of these sulfide inclusions within the two contrasting ruby-bearing regions. A high T stability for pyrrhotite, the main Mogok sulfide, at >743 °C suggested a protogenetic origin, based on a marble-related peak metamorphic T range of 620–670 °C. The Mogok rubies were generated during a lower T retrograde event. The binding of Fe by S before ruby formation may explain its low-Fe ruby nature and consequent undamped fluorescence effect. The rarer sphalerite inclusion within Mogok rubies was linked to low grade metamorphism of the host marble platform. In contrast, the more complex Montepeluez sulfide inclusions are accompanied by greater ranges in Fe contents within the rubies, giving less noticeable fluorescence effects [13].

2.3. Geographic Typing of Rubies

Locality determination for quality gemstones has become an important issue for tracing and confirming their sources and values, with an array of analytical techniques now marshalled to guide their scientific validation [20]. For ruby, its geographic origin can be determined with a high degree of confidence; with application of suitable statistical treatments, rubies from different deposits can be distinguished in up to 96% of cases [21]. In typing rubies from Appaluttoq deposits in SW Greenland, Krebs et al. [22] used sophisticated trace element and Sr–Pb isotope methods to distinguish two sets of rubies derived from two hosts of different host lithologies. They also, for the first time, age-dated ruby growth histories directly from the ruby compositions. Off-line laser ablation was combined with thermal ionizing mass spectrometry (TIMS) in analyzing the radiogenic isotopic compositions. These novel techniques are used in a wider study presented in this current Special Issue [10].

In terms of the wider study, Krebs et al. [10] examine the usefulness of trace element and radiogenic isotopes for geographic typing for gem corundum. They stress that distinction of host lithology is more reliable than in determining a precise geographic provenance, particularly for marble-type ruby. Studied samples came from three gem corundum deposit types. Amphibole-metamorphic ruby types included deposits from Montepeluez, Mozambique; Winza, Tanzania; Andilamena/Zahmena and Ampanihy/Toliara, Madagascar. Marble-ruby types included various deposits within the Mogok Gem Tract and Nama, Kachin State, Myanmar; Luc Yen, Vietnam; Jegdalek, Afghanistan; Morogoro, Tanzania. Metamorphic blue sapphire deposits included Andilamena and Andrebabe, Madagascar; various Mogo Gem Tract sites, Myanmar; Elahera, Sri Lanka.

Novel methodology developed to cater for low trace element abundances of the previous SW Greenland study [22] was employed again here, and the Greenland results were added in for comparison in the discussion section. The ppm data for 26 elements in the trace element array are provided in a Supplementary table, while a table in the text lists results for eight elements considered relevant or useful for geographic typing, viz. Mg, Ti, Cr, Fe, Ni, Zn and Ga. The analyzed values are plotted in several figures that include primitive mantle plots as comparative multi-element arrays, and box plots of Eu, Ce and Sr vs. Eu/Eu*, Ce /Ce* and Sr/Sr*; Ta vs. $(Ta/Nb)_N$; Pb vs. $(U/Pb)_N$; Th vs. $(Th/U)_N$; Hf vs. $(Zr/Hf)_N$.

Radiogenic isotope analyses are listed in a text table, shown as ranges in ratios of $^{87}Sr/^{86}Sr$ and $^{206}Pb/^{204}Pb$, $^{207}Pb/^{204}Pb$, $^{207}Pb/^{204}Pb$ and $^{208}Pb/^{206}Pb$ for samples from each types of corundum deposits. Bow and whisker diagrams in three figures plot the comparative ranges for these isotopes for each of the corundum types, while a further figure plots the isotopic values as $^{87}Sr/^{86}Sr$ vs. $^{207}Pb/^{206}Pb$ for the three corundum types, which showed no close correlation between these three suites.

In the Discussion, the authors plot their data on several typical diagrams previously used for corundum provenance studies. They use only LA-ICP-MS data for the comparisons in binary diagrams for Cr/Ga vs. Fe/Ti and Fe vs. Ga/Mg and for triangular diagrams for Fe–Ti $\times$ 10–Mg $\times$ 100; Fe–V–Ga; Fe/20–V $\times$ 3–Ga $\times$ 3. In the Cr/Ga vs. Fe/Ti diagram, high-Fe metamorphic ruby, marble-type ruby and blue sapphire fall into discrete fields with only minor overlaps. Different localities within these fields, however, significantly overlap. Among marble-type rubies, those from Mong Hsu are distinctive [19,22], though in general, none of the typical discrimination schemes are very effective in separating localities of the same deposit type.

Using broader trace element data, the authors evaluated other elements as discriminators, such as Ni, Zn and Pb, with Ni showing good discrimination among amphibole-ruby deposits. Combined in an Ni $\times$ 100–Ti–V $\times$ 10 triangular figure, it separated fields from Winza, Tanzania, Namehaca, Mozambique and Ampanihy and Zahmena, Madagascar. In contrast, Appaluttoq ruby, Greenland, showed a wide range and overlapped with the Namehaca and Zahmena fields. The Greenland field overlap was partly resolved in a Ga vs. V plot, but incompletely. None of the added elements proved useful for marble-ruby deposits. Instead, binary figures for V vs. Cr and Fe vs. V could roughly divide Myanmar and Morogoro area rubies, while ternary diagrams for Fe/Mg × 2–Cr/Ti–V × 10 and V–Cr/10–Ti achieved passable separations of Myanmar, Morogoro, Tanzania and Afghanistan rubies. For metamorphic blue sapphires, a figure using three binary plots, Mg v.s V, V vs. Cr × Ti and V–Cr/10–Ti, was employed to examine distributions of Myanmar, Andrebabe and Sri Lankan fields.

Multivariant statistical analysis, both Principal Component and Linear Discriminant, were applied by the authors to increase reliability of origin determination and detect elements of potential discriminatory use. Linear discriminant solutions are shown in a summary figure of element arrays for the main ruby and sapphire groups, and On-Line and Off-Line solutions were compared. Similarly, the most useful combinations of isotopic ratios and trace elements were also compared in a final figure.

In the Conclusions, the authors considered that geographic differentiation of amphibolite-type rubies is fairly simple but is more challenging for marble-type rubies and metamorphic blue sapphires. They emphasize the promise of using combined isotopic and trace element fingerprints, but for precise geographic origin, more powerful discriminating tools need development [10].

2.4. Gem Corundum Spectrum

In the paper by Palke [11], the author brings together the two main gem varieties of corundum. They have similar properties, although ruby differs in a relative excess of the chromophore ion Cr^{3+} that introduces a red color in comparison to the other colored variety sapphire. The two varieties, however, can occur together in the same gem deposit, and this theme is developed in the survey.

The Introduction indicates that changes in host rock chemistry and physical conditions during formation can enable Cr to enter the corundum structure. Many rubies form in platform carbonates, although the precise process is not well understood. In its outline, the study aims to focus on some important regions where deposits yield both ruby and sapphire suites. The studied samples were selected from the Gemological Institution of America (GIA) Colored Stones Collection and also gained from contacts associated with the Montana Bureau of Mines, mineral dealers and miners from MT, USA, sapphire fields. The sample sets included rubies largely from South East Asia: Thailand/Cambodia, Sri Lanka, Mogok and Myanmar, but also from more limited sources in Montana, USA. Transitional pink sapphires from Sri Lanka and Montana were also present, while the main blue sapphires were sourced from the Thailand/Cambodia, Sri Lanka, Mogok, Myanmar and Montana fields. The gemstones were largely recoveries from eluvial and alluvial deposits, with some Yogo, Montana, stones related to a primary deposit [11].

Analytical methods used for trace element data on the ruby-sapphire spectrum relied on LA-ICP-MS methodology adopted at the GIA Lab. The runs used ^{27}Al, NIST 610 and NIST612 glass as standards, for accuracies within 5–20%. Only main trace elements were run for the surveyed deposits and, with detection limits in ppm, were Mg (1.2–4.7), Ti (0.1–0.5), V (0.1–0.5), Cr (1.3–5.1), Fe (13.7–54.8) and Ga (0.1–0.2). Mineral inclusions in the rubies and sapphires were identified with a Renishaw, Raman microscope system. It had the capacity to analyze many inclusions beneath the exterior surface as well as others exposed on polished surfaces.

Each deposit was successively described in context of the host geological setting, trace element results and inclusion suites within the color groups. The trace element results for each constituent color group were accompanied by correlation matrices that brought out positive and negative trends. The listed data for each locality are placed within 11 text tables for their discussion. Plots of the trace element data from each deposit use specific trace element parameters that illustrate the relationships within color groups and occupy five figures within the text. Photo micrographs of typical inclusions in rubies and sapphires within suites occupy a further five figures within the text.

Thailand/Cambodia suites, studied from the important Chanthanburi and Pailin gem fields, suggest that this large region of ruby and sapphire deposits overlapping the border between the two countries differs from other deposits farther afield. Trace element contents, their correlation trends and inclusion characteristics mark significant separations between the color suites. The origin of the ruby sources remains in debate, either being in highly mafic metamorphosed rocks sampled by later alkali basalts or related to peritectic melting reactions caused by basalt magmas.

Mogok, Myanmar, suites include rubies associated with high-grade folded marble beds, where Cr and Al were introduced from mobilized molten-evaporate beds, while blue sapphires were generated where pegmatitic syenites intruded into gneisses and other metamorphic hosts. These source differences are reflected in trace element separations in several discrimination diagrams, but are less obvious in some plots, such as Ga vs. Mg which shows notable overlap. The correlation matrices bring out some unexpected features, where both rubies and sapphires both show significant positive correlation between Cr and V. The V-rich nature of Mogok rubies and sapphires are consistent with previous LA-ICP-MS imaging and analyses [23]. Differences between rubies and sapphires show up in their inclusions with carbonate, apatite and sulfide, dominant in ruby, and feldspars, zircon and polysynthetic twinning, common in sapphires.

Montana, USA, sapphire and ruby suites cover a number of spaced deposits across a wide region. The secondary suites are largely alluvial and are derived from rhyolitic and rare mafic hosts. They show a range of pastel colors mostly blue, green and lavender that pass into yellow, orange and ruby. Cr values vary by three orders of magnitude, above the two orders of magnitude for Mg, Ti, Fe and Ga. In Fe vs. Cr plots, good separation is achieved between blue sapphires, pink sapphires and rubies, whereas Ga vs. Mg plots only show large overlaps. Correlation matrices reveal a strong positive Ti, Mg trend. Inclusion suites across the color range show only minor differences.

Montana Yogo Primary suite is derived from a deep-seated lamprophyre intrusion and includes blue and violet sapphires and ruby. It is easily distinguished from the other Montana suites by trace element plots, correlation matrices and inclusion suites. Plots of Fe vs. Cr diagrams show good separations between the sapphire and ruby colors. Melt inclusions, however, show generally similar compositions across the color range.

Sri Lankan sapphire and ruby suites are mostly recovered from alluvial deposits. Host rocks are not well sourced. They probably represent amphibolitic and granulitic metamorphic rocks formed during Neoarchean-late Ordovician collision of E and W parts of continental Gondwana. The gem fields produced blue and pink sapphires and rubies among other colors. The sapphire to ruby range shows some separation with increasing Cr in a Ga vs. Cr plot, whereas a Ga vs. Fe plot shows much overlap. A similarity in inclusions is seen through the suite, mostly biotite, rutile silks and negative crystals.

In his discussion, the author considered the roles of inclusion suites and geochemistry within the studied gem corundum deposits. The inclusions are important direct clues to origins, although they have limits, while the path of geochemistry suggests controls related to the crystallizing environment but is not always fully understood and leads to breakdown in some assignments. The present survey shows two types of coexisting ruby and sapphire deposits, polygenetic and monogenetic. Polygenetic examples include the Thailand/Cambodia and Mogok, Myanmar deposits, although they may have overly common links, such as both being related to the Himalayan orogeny. Clear differences exist in Cr and Fe contents, though other elements such as Mg, Ti and Ga overlap in contents. Monogenetic examples include Montana and Sri Lanka deposits. A surprising observation is that Cr contents can range through extreme levels, with little other variation in other elements or within inclusion suites [11].

In conclusion, this study, though limited to several producing deposits, can be amplified through further studies in deposits elsewhere, such as in Australia, Colombia, Myanmar, Vietnam and Tajikistan. The present study suggests that rubies and sapphires within joint deposits do not necessarily reflect clear-cut tectonic or geological host controls in their formation [11].

2.5. Allied Mineral Assemblages

Ruby largely forms in metamorphosed/metasomatised ultramafic/mafic hosts and carbonate platform beds in fold belt sequences where Cr and Al enrichments are present, so that the presence of allied Cr-bearing minerals in host assemblages and in the ruby as inclusions are likely. In their paper, Kissin et al. [8] report the presence of a Cr mineral previously unrecorded as a genetic phase associated with ruby. In their Introduction, the authors identify the new allied mineral as eskolaite, a chromium oxide, Cr_2O_3, and give its location at the Kuchinsko ruby marble deposits in the southern Urals area, Russia. They suggest it is a useful find for discussion on the sources of Al and Cr in ruby-bearing marbles. The Introduction also provided preliminary surveys on ideas and references relating to formation of marble-hosted rubies and known types of global geological environments that record eskolaite.

In the geological setting, the authors describe the surroundings of the ruby deposit located in the Kochkar Anticlinorium, bounded by thrusts that dip below adjacent synclinorium belts. Granite gneissic domes form centers produced by dynamothermal metamorphism within the anticlinorium, framed by schists, amphibolites and marbles, intruded by granite and pegmatite dykes. Carboniferous prograde metamorphism that formed two types of marble was followed by Permian-Triassic retrograde metamorphism that formed a third marble type. The granite/pegmatite dykes were related to anatectic granites in the gneissic domes. Later Paleogene-Neogene karst deposits were formed that include eluvial rubies, showing no alluvial transport attrition. A geological map of the location and broad regional structural features accompanies the section [8].

The Materials and Methods outline sampling of ruby from the Kuchniskoe area where crystals were garnered from the karst deposits. Three different types of ruby were found, each related to the underlying marble type. Ruby grains with surface aggregates of a co-existing dark mineral phase were recorded by scanning electron microscopy (SEM) and identified using X-ray diffraction (XRD) at the State Mining University, Ekaterinburg. The eskolaite and ruby surface matrices were then subjected to electron microprobe analysis (EMPA) at the Russian Academy of Science laboratory, Ekaterinburg. Samples were run from both prograde and retrograde metamorphic ruby types. The XRD and EMPA results are listed separately in two text tables and the photomicrography and SEM imaging are illustrated in three composite text figures.

Discussion of the analytical results detailing the eskolaite-ruby association firstly considered the T–P conditions of its formation in relation to the regional geological events. The peak prograde metamorphism for the ruby-hosted marble, calculated by calcite-dolomite thermo-barometry, was 660 °C at 1.9–2.6 kbar. This was compared with slightly lower T–P for Type 3 ruby from the retrograde phase of metamorphism, estimated at T 550–600 °C, P 1.9–2.2 kbar, with P_{CO2} 0.4–1.4 kbar. The T–P for the inter dome region of the Kochlar Anticlinorium, where the ruby deposits lie, was based on mineral paragenesis of the assemblage; garnet + biotite + plagioclase + quartz ± staurolite ± sillimanite ± cordierite. This gave T 500–620 °C, P 3.0–4.0 kbar, and may reflect an ~estimate for ruby Type 1 prograde metamorphic formation conditions. Eskolaite in the marble deposit intergrowths is associated with high-Cr ruby, a relationship that was used to formulate an eskolaite-ruby geo-thermometer. This gave a T of 700–850 °C, higher than that known for the metamorphism in the Kochlar Anticlinorium, which lies between 670–800 °C. The cause of this discrepancy was unclear but may involve factors such as oxygen fugacity and pH conditions.

An extensive section was devoted to the Al and Cr sources for combined ruby and eskolaite formation by the authors. Several modes of potential formation were considered and thought unlikely on available evidence. Although redistribution of Al and Cr through metamorphism of sedimentary limestones with evaporate lenses fit some of the criteria, it did not fit the evidence of both the prograde and retrograde formational phases. The authors instead proposed that the dual ruby and eskolaite formation resulted from a hydro-metasomatism process where a high temperature fluid was generated during domal 'granitization'. This provided SiO_2, Na, K and H_2O and removed Mg, Fe, Ca and other components. The eskolaite formed in the final stages of each ruby growth, with maximum

Cr availability during prograde metamorphism and then after a transition Cr replenishment during retrograde metamorphism. In their Conclusion, the authors considered that the find of eskolaite in tandem with ruby in the Kuchinskoe marbles illustrated a new process of introducing Al and Cr into a mineral zone [8].

2.6. Multiple Ruby Assemblages

In a detailed study of the Snezhnoe ruby deposit, Central Palmir Mountains, Tajikistan, Litvenoko et al. [12] describe four ruby-bearing host assemblages intercalated within ruby-free assemblages. An introduction sets out the mineralogy of ruby as a corundum variety, aspects of ruby mineralization and the tectonic processes that make reconstructions of ruby formation a challenge. Features of the Snezhnoe marble-hosted ruby deposit, its earlier studies and comparisons with other similar ruby deposits of the Alpine-Himalayan fold belt followed. The Snezhnoe deposit, however, was considered understudied prior to the present project.

In the geologic setting, the ruby deposit site is pin-pointed in a figure of the large-scale geological map of the Palmir Mountains structures, where it lies within the Mazkul-Rangakul Anticlinorium. Two further figures show details of the Snezhnoe deposit in relation to other ruby deposits in a map of the marble layers in the southwestern limb of the Shatput Anticline and in a closer scale cross section. In this, the ruby deposit lies in steep-dipping en echelon lenses within a sequence of marbles intercalated with amphibole-pyroxene and scapolite calciphyres, gneisses and crystallized schists. The ruby lenses are cut by numerous late hydrothermal veins.

The Snezhnoe ruby-bearing rocks were sampled during field explorations from 2010 to 2017. A large array of instrumental methods at different institutions were employed for a multi-tasked gathering of data on the nature of the ruby deposit and its genetic formation. Selected mineral extractions were studied using XRF spectrometry at the Vernadsky Institute, Russian Academy of Sciences, Moscow, with mineral identifications made in XRD runs at the Russian State Geological Prospecting Museum, Moscow. Mineral composition data were collected by EMPA techniques at the Vernadsky Institute, with most elements being analyzed within detection limits of <0.01 wt %. LA-ICP-MS methodology was used on ruby samples for studying trace element values within internal zoning, at the Institut für Geowissenschaften, Johannes Gutenberg Universität, Mainz. Trace element and U–Pb isotopic compositions were analyzed using an ICP-MS unit coupled with an Analyte G2 excimer laser at the Westfälische Wilhelms Universität Münster. For rutile dating, ^{206}Pb, ^{207}Pb, ^{232}Th and ^{238}U isotope data allowed Concordia and age calculations at the Berkeley Geochronology Centre, USA. Minimum entrapment pressures for rutiles in rubies were estimated by shifts in Cr^{3+} R-lines, seen using a confocal Raman spectrometer coupled with an Olympus microscope and automatic XYZ-stage. Oxygen isotopic compositions of ruby grains were determined using a high-resolution ion probe at Heidelberg, Germany, after DSE imaging to avoid areas of inclusions. Ruby-bearing rocks were powdered for Rb–Sr and Sm–Nd isotope analyses, while mineral fractions of plagioclase and phlogopite were processed for Rb–Sr geochronology. Measurements were made using a multi-collector TIMS facility at the Russian Academy of Science facility, Moscow.

Results on one-mineral, three-mineral (2) and four-mineral ruby-bearing assemblages included: calcite; plagioclase + muscovite + margarite; muscovite + phlogopite + margarite; scapolite group + phlogopite + muscovite + margarite. Ruby-free assemblage results mostly included plagioclase + scapolite + phlogopite + muscovite. The micas were commonly enriched in Cr and V, with the greener varieties being indicators of ruby. Visible accessory mineral grains analyzed included graphite, corundophyllite, rutile and dravite-elbaite series, while a range of other minerals were identified under high magnifications. A table lists the major, minor and accessory minerals in assemblages in the text. Text figures illustrate macrophotography, photomicrography and a diagram of random ruby crystals in host rock illustrate the ruby-bearing assemblages. Results on pink to bright red and purple-hued ruby showed ranges in Cr up to 0.55 wt %, Fe_{total} up to 0.2 wt % (EMPA) and Ga analyses showed a significant range from 68–98 ug/g (LA-ICP-MS). Mineral element values and ratios of analyzed rubies in figure diagrams shear clear metamorphic association for ruby in marble in some diagrams, although in others, transitional overlapping towards magmatic trends is seen. The $\delta^{18}O$ isotopic compositions fall into a narrow range from +15.1–15.3, typical of crustal associations.

Compositional results on the ruby-bearing rocks showed variations between 38–98 wt % Al_2O_3, up to 12 wt % alkalis (Na_2O_3 + K_2O) and 3–10 wt % CaO. Crustal-normalized multi-element arrays of ruby-associated micaceous lenses and marbles were depicted in a figure diagram. Minor elements, mostly enriched in 3^+ and 4^+ and less so for 1^+, 2^+ and 5^+ charged lithophile elements, overall exceeded Earth's crust average values, particularly Ce (×248). F contents up to 4.6 wt % indicate significant inputs into mineral-forming activity of fluids. Using LA-ICP-MS U–Pb results on rutiles, a figure of their plots in a Concordia diagram showed a lower intercept at 12.0 ± 1.5 Ma and a potential upper intercept at ~4.9 Ma. Rutile grains inter-grown with zircon enabled thermometry and indicated a T range of ~830 ± 60 °C. Rb–Sr isotope results on ruby-bearing rocks plotted in a $^{87}Sr/^{86}Sr$ plotted in a figure indicated two error isochrones, one at 12 ± 3.0 Ma and another at 23 ± 1–2 Ma, the latter likely linked to alteration opening up the Rb–Sr system in phlogopite. An Nd isotopic result gave a bulk rock $\varepsilon Nd_{(20\ ma)}$ value of −9.6 [12].

Discussion was opened up with the authors reviewing different hypotheses on the origin of the ruby-bearing rocks, which included metasomatic, hydrothermal, and sedimentary-metamorphic scenarios, although all of these were previously controversial. The authors considered these using a figure in which two Ternary diagrams plotted element oxides against SiO_2 and Al_2O_3, plotting data from the present study. A sedimentary origin was discerned in both diagrams but had different overlaps, one that invoked Precambrian illitic clays and bauxitic ores while the other suggested illitic and kaolinitic clay sources and proximal lateritic bauxites. Considering the ruby geochemistry using trace element ratios, plotted oxide sums and O isotope data, the authors confirmed an earlier hypothesis—the ruby-bearing rocks were once an Al-enriched protolith, reworked during iso-chemical metamorphism [12].

Thermometry from zircon in rutile results and barometry from Raman mapping of rubies was plotted in a T (°C)–P (kbar) figure showing previous modelling of T–P fields, a peak metamorphism point, alumino-silicate stability fields and schematic Greenschist, Amphibolite and Granulite fields. The Rb–Sr isotope, U–Pb rutile Concordia and K–Ar muscovite age plots were linked to cooling and relaxing stages after peak metamorphism during the Alpine-Himalayan Orogeny, while the T/DM model age confirmed the hypothesis of a Proterozoic protolith for the ruby-bearing rocks. The ages of Snezhnoe and other ruby deposits in the orogenic region were compared in a figured map.

In their Conclusions, the authors summarize the outcomes related to the tectono-metamorphic development of the Snezyhnoe ruby deposit, the likely T–P formation conditions, the chromophore and genetic trace elements and inclusions in the rubies, and the nature of the ruby-bearing petrological assemblages, which confirm a crustal origin and offer prospecting indicators. The authors present a robust updated characterization and interpretation of the Snezhnoe ruby [12].

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