

SYMPOSIUM II

II: The Science of Gem Materials

December 2 - 3, 2003

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* Invited paper

8:30 AM III.1

The United States National Gem Collection. Jeffrey E. Post, Department of Mineral Sciences, Smithsonian Institution, Washington, District of Columbia.

The United States National Gem Collection at the Smithsonian Institution numbers more than 10,000 gems and jewelry pieces and continues to grow. Established in 1884 as a modest assemblage of American precious stones, the collection expanded considerably with the gift of 1,316 gems from the collection of Dr. Isaac Lea in 1894, and again with the acquisitions in 1926 of the Washington Roebling and Fredrick Canfield collections. Undoubtedly the most important event that established the world-wide reputation of the National Gem Collection was the gift in 1958 of the renowned Hope Diamond by Harry Winston. The Hope triggered a cascade of generous donations, and it remains the single most visited item in all of the Smithsonian collections, attracting more than 30,000 viewers each day. Most of our historically significant pieces, such as the Hope Diamond, the Napoleon Diamond Necklace, and the Star of Asia, appear on public display in the Janet Annenberg Hooker Hall of Geology, Gems and Minerals, which was renovated in 1997. In addition, the National Museum of Natural History maintains a reference collection of gems that is actively used by researchers from around the world, principally in the areas of gemology, mineralogy, physics, and the materials sciences. These specimens represent rough and cut stones from hundreds of classic and new gem localities, and they allow the Museum to fulfill its mission as an international leader in the pursuit of the gem sciences. For this purpose the Museum houses an extensive state-of-the-art materials characterization facility with capabilities in TOF-SIMS, ESEM, X-ray microdiffraction, and FTIR spectroscopy. This presentation will include an overview of the history of the U.S. National Gem Collection, with an emphasis on its most important pieces and the philosophy that has guided its creation.

8:45 AM III.2

The trade roots of gem materials in Caucasus and Eastern Europe in 1st Millennium AD. Vera Borisovna Kovalevskaia, Theory and Methods, Institute of Archaeology, Moscow, Russian Federation.

The stone-made artifacts spoken of are mostly beads, in a smaller measure amulets, signets and intaglios, found in Early Medieval sites of Caucasus and East Europe. They are incorporated in an archaeological-geographical database of BUS (97 sites - 311 types - 3 chronological layers - 48881 copies of beads and pendants and an atlas of 335 electronic maps). The basic attention will be inverted on the technological and morphological analysis, fractional dating on accompanying materials and on specificity of spatial distribution in studied territory. I shall show in the paper how large information it is possible to take from such a mass archaeological material as stone beads at the application of statistical and mathematical methods for analysis of their distribution in time and space. I see the main aim of the offered paper in disclosing of permitting opportunities of mapping of the mass archaeological materials made on the example of the analysis of the atlas of electronic maps. It was constructed for stone beads (127 maps) of the 1st Millennium AD of Northern Caucasus in comparison to materials of Asia and East Europe. With the use of the continuous interpolation function (spline-interpolation, average weight interpolation) it became possible to create quantitative models for the distribution of a number of leading forms of mass archaeological materials and compare them. With the growth of the database with aid of programs GGMag, Datstat, Mapstat, Map Developer Studio and others one will be able to trace trade routes and inter-regional cultural relations, the sequence of techniques and unknown workshops as well as to date more accurately both the funerary complexes and the artifacts proper. In the paper I show the basic ways of inflow of different beads (cornelian, garnet, amber, lapis lazuli, crystal etc.) constructed on the Eurasian cartographical basis by means of connected directed graphs on the base of all electronic maps on the territory of the Caucasus. It is the Black Sea Rout going through Constantinople and Trapezund, the overland transcontinental ways crossing of the Great Caucasus (Caucasian part of the Great Silk Rout), routs through the mountains to the Transcaucasia and Caspian rout through Derbend. In each case we bring that set of beads (on a matrix of factor of correlation such as beads and general components), which were imported to Ciscaucasus on these ways. After that we can determine a start point of readout - from what workshops of India or Iran, of Asia Minor or Mediterranean there were beads, which steadily went to the Caucasus by the same ways further to be distributed on Europe. The maps, shown in the paper, convince that computer mapping is the source of the new information, that formalizing and simulating process of distribution of new types of

stone beads and their combinations by various strategic and trade routs through the Caucasus to East Europe and down to Scandinavia.

9:00 AM *III.3

Recent Progress in Growth of Diamond Crystals. Reza Abbaschian¹, Carter W. Clarke² and Carlos Valeiras²; ¹Materials Science and Engineering, University of Florida, Gainesville, FL, Florida; ²Gemesis Corporation, Sarasota, Florida.

Diamond is considered to be the gem of gems because of its brilliance and other unique properties. Diamond is also the most difficult gem to manufacture because of the stringent requirements for high temperatures and high pressures. Growth of inclusion-free and clear diamonds also requires precise control of interfacial kinetics and chemistry of the starting materials. As a result, large-scale production of gem quality diamonds has not been commercially competitive with mined diamonds. This situation is changing rapidly with the introduction of the split sphere technology in commercial production of crystals with qualities that rival those of natural diamonds. In this presentation, an overview of the application of crystal growth fundamentals in the high-pressure high-temperature production of diamonds will be made, with particular emphasis on the recent developments in the production of 2.5-3.5 carat gem quality yellow Gemesis diamonds.

9:30 AM III.4

HPHT-Annealing of Gray Blue Type IIb Diamonds. Matthew S. Hall, Wuyi Wang and Thomas M. Moses; Gemological Institute of America, New York, New York.

The introduction of High Pressure/High Temperature (HPHT) annealed diamonds by the General Electric Company in 1999 created great anxiety within the gem and jewelry industry regarding their identification. As a result of this treatment process, naturally colored brown to gray diamonds (not considered valuable in the gem and jewelry trade) were changed into intensely colored or completely colorless diamonds (considered valuable in the gem and jewelry trade) largely dependant upon the starting material diamond type. HPHT-annealing reorganizes point and extended-defects in diamond, which also affects the diamond's color. All types of diamonds can be treated to improve their coloration; however, little is known about the very rare type IIb diamond (Hall and Moses, 2000). To improve our understanding, a systematic investigation of the HPHT-annealing of several type IIb diamonds was performed in this study. Four faceted gem-quality type IIb diamonds ranging in color from gray to gray-blue were HPHT-annealed, thus changing their colors to a more intense blue. The exact pressure, temperature and duration of HPHT treatment are unknown, however it is suspected that the run conditions were approximately 2200-2500°C, 7.6-8.4 GPa, for 60 minutes (Burnes, R., et al.). UV-visible, photoluminescence (PL), and infrared (IR) spectra were recorded for each diamond before and after HPHT-annealing. In general, the UV-visible spectra of the naturally colored gray-blue diamonds possess a gradual rise in absorption from 500 nm to high-energy, suggestive of a brown color component, in addition to a slight rise in absorption from about 600 nm into the near-IR, suggestive of a blue component. This absorption spectrum results in a gray-blue hue in the diamond. In general, after treatment the absorption from 500 nm to high-energy is depressed, while the absorption from 600 nm into the near-IR is intensified, resulting in a stronger blue hue. Before treatment, PL spectra revealed unassigned peaks at 566, 568, 579, 593, and 615 nm. After HPHT-annealing, these PL peaks were not present, suggesting these peaks may not be stable at annealing conditions. Boron-related absorptions at 2459, 2800, 2928, and 4092 cm⁻¹ were observed in IR spectra for both before and after HPHT-annealed diamonds. In almost all cases, the HPHT-annealed IR spectra show an increase in boron-related absorptions. One spectrum displays 50%, 360%, 380%, 860% increases in absorption at 2459, 2800, 2928, and 4092 cm⁻¹ respectively. These data suggest that after HPHT-annealing the concentration of IR-active boron increased. The samples' overall change in hue from gray (blue + brown) to blue after HPHT annealing is most likely attributed to the reduction in the plastic deformation of the diamond lattice. The apparent increase in boron concentration in the HPHT-annealed diamonds revealed by the IR data may be attributed to the liberation of hydrogen from pre-HPHT-annealing hydrogen-boron bonding.

9:45 AM III.5

New Challenge for jewelry industry: Laboratory grown CVD gem quality diamonds. Branko Deljanin^{1,3}, Robert Linares² and Dusan Simic³; ¹Research, European Gemological Laboratory, Vancouver, British Columbia, Canada; ²Apollo Diamonds, Boston, Massachusetts; ³Gem Identification and Research, EGLUSA, New York, New York.

In the early 1950s High Pressure High Temperature (HPHT) experiments culminated in the production of the first industrial

synthetic diamonds. Gem quality laboratory grown HPHT diamonds were produced by GE in 1971. In the late 1980s new technology was developed based on Chemical Vapor Deposition (CVD) of carbon atoms from a hydrogen rich, carbon-containing gas. This new technique is used to deposit thin polycrystalline diamond films on cutting tools and grow thick free standing polycrystalline diamond plates. Single crystal CVD diamonds over 0.5 mm thick were reported for the first time by Apollo Diamonds in 1998. These single crystal CVD diamonds were grown on natural, HPHT or CVD synthetic single crystal diamonds and had similar attributes as type IIa natural diamond crystals. These crystals found application in optical, mechanical and cutting applications, together with HPHT grown diamonds. Recent advances in the process have enabled the growth of high quality CVD diamond crystals in excess of 2 mm thick, from which gemstones have been cut. This paper will report on the properties of type IIa CVD grown gem quality diamonds. Several single transparent CVD crystals of various sizes were tested in gem laboratories before and after cutting. All samples were examined for internal and spectral characteristics using the following instruments: binocular gemological microscope, UV lamp, UV-VIS-NIR spectrophotometer, FTIR spectrophotometer and photoluminescence spectrometer. Results of gemological examinations: $\&\#61623$; Clarity of polished CVD diamonds is slightly included to clean at 10x magnification. $\&\#61623$; Colors are fancy light brown to near colorless. $\&\#61623$; No fluorescence to LW and SW UV radiation. $\&\#61623$; All samples are type IIa (no IR active nitrogen) $\&\#61623$; No absorption peaks in VIS-NIR spectra. $\&\#61623$; Photoluminescence spectra are very distinctive for CVD diamonds. Single crystal gem quality laboratory grown CVD diamonds are not possible to identify using standard gemological equipment, and is necessary to use photoluminescence spectrometers to detect very low level impurity states within the crystal structure. This new product is possible to use as gem material in the jewelry industry, especially if producers are improving techniques to growth larger single crystals. Keywords: CVD diamond, single crystal, gem testing, type IIa.

10:30 AM *II1.6

Spinel: deceitful crystals called to order? Simon A.T. Redfern and Richard J. Harrison; Department of Earth Sciences, University of Cambridge, Cambridge, United Kingdom.

Spinel has attracted attention to themselves for many centuries. They include *dramatispersonae* such as the Black Prince's "Ruby", now resident in the Imperial State Crown at the Tower of London, but with a long and colorful history of its own. Spinel, as lodestone, opened the way for navigation and exploration across the surface of the globe and its discovery and application can properly be thought of as an early "emerging technology". More recently, the relationship between spinel and science has overturned. Rather than providing the tools for new basic technologies, new scientific methodologies have been applied and tested inward on spinel, which has been exploited as a testing ground for ideas and methods. Examples include the application of neutron scattering at extreme conditions, and challenging quantum mechanical computational methods to understand the atomic-scale drivers for metal cation order within the structure. Magnetite- ulvospinel has recently come under the focus of electron holography, providing remarkable new images of the relationship between microstructure and magnetic properties. And understanding the coupling between microstructure, ordering, and physical properties in spinels may now open the way to developing new tools based on spinel for the emerging technologies of the future. Spinel's place in history seems assured.

11:00 AM *II1.7

Zircon: A Window into the Early History of the Earth. Bruce Watson, Earth and Environmental Sciences, Rensselaer Polytechnic Institute, Troy, New York.

Zircon (ZrSiO_4) is prized as a gemstone for its hardness, high refractive index and dispersion, but it is of immeasurably greater value for its unparalleled properties as a recorder of geologic and geochemical information. Despite the low abundance of Zr in the silicate Earth (~ 10 ppm), zircon crystallizes in virtually all igneous and metamorphic rocks, usually as small ($100\text{-}200\mu\text{m}$) tetragonal dipyramids. Zircons are ideally suited to age determinations because they incorporate several elements (U, Th, Sm, Lu) that have radioactive isotopes with long half-lives, and under most circumstances both the parent and daughter isotopes exhibit very sluggish diffusion in the zircon lattice (diffusivities can be as low as $1\text{E-}28$ m^2/s even at 1273K). Equally significant, however, is the fact that zircons are resistant to abrasion during sediment transport and remarkably durable chemically, even in extreme geologic environments. The solubility of zircon in supercritical H_2O at 1 GPa and 1273K , for example, is only about 0.2% – ~ 100 times lower than that of quartz. Even in molten granite, zircon reaches saturation at only ~ 20 ppm dissolved Zr. For these reasons, zircon can survive geologic "processing" and retain chemical and isotopic information as

no other mineral can. At 4.4 billion years old, some Australian zircons date back to the very early history of the Earth, and thus have the potential to tell us about the state of our planet when it was only ~ 150 million years old. Recent reports based on SIMS determinations of oxygen isotope ratios (Wilde et al. and Mojzsis et al., Nature 2001) suggest that oceans existed at this time, which raises the possibility that life may have been established on Earth significantly earlier than has generally been assumed. In a very real sense, zircon is our window into the early history of the Earth – and perhaps into the beginnings of life itself.

SESSION II2: The Science of Gem Materials II

Chair: Thomas Moses

Tuesday Afternoon, December 2, 2003

Liberty C (Sheraton)

1:30 PM *II2.1

Emerald Mineralization in the Northern Cordillera of Canada. Lee Groat¹, Heather Neufeld¹, Daniel Marshall^{2,1}, James Mortensen¹ and Hendrik Falck³; ¹Earth and Ocean Sciences, University of British Columbia, Vancouver, British Columbia, Canada; ²Earth Sciences, Simon Fraser University, Burnaby, British Columbia, Canada; ³C.S. Lord Northern Geoscience Centre, Yellowknife, NorthWest Territories, Canada.

In 1998 W. Wengzynowski discovered Cr-dominant (average 3208 ppm) emeralds in southeastern Yukon. The Regal Ridge showing occurs in metavolcanic rocks of the Yukon-Tanana Terrane, near their contact with a mid-Cretaceous granitic pluton. The emerald crystals occur where quartz veins cut mica-rich layers in a shallowly dipping mica schist of the Upper Devonian Fire Lake mafic metavolcanic unit. Most of the veins are surrounded by a much more extensive, overlapping mass of fine, dark tourmaline crystals. Green beryl crystals up to 4 cm in length occur in tourmaline zones and, rarely, in the quartz veins. Some of the smaller crystals, and sections of larger crystals, are gem-quality. The source of the Be is thought to be the granite, with 12-13.2 ppm Be, and the source of the Cr is the schist (~ 520 ppm Cr). In 1997 pale-green V-dominant (average 1137 ppm V) emerald crystals were discovered near the Lened granite in the southwestern Northwest Territories. The crystals occur in quartz-carbonate-muscovite veins in a garnet-diopside skarn. The skarn developed from limestone of the Rabbitkettle Formation (Cambrian-Ordovician). Other rocks in the immediate area include black shales of the Earn Group (Devonian). The source of the Be is thought to be the granite, with 6-7.3 ppm Be. The source of the V is the shale, with 2070-3170 ppm V. In most producing nations the emeralds come from a number of mines within a mineralized region. The discovery of emeralds at Regal Ridge and Lened along with numerous reports of anomalous levels of Be and/or the presence of beryl in the northern Cordillera suggest the potential for more emerald occurrences in northwestern Canada. This area could represent one (or possibly more) distinct beryl/emerald camp(s), as has been recognized at other places in the world.

2:00 PM *II2.2

First Report of the Identification of Naturally Deuterated Water Molecules in Emerald by Infrared Microspectroscopy: Application to Gem Origin Discrimination. Alain Cheilletz¹, Philippe de Donato² and Odile Barres²; ¹CRPG-ENSG, CNRS, Vandoeuvre-les-Nancy, France; ²LEM, INPL-CNRS, Vandoeuvre-les-Nancy, France.

FTIR micro-spectroscopy has been used to describe deuterated water molecules trapped in structural channels of ring silicates like beryl and emerald. At this very low level of deuterium content (natural dilution conditions: $\text{D}/\text{Hsmow} = 0.0156\%$), stretching vibrations of OD vibrators appear in the range $2900\text{-}2500\text{ cm}^{-1}$ (De Donato et al.1993). In beryl from Minas Gerais, the OD profile is characterized by four bands at 2735, 2686, 2672 and 2641 cm^{-1} . In emerald from Colombia and Brazil, the OD profiles are characterized by five or four bands at respectively 2816, 2737, 2685, 2641 cm^{-1} (Colombia) and at 2735, 2686, 2672, 2641 cm^{-1} (Brazil). These bands can be mainly assigned to type-II HOD molecules. Theoretically, each of these bands are related to a particular chemical surrounding of the HOD molecule within the ring-silicate channel. Practically, a strong reverse correlation appears between the Na_2O and H_2O content of emerald with the number of OD bands. Infrared profiles of HOD molecules have been investigated in 48 different emerald mines in the world. Each deposit is characterized by a specific and reproducible OD profile used to build up a representative spectral data base (2002 Copyright CNRS, Number IDDN FR 001 17016 000 DP 2002 000 10300). Gem origin discrimination is done by micro FTIR spectroscopy analysis of rough, cut, mounted emerald crystals and comparison with the data base. Four families of emerald mines can be distinguished, corresponding respectively to 5, 4, 3 and 2 bands OD

profiles. Within each family, individual mines are characterized by specific OD profiles showing distinct relative intensity ratio of OD bands. In case of overlapping, specific valence vibrations of $^{12}\text{CO}_2$ and $^{13}\text{CO}_2$ are used. These results open a new field of gemmological investigations particularly concerning the identification of archeological emeralds origin and gem expertises. Reference: de Donato Ph., Villieras F., Barres O. and Yvon J. (1993): Observation of OD stretching vibrations at natural dilutions: contribution of diffuse reflectance FTIR spectroscopy. C.R. Acad. S. Paris, 316, serie II, 1757-1662.

2:30 PM *II2.3

Lanthanides in Fluorite (REE:CaF₂): Probes of Crystal Surface Structure and Association in Color Centers. John Rakovan, Geology, Miami University, Oxford, Ohio.

Incorporation of lanthanide elements into natural fluorite crystals has been used as a probe of surface structural anisotropies and heterogeneous reactivity during crystal growth. The Ca site in fluorite is cubic, with eight nearest neighbor F-ions at a distance of 2.36 Å. The surface expression of this site is structurally different on symmetrically nonequivalent crystal faces. Differences in the atomic structure of Ca surface sites leads to a differential affinity for substituent elements such as the REE. During growth this causes differential incorporation of substituents, leading to sectoral zoning. The {100}, {111}, {110}, {210} and {321} all exhibit different affinities for incorporation of all of the REE studied. Intracrystalline partition coefficients range from 1.6 and 3.5. Once incorporated these elements can play an important role in the cause of color through their association with structural defects. Molecular complexes, of a cubically coordinated REE³⁺ and an adjacent fluorine vacancy, with two trapped electrons can absorb visible wavelengths of light, causing color. Complexes containing La and Ce lead to green color while those associated with Gd and Y produce blue to violet colors. Sectoral zoning of color results from the sectoral segregation for these trace elements.

3:30 PM II2.4

The Artificial Gems With Long Persistent Phosphorescence. Weiyi Jia, Physics, University of Puerto Rico, Mayaguez, Puerto Rico.

Gemstones with afterglow seen in dark are very rare in nature. They have been highly treasured all over the world in the human history. We have fabricated, for the first time, several types of single crystals and ceramics of rare earth doped aluminates of alkaline earths, such as SrAl₂O₄:Eu,Dy, SrAl₄O₇:Eu,Pr and CaAl₂O₄:Eu,Nd, with bright persistent phosphorescence in the green (520nm), blue-green (488nm) and violet (440nm)[1,2]. The persistent time can be more than 10 hours. The crystals were grown in form of fibers by laser heated pedestal growth (LHPG) method. The hardness of the crystal is close to that of sapphire. The crystals and ceramics may have potential applications to Jewelry industry. In this presentation, we will introduce the optical properties of the gems. We are interested in collaboration with investors to commercialize the gems. The author is thankful to the former collaborators: W.M. Yen, L. Lu, and H. Yuan. 1. W. Jia, W.M. Yen, L. Lu and H. Yuan, Patent No. US 6,117,362 and US 6,267,911 B1. 2. W. Jia, H. Yuan, L. Lu, H. Liu and W.M. Yen, J. Crystal Growth, 200 (1999) 179.

3:45 PM II2.5

Color of Variscite : Application to the Determination of Color and Mineralogical Origin of French Neolithic Jewels.

Laurence Galois¹, Georges Calas¹ and Ammonmat Kiratisin²;

¹Mineralogy, Mineralogy and Crystallography Laboratory, Paris, France; ²mineralogy, Mineralogy and Crystallography laboratory, Bangkok, Thailand.

The color of variscite has been investigated and the role of transition elements determined using spectroscopic methods and DRX. Diffuse reflectance measurements of variscite samples from various localities, show that the major coloring agent is Cr³⁺ with specific transitions that can be attributed unambiguously to this element as present in a distorted octahedral site. From EPR data, Cr³⁺ and Fe³⁺ are determined as diluted into the crystal structure or present into enriched domains depending on the origin of the variscite. Vanadium is present as vanadyl compound [VO₂⁺] and/or under the V⁵⁺ oxidation state in substitution of P⁵⁺. Using these data, the origin of color, the source and nature of the minerals used to make French Neolithic jewels has been investigated. In such jewels the use of non destructive methods is essential. Green beads has been found in megalithic monuments which were built about 4000-5000 BC. To understand the mineralogical nature and the origin of the green color of these beads which vary from dark green to pale green, some samples, from Carnac (Brittany, France), have been studied. Microprobe analyses were not discriminating because of the lack of specific preparation for such kind of sample. Variscite type M and metavariscite appeared to be the predominant phases. Using both optical absorption and EPR we show that Cr³⁺ is the major coloring

element and that some Fe³⁺ at the surface of the sample from secondary iron oxides can slightly modify the resulting color of the jewel. Some Fe²⁺ in octahedral sites are also identified on the optical spectra. From these results, the local origin usually claimed for the variscite material of these jewels is questioned.

4:00 PM *II2.6

Treatment of Natural Corundum by Beryllium Lattice Diffusion. Wuyi Wang¹, Matt Hall¹, Tom Moses¹ and Shane McClure²; ¹GIA-Gem Trade Lab, New York, New York; ²GIA-Gem Trade Lab, Carlsbad, California.

Defects in corundum that give rise to selective absorption in or extend to the range of visible light create various types of coloration. The artificial lattice diffusion of trace amounts of beryllium at high temperature can significantly alter the color of natural corundum by creating additional trapped-hole color centers (McClure et al., 2002; Emmett and Douthit, 2002), which has never been reported in natural corundum. In order to improve our understanding of the processes involved with beryllium diffusion, 21 selected natural corundums were treated and systematically analyzed by several spectroscopic techniques (SIMS, IR, and UV-VIS). The selected natural samples varied in color (colorless, pink, yellow, blue, green, purple, gray, and brown); most of them came from known geographic sources. All the samples were polished with parallel sides, a majority of which are parallel to crystallographic c-axis. Diffusion was performed by imbedding these samples in a Be-doped Al₂O₃ matrix, and heating them at 1850°C at one atmosphere pressure for 33 hours at high oxygen fugacity. Among the 21 samples, 13 showed sharp absorption lines at 3368, 3310, 3295, 3233, and 3185 cm⁻¹ with varying intensity (0.01 to 11.2 cm⁻¹ in absorption coefficient relative to the absorption line at 3310 cm⁻¹) due to hydrogen impurity in the corundum lattice. After diffusion treatment, all these H-related absorptions were entirely destroyed. Before the treatment, beryllium concentrations were about 1.0 ppm in all samples (close to the detection limit of SIMS). After treatment, beryllium concentration at the sample surfaces increased significantly and varied from 16 to 269 ppm. The beryllium concentration at sample surfaces was found to be heterogeneous in distribution. Colors of these sapphires changed significantly after treatment. An intense orange coloration was developed among colorless, yellow, and pink sapphires from Sri Lanka and Madagascar. Gray-brown sapphires from Songea, Tanzania, uniformly showed intense orange coloration after the treatment. However, no color change was observed in a pink sapphire from Vietnam despite of elevated beryllium concentration. In addition, in contrast to our expectations, two blue sapphires from northern Madagascar and one from an unknown source turned out to be darker blue after the treatment, probably due to dissolution of rutile inclusions by forming more Fe-Ti pair. Chemical interaction among chemical impurities in corundum is essential in determining its coloration, and data obtained from this study would be very helpful to explore the function of trace amounts of beryllium in corundum lattice as a cause of coloration.

4:30 PM *II2.7

The Origin of the Red Color of Ruby: The Importance of a Structural Relaxation Around Cr³⁺ and Fe³⁺. Emilie Gaudry¹, Bruno Boizot², Amonmat Kiratisin¹, Guillaume Morin¹, Christian Brouder¹, Laurence Galois¹, Philippe Saintavirt¹ and Georges Calas¹; ¹Mineralogy, University of Paris, PARIS, France; ²Laboratoire des Solides Irradies, Ecole Polytechnique, Palaiseau, France.

Trivalent Cr imparts minerals and gems a broad range of coloration, among which the red color of ruby and the green color of emerald has been the most described. The change in the color arises from a modification of the crystal field stabilization energy, generally described as decreasing with increasing average metal -O distances in the mineral structures hosting the trivalent Cr ions. We will review the location of trivalent Cr and Fe in ruby, using two spectroscopic methods. Electron paramagnetic resonance (EPR) spectra have been modelled using the superposition model. Natural x-ray linear dichroism absorption has been obtained at the Cr and Fe K edge on ruby single crystals. The two methods demonstrate the presence of a structural relaxation around trivalent Cr and Fe ions in ruby, with a structural surrounding similar to that of the pure end member of the solid solution. The site distortion is different around the two impurity cations, as expected from the structural differences between Fe₂O₃ and Cr₂O₃. The metal-ligand distances are not the only control of the crystal field intensity. The origin of the red color in ruby will be discussed at the light of complementary data on other Cr-containing minerals.

SESSION II3: The Science of Gem Materials III
Chair: Jeffrey Post
Wednesday Morning, December 3, 2003
Liberty C (Sheraton)

9:00 AM *II3.1

Computer Modeling of Appearance Aspects of a Faceted Diamond. T. Scott Hemphill¹, M L Johnson² and I M Reinitz¹;

¹Research, GIA, New York, New York; ²Research, GIA, Carlsbad, California.

Combining a computer model, that simulates the physics of light as it interacts with a faceted diamond, with computer graphics techniques produces images that are visually accurate. The same computer model serves as a framework for developing mathematical expressions (metrics) that describe aspects of the appearance of the round brilliant cut diamond. Varying the specific lighting and observing conditions yields differing metrics for a single appearance aspect. The observation of a real diamond depends on three factors: 1. The physical shape and optical properties of the diamond itself. 2. The environment the diamond is in, including the properties of the illumination and of the objects surrounding the diamond. 3. The location and characteristics of the observer. Each of these three factors can be modeled mathematically, and the laws of geometric optics can be applied in a physical simulation to produce images that are representative of actual diamonds. Several diamond appearance aspects are considered in the diamond trade, including: brilliance (the intensity and location of white light returned from the crown of a diamond); fire (the visible display of colored light returned from the crown); and scintillation (the flashes of light that are seen as the diamond, light source or observer moves). The trade also assesses details of the patterns of light and dark reflections seen within a round brilliant as part of the process of evaluating diamond appearance. Human observations of actual diamonds provided validation for a number of metrics for brilliance and fire. Observers from all levels of the diamond trade made pair-wise comparisons of suites of well-characterized diamonds in environments similar to those modeled. The relative ordering of these diamonds, based on the observations of brilliance or fire in each condition, shows good agreement with the order predicted by the metrics.

9:30 AM II3.2

Nanoindentation Behavior and Contact Properties of Gems and Minerals. Margaret E. Broz^{1,2}, Robert F. Cook¹ and Donna L.

Whitney²; ¹Department of Chemical Engineering and Materials Science, University of Minnesota, Minneapolis, Minnesota;

²Department of Geology and Geophysics, University of Minnesota, Minneapolis, Minnesota.

Contact properties have long been used to classify gems and minerals: the sequential Mohs "hardness" scale allows for rapid field identification of rocks and minerals as well as providing a tangible indicator of material behavior. Specimens are assigned Mohs numbers that reflect their scratch or single contact wear resistance. However, contact wear resistance is a property that comprises several other material properties: modulus (resistance to elastic deformation), hardness (resistance to plastic deformation) and toughness (resistance to fracture). Here we demonstrate the use of depth-sensing indentation ("nanoindentation") techniques and controlled-flaw indentation techniques (using microindentation) to determine independently the modulus, hardness and toughness of gems and minerals. Nanoindentation has an advantage over other techniques in that it offers sub-micrometer resolution of the indentation process. These techniques make available the fundamental mechanical properties of gems and minerals, allowing for identification of materials, analysis of chemical gradients and other microstructural features, as well as providing insight into the origin of the Mohs number and local contact responses in general. The techniques are demonstrated on the Mohs minerals and some common gems, including ruby, zirconia and garnet: hardness varies monotonically (but non-linearly) and modulus varies non-monotonically with Mohs number. Determination of the fracture conditions and properties of garnet has application in geologic studies of garnet-bearing rocks. Calculating the magnitude, path and rate of decompression associated with fracture of garnet is useful for tectonic studies of how rocks move from depth to the Earth's surface.

9:45 AM II3.3

Tiger's-eye and Pietersite: Fraternal Gems with Disparate Ancestries. Peter J Heaney and Donald M Fisher; Dept. of Geosciences, Penn State University, University Park, Pennsylvania.

Tiger's-eye is a popular gem material with lustrous golden-brown bands that exhibit a radiant chatoyancy in polished specimens. For well over a century, scientists had attributed its distinctive cat's-eye effect to quartz pseudomorphism after the fibrous amphibole crocidolite. Based on TEM, XRD, and light microscopy data, however, we proposed that tiger's-eye forms when a crocidolitic host rock cracks and columnar quartz is deposited from silica-saturated fluids antiaxially within the fissure (Heaney and Fisher 2003). Crocidolite inclusion trails created by this crack-seal process are responsible for the chatoyancy of tiger's-eye, and the variable orientations of the reflective cat's-eyes actually trace the displacement

of the host rock during the tectonic fracture events. Since its discovery in the Kuraman District of Namibia in 1962, the gem variety pietersite has been considered a close relative of tiger's-eye due to their mineralogical and optical similarities. Both contain quartz with inclusions of blue crocidolite that often is partly oxidized to brown hematite and goethite. Pietersite differs from the common South African tiger's-eye in its brecciated rather than banded texture, generating a lovely chaotic chatoyancy. Petrographic comparison of pietersite with tiger's-eye indicates that these gem materials formed by very different pathways, despite their close resemblance. Whereas tiger's-eye occurs as cm-thick layers within moderately metamorphosed Precambrian banded iron formations in South Africa and Australia, Namibian pietersite is found within limestone cobbles of unknown provenance. Microscopic examination reveals no evidence for crack-seal crystallization. Rather, the fabrics suggest that primary sideritic shales were infiltrated with siliceous hydrothermal solutions, which brecciated the parent rock by dissolution. The siderite partially reacted to precipitate crocidolite fibers, and subsequently length-fast chalcedony replaced the residual siderite while preserving the crocidolite. Monodisperse 10-micron carbonate spheruloids at the reaction boundaries provide evidence for this secondary silicification process.

10:30 AM *II3.4

Nano- To Micro-Structure of Natural Gem Opals: Relation to Deposition and Growth Conditions. Emmanuel Fritsch¹, Mikhail

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Gem opals offer a wider variety of micro- to nano-structures than usually thought. Most gem opals studied so far are sedimentary Australian play-of-color opals, which diffract visible light, and are opal A, that is amorphous in XRD. Less studied "volcanic" gem opals from Mexico or Ethiopia, with or without play-of-color, are opal CT, i.e. XRD shows diffraction peaks for disordered cristobalite. In general, the building blocks of these CT opals are roughly spherical silica particles about 10 to 40 nm in diameter. The nanoparticles can be fully disordered, as observed in all of the world's fire opals (orange and transparent). In some instances, nanoparticles can coalesce with a first degree of order to form small rods or fibers as in palygorskite-containing translucent pink opals. In a second degree of order, grains may coalesce to form platy crystals, about 20 nm thick. These platelets can be grouped according to a third degree of order into a roughly spherical aggregate called lepispheres. Play-of-color "volcanic" opals show a higher degree of organization, in which the nanoparticles form pseudospheres of appropriate size for diffraction of visible light (about 200 nm) in a matrix of less acid-soluble (probably better crystallized) particles. The more soluble particles also have necessarily a different index of refraction, so that light diffraction can occur. Sometimes, nanograins can form directly spheres, then of the order of the micron in diameter. Fresh breaks often show no particular organization. These microstructures are revealed only by attack with diluted hydrofluoric acid; one sees a network of holes in the residual matrix. There is a continuum of structures between opals with and without play-of-color. The more organized the structure and the more round the "spheres" are, the more noticeable the diffraction colors appear. The crystallinity of the opal does not increase with the degree of order. It is not a crystallization process. The major parameter controlling growth appears to be temperature of deposition, rather than geological environment.

11:00 AM *II3.5

Controlled Crystallization of Microparticles - A Tool for Making Opals, "Inverse Opals" and Advanced Coatings.

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The extraordinary optical properties and colors of opals arise from the diffraction of light in the microstructure of these gems. The opals are naturally synthesized colloidal crystals, in which submicrometer sized particles are stacked in periodic arrays in three dimensions. Colloidal crystallization has been studied for many years, due to its relevance to the fundamentals of colloid science. This field has, however, grown rapidly in the last few years, due to the possibility to use particle self-assembly as a tool for fabrication of "photonic crystals", structures that could guide and control the flow of light in photonic chips and devices. One promising route to making photonic structures is the synthesis of "inverse opals", using the colloidal crystals as templates that are backfilled with material of high refractive index, and then removed, leaving behind arrays of ordered cavities. This talk will present an overview of the techniques for colloidal crystallization in two and three dimensions and inside spherical templates. The strategies for using these crystals for making "inverse opals" will be

discussed. The major challenge at present appears to be the transition from the proof-of-concept stage to efficient, engineered fabrication. Assembly and deposition techniques must be developed that are fast, cost-effective and easy to control. The self-assembled photonic structures are best suited for applications which benefit from the efficient and inexpensive fabrication, while being tolerant to the intrinsic defects in the structure. Examples of how we aim to achieve this by developing techniques for fast electric field driven crystallization and for large scale deposition of crystal coatings will be presented.

11:30 AM *II3.6

Pearls, Natural and Cultured, Their Types, Localities, Growth and Treatment. Kenneth Scarratt, AGTA-Gemological Testing Center, New York, New York.

Pearls, natural or cultured, may be found in a variety of mollusks that live naturally, or are induced to live, in either freshwater or saltwater environments in various parts of the world. The natural pearl reigned supreme amongst gem materials prior to the introduction of the cultured pearl in the 1920s. Today the public's general perception of a pearl is that they are all cultured. However, natural pearls, i.e., those pearls that a mollusk produces without human interference, are available to those who search out these unique products of nature. The vast majority of cultured pearls created today are of the nacreous variety and are produced by various bi-valves, the one exception to this may be the abalone (Haliotidae genus *Haliotis*) which is a univalve. As with the cultured variety, natural pearls are mostly produced in bivalves and are nacreous but they may also be produced in a variety of univalves, in addition to the abalone, these include *Strombus gigas* and *Melo melo* both of which produce non-nacreous natural pearls. Separating the cultured from the natural is an increasingly difficult gemological challenge but one that the industry regard as essential to maintaining the integrity of both the natural and cultured products. Determining if either product has been treated in some way also creates unique challenges. This paper describes the differences between the natural and cultured products, where and how these are produced and in which mollusks, how they are separated and various treatments are identified, using microscopy, x-radiography, chemistry, Raman and UV/visible spectroscopy.