

## บทสรุปสำหรับผู้บริหาร

1. Final Report: Characteristics of Alexandrite and Emeralds Samples from Some Important Locality
2. Funding support for fiscal year B.E. 2550 in the amount of THB 1,500,000.00
3. Funding Period: 1 year starting July B.E. 2550
4. Details of research progress

### 4.1 Objectives

1) To better characterize alexandrite and emerald samples from major localities and to precisely specify their geographical origins.

2) To help GIT become internationally accepted for its expertise in grading and origin determination of gemstones.

4.2 Comparison between the expect result and the working result are summarized below

กิจกรรมตามแผน	ผลการดำเนินงาน
1. Literature survey	1. Scientific journal articles related to this study were obtained. Knowledge was also gained from consulting experts in the field.
2. Obtain (either buy or borrow) alexandrite and emerald samples from credible sources	2. Alexandrite samples are from Bahia, Brazil; Nova Era Brazil; Hematita Brazil; Sri Lanka; Malejuheva, Russia; Ural, Russia; Audhra, India; India; Lake Manyara, Tanzania. Emerald samples are from Santa Terezinha, Brazil, Carnaiba-Socoto, Brazil, Itabira, Brazil, Ndola Rural, Zambia, Sandawana, Zimbabwe, Mananjary region, Madagascar.
3. Analyze physical, optical and chemical properties of alexandrite and emerald samples	3. Physical, optical, photoluminescence, and some chemical properties of alexandrite and emerald samples were measured.
4. Analyze samples using various advanced	4. Samples were analyzed using advanced analytical instruments, such as, FTIR, UV-Vis-NIR, EDXRF, LA-

analytical instruments	ICP-MS, and Cathodoluminoscope.
5. Conclusion	5. Project concluded. The final report is being submitted
6. Publication	6. <b>Wathanakul, P.</b> , Homkrajae, A., Atichat W., Schwarz D., Sutthirat C., Sriprasert B. and Pisutha-Arnond, V. 2007. FTIR spectra as clues in geographic origins of emerald samples. Asia Oceania Geosciences Society holds 4th Annual Assembly (AOGS 2007), Bangkok, July 30 - August 03, 2007.

#### 4.3 Conclusion

The alexandrite samples from each source contain mineral and fluid inclusions reflecting mineralization styles as well as geological environment of each deposit.

Alexandrite samples from Brazil (Nova Era), Russia (Ural Mountain) and Russia (Malejuheva) showed infrared absorption peak at  $2166\text{ cm}^{-1}$ , stronger than those of other sources. UV-Vis-NIR spectra of alexandrite samples from Sri Lanka showed the strongest absorption peaks of  $\text{Fe}^{3+}$  and  $\text{Cr}^{3+}$  at 365, 375 nm and 435 nm, respectively. Samples from this source, however, showed the lowest  $\text{Cr}^{3+}$  absorption bands at 570 and 680 nm. Alexandrite samples from Bahia, Brazil, and Lake Manyara, Tanzania showed the strongest  $\text{Cr}^{3+}$  absorption peaks at 570 and 680 nm while those from India showed strongest  $\text{V}^{5+}$  absorption peak at 410 nm among others.

Based on EDXRF and LA-ICPMS results, alexandrite samples from India showed the highest content of V that related to the colour-changing phenomena. Alexandrite samples from Bahia, Brazil showed the highest content of Cr while those from Sri Lanka showed high contents of Mg, Ti and Ga. Alexandrite samples from Tanzania show high contents of Fe and Sn whereas those from Ural Mountain, Russia showed high content of Ta.

Studies of the effect of fluorescence features under UV and/or Cathodoluminescence (CL) found that alexandrite samples from Bahia, Brazil showed strong stretch glowing i.e., containing highest Cr among other sources, but the samples showed weak to inert in CL

because of their high Fe content. Alexandrite samples from Lake Manyara, Tanzania showed inert in CL which was in good agreement with their LA-ICPMS results with the highest Fe content. Alexandrite samples from India, Hematita, Brazil and Malejuheva, Russia showed strong red in CL due to high Cr and low Fe contents.

Mineral and fluid inclusions in emerald samples suggested paragenetic environments, which also reflected mineralization styles as well as geology of each deposit. The nonschist-hosted Nigeria and Colombia emerald samples showed different inclusion suites compared to those of the schist-hosted ones.

Studies of infrared absorption suggested that the crystal structure of beryl, when viewing through the c axis, consists of channels; these channels usually contain water molecules whose orientations are influenced by alkali-metal, e.g., mainly Na, K, Li, and Cs. Accordingly, the vibration modes of  $\text{H}_2\text{O}$  molecules in the crystal channels of emerald have occurred with respect to the absorbed resonance infrared radiation. The results showed that FTIR spectra could be used as a promising evidence for differentiating emerald samples of different localities. The Nigeria emeralds showed strong spectra of the non-alkali related water molecules (NA) whereas the samples from Pakistan showed strong alkali-related ones (AR). While other localities present both types of absorption. The samples from Columbia, Russia, and Afghanistan showed spectra of both types but tend to have NA>AR type while the samples from Santa Terezinha, Itabira, Zambia, Zimbabwe, and Madagascar showed AR>NA type. These were in good agreement with the results from UV-Vis-NIR and LA-ICPMS measurements. For example, Nigeria emeralds showed  $\text{Fe}^{3+}$  absorptions, and their LA-ICPMS results yielded high Fe content, which were in consistency with their UV-Vis-NIR results that showed more  $\text{Fe}^{3+}$  than  $\text{Fe}^{2+}$ . Most emerald samples showed two broad bands of  $\text{Cr}^{3+}$  and  $\text{V}^{3+}$  and iron-related absorption peaks at around 370 nm and in the NIR region. There were exceptions, however, for Colombia and Pakistan emeralds;  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  peaks were absent in their absorption spectra. Many samples from Santa Terezinha, Afghanistan, Zimbabwe, Itabira, Zambia, and Pakistan exhibited  $\text{Fe}^{2+}/\text{Fe}^{3+}$  charge-transfer transition, so called aquamarine component, which induced yellowish-green and bluish-green colours in emeralds.

EDXRF plotted diagram can be used for approximately distinguish between the high alkali-related emeralds from low alkali-related ones which was also confirmed by FTIR results. LA-ICPMS is excellent at detecting small quantity of an element, but cannot differentiate between, for example,  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  oxidation states. For the problem of overlapping localities, LA-ICPMS results are very helpful as Cs and Li contents can be used to completely discriminate the two overlapping localities from each other such as these from Madagascar vs Zambia and can be used a plot of Al vs Fe+Mg+Cr+V+Na+K to differentiate the samples from Colombia vs Afghanistan. Moreover, the plot of Fe+Mg versus Na+K including UV-Vis-NIR and FTIR absorptions are very useful for quick investigation.

Using all of those integrated instrumentation techniques has been proven that some of the overlapping emerald origins such as these from Colombia vs Afghanistan, or Madagascar vs Zambia by the absorption peak in FTIR result, that emerald samples from Colombia and Afghanistan yielded otherwise very close absorption spectra with only subtle difference in the direction perpendicular to the c-axis. The samples from Colombia showed absorption of  $\text{H}_2\text{O}$ -AR at  $3230\text{ cm}^{-1}$  and  $3910\text{ cm}^{-1}$  whereas that of samples from Afghanistan were shifted to  $3242\text{ cm}^{-1}$  and  $3924\text{ cm}^{-1}$ .

Study of the absorption spectra of emerald samples from various localities in the direction parallel to the c-axis showed that only the samples from Zambia and Zimbabwe absorbed at  $5590\text{ cm}^{-1}$  (NA). This method could therefore be used to distinguish Zambia and Zimbabwe emerald samples from other localities.

Emerald samples from Zambia, Zimbabwe, and Madagascar cannot be differentiated easily by their chemical compositions. However, it was found that measurement of absorption between  $7500\text{-}6500\text{ cm}^{-1}$  yielded interesting results. The samples from Zambia absorbed at  $7138\text{ cm}^{-1}$  (NA) with O-H stretching at  $7072\text{ cm}^{-1}$  whereas those from Zimbabwe and Madagascar only absorbed at  $7077\text{ cm}^{-1}$  (AR).

**Problems and Solution**

- More alexandrite samples from each locality should have been collected and analyzed for better representatives of the deposits.
- For more accuracy of the spectroscopic measurements, emerald samples from each source should be set and measured with respect to their c-axis.
- Inclusions could not be examined for all samples because the Raman spectroscope was down for an extended period of time.
- For more precise geographic determinations of alexandrite and emerald, samples from more diverse localities, such as China and Canada, should have been included in this study.

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