X-RAY AND OPTICAL METHODS APPLIED TO THE STUDY OF GEM MATERIALS

P. Carpenter, J. Armstrong, G. Rossman, E. Fritsch,** and R. Kane**

*Department of Earth and Planetary Sciences, California Institute of Technology,
Pasadena, CA 91125 **Gemological Institute of America, Santa Monica, CA 90404

Complimentary techniques have been used to study the relationship between color, chemical composition, and physical properties of gem materials, using single crystals of high optical quality. Faceted gems may be quite valuable and must be analyzed by non-destructive methods. Techniques have been developed for analysis of gems using EDS X-ray fluorescence (XRF) and WDS/EDS electron-probe microanalysis (EMP). Consumable material from the same locality is often available for optical absorption and infrared spectroscopy (IR). These methods are used for mineral classification, identification of chromophores and their oxidation state, and assignment of ions to structural sites.

Color in gems can be due to dispersed metal ions, charge-transfer between ions, color centers, band-gap phenomena, or combinations thereof. Transition elements are important chromophores, typically at trace levels, but a given element may cause various colors in different compounds due to differences in the coordination environment. For example, the red color of ruby, the red and green color of chrysoberyl, and the green color of emerald are due to Cr substitution for Al in these minerals. Conversely, the color 'green' is also due to Fe2+-Fe3+ charge-transfer in aquamarine, and Cu2+ in malachite. Irradiation and heating change colors due to activation or destruction of color centers, respectively, and it is believed that many natural gems have been treated in this way to improve their color. The identification of color mechanisms in gems is the subject of ongoing research. [1,2,3,4]

Emerald is the varietal name traditionally applied to green beryl (Be3Al2Si6O18) containing up to several weight percent Cr3+ substituting for Al. The structure consists of large Si6018 rings which form channels that are cross-linked by Be and Al in tetrahedral and octahedral sites, respectively. The crystal chemistry of beryl is complex, involving coupled substitution, including Li for Be in the tetrahedral site, and both trivalent and divalent ions for Al in the octahedral site. The large channel sites host a variety of ions and molecules, including up to 2.9% H2O, as well as large univalent ions (Na, K, Rb, Cs). The net result is a significant departure from the ideal formula $Be_3Al_2Si_6O_{18}$. The existing database of beryl chemistry is generally limited to gravimetric analyses, with few analyses obtained using modern techniques. Existing EMP analyses are typically incomplete due to both diverse chemistry and the historical inability to analyze light elements such as Be and O.[5]

A primary goal of gemologists is to discriminate natural emerald from synthetic material. Usually optical methods are used to identify mineral inclusions and zoning or growth bands, but in the absence of these features chemical techniques are used. Samples are typically screened using XRF in a semiquantitative manner for subsequent quantitative EMP analysis. Results of past work on suites of natural and synthetic emerald indicate specific trace element profiles and IR spectroscopy can aid in identification of natural vs. synthetic emerald. [7,8]

Natural emeralds from several important mines have been analyzed to improve the understanding of the crystal chemistry of beryl and further aid gemologists in chemical discrimination techniques. The trace element profile of these samples has been expanded and accuracy improved using peak overlap correction. Evaluation of light element analytical procedures is being carried out using synthetic beryl standards. Preliminary measurement of Be using a Mo_4C analyzing crystal shows large peak shifts for Be as a function of coordination environment, and substantial x-ray absorption relative to selected Be standards. Synthetic beryl mounted in known crystallographic orientation is being used to evaluate x-ray channelling. Analysis for oxygen has been initiated to directly measure both structural oxygen and channel molecular water.

The intensity of green color in emerald is normally attributed to the concentration of Cr (table 1, Transvaal for example). However, emerald from Eidsvold is colored dark green due to V, and other emeralds commonly contain low levels of V. Emeralds from Gravelotte and Conquista de Vitoria are pale green in color, due to much lower V and Cr, despite relatively high Fe. Scandium is reported only sporadically in beryl analyses, but is routinely detected in these emeralds. Comparison with an anhydrous synthetic beryl standard permits the conclusion that these emeralds contain at least 1.5 weight percent H_2O. Noteworthy also are Na and Mg which nearly span the observed range of these elements in beryl. The inverse relationship between trivalent octahedral cations (Al, Sc, Cr, and V) and either (Na + K) or Mg point to coupled substitution involving octahedral Mg balanced by univalent ions in the channel sites (figures 1 and 2). This relationship has also been observed for emeralds from the Ural Mountains[9] but is less clearly followed by other beryls, presumably due to other substitutional schemes. It is evident that the chemistry of beryl in general, and emerald in particular, deserves further work.

References

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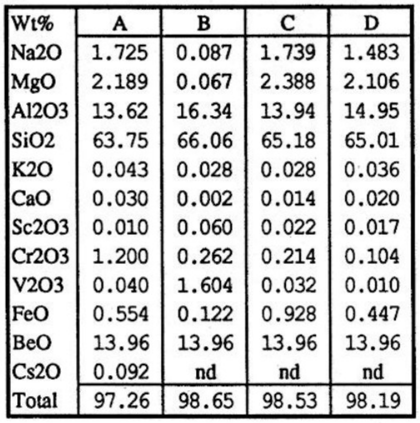

Wt%	A	B	C	D
Na2O	1.725	0.087	1.739	1.483
MgO	2.189	0.067	2.388	2.106
Al2O3	13.62	16.34	13.94	14.95
SiO2	63.75	66.06	65.18	65.01
K2O	0.043	0.028	0.028	0.036
CaO	0.030	0.002	0.014	0.020
Sc2O3	0.010	0.060	0.022	0.017
Cr2O3	1.200	0.262	0.214	0.104
V2O3	0.040	1.604	0.032	0.010
FeO	0.554	0.122	0.928	0.447
BeO	13.96	13.96	13.96	13.96
Cs2O	0.092	nd	nd	nd
Total	97.26	98.65	98.53	98.19

Table 1.--Electron microprobe analyses of emeralds. (a) Transvaal, South Africa USNM 139551, green-blue; (b) Minne, Eidsvold, Norway USNM R6983-1, dark green-blue; (c) Gravelotte, South Africa USNM 120556, pale green; (d) Conquista de Vitoria, Bahia, Brazil USNM C5979, pale blue-green. Conditions of analysis: 15KV, 100nA, 120 sec per element (precision 1-5%), CITZAF/Armstrong correction.

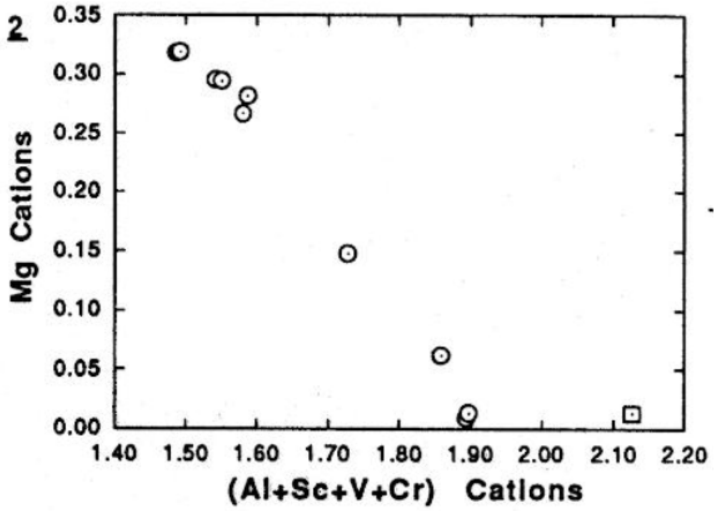

FIG 2.--Plot of (Al+Sc+V+Cr) octahedral cations vs. Mg cations. Circles: natural emeralds this study, Square: synthetic Chatham emerald. Magnesium substitutes in octahedral site of beryl. Synthetic Chatham emerald exhibits high Cr and trivalent ions in channel site.

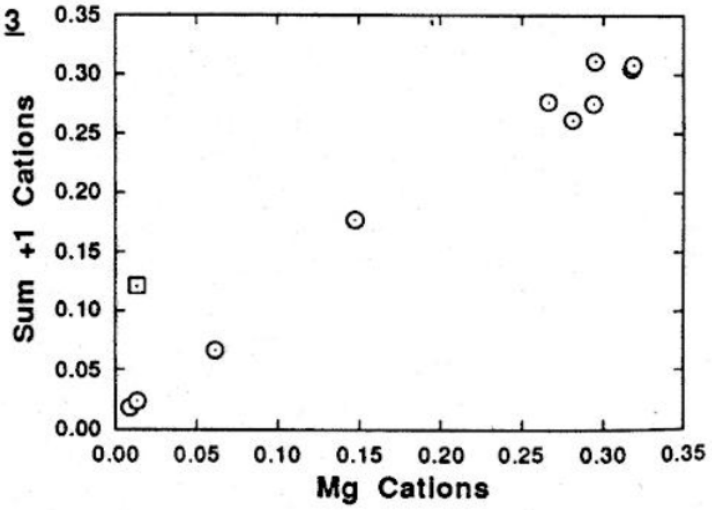

FIG 3.--Plot of Mg cations vs. (Na+K+Rb+Cs). Symbols as in fig 2. Substitution of Mg in octahedral site is balanced by univalent ions in channel site of beryl.