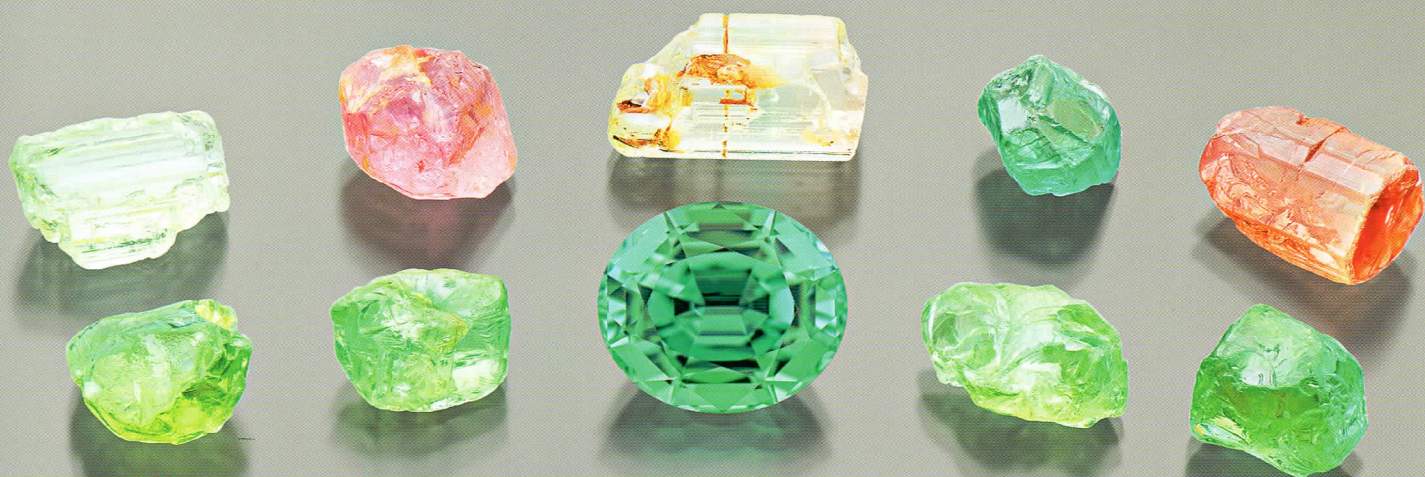


n° 5

2018
INTERNATIONAL
EDITION

IGR

RIVISTA ITALIANA DI GEMMOLOGIA
ITALIAN GEMOLOGICAL REVIEW



(Cover photo: rough tourmalines pastel color from Congo, green tourmaline from Nigeria and, on the center, a 14 ct. nigerian tourmaline oval cut tormaline - Photo by Arjuna Irsutti, gemstones courtesy from Tales of Gemstones)

THE CAUSES OF COLORS OF FLUORITE, A GEM EMPEROR NERO PAID ONE MILLION SESTERCES

Enrico Butini, Flavio Butini, Francesca Gaeta

Fluorite, a super gem in the ancient world

In the first century after Christ, Pliny the Elder (23 - 79 AD), Roman writer, admiral and naturalist, in his *Naturalis Historia* reports of an inestimable material, unknown before then, brought to Rome as spoils of war, by Pompeo Magno from the East "[...] the same victory introduced the *murra* vases for the first time in Rome [...]". Pliny refers to the victory that Pompeo Magno obtained during the campaign of 66 b.C. against Mithridates VI Eupator King of Pontus, a region currently comprising the geographic areas of Cappadocia, the Black Sea coasts and part of Iran. The ancient author also records: "[...] this type of pottery immediately became in common use [...] and this luxury grows day by day [...]" and also makes precise economic references, writing: "[...] a former consul was used to drink in a cup of *murra* bought for 70,000 sesterces [...] Tito Petronio [...] broke a ladle of *murra* he had bought for 300,000 sesterces [...] but Nero, as befits an emperor, surpassed all paying only one cup 1.000.000 sesterces"¹.

These figures, if related to current currency, should amount to 3 to 12 million euros. The reason why such a huge value was given to the *murrina* vases is certainly attributable to the multitude of colors that presented this material (fluorite), never seen in another gem before then, and its rarity. Just consider that to date only three *murrina* vases are known in the world. Two of these are kept at the British Museum of London (Figure 1) and one at the Ashmolean Museum of Oxford (Figure 2).

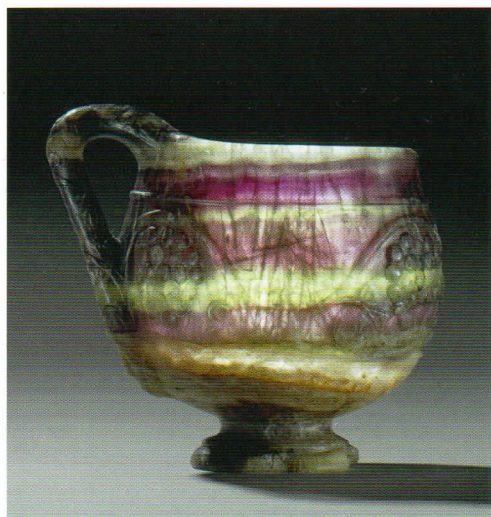


Fig. 1 Murrina vases kept at the British Museum of London.

¹ Pliny, *Naturalis Historia*. XXXVII, 7 (Corso et al. 1988, p. 755 e 757).

The enigma of Vasi Murrini

While carrying out the study on *Murrina Vasa*², IGR gemologists had the opportunity to deepen the analysis of this gem. This paper summarizes the results of gemological tests conducted on different samples of fluorite, focusing on the determining causes of the great variety of its colors.

The causes of colors of fluorite

Fluorite (CaF_2) is a very common mineral found both in igneous formations, such as granites rich in fluorine, and in metasomatic metamorphic rocks, as accessory mineral, in greisen and secondary quartzites. The gem varieties of fluorite are extracted in numerous countries including, for example, China, Britain, Russia and others.

It is not a widespread faceted gem, because of its low hardness (4 on the Mohs scale), it is however much appreciated as a material for carvings and sculptures thanks to its variety of colors (Figure 3).

In its pure state, fluorite is colorless and perfectly transparent (Figure 4), therefore owes its colors to impurities and imperfections of its crystal lattice (allochromatic mineral).

Understanding the causes of color in fluorite is no easy task and the debate about their origin is still ongoing. However, three are the most reliable hypotheses:

- a. presence of impurities of organic origin;
- b. presence of impurities of inorganic origin;
- c. color centers and structural defects.

The presence of small traces of organic compounds in the fluorites of various colors has been widely demonstrated through the use of different analytical techniques (Mueller 1954), however the direct relationship between the presence of such compounds and the formation of color has not been clarified yet.

The second theory is based on the presence of ions that can cause light absorption through electronic transitions or charge transfers, the presence of Mn^{2+} and S^{2-} has been repeatedly found but the concentration of such elements alone does not fully justify the incredible color varieties of fluorite (MacKenzie and Green 1971).

The third and more complex hypothesis, which does not exclude the first two, suggests a mechanism of structural defects, due to irradiation, such as the well known F-center consisting of an electron trapped in an anionic vacancy (Figure 5). The common presence of colloidal calcium (in particles in the order of 30 nm) associated with such structural defects can give rise to important scattering



Fig. 2 Murrina vase kept at the Ashmolean Museum of Oxford.



Fig. 3 Multicolor fluorite sample.



Fig. 4 Colorless fluorite sample.

² A text entitled "L'enigma dei Vasi Murrini" is about to be published by Enrico Butini who also contributed to this article.

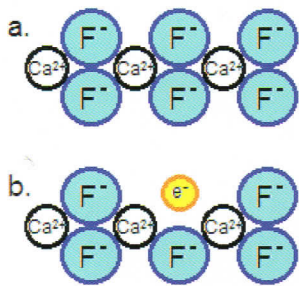


Fig. 5 Example sketch of the F-center: a. intact portion of the crystal lattice; b. dislocation of an F atom substituted by an electron.



Fig. 6 Rough pink fluorite. (Photo:Trinityminerals.com)



Fig. 7 Rough yellow fluorite. (Photo:Trinityminerals.com)

phenomena and Tyndall effect, able to absorb in the visible (Braithwaite et al 1973). In addition to what just said above, the common presence of rare earths in fluorite (e.g. Samarium - Sm, Europium - Eu, Erbium - Er, Ytterbium - Yb) increases the variety of characteristic absorptions both in the visible and in the ultraviolet spectra. Examples of such mechanisms are the Y / O_2 - color center, which can contribute to pink hue (Figure 6) and the O_3 or O_3^- color centers which can contribute to yellow hue (Figure 7).

These colors seem to be caused by forms of radioactivity, and subsequently modified by light or impurities of an unidentified nature; in the green ones there were traces of Eu^{2+} , in the "amethyst purple" ones there were traces of Mn^{3+} and impurities from hydrocarbons. It is not excluded that such impurities, as already mentioned, are constituted by radioactive substances (Przibram 1938).

The absorption bands and peaks that determine the wide range of colors in fluorite, deriving from the mechanisms described above, can be easily eliminated by heating. In particular, the bands in the visible region are eliminated, with consequent bleaching, at temperatures as low as 300°C or even below. Absorptions in the ultraviolet region, on the other hand, are more resistant, but can however be removed by heating to about 500°C. For this reason the heat treatment is not practiced since the only obtainable effect would be the loss of the much appreciated colors typical of fluorite.

Gemological analysis

Fluorite is a relatively simple gem to be identified thanks to its isotropic behavior under the polariscope, to its low refractive index (1,430), to its low variability of the specific

gravity (3.18 - 3.20 gr / cm³) and to its scarce hardness (it can be scratched with the tip of a small knife).

The study and understanding of colors, however, are only possible through more advanced gemological techniques such as UV-Visible spectrophotometry and PL (photoluminescence) spectroscopy.

PL Spectroscopy

We analyzed numerous fluorites both at room and liquid nitrogen temperature (about -190°C), using various sources of excitation, in particular a 365 nm LED for the graph in figure 8 and a 532 nm laser for the graph in figure 9. The two examples shown here have highlighted the presence of elements belonging to the group of the rare earths such as Sm and Eu, to which we can certainly attribute the cause of yellow and green colors, respectively, of the two samples.

UV-Visible Spectrophotometry

The samples were subjected to UV-Vis analysis, in particular the two gemstones reported in the present work show absorption bands and peaks respectively responsible for a pleasant "sapphire blue" (Figure 10) and a valuable "amethyst purple" (Figure 11). The broad absorption band between 550 and 600 nm is attributable to colloidal aggregates of Ca, which, on the basis of their size and concentration, shift the band, determining substantial color changes in the visible spectrum; the absorptions at 399 and 334 of figure 10, are attributable to structural defects color centers, poorly active since they fall into the ultraviolet or near ultraviolet spectrum.

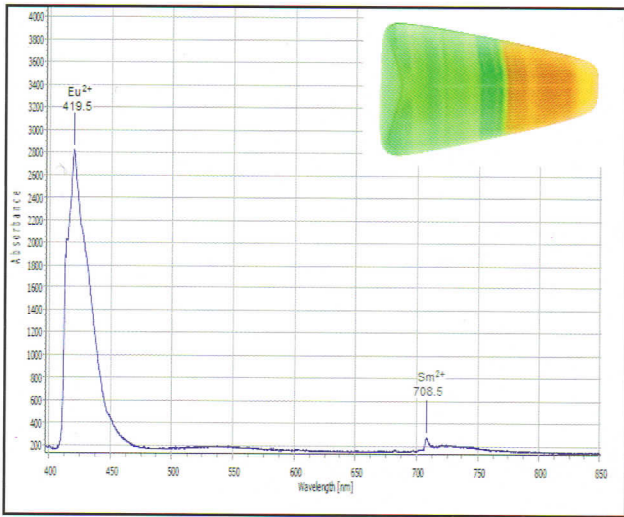


Fig. 8 PL spectra of the yellow part of this sample.

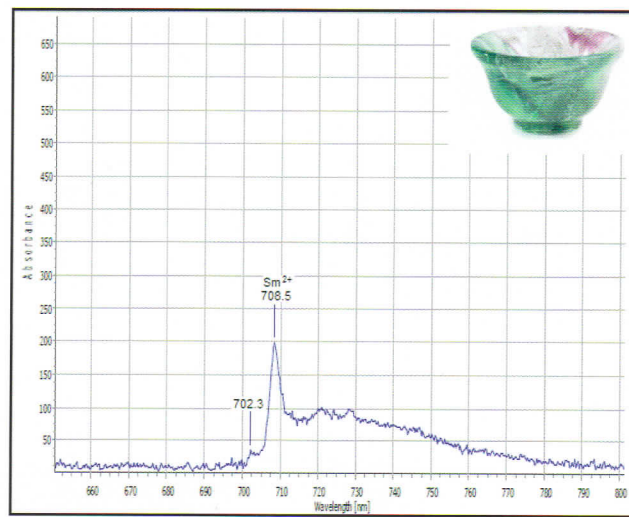


Fig. 9 PL spectra of the green part of this sample.

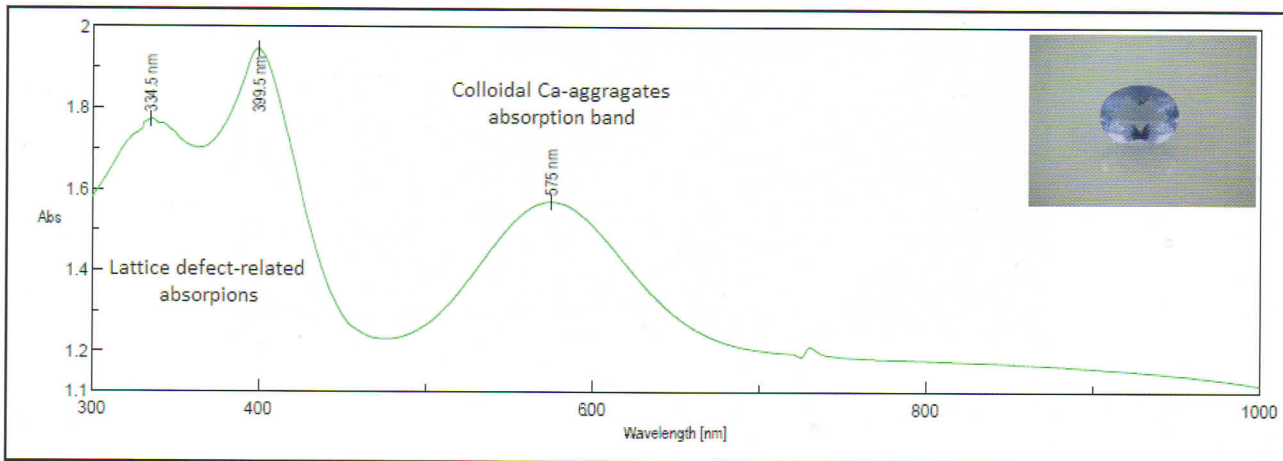


Fig. 10 UV-Visible spectra of a blue gem quality sample.

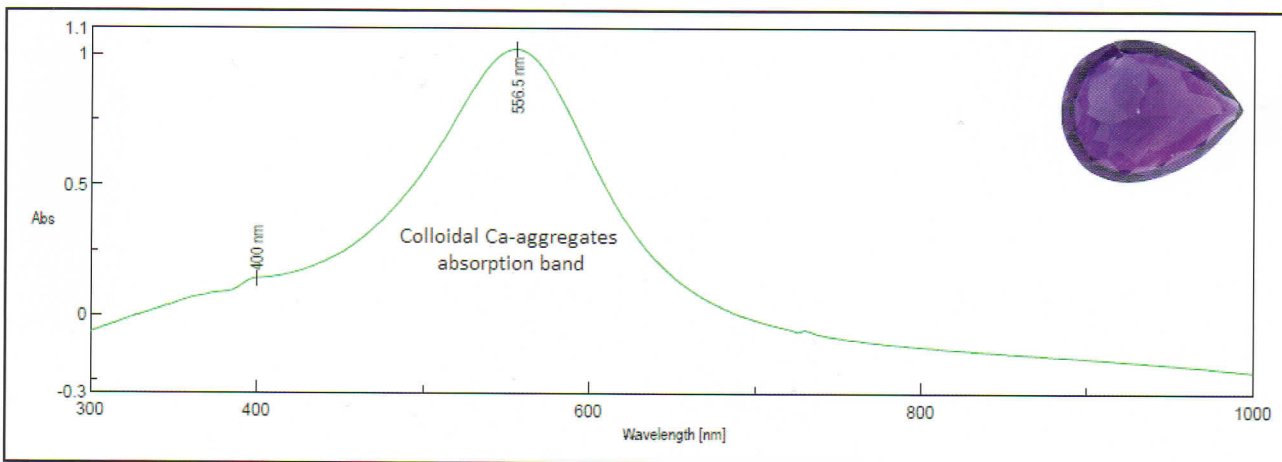
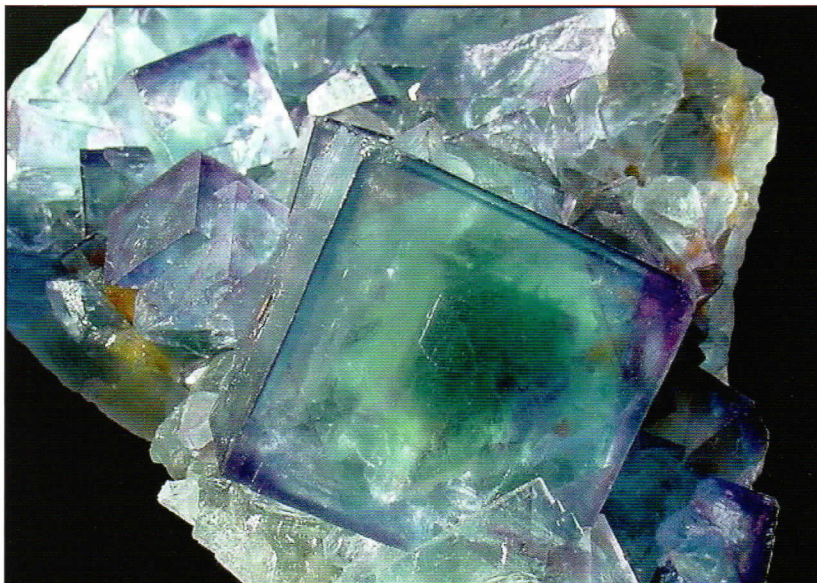


Fig. 11 UV-Visible spectra of a purple gem quality sample.

Conclusions

This fascinating material, characterized by a multitude of colors, has been appreciated since ancient times and is mentioned in Pliny's *Naturalis Historia* which exalts its chromatic varieties: "[...] Their value is the variety of colors [...] the edges and certain reflex nuances are highly appreciated and are similar to what it is seen on the inside of the rainbow [...]"³.

Although the characteristics of this mineral are not the best for the use in jewelry, this work is still intended to support the gemologist who has to analyze gems or carvings in fluorite.



Bibliography

Cavenago-Bignami Moneta, S., 1980. *Gemmologia*, I-III, Hoepli, Milano

Cavallini, M., Gigante, G.E. 2006. *De re metallica: dalla produzione antica alla copia moderna*, L'Erma di Bretschneider, Roma

Corso A., Mugellesi, R., Rosati, G., 1988. *G. Plinio Secondo, Storia Naturale, V. Mineralogia e storia dell'arte, Libri 33-37*, Einaudi, traduzioni e note di A. Corso, R. Mugellesi, G. Rosati

Loewental, A.I., Harden, D.B., 1949. *Vasa Murrina*, with a note by C.E.N. Bromehead, in *JRS*, 39, pp. 31-37.

Mackenzie, K.J.D., Green, J.M., 1971. *The Cause of Coloration in Derbyshire Blue John Banded Fluorite and Other Blue Banded Fluorites*, in *Min. Mag.* 38, 459-470

Mueller, G. 1954. *Cong. Geol. Internat. Compt. Rend. 19me Sess., Algérie*, 15, 523-39

Ogden, J.M., 1982. *Jewellery of the ancient world*, Rizzoli

Pasto, A.E., 2009. *Collector's guide to fluorite*, in *Schiffer Earth Science Monographs*, 3

Przibram, K., 1938. in *Nature*, 141, 970

Starnes, X.B., 1947. *Fluorite and zinc on the Eva Tanguay property, Crittenden County, Ky*, Department of the Interior, Bureau of Mines

³ Pliny, *Naturalis Historia*. XXXVII, 7 (CORSO et al. 1988, p. 759).