

"Rainbow Calsilica"

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Abstract

An ornamental stone with bands in various colours was investigated with traditional gemmological as well as sophisticated analytical methods. The analysis of the various colours with Raman spectroscopy showed that the material was not of natural origin, as stated by the vendors, but an artificial product, partly coloured by artificial pigments. The material is stabilised using a waxy/resinous material.

Introduction

An ornamental material, reportedly from Mexico, has been on sale at gem and mineral shows in Europe since 2002. The material shows spectacular colour distribution (Fig. 1) and is marketed under the name "Rainbow Calsilica", "Calsilica", "Calcilica", or "Fossilized Clay". Prior to this, the material had been on sale in the US mainly via the Internet, in the form of talismans, amulets and figurines. All dealers handling the material, offer what they claim is proof of its natural origin with photos of the "mine" it is said to come from, a "Certificate of Authenticity" from a geological laboratory in Arizona, as well as specimens of "rough" (Fig. 2). According to this certificate, the Rainbow Calsilica is composed of microcrystalline calcite, with the amorphous clay mineral allophane as the binding material; the pigmentation is associated with the allophane. The colour is reportedly the result of a "copper push" that

crosscuts rhyolite. In fact, after extensive chemical and physical analyses this material has been shown to be an artificial product.

Analytical methods

As well as using standard gemmological analyses, two polished pieces of the material (Fig. 1) weighing 46.11 and 36.14 ct were analysed with Raman spectrometry to distinguish the different components of the material. The Raman spectra were performed with a Renishaw Raman System 1000 Spectrometer with Peltier-cooled CCD camera and argon-ion laser (514 nm, 25 mW). X-ray fluorescence analyses were performed in differently coloured areas using a Tracor Spectrace 5000 energy-dispersive X-ray Fluorescence Spectrometer. Infrared spectra were recorded with a Phillips PU9800 FTIR spectrometer.

Results

Gemmological analysis

Macroscopically, the material showed irregular bands of blue, green, light yellowish green, yellow, orangey yellow, white, black, and reddish brown, and somewhat resembled the brightly colored sands found in bottles in curio shops (Fig. 1). The width of the bands ranged from 0.1 to 2.7 mm, with variations not only between the bands, but also within a given band. The colour range of the bands included white, yellow, light blue, bluish green, various shades of green, red, brown and dark grey. In

places, rounded "droplets" with the same granular texture as the surrounding bands, but of a different colour, were present. The rough material appeared sandy and dull in colour. The material has to be stabilised before it can be worked in order to obtain a good polish and its intense colours.

The S.C. values of the samples (measured hydrostatically) were 1.88 and 1.92. The fluorescence depended on the intensity of the colour. When exposed to long-wave UV radiation, white bands fluoresced white, light green and light blue bands fluoresced a weaker white, and brown and black bands were inert. A similar, but weaker, result was observed with short-wave UV.

With a gemmological microscope, we were able to distinguish broken, irregularly shaped, and sometimes rhombic white grains in all of the colored bands. Also present were grains of various colours (Fig. 3), the quantities and proportions of which corresponded to the overall colour and intensity of each layer. Blue bands contained dark blue grains and, in some cases, thin layers of concentrated colour (Fig. 4), along with white grains and a colourless bonding material. The green bands contained yellow as well as blue pigments. Occasionally, we observed a transparent band of a soft plastic-like material, sometimes with bubbles, between the coloured bands and in irregular patches (again, see Fig. 4). Bands and other areas that appeared black to the unaided eye were dark greyish green with 50x magnification, and showed a multitude of different-coloured grains, transparent plastic-like areas, and pigments.

Instrument analysis

EDXRF analyses showed that Ca was the major constituent (approximately 80-90%) in

two randomly chosen bands, as well as in representative layers of various colours (i.e., blue, green, reddish brown, and black). Minor constituents were Si, Ba, and Fe (similar values in all samples). In addition, there was approximately 1-2% Sr in the blue, brown and green bands. A black band contained over 13% Sr. Traces of Mg, Al, P, S, Cl, Mn, Cu, Zn, and As were detected in various amounts, with no obvious correlation to colour.

Raman analysis showed that the white grains were calcite. This mineral was also a major constituent of the fine-grained groundmass. Analysis of two red layers showed the presence of hematite, which was consistent with the colour of these bands. Celestine (SrSO_4) was identified in the black areas, and is probably the cause of the high Sr content measured with EDXRF. Raman analysis of concentrated blue areas within blue layers gave the strongest peaks above 1300 cm^{-1} (Fig. 5), which suggests that this material is organic. When this Raman spectrum was compared to those of 20th century blue artists' pigments, the material was identified as a copper phthalocyanine pigment called PB15 (again, see Fig. 5), a synthetic pigment that was developed in the 1930s. Similarly, the light greenish-yellow areas contained the yellow mono-azo pigment PY1 (or Hansa Yellow; Fig. 6) (Vandenabeele et al., 2000). The other coloured bands contained one or both of these pigments to produce the corresponding colour.

The infrared spectra of the colourless areas and layers revealed features similar to paraffin wax, together with some additional, unidentified absorption bands (Fig. 7 top). Raman analysis also showed bands that are consistent with paraffin, with the major bands at 2928 and 2868 cm^{-1} (Kiefert et al., 1999). Additional bands were observed at 1444 , 1462 , and 1732 cm^{-1} (paraffin), as well as at

1279, 1306, and 1352 cm⁻¹ (due to unknown phases)(Fig. 7 bottom). Despite the spectral similarities to paraffin, the material was more elastic and it appears that the substance is an aliphatic polymer or a paraffin derivative mixed with other compounds unknown to us.

Conclusions

Our examination of the two Rainbow Calsilica samples proves that this is a manufactured material. Extensive microscopic analyses show larger and smaller angular rock fragments together with a bonding agent and colour pigments around grain boundaries or parallel to the layers.

The chemical composition, with Ca as the major element and Al, Si, Sr, Ba and Fe as minor elements as well as trace elements, shows no correlation with the differently coloured layers. The Cu concentration, which lies between 0.05 and 0.14% was explained by a "copper push" in the American certificate of authenticity. The identification of the blue pigment, shows, however, that the copper must be derived from the pigment copper phthalocyanine PB15. An examination that considering only the inorganic composition of the material would not have been able to disprove natural origin. However, Raman spectrometry was able to detect both the colouring agents used for producing this artificial sedimentary rock and the stabilizing resin. This non-destructive method of gemstone analysis has once again shown its versatility (Hänni et al., 1997; Kiefert et al., 2001).

Although the identification of pigments with Raman spectroscopy is new in gemmology, this technique has been extensively used in the identification of artists' paints. Raman

spectrometry is used for the identification of pigments in mediaeval manuscripts (Edwards et al., 1999; Vandenabeele et al., 1999; Burgio et al., 1997), for sculptures of different colours (Vandenabeele et al., 2000), wall paintings (Edwards et al., 1997; 2001) and oil paintings (Vandenabeele et al., 2001 a, b).

In our case, the presence of synthetic pigments and of a paraffin-like substance precluded a natural origin. The latter substance had apparently been used to stabilise the material; Samples that lack this polymer reportedly separate easily along colour layers (S.F. McClure, pers. comm., 2002). The Rainbow Calsilica appears to have been made of pulverised carbonate rock mixed with pigments and stabilised with a polymer.

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Fig. 1: These two pieces of "Rainbow Calsilica" weigh 46.11 and 36.14 ct. The larger sample is 35.6 mm long.



Fig. 2: Unstabilised "Rainbow Calsilica" is supposed to emphasise the "natural" origin of the material. The colours in this sample are much paler than in the stabilised samples.

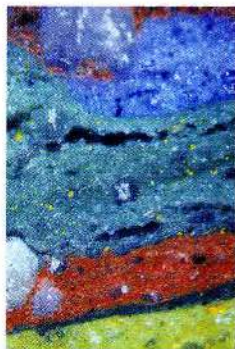


Fig. 3: White grains of various sizes are present in all colour layers of the Rainbow Calsilica, together with smaller grains of blue, green, yellow, and other colours. - Magnification 50x.

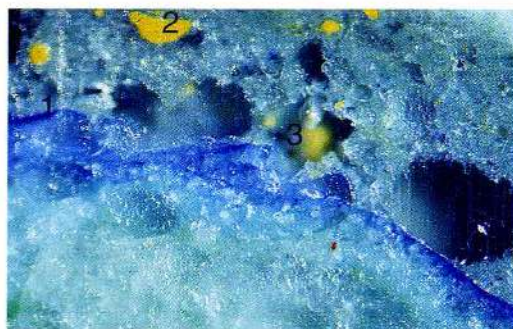


Fig. 4: A thin layer of concentrated blue is visible in this view of the Rainbow Calsilica (1), as are areas of yellow pigment (2) and a clear plastic-like material (3). - Magnification 100x.

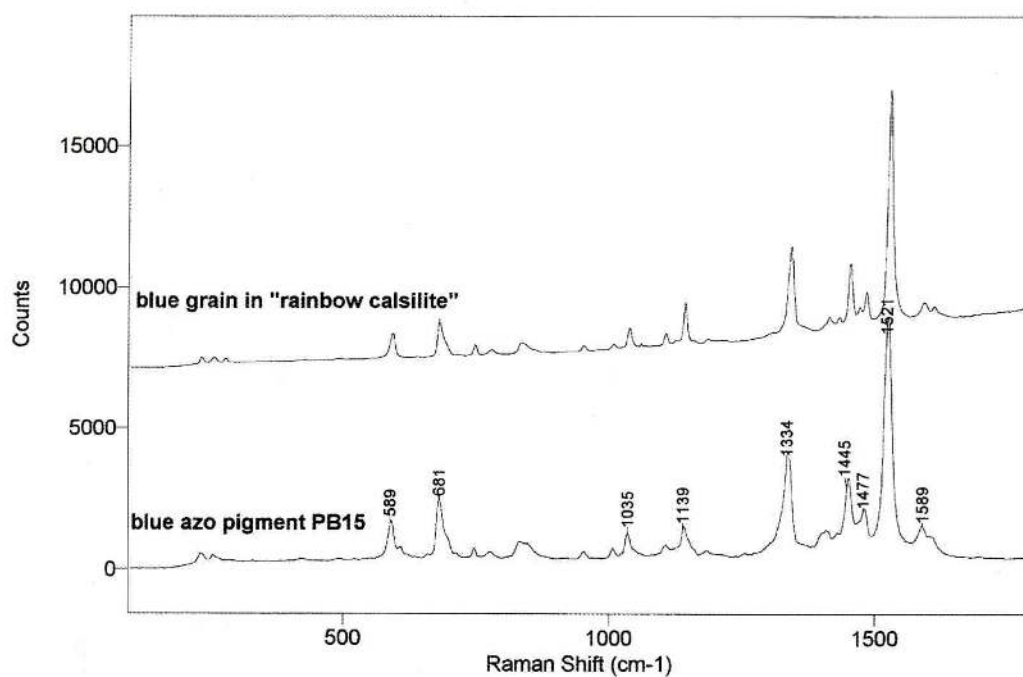


Fig. 5: The Raman spectrum of the blue pigment in Rainbow Calsilica is identical to that of the blue copper phthalocyanine pigment PB15.

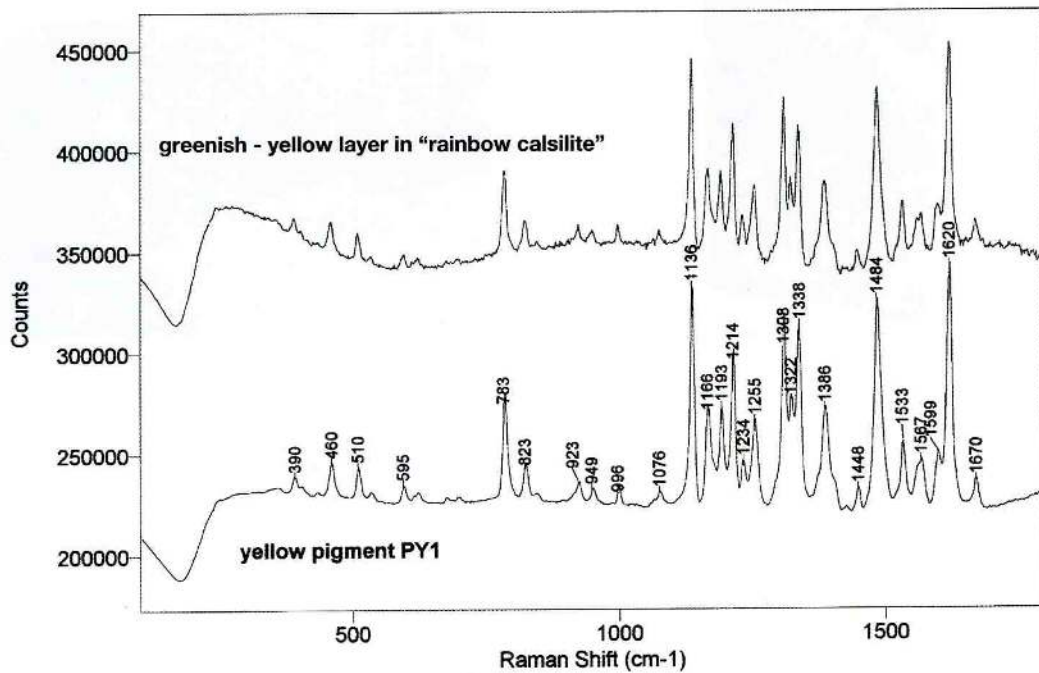


Fig. 6: The spectrum of the yellow pigment matches that of the yellow mono-azo pigment PY1 (Hansa Yellow).

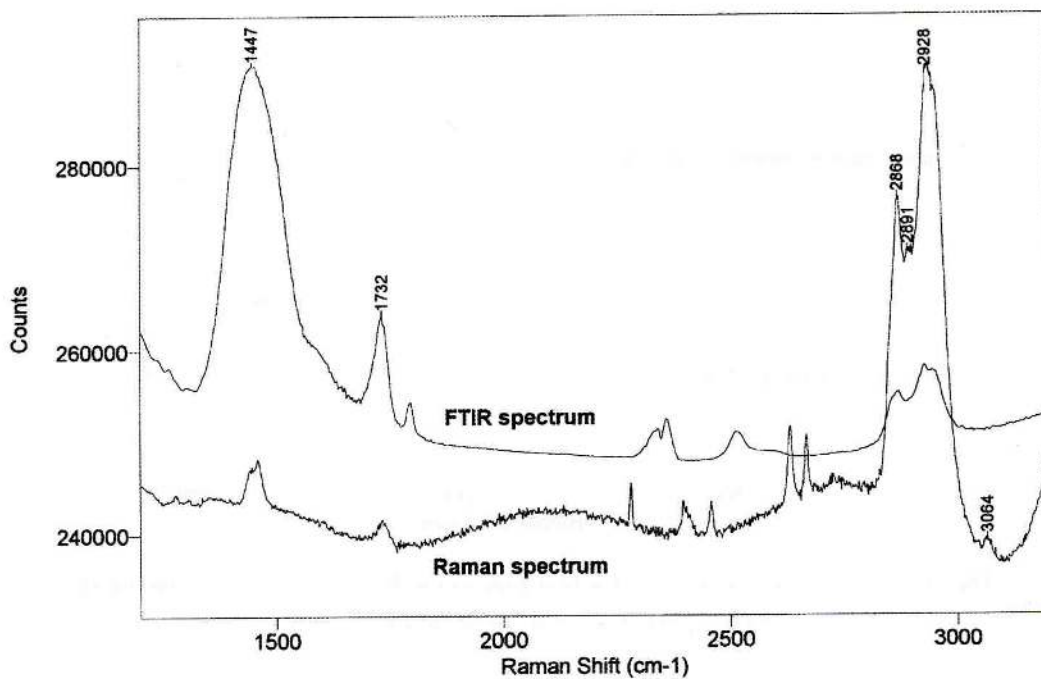


Fig. 7: Top: Infrared spectrum of the stabilising agent in Rainbow Calsilica;
Bottom: Raman spectrum of the stabilising agent in Rainbow Calsilica.