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***NOTE***

# Role of Trace Elements in Natural Amethysts in Colouring

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In this study, a research has been conducted on trace elements that are likely to colour natural amethyst, a semi-precious gemstones. The trace elements of two amethyst samples, one in purple and the other one in lilac, which were procured from Dursunbey (Balikesir, Turkey) were defined. Comparing the trace elements obtained with the previous studies, it was concluded that the colour purple intensified as Fe and Mn proportions in amethysts increased and the colour purple turned into a lighter purple, which was lilac as the proportion of Sb element diminished.

**Key Words: Amethyst, trace elements, Fe, Mn, Sb.**

The mingling of hot hydrothermal water with oxygen-rich cold meteoric water in relatively near surface conditions results in the formation of amethyst because these oxidizing conditions form trivalent iron which provides the colour purple to amethyst[1]. It has been stated that the colour centers related to Fe impurity cause the colour purple in amethyst[2,3]. Iron may be present in quartz in three valence states, $Fe^{2+}$, $Fe^{3+}$ and $Fe^{4+}$. All three states may be present in interstitial sites, only $Fe^{3+}$ being in a substitutional $Si^{4+}$ site[4]. Cohen and Makar[5] found that the $Ti^{3+}$ related rose colour in single crystal rose quartz.

**Sampling and analyses:** Two natural massive amethyst samples utilized in this study were procured in Dursunbey (Balikesir, Turkey) samples, located in Western Anatolia. Amethysts were coloured according to criteria in Taylor *et al.*[6]. According to these criteria, two samples were fixed as purple and lilac amethysts. Semi-quantitative analyses of trace elements in the samples were carried out in Philips PW-2404 wavelength dispersive X-Ray Fluorescence Spectrometer instrument. In analyses, Al, As, Ca, Cl, Cr, Cu, Fe, K, Mg, Mn, Na, Ni, P, Rb, S, Sb, Ti and Ga elements were determined as ppm.

According to the results of analyses (Table-1) conducted on purple and lilac amethysts, the elements (ppm) in natural amethyst in purple were concluded to be as: Al: 965, As: 2, Ca: 118, Cl: 41, Cr: 12, Cu: 2, Fe: 163, K: 228, Mg: 31, Mn: 6, Na: 20, Ni: 2, P: 30, Rb: 1, S: 75, Sb: 32 and Ti: 15. On the other hand, in natural lilac amethyst, it was determined as: Al: 476, Ca: 61, Cl: 51, Cr: 19, Fe: 125, K: 18, Mg: 66, Mn: 7, Na: 22, P: 2, Rb: 5, S: 313, Sb: 58 and Ga: 30. As, Cu and Ti elements found in purple sample do not exist in the lilac one. In addition, Ga element found in lilac sample does not exist in the purple one. The proportions of values (C = A/B) obtained in the analyses were fixed as Al: 2.02, Ca: 1.93, Cl: 0.80, Cr: 0.63, Fe: 1.30, K: 12.66, Mg: 0.46, Mn: 0.85, Na: 0.90, P: 15. Rb: 0.20, S: 0.23 and Sb: 0.55.

TABLE-1
DURSUNBEY (BALIKESIR, TURKEY), TRACE ELEMENTS (ppm) CONTENTS OF NATURAL AMETHYSTS

| Al | As | Ca | Cl | Cr | Cu | Fe | K | Mg | Element/ samples |
|---|---|---|---|---|---|---|---|---|---|
| 965.00 | 2 | 118.00 | 41.00 | 12.00 | 2 | 163.00 | 228.00 | 31.00 | A |
| 476.00 | – | 61.00 | 51.00 | 19.00 | – | 125.00 | 18.00 | 66.00 | B |
| 2.02 | – | 1.93 | 0.80 | 0.63 | – | 1.30 | 12.66 | 0.46 | C = A/B |
| **Mn** | **Na** | **Ni** | **P** | **Rb** | **S** | **Sb** | **Ti** | **Ga** | **Element/ samples** |
| 6.00 | 20.00 | 2 | 30 | 1.0 | 75.00 | 32.00 | 15 | – | A |
| 7.00 | 22.00 | – | 2 | 5.0 | 313.00 | 58.00 | – | 30 | B |
| 0.85 | 0.90 | – | 15 | 0.2 | 0.23 | 0.55 | – | – | C = A/B |

A: Purple amethyst; B: Lilac amethyst.

Trace elements and the proportions of the mentioned elements (C* = A*/B*) in natural amethysts concluded in a study conducted by Birsoy[7] on the same colour formation amethysts in the same region are shown in Table-2.

TABLE-2
TRACE ELEMENTS (ppm) DEFINED IN THE STUDY ON NATURAL AMETHYSTS IN THE SAME REGION [Ref. 7]

| Al | Fe | K | Mg | Mn | Na | Sb | Ti | Element/ samples |
|---|---|---|---|---|---|---|---|---|
| 31.00 | 33.00 | 12.50 | 1.0 | 4.20 | 15.00 | 51.40 | 1.20 | A* |
| 424.50 | 23.40 | 33.80 | – | 8.60 | 35.10 | 115.70 | 8.70 | B* |
| 0.07 | 1.41 | 0.37 | – | 0.49 | 0.43 | 0.44 | 0.14 | C* = A*/B* |

A*: Purple amethyst; B*: Lilac amethyst.

In previous studies, $Fe^{4+}$ was defined as the cause of the colour purple[3,8]. In addition, Lehman and Bambuer[9] stated that the colour purple could be formed only when $Fe^{3+}$ ion was placed in space between atoms which was its tetraedric symmetry. The quasi-complete relationship between the iron quantity and the intensity of the colour purple in amethyst was suggested to result from the existence of iron in different places in the frame structure[7]. Iron in amethyst does not always exist in the suitable place in the frame and with the proper charge stabilizer[9]. It was also noted that other charge stabilizers other than $Fe^{3+}$ that could cause an error could exist as well[10]. In terms of atomic diameter and charge, $Sb^{5+}$ and $Mn^{3+}$ ions within amethyst have the adequate properties to be placed in the place of $Si^{4+}$ and in space between atoms in quartz's composition[11].

In comparison trace elements in Tables 1 and 2, it was concluded that Fe, K, Mg, Mn, Na, Sb and Ti elements were detected in both studies. Having compared Al, K, Mg, Na and Ti elements which were common in both data obtained in this study and data of Birsoy[7], it was stated that there was no parallelism in distributions of proportions of these elements. It was also observed that the C proportions estimated for Fe, Mn and Sb elements which were common were similar. Consequently, the increase in the proportion of Fe and Mn elements in amethyst results in a more dark purple other than lilac. On the other hand, with the rise in Sb elements, the colour turns into a lighter lilac from purple.

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