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The influence of Vietnam and Sri Lanka spinel mineral chemical elements on colour

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The chemical composition of 42 various colour spinel minerals from the Vietnam Luc Yan locality and the Sri Lanka Ratnapura locality were investigated and according to the results of the research the chromophore influence on colour was interpreted. It was established that the colour of spinel mineral is determined not only by chromium, iron, cobalt but also by vanadium. We assume that V^{3+} determines the brown or yellow spinel colour, since a relatively high content of V_2O_3 (0.44–0.88%), which may determine the orangey hue of mineral, was found in the investigated orangey pink samples from the Ratnapura locality. Other chromophores found in these samples, such as chrome oxide (0.05–0.36%), iron oxide (0.08–0.28%) and cobalt oxide (0.05–0.20%), show low or medium contents, which determined the pink hue of spinel. After carrying out the research on the samples of dark red spinel, it was established that the red colour is determined by a high content of Cr^{3+}. The purple/violet colour of samples is determined by Fe^{2+} and a low content of Co^{2+}, whereas the pink hue of samples is determined by Cr^{3+} and a high content of Fe^{2+}, which saturation depends on the quantitative ratio of Fe^{2+} and Cr^{3+}. Relatively low contents of chromophores V^{3+}, Cr^{3+}, Fe^{2+} and Co^{2+} were found in the pinkish grey spinel, thus their hue is grey.

Keywords: spinel, magnesium spinel, orange pink spinel, yellow spinel, magnesium spinel with vanadium

INTRODUCTION

A whole group of minerals, whose general chemical formula can be expressed as $A^{2+}B_2^{3+}O_4^{2-}$, is named after the spinel mineral. The bivalent ions are housed in A sites in 4-fold coordination (tearahedral) while the trivalent ions occupy octahedral B sites [1]. In spinel group minerals both tetrahedral and octaedral sites are occupied by metal ions [2] and thus it leads to a coloured product [3, 4]. A site can be occupied by such ions as Mg^{2+}, Fe^{2+}, Zn^{2+}, Mn^{2+}, Ni^{2+}, Co^{2+} or Cu^{2+}, whereas B sites can be filled by Al^{3+}, Fe^{3+}, Cr^{3+}, V^{3+}, Ti^{4+}, germanium or antimony ions [5]. The main metal ions that determine the colours of spinel are Fe^{2+}, Fe^{3+}, Cr^{3+}, Co^{2+} [1, 6–8] and V^{3+} [9], the existence of Zn^{2+}, Mn^{2+} [10], Cu^{2+} [3] ions in crystal gratings may also influence the colour. However, the question of what kind of metal ions and their combinations may influence the colour of spinel is not fully answered.

Taking into consideration Cr^{3+}, Al^{3+}, Fe^{3+} ions, the spinel group is divided into aluminium spinel, iron spinel and chrome spinel [5]. Spinel ($MgAl_2O_4$) is the mineral from the magnesium aluminium group of minerals, which belongs to aluminium spinel or "Inverse" spinels [2]. Its name may have derived from the Latin word *spina*, which can be translated into *thorn* that resembles the form of the crystal [2] (Fig. 1), or the name is apparently derived from the Latin *spinella*, or "*little thorn*", in allusion to its dipyramidal crystal [11] (Fig. 2). Spinel is distinguished by a variety of colours, however, the most popular is red (Fig. 3) or pink (Fig. 2), thus due to its colour spinel was frequently confused with ruby. The ancient Indians knew the difference between *manek* (ruby) and *narmal manek* (red spinel) [1]. For hundreds of years various written sources described big rubies that were encrusted in the crowns of rulers. Red, shining, big minerals that look like rubies and embellish the regalia of noblemen are in fact spinels and not rubies. Since antiquity, brilliant red spinels from Afghanistan, India, and Southeast Asia were widely traded as "Balas rubies"; an example is the particularly fine 5 cm wide spinel in the British Imperial Crown, still called the "Black Prince's Ruby" [11], this spinel is described by V. Pardieu and R. W. Hughes [12], and R. V. Karanth [1]. It was not until 1783 that spinel was identified as a distinct mineral species [11]. Spinel is very similar to ruby not only in its appearance but also in its chemical composition (Al_2O_3), thus it is still believed that

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the crowns are encrusted by big rubies. This information still remains false even in the most of the museums.

Fig. 1. Spinel crystals from Vietnam. Picture by Irzhi Korn

Fig. 2. Dipyramidal crystal of pink spinel from Vietnam. Picture by Irzhi Korn

Fig. 3. Red spinel from Vietnam. Picture by Irzhi Korn

Noble spinel is characterized by a variety of colours (Fig. 4), the range of colours depends on the composition of chromophores. According to their colour, the spinels are divided into red spinel ("ruby spinel" – blood red, "Balas" – pinkish red (Fig. 5), "almandine spinel" – purple red (Fig. 6)), pink spinel ("iris" – light pink, vivid pink) (Fig. 7), orange spinel ("rubicelle" – orangey red or orangey pink (Fig. 8), yellow), purple and violet spinel (purple colour and violet colour in spinel occurs primarily due to a mix of blue colour with pink and red colour) (Figs. 9, 10), grey spinel, green spinel (chlorospinel – brightly green, pleonaste, ceylonite pleonaste – dark green), blue spinel (sapphire spinel – sky blue, blue (Fig. 11), "cobalt blue" spinel – blue (Fig. 12), hanospinel – dark blue), near-colouress spinel (Fig. 13), hercynite ($FeAl_2O_4$) – black, brown (Figs. 14) [6–8]. Up to this day, scientists have been interested in a variety of spinel colours and factors that determine its colours and hues. Therefore, this study investigates Sri Lanka Ratnapura and Vietnam Luc Yen spinel in order to determine which metal ions and their combinations may affect colours and hues of spinel.

Fig. 4. The range of spinel colours from Vietnam. Picture by Irzhi Korn

Fig. 5. Pinkish red spinel from Sri Lanka. Picture by Irzhi Korn

Fig. 6. Purple red spinel from Sri Lanka. Picture by Irzhi Korn

Fig. 7. Vivid pink spinel from Sri Lanka. Picture by Irzhi Korn

Fig. 8. Orange pink spinel from Vietnam. Picture by Irzhi Korn

Fig. 9. Purple spinel from Vietnam. Picture by Irzhi Korn

Fig. 10. Violet spinel from Vietnam. Picture by Irzhi Korn

Fig. 11. Blue "sapphire spinel" from Vietnam. Picture by Irzhi Korn

Fig. 12. Cobalt blue spinel from Sri Lanka. Picture by Irzhi Korn

Fig. 13. Near-colourless spinel from Sri Lanka. Picture by Irzhi Korn

Fig. 14. Brown spinel from Vietnam. Picture by Irzhi Korn

RESEARCH MATERIALS AND METHODS

26 Sri Lanka Ratnapura locality and 16 Vietnam Luc Yen locality spinel minerals of various colours were investigated. The chemical analysis was carried out using a scanning electron microscope Quanta 250/450/650. Instead of light, this microscope (the magnification is from ten to few hundred thousand times) uses the electron beam, which is created in vacuum. The samples were grinded to meet the form of the plate, mounted on the holder on the carbon strip and coated by carbon (Fig. 15). An Emitech SC7620 Mini Sputter Coater was used for the carbon coating. While carrying out the tests, the electron beam in the scanning electron microscope was acquired in the electron gun using various cathodes. Under the influence of the anode, the electron beam spread vertically through the electromagnetic lenses and the focused beam was diverted to the sample. The reflected electrons were collected by detectors, which turned them into such signal that was appropriate to form the image. Two different detectors were used. One of them is the secondary electron detector, which is designed to respond to the electrons that spread from the test sample. The second detector is the detector of scattered or primary electrons, which collects and registers electrons that are reflected from the test object, and forms the surface image on the screen. After receiving an image on the screen, a point on the surface of the sample was chosen, and the electron beam as well as the INCA program was started, which generated a chart showing the atomic percentage of chemical elements. 4–10 points were evaluated in the tested samples. Concentrations of chemical elements in different spots were obtained with the accuracy of 0.01–0.1%. 0.1% accuracy results were discarded and the final results were presented after calculating the average with up to 0.01% accuracy combined with the oxides.

Fig. 15. Samples in the holder: not coated with carbon (a), coated with carbon (b). Picture by A. Daukšytė

RESULTS AND DISCUSSION

After carrying out the tests of 16 samples from the Vietnam Luc Yan locality and the Sri Lanka Ratnapura locality, chemical elements, following contents of Al_2O_3 64.40–72.70% and 51.86–73.30% (Fig. 16) as well as MgO 26.80–35.34% and 22.95–30.96% (Fig. 17), respectively, were found, which correspond to the mineral of the spinel group, i. e. spinel or magnesium spinel. All the tested samples show slightly variable contents of SiO_2, TiO_2, FeO[1], MnO, CaO, K_2O, CoO, ZnO, Cl, Cr_2O_3, NiO, V_2O_5, ZrO_2, P_2O_5, Ce_2O_3, Na_2O, Sc_2O, La_2O_3, SeO_2, HfO_2, UO_2, ThO_2, PbO, La_2O_3, Sm_2O_3, Eu_2O_3, however, their contents are essentially low (Figs. 16, 17).

After the comparison of the tested differences of spinel chemical elements in the Ratnapura locality (Sri Lanka) was carried out, the following elements have been found: hafnium, uranium, thorium, lead, samarium, europium, however, they were not found in the Luc Yan locality (Vietnam), and the samples from Vietnam featured such elements as potassium, chlorine, nickel, sodium, caesium, selenium, which were not found in the samples from Sri Lanka. However, these elements are not chromophores, thus it may not influence the colour.

Various written sources claim that the colour of spinel mineral is determined by the chromophores Cr^{3+}, Fe^{2+}, Fe^{3+}, Co^{2+}. However, after the analysis of the chemical composition of Vietnam's and Sri Lanka's minerals as well as its influence on the colour has been carried out, it can be assumed that without the abovementioned chromophores, V^{3+} is also influential to the colour. It is mentioned in the articles of some scholars, whereas Fe, V, and Cr cumulated as the principal factors responsible for the dominant red colour [9]. However, we would like to complement this statement, since V^{3+} determines the brown and yellow colour of spinel. After tests have been carried out, the highest content of V_2O_3 (0.44–0.88%) was found in four spinels from the Ratnapura locality (Sri Lanka) (Table 1), whose colour is orangey pink, and not red, as claimed by the abovementioned authors. We believe that the orangey hue is determined by V^{3+}, together with a low or medium content of Cr_2O_3 (0.05–0.36%), where Cr^{3+} determines the red and pink colour [1, 7, 9, 13]. These samples feature a relatively low content of iron oxide (0.08–0.28%) and cobalt oxide (0.05–0.20%), where Fe^{2+} and Co^{2+} determines the blue colour of spinel [1, 7, 13, 14, 15], hence together with Cr^{3+} these minerals can acquire the pink hue. It is known that V^{3+} influences the green colour of various minerals, such as beryl (emerald), tourmaline, garnet (demantoid), which are coloured by Cr^{3+} and V^{3+} [8, 13]. Cr^{3+} determines the red colour of spinels, however, we believe that V^{3+}, differently than Cr^{3+}, can determine the yellow and brown colour. We can claim that if V^{3+} determined the red colour of spinel or, as in the case of other minerals, the green colour, the tested samples would not have the orange hue. It is perfectly illustrated by the orangey pink spinel sample from the Ratnapura locality (Sri Lanka) (Table 1, No. 25), which features a high content of vanadium oxide 0.88%, whereas

[1] Submitted together with FeO and Fe_2O_3 contents.

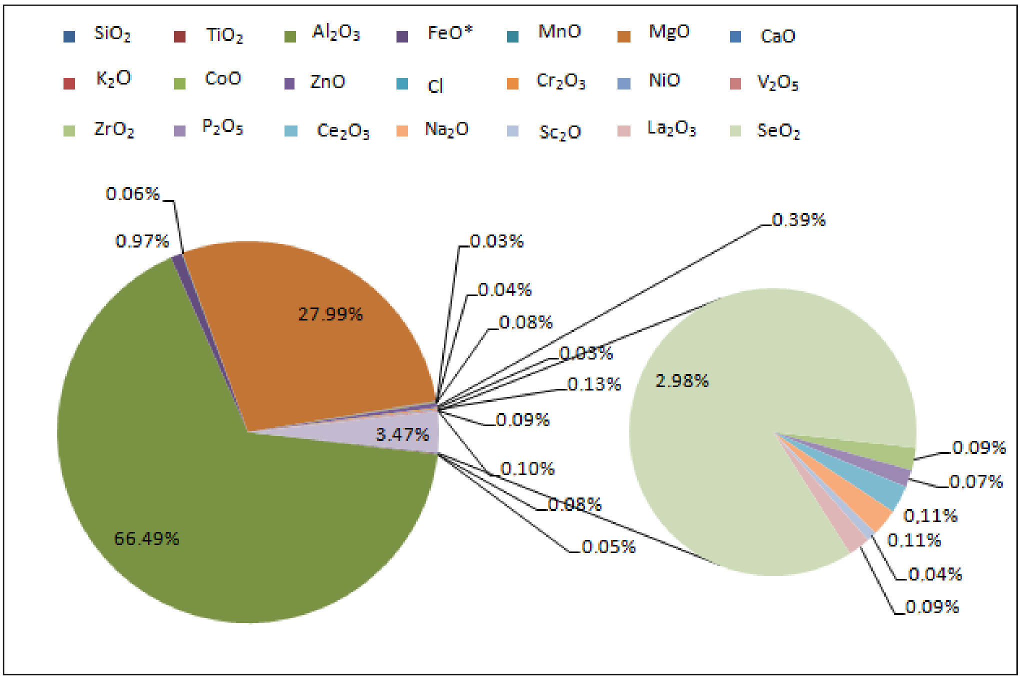

Fig. 16. The means of oxides of Vietnam Luc Yan locality chemical elements

(* submitted together with FeO and Fe_2O_3 contents)

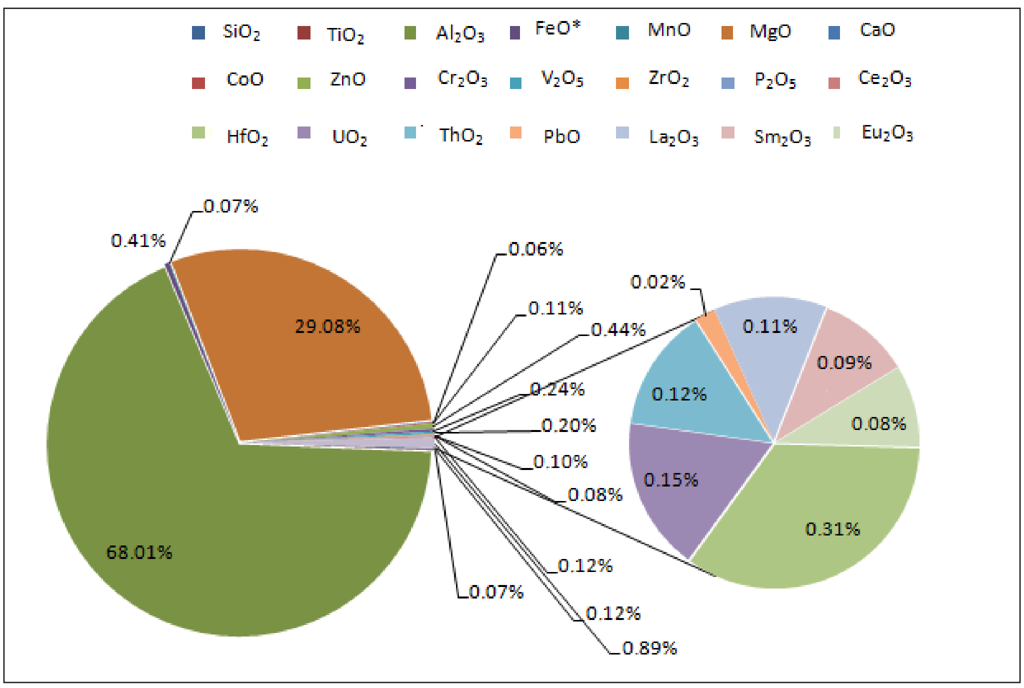

Fig. 17. The means of oxides of Sri Lanka Ratnapura locality chemical elements

(* submitted together with FeO and Fe_2O_3 contents)

the contents of chrome, iron and cobalt oxides (0.5, 0.08 and 0.08%, respectively) are very low (Table 1). Vanadium ions can determine the brown and yellow colour in unheated Tanzanite (zoisite) [8]. Thus, we believe that V^{3+} can determine the brown and yellow colour of spinel.

The fact that Cr^{3+} determines the red colour of spinel is very well illustrated by two dark red spinel samples from the Ratnapura locality (Sri Lanka) (Table 2), where the content of Cr_2O_3 (1.63–1.85%) is very high, whereas the contents of vanadium, iron and cobalt oxides are relatively low (0.26–0.29,

Table 1. **The means of chromophore oxides of orangey pink Sri Lanka's spinels**

No/Colour	V_2O_3%	Cr_2O_3%	FeO*%	CoO%
22. Orangey pink	0.50	0.32	0.19	0.07
23. Orangey pink	0.53	0.36	0.28	0.20
24. Orangey pink	0.44	0.11	0.08	0.05
25. Orangey pink	0.88	0.05	0.08	0.08

* Submitted together with FeO and Fe_2O_3 contents.

Table 2. **The means of chromophore oxides of dark red Sri Lanka's spinels**

No/Colour	V_2O_3%	Cr_2O_3%	FeO*%	CoO%
27. Dark red	0.29	1.63	0.09	0.02
28. Dark red	0.26	1.85	0.11	0.08

* Submitted together with FeO and Fe_2O_3 contents.

0.09–0.11 and 0.02–0.08%, respectively), which shows that compared to the content of Cr_2O_3 their contents are too low to influence the colour.

According to the test results and the sources used [7, 13], the purple/violet colour of spinel is determined by Fe^{2+}. Two Luc Yan locality samples and one Ratnapura locality sample feature a relatively high content of FeO (1.16–2.86%) (Table 3), which should influence the purple/violet colour, since the contents of other chemical elements that may influence the colour are very low, i. e., respectively, V_2O_3 0.02–0.04%, Cr_2O_3 0.01–0.06%, CoO 0.03–0.08%. The light purple/violet colour of spinels can be determined by a relatively medium content of iron oxide (0.58–0.65%) and a low content of cobalt oxide (0.02–0.11%), without chrome or with low contents of chrome and vanadium oxide (respectively, 0–0.15 and 0.2–0.08) (Table 3).

Table 3. **The means of chromophore oxides of purple/violet, light purple/violet spinels**

Colour	Locality	V_2O_3%	Cr_2O_3%	FeO*%	CoO%
Purple/violet	Vietnam	0.02–0.04	0.01–0.06	1.86–2.86	0.06–0.08
Light purple/violet	Vietnam	0.08	0.13–0.14	0.62–0.65	0.02
Purple/violet	Sri Lanka	0.02	0.04	1.16	0.03
Light purple/violet	Sri Lanka	0.02–0.03	0–0.15	0.58–0.65	0.03–0.11

* Submitted together with FeO and Fe_2O_3 contents.

The pink colour of spinel is influenced by Cr^{3+} [7, 8, 13]. The test results show that Fe^{2+} can also influence the pink colour and its saturation. It was estimated that the vivid pink colour is influenced by a high content of FeO (0.87–2.17%) and a relatively fair content of Cr_2O_3 (0.10–0.20%) (Table 4). According to the earlier researches [16], the sufficient content of Cr^{3+}, which determines the colour of the mineral, is 0.1%, whereas its saturation may be influenced by a high quantity of Fe^{2+}. Medium saturation pink spinels have a relatively medium content of FeO (0.75–0.76%) and a relatively fair content of Cr_2O_3 (0.04–0.11%), which may determine the pink hue, however, it does not feature the vivid pink saturation. The saturation of light pink spinels depends on the quantitative ratio of Fe^{2+} and Cr^{3+}. Although FeO is relatively low (0.07%), the pink colour is determined by a low content of Cr_2O_3 (0.03%), and if the content of FeO is slightly higher (0.15–0.24%), the relatively low content of Cr_2O_3 (0.09–0.11%) is sufficient to determine the pink colour. The tested spinels with pink hue showed very low or low quantities of Co^{2+} (0.02–0.10%). They can determine the slightly blue hue, and together with Cr^{3+} they can determine the pink hue.

Table 4. **The means of chromophore oxides of pink hue spinels**

Colour	Locality	V_2O_3%	Cr_2O_3%	FeO*%	CoO%
Vivid pink	Vietnam	0.05–0.23	0.10–0.20	0.86–2.17	0.02–0.07
Pink	Vietnam	0.05–0.22	0.04–0.11	0.74–0.76	0.03–0.06
Light pink	Vietnam	0.04–0.33	0.10–0.11	0.22–0.24	0.05–0.10
Light pink	Sri Lanka	0.06–0.23	0.03–0.11	0.07–0.24	0.02–0.08

* Submitted together with FeO and Fe_2O_3 contents.

The content of V_2O_3 in pink spinels is from 0.04 to 0.33%, however, it may not influence the colour. The content of V_2O_3 is from 0.44 to 0.88%, which supposedly determines the yellow or brown colour. Comparing the V_2O_3 content of the tested spinels, the assumption can be made that the content of V_2O_3 that can determine the brown or yellow colour starts at 0.4%, whereas together with a low content of Cr^{3+}, it determines the orange colour. It can be related to the magnetic features of vanadium. Vanadium is not magnetically detectable in concentrations less than approximately 0.4% vanadium oxide [8], thus even lower content of V_2O_3 than 0.4% may influence the colour.

In the tested pinkish grey spinels the contents of chromophore V^{3+}, Cr^{3+}, Fe^{2+} and Co^{2+} oxides, which determine the colour, are low or fair (0.02–0.08%, 0.02–0.04%, 0.18–0.31% and 0.03–0.04%, respectively) (Table 5). The chromophore contents in them are relatively low, thus they are either colourless or grey with faint pink hue.

Table 5. **The means of chromophore oxides of grey hue spinels**

Colour	Locality	V_2O_3%	Cr_2O_3%	FeO*%	CoO%
Near-colourless pink	Vietnam	0.06	0.05	0.23	0.04
Near-colourless gray	Sri Lanka	0.06	0.08	0.14	0.02
Near-colourless pink	Sri Lanka	0.09	0.05	0.24	0.13
Pinkish grey	Sri Lanka	0.02–0.08	0.02–0.04	0.18–0.39	0.03–0.04

* Submitted together with FeO and Fe_2O_3 contents.

CONCLUSIONS

According to the test results it can be assumed that in spinel V^{3+} determines either the yellow or brown colour and the concentration of V_2O_3 should be no less than 0.4%. The orange colour of orangey pink samples is determined by the co-existence of V^{3+} (yellow colour) and Cr^{3+} (red colour), whereas the pink colour is influenced by Fe^{2+} (pink, blue colour) and Co^{2+} (blue) as well as Cr^{3+}.

The low content of Cr_2O_3 0.1% is sufficient to determine the colour, however, the concentration of FeO/Fe_2O_3 and CoO should be significantly higher.

The pink colour of spinel minerals and its saturation may also be influenced by Fe^{2+}, but it should be together with Cr^{3+}. The concentration of Fe^{2+} should be higher than that of Cr^{3+}.

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Arūnas Kleišmantas, Aistė Daukšytė

VIETNAMO IR ŠRI LANKOS ŠPINELIO MINERALO CHEMINIŲ ELEMENTŲ ĮTAKA SPALVAI

Santrauka

Ištirta 42 įvairių spalvų špinelio mineralų iš Vietnamo Luc Yan vietovės ir Šri Lankos Ratnapura vietovės cheminė sudėtis skenuojančiu elektroniniu mikroskopu Quanta 250/450/650 ir remiantis tyrimų rezultatais interpretuota chromoforų įtaka spalvai. Nustatyta, kad špinelio mineralo spalvas lemia ne tik chromas, geležis, kobaltas, bet ir vanadis. Remdamiesi tyrimų rezultatais manytume, kad špineliui V^{3+} cheminiai elementai gali suteikti ir rudą ar geltoną spalvą, kitaip negu teigia kiti autoriai. Tačiau vanadžio oksido kiekis turi būti ne mažesnis kaip 0,4 %, kad lemtų špinelio spalvą. Ištyrus tamsiai raudonos spalvos špinelių pavyzdžius, nustatyta, kad raudoną spalvą lemia didelis Cr^{3+} kiekis. Purpurinių / violetinių pavyzdžių spalvai suteikia Fe^{2+} ir mažas Co^{2+} kiekis, o rožinį atspalvį turintiems pavyzdžiams gali suteikti Cr^{3+} ir didelis Fe^{2+} kiekis, kurių sodrumas priklauso nuo Fe^{2+} ir Cr^{3+} kiekybinio santykio. Rausvai pilkuose špineliuose nustatyti chromoforų V^{3+}, Cr^{3+}, Fe^{2+} ir Co^{2+} oksidų kiekiai yra santykinai maži, todėl ir jų atspalvis yra tik pilkas.