



Discussing the Coloration Mechanism of Luodian Jade from Guizhou

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Abstract

In this paper, we have discussed the coloration mechanism based on visible absorption spectra testing by selecting three typical samples of Luodian jade with white, pallor and cyan. The attribution analysis of absorption spectra showed that absorption of Luodian jade in visible light mainly includes charge transfer spectrum of $\text{Fe}^{2+} \rightarrow \text{Ti}^{4+}$ (at 490 nm - 500 nm) and $\text{Fe}^{2+} \rightarrow \text{Fe}^{3+}$ (at 523 nm - 536 nm, 646 nm - 657 nm), electron transition ${}^6\text{A}_1 \rightarrow {}^4\text{T}_2$ (${}^4\text{G}$) of Fe^{3+} (at 615 nm - 632 nm, 685 nm - 694 nm) and ${}^4\text{T}_1$ (${}^4\text{G}$) \rightarrow ${}^6\text{A}_1$ (${}^6\text{S}$) of Mn^{2+} electron transition (at 549 nm - 560 nm). The color of Luodian Jade is the mixed color of complementary color caused by light-absorbing at these frequencies; moreover, different frequency absorption intensity determines the purity and brightness of color. At the same time, The results also confirmed that iron ions play an important role in the coloring mechanism especially with cyan color samples.

Subject Areas

Material Experiment, Metal Material

Keywords

Guizhou, Luodian Jade, Absorption Spectra, Coloration Mechanism

1. Introduction

As to the origin of nephrite color, it is generally agreed that the cyan is in direct proportion to the content of Fe^{2+} , and the green is related to Cr, Ni, Co and other trace elements. Li Wen-wen *et al.* [1] and Na Bao-cheng *et al.* [2] considered

that the color of Hetian jade was mainly determined by the total iron content in the structure by combining the visible absorption spectrum with the EPMA: the green-turquoise blue series is decided by Fe^{2+} and yellow-red-brown red series is namely by Fe^{3+} , and in the meantime, trace amounts of Cr, Mn, etc., are also a factor to color in Hetian jade; the yellow-green characteristic of Longxi jade in Sichuan province is caused by two charge transfers in the form of $\text{O}^{2-} \rightarrow \text{Fe}^{3+}$ and $\text{Fe}^{2+} \rightarrow \text{Fe}^{3+}$, and the spin-forbidden transition of Fe^{2+} (possibly Mn^{2+} and Fe^{3+}) also has some influence [3]. Qian Xiang-li *et al.* [4] analyzed five colors (gray, light green, grey green, dark green and brown) of nephrite-cat-eye in Sichuan province by EMAP and XRD and concluded that the Fe and trace Cr contents in the color origin structure were determined. White, light yellow, green, gray-green to yellow-green in Hualien nephrite is the result of the increasing content of Fe^{2+} [5]. The study on the coloration mechanism of nephrite from Qinghai province also shows that Fe^{2+} is directly related to the origin of color [6]. Chen Tu-hua *et al.* [7] believed that the color of Hetian jade and Canadian nephrite was caused by the actinolitization in tremolite. Wilkins C.J. *et al.* [8] confirmed that the cause of nephrite color from New Zealand was directly related to the content of total iron in its composition by studying the infrared spectrum, visible absorption spectrum and Mössbauer spectrum. The color of Australian nephrite is mainly caused by the isomorphism substitution between Cr and Fe and Mg [9].

Generally, the study of the nephrite's coloration mechanism is mostly based on that occurs in basic-ultrabasic deposit. Luodian jade, which is related to the contact metamorphism between basite and carbonatite, is a new genetic type of nephrite and completely different from other discovered nephrite deposits. As a kind of nephrite resource, it is mainly distributed in the south of Luodian county and Wangmo county in Guizhou province; its mineral composition, structure and other physical characteristics are similar to those of Hetian jade. Moreover, the differences in chemical composition and material composition of the white, cyan and cyan series in Luodian jade result in some differences in the basic characteristics of jadeology. Chemical analysis results of Luodian jade show that the chemical composition of Luodian jade contains some transition metals, which incompletely filled d electron orbit, such as Mg, Fe, Mn, Ti, etc. [10]. Based on the mineral physics theory, however, after the electron located in the split orbitals absorbed light irradiation energy would cause its transition to a higher energy state from lower energy state, so the mineral color is a kind of complementary colour that some frequency of visible light is absorbed selectively by its internal electron transition [11]. Accordingly, we selected some samples (**Photo 1**) with different color to discuss the coloring mechanism of Luodian jade, which is based on the perspective of mineral physics theory, by testing UV-VIS absorption spectra, so as to more clearly explain the mechanism of the transition metal in its color genesis, at the same time, the research results to enrich the content of the basic theoretical research about Luodian jade.

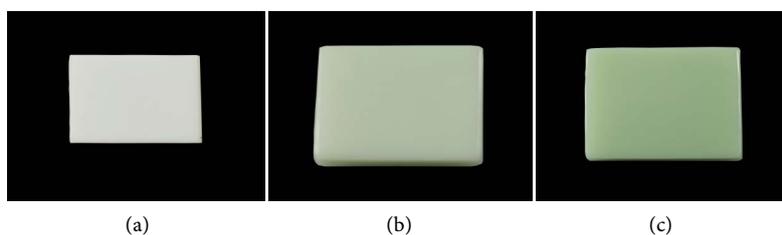


Photo 1. Samples (from (a) to (c): white, pallor and cyan).

2. Samples and Testing

Generally, Luodian jade's color can be divided into three types including white, pallor (bluish white) and cyan, and make three samples contains of each one into rock section to testing absorption spectra at the 350 - 750 nm wavelength by using QDI302 micro spectrophotometer. All tests are completed in the Guiyang Supervision Testing Center for Mineral Resources, Ministry of Land and Resources (MLR).

The test results as shown in **Figure 1**. According to **Figure 1** that all samples are not absorption spectra while frequency is less than 450 nm, on the other hand, its absorption spectrum becoming complicated as the sample color from white change to pallor or cyan. Among them it is widespread that the absorption at 490 - 500 nm, 550 - 560 nm, 610 - 640 nm, and ± 690 nm in all samples, besides, shoulder absorption is also spread at 523 - 533 nm, 596 - 606 nm and 648 - 657 nm in samples, appear at 511 nm and 584 nm only in pallor sample (**Table 1**).

3. Spectra Attribute Classification

The spectral characteristics of mineral are determined by the interaction between mineral electrons and crystal field along with molecular vibration. According to the theory that the absorption frequency of transition energy, which can be calculated as a electronic transition of Fe^{3+} when ${}^6\text{A}_{1g} \rightarrow {}^4\text{T}_2$ (G) and ${}^6\text{A}_{1g} \rightarrow {}^4\text{T}_1$ (G) in the octahedral crystal field, are 680 nm ($14,702 \text{ cm}^{-1}$) and 14,702 nm (9950 cm^{-1}) respectively. Whenever, that belongs to spin forbidden transition when Fe^{3+} as in form of isomorphism to displacement Al in AlO_6 octahedral can produce three weak absorption at 430, 450 and 460 nm [12] [13] [14] [15].

Some researchers pointed out by different experiments that the electronic transition of Fe^{2+} can mainly form absorption band near 945 nm ($10,582 \text{ cm}^{-1}$) while octahedral distort to trigonal field [13] [16]. As a rule, in tremolite the absorption spectrum frequency of $\text{Fe}^{2+} \rightarrow \text{Fe}^{3+}$ in range of 570 - 840 nm which is formed by the charge transfer [8] [17] [18] [19] [20] [21]; in another case, the charge transfer spectrum of $\text{Fe}^{2+} \rightarrow \text{Ti}^{4+}$ cause to absorption near to 500 nm ($18,040 \text{ cm}^{-1}$) [22].

In Luodian jade, that is ubiquity such as Mg^{2+} in octahedral sites be replaced by Mn^{2+} as in form of isomorphism. However, on this occasion Mn^{2+} with typical d^5 electron configuration in case of electron transition will lead to absorption in visible light whether which is a absorption band mainly at 450 nm, 450 nm

and three absorption characteristics in the region of 360 - 410 nm or to produce a relatively steep half absorption in 400 - 600 nm region.

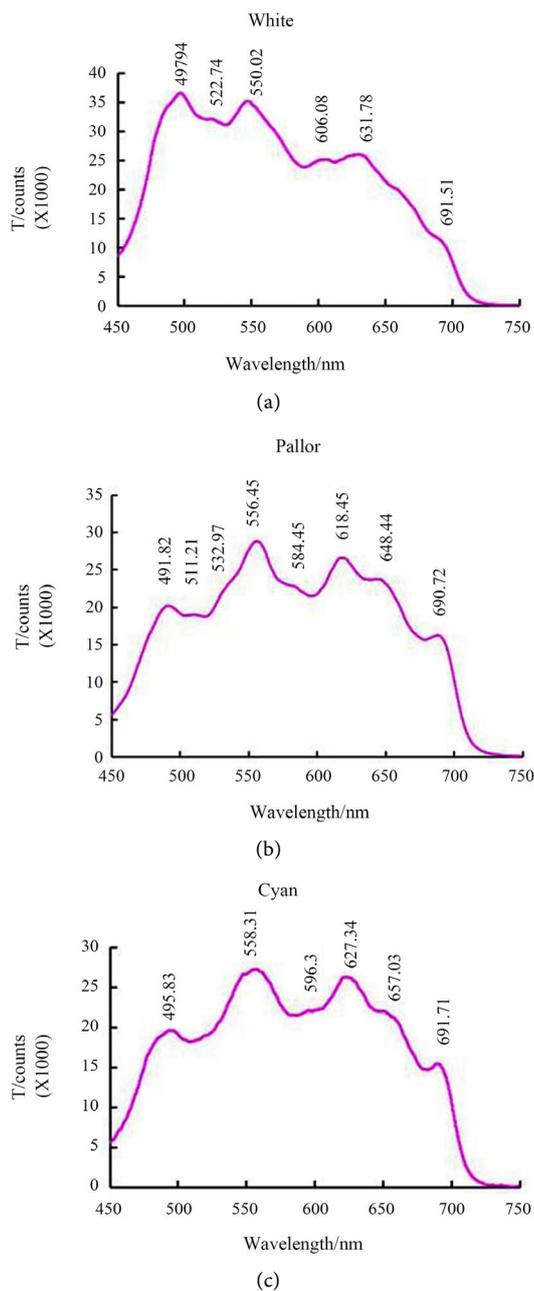


Figure 1. VIS spectra of Luodian jade (from (a) to (c): white, pallor and cyan).

Table 1. VIS spectra absorption frequency.

Samples	Absorption Frequency/nm								
White	498	—	523	550	—	606	632	—	692
Pallor	492	511	533	556	584	-	618	648	691
Cyan	494	—	—	558	—	596	627	657	692

In addition, Yan, *et al.* [22], Gan, *et al.* [23] summarized the VIS characteristics of ions in mineral such as Fe^{2+} , Fe^{3+} , Mn^{3+} , Ti^{4+} , Cr^{3+} and so on (Table 2). The other achievements obtained show that there some absorption in crystal field of Fe^{3+} are located at 530 nm, 630 nm and 860 nm from Mars hematite ($\alpha\text{-Fe}_2\text{O}_3$) [24], and on pyroxene Fe^{2+} which occupies M_2 sites causes some absorption at 425 nm, 445 nm, 480 nm, 505 nm and 545 nm [25]. Whatever, the absorption properties of the three samples of frequency range is 450 - 750 nm are shown in Table 3 based on the integrated pre-research results. It attributable to charge transfer spectrum between in valence-state of Fe^{2+} and Fe^{3+} that optical absorption spectra of the cyan and pallor are characterized by two broad bands in range of 530 - 540 nm and 640 - 657 nm, further, it may be a superposition of a few charge transfer spectrums either is $M_1 (\text{Fe}^{2+}) \sim M_2 (\text{Fe}^{3+})$ and $M_1 (\text{Fe}^{2+}) \sim M_2 (\text{Fe}^{2+})$ or $M_3 (\text{Fe}^{2+}) \sim M_1 (\text{Fe}^{3+})$. Because the samples tested contain minor amounts of Cr so the absorption of 492 - 498 nm cannot be ruled out spin forbidden transition of Cr^{3+} .

4. Coloration Mechanism

In fact, each of the frequency or wavelength of visible light corresponds to one color (Table 4). According to the different scale and strength of the three primary colors red, green and blue, which wavelength is 700 nm, 546.1 nm and 435.8 nm respectively, can produce all kinds of change color in nature.

As indicated in Table 5, the mainly color after absorbing visible light frequency Luodian jade of white color is in the range of the three primary colors, when three kinds of color red, blue and green mixed up with equal proportion and intensity which color is white and belongs to the charge transfer of Fe^{2+} and Fe^{3+} in white sample at 523 nm and 608 nm also into this color range, when the proportion and intensity of these three kinds of color is inconformity then would form white-grey color, for this reason, we can concluded that Luodian jade of white color is mainly due to the absorption of this type; besides above the absorption of that it also has absorption at 627 nm to 657 nm in cyan Luodian jade, the intensity of the color of this kind of sample becomes to larger after to absorb visible light which frequency is greater than 540 nm, on the whole, whose color is mainly present blue or green and made blue-green to be gave priority to increase, the blue-green enhanced mixes the green after being absorbed at 685 nm

Table 2. VIS spectra of some ions.

Ions	VIS absorption frequency/nm
Fe^{2+}	550, 510, 450, 430
Fe^{3+}	700, 520, 490, 450, 400
Mn^{2+}	550, 450, 410, 370, 340
Ti^{4+}	640, 600, 550, 450
Cr^{3+}	700, 550, 400

Table 3. The location and identification of VIS.

Attribute	Samples/Frequency/nm		
	White	Pallor	Cyan
Fe ²⁺ → Ti ⁴⁺ (charge transfer)	498	492	494
Fe ³⁺ : ⁶ A ₁ → ⁴ T ₂ (⁴ G) (electronic transition)	632 692	618 691	627 692
Fe ³⁺ : 2(⁶ A ₁) → 2 (⁴ T ₁ (⁴ G)) (electronic transition)	—	511	—
Fe ²⁺ → Fe ³⁺ (charge transfer)	523 608	533 584 648	596 657
Mn ²⁺ : ⁴ T ₁ (⁴ G) → ⁶ A ₁ (⁶ S) (electronic transition)	550	556	558

Table 4. The relationship between wavelength and corresponding colors.

Wavelength/nm	400	425 - 450	490 - 510	540	590	640	680-
Coloring	Greenish-yellow	Orange-Yellow	Red-Rose	Purple-Blue	Blue	Blue-green	Green

Table 5. The coloration mechanism of Luodian jade.

Color	Coloration Mechanism	Coloring & absorption frequency/nm
White	electron transition: Fe ³⁺ , ⁶ A ₁ → ⁴ T ₂ (⁴ G)	Red~Rose~Purple: 498, 523
	Mn ²⁺ , ⁴ T ₁ (⁴ G) → ⁶ A ₁ (⁶ S) charge transfer: Fe ²⁺ → Ti ⁴⁺ , Fe ²⁺ → Fe ³⁺	Blue~Blue-green~Green: 550, 608, 632, 692
Pallor	electron transition: Fe ³⁺ , 2 (⁶ A ₁) → 2 (⁴ T ₁ (⁴ G)), ⁶ A ₁ → ⁴ T ₂ (⁴ G)	Red~Rose~Purple: 492, 511, 533
	Mn ²⁺ , ⁴ T ₁ (⁴ G) → ⁶ A ₁ (⁶ S)	Dark blue~Blue~Blue-green: 556, 584, 618
	charge transfer: Fe ²⁺ → Fe ³⁺ , Fe ²⁺ → Ti ⁴⁺	Blue-green~Green: 648, 691
Cyan	electron transition: Fe ³⁺ , ⁶ A ₁ → ⁴ T ₂ (⁴ G)	Red~Rose: 494
	Mn ²⁺ , ⁴ T ₁ (⁴ G) → ⁶ A ₁ (⁶ S) charge transfer: Fe ²⁺ → Fe ³⁺ , Fe ²⁺ → Ti ⁴⁺	Dark blue~Blue: 558, 596 Blue~Blue-green~Green: 627, 657, 692

to 694 nm could produce the cyan color of Luodian jade. The most prominent is what one absorption at 511 nm to make red~rose color while bluish white jade is compared with cyan and white sample, which is the result of adding white tones to green.

5. Conclusions

1) The absorption of Luodian jade in visible light area mainly is the charge transfer as well by Fe²⁺ → Ti⁴⁺ (490 nm to 500 nm) and Fe²⁺ → Fe³⁺ (523 nm to 608 nm, 533 nm to 648 nm and 596 nm to 657 nm) as the electron transition inclusion ⁶A₁ → ⁴T₂ (⁴G) of Fe³⁺ (618 nm to 632 nm, 691 nm or 692 nm) and ⁴T₁ (⁴G) → ⁶A₁ (⁶S) of Mn²⁺ (550 nm to 558 nm).

2) Iron ion plays a very important role in the coloring Mechanism of Luodian jade especially in the cyan color samples (Tables 1-5). On the one hand it is widespread on the earth; on the other hand, it can replace Mg²⁺ and Al³⁺ in the shape of Fe²⁺ or Fe³⁺ in nature.

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Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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