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FT-IR, XRD, Porosity and TG-DTA Analysis of Archaeological Potteries Excavated from Kottapuram, Kerala, South India

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ABSTRACT

The mineralogical analysis of five pottery shards from the Kottapuram site, Kerala using interdisciplinary analytical techniques such as Fourier Transform Infrared (FT-IR), XRD, thermal analysis and porosity has been carried out. The above techniques show the clear presence of inclusions of clay minerals were used for the study of characteristic reactions, associated with the course of heating. The evidence for the decomposition of calcite and kaolinite in some of the samples were found so that the earthenware may be produced the high temperature ceramics.

Introduction

It is a common fallacy that archaeology is about things – objects, monuments, landscapes. It is not: archaeology is about people, i.e. archaeology is concerned with the full range of past human experience – how people organized themselves into social groups and exploited their surroundings; what they ate, made, and believed; how they communicated and why their societies changed. Thus, in many cases, by the way of detailed structural characterization and identification of key chemical constituents, important information of historical is uncovered. For example, communication, technology sharing, and trade between different ancient cities can be revealed on the basis of similarity of materials found in archaeological sites.

A large variety of modern analytical techniques have been successfully applied in the analysis ancient materials, uncovering information of historical and artistic significance. Some information on the firing temperatures, one of the most intriguing aspects in the investigations on ancient pottery, could also be inferred by the above mentioned techniques. The vibrational spectrum of a molecule is considered to be a unique physical property and is characteristic of the molecule. As such, the infrared spectrum can be used as a fingerprint for identification by the comparison of the spectrum from an unknown with previously recorded reference spectra. The qualitative aspects of infrared spectroscopy are one of the most powerful attributes of this diverse and versatile analytical technique. In the present work, XRD analysis is used for the complementary study for FT-IR analysis. The X-ray patterns were examined with the help of JCPDS data. Similarly the other studies such as TG-DTA and porosity were used to investigate the firing temperature range. Finally all the results reveal that the firing temperature ranges of the relics. The similar studies were carried out by the other authors are following.

Rutherford et al [1] have used infrared and XRD techniques to investigate the inclusions in the potteries. Keller and Picket [2] have done infrared absorption studies for the identification and classification of clays and clay minerals. Similarly, Legodi and Waal [3] are analyzed the clay minerals present in the archaeological pottery samples excavated in South Africa by using the infrared spectroscopy along with XRD. The thermogravimetric (TG) and differential (TG-DTA) analysis is an adequate tool for analyzing ancient pottery; it allows one to control the process of firing and record variations due to the thermal process simultaneously [4]. DTA curves enable detection of exo and endothermic peaks due to the effects of gain/loss of enthalpy occurring in the sample when undergoing controlled heating. Joachim Schomburg [5] studied that the different thermal reactions of clay minerals on temperatures ranging from 500°C to 1100 °C are important for the formation of potteries as well as for the reconstruction of their production conditions. Tite and Mureson correlated the porosity of archaeological samples with firing temperatures [6, 7]. Thermal analysis in conjugation with FT-IR and XRD provides information for the estimation of original firing temperature of the ancient pottery as evidenced from the studies done by the earlier investigations [8].

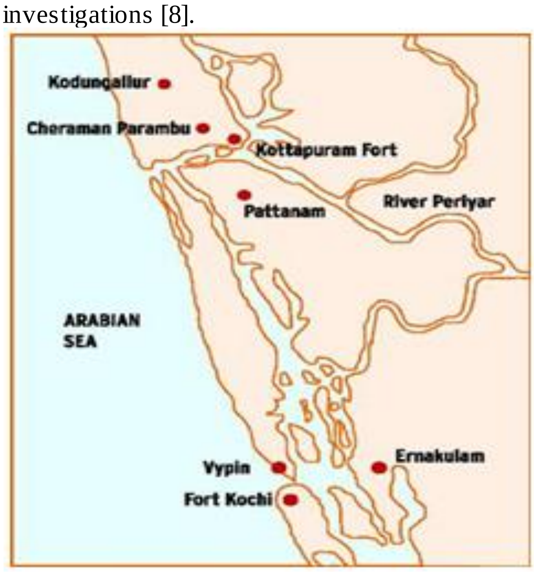

Figure 1. Archaeological Site map of Kottapuram Fort in Kerala, India

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Site details

Archaeological Kottapuram Fort site and the collected pottery samples for the present work are shown in Fig.1 and Fig.2 respectively. Kottapuram Fort or Cranganur fort is an old fortification area near Kodungalur Taluk, Thrissur district. Thrissur is referred as the "Cultural Capital of Kerala". Many important historical sites and monuments, like Cheramanparambu, Thiru Vanchikulam temple, Kottapuram fort etc. Muziris has the distinction of having yielded a complete human skeleton for the first time in India, from the Kottapuram fort area.

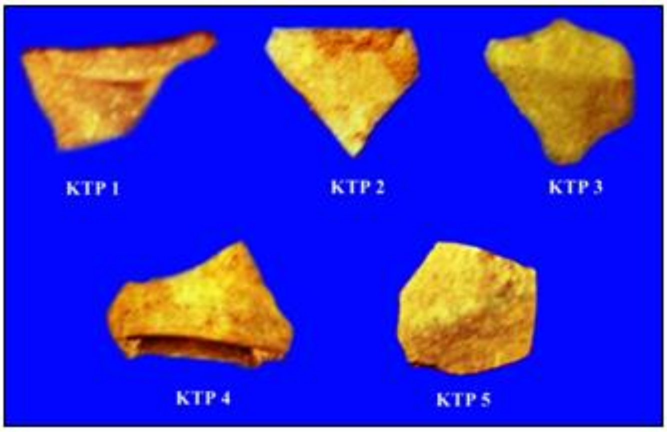


Figure 2. Pottery shards of Kottapuram site (KTP1-KTP5)

As the focal point of commerce for over 2500 years, this bustling seaport traded in everything from spices to precious stones with the Greeks, Romans and the rest of the world. It was also the doorway to India for varied cultures. These pot shards were excavated by the archaeological survey of India, Trivandrum, in the year April 2007.

Experiment details

Fourier Transform Infrared spectroscopy (FT-IR)

The pottery samples were analyzed from the FT-IR absorption spectra in transmittance mode to characterize their mineralogical composition from the specific transmittance peak observed. The samples were powdered, pelletized with spectra grade KBr in the ratio of 1:20. The spectra were recorded at room temperature using Perkin Elmer FT-IR spectrometer with resolution of ±4 cm^{-1} in 4000-400 cm^{-1} region.

X-Ray Diffraction Analysis (XRD)

The representative samples for this study were subjected to X-ray diffraction patterns of potteries (powdered samples) were recorded at room temperature by using JEOL-JDX 8030 X-ray computer controlled diffractometer system, having a curved graphite crystal diffracted monochromator, with a source of CuKα radiation of wavelength λ=1.5418A° and NaI (T1) scintillation detector. The diffractograms were recorded that run between 20°-80° as the angle with proportional counter 1600V, scanning speed of 1° per minute.

Thermo Gravimetric – Differential Thermal Analysis (TG-DTA)

The experiment was carried out by heating the samples from 30 to 1200°C in steps of 10°C min^{-1} with flow of high purity Nitrogen. A sample is placed into a tarred TGA sample pan attached to a sensitive microbalance assembly. The sample holder portion of the TGA balance assembly is subsequently placed into the high temperature furnace.

Porosity

The samples were heated continuously in boiling water for about six hours and left to cool overnight which enable the pores to get filled up with water to saturation. The saturated specimens were then weighted by immersing in water and in air. The samples were then placed in hot air oven at 200°C and dried for about six hours to remove the water contents completely and then weighed. The open or apparent porosity is calculated.

Result and Discussion

The firing temperature analysis using FT-IR and XRD

The FT-IR spectra of Kottapuram pot shards (KTP1-KTP5) are given in Fig.3.

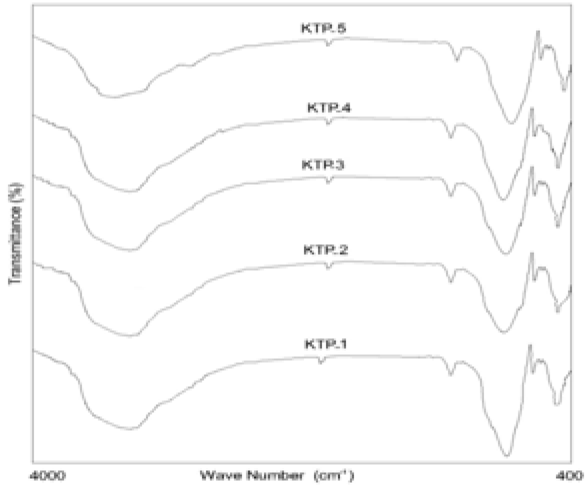


Figure 3. FT-IR Spectra of KTP1-KTP5

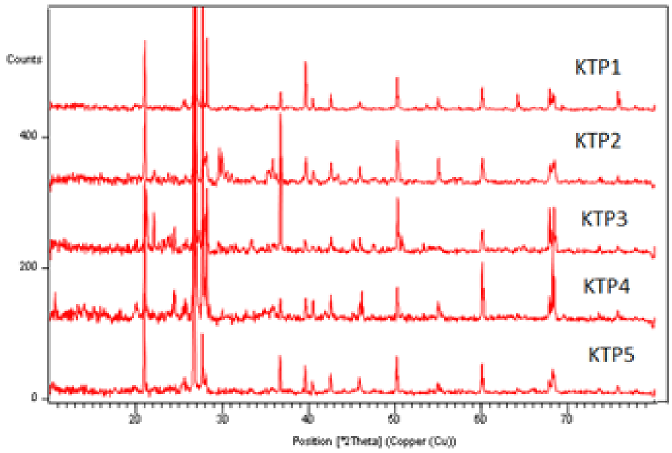


Figure 4. XRD Spectra of KTP1-KTP5

The band around 3812, 3741 and 3449 cm^{-1} is due to OH stretching of hydroscopic water [9]. The weak bands at around 2593 and 2516 cm^{-1} could also be attributed to calcite overtone/combination bands given in table.1 [10]. The spectra dominated with the calcite bands 1425, 1426 and 1463 cm^{-1} [11, 12]. The pot shards contain quartz, as identified by the bands around 784 cm^{-1} [9]. The bands 1036, 1040 and 1071 cm^{-1} is assigned to Si-O stretching mode of kaolinite [9]. Kaolinite dehydroxylates and transforms to metakaolinite at about 450-650°C [13, 14]. Metakaolinite has broad vibrational bands around 1098 cm^{-1} (Si-O stretching) [15]. Since we observed vibrational modes of kaolinite and those of metakaolinite (1090 & 1092 cm^{-1}), the firing temperature should be higher than 650°C for KTP1 and KTP5, the firing temperature may below 650°C for remaining samples [13, 14].

FT-IR and XRD results indicated that all samples contain calcite in different amounts. Decomposition of calcite in clayey matrixes begins at 600°C mainly occurs around 650-750°C [16]. At higher temperatures (900°C), high temperature calcium-silicate phases appear; it formed due to thermal reaction of the calcite decomposition products with the fired clay. After firing, deformed calcite may be recarbonated from the remaining decarbonation products of original calcite and/or by a reaction with atmospheric CO_2 [17]. Reformed calcite is characterized by a broad band around 1450 cm^{-1}, although at original calcite this CO_3 stretching vibration occurs around 1420-1430 cm^{-1}. The vibrational wave number of carbonate stretching vibration found in the range of 1425-1463 cm^{-1}. Observations of calcite (CaCO3) bands allow depicting the conclusion on firing temperature. In the samples KTP2, KTP3 and KTP4 have the calcite band and the remaining samples did not observed that kind of bands. Also KTP2 have the very weak calcite absorption band. It may disappear in the higher temperature, because it doesn't absorb in XRD studies. Thus the samples might have been fired below 800°C. It is evidenced by the kaolinite peak that was citing above. But the sample KTP2 may be allowed at higher temperature.

Table 1. FT-IR absorption frequencies (cm^{-1}) and relative intensities of ancient potteries

Frequency with relative Intensity (cm^{-1})					Tentative Vibrational assignments
KTP1	KTP2	KTP3	KTP4	KTP5	
-	3828S	3812S	3812W	3812S	(O-H) str. Of water molecule
-	3742S	3741VS	3740S	3741W	(O-H) str. Of water molecule
3449M	3449VS	3436W	-	3448VW	(O-H) str. Of water molecule
2597S	2516S	2593S	2597S	2512W	Overtones of carbonate
1644S	1637VS	1644S	1643W	1643W	(O-H) str. Of water molecule
-	-	-	1463W	-	Calcite
-	1426VW	1425S	-	-	Calcite
1092VS		-	-	1090S	Metakaolinite
-	1071M	-	-	-	Si-O str. Of kaolinite
-	-	1040VS	1036VS	-	Si-O str. Of kaolinite
790S	784S	784VS	786S	787S	Quartz
688VW	685VW	-	-	688W	Quartz
-	525VW	-	-	-	Hematite
-	-	538VW	538VW	-	Hematite
466S	-	469VS	472VS	-	(Si-O-Si)
-	459S	-	-	459VS	Microcline
-	431M	-	-	-	Kaolinite

VS-Very Strong, S-strong, M-Medium, W-Weak, VW-Very Weak

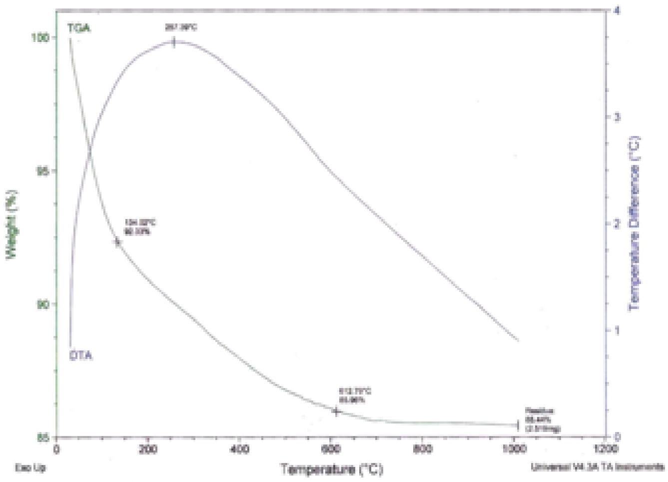
In XRD pattern of the Kottapuram pot shards have all the minerals that observed in FT-IR along with other clay minerals orthoclase and orthopyroxene in few of the samples. All these observations from XRD patterns (given in Fig.4) made from the matching JCPDS files [18]. All the high intensity peaks in the pattern (3.33 Å, 2.45 Å and 1.81 Å) are assigned to quartz in all the samples of Kottapuram site. The other importance peaks of calcite d-spacing values are 1.96 Å, 2.43 Å, 0 .66 Å and the metakaolinite peaks are 4.19 Å, 2.28 Å, 2.09 Å, 1.72 Å, and 1.30 Å present in the KTP2-KTP4 and KTP2 and KTP5 samples respectively. In the other samples the calcite peaks and the metakaolinite peaks were absent as resulted by the FT-IR. Presence of hematite indicates probably open air firing in the oxidizing atmosphere. The red colour of the potteries is due to the more amount of hematite present in the sample [19]. Kottapuram potteries that were red ware/red slipped ware in colour and showed the presence of hematite and hence they might have been fired in the oxidizing atmosphere. But magnetite is not observed any of the FT-IR spectra and also in XRD studies. Then the presence of clay minerals and observation of O-H stretching and vibration bands in all the shards allows to draw a conclusion that the firing temperature of the investigate samples should be less/more than 650°C.

The firing temperature analysis using TG-DTA and Porosity

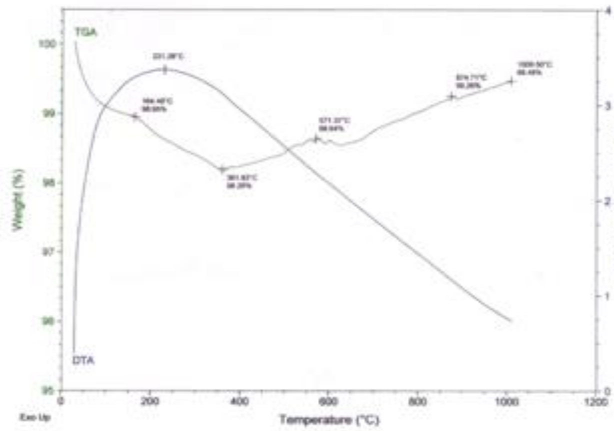
The weight loss/gain and the temperature difference between the pot shards were monitored by TG-DTA. It is well known that thermal analysis (TG-DTA) is a very important characterization method used to study the action process and of the properties of the materials obtained. TG coupled with porosity and FTIR provides very important information about the decomposition products of pot shards.

Both weight loss/gain and the porosity values are given in table 2. The thermal curves (shown in Fig 5) were recorded in the temperature range 25-1200°C in the air and nitrogen atmosphere. The weight loss band around 100-200°C is induced by hygroscopic water (i.e. physically absorbed water) and the exothermic peal in the temperature region 250-500°C is due to the combustion of organic materials in DTA curves [8, 20, 21]. The endothermic peak observed between 100-200°C characterizes the hygroscopic water in all the potteries whereas the broad exothermic band found in the range of temperature 250-500°C in the characteristics DTA curves of KTP2, KTP3 and KTP4 samples represent combustion of organic materials. The exothermic band appearing the temperature at around 600°C is attributed to the decomposition of kaolinite [8, 22]. Then, the decomposition of kaolinite was evidenced by the appearance of exothermic band in all the Kottapuram pot shards except in KTP2. The band on decomposition of kaolinite is the indication that the pottery is not fired above 800°C. Decomposition of calcite mineral is associated with the 700-900°C range. In this case, the exothermic band appearing at the temperature of 874°C in KTP2 sample.

In agreement with previous statements [4, 23], the KTP2 sample may be fired above 800°C and the other samples are may be fired in below 800°C as they are not possessing or minimal amount of calcite mineral in their well evidenced by the absence of peak in this respective region of temperature. It is evidenced by FT-IR analysis and porosity (discussed later). The total weight loss (%) and porosity were estimated with the different temperature range is given in table 2. The total weight loss range is 10.23-19.71% to the corresponding samples and 0.52% in KTP2 due to the weight gain in the exothermic band. The mass loss found is more in dehydroxylation and less in dehydration.



(a)



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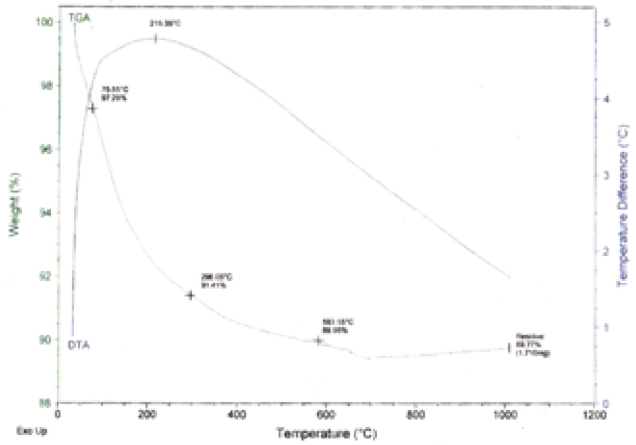

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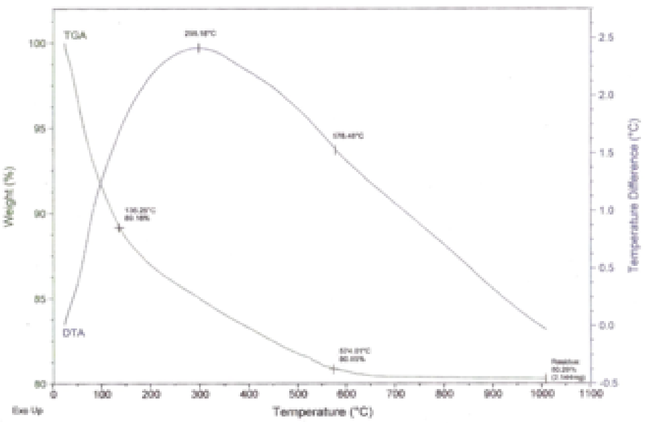

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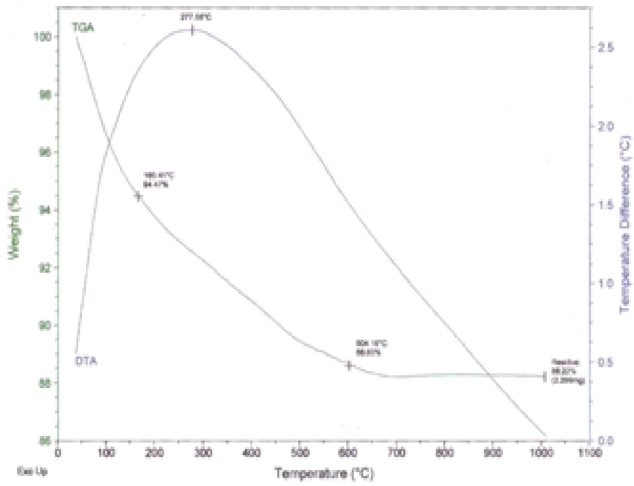

(e)

Figure 5. TG-DTA curve of KTP1-KTP5

Porosity is the prime factor to differentiate clay bodies after firing. High firing temperature will lead to low porosity especially if the bodies are glazed. The porosity ranges in the Kottapuram samples of the present study from 26% to 42%. The samples are classified into two groups with low porosity (fine particle) and high (coarse particle) porosity. The difference in porosity is attributed to the nature of the particles. The potteries made of coarse particles might have been fired below 1000°C whereas fine particle is fired to less than 900°C [24]. Thus, in all the Kottapuram samples made of coarse particle were fired below 1000°C.

The results of thermal analysis and porosity were compared are given in table.2. The clay minerals, calcite, kaolinite and iron oxides are the imperative minerals in the case of potteries to expound about that material such as firing temperature and the techniques during manufacturing. The minerals not devastate at anymore and it transform to any other state with regards to temperature. The science in behind that is the clay minerals change with respect to temperature and the techniques. This is applicable to establish the ancient people lifestyles they were living. The porosity measurement, which is used to exhibit the porous state of the pot shards. As mentioned above, at low temperature, the porosity is increased and vice versa[25].

Table 2. Thermal & Porosity analysis with estimated firing temperature of Archaeological pottery shards

Thermal Analysis			Porosity Analysis				Estimated firing temperature range °C
Sample code	Total weight loss/gain (%)	Estimated firing temperature °C	Colour	Particle nature	Porosity (%)	Estimated firing temperature °C	
KTP1	14.56	<800	Red ware	Coarse	42.14	<1000	650-800
KTP2	0.52	>800	Red ware	Coarse	26.94	<1000	800-900
KTP3	10.23	<800	Red slipped ware	Coarse	38.69	<1000	500-650
KTP4	19.71	<800	Red slipped ware	Coarse	29.08	<1000	500-650
KTP5	11.78	<800	Red slipped ware	Coarse	40.82	<1000	650-800

Conclusion

The IR spectra of the samples show very weak OH bands, while those of the others have OH bands higher intensity; the results indicate that due to open-air firing technique samples are not fired uniformly. The destruction of kaolinite and calcite in Kottapuram samples leads to the high temperature of the samples. The high porous pottery wares were used for keeping dry contents whereas the wares with fine pores and low porosity might have been used for storing oils, cooking purposes, carrying water or potable materials. The potteries of porosity values of more than 25% indicate that these pottery wares might have been used for preserving food materials. So in this period people perhaps learnt to store the foods for the future purpose.

From the above analysis it can be recorded that the Kottapuram samples KTP1 and KTP5 may be fired in the range of 650-800ºC whereas KTP2 were fired between 800-1000ºC and this high firing temperature lead to low porosity. Thus the KTP3 and KTP4 may be fired in the range of 500-650ºC due to the presence of kaolinite and calcite. These non uniform firing temperatures lead us to conclude the firing may be in open air. This combination of these techniques allows a thorough characterization of the pottery samples to be made and allows the origin of the clay used for the pottery samples to be explored. It comes to know that the artisans of this site aware of open air firing technique.

Acknowledgements

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