



Study on effect of sodium based buffers on the isotopic measurement of boron using Na_2BO_2^+ by thermal ionization mass spectrometry

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Abstract

Alkali metaborate ions are usually monitored for the isotopic measurement of boron by positive thermal ionization mass spectrometry. Large variations in the of $^{10}\text{B}/^{11}\text{B}$ isotopic ratios are observed with the change in the mole ratios of B/Na when sodium carbonate solutions are added when compared with solution of neutral salt of sodium (NaCl). To understand the reason for the variations observed in the isotopic ratio of $^{10}\text{B}/^{11}\text{B}$ with the change in the mole ratio of B/Na, various sodium containing buffers effective in the pH range 3–9 were employed in the present studies instead of the conventionally used sodium carbonate for formation of Na_2BO_2^+ ions in the ion source. NIST SRM-951 having certified $^{10}\text{B}/^{11}\text{B}$ ratio 0.2473 ± 0.0002 was used for all isotopic measurements by TIMS. It could be concluded that irrespective of the pH, the foremost reason for variations in the isotopic ratio of $^{10}\text{B}/^{11}\text{B}$ is the amount of Na present as Na_2O on the filament.

Keywords Sodium buffers · Na_2BO_2^+ · pH · TIMS · $^{10}\text{B}/^{11}\text{B}$ isotopic ratio

Introduction

Thermal ionization mass spectrometry is a very useful technique for the precise and accurate determination of isotopic composition of different elements in the periodic table. Conventionally singly charged positive atomic ions are monitored for the isotopic measurements of various elements using either single filament or multiple filaments assemblies. In some cases, polyatomic ions have also been employed for the isotopic measurement using thermal ionization source. Isotopic analysis using polyatomic ions is very common practice for most of the elements analyzed by negative ion mode of Thermal ionization source (NTIMS) such as BO_2^- , ReO_4^- , OsO_3^- , MoO_3^- etc. [1–5]. In the Positive ion Thermal Ionization method (PTIMS), with the application of the polyatomic ions for certain elements, a few of the following mentioned limitations in the atomic ion measurements are overcome such as high ionization potentials of the non-metals like B, S etc. and isobaric interferences such

as ^{238}U – ^{238}Pu [6–18]. It also minimizes the large isotopic fractionation particularly for the lighter elements.

Isotopic measurement of boron is essential in wide areas of research including hydrology, marine biochemistry, geochemistry, cosmo-chemistry, environmental sciences, health sciences, nuclear technology, etc. A comprehensive review on determination of isotope ratios of boron by mass spectrometry discusses the different mass spectrometric techniques used, along with their advantages and limitations [19]. Due to its high ionization potential (8.3 eV), boron is analysed as alkali metaborate (M_2BO_2^+ where M=Li, Na, Rb or Cs) by P-TIMS and as BO_2^- ions by N-TIMS. Even though N-TIMS is highly sensitive, a high level operator skill and strict analytical protocols (such as amount of boron loaded on the filament and heating condition) are required to achieve good precision in the measurement. When the amount of boron in the sample is sufficient (ppb or higher), analysis by P-TIMS is preferred over N-TIMS, as the monitoring species has relatively higher molecular weight, which reduces the severity of the isotopic fractionation. For P-TIMS isotopic measurement of boron, the choice of alkali used for the formation of M_2BO_2^+ depends on certain criteria. Among all the alkali metals, Lithium is least preferred alkali metal for the measurement using Li_2BO_2^+ ion because of the following reasons: (1) choice of polyatomic ion ratio is very crucial because of error systematics in the

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formulation of $^{10}\text{B}/^{11}\text{B}$ isotopic ratio from polyatomic ion [7] and (2) Polynomial equations have to be solved to obtain the boron isotopic ratios, since both boron and lithium have two isotopes with a mass difference of one resulting in a complicated isotope distribution pattern among the various polyatomic ions formed [8–12]. Alkali borate using cesium would be ideal as cesium is mono isotopic and the cesium metaborate ions have high ionic masses at m/z 308 and 309. But due to the restriction in the physical movement of the faraday cups at such higher masses, instruments with facility for simultaneous collection of the ions are available only in very few laboratories around the world. Accuracy in TIMS is limited due to the inherent systematic uncertainty such as isotopic fractionation. Various correction methodologies exist to account for the isotopic fractionation, such as external normalization, internal normalization and total evaporation with ion integration [20]. Total evaporation and ion integration method requires the production and collection of single ionic species and internal normalization requires minimum of three isotopes of which one isotopic ratio is invariable. Therefore for isotopic measurements of boron only external normalization method can be employed using isotopic reference material. Using Rb_2BO_2^+ a linear correlation between the fractionation factors of rubidium isotopes and boron isotopes using Rb_2BO_2^+ as monitoring ion was established which improved the precision in $^{10}\text{B}/^{11}\text{B}$ ratio [13]. The advantage of using Na_2BO_2^+ is that mono isotopic sodium restricts the number of polyatomic species and simultaneous collection at m/z 88 and 89 is possible [14, 15]. With appropriate loading techniques the sensitivity was improved to sub microgram levels of boron [14, 16].

The alkali borates are prepared by reaction of the boron sample with alkali carbonate. Various sample treatment and preparation procedures have to be employed depending upon the nature of the sample. For B_2O_3 and H_3BO_3 , the sample is made to react with sodium carbonate so that B/Na ratio is ~ 2 [14]. For refractory material or irradiated alloys of boron, it is fused with alkali carbonate on the filament, graphite coating on the filament after fusion is helpful in the enhancing the signal intensities of alkali borate formed [16]. Isotopic measurement of ground, fresh and downstream water samples requires anion ion exchange separation of boron from sodium and other elements. For this, the elution of boron is done with 0.1 M HCl so the addition of Na_2CO_3 or NaCl along with mannitol is required during pre-concentration of boron from the large eluted volume. 2-Ethyl-1, 3 hexanediol (EHD) solvent extraction is a preferred separation method when boron is present as impurity at ultra-trace levels in wide variety of matrices. As boron extracts into organic phase, the removal of organic phase is very essential step prior to the sample loading for the isotopic measurement [17]. Irrespective of the sample treatment and preparation procedures, boric acid being weak acid ($K_a = 6.4 \times 10^{-10}$)

requires a base such as MOH or M_2CO_3 (M can be any alkali metal) for formation of alkali metaborates. B/M ratio is usually maintained as 1 to 2 for the precise and accurate isotopic measurement, when the boron content in the sample solution is known. It has been observed that the $^{10}\text{B}/^{11}\text{B}$ ratio usually increases with B/Na mole ratio and for B/Na in the range 0.01–25, the $^{10}\text{B}/^{11}\text{B}$ ratio can change by 0.8% which can be an expected situation when boron concentration is not known. In our laboratory it was also observed that with the addition of sodium in the form of a neutral salt such as NaCl with mannitol this spread in the isotopic ratios for B/Na 0.01–5 is minimized to 0.08%. It is found very interesting that addition of sodium in the form of neutral salt improves the precision of the measurement drastically compared to addition of basic salt of sodium. The question arises that, the observed variations in the isotopic ratio of $^{10}\text{B}/^{11}\text{B}$ with the change in the mole ratios of B/Na, is due to the amount of sodium added or the pH of the resultant solution. In order to check this, present studies have been carried out with various sodium containing buffers with pH range 3–8.6 instead of sodium carbonate. The B/Na mole ratio was varied from 0.01 to 5 using each of these buffers to study the effect of changing B/Na ratio on the $^{10}\text{B}/^{11}\text{B}$ ratio at the constant pH of the buffer. Calculated quantities of these buffers were added to the NIST standard SRM-951 Boric Acid. Citric acid-sodium citrate [CA] (pH ~ 3), tartaric acid-sodium tartarate [TA] (pH ~ 3), acetic acid-sodium acetate [AA] (pH ~ 3.5) and glycine-sodium hydroxide [Gly] (pH ~ 8.6) were the different buffers employed during the present work.

Experimental

A single focusing TIMS (Isoprobe-T, Micromass, UK) with nine faraday collectors each connected to $10^{11} \Omega$ resistor for simultaneous collection of ions was used in the present work. Zone refined high purity Re single filament assemblies with dimensions (10 mm \times 1 mm \times 0.04 mm) were used for loading of the samples. Isotopic reference material for boron NIST-SRM 951 and high purity B_2O_3 have been used. 0.2 M Glycine + 0.2 M NaOH (pH 8.6), 0.2 M Acetic acid + 0.2 M Sodium acetate (pH 3.6), 0.1 M Citric acid + 0.1 M Sodium citrate (pH 3) and 0.1 M Tartaric acid + 0.1 M Sodium tartarate buffer (pH 3) solutions have been prepared using high purity chemicals (purity $> 99\%$) obtained from Merck. pH of B and Na solution mixtures were measured using pH meter model CL 54+, make: Toshcon Industries Pvt. Ltd. pH values were measured for each of the buffer solutions before and after the addition of boric acid to the buffers such that B/Na mole ratio varied from 0.01 to 5.

Experiments were carried out for the isotopic measurement of boron using all of the above mentioned four buffers and Na_2CO_3 , by mixing boron NIST standard SRM-951

solution with sodium containing solutions on a Teflon sheet so that B/Na varied from 0.01 to 5. These solutions were treated with Millipore water and evaporated to dryness for proper mixing. 5 μL of this solution containing 2 μg of boron (NIST-SRM 951) was loaded onto the centre of the Re filament. Sample was dried at 1 Amp and then slowly heated to 1.6 Amp and kept for 5 min for the complete conversion to alkali metaborate and then heated to red hot before bringing the filament current to zero Amp. The samples were mounted into the ion source housing and after achieving sufficient vacuum, filament was programmed to heat the sample to 1.3 Amp for 10 min and then slowly heated to obtain a steady signal for the data acquisition. Samples were run in static mode using Axial and H1 Faraday cups for collection of Na_2BO_2^+ ions at m/z 88 and 89. Data was collected for 3 blocks, each block consisting of 12 scans. Signal was integrated for 5 s in each scan.

Results and discussion

For analysis by TIMS normally alkali borates are formed by reaction of boric anhydride or boric acid with alkali carbonate. The B/Na mole ratio in the borate depends on the ratio of boric acid to alkali carbonate. Good ion intensities are obtained for B/Na ratio from 5 to 0.5. The pH of these solutions increases with decrease in B/Na ratio and the observed $^{10}\text{B}/^{11}\text{B}$ ratio has been found to decrease. Our earlier studies have shown graphite coating on the filament is required to obtain stable ion intensities and $^{10}\text{B}/^{11}\text{B}$ ratios during data acquisition especially when $\text{B}/\text{Na} \leq 0.5$ [14]. In the present studies different buffers in the acidic and basic range (pH 3, 3.6 and 8.6) as given above were used. The idea was to measure the $^{10}\text{B}/^{11}\text{B}$ at constant pH over a wide B/Na mole ratios. pH values of the boron mixed buffer solutions, do not change from the initial pH values unlike in the case of Na_2CO_3 where the basicity of solution mixture increases with decreasing B/Na ratio [14]. Boric acid being a weak acid, the buffer capacity of the buffer is not exceeded even when significant amount of boron is added to the buffer solutions. Irrespective of the buffers used, good signal intensities around 2–3 V were obtained at m/z 89 for mole ratios of B/Na from 5 to 0.5, below 0.5 poor signal ion intensities resulted in poor precision in the observed $^{10}\text{B}/^{11}\text{B}$ ratio. Based on experiments carried out earlier in our laboratory using sodium carbonate, for B/Na mole ratios below 0.5, the heated filament was coated with graphite to increase the signal intensities of M_2BO_2^+ [14, 16]. Graphite was not required for B/Na mole ratios > 0.5 , in fact we have observed reduction in ion intensity at B/Na mole ratio 5. Use of graphite enhanced the signal intensities for B/Na mole ratios of 0.1 to 0.01 for glycine + sodium hydroxide[Gly] and acetic acid + sodium acetate buffers[AA]. Increase in ion intensities

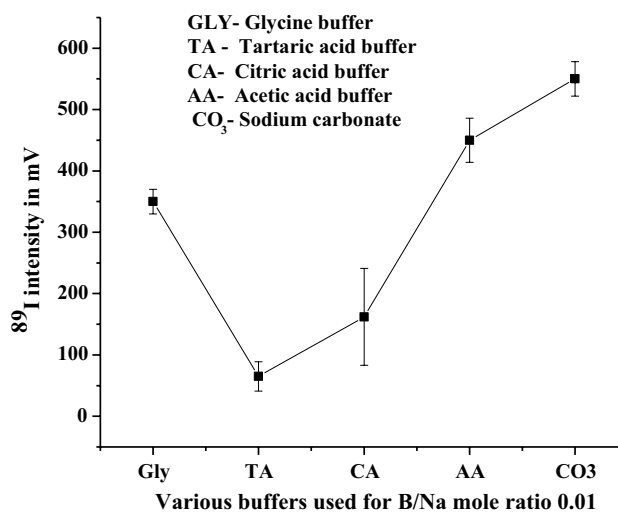


Fig. 1 Ion intensities at m/z ^{89}I for different buffers at B/Na mole ratio 0.01 using graphite during loading

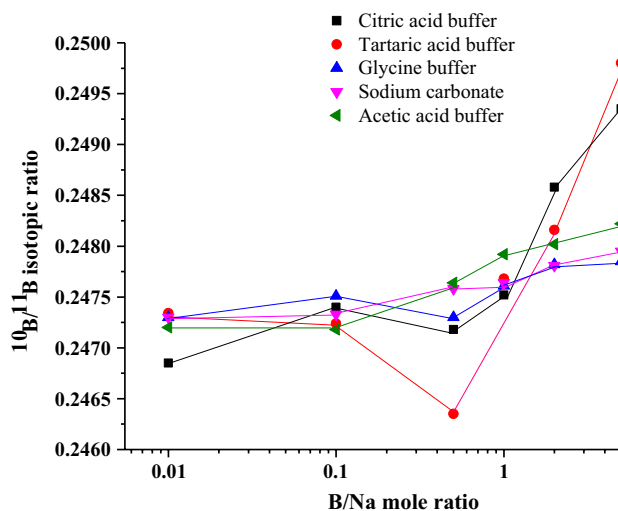


Fig. 2 B/Na ratio varied from 5 to 0.01. Graphite added on the filament for B/Na 0.1 to 0.01. Precision of better than 0.03% was obtained during $^{10}\text{B}/^{11}\text{B}$ measurements

was not as much for citric acid + sodium citrate[CA] and tartaric acid + sodium tartarate[TA] buffers inspite of using graphite which could be due to larger residue on the filament due to higher carbon content of these two buffers. This is shown in Fig. 1 which shows the signal intensities for all the buffers used with mole ratios of B/Na = 0.01 using graphite.

Figure 2 shows the variations in the isotopic ratio of $^{10}\text{B}/^{11}\text{B}$ with the change in the mole ratio of B/Na from 0.01 to 5 for the different buffers as well as sodium carbonate. The precision for all the measurements of $^{10}\text{B}/^{11}\text{B}$ ratio was better than 0.03%. It can be seen from the Fig. 2 that individually each of the buffers show decrease in $^{10}\text{B}/^{11}\text{B}$ ratio with

decrease in B/Na ratio. However, the variation in $^{10}\text{B}/^{11}\text{B}$ ratio with B/Na ratio is large for tartaric acid buffer at 1.4% and about 0.8% for citric acid buffer. This could be due to the high carbon residue on the filament for both citric acid and tartaric acid buffers resulting in incomplete formation of borates on the filament. From these graphs it is obvious that, isotopic ratio of $^{10}\text{B}/^{11}\text{B}$ decreases with the decrease in the B/Na from 5 to 0.5 irrespective of the buffers used, but when graphite coated filament was used, negligible change in isotopic ratios of $^{10}\text{B}/^{11}\text{B}$ was seen with further decrease in the B/Na mole ratio from 0.5 to 0.01. The overall trend in $^{10}\text{B}/^{11}\text{B}$ ratio obtained using the buffers is similar to sodium carbonate as seen in Fig. 2. This means that even at constant pH of a particular buffer solution variation in $^{10}\text{B}/^{11}\text{B}$ ratio with B/Na mole ratio is observed suggesting that the isotopic ratio is possibly dependent on B/Na mole ratio rather than pH. However the plot (in Fig. 3) of $^{10}\text{B}/^{11}\text{B}$ ratio vs pH shows that even at constant B/Na ratio the $^{10}\text{B}/^{11}\text{B}$ ratio does vary with pH as seen for B/Na = 5 and B/Na = 0.5. Figure 4 gives the uncertainty on the average value of $^{10}\text{B}/^{11}\text{B}$ ratio obtained for B/Na from 0.01 to 5 for the different buffers which gives an indication of the spread in $^{10}\text{B}/^{11}\text{B}$ ratio. Both glycine and acetate buffers, two different pH buffers at 8.6 and 3.6 show similar spread in the $^{10}\text{B}/^{11}\text{B}$ ratio with B/Na mole ratio of about ($\pm 0.15\%$) like carbonate, whereas this spread is significant in the case of citric acid and tartaric acid buffers (about $\pm 0.5\%$) due to reasons mentioned above.

Stable $^{10}\text{B}/^{11}\text{B}$ ratios are obtained during data acquisition with external precision better than 0.03% for all borates having a certain B/Na mole ratio. The observed $^{10}\text{B}/^{11}\text{B}$ ratio is specific to the borate formed on the filament, and shows negligible change with time or amount of sample on the filament which is expected from a normal fractionation behavior in TIMS. From these observations it appears that variations

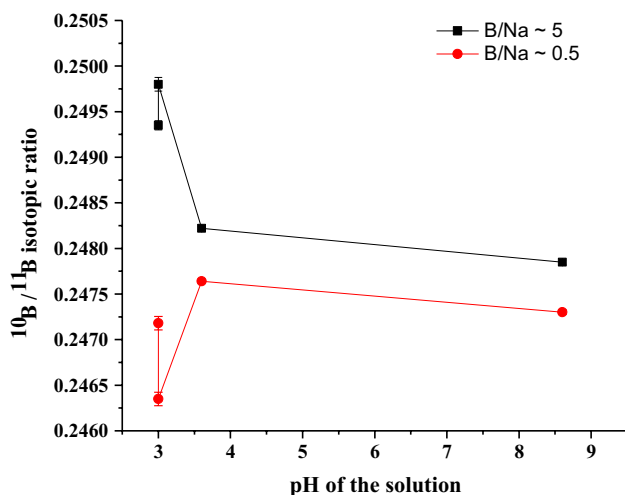


Fig. 3 Variation in boron isotopic ratio with pH at constant B/Na ratio

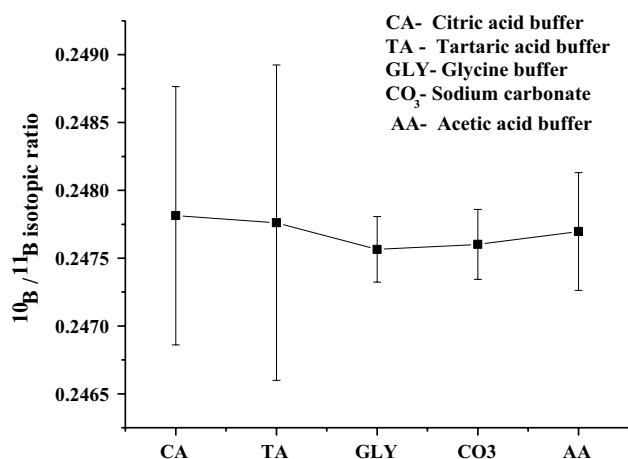


Fig. 4 Spread in the isotopic ratios of $^{10}\text{B}/^{11}\text{B}$ for various buffer solutions for B/Na from 5 to 0.01

in the isotopic ratio of $^{10}\text{B}/^{11}\text{B}$ with the change in mole ratio of B/Na is due to the existence of different boron species on the heated filament which have different physical characteristics such as volatility which causes the borate to fractionate differently during mass spectrometric analysis. Table 1 shows the various sodium borates reported in the literature. It is expected that sodium rich borates (B/Na < 1) will be highly alkaline (higher pH) when compared to the boron rich borates (B/Na > 1 Column 1 of Table). Measuring the pH of the residue formed on the filament after heating the filament to red hot will help to confirm the formation of different borates on the filament. This may be different from pH of the buffer solution used for loading. The residue formed was dissolved in 50 μL of Millipore water and pH measured using pH paper with resolution of 0.5 pH (Sigma Chemical Company USA). Though this data was measured for acetic acid buffer it is expected to be the representative for the rest of the buffers. Irrespective of the pH of buffer solution (pH 3.6 for acetic acid buffer), pH values of dissolved sodium borate residues were observed to vary with B/Na ratio. The measured pH of the residues are given in Column 4 of Table 1. The pH of the solution of the residue was observed to vary from 6 to 11 as B/Na mole ratio was changed from 5 to 0.5. Thus it is apparent that different sodium borates are formed on the filament with the amount of Na added as buffers. Also one can conclude that irrespective of the buffer used, it is the type of borate formed on the filament that decides the $^{10}\text{B}/^{11}\text{B}$ and other characteristics such as fractionation, signal intensity etc. obtained during analysis. Generally in TIMS the fractionation pattern of measured isotopic ratio of the element under study is affected by the physical properties such as volatility and molecular weight of the chemical species from which it is evaporated. With the decrease in the mole ratio of B/Na from 5 to 0.5, various sodium rich borates may be formed which may have different

Table 1 pH of the borate buffer solution and the dissolved residue

B/Na mole ratio	Formula of Compound expected to be formed	pH of buffers used	pH of residue on heated filament dissolved in 50 μ L water
0.5 ($2\text{Na}_2\text{O}\cdot\text{B}_2\text{O}_3$)	$\text{Na}_4\text{B}_2\text{O}_5$	8.6, 3.6, 3	11
1 ($\text{Na}_2\text{O}\cdot\text{B}_2\text{O}_3$)	NaBO_2	8.6, 3.6, 3	10
2 ($\text{Na}_2\text{O}\cdot 2\text{B}_2\text{O}_3$)	$\text{Na}_2\text{B}_4\text{O}_7$	8.6, 3.6, 3	9
5 ($\text{Na}_2\text{O}\cdot 5\text{B}_2\text{O}_3$)	$\text{Na}_2\text{B}_{10}\text{O}_{16}$	8.6, 3.6, 3	7

vapor pressures which would affect the pattern of observed $^{10}\text{B}/^{11}\text{B}$ ratio. The sodium salt of the buffers gets converted to sodium oxide, forming different sodium borates as given in Table 1. As reported earlier from our laboratory, coating of graphite on the heated sample filament may help reduce the volatility of these sodium rich borates, also graphite may possibly be reducing excess sodium oxide to sodium resulting in the formation of boron rich borates and higher observed $^{10}\text{B}/^{11}\text{B}$ ratio [14, 16]. The increase in $^{10}\text{B}/^{11}\text{B}$ ratio for B/Na of 0.1 and 0.01, when graphite is used (as seen in Fig. 2) does indicate the formation of boron rich borates in contrast to borates formed when graphite is not used. This also means that formation of sodium rich borates should be avoided for better precision in $^{10}\text{B}/^{11}\text{B}$ ratio. Therefore, the strategy followed is to use graphite when B/Na ratio is less than 0.5 but for B/Na in the range of 5–0.5, direct loading without using graphite gives best results.

Conclusion

During the present experiments with different buffers, it has been observed that when using buffer solution at constant pH, the $^{10}\text{B}/^{11}\text{B}$ ratio changes with B/Na ratio for all four buffers used. Although $^{10}\text{B}/^{11}\text{B}$ ratio variations with B/Na ratio are similar for all buffers used, variations in the isotopic ratio of boron with pH are observed, even at constant B/Na ratio. Based on the above observations, we can infer that the variations observed in the isotopic ratio of $^{10}\text{B}/^{11}\text{B}$ are most likely to be due to the different borates formed on the filament which show different fractionation pattern. The decomposition of Na_2CO_3 or sodium based buffers to different amounts Na_2O , forming sodium rich borates (lower B/Na ratios), whose volatility is high or boron rich borates (higher B/Na ratios) which are less volatile results in variations in the observed isotopic ratio of $^{10}\text{B}/^{11}\text{B}$. By using graphite during loading, the volatility is reduced either by trapping these species in the layered structure of graphite or by reducing Na_2O leading to formation of boron rich borates which improves the overall precision of analysis. Irrespective of the sample pretreatment procedures followed for separation or pre-concentration of boron, an understanding of the borate formation mechanism on the filament has led to enhancement in the achievable precision in $^{10}\text{B}/^{11}\text{B}$.

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