

Past rainfall and trace element variations in a tropical speleothem from India

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सार - मध्य प्रदेश की दंडक गुफा से 1996 में सक्रिय रूप से संवर्द्धित स्टैलैग्माइट (गुहा निक्षेप) एकत्रित किया गया। इनकी पुराजलवायु संबंधी विशिष्टता का मूल्यांकन करने के लिए मैग्नेशियम (Mg), स्ट्रॉन्टियम (Sr) और बैरियम (Ba) के सूक्ष्म मात्रिक तत्व मापे गये। इनमें इनकी वृद्धि की अवधि के दौरान सान्द्रण में शतप्रतिशत से भी अधिक भिन्नताएं पाई गई हैं। सूक्ष्म मात्रिक तत्वों के रसायनिक और भौतिक गुणों के साथ-साथ इस क्षेत्र में हमारे द्वारा किए गए प्रारम्भिक कार्य से प्राप्त हुए आक्सीजन और कार्बन के स्थायी समस्थानिक अनुपात के आंकड़ों के संबंध में भी इस शोध पत्र में बताया गया है। बैरियम और स्ट्रॉन्टियम की सान्द्रताओं के अनुपात स्थिर रहे जिससे यह पता चलता है कि गुफा के निरस्यंद जल के लिए मिट्टी की परतों और आधार शैल के विलयन में सूक्ष्म मात्रिक तत्वों का योगदान समान मात्रा में है। मैग्नेशियम, स्ट्रॉन्टियम और बैरियम की सान्द्रताओं और δ^{13} कार्बन के प्रोफाइलों के क्रमिक रूप से परिवर्तित होनेवाले घटकों से प्रगाढ़ सहसंबंधों का पता चलता है। यह देखा गया है कि सूक्ष्म मात्रिक तत्वों में आए परिवर्तनों का मुख्य कारण पहले हुई वर्षा की तीव्रता में आए परिवर्तन हैं। उष्णकटिबंधीय प्रदेशों में गुहा गौण निक्षेपों के सूक्ष्म मात्रिक तत्व की भिन्नताओं को पहले हुई वर्षा की तीव्रता के संकेतकों के रूप में देखा जा सकता है। विभिन्न जलवायु अंतरालों को सूक्ष्म मात्रिक तत्वों और स्थायी समस्थानिकों के आधार पर अभिलक्षित किया गया है। 3700 से 3350 वर्ष पूर्व की अवधि शुष्क पाई गई है। 3350 से 3200 वर्ष पूर्व के मध्य अधिक वर्षा का पता चला है। जलवायु से इतर प्रक्रियाओं से प्रभावित 2000 वर्ष की अवधि के अंतराल के पश्चात् 1200 से 400 वर्ष पूर्व के मध्य वर्षा अधिक हुई इसी समय ~ 650 वर्ष पूर्व की अवधि में वर्षा सर्वाधिक हुई। ~ 200 वर्ष पूर्व की अल्प अवधि में अधिक वर्षा होने तथा ~ 90 वर्ष पूर्व की अल्प अवधि में अल्पवृष्टि होने का भी पता चला है।

ABSTRACT. An actively growing stalagmite (cave deposit) was collected in 1996 from the Dandak cave in Madhya Pradesh. Trace elements Mg, Sr and Ba were measured in order to assess their palaeoclimatic significance. More than 100% variations in the concentrations of trace elements have been observed during the growth period. The chemical and physical properties of the trace elements along with the data of stable isotope ratios of oxygen and carbon from our earlier work has been discussed in this paper. Ratio of Ba to Sr concentrations has remained constant suggesting that the soil layers and bedrock dissolution have contributed the same proportion of trace elements to the cave seepage water. Slowly varying components in the Mg, Sr and Ba concentrations and $\delta^{13}\text{C}$ profiles show high degrees of correlations. It is found that changes in the trace elements are mainly driven by the varying intensity of past rainfall. Trace element variations of speleothems in tropical regions can be used as indicators of the past rainfall intensities. Different climatic intervals are characterised based on trace elements and stable isotopes. Period 3700 to 3350 yr BP was found to be arid. High rainfall was observed between 3350 to 3200 yr BP. After a hiatus period of 2000 yr due to non-climate dependent processes, again a high rainfall phase between 1200 to 400 yr BP was observed with a peak level at ~650 yr BP. A short enhanced rainfall phase at ~ 200 yr BP and a short arid phase at ~90 yr BP was also observed.

Key words – Speleothems, Stable isotopes, Trace elements, Tropical climate, Palaeomonsoon.

1. Introduction

Eventhough speleothems are important proxies of past environment their palaeoclimatic potential remains unexplored in India. Recently, a first detailed study of stable isotopes of carbon and oxygen was reported by Yadava and Ramesh (1999) for speleothems from Orissa and Madhya Pradesh. In this paper we report trace element measurements on a stalagmite from the Dandak cave in Madhya Pradesh.

1.1. Sample description

An active (*i.e.* cave water was dripping on the tip part of the sample) stalagmite (length ~28 cm) was collected from the Dandak cave (19°00' N, 82°00' S) in the Jagdalpur district of Madhya Pradesh in February 1996 (Yadava and Ramesh 1999). It was cut along the growth direction by a diamond cutter. A schematic diagram of the cross sectional view is shown in Fig. 1.

1.2. *Speleothems*

These are hanging columnar CaCO_3 deposits found in karst formations. Rain water percolates the porous soil zone with high pCO_2 (due to root respiration and bacterial decomposition of organic matter) and becomes acidic. The water flowing through cracks and fissures dissolves carbonates in bedrock strata. It is laden with HCO_3^- , CO_3^{2-} , Ca^{2+} and several soluble components derived mainly from the carbonate bedrock strata. The same water carrying dissolved ionic species, when drips through the fissures on the roof of a cave, encounters a low pCO_2 environment (as inside there is air circulation which links the cave with the outside atmosphere which has low pCO_2). The dissolved CO_2 slowly leaves the liquid phase which makes the drip water supersaturated with calcite. This results in the precipitation of calcium carbonate, forming a thin lamina of CaCO_3 at the dripping spot on the roof (stalactites, growing downward) and on the floor (stalagmites, growing upward). The seepage water acts as a transferring medium, carbonate in the bedrock strata is redeposited as speleothem in the cave gallery.

1.3. *Stable isotopes in speleothems*

During CaCO_3 precipitation stable isotope ratios of oxygen ($^{18}\text{O}/^{16}\text{O}$) and carbon ($^{13}\text{C}/^{12}\text{C}$) in the HCO_3^- ions in the dripping water are affected by the cave environment. These ratios are preserved in the CaCO_3 laminae and are used to decipher past cave environment. The ratios are measured relative to laboratory standard on a mass spectrometer and expressed as $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ where,

$$\delta^{18}\text{O} = [\{ (^{18}\text{O}/^{16}\text{O})_{\text{sample}} / (^{18}\text{O}/^{16}\text{O})_{\text{standard}} \} - 1] \times 1000 \text{ permil}$$

similarly,

$$\delta^{13}\text{C} = [\{ (^{13}\text{C}/^{12}\text{C})_{\text{sample}} / (^{13}\text{C}/^{12}\text{C})_{\text{standard}} \} - 1] \times 1000 \text{ permil}$$

The standard used is V-PDB supplied by IAEA. The oxygen isotopic composition, $\delta^{18}\text{O}$, of cave calcite is found to be very well correlated with the annual mean air temperature outside the cave in the mid and high latitude regions (Gascoyne 1992, Lauritzen 1995 and Repinski 1999). In semiarid climatic zones, oxygen isotopes have shown dominant dependence on intensity of rainfall (Bar-Matthews *et al.* 1996, 1999). The temperature induced $\delta^{18}\text{O}$ change is overridden with the rainfall induced component, as $\delta^{18}\text{O}$ decreases by increase in both temperature and rainfall. Earlier work on two tropical Indian speleothems have shown large fluctuations on $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ derived due to varying intensity of past rainfall (Yadava and Ramesh 1999).

TABLE 1

Several divalent ions and their radii from Rimstidt *et al.* 1998

Element	Ionic Radius $\text{\AA}^\circ (\text{M}^{++})$
Mg	0.72
Ca	1.00
Sr	1.16
Ba	1.36
Cd	0.95
Mn	0.67
Co	0.65

1.4. *Trace elements in speleothems*

The seepage water contains dissolved organic compounds and several ions at trace levels (Gascoyne 1983 and Goede 1994). While calcite is precipitated they are incorporated in speleothem laminae. As their chemical properties are similar and ionic radius are comparable (Table 1), substitution of Ca^{++} ion is possible in the growing speleothem (Tesoriero and Pankow 1996).

As ionic radius of Mg is (0.72\AA°) less than that of Ca (1.00\AA°), it is very likely to be substituted for Ca in the calcite lattice. Also, being smaller in size, the temperature increase may raise the rate of diffusion. This may enhance the substitution of Ca by Mg in the calcite precipitated. Sr and Ba have larger but comparable radii relative to the Ca ion and hence non-lattice substitution may be possible for them (Tesoriero and Pankow 1996). These effects should be observed in controlled laboratory experiments and also in natural calcite samples.

A summary of trace metals in speleothems and their temperature dependence is given by Gascoyne (1983). Following are the main sources of contribution of TE (trace elements) in cave seepage water.

- (i) The bedrock will contribute mainly to TE content in the seepage water during dissolution. It is expected that the contribution from bedrock will remain constant over long periods of time unless seepage water pathways have changed in the course of time.
- (ii) Dissolved organic complexes are also a source of TE. This dissolved organic material originates from different kinds of vegetation and the overlying soil zone.

The presence of trace elements in speleothem calcite may be due to following processes.

- (i) Drip water may contain particulate material which is trapped during calcite formation.

- (ii) TE may be adsorbed on the growing surface of the calcite.
- (iii) Direct substitution of the Ca^{++} by trace elements.

Speleothems free from particulate materials will incorporate TE by processes no. ii and iii. Adsorption process is expected to be temperature dependent and increase in temperature should result in less adsorption. At the same time the diffusion process will enhance substitution for the Ca^{++} ion (process no.iii). For a pure substitution process degree of incorporation is defined (Gascoyne, 1983) as

$$K = [\text{Conc. of TE in solid phase}] / [\text{conc. of TE in co-existing liquid phase}]$$

For a very dilute and infinite volume system the homogeneous distribution coefficient is defined as

$$D_{\text{TE}} = [\text{TE/Ca}]_{\text{solid}} / [\text{TE/Ca}]_{\text{liquid}}$$

Because free energies may differ in different phases the D_{TE} may be temperature dependent. This property can be utilised for palaeotemperature reconstruction.

Although the real solution may not be dilute and the TE ions precipitated in calcite may not be insignificant compared to ions in leftover seepage water, activity term should be used for the concentration. In reality the heterogeneous distribution coefficient will obviously differ from D_{TE} .

But, for simplicity it is assumed that the seepage water is a dilute system and the amount of precipitated calcite is insignificant compared to the ionic content of the coexisting liquid and hence, properties of TE are considered only in terms of D_{TE} .

1.5. Variations of TE in speleothems

During the deposition of calcite TE concentration may vary because of the temperature dependence of D_{TE} . Changed water pathways may also contribute to the different TE/Ca ratio. Varying residence time of seepage water in the soil and bedrock will change the degree of saturation and hence calcite TE/Ca. However varying TE/Ca of the seepage water may interfere with the temperature induced component.

1.6. Summary of previous TE work on speleothems

Behaviour of trace elements in cave deposits and their potential in paleoclimate is still under investigation.

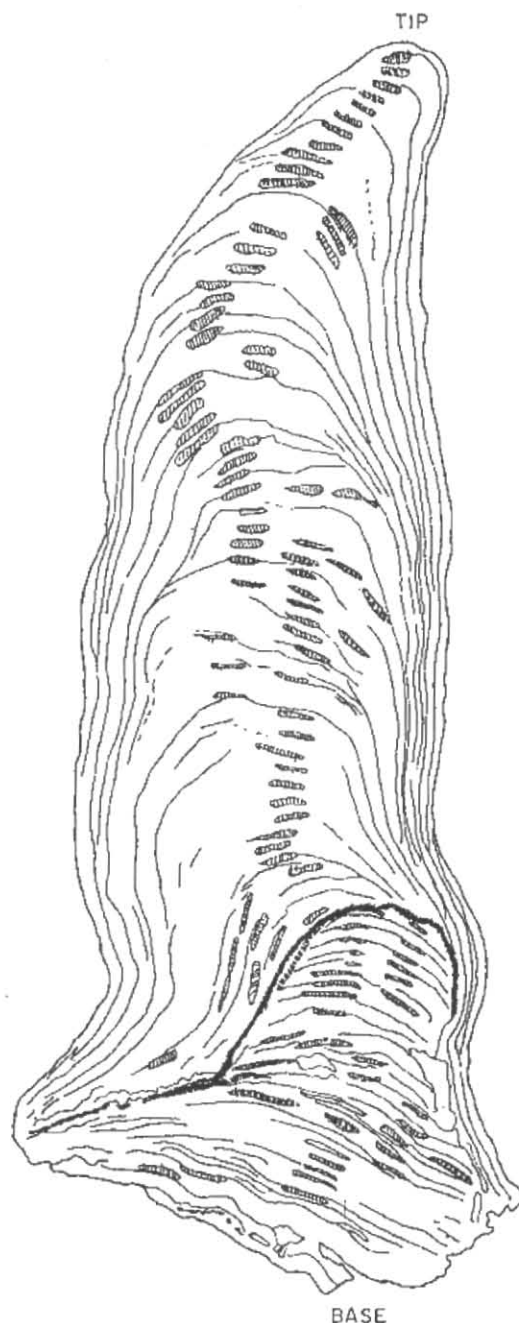


Fig. 1. Cross sectional view of the stalagmite from Dandak cave (19°00' N, 82°00' S). Dark patches show the sampling areas for trace element measurements

Work reported in the literature so far is limited, while Indian speleothems have not been studied.

Gascoyne (1983) measured TE/Ca ratio in the modern seepage water and calcite deposited in different caves which had different ambient temperatures. It was found that the Mg/Ca ratios in speleothems deposited at different temperatures are

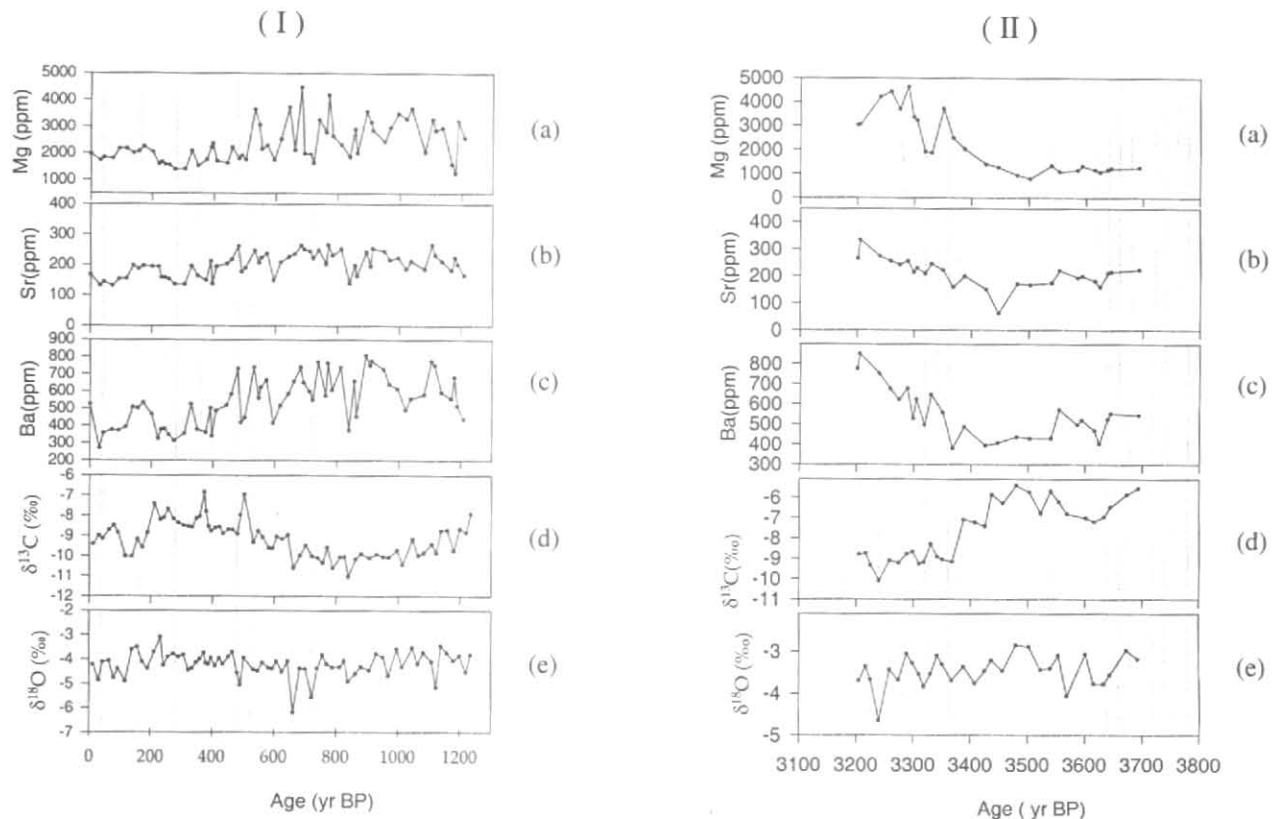


Fig. 2. Mg, Sr and Ba concentrations along the growth direction are shown in Figs. a, b and c respectively. Stable isotope data from Yadava and Ramesh (1999) (Figs. d & e). Data for post-hiatus is shown in Fig. 2-I and pre-hiatus period is shown in Fig. 2-II

correlated with the ambient temperatures. Between temperatures ranging from 7 to 24°C, $dD_{Mg}/dT = +0.0017/°C$. Also, D_{Mg} has not shown any clear dependence on the seepage water conditions *i.e.* different Mg/Ca ratios. In the same study the D_{Sr} was not found to have any clear temperature dependence, although it showed sensitivity to the seepage water conditions. Based on such observations it was proposed that Mg and Sr concentrations could be utilised for past temperature reconstruction. On the contrary, magnesium content showed significant correlation with $\delta^{13}C$ and little correlation with $\delta^{18}O$ in a study on stalagmite from Tasmania by Goede (1994). In the same study Sr content and $\delta^{18}O$ showed significant correlation and virtually no correlation with $\delta^{13}C$. It was suggested that the Mg content in speleothems may not be suitable for palaeotemperature reconstruction.

Four elements Mg, Sr, Ba and Br among thirteen studied in a speleothem by Goede and Vogel (1991) were shown to be potential paleoclimatic indicators.

Further work on fossil flow stone deposit from Ingleborough cave, northern England (Gascoyne 1992)

showed no correlation between trends in $\delta^{18}O$ and Mg content, possibly as the Mg in the feed water content varied in the past.

High resolution analysis by secondary ionisation mass spectrometry on a Holocene stalagmite from Tartair cave in north-west Scotland (Roberts *et al.* 1998) revealed annual cyclicity in the Mg/Ca, Sr/Ca and Ba/Ca. High frequency oscillations show anti correlations between Mg/Ca and Sr/Ca and positive correlation between Sr/Ca and Ba/Ca.

2. Experimental method and results

2.1. Sub-sample dissolution

Variations in the concentrations of trace elements Mg, Sr and Ba were studied in the Dandak stalagmite. As shown in Fig.1, 105 sub-samples weighing between 30 to 100 mg were recovered from stalagmite along the main growth direction.

The Inductively Coupled Plasma of argon gas has very high temperature between 6000 to 8000°K. Under these conditions any dissolved solution introduced in to

TABLE 2

Method of addition for determining the absolute Mg concentration for a typical speleothem sample

Aliquot	Mg added ($\mu\text{g/ml}$)	Relative line intensities at 279.806 nm	Mg in the sub-sample solution ($\mu\text{g/ml}$)
1	0	4725.8 \pm 70.9	28.4 \pm 0.6 / 0.9998* 26.4 \pm 0.5**
2	20	7932.1 \pm 119.0	
3	40	11368.6 \pm 132.8	

* correlation coefficient for the best fit line [emission line intensity (column-3) vs $\mu\text{g/ml}$ (column-2) plot].

** values obtained using the calibration method.

TABLE 3

Method of addition for determination of the Sr concentration for a typical speleothem sample

Aliquot	Sr added ($\mu\text{g/ml}$)	Relative line intensities at 421.552 nm	Sr in the sub-sample solution ($\mu\text{g/ml}$)
1	0	6304.5 \pm 94.6	0.5659 \pm 0.0106 0.9992* 0.6018 \pm 0.0141 **
2	0.465	11157 \pm 36.8	
3	0.929	16444.1 \pm 106.9	

* correlation coefficient for the best fit line [emission line intensity (column-3) vs $\mu\text{g/ml}$ (column-2) plot].

** values obtained using the calibration method.

the argon plasma in the form of aerosols using appropriate nebulizer gets efficiently atomised. Ionic and atomic line spectra are generated, which can be used to measure concentrations of major and trace elements, using a suitable spectrometer (Potts 1992).

In the present study all sub-samples were dissolved by 1N HNO₃ and heated at 50°C for about an hour to completely dissolve the carbonates. The solution volume was later made to precisely 25ml by adding 1N HNO₃ in a volumetric flask. After dissolution the solution doesn't show any particulate matter (except in the hiatus layer discussed later), which suggests that the TE in calcite are totally derived from seepage water and not from any detrital material.

Emission lines selected for the TE measurements are 279.806 nm for Mg, 421.552 nm for Sr and 455.403 nm for Ba. Measurements were carried out on ICPAES-JY-38S (Jobin Yvan-38S) machine at PRL, Ahmedabad. A calibration line *i.e.* emission line intensity vs. concentration ($\mu\text{g/ml}$) for Mg was generated using 1, 5 and 10 $\mu\text{g/ml}$ Mg standards. Similarly, both for Sr and

TABLE 4

Method of addition for determination of Ba concentration for a typical speleothem sample

Aliquot	Ba added ($\mu\text{g/ml}$)	Relative line intensities at 455.403 nm	Ba in the sub-sample solution ($\mu\text{g/ml}$)
1	0	11424.1 \pm 51.4	1.0166 \pm 0.0132 0.9993* 1.1310 \pm 0.0142 **
2	20	22126.1 \pm 143.8	
3	40	31271.3 \pm 437.8	

* correlation coefficient for the best fit line [emission line intensity

(column-3) vs $\mu\text{g/ml}$ (column-2) plot].

** values obtained using the calibration method.

TABLE 5

Correlation coefficients significant at 0.05 level are listed for low (bold) and high frequency variations for different parameters. Vacant spaces show no significant correlations

	Mg	Sr	Ba	$\delta^{18}\text{O}$	$\delta^{13}\text{C}$
Mg			0.27		
Sr	0.73		0.83		
Ba	0.75	0.92			
$\delta^{18}\text{O}$	-0.27		-0.25		0.45
$\delta^{13}\text{C}$	-0.73	-0.43	-0.53	0.72	

Ba 1, 2 and 5 $\mu\text{g/ml}$ standards were used to generate calibration lines. For samples with unknown concentration, first, specific emission line intensity was measured on ICP-AES and then from the calibration line, its solution concentration ($\mu\text{g/ml}$) was estimated. This value was later converted into TE concentration in the sub-samples.

TE concentration ($\mu\text{g/gm}$ or ppm) = solution concentration ($\mu\text{g/ml}$) \times (25/w)

where, w is the weight (in grams) of the sample dissolved in 25 ml 1N HNO₃.

2.2. Carbonate matrix problem

The dissolved sub-sample solution has many ionic species particularly the calcium ions. The carbonate matrix may either enhance or suppress the emission line intensities of specific interest. Calibration for Mg, Sr and Ba lines are generated using standards prepared from pure 1N HNO₃ where carbonate matrix is not present. If the matrix effect is dominant then it may not be possible to estimate absolute concentrations of TE using the method

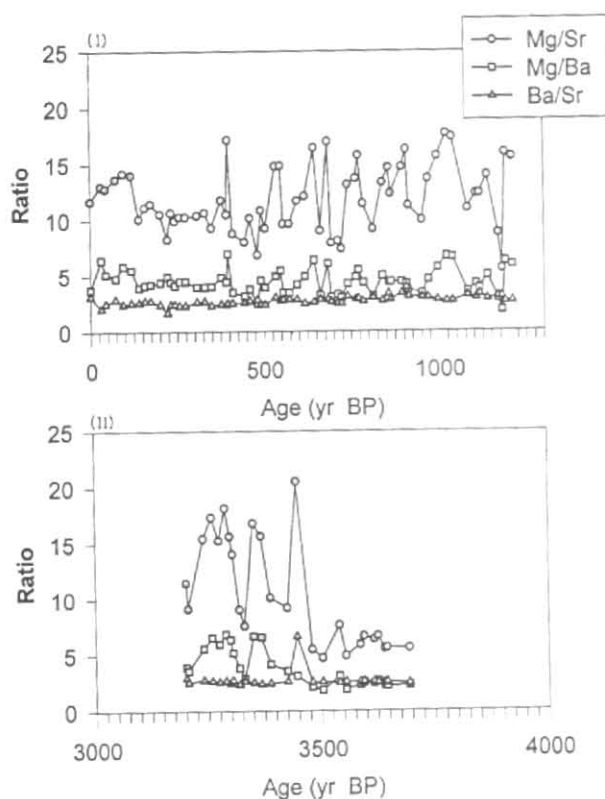


Fig. 3. Ratios of elements Ba/Sr, Mg/Ba and Mg/Sr are shown. Fig. 3-I shows post-hiatus period. Pre-hiatus period is shown in Fig. 3-II

of calibration discussed above. Method of addition which can estimate absolute concentrations was applied for a few sub-samples and then the results were compared with those obtained using the method of calibration. For this three separate aliquots were taken from the 25ml volume sub-sample solution. Leaving one of them, two of the aliquots were added with known ($\mu\text{g/ml}$) amount of TE. After measuring the respective line intensities absolute concentration of TE is estimated from the abscissa cut on one of the sub-samples is given in the Table 2. As shown in Table 2 the solution concentration values 28.4 ± 0.6 obtained from method of addition and 26.4 ± 0.5 from method of calibration are in good agreement at 2σ level. Similarly, in Tables 3 and 4 results obtained for Sr and Ba are given. The results obtained for Sr using the method of addition and the method of calibration are in good agreement at 2σ level, but for Ba it is somewhat different. Considering the overall uncertainty of 10% in the concentration measurements, this small difference is not significant.

This proves that concentration values can be measured using the calibration lines without any

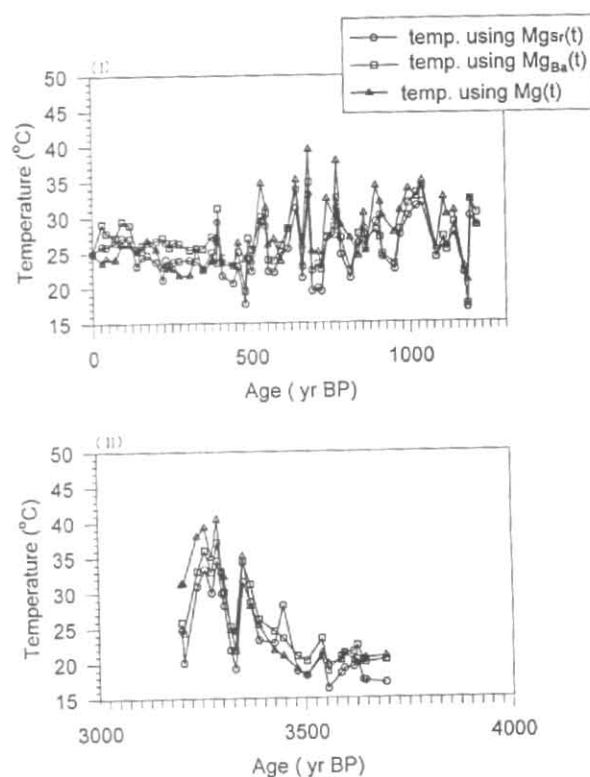


Fig. 4. Temperature reconstruction based on Mg concentration variation for post-hiatus (Fig. 4-I) and pre-hiatus (Fig. 4-II) periods. The $\text{Mg}(t)$ is original Mg concentration data where as $\text{Mg}_{\text{Sr}}(t)$ and $\text{Mg}_{\text{Ba}}(t)$ are rainfall corrected Mg concentration reconstruction. See text for more details

significant deviation from the absolute values. Subsequently, TE concentrations in all the sub-samples were measured using the calibration method. The Mg, Sr and Ba concentrations with depth from tip to base part are shown in Figs. 2 I & II(a-c). During the growth period more than 100% fluctuation is observed in the TE concentrations. The overall uncertainty in the concentration value is 10%. The chronology and measurements of stable isotopes of oxygen and carbon of successive layers are discussed elsewhere (Yadava and Ramesh 1999). The $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ taken from Yadava and Ramesh (1999) are shown in Figs. 2 I & II(e & d) respectively, for comparison.

3. Data analysis and discussion

3.1. Correlations between different parameters

To check any similarity in the behaviour of trace elements and stable isotopes, correlation coefficients between different parameters were calculated. The amplitude of variations in trace element content is

more than 100% compared to the present level (Fig.2). To suppress high frequency components a, five-pt. moving average was taken. As the central points of the sampling spots for stable isotopes (Yadava and Ramesh 1999) and trace elements are at about 20 yr intervals, this moving average will yield components of 100 yr period and above. High frequency (less than 100 yr) components are obtained by subtracting smoothed data from the originals. Correlation coefficients for the high and low (bold numbers) frequency components are listed in Table 5.

3.1.1. Low frequency changes

At low frequencies, changes are brought out by the slowly varying precipitation. This is confirmed by the values of correlation coefficients for different pairs discussed later, between $\delta^{13}\text{C}$ and Mg it is -0.73, between $\delta^{13}\text{C}$ and Sr it is -0.43 and between $\delta^{13}\text{C}$ and Ba it is -0.53 (correlations significant at 0.05 level, after adjusting for autocorrelations). Correlation coefficients for Mg and Sr is 0.73, between Mg and Ba is 0.75 and Ba and Sr it is 0.92 (correlations significant at 0.05 level, after adjusting for autocorrelations). As D_{Mg} depends only on temperature whereas D_{Ba} and D_{Sr} are dependent on source conditions and not on temperature, the Sr and Ba contents are significantly correlated. Oxygen isotopic composition may vary with temperature and amount of rainfall. There is weak negative correlation between $\delta^{18}\text{O}$ and concentrations of trace elements. For $\delta^{18}\text{O}$ and Mg, r is -0.27, with Ba it is -0.25 (correlations significant at 0.05 level, after adjusting for autocorrelations). No significant correlation between $\delta^{18}\text{O}$ and Sr is observed.

3.1.2. High frequency changes

Between Mg and Ba, r is 0.27. Sr and Ba are significantly ($r = 0.83$) correlated. Oxygen and carbon isotope ratios have significant positive correlation ($r=0.45$, correlations significant at 0.05 level, after adjusting for autocorrelations). For other pairs r is insignificant.

3.2. Temperature reconstruction

In Figs.3 (I & II) ratios of Mg/Sr, Mg/Ba and Ba/Sr are shown. It is clear that the Ba/Sr has remained essentially constant during growth of stalagmite. This proves that the bedrock constituents and seepage water pathways have not changed significantly during growth except a major change in Ba/Sr ratio around 3450 yr BP (Fig.3). Therefore, it appears that the source area for trace elements has remained the same throughout and the observed variations in Mg/Sr, Mg/Ba are solely due to climatic effects Figs. 2(a, b and c).

We do not have the value of present day $(\text{Mg}/\text{Ca})_{\text{water}}$ of the Dandak cave. Its value is estimated by taking D_{Mg} at 25°C from Gascoyne (1983) and using the present day $(\text{Mg}/\text{Ca})_{\text{calcite}}$ value of the tip part of the Dandak stalagmite. Using $\Delta D_{\text{Mg}}/\Delta T = 0.0017$, from Gascoyne (1983), the estimated change in Mg concentration in calcite deposited for 1 °C change in ambient cave temperature is 173.4 ppm (Table-6). We have further used this value for the temperature reconstruction.

Annual average temperature for the cave area is 25°C and Mg. conc. for the tip part is 1955.5ppm. Cave temperature $T(t)$ was reconstructed by assuming that all variations in Mg concentration are due solely to temperature Figs.4 (I & II).

$$T(t)=25+[\text{Mg}(t)-1955.5] / 173.4$$

Part of large variations in Mg, Sr and Ba concentrations have originated presumably due to changes in rainfall above the cave area. Concentration of trace elements in dripping water is constant as shown by consistent ratio of Ba/Sr (Fig. 3). The rate varies with the amount of water available in the seepage zone or bedrock which essentially is directly related to the amount of rainfall above cave area. The measured Mg concentration is a resultant of both past temperature and rainfall variations above the cave area. As D_{Ba} and D_{Sr} depend primarily on source conditions and not on the temperature variations (Gascoyne 1983 and Roberts *et al.* 1998) their past changes are expected due solely to rainfall fluctuations. To decouple the two we have taken the modern value of $\text{Mg}/\text{Sr}=11.6956$ and $\text{Mg}/\text{Ba}=3.7376$ at 25°C from tip part and reconstructed the Mg profile Mg_{Sr} and Mg_{Ba} from past Sr and Ba data. Mg_{Sr} and Mg_{Ba} represent purely temperature induced variations in Mg concentration.

$$\text{Mg}_{\text{Sr}}(t)=\text{Mg}(t) - \text{Sr}(t) \times 11.6956$$

$$\text{Mg}_{\text{Ba}}(t)=\text{Mg}(t) - \text{Ba}(t) \times 3.7376$$

Temperatures reconstructed from Mg_{Sr} and Mg_{Ba} are also shown in Fig. 4.

Table 6 shows wide uncertainty in the estimated $\Delta D_{\text{Mg}}/\Delta T$ from a cave system and inorganic precipitation experiments. Considering different $\Delta D_{\text{Mg}}/\Delta T$ values given, change in speleothem Mg content for 1°C change in ambient cave temperature varies from 173.4 to 42.8 ppm. We have chosen 173.4 ppm because it is based on actual measurements in cave system; in general lab experiments have underestimated this value (Table 6).

3.3. Discussion

3.3.1. Effect of temperature fluctuation

Partitioning of Mg between water and calcite is found to be temperature dependent and experimental studies have attempted to quantify this temperature dependence (Table 6). Sr and Ba incorporation is found to be temperature independent (Katz *et al.* 1972, Mucci and Morse 1983 and Roberts *et al.* 1998). Temperature reconstruction based on Mg concentration have given large amplitudes (up to 10°C, Fig. 4) in the past fluctuations. Past global temperatures for last 2000 yr have not changed by more than 0.5°C from the present level (Briffa and Osborn 1999). High temperatures around 800 yr BP could be due to the Medieval Warming. However, temperature could be indirectly involved in controlling the partitioning of trace elements as suggested by Roberts *et al.* 1998. As temperature increases D_{Mg} increases raising Mg concentration in calcite subsequently precipitated. Temperature also increases the calcite precipitation rate and hence indirectly increases the D_{Sr} and D_{Ba} (Roberts *et al.* 1998) raising Ba and Sr. This is observed in our data indicating high correlations between slow changes in Mg, Sr and Ba (Table 5). Hence, we can conclude that part of the fluctuations experienced are due to past temperature changes.

3.3.2. Effect of rainfall

3.3.2.1. Stable isotopes

Rate of dripping is directly related to the annual rainfall in the karst area. Stable isotopes of C and concentration of trace elements are affected by the dripping rate. $\delta^{13}C$ of calcite precipitated from a single droplet is found to be a function of time, with time, loss of CO_2 increases, which will continuously enrich the calcite precipitated in isotopic equilibrium with the ionic species. This follows Rayleigh type loss (Dulinski and Rozanski 1990). Oxygen isotopes in the calcite will not be affected with time as ionic species remaining in the drop immediately exchange with oxygen of bulk H_2O . However, $\delta^{18}O$ is depleted as intensity of rainfall increases, an effect observed in many regions and called amount effect (e.g. Bar-Matthews *et al.* 1996,1999).

3.3.2.2. Trace elements

Concentration of trace elements is also function of time. Calcite precipitation rate increases due to enhanced rainfall. This leads to increase in D_{Sr} and D_{Ba} (Lorens 1981; Tesoriero and Pankow 1996). Hence, the successive calcite lots will have more Ba/Ca and Sr/Ca ratio. Calcite precipitation rate dependence of

TABLE 6

Temperature and D_{Mg} relations obtained from inorganic calcite precipitation experiments (nos. 1, 3, 4 and 5) and from cave systems (no. 2). Third column represents estimated $\Delta Mg/\Delta T$ (ppm / °C)

Reference	$\Delta D_{Mg}/\Delta T$	$\Delta Mg/\Delta T$
1-Katz, 1973	0.0009	91.8
2-Gascoyne, 1983*	0.0017	173.4
3-Oomori <i>et al.</i> 1987	0.007	71.4
4-Mucci, 1987	0.00042	42.8
5-Burton and Walter, 1991	0.00043	43.9

* Derived from cave seepage water, speleothems and ambient cave temperature.

Cd^{2+} (0.95A⁰), Mn^{2+} (0.67A⁰) and Co^{2+} (0.65A⁰) all having lower effective ionic radii compared with Ca^{2+} , have shown inverse relations in inorganic precipitation experiments (Lorens 1981 and Tesoriero and Pankow 1996). A review of factors affecting Mg^{2+} partitioning when calcite is precipitated from sea water is given by Hartley and Mucci (1996). The literature is abundant but frequently marked by controversy. The Mg^{2+} partitioning is found to be independent of calcite precipitation rate from the sea water (Mucci and Morse 1983). But, as seen in the Table 5 slow changes in the Mg, Sr and Ba have high correlations which means that behaviour of Mg is very similar to Sr and Ba when calcite precipitation rate is changing in a cave system. Presumably, the sea water based results where high concentrations of elements are involved is not applicable to seepage water-calcite system in a cave.

Recently, Rimstidt *et al.*(1998) have proposed that both set of divalent ions, having larger and smaller radii compared with Ca and with equilibrium distribution coefficients $D_{TE} < 1$ (e.g. for Mg, Sr and Ba) are affected by the calcite precipitation rate in the same way. It has been shown that due to the kinetics related processes occurring at the solution-calcite boundary, the distribution coefficient D_{TE} measured for such divalent ions in an experiment are systematically increased by increasing calcite precipitation rate. This means that distribution coefficients of Mg should also increase with increasing calcite precipitation rate in a cave system similar to Sr and Ba.

In the light of such observations we believe that,

- (i) Only part of the changes in the trace element and stable isotope data are due to temperature fluctuations, major changes are due to the amount of water received by the surface area.

- (ii) Changes in $\delta^{18}\text{O}$ of speleothem are due to the amount effect which is presumably the outcome of the evaporations occurring at the surface above the cave area.
- (iii) Change in $\delta^{13}\text{C}$, Mg, Sr and Ba are derived by fluctuating drip rate inside the cave which is indirectly related to the rainfall above the cave.

The following explanation of the cave data can be given. When rainfall received by the catchment area increases, the dripping rate from the fissures increase, this also increases calcite precipitation rate. Each drop will stay for shorter period of time, on the tip of an actively growing speleothem as it is splashed away by a new drop. The $\delta^{13}\text{C}$ of the calcite depletes due to Rayleigh type loss (Dulinski and Rozanski 1990). While Mg, Sr and Ba concentration increases due to increased D_{TE} , increase in the rainfall is also shown by depletion trend in the $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ data (Fig. 2). When rainfall decreases, dripping rate is reduced. The drop stays for longer period of time, speleothem will have more enriched $\delta^{13}\text{C}$ and less of Mg/Ca, Ba/Ca and Sr/Ca ratios. The $\delta^{18}\text{O}$ will enrich due to the amount effect. The cumulative effect will be enriched $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ and reduced Mg/Ca, Ba/Ca and Sr/Ca.

All these processes leads to significant correlations between slow changes in Mg, Sr, Ba, $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ as shown by bold numbers in the Table 5.

3.3.3. Effect of residence time on trace element concentrations

The residence time of seepage water in overlying strata affects concentration of trace elements. Generally, dolomites have lower Sr and Ba compared to calcite but higher Mg content. Also, they dissolve slowly compared to calcites and hence saturation with respect to calcite or dolomite is a time dependent process. Increased residence time of water in bedrock strata will dissolve more of dolomites (Roberts *et al.* 1998). If residence time is affecting the trace element concentrations then the Ba and Sr together should show inverse correlations with Mg concentration data. This is not observed in our study hence we rule out the possibility of differential calcite / dolomite dissolution to be playing any roll.

3.3.4. Rainfall reconstruction

As the temperature reconstruction shows large values, considering the significant correlation coefficients of the slow changes among all the parameters studied we infer that major changes in TE are driven by the past rainfall variations. Based on characteristic changes in Mg,

Sr and Ba and $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ compared in Figs.2 (a,b,c,e and d) the deposit can be divided in to five different zones.

Period 3700 to 3350 yr BP : Arid phase

Growth of speleothem originated at ~3700 yr BP when rainfall was comparatively lower than present level as Sr, Ba and Mg contents are all low. High aridity makes $\delta^{13}\text{C}$ enriched due to reduced rate of dripping in cave environment and due to increased abundance of C_4 type plants. $\delta^{18}\text{O}$ is enriched due to amount effect.

Period 3350 - 3200 yr BP : High rainfall

Rainfall started increasing from 3350 yrBP as Mg, Sr and Ba all have increasing trend. $\delta^{13}\text{C}$ shows a depletion trend due to 'Rayleigh Distillation' loss of CO_2 and increasing C_3 type plant abundance. The change in $\delta^{18}\text{O}$ is ~1% which is equivalent to increase of 378 mm of rain per year (Yadava and Ramesh 1999).

This high rainfall phase presumably disturbed the intake part and at about 3200 yr BP, the stalagmite experienced a break in growth. The high flow conditions filled the seepage path and due to choking the dripping stopped. The hiatus layer is associated with fine clay particles which supports this argument.

1200 to 400 Yr BP : Increasing trend in the rainfall

Between this period rainfall was high with peak level around 650 yr BP. This is indicated by increasing trends in Mg, Sr and Ba concentrations and depletion trends in $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$, all attain peak levels around 650 yr BP. Already reported aridity during this period (Yadava and Ramesh 1999) is confirmed. In the Gupteswar cave, humid phase starts around 1.2 ka. Probably, the Dandak stalagmite formation restarted due to increased precipitation ~1200 yr BP. $\delta^{18}\text{O}$ shows high precipitation around this period due to the amount effect.

400 yr BP to present day : Short arid and enhanced rainfall events.

After a little enhanced rainfall phase around 200 yr BP again low rainfall event near 90 yr BP is observed.

3.4. Conclusions

We have reconstructed the past rainfall patterns of central India using a speleothem. Through this study we have seen that both changes in temperature and rainfall affect the stable isotopes and trace element concentration

in the same way. However, the temperature induced component is likely to be small and major variations are derived by fluctuating amounts of the past rainfall. Different growth zones are characterised with high or low intensity rainfall. Period 3700 to 3350 yr BP shows aridity phase. From 3350 to 3200 yr BP it was a high rainfall phase. From 1200 to 400 yr BP high rainfall with a peak level at ~650 yr BP is observed. A short duration enhanced rainfall at ~200 yr BP and low rainfall at ~90 yr BP is markedly observed. This study has shown that trace elements can be used for reconstructing high resolution hydrological changes in the karstic area. Further calibration studies in a cave environment and laboratory experiments are required for a quantitative reconstruction of the precipitation record.

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