Uranium-bearing magnesian-calcrete in surficial environment from Khemasar, Churu district, Rajasthan, India

A. Yugandhara Rao[1,*], K. Vijay Raj[2], O. P. Yadav[2], L. K. Nanda[3], A. K. Rai[3] and P. S. Parihar[3]

[1]Atomic Minerals Directorate for Exploration and Research, Vishakapatnam 530 007, India
[2]Atomic Minerals Directorate for Exploration and Research, Jaipur 302 033, India
[3]Atomic Minerals Directorate for Exploration and Research, Hyderabad 500 016, India

Magnesium-bearing calcretes of soft-gritty and hard pan varieties containing uranium concentrations from 16 to 74 ppm with <10 ppm of thorium are located along the Saraswati palaeochannel at Khemasar village, Churu district, Rajasthan. The uranium-bearing calcretes are exposed over an areal extent of 300 m × 200 m with thickness of up to 2 m in an interdunal depression. The silty sand layer occurring below the calcrete horizon suggests that it is a valley-fill calcrete, deposited along a palaeochannel. This occurrence of uraniferous Mg-calcrete in the Saraswati river palaeochannel opens up a large area for uranium exploration in the calcrete environment of Thar Desert. These calcretes are composed of 15.94% to 25.39% CaO, 7.15% to 22.39% MgO and Sr/Ba ratio up to 66.98. There is a positive correlation of U with Sr/Ba and MgO. The high Sr/Ba ratio and MgO indicate water of saline nature and high rate of evaporation. Ephemeral centripetal drainage mixing with the dissected palaeochannel waters and groundwaters, under arid climatic conditions might have resulted in the formation of this kind of uranium-bearing calcrete in fluvio-lacustrine environment.

Keywords: Fluvio-lacustrine environment, Khemasar, magnesian calcrete, surficial type uranium.

SURFICIAL-TYPE uranium deposits related mainly to evaporites and associated with calcretes (calcium and magnesium carbonate) are known in late Tertiary to Quaternary geological settings[1]. Calcretes occur in powdery, nodular and indurated forms. They show characteristics of cementation and accumulation by replacement in soil, rock or weathered material primarily in the 'vadose zone'[2]. These are incidentally the most studied types of palaeosoils as they provide information for sedimentalogical, palaeogeomorphological and palaeoclimatic reconstruction[3]. Uranium mineralization in the surficial-type deposits is typically in the form of carnotite ($K_2(UO_2)_2(VO_4)_2 \cdot 3H_2O$) and is commonly cemented by minerals such as calcite, gypsum, dolomite, ferric oxide and halite[4,5].

A number of mechanisms including sorption, colloidal precipitation, changes in vanadium redox state, CO_2 partial pressure and pH have been proposed to explain precipitation of carnotite[4]. Some of these changes may result from mixing of different groundwaters and/or evaporation and deposition of cementing minerals, resulted mainly from fluctuation of the groundwater table and evaporation under semi-arid climatic conditions in the closed basins[1].

Subsequent to the discovery of the Yeelirrie deposit in Australia in 1972, surficial type uranium deposits are continuing to receive attention. During recent times, in the southern hemisphere, a similar type of uranium deposit has been located in Langer Heinrich and Klein, Trekkopje in Namibia and lake Maitland in Western Australia. As similar tropical conditions and uranium-rich granitic and volcanic rocks also occur in parts of Northern Hemisphere, such type of deposits should exist in addition to the few occurrences already known in Mauritania, Somalia and the United States[1]. Favourable geological factors such as the occurrence of uranium-bearing Malani Igneous Suite (MIS) rocks and well-defined palaeochannels coupled with arid climatic conditions in Thar Desert of western Rajasthan have paved the way for exploration of such surficial-type uranium deposits in Rajasthan. Recent studies have resulted in delineating magnesium-bearing (avg. 13.28%) calcrete from Lachheri area, Nagaur district, in Playa lake environment[6]. Calcretes in Thar desert occur in a variety of settings, including piedmonts, sheet wash aggraded plains and colluvial plains formed through hybrid process[7]. Calcretes in the interdunal calcpan sites near Didwana are formed by a process of re-precipitation and re-cementation and are pedo-sedimentary and affected by groundwater during their origin[8]. The source of most of the calcium is groundwater and calcite nodule formation was largely dependent on pedogenic process associated with evaporation, microenvironmental changes in pH and CO_2 partial pressure[9].

Palaeo drainages of Saraswati–Drishadvati river system in north western part of Rajasthan concealed under aeolian sand cover[10,11] were delineated through remote sensing techniques (Figure 1). Based on the favourable geological and geomorphological conditions, regional radiometric and hydrogeochemical surveys were conducted and calcrete sampling was initiated along the Saraswati river palaeochannels.

The area under study lies in the semi-arid zone with annual rainfall of <300 mm and evapotranspiration of around 1500–1800 mm. The minimum and maximum temperatures recorded from Churu district are –3°C and 50°C respectively. The area is covered by sand dunes with no rock exposures and even the youngest calcrete

*For correspondence. (e-mail: ayugandhararao.amd@gov.in)

formations are concealed under sand cover. However, at places, a few exposures of calcretes can be noticed along this tract. Calcrete exposure at Khemasar village is one among them hosting considerable amounts of uranium, and it is one of the oldest working quarries for calcrete in this region. The Khemasar village, locally pronounced as 'Khevinsar' (lat. 28°23′N; long. 74°39′E) is about 36 km from Churu due northwest on the Churu–Sardarsahar road (Figure 2).

Due to its hard and compact nature, local villagers use this calcrete for road metal as well as construction. Physiographically, it is a low lying valley of nearly 1 sq. km developed within the interdunal depression. Within this valley, the calcretes are exposed over an areal extent of 300 m × 200 m and are sandwiched between aeolian sand cover and khaki-green colour silty sand horizon (Figure 3).

There are two types of calcretes: one is pale white, soft and friable, nodular to columnar 'gritty' type. The other variety is a white, hard and compact 'hardpan' type. Both these varieties contain uranium concentration and the soft variety holds higher concentration than hardpan. Thickness of calcrete horizon varies from 0.50 to 2.50 m with an average of 2 m and the contact between calcrete and the underlying khaki-green silty-sand unit is sharp. It is suggested that the green sand below the calcrete in the interdunal areas represents vestiges of an earlier disorganized drainage system[12].

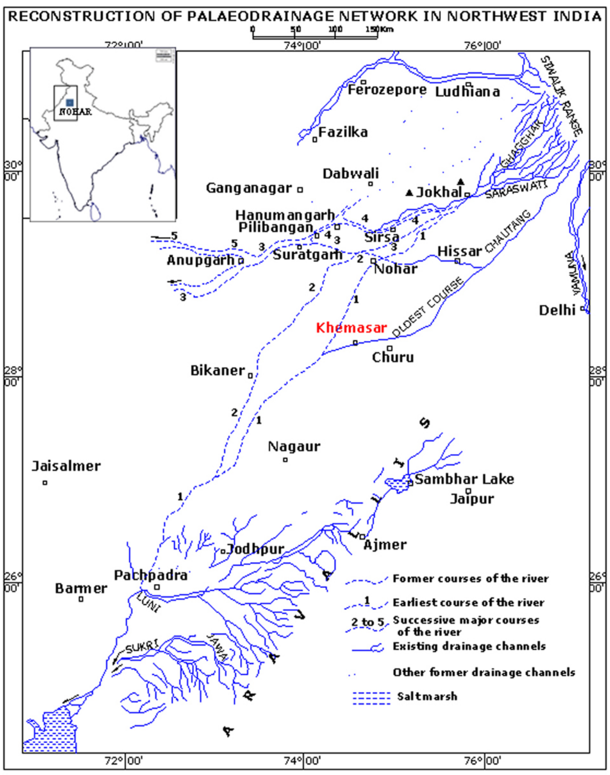

Figure 1. Palaeodrainage map of Saraswati river (source: ref. 11).

Three cross-sectional profiles were selected within the quarry and systematic grab samples ($n = 18$) were collected from both these calcrete and silty-sand horizons. Uranium was estimated through standard flourimetry[13], and thorium, strontium, barium, calcium and magnesium were estimated though ICP-AES and potassium by flame photometry. These analytical results are provided in Table 1. The analysis of data reveals that uranium values in calcretes vary from 16 to 74 ppm and in silty-sand horizon it is <5 ppm. Thorium concentration in both these units is <10 ppm. The CaO ranges from 15.94% to 25.39% and MgO from 7.15% to 22.39%. Literature survey shows that the world average of CaO content in calcretes varies from 39.5% to 44.5% and MgO does not exceed 3% and average Indian calcretes are less calcareous as

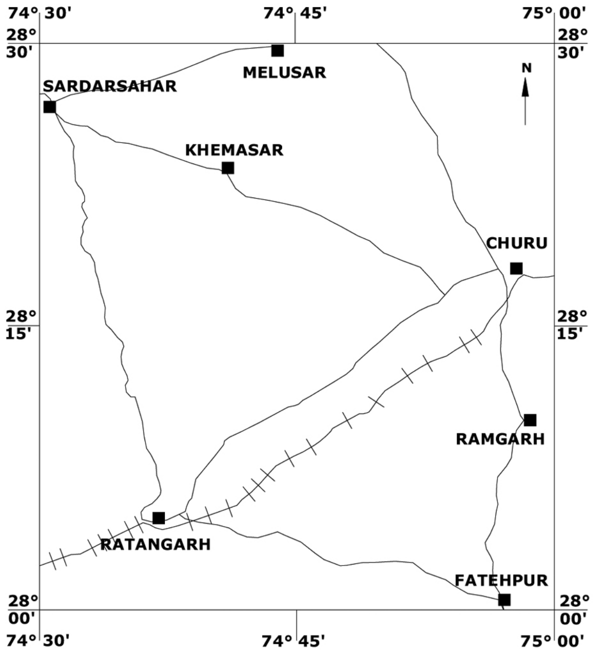

Figure 2. Location map of Khemasar.

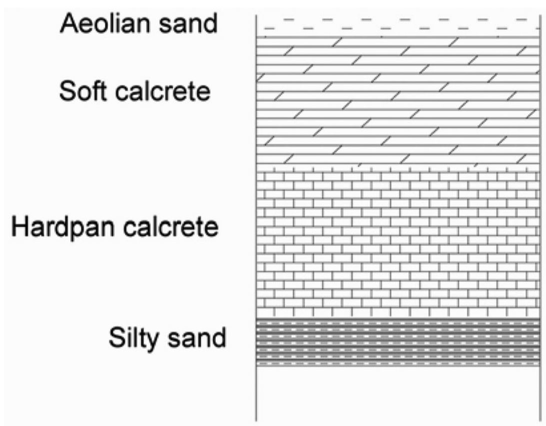

Figure 3. Schematic view of Khemasar calcrete profile.

Table 1. Chemical analysis data of calcretes from Khemasar, Churu district, Rajasthan

Sample no.	Rock type	U (ppm)	Th (ppm)	CaO (wt%)	MgO (wt%)	Sr (ppm)	Ba (ppm)	Sr/Ba	V (ppm)	K_2O (%)
KMR/104A	Soft powdery calcrete	30	<10	20.50	17.32	3514	90	39.04	11	0.32
KMR/104B	Hardpan calcrete	16	<10	16.76	12.66	3574	87	41.08	14	0.17
KMR/104C	Silty-sand	<5	<10	2.20	1.32	238	247	0.96	36	1.24
KMR/105A	Soft powdery calcrete	31	<10	21.80	13.93	3367	125	26.94	10	0.38
KMR/105B	Hardpan calcrete	20	<10	24.09	14.04	1649	83	19.87	<10	0.29
KMR/105C	Silty-sand	<5	<10	2.40	1.56	231	249	0.93	28	1.15
KMR/106A	Soft powdery calcrete	31	<10	16.37	19.64	5608	118	47.53	20	0.23
KMR/106B	Hardpan calcrete	16	<10	25.39	7.15	1946	149	13.06	13	0.51
KMR/106C	Silty-sand	<5	<10	2.43	1.51	273	300	0.91	21	1.05
KMR/107		72	<10	19.78	19.72	5247	109	48.14	13	0.19
KMR/108		74	<10	20.42	19.68	6013	101	59.53	12	0.16
KMR/109	Soft powdery calcrete	42	<10	23.39	13.06	4993	139	35.92	14	0.24
KMR/110		64	<10	16.37	22.39	6229	93	66.98	16	0.26
KMR/111		36	<10	19.18	19.49	5159	111	46.48	12	0.22
KMR/112		18	<10	23.63	14.41	2528	121	20.89	11	0.36
KMR/113	Hardpan calcrete	22	<10	21.44	13.81	2248	107	21.01	13	0.42
KMR/114		18	<10	15.94	18.00	2359	176	13.40	39	0.15
KMR/115		21	<10	17.73	17.89	4582	135	33.94	17	0.23

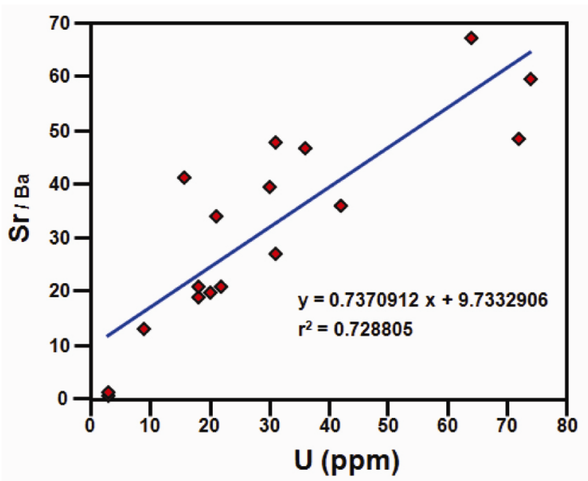

Figure 4. U (ppm) versus Sr/Ba.

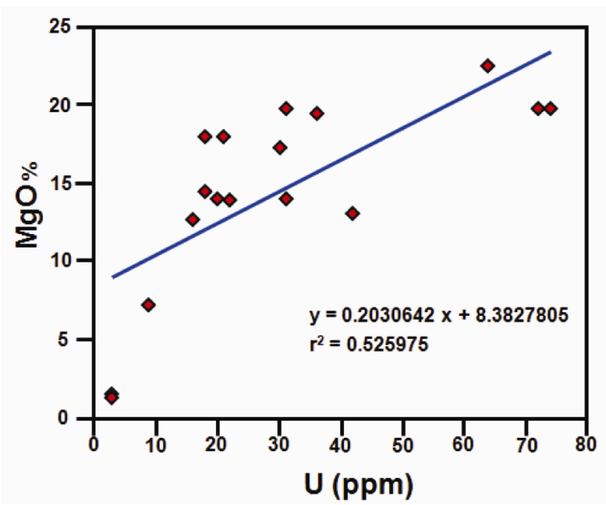

Figure 5. U (ppm) versus MgO (%).

compared to global average. Mg-rich calcretes have been reported from Australia, South Africa and Namibia[14].

The analysis of data indicates that strontium content varies from 1649 to 6229 ppm, barium ranges between 83 and 176 ppm. Sr/Ba ratio varies from 13.06 to 66.98. Strontium is generally associated with calcium-bearing evaporate sediments, whereas barium is associated with clastic sand; the higher Sr/Ba ratio indicates the non-clastic nature of sediments. Accordingly, analysis of the silty-sand (clastic sediment) horizon at the base of calcrete showed low MgO up to 1.56% and accordingly uranium <5 ppm and Sr/Ba ratio up to 0.96. There is a distinct chemical variation, especially in Sr/Ba ratio between clastic and non-clastic (evaporatic) sediments. Silty-sand horizon contains high potassium concentration up to 1.24% and accordingly there are moderate levels of barium concentration up to 300 ppm. This may occur due to presence of clay minerals within the silty-sand horizon. The linear association relationship of U with Sr/Ba and MgO using co-efficient of correlation analysis is shown in Figures 4 and 5 respectively.

There is a moderate positive correlation between U and MgO and Sr/Ba with the co-efficient of correlation (r^2) values of 0.525 and 0.728 respectively. Studies carried out on sub-surface playa sediment-calcrete from different playas in western Rajasthan, suggest that the prevalence of higher evaporation and salinity conditions favours high Sr/Ba ratio and strontium is associated with carbonate and sulphate bearing minerals and these are genetically contain evaporates, whereas barium is derived from clastic sediments[15]. Similar studies on calcrete from Kalahari Desert area attributed high magnesium concentration in calcretes to high rate of evaporation[16]. The high Sr/Ba ratio and MgO contents indicate the high rate of evaporation which favours the dissociation of uranylcarbonate complex in the waters forming uranyl ions in solutions.

It is established that hydrogeochemical surveys play a major role in exploration for uranium-bearing calcretes[17]. For this purpose, eight water samples were collected from different open wells, hand pumps and tube wells along the palaeo-channels. The general water table depth varies between 15 and 25 m. Samples were collected in duplicate in 250 ml prewashed polythene bottles. The waters were filtered through 0.45 micron filter paper and one set of samples was acidified to pH 2 using 10% nitric acid, to prevent flocculation and fungus formation, thus arresting the adsorption of uranium. This facilitated the reliability and precision of uranium values. The acidified samples were used for estimation of uranium through laser flourimetry[18].

The other set of non-acidified samples were used for estimation of major cations (Ca^{++}, Mg^{++}, Na^{+}, K^{+}) and major anions (HCO_3^-, Cl^{2-}, SO_4) using standard procedures[19]. The results indicate that Ca^{++} ranges from 145 to 212 ppm, Mg^{++} ranges from 15 to 102 ppm, Na^{+} ranges from 45 to 212 ppm, K^{+} ranges from 3 to 12 ppm, HCO_3^- ranges from 257 to 565 ppm, Cl^{-} ranges from 250 to 1415 ppm, SO_4^{--} ranges from 123 to 248 ppm and V ranges from 16 to 55 ppb. During sample collection itself, the Eh and pH values were measured using ORP and pH meters respectively. The Eh values vary between +125 and +275 mV and pH values range between 7.5 and 8.

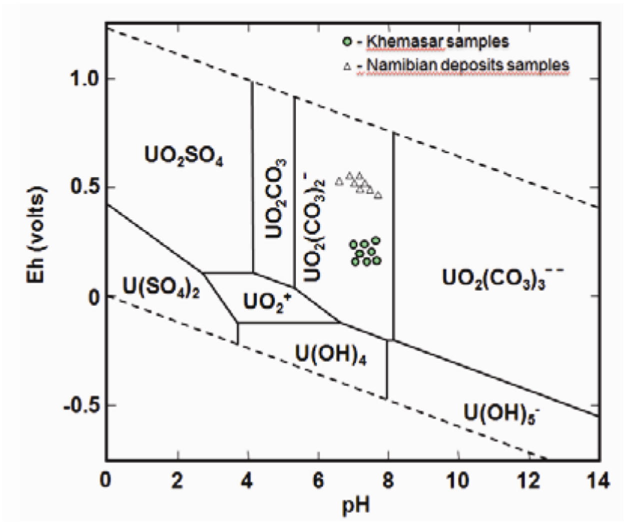

Figure 6. Eh–pH diagram for system U–H–O–S–C at 25°C. (Source ref. 20.)

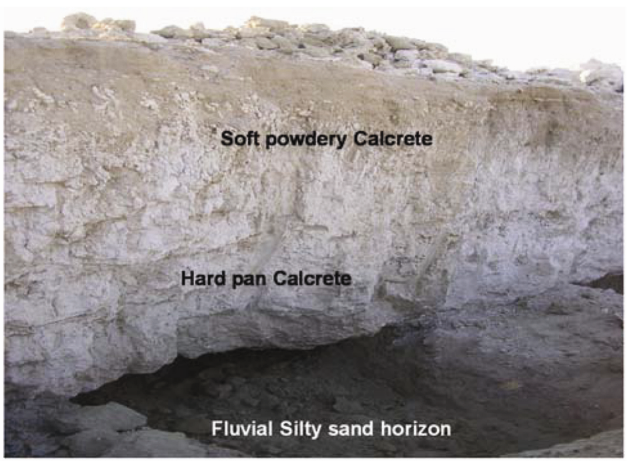

Figure 7. Photograph of calcretes, Khemasar, Churu district, Rajasthan.

The data indicate that waters are oxidized, saline and alkaline. Uranium-bearing calcretes generally formed from mildy oxidizing, saline alkaline groundwaters. In constricted drainages to semi-enclosed basins under variable evaporative conditions[20]. The present uranium-bearing calcretes were identified in the dry small playa along the channel with green silty sand at the base (Figure 6). This kind of semi-enclosed loci is of fluvio-lacustrine nature and formed by the dissection/segmentation of palaeochannels and was admixed with fluctuating ground waters and centripetal ephemeral drainages draining through sand dunes, during seasonal rains. It is suggested that the green silty-sand in the inter-dunal areas represents vestiges of an earlier disorganized drainage system[12]. The high rate of evaporation under arid conditions resulted in an increase of total dissolved solids (TDS, 1225–3075 ppm) and waters gradually become brackish to saline. Accordingly, calcium and carbonate ions were enriched and saturated within the waters. Subsequently, calcrete formation occurred by chemical precipitation. Similar to other ions, uranium concentration in waters also got enriched during evaporation. The uranium values range between 18 and 46 ppb. Eh versus pH plot was prepared to understand the complexes of uranium. The plot (Figure 7) indicates that uranium in groundwater is found in the carbonate complex. In uranyl–hydroxide–carbonate system, the $UO_2CO_3^0$, $UO_2(CO_3)_2^{2-}$ and $UO_2(CO_3)_3^{4-}$ complex predominate in the pH range of 6–8 (ref. 21). These carbonate complexes are most important for the formation of surficial uranium deposits and dissociation of uranyl carbonate complex is considered to be vital for the formation of calcrete and gypcrete bearing uranium deposits[7]. Under high rate of evaporation, uranium carbonate complex dissociates and gives rise to uranyl ion and with the existing available cations and anions uranium vanadates, sulphate and phosphate complexes are formed in the secondary environment. High magnesium concentration in calcretes indicates high rate of evaporation[16]. Probably, this kind of high rate of evaporation may have been prevalent during the geological past, as supported by the existence of high magnesium calcretes. Petrographic and mineralogical data on uraniferous calcrete from major world surficial uranium deposits indicate that calcite in calcrete is magnesian and development of dolomite at the expense of calcite has been proven in Yeelirrie deposit[22]. Waters raising towards the surface undergo evaporation, including increasing salinity and CO_2 degassing, and finally leading to breakdown of the uranyl carbonates.

The Saraswati palaeochannel has been traced by earlier researchers across the entire Thar Desert and the present occurrence of Mg-rich uraniferous calcrete at Khemasar brings out the importance of the palaeochannel as a future exploration target for surficial uranium concentrations.

1. Michel Cuney, Evolution of uranium fractionation processes through time driving the secular variation of uranium deposit types. *Econ. Geol.*, 2010, **105**, 553–589.
2. Mann, A. W. and Deutscher, R. L., Genesis principles for the precipitation of carnotite in calcrete drainages in Western Australia. *Econ. Geol.*, 1978, **73**, 1724–1737.
3. Wright, V. P. and Wilson, R. C. L., A terra rosa-like paleosoil complex from upper Jurassic of Portugal. *Sedimentology*, 1987, **34**(2), 259–273.
4. Boyle, D. R., The genesis of surficial uranium deposits. Surficial Uranium Deposits. Report of the Working Group on Uranium Geology, IAEA-TECDOC-322, 1984, pp. 45–52.
5. Carlistle, D., Surficial uranium occurrences in relation to climate and physical setting. Surficial Uranium Deposits. Report of the Working Group on Uranium Geology, IAEA-TECDOC-322, 1984, pp. 25–35.
6. Misra, A., Pande, D., Ramesh Kumar, K., Nanda, L. K., Maithani, P. B. and Chaki, A., Calcrete-hosted surficial occurrence in Playa-lake environment at Lachhri, Nagaur District, Rajasthan, India. *Curr. Sci.*, 2011, **101**, 84–88.
7. Dhir, R. P., Tandon, S. K., Sareen, B. K., Ramesh, R., Rao, T. G. K., Kailath, A. J. and Sharma, N., Calcretes in the Thar desert: genesis, chronology and palaeoenvironment. *Proc. Indian Acad. Sci.* (*Earth Planet. Sci.*), 2004, **113**(3), 473–515.
8. Raghavan, H., Galliard, C. and Rajaguru, S. N., Genesis of calcretes from calc-pan site of Singi Talav near Didwana. *Geoarchealogy*, 1991, **6**(2), 151–168.
9. Achyuthan, H., Petrologic analysis and geochemistry of Late Neogene–Early Quaternary hardpan calcretes of Western Rajasthan, India. *Quarternary Int.*, 2003, **106–107**, 3–10.
10. Kar, A., Drainage desiccation, water erosion and desertification in northwest India. *Desertification in the Thar, Sahara and Sahel Regions* (ed. Send, A. K.), Region Scientific Publishers, Jodhpur, 1993, pp. 49–72.
11. Rajawat, A. S., Verma, P. K. and Nayak, S., Reconstruction of palaeodrainage network in Northwestern India: retrospect and prospects of remote sensing based studies. *Proc. Indian Natl. Sci. Acad.*, 2003, **69A**, **2**, 217–230.
12. Sundaram, R. M., Rakshit, P. and Pareek, S., Regional stratigraphy of Quaternary deposits in parts of Thar Desert. *J. Geol. Soc. India*, 1986, **48**, 203–210.
13. Analytical techniques in uranium exploration and ore processing, IAEA Tech Report Series, 1992, No. 341, pp. 74–76.
14. Gouide, A. S., The chemistry of world calcrete deposits. *J. Geology*, 1972, **80**, 449–463.
15. Roy, P. D., Nagar, Y. C., Juyal, N., Smykotz-k loss and Singhvi, A. K., Geochemical signatures of Late Holocene palaeohydrological changes from Phulera and Pokhran playas near the eastern and western margins of the Thar Desert, India. *J. Asian Earth Sci.*, 2009, **34**, 275–286.
16. Watts, N. L., Quaternary pedogenic calcretes from Kalahari (South Africa) Mineralogy, genesis and diagenesis. *Sedimentology*, 1980, **27**, 661–686.
17. Middleton, W. G., An assessment of the use of hydrogeochemistry exploration for calcrete uranium in Australia. Surficial Uranium Deposits, Report of the Working Group on Uranium Geology, IAEA-TECDOC-322, 1984, pp. 75–79.
18. Danielson, A., Flourimetric method for determination of uranium in natural waters. *Talanta*, 1970, **20**, 185–192.
19. American Public Health Association (APHA), Standard method for examination of water and wastewater, 2002.
20. Bowell, R. J., Barnes, A., Grogan, J. and Dey, M., Geochemical controls of uranium precipitation in calcrete palaeochannel deposits of Namibia, 24th IAGS Symposium, Canada, 2009, pp. 1–4.
21. Choppin, G. R., Actinide speciation in the environment. *J. Radioanal. Nucl. Chem*., 1984, **273**(3), 695–703.
22. Pagel, M., Petrology, mineralogy and geochemistry of surficial uranium deposits. Surficial Uranium Deposits, Report of the Working Group on Uranium Geology, IAEA-TECDOC-322, 1984, pp. 37–44.

ACKNOWLEDGEMENTS. We thank the Director, AMD and Additional Director (Op. I), AMD for granting permission to publish this article. We also thank the officers and staff of Chemical Laboratory, AMD, WR, Jaipur, for providing chemical analysis of the samples.

Received 1 March 2014; re-revised accepted 24 February 2015

Ant larvae silk fibres mat

M. Prajwal[1], M. A. Sangamesha[2] and K. Pushpalatha[2,*]

[1]Department of Physics, NIE First Grade College, Mysuru 570 008, India
[2]Department of Chemistry, The National Institute Engineering, Mysuru 570 008, India

Weaver ants (*Oecophylla smaragdina*) are mostly seen in open forests of India, Australia, China and South-east Asia. The nests of weaver ants are built with silk secreted by their larvae. Silk fibre mat is a biopolymer, containing proteins produced by a broad array of spiders and other insects. In this study some hidden properties of weaver ant silk mat have been examined. The surface and structural studies reveal that the mat possesses very good chemical resistance.

Keywords: FT-IR, scanning electron microscope, silk fibre, weaver ant.

ANTS are the most commonly seen insects in our surroundings. Identifying ants is an easy task because they will have three pairs of legs, antennae and their disciplined march is enough to recognize them. They are highly social creatures and also referred to as 'super organisms'. In our society, ants are considered as a symbol of hard work and disciplined life. A typical ant colony

*For correspondence. (e-mail: kplnie@hotmail.com)