RESEARCH COMMUNICATIONS

Prehistory (eds Misra, V. N. and Bellwood, P.), Oxford–IBH, New Delhi, 1985, pp. 19–28.

23. Marathe, A. R., *Geoarchaeology of the Hiran Valley, Saurashtra, India*, Deccan College, Pune, 1981.

24. Chakrabarti, S., The Prehistory of Bhavanagar Distict, Saurashtra, Gujarat State, Ph D dissertation, University of Poona, Pune, 1978.

25. Marathe, A. R., Deodhar, P. G. and Rajaguru, S. N., Miliolite Formation and history of early man in Southern Saurashtra. *Quaternary Deserts and Climatic Change* (eds Alsharahan, A. S., Glennie, K. W. and Whittle, G. L.), A.A. Balkema Publishers, Netherlands, 1995, pp. 701–711.

26. Joshi, R. V., *Stone Age Cultures of Central India: Report on the Excavations of Rock-shelters at Adamgarh, Madhya Pradesh*, Deccan College, Pune, 1978.

27. Misra, V. N., The acheulian industry of rock shelter III F-23 at Bhimbetka, Central India: A preliminary study. *Puratattva*, 1978, **8**, 12–36.

28. Misra, V. N., The acheulian succession at Bhimbetka, Central India. *Recent Advances in Indo-Pacific Prehistory* (eds Misra, V. N. and Bellwood, P.), Oxford–IBH, New Delhi, 1985, pp. 35–48.

29. Corvinus, G., *A Survey of Pravara River System in Western Maharashtra, India*, Institute for Urgeschichte, Tubingen, 1981, Volume I.

30. Corvinus, G., *A Survey of Pravara River System in Western Maharashtra, India*, Tubingen, Institute for Urgeschichte. 1983, Volume II.

31. Paddayya, K., Excavations of an Acheulian site at Hunsgi, South India. *Curr. Anthropol.*, 1976, **17**, 760–761.

32. Paddayya, K., The acheulian culture of the Hunsgi–Baichbal valleys, Peninsular India: A processual study. *Quartar*, 1991, **41/42**, 111–138.

33. Singh, R., Palaeolithic Industries of Northern Bundelkhand, Ph D dissertation, University of Poona, Pune, 1965.

34. Paddayya, K. and Petraglia, M. D., Isampur – an Acheulian workshop site in the Hunsgi valley, Gulbarga District, Karnataka. *Man Environ.*, 1997, **XXII[2]**, pp. 94–100.

35. Paddayya, K. and Petraglia, M. D., *Acheulian Workshop at Isampur, Hunsgi Valley, Karnataka: A Preliminary Report*, Bulletin of the Deccan College Research Institute, 1998, vol. 56–57, pp. 3–26.

36. Rajaguru, S. N. and Marathe, A. R., Chronology of early man in Saurashtra, Gujarat. Proceedings of the Symposium on Quaternary Episodes, Department of Geology, M.S. University, Baroda, 1984, pp. 1–10.

37. Hashmi, N. H., Nigam, R., Nair, R. R. and Rajagopalan, G., Holocene sea level fluctuations on Western Indian continental margin: An update. *J. Geol. Soc. India*, 1995, **46**, 157–162.

FTIR signatures of type-II clathrates of carbon dioxide in natural quartz veins

P. S. R. Prasad*, K. Shiva Prasad and N. K. Thakur

Gas Hydrates Group, National Geophysical Research Institute, Hyderabad 500 007, India

In situ FTIR spectroscopy is used to probe the clathrate formation in H_2O–CO_2 inclusion in quartz veins by monitoring the spectral variations in 300–93 K. The characteristic spectral signatures of asymmetric stretching mode (v_3) of CO_2 clathrates in both structure-I and structure-II are doublets at 2336, 2348 cm^{-1}, and 2337, 2349 cm^{-1} respectively. Further, structure-II for CO_2 clathrate is metastable (it is stable in 93–215 K range), and it transforms into structure-I before melting.

Keywords: Carbon dioxide, clathrates, FTIR, quartz veins, spectral signature.

METHANE hydrates (clathrates) are the non-stoichiometric inclusion compounds encaging a small, normally a polar (guest) molecule in the framework of hydrogen-bonded, ice-like host molecules, and exist as a stable solid phase at high gas pressures and/or low temperatures. Methane hydrates occurring in marine sediments are considered as an alternate energy source. Two main crystallographic structures of gas hydrates, cubic structures-I and II, are distinguished[1]. The basic difference between these two types is in the occupancy ratio of the cages. The ratio of large to small cages in structure-I (sI) is 3 : 1, while that in structure-II (sII) is 1 : 2. Guest molecules such as methane (CH_4) and carbon dioxide (CO_2), most abundant in natural gas hydrates, are not known to form sII hydrates under moderate temperature and high-pressure conditions. Generally it is accepted that these guest molecules form sI in natural gas hydrates and in synthetic hydrates grown under conditions of similar geological occurrence. It is well known that Raman spectroscopy has distinct signatures of gas hydrates. Raman spectroscopy and infrared (IR) spectroscopy are complimentary tools. Use of IR in case of gas hydrates (IR) is difficult because of stronger nearby water modes. But, for CO_2 clathrates, as the modes of CO_2 and H_2O are well separated, IR spectroscopy provides vital information[2–5].

Some Raman spectroscopic investigations[2] on synthetic methane hydrates, in the pressure range 3.0–9.0 MPa and temperature range –15 to 15°C, have shown the signature of sII. Staykova[3] observed transient formation of sII CO_2 hydrates during the growth of pure CO_2 hydrates on grains of ice. Fleyfel and Devlin[4] have reported sII CO_2 hydrates on tetrahydrofuran (THF) hydrate in cryogenic condition

and also sI CO_2 hydrates on ethylene oxide. The present study is aimed at providing Fourier transform infrared (FTIR) spectroscopic evidences for clathrate formation in natural minerals. Though the formation of clathrates is of no concern while investigating the behaviour of fluid inclusions, it is unavoidable due to favourable pressure and temperature conditions[5]. The H_2O–CO_2–NaCl system is common in quartz veins and is one of the extensively studied systems for clathrate formation. In the present investigation we report infrared spectroscopic studies on this system in quartz veins from Dharwad schist belt, in the temperature range 90–303 K.

FTIR studies were carried out on a NEXUS FTIR spectrometer (with sealed and desiccated optics) from Thermo-Nicolet, using a thermo electrically cooled deuterated triglycene sulphate (DTGS) detector, extended range KBr (XT-KBr) beam splitter, and a dual source working in the wave number range 375–12500 cm^{-1}. The samples, 50-μm thick doubly polished wafers, were placed in LINKAM FTIR-600 stage, modified for transmission FTIR studies. This stage can be operated in the temperature range of –190 to 600°C. The sample was cooled to sub-ambient temperature at a rate of 5°C/min, while it was brought back to ambient temperature at a rate of 2°C/min. Temperature stability was better than 0.1° during measurements. Spectra were recorded in the wave number region 400–7400 cm^{-1} using NEXUS Ever-Glo source and each spectrum is an average of 128 scans and with 2 cm^{-1} resolution. The size of the aperture is 1.3 mm diameter, and hence this area of the sample is always exposed to IR radiation. We restrict our investigations to asymmetric stretching mode (v_3) of CO_2 molecules, since spectral features below 2000 cm^{-1} are saturated because of fundamental modes of quartz.
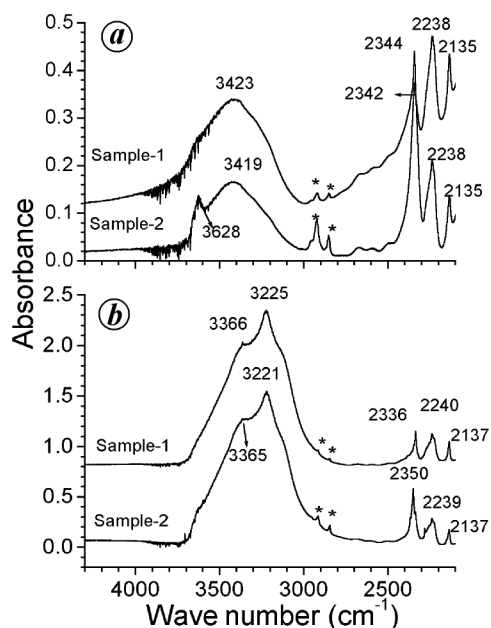

Figure 1. FTIR spectra of quartz veins at 300 K (*a*) and 93 K (*b*). Spectral features marked with star are artifacts.

The FTIR spectra of quartz veins in the 2000–4000 cm^{-1} range at ambient temperature (300 K) and lowest temperature (93 K) are shown (Figure 1). A sharp band around 2344 cm^{-1} due to (v_3) of CO_2 and the broader mode around 3420 cm^{-1} is due to (v_3 and v_1) of H_2O molecules. The other two modes around 2135 and 2238 cm^{-1} are the overtone modes characteristic of SiO_2 (quartz) matrix. The weaker IR band around 3628 cm^{-1} shows the presence of Si-OH bonding[6]. All these characteristic IR modes are identical to those reported in our previous studies[7]. It is interesting to note that the peak positions of all these modes are almost identical in these two samples at ambient conditions, the only exception being the width of (v_3) of CO_2 around 2344 cm^{-1}, which is broader in sample 1 than in sample 2. However, the spectra of samples cooled to cryogenic temperatures showed marked variations. The spectral features of H_2O molecules are almost identical and these are typical of polycrystalline ice Ih, reported earlier[8]. Spectral variations of the (v_3) band of CO_2 are more acute. For better clarity, the recorded spectra in these two samples in the wave number region 2250–2450 cm^{-1} are shown in Figure 2. Spectral traces are deconvoluted using GRAMS software. At lower temperature, the (v_3) band of CO_2 molecules is upshifted (blue) by about 7 cm^{-1} in sample 2, while that in sample 1 is downshifted (red) by about 8 cm^{-1}. The red shift for the IR mode while cooling is more commonly observed. The blue shift is reported[4] in sII and in small clusters[9] of CO_2.

As already stated, CH_4 and CO_2 clathrates are mostly formed in sI. Spectroscopic evidences in natural systems, such as mixed H_2O–CO_2–CH_4 inclusions in quartz veins support sI. The Raman spectrum of methane hydrates consists of two peaks at 2913 cm^{-1} (large cage) and 2903 cm^{-1} (small cage) in symmetric C–H symmetric stretching mode region. However, such splitting has not been reported[10] for corresponding C–O stretching mode in CO_2 hydrate in sI. Fleyfel and Devlin[4] reported two, IR-active asymmetric stretching modes for CO_2 clathrate at 2335 cm^{-1} (large cage) and at 2347 cm^{-1} (small cage). From Figure 2, it is clear that the v_3 mode of CO_2 for sample 1, at low temperature (93 K) has two prominent bands at 2336 and 2348 cm^{-1}. These two modes compare closely with earlier results[4,11] (2335 and 2347 cm^{-1}). These two modes are due to large and small cages in sI. The occupancy of these cages must follow a 3 : 1 ratio in an ideal case. The asymmetry of this band towards the higher wave number region is because of two weak and broad bands. It is clear that the v_3 mode of CO_2 due to the large cage is downshifted by about 8 cm^{-1} (Figure 1). This shift is gradual and significant around 220 K, while cooling to 93 K. In the warming-up cycle, recovery of the spectral shift is around 278 K, indicating complete melting of clathrates.

The observed spectral shifts at 93 K for sample 2 are interesting. Two bands characteristic of clathrate structure are observed at 2337 and 2349 cm^{-1}. The band at 2337 cm^{-1} is comparable with that of the large cage mode for sI.

However, the one at 2349 cm^{-1} is up-shifted by 7 cm^{-1}. It could be due to sII or due to clustering of CO_2 molecules[9]. Reasons for the formation of sII hydrate are not known. However, it has been reported that CH_4-hydrates form sII as a metastable structure[2]. Also transient formation of sII clathrates has been reported during the growth of
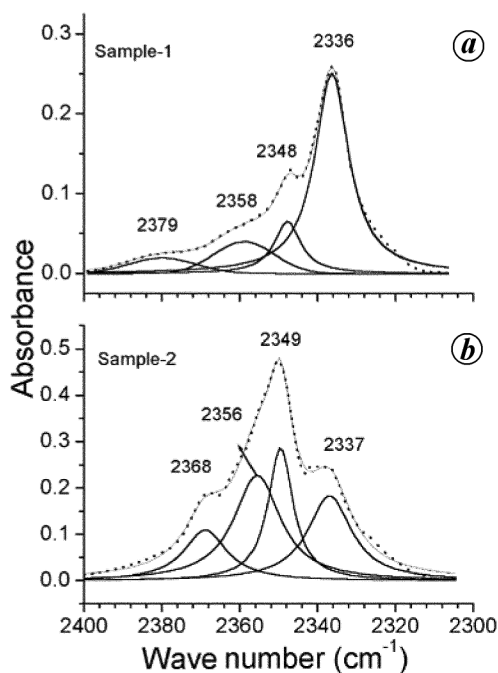

Figure 2. Deconvoluted FTIR spectral traces of CO_2 asymmetric stretching (v$_3$) mode for sample 1 (*a*) and 2 (*b*). Spectra recorded at 93 K are shown by dotted line, whereas continuous lines show fitted profiles.
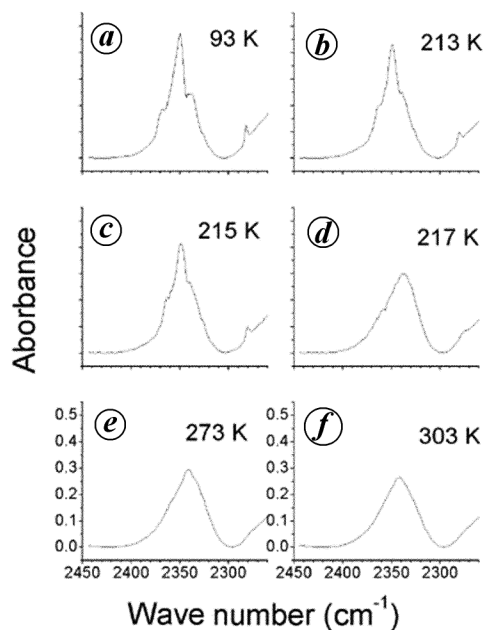

Figure 3. Spectral evolution of CO_2 asymmetric stretching (v$_3$) mode for sample 2 indicating transformation of sII.

pure CO_2 hydrates on small grains of ice of size 28–38 μm^3. It is also reported that the reactivity of CO_2 is at least three times faster than that of CH_4 in hydrate formation on such porous medium[3]. Thus one may find both types of clathrates in the quartz veins having CO_2–H_2O inclusions. However, sII hydrates, if found in quartz veins (with smaller inclusions), eventually transform to sI before melting. Fleyfel and Devlin[4] have reported the growth of sII CO_2 hydrates in the presence of THF. In sII, the occupancy ratio of large to small cages is 1 : 2. The FTIR spectrum reported by these authors has a band at 2345 cm^{-1} (at 13 K) and this was attributed to small cage. Using the same analogy, we can attribute the band at 2349 cm^{-1} in sample 2 to the small cage of sII. Interestingly, the peak absorbance ratio of two deconvoluted bands (see Figure 2) at 2349 and 2337 cm^{-1} is about 1.69.

The sII of CO_2 hydrate is transformed into sI prior to melting. In order to understand this clearly, we probed the spectral features more closely during the warm-up cycle. As shown in Figure 3 *a–f*, the characteristic features of sII show marginal variations till about 215 K. At 217 K, all the higher wave number bands became much weaker and broader, while the prominent peak is shifted to around 2336 cm^{-1} (large cage of sI), indicating the transformation to sI. Upon further warming, it completely transformed to vapour phase around 303 K. These observations indicate the metastable nature of sII. These results are similar to those of CH_4-hydrates, wherein it was observed that sII converts to sI at high temperatures[2].

In summary, we demonstrate the growth CO_2 clathrates in both sI and sII in naturally occurring quartz veins using FTIR spectroscopy. Visual observations show that the sizes of inclusions in quartz veins forming sII are smaller. In fact, FTIR spectroscopic evidence for cluster formation in these samples vindicates the smaller size of inclusions. Observed FTIR evidences for both forms of CO_2 clathrates are comparable with earlier reports. The metastable nature of sII CO_2 hydrate is clearly observed in the warming-up cycle and it is converted to sI before melting.

1. Sloan, Jr. E. D., *Clathrate Hydrates of Natural Gases*, Marcel Dekker, New York, 1998.
2. Schicks, J. M. and Ripmeester, J. A., The coexistence of two different methane hydrate phases under moderate pressure and temperature conditions: Kinetic versus thermodynamic products. *Angew. Chem. Int. Ed. Engl.*, 2004, **43**, 3310–3313.
3. Staykova, D. K., Kuhs, W. F., Salamatin, A. N. and Hansen, T., Formation of porous gas hydrates from ice powders: Diffraction experiments and multistage model. *J. Phys. Chem. B*, 2003, **107**, 10299–10311.
4. Fleyfel, F. and Devlin, J. P., Carbon dioxide clathrate hydrate epitaxial growth: Spectroscopic evidence for formation of the simple type-II CO_2 hydrate. *J. Phys. Chem.*, 1991, **95**, 3811–3815.
5. Roedder, E., *Fluid Inclusions, Reviews in Mineralogy*, Mineralogical Society of America, 1984, vol. 12.
6. Prasad, P. S. R. and Sarma, L. P., A near-infrared spectroscopic study of hydroxyl in natural chondrodite. *Am. Mineral.*, 2004, **89**, 1056–1060.

7. Rammohan, M. and Prasad, P. S. R., FTIR investigation on the fluid inclusions in quartz veins of the Penakacherla schist belt. *Curr. Sci.*, 2002, **83**, 755–760.
8. Bergren, M. S., Schuh, D., Sceats, M. G. and Rice, S. A., The OH stretching region infrared spectra of low density amorphous solid water and polycrystalline ice Ih. *J. Chem. Phys.*, 1978, **69**, 3477–3482.
9. Barnes, J. A. and Gough, T. E., Fourier transform infrared spectroscopy of molecular clusters: The structure and internal mobility of clustered carbon dioxide. *J. Chem. Phys.*, 1987, **86**, 6012–6017.
10. Seitz, J. C., Pasteris, J. D. and Wopenka, B., Characterization of CO_2–CH_4–H_2O fluid inclusions by microthermometry and laser Raman microprobe spectroscopy: Interferences for clathrate and fluid equilibria. *Geochim. Cosmochim. Acta*, 1987, **51**, 1651–1664.
11. Ratcliffe, C. I. and Ripmeester, J. A., ^1H and ^{13}C NMR studies on carbon dioxide hydrate. *J. Phys. Chem.*, 1986, **90**, 1259.

On the Holocene record of phytoliths of wild and cultivated rice from Ganga Plain: evidence for rice-based agriculture

A. Saxena[1,*], V. Prasad[2], I. B. Singh[1], M. S. Chauhan[2] and R. Hasan[1]

[1]Department of Geology, Lucknow University, Lucknow 226 007, India
[2]Birbal Sahni Institute of Palaeobotany, 53 University Road, Lucknow 226 007, India

Evidence of rice-based agriculture is recorded in the form of phytoliths from about 10 kyrs BP to present succession of Lahuradewa lake deposits, Sant Kabir Nagar district, Ganga Plain. Bulliform phytoliths are considered to be of rice, where distinction between wild rice (*Oryza rufipogon*) and cultivated rice (*Oryza sativa*) has been made using the criterion of number of scale-like ornamentation on the edges of fan-shaped phytoliths. The wild rice phytoliths are present since about 10300 cal. yrs BP, while cultivated rice phytoliths appear 8350 cal. yrs BP. Upward in the profile, cultivated rice phytoliths increase with a simultaneous decrease in the wild rice phytoliths. This indicates the beginning of rice cultivation in the Ganga Plain around 8350 cal. yrs, which supports the presence of cultivated rice at Lahuradewa archaeological site, dated 8360 cal. yrs BP.

*For correspondence. (e-mail: anju_saxena2002@yahoo.co.in)

IN this study, we describe the phytoliths in a Holocene lake fill succession of Ganga Plain, where identification of phytoliths of Oryzeae tribe of Oryzoideae subfamily and distinction between wild and domesticated rice have been done. Lahuradewa lake is located adjacent to the Lahuradewa archaeological site where archaeological excavation is being carried out by the Uttar Pradesh State Department of Archaeology[1]. The study of rice phytoliths in lake deposits and archaeological sites can be useful in understanding the anthropogenic activity and the beginning of agriculture in the Ganga Plain.

The Ganga Plain occupies a central position in the Indo-Gangetic plains. It exhibits many fluvial landforms, namely abandoned channels, meander cut-offs, lakes and ponds. The present-day highly diversified fluvial geomorphology of the Ganga Plain is a consequence of climate changes, tectonic activity and base-level changes during Late Quaternary[2–4]. The lakes and ponds have been mostly formed during Late Pleistocene–Early Holocene due to channel abandonment, in response to tectonics and changing climatic conditions[3–5].

The vegetation of the Ganga Plain must have witnessed changes in the last few millennia under climate change and anthropogenic influence. Information on changing palaeovegetation pattern in the Ganga Plain is scanty. Only recently, attempts have been made to reconstruct the palaeovegetation in the Ganga Plain using mainly pollen studies in lake deposits[6–8]. These studies demonstrate that for the last 15,000 yrs, the Ganga Plain was a grassland with few thickets[9–11].

Lahuradewa lake (lat. 26°46′N; long. 82°57′E) (Figure 1) and Lahuradewa archaeological site are located in the vicinity of Lahuradewa village, Sant Kabir Nagar district, UP[1]. The mean annual rainfall of this area is about 1400 mm. The lake is situated on the upland interfluve surface and receives its water budget mainly from the monsoon. Generally the lake holds water throughout the year; but in the extremely dry years it may dry out completely. The northern and eastern parts of the lake are shallow due to high siltation, mainly as a consequence of intense agricultural activity. The western portion of the lake holds sufficient water during all the seasons. The region of Lahuradewa is characterized by shrubs and grasses with scattered trees. At present, the surrounding area of the lake is influenced by intense agricultural activity and large inhabitation.

A 2.80 m deep trench was dug on the eastern dried flank of the lake, about 150 m north of the Lahuradewa archeological site. Twenty-eight samples were collected from this profile at 10 cm interval. All the samples were analysed for grain size and phytolith assemblage. Samples were also collected from the same trench at larger intervals for radiocarbon dating.