

25. Tang, M. S. *et al.*, Both (+) syn acti-7-12-DMBA-3,4-diol-1,2-epoxide initiate tumours in mouse skin that possess-CCA-to CTA mutations at codon61 of CC-H-ras. *Cancer Res.*, 2000, **60**, 5688–5695.
26. Smith, W. A. and Gupta, R. C., Use of microsome-mediated test system to assess efficacy and mechanism of cancer chemopreventive agent. *Carcinogenesis*, 1996, **17**, 1285–1290.
27. Arif, J. M., Gairola, C. G., Kelloff, G. J., Lubet, R. H. and Gupta, R. C., Inhibition of cigarette smoke related DNA adducts in rat tissues by indole-3-carbinol. *Mutat. Res.*, 2000, **452**, 11–18.
28. Mollerup, S., Ryberg, D., Hewer, A., Phillips, D. H. and Haugen, A., Sex differences in lung CYP1A1 expression and DNA adduct levels among lung cancer patients. *Cancer Res.*, 1999, **59**, 31337–33320.
29. Ajith, T. A. and Janardhanan, K. K., Chemopreventive activity of a macrofungus, *Phellinus rimosus* against N-dimethylamine induced hepatocellular carcinoma in rat. *J. Exp. Ther. Oncol.*, 2006, **5**, 309–321.
30. Zhou, X., Lin, J., Yin, Y., Zhao, J., Sun, X. and Tang, K., *Ganoderma* spp.: Natural products and their related pharmacological functions. *Am. J. Chinese Med.*, 2007, **35**, 559–574.

Received 16 March 2009; revised accepted 10 November 2009

## Discovery of minamiite from the Deccan Volcanic Province, India: implications for Martian surface exploration

N. Siva Siddaiah\* and Kishor Kumar

Wadia Institute of Himalayan Geology,  
33, General Mahadeo Singh Road, Dehradun 248 001, India

**Discovery of minamiite, a Ca-bearing hydrous sulphate mineral, is reported for the first time in India from the Deccan Volcanic Province at Matanumadh (Kachchh, Gujarat), western India. Minamiite was identified by X-ray diffraction and chemical analyses. The hydrous sulphates at Matanumadh occur associated with Paleocene sediments as soft powdery deposits and consist dominantly of minamiite  $[(\text{Na,K,Ca})\text{Al}_3(\text{SO}_4)_2(\text{OH})_6]$  and natroalunite  $[\text{NaAl}_3(\text{SO}_4)_2(\text{OH})_6]$  with traces of alunite and kaolinite. The geological setting, mineralogy and geochemistry suggest that the sulphate layers at Matanumadh were produced via solfataric alteration of volcanic ash. Hydrous sulphates are abundant on the planet Mars but not common on Earth because they form under extreme conditions (low pH and high Eh). Results of our study suggest that the Deccan Volcanic Province with its gigantic flood basalts of thermal plume origin, craters of both volcanic and impact origin, and hydrous sulphates of secondary origin can serve as a potential Earth analogue for the Mars and the Martian condi-**

**tions. This may help us better understand the geology of the planet Mars and compare the geologic processes on Mars and the Earth.**

**Keywords:** Deccan Volcanic Province, Earth analogue, Mars, fumarole activity, hydrous sulphates, minamiite.

THE discovery of liquid water-related sulphates in the Meridiani Planum region of the planet Mars has stimulated interest in studying the Martian analogues on Earth in order to elucidate the mineralogical and chemical makeup of the Martian surface, and to get insights into the processes that may have operated on Mars<sup>1–12</sup>. In the international arena, it is widely recognized that interpretations of Mars must begin by using the Earth as a reference, because Earth analogues can provide ground truth to constrain interpretations on the geological history of Mars. Accordingly, several sites such as Rio Tinto and Jaroso Ravine (Spain), Dry Valleys (Antarctica), Devon Island (Canada), Valley of Ten Thousand Smokes (USA), and Payun Matru Volcanic complex (Argentina), among others, are under investigation the world over.

In India, the Deccan Volcanic Province (DVP) spread over the large tracts of west-central parts of the country<sup>13</sup> could be a potential analogue for Mars, because of the similarity of its characteristic flood basalts, craters of both impact and volcanic origin<sup>14</sup>, and extensive hydrous sulphate layers to those observed on Mars. The Deccan volcanic flows represent some of the largest sub-aerial lava flows on the Earth surface, and show a multiplicity of flow surface morphologies linked to different lava types and related emplacement mechanisms. Interestingly, the Deccan basaltic volcanism on Earth as well as the volcanoes of the Tharsis region, in general and the Olympus Mons in particular, on Mars were produced by the thermal plume process (hotspot). However, the mammoth size of volcanoes on the Mars compared to those on the Earth is considered to be due to the absence of active plate tectonics on the Mars<sup>15</sup>. Therefore, the DVP can represent an outstanding analogue of several Martian flows. In addition, the understanding of propagation processes of widespread Deccan basalt flows can give important clues in the comprehension of emplacement mechanisms of the long flows on Mars.

The Deccan basalts, by virtue of their thickness, spatial extent and eruption timing coinciding with the Cretaceous–Tertiary (K–T) boundary event have been studied extensively for petrological, geochemical, biotic and paleomagnetic aspects to understand their impact on climate at the K–T boundary<sup>16–23</sup>. However, very little is known about the nature of rock-alteration assemblages formed due to aqueous processes that operated during the gigantic volcanic activity. Alteration phases are important recorders of atmosphere–fluid–rock interactions, specific surface processes, environments and fluid compositions during the volcanism, and thus, can provide a template

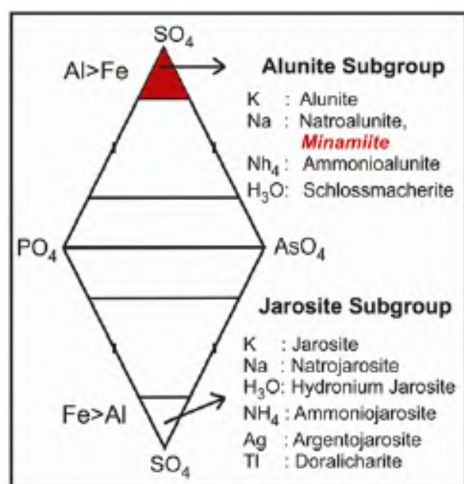
\*For correspondence. (e-mail: nssiddaiah@rediffmail.com)

for identification of phases and conditions analogous to those on Mars.

We report here the discovery of minamiite [(Na,K,Ca)  $\text{Al}_3(\text{SO}_4)_2(\text{OH})_6$ ], a hydrous sulphate mineral, from India, and present results of mineralogical and geochemical studies of hydrous sulphates associated with the Deccan flood basalts, discuss probable mode of their formation, and highlight their significance in understanding the Martian surface. Prior to this report, Chitale and Guven<sup>24</sup> had recorded the occurrence of another hydrous sulphate mineral, natroalunite [ $\text{NaAl}_3(\text{SO}_4)_2(\text{OH})_6$ ] from the same Matanumadh area. However, the significance of that find in the context of Martian surface was not indicated.

Elsewhere in the world, minamiite has been reported from an ancient subvolcanic hydrothermal system exposed at Mt Schimkura in northeastern Japan<sup>25</sup>, from highly altered andesitic and dacitic volcanics of southwest Turkey<sup>26,27</sup>, and from andesitic stratovolcanoes of the Cascade Range in Western USA<sup>28</sup>.

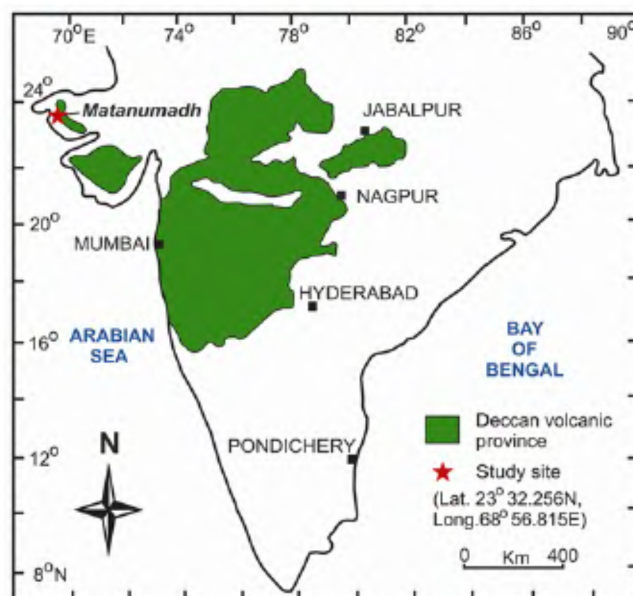
Hydrous sulphates belong to the alunite family, which is divisible into an alunite subgroup where aluminium is greater than iron ( $\text{Al} > \text{Fe}$ ), and a jarosite subgroup, where iron is greater than aluminium ( $\text{Fe} > \text{Al}$ )<sup>29–32</sup> (Figure 1). Alunite has the ideal formula  $\text{KAl}_3(\text{SO}_4)_2(\text{OH})_6$  with the possibility of Na, Ca or  $\text{H}_3\text{O}$  substituting for K, forming natroalunite, minamiite and hydronium alunite respectively. In the jarosite subgroup, Fe substitutes for Al forming jarosite, and  $\text{PO}_4$  substitutes for sulphate forming woodhouseite, crandallite and others, depending on available ions in the solution and in the host rocks<sup>33,34</sup>. Occurrence of hydrous sulphate minerals is not common on Earth, as they occur only in alteration zones formed in acid-sulphate environment (i.e. low pH, high Eh) in some volcanic settings. They have also been observed in fluid–rock interaction experiments conducted in near-Martian conditions in some Earth-based laboratories<sup>35,36</sup>.



**Figure 1.** Classification of alunite–jarosite group members containing monovalent ions in the alkali site, showing the  $\text{XO}_4$  compositional limits<sup>30,46</sup>.

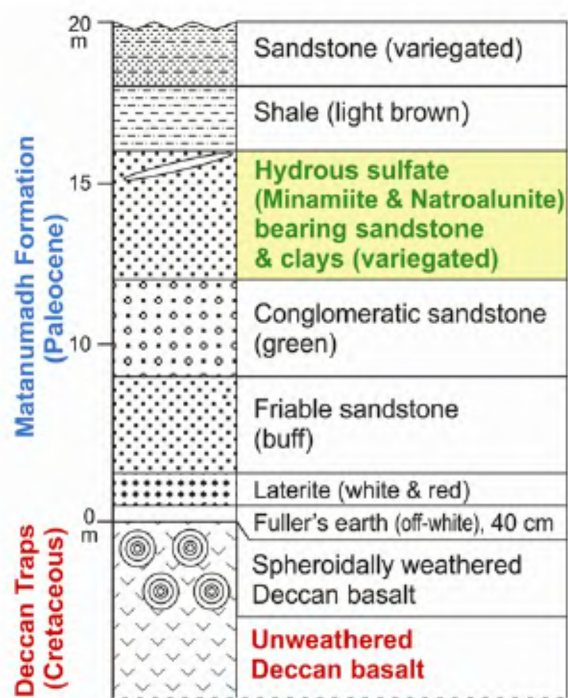
Figure 2 is a geological map of a part of peninsular India showing the present distribution of Deccan volcanic flows. Towards the north, the flows extend up to the southern part of the Kachchh District of the state of Gujarat (western India), where erosion of upper flows has exposed not only the older flows of the volcanic activity but also several feeder plugs and volcanic vents<sup>23</sup>. The flows here are mainly of alkali and tholeiitic basalts<sup>23,37,38</sup>. At Matanumadh, a village ~80 km northwest of Bhuj, in the Kachchh region, hydrous sulphates occur as layers and/or lenses in association with Paleocene sedimentary package that overlies the Deccan traps<sup>24,39,40</sup>. The Paleocene sediments overlying the Deccan basalts at Matanumadh are referred to as the Matanumadh Formation<sup>41</sup>. They consist of laterites, bright coloured tuffaceous clays, Fuller's earth (bentonite), sandstones and trap-pebble conglomerates with occasional layers of lignite (Figure 3). The Matanumadh Formation is unconformably overlain by the Naredi Formation. The hydrated sulphates at Matanumadh are relatively pure, soft and powdery in nature, and occur within coarse-grained bedded sandstone units (Figure 4). The sulphate layers are up to 1 m thick, white to cream-yellow and reddish in colour, and extend laterally for over a kilometre on both sides of Matanumadh–Lakhpur road (Figure 5). Their physical appearance including texture is distinct from that of the surrounding relatively unaltered, denser and coarser-grained sedimentary rocks. They are spectacular in the field with complete textural and mineralogical destruction of precursor lithologies.

Bulk sulphate samples from freshly cleared outcrops were collected for laboratory studies. Samples were hand-powdered gently in an agate mortar and pestle to ~200



**Figure 2.** Peninsular India showing the location of Matanumadh within the Deccan Volcanic Province.

mesh size for mineralogy, texture and geochemistry by X-ray diffractometry (XRD), scanning electron microscopy (SEM) and X-ray fluorescence spectrometry (XRF) respectively, in the central laboratory facility of the Wadia Institute of Himalayan Geology. Twenty bulk hydrous sulphate samples were analysed by XRD with Ni-filtered  $\text{CuK}\alpha$  radiation from  $10^\circ$  to  $75^\circ$   $2\theta$ . Morphology of the individual sulphate minerals was studied with the SEM. Powder pellets of four representative bulk sulphate samples were analysed for their major oxides by



**Figure 3.** Lithological log of the studied section at Matanumadh showing the stratigraphic position of the minamiite-bearing hydrous sulphate layer.



**Figure 4.** Hydrous sulphate layer/lens (white) within variegated sandstone at Matanumadh.

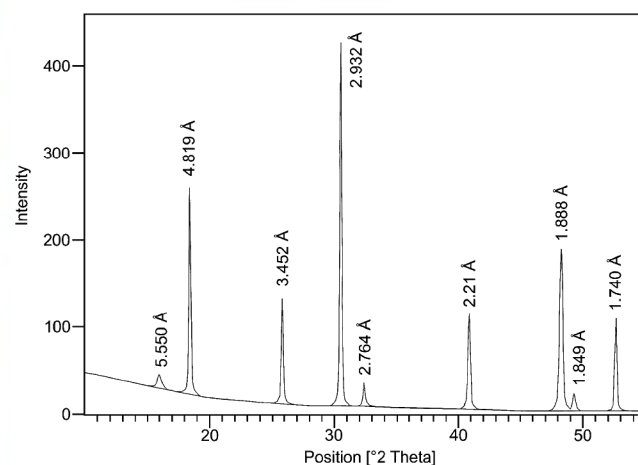
XRF. The spectrometers were calibrated using USGS rock standards. Loss on ignition (LOI) was obtained by heating 5 g of sample powders to  $950^\circ\text{C}$  for one hour.

The hydrous sulphate deposits at Matanumadh consist dominantly of minamiite and natroalunite with trace amounts of alunite and kaolinite. Minamiite is identified by its characteristic  $d$ -values and relative peak intensities (Table 1, Figure 6), which are in good agreement with the minamiite patterns given by other workers<sup>42–44</sup>. Minamiite is pseudocubic or rhombohedral in habit and its crystal size generally ranges between 1 and  $2\ \mu\text{m}$ , but a few  $5\text{--}6\ \mu\text{m}$  crystals have also been found (Figure 7). Minamiite morphology is similar in all the samples examined during the present study. Individual crystals are white to colourless with vitreous lustre but without any dissolution marks on their surfaces, indicating absence of late stage acid sulphate or meteoric weathering (Figure 7). Euhedral morphology of crystals of hydrous sulphate minerals from Matanumadh indicates their authigenic origin.

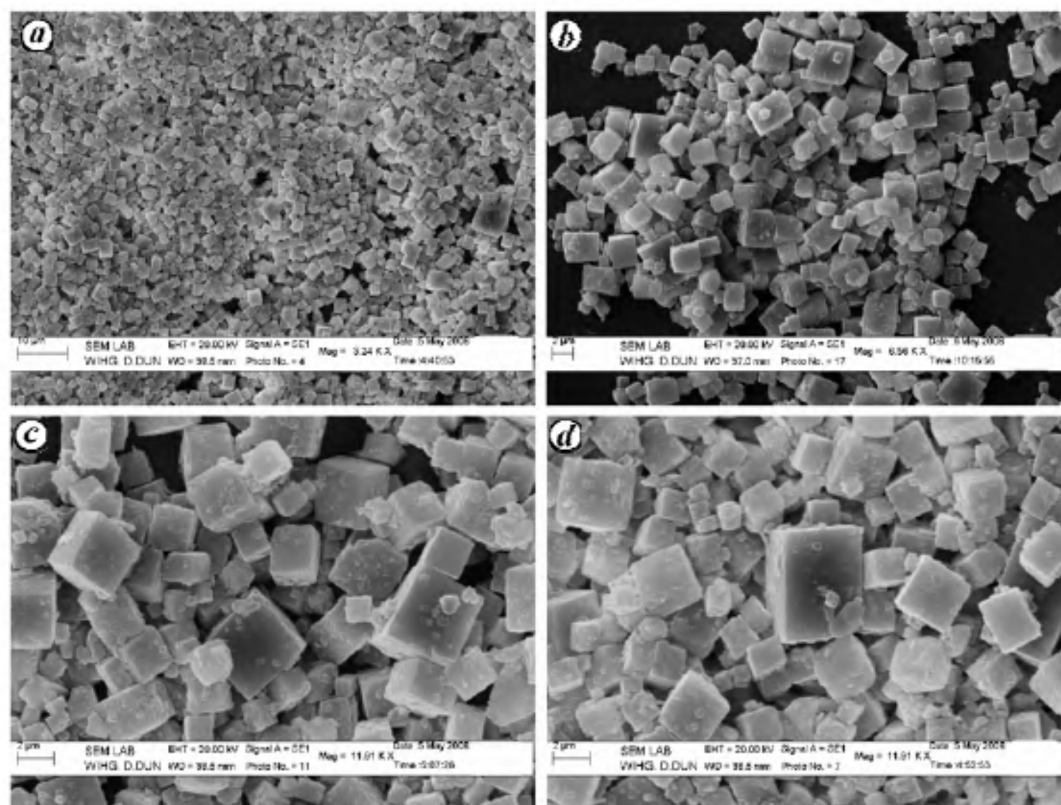
The results of the chemical analysis of four bulk sulphate samples (MC 1 to 4) from Matanumadh are shown



**Figure 5.** Specimen (a) and powder (b) of hydrous sulphate consisting of minamiite and natroalunite assemblages from Matanumadh, DVP. Scale bar equals 1 cm.



**Figure 6.** X-ray powder diffraction pattern for minamiite sample from Matanumadh.



**Figure 7.** Scanning Electron Microscope images of hydrous sulphate sample from Matanumadh showing well-developed crystals of minamiite. *a–b*, Low-magnification views of minamiite crystal morphology displaying pseudocubic structure. *c–d*, Minamiite crystals showing their pristine nature and clear vitreous lustre.

**Table 1.** X-ray powder diffraction data for minamiite from Matanumadh, DVP

<i>d</i> (Å)	<i>I</i>	<i>hkl</i>
5.550	5	006
4.819	48	014
3.452	26	110
2.932	100	202
2.764	5	0012
2.21	25	0114
1.888	30	306
1.849	3	0018
1.740	24	220
1.637	5	134
1.552	2	318
1.537	3	2116
1.499	3	042
1.475	7	2212
1.457	10	2020
1.418	4	048
1.365	8	324

**Table 2.** Major elements composition (in wt%) of bulk hydrous sulphate samples (MC 1 to MC 4) from Matanumadh, DVP

	MC 1	MC 2	MC 3	MC 4
Na <sub>2</sub> O	3.35	3.29	3.27	3.30
K <sub>2</sub> O	1.33	1.33	1.33	1.33
CaO	0.45	0.46	0.50	0.50
Al <sub>2</sub> O <sub>3</sub>	35.99	36.53	36.65	36.87
SO <sub>3</sub>	38.1	38.2	38.5	38.4
Fe <sub>2</sub> O <sub>3</sub>	0.11	0.10	0.61	0.62
SiO <sub>2</sub>	4.42	4.16	3.70	3.62
TiO <sub>2</sub>	0.29	0.29	0.29	0.29
MnO	0.01	0.011	0.01	0.01
MgO	0.38	0.32	0.26	0.28
P <sub>2</sub> O <sub>5</sub>	0.026	0.025	0.051	0.052
H <sub>2</sub> O	13.5	13.6	13.2	13.7
Total	97.96	98.3	98.4	98.97

in Table 2. The samples are characterized by higher SO<sub>3</sub> (38.1–38.5 wt%), Al<sub>2</sub>O<sub>3</sub> (35.99–36.8 wt%) and loss on ignition (13.2–13.7 wt%). Calcium (CaO = 0.45–0.5 wt%) and iron (Fe<sub>2</sub>O<sub>3</sub> = 0.1–0.62 wt%) contents are relatively high, whereas TiO<sub>2</sub> (0.29 wt%) and MgO (0.26–0.38 wt%) contents are low (Table 2).

The lack of alteration in the sediments associated with the hydrous sulphates at Matanumadh suggests that the sulphate layers were originally mineralogically and texturally distinct with a unique chemical composition that made them susceptible to alteration under extreme conditions (e.g. extremely acidic conditions, pH ~1–2). The sulphate layers at Matanumadh, therefore, may not have developed from beds with lithologies similar to the surrounding sandstones, but probably represent an altered



product of beds deposited under different conditions, and derived from a different source than the surrounding sediments. The most likely precursor for the hydrous sulphates at Matanumadh could be a volcanic ash fall deposit. This would contain the necessary clays and K-feldspars required for alunite formation. The hydrous sulphate layers of Matanumadh with minamiite and natroalunite as dominant phases suggest that they may have been derived from volcanic ash of dacitic to andesitic composition. Although occurrence of volcanic ash beds in Matanumadh area has been mentioned by several workers, no detailed analysis to characterize its mineralogical and geochemical composition has been carried out. In this context, it is interesting to note that the first and the best documented occurrence of minamiite in the world, from Okumanza (Japan), is also believed to have derived from hydrothermal alteration of andesite<sup>33</sup>. The mineralogy, texture and mineral stability relation of the hydrous sulphate layers at Matanumadh suggests that they were formed under acidic conditions in steam-heated environment.

On the basis of the geological occurrence, mineralogy and crystal form of Matanumadh hydrous sulphates, and the distinct characteristics of Deccan basalts (cones, craters and calderas) with known fumarole activity during their eruption, we suggest that the sulphate layers in the Matanumadh area could be a product of reactions between volcanic gases and acid hydrothermal solutions with the volcanic rock/ash, because large volumes of low pH solutions are required to cause acid sulphate alteration and such fluids can be produced in steam-heated environment. Matanumadh hydrous sulphates are similar to those found on the surface of Mars. The Martian hydrous sulphates are also considered to be of secondary origin because basaltic magmas have relatively lower abundance of sulphur<sup>45</sup>.

Although sulphates were found in abundance on Mars by both surface explorations and orbital remote sensing, discrepancies exist in results of these two sets of observations. Mars Exploration Rovers indicated dominance of Fe, Ca and Mg sulphates in the vicinities of their landing sites on Mars. Jarosite [ $\text{KFe}_3^{3+}(\text{SO}_4)_2(\text{OH})_6$ ] was identified by Mössbauer spectroscopy and accounts for ~10 wt% of the material in Meridiani outcrop<sup>4</sup>. On the other hand, orbital remote sensing based on NIR reflectance spectra by OMEGA on Mars Express and by CRISM on MRO showed the presence of only Mg and Ca sulphates and no jarosite<sup>11</sup>. This underlines the importance and need of understanding how similar minerals form in Earth environments in interpretation of Martian data.

The hydrous sulphate minerals (minamiite and natroalunite) found in the DVP are similar in terms of their geologic association, depositional environment and genesis to those described from the planet Mars. It may, however, be mentioned here that minamiite has not been reported so far from the Martian surface. Systematic explo-

ration and examination of hydrous sulphate deposits from the DVP are warranted for better comparative analysis with those on Mars.

The DVP approximates the geological (including thermal plume origin), geomorphological and environmental conditions on Mars and other planetary bodies, either of the present-day or sometime in the past, and thus appears to be a promising analogue site for improving understanding of the Martian surface mineralogy, volcanism, related aqueous hydrothermal processes, etc. Further studies on the DVP, which has several similarities with Mars including extensive volcanic plains, cones and craters as well as abundant hydrous sulphate layers, will help in better understanding the physicochemical conditions necessary for formation of hydrous sulphates. This, in turn, will provide insights into the interpretation of remote sensing data on Mars including modelling of planet's interior and its bulk composition. This is important because (1) the microscopic imager currently in use on board the Mars Exploration Rovers does not have enough resolution to provide detailed textural/morphological features of sulphate crystals on par with those shown in Figure 7, and (2) the non-availability of Martian samples in their original condition for investigations in Earth-based laboratories. Therefore, to understand Mars, it is imperative to focus our studies on appropriate Earth analogues such as the DVP so as to get the first approximation to assessing conditions on Mars.

1. Morris, R. V. *et al.*, Mineralogy, composition, and alteration of Mars Pathfinder rocks and soils: evidence from multispectral, elemental, and magnetic data on terrestrial analogue, SNC meteorite, and Pathfinder samples. *J. Geophys. Res.*, 2000, **105**, 1757–1817.
2. Christensen, P. R. *et al.*, Mineralogy at Meridiani Planum from the Mini-TES experiment on the opportunity rover. *Science*, 2004, **306**, 1733–1739.
3. Herkenhoff, K. E. *et al.*, Evidence from opportunity's microscopic imager for water on Meridiani Planum. *Science*, 2004, **306**, 1727–1730.
4. Klingelhöfer, G. *et al.*, Jarosite and Hematite at Meridiani Planum from opportunity's Mössbauer spectrometer. *Science*, 2004, **306**, 1740–1745.
5. Rieder, R. *et al.*, Chemistry of rocks and soils at Meridiani Planum from the alpha particle X-ray spectrometer. *Science*, 2004, **306**, 1746–1749.
6. Squyres, S. W. *et al.*, *In situ* evidence for an ancient aqueous environment at Meridiani Planum, Mars. *Science*, 2004, **306**, 1709–1714.
7. Clark, B. C. *et al.*, Chemistry and mineralogy of outcrops at Meridiani Planum. *Earth Planet. Sci. Lett.*, 2005, **240**, 73–94.
8. Gendrin, A. *et al.*, Sulfates in Martian layered terrains: the OMEGA/Mars Express view. *Science*, 2005, **307**, 1587–1591.
9. Langevin, Y., Poulet, F., Bibring, J. P. and Gondet, B., Sulfates in the North Polar Region of Mars detected by OMEGA/Mars Express. *Science*, 2005, **307**, 1584–1587.
10. Poulet, F. *et al.*, Phyllosilicates on Mars and implications for early Martian climate. *Nature*, 2005, **438**, 623–627.
11. Bibring, J. P. *et al.*, Global mineralogical and aqueous Mars history derived from OMEGA/Mars express data. *Science*, 2006, **312**, 400–404.

12. Papike, J. J., Karner, J. M., Spilde, M. N. and Shearer, C. K., Terrestrial analogs of Martian sulfates: major and minor element systematics of alunite–jarosite from Gold Field, Nevada. *Am. Mineral.*, 2006, **91**, 1197–1200.
13. Wadia, D. N., *The Geology of India*, Tata-McGraw Hill, New Delhi, 1975, 4th edn, p. 508.
14. Sheth, H. C., Mathew, G., Pande, K., Mallick, S. and Jena, B., Cones and craters on Mount Pavagadh, Deccan traps: rootless cones? *Proc. Indian Acad. Sci. (Earth Planet. Sci.)*, 2004, **113**, 831–838.
15. Scott, D. H. and Tanaka, K. L., Mars Tharsis region: Volcanotectonic events in the stratigraphic record. *Proc. 11th Lunar Science Conference*, Houston, Texas, USA, 1980, pp. 2403–2421.
16. Courtillot, V., Féraud, G., Maluski, H., Vandamme, D., Moreau, M. G. and Besse, J., The Deccan flood basalts and the Cretaceous–Tertiary boundary. *Nature*, 1988, **333**, 843–846.
17. Khadkikar, A. S., Sant, D. A., Gogte, V. and Karanth, R. V., The influence of Deccan volcanism on climate: insights from lacustrine intertrappean deposits, Anjar, western India. *Palaeogeogr. Palaeoclimatol. Palaeoecol.*, 1999, **147**, 141–149.
18. Krishnamurthy, P., Pande, K., Gopalan, K. and Macdougall, J. D., Mineralogical and chemical studies on alkaline basaltic rocks of Kutch, Gujarat, India. In *Deccan Volcanic Province* (ed. Subbarao, K. V.), Mem. Geol. Soc., 1999, pp. 757–783.
19. Mahoney, J. J., Sheth, H. C., Chandrasekharam, D. and Peng, Z. X., Geochemistry of flood basalts of the Toranmal section, Northern Deccan traps, India: implications for regional Deccan stratigraphy. *J. Petrol.*, 2000, **41**, 1099–1120.
20. Khosla, A. and Sahni, A., Biodiversity during the Deccan volcanic eruptive episode. *J. Asian Earth Sci.*, 2003, **21**, 895–908.
21. Ravizza, G. and Peucker-Ehrenbrink, B., Chemostratigraphic evidence of Deccan volcanism from the marine osmium isotope record. *Science*, 2003, **302**, 1392–1395.
22. Chenet, A. L., Fluteau, F., Courtillot, V., Gerard, M. and Subbarao, K. V., Determination of rapid Deccan eruptions across the Cretaceous–Tertiary boundary using paleomagnetic secular variation: results from a 1200-m-thick section in the Mahabaleswar escarpment. *J. Geophys. Res.*, 2008, **113**, B04101.
23. Paul, D. K., Ray, A., Das, B., Patil, S. K. and Biswas, S. K., Petrology, geochemistry and paleomagnetism of the earliest magmatic rocks of Deccan Volcanic Province, Kutch, Northwest India. *Lithos*, 2008, **102**, 237–259.
24. Chitale, D. V. and Guven, N., Natroalunite in a laterite profile over Deccan trap basalts at Matanumad, Kutch, India. *Clays and Clay Minerals*, 1987, **35**, 196–202.
25. Ohba, T. and Kitade, Y., Subvolcanic hydrothermal systems: Implications from hydrothermal minerals in hydrovolcanic ash. *J. Volcanol. Geotherm. Res.*, 2005, **145**, 249–262.
26. Celik, M., Minamiite and alunite occurrences formed from volcanic emanations, west-southwest of Konya, Turkey. *Geol. Bull. Turkey*, 1999, **42**, 89–97.
27. Karakas, Z. and Kadir, S., Devitrification of volcanic glasses in Konya Volcanic Units, Turkey. *Turk. J. Earth Sci.*, 2000, **9**, 39–46.
28. Zimbelman, D. R., Rye, R. O. and Breit, G. N., Origin of secondary sulfate minerals on active andesitic stratovolcanoes. *Chem. Geol.*, 2005, **215**, 37–60.
29. Stoffregen, R. E. and Alpers, C. N., Woodhouseite and svanbergite in hydrothermal ore deposits: products of apatite destruction during advanced argillic alteration. *Can. Mineral.*, 1987, **25**, 201–211.
30. Scott, K. M., Nomenclature of the alunite supergroup: discussion. *Can. Mineral.*, 2000, **38**, 1295–1297.
31. Dutrizac, J. E. and Jambor, J. L., Jarosites and their application in hydrometallurgy. *Rev. Mineral. Geochem.*, 2000, **40**, 405–452.
32. Dill, H. G., The geology of aluminium phosphates and sulphates of the alunite group minerals: a review. *Earth Sci. Rev.*, 2001, **53**, 35–93.
33. Ossaka, J., Hirabayashi, J., Okada, K., Kobayashi, R. and Hayashi, T., Crystal structure of minamiite, a new mineral of the alunite group. *Am. Mineral.*, 1982, **67**, 114–119.
34. Li, G., Peacor, R., Essene, E. J., Brosnahan, D. R. and Beane, R. E., Walthierite,  $\text{Ba}_{0.5}\square_{0.5}\text{Al}_3(\text{SO}_4)_2(\text{OH})_6$ , and huangite,  $\text{Ca}_{0.5}\square_{0.5}\text{Al}_3(\text{SO}_4)_2(\text{OH})_6$ , two new minerals of the alunite group from the Coquimbo region, Chile. *Am. Mineral.*, 1992, **77**, 1275–1284.
35. Banin, A., Han, F. X., Kan, I. and Cicelsky, A., Acidic volatiles and the Mars soil. *J. Geophys. Res.*, 1997, **102**, 13341–13356.
36. Golden, D. C., Ming, D. W. and Morris, R. V., Laboratory hydrothermal alteration of basaltic tephra by acid sulfate solutions: an analog process for Martian weathering. *Lun. Planet. Sci.*, 2003, **34**, 1–2.
37. Basu, A. R., Renne, P. R., Dasgupta, D. K., Teichman, F. and Poreda, R. J., Early and late igneous pulses and a high- $^3\text{He}$  plume origin for the Deccan flood basalts. *Science*, 1993, **261**, 902–906.
38. Guha, D., Das, S., Srikarni, C. and Chakraborty, S. K., Alkali basalt of Kuchchh: its implication in the tectonic framework of Mesozoic of western India. *J. Geol. Soc. India*, 2005, **66**, 599–608.
39. Biswas, S. K., A new classification of the Tertiary rocks of Kutch, Western India. *Bull. Geol. Min. Metallurg. Soc. India*, 1965, **35**, 1–6.
40. Biswas, S. K. and Deshpande, S. V., A note on the mode of eruption of the Deccan trap lavas with special reference to Kutch. *J. Geol. Soc. India*, 1973, **14**, 134–141.
41. Biswas, S. K. and Raju, D. S. N., Note on the rock stratigraphic classification of the Tertiary sediments of Kutch. *Bull. Geol. Min. Metallurg. Soc. India*, 1971, **43**, 177–180.
42. Okada, K., Soga, H., Ossaka, J. and Otsuka, N., Synthesis of minamiite type compounds,  $\text{M}_{0.5}\text{Al}_3(\text{SO}_4)_2(\text{OH})_6$  with  $\text{M} = \text{Sr}^{2+}$ ,  $\text{Pb}^{2+}$  and  $\text{Ba}^{2+}$ . *N. Jb. Miner. Mh.*, 1987, **2**, 64–70.
43. Ossaka, J., Otsuka, N., Hirabayashi, J., Okada, K. and Soga, H., Synthesis of minamiite,  $\text{Ca}_{0.5}\text{Al}_3(\text{SO}_4)_2(\text{OH})_6$ . *N. Jb. Miner. Mh.*, 1987, **2**, 49–63.
44. JCPDS, *Mineral Powder Diffraction File Databook*. Joint Committee on Powder Diffraction Standards, Swarthmore, Pa., 1993, p. 781.
45. Wallace, P. and Carmichael, I. S. E., Sulfur in basaltic magmas. *Geochim. Cosmochim. Acta*, 1992, **56**, 1863–1874.
46. Jambor, J. L., Nomenclature of the alunite supergroup. *Can. Mineral.*, 1999, **37**, 1323–1341.

ACKNOWLEDGEMENTS. We thank Allen Treiman, Richard V. Morris, Mikki Osterloo, David Vaniman, William Ferrand, Benton C. Clark, Donald J. Rimstidt, Laurence E. Nyquist, Andrew H. Knoll and Kenneth E. Herkenhoff for commenting on our manuscript. We also thank Dr B. R. Arora, Director, Wadia Institute of Himalayan Geology, Dehradun for providing facilities, and N. K. Saini, B. Chandrasekhar and N. K. Juyal for analytical assistance. K.K. thanks Professors Ashok and Neera Sahni and Lachham Singh for field assistance.

Received 27 August 2008; revised accepted 9 October 2009