ELECTRONIC SUPPLEMENTARY MATERIAL

Analytical procedures used to analyze Kamchatka and Lassen samples.

All solvents and reagents such as phenacyl bromide, 2-naphthoyl chloride and triethylamine were purchased from Aldrich Chemical Company and used without further purification. Myristic acid, amino acids and nucleobases were purchased from Sigma Chemical Company, and glycerol from EM Science.

HPLC analysis was carried out using a Waters 2695 Separations Module Instrument with a Waters UV detector. An Alltima C18 column (Alltech) of 25mm x 4.6 mm was used for the reverse phase chromatography and separation of solutes. Water-acetonitrile (with 0.1% TFA) served as eluents and the instrument was programmed to deliver the solvents from 0-100% in 40 minutes. Flow rate set at 0.75ml/min. Colorimetric analyses of phosphate was carried out by a standard molybdic acid method (Horwitt, 1952).

Derivatization procedures.

For the amino acids and myristic acid, it was necessary to prepare derivatives that absorbed UV light in order to provide the sensitivity required for microgram scale analysis by HPLC. Amino acids were converted into 2-naphthoyl derivatives. In a typical run 100μl of the Kamchatka water samples was mixed with 200μl of 0.2M borate buffer (pH 8.5) for 45 seconds followed by addition of 200ul of 2-naphthoyl chloride (15mM in acetone). After vortexing for 45 seconds, the unreacted naphthoyl chloride was extracted with ethyl acetate (3 X 0.5ml).The organic layer was removed and an aliquot of the aqueous portion was injected into the liquid chromatograph.

Myristic acid was analyzed by HPLC as its phenacyl ester. The water samples were first vortexed for 1 minute to disperse the myristic acid and 10ml was then extracted with 10 ml diethyl ether (10ml). The organic layer was separated and evaporated to dryness. The residue was then mixed with 400μl of phenacyl bromide solution (1mg /ml acetone) and 2 ml of triethyl amine solution (1μg/μl acetone). The contents were kept at room temperature for 24 hrs and then evaporated to dryness to remove the solvent and triethyl amine. The residue was redissolved in 2 ml of acetone and an aliquot was injected into HPLC.

Nucleobases. Since the bases are UV absorbing chromophores the Kamchatka water samples were analyzed as such in HPLC.

*Phosphate***.** The inorganic phosphate was estimated by the molybdic acid method with stannous chloride as reducing agent. To 0.5 ml of water samples 0.5 ml of ammonium molybdate (2.5g /100 ml in 3N sulphuric acid) was added and mixed. To this was added 0.5 ml of stannous chloride (3g/100 ml 37%. HCl diluted 1 : 500 before addition). After 15 minutes the blue solutions were analyzed by their absorption at 750 nm, using a standard curve of phosphate to determine the amounts present.

Adsorption of organics and phosphate to clay.

We found that organic solutes and phosphate rapidly disappeared as soluble species. For this reason we also analyzed samples of clay taken from the edge of the puddle at 0, 5, 30, 120 minutes. Clay aliquots (2.0 g) were extracted either with 0.1 M HCl or in 0.1 M NaOH (20 ml) then centrifuged to remove the clay minerals. The dissolved compounds were analyzed by the same procedures described above.

Control experiment.

The experiment conducted in Kamchatka hydrothermal pond was repeated in the laboratory to compare the fate of the chemicals added. By maintaining similar concentrations to those in the Kamchatka pool, one tenth of the weight of the chemicals was added to boiling 700 ml of water (pH 3.1) in a glass beaker. Water samples (10ml) were taken before the addition of chemicals and after 1min, 5 min. 30 min and 2 hr. The samples were analyzed for the amino acids and nucleobases only, because phosphate and myristic acid would not be affected under these conditions.

Clay analysis.

Samples (obtained from buffered solutions at pH values of 3.2, 4.5, and 12) were prepared for X-ray diffraction (XRD) by following standard clay mineralogy techniques (e.g., Moore and Reynolds, 1997). Each sample was prepared first by sonification for 4 minutes, centrifugation, and decantation of the clear supernatant, followed by sonification for an additional 4 minutes in two-minute steps. This procedure was repeated three additional times, but with sonification for 3 minutes instead of 4 minutes. An $AgNO_3$ test showed that there were no residual salts present. Sodium pyrophosphate was used to produce dispersion by increasing the pH, which was followed by 4 minutes of sonification (in two-minute steps), and then appropriate settling was allowed to produce a fraction of clay particles in the size range of ~2 μm or less. The resulting supernatant containing this size fraction was then centrifuged, the clear supernatant discarded, and the residual thick slurry was used to prepare mounts for diffraction by the smear-mount technique, which involved forced-air drying. A low sodium glass (“quartz” glass) was used as the substrate so that the

sample could be heated to high temperatures. One smear mount was exposed to X-rays directly after mounting and drying, and then after heating at 300 ^{o}C for one hour, and after heating at 550 ^{o}C for one hour. A second smear mount was exposed to X-rays directly after mount preparation and then after this mount was subjected to an ethylene-glycol vapor for 90 hours at 60-80 ^{o}C. A smear mount was prepared also after Mg saturation and then the mount was subjected to X-rays before and after glycerol solvation; the same procedure was used for a mount with a K-saturated sample. Mg exchange was accomplished by treating the clay with 0.1 M solution of $MgCl_2$ (K exchange involved 1 M solution of KCl). Approximately 50 mL of the solution was added to the clay, treated by sonification for two minutes and then centrifuged. The clear supernatent was removed and the exchange process was repeated an additional two times, and then all chloride ions were removed by washing multiple times in distilled water with each washing followed by centrifugation, and this was repeated until the $AgNO_3$ test showed that no chloride ions remained. A final washing was accomplished with 50/50 mixture ethanol/water to avoid hydrolysis.

The conditions for X-ray diffraction in a Siemens (Bruker) D-5000 powder diffractometer were as follows: graphite monochromatized copper (1.5418 Å) radiation, 40 kV, 25 mA, step scan at 0.02 ^{o} steps and an exposure for 1 sec/step using a Peltier-cooled detector. Diffraction patterns were obtained in the range from two theta of 2 - 35.