would be increased in alkaline solutions.

This proved to be the case. In an experiment 76.5 mg of krypton tetrafluoride (0.48 mmole) were hydrolyzed at 0° to 5°C with 50.0 cm^3 of 0.346*N* barium hydroxide solution. The reaction proceeded with the evolution of gas and the formation of a white precipitate of barium fluoride, BaF_2, and barium kryptate. After completion of the reaction, the precipitate was filtered off, washed with small amounts of ice water, and dried (all at 0°C). The weight of the dry precipitate was 181.5 mg. The filtrate was titrated for unreacted barium hydroxide; the difference was equal to 1.10 mmoles of combined barium fluoride and barium kryptate.

The gas evolved during the reaction was 19.0 cm^3 (at N.T.P.) and it contained 49.6 percent krypton and 50.4 percent oxygen corresponding to 0.425 mmole of the original krypton tetrafluoride. The difference from the original amount of krypton tetrafluoride, or approximately 0.05 mmole, apparently reacted with the barium hydroxide, forming *insoluble* barium kryptate.

The dry precipitate of BaF_2 and barium kryptate showed no noticeable thermal decomposition either at 0°C or at room temperature; it started decomposing at approximately 50°C, and the decomposition was complete at 200°C. The total gas collected was 1.9 cm^3 (N.T.P.); if the decomposition is assumed to be as follows:

$$BaKrO_4 \rightarrow BaO + Kr + 1.5\,O_2, \tag{3}$$

this amount of gas is equivalent to 0.034 mmole or 9.7 mg of barium kryptate. The yield of barium kryptate based on the original amount of krypton tetrafluoride is 7.1 percent (mole); this is in reasonable agreement with the value of approximately 0.05 mmole from the krypton recovery. Furthermore, the total barium fluoride formed from the original krypton tetrafluoride should be 0.96 mmole or 168.3 mg and with the weight of barium kryptate (about 9.7 mg) the total weight (178 mg) is in reasonable agreement with the weight of the combined barium fluoride and kryptate actually recovered (181.5 mg), when consideration of the washing is taken into account. Small amounts (about 1 percent or less) of barium carbonate are also present in the precipitate. The amount of barium oxide produced by thermal decomposition was determined by titration and was also in agreement with Eq. 3.

In another experiment, the yield of barium kryptate was determined by reacting it, in hydrochloric acid solution, with potassium iodide solution and back-titrating with standard thiosulfate solution (*4*). If the reaction is

$$BaKrO_4 + 8\ HCl + 6\ KI \rightarrow BaCl_2 + 6\ KCl + 3\ I_2 + Kr + 4\ H_2O \tag{4}$$

the yield equals 9.0 percent (mole) of the original krypton.

Barium kryptate was further identified by isolating the *krypton* formed in the thermal decomposition and identifying it as such by (i) determining the vapor pressure of the pure gas evolved, (20 mm at 90°K and 2 mm at 77°K identical with an authentic sample of krypton, xenon at the same temperatures has a vapor pressure of 0.05 mm and 10^{-3} mm) and (ii) by mass-spectrometer analysis, which showed nearly 100 percent krypton. Thus the presence of barium xenate is excluded.

The alkali salts of kryptic acid can be expected to be even more stable thermally than barium kryptate, in analogy to the corresponding xenates or perxenates (*4, 5*). Thus it may be expected that krypton, like xenon (*4*), may be found in nature not only in the atmosphere but in hydrothermal minerals and in waters of the ocean.

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Pleistocene Chipped Stone Tool on Santa Rosa Island, California

Abstract. *Santa Rosa Island, California, has been the site of numerous discoveries of evidence of Pleistocene Man. The recent finding of a well-made chipped stone tool* in situ *in the mammoth beds adds further evidence.*

Since 1946 (*1*), excavations and studies have been made of the Santa Rosa Island formation which contains the charred bones of dwarf mammoths and birds as well as more than 100 "fire areas" suggesting "barbecue pits."

Human bone, found at a depth of 11 m at Arlington Springs, has been dated by Broecker (*2*) as 10,400 years old. It was analyzed for fluorine by Oakley, who reported the bones as fossil (*3*). In a narrow area of about 1000 m along the sea cliffs, more than 40 radiocarbon dates have been secured from five laboratories. These dates spread through the entire range of radiocarbon.

In September 1963, while searching for radiocarbon material, Gordon Fergusson, Rainer Berger (*4*), and I discovered a well-made chipped stone implement 145 mm by 103 mm, projecting about 45 mm from the compact clays of the Tecolote member of the Santa Rosa Island formation (*5*), and at a depth of approximately 2½ m below the grass roots.

The implement was in a small badland type of gully, and lay stratigraphically between two separate mammoth deposits. The upper one, consisting of a few weathered bones, has been known

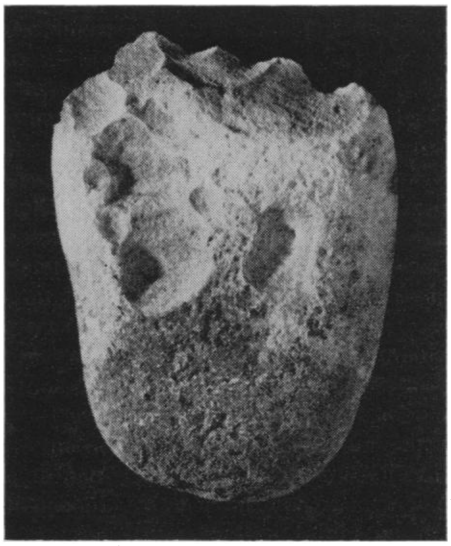

Fig. 1. Pleistocene chipped Stone tool found at Santa Rosa Island.

to be in evidence for 17 years, the lower bones constituted quarry No. 2, and contained the partial burned skeletal parts of a young mammoth which I excavated in 1946. On the opposite side of the erosional channel are several fire areas in which erratic chips, which may be discards of tool making, or, in some cases, thermal fractures, occur in considerable numbers.

This tool is made from a beach cobble naturally rounded on all sides except where it is bifacially chipped by percussion. The upper side (as it lay in the ground) has six distinct chips, the lower side has one large chip and two smaller ones. There is evidence of some retouching.

Numerous chipped-stone implements have been found on the surface, some in association with weathered mammoth bones. Other chipped stones have been found with buried mammoth bones, but are controversial as to whether they were "thermal fractures" or man-made. There is no doubt that this last find is man-made, and *in situ* in the mammoth beds.

While no radiocarbon age can as yet be assigned to this particular specimen, it lies stratigraphically about 120 m east of Lamont's L. 290-T, 12,500 years old, made on charcoal from a mammoth "kill," and at an equal distance west of sample UCLA 141, made from carbon in an Indian midden and dated as 12,620 years ago. From about 90 m away and slightly higher stratigraphically, charcoal from a buried midden was dated at 11,900 years ago (sample UCLA 661).

Further dating and excavation will be carried out in the future, and this and other artifacts will be described elsewhere.

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Infrared Study of the OH Groups in Expanded Kaolinite

Abstract. *Expansion of kaolinite with potassium acetate and with hydrazine followed by deuteration, shifts the absorption frequency at 3695 cm^{-1} to lower values, but does not affect the intensity of the 3620-cm^{-1} absorption band. The band at 3695 cm^{-1} is correlated predominantly to inner-surface hydroxyls with the dipole at right angles to the basal plane and the band at 3620 cm^{-1} is related to inner hydroxyls with the dipole inclined toward empty octahedral sites.*

In spite of a rather considerable amount of work done with infrared spectroscopy, only limited correlations have been made between the hydroxyl stretching frequencies and the hydroxyl sites in the clay lattices. Our report includes results obtained with infrared spectroscopy on expanded kaolinite complexes and suggests absorption band assignments for the hydroxyl groups.

The terminology used to specify the OH groups in kaolinite structure (Fig. 1) is as follows. "Outer hydroxyls" refer to structural OH groups at the surface of micro crystals, including both hydroxyls at the broken edges (*A*), and hydroxyls of the octahedral sheet found at the upper surface denoted by (*B*). "Inner-surface hydroxyls" refer to OH groups located at the surface of the octahedral sheets opposite the tetrahedral oxygens of the adjacent kaolinite layer and having their OH dipole normal or nearly normal to the (001) plane; they are indicated by (*C*). "Inner hydroxyls" are designated by (*D*) and refer to the OH groups in the plane common to octahedral and tetrahedral sheets and to OH groups at 4.37 Å, both having their dipole directed towards an empty octahedral site.

Each oxygen atom not bonded to Si has two free orbitals which can interact with one proton to form an OH group. The choice of the specific oxygen orbitals interacting with the protons was based upon consideration of (i) the length and the proportion of each type of oriented O-H ··· O bond necessary to account for the number and the relative intensity of the infrared absorption bands, and (ii) the electrostatic repulsion between the aluminum and the proton. The probability of finding a proton associated with the remaining free orbitals is small.

We have attempted to correlate the OH absorption frequencies to the OH sites in the lattice of kaolinite by studying the manner in which the OH vibration frequencies are affected when the mineral is expanded by intersalation and then deuterated.

Andrew *et al.* (*1*) expanded kaolinite from 7 Å to 14 Å simply by grinding and hydrating a mixture of potassium acetate (CH_3COOK) and kaolinite, and proposed the term "intersalation" for the phenomena of entrance of such salts between lattice layers of clay minerals. The intersalated kaolinite for our study was prepared by grinding a 1 g sample of the mineral (*2*) with 15 mmoles of (CH_3COOK) for 20 minutes in a Fisher mechanical mortar-and-pestle grinder and allowing the mixture to stand overnight over a water bath. A large proportion of the kaolinite crystals were expanded, although a significant amount remained in the collapsed state. The specimens were prepared so that it would be possible to record the infrared spectra and the x-ray patterns, and to allow dipole orientation studies. A small portion of the hydrated (CH_3COOK)-kaolinite complex was dispersed in distilled water and a film specimen was prepared by evaporating, in a desiccator, 1 ml of suspension that had been placed on a cover glass (*3*). The cover glass with the mounted specimen was inserted as a window into a cylindrical infrared cell with the specimen surface inside the cell. Thin cover glasses are very suitable window material; excellent compensation is easily obtained between 4000 and 2400 cm^{-1} by using four matched windows in the reference and sample cells. Since the specimen had to be removed from the cell for x-ray determination, a mark was made on the edge of the cover glass to insure replacement of the sample in exactly the same position.

The infrared spectra (*4*) were obtained after the sample and the reference cells had been heated at 110°C. The sample was removed from the cell, reheated at 110°C for 1 hour, and an x-ray diffraction pattern was recorded (see *4*) while a stream of dry nitrogen was passed through the sample chamber.

In the infrared spectrum of pure