society (*10*)? This appears to be the most promising line of investigation in the present state of our knowledge.

Occupational specialization, proliferating craft industries, high urban density, and a large population are differing manifestations of the same intense process of urbanization. Taken in conjunction with the scope of Teotihuacán's exports and imports, they argue that Teotihuacán society was more complex than recent estimates have suggested. The intensity of the urbanization process appears to set Teotihuacán apart from other contemporary centers in Middle America. At the same time, it makes it more similar to Tenochtitlán, the capital of the Aztecs, which rose 40 km from Teotihuacán on the site of modern Mexico City over 500 years after Teotihuacán's fall. Until equivalent comparative data from other parts of the New World are available, comparisons with early Old World centers may be more useful in trying to understand pre-Hispanic urbanization in the Valley of Mexico.

Teotihuacán stands for the present as the most highly urbanized center of its time in the New World (*11*). The extraordinary extent and pervasiveness of its influence through so much of Middle America in the early centuries of the Christian era are now more understandable.

RENÉ MILLON
University of Rochester,
Rochester, New York 14627

References and Notes

1. Computer analyses are being carried out by G. Cowgill.
2. See H. Saalman, *Medieval Cities* (Braziller, New York, 1968), pp. 44–45.
3. See W. Sanders, *The Cultural Ecology of the Teotihuacán Valley* (Dept. of Sociology and Anthropology, Pennsylvania State Univ., State College, 1965).
4. R. Millon, *Bol. Inst. Nac. Antropol. Hist.* **29**, 42 (1967); *Gac. Med. Mex.* **98**, 339 (1968).
5. ———, *Sci. Amer.* **216** (6), 38 (1967).
6. D. Robertson, *Pre-Columbian Architecture* (Braziller, New York, 1963), pp. 25–27, 35–36; J. E. Hardoy, *Ciudades Precolombinas* (Infinito, Buenos Aires, 1964), pp. 89–93; *Urban Planning in Pre-Columbian America* (Braziller, New York, 1968), pp. 9, 12, 22–23.
7. G. Kubler, *The Art and Architecture of Ancient America* (Penguin, Baltimore, 1962), pp. 29, 328.
8. R. Millon, *37th Int. Congr. Americanists Actas Memorias* **1**, 113 (1968).
9. For the past several years M. Spence of Southern Illinois University has been analyzing obsidian, obsidian workshops, the obsidian industry, and specialization within the industry in Teotihuacán on the basis of what was found in our excavations and surface survey.
10. This is suggested in part by the stimulating ideas of J. Jacobs on the economic growth of early cities [*The Economy of Cities* (Random House, New York, 1969]. See also R. Millon, in *Teotihuacán, XI Mesa Redonda* (Sociedad Mexicana de Antropología, Mexico, 1967), pp. 149–155.
11. Other contemporary Middle American centers, such as Tikal in Guatemala or Dzibilchaltun in Yucatán, seem to have covered larger areas than Teotihuacán [W. Coe, *Tikal* (University Museum, Philadelphia, 1967); W. Haviland, *Amer. Antiquity* **34** (4), 429 (1969); E. Andrews, Map of Dzibilchaltun, Yucatán, Mexico (Middle American Research Institute, Tulane Univ., New Orleans, 1965); *Archaeology* **21** (1), 36 (1968)]. But so far as is now known, none seems to have been so highly urbanized as Teotihuacán; that is, none seems to have combined great size, high population density, large populations, foreign enclaves, and thousands of craft specialists in a marketplace and ritual center of immense, monumental proportions. Chan Chan, an immense urban center on the north coast of Peru, is now under intensive study by M. Moseley and others. From what is now known of it, Chan Chan, although of great size, also does not appear to have been so highly urbanized as Teotihuacán [see M. West, *Amer. Antiquity* **35** (1), 74 (1970)].
12. Supported by NSF grants G23800, GS207, GS641, GS1222, and GS2204. Principal participants with R.M. on the project are G. Cowgill (Brandeis University) and R. B. Drewitt (University of Toronto). J. A. Cerda is chief draftsman. I gratefully acknowledge the assistance of P. Baños, W. Barbour, J. Bennyhoff, D. Blucher, H. Castañeda, J. Dow, A. German, E. Ekholm, P. Krotser, G. R. Krotser, D. Massey, E. Rattray, S. Reichlin, S. Sharnoff, M. Spence, J. Vidarte, M. Wallrath. I thank I. Bernal, I. Marquina, J. Cortina, J. Acosta, J. L. Lorenzo, P. Salazar, E. Matos, E. Contreras, F. Müller, and E. Taboada of Mexico's Instituto Nacional de Antropología e Historia for their assistance in our work. This report benefited from readings and criticisms by W. Barbour, E. Calnek, G. Cowgill, R. B. Drewitt, A. Green, and C. Millon.

15 April 1970

■

Sulfur Isotope Distribution in Solfataras, Yellowstone National Park

Abstract. *Sulfur isotope data on hydrogen sulfide, native sulfur, and sulfates from acid hot-spring areas at Yellowstone National Park suggest that hydrogen sulfide oxidizes to sulfur abiologically, whereas sulfur undergoes biological oxidation to sulfuric acid. An exception occurs at Mammoth Hot Springs where hydrogen sulfide apparently undergoes biochemical oxidation to sulfur.*

Fumarolic hydrogen sulfide, discharged in sulfurous hot-spring areas known as solfataras, oxidizes to form large quantities of sulfuric acid. Previous studies suggest that bacteria may produce virtually all this sulfuric acid by catalyzing the oxidation of geothermal hydrogen sulfide. These studies dealt with the distribution of sulfur-oxidizing bacteria in solfataras (*1*) and the quantities of sulfuric acid produced in solfataras as compared with the quantities produced by bacteria in the laboratory (*2*). The relative importance of a biochemical versus an inorganic oxidation mechanism, however, has been difficult to determine. The success achieved with the use of sulfur isotope ratios to confirm bacterial processes of sulfate reduction led naturally to their use in studies of the oxidation of sulfides in nature (*3, 4*). Results thus far, however, have been only suggestive of biochemical involvement.

Because the masses of the S^{32} and S^{34} nuclei are different, these isotopes react at different rates in chemical reactions. If, during the formation of sulfur compounds, the reaction does not go to completion, the ratio of the isotopes in the products will be different from that in the remaining reactants. It is this enrichment or depletion of one of the isotopes that can sometimes be used to infer the genesis of a sulfur compound. Oxidation-reduction reactions in which organisms participate usually show diagnostic shifts in the ratios of isotopes of the reacting elements (*5*). In order to see if the ratios of sulfur isotopes would show shifts that we could interpret as diagnostic of biochemical, as contrasted with inorganic, oxidation, we collected samples of sulfide, sulfur, and sulfate from various hot-spring localities within Yellowstone National Park (*6*).

Table 1 lists the results of our sulfur isotope analyses in terms of δS^{34} values [difference (in parts per thousand) between the S^{34}/S^{32} ratio in the sample and that in the Cañon Diablo meteorite standard]. Table 1 shows that the δS^{34} values of hydrogen sulfide from localities 1 through 5 range from $+0.7$ to $+2.6$ per mil. This small range of δS^{34} values indicates a well-homogenized source and is in agreement with values generally considered to be those of deep-seated sulfur (*7*). Most of the hydrogen sulfide rising to the surface in these areas may come from either a body of degassing magma beneath the park or igneous rocks containing unfractionated sulfur.

The hydrogen sulfide values from localities 6, 7, and 8, however, range from -3.0 to -5.5 δS^{34} per mil. A thick sequence of sedimentary rocks underlies locality 6, Mammoth Hot Springs (*8*). Sulfide minerals in sedimentary rocks usually show depletions of S^{34} because of the biologic reduction processes involved in their genesis (*9*). For these reasons, the hydrogen sulfide at Mammoth Hot Springs (locality 6) may be a mixture of magmatic hydrogen sulfide with hydrogen sulfide baked out of underlying sedimentary rocks by high geothermal temperatures. Although no sediments crop out at localities 7 and 8, a similar explanation involving buried sedimentary rocks may be suggested to explain these low δS^{34} values of the hydrogen sulfide as well.

The laboratory experiments on sulfur isotope fractionation by sulfur-oxidizing bacteria show δS^{34} fractionations of about − 6 per mil in sulfur formed from hydrogen sulfide and − 6 per mil to as much as − 18 per mil in sulfate formed from hydrogen sulfide (*10, 11*). But all the experiments show that bacterial oxidation of sulfur, rather than of hydrogen sulfide, to sulfate results in either no fractionation or a slight positive fractionation of about + 2 per mil with respect to the sulfur (*11*). In contrast, equilibrium inorganic oxidation of hydrogen sulfide to sulfate should yield large positive fractionations (*12*).

Native sulfur in all localities except Mammoth Hot Springs (and Pocket Basin, where we were unable to find sulfur) possesses sulfur isotope values ranging from − 1.7 to + 1.4 δS^{34} per mil with respect to the local hydrogen sulfide source. Other studies in geothermal areas show that inorganic oxidation of hydrogen sulfide to sulfur does not appreciably change the ratio of sulfur isotopes (*3*, p. 216; *13*). The small variation exhibited by our samples probably reflects analytical errors, fractionation caused by partial oxidation of the sulfur, and variation of the sulfur isotope ratio of the hydrogen sulfide with time. The samples of sulfur and sulfate represent hydrogen sulfide emitted at some time in the past that may not correspond exactly in sulfur isotope ratio with the hydrogen sulfide we collected. Despite these small differences, we believe that all these sulfur samples (a few of which come from > 90°C fumaroles) probably formed by purely inorganic oxidation of hydrogen sulfide.

The sulfur from Mammoth Hot Springs is clearly much lighter (− 5.4 per mil) than the local hydrogen sulfide. The similarity of this fractionation to that observed in laboratory measurements of the bacterial oxidation of hydrogen sulfide, and the distinct difference from the positive fractiona-

Table 1. Distribution of sulfur isotopes in solfataras, Yellowstone National Park, Wyoming. Locations of numbered sampling sites are shown on Fig. 1 and described in reference (*16*). Delta values listed in columns 2 and 5 are differences (in parts per thousand) between the S^{34}/S^{32} ratio in the sample and that in the Cañon Diablo meteorite. A positive value indicates more heavy sulfur (S^{34}) and a negative value indicates more light sulfur (S^{32}) in the sample than in the meteoritic standard. Columns 3 and 6 show the differences between the S^{34}/S^{32} ratio in the sample and the sulfur isotope ratio in the local source of hydrogen sulfide.

Sample description	δS^{34} with respect to Cañon Diablo (‰)	δS^{34} with respect to local H_2S (‰)
Norris Junction (locality 1)		
H_2S	+2.6	
S^0 (needles, fumarole)	+3.2	+0.6
S^0 (massive, fumarole)	+1.1	−1.5
SO_4 (soil)	+3.1	+0.5
SO_4 (stream)	+3.2	+0.6
Norris Ranger Station (locality 2)		
H_2S	+2.3	
S^0 (surface soil)	+0.6	−1.7
SO_4 (soil)	+2.8	+0.5
SO_4 (stream)	+3.3	+1.0
Roaring Mountain (locality 3)		
H_2S	+0.7	
S^0 (fumarole)	+1.6	+0.9
S^0 (surface soil)	+1.1	+0.4
S^0 (soil, 1 foot deep)	+1.7	+1.0
SO_4 (surface soil)	+1.5	+0.8
SO_4 (soil, 4 feet deep)	+1.1	+0.4
SO_4 (stream, southern end)	+2.1	+1.4
SO_4 (Lemonade Lake)	+2.0	+1.3
SO_4 (hot spring, northern end)	+1.8	+1.1
Amphitheater Springs (locality 4)		
H_2S	+1.7	
S^0 (fumarole)	+0.7	−1.0
SO_4 (soil)	+1.7	0.0
SO_4 (stream)	+2.6	+0.9
Pocket Basin (locality 5)		
H_2S	+1.8	
SO_4 (soil)	+2.7	+0.9
Mammoth Hot Springs (locality 6)		
H_2S	−3.0	
S^0 (fumarole)	−8.4	−5.4
SO_4 (soil)	−6.2	−3.2
SO_4 (New Highland Terrace Spring)	+20.5	+23.5
Washburn Hot Springs (locality 7)		
H_2S	−4.0	
FeS_2 (Devil's Inkpot)	−3.2	+0.8
S^0 (fumarole)	−2.6	+1.4
SO_4 (soil)	−2.2	+1.8
SO_4 (stream)	−0.1	+3.9
Turbid Hot Springs (locality 8)		
H_2S	−5.5	
S^0 (fumarole)	−4.7	+0.8
SO_4 (soil)	−5.7	−0.2

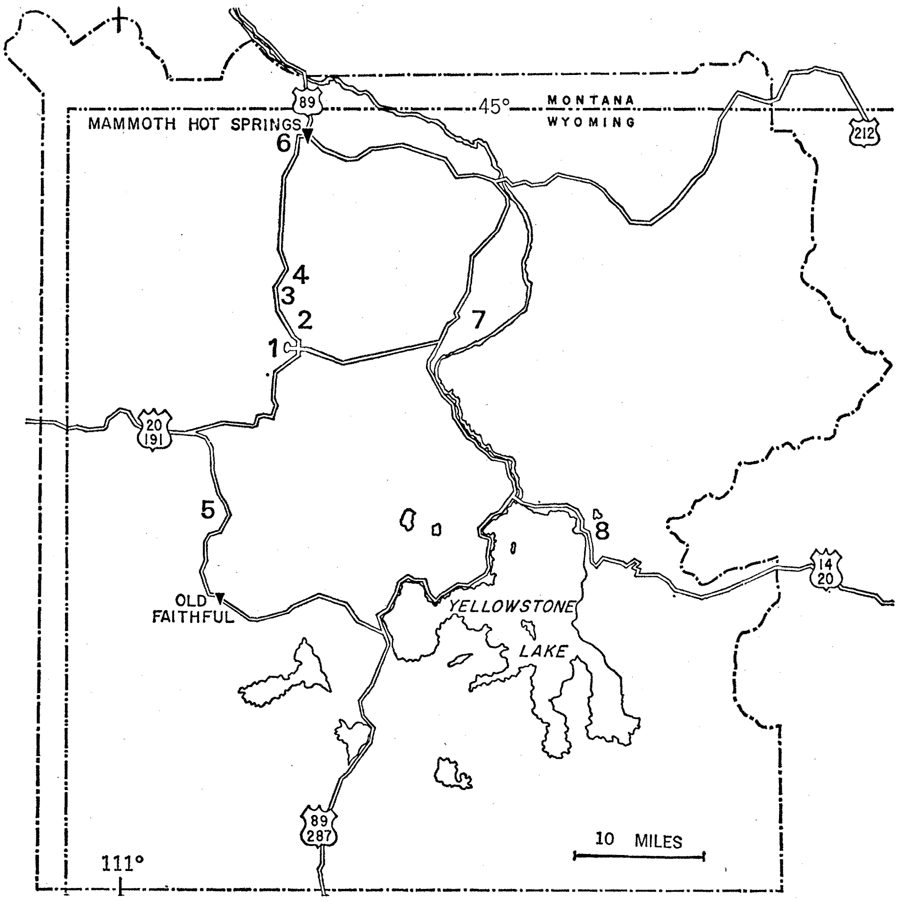

Fig. 1. Map of Yellowstone National Park, Wyoming, showing locations of numbered sampling sites [Table 1 and reference (*16*)].

tions predicted for equilibrium inorganic fractionations, suggests that the sulfur at Mammoth Hot Springs is biogenic.

Mammoth Hot Springs (locality 6) is unique. The surrounding rocks are sedimentary rather than volcanic, and, in addition, the hot-spring deposits are travertine rather than siliceous sinter. Temperatures below 70°C at Mammoth contrast with temperatures of over 90°C at the other localities. The rate of emission of hydrogen sulfide is very much slower at Mammoth. These conditions may favor the direct oxidation of hydrogen sulfide by bacteria.

With the exception of the sulfate from New Highland Terrace Spring at locality 6, all our sulfate samples show sulfur isotope fractionations close to zero or slightly positive with respect to either hydrogen sulfide or sulfur. These fractionations agree with those previously described laboratory values for biogenic sulfate derived from sulfur, not from hydrogen sulfide, and differ greatly from theoretical inorganic fractionations (*12*). The abundance of heavy sulfur in the water of New Highland Terrace Spring ($\delta S^{34} = +20.5$ per mil) comes from marine gypsiferous beds that underlie this part of the park (*14*). The area in which we find oxidizing hydrogen sulfide is well above the water table, and none of the deep sulfate contaminates the soil sulfate.

Roaring Mountain, a high-discharge hot spring at the north end of the park, contains 500 mg per liter of sulfate whose δS^{34} value approximates that in the nearby soil. This suggests that most of the sulfate in the hot spring derives from biogenic oxidation of sulfur on the surface of the ground and enters the hot spring by percolation of groundwater. The similarity in the δS^{34} values of soil and stream sulfate at the other localities supports this hypothesis.

We cannot explain why the soil sulfate at Mammoth is slightly heavier than the sulfur. The oxidation of hydrogen sulfide to sulfur and sulfate by sulfur-oxidizing bacteria in the laboratory (*10, 11*) yielded negative δS^{34} fractionations. Instead, we find a negative fractionation of the sulfur, which agrees with a biologic origin, but a small positive fractionation of the sulfate with respect to the sulfur. A possible explanation is that a very different ecology exists at Mammoth Hot Springs, where soil *p*H's buffered by travertine are close to neutral, by comparison with the other solfataras that are strongly acid. Therefore, the sulfur-oxidizing bacteria may be different. Other studies in *p*H-buffered, sulfur-oxidizing soils show the reasonableness of such an explanation for seemingly anomalous bacterial populations (see *15*).

Our data imply that, at Yellowstone Park, most of the hydrogen sulfide oxidizes to sulfur abiologically, whereas sulfur oxidizes to sulfuric acid biologically. The reason for this is unclear. Perhaps geothermal hydrogen sulfide is generally too hot for bacteria to oxidize directly, and instead it oxidizes to sulfur vapor which then precipitates in the cooler parts of the soil. The data also indicate that, except at Mammoth, most of the sulfate in hot springs and streams draining the solfatara percolated down from a biochemical origin on the surface.

Although the isotope ratios support a biochemical origin for the sulfuric acid, and differ greatly from the isotope ratios for an inorganic equilibrium reaction (*12*), the possibility that an inorganically catalyzed nonequilibrium reaction might produce identical isotope ratios cannot be excluded at this time. It seems unlikely, however, that a nonequilibrium reaction would produce the very uniform grouping of δS^{34} values in the different sulfur species over widely separated areas.

ROBERT SCHOEN
U.S. Geological Survey,
Menlo Park, California 94025

ROBERT O. RYE
U.S. Geological Survey,
Denver, Colorado 80225

References and Notes

1. G. G. Ehrlich and R. Schoen, *U.S. Geol. Surv. Prof. Pap. 575-C* (1967), p. C110; G. A. Zavarzin, L. V. Vasil'eva, V. V. Trykova, *Izv. Akad. Nauk SSSR Ser. Biol.* **4**, 605 (1967); R. Schoen and G. G. Ehrlich, *Proc. Int. Geol. Congr., 23rd, Prague* (1968), vol. 17, p. 171.
2. R. Schoen, *Geol. Soc. Amer. Bull.* **80**, 643 (1969).
3. T. A. Rafter, I. R. Kaplan, J. R. Hulston, *N.Z. J. Sci.* **3**, 209 (1960).
4. I. R. Kaplan, T. A. Rafter, J. R. Hulston, *ibid.*, p. 338; A. Nissenbaum and T. A. Rafter, *J. Sediment. Petrol.* **37**, 961 (1967); V. A. Grinenko and A. Yu. Lein, *Geochem. Int.* **4**, 250 (1967); M. V. Ivanov, V. A. Grinenko, A. Yu. Lein, *ibid.* **5**, 1133 (1968).
5. G. E. Jones and R. L. Starkey, *Appl. Microbiol.* **5**, 111 (1957); R. M. Lloyd, *Science* **156**, 1228 (1967); R. Park and S. Epstein, *Geochim. Cosmochim. Acta* **21**, 110 (1960).
6. We collected hydrogen sulfide by leading the natural gases from a fumarole into an inverted Pyrex funnel, through Tygon tubing, into a 1-gallon (3.785-liter) Pyrex bottle cooled by evaporation where steam condensed, and then into a 4-ounce (118.3-cm^3) bottle of 5*N* silver nitrate solution where silver sulfide precipitated. If natural pressures were low, we applied a vacuum with a rubber-bulb syringe to move the hydrogen sulfide to the silver nitrate solution. Samples of yellow native sulfur, from the throats of fumaroles and dispersed in acid-bleached soils, were purified by solution in hot benzene, filtration, and recrystallization. We obtained soluble sulfate from acid-bleached soils by leaching with distilled water. Abundant gypsum in one of the soils required the addition of hydrochloric acid to ensure solution. We used standard gravimetric analytical procedures to precipitate the sulfate as barium sulfate. Where possible, we sampled sulfate-rich streams draining the solfataras and precipitated the sulfate directly. One sample of black iron sulfide, from Devil's Inkpot, required oxidation with hot aqua regia and filtration before sulfate precipitation. Sulfur dioxide was prepared from the silver sulfide, sulfur, and barium sulfate by standard techniques and isotopically analyzed on a mass spectrometer (Nuclide RMS-60). The precision of replicate analyses of sulfur isotope ratios is ± 0.2 per mil.
7. A. Polanski, *Geochemistry of Isotopes* (Scientific Publications Foreign Cooperation Center of the Central Institute for Scientific, Technical, and Economic Information, Warsaw, 1965), pp. 130–132.
8. G. D. Fraser, H. A. Waldrop, H. J. Hydan, *U.S. Geol. Surv. Bull. 1277* (1969); I. J. Witkind, *U.S. Geol. Surv. Prof. Pap. 609* (1969).
9. H. G. Thode, R. K. Wanless, R. Wallouch, *Geochim. Cosmochim. Acta* **5**, 286 (1954); M. L. Jensen, *Econ. Geol.* **53**, 598 (1958).
10. I. R. Kaplan and T. A. Rafter, *Science* **127**, 517 (1958).
11. I. R. Kaplan and S. C. Rittenberg, *Nature* **194**, 1098 (1962).
12. H. Sakai, *Geochim. Cosmochim. Acta* **12**, 151 (1957); our calculations indicate that enrichments of S^{34} in the sulfate should be 68.0 per mil at 25°C and 48.0 per mil at 100°C, if we assume equilibrium inorganic oxidation of hydrogen sulfide with a $\delta S^{34} = 0.0$.
13. H. Sakai, *Geochim. Cosmochim. Acta* **12**, 160 (1957).
14. W. T. Holser and I. R. Kaplan, *Chem. Geol.* **1**, 93 (1966).
15. M. V. Ivanov, *Microbiological Processes in the Formation of Sulfur Deposits* (Israel Program for Scientific Translations, Jerusalem, 1968), pp. 225–231; J. M. Sharpley, *Applied Petroleum Microbiology* (Buckham Laboratories, Inc., Memphis, 1961), pp. 133–134.
16. Localities sampled were the following: locality 1, Norris Junction, west of the Norris Junction–Mammoth highway, about 300 feet (91.4 m) north of the new Norris Junction bypass; altered area is about 600 feet northeast of Nuphar Lake, 44°43½′N, 110°42′W; locality 2, Norris Ranger Station, northeast of the Norris Junction–Mammoth highway, about 600 feet north of the intersection with the road leading to the Norris Ranger Station and campground, 44°44½′N, 110°42′W; locality 3, Roaring Mountain, immediately east of the Norris Junction–Mammoth highway, about 5 miles (8 km) north of Norris Junction, 44°47′N, 110°44′W; locality 4, Amphitheater Springs, approximately 1 mile by trail southeast of a point on the Norris Junction–Mammoth highway, 7.5 miles north of Norris Junction, and approximately 1.5 miles due north of the highest point on Roaring Mountain, 44°48′N, 110°-43½′W; locality 5, Pocket Basin, a large group of mud pots about 500 feet east of Pocket Basin and 500 feet west of Rush Lake, about 0.4 mile east of the iron bridge where Fountain Freight Road crosses Firehole River, 44°34′N, 110°50′W; locality 6, Mammoth Hot Springs, about 100 feet east of the paved sightseeing road and about 200 feet northwest of the middle part of White Elephant Terrace (extinct), 44°58′N, 110°43′W; locality 7, Washburn Hot Springs, about 2 miles south of the highest point on Mount Washburn and just north of the Howard Eaton trail, 44°46′N, 110°25½′W; locality 8, Turbid Hot Springs, on the left bank of Bear Creek about 1000 feet above the mouth at Turbid Lake, 44°32½′N, 110°15½′W.
17. We thank the National Park Service for permission to collect these samples. Publication authorized by the director of the U.S. Geological Survey.

18 June 1970