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17. H. Craig, L. I. Gordon, D. E. White, in preparation. Surprisingly, lithium obeys the same equation as chloride; the ratio of lithium to oxygen-18 atoms added to the water is 0.77, 7.7, and 425 at the three stages listed for chloride. Lithium is therefore continuously extracted from the sediments in constant proportion to chloride. By using the isotopic data for identification of waters in a related sequence and as a scaling function, it is possible to unravel a large amount of detail on processes affecting the individual elements in a system.
18. The Red Sea water samples were collected by me in September 1962 on Scripps Institution Expedition Zephyrus; the hydrographic data (16 stations) are available on computer print-out. North Atlantic and North Pacific waters have very similar isotopic relationships, with slopes of about 6.5 and 7.5 and zero intercept. Ocean waters are offset from the precipitation locus because of the kinetic effects in evaporation and air-sea exchange (*15*).
19. The brine is found in approximately 150-m isothermal, isohaline layers at the bottom of the Discovery Deep (*3*) and the Atlantis II Deep (7), about 5 miles (8 km) apart in the center of the Red Sea. Temperatures of the brine layers are 44.8° and 55.9°C respectively, but the chloride concentrations are identical in both deeps; reported data (*5, 6*) agree within experimental error with the present measurements. The Discovery brine sample was obtained through the courtesy of E. C. Bullard; the Atlantis II sample was provided by A. Jokela.
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21. H. Craig, "The measurement of oxygen isotope paleotemperatures," in volume cited in (*15*). The melting of present continental ice (4.71 kg/cm^2, assumed composition $\delta O^{18} = -30$, $\delta D = -230$) would make the present ocean water 0.5 per mil lower in oxygen-18 and 4.0 per mil lower in deuterium. The water removed from the sea in excess of present continental ice during times of maximum Pleistocene glaciation (about 14.9 kg/cm^2, assumed composition $\delta O^{18} = -17$, $\delta D = -126$) would increase the oxygen-18 and deuterium content of the present ocean by 1.0 and 7.4 per mil respectively.
22. This value is calculated assuming melting of all present continental ice during interglacial periods. W. Broecker has pointed out that sea level during the last two interglacials was probably close to the present level; if the present amount of continental ice was maintained during interglacials, the calculated mean brine composition is $\delta D = +11.2$, $\delta O^{18} = +1.7$, even more different from the present values. This calculation also assumes that the position of the brine relative to SMOW is maintained as the locus shifts.
23. I assume two brine depressions, each with a diameter of 2 km and depth of 150 m (*7*) and a salinity of 255 per mil (*5*); together they contain 10^9 tons of brine and 2.5×10^8 tons of salts. The Red Sea contains 2.2×10^{14} tons of sea water and 9×10^{12} tons of salts; the evaporation rate is 2 m a year, over an average depth of 500 m.
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27. Brewer, Riley, and Culkin (*5*). The analysis in (*7*) has 9 percent too much chloride for neutrality and was not used. In calculating the salt balance I have removed SO_4 entirely as $MgSO_4$; there is actually a slight excess of SO_4 over Mg in the salts which were lost, so that a small amount of Mg also appears in the composition of added salt.
28. An oil field brine, of composition very similar to Red Sea brine, has been found at a depth of 2500 m in Louisiana [(*11*), analysis No. 3 in Table 13), only 66 m from salt near the crest of a salt dome lacking an anhydrite cap, with a temperature of 87°C. These brines have surely dissolved salt from the same type of deposit.
29. I thank L. I. Gordon, D. E. White, and H. C. Helgeson for aid in the field work at Salton Sea, N. Anderson for the hydrographic work in the Red Sea, and W. Broecker for discussion. Supported from NSF grants GP-1885, GP-3347, and G-24479, and by ONR grant NONR-2216(23).

22 August 1966

Fluorine Content of Microsaur Teeth from the Carboniferous Rocks of Joggins, Nova Scotia

Abstract. *Because the Carboniferous deposits at Joggins, Nova Scotia, contain the earliest fauna of terrestrial vertebrates, the extremely well-preserved teeth of these ancient animals are of special interest. The "mineral" composition of teeth from the Joggins microsaur* Hylerpeton dawsoni *is crystallochemically identical with francolite, a carbonate fluorapatite. The fluorine content of the fossilized dentin is 3.1 percent, which is much higher than any previously recorded for fossil teeth.*

The oldest fossil vertebrates that were land animals have been found in the Carboniferous sedimentary rocks of Joggins, Nova Scotia. These vertebrates include the earliest terrestrial labyrinthodonts, the earliest known reptiles, and the earliest typical microsaurs, and all have teeth that are in an excellent state of preservation. Carroll (*1, 2*) has restudied all known vertebrate specimens from Joggins, and as a follow-up to his work, we have made a mineralogical study of the teeth. We have identified dentin from microsaur teeth as francolite, with a fluorine content much higher than any previously reported from analyses of fossil teeth.

These fossils occur in rocks of the Cumberland group, facies B (*3*), exposed along 40 miles (64 km) of sea cliffs on the south shore of Chignecto Bay at the head of the Bay of Fundy. They were first studied by W. M. Dawson who, with Sir Charles Lyell, visited the site in 1851 and discovered vertebrate fossils in one of the fossil tree stumps that had fallen to the beach from the cliff near Coal Mine Point. A series of papers by Dawson (*4*), Lyell (*5*), and Sir Richard Owen (*6*) were culminated in Dawson's comprehensive work (*7*), published in 1882. Despite the development of geology and paleontology since then, and the extensive field work that has been carried on in Nova Scotia and elsewhere during the intervening years, this fauna continues to be of unique interest since there are no terrestrial deposits earlier than Joggins (*2*) that contain remains of vertebrates. Because the rocks also contained well-preserved plant fossils, Bell (*8*) was able to date the sediments as Westphalian B (similar in age to the Pottsville deposits of Pennsylvania); hence these animals lived approximately 250 million years ago.

Most Carboniferous deposits throughout the world are from coal swamps. Although they present a fairly complete record of aquatic forms, they furnish little information about life on land. However, during Westphalian B, the Joggins area was apparently a restricted basin of rapid deposition. Sediments approximately 3.2 km thick are exposed along the cliff, and all were deposited in a relatively short period of time. At least 40 successive forests were buried so rapidly that the trees remained upright in their original position. Most of the trees were lycopods of the genus *Sigillaria*, and they formed stumps that were particularly favorable for trapping land animals. During the deposition of several layers, conditions were such that the broken ends of the trees remained exposed at the level of a new land surface. Since the interior of the stumps had a rather pulpy composition, it rotted out, leaving large well-like holes. These hollow cylinders served as traps for animals living on the new land surface; they fell in and could not climb out again (Fig. 1). Such a method of entrapment would favor the preservation of terrestrial rather than aquatic animals, as Carroll (*2*) has pointed out. In addition to the vertebrates, the fossil material that has been found at the base of these stumps includes the earliest terrestrial gastropods, many millipeds, some insects, and many eurypterids.

Dawson appears to have been particularly interested in the teeth of the tetrapods. No doubt the excellent preservation of many of the teeth, in contrast to the crushed and intermingled condition of many of the bone fragments, led to a natural emphasis on

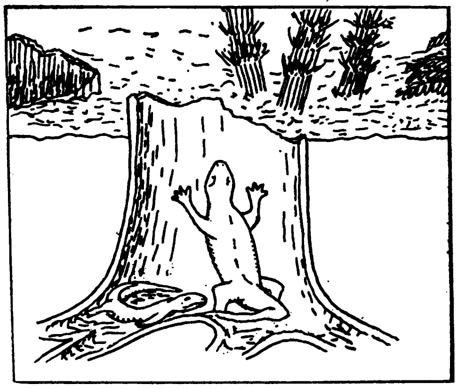

Fig. 1. Reconstruction of the Carboniferous forest at Joggins, showing microsaurs trapped in a *Sigillaria* stump.

study of the teeth. However, because of the limited facilities for mineralogical research during the 19th century, most of Dawson's work was confined to careful figuring of many of the teeth and to some study with the biological microscope (*7*).

We were greatly restricted because much of the Joggins collection consists of type fossils in which the jaws and teeth must remain intact. In addition, microsaur teeth were small in contrast to the teeth of other fossil animals that have been studied mineralogically. For example, Brophy and Hatch (*9*) worked with fossil horse teeth while McConnell (*10*) worked with dental enamel from a mastodon.

Although the Joggins vertebrates ranged in size from approximately 5 inches (12.7 cm) to 4 feet (1.3 m) from nose to tail, it was rather discouraging to discover that some of the largest species had the smallest teeth. Furthermore, a number of the larger specimens were labyrinthodont amphibians, animals characterized by teeth in which the enamel surface is infolded in a complicated way into the tooth itself, and in such species it is difficult to separate enamel from dentin. However, we made general studies of all tooth material available, and found only minute, but possibly significant, variations in mineralogical constants among the species. In their studies of recent and fossil vertebrate teeth, Osmund and Sawin (*11*) also noted small mineralogical variations among the teeth of various animals. However, the significance appears uncertain.

We confined our detailed studies to the teeth of the gymnarthrid microsaur *Hylerpeton dawsoni* because the best tooth material for our work was obtainable from this species. This is a small amphibian (*12*) with crushing, rather than grinding, teeth and small limbs. Although this animal was only about 30.5 cm long, its teeth were relatively large, simple conical structures that yielded good material for study. We were able to work with portions of a few teeth and one whole tooth from the mid-region of the upper jaw (Fig. 2).

Both thin sections and mineral grains of teeth were studied. The enamel consisted of bundles of fine apatite fibers; the dentin showed a radial pattern and the larger crystallites were between 0.002 and 0.005 mm in diameter. The refractive indices were determined as 1.605 and 1.608; x-ray powder diffraction data were satisfactorily obtained (*13*), and it appeared that the tooth apatite might contain relatively large amounts of both fluorine and carbon dioxide.

Since, as McConnell (*14*) has emphasized, the x-ray diffraction method is not reliable for determining fluorine, the remaining dentin was sent to W. D. Armstrong, Department of Biochemistry, Medical School, University of Minnesota, who was able to determine the fluorine content by the microchemical method he developed for use on teeth and bones. The fluorine content of the tooth dentin was 3.1 percent, establishing that the material was crystallochemically identical with francolite, a carbonate fluorapatite. The point of distinction between dahllite and francolite is arbitrarily set at a fluorine content of 1 percent by weight, in accordance with the observation that most specimens fall distinctly into one category or the other (*15*). This high percentage of fluorine is in contrast to 0.03 percent that was found for fossilized dental enamel from a mastodon tooth (*10*) and 0.10 percent for *Parahippus* tooth enamel (*9*).

The surrounding rock from the tree stump under study had an average fluorine content of 0.29 percent. Although this is less than one-tenth of the fluorine found in the tooth material, it is nevertheless quite high for sedimentary materials. This suggests that the seemingly nonfossil portion of the rock that filled the stump was "contaminated" by minute tooth and bone fragments that would have given the rock a small francolite component, since apatite materials, such as tooth and bone, will extract fluoride ions from waters that contain only a few parts of fluorine per million (*14*). In fact, bone char has sometimes been used for the defluoridation of drinking water.

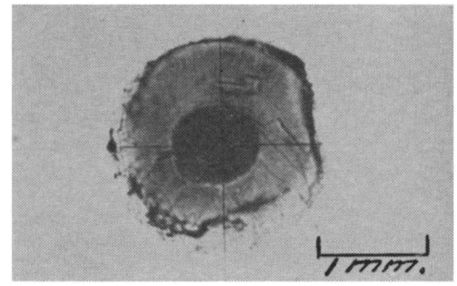

Fig. 2. Cross section of a tooth of *Hylerpeton dawsoni* in 1.610 immersion oil, plane light. The tooth is composed largely of dentin, with enamel forming a very narrow coating around it; coal-like material forms discontinuous black segments at or near the periphery. The pulp chamber in the center is filled with resinous material.

McConnell and others have established the fact that, in all living, tooth-bearing animals, dental enamel and dentin are composed of a single crystalline phase, dahllite, a carbonate hydroxyapatite, in which there is substitution within the crystal lattice of carbonate groups for the phosphate groups (*14*). Fossil teeth are presumed to have been formed originally of dahllite, and in previous studies of younger fossil teeth the composition has also been found to be that of dahllite (*9, 10*).

It seems likely that these well-preserved microsaur teeth were originally composed of dahllite and were converted from dahllite to francolite through interaction with fluorides in ground water, sea water, or connate water (*14*). Work by Eanes, Posner, and others (*16*) has suggested that a rise in fluoride content in apatites in the human body produces a more stable apatite by improved crystallinity and by the isomorphous substitution of fluoride in the apatite structure. A similar process appears to have occurred since the teeth of *Hylerpeton dawsoni* were first buried in the Joggins tree stumps.

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19 August 1966

Helium-Neon Laser: Thermal High-Resolution Recording

Abstract. *Scan-line recording by means of a moving laser spot has been achieved on metallic and organic thin films. Recording rates of the order of one million spots per second were obtained with a laser beam power of 38 milliwatts at the recording surface. Typical recorded line widths were of the order of 2 microns.*

Basic considerations indicated that laser recording of very high resolution (> 400 lines per millimeter) should be possible with what we now term heat-mode recording. We define laser heat-mode recording as any detectable physical or chemical change in the recording medium caused by a temperature rise due to absorption of energy from the laser beam. In general, such a recording is "real time" since the recorded data is immediately available for sensing and does not make use of a latent image effect requiring subsequent processing or treatment.

Our preliminary theoretical studies indicated that high-resolution, heat-mode recording should be possible on thin films with optics of reasonable numerical aperture (> 0.2) with a low divergence, uniphase laser beam with an output greater than 20 mw. Practical considerations dictated that the laser should be continuous wave. The particular wavelength of the laser was of minor concern in that we were free to select recording media that showed adequate absorption at the laser wavelength. We preferred a laser wavelength in the visible range because of the availability of suitable optics, the convenience of working in the visible portion of the spectrum, and the high resolution possible with visible radiation.

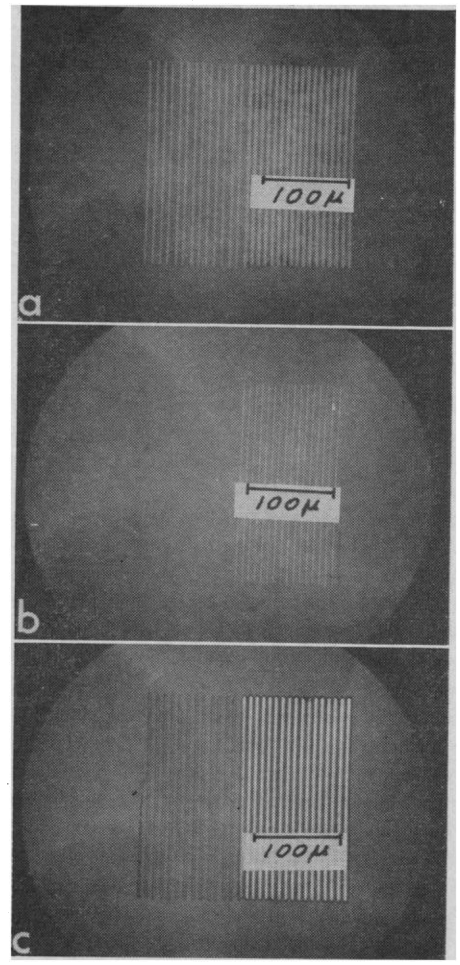

Fig. 1 (top right). High-resolution recording by laser thermal effects on thin films, illustrating (a) lead, (b) tantalum, and (c) a triphenylmethane dye in a plastic binder. Left half of a, b, and c at 0.1 msec per scan line, and right half at 1.0 msec per scan line; beam power 38 mw.

A Spectra-Physics model 125 helium-neon laser was used for our initial experiments. Its uniphase power output at 6328 Å exceeded 50 mw with a beam divergence that was within a factor of 2 of being diffraction-limited. Apparatus was constructed to move a focused spot at the recording medium through a series of parallel lines. The optical system was carefully designed to conserve power and to limit losses to unavoidable reflections. Although desirable, optical surfaces were not coated with antireflection films for the 6328-Å wavelength. The system could also operate without the scanning motion to record single spots.

The cross-sectional distribution of energy in the laser beam has been assumed to be gaussian. The radius of the beam is defined as the distance from the center of the beam to the point where the flux density has fallen to 0.135 of its peak value. When the laser beam is focused to a small spot, its distribution remains gaussian. The final recording lens had a 0.4 numerical aperture and produced a focused spot, as defined, which was 1.8 μ in diameter. The maximum power of the beam transmitted to the recording medium was 38 mw. This corresponds to an average power density of 1.5×10^6 watts/cm^2.

The recording media have been in the form of thin films on glass sub-

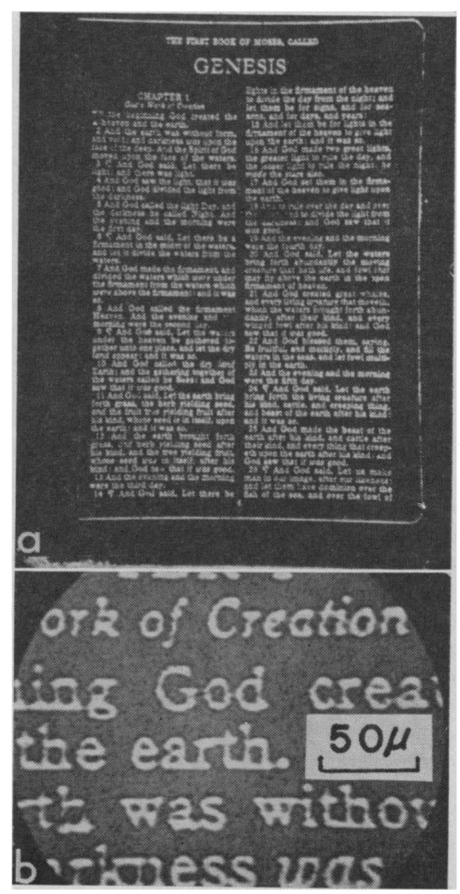

Fig. 2 (bottom right). A facsimile-type laser thermal recording of the first page of the Bible, showing (a) the complete page, and (b) a portion of the page to illustrate detail.