are also used by taxonomists and paleontologists to distinguish species of living and extinct representatives of several different phyla of invertebrate organisms (for example, mollusks, brachiopods, ostracods). Similar uses for patterns of attachment scars should now be considered by specialists dealing with scleractinian corals (*9*).

SHERWOOD W. WISE, JR.
Department of Geology,
Swiss Federal Institute of Technology,
CH-8006, Zürich, Switzerland

References and Notes

1. J. W. Wells, in *Treatise on Invertebrate Paleontology, Coelenterata*, R. C. Moore, Ed. (Univ. of Kansas Press, Lawrence, 1956), part F, p. 328; T. Sato, *Earth Sci. (Chikyu Kagaku)* **66**, 9 (1963); S. A. Wainwright, *Quart. J. Microscop. Sci.* **104**, 169 (1963); ———, *Exp. Cell Res.* **34**, 213 (1964); A. v. Schouppé and P. Stacul, *Palaeontogr. Suppl.* **11**, 1 (1966); J. Vahl, *Z. Morphol. Oekol. Tiere* **56**, 21 (1966).
2. J. E. Sorauf, *Abstracts with Programs for 1969* (Geological Society of America, Denver, Colorado, 1969), part 7, p. 210.
3. S. W. Wise, Jr., in *Scanning Electron Microscopy 1969*, O. Johari, Ed. (Illinois Institute of Technology Research Institute, Chicago, 1969), p. 205; ———, *Abstracts with Programs for 1969* (Geological Society of America, Denver, Colorado, 1969), part 7, p. 241.
4. G. C. Bourne, *Quart. J. Microscop. Sci.* **41**, 499 (1899).
5. M. M. Ogilvie, *Phil. Trans. Roy. Soc. London Ser. B Biol. Sci.* **187**, 83 (1896). Ogilvie's illustrations of "calcareous scales" show granular elements 10 to 15 μm in diameter which are oriented at an oblique angle to the skeletal surface (fasciculi commonly have the same dimensions and orientation). Ogilvie believed that the "calcareous scales" were calcioblast cells which were first formed by the epidermal layer and then deposited *in toto* on the skeletal surface where they calcified to form skeleton. This theory was disproven by the work of K. Hayasi, *Palao Trop. Biol. Sta. Stud.* **2**, 169 (1937).
6. G. Matthai, *Trans. Linn. Soc. London Ser. 2 Zool.* **17**, 1 (1914); *Quart. J. Microscop. Sci.* **67**, 101 (1923).
7. Mesenteries are radially disposed partitions of living tissue attached to the inner surface of the oral disk and the column wall of the polyp.
8. A. L. McAlester, *Palaeontology* **8**, 231 (1965).
9. In reviewing this report, Dr. J. W. Wells noted that "if these scars could be detected in fossil corals, some problems, such as where the tabulate corals belong, might be solved" (J. W. Wells, personal communication, 1970).
10. Supported by NSF grants GP-1991 and FP-5056 to Dr. W. W. Hay and by a summer research grant from the Department of Geology, University of Illinois. Dr. B. V. Hall, director of the Central Electron Microscopy Laboratory, University of Illinois, kindly made available the Cambridge Mark IIA scanning electron microscope used in the study. The instrument was purchased with funds from NSF (NSF GA-1239), PHS (PH FR-07030), and the University of Illinois Research Board. I especially thank Dr. J. W. Wells (Cornell University) and Dr. W. W. Hay (University of Illinois) for critical readings of the manuscript, and Dr. Wells for identifying the coral specimens.

11 June 1970

Inorganic Liquid Photovoltaic Cell: Tetravalent Molybdenum in Water

Abstract. *An inorganic liquid photovoltaic cell is described. The cell is based on the reaction* $2Mo^{4+} \leftrightarrows Mo^{5+} + Mo^{3+}$, *with pentavalent molybdenum formed in the illuminated half-cell and trivalent molybdenum formed in the dark half-cell. In the photochemical reaction pentavalent molybdenum precipitates. Consequently, the cell has the capability of storing energy.*

We report a new liquid photovoltaic cell based on the disproportionation of excited Mo^{4+} to Mo^{3+} and Mo^{5+}. The sequence of reactions in the illuminated side of the cell is

$$Mo^{4+} \xrightarrow{h\nu} (Mo^{4+})^*$$

$$(Mo^{4+})^* \rightarrow Mo^{5+} + e$$

The reaction in the dark side is

$$Mo^{4+} + e \rightarrow Mo^{3+}$$

The net reaction is

$$2Mo^{4+} + h\nu \rightarrow Mo^{3+} + Mo^{5+}$$

The photovoltaic effect is due to the accumulation of Mo^{5+} in the illuminated side and the simultaneous accumulation of Mo^{3+} in the dark side.

The experimental cell is shown in Fig. 1. The cell is made of two Pyrex test tubes 25 mm in inside diameter connected by glass tubing 6 mm in inside diameter with a very fine glass frit. The two sidearms are used to flush the solutions with nitrogen, the stream of which also stirs the solution. The platinum electrodes have an area of 0.5 cm². The thermometers in the two sides are necessary so that the temperature in the illuminated side does not exceed the temperature in the dark side.

To ensure temperature uniformity and to rule out thermal potential differences, the whole cell is immersed in a thermostated water bath (25.0° ± 0.5°C). The light source used is a tungsten halogen lamp (General Electric "quartzline," model FAL). The 420-watt lamp is kept at a distance of 15.3 cm from the cell. To exclude light from the dark side, one of the test tubes is wrapped with aluminum foil.

The materials used were colorless hydrated ammonium molybdate $(NH_4)_6$-$Mo_7O_{24} \cdot 4H_2O$, and red "$(NH_4)_2MoCl_5 \cdot H_2O$." In the first compound, which is commercially available, molybdenum is hexavalent. The second compound, in which molybdenum is trivalent, was prepared as described by Palmer (*1*, pp. 413–415), except that we used nitrogen rather than carbon dioxide as our oxygen-free atmosphere. We obtained Mo^{4+}, also as described by Palmer (*1*, pp. 410–413), upon mixing a solution containing one equivalent of the Mo^{6+} compound with two equivalents of the Mo^{3+} compound. The formation of Mo^{4+} requires about 5 minutes. By mixing equal amounts of an 0.05*M* Mo^{3+} solution and an 0.025*M* Mo^{6+} solution, we obtained an Mo^{4+} concentration of 0.0375*M*. The Mo^{4+} solution, which has a deep green-black color, was used to fill both sides of the photovoltaic cell.

Figure 2 shows the voltage development after the light is switched on. A plateau of 88 mv is reached in about 15 minutes. The cell is capable of storing electrical energy. When the light is switched off, the drop in the cell's voltage is very slow unless a current is drawn (there is no substantial drop in potential in 2 hours). As the voltage develops, the color of the solution changes from dark green to light brown in the illuminated side and from dark green to brown-green in the dark side. We assign, by polarographic experiments, the yellow-brown solution and the crystals precipitated in the illuminated side to Mo^{5+}, and the brown-green solution in the dark side to Mo^{3+}. The color changes are consistent with the formation of Mo^{5+} and Mo^{3+}. On the illuminated side the Mo^{5+} precipitates as the light brown "$MoO(OH)_3$," which dissolves in concentrated hydrochloric acid to give the dark green Mo^{5+} solution (*1*, pp. 406–407). If ammonium carbonate is added to the solution in the dark side, a red compound, characteristic of Mo^{3+}, precipitates (*2*).

To prove the nature of the light-induced reaction, we subjected the starting solution and its photoproducts to a polarographic study. The solvent and supporting electrolyte for the polarography in all cases was 3*N* HCl. All of the reactions described below were carried out in a nitrogen atmosphere.

To establish that the molybdenum was indeed in the tetravalent state prior to irradiation, the molybdenum in the solution was precipitated as "py_2H_2Mo-$(CNS)_6$" (where py represents pyridine), and then converted to "Cd_2Mo-

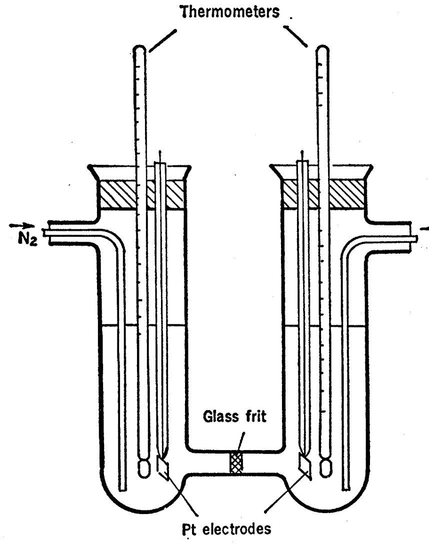

Fig. 1. Schematic drawing of the experimental cell.

$(CN)_8 \cdot 8H_2O$," and finally to "$K_4Mo(CN)_8 \cdot 8H_2O$" (*1*, pp. 410–413). In parallel, the same preparative route to "$K_4Mo(CN)_8 \cdot 8H_2O$" was followed, starting with a concentrated HCl solution of "$MoCl_4$" (Research Organic/Inorganic Chemical Corporation, Sun Valley, California). The polarograms of the two substances were identical, showing a half-wave potential $E_{1/2}$ of −0.12 volt.

The formation of Mo^{5+} on the illuminated side of the cell was established as follows: The brown precipitate formed upon irradiation was dissolved in HCl and reprecipitated with ammonium carbonate as brown "$MoO(OH)_3$" (*1*, pp. 406–407). The polarogram of this substance in 3*N* HCl was identical with a polarogram obtained from a sample of "$MoO(OH)_3$" prepared by adding ammonium carbonate to a concentrated HCl solution of "$MoCl_5$" (Research Organic/Inorganic Chemical Corporation). Both samples show polarograms with half-wave potentials of −0.11 volt and −0.45 volt.

That Mo^{3+} was formed in the dark side of the cell was shown by comparing the polarogram of a known sample of "$(NH_4)_2MoCl_5 \cdot H_2O$" with that of the dark red precipitate obtained by adding ammonium carbonate to the solution in the dark side (*1*, pp. 413–415). The polarograms of these two materials were identical ($E_{1/2} = -0.43$ volt).

The concepts that we applied to identify the present photovoltaic liquid were the following:

1) Ions, atoms, and molecules all become stronger reducing agents upon excitation: The electron promoted to a higher energy level requires less energy for its removal.

2) To obtain efficient electron transfer reactions it is necessary to have relatively long-lived excited states. If either the radiationless or the radiative transitions are excessively rapid relative to the electron transfer reaction, the quantum yields are small and the effects negligible. Criteria for adequately long life are (i) photochemical reactivity of the excited species and (ii) luminescence with long decay. Molybdenum (IV) is known to undergo photochemical reactions, and photoelectron ejection has been reported in the cyano complex of Mo^{4+} (*2*).

3) The absorption spectrum of the product in the illuminated cell must not mask the spectrum of the reactant. The Mo^{4+} ion is deep green; the product (the Mo^{5+} formed in the illuminated side) is light brown and precipitates out.

4) The rate of reverse reaction, in which the photooxidized species is reduced by the ejected solvated electron, or by a reduced material that is produced, must be slow relative to the diffusion of the solvated electron to the electrode or the diffusion of the reduced intermediary to the electrode. This criterion is met in our experiment because the solubility of Mo^{5+} in our solution at *p*H 4 is limited and the oxidized product is removed from the equilibrium when formed. Indeed, our photovoltaic cell cannot be operated in strongly acid solutions, in which Mo^{5+} dissolves.

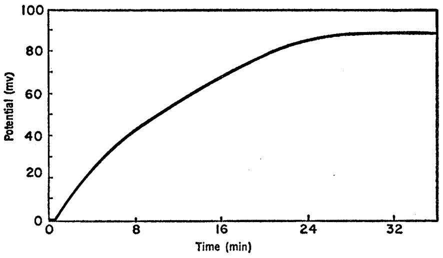

Fig. 2. Development of the potential after exposure of the half-cell to light.

MARJORIE H. NAVIDI
HARRY G. BRITTAIN
Chemistry Department, Queens College, City University of New York, Flushing 11367
ADAM HELLER
Bayside Research Center of General Telephone & Electronics Laboratories, Inc., Bayside, New York 11360

References

1. W. G. Palmer, *Experimental Inorganic Chemistry* (Cambridge Univ. Press, London, 1965).
2. W. L. Waltz, A. W. Adamson, P. D. Fleischauer, *J. Amer. Chem. Soc.* **89**, 3923 (1967).

5 June 1970; revised 2 July 1970

Garnet: First Occurrence in the Lunar Rocks

Abstract. *Three grains of almandine-rich garnet isolated from lunar sample 12021 have the composition* $Alm_{70.7}Gro_{25.0}Sp_{2.7}Pyr_{1.6}$, *with cell edge of 11.624 angstroms and refractive index of 1.81. The garnet probably formed late in the crystallization sequence.*

In our study of lunar sample 12021 returned by the Apollo 12 mission, we have identified three grains of garnet. This rock was described by the Lunar Sample Preliminary Examination Team (*1*) as a porphyritic gabbro, and we have examined a small rock chip (12021,22) and a polished thin section (12021,2). The rock chip, wrapped in aluminum foil, was partly disaggregated when received, and the enclosing foil contained several hundred mineral and rock fragments ranging in size from a few micrometers to a millimeter. During examination of the fragmental material under a binocular microscope, three distinctive grains were observed and isolated (*2*). These grains were pale brown in color with a distinct pink tinge and were free from inclusions, having a gem-quality appearance. They were anhedral and somewhat flattened, varying from 100 to 300 μm in the largest dimension and averaging less than 40 μm in thickness.

The three grains were used for an x-ray powder pattern, microprobe analysis, and refractive index determination. The x-ray powder pattern (*3*) identified the grain as garnet, with a cell edge of 11.624 ± 0.005 Å. The electron microprobe analysis (*4*) showed that the garnet is rich in iron and calcium, with minor amounts of manganese and magnesium (see Table 1). No evidence of chemical zoning was detected in this grain. In calculating the atomic formula (Table 1), all of the iron is assumed to be divalent. This assumption is reasonable in view of the highly re-