

# USES OF LUNAR SULFUR

N 9 3 - 1 3 9 8 1

D. Vaniman, D. Pettit\*, and G. Heiken

EES-1 (\*M-9)

Los Alamos National Laboratory

Los Alamos NM 87545

*Sulfur and sulfur compounds have a wide range of applications for their fluid, electrical, chemical, and biochemical properties. Although known abundances on the Moon are limited (~0.1% in mare soils), sulfur is relatively extractable by heating. Coproduction of sulfur during oxygen extraction from ilmenite-rich mare soils could yield sulfur in masses up to 10% of the mass of oxygen produced. Sulfur deserves serious consideration as a lunar resource.*

## INTRODUCTION

Volatile constituents such as molecular oxygen, nitrogen, water, and hydrocarbons are rare on the Moon. The absence of such molecules is one of the problems that confronts prolonged lunar exploration or permanent lunar bases. The lightweight compounds of the elements from hydrogen to oxygen are vital for life, and many of these elements play important roles as fuels, solvents, and industrial chemicals in processes that have become the necessities of industrialized life on Earth. The scarcity of these elements on the Moon thus raises two barriers against easy expansion into space: one against the simple need to stay alive and the other against easy transplantation of Earthbound industrial processes.

With imagination this assessment need not be so bleak. Living in space will require adaptation, but it also opens opportunities to reassess the ways in which we live and use available resources. Sulfur on the Moon may well prove a satisfactory replacement for lighter volatile elements and their compounds in some applications. It may even open new possibilities and uses that surpass a mere duplication of what is already done on Earth.

Our present knowledge of lunar samples suggests that the best place to collect sulfur on the Moon is from mare soils and rocks. Although sulfur is not so abundant that it is available without effort, it does rank eleventh in weight abundance among the elements in average lunar mare rocks. *Gibson and Moore* (1974) found that the high-Ti mare basalts, in particular, have high sulfur contents, in the range of 0.16% to 0.27% by weight. These authors also make the important point that lunar basalts actually have more sulfur than terrestrial basalts, which seldom have more than 0.15%.

Although terrestrial basalts are relatively low in dispersed sulfur content, this sulfur is extracted and concentrated by circulation of heated water. This process results in the remarkable sulfur-rich environments at midocean spreading ridges, where base-metal sulfides are deposited in great abundance and "unearthly" sulfur-metabolizing organisms proliferate. Clearly, we cannot expect heated water to have concentrated sulfur on the Moon. The relatively high sulfur content of lunar mare basalt 12036, however, led *Gibson et al.* (1977) to speculate on the possibility of Fe-FeS liquid segregation and accumulation in some mare magmas. Discovery of sulfur-rich ore bodies on the Moon would be a major find that could accelerate exploitation immensely, but until their existence is actually proven, it would be unwise to plan on their use.

Another possible means for natural concentration of lunar sulfur may be vapor transport and deposition; the abundance of sulfur in volatile coatings on lunar pyroclastic glass droplets strongly suggests that sulfur was involved as a propellant gas in fire-fountain types of eruptions (*Butler and Meyer*, 1976). However, the analyses of volatile coatings on glass droplets suggest that significant amounts of sulfur are lost rather than trapped on droplet surfaces as a result of pyroclastic eruption. For example, the sulfur contents of the famous pyroclastic "orange glass" deposit of Shorty crater at Apollo 17 contains only 0.06-0.08% sulfur (*Gibson and Moore*, 1974), whereas comparable chilled Apollo 17 lavas retain more than 0.16% sulfur. Unless geologic traps for volatile sulfur are found on the Moon (perhaps in vesicle pipes or lava tubes?), there is reason to believe that lunar volcanic gases have acted more effectively in the dispersal of sulfur than in its concentration. The formation of soil on top of sulfur-rich lava flows also results in decreased sulfur content, through the combined processes of sulfur volatilization by small meteoritic impacts and of dilution by addition of sulfur-poor highland materials (*Gibson and Moore*, 1973, 1974). For practical purposes, the ranking of sulfur contents presently known in lunar samples is about as shown in Table 1.

TABLE 1. Sulfur in lunar samples.

Rock or Soil Type	Sulfur Content (wt%)
High-Ti mare basalts (A-17)	0.16-0.27 (avg 0.21)
Low-Ti mare basalts (A-12)	0.06-0.15 (avg 0.11)
High-Ti mare soils (A-17)	0.06-0.13 (avg 0.10)
Low-Ti mare soils (A-15)	0.05-0.06 (avg 0.05)
Highland rocks (A-16)	0.01-0.14 (avg 0.07)
Highland soils (A-16)	0.03-0.09 (avg 0.06)

Data from *Gibson and Moore* (1973, 1974), *Gibson et al.* (1977), *Kerridge et al.* (1975), and *LSPET* (1972). Note that the ranges and averages cited are for specific Apollo sites (12, 15, 16, and 17); the data include possible analytical differences between laboratories.

Although the richest known sources of sulfur are the high-Ti mare basalts, extraction of this sulfur would require energy-intensive crushing of hard rock. Most of the sulfur in the basalts occurs as sulfide in the mineral troilite (FeS). The easiest source of sulfur is high-Ti mare soils, which need not be crushed prior to processing. In addition to the sulfur in troilite, some surface-correlated sulfur can be found in soil samples. In pyroclastic soils, surface-correlated metal sulfides probably occur (*Butler and*

Meyer, 1976; Cirlin and Housley, 1979), but sulfur may also occur as metal sulfates that are readily volatilized to produce  $\text{SO}_2$  (D. McKay, personal communication, 1988). The heating experiments of Gibson and Moore (1973) on Apollo 15 and 16 samples indicate that 12-30% of the total soil sulfur can be extracted at  $750^\circ\text{C}$ , 50-70% of the total sulfur is extracted at  $950^\circ\text{C}$ , and 85-95% of the total sulfur is extracted at  $1100^\circ\text{C}$  (vacuum conditions,  $<2 \times 10^{-6}$  torr). Gibson and Moore (1974) suggest that the 12-30% of the sulfur extracted at  $750^\circ\text{C}$  is surface correlated. Most of the higher temperature sulfur is probably derived from troilite. The sulfur is given off as  $\text{SO}_2$  and  $\text{H}_2\text{S}$ , which Gibson (1973) attributes mainly to reaction between troilite and other phases at high temperatures.

Sulfur is not the only volatile element to be won. Heating of typical lunar soils will be useful in the cogeneration of small amounts of hydrogen (about 0.001-0.020%), helium (0.001-0.006%), carbon (0.001-0.028%), and nitrogen (0.001-0.016%) that are the solar-wind constituents of lunar fines (Williams and Jadwick, 1980). Heating of high-Ti pyroclastic deposits to  $1200^\circ\text{C}$  will also provide some cogeneration of Zn (0.01-0.03%), Na, K, Cl (0.002-0.010%), F (0-0.02%), and other vapor-transported elements (Cirlin and Housley, 1979; Butler and Meyer, 1976; Meyer et al., 1975).

Thus, although sulfur is not richly concentrated on the Moon, it is present in sufficient abundance and associated with other potentially useful elements that make the mining of lunar sulfur worth serious consideration. However, this consideration will not go very far if there is not a well-established set of end uses for the sulfur and its codeposited elements. Sulfur has a broad range of chemical and physical properties that may make it extremely useful. Perhaps most importantly, sulfur and sulfur compounds have the capacity to substitute for water in many aqueous-based mechanical and chemical processes on Earth. Sulfur research is so broad and diverse that we cannot fully cover its terrestrial applications in this short paper. Moreover, we can only begin to speculate on the possible uses of sulfur in space. Our purpose is rather to suggest several starting points for more imaginative studies on the uses of lunar sulfur. These starting points are discussed below under three broad categories: (1) the use of sulfur fluid and physical properties, (2) the use of sulfur electrical properties, and (3) the use of sulfur chemical and biochemical properties.

### THE USE OF SULFUR FLUID AND PHYSICAL PROPERTIES

Pure sulfur is fluid over a broad range of temperatures. Depending on crystal form, sulfur melts at  $112.8^\circ\text{C}$  (orthorhombic) or  $119^\circ\text{C}$  (monoclinic; Weast, 1982). Although the liquid does not boil until  $444.6^\circ\text{C}$ , it begins to lose its low-temperature fluidity and become very viscous at about  $160^\circ\text{C}$ . Figure 1 shows the variability of viscosity with temperature. At average lunar daytime temperatures ( $\sim 107^\circ\text{C}$ ) minimal heat input would maintain sulfur as a low-viscosity liquid. At the maximum lunar equatorial daytime temperature ( $123^\circ\text{C}$ ) no additional heat would be necessary to keep sulfur molten.

#### Sulfur Concrete

A direct application of liquid sulfur on the Moon would be in the production of sulfur concrete (Crow and Bates, 1970). Sulfur concrete has found many applications on Earth and is being used in areas where corrosion resistance is important or in extreme

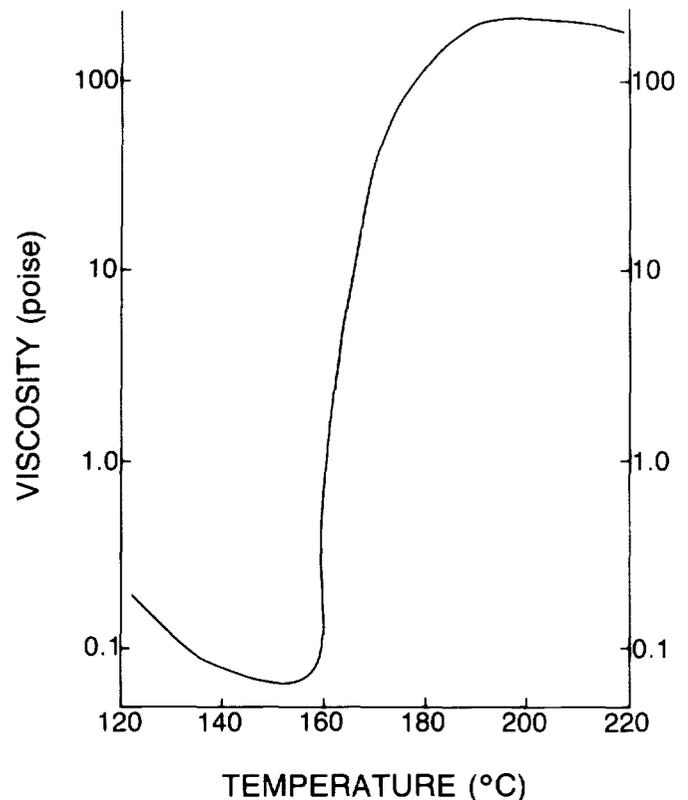


Fig. 1. Viscosity of liquid sulfur (gas free) as a function of temperature (data from Weast, 1982).

desert environments (Sulphur Institute, 1979). A particular advantage of sulfur concrete on the Moon is that it needs no water in its production and is best poured hot at temperatures of  $125^\circ$  to  $140^\circ\text{C}$ , which are only slightly higher than the average lunar daytime temperature. Contrasted with water-based concrete, sulfur concrete attains most of its final strength within hours rather than weeks and has more than twice the compressive and tensile strength. Weight ratios of sulfur to aggregate are approximately 1:3, so that the amount of sulfur concrete produced could be about four times the amount of sulfur mined on the Moon. Thermal stability is a concern; Crow and Bates (1970) suggest that sulfur concrete be used only in buried structures on the Moon where full-sun thermal exposure will not be a problem.

#### Sulfur Sealants

Lunar habitats must be capable of maintaining a pressurized atmosphere. Some redundancy in sealants to contain the atmosphere is desirable, and a method of spray-impregnating walls of regolith or the internal surfaces of lava tubes might be useful. Thioelastomers (thiokols) can be mixed with small amounts of molten sulfur to make extremely tough materials (Leclercq, 1972). The production requirements of hard or rubbery coatings are presently too complex for simple extension to the Moon, but imaginative use of organic waste with lunar sulfur might produce a useful sealant.

#### Sulfur Dioxide for Fluid Uses

As noted in the introduction, Gibson (1973) found that most sulfur released from lunar samples by heating in vacuum is not released as S but as  $\text{SO}_2$  or  $\text{H}_2\text{S}$ . Contrasted with pure sulfur,  $\text{SO}_2$

has a more useful range of fluid properties and has physical-chemical properties that can fit special fluid-application requirements. Sulfur dioxide is liquid between  $-75.52^{\circ}\text{C}$  and  $-10.08^{\circ}\text{C}$ , with corresponding viscosities between 0.0068 and 0.0043 poise. This liquid is a polar solvent, although its dipolar attractive field is weaker than that of water. Where water is an excellent solvent for strong dipoles, liquid  $\text{SO}_2$  is a better solvent for nonpolar or easily polarized molecules. Sulfur dioxide is a good solvent for halogens and for olefinic and aromatic hydrocarbons, but it is a poor solvent for aliphatic hydrocarbons (Burou, 1970). The halogens are quite soluble in liquid  $\text{SO}_2$ ; metal chlorides are highly soluble and this property may be particularly important on the Moon. There is strong evidence that many of the metals with high boiling points (e.g., Zn and Ga) that are found on the surfaces of lunar pyroclastic particles were transported and deposited as more volatile metal chlorides (Meyer et al., 1975). If this is the case, then these deposits might be easily stripped and collected from pyroclastic deposits using an  $\text{SO}_2$  washing process.

There are many potential uses of  $\text{SO}_2$  as a fluid. Some attractive possibilities are in refrigerant systems, in turbines (Rankine cycle), in heat transfer systems (liquid phase), in heat pipes (gas phase), in slurry lines for regolith or waste transport, and in hydraulic systems. Availability of  $\text{SO}_2$  will open a broad range of possibilities for controlling energy and materials on the Moon. An important caveat in the use of  $\text{SO}_2$ , however, is its extreme toxicity. The fluids in use would have to be isolated from habitats.

## THE USE OF SULFUR ELECTRICAL PROPERTIES

Sulfur, especially in Na-S combinations, has potential use in both solar energy collection systems and in storage batteries.

### Solar Energy Conversion

There is considerable active research into  $\text{Cu}_2\text{S}$ -based thin-film solar cells and several sulfur-bearing photoelectrochemical (PEC) cells (Chopra and Das, 1983). The thin-film solar cells employ a heterojunction between two metal sulfides, one of which is  $\text{Cu}_2\text{S}$  (p-junction) and the other a sulfide of Cd or ZnCd (n-junction). Such cells are still being perfected; efficiencies were around 7% in the mid 1970s but had risen to about 10% by 1981. One advantage of these cells is that they are, as the name implies, thin films of relatively light mass. The cells are layered structures, with layers as thin as a few tens or hundreds of angstroms deposited in sequence. Total thickness of the cell would typically be 5-50  $\mu\text{m}$ . The efficiency of present  $\text{Cu}_2\text{S}/\text{CdS}$  cells crests at light intensities between 20 and 120  $\text{mW}/\text{cm}^2$ , a range that includes the one-sun intensity of 50  $\text{mW}/\text{cm}^2$ . Although the efficiency of this system is currently less than half that of some advanced photovoltaics systems now under investigation (InP or GaAs; Flood, 1986), there is a possible advantage in that the sulfur would not have to be imported.

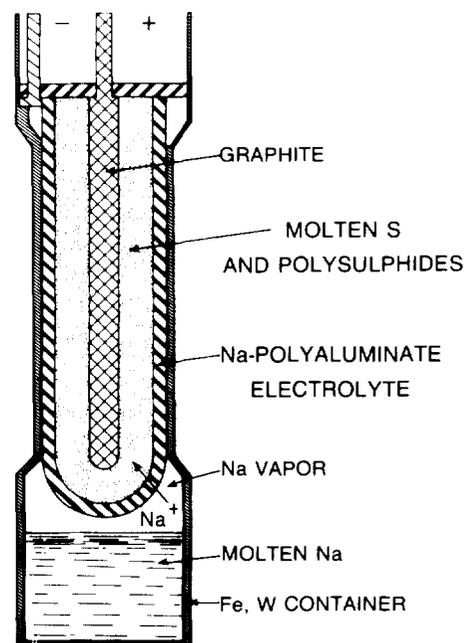
In practice, the need for some material imports (mostly Cd) may be a potential problem in production of thin-film solar cells on the Moon. Most of the cell mass is Zn and Cd, and Cd is critical to efficient thin-film cells. Although there is good reason to believe that both S and Zn occur in extractable quantities in lunar pyroclastic deposits (0.07% S and 0.02% Zn; Gibson and Moore, 1974; Butler and Meyer, 1976), Cd is not comparably enriched. In addition, once the cells are produced, it is not known how well they might survive in the space environment. Still, this is an energy conversion system that is worth serious consideration. One

potentially advantageous aspect of the thin film cells is the evidence that vacuum evaporation is probably the best method for cell production (Chopra and Das, 1983). High-vacuum systems should be relatively easy to operate in space.

An alternative approach to the use of sulfur in solar energy collection is through a photoelectrochemical (PEC) effect. Sulfur is important in the electrolyte solution as a "hole scavenger" at the photoanode. A well studied PEC cell configuration uses a CdSe photoanode with a CdS interface against an electrolyte (Chopra and Das, 1983). One practical electrolyte contains various proportions of  $\text{Na}_2\text{S}$ , S, and NaOH (Russak et al., 1980). The cell efficiencies observed range from 3% to 8%. As with the thin film cells, a potential drawback may be the need to import Cd and, in this case, Se for lunar production. Economic study may well show that it would be more advantageous to form light photocells on Earth and export them intact to the Moon, or to rely on possible crude but rugged cells such as those that might be made out of minimally processed lunar ilmenite (Meet et al., 1987).

### Electrical Energy Storage

The greatest payoff in the use of indigenous lunar sulfur for electrical applications may be in the *in situ* production of relatively massive storage batteries. Sulfur-based storage batteries have widespread applications on Earth. In addition to the ubiquitous Pb-PbO<sub>2</sub>-H<sub>2</sub>SO<sub>4</sub> battery (which, unfortunately for lunar use, requires precious water), there is active research in the development of molten electrolyte Na-S storage cells for electric vehicles. These cells operate at about 300-350 $^{\circ}\text{C}$ , with a two-stage discharge that derives electrons from Na-to- $\text{Na}^+$  oxidation by (1)  $5\text{S} + 2\text{Na} \rightarrow \text{Na}_2\text{S}_5$  and (2)  $3\text{Na}_2\text{S}_5 + 4\text{Na} \rightarrow 5\text{Na}_2\text{S}_3$ . The discharge voltage of the cell varies with the reaction stage, from about 2.08 V for reaction (1) to 1.76 V for reaction (2) (Bagotzky and Skundin, 1980, pp. 320-337). The predicted cell performance for the near future is 150-200 W-hr/kg. A schematic cross section of a Na-S storage battery is shown in Fig. 2.



after Bagotzky and Skundin, 1980

Fig. 2. A molten electrolyte Na-S battery (after Bagotzky and Skundin, 1980).

The electrolyte for the cell is a sodium polyaluminate (with  $n = 3-11$  in the formula  $\text{Na}_2\text{O} \cdot n\text{Al}_2\text{O}_3$ ) that is porous to  $\text{Na}^+$ . This electrolyte is formed as a ceramic and is difficult to manufacture (Bagotzky and Skundin, 1980); this component and the porous graphite positive electrode would probably have to be supplied from Earth. The requirement for Na as well as S may be viewed critically in terms of availability on the Moon, but there is some evidence for Na associated with the surface-deposited volatiles of lunar pyroclastic deposits (Cirtin and Housley, 1979). The sodium mineralogy and abundances in these deposits are poorly known, but the possible use in batteries justifies further study. Should the indigenous lunar sodium be found insufficient, a useful alternative may be to import NaOH, which could be processed after arrival to provide Na,  $\text{O}_2$ , and  $\text{H}_2\text{O}$  (all of great value on the Moon).

## THE USE OF SULFUR CHEMICAL AND BIOCHEMICAL PROPERTIES

The chemical uses of sulfur are so varied that we can only touch on a few in this paper. The examples chosen are those that appear to the authors to have important potential applications on the Moon.

### Sulfuric Acid

Sulfuric acid usage is a common measure of industrial capacity on Earth; this acid has so many uses that it is practically a generic guide to productivity. A large number of potential uses on the Moon might be considered, but these must be weighed against the need to consume water in the production of sulfuric acid. As one example of possible uses, the acid could be employed in thermochemical splitting of water to produce  $\text{H}_2 - \text{O}_2$  for propellant or for fuel cells (see below). A very different example of sulfuric-acid use would be the destruction of organic waste as part of a Closed Ecological Life Support System ("CELSS"; MacElroy et al., 1985). Highly concentrated sulfuric acid can remove hydrogen and oxygen from some organic compounds to produce water; simple plant sugars might be processed in this manner.

The production of sulfuric acid on the Moon might occur as a variant of the terrestrial contact process, in which  $\text{SO}_3$  is made by catalytic oxidation of  $\text{SO}_2$  (over platinum or vanadium pentoxide) and bubbled through relatively dilute sulfuric acid to produce concentrated acid. This process would require oxygen input to oxidize the relatively reduced sulfur that occurs in lunar regolith. Sulfuric acid can also be produced by electrolysis of  $\text{SO}_2$  in water (see section on thermochemical water splitting, below). In a closed system the depletion of water and oxygen could be minimized, but some loss will probably be incurred and the benefits must be weighed against this loss.

Sulfuric acid production and control is almost a necessary adjunct industry if oxygen is to be produced from lunar ilmenite. Sulfur is a serious contaminant in the reduction of lunar ilmenite;  $\text{H}_2\text{S}$  and sulfur-based acids would pose serious problems through corrosion and induced electrolysis of water. The most direct way to avoid such problems would be to extract (and use) the sulfur before the ilmenite concentrates are processed for oxygen.

### Thermochemical Water-Splitting

Water can be split into  $\text{H}_2$  and  $\text{O}_2$  for collection and cooling to provide liquid rocket propellant. On a smaller scale, water might be split for use in hydrogen fuel cells. Fuel cells may be

particularly useful if the water is reclaimed at the exhaust. There are several options for producing  $\text{H}_2$  from water on the Moon; extraction from waste methane and electrolysis of water are both possible. Thermochemical splitting of water, however, would be advantageous where reactor power is available to provide a high-temperature heat source. Doktya et al. (1979) describe both an  $\text{SO}_2$  hybrid cycle and a  $\text{SO}_2\text{-H}_2\text{S}$  cycle for thermochemical splitting of water. The  $\text{SO}_2$  hybrid cycle uses electrolysis of  $\text{SO}_2 + 2\text{H}_2\text{O}$  to produce  $\text{H}_2\text{SO}_4 + \text{H}_2$ , followed by thermal dissociation of the sulfuric acid at  $800^\circ\text{-}850^\circ\text{C}$  to produce  $\text{H}_2\text{O} + \text{SO}_2 + 1/2\text{O}_2$ . The  $\text{SO}_2\text{-H}_2\text{S}$  cycle requires only heat energy ( $830^\circ\text{C}$ ) but has four steps and requires input of both  $\text{H}_2\text{S}$  and  $\text{SO}_2$  as well as water. For lunar applications the  $\text{SO}_2$  hybrid cycle is probably most attractive because of its relative simplicity (two steps instead of four) and the relative conservation of sulfur as  $\text{SO}_2$  (output ideally equals input but is limited by 70-80% conversion efficiency). The most significant drawback of this method is the requirement for use of electrical as well as thermal energy.

### Sulfur as a Fluxing Agent

Sulfur is used terrestrially as a fluxing agent in reducing the melting points of glasses. This use may also be practical on the Moon, where glass production may be sought for structural uses (Blacic, 1985). Experiments with a variety of regolith-sulfur mixtures are needed to determine the utility of such a process.

### The Brimstone Rocket

Production of rocket propellants from lunar resources would be a major boon for expanded space exploration (National Commission on Space, 1986). There has been considerable study of systems to produce oxygen from lunar regolith, particularly from concentrates of lunar ilmenite (Cutler and Krag, 1985; Gibson and Knudsen, 1985). Lunar sources of fuels to be oxidized, however, are extremely scarce. Hydrogen is so rare that extensive use for propellant may require expensive imports, perhaps as methane or ammonia from Earth (Friedlander, 1985). Other fuels such as silane ( $\text{SiH}_4$ ; Rosenberg, 1985) might be produced in part from lunar feedstocks but would still require hydrogen imports. In contrast, sulfur might provide a truly indigenous lunar fuel.

Some sulfur release will be an inevitable byproduct of lunar oxygen production. Lunar oxygen production is targeted on mare regoliths with high ilmenite content; these are also the regoliths with highest sulfur content (0.06% to 0.13%; see Table 1). In an oxygen production plant such as Cutler and Krag (1985) envisioned, the sulfur byproduct would be about 1% of the  $\text{O}_2$  mass produced, assuming 0.1% collectable S in the ilmenite-enriched feedstock. If the tailings from ilmenite enrichment are also processed for sulfur, then the total sulfur production would be about 10% of the  $\text{O}_2$  mass. These proportions permit serious consideration of a sulfur-oxygen propulsion system (a "brimstone" rocket).

The brimstone rocket could be fueled with liquid sulfur and liquid oxygen, the sulfur being kept between  $150^\circ$  and  $160^\circ\text{C}$  where its viscosity is lowest and it is easiest to pump. Atomized droplets of liquid sulfur would be introduced with gaseous oxygen into the combustion chamber. Here the exothermic reaction to  $\text{SO}_2$  would liberate about 4600 kJ/kg  $\text{SO}_2$ . Isotropic expansion would result in an ideal exhaust velocity near 3000 m/sec, giving a specific impulse ( $I_{sp}$ ) of  $\sim 300$  sec.

The performance of the brimstone rocket would be sufficient for pogosticking from one point to another on the lunar surface or for putting payloads into lunar orbit. To place a payload into a 100-km lunar orbit requires that the initial rocket mass at launch be about 44% propellant at lift off.

The exhaust gases from the brimstone rocket would be compatible with the lunar environment. Sulfur dioxide is a condensable gas, which would ultimately be chemisorbed as coatings on the regolith rather than accumulating as a gas to increase the lunar atmosphere. In contrast, rockets based on combustion of metals and excess oxygen will liberate large quantities of oxygen into the lunar environment. This oxygen might build up to a significant atmosphere and provide oxidizing conditions that could alter the pristine state of the lunar regolith.

### Sulfur for Plants, Animals, and People

Sulfur is a necessary trace element in the diets of many organisms, including people. Powdered sulfur also has uses in plant fertilization (*Leclercq*, 1972). These uses could probably be met simply by the use of unprocessed lunar soil in CELSS systems. For radiation protection, however, it is worth considering the inclusion of small-scale pharmaceutical production of sulphhydryl compounds in space for advanced CELSS systems.

Because nitrogen and other inert gases will be scarce on the Moon, it is likely that the atmospheres in lunar habitats will be oxygen-rich. One consequence of this may be a long-term increase in susceptibility to sickness and biological damage from ionizing radiation (*von Sonntag*, 1987). Sulphydryl compounds are the most extensively studied and effective means of chemical prophylaxis against radiation damage (*von Sonntag*, 1987; *IAEA*, 1969). The action of these compounds is still incompletely understood, but there is considerable evidence that one of their effects is not entirely unlike the role of sulfur in photocells, where the ability of sulfur to assume a large variety of electron shell configurations will not abide an association with electron holes or active charged radicals (see section on PEC photocells, above). Energy transfer from ionizing radiation into biological materials produces target radicals, which will produce cellular damage if left "unquenched." Potentially damaging hydrogen ionization induced in a biological target can release a proton, leaving a target radical with chemical activity that may eventually result in permanent damage. The sulphhydryl compounds can split rapidly to donate a replacement hydrogen before permanent damage occurs (*von Sonntag*, 1987).

The amount of sulfur in sulphhydryl compounds is actually quite small. Glutathione, a well-studied example, has only one sulfur in a molecule of 37 atoms (the rest being H, O, N, and C). These compounds are not heavy users of sulfur resources, and for the near future are probably best produced on Earth even if a use is found for them in space. On the other hand, a flurry of early research into new sulphhydryl compounds has now stagnated (*von Sonntag*, 1987) but might be renewed if considered in terms of the space environment. The advances made in synthesizing pharmaceuticals under microgravity conditions may be applicable to advances in chemical protection from ionizing radiation. Ultimately, the use of lunar sulfur may play a role in expanded human occupation of near-Earth space.

A sulfur-based life cycle may prove useful on the Moon. Such a cycle may be modeled on the sulfur life cycles found in midocean spreading ridges where sulfur-metabolizing bacteria support a host of higher organisms including giant tube worms,

vent crabs, clams, and snails. These midoceanic life centers are unusual in that the food chain is entirely based on sulfur compounds released from volcanic fumaroles. Sunlight, the energy source that was once thought to be the sole basis of life, is absent from this deep ocean microcosm.

There are several advantages of the use of a lunar sulfur life cycle compared to photosynthesis. Such a cycle could operate without artificial light, which would be a requirement for photosynthesis-based life systems at any nonpolar lunar base over the 14-day lunar night. Artificial light may be a permanent requirement for photosynthesis if life systems have to be deeply buried for radiation shielding. The energy efficiency of making electricity into light is poor, resulting in the release of significant quantities of low-temperature heat. The photosynthetic efficiency of using light energy is also poor, resulting in the release of more low-temperature heat. Rejection of low-temperature heat on a lunar base is troublesome because it ultimately hinges on radiation into space. Radiation is inefficient at low temperatures, requiring large radiation areas or the use of heat pumps to increase the temperature of the waste heat. The heat pumps in turn will generate 8 to 10 times the original heat load, which must also be radiated away.

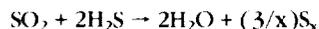
The sulfur life cycle is based on hydrogen sulfide as the energy source, which can be produced from lunar sulfur or recycled from the biota using chemical processes that reject waste heat at high temperatures. The oxidation of the sulfur occurs in aqueous solution where the chemical energy in hydrogen sulfide is efficiently used by the bacteria. Subterranean lava tubes or man-made tunnels could be sealed and flooded with aqueous solutions necessary to support a modified low-pressure sulfur life cycle without need for lighting. Heat transfer between the liquid solution and the tunnel walls may be sufficient to dissipate the small amounts of low-temperature waste heat. A lunar colony's need for a variety of food will certainly dictate the production of familiar photosynthetically based food chains, but the staples required to support a lunar base could well be supplemented by a sulfur-based system. Bioengineering would be required to adapt the existing high-pressure sulfur-metabolizing organisms to a low-pressure lunar system, and to produce palatable foods (unless the lunar inhabitants develop a taste for tube worms and vent crabs). Separate food systems based on photosynthesis and sulfur would provide a redundancy that could increase the security or, in crisis, ensure the survival of a large lunar colony.

### PRACTICAL PRODUCTION OF SULFUR

A wide variety of schemes could be proposed for extracting sulfur from lunar rocks and soils, but not all may be cost effective or practical on the Moon. Procedures requiring multiple complex processing steps are probably too cumbersome to be practical—especially if they cannot be automated and run as autonomous systems. Heating lunar feedstocks to over 1100°C is probably one of the simplest of possible extraction procedures. Moreover, this method has already been tested and proven. *Gibson* (1973) used thermogravimetric-quadrupole mass-spectrometric analysis to determine that Apollo 14 and 15 soil samples release their sulfur as SO<sub>2</sub> and H<sub>2</sub>S on heating to 1000°–1300°C. His experiments were run at vacuum conditions close to those that would be expected on the Moon. These gases are thus the sulfur products to be anticipated on simple heating of lunar feedstocks.

Some direct uses of SO<sub>2</sub> liquid are discussed above. Many applications of sulfur, however, would require its production as

pure S. This would be particularly true for the brimstone rocket. Fortunately, the sulfur-bearing gases that are liberated from lunar feedstocks can be combined in the Claus reaction to produce pure sulfur and water.



where  $x$  varies between 2 and 8. This reaction has been studied intensively and used in the treatment of  $\text{SO}_2$  waste gases on Earth (Pfeiffer, 1975). The Claus reaction is of particular interest not only because it uses exactly those sulfur gases expected from lunar feedstock, but also because it produces valuable water.

Since the Moon is such a different environment, it is important to consider how terrestrial processes might be perturbed on this new industrial frontier. For example, radiolysis of  $\text{SO}_2$  can produce small amounts of S and  $\text{SO}_3$  (Rothschild, 1964). Will this effect be a problem in  $\text{SO}_2$  liquid management, or might it be used to advantage in boosting the production of S from  $\text{SO}_2$ ? Model industrial processes must be considered in terms of the environment where they will be used, and in many cases may require small pilot-plant tests on the Moon before full-scale production is sought.

Finally, sulfur production should not be viewed as an alternative to the extraction and use of other gases (such as  $\text{O}_2$ ,  $\text{H}_2$ , and He) on the Moon. Schemes for extracting one of these gases will often provide some of the others as well. Each gas has its own set of uses, and thus a special value for exploitation in space. Extraction schemes that combine cogeneration with multiple uses will obtain the maximum benefit and minimum wastage of these rare lunar resources.

## CONCLUSIONS

It is fortuitous to find small but useful amounts of extractable sulfur on the Moon. In an environment devoid of gas-forming elements, sulfur has the potential to provide as significant an impact on lunar development as coal and petroleum had for the industrialization of society on Earth.

Even at its low abundance in lunar regolith, the ~0.1% of sulfur available across many thousands of square kilometers of high-Ti mare regolith may be useful. Thermal processing of mildly crushed regolith from high-Ti basaltic lava areas at  $1100^\circ\text{C}$  could yield about 1000 kg of sulfur from a patch of regolith  $100\text{ m} \times 100\text{ m}$  and 10 cm deep. Figure 3 shows the possible scars that would be left by much more extensive mining in two types of regolith at the Apollo 17 site. Each scar has an area of about  $10\text{ km}^2$ , but patch A would produce ~1,000,000 kg of sulfur from high-Ti basaltic lava regolith, whereas patch B would produce ~700,000 kg of sulfur with cogeneration of the metals and sodium that occur on the surfaces of pyroclastic glasses. Either patch would produce sufficient sulfur to lift a payload of several hundred metric tons off the Moon using the brimstone rocket.

In practice these patches would not be nearly so regular or well contained; patch A in particular would have to be gerrymandered to avoid large craters in the basaltic lava regolith (the pyroclastic mantle is much smoother, and crater avoidance would be less of a problem in patch B). It is possible that these mined areas would not leave visible scars. The most efficient extraction

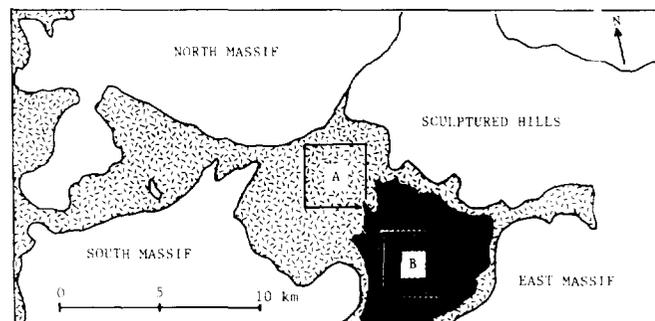


Fig. 3. A simplified version of an albedo map of the Apollo 17 landing site (modified from Muehlberger et al., 1973). Massifs and hills of the nonbasaltic highlands surround an embayment flooded by high-titanium, high-sulfur basalts (light pattern); the eastern part of the embayment includes a terrain of very low albedo (dark pattern), which is attributed by Muehlberger et al. to an extensive pyroclastic mantle. Squares A and B show the dimensions of  $10\text{-km}^2 \times 10\text{-cm}$ -deep patches mined out of the regolith; A would yield  $\sim 10^3$  MT of sulfur and B would yield  $\sim 7 \times 10^2$  MT.

system could be a mobile processing plant that would return more than 99% of the processed regolith and leave no trench. Such a system would be merely one more gardening event at the lunar surface. The depth of excavation would be strongly process dependent (considering plant mobility vs. plant simplicity); shallow excavation simplifies the mining equipment at the cost of making the plant more mobile.

If dedicated solely to sulfur and associated volatile-element production, the thermal energy required for this plant would be about 0.1 MW-yr per metric ton of sulfur (assuming 100% duty cycle). Significant energy savings might be realized if sulfur production were piggybacked with oxygen production, or if low-energy solvent extraction of sulfur were developed to replace thermal extraction. Clearly, process development with a clear definition of end use is necessary if lunar sulfur is to be taken seriously as a potential resource.

**Acknowledgments.** This study was completed with the support of the National Aeronautics and Space Administration and the U.S. Department of Energy. Reviews by E. Jones, W. Field, E. Cameron, and L. Taylor helped to improve the text and the technical content of the paper.

## EPILOGUE

### Fire and Brimstone

A mechanical dragon, breathing fire and smoke,  
But it lives off of sulfur instead of off coke.  
It rolls down the rails of St. Lucifer's line  
On a journey to a place that is far from divine.

But the fire and brimstone that makes up our hell  
May some day prove useful to mankind as well,  
For brimstone-based rockets reaching out into space  
Could open the heavens for the human race.

DP 4/88

## REFERENCES

- Bagotzky V. S. and Skundin A. M. (1980) *Chemical Power Sources*. Academic, New York. 387 pp.
- Blacic J. D. (1985) Mechanical properties of lunar materials under anhydrous hard vacuum conditions: Applications of lunar glass structural components. In *Lunar Bases and Space Activities of the 21st Century* (W. W. Mendell, ed.), pp. 487-495. Lunar and Planetary Institute, Houston.
- Burow D. F. (1970) Liquid sulfur dioxide. In *The Chemistry of Non-aqueous Solvents, Vol. III* (J. J. Lagowski, ed.), pp. 137-185. Academic, New York.
- Butler P. Jr. and Meyer C. Jr. (1976) Sulfur prevails in coatings on glass droplets: Apollo 15 green and brown glasses and Apollo 17 orange and black (devitrified) glasses. *Proc. Lunar Sci. Conf. 7th*, pp. 1561-1581.
- Chopra K. L. and Das S. R. (1983) *Thin Film Solar Cells*. Plenum, New York, pp. 349-389 and 391-481.
- Cirlin E. H. and Housley R. M. (1979) Scanning auger microprobe and atomic absorption studies of lunar volcanic volatiles. *Proc. Lunar Planet. Sci. Conf. 10th*, pp. 341-354.
- Crow L. J. and Bates R. C. (1970) Strengths of sulfur-basalt concretes. *U.S. Dep. Inter., Bur. Mines, RI 7349*. 21 pp.
- Cutler A. H. and Krag P. (1985) A carbothermal scheme for lunar oxygen production. In *Lunar Bases and Space Activities of the 21st Century* (W. W. Mendell, ed.), pp. 559-569. Lunar and Planetary Institute, Houston.
- Dokiya M., Fukuda K., Kameyama T., and Yokokawa H. (1979) A feasibility study on thermochemical water-splitting cycles using sulfur compounds. In *Hydrogen Energy System, Vol. 2. Proceedings of the Second World Hydrogen Energy Conference*. pp. 499-512. Pergamon, New York.
- Flood D. J. (1986) Space solar cell research: Problems and potential. In *SPIE Vol. 706, Photovoltaics for Commercial Solar Power Applications* (D. Adler, ed.), pp. 34-39. Proceedings of SPIE—The International Society for Optical Engineering, SPIE, Bellingham, Washington.
- Friedlander H. N. (1985) An analysis of alternate hydrogen sources for lunar manufacture. In *Lunar Bases and Space Activities of the 21st Century* (W. W. Mendell, ed.), pp. 611-618. Lunar and Planetary Institute, Houston.
- Gibson E. K. Jr. (1973) Thermal analysis-mass spectrometer computer system and its application to the evolved gas analysis of Green River shale and lunar soil samples. *Thermochim. Acta*, 5, 243-255.
- Gibson E. K. Jr. and Moore G. W. (1973) Carbon and sulfur distributions and abundances in lunar fines. *Proc. Lunar Sci. Conf. 4th*, pp. 1577-1586.
- Gibson E. K. Jr. and Moore G. W. (1974) Sulfur abundances and distributions in the valley of Taurus-Littrow. *Proc. Lunar Sci. Conf. 5th*, pp. 1823-1837.
- Gibson E. K. Jr., Brett R., and Andrawes F. (1977) Sulfur in lunar basalts as a function of bulk composition. *Proc. Lunar Sci. Conf. 8th*, pp. 1417-1428.
- Gibson M. A. and Knudsen C. W. (1985) Lunar oxygen production from ilmenite. In *Lunar Bases and Space Activities of the 21st Century* (W. W. Mendell, ed.), pp. 543-550. Lunar and Planetary Institute, Houston.
- IAEA (International Atomic Energy Association) (1969) *Radiation Damage and Sulphydryl Compounds*. IAEA Panel Proceedings Series, Vienna. 191 pp.
- Kerridge J. F., Kaplan I. R., and Petrowski C. (1975) Evidence for meteoritic sulfur in the lunar regolith. *Proc. Lunar Sci. Conf. 6th*, pp. 2151-2162.
- Leclercq R. (1972) Commercially important sulfur compounds. In *Sulfur in Organic and Inorganic Chemistry* (A. Senning, ed.), pp. 207-221. Marcel Dekker, New York.
- LSPET (Lunar Sample Preliminary Examination Team) (1972) Preliminary examination of lunar samples. In *Apollo 16 Preliminary Science Report*, pp. 7-1 to 7-58. NASA SP-315, Washington, DC.
- MacElroy R. D., Klein H. P., and Averner M. M. (1985) The evolution of CELSS for lunar bases. In *Lunar Bases and Space Activities of the 21st Century* (W. W. Mendell, ed.), pp. 623-633. Lunar and Planetary Institute, Houston.
- Meek T. T., Vaniman D. T., Blake R. D., and Cocks F. H. (1987) Electromagnetic energy applied to and gained from lunar materials. In *Symposium '86: The First Lunar Development Symposium* (G. M. Andrus, ed.), pp. S86-40a to S86-40e. Lunar Development Council, Pitman, New Jersey.
- Meyer C. Jr., McKay D. S., Anderson D. H., and Butler P. Jr. (1975) The source of sublimates on the Apollo 15 green and Apollo 17 orange glass samples. *Proc. Lunar Sci. Conf. 6th*, pp. 1673-1699.
- Muchlberger W. R. et al. (1973) Preliminary geologic investigation of the Apollo 17 landing site. In *Apollo 17 Preliminary Science Report*, pp. 6-1 to 6-91. NASA SP-330, Washington, DC.
- National Commission on Space (1986) *Pioneering the Space Frontier*. Bantam, New York. 211 pp.
- Pfeiffer J. R., ed. (1975) *Sulfur Removal and Recovery from Industrial Processes*. Advances in Chemistry Series 139, American Chemistry Society, Washington, DC. 221 pp.
- Rosenberg S. D. (1985) A lunar-based propulsion system. In *Lunar Bases and Space Activities of the 21st Century* (W. W. Mendell, ed.), pp. 169-176. Lunar and Planetary Institute, Houston.
- Rothschild W. G. (1964)  $\gamma$ -ray decomposition of pure liquid sulfur dioxide. *J. Am. Chem. Soc.*, 86, 1307-1309.
- Russak M. A., Reichman J., Witzke H., Deb S. K., and Chen S. N. (1980) Thin film CdSe photoanodes for electrochemical photovoltaic cells. *J. Electrochem. Soc.*, 127, 725-733.
- Sulphur Institute (1979) *Sulphur Research and Development 2* (J. S. Platou and R. Pond, eds.). The Sulphur Institute, Washington, DC. 20 pp.
- von Sonntag C. (1987) *The Chemical Basis of Radiation Biology*. Taylor and Francis, New York. 515 pp.
- Weast R. C., ed. (1982) *Handbook of Chemistry and Physics*, 63rd edition, F-46. CRC, Boca Raton, Florida.
- Williams R. J. and Jadwick J. J., eds. (1980) *Handbook of Lunar Materials*. NASA RP-1056. 120 pp.