stresses might have serious consequences. Since the medium properties, and not the shot yield, control the proportion of energy release, a large explosion could release large amounts of tectonic strain energy. For example, with the energy factor of Pile Driver or Hardhat, a 1-megaton explosion could release energy equivalent to that of a magnitude  $M_{\rm S} = 6.3$  earthquake. For a 10-megaton explosion, this could be equivalent to a magnitude  $M_{\rm s} =$ 7.2 earthquake, indeed a potentially destructive earthquake. Thus, in any testing program, these factors must be taken into account, and hard media should be avoided unless the ambient stress levels are known to be low.

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Fossil Fuel Combustion and the Major

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of movement of these elements with

those observed for elements entering

the oceans each year by way of the

rivers as a result of weathering proc-

produced in 1967 and presumably the

amounts consumed in 1967 were as

follows (3): coal,  $1.75 \times 10^{15}$  g; lig-

nite,  $1.04 \times 10^{15}$  g; fuel oils,  $1.63 \times$ 

 $10^{15}$  g; and natural gas,  $0.66 \times 10^{15}$  g.

The estimated world production of

crude oil (1969) amounted to  $2.13 \times$ 

 $10^{15}$  g, of lignite (1970) to  $0.77 \times$ 

1015 g, and of bituminous plus anthra-

citic coal (1970) to  $2.18 \times 10^{15}$  g (5).

Although the yearly production figures

for solid fuels, that is, coal plus lignite,

appear to be static at the present time,

there is a substantial yearly increase in

the production and consumption of

the world's oceans yearly as a result

of the weathering cycle can be obtained

from river discharge and composition

data or from rates of sedimentation in

marine areas (6). The river data reflect

The amount of an element entering

petroleum.

The total amounts of fossil fuels

esses upon the continents.

8 March 1971

Abstract. The combustion of the fossil fuels coal, oil, and lignite potentially

can mobilize many elements into the atmosphere at rates, in general, less than but comparable to their rates of flow through natural waters during the weather-

ing cycle. Since the principal sites of fossil fuel combustion are in the mid-lati-

tudes of the Northern Hemisphere, changes in the composition of natural waters

and air, as a consequence of this activity, will be most evident at these latitudes.

the transfer of dissolved phases, whereas the sedimentation data take into account the movement of both the dissolved and the particulate loads of rivers. Both techniques depend upon global averages of geologic parameters, and these numbers are characterized by a certain degree of uncertainty.

Since the river load of particulate matter is, on the average, four times higher than that of the dissolved phases, the mobilization calculated from the dissolved contents of rivers would be expected to be less than that from sedimentation values. Such is the case for two-thirds of the elements considered in Table 1. However, the significance of the exceptions is difficult to evaluate. More important for this study is the order of magnitude and the relative rank for the dispersion of a given element during the weathering cycle.

It is possible to determine only approximately the percentage of the ash from the fuel burning that actually enters the atmosphere as compared with the percentage that is incorporated in the furnace residues, the so-called bottom ash. Estimates made over the past several decades at the U.S. Bureau of Mines (5) suggest that the fly ash released to the atmosphere appears to be about 10 percent of the total ash in coals and perhaps a similar value is applicable to the combustion of liquid petroleum fuels. Thus, for the elements listed in Table 1 we have reduced by a factor of 10 the potential amount of material that might enter the atmosphere from the burning of coal and oil.

An additional correction on the computations for coal involves the amounts that are combusted in power production and in the manufacture of coke. Estimates at the U.S. Bureau of Mines (5) suggest that there is about an equal division of the bituminous and anthracitic coals between these two uses. Hence, for the elements listed in Table 1 we have applied a reduction factor of 2 to the potential amount of material that might enter the atmosphere from the combustion of coal and lignite.

Thus far, we have assumed that the elements are accommodated in either the fly ash or the bottom ash during the combustion process and are not introduced as volatile species to the atmosphere. Clearly, selective volatilization can introduce the readily distillable materials into the atmosphere at concentrations far above those indicated in Table 1. An indication of what

## is introduced into the atmosphere by

**Sedimentary Cycle** 

fuel burning appears to be the same as that for the combined emissions from anaerobic areas and from volcanism, two processes that do not involve man (1). The amount of carbon dioxide introduced into the atmosphere in 1967 by energy production,  $13 \times 10^{15}$  g, is close to the amount of carbon dioxide produced by photosynthesis on land and on sea,  $50 \times 10^{15}$  g (2, 3). More lead has been transferred from the land to the oceans by the use of tetraethyl lead as an antiknock additive in gasolines than has been added to the marine environment through rivers (4).

The combustion of fossil fuels (fuel

oils, lignite, coal, and natural gas) may

introduce some elements into the atmo-

sphere and subsequently into the

oceans at rates comparable to those of

natural processes. Previous work has

indicated that the rate at which sulfur

Such figures prompted us to investigate what other elements might be mobilized about the surface of the earth as a result of fossil fuel combustion and to compare the potential rates

elements may be mobilized more effectively through the volatilization process may be found in observations of emissions from the d-c arc observed by spectrographers (7). The general order of volatility of these elements, listed as volatile oxides, sulfates, carbonates, silicates, and phosphates, is as follows: As, Hg > Cd > Pb, Bi, Tl > In, Ag, Zn > Cu, Ga > Sn > Li, Na, K, Rb, Cs. For the elemental states the order is as follows:  $Hg > As > Cd > Zn > Sb \ge$ Bi > Tl > Mn > Ag, Sn, Cu > In, Ga, Ge. For the sulfides we have the following order: As, Hg>Sn, Ge $\geq$ Cd> Sb,  $Pb \ge Bi > Zn$ , Tl > In > Cu > Fe, Co, Ni, Mn, Ag.

Thus, one would expect a preferential transfer of As, Hg, Cd, Sn, Sb, Pb, Zn, Tl, Ag, and Bi, for example, to the atmosphere during fuel burning. Such elements could be introduced in amounts as much as 20 times greater than those shown in Table 1, if the effects of selective volatilization override the two correction factors.

Today, the combustion of fossil fuels potentially can mobilize many elements into the atmosphere at rates, in general, less than but comparable to those of flow through natural waters during the weathering cycle (Table 1). Since the principal sites of fossil fuel combustion are in the mid-latitudes of

the Northern Hemisphere, changes in the compositions of natural waters and air will be most evident at these latitudes. Amounts of such products from fossil fuel combustion as S, Pb, and Hg that are increasing with time are being found in the Greenland glacial deposits (1, 8). The surface sediments of the Sierra Leone Rise in the Atlantic Ocean contain detectable amounts of elemental carbon produced from fossil fuel burning (9). Airborne dusts collected from the prevailing westerlies and northeast trades in the Atlantic contain measurable amounts of fly ash, consisting mainly of colorless glass spheres with occasional red, yellow, or

Table 1. Amounts of elements mobilized into the atmosphere as a result of weathering processes and the combustion of fossil fuels; ppm, parts per million.

Ele- ment	Fossil fuel concentration*,† (ppm)		Fossil fuel mobilization <sup>†</sup> , <sup>‡</sup> ( $\times 10^9$ g/year)			Weathering mobilization $(\times 10^9 \text{ g/year})$	
	Coal	Oil	Coal	Oil	Total	River flow§	Sediments]
Li	65		9			110	12
Be	3	0.0004	0.41	0.00006	0.41		5.6
В	75	0.002	10.5	0.0003	10.5	360	
Na	2,000	2	280	0.33	280	230,000	57,000
Mg	2,000	0.1	280	0.02	280	148,000	42,000
AŬ	10.000	0.5	1,400	0.08	1,400	14,000	140,000
Р	500	0.0	70			720	,
S	20.000	3,400	2,800	550	3,400	140,000	
Cl	1.000	5,100	140		,	280,000	
ĸ	1,000		140			83.000	48.000
Ĉa	10,000	5	1.400	0.82	1.400	540,000	70.000
Sc	5	0.001	07	0.002	0.7	0.14	10
Ti	500	0.001	70	0.0002	70	108	9 000
V	25	50	35	82	12	32	280
Č.	10	30	1.1	0.2	15	36	200
Mn	10	0.3	1.4	0.03	7	250	200
	10,000	0.1	1 400	0.02	1 400	24 000	100,000
Fe Ca	10,000	2.5	1,400	0.41	1,400	24,000	100,000
CO N:		0.2	0.7	0.03	0.7 2 <b>7</b>	1.2	10
N1	15	10	2.1	1.6	5.7	250	160
Cu	15	0.14	2.1	0.023	2.1	230	80
Zn	50	0.25	7	0.04	1	720	80
Ga	7	0.01	1	0.002	1	- 3	30
Ge	5	0.001	0.7	0.0002	0.7		12
As	5	0 01	0.7	0.002	0.7	72	
Se	3	0.17	0.42	0.03	0.45	7.2	
Rb	100		14			36	600
Sr	500	0.1	70	0.02	70	1,800	600
Y	10	0.001	1.4	0.0002	1.4	25	60
Мо	5	10	0.7	1.6	2.3	36	28
Ag	0.5	0.0001	0.07	0.00002	0.07	11	0.03
Cd		0.01		0.002			0.5
Sn	2	0.01	0.28	0.002	0.28		11
Ва	500	0.1	70	0.02	70	360	500
La	10	0.005	1.4	0.0008	1,4	7.2	40
Ce	11.5	0.01	1.6	0.002	1.6	2.2	90
Pr	2.2	0.01	0.31			1.1	11
Nd	4.7		0.65			7.2	50
Sm	1.6		0.22			1.1	13
En	0.7		0.1			0.25	2.1
Gđ	1.6		0.22			1.4	13
Th	0.3		0.042			0.29	10
Ho	0.3		0.042			0.25	23
Fr	0.6	0.001	0.085	0.0002	0.085	1.8	5.0
Tm	0.1	0.001	0.014	0.0001	0.000	0.32	0.4
Yh	0.5		0.07			1.8	5 3
10	0.07		0.07			0.29	15
Re	0.07		0.007			0.29	0.001
Нa	0.03	10 4	0.007	16	16	25	1.0
Ph	25	03	2.5	0.05	3.6	2.3	21
R;	55	0.5	0.75	0.05	5.0	110	∠ı 06
1	J.J 1 0	0.001	0.75	0.001	0.14	11	0.0
0	1.0	0.001	0.14	0.001	0.14	11	ð

\* These average values were obtained from a review of published values for the abundances of elements in coal (11, 12) and fuel oils (13). Wide variations exist for a given element and the figures are presented as reasonable estimates from available data.  $\dagger$  Coal and lignite are combined in this representation.  $\ddagger$  Based upon 1967 production figures. \$ In the main calculated from the data of Turekian (14). || In the main calculated from the data of Goldberg (6).  $\P$  This Hg value may be unrepresentative of petroleums in general. It is the only published value for Hg in fuel oils of which we are aware. The samples came from the Cymric oil fields of California, an area near known Hg deposits (15).

brown particles (9, 10). These spherules constitute over 60 percent of the dust particles greater in size than 3  $\mu$ m near the North American continent and about 5 percent of the particles of this size over the open ocean.

The Northern Hemisphere is about half land and half water. Thus, about half of the fallout will initially enter the hydrosphere. A portion of the land fallout will eventually reach the marine environment by way of the rivers. Expected alterations in the composition of rivers, lakes, and coastal seawaters as a result of fossil fuel combustion may be most difficult to document inasmuch as any such changes must be distinguishable from those that have resulted from industrial or domestic waste disposal or from natural processes.

The above observations emphasize the need for detailed studies of the sedimentary record over the past 100 years or so, with special emphasis on those elements that may be selectively volatilized. Permanent snowfields, lakes, and inshore marine areas can provide datable sedimentary strata, separable into time units, that may furnish information about man's injections into the atmosphere. Furthermore, the atmospheric burdens of such elements in the major wind systems should be investigated to provide information on the long-range transfer processes.

Note added in proof: Joensuu (16) has measured the Hg contents of 36 U.S. coals and found an average of 3.3 parts per million, about 300 times the literature value used in Table 1. This figure is most probably a better estimate as a result of the very careful analytical procedures which took into account the ready volatility of Hg. Joensuu's mobilization value of  $3.0 \times 10^9$  g/year is clearly preferable to the one we derive even though no correction is made for the Hg retained in the bottom ash or incorporated in coke.

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## Synthetic Calcareous Pseudomorphs Formed from Siliceous Microstructures

Abstract. Individuals of the diatom Coscinodiscus have been treated hydrothermally in the presence of lime and carbon dioxide with the result that they have been pseudomorphed by calcite. The silica of the original diatoms has been replaced while the intricate reticulations of the alveoli have been preserved down to submicroscopic detail.

Technical advances in high-temperature, high-pressure systems have made it possible to simulate conditions far beneath the earth's surface, and there are few minerals of the earth's crust that have not been synthesized in the laboratory. The wealth of data on phase equilibria in natural systems has revealed many of the mechanisms involved in the formation of igneous, metamorphic, and sedimentary rocks. However, one of the most interesting types of mineral transformations, about which relatively little is yet known, is the formation of pseudomorphs.

A pseudomorph may be defined as "any substance or structure of definite or characteristic form which is represented or defined by another substance to which the form does not properly belong" (1), (A later-formed material B, which has replaced but preserved the structure of an earlier material A, is said to produce a pseudomorph after A.) To be sure, there is a substantial amount of literature on ion exchange in which major chemical changes are being effected with little or no modification of the crystal structure. And there are several very significant papers on topotactic transformations in which the chemical compositions, at least with respect to nonvolatile components, are essentially maintained, while substantial changes are induced in the crystal structures (2). In both of these types of transformations the morphology, that is, the external shape, of the starting material may be preserved. However, a great deal remains to be learned about much more drastic transformations such as the silicification of wood, the metallization of organic fossils, and the calcification of siliceous forms. It is with a transformation of the last type that this report is concerned.

My interest in pseudomorphing arose from a desire to explore certain reactions in set, low-alkali mortars containing reactive silica. Reduced to its simplest components, lime liberated by the hydration of anhydrous lime-rich calcium silicates in cement reacts with such silica of the aggregate to produce calcium silicate hydrates with hydraulic properties. Carbon dioxide, which has a great affinity for lime, particularly slaked lime, and for calcium silicate hydrates, plays an important role in the formation of carbonates in many cement and concrete products which are usually cured and used in air.

The strength and corrosion resistance of aged cement structures are also affected to some degree by reac-