On the absorption of SO_2 in ocean water

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ABSTRACT

The role which the ocean plays with respect to the atmospheric sulfur budget is still unclear. It is known that the ocean is an important source of sulfat-containing particles, but opinions differ on the question: Is the ocean a sink or a source of SO_2 and H_2S? In this paper, on the basis of laboratory investigations, the absorption and desorption of SO_2 by sea water is discussed. The results of our measurements show that the ocean is an SO_2-sink and presumably cannot be a direct SO_2-source. The possibility of an indirect source of SO_2 is considered in a discussion of current literature on H_2S-oxidation in ocean water.

It is often assumed that cloud and rain drops, wet soils, rivers, lakes, and oceans are important sinks of the SO_2 emitted into the atmosphere. Although cloud and rain drops can indeed absorb SO_2 to a great extent, Hales et al. (1970) have shown that, under certain circumstances, some of the SO_2 can also be desorbed. Less well known is the absorption–desorption behavior of wet soils and oceans. Despite the fact that the oceans contain much sulfate and are an important source of sulfate-containing particulates, the question of the ocean being a source or a sink of SO_2 and H_2S remains open. In order to balance the terrestrial sulfur budget some authors have considered the oceans to be a source (Kellog et al., 1972). Further investigations of this matter are indicated.

In this paper the absorption–desorption characteristics of sea water are considered on the basis of simple bubble column experiments. Fig. 1 shows the essentials of the experimental set-up. As the bottled air passes through a large ($2 \times 1 \times 1$ meters) chamber containing sulfurous acid, it picks up SO_2 and water vapor. The mixture is then bubbled continuously through two absorption columns connected in series. The concentration of SO_2 is monitored constantly by a Picoflux electroconductivity meter. In the first column, containing 40 ml of ocean water, the pH is recorded continuously by means of an Ingold glass electrode. The second column contains an SO_2 absorption solution stabilized against changes in the concentration of CO_2. By recording the change in the specific electroconductivity of this latter solution, one can determine the fraction of SO_2 which was desorbed or not absorbed by the ocean water in the first column. So as to eliminate the influence of sulfate formation on the up-take rates, experimental runs were also conducted in the absence of O_2 using a mixture of SO_2 in $N_2 + 315$ ppm CO_2. The CO_2 was necessary to avoid upsetting the carbonate buffering action of the sea water.

Fig. 2 shows a typical experimental run. Time is expressed along the ordinate in minutes after the first introduction of SO_2 into the wash bottles. The time required for an air parcel to travel between the two bottles is on the order of seconds and so can be neglected on the scale of these experiments. The abscissa shows the measured pH (curve I) of the ocean water in the first column as well as the conductivity (curve II) of the solution in the second column. The pH trace shows the two inflection points commonly associated with a buffered system. One sees readily that the buffer capacity becomes exceeded after enough SO_2 has been absorbed to lower the pH below about 7. The curve of specific conductivity indicates that the ocean water is very effective in absorbing the SO_2 out of the air mixture until the pH has dropped

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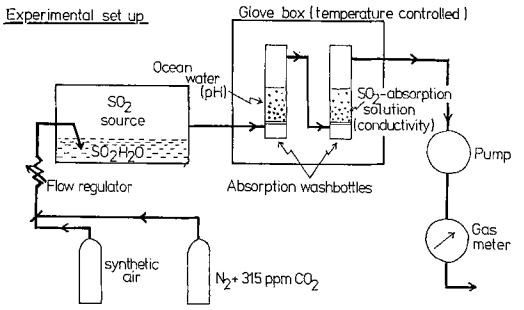

Fig. 1. Experimental set-up to study the oxidation of SO_2.

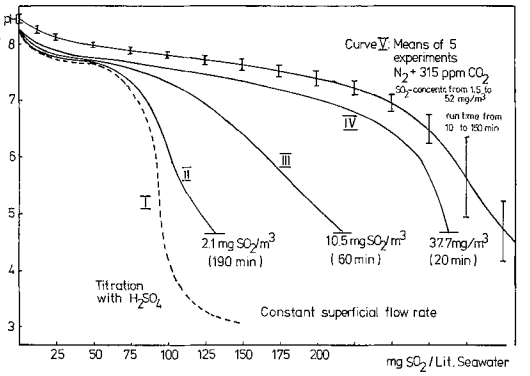

Fig. 3. pH as a function of the total amount of SO_2. Absorbed by ocean water. Curve I: A titration curve for H_2SO_4 (dashed curve). Curves II, III, IV: pH-decrease of sea water using an SO_2-air-mixture. Curve V: A mean of five separate runs using an $N_2 + 315$ ppm CO_2 mixture as a carrier of the SO_2.

below 5. At the lowest pH values the absorbing ability of the ocean water is very weak.

In the real ocean the pH cannot change this drastically, of course, due to the exceedingly large mass capacity. Any changes in pH would most likely be a result of variations in the CO_2 system. Nevertheless, it is useful not to simulate the ocean-atmosphere system with such experiments, but to exaggerate the SO_2 concentration, transport, and the changes in pH so as to investigate the mechanism of the absorption process.

To summarize these experimental results the pH has been plotted in Fig. 3 as a function of the total amount of SO_2 absorbed by the ocean water. A titration curve for H_2SO_4 (dashed curve, I) has been added for reference since this is the curve one would expect had all the SO_2 taken up by the ocean water been oxidized instantaneously to sulfate. Curves II, III, and IV show the pH decreases arising from the use of an SO_2-air mixture with concentrations ranging from 2 to 37 mg SO_2/m^3 and corresponding run times (times to attain a certain pH) of from 190 to 20 minutes. Curve V is a mean of five separate runs all using the $N_2 + 315$ ppm CO_2 mixture as a carrier. The SO_2 concentrations for these runs ranged from 1.5 to 52 mg/m³ and the corresponding run times varied from 150 to 10 minutes. Two points may be noted from these results:

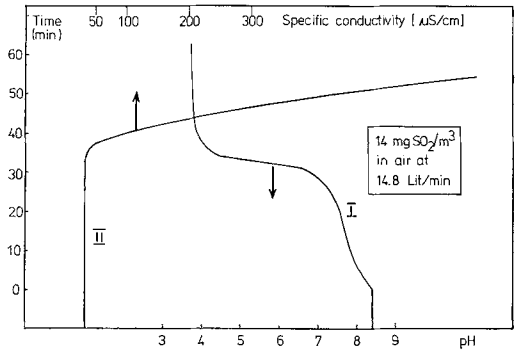

Fig. 2. A typical experimental run. Curve I: Decrease of pH in ocean water. Curve II: Increase of specific conductivity in the second bubble column.

(*a*) The curve (V) for absorption without any oxygen does not depend on time, meaning that the formation of the HSO_3^- and $SO_3^=$ ions from the physically dissolved SO_2 must occur very rapidly. This implies that, despite the rapid rate with which SO_2 is supplied to the system (about two orders of magnitude faster than in the atmosphere), the liquid phase resistance remains negligible and the up-take, both in the bubble column and in the atmosphere, must be limited by the transport of SO_2 through the gas phase. These results are consistent with the findings of Spedding (1972) using a different approach.

(*b*) When oxygen is present (curves II, III, and IV), sulfate can form, but the $SO_4^=$ formation rate is very slow in contrast to the hydrolysis of the SO_2 itself. Due to extreme experimental difficulties no reaction rates have been measured in ocean water as yet. In any case, the ability of the ocean to absorb SO_2 does not seem to depend on sulfate formation as a significant step in the absorption mechanism.

Another way to investigate the buffering ability of ocean water is to pass the same concentration of SO_2 into both ocean water and distilled water. Such a comparison experiment was made in the course of this study and emphasized the enormously greater (about two orders of magnitude) buffer capacity[1] of sea water compared with distilled water. Spedding, in comparing his results with those of Terraglio & Manganelli (1967), also formed the same conclusion. Again, because our results were reproduced in the absence of atmospheric oxygen, the ability of the ocean to absorb SO_2 is seen not to depend on its ability to oxidize SO_2 to sulfate.

To investigate the actual mechanism of uptake more thoroughly a series of absorption–desorption experiments were also carried out. Fig. 4 exemplifies such an experiment. The pH of the ocean water is plotted on an expanded scale along the abscissa, while the time relative to the first introduction of SO_2 into the system is plotted along the ordinate. After the SO_2-air mixture had been allowed to bubble through the bottles for 4 minutes, the SO_2 supply was cut off so that only pure air was bubbled through. Although the pH changes as expected, the electroconductivity, as measured in the absorbing solution (second bubble column), changed conspicuously little when only air was passed. Had the pH increase during the latter part of the run been caused by a desorption of the SO_2 itself, the specific conductivity would have followed the dashed curve. Such results suggest that CO_2 is the component released, not SO_2.

Despite the suggestion of others that at least certain parts of the oceans may release SO_2, all our results indicate rather strongly that, because of its high pH and good carbonate buffering action, the oceans are actually good sinks of SO_2 and may never be direct sources. This does not, however, exclude the possibility that some parts of the ocean, such as shallow coastal areas, may act as indirect sources perhaps by the release and subsequent oxidation of H_2S. This idea is supported by the results of others (Östlund & Alexander, 1963; Cline & Richards, 1969) who have found that H_2S oxidizes with half-concentration times which are long compared with the half-concentration times for SO_2 and, in any case, long enough to allow for a significant transport away from the source before possible oxidation to SO_2. We conclude that any SO_2 which is found over the open ocean will tend to be of continental or coastal origin and that the resulting transport from the continents implies an SO_2 profile with increasing concentrations with height.

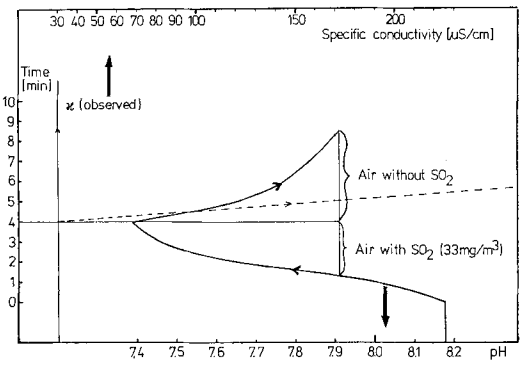

Fig. 4. An example of an SO_2-desorption experiment. Thick solid curve: pH curve in sea water. Thin solid curve: Observed specific conductivity in the second column. Dashed curve: Calculated specific conductivity in the second column had the pH increase of the sea water been caused by a desorption of SO_2.

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[1] Buffer capacity, a measure of how much of a substance must be added to a solution to cause a given change in pH, is generally defined as

$$\beta = \frac{1}{V} \cdot \frac{dn}{d\mathrm{pH}},$$

where V is the volume of the solution, dn is the gram-equivalent addition, and dpH is the resultant change in pH. For solutions buffered by the CO_2 system, $dn = d\Sigma CO_2$, where ΣCO_2 represents the sum of the ionic species.

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О ПОГЛОЩЕНИИ SO_2 В ВОДЕ ОКЕАНА

Роль, которую играют океаны в балансе серы в атмосфере, все еще не ясна. Известно, что океан является важным источником частиц, содержащих сульфаты, но мнения расходятся по вопросу — является ли океан источником или стоком для SO_2 и H_2S. В данной статье на основе лабораторных исследований обсуждается абсорбция и десорбция SO_2 морской водой. Результаты наших измерений покаюывают, что океан является стоком для SO_2 и не может быть прямым источником этого газа. При обсуждении текущей литературы по окислению H_2S в воде океана рассматривается возможность того, что океан является косвенным источником SO_2.