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ARTICLE *in* THE JOURNAL OF PHYSICAL CHEMISTRY · APRIL 1995

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Periodic Convection in the Bromate–Sulfite Reaction: A "Jumping" Wave

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Received: November 4, 1994; In Final Form: January 3, 1995[⊗]

An unusual spatiotemporal phenomenon was observed in propagating fronts in the bromate–sulfite system with an initial pH gradient, but not in chlorate–sulfite nor iodate–sulfite systems. Periodic acceleration and deceleration of the front were observed, which appeared as a "jumping" wave. An experimental method was developed to produce the pH gradient systematically and reproducibly in a tube. The effect of the gradient was studied. With the use of infrared and visible imaging the competition between chemically and thermally induced convection was observed. A qualitative model is proposed that includes the effect of pH gradient and the specific mechanism of the bromate oxidation of sulfite.

Introduction

In the preceding work, we presented anomalous results for the iodat–-sulfite system.[1] The experiments for the bromate–sulfite system were completely in accord with earlier work.[2–5] While investigating the latter system, we discovered a novel mode of propagation down an initial pH gradient in which the front "jumps" as much as several centimeters in a few seconds. We discovered this accidentally when the initial sulfite–bisulfite solution was prepared but not mixed completely. Nagy and Pojman[3] observed periodic double-diffusive convection when fronts in the chlorate–sulfite system propagated down a separatory vertical funnel but the front did not periodically change its velocity. We therefore set out to systematically study this periodic reaction–convection phenomenon in the bromate–sulfite system using both IR and visual imaging. We have developed a technique to produce pH gradients reproducibly and to characterize them semiquantitatively.

Experimental Section

Chemicals and Apparatus. Reactant solutions were prepared with analytical grade chemicals that were used as received: Na_2SO_3, $NaHSO_3$, Na_2SO_4, H_2SO_4, phenolphthalein from Fisher; $NaBrO_3$, bromophenol blue from Aldrich; Universal Indicator from BANCO Laboratories Inc.; and deionized water. The stock solution of Bromophenol Blue was 8 w/v%.

Wave experiments were carried out using a 100 mL graduated cylinder (TEKK USA No. 20025-H, inside diameter of 2.606 cm, 1 vertical scale unit is 0.187 cm). To achieve a reproducible pH gradient we used a glass rod with a round plastic plate attached. Two types of plates were prepared: one with 18 holes, the other with six holes, shown in Figure 1. This device was immersed into the solution, and a counterweight (45.8 g) was used to raise it at a constant and reproducible rate.

Imaging. Visible images from a Hitachi KP-C501 solid state color camera equipped with a Cosmicar zoom lens were digitized with a RasterOps 364 board on a Macintosh Quadra 800. Analysis of captured images was performed with Image 1.41 (from NIH). Infrared imaging was carried out using an Inframetrics Model 760 infrared camera with a mercury–cadmium–telluride detector with closed circle cooling and equipped with germanium 3× zoom lens.

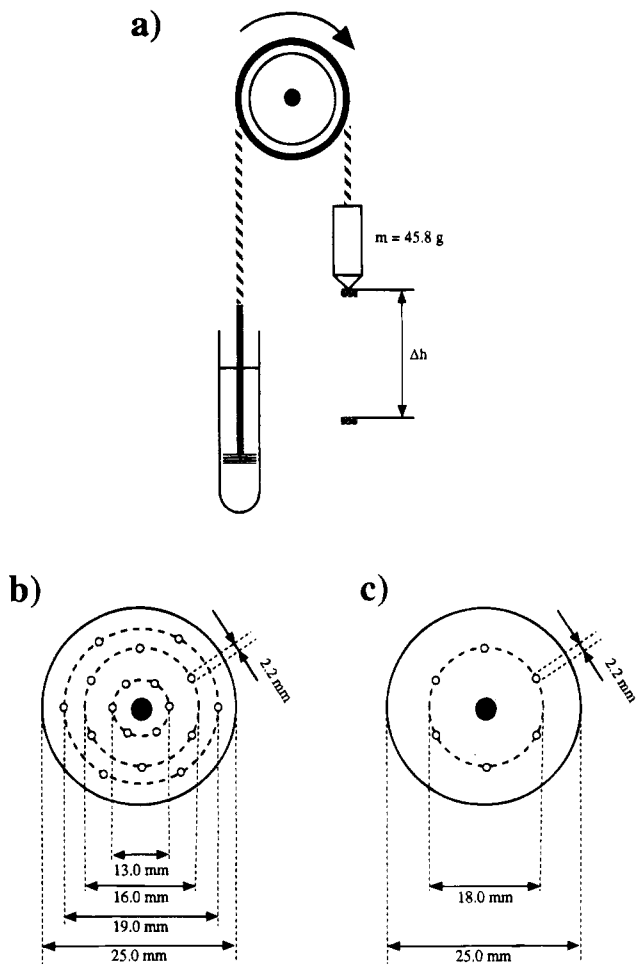

Figure 1. Apparatus: (a) device used to mix solutions, (b) 18 hole plate, and (c) 6 hole plate.

Observations of the Jumping Wave. The reaction mixture was prepared in the following way: we pipetted 40 mL of 2.08 M Na_2SO_3 solution, 40 mL of 0.813 M $NaBrO_3$ solution, 4 mL of bromophenol blue solution, and 0.1 mL of 0.72 M H_2SO_4 solution into a 100 mL graduated cylinder and mixed them thoroughly. This produced an initial lower solution with the following composition: 0.99 M Na_2SO_3, 0.39 M $NaBrO_3$, and 0.86 mM H_2SO_4. The mixer plate was immersed into this solution to the 50 mL scale unit. A mixture of 1.0 mL of 0.72

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[⊗] Abstract published in *Advance ACS Abstracts*, March 1, 1995.

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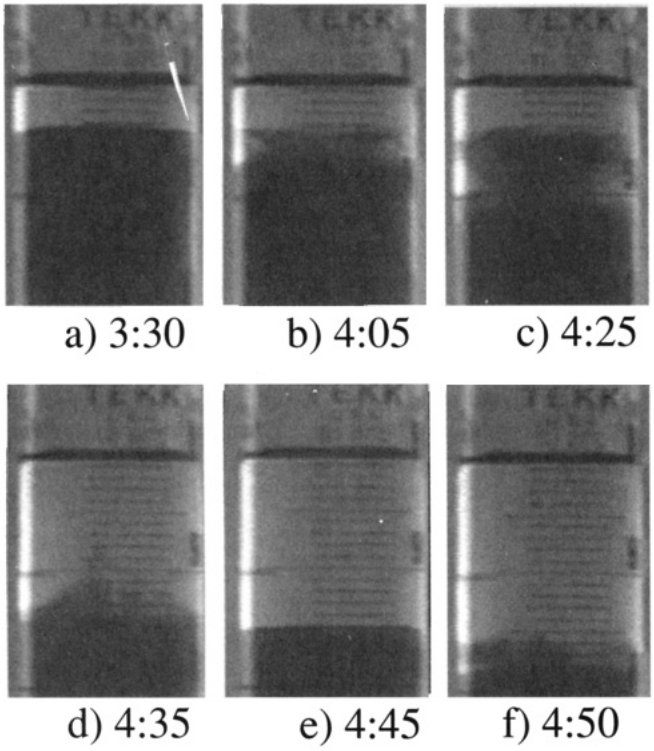

Figure 2. Evolution of the jumping wave and shape of the jumping wave at different times. Composition of the solution before creation of the pH gradient: 0.99 M Na_2SO_3, 0.387 M $NaBrO_3$, 0.4 w/v% bromophenol blue, 0.48 mM H_2SO_4. The top solution was 16 mL of 45 mM H_2SO_4. The 18 hole plate was used to create the initial pH gradient. Time is indicated in minutes:seconds.

M H_2SO_4 and 15 mL of distilled water was carefully poured into the cylinder, and the mixer plate was pulled up immediately a distance of 0.2 m. The front was initiated with 0.9 mL of 0.1 M H_2SO_4 solution layered on the reactant solution.

We observed that the front was flat and stable after initiation and traveled downward, but after 4−5 min it became unstable and fingering (double-diffusive convection) began (Figure 2). The fingering did not develop completely but a large section of solution (from scale units 95 to 85) reacted, leaving a flat front at a lower scale. After this first long jump (the front jumped down about 10 scale units, from the 95th to the 85th scale unit), 10−12 shorter jumps (2−4 scale units) occurred. We tested if similar systems would exhibit the same periodic behavior. Neither the chlorate−sulfite nor iodate−sulfite systems did.

Measurement of the pH Gradient. We carried out experiments with nonreactive solutions. Values in parentheses indicate concentrations after mixing: 40 mL of 2.08 M (0.98 M) Na_2SO_3 solution, 40 mL of 1.35 M (0.696 M) Na_2SO_4 (we used Na_2SO_4 to produce a solution of the same density as the reaction mixture), 0.1 mL of 0.72 (0.85 mM) M H_2SO_4 solution, 4 mL distilled water, 0.6 mL phenolphthalein solution, and 1.0 mL universal pH indicator were pipetted into the 100 mL graduated cylinder and mixed thoroughly. The color of the mixture was dark pink. The 18 hole plate was immersed into the solution to the 50 mL scale unit, and 16 mL of 45 mM H_2SO_4 was slowly poured into the cylinder. The mixer was pulled out from the solution, and the color change was recorded using a color camera. The pH was analyzed by digital image processing (Figure 3), and the gray scale (proportional to the pH change) vs distance relationship was plotted. After five experiments, everything was repeated with the six hole plate.

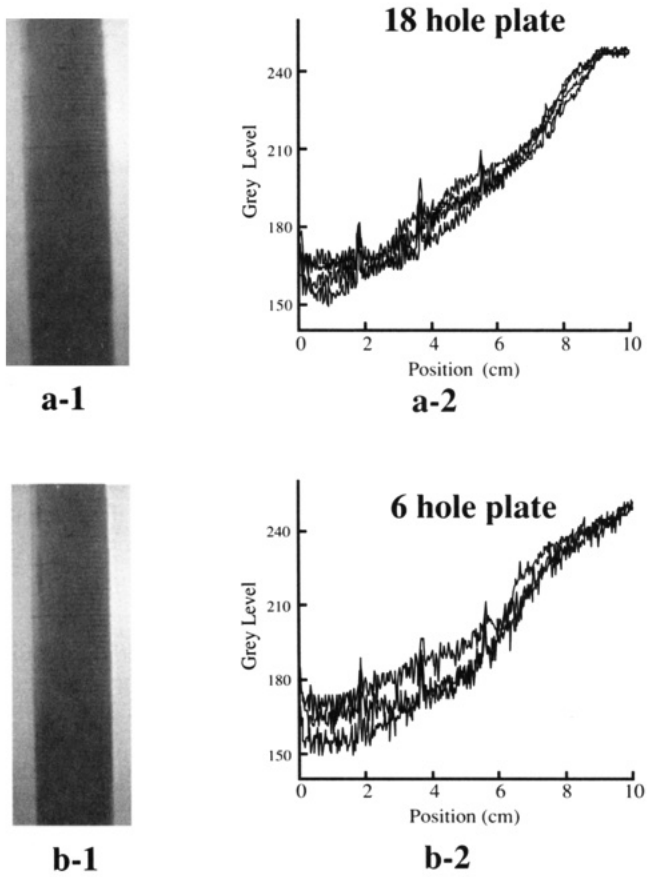

Figure 3. Reproducibility of pH gradient. (a-1) pH gradient in the 100 mL graduated cylinder produced by the 18 hole plate, composition of the initial lower solution, is 40 mL of 0.99 M Na_2SO_3 solution; and the top solution is a 44.1 mL of 1.22 M Na_2SO_4 and 1.63 mM H_2SO_4 solution, to which was added 0.6 mL phenolphthalein solution and 1.0 mL universal pH indicator. The mixing started at the 50 mL scale unit. (a-2) Gray level (proportional to the pH) vs position plot for five parallel experiments. pH at 0 pixel is 8 and 5.5 at pixel 350. Small peaks on the curves are the scale units on the cylinder. (b-1) pH gradient with the same conditions as in a except the six hole plate was used b-2. Gray level vs position plot for five parallel experiments.

Results

pH Gradient Effect. We tested the effect of the pH gradient by varying the initial position of the 18 hole plate (Figure 4). Positioning the plate a longer distance from the top decreased the gradient. The lower solution had the same composition as described in "Observations of the Jumping Wave": 40 mL of 2.08 M Na_2SO_3 solution, 20 mL of 1.63 M $NaBrO_3$ solution, 4 mL of bromophenol blue solution, and 0.1 mL of 0.72 M H_2SO_4 solution; the upper solution consisted of 36.0 mL of 2.0 mM H_2SO_4 solution. The jumping phenomenon did not occur. When the starting position was the 40 mL scale unit, we observed the jumping phenomenon, which began with a long jump (the amplitude of which was almost the same as found in the case of mixing from the 50 mL scale unit) and continued with many shorter ones. Two significant differences should be mentioned: the number of the shorter jumps after the first long one was smaller (7−8), and the last jump occurred between the 70 and the 60 mL scale unit. In the case of mixing from the 50 mL scale unit, the last jump ended under the 60 mL scale unit.

We repeated this experiment (starting from the 40th scale unit) using the six hole plate. The phenomenon began with a long jump (the amplitude of it was the same as in the case when the mixing began at the 50th scale unit), which was followed

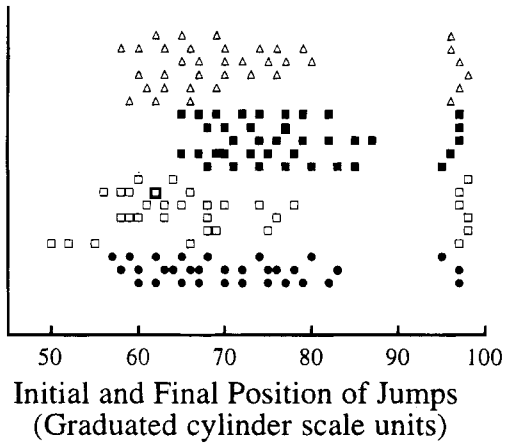

Figure 4. Effect of mixing on the jumping wave. The symbols indicate where the front started and stopped its jump. The top of the tube corresponds to scale unit 100: (△) mixing was begun at the 50 mL scale unit with the 18 hole plate; (+) mixing was begun at the 50 mL scale unit with the six hole plate; (●) mixing was begun at the 40 mL scale unit with the 18 hole plate; and (X) mixing was begun at the 40 mL scale unit with the 6 hole plate.

by shorter jumps; no significant differences can be mentioned when compared to the phenomenon observed in the case of mixing starting at the 50 mL unit with the six hole plate.

We studied the effect of the pH gradient by varying the geometry of the mixing plate holes because this affects the flow pattern. We carried out experiments using the six hole plate, which produces a sharper pH gradient (in the region from 6 to 8 cm from the top) than the 18 hole plate (Figure 3). The phenomenon began similarly to that observed with the 18 hole plate, but after 5 min the front jumped an additional 20 scale units (to the 75 scale unit). After the first long jump additional shorter jumps could be observed (3−4 scale units), but their number was less than in the case of the 18 hole plate.

Effect of Acid Concentration. We carried out experiments with the 18 hole plate using various acid concentrations in the upper solution with the same lower solution composition described in the section "Observation of the Jumping Front". With 16 mL of 23 mM H_2SO_4 the phenomenon was very slow. The jumps of the front were no more real jumps but only fingering. The front did not become flat between two "jumps". With 68 mM H_2SO_4, the front just traveled downward in the cylinder with a flat shape.

Reactant Concentration Dependence. We repeated the experiments described above at several dilutions of the initial sulfite/bromate using the 18 hole plate. With 0.25 M Na_2SO_3 and 0.097 M $NaBrO_3$, no jumps were observed; the front traveled downward and fingering formed. With a 0.50 M Na_2SO_3 and 0.19 M $NaBrO_3$ solution the front was not flat even after initiation, and it did not become flat between jumps. The phenomenon could be described as "turbulent" with faster propagation followed by slower propagation. Under these conditions, the phenomenon began with a long jump followed by shorter jumps. With a 0.75 M Na_2SO_3 and 0.30 M $NaBrO_3$ solution, we observed the following phenomenon: after initiation the front was flat, the first jump occurred followed by shorter jumps but the front did not become flat between successive jumps.

IR Camera Studies of the Jumping Wave. Because double-diffusive convection arises from the competition between isothermal and thermal density changes, we wanted to determine the relationship between the jumping behavior and the thermal condition of the system. Temperature measurements using a single thermocouple are not sufficient to obtain information on the heat transport throughout the solution. Therefore, we used infrared and visible imaging simultaneously to see the pH and temperature changes. The comparison of sequences a and b in Figure 5 indicates that the pH and the temperature changes occur on different time scales; heat transfer to the unreacted region occurs before the pH decreases.

Discussion

Any mechanism of the periodic front must be consistent with three observations.

(1) The phenomenon only occurred with bromate and sulfite but not with chlorate or iodate.

(2) For a fixed acid concentration, a sharper gradient (with the six hole plate) produced a longer first jump but fewer short ones.

(3) The initial concentrations of sulfite and bromate affect the appearance of jumps. Low initial concentrations eliminate the phenomenon, and high concentrations cause such rapid jumps that the front cannot stabilize between them.

Calorimetric data show that some reactions occur sequentially.[1] Edblom et al. studied the kinetics and mechanism of the oscillatory bromate−sulfite−ferrocyanide reaction.[6] They used concentrations close to those in our experiments, and they carried out the experiments at pH of approximately 6. The pH in our initial reaction mixture was between 6 and 7. Therefore, we assumed the same reaction mechanism for our system as well.

Using the mechanism in Table 1, we are able to explain the interesting phenomenon found during the measurement of the reaction heat, i.e., after preparing the reaction mixture the reaction starts immediately, and heat is generated, but the bromophenol blue indicator shows no pH change. This first step of the reaction may be described by R1 because it is slow in comparison to the other steps, and no pH change occurs during this reaction. Steps R2 and R3 are fast and consume protons. Steps R4 and R5 are slower and produce protons. The main proton-producing reaction step is the R6, so this is responsible for the overall pH change of the reaction.

We therefore propose a mechanism for the periodic convection. At the top of the tube, a lower pH exists, and the reaction is less buffered and occurs more quickly. Because of heat losses the solution temperature is a function not only of the reaction enthalpy but also of the rate of heat production. As we showed in the preceding paper, double-diffusive convection occurs, which transports heat faster than mass. (The difference in transport coefficients between heat and solute causes the double-diffusive instability.) Figure 5(a-2) shows that the region that will react rapidly during the jump is heating up before any pH change.

The periodicity arises because of the pH gradient. Heat that diffuses from a reacted region into unreacted solution does not increase the rate of reaction as effectively because of the gradient. The solution is more buffered in the unreacted regions. The region below is preheated before enough protons are transported to form bisulfite. The increased temperature accelerates the rate of R1, which leads to a build up of Br_2. When protons do diffuse into the region, the reaction occurs very rapidly leading to the appearance of a jump in the front position.

The sharper the gradients the greater the difference in time scales between the heat transport and its effect on the reaction rate. Therefore, as the front proceeds down the tube the solution is more buffered, and the heat from above will have more time to dissipate before the autocatalytic acid-producing reactions take over. Although the pH gradients do not appear very different for the different mixers (except in the 6−8 cm region),

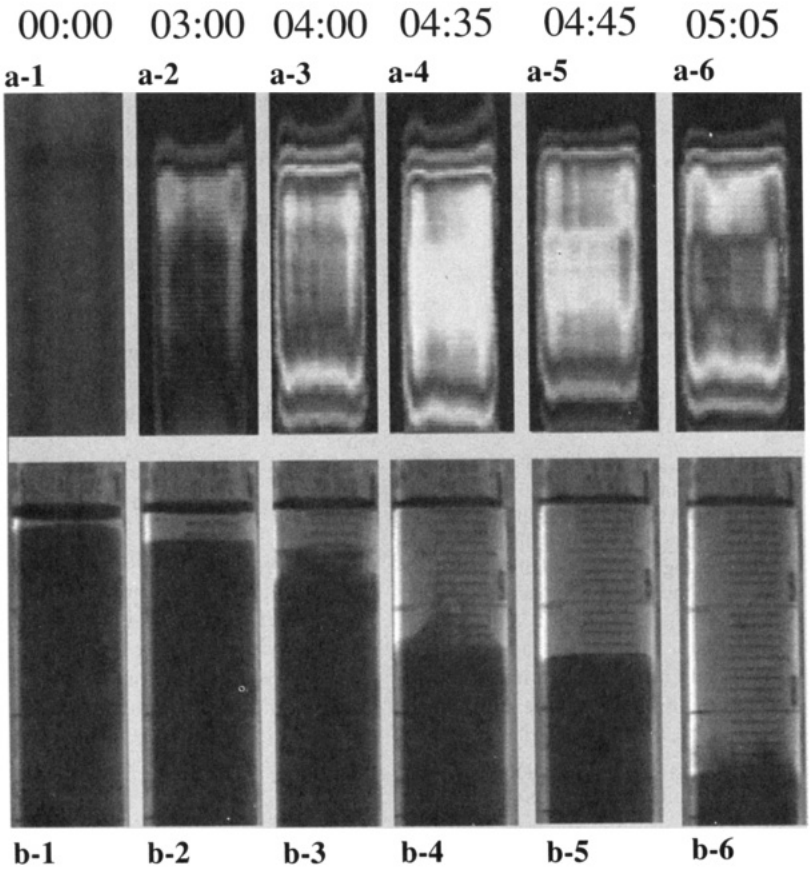

Figure 5. pH and temperature distributions during the jumping phenomenon in the first 5 min of the reaction. Sequence a-1−a-6 (top): temperature distribution during the jumping phenomenon; black indicates regions below 30 °C, white indicates temperature above 50 °C Intermediate gray levels indicate transition temperatures in the 30−50 °C region. Sequence b-1−b-6 (bottom): pH distribution indicated by the color change of bromophenol blue. Dark region shows blue (basic), light indicates yellow (acidic). Time is indicated in minutes:seconds.

TABLE 1: Reaction Mechanism for the Bromate−Sulfite Reaction[6]

	reaction	rate constant
R1	$BrO_3^- + HSO_3^- \rightarrow HBrO_2 + SO_4^{2-}$	$8.0 \times 10^{-2}\ M^{-1}\ s^{-1}$
R2	$HBrO_2 + Br^- + H^+ \rightarrow 2HOBr$	$9.5 \times 10^{6}\ M^{-2}\ s^{-1}$
R3	$HOBr + Br^- + H^+ \rightarrow Br_2 + H_2O$	$1.6 \times 10^{10}\ M^{-2}\ s^{-1}$
R4	$Br_2 + H_2O \rightarrow HOBr + Br^- + H^+$	$1.1 \times 10^{1}\ s^{-1}$
R5	$2HOBr_2 \rightarrow BrO_3^- + HOBr + H^+$	$3.0 \times 10^{3}\ M^{-1}\ s^{-1}$
R6	$Br_2 + HSO_3^- + H_2O \rightarrow 2Br^- + SO_4^{2-} + 3H^+$	$1.0 \times 10^{6}\ M^{-1}\ s^{-1}$
R7	$H^+ + SO_3^{2-} \rightarrow HSO_3^-$	$5.0 \times 10^{10}\ M^{-1}\ s^{-1}$
R8	$HSO_3^- \rightarrow H^+ + SO_3^{2-}$	$3.0 \times 10^{3}\ s^{-1}$

the behavior is different. This difference indicates that the sensitivity of the front to pH gradients is greater than the resolution of the our imaging technique.

The initial concentrations have an effect because the jumps arise from the difference in time scales between thermal and mass transport. Low concentrations mean that the heat produced has time to dissipate, suppressing the jumps. High initial concentrations mean that the lag between the buildup of Br_2 and the proton producing reactions is less; the jumps are not well separated in time or space.

A complete model of this phenomenon will require simulating in three-dimensions the double-diffusive instability with chemical reactions in the presence of a pH gradient.

Acknowledgment. This work was supported by the U.S.−Hungarian Science and Technology Joint Fund (Grant J. F. No. 247/92a), the National Scientific Research Fund of Hungary (OTKA Grant No. F-4024), the Ministry of Education of the Hungarian Government (MKM Grant Number 9/94), the National Science Foundation's Mississippi EPSCoR Program, and NASA's Microgravity Materials Science Program (NAG8-973). We thank Reuben Simoyi, Cordelia Chinake, and Marcus Hauser for critical readings of the manuscript. Special acknowledgment is made to NASA (Stennis Space Center) for providing the IR imaging equipment and to Charles Thurman and Joe Whitehead for helpful consultation on IR imaging.

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JP943002C