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DISSOLUTION KINETICS OF CALCIUM CARBONATE IN SEA WATER. III: A NEW METHOD FOR THE STUDY OF CARBONATE REACTION KINETICS

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ABSTRACT. A new method for the study of carbonate reaction kinetics has been developed based on a pH-stat technique which allows accurate and automatic measurement of dissolution rates under conditions of steady-state disequilibrium. This method has evolved during three years of experimentation and from over 500 runs. It has been used for study of the dissolution kinetics of synthetic calcite and carbonate oozes (Morse and Berner, 1972; Berner and Morse, 1974; Morse, 1974). Presently, dissolution rates as slow as 6×10^{-11} g calcite/cm^2/sec can be measured with a reproductability of better than ± 10 percent. The degree of saturation can be held constant to within 1 percent, and up to six runs can be done in a day. This technique has important advantages over the "free drift" approach previously used for the investigation of carbonate dissolution kinetics, and it also should be well suited for studies of calcium carbonate precipitation.

INTRODUCTION

Previous studies of the reaction kinetics of calcium carbonate, in aqueous solution under various conditions, have all employed the same basic approach (Weyl, 1958, 1967; Terjesen and others, 1961 Pytkowicz, 1965; Nestaas and Terjesen, 1969; Nancollas and Reddy, 1971; Cooke, ms; Plummer, ms; Pesret, ms). In all cases the system was started at either supersaturation or undersaturation and allowed to react toward equilibrium. However, the carbonate system presents a rare opportunity to maintain a nearly constant state of disequilibrium. By utilizing this unique feature, it is possible to obtain accurate reaction rates and to study adsorption and the effects of possible inhibitors under constant conditions.

The basis for the maintenance of a constant state of disequilibrium comes from consideration of the dissolution or growth of calcium carbonate via reaction 1. Equation 2 shows that there are only three concentration variables in the dissolution or growth of calcium carbonate, (assuming the activity of water is close to constant) when reaction 1 is followed — $m_{Ca^{++}}$, a_{H^+}, and P_{CO_2}.

$$CaCO_3 + 2H^+ \rightleftharpoons Ca^{++} + H_2O + CO_2 \text{ (gas)} \qquad (1)$$

$$\Omega = \frac{a_{Ca^{++}}\, a_{CO_3^{--}}}{K_c} = K' \left(\frac{m_{Ca^{++}}\, P_{CO_2}}{a_{H^+}{}^2} \right) \qquad (2)$$

Where: Ω = the degree of saturation

a = activity

m = the total molality (free ions plus ion pairs)

$$K' = \frac{K_{012}\,\gamma_{T_{Ca^{++}}}}{K_c}$$

K_c = equilibrium ion activity product of calcite under the experimental conditions

K_{012} = the activity equilibrium constant for the reaction:

$$CO_2\ (gas) + H_2O \rightleftharpoons 2H^+ + CO_3^{--} \qquad (3)$$

$\gamma_{T_{Ca^{++}}}$ = total activity coefficient of calcium ion

P_{CO_2} = partial pressure of carbon dioxide

Thus, at constant a_{H^+}, $m_{Ca^{++}}$, and P_{CO_2}, the degree of saturation is constant.

It is possible to hold P_{CO_2} constant by bubbling a CO_2-air mixture of constant composition through the solution during reaction. The concentration of calcium ($m_{Ca^{++}}$) is essentially constant because a negligibly small amount of $CaCO_3$ can be dissolved or precipitated relative to the amount of calcium originally present in the solution. For example, the dissolution of 1 mg of calcite in a liter of sea water, in equilibrium with the atmosphere, would result in a change in the calcium concentration by a factor of only 1.0005. Although the change in the calcium concentration in this example would be negligibly small, the change in hydrogen ion concentration would be by a factor of approximately 1000. It is, therefore, necessary to add either acid or base to the solution in order to maintain a nearly constant pH and, consequently, a close to constant degree of saturation. The hydrogen ion activity can be continuously monitored on a pH meter, and the rate of addition of either acid or base necessary to maintain a constant pH can then be used as a precise method of determining the reaction rate via the stoichiometry of reaction 1.

CONSTRUCTION OF A pH-STAT

Figure 1 is a schematic diagram of the arrangement of the components of the pH-stat system that has been developed for the study of carbonate reaction kinetics at constant disequilibrium. In the configuration shown, the pH is continuously monitored on a controller and recorded on a dual pen recorder. Whenever a set pH limit is exceeded, the controller activates an automatic syringe which adds either acid (HCl) or base (NaOH) to the test solution. The amount of titrant added is constantly recorded on the dual pen recorder.

A number of different reaction vessel designs and materials have been tried. The design presently being used is shown in figure 2. It is important to use "non-reactive" materials in the construction of the reaction vessel if reproducable results are to be obtained. Rubber should be avoided, as it adsorbs a large variety of compounds and may give off organics. This adsorption leads to a disastrous increase in the "memory" of the system. Even the best stainless steel was found to rust with con-

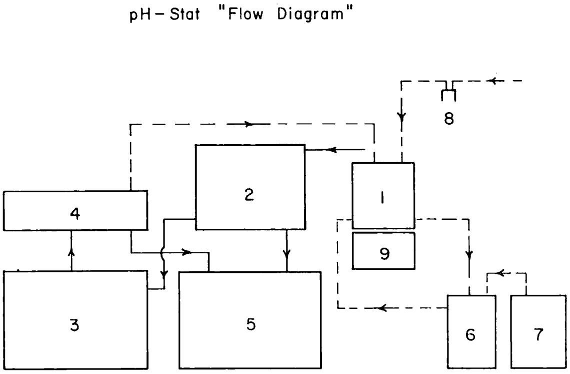

Fig. 1. Schematic "flow diagram" of the apparatus used in the pH-stat. The solid connecting lines indicate electrical linkage, and the dashed lines indicate fluid and gas connections.

(1) Reaction vessel; (2) pH meter; (3) controller; (4) automatic syringe; (5) dual-pen recorder; (6) temperature control; (7) refrigeration unit; (8) gas moisturizing chamber; (9) magnetic stirrer.

tinuous use. Rusting resulted in intermittent addition of fresh iron oxide and lead to poor reproducibility.

Another source of problems was the bubbler. Normal sintered glass bubblers trap calcium carbonate and serve as sinks for inhibitors that are subsequently given off in an irregular manner. Even boiling the sintered glass bubblers in acid does not clean them sufficiently. They are a great source of irreproducibility and should not even be used in pre-equilibration (see discussion on procedure). The bubbler used in this system was constructed from pyrex glass tubing.

A constant temperature is maintained by a "flow-through" type water bath. This water bath is completely covered with 1 cm thick foam rubber for thermal insulation, which is especially necessary at low temperatures. The tubing connecting the water bath to the temperature controller is also covered with foam insulation. It is important to insulate the bottom of the water bath as the magnetic stirrer becomes warm with extended use and causes gradual heating during long runs at low temperatures. The walls and bottom of the water bath have been indented to hold the reaction vessel in a manner that allows water to flow around it on all sides and the bottom.

The reaction vessel presently being used is made of pyrex glass and has a volume of 450 ml. It is covered with a snugly fitting teflon cap which is approximately 2 cm thick. Holes have been drilled through the cap at diameters very close to the diameters of the various pieces that must extend into the interior. Tygon tubing is used for support collars that allow these pieces to be positioned at the desired level. The top has also been fitted with a threaded teflon rod that allows precise height adjustments to be made on a suspended magnetic stirring bar. Suspension of the magnetic stirring bar is important to prevent grinding of particles against the bottom of the vessel which can cause a change in reaction rate. Problems can arise in the use of a suspended magnetic stirring bar if a flatbottomed reaction vessel is used due to settling out of material in the low velocity zone that occurs immediately below the center of the stirring bar. To avoid this problem a reaction vessel with an indented bottom is used.

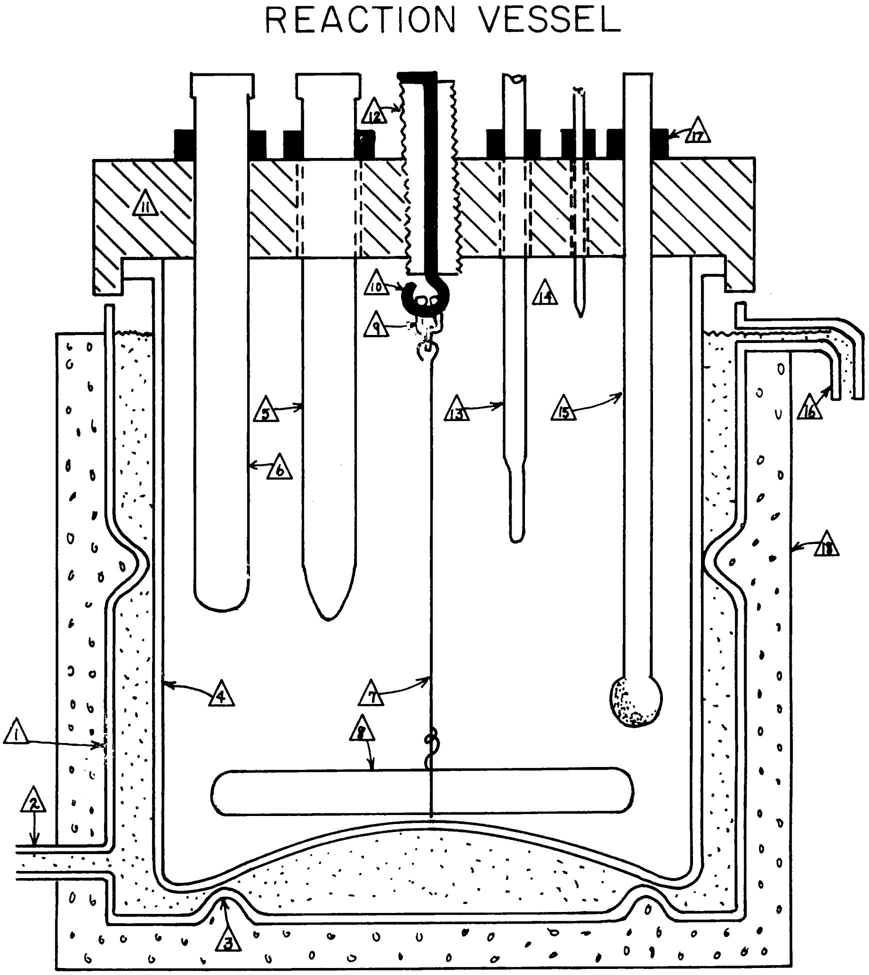

Fig. 2. Diagram of reaction vessel (not to scale).

(1) Water bath; (2) water inlet; (3) vessel support; (4) reaction chamber; (5) pH electrode; (6) calomel electrode; (7) platinum magnetic stirrer support wire; (8) magnetic stirrer bar; (9) teflon swivel; (10) platinum swivel support wire; (11) teflon vessel top; (12) teflon stirrer adjuster; (13) thermometer; (14) avid or base inlet; (15) glass bubbler; (16) water outlet; (17) tygon collar; (18) foam insulation.

PROCEDURE FOR STUDYING DISSOLUTION

In carrying out a procedure that will yield reproducible results the most important factor is to perform every step in the most consistent manner possible. If a series of runs is to be done, it should be carried out in the shortest possible time interval, and enough of the reaction medium and reagents should be prepared so that the same stock solution can be used for the entire series. Failure to do this can result in non-reproducible, altered reaction rates (due, at least partly, to unavoidable contamination by trace species).

Before adding calcium carbonate to the solution, the solution must first be equilibrated with the gas and have obtained a pH very close to that at which the run is to take place. Failure to do this will result in a false reaction rate due to titration of preexisting alkalinity. Just how far from the run pH it is permissible to start depends on the precision desired, the rate that is to be encountered, and the pH at which the run is to be carried out. However, if the runs are carried out within 0.30 pH units of the equilibrium pH value it is generally necessary to have the pH within ± 0.01 of the run pH before starting. One way to accomplish this, although somewhat time consuming, is to get the pH close to the desired value (on the high side for dissolution) and set the controller at the desired pH limit and allow it to bring the solution to the exact pH at which the run is to take place. A low rate of addition must be set on the automatic burette so as not to overshoot. It is helpful to monitor the pH on the recorder throughout pre-equilibration so it can be determined when solution-gas equilibrium is reached. If an entire series of runs is to be carried out at relatively small differences in the degree of saturation, it is very helpful to pre-equilibrate the entire stock solution to a pH near the center of the range. This not only saves time but results in greater reproducibility due to less chance of variable contamination. Frequently a certain amount of "trial and error" is involved in arriving at the correct pH. The time it takes to reach the desired pH depends on how much the pH of the solution is to be changed and the value of the P_{CO_2} that is being used, with equilibration being slower at low P_{CO_2} values. Consequently, the amount of time that the solution spends reaching the required pH can vary from a few minutes to several hours. The best results (although certainly not the quickest) are obtained by waiting for the same period of time in all runs before starting the reaction.

In carrying out this procedure, it is very important to avoid contamination by the standard buffer solution in which the electrodes are immersed for calibration. Most buffer solutions used to standardize electrodes in the intermediate pH range utilize a phosphatic buffering compound. Phosphate, even at low concentrations, has a large effect on calcite dissolution kinetics (Morse and Berner, 1972; Berner and Morse, 1974; Morse, 1974). To avoid this problem the electrodes must be carefully washed with distilled water after removal from the buffer solution.

A major consideration is the balance to be set up between acid or base strength, the amount of carbonate to be reacted, the time period over which the reaction is to occur, and the amount of pH variation that is permissible. It is important to remember that the calcium concentration must remain constant to within a few percent in order to maintain a constant degree of saturation at constant pH. The amount of material that is to dissolve must, therefore, not be so large to alter seriously the calcium concentration. If large amounts of titrant are to be used, the titrant should be made out of the stock solution so that it will not alter original concentrations. For very precise work, where it is necessary to dissolve a relatively large amount of material, the calcium concentration can be held constant by setting the calcium concentration in a titrant, of composition similar to that of the stock solution, at a level such that the calcium that comes from the dissolving carbonate is balanced by the dilution caused by the addition of titrant.

In order to maintain a nearly constant state of disequilibrium, one of the three chemical components, involved in the carbonate reaction, that must be kept constant is the P_{CO_2} (see eq 2). The method used to keep the P_{CO_2} constant during dissolution was to bubble a gas of known P_{CO_2} through the solution. The effectiveness of this method depends on the rate at which dissolved carbon dioxide is produced in the solution by dissolution of calcium carbonate as compared with the rate of transport of carbon dioxide between the solution and bubbles. Under the experimental conditions used in this work, gases with P_{CO_2} values of less than $10^{-2.6}$ did not remain in equilibrium with the solution during runs in which very rapid dissolution took place.

The gases used were nitrogen-carbon dioxide mixtures. Each tank of gas was calibrated by bubbling the gas through a 10^{-3} molar solution of sodium bicarbonate at 25°C and monitoring the pH. When the equilibrium pH was obtained the P_{CO_2} of the gas mixture was calculated from known carbonate equilibrium constants and the Debye-Hückel equation for converting HCO_3^- concentration to activity. Since these gas mixtures were waterfree, the gas was bubbled through distilled water before being bubbled through the solution used for the experiment.

The carbonates that have been studied generally have had a characteristic curve shape, for percent of starting material dissolved versus time, that has been useful in comparing reactions. As shown in figure 3, for up to approximately 20 percent complete dissolution of a synthetic calcite sample, a nearly straight line is approximated. In cases where the curve has this shape, it is possible to measure the reaction rate after only a small percentage of the material has been dissolved. This method should be used with caution, and the dissolution curve for each sample must be determined to see if it can be reasonably approximated by a linear curve over a significant portion of the reaction. Special care should be used when applying this method to natural materials of mixed composition, as phases of different composition dissolve out at different rates, and abrupt changes in reaction rate can occur within a run.

Different amounts of sample can be used in order to bring about sufficiently slow or rapid rates of acid (or base) addition. This is possible

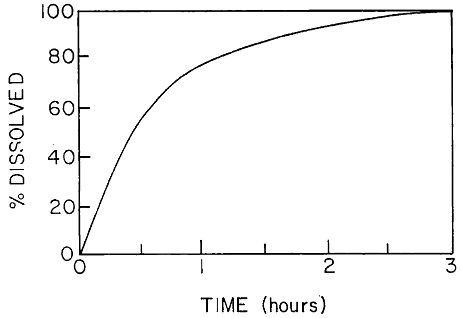

Fig. 3. Plot of percent dissolution versus time. Note that the plot is very close to linear up to approximately 20 percent completion. The plot was obtained from the continuous recording of the amount of hydrochloric acid added with time.

because, for a given sample of $CaCO_3$, this rate was found to vary linearly with sample size (that is, surface area), as shown in table 1.

CHECKS ON THE VALIDITY OF THE pH-STAT METHOD

A possible source of error in the pH-stat method could arise from increases in dissolution rates caused by the very short term inhomogeneities that occur in the solution immediately after the addition of acid. If this is a source of error, the rate of dissolution should be dependent on the amount of material present per unit volume of solution, for a given titrant concentration, or dependent on the concentration of the titrant for a given amount of material per unit volume of the solution. Table 1 contains data that indicates that, within the reproducibility (± 10 percent) of the method, the rate of dissolution is independent of both the titrant concentration and the amount of material present per unit volume of the solution. It is therefore unlikely that the short term variations in the degree of saturation, in the immediate vicinity of where a drop of titrant enters the solution, result in false dissolution rates.

A check was made to determine if dissolution rates measured at constant pH values, close to the equilibrium pH for the conditions of

TABLE 1

Constancy of dissolution rate with surface area

Area (m^2)	Rate ($mg/cm^2/yr$)	Acid normality (HCl)
0.008	67	0.05
0.025	63	0.05
0.075	80	0.05
0.150	77	0.10
0.300	74	0.10

ph = 7.17; $P_{CO_2} = 10^{2.58}$, reagent grade calcite
Done in 350 ml of $NaCl$–$CaCl_2$ solution with same ionic strength and calcium concentration as sea water of 35‰ salinity.

the experiment, are real, and that the calculated equilibrium pH values used were correct. Artificial sea water (see Kester and others, 1965), low in phosphate, nitrate, and silica, was equilibrated to a pH of 7.45 at a $P_{CO_2} = 10^{-2.58}$ and synthetic calcite added. After 12 hours the pH had drifted upward to a value of 7.49. The same procedure was carried out with a starting pH = 7.55. This time the pH drifted down to a value of 7.52. These values closely bracket the calculated value of equilibrium pH at this P_{CO_2} of 7.51. They indicate calcite dissolution on the low side and precipitation on the high side of the calculated equilibrium value and reinforce the argument that the dissolution rates measured close to equilibrium are real and not the result of self-titration.

DISCUSSION

The "free drift" type experiments on carbonate reaction kinetics have generally been carried out in a manner that allowed the reaction rate to be determined by monitoring the change in pH of the solution with time (Weyl, 1958, 1967; Plummer, ms; Pesret, ms). Rates determined by this method are dependent on calculating the hydrogen ion consumption from the change in slope plot of pH versus time (see fig. 4). The hydrogen ion consumption involved in the reaction of calcium carbonate with the solution is not simply related to the change in pH of the solution, since the carbonate alkalinity of the solution is also changing due to dissolution of $CaCO_3$. The relation between the carbonate alkalinity change and the change in pH of the solution is given in equation 4.

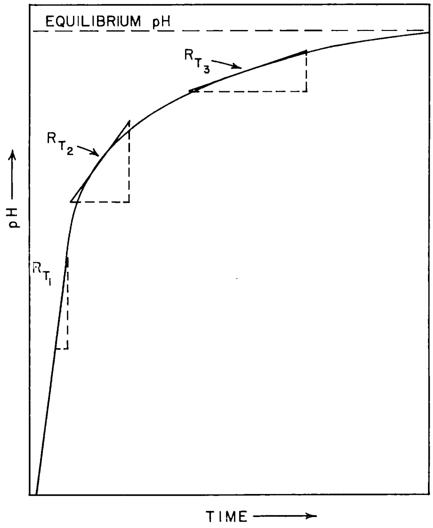

Fig. 4. Time versus pH for free drift type of kinetic experiment. The rate of pH change is the slope of the line.

$$\Delta A_c = (m_{HCO_3^-{}_2} - m_{HCO_3^-{}_1}) + 2(m_{CO_3^{--}{}_2} - m_{CO_3^{--}{}_1})$$

$$= \frac{K_0K_1P_{CO_2}}{\gamma_{T_{H_2CO_3}}\ \gamma_{T_{HCO_3^-}}}\left[\frac{1}{a_{H_2^+}} - \frac{1}{a_{H_1^+}}\right]$$

$$+ \frac{2K_2}{\gamma_{T_{CO_3^{--}}}}\left[\frac{1}{a_{H_2^+}{}^2} - \frac{1}{a_{H_1^+}{}^2}\right] \qquad (4)$$

where:

$$A_c = \text{carbonate alkalinity} = m_{HCO_3^-} + 2m_{CO_3^{--}}$$

K_0 is the thermodynamic equilibrium constant for the reaction

$$CO_2 + H_2O \rightleftharpoons H_2CO_3$$

K_1 and K_2 are the first and second thermodynamic disassociation constants for carbonic acid.

For sea water at a $P_{CO_2} = 1$ atm and a pH less than the equilibrium value for calcite of approximately 6, the bicarbonate ion term is dominant, and the carbonate ion term can be dropped. Equation 4 can then be written as:

$$\Delta A_c \cong \left(\frac{K_0K_1P_{CO_2}}{\gamma_{T_{H_2CO_3}}\ \gamma_{T_{HCO_3^{--}}}}\right)\left(\frac{1}{a_{H_2^+}} - \frac{1}{a_{H_1^+}}\right)$$

$$\cong (3 \times 10^{-8})\left(\frac{1}{a_{H_2^+}} - \frac{1}{a_{H_1^+}}\right) \qquad (5)$$

Table 2 gives numerical data on the amount of hydrogen ion that must be consumed in order to change the pH by 0.1, using a borate-free sea-water approximation, at several different pH values within the interval generally studied for dissolution kinetics. Note that the direct relation between rate of reaction (that is H^+ consumption) and pH change decreases greatly as equilibrium with $CaCO_3$ is approached. This problem is compounded by the fact that as equilibrium is approached, it becomes

TABLE 2

pH change	Moles of hydrogen consumed per liter
4.0-4.1	7.8×10^{-5}
4.5-4.6	2.4×10^{-4}
5.0-5.1	7.8×10^{-4}
5.5-5.6	2.4×10^{-3}
6.0-6.1	7.8×10^{-3}

increasingly difficult to measure accurately changes in the slope of a plot of pH versus time (that is, the second derivative of pH with respect to time becomes hard to determine accurately). In order to obtain the difference in the carbonate reaction rate, this change must be multiplied by very large numbers (on the order of 10^4). It consequently becomes increasingly difficult to obtain information as equilibrium is approached from undersaturation.

In approaching equilibrium from supersaturation, the situation is somewhat different since alkalinity is decreasing as equilibrium is approached. However, the measured growth rates near equilibrium can be no more accurate than the near equilibrium dissolution rates, since they are obtained at even higher alkalinities.

Fortunately, the alkalinity problem does not assail the determination of carbonate dissolution rates in the pH-stat type experiments, since the alkalinity remains constant. As a result, hydrogen ion consumption or production exactly follows the stoichiometry of equation 1. It may be necessary to obtain reaction rates at only very small differences in pH between the data points (0.01-0.03 pH units spacing). Under these conditions the reaction rate can be determined at one stated pH, and then the pH-stat turned off, and the pH allowed to drift a few hundredths of a pH. Then the stating can be begun at the new pH. When this is done the rate of drift up to the new pH is not used for the reasons that have just been discussed. However, if sufficient time is allowed for the carbonic acid system to come to equilibrium at the new pH the rate can again be accurately determined.

SUMMARY

The pH-state method presented in this paper represents a new approach to the study of carbonate reaction kinetics. Unlike the previously used "free drift" methods, in which the state of saturation continuously changes, it allows an accurate measurement of dissolution rates under conditions of constant disequilibrium. The method has been developed so that it is now possible to maintain the degree of saturation constant to within 1 percent and measure dissolution rates as slow as 6×10^{-11} g calcite/cm^2/sec with a reproducibility of better than ± 10 percent. Up to six runs can be carried out in a day. Special advantages for the study of adsorption and desorption phenomenon are presented by this method due to the conditions of constant disequilibrium. It also makes possible the detailed study of effects of inhibitors under steady state conditions.

ACKNOWLEDGMENTS

Professor R. A. Berner originally suggested the possibility of measuring carbonate reaction kinetics by a pH-stat technique and has contributed greatly to the development of the method as presented here. Research support was provided to the author by NSF Grants GA 1441 and GX 30288X.

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