CMS News

A Publication of The Clay Minerals Society

March 1991

Letter from the President

CMS stalwarts thanked

The preamble to the CMS by-laws states in part that "the particular business and objectives of the Society shall be to encourage ... the advancement of clay mineral science ... the promotion of research ... the increase and diffusion of knowledge ... and to promote scientific interest and inquiry thereby fostering public welfare and education, aiding the development of industries and natural resources, and adding to the material prosperity and happiness of all people." These are noble goals!

CMS volunteer Pat Costanzo: Council Member and Program Development Chair High Iron Photos

Soon after returning from our annual meeting last October, I realized what was required to keep the Society founded on these objectives. Commitment! Not only by me, but also by you, the membership.

In addition to a seven-member executive committee and a twelve-member council, the Society depends heavily on the services of five standing committees and eleven ad hoc committees. My first concern as president was finding the individuals to fill the 79 positions on these committees! I was delighted to discover that nearly everyone responded positively, even enthusiastically, to my invitation to serve the Society. Moreover, I know that there are many more of you willing to serve, and I'm sure Bob Reynolds will seek you out when he replenishes the committees as president of CMS next year.

The point that I want to emphasize is that it requires the efforts of a huge number of people to make CMS the thriving professional organization it is today. If we include our liaison representatives, our office advisor, and the members of the local organizing committee for the annual meetings, there are more than 100 positions that must be staffed to make the Society function in accord with its objectives. Having a

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Volume 3 published

Thermal Analysis of Clays, edited by D. L. Bish, J. W. Stucki, and F. A. Mumpton, has just been published. The third volume in the CMS Workshop Series, this book includes an introduction by R. F. Giese and the following chapters: "Precision Scanning Calorimetry of Clay Minerals and Their Intercalates," by R. F. Giese, "High Pressure Differential Thermal Analysis: Applications to Clay Minerals," by A. F. Koster van Groos and Stephen Guggenheim, "Thermogravimetric Analysis of Minerals," by D. L. Bish and C. J. Duffy, "Vaccum Thermogravimetric Analysis and Evolved Gas Analysis by Mass Spectrometry," by F. J. Wicks and R. A. Ramik, and "Mineral Index" by J. W. Stucki.

Thermal Analysis of Clays is available from the CMS Office in Boulder for $10.00 plus $2.00 postage, in U.S. funds drawn on a U.S. bank.

Did you send in your request for more information on the annual meeting?

If not, you won't receive subsequent mailings concerning registration and abstracts. A similar form on page 14 can also be sent.

Inside ...

The Clay Minerals Society

President Thomas J. Pinnavaia, Michigan State University
Vice President Robert C. Reynolds, Jr., Dartmouth College
Secretary Don Scafe, Alberta Research Council
Treasurer and Editor-in-Chief Kenneth M. Towe, Smithsonian Institution
Immediate Past Pres. Brij L. Sawhney, Connecticut Agricultural Experiment Station
Vice President Elect David R. Pevear, Exxon Production Research Company
Office Manager/Newsletter Editor Patricia J. Eberl

CMS News is published quarterly by The Clay Minerals Society. Contributions of articles, letters, commentary, photographs, and drawings are welcome.

The newsletter is distributed to all CMS members. Membership rates are as follows: full membership, including a subscription to *Clays and Clay Minerals*, $35.00/year; student membership, $17.00/year; nonsubscribing membership, $10.00/year. Institutional subscriptions to *Clays and Clay Minerals*, $125.00/yr ($140.00 overseas). Please contact the Society Office for information regarding membership and subscriptions, and for a copy of our publications list.

CMS News welcomes advertising. Inquire about rates to the Society Office. Articles and other contributions submitted to *CMS News* are subject to editing and are published on a space available basis. All opinions expressed herein are the opinions of individual contributors, and not of The Clay Minerals Society.

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Letters

Orchids to Bull

Editor:

Although you know that Bull Bailey received both the Miner and Roebling Awards, I call attention to this "double whammy" as proving that he is at the top as both a *teacher* and *researcher*—in these days of argument about teaching vs. research in our universities and the objectives of education. Maybe this feat of double excellence in antipathetic capabilities should be mentioned in the newsletter. Orchids to Bull!

Walter D. Keller
Columbia, Missouri

The Same to You, Walt

Editor:

The Keller 90 Kaolin Symposium in Missouri was more than clay, as important as that is. For those who have reached 60 and those who are just thinking about it, it may well have added decades to our productivity. Just think of it! If each of us begins to target 90 as our productivity goal, as Dr. Walt Keller has done, what a boost that will be for the study of clays. I like the idea. I hope you find it attractive, too.

J. B. Dixon
College Station, Texas

Kaolin question

Editor:

Please ask the Clay Doctor, or the general membership of the Society if the CD is too modest to enlighten us, several questions about the origin of kaolinite, the answers to which I did not hear at the Kaolin Symposium.

Is there a commercial-size deposit of kaolin geologically older in time of origin than the Carboniferous (Pennsylvanian over here)? If not, why not? Is an abundance of land plants necessary for large deposits of kaolin to form? If so, are large quantities of the organic (chelating) acids from plants necessary; or is a high concentration of gaseous O_2, from photosynthesis by many plants, in the atmosphere necessary to form kaolin?

How does a thick stack (book, or vermicule) of kaolinite that formed from direct *weathering* of feldspar *recognizably* differ from a vermicule or stack formed by *recrystallization* of kaolinite in a secondary deposit?

In a stack of kaolinite flakes where the c-axes of the crystals are in line, are the a and b axes of the crystals likewise superimposed in line?

W. D. Keller
Columbia, Missouri

Errata

Editor:

Sam Patterson informs Robert Hall that Hall erred in his mention of the paleobotany "lesson" on page 17 of the December 1990 issue of *CMS News*. First, it was David Keller,

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Thanks...

To the following people who contributed to this issue:

Joe B. Dixon
Dennis D. Eberl
Jessica Elzea
Robert B. Hall
Warren D. Huff
Walter D. Keller
Bruno Lanson
M. J. Nash
David R. Pevear
Thomas J. Pinnavaia
Richard M. Pollastro
J. L. Post
C. B. Roth
Don Scafe
Garrison Sposito
Kenneth M. Towe
Jeffrey R. Walker
Joe L. White
Gene Whitney

Letter from the President,

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membership willing to serve makes it all possible. As president, I want to express my appreciation of your commitment to CMS and for making it the dynamic professional organization that it is today.

At the risk of adding yet another layer of administrative responsibility, I have appointed this year a new Ad Hoc Committee on Regulatory Issues. I believe this will be a valuable committee for CMS, because increasing government regulations on finely divided materials will continue to have an impact on the use of clay minerals in commerce and research. This committee will keep us informed of federal and state regulatory activities and provide us a means of responding as a Society when appropriate.

I should also like to report that Ken Towe is doing an outstanding job as Interim Editor of our journal. The processing of new manuscripts is being efficiently handled, and the publication of new issues of *Clays and Clay Minerals* for 1991 is on schedule. A vigorous executive committee search for a permanent editor is underway. *Clays and Clay Minerals* established a world-wide reputation as the best journal in its field under the editorial leadership of Fred Mumpton. I am confident that we soon will have a capable new editor to continue this CMS tradition of excellence. To help us in meeting our publishing commitments, Rich Pollastro has agreed to serve as Special Publications Editor. He will edit two issues of the workshop lecture notes.

The Annual Meeting in Columbia last October was a great success, thanks to the thorough organizing efforts of Bill Johns, Jack Burst, and their colleagues. Dave Pevear and Joe Dixon are working hard on our next meeting in Houston on October 6-10, 1991. I hope to see you there!

Tom Pinnavaia
East Lansing, Michigan

Letters,

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student at University of Missouri—Rolla, who discovered the fossil and not Patterson. Second, the fossil was *Stigmaria* (root scars associated with *Lepidodenron* and *Sigillaria*) and not *Calamites*, as reported by Hall. *Calamites* does not yield root scars. A red-faced Hall admits his errors.

Futhermore, Glen Goulson should have been spelled Glenn Golson, peludal should be paludal, and salutory should be salutary.

Bob Hall
Lakewood, Colorado

Notices

S. W. "Bull" Bailey is recuperating at home after surgery this winter. Friends and colleagues can write him at 5049 LaCrosse Lane, Madison, WI 53706.

The Regulatory Issues Committee is interested in gathering any available data (published and unpublished) on the CMS Source Clays. This data, which may include, but need not be limited to, results from XRD, SEM, DTA, TEM, and chemical analyses, will be used to update the Source Clay Files. Please send references or other information to Jo Eberl at the Society Office.

Jessica Elzea

I've sent about 150 pounds of beidellite to the Source Clays Repository. The material contains about 18 percent quartz and about 5% poorly crystalline kaolinite, but was the best material readily available. The material has been analyzed and found to contain about 31 percent Al_2O_3, by weight. The quartz is readily removed by sedimentation.

The material was secured by Barrett Cupp, Senior Geologist, and donated by the NERCO DeLamar Mining Company where he is employed.

J. L. Post

The Pioneer Lecturer is to be chosen by the local annual meeting organizing committee, not by the Awards Committee, as incorrectly stated in the December 1990 issue of *CMS News*.

The organizing committee of the CMS-Columbia Meeting reports a surplus of $8444.73, which goes into CMS endowment funds to support grants and lectureships. This surplus was due, in part, to the large number of walk-on registrants.

Positions Available

A large international industrial group is seeking recent PhDs from U.S. and Canadian universities for year-long post-doctoral appointments in France. The selected candidates will work either in our labs in France or in a French University in collaboration with our labs. Knowledge of French is desired but not mandatory.

Research topics for the positions are areas of pattern recognition applied to geophysical characterization of sedimentary rocks for oil and gas exploration, and all areas of geochemistry applied to sedimentary rocks: characterization methods (ESCA, X-rays...), clay minerals, stable or unstable isotopes, and fluid inclusions.

Send résumé, a research proposal, and possibly, the name of the desired university to: Ms. Mélisende Bart, 1899 L Street, N.W., Suite 500, Washington, D. C. 20036.

Student Research Grants

CMS research grants of up to $2500 each are available to masters and doctoral students of clay science or technology. The deadline for applying for the grants is August 1, 1991. Contact the CMS Office for information and applications.

Interviews with the clay scientists

Joe L. White

Dr. Joe L. White, the 1990 Distinguished Member of The Clay Minerals Society, taught and carried out research in soil mineralogy and chemistry at Purdue University from 1947 to 1988. The interview was conducted by Dennis Eberl and Charles Roth at Columbia, Missouri.

Drawing by M. J. Nash

CMS: In your career you have studied many diverse subjects dealing with clays, including soil science, medicine, chemistry, and so on. Is there an underlying agenda to what you've been studying?

WHITE: No, there really is no underlying agenda. For a while I was trying to do quantitative clay mineral analysis by X-ray diffraction. Then I got interested in the reaction of molten salts with mica systems. That study opened up a method for studying the mica weathering sequence by taking potassium out of mica in increments, and by putting it back in again, and looking at the diffraction effects. I did not purposely sit down and say, "Well, I'm going to study mica weathering by this technique." In fact, the reason I even got started looking at the molten salt idea was because of John Wear's preliminary examination. I tried to think of a difficult question or two for him, so I was browsing through Emeleus and Anderson's book on inorganic chemistry. I saw that the German scientist, Thilo, had published information about metal oxides and chlorides reacting with pyrophyllite; he thought that he had evidence that magnesium went into the lattice. So I thought that since lithium is quite small, it might react with mica. I had been using sodium cobaltinitrite to extract the potassium out of mica, but that is a very, very slow reaction; so I tried lithium chloride, and sure enough I got a reaction. However, the high temperature of the melt resulted in formation of spinel. I mentioned the experiment to Phil Low, and he said that I should try a salt having a lower melting point, like lithium nitrate. I tried lithium nitrate and voila! It worked.

CMS: The idea is that the lithium ion is not hydrated if you use a molten salt; so it goes into the inner layer more easily and replaces the potassium.

WHITE: Yes, that's right. In addition, the lithium ion migrates into empty octahedral sites, thereby lowering the charge and facilitating further removal of potassium. The concentration of lithium in that melt is about 32 molar, so there is a very strong driving force. You have to keep the potassium activity down by removing the material as the potassium comes out, because the system reaches a point at which the potassium level in the melt inhibits further potassium removal.

CMS: Did this idea have some practical application?

WHITE: Illite is one of the main minerals present in the soils in Indiana, where it weathers to a 14 angstrom material in many situations. If I could do that in the laboratory, it might be a way of studying artificially-induced mica weathering. Significant potassium removal under natural conditions takes thousands of years. J. B. Peterson, who was head of the department at that time, encouraged me to try to get a National Research Council Fellowship to study this. Dr. Peterson mentioned that he had had a wonderful experience on such a fellowship, working at Berkeley with Hans Jenny; so he encouraged me to apply. I wrote up a little proposal to NRC and, sure enough, I got a wonderful letter saying that I was going to be awarded the fellowship. I had proposed to work with MacEwan at Rothamsted.

CMS: At what stage in your career were you then?

WHITE: Well, this was just in time for my first sabbatical. I went to Purdue in '47, and this was in '53-'54. I consciously chose to go to Europe. At that time it was

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quite an adventure of faith, because we had three children who were not in school yet, and my salary was pretty meager. We decided that we would do it—we never really had traveled very far— but we went, and it turned out to be a very wonderful experience. As a result of that, I made it a practice to go on sabbaticals to foreign labs any time I had an opportunity.

At that time George Brown, Robin Greene-Kelly, and Douglas MacEwan had been recruited by Alex Muir as part of the pedology department at Rothamsted, and they were the tops. During subsequent trips to Europe (I went to international meetings as often as I could), I always would make a tour of the laboratories; so I visited Fripiat's laboratory at Leuven frequently, as well as Chaussidon (Versailles), Rothamsted, Macaulay, and Udo Schwertmann (Freising) every time I had an opportunity. As a result, it was possible to know what these laboratories were doing, and you could anticipate what they were going to publish in the near future, and you could get ideas from discussions with the researchers. You found out not only what was going on now, but also what they were planning for the future. It was a way of keeping your finger on the pulse of research in Europe.

CMS: Recently, Macaulay and Rothamsted have lost their clay groups.

WHITE: Yes, that was most unfortunate, because these two groups were really premier groups. They had made contributions to clay mineralogy like no other groups had made. Many people in The Clay Minerals Society and the soils groups wrote letters of protest to the government, pointing out that these people were really an international treasure, something that should be maintained at all costs.

CMS: Some of your more interesting work was in aluminum complexes. Would you describe that work, and how you got involved in it?

WHITE: I had noticed in some consulting research I had done on soils from Costa Rica that there were some precursors for gibbsites that were amorphous to X-rays, but that could be studied by infrared. This was a little bit of information for the database. Later I saw a note in the *Purdue Monday Memo,* the faculty paper, that a scientist in Physical Pharmacy by the name of S. L. Hem had written a paper about the acid reactivity of aluminum hydroxide gels as affected by anions. I called him. We met, and we saw right away that we had many common interests. This resulted in a collaborative research effort that has continued now for about 20 years. This was one of the high points in my career.

CMS: You have several patents in that area. What are your patents?

WHITE: These are patents which cover the composition of matter and processes for producing aluminum hydroxyl carbonate, and a method for drying it so that the dry powders have acid reactivity comparable to that of the liquid aluminum hydroxycarbonate gels.

CMS: What are these powders used for?

I made it a practice to go on sabbaticals to foreign labs any time I had an opportunity....It was a way of keeping your finger on the pulse of research in Europe.

WHITE: They're used primarily for the treatment of stomach acidity, and are found in products like Maalox and Mylanta. We found right away that the so-called aluminum hydroxide really wasn't $Al(OH)_3$. That astounded us. We didn't know very much about it, but found that whenever you precipitated it, whatever the anion was, some of that anion was incorporated into the lattice. For example, you would get $Al(OH)_{2.5}$, plus $Cl_{0.5}$ to satisfy the charge.

CMS: So when carbonate is incorporated into the complex, it will block crystal growth centers?

WHITE: Yes. The carbonate had been considered to be a contaminant in these materials. From the infrared spectra we could see the splitting of the carbonate band, indicating that it was bonded to aluminum rather tightly. We discovered that carbonate was an integral part of the structure. The size of the carbonate ion prevented the crystal lattice of the hydroxide from continuing to grow. The particle size stayed quite small, and it was amorphous to X-rays.

CMS: The fine particle size kept it highly reactive?

WHITE: It stayed highly reactive. So this discovery was quite a breakthrough in understanding the nature of these compounds that were being made commercially.

CMS: I can see how work on these compounds developed from your interest in soil science. How did you get interested in soil science to begin with? Were you always interested in agronomy ?

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Ralph E. Grim, John Gieseking, Joe White, and S. W. Bailey during the 1969 International Clay Conference, Tokyo.

Courtesy Joe White

WHITE: I had a friend who lived across the street in Checotah, Oklahoma, who went to work for the Soil Conservation Service (SCS) as an agronomist. I had been interested in science and chemistry in high school, and I knew I wanted to do something that involved chemistry. I told myself that if he could get a job in agronomy, then maybe I could too. I really had wanted to go to Oklahoma A&M to study aeronautical engineering. I went there, and they said don't write us, we'll write you, and they never did. So I went to Connors State Agricultural School near Warner, Oklahoma, for two years in the area of agronomy and soils, and then continued at Oklahoma State at Stillwater. This work enabled me to continue studying chemistry.

After completing BS and MS degrees at Oklahoma State, I went to work at the SCS as a supervisor trainee. After a few months I saw that everything that you used to make decisions could be put on a small 4 x 6 index card, and I said that's not for me. Advancement in SCS work units was a matter of politics. My advisor at Oklahoma State, Dr. Horace J. Harper, had said that if I decided to go to graduate school to let him know, and he would see if he could help me get a fellowship at Wisconsin or Iowa. I chose Wisconsin to study clay minerals with M. L. Jackson. I didn't know much about clay minerals; I remembered having read a paper by Marshall that had these little ball and stick structural diagrams, and that was all I knew about clay minerals at that time.

Jackson was the one who gave me the concept that ideas are the currency of research.

CMS: That would have been early then in Jackson's career?

WHITE: Very early. He had had two PhD students: N. Hellman and Dan Aldrich. Jackson went to Purdue for a year at the very time that I went to Wisconsin. He gave me brief instructions on the operation of the XRD unit and sample preparation and showed me XRD patterns of standard mineral mixtures. He gave me about twenty samples and asked if I would run them and get the data to him by the end of December. I had never seen an X-ray diffraction machine before, but I followed instructions and got the results to him on schedule.

CMS: Jackson has had so many talented students. Why do you think that he was so successful in attracting students, and in training them so well?

WHITE: Dr. Jackson is a person who is just full of ideas. He was the one who gave me the concept that ideas are the currency of research. The more ideas you have, the greater the possibility that you'll have some good ones.

CMS: Pauling said something like that: to do research you just have to have a lot of ideas, and throw away the bad ones.

WHITE: That's right. Jackson had a tremendous breadth of interest; he just covered the waterfront. He knew the areas of suface chemistry, mineralogy, and geology; so it was really stimulating to be a part of his research group.

CMS: Did you go right from Wisconsin to Purdue ?

WHITE: Yes. In fact, that was the only job offer that I had. So I didn't have much choice, but it turned out to be best in the long run. N. J. Volk, who also graduated from Wisconsin, was the director of the experiment station at Purdue at the time. He had a great interest in potassium fixation, because he had made the observation several years before that there was an increase in the mica content in soils that could be attributed to addition of potassium fertilizer; so he was interested in my background in clay mineralogy. It was a very good environment in which to work, in terms of support and the personal involvement of the administrators. They all had a personal interest in you because the subject matter you were working on was of direct concern to them. This was true of Dr. Peterson as well; so you had the feeling that you had people behind you, supporting you.

CMS: The University gave you financial support to pursue your research?

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White, *continued*

WHITE: Yes. They provided the funds for graduate students. There were a couple of graduate students funded by the experiment station at that time. Unfortunately, we didn't have an X-ray machine. I went over to the physics department and found they had an air-cooled Phillips XRD unit. We would use it when they weren't using it. Things went along pretty well until they got pretty busy on the instrument. Several times I went over at two o'clock in the morning to start when the student would quit. Then a student in physics got assigned to a project in which they tied up the only machine for three years solid; so that was the end of that. As a result of going to Rothamsted, and of having some ideas about mica weathering, I was able to get an NSF grant that funded the diffraction unit. It became the X-ray facility for soil clay mineralogy at Purdue.

CMS: How is funding today ?

WHITE: Funding is very, very difficult. Most of the equipment is anywhere from ten to thirty years obsolete. In fact, funding is virtually non-existent. There are hardly any federal agencies that will support basic research in the field of soil mineralogy at the present time.

CMS: Why is this? Do people not think that soil research is important, possibly because of overproduction in food?

Toshio Sudo and Joe White during the 1961 Conference on Clay Mineralogy and Petrography, Prague.
Courtesy Joe White

WHITE: The problem is that people at the higher levels of government do not really understand the role that scientific research plays in providing the support for decisions and strategies in agriculture.

CMS: You got interested in X-ray diffraction very early, but probably some of your best work in the area of clays and soils has been in infrared spectroscopy. When did you get interested in infrared, and for what reason?

WHITE: I became interested in it because I was able to visit Fripiat's laboratory, and some of the other laboratories in Europe, where I became aware that surface chemistry had an important role to play in understanding interactions in soils, especially pesticide-soil interactions. The Europeans were using infrared as one of their main techniques. George Bailey finished studying with me in soil mineralogy, and he stayed on at Purdue as a post doctoral. We wrote a proposal to the National Institute of Health to study soil-pesticide interactions using infrared and X-ray techniques to get an understanding of how these

The problem is that people at the higher levels of government do not really understand the role that scientific research plays in providing the support for decisions and strategies in agriculture.

were interacting at the mineral surfaces, how they would be degraded and held, and so on. The grant was written at the beginning of the era of the sixties, so we were able to get funding for an infrared instrument that made it possible to go all out in looking at clay organic interactions by infrared techniques.

CMS: Is it the Bronsted acidity of clays that breaks down pesticides ?

WHITE: Well, that's one of the concepts. But Joe Feldcamp did work in which it appeared that Le Chatelier's principle was involved, that it wasn't surface acidity as such. If you have material that has very low solubility, when that material is absorbed, you upset the equilibrium. If the clay preferentially takes out one of those ionized moieties, then the equilibrium keeps on pulling more of the material into solution. You can place compounds that are absolutely insoluble, in solvents like chloroform, and if you put a clay film in with them, you may observe very significant absorption just from the driving force of that molecule being absorbed.

CMS: Is it the ion exchange reaction that decomposes the pesticide ?

WHITE: Well, the pesticide has a pK; so that means that it does dissociate. If you have a sink to absorb the dissociated species, the pesticide just keeps on being dissociated and absorbed. It's really amazing. In some cases, the apparent pK of the molecule in the presence of the clay surface is shifted up by 5 units; so reactions happen that at first glance you would not predict should happen. Adsorption of the pesticide by ion exchange

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doesn't necessarily cause decomposition or loss of biological activity. Some protonated s-triazine herbicides show biological activity when they are desorbed; others tend to undergo hydrolysis and lose their biological activity.

Our discussion reminds me that I have changed my research topic about every ten years. This pattern probably is by chance. Nevertheless, by going into a new area, I had to declare that I was completely ignorant, and had to start from scratch to learn about it. It is exciting and stimulating, and a real learning experience.

G W. Bailey, Robert Ledoux, and Joe White during the 1969 International Clay Conference, Tokyo. *Courtesy Joe White*

CMS: There often seems to be a lot of resistance from people who are in a field to accept contributions from a newcomer.

WHITE: That is very true, but it is sad because nature and science are each a continuum. There are no pigeon holes that say that this is where earth science starts, and this is where it stops. Because people are in departments, they have blinders on their eyes. They fail to look outside their area. People need to be encouraged to do interdisciplinary studies, and to view things from a different standpoint.

I found that it was exciting and stimulating to go to what started out to be the Pittsburgh Conference. Instead of going there with a specific problem and trying to find some way to measure it, to go down the aisles and say, "Well now, here's an instrument. What does it measure? How can I use that in soils research?" You'd come up with some ideas you'd never usually think about. So I encouraged graduate students and younger staff to go to those kinds of exhibits.

CMS: That might be an idea you learned from Fripiat?

WHITE: Well that may be, because in his lab we used every kind of instrument you could think of: UV, infrared, high vacuum systems, X-ray diffraction, NMR. I'm sure exposure to that kind of environment made me aware of the power of instrumentation.

CMS: Are there any instruments that you are interested in now that you think may open up the field?

WHITE: Yes, I know of one that has a great deal of potential. Unfortunately, it is not commercially available as yet, but hopefully it will be in the near future. It is a device called FODA, Fiber Optic Doppler Anemometer, which uses a laser beam to measure the scattering of light by particles. The doppler shift can be used to determine particle size, and FODA can be used in concentrated suspensions. No other laser instrument allows you to do that. This instrument makes it possible to measure the number of particles showing Brownian motion, so that when particles interact to form some kind of a three-dimensional structure, and the Brownian motion stops, the signal goes to zero. So we can precisely measure the point of gelation. We have used it to develop an understanding of the rheological nature of aluminum hydroxide gels.

This could be a critical tool for every industry that uses suspensions and emulsions, because you can adjust things until particle interactions are happening the way you want them to happen. Control of viscosity is essential in many products, and we don't really have a good theoretical handle on it. Each batch is tailor-made by adding some kind of material to make it more or less viscous. It is one of the important instruments that could revolutionize rheological studies of clays and other kinds of suspensions and emulsions.

CMS: You mentioned the aluminum hydroxides, and that reminded me of your work with liming practices, and how they would affect aluminum toxicity.

WHITE: When I started doing these studies, I was spending a great deal of my time in the pharmacy department, while being supported by agronomy. I had to apologize to the head of the department for several years because I could not say that I was directly studying soil chemistry. When we found that the carbonate was involved in Al-complex stability, it suddenly dawned on us that this work had a spin-off in terms of agronomy. There are crops that are quite sensitive to aluminum toxicity, which usually occurs in acid soils. Soil is acid because it has been leached over long periods of time, and so the common practice is to add calcium carbonate to

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White, *continued*

lime the soil. Sometimes people think that if a little bit is good, more is better; so they raise the pH to 7 or higher. In many acid soils, aluminum dissolves, and it becomes an exchangeable hydroxy cation. The usual idea is to add lime to raise the pH to precipitate $Al(OH)_3$. But when you think about it, that may not be what is happening. Al is present on the exchange sites in the interlayer space as Al-hydroxy complexes that are physically isolated and thus are not affecting plants. But when you raise the pH above 6.5, you expel Al-hydroxy interlayers. We think that aluminum hydroxy carbonate is being made right there in the soil. With these carbonate complexes, the activity of the aluminum is higher than before the soil was limed. I think that this mechanism explains observations made by Malcolm Sumner in Georgia. He plotted the yield of corn as a function of pH. On adding lime, at first the yield went up, but when a pH of 6.5 was reached, the yield decreased. Experiments we have done with grasses suggest that you shouldn't lime soils above pH 6.5. It makes me wonder what's going to happen when limestone is added to lakes that have soluble Al in them.

CMS: Do you think that our soil resources are, on the whole, being managed correctly?

WHITE: I believe soils are being managed more carefully today than they have in the past; I think erosion has been decreased very considerably. The big concern is the movement of fertilizers, herbicides, and pesticides into the groundwater. The practical solution to the problem is very simple, and that is not to try to upgrade water treatment plants to give drinking water quality for flushing toilets and washing cars and irrigating land, but rather let people either have very safe filtration devices, or drink bottled water that has been produced under supervision and is certified as really being pure. There is no way that you can justify infrastructures that purify water to the nth degree to be used for things other that human consumption.

CMS: What about preventing the pollution in the first place by changing agricultural practices?

WHITE: Well, there is a move being made in this direction. The amount of fertilizers are being reduced, and there is more minimum tillage operation in which the soil surface is disturbed very little. I think that you can't go to organic farming because there is not enough manure for all farmers to farm in a completely natural way.

CMS: What was your most exciting contribution? Is there one that stands out in your mind?

WHITE: The most satisfying work is that which Robert LeDoux and I did with the kaolin intercalation complexes with hydrazine, urea, and acetate. By infrared we could actually see the nature of the bonding that was developing. This made it possible to selectively deuterate kaolinite's outer hydroxyls, so that we could assign the inner hydroxyl positions with real certainty. Then we heated the kaolinite to show that proton migration occurs, even at temperatures as low as 150 degrees. Fripiat once said that the hydrogens are so mobile in kaolinite that they behave like a proton gas.

CMS: Do you have any advice for students?

WHITE: During my years of teaching, I developed a few little sayings that I tried to pass on to the students. One is that every experiment turns out right. Many times students think they know what the teacher or the advisor wants. If the experiment doesn't turn out that way, they throw the results out and start all over again. I try to tell them that when you do an experiment, and you record the data properly, what you see is right. You may not

There are no pigeonholes that say this is where earth science starts, and this is where it stops. Because people are in departments, they have blinders on their eyes.

recognize all the parameters that were involved (a fly might have fallen in the phosphate solution you were analyzing or something else may have happened), but if everything is known, that entry is correct. You need to change your idea, to have confidence in yourself that you did the experiment right, and to try to understand why it came out like it did.

Another little bit of philosophy is to be careful what you ask for, because you might get it. Research is not planned by somebody sitting at a desk who understands everything, who has it all figured out, so he knows how it's going to come out before he starts. The chronological order in getting material together to write a paper usually is not expressed in the paper itself. The paper reads as though the person proceeded very logically. It's very important to realize the role of serendipity: that you're not looking for something, but if you observe carefully, you may see something unusual, and you investigate it. You have curiosity enough to wonder why this happened.

CMS: Is there a clay scientist whose work you particularly admired?

continued on next page

White, *continued*

WHITE: I admired Bill Bradley's approach to science, and his intuition. When you would ask Bill a question, he had had so much experience and he knew things so well, that what he said would come out in a very measured way, as though it was coming out for publication in the final form. He would put his foot on the seat of the chair, and cup his hand under his chin, or maybe use his fingers to illustrate the answer to the problem. He had a special kind of insight when he focused on a problem.

CMS: It's not a subject that scientists usually talk about, but in your talk as Distinguished Member, you used quotes from the Bible. Do you think that there is a general opinion among scientists that science and religion don't mix?

WHITE: I get the impression that there is a general feeling of that sort, but I have come to an understanding about this so-called problem of creation and science I was pleased to see in a recent Memorial of Martin J. Buerger by Clifford Frondel (Amer. Min. 1988 73:1483-85) that Buerger was a devout believer in God. Of Buerger's belief in the Bible, Frondel wrote, "He also recognized that the content of order and its expression by rules that characterizes crystallography as a science were the bases of its appeal to him." I believe the statements in the Bible, and so it doesn't bother me that I don't understand *how* this happened, but it is obvious that the kind of energy that was involved in creation isn't going to come out of nothing. It has to have an origin. So when the Bible says that God created the world out of nothing, I can understand that; and when it says the world will be consumed with fervent heat, I can understand that because that's converting matter back to energy. So I don't really have any problem with this. I think that if a person tried to explain scientifically how all these things happened, then he could run into some problems, but that really is not a concern of mine. When I see God's handiwork in terms of the beauty of crystal chemistry and the complexities of DNA and of life itself, why, it's obvious there's no way that this just happened. My belief in God is not based on so-called scientific facts, because if it were, that would remove the role that faith plays. So this belief has made me enjoy science even more, because I know there is order and rhyme and reason in nature. Evidence in the Bible is expressed as inspired and eyewitness accounts recorded by people over hundreds of years. I accept their testimony. If you could prove it, then there would be no role for faith.

CMS: Do you have any advice to those who are just graduating and starting out in a career in soil science?

WHITE: Particularly in the area of soil science, I would say broaden your spectrum of interests and try to keep up with some of the basic science areas so that you can apply new developments, techniques, and instrumentation.

CMS: What about advice to teachers ?

WHITE: Well, teaching is a very difficult situation right now because the person who teaches is at a tremendous disadvantage, especially starting out. Rewards and promotions too often are based on research accomplishments, and until universities develop an objective way of evaluating teaching and rewarding teaching, teaching is going to get the short end of the stick. Teachers are being driven to neglect teaching because they are struggling to find some way to get enough money to satisfy a $100,000- or $200,000-a-year grant minimum that you ought to raise, and the five papers that you ought to publish every year. People who are teaching just can't do that.

CMS: As Keller said, Mammon has replaced Athena in academia.

WHITE: Yes, that is very true. I was very fortunate to come up in an era when excellence in teaching was recognized, because administrators had the authority and the power to reward people. It did not depend on peer review.

CMS: What do you think about the role of the small scientific society, such as The Clay Minerals Society ?

WHITE: In the case of the CMS, I think it's a very, very important role, because it is big enough that it can publish an excellent journal. It has a central office that keeps people in touch with each other very effectively, and at the same time it's small enough that people can get to know each other quite well; the national meetings, as well as the international meetings, encourage this personal relationship. So the meetings are like a family affair, a family reunion. These meetings contrast with those of the American Chemical Society or even the Agronomy Society, where there may be 5,000, 10,000 or 50,000 people getting together, and you can't even find the people you know. The CMS functions like a prism in reverse: it takes diverse disciplines into the prism, and it focuses them on clay science and technology. We have a common material to work on and to talk about, and everybody has a common language. The CMS is the most effective, the most interdisciplinary society that I know. It is absolutely unique.

White's Students

Among Dr. White's students in soil mineralogy and chemistry have been John I. Wear, Gerhardt Talvenheimo, Maurice M. Phillippe, W. L. Parks, James M. Spain, Robert T. Smith, Robert E. Caldwell, Murray G. Klages, James U. Anderson, Cyril B. Brown, George W. Bailey, Dale R. Hensel, Roy D. Bronson, James L. Ahlrichs, Glenn C. Lewis, Allan F. Burns, Sidney Diamond, Robert L. Ledoux, Marion F. Baumgardner, Joe B. Fehrenbacher, Donald F. Post, Alvin L. Zachary, Mark A. Lucas, Lupo A. Montecillo, and Joe R. Feldkamp. In his collaboration with Professor Stanley L. Hem, Department of Industrial and Physical Pharmacy, since 1970, Dr. White has served as co-advisor for the following students in physical pharmacy: Steven L. Nail, Nicholas J. Kerkhof, Linda S. Porubcan, Roger K. Vanderlaan, Edward A. Lipka, Jeffrey E. Browne, Dhiren N. Shah, Dirk L. Teagarden, Mary I. Zapata, Edward C. Scholtz, Robert J. Sepelyak, Jue-Chen Liu, Paul P.-L. Wu, Elaine M. Morefield, Mariela M. Salazar-Gutierrez, Barbara Floy, Neil A. Partridge, Phillip R. Nixon, Suhag Shirodkar, Rosemary Kos, Sally J. Seeber, William J. McLaughlin, Archani Deasai, and Ragheb H. Al-Shakhshir.

Ask the Clay Doctor

(Not a real doctor)

Dear Clay Doctor: When fixed potassium ions are removed from the interlayer position in micaceous clays, it is my understanding that the ditrigonal openings suddenly revert to the slightly smaller hexagonal symmetry and will no longer accept potassium as a fixed ion. My question is, has anyone ever suffered bodily injury during the readjustment of tetrahedral sheets?

Frightened in Flagstaff

Dear Frightened: As a matter of fact, there is one documented incidence of injury due to sudden tetrahedral rotation. Its recipient, strangely enough, was none other than the original discoverer of tetrahedral rotation, A. W. "Lefty" Steinmetz, in the early 1800's. Steinmetz was a peripatetic clay mineralogist in a small village in the Bavarian Alps and had managed to construct in his basement a rather incredible device with which he was able to discern the atomic structure of layer silicates. This was prior to the discovery of X-rays, so he didn't have a name for it. Anyway, on a long holiday week-end when the rest of his family was visiting relatives in a nearby village, Lefty was toying rather daringly with potassium removal in some high-charge illites just to see what would happen. Little did he know of the danger that lay ahead. As he progressively leached out potassium with a sodium borate compound, the internal stresses in the illite increased. Finally, the last ion was removed and for one brief, shining moment, he held a lump of zero-K illite with severely rotated tetrahedra in his right hand. Then with a resounding snap that could be heard all the way to Munich, the tetrahedra readjusted to hexagonal symmetry and Steinmetz's hand was cruelly mangled beyond recognition. The surgeons shook their heads and said nothing could be done and Steinmetz, disillusioned and angry, turned to computer modeling, and, of course, the rest is history.

Dear Clay Doctor: As a first-year student in clay mineralogy, I must confess I am shocked and dismayed to learn that clay minerals suffer from broken bonds. Has this always been the case, and can anything be done to help them?

Forlorn in Fargo

Dear Forlorn: No, clay minerals have not always been victimized by broken bonds. During the Middle Ages, for example, records show that most clays were well-adjusted and reasonably content. Lamentably, the hustle and bustle of the 20th century has inflicted upon them new and unforeseen handicaps. A decade ago I would have said there is nothing to be done outside of collective hand-wringing. But in recent years some startling breakthroughs in surgical procedures offer renewed hope. French doctors have developed prosthetic devices which look remarkably like hydroxyls when connected to the edge of clay plates and cannot be distinguished from the real thing by the casual observer. Belgians, working overtime under the most arduous conditions, have perfected microsurgical procedures for reconnecting broken bonds with minimal scar tissue. And, as you may know, in South Africa they plant little window boxes around the plates to hide the deformities. But I suppose the real answer lies in parapsychology and in helping clays to live with reality, so to speak.

The Clay Doctor is available for consultation. Please send contributions to CMS News.

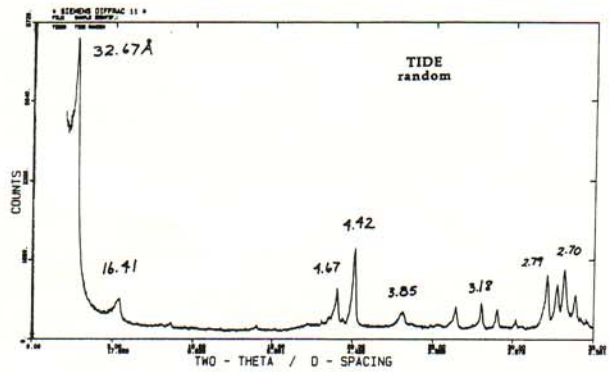
Structure of the Everyday

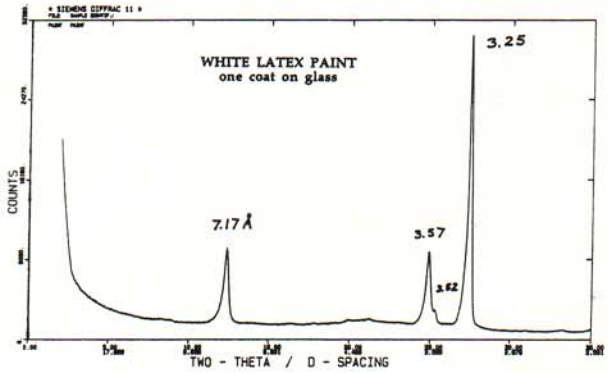
by Levi Pratt

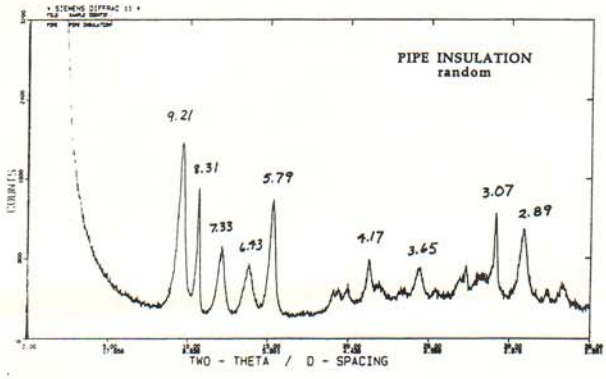
This article was inspired by a rumor that David Pevear, as a graduate student, X-rayed a chocolate bar and found a peak for montmorillonite. Is Kaopectate really kaolinite? Is children's modelling clay actually clay at all? What is the "aluminosilicate" listed in the ingredients of a can of paint? What, exactly, is in a McDonald's milkshake? A few X-ray patterns provide some answers. Listed below are the identifiable ingredients in a few common products. Some are surprising. Some are, well, uninteresting. But at least now you know the answers to some of those questions about "what's really in it?"

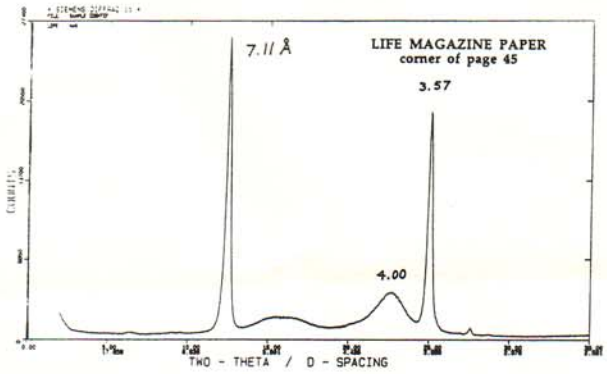
SUMMARY OF PRODUCT MINERALOGY

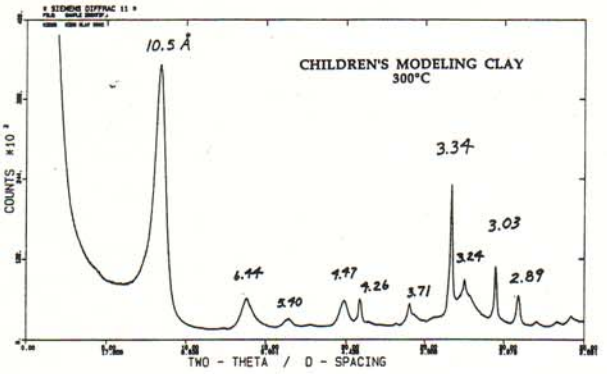
PRODUCT	MINERALOGY AND COMMENTS
Tide detergent	Insoluble residue (a very small proportion of the detergent) appears to contain kaolinite, smectite, and mica. Evidently, Tide comes with pre-dirt. An organic compound in the detergent produces a beautiful peak at 32.67Å.
Pipe insulation	Mixture of serpentine and amphibole (grunerite) asbestos, plus hydromagnesite.
Paint (Colony Satin flat latex enamel)	Kaolinite and titanium dioxide (mixture of rutile and anatase).
Shiny paper *(Life Magazine)*	Kaolinite. When you look at *Life Magazine*, you are also looking directly at kaolinite's c*-axis.
Children's modelling clay	Palygorskite, quartz, calcite, dolomite, organics.
Flavored Kaopectate	Palygorskite, quartz, dolomite, organics. Plain Kaopectate contains kaolinite.
Pepto Bismol	Organics, plus peaks at 9.36, 3.85, and 3.03Å when heated to 300 °C. Organics give beautiful 17Å peak which does not shift upon glycolation and disappears when heated to 300 °C.
Kitty litter (Tidy Cat)	Smectite, quartz, opal C-T (?), kaolinite, mica, clinoptilolite.
Kitty litter (Fresh Step)	Randomly interstratified illite/smectite, which, based on low angle scattering, appears to be about 70% expandable. Actually, Nadeau thinks that it is composed of very thin fundamental illite particles. I asked my cat about this problem, but he didn't know diddly squat.
MacDonald's milkshake	No crystalline components. Rumors of smectite are unfounded. Urp!

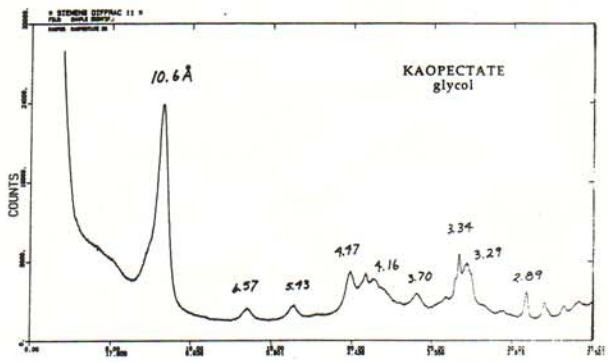


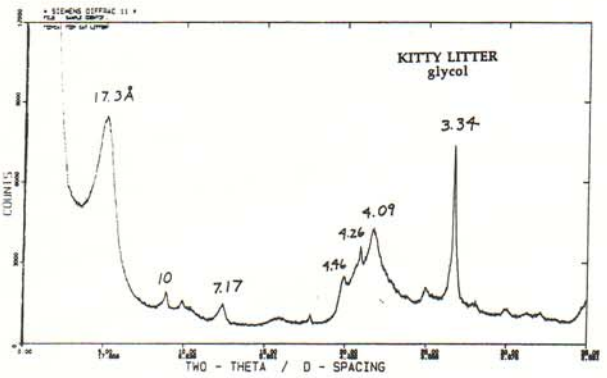












MSA Grant Available

The Mineralogical Society of America offers a grant of $3500 to defray the expenses of research in crystallography. Application deadline: July 1, 1991. For information, contact the MSA, 1130 Seventeenth Street N.W., Suite 330, Washington, D.C. 20036; (202) 775-4344.

Thompson publishes geology text

Graham Thompson has recently co-authored a new geology textbook, *Modern Physical Geology*, with Jonathan Turk. Looking as much like a coffee-table book as a textbook, it is full of color photos and graphs. Divided into four main units, *The Earth: Its Origin and Its Materials, Earthquakes and Plate Tectonics, Surface Processes*, and *Special Topics in Geology*, it includes the unusual chapters "Fossils, Evolution, and Extinction" and "Geologic Evolution of North America," interviews with prominent geologists, and a number of teaching aids such as anecdotes, environmental topics, focus areas, memory devices, analogies that help explain geological processes, and a study guide. Also available are an accompanying slide set, overhead transparency set, and lab manual.

Over 600 pages long, *Modern Physical Geology* is available from Saunders College Publishing, a division of Holt, Rinehart and Winston, Inc. ISBN 0-03-025398-5.

Feats of Clay

Walt Keller was honored with the 1991 Distinguished Alumni Award from the University of Missouri at Columbia, for those whose professional contributions have enhanced their respective disciplines and the quality of life for humankind.

Jim Wood, his wife Jennifer, and sons Collin and Phillip have a new baby in the house, a little girl named Elizabeth.

Eric Eslinger is starting his own consulting business, Alpha Earth, Inc., which will provide services in environmental and petroleum-related fields.

New Members

We welcome the following new members of The Clay Minerals Society.

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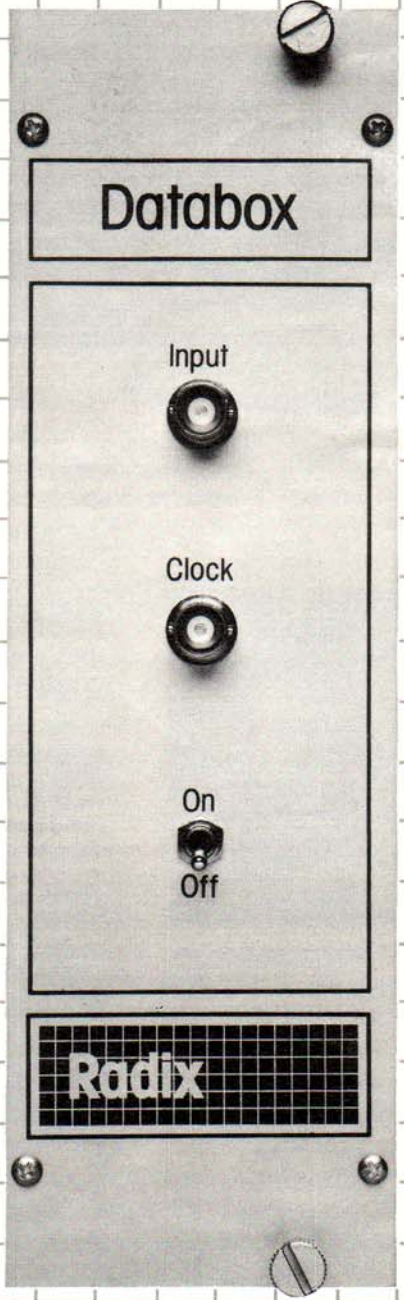

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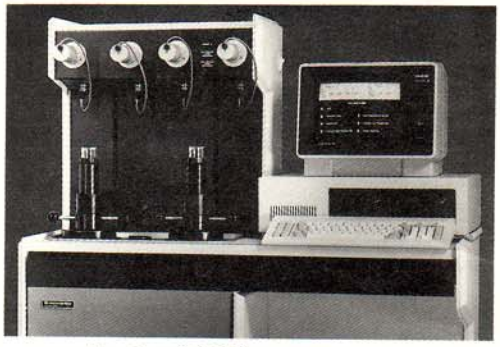

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Commentary

Thoughts on Measuring the Surface Charge of Hydroxylated Minerals Suspended in Aqueous Solution

Oxides, hydroxides, and oxyhydroxides of aluminum, iron, manganese, and silicon abound in terrestrial environments as products of mineral weathering processes. When in contact with water, these solid compounds have in common the property of exposing reactive hydroxyl (OH) functional groups at their surfaces. Some of these OH groups (depending on the nature of their bonding to the solid structure) function as Brønsted acids in the pH range of natural waters. They can dissociate protons to create negatively-charged oxide sites, or they can bind additional protons to create positively-charged water molecules (Lewis acid sites). These two kinds of charged species are, in turn, very reactive with metal cations or with anions in aqueous solution, leading to ion adsorption on the hydroxylated solid surface. The same kind of Brønsted acidity and consequent adsorption reactivity also exists for hydroxyl groups at the edges of crystallites formed by clay minerals, such as kaolinite or illite. Thus, the acidic surface hydroxyl group is a very important contributor to the charge and adsorptive capability of the solid products of weathering in the clay fractions of soils and sediments.

A key property of hydroxylated solid surfaces is their *net proton surface charge density*. This property has been measured electrometrically and reported in literally hundreds of published articles over the past 40 years. The procedure for measurement is described in standard textbooks on the surface chemistry of natural solids. One titrates an aqueous suspension of the solid using an electrode that is reversible with respect to protons (e.g., a glass electrode) coupled to a reference electrode that either is reversible to an anion in the suspension (e.g., Cl^-) or functions irreversibly because of associated liquid junctions. Regardless of the nature of the electrode assembly, the experimental data comprise electromotive force (emf) values that ultimately must be interpreted in terms of the *concentration* of free protons in the aqueous suspension under changing conditions of pH and ionic concentration or composition. Once this is done, the *net proton surface excess* can be calculated with the standard expression (or a near relative of it): net proton surface excess = $(c_A - c_B + [OH^-] - [H^+])V$, where V is the volume of a suspension in which the concentration of strong acid (e.g., HCl) added is c_A, that of strong base (e.g., KOH) added is c_B, that of the free hydroxide ion is $[OH^-]$, and that of the free proton is $[H^+]$. With $[H^+]$ known from emf data, $[OH^-]$ can be calculated with the conditional ionization product constant for liquid water appropriate to the composition of the aqueous solution phase in the suspension. The strong acid or base concentrations are known directly from the titration manipulations themselves.

Garrison Sposito with two of his daughters, Jenny (left) and Sara (right) at the Getty Art Museum in Malibu. Sposito is an occasional consultant to the Getty Conservation Institute for clay mineralogy problems they encounter in the preservation of adobe structures.

Courtesy G. Sposito

Careful published treatments of titration methodology describe the unwanted side-reactions (e.g., proton consumption by aqueous species; solid dissolution or precipitation; particle coagulation or dispersion) that can interfere with the use of a $[H^+]$ determined electrometrically to calculate the net proton surface excess. These interferences, in principle, can be reduced to an acceptable level depending on the perspicacity of the experimentalist. Numerous recipes for doing this are to be found in the literature of natural colloid surface chemistry.

The fundamental experimental issue surrounding the use of $[H^+]$ to calculate the net proton surface excess does not involve the interfering side-reactions, but instead concerns the operartional significance of the relation between emf and $[H^+]$. In plain terms, one needs to calibrate an electrode assembly unambiguously (i.e., without making unverified assumptions) to obtain reliable proton concentrations from a set of emf values. Suppose that the reference electrode in the electrode assembly functions irreversibly because of associated liquid junctions. Then we know from standard electrode theory that nonequilibrium diffusive processes involving the charged species in the aqueous system into which the reference electrode dips will contribute importantly to the resulting emf for a

continued on next page

Sposito, *continued*

suspension with both the proton-reversible and the reference electrode immersed in the suspension itself, then repeat the measurement with the proton-reversible electrode remaining in the suspension while the reference electrode is immersed in an overlying supernatant solution. It has been known for many years that the two emf values so measured will differ. Standard electrode theory, applied under the condition that equilibrium exists with respect to proton transfer between the suspension and its supernatant solution, shows readily that this emf difference arises because of differences in nonequilibrium ion-diffusion processes (for ions other than H^+) in the two aqueous systems with respect to the liquid junction at the reference electrode. This is the famous *suspension effect*. It has nothing to do with the proton-reversible electrode, nor with the suspension-supernatant solution boundary.

If there is a suspension effect, then an electrode assembly cannot be calibrated for use *in a suspension* by, say, measuring the emf values developed in a pure solution to which known amounts of strong acid or base are added. Worse yet would be to calibrate the electrode assembly with standard pH buffer solutions. Not only would there be significant emf inaccuracy because a buffer solution differs considerably from a suspension of natural particles, but there would also be the need to convert pH to $[H^+]$, which, as all good thermodynamics textbooks show, cannot be done unambiguously. One might think of overcoming these problems by suspending the particles to be titrated in a strong electrolyte solution (e.g., KCl) whose concentration is high enough to "swamp" the suspension effect (i.e., the charge concentration of the electrolyte is much larger than that of the suspended particles or other ions in suspension, such that the diffusion processes of the "swamping" electrolyte ions control the response of the reference electrode). This is a possible resolution of the calibration issue vis-à-vis the electrode assembly, but now one faces the non-trivial question of whether net proton surface excesses determined in "swamping" background electrolyte solutions bear any resemblance to those developed in dilute natural waters.

Suppose, instead of an irreversible reference electrode, that a reversible reference electrode is used along with proton-reversible electrode to measure emf. Then, without liquid junctions, nonequilibrium ion diffusion effects are irrelevant and the electrode assembly could be calibrated in solutions of strong acid or base. The problem now is how to interpret the emf values in terms of $[H^+]$ alone, since we know from standard electrode theory that the emf must depend on both $[H^+]$ *and* the concentration of the ion toward which the reference electrode functions reversibly (e.g., Cl^-). In fact, emf in this case is proportional to the chemical potential of the strong electrolyte H_nA, where A^{n-} is the anion sensed by the reference electrode. Therefore, what one needs is a relationship between the chemical potential of H_nA and the free proton concentration. Chemical thermodynamics tells us that no unambiguous relationship of this kind exists. Operationally, one might get around this theoretical problem by calibrating the electrode assembly in synthetic solutions of H^+ added to a "swamping" electrolyte like KCl. The idea here is that a proton titration of the synthetic solution would yield emf values with constant (if unknown) contributions from the non-protonic ions. If the charged particles in the suspension (also containing the "swamping" electrolyte) make a negligible contribution to the emf, this approach will be successful. In molecular terms, one is assuming that the ionic atmosphere around H^+ and A^{n-} has no significant contribution from the charged particles, but only from the solution ions. One has made this assumption with reasonable certainty by adding a "swamping" background electrolyte, but again there spectre of the "baby-with-the-bath-water" problem, noted above, is raised. In all, the accuracy of a calibration in the absence of suspended particles remains largely an article of faith.

Besides the difficulty of determining $[H^+]$ accurately in particle suspensions, which is an experimental problem, there is also a basic conceptual issue concerning the calculation of the net proton surface excess. Speaking strictly, what is calculated with the equation given above is the difference between the surface excess (i.e., adsorption of protons and that of hydroxide ions, *relative to the value of this difference before strong acid or base was added.* This initial value of the net proton surface excess usually is not known experimentally, so the values calculated with titration data must be renormalized by adding (algebraically) to them some reference value that is accessible to experimental determination. For example, at very low pH, it might be possible to set the net proton surface excess equal to a maximum positive value. In practice, unless a well-defined plateau appears in the titration data as pH decreases and the number of protonatable surface hydroxyl groups is known independently, this kind of renormalization procedure is ambiguous. Alternatively, it might be possible to determine a pH value at which the true net proton surface excess should be zero ("point of zero net proton charge" = p.z.n.p.c.). In this case, an "absolute" value of the net proton surface excess would be calculated by subtracting the apparent net proton surface excess at the p.z.n.p.c. from the apparent value at all other pH values. It is common practice, unfortunately, that the titration net proton surface excess is automatically equated with the absolute

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Sposito, *continued*

net proton surface excess, which is correct only if the net proton surface charge happens to be zero when a titration is begun. Equally problematic is the common procedure of plotting the titration net proton surface excess as a function of pH for two (or more) different background electrolyte concentrations, then setting it equal to zero at the point of intersection of the curves. If the value of the titration proton surface excess at the p.z.n.p.c. depends on electrolyte concentration, it follows that the point of intersection of the true proton surface excess curves will not be the same as that of the titration proton surface excess curves. Even if it were the same, equating the pH value at the point of curve intersection with the p.z.n.p.c. is well known to require either additional assumptions about the chemical speciation of particle surfaces or auxiliary measurements of components of the particle surface charge, other than the net proton surface charge.

These considerations would appear to cast doubt on the accuracy of most reported measurements of the net proton surface excess for oxide and clay mineral particles in suspension, since few published data are free of the ambiguities in electrode calibration and net proton surface excess renormalization that have been discussed here. However, if the particles titrated possess no permanent structural surface charge (i.e., no surface charge created by isomorphic substitutions among the structural ions) and if the electrode assembly is immersed solely in an overlying supernatant solution during the titration, most of the fundamental issues raised in this commentary are resolved. At equilibrium, the electrochemical potentials of any aqueous species to which the electrode assembly responds reversibly are the same in the suspension and its supernatant solution, so emf measurements and an electrode calibration performed solely in the latter aqueous system will suffice to determine $[H^+]$. If there is no structural charge (generally the case for oxide minerals), the p.z.n.p.c. can be shown to be the same as the pH value at which the surface excess of cations (other than H^+) equals that of anions (other than OH^-) adsorbed by the particles. This latter pH value can be measured independently, and then used to renormalize the titration proton surface excess to "absolute" values. The problem of how to renormalize in the case of particles (like most clay minerals) which do possess structural charge remains an open question.

Garrison Sposito
Berkeley, California

Meeting Calendar

July 21-26, 1991, Toledo, Ohio: **Annual Meeting of the American Crystallographic Association**. Contact: Margaret C. Etter, Dept. of Chemistry, University of Minnesota, 78 Kolthoff Hall, Minneapolis, MN 55455. Phone: (612) 624-5217.

August 12-16, 1991, Ithaca, New York: **Clay Swelling and Expansive Soils,** NATO Advanced Research Workshop. Application deadline April 15, 1991. Contact: Dr. Philip Baveye, Dept. of Soil, Crop, and Atmospheric Sciences, Bradfield Hall, Cornell University, Ithaca, NY 14853 USA.

August 23-24, 1991, Berlin: **Euroclat '91,** 5th International Meeting. Topics: Supergene Ore Deposits and Mineral Formation, General Aspects of Laterite Research. Abstract deadline: April 31, 1991. Contact: Technische Universität Berlin, FG Lagerstättenforschung, BH , Euroclat '91, Ernst-Reuter-Platz 1, D-1000 Berlin 12.

August 26-30, 1991, Dresden: 7th Meeting of the European Clay Groups, **Euroclay Dresden '91.** Contact: Prof. Manfred Störr, Mehringstrasse 48, Griefswald DDR-2000, GDR.

September 16-21, Manchester: **15th International Meeting on Organic Geochemistry.** Contact: Dr. D.A.C. Manning, Dept. of Geology, The University, Manchester, M13 9PL. FAX: (44) 61 275 3947.

September 18-21, Cologne: International Congress for Geo-Sciences and Technology, **Geotechnica 91.** Contact: Cologne Congress Management GmbH, Geotecnica, Postfach 180 180, D-5000 Köln 1, Germany.

October 5-10, Houston: **28th CMS Annual Meeting.** Symposia: Clay Chemistry, Clay Geothermometers and Geochronometers, Extraterrestrial Clays, and Soils & Clays in Environmental Research. Contact: D. R. Pevear, P.O. Box 2189, Houston, TX 77055; (713) 965-4452.

October 21-24, 1991, San Diego: **GSA / MSA Annual Meeting.** Contact: GSA, Meetings Dept., P.O. Box 9140, Boulder, CO 80301.

November 4-8, 1991, Strasbourg: **15th International Symposium on the Scientific Basis for Nuclear Waste Management.** Abstract deadline: May 30, 1991. Contact: Prof. A. Meunier, Lab. Pétrologie URA 721, CNRS, Université de Poitiers, 40, avenue du Recteur PINEAU, 86022 Poitier Cedex, France.

November 8-21, 1991, Auckland: IGCP Project 294 International Symposium, **Low Temperature Metamorphic Processes in Contrasting Geodynamic Settings.** Abstract deadline May 31, 1991. Contact: Conveners, LTMP, Geothermal Institute, University of Auckland, Private Bag, Auckland, New Zealand.

The Clay Minerals Society
28th Annual Meeting

October 5-10, 1991 Houston, Texas

SYMPOSIA: Clay Chemistry, Clay Geothermometers & Geochronometers, Extraterrestrial Clays, Soils & Clays in Environmental Research
WORKSHOP: Mössbauer Spectroscopy
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General Chair: D. R. Pevear (713) 965-4452, P.O. Box 2189, Houston, TX 77001
Program Chair: J. B. Dixon (409) 845-8323

Computer information needed by Continuing Education Committee

The Continuing Education Committee of The Clay Minerals Society is compiling a list of computer software that would be of interest to members and others involved in the study of clay and zeolite minerals.

If you are interested in sharing a computer program with your fellow researchers or in informing them of one, send the following information:

Name of program or package
Short paragraph describing what it does
Any hardware or software requirements
Where and how to obtain it
Any applicable fees

to: Steve Chipera, Los Alamos National Laboratory, Mail Stop D469, Los Alamos, NM 87545.

There are several companies and organizations that deal in geoscience software that may be of potential interest to our members:

Rock Ware, Inc.
4251 Kipling Street, Suite 595, Wheat Ridge, CO 80033
(303) 423-5645
(Geologic programs which include well logging, plotting, graphing, hydrogeologic, geophysical, etc., programs for a fee.)

GEOTECH Computer Systems
7338 S. Alton Way, Ste. 16F, Englewood, CO 80112
(303) 740-9432
(Hardware, software, consulting, and training.)

Computer Oriented Geological Society (COGS)
P.O. Box 1317, Denver, CO 80201-1317
(Public Domain Geologic software for a nominal fee.)

COGS also offers the following publication for $18.50:
Geology Programs for Microcomputers, A Catalog of Known Geological Software, 6th Edition.
(Contains more than 600 listings of geological programs, grouped according to area of application and type of computer. Lists both commercial and public domain software. Gives names of program, brief description, and name, phone number, and address of publisher.)

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