SOCIEDAD ESPAÑOLA DE ARCILLAS

Conferencias

XI REUNION CIENTIFICA

Homenaje al Profesor

JOSE MARIA SERRATOSA MARQUEZ

Madrid, 1991

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Pelicier

SOCIEDAD ESPAÑOLA DE ARCILLAS

CONFERENCIAS

XI Reunión Científica
Homenaje al Profesor José María Serratosa Márquez

Madrid, 11 y 12 de Abril de 1991

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INDICE

I. PRESENTACION

PRESENTACION

La Undécima Reunión Científica de la Sociedad Española de Arcillas, celebrada en Madrid los dias 11 y 12 de Abril de 1991, en la Facultad de Geología de la Universidad Complutense, fue algo especial. Por una parte, la Sociedad quiso rendir un pequeño homenaje al Profesor José María Serratosa Márquez, y por otra, nombró Socios de Honor a los Profesores José Antonio Rausell-Colóm, Celso de Sousa Figueiredo Gomes, Jiri Konta y Henry Van Damme.

El Profesor Serratosa, administrativamente jubilado pero intelectual y científicamente activo, es actualmente Presidente de la AIPEA (1989-1993), y Socio de Honor de la S.E.A. desde 1987. En su larga e intensa vida investigadora ha dedicado sus mejores aportes científicos a la cristalquímica y físico-química de los filosilicatos. Como científico completo que es, une a su amplia capacidad de trabajo y constante deseo de aprendizaje, un perfecto equilibrio y eficacia en sus decisiones, una brillante personalidad cargada de humanidad y comprensión para todos cuantos gozamos de su amistad, una extensa formación humanística y una filosofía vital en la que se conjugan la sobriedad y la elegancia, con la libertad de pensamiento, el respeto y la independencia.

Serratosa ha sido uno de los más importantes impulsores de la Mineralogía de Arcillas a nivel nacional, con una evidente proyección internacional reflejada especialmente en la literatura y en la vida científica de los últimos treinta años. Creemos que este homenaje que ha recibido de la Sociedad Española de Arcillas, apenas puede compensar lo que la propia Sociedad y nosotros le debemos.

En este Volumen se incluyen las tres conferencias que pronunciaron los Profesores Gomes, Konta y Van Damme, -el Profesor Rausell-Colóm no pudo estar presente por un compromiso profesional ineludible-, que son exponentes de la investigación actual que están desarrollando, y una biografía del Profesor Serratosa preparada por Ramón de Dios, viejo amigo y compañero, y Eduardo Ruiz Hitzky, brillante discípulo y colaborador.

Esperamos que esta nueva Publicación de la Sociedad Española de Arcillas sea especialmente bien acogida y difundida por el recuerdo entrañable que encierra, y por su alto contenido científico.

Febrero, 1992

Emilio Galán Huertos

II. BIOGRAFIA DEL PROFESOR JOSE MARIA SERRATOSA MARQUEZ

José María Serratosa, nace en Ronda donde recibió su educación primaria y estudió el Bachillerato. Se traslada a Granada en cuya Universidad realiza sus estudios universitarios, obteniendo la Licenciatura en Ciencias Químicas en 1946. Fué nombrado Profesor Ayudante de dicha Universidad, cargo que ocupó durante un año, lo que le proporcionó la primera oportunidad de dedicarse a la Investigación. Su etapa inicial de formación en la Investigación continúa en Madrid, como Becario del Consejo Superior de Investigaciones Científicas, ampliando estudios por un año en la Universidad de Utrech, bajo la dirección del Profesor J.Th. Overbeek. En 1953 retorna a Madrid donde prosigue sus investigaciones en el Instituto de Edafología del CSIC, colaborando con el Dr. Jiménez-Salas en estudios sobre hinchamiento y compresibilidad de suelos.

Obtuvo el título de Doctor en Ciencias Químicas por la Universidad de Madrid en 1953, consecuencia de sus investigaciones en Fisico-Química de sistemas coloidales.

Después de dos años de estudios postdoctorales en Estados Unidos - Departamento de Química-Física de la Universidad de Illinois y en el Illinois State Geological Survey- vuelve al CSIC donde obtiene la plaza de Investigador Científico en el año 1958. En 1963, regresa a Estados Unidos donde trabaja como Research Scientist, en la Universidad de Texas durante cinco años (1963-1968), y como Visiting Research Scientist en la Washington University de St. Louis Missouri. En 1968, vuelve al CSIC y como Profesor de Investigación, prosigue su actividad científica de gran repercusión en la especialidad.

Su actividad investigadora se incluye dentro de la Físico-Química de Estado Sólido, teniendo como objetivo fundamental alcanzar un conocimiento profundo del comportamiento microscópico de distintos tipos de materiales sólidos, especialmente los filosilicatos (minerales de la arcilla), y de la influencia que su microestructura ejerce sobre sus propiedades macroscópicas.

Al tratar de resumir su labor científica, hemos creído de interés seguir un orden que, de alguna manera, explique la evolución en el tiempo de su interés por los temas científicos que ha desarrollado en las distintas etapas de su carrera profesional. Así, dedica esencialmente su atención a los siguientes aspectos:

1. Coloidequímica: estabilidad de suspensiones, hinchamiento y fuerzas interparticulares.

Esta investigación comprende el período 1949-1954 y se desarrolló en los laboratorios del CSIC en Granada y Madrid y en la Universidad de Utrecht, donde permaneció el año 1953 trabajando en colaboración con el Prof. Overbeek.

En los años 40 la Ciencia de coloides experimenta un auge espectacular, desarrollándose teorías cuantitativas que tratan de explicar el comportamiento de los coloides, basado, hasta entonces, en correlaciones exclusivamente empíricas. Los centros de este desarrollo estaban en Holanda (Verwey y Overbeek, Universidad de Utrecht y Laboratorios de investigación de la Philips) y en la Unión

Soviética (Derjaguin y Landau, Academia de Ciencias). Este auge culminó con la publicación del libro "Theory of stability of lyophobic colloids" por Verwey y Overbeek en 1948.

Como es bien conocido, las arcillas dan lugar a sistemas coloidales (suspensiones y pastas), cuyas propiedades son de especial interés y repercusión en Cerámica, origen y explotación del petróleo, Mecánica de suelos, Agricultura, etc. La contribución de Serratosa en este área se refiere al conocimiento de la estructura y propiedades de la doble capa eléctrica en halogenuros de plata, y al estudio de las suspensiones de arcillas cuyo comportamiento puede explicarse por la teoría DLVO (Derjaguin-Landau-Verwey-Overbeek).

2. Espectroscopia vibracional de sólidos: caracterización de grupos OH localizados en silicatos laminares.

Esta investigación comprende el período 1955-1962 y se desarrolla esencialmente en el CSIC (Madrid), y parcialmente en la Universidad de Illinois y en el "Illinois Geological Survey" USA, en colaboración con el Prof. R.E. Grim y el Dr. W.F. Bradley.

Las estructuras cristalinas de los filosilicatos eran conocidas en sus características generales desde los estudios de Linus Pauling en los años 20 y 30. Sin embargo, quedaban por dilucidar ciertos aspectos sobre los que los métodos de difracción de rayos X no daban información fiable. Uno de estos aspectos se refiere a la localización de átomos de hidrógeno. La contribución de Serratosa se refiere a la aplicación de la espectroscopía infrarroja para determinar la orientación de los enlaces O-H respecto a los ejes cristalográficos del cristal y por tanto localizar los átomos de H en estructuras de silicatos y otros compuestos inorgánicos. Asímismo, Serratosa aplicó la espectroscopía infrarroja al estudio de la evolución de compuestos inorgánicos durante el tratamiento térmico, procesos que son de interés fundamental en Cerámica. Estas investigaciones tuvieron una gran repercusión a nivel internacional y propiciaron el desarrollo de la espectroscopía de sólidos, especialmente en el área de la Mineralogía.

3. Caracterización de superficies de sólidos mediante técnicas espectroscópicas. Mecanismos de interacción de moléculas adsorbidas en silicatos: intercalación, reactividad y catálisis.

Estas investigaciones comprendidas en el período 1963-1974, se realizaron en Madrid, en los laboratorios del CSIC, así como en la Universidad de Texas en colaboración con el Prof. W.D. Johns de la Washington University de St. Louis, Missouri.

La aplicación de las técnicas espectroscópicas al estudio del fenómeno de la adsorción se desarrolló especialmente en los años 60 siendo Serratosa uno de los pioneros en este tipo de investigaciones. Su contribución científica en este área se refiere a la aplicación de la espectroscopía infrarroja e incluyen los siguientes

aspectos: caracterización de la superficie de sólidos microcristalinos; interacción superficie-molécula adsorbidas; centros activos de adsorción; moléculas adsorbidas: disposición y reactividad de las mismas (catálisis). En compuestos laminares fué posible determinar la orientación de las moléculas adsorbidas mediante el uso de agregados orientados en las que las partículas del sólido tienen una orientación preferencial de los planos de las láminas.

Estas investigaciones han conducido a la preparación de nuevos materiales orgáno-inorgánicos con propiedades predeterminadas para aplicaciones específicas (materiales para procesos de Química fina) y han dado lugar a varias patentes.

4. Cristaloquímica de zeolitas y filosilicatos. Orden-desorden en la distribucion de iones: aplicación de la RMN de alta resolución.

Sus actividades en este campo iniciadas en 1976 se realizaron en el Instituto de Ciencia de Materiales del CSIC en Madrid, en colaboración con los Dres. J. Sanz y C.P. Herrero.

La distribución de iones es una importante característica cristaloquímica que controla la estabilidad termodinámica y las propiedades físicas y químicas de los sólidos. Su determinación por métodos de difracción presenta dificultades porque las sustituciones isomórficas no siguen necesariamente una periodicidad regular y también porque en ciertos casos (Si y Al por ejemplo) los factores atómicos de difusión son muy semejantes. La contribución en éste área se refiere a la determinación de la distribución de Si y Al en filosilicatos y su relación con la energía elctrostática del cristal. Asímismo es de destacar la contribución referente al estudio por RMN de procesos de gran interés en materiales cerámicos (formación de mullita) que han permitido establecer los mecanismos de dichos procesos a nivel atómico.

Todos estos logros muestran por sí solos su extensa dedicación científica dentro del área de Físico-Química del sólido y de su capacidad de trabajo, proporcional a su disposición intelectual, que se caracteriza por la brillante aplicación de técnicas experimentales y convincentes resultados. Además de los pináculos de éxito de una brillante carrera científica, como investigador, experimentador y observador, existe el valor personal de inspiración a sus anteriores y actuales cooperadores.

Serratosa permaneció siempre activo en el laboratorio y se mantiene en acción en su despacho, no cansándose nunca de las emociones de los hallazgos de sus numerosos colaboradores y doctorandos, celoso siempre de reconocer su contribución y ayuda, revelados por sus comentarios de amplia consideración y comprensión. Su entusiasmo e interés se contagió a aquellos, lo que dió lugar a grupos sucesivos de excelentes científicos que le rodearon. Prestó gran interés a los seminarios de investigación, animando a pensar críticamente, recibiendo con beneplácito las sugerencias a sus propias ideas, dando confianza a los saberes de los principiantes -becarios- de trabajos de investigación.

Sus éxitos científicos y su destacada personalidad le llevaron a obtener diversos nombramientos en cargos de responsabilidad, tanto en España como en el extranjero, entre las que cabe destacar el de Director de Investigación de la División de Ciencias del CSIC (1973-76), Subdirector General de Política Científica (1977-79), representante español en el Programa de Materiales de la Comunidad Europea (1986-92), Consultor Científico de la Comisión de la Comunidad Europea (Dirección General XII) para la investigación en Materiales.

En el año 1984, Serratosa fué nombrado Director del Programa Movilizador de Ciencia de Materiales del CSIC, desde donde contribuyó decisivamente al desarrollo de este área. Desde este puesto contribuyó eficazmente a la creación de una red de Centros de Investigación dedicados a la Ciencia de Materiales. En 1986 fué nombrado Director del Instituto de Ciencia de Materiales de Madrid.

Actualmente, desempeña funciones de asesoramiento científico tanto en el ámbito nacional como en el de la Comunidad Europea.

RAMON DE DIOS
EDUARDO RUIZ-HITZKY

III. NOMBRAMIENTO Y PRESENTACION DE LOS NUEVOS SOCIOS DE HONOR DE LA SOCIEDAD ESPAÑOLA DE ARCILLAS

NOMBRAMIENTO DE SOCIOS DE HONOR DE LA SOCIEDAD ESPAÑOLA DE ARCILLAS

El Artículo 15, apartado C, de los Estatutos de la Sociedad Española de Arcillas dice:

"Socios de Honor: Podrán ser Socios de Honor todas las personas que por su relevante prestigio científico en el campo de las Arcillas o por su demostrado apoyo a la Sociedad, se hagan acreedores de tal distinción. Serán propuestos por la Junta Directiva o diez socios y su admisión deberá ser acordada por la mayoría de las dos terceras partes de la Asamblea General".

De acuerdo con el mencionado artículo, la Junta Directiva de la Sociedad, reunida en Madrid el 13 de Diciembre de 1990, decidió proponer a la Asamblea General, el nombramiento de los siguientes Socios de Honor:

* Prof. Dr. José Antonio Rausell-Colóm
* Prof. Dr. Celso de Sousa Figueiredo Gomes
* Prof. Dr. Jiri Konta
* Prof. Dr. Henry Van Damme

En la Asamblea General de la Sociedad Española de Arcillas, celebrada en Madrid el 11 de Abril de 1991, fueron expuestos por el Presidente los méritos científicos y humanos de los candidatos a Socios de Honor, así como las relaciones con los investigadores españoles, en el caso de los extranjeros. Tras esta presentación, se acordó por unanimidad nombrar a los Profesores antes citados como nuevos Socios de Honor de la Sociedad Española de Arcilla.

PRESENTACION DE LOS SOCIOS DE HONOR

Prof. Dr. José Antonio Rausell-Colóm

El Prof. Rausell-Colóm es Doctor en Ciencias Químicas por la Universidad Complutense de Madrid (1950) y Profesor de Investigación del Consejo Superior de Investigaciones Científicas, y desde su Licenciatura en 1954 (Universidad de Valencia) ha tenido una dedicación total a la investigación.

En su etapa de postgrado trabajó con el Prof. Martín Vivaldi y con el Dr. Mac Ewan en la caracterización de los minerales de la arcilla, coloidequímica de arcillas, y principios ópticos de la difracción de rayos X por la materia condensada y por sustancias imperfectamente cristalizadas y amorfas.

Su etapa postdoctoral comienza con su estancia en la División de Suelos del CSIRO, Adelaida, Australia, (1958-1963), junto a los Dres. K. Norrish, E.W.

Radoslovich y R.E. Taylor, donde trabaja esencialmente en estabilidad de coloides de arcillas, mecanismos de intercambio iónico en micas, alteración mineral, cristalquímica de filosilicatos, etc. De vuelta a España comienza su formación en Cristalografía Estructural en el Instituto de Química Física Rocasolano del C.S.I.C. (1963-1966), con la determinación de estructuras de compuestos inorgánicos, etapa que completa con el aprendizaje de otras técnicas físicas de análisis instrumental enfocadas a la determinación de minerales (Absorción Atómica, Fluorescencia de rayos X, Microsonda Electrónica), durante su estancia en el Instituto Geológico y Minero de España (1966-1969).

En 1969 se incorpora al Instituto de Físico-química Mineral del C.S.I.C., trabajando con los Dres. Serratosa, Ruíz Hitzky, Sanz, Mifsud, Fornés, Rodríguez Pascual, etc. en los dominios de la interacción arcilla-materia orgánica y arcilla-agua, donde ha desarrollado una intensa y fructífera investigación, que viene reflejada en su impacto nacional e internacional.

Finalmente, pasa a formar parte del Instituto de Ciencia de Materiales desde su creación (1982) investigando esencialmente sobre propiedades de superficie y reactividad de silicatos de estructura laminar.

El Dr. Rausell-Colóm ha sido Presidente de la Sociedad Española de Arcillas (1979-1984), Miembro del Comité Editorial de la Revista "Clay Minerals" y Miembro del Comité de Nomenclatura de la AIPEA.

Fue Coordinador del Area Científica de la CAICYT y atualmente reside en Bruselas, donde desempeña el cargo de Director del Programa Científico de la NATO (Colloborative Research Grants).

La Junta Directiva de la Sociedad Española de Arcillas en su Reunión del 13 de Diciembre de 1990, acordó proponer a la Asamblea General, nombrar como Socio de Honor al Prof. José A. Rausell-Colóm, considerando fundamentalmente su destacada contribución al desarrollo en España de la investigación de arcillas, su proyección y prestigio internacionales en este campo, y su dedicación a la Sociedad, especialmente durante su etapa como Presidente.

Prof. Dr. Celso de Sousa Figueiredo Gomes

El Prof. Gomes, natural de Viana do Castelo, es Licenciado en Ciencias Geológicas por la Universidad de Coimbra y Doctor en Ciencia de Materiales, especialidad en Materiales Cerámicos por la Universidad de Leeds, Inglaterra. Actualmente es Catedrático de la Universidad de Aveiro, Portugal.

El Prof. Gomes inició su actividad científica en la Universidad de Coimbra, pasando después a ocupar diversos puestos profesionales en el Servicio de Geología de Minas de Angola, de donde llegó a ser su Director, al mismo tiempo que fue Profesor en la Universidad de Angola y Colaborador Científico del Instituto de Investigaciones Científicas de aquel país. Posteriormente, en Portugal continua su carrera docente en la Universidad de Aveiro, hasta llegar a ser Catedrático y Director del Departamento de Geociencias.

Sus actividades científicas se centran fundamentalmente en la caracterización cristalquímica de minerales del grupo del caolín, en las aplicaciones industriales de las arcillas, especialmente en las industrias cerámicas y del papel, y en geología y geoquímica de arcillas. Es autor de numerosos trabajos y de varios libros de arcillas de gran interés didáctico.

Es Socio de la Sociedad Española de Arcillas; organizó la Reunión Luso-Española de Arcillas en Aveiro en 1989 con gran éxito y transcendencia científica a nivel portugués, -de allí partió la creación del Grupo Portugués de Arcillas, que formalmente se ha constituído en 1991-, ha participado en la mayor parte de las Reuniones Científicas de la S.E.A., y en su Departamento ha recibido a varios investigadores españoles para su especialización.

La Junta Directiva de la Sociedad Española de Arcillas en su Reunión del 13 de Diciembre de 1990, acordó proponer a la Asamblea General, nombrar Socio de Honor al Prof. Celso de Sousa Figueiredo Gomes, considerando sus destacados méritos científicos en el campo de las Arcillas, su colaboración con la Sociedad Española de Arcillas, a la que pertenece desde hace muchos años, y sus estrechas relaciones científicas y humanas con un gran número de investigadores españoles, lo que ha contribuido a mejorar las relaciones entre las comunidades científicas de España y Portugal.

Prof. Dr. Jiri Konta

El Prof. Konta nació en Zleby, Checoslovaquia, es Licenciado en Ciencias Geológicas y en Química (1948), Doctor en Mineralogía y Petrología (1954) y en Ciencias Geológicas (1961) por la Universidad de Praga (Charles University). Actualmente es Profesor Emérito de esta misma Universidad.

En su larga vida profesional ha compatibilizado siempre la docencia con la investigación. Desde 1948, en que comienza su carrera docente en la Universidad de Praga, ha ocupado diversos puestos hasta que en 1961 fue nombrado Catedrático de Petrología Sedimentaria en la Facultad de Ciencias. En el Curso 1965-1966 fue Profesor Visitante en la Universidad de Pensilvania, U.S.A., Departamento de Geoquímica y Mineralogía; y en 1971 fue también Profesor Visitante de Tecnología de Materias Primas en la Universidd de Skopje, Yugoslavia.

Los temas de investigación del Prof. Konta han sido muy variados, y van desde la sedimentología, la geología de arcillas, la petrología y mineralogía de materias primas para cerámica y vidrio y los productos cerámicos, la geoquímica, la metodología para la investigación en el laboratorio de minerales y rocas, la alteración de la piedra de monumentos, etc. Es autor de más de doscientos trabajos y autor o coautor de ocho libros publicados en Checoslovaquia y Alemania. Entre estos últimos destacan: "Minerales de la Arcilla de Checoslovaquia" (1951) e "Imbibometría. Un nuevo método para la investigación de arcillas" (1961), y sus colaboraciones en "Materias primas para Cerámica y Vidrio" (1982) y "Handbook de Cerámica" (1979-1981).

El Prof. Konta ha tenido una dilatada trayectoria como Editor, publicando los Proceedings de las diez Conferencias Internacionales sobre Mineralogía y Petrología de Arcillas, celebradas en Checoslovaquia (1959-1991), y de la EUROCLAY'83, de la que fue su Presidente.

Es Miembro del Comité Editorial, o Consultor Editorial, de las siguientes revistas: Silikaty, Ceramics, Clay Minerals, Applied Clay Science, y Transaction of the Royal Society of Edinburg, Eart Sciences.

Ha sido Miembro del Comité de Nomenclatura de la AIPEA, y Presidente de esta Asociación en el período 1985-1989.

El Profesor Konta ha sido durante muchos años el "representante internacional" de la investigación checoslovaca de arcillas, manteniendo contactos con el mundo entero, y en especial con los paises de Europa Occidental, e invitando regularmente a numerosos investigadores extranjeros a las Conferencias sobre Mineralogía y Petrología de Arcillas que periódicamente organizaba en Checoslovaquia. Entre estos invitados se cuenta un gran número de españoles, que siempre han sido acogidos con la hospitalidad que caracteriza al Prof. Konta, hombre de gran cultura y exquisita educación.

La Junta Directiva de la Sociedad Española de Arcillas en su Reunión del 13 de Diciembre de 1990, acordó proponer a la Asamblea General, nombrar Socio de Honor al Prof. Jiri Konta, considerando fundamentalmente: a) sus importantes aportaciones a la Ciencia de las Arcillas, especialmente en sus aspectos docentes, metodológicos, geoquímicos, petrológicos y aplicados; b) la organización periódica durante más de treinta años de Conferencias Internacionales de Arcillas en Checoslovaquia, en las que por su iniciativa se daban cita los más prestigiosos científicos del Este y del Oeste, y c) las relaciones mantenidas con investigadores españoles, especialmente en estos encuentros de Checoslovaquia.

Prof. Dr. Henry Van Damme

El Prof. Van Damme nació en Uccle, Bélgica, es Ingeniero Químico (1969) y Doctor en Ciencias Naturales Aplicadas y Ciencias de los Materiales por la Universidad de Lovaina (1973). Desde 1970 hasta la actualidad se ha dedicado exclusivamente a la investigación, primero como Investigador Asociado de los Fondos Nacionales de Investigación Científica (FNRS) en Bélgica, con el Prof. Fripiat, quien le dirigió su Tesis Doctoral (1970-1973), y luego en el Centro de Investigación de Sólidos con Organización Cristalina Imperfecta (CRSOI) del CNRS en Orleans, Francia, donde en 1985 llegó a ser su Director. Actualmente, desde 1990, es el Director del Centro de Investigación de la Materia Dividida (CRMD) del CNRS de Orleans.

La investigación del Dr. Van Damme se puede dividir en dos períodos. En el primero, desde 1971 a 1984, la investigación estuvo centrada en los aspectos biomiméticos de la química de la superficie de las arcilas, y en especial en el almacenamiento fotoquímico de la energía solar por disociación del agua. En esta línea se situan sus trabajos sobre la adsorción, fotoquímica y fotofísica de moléculas orgánicas fotoactivas en el espacio interlaminar de esmectitas, así como de otros iones inorgánicos y compuesto de coordinación. Durante esta etapa colaboró con los Dres. J. Fripiat, M.I. Cruz Cumplido, F. Bergaya, D. Krenske y otros, y también con los españoles B. Casal y E. Ruiz Hitzky con quienes desarolló un sistema para protooxidar el agua, usando arcillas como soporte de catalizadores.

El segundo período se extiende desde 1984 hasta la actualidad, y durante este tiempo la investigación fundamental ha girado en torno a aspectos estadísticos de los materiales desordenados y, en particular, de arcillas, y en la modelización de propiedades de superficie de la arcilla en relación con problemas de fracturación, microporosidad, etc. En esta etapa colabora con los Dres. J. Fripiat, P. Levitz, L. Gatineau, D. Tchoubar, etc. Actualmente se dedica a los aspectos micromecánicos de la compactación y reología de arcillas, y continua colaborando con grupos españoles (Madrid, Málaga) en la investigación de compuestos orgánicos e inorgánicos de las arcillas.

El Dr. Van Damme es autor de más de sesenta trabajos, publicados en su mayoría en las más importantes revistas de arcillas, coloidequímica, físico-química y catálisis.

La Junta Directiva de la Sociedad Española de Arcillas en su Reunión del 13 de Diciembre de 1990 acordó proponer a la Asamblea General, nombrar Socio de Honor al Prof. Henry Van Damme, considerando fundamentalmente sus importantes aportaciones al conocimiento de la química de la superficie de las arcillas y sus aplicaciones, y a la intensa colaboración científica y relaciones humanas, que mantiene con diversos investigadores españoles.

IV. CONFERENCIAS

DELAMINATION OF KAOLIN FOR THE PAPER INDUSTRY: ASSESSMENT OF A NEW CHEMICAL-MECHANICAL METHOD

C.S.F. Gomes

DELAMINATION OF KAOLIN FOR THE PAPER INDUSTRY: ASSESSMENT OF A NEW CHEMICAL - MECHANICAL METHOD

C.S.F. Gomes
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INTRODUCTION

Kaolin, within mineral pigments, is the most utilized for paper fabrication, either as coating or as filler. Characteristics such as: white colour, adequate particle size and shape, chemical inertia and favourable price convert kaolin into a very attractive pigment in the paper industry.

Kaolin improves so much paper surface that allows high quality printing, particularly important whenever various colours are utilized.

Micronized calcium carbonate, particularly in Europe, is becoming more and more competitive with kaolin in the paper industry; being whiter and cheaper it substitutes very conveniently kaolin for filler applications. However, for high quality coated papers kaolin is still essential.

Coated papers are being produced more and more. For instance, production in West Europe is about 20 m.t. / year.

The reasons for the continued increase in the coated papers production are essentially three:

1.- the improvement verified both in the standard of living and in literacy, requiring greater demand of better quality papers;
2.- the progress verified on coating and printing techniques;
3.- the availability of new retention agents for pigments and of kaolins with various quality grades.

Table I contains, in a short form, the main requirements kaolin should fulfil for paper coating applications. Small differences in the requirements can affect greatly kaolin properties. Therefore, kaolin intrinsic properties and their beneficiation should be the object of appropiate studies.

QUALITY GRADES OF COATING KAOLINS

Up to few years ago, only 3-4 types of coating kaolin were available, distinguished by their brightness and grain size distribution.

Nevertheless, in a matter of few years, several new types of kaolin were produced for writing and printing paper: magazines, catalogues, books, periodicals, etc. In U.S.A. about 10% of writing and printing papers is used on books whereas 90% is used in publicity.

Recent years are characterized by the development of kaolin treatment techniques every time more sophisticated, such as: aeroflotation, hydroflotation, calcination and delamination.

The new treatment processes of kaolin are justified due to three main reasons:

1.- the need to fulfil the demands of the paper industry;
2.- the important added value of treated kaolin;
3.- the convenience of reducing kaolin imports and to upgrade national kaolins.

These reasons have transformed kaolin producing industries in highly competitive activities both in process and in technologies (equipments, new production processes, etc.).

These days, coating kaolins can be classified in four main groups on the base of brightness and grain size values: normal, delaminated, premium and special.

Each group comprises classes established on a quality base (table II). Within the grades of commercial kaolin available, twenty three were specially designed for coating, being characterized by three main properties: brightness, yellowness and % of particles under 2 μm. According to the variety of paper we wish to produce, an appropiate grade of kaolin has to be selected. For instance, whenever would be important to enhance brightness, smoothness, low weight and opacity, a delaminated kaolin should be selected.

In fact, actual trends points out toward specific kaolins for specific perfomances. Therefore, five technological development lines could be defined in regard with coating kaolins:

1.- delamination kaolin
2.- mate kaolin
3.- high gloss kaolin
4.- calcined kaolin
5.- blended kaolin

Experimental studies have been carried out in regard with delaminated kaolins and some results are reported in this paper.

TABLE I

Properties	Conditioning
Brightness	Higher as possible (> 83 %); high brightness can reduce opacity
Opacity	Improves with high crystallinity kaolin; better when grain size is around 0.3 μm. Improves at high shear rate viscosities.
Abrasivity	Lower as possible; smoothness is quartz and halloysite dependent
pH	5.5-6
Grain size	Material retained on 200 # : 0.005 % Grain size > 3 μm : < 8 % Grain size < 5 μm : > 90 % Grain size < 2 μm : > 70 % Particles selection around 2 μm Very fine particles (< 0.25 μm) are not convenient
Retention	Stable suspensions with high solids concentration
Chemical Composition	SiO_2 : 45-55 % ; Al_2O_3 : 37-40% ; Fe_2O_3 :< 0.3 % ignition loss : > 12 %
Viscosity	Good rheological characteristics for high shear rates in suspensions with 70 % solids Depends of particle size and particle texture

TABLE II

			Brightness	Yellowness	% < 2 µm				Brightness	Yellowness	% < 2 µm
NORMAL	4	Dinkie B+	82.5	-	65-68	DELAMINATED	C	Superclay+	81.5	-	-
	3	NCC+	85.5	4.7	74		M	Hydraprint*	86-87	-	-
		Dinkie A+	86.6	-	72		F	Hydrasheen 90*	88-90	-	-
	2	Alphaplate+	86.0	5.1	80	PREMIUM	2	Hydrasperse90*	88.5	-	80-84
		SPS+	85.5	4.7	80			Arvor 7 A "	87-88	2-3	75
		Hydrasperse*	84.5	-	80-82						
	1	Supreme+	87.5	4.2	94		1	Hidrafine 90*	88-90	-	90-92
		Hidrafine*	85.5	-	90-92						
		Alphacrate+	89.0	4.4	92-94		1F	Hydragloss 90*	88-90	-	96-99
	1F	Hydragloss*	85.0	-	94-97	SPECIAL	M	Hydramatte*	88	-	-
		Betagloss+	84.7	6.7	94						
		Alphagloss+	88.0	4.0	90-95		CD	Alphatex+	90.7	4.1	89
		Amazon 88|	85.4	6.0	97			Ansilex #	92.5	-	86-90

* J. Huber (USA)
\+ ECCI (UK and USA)
| Caulim da Amazónia (CADAM),(Brazil)
" Société des Kaolins d'Arvor (France)
\# Engelhard Minerals & Chemicals (USA)

C = coarse
M = medium
F = fine
M = mate
CD = calcined

DELAMINATED KAOLIN

Delamination promotes basal exfoliation of kaolinite crystals and provides the formation of more but less thick crystals. The cleavage plates exhibit high diameter (up to 5 μm or even more) and low thickness (mean thickness of 0.2 μm). Crystals get so thin that become flexible. In regard with grain size, exfoliation produces kaolin with grain size better calibrated.

Suspensions (slips) prepared with delaminated kaolins display higher viscosities and provide less packed, more compressible and flexible sediments. On the other hand, such suspensions are more easily retained on paper surface avoiding disruption through macropores sites.

Grain size distribution of delaminated kaolins can be handled in order to obtain three types of delaminated kaolins: fine, medium and coarse. Coarse kaolin is the most appropiate to improve paper printing quality despite a reduction in gloss.

Higher viscosity of delaminated kaolin suspensions prevents their applications at high speeds. Therefore, delamination, viscosity and solids concentration (higher as possible) have to be conveniently controlled.

Delaminated kaolin was introduced for the first time in the paper industry by the end of the sixties. It started being applied in paper coating due to excellent qualities of brightness, smoothness and opacity. These characteristics being much better in delaminated kaolin than in the kaolins so far available were responsible for the belief that delaminated kaolin would be the kaolin of the future.

Delaminated kaolin is preferently utilized for low weight coatings, usually less than 10 g/m^2, because it shows advantages in terms of gloss and smoothness. It is utilized in low weight papers derived from pulps made with softwood having coarse fibers which produce irregular surfaces.

As far as the coating weight increases, delaminated kaolin, both in gloss and in economic terms, become less efficient being overcomed by commercial kaolins of premium and n° 1 F types, since these kaolins due to their very fine particles produce smooth and compact coatings.

DELAMINATION PROCESSES

Delamination as other kaolin treatment processes have their proper place in treatment flowsheets.

So far, the kaolin delamination processes available can be classified as mechanical processes. Indeed mechanical actions promote the cleavage of the thick kaolinite crystals (books). Specific surface increases and as a consequence rheological properties of the

kaolin-water system will change. Also kaolin brightness will improve since after cleavage crystal internal surfaces free of any coating coloured pigments will become exposed.

Delamination processes should not include any type of grinding since it would modify kaolinite grain size and shape as well as its structural organization.

Current kaolinite delamination processes are the following:

a) sand attrition: consists of attrition through collisions between kaolinite crystals in water suspensions with sand grains of plastic/glass beads with special characteristics, till convenient changes of rheological properties take place.

b) extrusion: consists of forcing the passage of high concentrated kaolin suspensions (18-25% water) through a narrow nozzle under pressure.

c) pug-milling or kneading: consists of kneading a thick kaolin slip.

In all these processes inter-particle attrition promotes the cleavage of kaolinite crystals and the rectification of their edges. In any case, the number of the particles increases, because besides basal cleavage, prismatic cleavage and rupture along other planes takes place as well.

PRINCIPLES OF A CHEMICAL-MECHANICAL DELAMINATION PROCESS

Delamination treatments where carried out on four kaolins, two of sedimentary type (PUGU D from Tanzania and ALVARÃES D from Portugal) and two of the residual type (ALVARÃES from Portugal, SPS from England).

In a first phase, for each kaolin, samples less than 38 μm, 10 μm and 2 μm were characterized in regard with mineral composition (by XRD), chemical composition (by XRF), grain size analysis (by laser particle size analyser) and kaolinite crystanillity (by XRD and Hinckley crystanillity index).

In a second phase, kaolin samples were submited to a chemical-mechanical treatment consisting of two mechanism:

1) intercalation of kaolinite with a complexing agent (hydrazine hydrate was selected due to its easy intercalating capacity); a ratio 1/3 of kaolinite/intercalating agent has been used, warmed up to 80°C in a sand bath and dispersed in a ultrasound bath;

2) water-washing of the complex being formed and submission of it to mechanical agitation using medium energetic ultrasounds.

Hydrazine hydrate intercalation followed by water-washing would promote change of the cohesion energy between kaolinite structural layers, whereas mechanical agitation would promote crystal cleavage.

For each kaolin four preparations have been considered, when hydrazine was the intercalating agent, exemplified in table III.

TABLE III

Kaolin Preparations

A	Kaolin suspension (76 % solids) + hydrazine hydrate + ultrasound agitation (200 W up to 3 hours)
B	Kaolin suspension (76 % solids) + ultrasound agitation (200 W up to 3 hours)
C	Kaolin suspension (38 % solids) + hydrazine hydrate + ultrasound agitation (200 W up to 3 hours)
D	Kaolin suspension (38 % solids) + hydrazine hydrate + ultrasound agitation (100 W up to 3 hours)

DELAMINATION EFFECTS ON KAOLIN PROPERTIES RELEVANT FOR PAPER COATING

Delamination effects can be revealed on kaolin properties, such as: colour, specific surface and viscosity.

Preparation A appears to be the most effective. It provides a reduction down to about 1/3 in average, of the initial kaolinite mean crystal thickness (table IV). This has been evaluated from shadow measurements taken on a significant number of kaolinnite crystals in transmission electron-micrographs of specimens (dried drops of very diluted kaolin-water dispersions) shadow casted with evaporated gold at 45°. Crystal thickness reduction values evaluated by this technique correspond to the values estimated on XRD traces using the effect of coherent diffusion of the kaolinite (001) reflection.

TABLE IV

Kaolin Preparation	Improvement (%) Delamination	Improvement (%) S.S.A.
A	26	60.0
B	16	29.8
C	10	18.2
D	9	16.8

Specific surface area determinations, before and after delamination express quite well the cleavage degree of kaolinite crystals.

Brightness of delaminated kaolin shows small increase. However, yellowness shows appreciable decrease. Therefore, in preparation A delamination favours clearly kaolin colour. The same happens with specific surface and viscosity. There is an increase in the number of individual particles and a decrease of the mean particle size due to the crystal cleavage (Fig. 1).

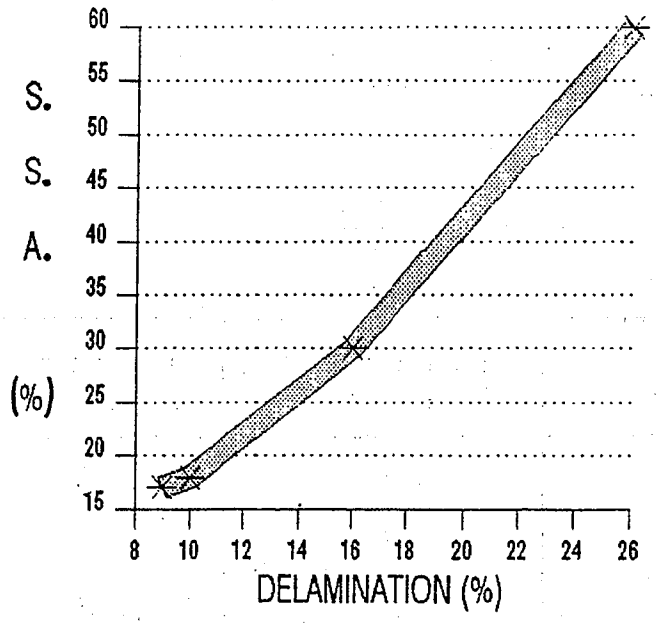

Fig. 1 - Delamination increase vs. S.S.A. increase

CONCLUSIONS

Delamination through the chemical-mechanical method herin reported is more developed in residual kaolins than in sedimentary kaolins. This could be explained by their partial intercalation of sedimentary kaolinites allied to their smaller mean crystal thickness.

High solids concentration favour clearly the increase of fine particles. Crystal breakdown would be more developed due to the easier mechanical energy propagation. Particle cleavage would take place along basal planes and along other planes.

For low solids concentration and low mechanical energies the production of fine particles results essentially from delamination.

The chemical-mechanical method does not affects much kaolinite structural order-disorder. However, to the increase of fines corresponds a decrease on kaolinite crystanillity (Fig. 2).

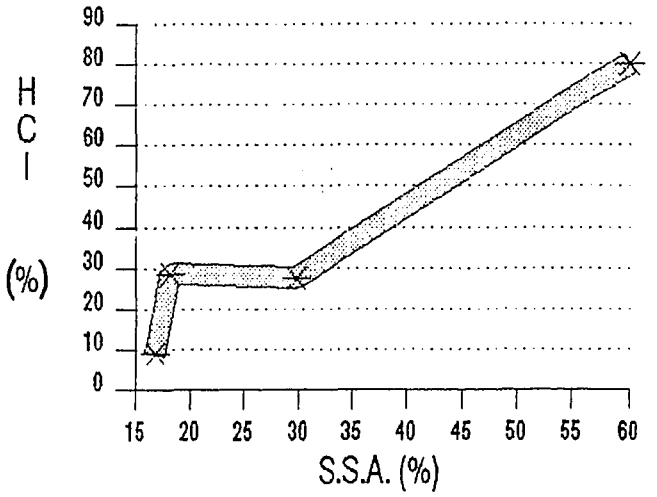

Fig. 2 - S.S.A. increase vs. HCl decrease

In order to maximize delamination it was found necessary to find out the best working conditions, such as: solids concentration, kaolinite/intercalating agent ratio, intercalation time, intensity and time of mechanical agitation.

ACKNOWLEDGEMENTS

I rather did appreciate the invitation issued by the Board of Directors of the Sociedad Española de Arcillas to deliver a conference during its annual meeting held in Madrid. On the one hand, due to the fact that the meeting was been elected to pay homage to Professor José María Serratosa Márquez, a clay scientist of enormous worldwide reputation. On the other hand, due to the fact that in the same meeting I would be distinguished as a member of honour of a Scientific Society of so great prestige.

The investigations reported in my conference were undertaken, with my supervision, by José Antonio Ganilho Lopes Velho, post-graduate student of University of Aveiro. They are part of a research programme carried out in order to accomplish the Ph. D. degree, programme that deserved the fundamental support of J.N.I.C.T. (Junta Nacional de Investigação Científica e Tecnológica) and I.N.I.C. (Instituto Nacional de Investigação Científica).

PHYLLOSILICATES IN RIVERS: RESULTS OF WEATHERING, EROSION, TRANSPORTATION AND DEPOSITION

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PHYLLOSILICATES IN RIVERS: RESULT OF WEATHERING, EROSION, TRANSPORTATION AND DEPOSITION

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INTRODUCTION

Minerals and, together with them, fragments of their parent rocks exposed to the weathering in river catchments and transported in rivers are the dominant supply of the sediments of lakes, seas and oceans (Fig. 1). This holds true of the known geological history from the youngest to the oldest sedimentary sequences. Phyllosilicates are omnipresent in any layer of the sedimentary accumulations. Clay matter composed mainly of the phyllosilicates constitutes about 50 or even 75% of the sedimentary lithosphere according to the stratigraphic or geochemical data, respectively. Phyllosilicates, mostly clastic muscovite, biotite and chlorite, in silt, sand and gravel fractions are usually derived from different igneous, metamorphic and sedimentary rocks. Chamley (1989) in his excellent monograph "Clay Sedimentology" compiled enough original papers showing that sheet silicates even in the clay fraction of river sediments have their sources mostly in local parent rocks. In suspended solids and muds of rivers the newly formed sheet silicates from soils only accompany the prevailing portion of preexisting phyllosilicates (micas, kaolinite, chlorites, smectites, vermiculites as the main groups). This fact needs explanation based on the knowledge of weathering, erosion, transportation and deposition in rivers. Quartz, sodium-rich plagioclase, potassium feldspar, somewhere amphibole, calcite and/or dolomite are the commonest subordinate or accessory clastic minerals in suspended matter and muds of rivers (Konta, 1988)

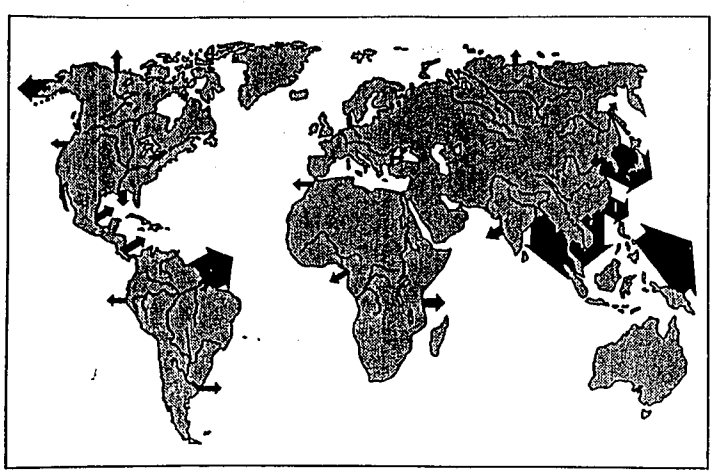


Fig. 1.- Relative year supply of solid particles in suspension by rivers into the seas in different regions of the world (Milliman and Meade, 1983).

EVERYTHING STARTS IN WEATHERING CRUST

Phyllosilicates are the most stable silicates in aqueous environments (Konta, 1984). While many common igneous and metamorphic rocks-forming silicates are destroyed by weathering processes, the phyllosilicates, quartz and some heavy minerals are highly resistant. The environment during the weathering of different rocks is favorable even for crystallization and growing of phyllosilicates, usually called clay minerals. These newly formed phyllosilicates in soils, deep weathering crusts and hydrothermal occurrences crystallize under well defined thermodynamic conditions (e.g. Lippmann, 1981).

Quartz is less resistant to chemical weathering than the phyllosilicates rich in silicon and aluminium. Chemical resistivity of quartz is also supported by its limited cleavage. This property acts against the increase of specific surface area and the penetration of aqueous solutions into quartz grains. Feldspars due to their excellent cleavage soak up aqueous solutions by capillary forces. Specific surface area of feldspar grains exposed to weathering increases with the cleavage abundance. The different resistivity of the commonest rock-forming silicates against weathering is illustrated in Fig. 2. Its shows a correlation between the calculated index of corrosion (I_{KO}) and the determinated (SiO_2 + Al_2O_3)% in these minerals (Konta, 1984). Index I_{KO} of each crystalline silicate is calculated from its chemical composition according to the equation

$$I_{KO} = \frac{200\left[\Sigma A_i\left(\frac{Z_i}{r_i}\right) - \frac{C\left(\frac{Z_{H^+}}{r_{H^+}}\right)}{10}\right]}{\Sigma A_i\left(\frac{Z_i}{r_i}\right) + \Sigma B_i\left(\frac{Z_i}{r_i}\right)}$$

where A_i is the mol concentration of oxides of those cations which are easily removed, i.e. alkaline and alkaline earth and other divalent cations plus some of the smaller cations (C^{4+}, P^{5+}, S^{6+}) which easily form complex anions, while B_i are the mol concentrations of oxides of the more insoluble tri-, tetra- and pentavalent cations such as SiO_2, ThO_2, ZrO_2, TiO_2, Al_2O_3, Fe_2O_3, Cr_2O_3, B_2O_3, Ti_2O_3, V_2O_3; C is the mol concentration of the chemically bound water (OH plus zeolitic H_2O multiplied by 2.703); Z_i is the cation charge and r_i the ionic radius of the respective ion i; Z/r for $H^+/10$ = 2.703 (for more detail see Konta, 1984).

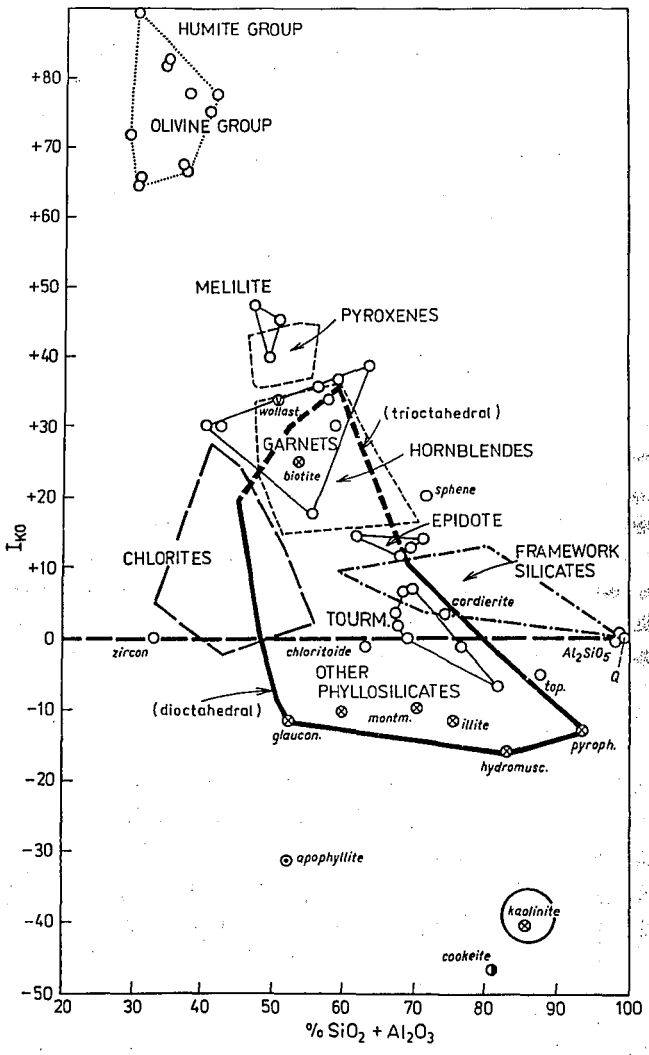


Fig. 2.- Simplified diagram showing correlation between the corrosion index (I_{KO}) and % (SiO_2 + Al_2O_3) in the commonest rock-forming silicates. Chemical stability of the silicates during weathering increases with the SiO_2 + Al_2O_3 contents and the decreasing I_{KO} values (more see in Konta, 1984).

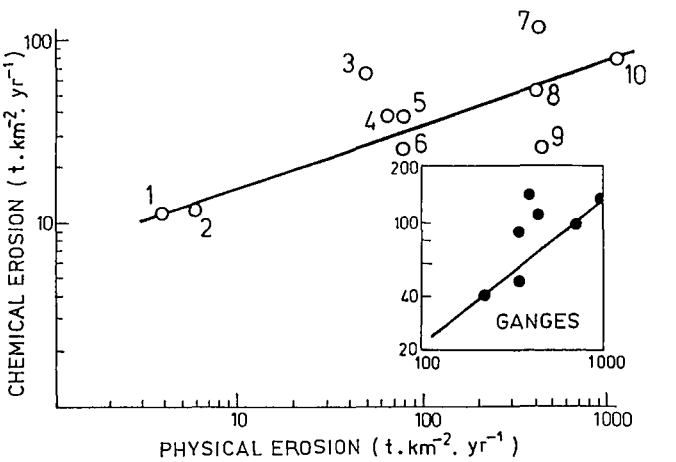
The I_{KO} value of a rock-forming silicate decreases with the increasing percentage content of (SiO_2 + Al_2O_3) while its stability in aqueous environment increases. The negative I_{KO} value always means that the mineral is ultrastable in aqueous environment. As a proof of the extremely high chemical stability, especially of dioctahedral micas, Al-rich smectites and kaolinite, is their common occurrence in the detrital pelite up to arenite sediments. The micromilieu strongly differing from that of pH $\approx$ 7 in some weathering profiles may destroy even the Al-rich phyllosilicates.

OUTFLOW AND TRANSPORTATION, THE MAIN ROLE OF RIVERS

For a geologist the primary function of rivers is to drain meteoric water from the continents to lacustrine and marine basins. Considerable volumes of water penetrate into soils or evaporate. Each part of nonarid regions is interwoven by dense net of the initial transport tiny rills during rains or thaw. They finely end in a mighty river system. The constituents of soils and mechanically disintegrated rocks on the earth surface easily get loose in the erosion process. The finest of them disperse and make the streams muddy. The apparent viscosity of the muddy water increases with the amount of suspended matter and so does its transport capacity. The loose solid material transported in rivers represents globally more than 90% of the eroded earth surface. The rest is shared by landslides, avalanches, glaciers, solifluction movements and wind erosion.

The rate of weathering and also erosion in central and southern Europe varies in magnitude from several millimeters up to 10 mm per 100 years (Petrov, 1967; Manickam et al., 1985). Due to acid rains in the Elbe catchment area the rate of weathering has increased three times over the last less than 100 years (Pačes, 1983). The rate of erosion generally rises with the height above sea level, with the increasing volume of atmospheric precipitations and with the decrease of the vegetation mantle.

Quite considerable portion of the inorganic material is transported in solution (Fig. 3). In any river, the ration of transported inorganic solid matter in suspension to the content of inorganic matter in solution increases with the rising discharge. Sedimentary and volcaniclastic terrains, however, yield rather high amounts of soluble matter. The riverine water contains also organic matter in solution and in particulate state.



1 - Yenisey 2 - Ob 3 - Columbia
4 - Mississippi 5 - Amazon 6 - Zaire /Congo/
7 - Ganges 8 - Indus 9 - Colorado
10 - Mekong

Fig. 3.- Relationship between transported inorganic solid matter in suspension (physical erosion) and the content of inorganic matter in solution (chemical erosion) for ten major world rivers (Subramanian, 1985). Insert: variations for the Ganges.

MOVEMENT OF THE SOLID MATERIAL IN STREAMS AND ITS DEPOSITION

The classic Hjulströms (1935) graph explains the behavior of cohesive and loose accumulations composed of different grain sizes in the interaction with flows of different velocities in three sedimentological categories: erosion, transportation and deposition (Fig. 4). The movement of eroded solid components in rivers runs by traction (mostly gravel, > 2 mm), saltation (mostly sand, 2 - 0.063 mm) and in suspension (mostly silt, 0.063 - 0.004 mm and clay, < 0.004 mm). Phyllosilicates occur in any size category of these detrital sediments (Fig. 5). The largest amount of phyllosilicates is transported in suspension.

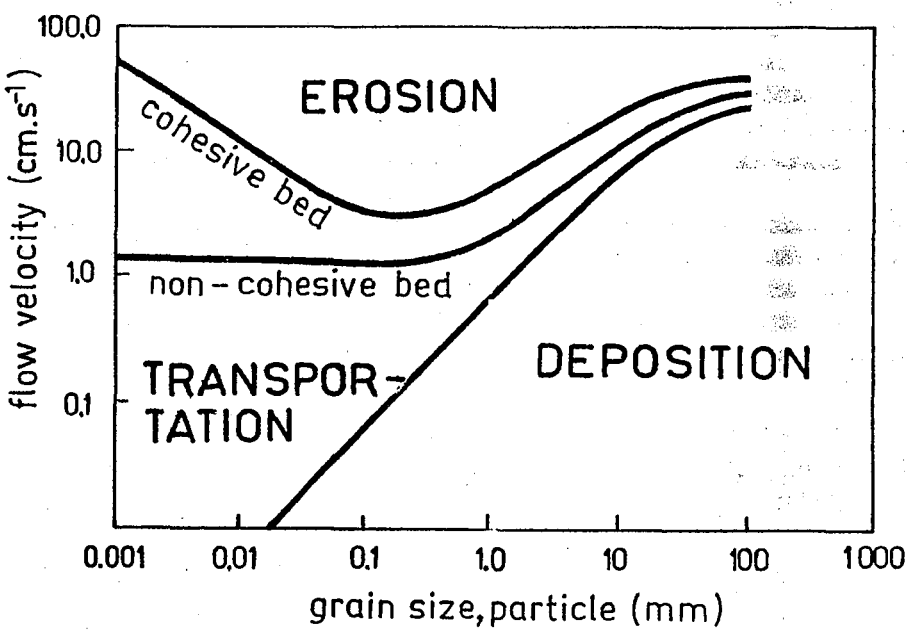


Fig. 4.- The classic Hjulström (1935) graph for erosion, transportation and deposition of different grain sizes of cohesive and loose accumulations under the action of flows of different velocities.

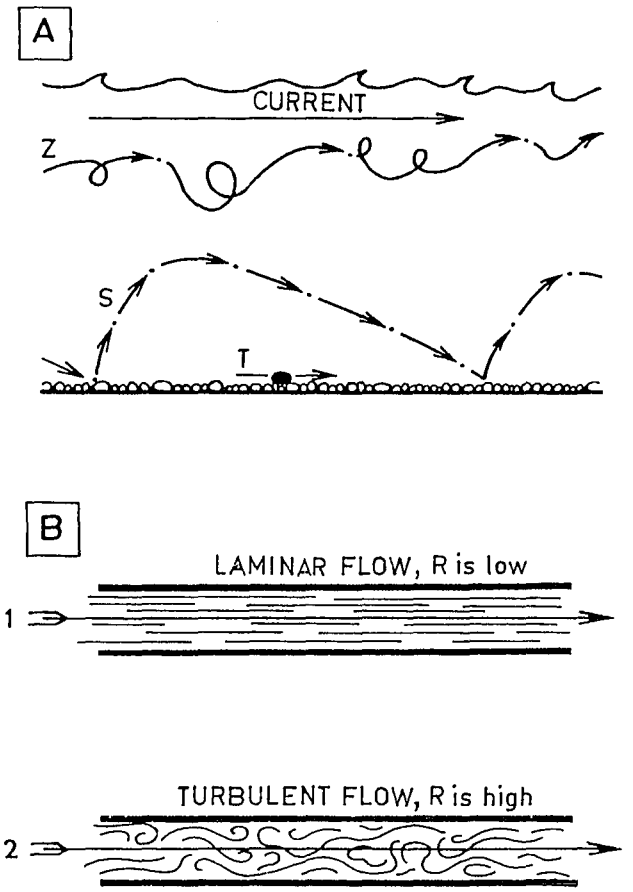


Fig. 5.- A three basic mechanics of particle movements in a stream: Z, in suspension; S, saltation (bouncing or periodical suspension); T, traction (rolling). B-1, laminar flow, characteristics by low Reynolds number; 2, turbulent flow, high Reynolds number (Illustrative of the flows in tubes, Selley, 1976).

Large amounts of primary phyllosilicates in original shapes may be embedded in gravel fragments of different rocks. The most common muscovite- and biotite- bearing rocks are granitoids, their volcanic equivalents, gneisses and migmatites. Muscovite is the main mineral in mica-schists. Fine flakes of muscovite (sericite) and chlorite are typical constituents of shales, slates, phyllites, porphyroids, etc. Representants of any group of phyllosilicates may be eroded from argillaceous or similar sediments, e.g. clays, claystones, clay shales, marls or marlstones, unconsolidates lutites up to shales and their anchimetamorphic equivalents. Many of the phyllosilicates occurring in different rocks easily survive chemical weathering due to their crystal structure and chemical composition. The least stable are biotite and chlorites rich in iron and magnesium (Fig. 2). They are relatively rapidly destroyed in tropical soils.

Coarser crystals of micas, chlorites or kaolinite in different stages of mechanical weathering disintegrate during continual transportation (Fig. 6). The turbulent flow of any river contributes to this partition (Fig. 5, B2). The microscopic or submicroscopic fissures are controlled by the best developed crystal structure planes, but not only along the basis. Therefore, phyllosilicates in clay fraction mostly occur in very thin, irregular flakes. Aggregates of swelling sheet silicates disperse still better. The preexisting fine aggregates of phyllosilicates also disintegrate during the transportation. The clay minerals newly formed in soils build a rather small portion of suspended solids and muds in rivers compared to the amount of the preexisting highly stable species (Fig. 7).

The log-probability size distribution curves of river sediments help to recognize several size subpopulations. Each of them is transported by a specific mode (fig. 8).

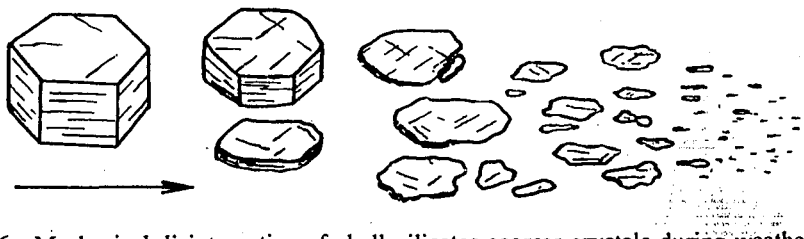


Fig. 6.- Mechanical disintegration of phyllosilicates coarser crystals during weathering and continual transportation, one of the commonest phenomena.

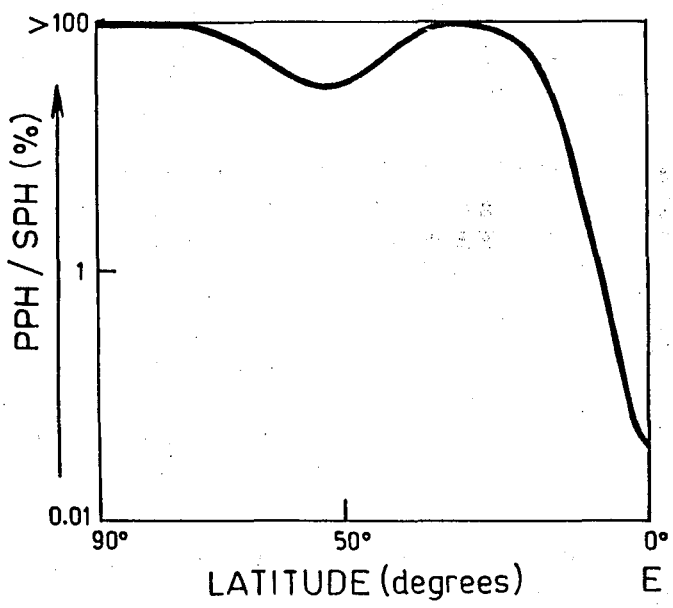


Fig. 7.- Graph globally generalizing the ratio between the preexisting (PPH) and newly formed soil (SPH) phyllosilicates in clay fraction of river sediments. E = Equator.

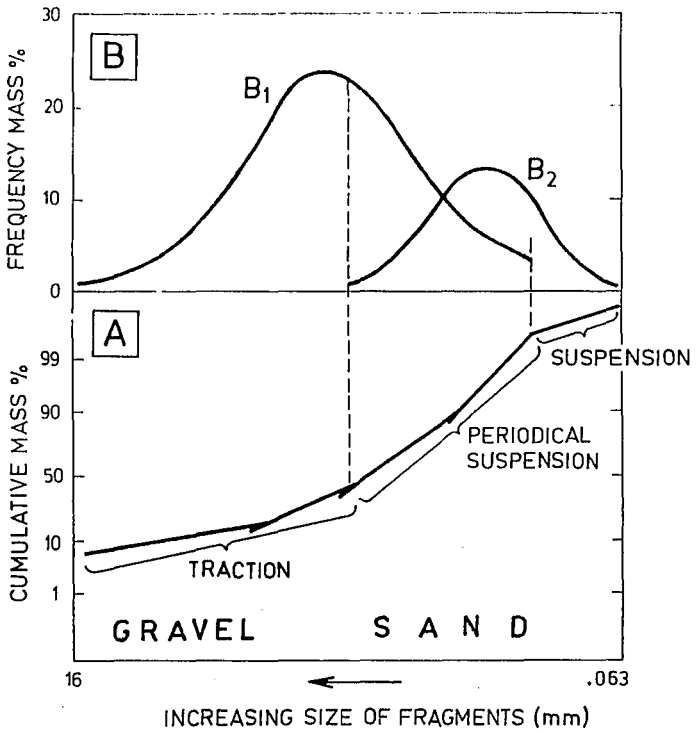


Fig. 8.- A. Log-probability cumulative distribution curve and B: frequency curve of a river sediment from the bottom (B1) and the suspension (B2) without silt and clay. The curves represent only a gravel and sand material in rivers of the discharges approaching flood state (Eschner and Kircher, 1984).

Deposition of phyllosilicates and clay fraction occurs in any river segment considering the longitudinal or transversal profiles. The physical behavior or transported clastic material in a aqueous flow can be expressed by a dimensionless coefficient, the Reynolds grain number (R):

$$R = \frac{U d p}{\mu}$$

where
- U is the velocity of the particle ($cm.s^{-1}$),
- d is the diameter of the particle (cm.),
- p is the density of the particle ($g.cm^{-3}$),
- μ is the viscosity of the fluid (poise).

R varies between 1 and 1000. Laminar, extremely slow flows are characteristics by very low R. In a flow, during decreasing velocity and turbulence and apparent viscosity of the aqueous suspension, the fragments fall to the bottom starting with the heaviest and successively continuing to the lightest. R usually decreases with the length of a river.

A second important coefficient of fluid dynamics is the Froude number (F) which is expressed by the following equation:

$$F = \frac{U}{\sqrt[2]{gD}}$$

where U is the average velocity of the flow (m),
g is the gravitational acceleration ($m.s^{-2}$ = 9.82 for Central Europe),
D is the depth of the flow (m).

The largest amounts of clays settle from flows of very low R and F. They approach more the laminar than the turbulent flows. This is best fulfilled in the terminal sedimentation basins.

Clay particles, however, may settle in streams in many energetic "shades", especially behind some barrier or on the alluvial planes together with silt and sand grains. The R and F numbers of a river strongly vary not only with sites but also with its seasonal discharge changes (Fig. 9). Smectite occurring as extremely fine flakes cannot settle under strong hydrodynamic conditions, i.e. on sites of high R and F numbers.

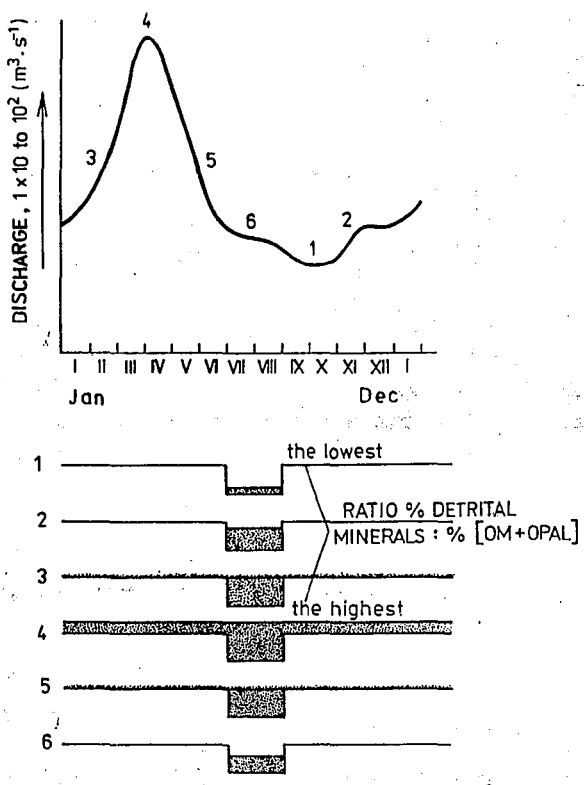


Fig. 9.- Generalized time depending discharge curve for rivers in Bohemia and Moravia. The corresponding changes of water levels are indicated by numbers on the curve and shown below: 1, low water; 2, rising water; 3, initial overbank; 4, high water; 5, receding water; 6, draining water. Modification from monographs by Netopil (1972) and Richey (1982). OM = Organic Matter.

THE SUSPENDED SOLIDS ARE THE RICHEST IN PHYLLOSILICATES AND AMORPHOUS MATTER

The finest clastic material transported in suspension contains the largest amounts of phyllosilicates (Konta, 1988). Amorphous matter, i.e. mainly particulate organic matter and the opal skeletons of organisms, mostly diatoms, living in rivers and Fe(III) - oxyhydroxides may highly enrich water suspension as well as the finest river sediments. The ratio between the crystalline minerals content (CM) with clay minerals prevailing and amorphous matter content (AM) in river suspensions varies from 5:0 to 1:4. Scanning electron micrographs of Czechoslovak rivers show these extreme ratios (Fig. 10) among which many transitions exist. The %CM:%AM ratio is controlled by the seasonal changes of the river discharge (Fig. 9). More watery and turbid major world waterways, e.g. the rivers Amazon, Paraná, Orinoco, Mackenzie, St. Lawrence, Niger, Indus, Ganges, Brahmaputra, with their different seasonal discharge curves carry many times larger amounts of eroded minerals than any European rivers, including the Danube (Fig. 11). Also these major world rivers reveal similar %CM:%AM variations (Figs. 12 to 15).

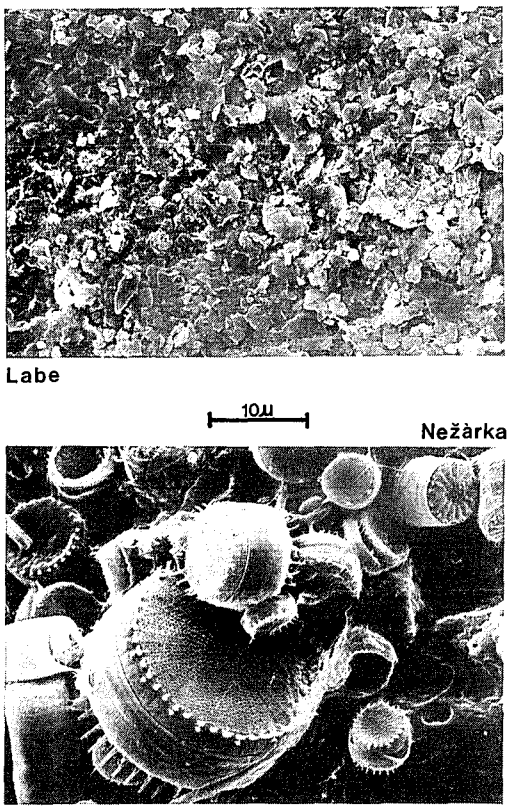


Fig. 10.- Scanning electron micrographs of suspended matter of the Czechoslovak rivers (the Labe and Nežárka) showing the extreme %CM : %AM ratios. CM: Crystalline minerals, AM: Amorphous matter.

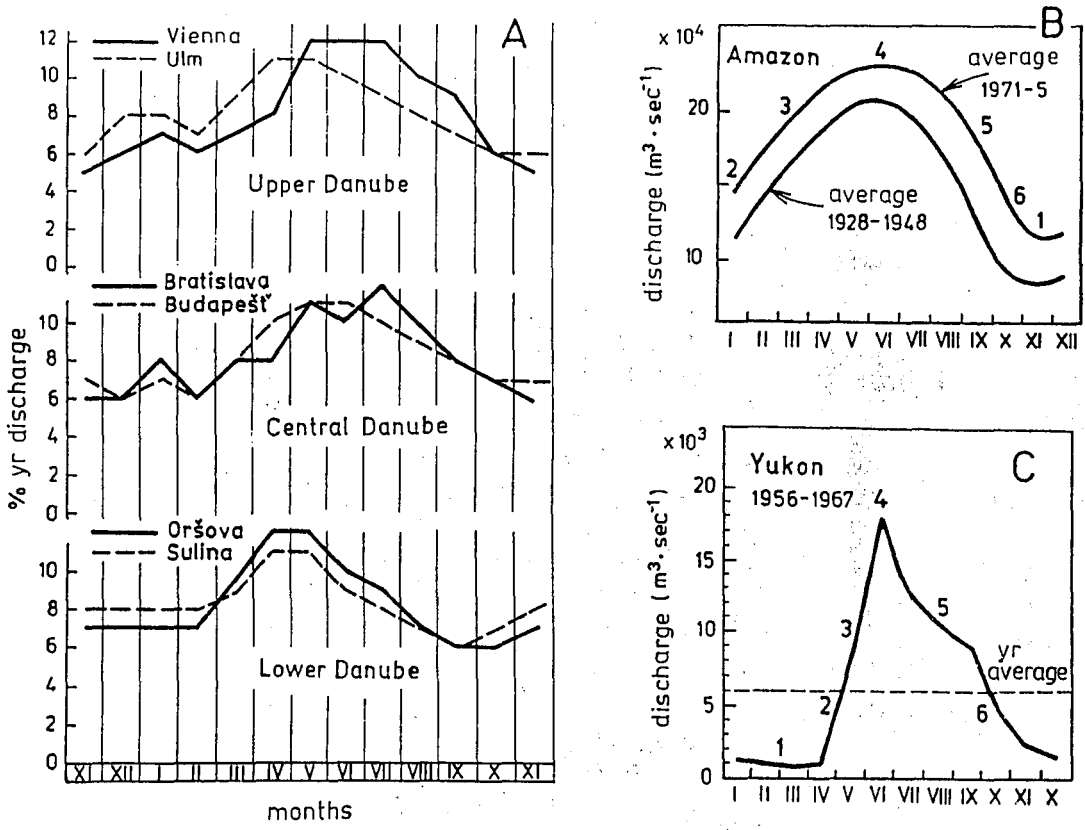


Fig. 11.- Time depending discharges in several sites of the Danube (A, Netopil 1972) with the maxima in the late spring up the summer, the discharge curves of the Amazon (B, Meade et al., 1979; Richey, 1982) and the Yukon (C, Kempe, 1982). Numbers 1 to 6 are explained below Fig. 9.

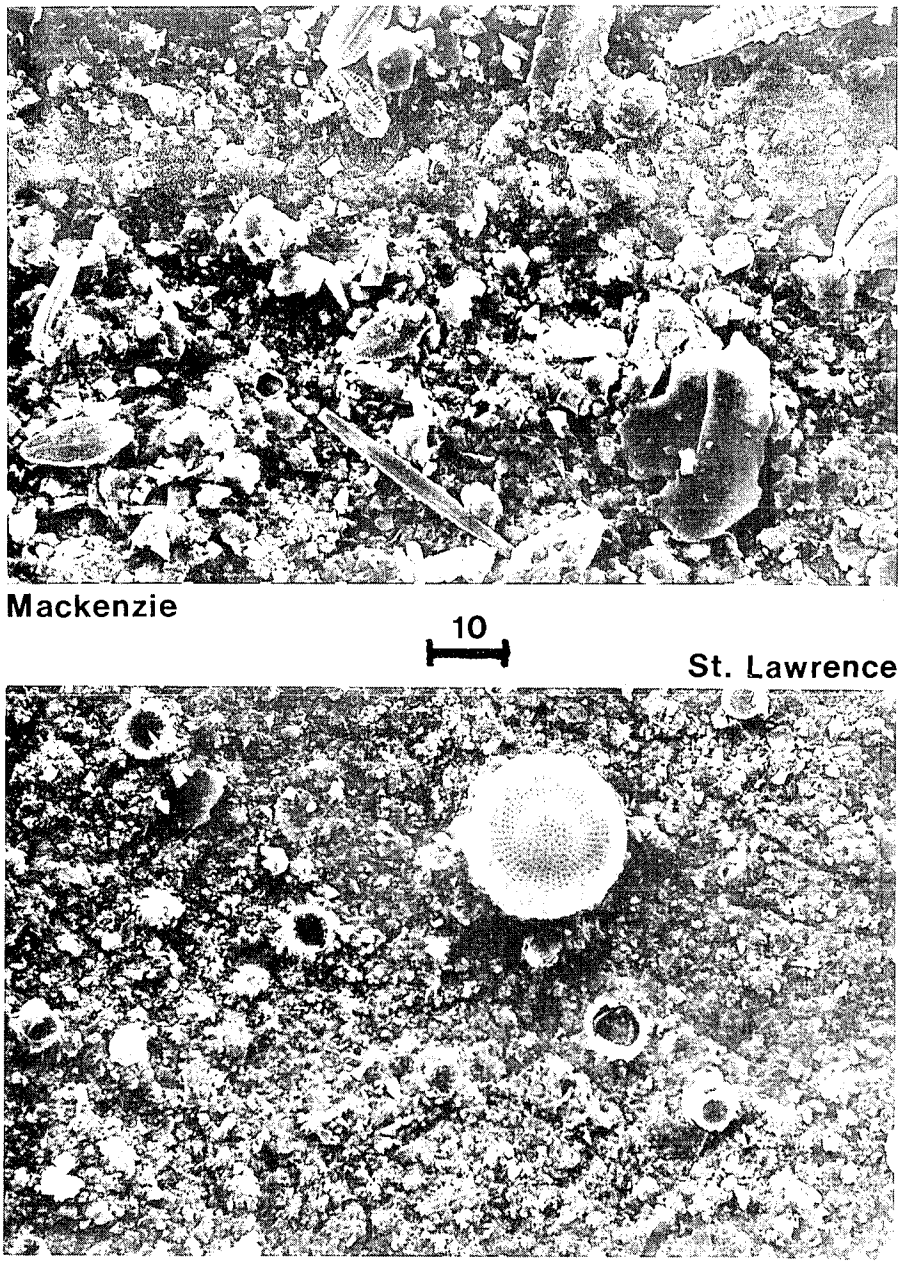
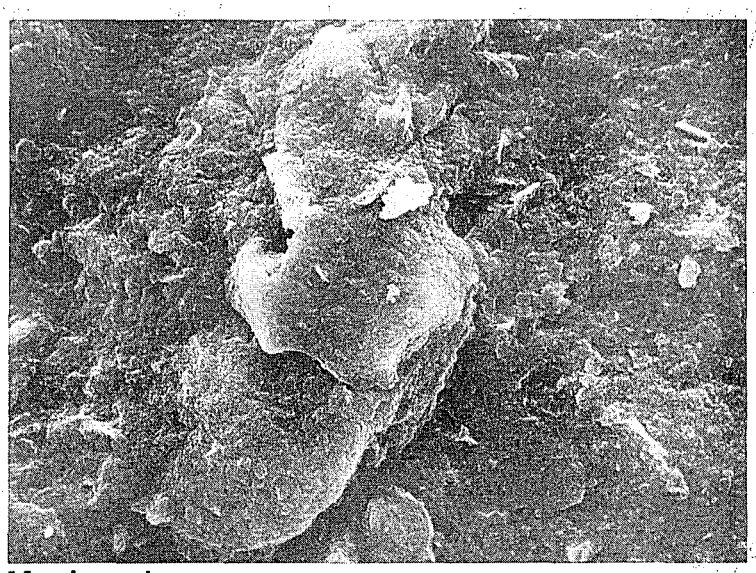


Fig. 12.- SEM micrographs of suspended matter of the Mackenzie and the St. Lawrence, Canada. The bar in all micrographs is in μm.

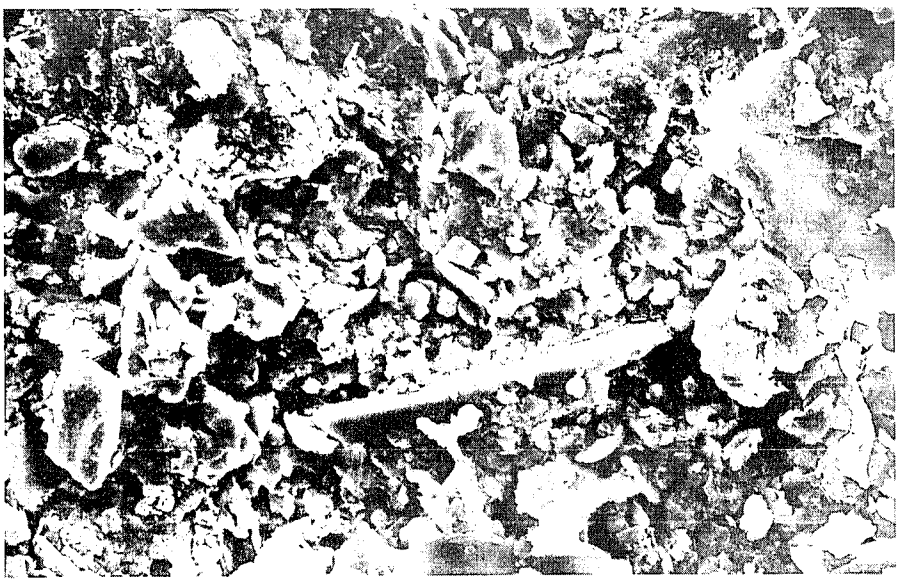


Mackenzie

3

Paraná

Fig. 13.- SEM micrographs of suspended matter with very fine particles and rounded clay intraclasts in the Mackenzie (Canada) and coarse flat sheet silicate fragments in the Paraná (Argentine).



Orinoco

10

Niger

Fig. 14.- SEM micrographs of suspended matter of the Orinoco (Venezuela) and the Niger (Nigeria).

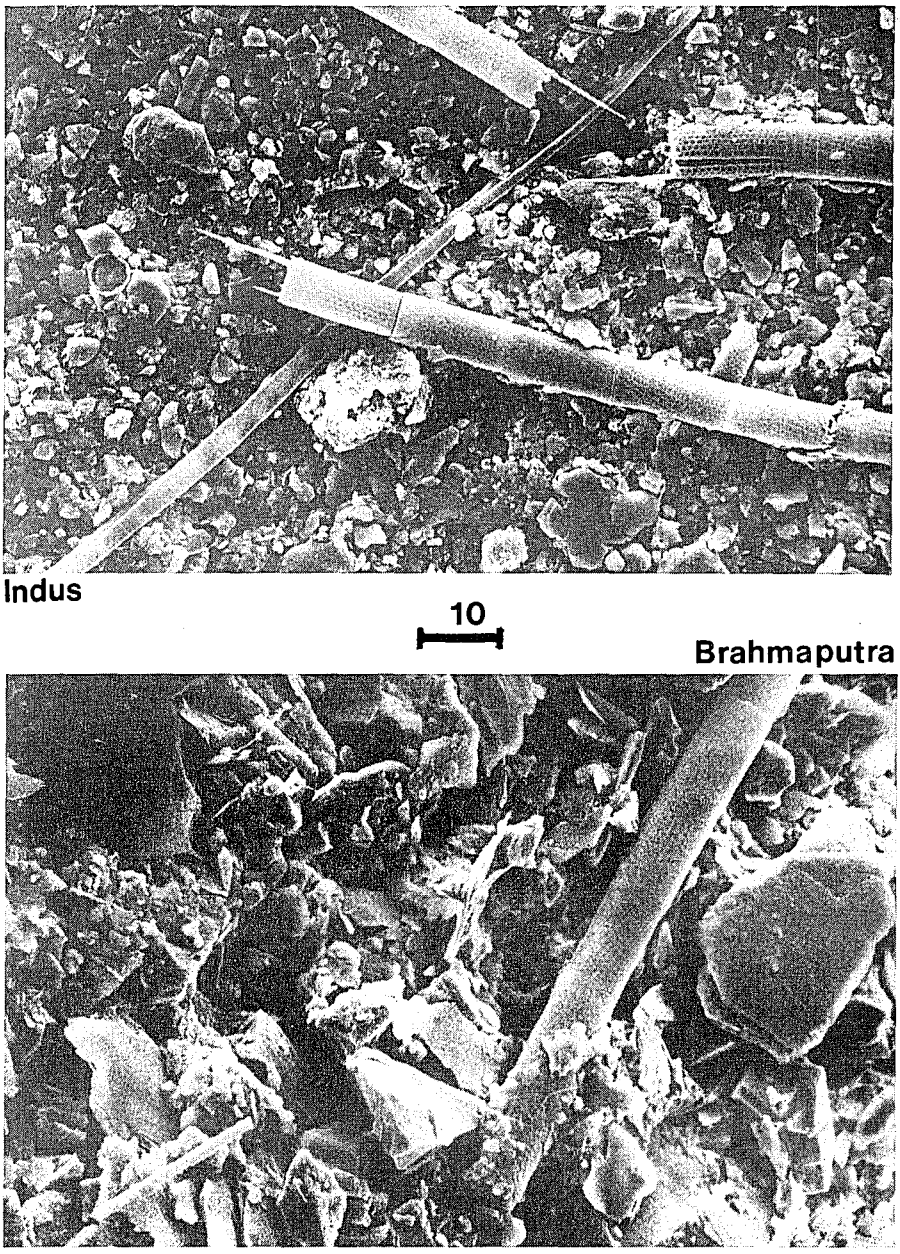


Fig. 15.- SEM micrographs of suspended matter of the Indus (Pakistan) and the Brahmaputra (Bangladege).

The varying %CM:%AM ratios in suspended matter are sensitively expressed not only by X-ray diffractograms (Fig. 16) but also by EDAX spectra (Fig. 17) and EDAX quantitative data. Samples with higher amount of organic combustible substance give EDAX spectra with rather intense lines of detectable biophile elements (P, S, Cl, Ca). Samples rich in opal tests of diatoms and other opal- bearing organisms give EDAX spectra with high Si/Al ratios. Suspended matter without these amorphous materials and rich in common crystalline detrital silicates gives EDAX spectra of lower Si/Al or Si/(Al+Mg) ratios.

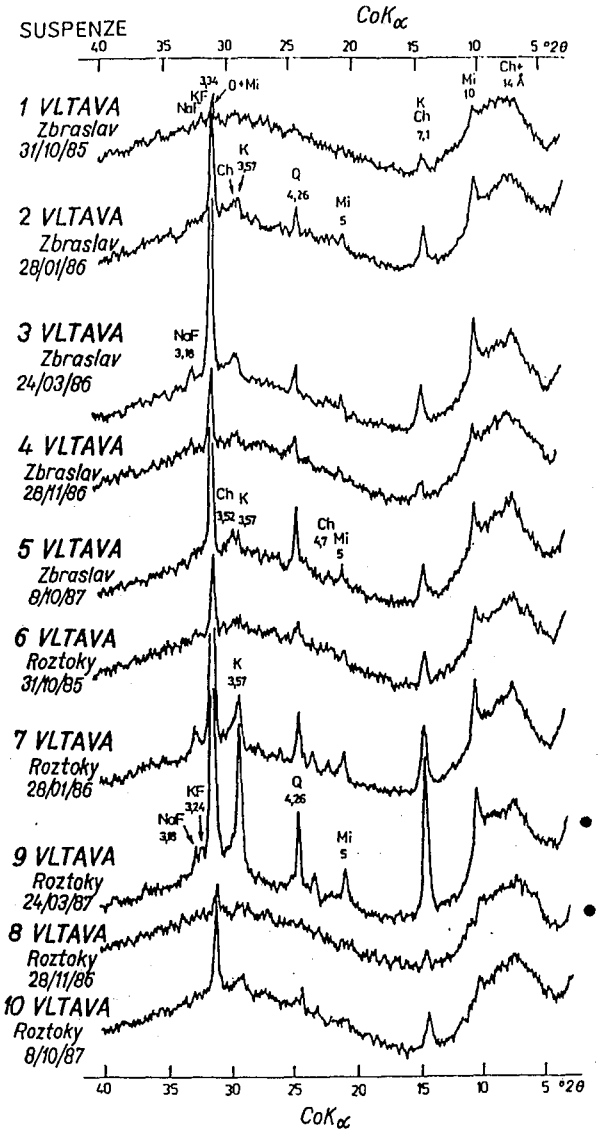


Fig. 16.- X-ray diffractograms of suspended matter from the Vltava (Moldau), Zbraslav station, upstream of Prague (1 to 5) and from the Vltava, Roztoky station, downstream of Prague (6 to 10). Konta (1990a).

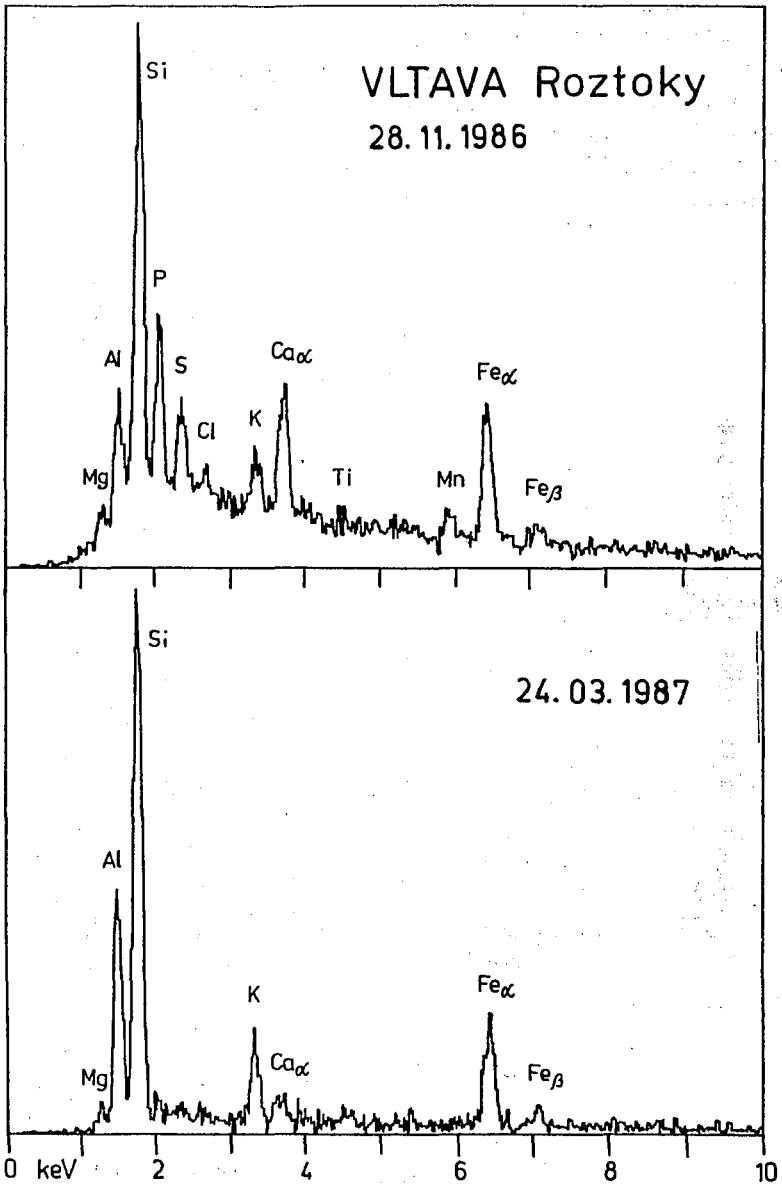


Fig. 17.- Two differing EDAX spectra of suspended matter from the same river, the Vltava (Moldau), from the same sampling site (Roztoky, downstream of Prague): the upper spectrum is for the November sample richer in organic matter, while the lower one is for the March sample poor in organic matter but rich in phyllosilicates (mica-illite, kaolinite, chlorite).

The mixed-layer structures of phyllosilicates are less abundant in suspended matter and muds of rivers than in soils,

The silt fraction of river sediments is usually rich in phyllosilicates released from parent rocks and highly disintegrated and broken. Many silts are rich in muscovite and quartz but biotite or chlorite and feldspars fragments may also be common.

Some microflora of rivers, especially specific algae, are important acceptors of heavy metals. That is why suspended matter and clay fraction of muds in rivers are usually enriched in Mn, Zn, Cu and less in other heavy metals (Figs. 18 and 19).

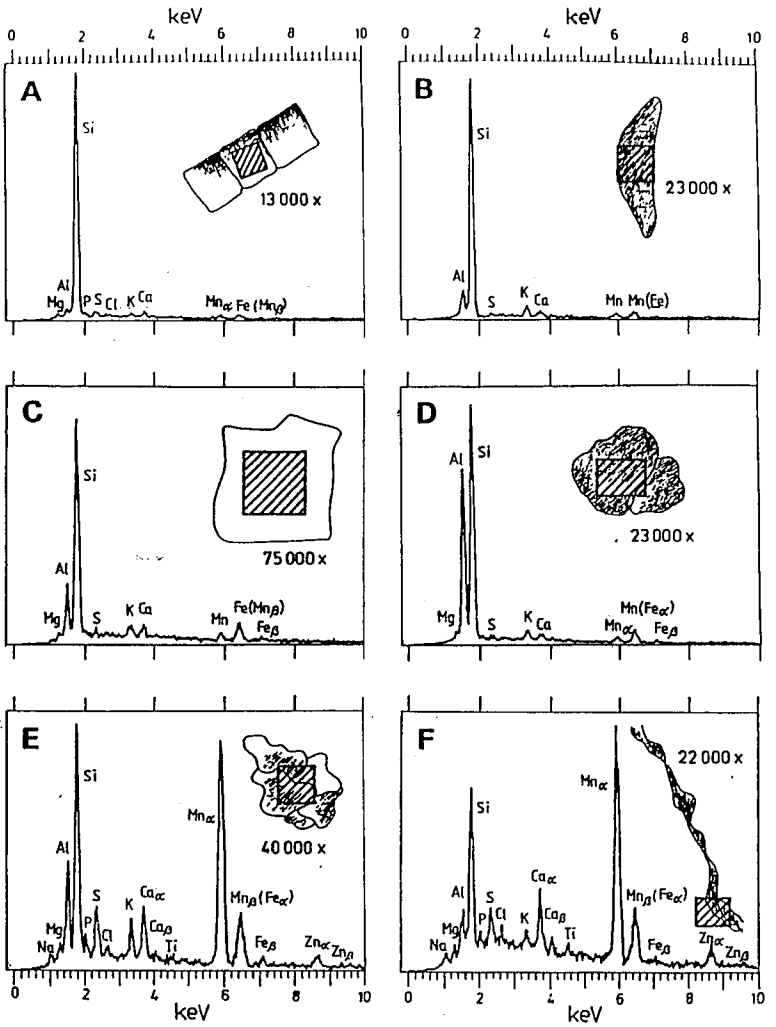


Fig. 18.- EDAX spectra of different particles in suspended matter of the Mže (collected at Plzeň-Křimice, June 15, 1988, Bohemia), at the magnification 1000x. The dashed square in each particle represents the analyzed area (Konta, 1990b).

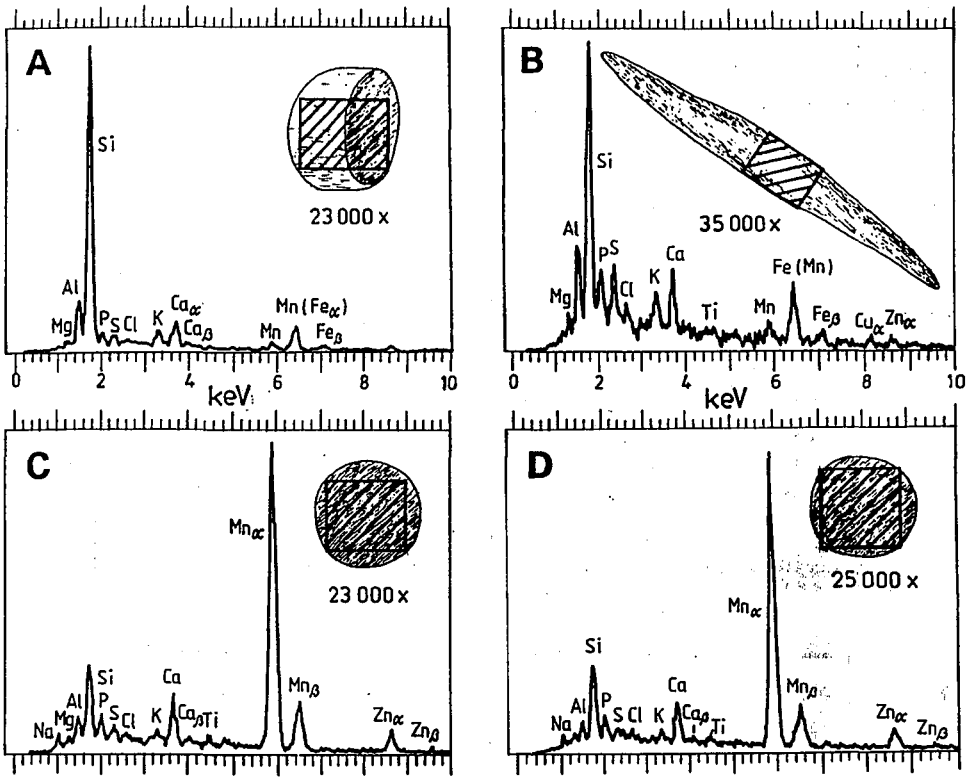


Fig. 19.- EDAX spectra of different particles in suspended matter of the Radbuza (Plzeň, June 15, 1988, Bohemia), at the magnification 1000x. The dashed square in each particle represents the analyzed area.

DEFLOCCULATION AND COAGULATION OF CLAY PARTICLES

Deflocculation and coagulation of clay particles in rivers are known from nature and their physics is recognized by experiments. The equilibrium diameter (D_E) of transported clay flocs or individual particles depends on two processes acting against each other: a) aggregation, caused by the collision of particles, b) dispergation, enabled by erosion and splitting. D_E is a multidimensional function, depending on at least seven variables:

$$D_E = f\,(\,C,\ S,\ \nu,\ \rho,\ D,\ N,\ D_O)$$

where C is the concentration of particles ($mg.litre^{-1}$),
S is the salinity of water (‰),
ν is the kinematic viscosity of fluid ($cm^2.s^{-1}$),
ρ is the density of particle ($g.cm^{-3}$),
D is the diameter of agitator at the experiment (cm),
N is the agitator speed (revolution $number.min^{-1}$),
D_O is the initial diameter of flocs (μm).

The equilibrium state is attained when the diameter of flocs does not change with time under existing agitation energy.

The humus compounds and especially the sodium humate, keep fine clay particles in suspension for a long time. This may occur in rivers and especially in artificial dams. The resuspensation of deposited mud and deflocculation of clay aggregates occurs e.g. during a strong storm or flood. The increased cloudiness of the water column reduces the penetration of light into the depth. Long-lasting turbidity and reduction of light in water basin may have a far-reaching impact on its ecology. Industrial or agricultural waste let out into rivers may change flocculation and deflocculation conditions of clay particles and thus also the physical and chemical behaviour of one of the most effective natural sorbents.

A mighty coagulation of clay particles takes place in estuaries due to the electrolytic action of salts from marine water onto the electric outer double-layer of clay minerals. This phenomenon leads to a depositional acceleration of clay particles. It is also the reason why the estuary muds are richer in heavy metals.

CONCLUSION

Phyllosilicates, especially the Al-rich species, are chemically the most stable rock-forming silicates in aqueous environment. They survive chemical weathering due to their crystal structure and chemical composition. The preexisting crystals and fine aggregates of phyllosilicates disintegrate during the erosion and transportation. Therefore, the clay minerals newly formed in soils build a rather small portion of suspended solids and muds in rivers compared to the amount of preexisting highly stable species.

The seasonal pulsation of a river discharge is accompanied by several characteristic changes in suspended solids, where the largest portion of phyllosilicates is transported. The decrease of water level leads to:

1) the decrease of the content of transported clastic particles including the phyllosilicates;

2) the decrease of the % CRISTALLINE MINERALS : % AMORPHOUS MATTER ratio (i.e. %CM : %AM, where AM means mainly organic combustible substance + opal tests);

3) the increase of the concentration of heavy metals, especially Mn, Zn and Cu, which are extracted by some specific microorganisms.

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STACKING, DEFORMATION AND RUPTURE IN SMECTITE CLAYS

H. Van Damme

STACKING, DEFORMATION AND RUPTURE IN SMECTITE CLAYS

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Before starting this lecture, let me thank the Sociedad Espanola de Arcillas for inviting me to this meeting organized in honor of Professor J.M. Serratosa. The collaboration of the French Clay Group with the Spanish Group and, in particular, of our group in Orléans with Professor Serratossa's group in Madrid is a long standing habit, which allowed me to have many faithful friends. It is a real pleasure and an honor for me to be here today.

I. INTRODUCTION

My lecture will be a modest attempt to detect general phenomena in the forest of fascinating behaviours which clays, and smectite clays in particular, exhibit. Like many other finely divided materials, clays raise the problem of understanding, in terms of interparticular interactions at colloidal and molecular levels, the behaviour of a macroscopic system which can go from a dilute suspension to a porous and brittle solid. However, with respect to other inorganic or organic colloids, clays present an exceptionaly broad spectrum of morphologies and surface properties. The elementary crystals may be hollow spheres, fibers, hollow fibers, thick polygonal platelets, or thin and flexible sheets, with sizes ranging from a few nanometers to several microns. Most of these particles are very anisotropic and, in this respect, clay materials bear a close resemblance to liquid crystals. As far as surface properties are concerned, one encounters several types of surface atomic planes (oxygen atoms, hydroxyl groups, lacunar or compact planes,...) with physico-chemical properties ranging from hydrophobic to hydrophilic, from apolar to very polar, from neutral to highly charged, and from permanently charged to pH-dependent.

The purpose of this contribution is not to give a "comprehensive behavioural theory" of such a complex family of materials, but to provide a few clues based on the consideration of interactions and phenomena which are often neglected: *steric constraints* on one hand and *micromechanical deformations* on the other hand. In random (disordered) *macroscopic* media, such as slurries or powders of millimetric particles, the texture of the system is determined essentially by the hydrodynamic interactions, the contact mechanics, the steric constraints and, in the case of deformable particles, the particle rheology. Intermolecular and surface forces other than capillary forces are of negligible importance. Surprisingly, in random *microscopic* (colloidal) media, contact mechanics, steric constraints and internal particle rheology are usually completely neglected and the texture is often thought to stem solely from van der Waals and electrostatic interactions. The main purpose of this lecture is to show that

geometrical and mechanical constraints may be just as strong in colloidal liquids and solids as in macroscopic media.

A basic concept which I will develop is that of *scaling*. Rather than looking to the average properties or to the texture of a material at a given scale, it is often advantageous to look to their evolution as the observation scale is changed. The main benefit is that the rules which allow to go from one scale to another are usually revealing features which are more "universal" than those which one can detect at a single scale.

As sketched in scheme 1, I will try to analyse several phenomena, some of them dealing essentially with *particles*, such as stacking, sedimentation and swelling, the others dealing more specifically with *molecules*, such as surface area and porosity measurements. Most of the discussion will be devoted to smectite (swelling) clays, but the concepts may be applied to other clays as well. Hopefully the approach will be of interest both for earth scientists and for chemists.

Before starting, I would like to stress that the results and the ideas which will be presented are the fruits of a collaborative effort with students such as Mohsine Ben Ohoud (section III), Bachir Barriki and Mohend Chaouche (section IV) and with colleagues at the CNRS or at the University of Orléans such as Pierre Levitz, Faïza Bergaya, Daniel Tinet, Freddy Delville, Lucien Gatineau, Jean-François Alcover and Charles Pons.

II. GEOMETRICAL CONSTRAINTS

Particles in suspensions and sediments

Putting an increasing number of objects (molecules or particles) in a finite volume is not an innocent process. The arrangement which is produced is strongly dependent on the shape of the objects and on the distance from the walls. Even if the interactions are limited to *contact* interactions (in other words, even if an object does not detect the presence of other objects, including the walls of the box, before touching them), the presence of one object at a given place influences the position and the orientation of other objects within a volume which is usually much larger than the volume of the object itself. As shown by Lars Onsager several decades ago, this may induce the simplest order-disorder transitions which are known.

The central concept which permits to quantify this effect is the so-called *excluded volume*, which can be defined as the volume surrounding the center of a first object within which one cannot place the center of a second object without statistically experiencing steric hindrance. For anisotropic objects, their excluded volume can be visualized as a sort of gyration volume. For infinitely thin disks or platelets of size R, the excluded volume is increasing as $\sim R^3$. For rods of length R and diameter r, V_e is

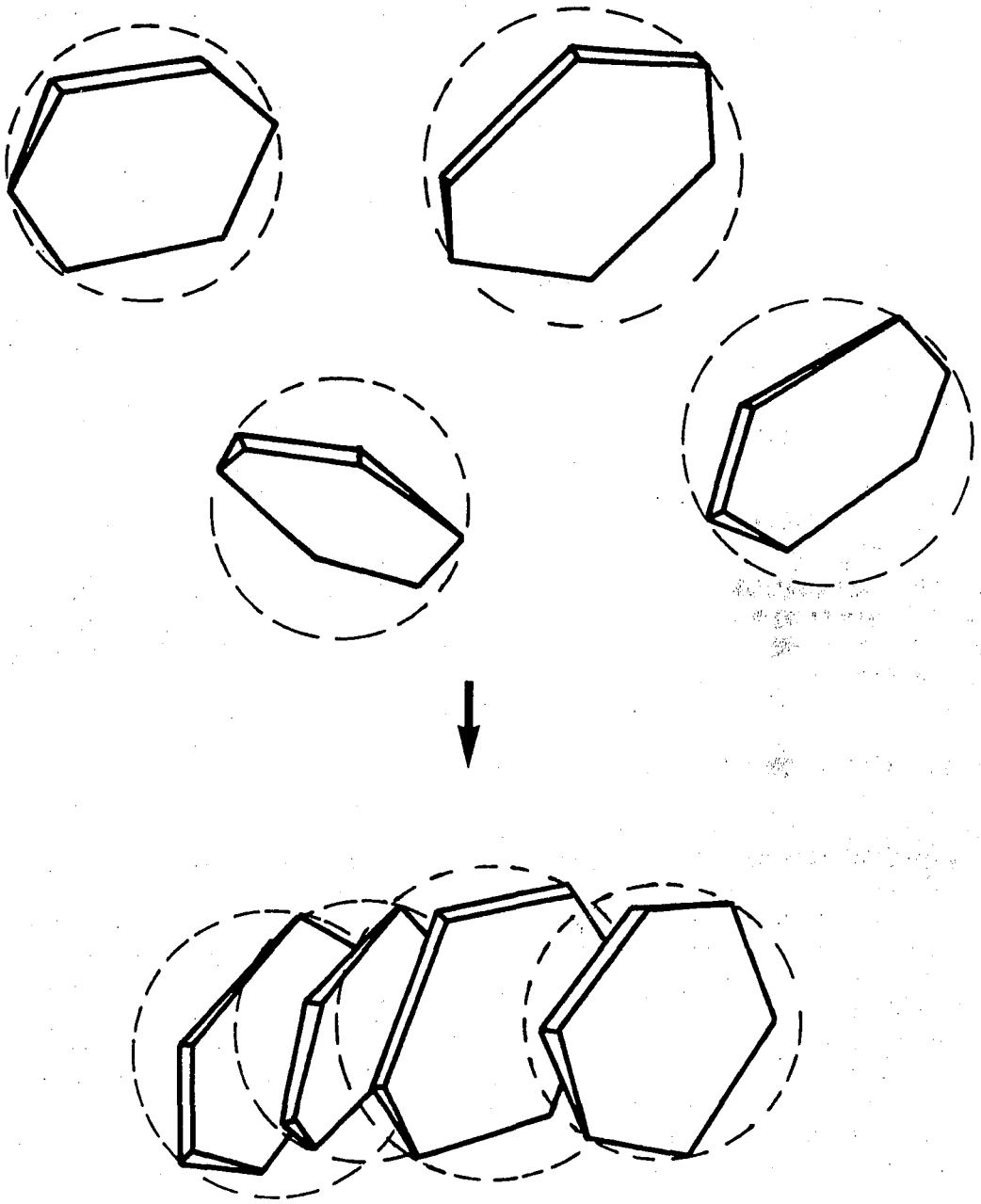


Fig. 1. By confining several platelets in a small volume, one forces the gyration or envelope volume of these platelets to overlap each other. This induces a mutual orientation effect due to steric hindrance.

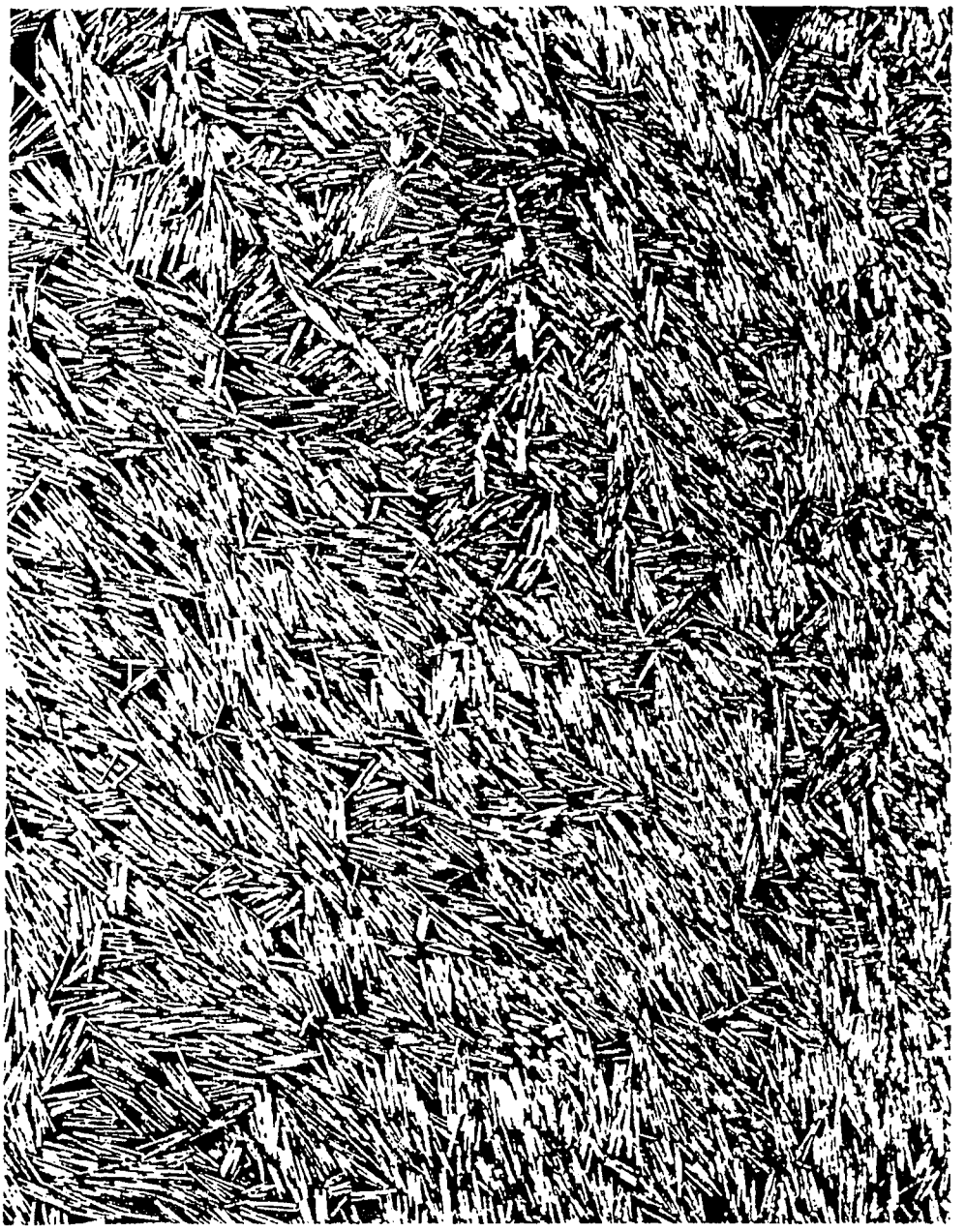


Fig. 2. Disordered dense packing of tree logs floating on a river (adapted from D. Hogstadter, "Metamagical Themas")

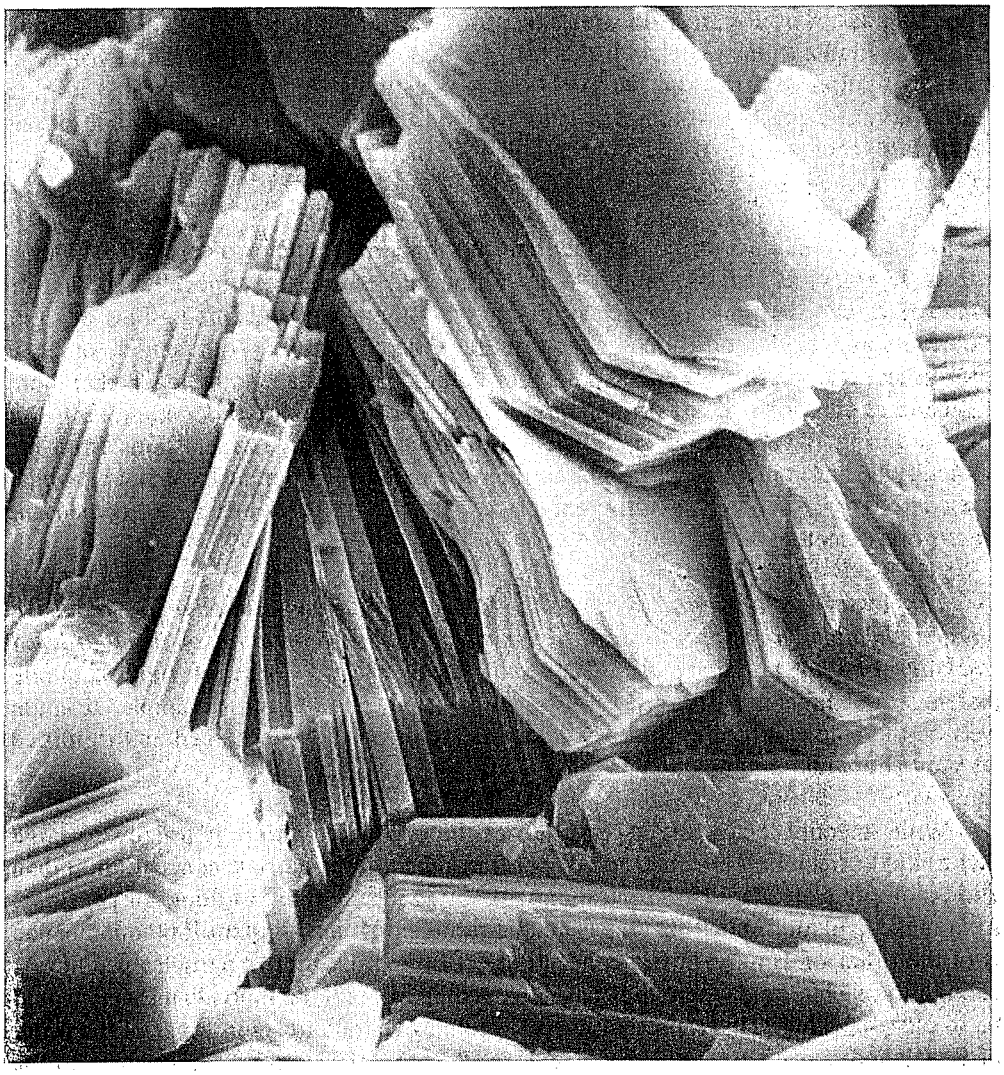


Fig. 3. Kaolinite platelets in a sandstone pore.

increasing as $\_R^2r$. Figure 1 illustrates this for hexagonal platelets. As long as the total volume available to the platelets is much larger than the sum of their gyration volumes, their orientation is at random. However, as soon as the system is concentrated up to a point where the gyration volumes start to overlap each other, the platelets tend to orient parallel to each other. If the concentration is increased further, ordered stackings appear.

Liquid crystals are of course familiar and modern examples of excluded volume effects at work, at length scales where the thermal motion of molecules allows for almost perfect ordering to be reached (gently vibrating a bag containing grains or rigid plates always leads to a denser and more ordered state). With larger objects, inter-object friction or wall effects may prevent this perfect stage to be reached. Figure 2 illustrates this for tree logs floating on a river. No long range order is present, but local ordering is very clear. The difficulty to reach long range order stems from the difficulty to harmonize the position and the orientation of different local stacks which started to grow randomly at different places. It may be described as a *geometrical frustration* effect.

The lesson to be learned from this is that no strong attractive or repulsive physico-chemical forces are necessarily involved in the generation of local ordered stackings of clay microcrystals. The strong local stacking order of rigid kaolinite platelets in sedimentary rocks, as illustrated in fig. 3, is a beautiful example. It might well be the sole result of excluded volume effects (eventually reinforced and rigidified later by short range interactions).

With smectitic clays, the aspect ratio of the crystalline sheets is usually so large that mutual orientation effects start to appear at much lower particle concentration than with kaolinite platelets, in concentration regimes which are those of dilute suspensions. A simple calculation shows that the excluded volume of 1nmx1000nmx1000nm lemellae is of the order of $1\mu m^3$. Thus, a concentration of the order of 10^{15} particles per liter is enough to reach a state where the "envelope" volumes of all the individual sheets would be in close packing. This represents a real volume fraction of clay in water of the order of 0.001 and a mass fraction of the order of 0.25%. This is remarkably close to the point where the rheological properties of a well dispersed Na-smectite start to show marked departure from simple Newtonian behaviour. From such simple excluded volume considerations, one can also predict that going beyond this concentration would unavoidably lead to mutual orientation of the sheets and, finaly, to a orientationaly ordered sediment fabric.

To close this section, let us keep in mind that excluded volume effects are universal interactions which provide a valuable clue for understanding the texture of clay sediments and the properties of the clay-water system. However, in order to apply this approach validly, one needs to know accurately the nature of the objects which are interacting. In this respect, flexibility of the crystaline sheets, long range repulsive forces of electrostatic origin and, most important, aggregate (tactoid) formation by short

range attractive forces, may deeply modify the nature of the "individual units" which have to be considered for their excluded volume.

Molecules in the interlayer space

As another example of steric interactions, let us consider the packing of spheres in a narrow gap. "Narrow" means a gap which is of the order of a few sphere diameters, i.e. a gap where the walls are never very far from the molecules (something like the microporous and the beginning of the mesoporous regime). This may represent, for instance, the packing of water molecules in the interlayer space of smectites or the packing of nitrogen molecules in the galeries of so-called *pillared smectites*, i.e. smectites where the sheets have been permanently propped apart by bulky ions or molecules. Al_{13} polyoxy cations are frequently used for that purpose.

The question to be addresed is the influence of the walls on the packing of the molecules. More specifically, one might wish to know the evolution of the density of the confined fluid (interlayer water; adsorbed nitrogen) as the distance between the wall, D, is increased. Obviously, one knows that the density of the confined fluid has to tend towards that of the bulk fluid as D becomes very large, but what about regimes where D is only a few molecular diameters? Direct experimental results are difficult to obtain, but a simple macroscopic simulation study shows clearly the trends and illuminates some real studies.

The experience is performed as follows. Take two pieces of glass of 0.5mx0.5m. Separate them by three pieces of wood of thickness D. This produces a slit-shaped pore (fig.4) in which glass beads of diameter $2a$ can be poured. The same experiment may be performed with a few fixed cylinders in the cell simulating pillars in the case of pillared smectites (fig.5). After gentle vibration, the saturated set-up is weighted and, knowing the weight of one glass bead, the total weight converted into the total volume occupied by the glass beads.

Figure 6 shows the evolution of the volume *fraction* occupied by the beads, $1-U$, as a function of the dimensionless distance between the walls, $D/2a$. The curve, which is the result of a number of measurements performed with several sphere diameters, shows two remarkable features. The first is that the density of the confined "fluid" is always lower than that of the bulk "fluid". Clearly, the presence of walls prevents the packing from reaching its optimum density which, for an infinite random close packing of spheres, is close to 0.65 (the porosity is of the order of 35%). Not surprisingly, this is precisely the asymptotical value measured at large $D/2a$, when the gap is of the order of 10 "molecular" diameters or more. In other words, the steric hindrance due to the presence of walls vanishes at distances of the order of 10 molecular diameters.

The second remarkable feature of fig.6 is that the evolution of $1-U$ is not smooth. It shows several well defined minima and maxima, with a periodicity of the order of 0.95 $D/2a$. The amplitude of the min-max difference decreases as the confinement

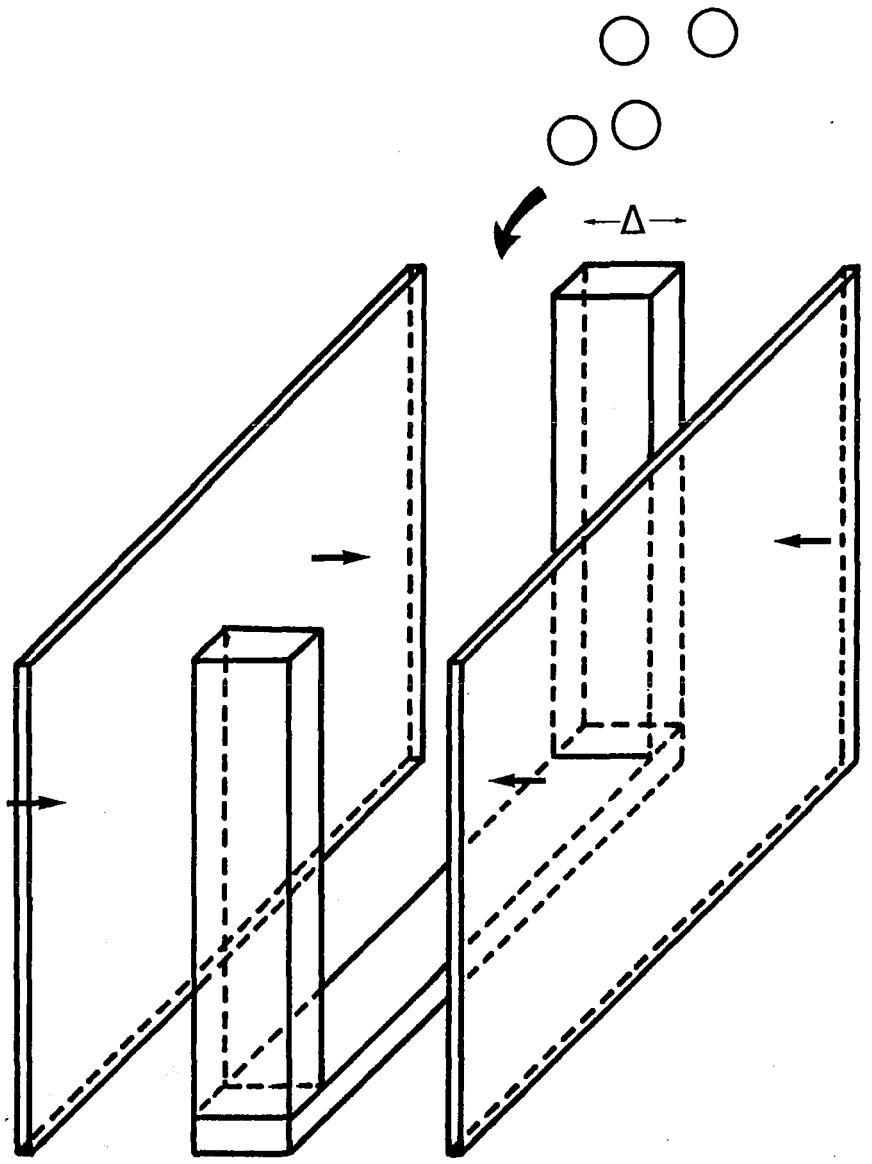


Fig. 4. Schematic view of the construction of an experimental cell for studying the packing of glass beads in a narrow gap.

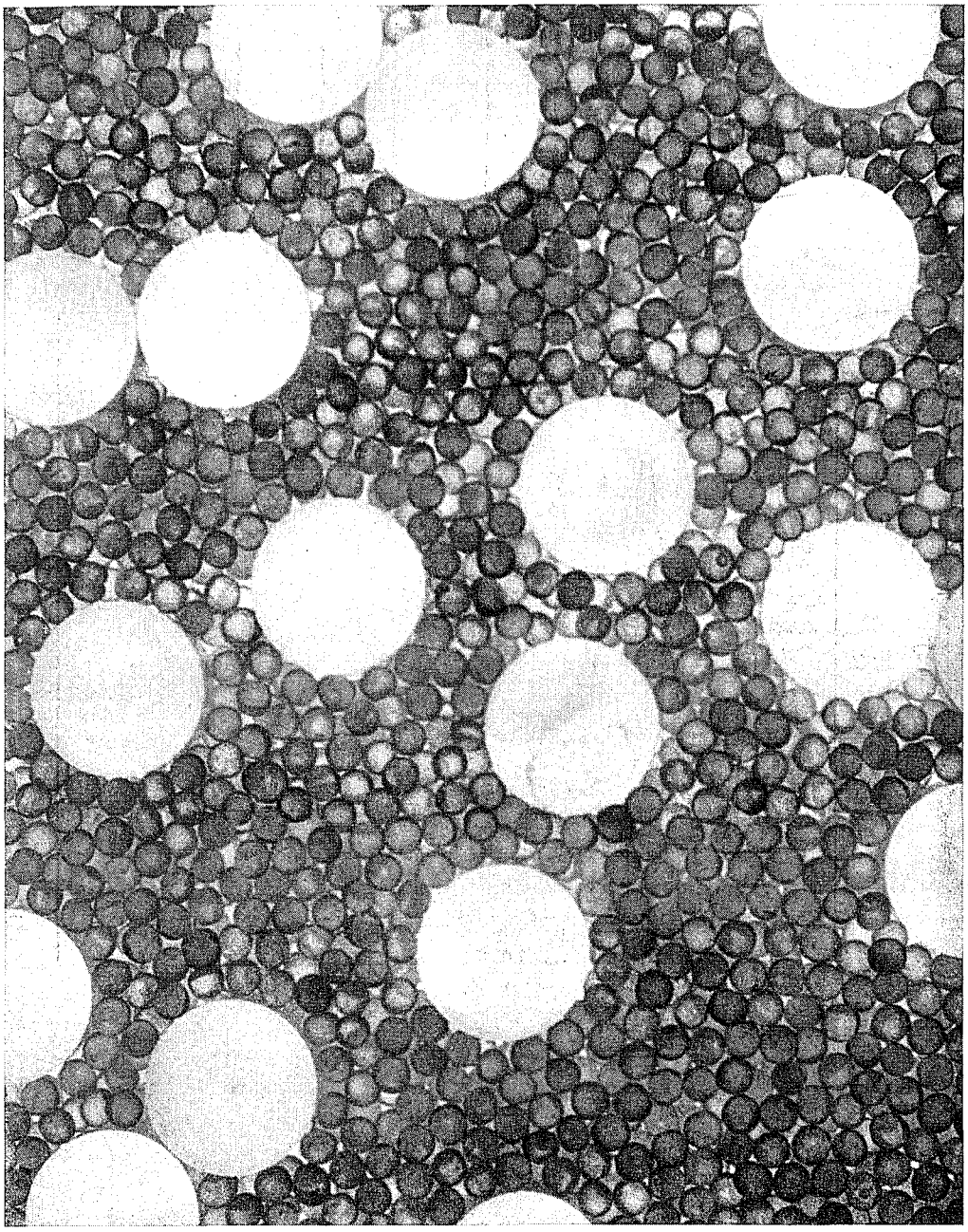


Fig. 5. Top view of glass spheres filling a cell like in fig.4, with cylindrical obstacles simulating pillars in a pillared smectite.

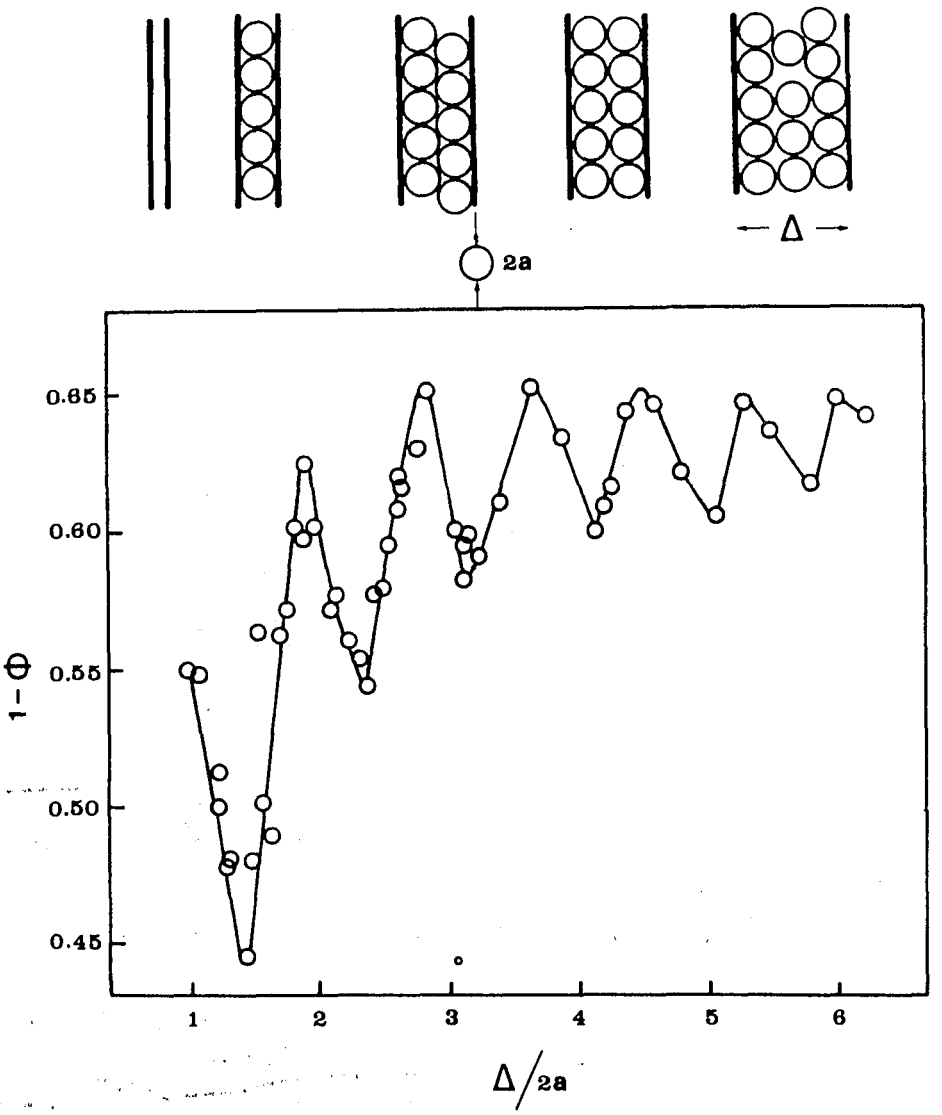


Fig. 6. The structure of a packing of spheres between two walls is strongly dependent on the distance D between the walls. The density (U is the porosity) oscillates with a period which is sligthly smaller than the sphere diameter 2a. The influence of the walls vanishes for about ten diameters.

effect diminishes. This is nothing else than the development of the three-dimensional disorder in the system, starting from a single monolayer with (at least local) two-dimensional order. In small gaps, the build-up of a new monolayer requires a minimum free volume. As long as this threshold is not reached, the average density decreases. The dimensionless distance of 0.95 is clearly reminiscent of the distance between "111" planes in a closed packed assembly.

As far as practical consequences are concerned, what fig.6 tells us is that surface area or microporous volume measurements in layered materials like many clays should take into account a correction factor which, in the worst situation (the density minimum between one and two monolayers), may be as large as 0.45/0.65=0.7.

III. SCALING PROPERTIES

I would like to leave now the local or semi-local scale for exploring larger length scales. Like other colloidal solids (hardened cement, silica gel), a macroscopic piece of solid clay rock or sediment is in fact a coherent but porous packing of submicronic particles held together by short range surface forces. The same is true within the individual grains obtained by crushing (not too extensively) a piece of rock or sediment. The problem is to describe the structural and textural hierarchy which leads to a macroscopic body or to a powder grain starting from elementary nanometric lamellae, platelets or fibers. This may be approached by two types of techniques: direct structural or textural techniques such as X-ray diffraction or scattering and electron microscopy, or indirect probing techniques such as surface area or porosity measurements. In the later case, the accessibility of the fabric to the molecular probes is an important aspect of the problem.

Fractals and characteristic length scales

Before analysing the fabric of clays, it may be useful to have a general look on the main types of disorder one may expect in porous materials. Perhaps the simplest type of disorder in a porous material is the one which is illustrated by fig.7. What is shown is a consolidated sand of submillimetric quartz particles. Although there is no long range order in the system, it is quite clear that, in order to have a statistically satisfying description of the texture, one does not need to describe the size and the position of *all* the quartz particles and *all* the pores of the system. Knowing the average particle size and the average local texture in a "elementary" volume or cell containing, say, a few particles and a few interparticle pores is enough to understand the texture and the properties of the whole system. In other words, the system is characterized by a well-defined characteristic length scale, L_c, such that the whole system can be statistically reproduced by simple *translation* of cells of size L_c. In the example, L_c is of the order of one average particle diameter + one average pore diameter. The symmetry operation which allows one to go from small length scales to large length scales is *translation*.

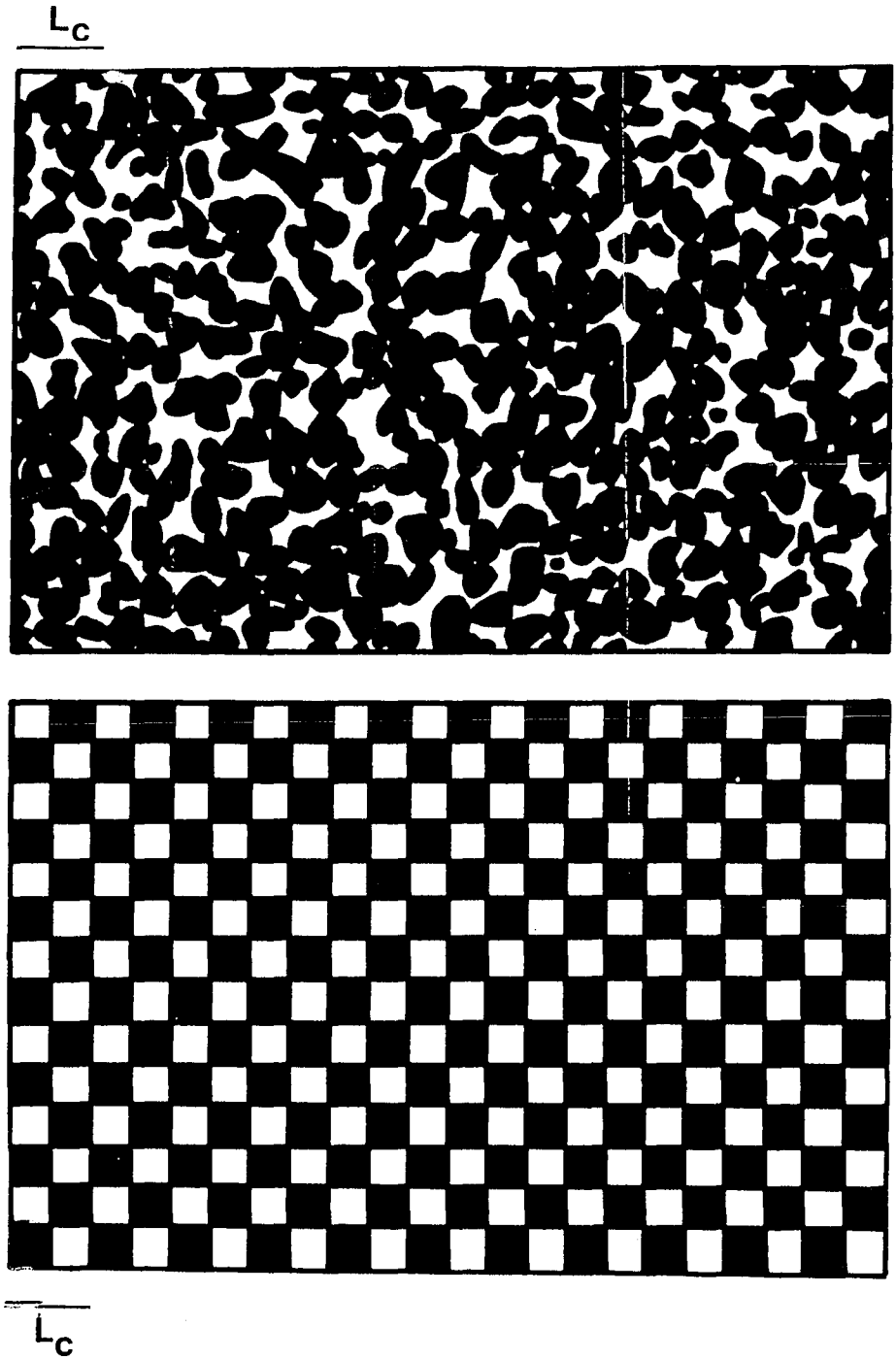


Fig. 7. Polished section of a consolidated sand and a simple model with a regular (translationaly invariant) porous lattice having the same characteristic length as the original material.

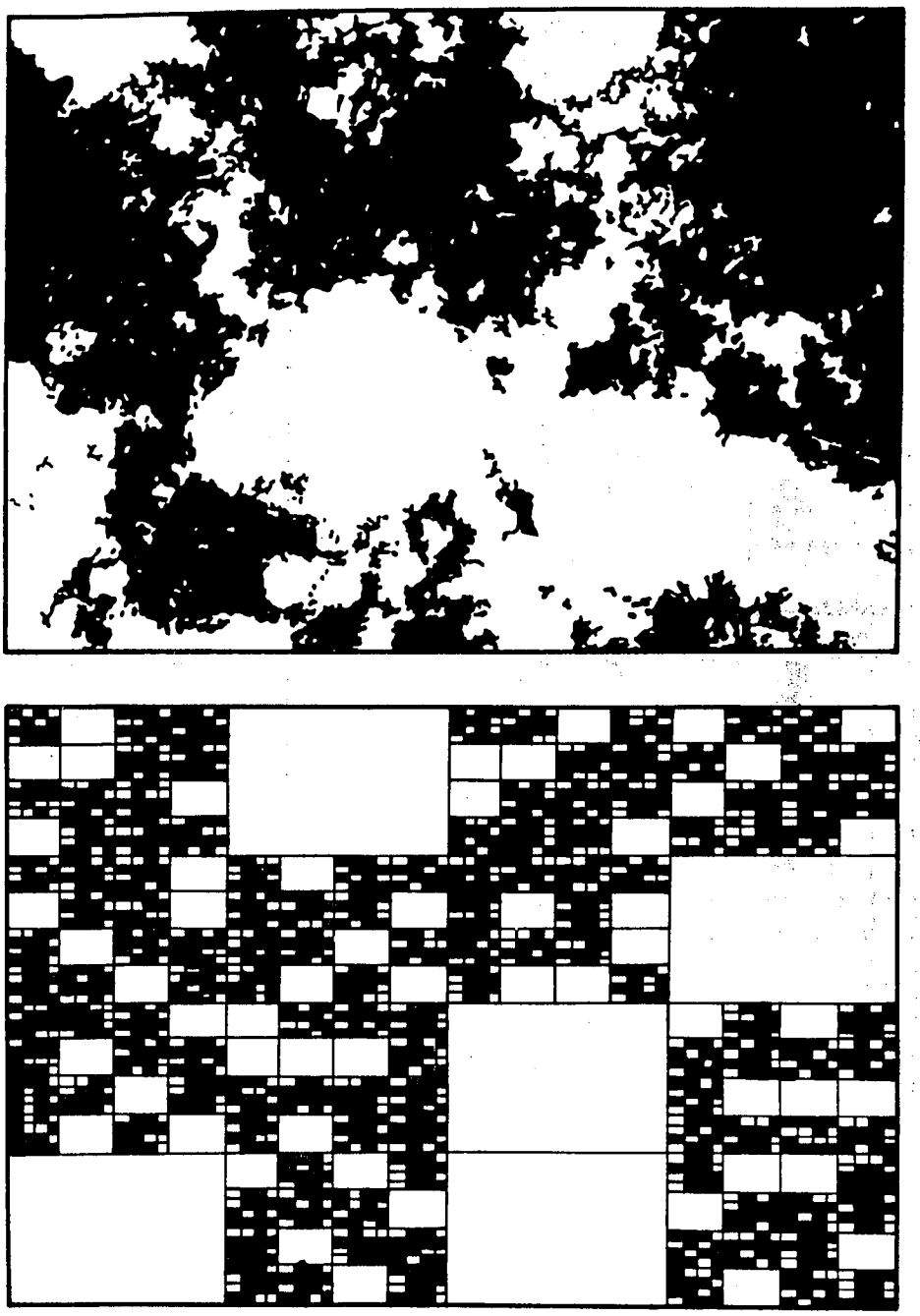


Fig. 8. Transmission electron micrograph of amorphous calcium silicate hydrate and modelisation by a porous network with dilational symmetry. The real material and the model are characterized by the same total porosity and the same scaling exponents.

Fig.8 shows a totally different porous material. It is a calcium silicate hydrate (the elementary units are not visible at the observation scale). The main difference with respect to fig.7 is that no characteristic length scale is clearly apparent. There is no elementary volume which, by translational symmetry, is able to generate the whole system. To characterize this texture by an average pore size and/or an average particle size would be a very poor description. The system contains domains of matter and pores of all sizes between the resolution of the image and the size of the image itself. Thus, a satisfying textural description would require to take into account the texture of the system at *all* length scales.

Fortunately, there is a hidden "logic" or symmetry in this texture which saves a lot of work. Just like in fig.7, one can still statistically generate the texture of the system at large scale starting from small scales, but the nature of the symmetry operation to be applied is different. Translational symmetry is here replaced by *dilational symmetry*. The distribution of matter and voids is statistically the same at different observation scales. This property is called *self-similarity*. Mathematical or real objects which display this property (or related properties) have been called "fractals" by Benoit Mandelbrot and defined as systems where "parts are the image of the whole".

Quantitatively, fractals are characterized by at least one number: the *fractal dimension*, D, which is usually a non integer number. The meaning of D follows directly from a measure process or, more precisely, from the relationship between the linear size of the object to be measured and the linear size of the yardsticks which are used to measure it. As illustrated in fig. 9, in order to measure the length of an object of topological dimension 1, such as a straight line of length R, with yardsticks of length r, one needs to use $N \sim (R/r)^1$ yardsticks. Similarly, measuring the area of an object of topological dimension 2, such as a square surface of side R, with square yardsticks of side r, requires $N \sim (R/r)^2$ yardsticks. This is easily generalized to $N \sim (R/r)^d$, where d is the euclidean dimension of the ensemble (or object) on which a d-dimensional measure (length, area, volume) is performed.

This apparently obvious logic is not followed by fractals. Fig.10 shows an example of a porous fractal surface and an example of a broken fractal curve. Measuring the area of this porous surface or measuring the length of this broken curve leads to a relationship which is still of the same general form as previously, but the exponent which relates N and R/r is no longer the euclidean dimension d. This exponent is Ln3/Ln2 in the first case and Ln4/Ln3 in the second case. In general, one has

$$N \sim (R/r)^D$$

with D different from d. Thus everything happens as if the "effective" dimensionality of the porous surface was lower than its topological dimension and that of the broken line larger than its topological dimension. This is a direct consequence of the dilational symmetry of these objects.

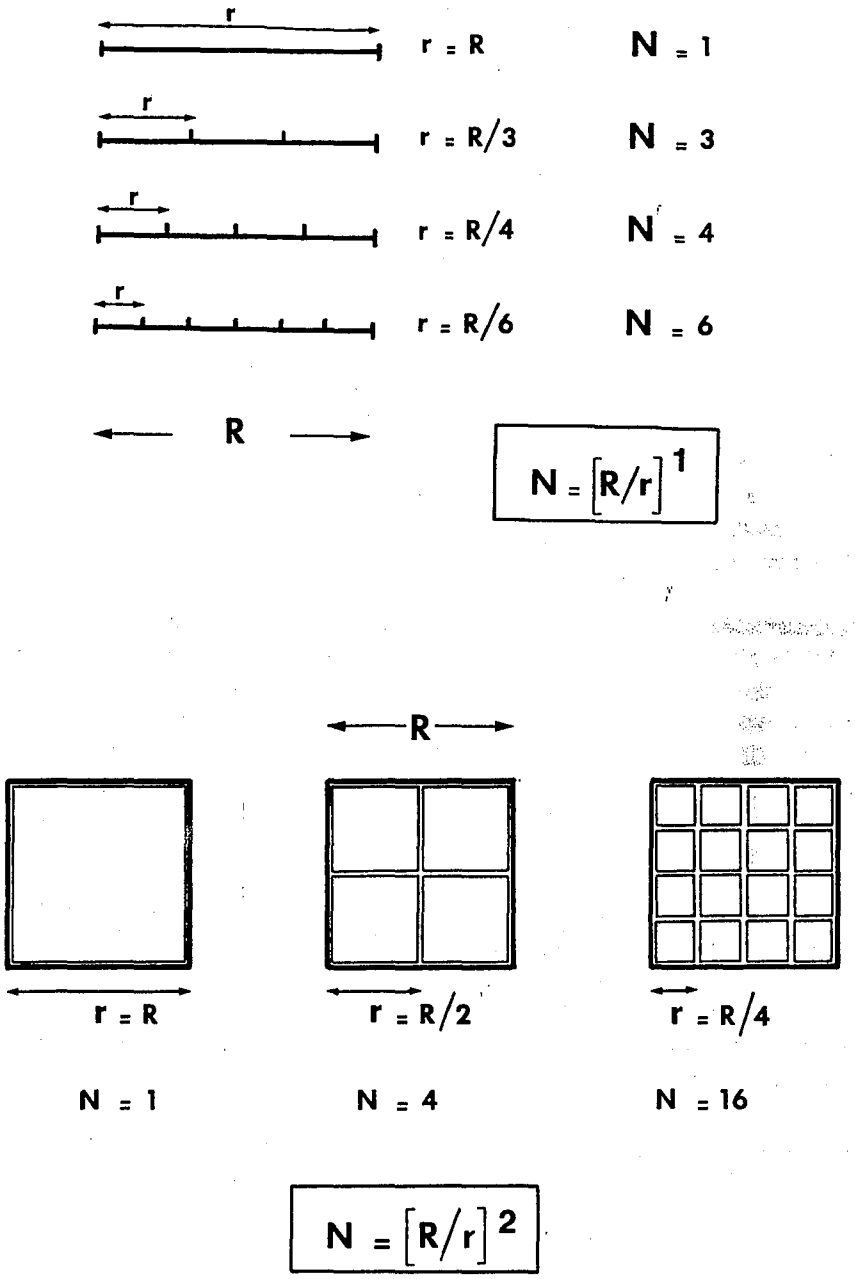
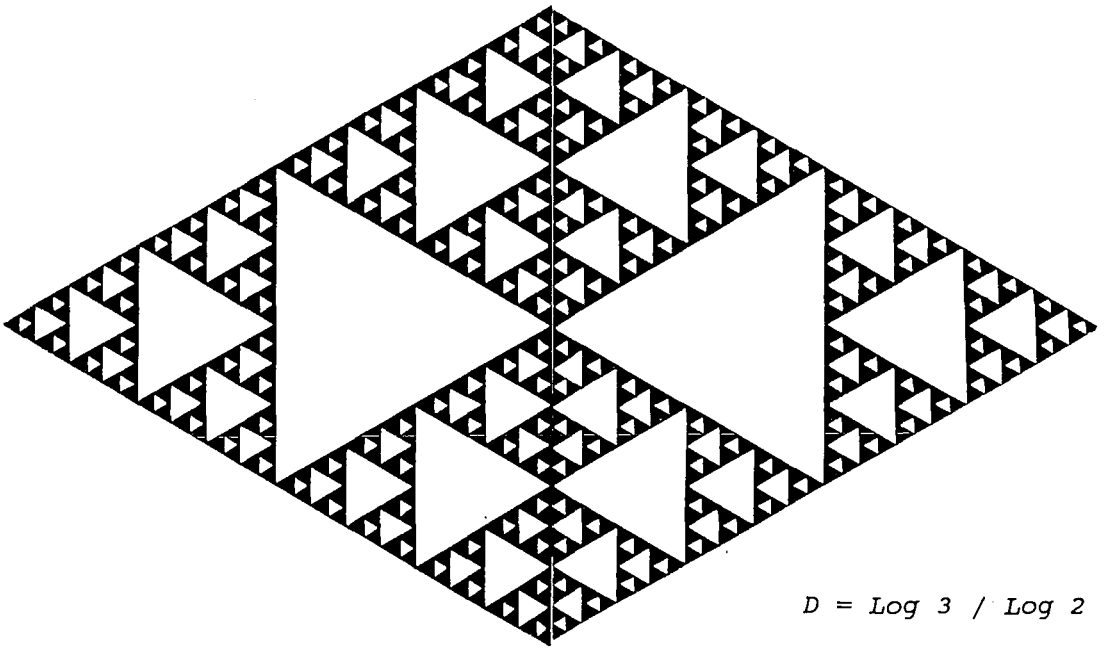
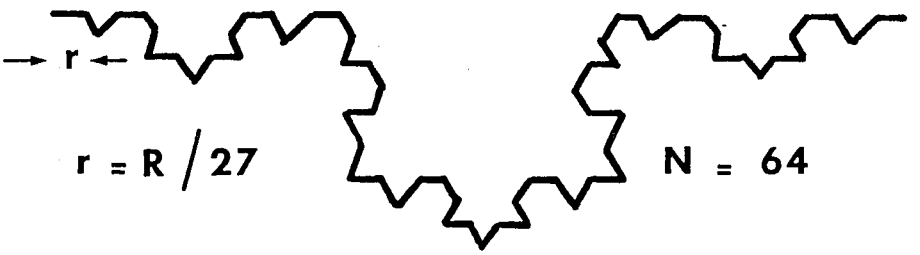


Fig. 9. Relationship between the number N of parts of size r in an object of size R and the dimensionality of space. In the present case, the exponent which relates N and R/r is the Euclidean dimension, which is itself equal to the topological dimension.





$$N = [R/r]^{D}$$

$$D = \text{Log } N / \text{Log}[R/r] = \text{Log}4/\text{Log}3 = 1.26$$

Fig. 10. For a fractal (here a porous surface and a broken curve), the number N of parts is often related to their relative size (r/R) by a non integer exponent, D, the fractal dimension.

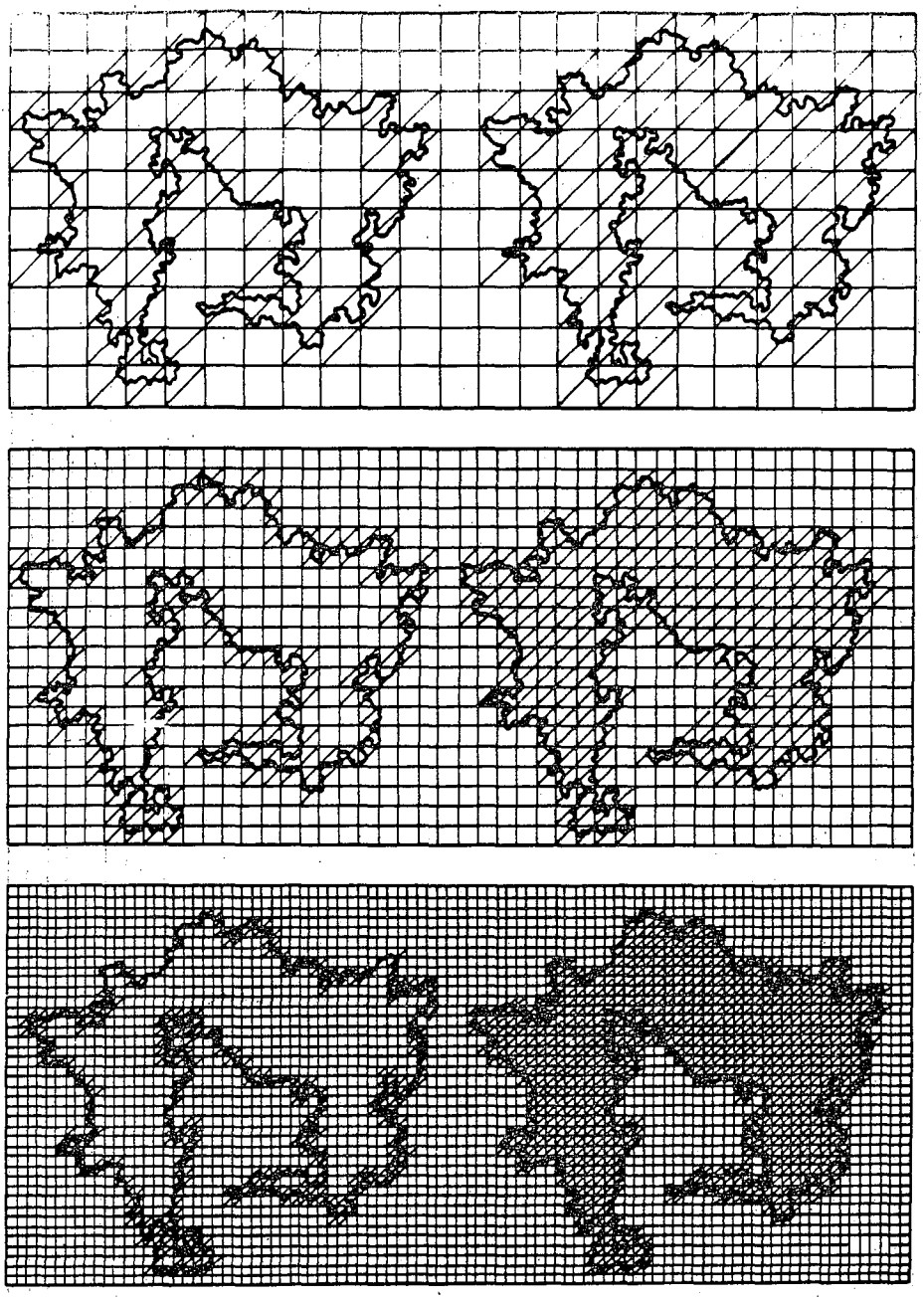


Fig. 11. The measure of the box fractal dimension of an object by covering it with boxes of decreasing size, r . One expects N_r^{-D}. In the left row the method is applied to the boundary of the object. In the right row to its "mass".

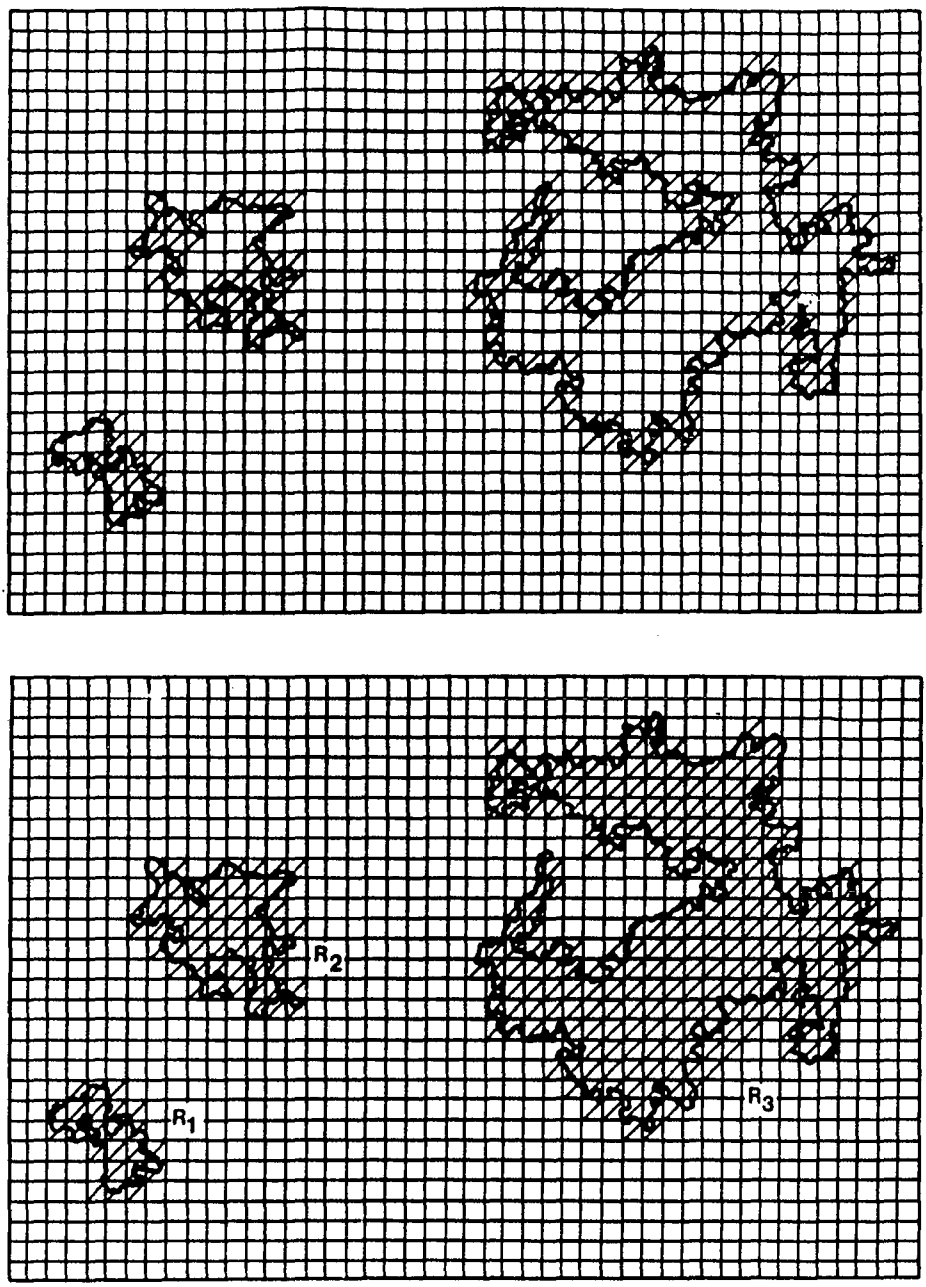


Fig. 12. The measure of the box fractal dimension D of a series of objects of sizes R_1, R_2,...R_i belonging to the same family by covering them with boxes of constant size r. One expects N _ R^D. The method can be applied to the boundary (above) or to the bulk part (below)

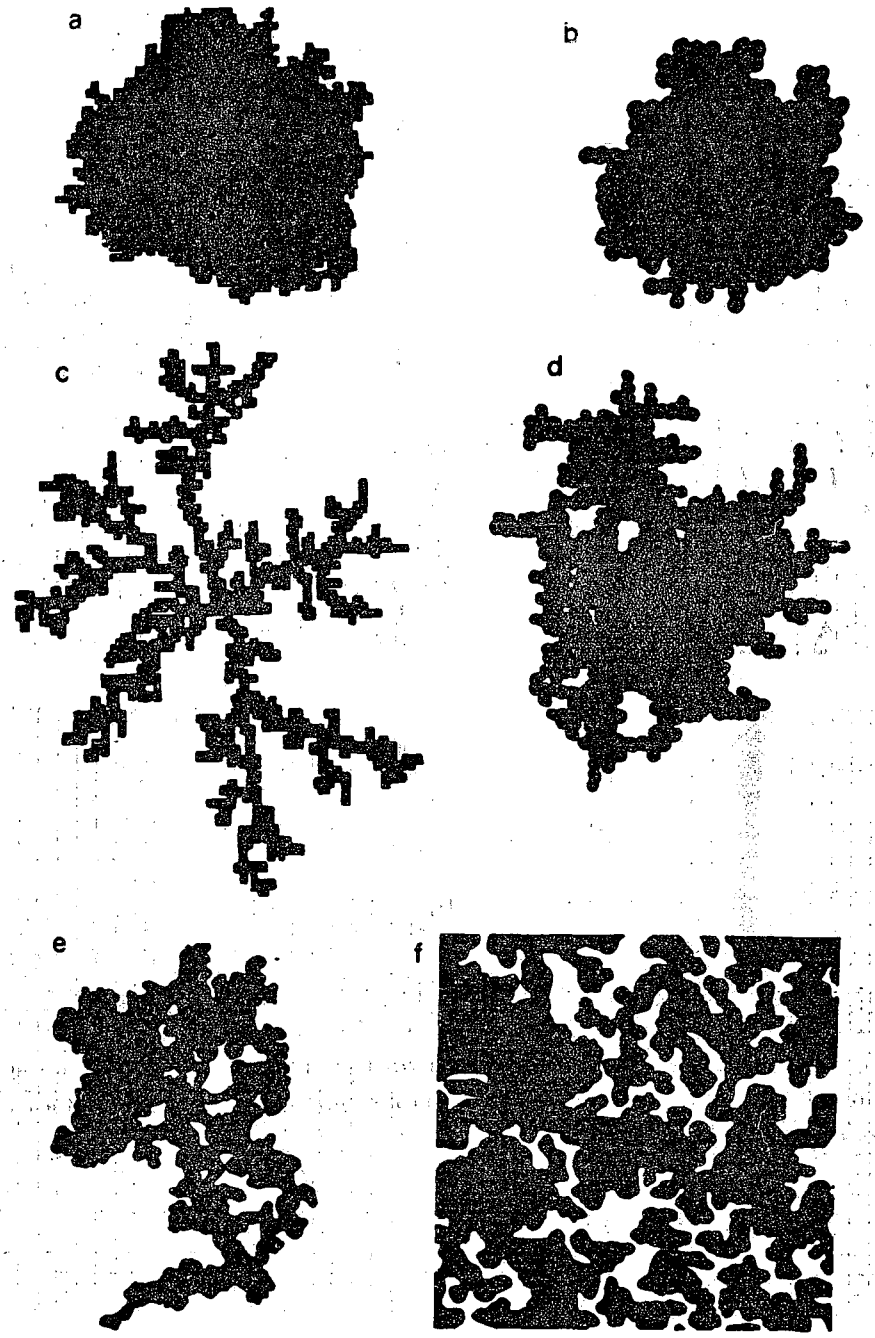


Fig. 13. Examples of two surface fractals (a and b), one mass fractal with $D_m = D_s$ (c and d, but d is the projection on a plane of an aggregate in three dimensional space and this projection is compact), a mass fractal with D_m different from D_s (e) and, finally, a pore volume fractal (f).

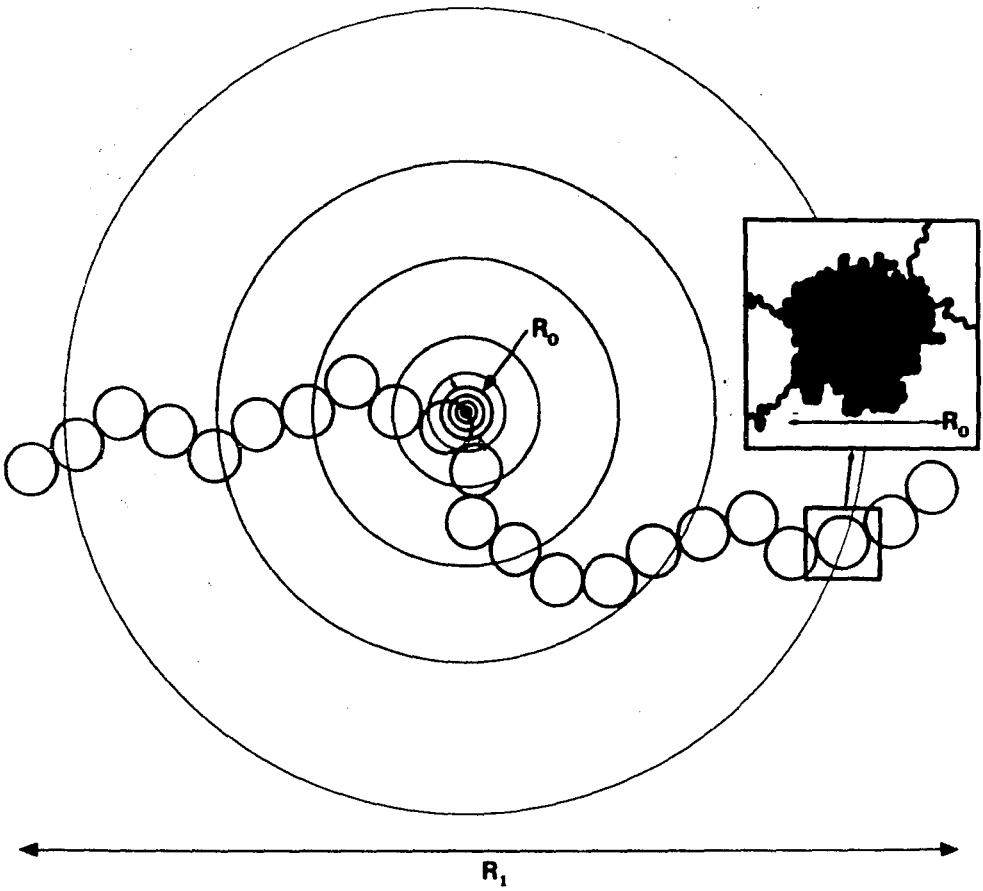


Fig. 14. A single material may be characterized by different scaling exponents at different length scales. Here an aggregate which is surface fractal below R_0 and mass fractal between R_0 and R_1.

The surface or the shape of real material are of course not as simple as the examples of fig.10, but the principle of the measuring process which leads to D can nevertheless be applied by counting the number of d-dimensional boxes of size r necessary to cover the object or the part of object to be analyzed. This leads to the so-called fractal "box" dimension. The application of this method is straightforward in image analysis. One covers the image with a regular square or hexagonal grid (2-dimensional boxes or cells of size r) and one counts the number of cells intercepting the object to be analyzed. The size of the cells is then changed and the counting procedure repeated. D is obtained from the scaling relationship:

$$N \sim r^{-D}$$

Alternatively, if one has a collection of objects belonging to the same family, one can apply the box counting procedure with the same cell size to the different objects and derive D from the relationship between N and the size R of the objects:

$$N \sim R^{D}$$

Both procedures are illustrated in fig.11 and in fig.12.

Before leaving this short general introduction to fractals, let us mention two important points:

- The first is that self-similarity or dilational symmetry does not necessarily apply to *all* parts (or, in mathematical terms, subsets) of an object. It may only apply to its interfaces or to its volumic parts: its matter or its pore space. Thus, one can define *surface fractals* and *volume fractals* (which may themselves be *mass fractals* or *pore volume fractals*), as illustrated in fig.13.
- The second is that, in real materials, dilational symmetry is usually observed between two limits: a microscale one one hand and a macroscale on the other hand. Going beyond the macroscale may lead either to another fractal regime with different exponents or, more often, to a euclidean (statistically translationaly invariant) regime, as illustrated in fig.14. In the later case, the macroscale is nothing else than the characteristic length, L_c, which was introduced in the beginning of this section.

Surface area and packing texture: classical models

Measuring the box dimension of an object by image analysis with boxes of size r is just one among the many methods which use the same principle. For instance, the "box" may also be a molecule and the counting method may be physical adsorption and monolayer coverage determination. One may change either the molecular diameter (variable r) while keeping constant the size of the particles on which adsorption is performed (constant R), or change the particle size (variable R) while keeping the molecular diameter constant (constant r). The first method is very limited and dangerous because it is not easy to change the molecular diameter over a wide range

without also changing the physical and chemical properties of the molecules. The second method is easy and safe to apply, provided one can prepare monodisperse granulometric fractions of the same material over a wide range of grain sizes. It merely involves physical adsorption of nitrogen or krypton for instance, followed by monolayer coverage (N_m) determination by the classical BET method. This method has been initiated by D. Avnir and coworkers and developed by ourselves.

Before discussing the experimental evidence for scaling properties, let us examine the classical (non fractal) models which are usually used to interpret surface area data on materials which are in fact coherent packing of smaller units. Two limiting trivial cases might be considered, as sketched in fig.15. The first model may be considered as an idealy porous packing. The second as an idealy compact packing. In the first case, each grain of size R is a fragile and disordered assembly of quasi-independent subunits. Like in fig.7, there is a characteristic length, L_c, for the mass and void distribution, much smaller than the size of the grain on which the measurements are performed. Most of the surface area developed by the subunits is accessible from outside. Thus, whatever the size, R, of the grain, properties such as its surface area per unit mass, $S_m(R)$, or its pore volume per unit apparent volume, U, are expected to remain constant as long as R is large compared to L_c. The surface area per unit mass, S_m of a grain of rock or sediment like this, containing N subunits, is very close to the surface area per unit mass of each subunit, s_m:

$$S_m = N.\text{area(subunit)}/N.\text{mass(subunit)} = s_m$$

Thus, S_m is independent of N and of R. In other words, even though N is scaling as R^3, S_m is scaling as R^0.

The other trivial model (fig.15) is an ordered, compact and mechanically strong assembly of subunits packed so closely that no "internal" surface area is accessible. Only the envelope of the packing contributes to the adsorption of molecules. S_m is scaling as $N^2/N^3=N^{-1}$ or R^{-1}, as for any non porous granular material.

Most often, surface area data obtained on clay material are interpreted in terms of the first, ideally porous, model. Each subunit may a fiber (sepiolite, palygorskite), a rigid platelet (kaolinite) or, in the case of smectites, a stack ("quasi-crystal" or "tactoïd") of elementary 1nm thick sheets). In the later case, the one-dimensional orientational and translational order is assumed to be strong within the stacks, along the axis of the stack, whereas there is symmetry breaking when passing from a stack to a collection of stacks.

Assuming further that the thickness, e, of the stacks is much smaller than their width and, consequently, that the area of the lateral surfaces is negligible compared to the area of the basal surfaces, it is easy to relate S_m to e and to calculate the average number of crystaline sheets in each "quasi-cristalline" stack.

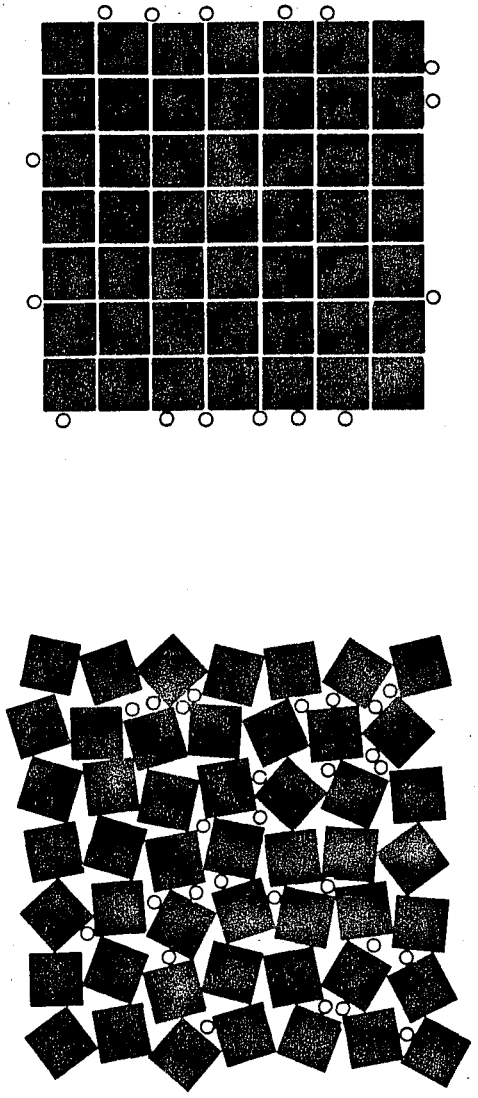


Fig. 15. Two simple limiting models for interpreting surface area data on materials which are coherent packings of smaller and rigid subunits. In the first case, the packing is compact and molecules have access only to the external surface. In the second case, the packing is disordered and the total -internal and external- surface area is accessible (except very tiny contact areas).

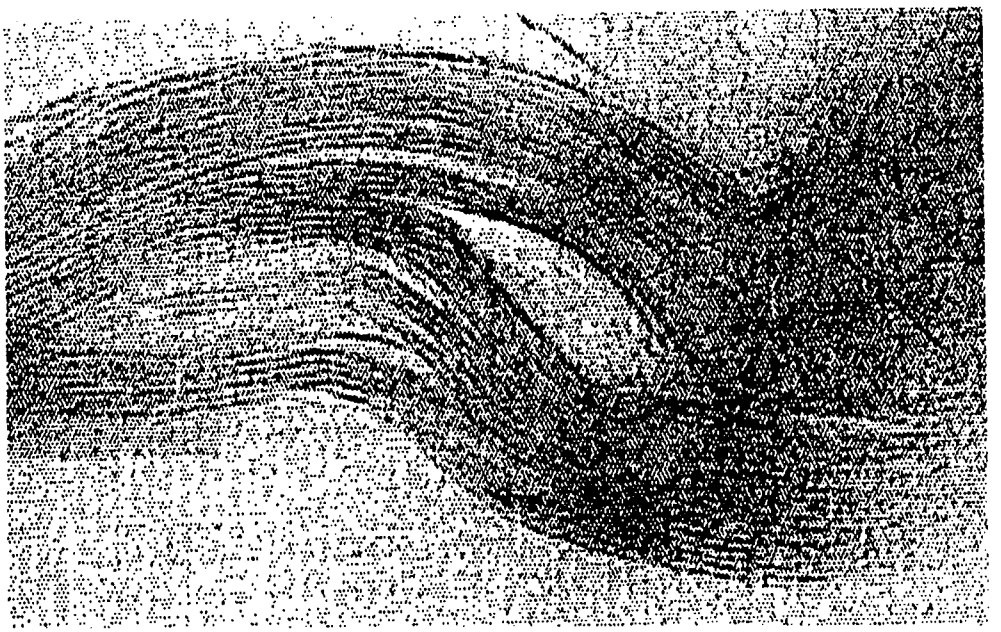


Fig. 16. Illustration of the general face-to-face connectivity and the lenticular porosity in Ca-smectite/water slurries (courtesy D. Tessier).

Surface area and scaling properties

What might be wrong with using the idealy porous packing model for interpreting surface area measurements on clays? Very little in the case of more or less rigid fibrous clays and in the case of thick and rigid kaolinite platelets, except perhaps the assumption that the lateral surface area is negligible compared to the basal surface area. Very much in the case of smectites. It is quite obvious, from a look to electron micrographs of smectite slurries that the assumption of quasi-independence of the structural subunits is a very poor assumption. Even the simple identification of subunits is not obvious. Multiple face-to-face connectivity of the sheets is the rule. even in rather dilute smectite/water systems (fig.16) *and a fortiori*, in dense sediments.

Rather than assuming *a priori* a given type of model, one can look whether simple power law relationships between the size of macroscopic grains, R, and their mass, $M(R)$, their surface area, $S(R)$, and their pore volume, $U(R)$, are valid. In practice, the measurements are made on a powder bed containing N_g grains belonging to the same granulometric fraction. If the grains have a spheroidal shape, N_g, is related to the apparent volume of the powder bed, V_a, and to the size of the grains by $N_g(R) \sim V_a / R^3$. Thus, if $M(R)$, $S(R)$ and $u(R)$ are scaling as R^{Dm}, R^{Ds}, and R^{Dp}, respectively, for single grains, the following relations can be derived for the apparent volumic mass, $M_v(R)$, for the specific surface area, $S_w(R)$, and for the internal porosity, $U(R)$, of a collection of $N(R)$ grains:

$$M_v(R) = N(R)W(R) / V_a \sim R^{(Dm-3)}$$

$$S_w(R) = N(R)S(R) / N(R)W(R) \sim R^{(Ds-Dm)}$$

$$U(R) \sim N(R)U(R) / N(R)R^3 \sim R^{(Dp-3)}$$

In this framework, the idealy porous model is characterized by $D_s=D_m=D_p=3$ and the idealy compact model by $D_s=2$ and $D_m=3$.

One kaolinite, one sepiolite, one palygorskite and twenty monoionic montmorillonites were prepared by performing an ion-exchange (for 19 materials) or an adsorption (for humic acid) treatment on the same parent material (a Na-exchanged clay from N.L. Industries). The samples were prepared by allowing several liters of slurries containing about 10% dry matter to dry by slow evaporation at 353K. The resulting lumps of what might be called "mud rocks" were first fragmented with a hammer and with a ball mill afterwards. For each material, about twenty granulometric fractions were isolated by sieving, with mesh sizes ranging from 20 to 4500 μm, as sketched in fig.17. The shape of the grains was examined by scanning electron microscopy (SEM) and found to roughly spheroidal in all cases, as examplified in fig.18.

$M_v(R)$ was calculated by measuring the volume occupied by a given mass of powder in a simple measuring glass tube, after gentle vibration for a fixed time. The accessible

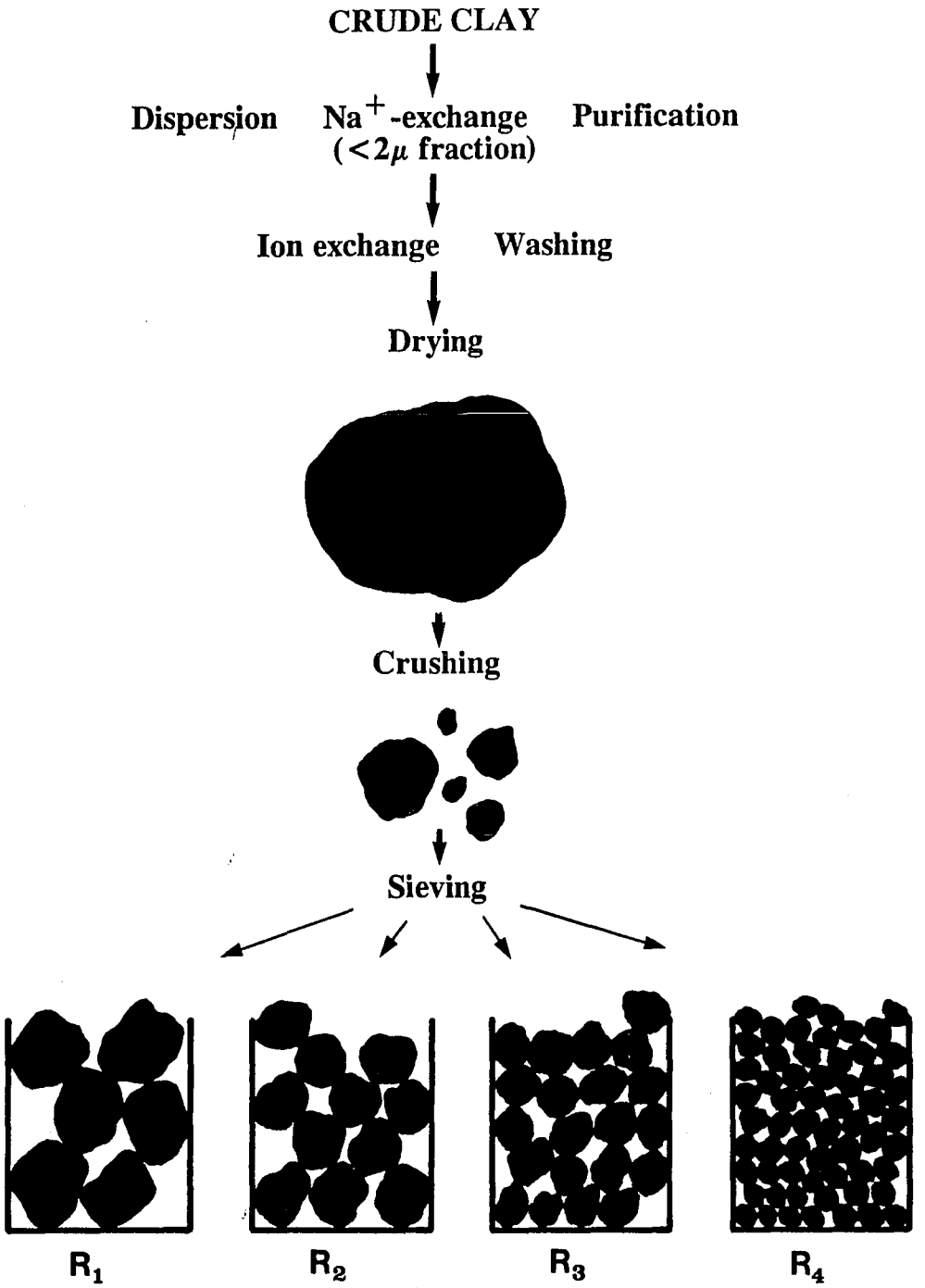


Fig. 17. Schematic description of the preparation of the montmorillonite samples for scaling exponent determination, from the crude clay to the monodisperse granulometric fractions of ion-exchanged samples.

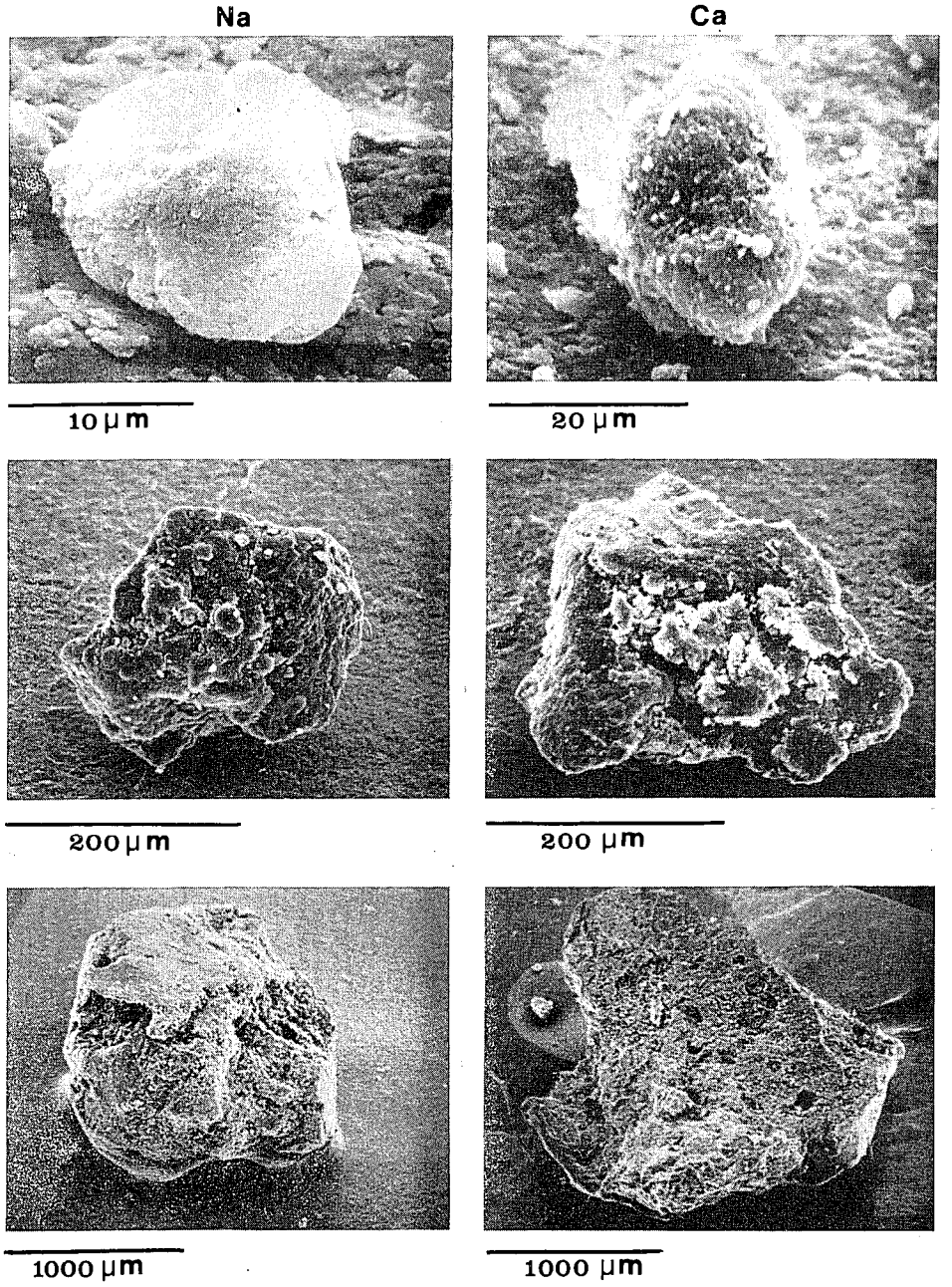


Fig.18. Scanning electron micrographs of Na- (left column) and Ca-(right column) montmorillonite particles in three granulometric fractions.

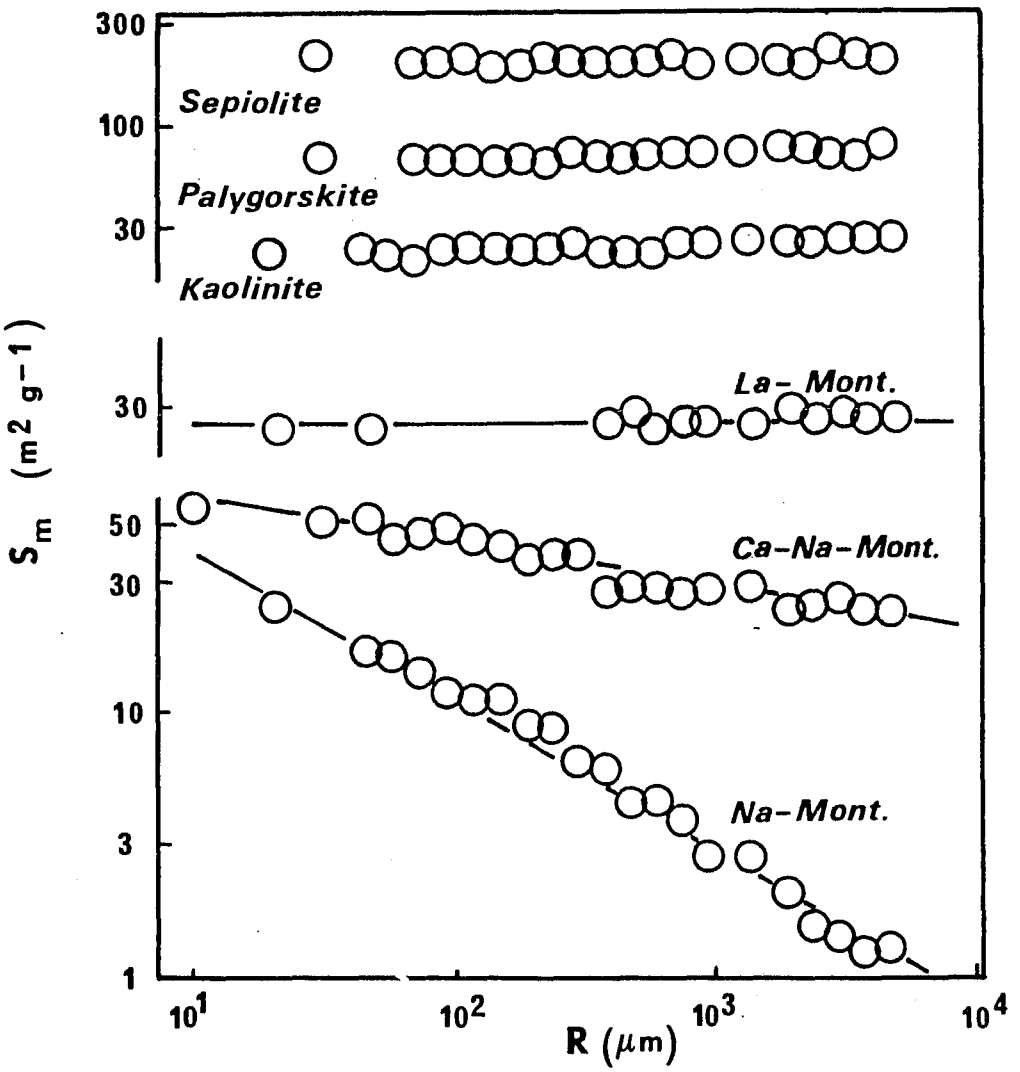


Fig. 19. Particle size dependence of the surface area of various clays measured by nitrogen adsorption. Note that all the montmorillonite samples were prepared from the same $<2\mu$ fraction of parent material.

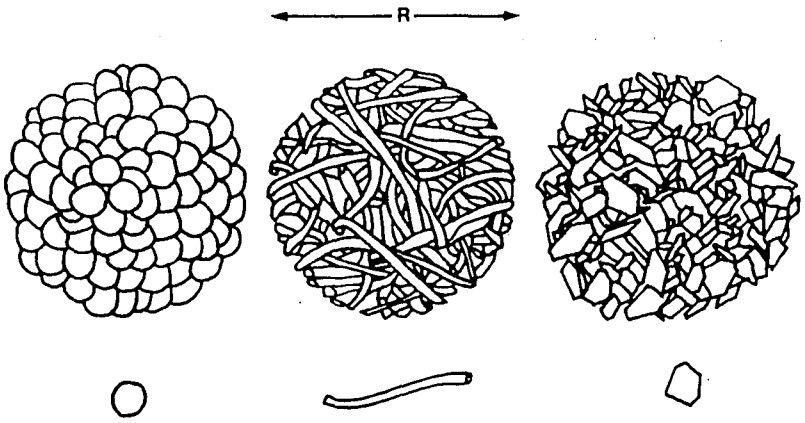


Fig. 20. Illustration of the structure of particles which are coherent packings of spheres, platelets or fibers. As in the sketch of the disordered porous packing of fig. 15, most of the surface area is internal and accessible from outside.

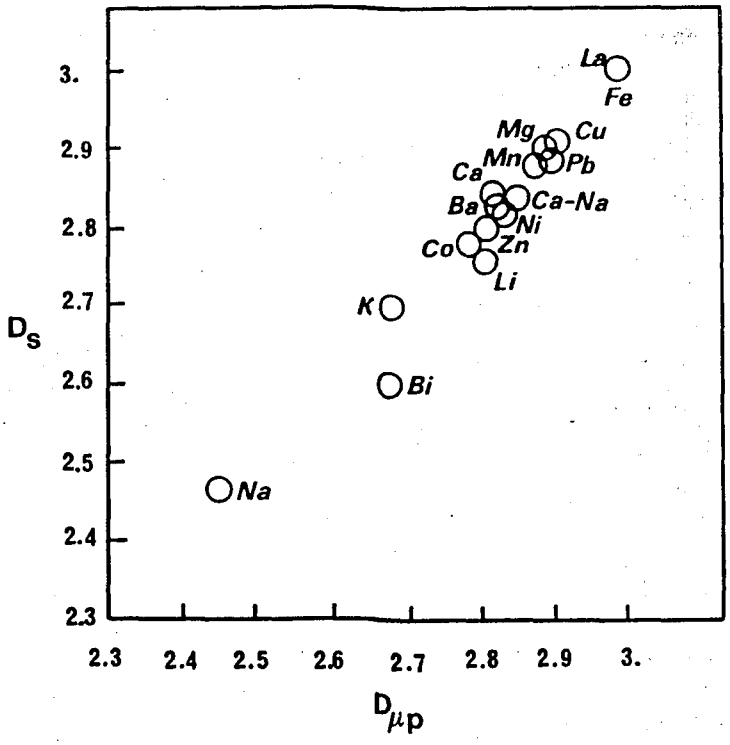


Fig. 21. Correlation between the surface fractal exponents of ion-exchanged montmorillonites particles and the fractal exponents describing the scaling of microporosity (pore size less than 10 nanometers) in the same samples.

surface area was measured by nitrogen adsorption at 77K, using the classical BET method. The open porosity of the grains was also determined by physical adsorption, by measuring the total volume of liquid nitrogen adsorbed at a relative vapor pressure of 0.99. This corresponds to pores smaller than 10 nm.

Within experimental error, the slope of Log $M_v(R)$ vs Log R plots was found to be zero in all cases, so that $D_m=3$ for all the clays that were studied. In other words, the mass distribution and the *total* (open + closed) pore volume distribution within the grains are homogeneous. Thus, solid clay samples are neither mass- nor *total* pore volume fractals. They behave, as far as *total* mass and porosity distribution is concerned, as ideal porous solids.

Much more interesting is the behavior of the *accessible* surface area and *open* porosity of the grains. For fibrous clays and kaolinite, S_m and U are independent of the grain size (fig.19). Thus, for these clays, the ideally porous model is applicable, as illustrated in fig.20. However, for most smectite samples, *neither* S_m nor U are independent of the grain size. Only a few of the twenty samples follow the idealy porous model. All the samples are characterized by linear Log S_m vs Log R plots, over almost three decades, but, in the overwhelming majority of cases, the slopes lead to non trivial D_s exponents for the accessible surface between 2.4 and 3. No samples are found to follow the idealy *compact* model (which would require $D_s=2$).

Equally remarkable is the fact that the same power laws are obtained for the open porosity smaller than ~10 nm, with scaling exponents which are in good agreement with the surface fractal exponents (fig.21). *Thus, most solid smectite clays are surface and pore volume fractals. However, the surface and the void volume which exhibit this fractal character are not the total surface and void space, but the open surface and the open porosity.*

Scaling, local order and morphomechanics

What are the structural and textural features which are at the origin of these non trivial scaling properties of most smectites? One knows, often from simulation studies, that many physical processes are able to produce fractal structures. Diffusion-limited aggregation is among the best known, but it does not correspond to what is observed with clays. Indeed, it leads either to mass fractals or to compact surface fractals, but not to surface and pore volume fractals. *Cracking by drying* is a better candidate. It has been shown by Skjeltorp and P. Meakin, in two-dimensional experiments and simulations with spherical particles, to lead to a fractal hierarchy of cracks, within certain limits, but the cracking patterns of smectite-rich soils have been known for long by soil scientists!

In any case, a close look to the SEM micrographs of the smectite grains shows that the structural features responsible for the scaling properties of smectites cannot be *large* voids. Clearly, they ought to be much smaller than the grain size.

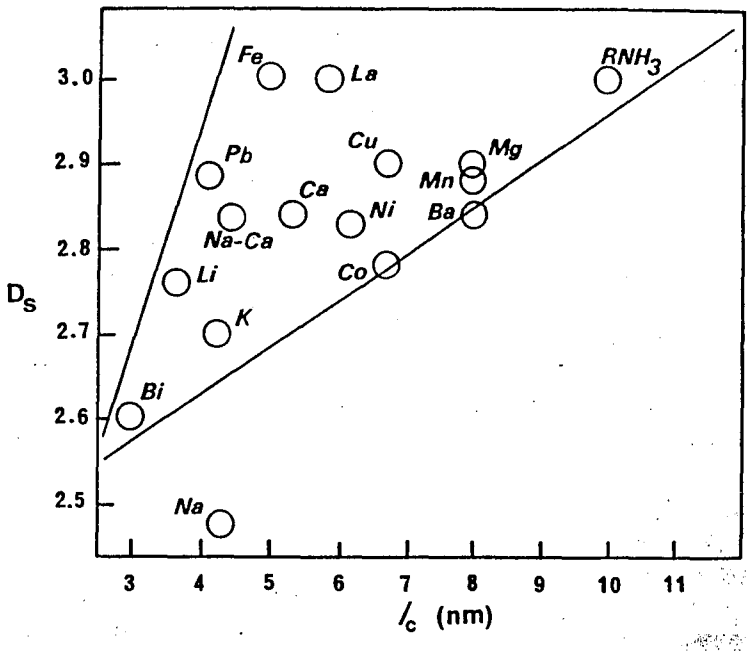


Fig. 22. Correlation between the surface fractal exponents of various ion-exchanged montmorillonites, determined by nitrogen adsorption, and their coherence length, determined from X-ray diffraction.

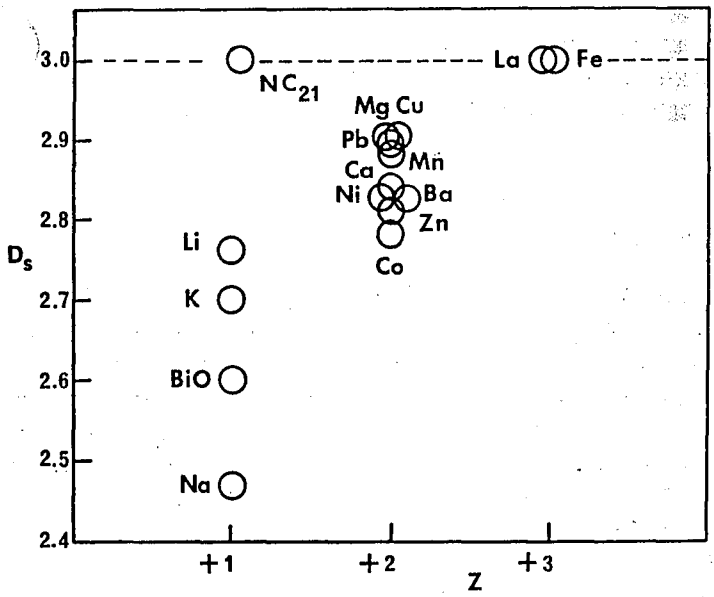


Fig. 23. Correlation between the surface fractal dimension of ion-exchanged montmorillonites and the cationic charge. "NC_{21}" is a long chain quaternary ammonium ion.

A plausible hypothesis is that they are *stress-induced micro- or nanocracks* or, more generaly, *defect zones or zones of weak connectivity separating more compact nano- or micro(stacked) domains*. This hypothesis finds indirect support in the correlation between the scaling exponents and the nanometric stacking order of the elementary lamellae in the solid. This is shown in fig.22, where the scaling exponents derived from the adsorption data have been plotted vs the coherence length, l_c, for X-ray diffraction, calculated from the line broadening of the 00l reflection lines. l_c is a direct estimate of the thickness of the ordered stacks in the solid. Although the data are scattered, the general trend is clear: D_s and D_p increase as l_c increases. Thus, as l_c increases, each grain looks increasingly like a simple disordered three-dimensional mechanically coherent (but fragile) packing of quasi-independent building blocks.

All this can now be rationalized in morphomechanical terms, since the thickness of stacks is expected to be related to their stiffness (this will be explicitely shown in section IV). The two reference microstructural situations which we have to consider are the following. The first, which is valid only with a few cations, is the first "trivial" model introduced above: an open card-house-type structure of *thick and rigid* "quasi-crystals", with (trivial) scaling exponents equal to 3. The other, which would be closer to reality in many more cases (in particular in natural smectites) is a much more compact packing but, unlike the second "trivial" model of fig.15, it would be obtained by *thin and flexible* units, with a non vanishing crack-like open porosity, along the interfacial defect zones between more ordered domains. In the former case, the orientational correlation between elementary layers is at its maximum within the "quasi-crystals", but drops suddenly beyond $l_c = L_c$. In the latter case, the orientational correlation is weaker but the characteristic length is larger, up, eventually, to the size of the macroscopic aggregate. $l_c << L_c$ and D_s and $D_p < 3$.

An open question is the relation between the properties of the exchangeable cations and their capacity to generate stacks of smectite lamellae. At first sight, one might think that highly charged and/or small cations, with a large polarizing power, would have a strong local ordering tendency and would be able to form thick stacks. As shown in fig.23, the trend is satisfying since highly charged (trivalent) ions do indeed yield large (trivial) scaling exponents (=3), divalent ions yield intermediate values (between 2.9 and 2.8), whereas monovalent ions yield generally even lower values. However, a closer look shows that the correlation between the polarizing power and l_c, D_s or D_p is not simple. The fine structure of the hydration shells in the interlayer space has most probably to be taken into account.

From suspensions to solids

It would be very surprising not to find the seeds of the textural features of solid smectite "rocks" in the suspensions from which they were prepared. Very qualitatively, I would like to show now that there is indeed a strong correlation between the properties of suspensions or soft sediments and the morphomechanical models of the solid rocks.

Fig. 24. Sketch of the two extreme model microtextures of smectites: stacked smectites, originating from suspensions with thick and rigid tactoïds (top), and entangled smectites, originating from delaminated suspensions of thin and flexible lamellae (bottom). (the orientational disorder between stacks in the stacked smectite is expected to be much smaller in reality, due to the excluded volume effects described in II).

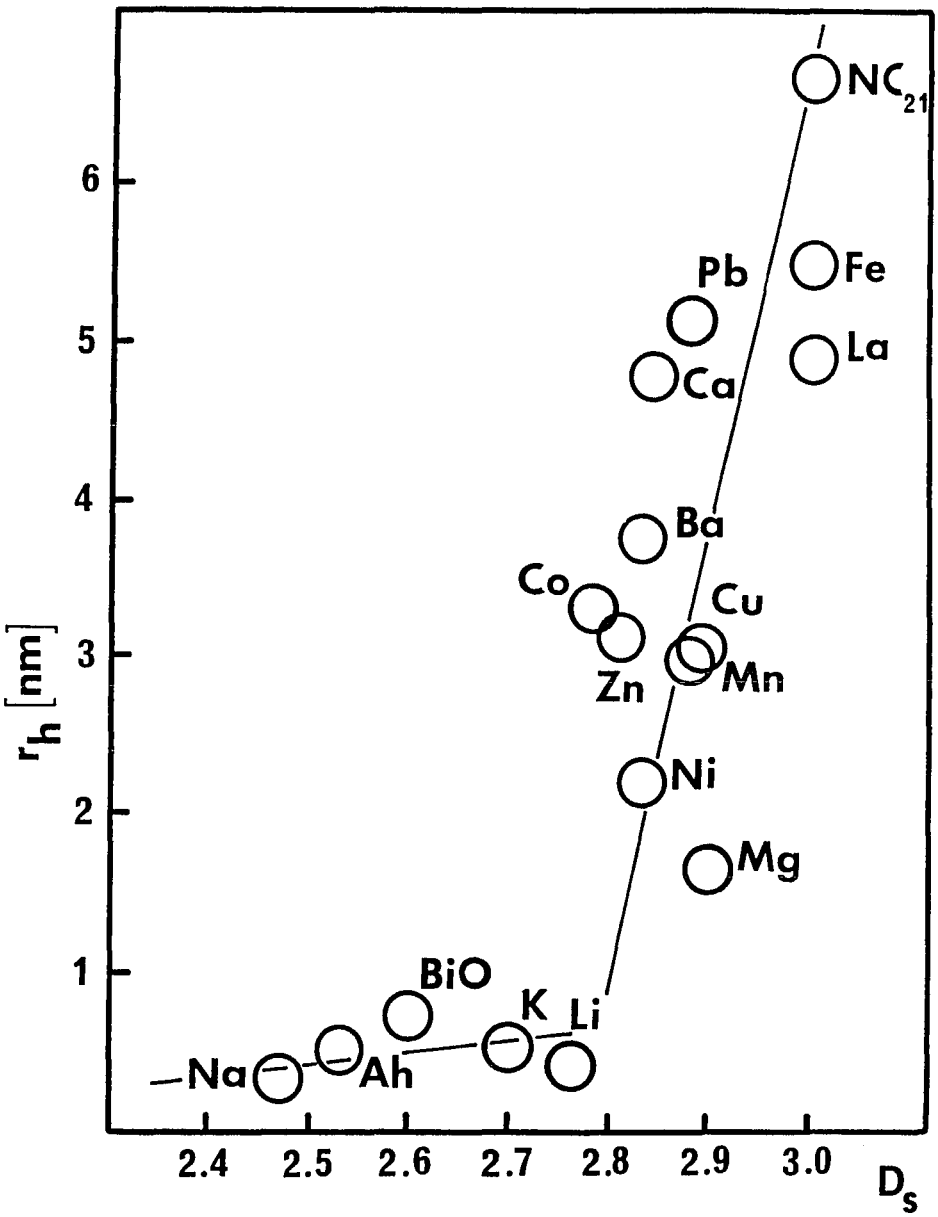


Fig. 25. Correlation between the hydraulic radius of the water saturated filtration cakes obtained by filtering slurries of ion-exchanged montmorillonites under a presure of 6 bars and the surface fractal dimension of the dry solid samples obtained by drying the same slurries.

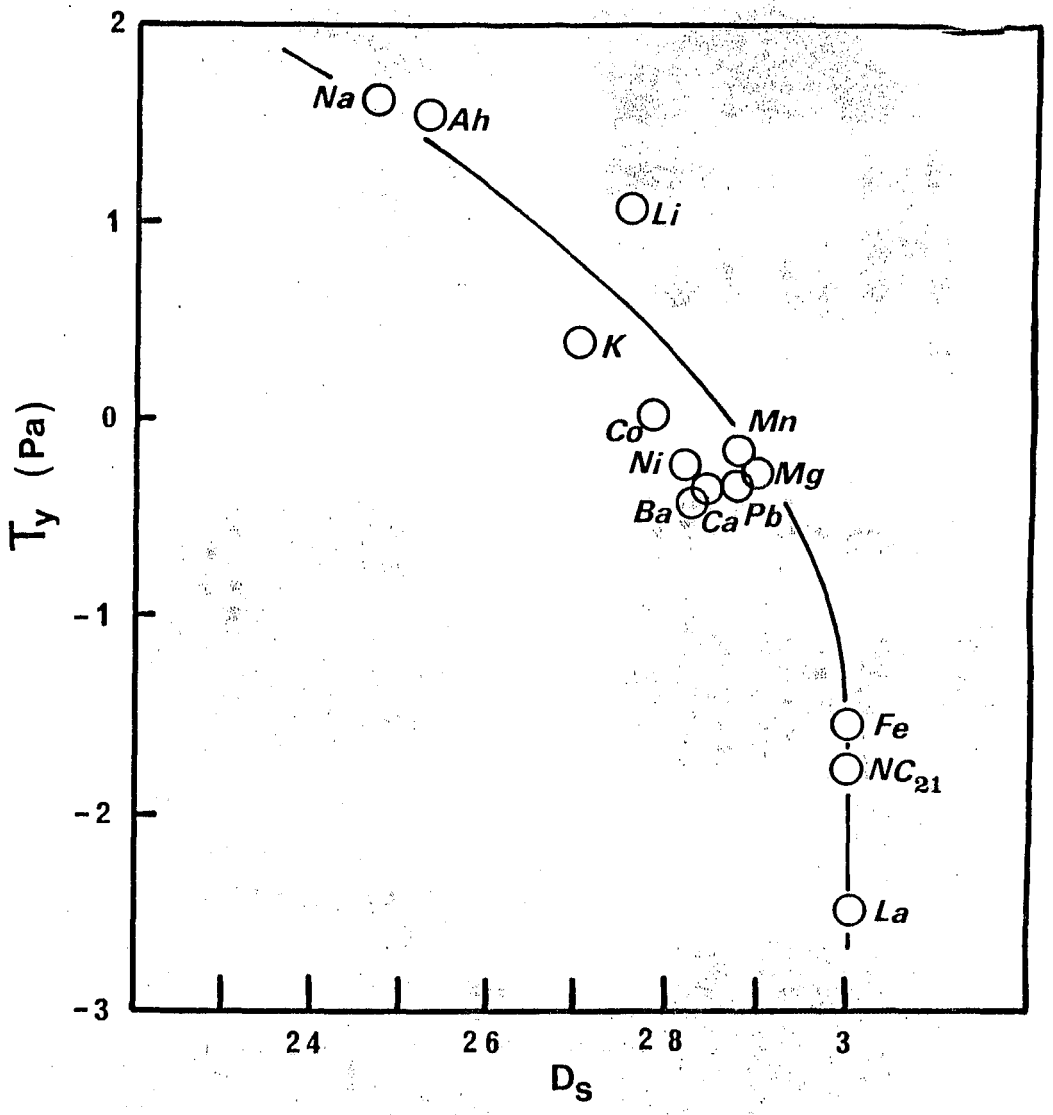


Fig. 26. Correlation between the Bingham yield stress of ion-exchanged montmorillonite suspensions and the surface fractal dimension of the solid samples obtained by drying the same slurries.

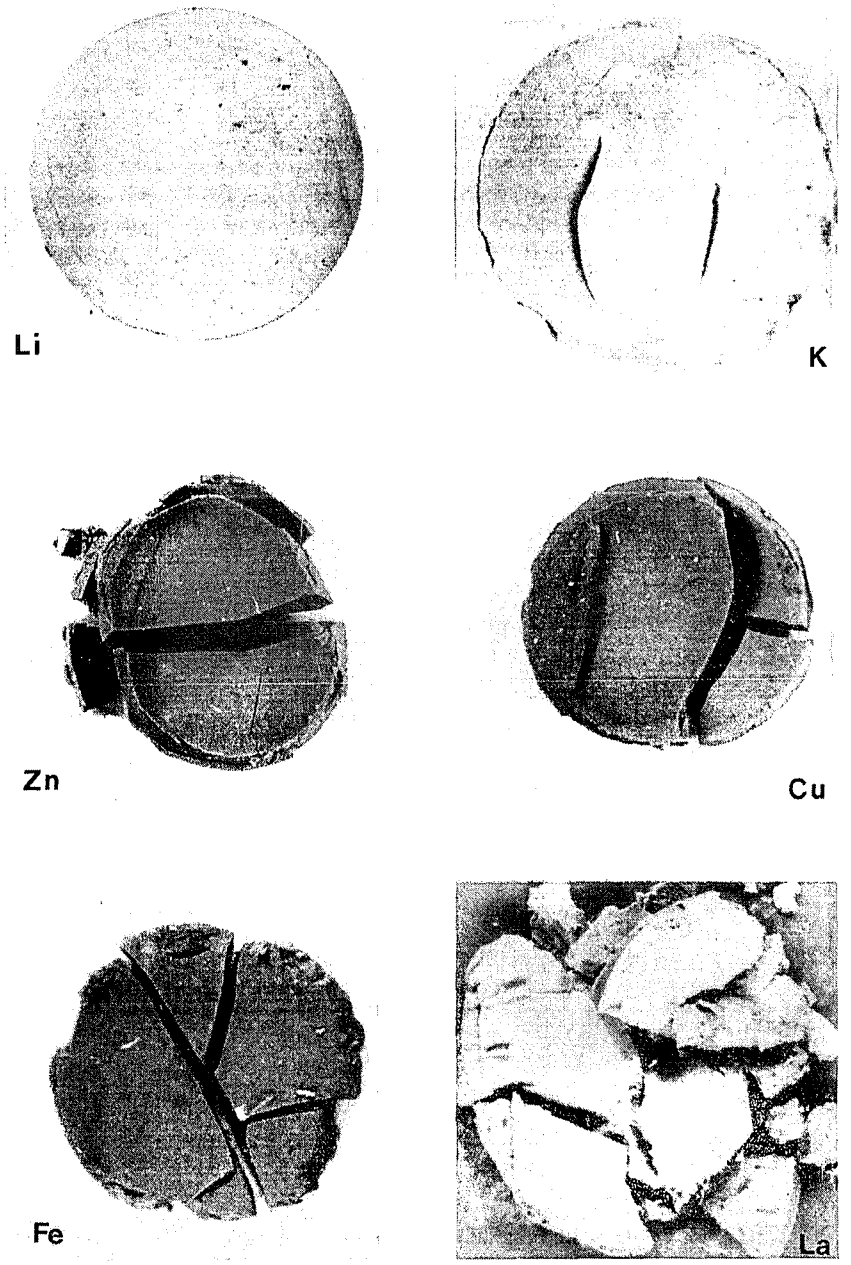


Fig. 27 Cracking patterns obtained by drying the filtration cakes of a few ion-exchanged montmorillonites suspensions. Note the extensive cracking of the "stacked" clays and the absence of cracking in the "entangled" clays.

Generally speaking, one expects the following trends:

- smectites which give rise to fragile book house-type arrangements of thick and well ordered stacks in the solid state with $D_s=D_p=D_m=3$ (I will call those "stacked" smectites) are also expected to come from thick tactoids in suspensions, with a small water-tactoid interface area. Those which form compact packings of flexible units ("entangled" smectites) with non trivial scaling exponents are expected to come from well dispersed, delaminated suspensions, with a large solid-liquid interface area (fig.24).
- since the total excluded volume of one thick tactoid containing n elementary lamellae is much smaller than the total excluded volume of n individual lamellae, one expects suspensions of "stacked" smectites to have lower plastic viscosity and gel strength (yield stress) than the "entangled" smectites.
- assuming that thick rigid units form less coherent and more porous sediments than thin flexible units, "stacked" clays should form more permeable filtration cakes than "entangled" clays. Upon drying, "stacked" filtration cakes are also expected to crack extensively under the action of the capillary stress, since the units have only very limited contact areas. "Entangled" clays should withstand much better the stresses.

As shown in fig.25, fig.25 and fig.27 for the permeability of filtration cakes, the yield stress of suspensions and the drying cracking patterns of cakes respectively, all these trends are experimentally confirmed, in spite of a relatively large scatter of the data.

IV. DEFORMABILITY

In the last part of this lecture, I would like to address directly the question of the flexibility of smectite stacks and of its consequences. I will successively present a few experimental results, a simple simulation and, finally, what in its present state is merely a conjecture.

Stiffness and curvature

The assumption that the rigidity of an aggregate of lamellae increases with the number of lamellae in the aggregate is a reasonable assumption, but one might wish to have direct evidence. Measuring from place to place the local curvature radius of a folded surface in a three-dimensional space is not at all an obvious problem, but one can design approximate methods. For instance, one can prepare a relatively thin (~ 0.1 mm) deposit of a cation-exchanged smectite by filtering a dilute suspension on a millipore filter. This deposit may then be fractured and the fracture surface examined by scanning electron microscopy (SEM). Putting the sample in the high vacuum of the microscope (or, before that, in the vacuum of the evaporator) induces a brutal dehydration of the sample which expands the film and deforms the smectite lamellae.

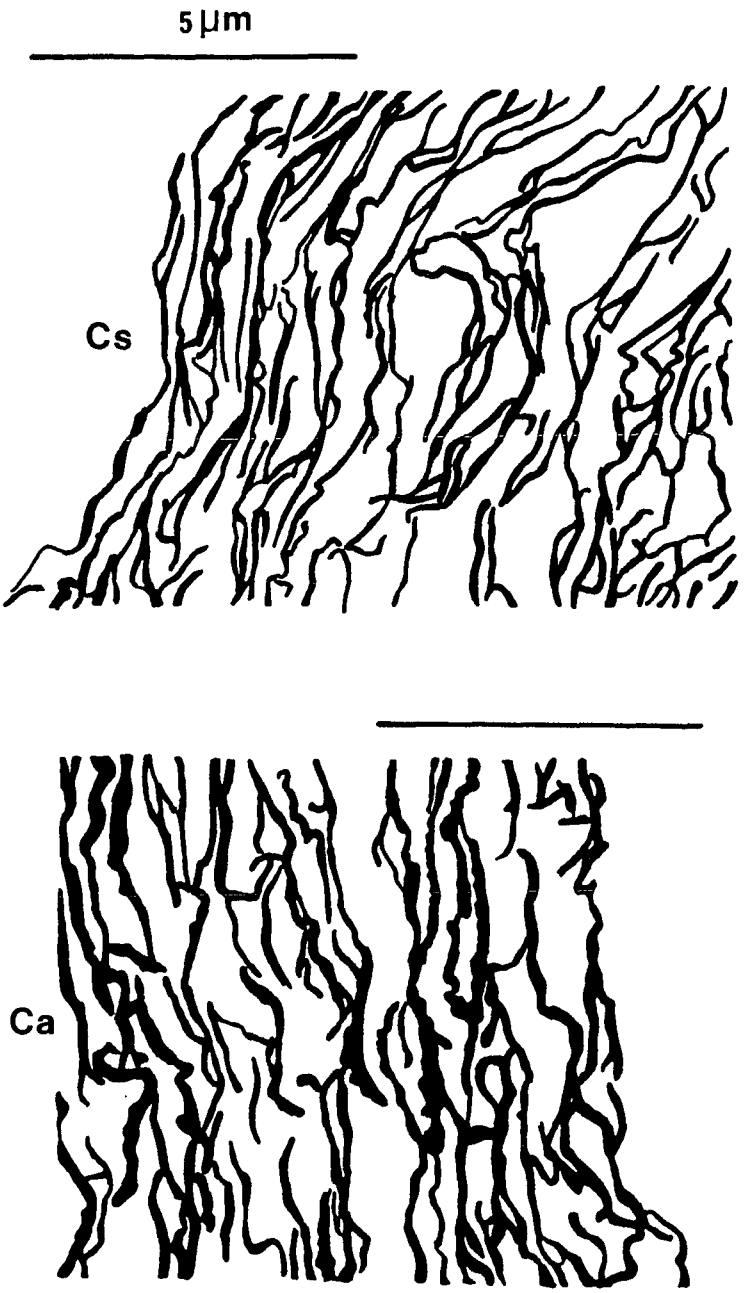


Fig. 28. Profiles of the scanning electron micrographs of the fracture surface of ion-exchanged montmorillonite films. The Cs-exchanged sample exhibits rather short local curvature radii, whereas the Ca-exchanged sample looks more rigid.

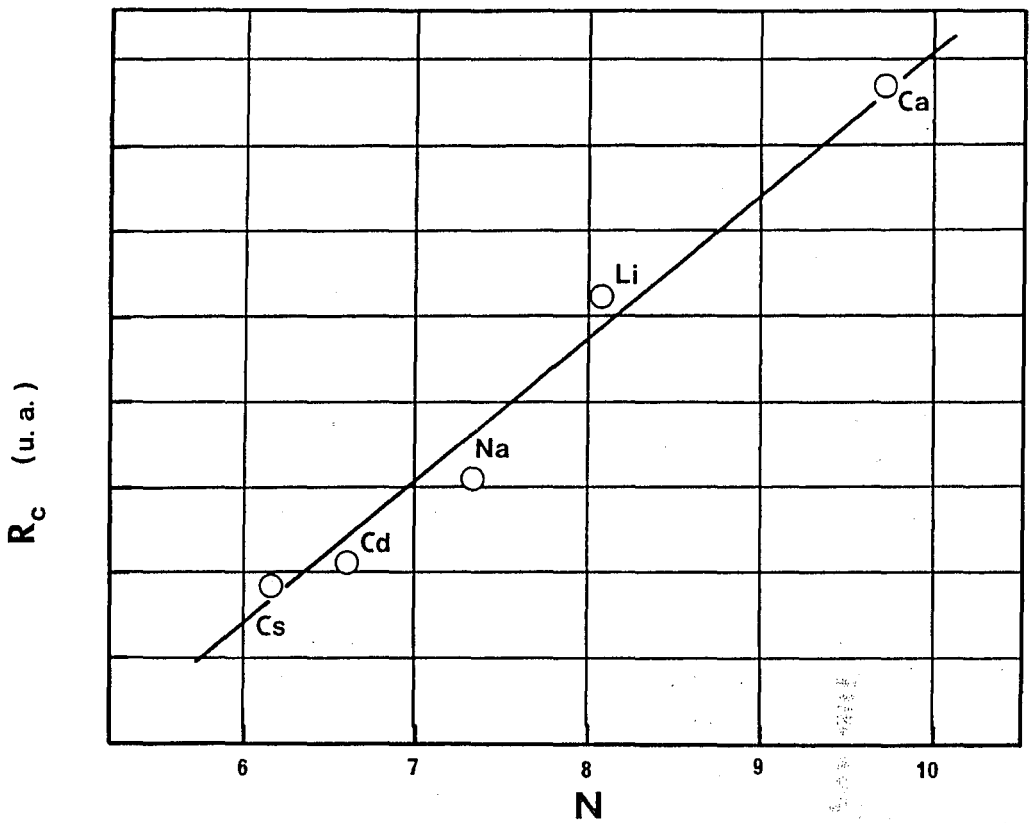


Fig. 29. Correlation between the average value of the local curvature radius (arbitrary units) of the lamellae packets measured on digitized electron micrographs of montmorillonites at the micrometer scale, and the number of elementary clay lamellae in organized stacks at the nanometer scale, derived from the line width of the 001 diffraction line.

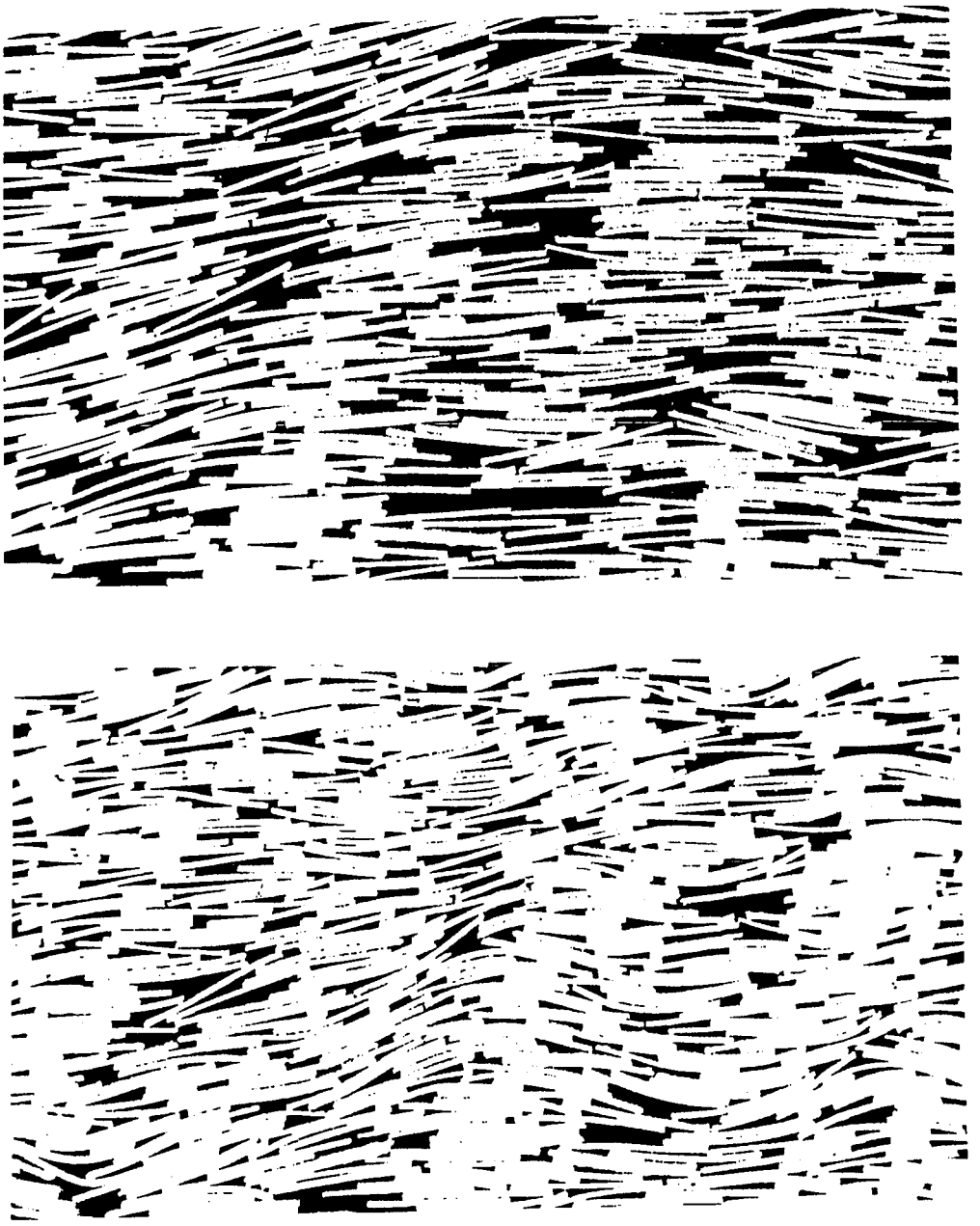


Fig. 30. Uncompacted and compacted layered packing obtained by randomly sedimenting thick (and relatively rigid) cardboard lamellae. Note the presence of piles transmitting the applied stress.

The SEM image may then be digitized and the local curvature of each individualized part of the expanded film be measured.

Fig.28 shows the results of such measurements on a few cation-exchanged montmorillonites (Cs, Li, Na, Cd, Ca). Although the curvature differences are not very clear upon simple visual examination, a quantitative image analysis treatment shows that the differences are quite large. Remarkably, these average curvature radii, measured in the micrometer range, are very well correlated to the coherence length, l_c, of the lamellae stacks in the nanometer range, as calculated from the line broadening of the OO1 reflection. As shown in fig.28, there is a surprisingly simple linear relationship between the average (absolute value) of the curvature radius and the average number of lamellae involved in X-ray diffraction. To my best knowledge, this is the first quantitative bridge between micromorphology, structure and mechanics in the field of clays!

Local order and flexibility

The previous results suggest that, after all, the type of macroscopic mechanical concepts we use in building material for instance might well be applicable on the nanometer scale or, reciprocally, that useful structural or microtextural information could be gained from macroscopic mechanical simulations. An example of this type is the two-dimensional simulation of sediment compaction which is shown in fig.30 and fig.31 for relatively thick and relatively thin cardboard platelets, respectively.

The simulation is performed as follows. Make a narrow 10mmx300mmx300mm gap between two glass sheets, as in fig.4. Take five thousand 10mmx30mm pieces of cardboard. Use a random number generator to choose an abcissa between 1 and 300 (the width of the cell) and put a cardbord at the choosen place. After placing all the pieces of cardboard, compress progressively the whole system from above, while following the textural evolution by image analysis.

A first interesting observation, which is most clear on fig.30, is that although the "sedimentation" is performed at random, one can see the formation of stacks which, upon compaction, will transmit most of the stress. A second observation is that, as assumed previously in this lecture, uncompacted "sediments" of the more rigid thick platelets are more porous than those of thiner and more flexible platelets.
Much more could be done with this type of simulation but, for the moment, let us leave it here.

Flexibility and swelling

A simple look to fig.16 is enough to be convinced that the swelling of a smectite/water medium is not the separation of perfectly parallel individual lamellae at increasing distances. A smectite/water slurry is in fact a multiply connected network of

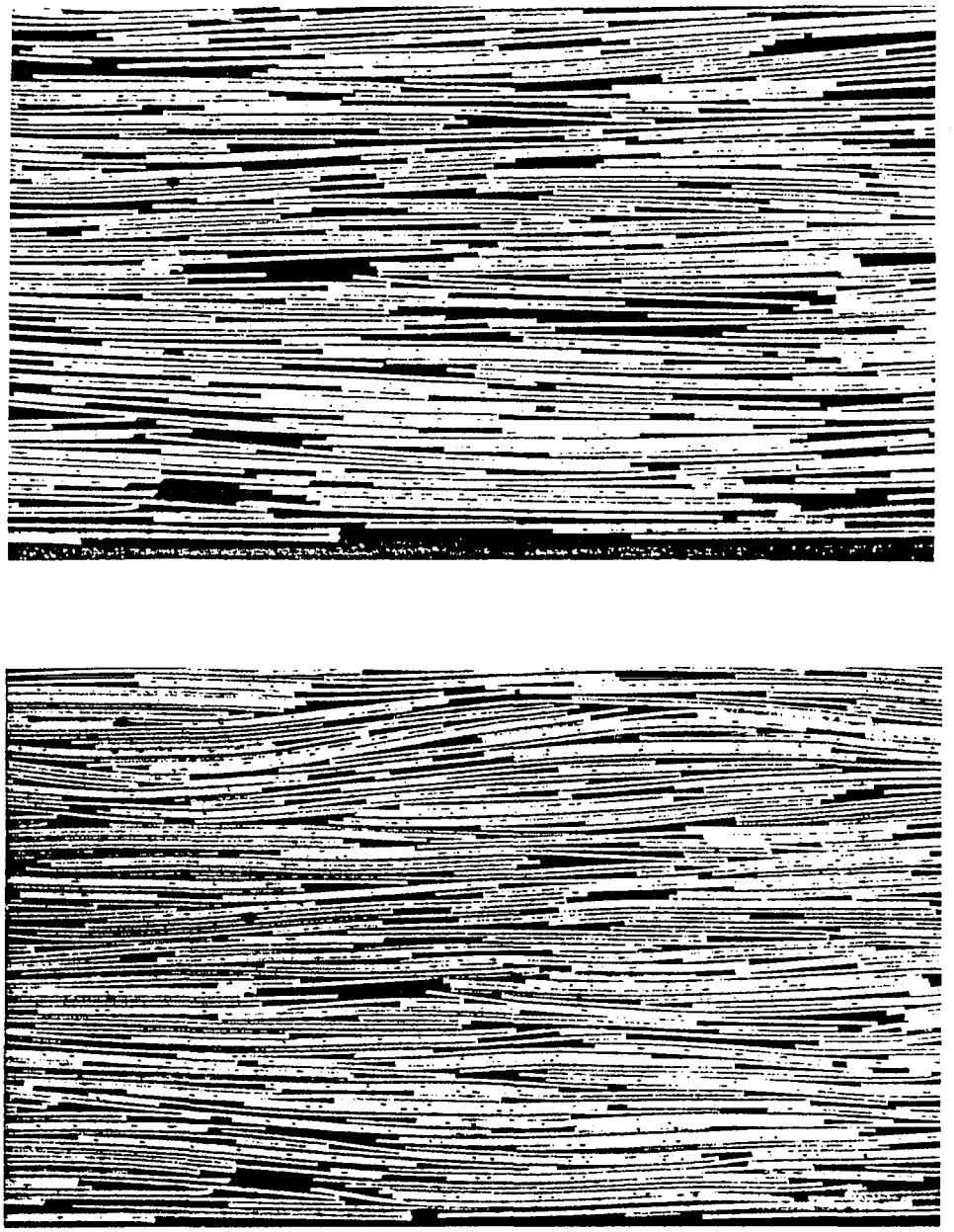


Fig. 31. Uncompacted (top) and compacted (bottom) layered packing obtained by randomly sedimenting relatively thin and flexible cardboard lamellae (as compared to the packing of fig. 30).

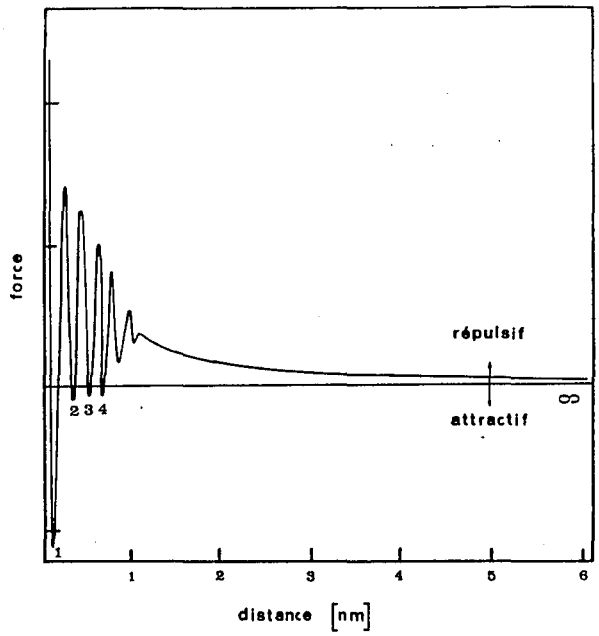


Fig. 32. Separation dependence of the force between two mica surfaces in an aqueous medium (after J. Israelachvili, "Intermolecular and Surface Forces). Note the presence of several stable minima at short distances, corresponding to 1, 2, 3 or 4 layers of water molecules (to be compared to the oscillations in fig. 6), as in the swelling of smectites. This short range regime is followed by a "swelling gap", where no stable interlayer distance is found, except infinite separation (in smectite suspensions, this would be the distance corresponding to the maximization of the entropy allowed by the total volume of the system and the number of particles, and to the minimization of the elastic energy stored in the lamellae.

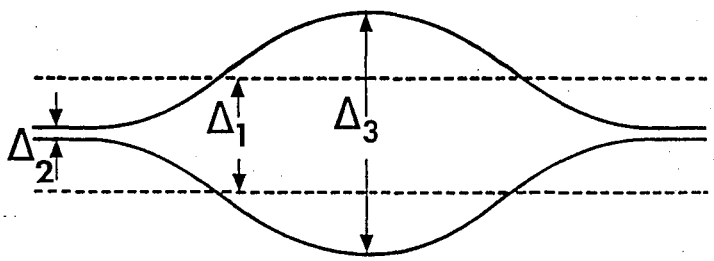


Fig. 33. Two smectite lamellae separated by a distance D_1 located in the swelling gap (fig. 32) may jump into a buckling regime, where part of the lamellae would be separated by only a few layers of water molecules (typically 4, which would give a 001 distance around 2.1 nm) whereas another part would be separated by the maximum distance allowed by the elastic energy stored in the deformation and by the entropy of the system.

bended lamellae involved in aggregates at some places and individualized at other places. In fact, only two types of local swelling situations seem to exist: lamellae involved in stacks and separated from each other by a few layers of water molecules (one to three) on one hand, and lamellae separated by much larger distances on the other hand. The presence of what might be called a "swelling gap" of forbidden distances in the intermediate range (interlayer distances between, say, 2 and 4 nm) was already detected by Norrish in his pioneering investigations of swelling and confirmed later by Pons and Rausell Colom. There is little doubt that the flexibility of the lamellae and their (not too thick) aggregates is a key parameter for allowing variable local swelling states along a single lamella, but is there a fundamental reason for having a "swelling gap"?

The conjectural answer to this question is "yes". As the remarkable measurements of surface forces between mica surfaces by Israelashvili and coworkers have shown, the force between two charged surfaces exhibits at short distances several stable minima due to hydration forces corresponding to an integer number of water layers between the two surfaces (fig.32) (this is by the way clearly reminiscent of the density oscillations observed in the simple macroscopic simulation with glass beads of fig.6). At larger distances, this oscillating attractive-repulsive regime is followed by a smoothly repulsive regime of electrostatic origin. Thus, there are two admissible situations for an interlayer gap: either to be trapped in one of the short range hydration state, or be as large as allowed by the volume of solvent available. Provided the lamellae are flexible enough, one might very well imagine that the same lamella would be involved at some places in one of the short range minima and, at other places, in the long range repulsive regime (fig.33).

This ends the sort of medley which I wanted to present to you. As emphasized in my introduction, most of the points which were presented should only be regarded as clues. Much remains to be done to put the relationships between micromechanics, scaling and physico-chemical interactions in a unified quantitative framework.

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