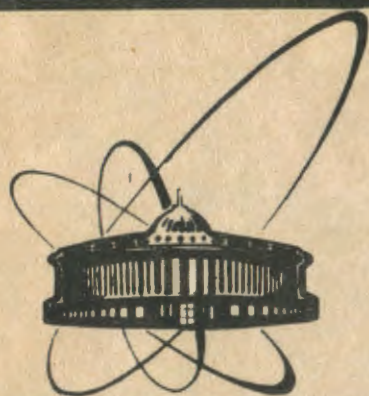


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ON THE FRACTAL NATURE OF CARBONATE
AND APATITE ROCKS

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1. INTRODUCTION

Many minerals in nature can be regarded as porous media with surface or volume fractal properties^{/1/}. Their scaling characteristics play an important role in formation of physical properties of these media and the processes of flow through porous media^{/1,2/}, water-oil distribution^{/3/}, dielectric properties of brine-saturated rocks^{/4/}, elastic properties^{/5/} and fracture^{/6/}. Identification of the fractal dimension is thus the "preparative" stage in these studies.

Small angle scattering (of neutrons, X-rays, etc.) has been widely used for this goal^{/7-12/}. It is well established that the scattering intensity as a function of the scattering vector length q , $I(q)$, for q^{-1} corresponding to the medium scaling diapason falls of as

$$I(q) \sim q^{-D} \quad (1)$$

for volume fractals and as

$$I(q) \sim q^{-(6-D)} \quad (2)$$

for surface fractals^{/7-12/}.

Here $2 < D < 3$ is the fractal dimension of either topological 3-d porous particle or 2-d surface of the particle, respectively. The "cut-off" of these laws bound them both from the very large q and very small q sides^{/7/}. The former is due to finite size of the particle and the latter due to the breakdown of self-similarity, usually, approaching the inter-atomic distances range.

The treatment of the scattering data in $\log I$ versus $\log q$ plots thus enables one to identify the fractality and to distinguish between the volume and surface fractal behaviour. Indeed, when we deal with volume fractals the exponent lies between 2 and 3, while for surface fractals $3 < \alpha (=6-D) < 4$. The case of a homogeneous volume corresponds to $\alpha = D = 3$. Smooth surfaces give $D = 2$ and $\alpha = 4$, i.e. the Porod law^{/13/}. The more developed is the surface, the more D deviates from 2 towards 3 and the smaller is α with respect to its porod limiting value of 4.

Fractal nature of pore-space surfaces of sandstones, limestones and dolomites^{/11/}, lignite coals^{/12/} was identified together with measuring the surface fractal dimensions. Qualitatively, results of this kind are supported by the real space measurements^{/1,14-16/}. In this paper we investigate mineral components of apatite-carbonate ores. The interest to these systems is caused by their particular colloid properties relevant for selective flotation. To build a theory of elementary act of heterocoagulation between the mineral particle and the gas bubble we need a picture of the particle pore structure.

In this work, the small angle neutron scattering (SANS) will be taken as a tool for the study of this picture. The efficiency of SANS for the study of rocks and other strongly inhomogeneous structures is due to two main features of interaction of neutrons with matter. Firstly, neutrons are capable to penetrate deep inside the sample which allows one to probe its inner structure. Secondly, since the scattering amplitudes of the basic elements of rock substances, viz. carbon, oxygen, silicon, phosphorous, calcium, etc., are close*, in small wave vector transfer (q) experiments porous rocks behave like two phase systems exhibiting the interior "rock space" and "pore space".

As we shall see, the mineral grains under study in SANS experiments possess surface fractal properties, and the data obtained provide a useful nomenclature of these properties by their fractal dimension.

2. MATERIALS AND METHODS

The object of studies were the pure monomineral fractions of apatites and calcites from the apatite-carbonate ores of different genesis. The taken ores differed in technological characteristics of enrichment, i.e. flotation extraction of the valuable component (apatite), with practically invariant chemical composition. The chemical composition was established by standard methods of chemical analysis.

*Indeed, the coherent neutron scattering length for carbon, oxygen, silicon, phosphorous and calcium are respectively, 0.66, 0.58, 0.40, 0.50, 0.49 in units of 10^{-12} cm. For comparison the X-ray scattering factors ($\theta = 0^\circ$) for the same elements differ substantially and are, respectively, 1.13, 2.25, 3.95, 4.23 and 5.6.

The samples were monodisperse powders of $\sim 40 \mu\text{m}$ (calcites) and $\sim 100 \div 200 \mu\text{m}$ (apatites) average size controlled by sedimentation. The powders were filled in a cylindrical quartz glass cuvette 2 mm thick and 32 mm in diameter.

5 types of calcite and 2 types of apatite grains taken from different ores which will be hereafter denoted as 11c, 12c, 13c, 14c, 15c and A1, A2, respectively.

For the verification of unimportance of the multiple-scattering the 11c sample was also studied in cuvettes of 1 and 4 mm thickness.

Scattering measurements were performed on the time-of-flight SANS spectrometer^{/17/} at the pulsed reactor IBR-2 the Joint Institute for Nuclear Research in Dubna^{/18/}. Sample-detector distance was ~ 10 m; collimation diameter of the primary beam was 16 mm. Under these conditions the range of the scattering vector length, $q = \frac{4\pi}{\lambda} \sin(\theta/2)$ (θ - the scattering angle; λ_0 - the wave length of the incident neutron), was $10^{-2} - 5 \cdot 10^{-1} \text{ \AA}$, i.e. corresponded to real space scale, $2\pi/q$, of 12 to 600 \AA . The mean neutron flux on the sample was about $3.2 \cdot 10^7$ neutrons/ cm^2s . The time of measurement for each sample (exposition) was about 3 hours. The background spectrum was that of an empty cuvette.

3. RESULTS AND DISCUSSION

Figures 1 and 2 show the scattering intensity $I(q)$ curves for calcites and apatites, respectively. Within the q variation range between 10^{-2} to $8 \cdot 10^{-2} \text{ \AA}^{-1}$ the experimental error is less than 0.5% and $\log I - \log q$ plot looks linear, i.e. $I \sim q^{-\alpha}$ where the exponent α is determined from the slope of the line drawn through experimental points. Deviation from linearity in the large q limit ($q > 0.1 \text{ \AA}^{-1}$) is evidently due to arrival of interatomic scale (e.g. average interatomic distance or lattice constant). No cut-off is expected in the smallest q range due to Guinier-like scattering from the grain as a whole^{/7,9/}, because in our case $q_{\min} R_{\min} = 4 \cdot 10^3 \gg 1$ (here R_{\min} is the smallest size of the grain $\sim 4 \cdot 10^5 \text{ \AA}$).

The possibility of multiple scattering was checked for C11 samples by varying the thickness of cuvette (1, 2 and 4 mm). Within the experimental accuracy (± 0.02) the same values of α were obtained: 4.00, 4.00, 3.98 respectively. The values of α determined for 11c samples extracted from the experimental data obtained with the help of 7 detectors which correspond

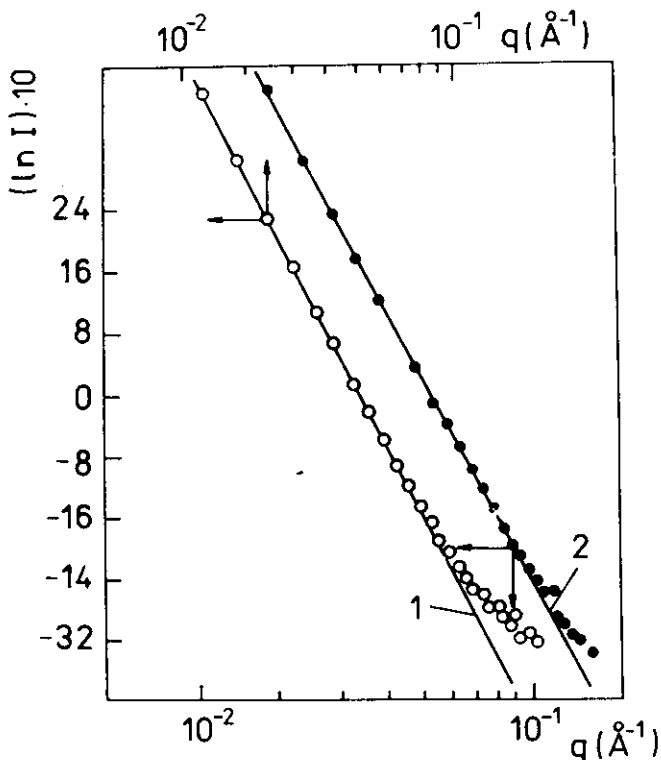


Fig.1. The neutron scattering intensity dependences on q for carbonates: 1 - 11c sample, 2 - 12c sample.

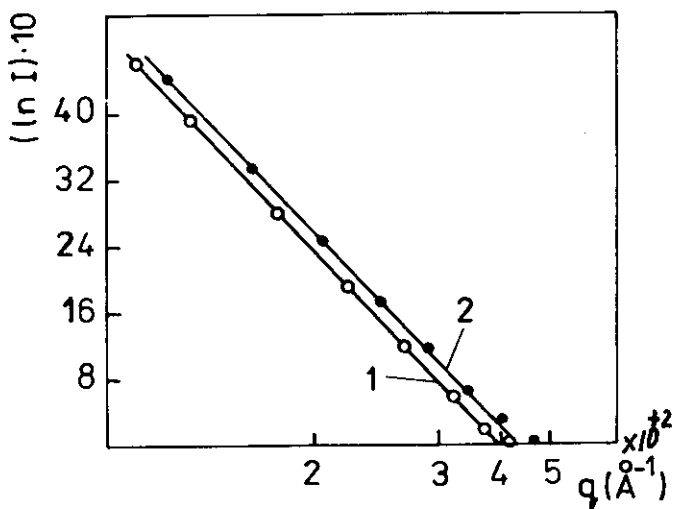


Fig.2. The neutron scattering intensity dependences on q for apatites: 1 - A1 sample, 2 - A2 sample.

SANS data for scattering intensity exponents

Sample	Average linear size (μm)	α (the accuracy ± 0.02)	$D = 6 - \alpha$
11c	40	4.00	2.00
14c	40	3.97	2.03
15c	40	3.90	2.10
12c	40	3.85	2.15
13c	40	3.79	2.25
A1	100 \div 200	3.81	2.19
A2	125 \div 160	3.61	2.39

to different scattering angles, also coincide within the experimental error. We thus conclude that the contribution of multiple scattering is negligible.

The observed values of α and the corresponding values of $D = 6 - \alpha$ are given in the table. We see that $q^{-\alpha}$ law represents well the $I(q)$ data, and there is no reason to apply more complicated approximations (c.f.^{10,11/}). Really, the deviation of log-log plots from linearity is observed only at approaching the lattice constant. Some influence of the incoherent scattering is not excluded here.

Noteworthy, that for one of the carbonate rocks (11c) Porod's law is ideally valid (a rare case!). In the table, the calcites and apatites are set in a sequence of decrease of α or increase of D which indicates the development of the surface. We see that surfaces of calcites range from very smooth ones (with surface fractal dimension $D = 2$) to moderately developed surfaces ($D \approx 2.2$). One of the considered apatites exhibits a more developed surface ($D \approx 2.4$). The results are in "visual" correlation with microphotographs presented in Figs.3 and 4. It should be noted that the fractal character of the surfaces of the studied samples is associated not only with intrinsic properties of crystallite surfaces, but also with the aggregation on these surfaces of smaller fractions of the same nature. The values of surface fractal dimensions, D , obtained are not too large. This gives evidence that this is not the case of diffusion limited aggregation, but rather some kind of ballistic aggregation^{18/}. It is not excluded that aggregation of smaller particles on larger ones occurs on the surfaces of crystallites which are already fractal^{16,19/}.



Fig.3. The scanning electron microscopy of carbonate 12c crystal surface. $\alpha = 3.85$. Magnification 18000.

4. CONCLUSION

We thus found that the series of carbonate and apatite rocks of the same chemical composition are typical of different surface fractal structures. In order to explain why it is so, we should at least know its geological origination. The surface crystallite growth depends on many factors determining



Fig.4. The scanning electron microscopy of apatite A2 crystal surface. $a = 3.61$. Magnification 19200.

aggregation (sticking probability, pressure, temperature, the speed of the liquid flux, laws of random environmental changes, etc.) and, not excluded, on way of fracture and powder grinding too.

In the further work we shall apply these results to the theory of selective flotation. Another development of this work would be the expansion of the range of q to a lower values in order to test the linearity of log-log plots on a broader scales.

REFERENCES

1. Thompson A.H., Katz A.J., Krohn C.E. - Adv.Phys., 1987, v. 36, p. 625.
2. Guyon E. - "On the Reology of Random Media", in: H.E.Stanley and N.Ostrowsky, Eds. "On Growth and Form", Martinus Nijhoff Pbls., Boston, 1986, p.163.
3. Strong D., Milton G.W., De B.R. - Phys.Rev., 1986, v.34, p.5145.
4. Browsers F., Ramsamugh A., Dixit V.V. - J.Phys.C, 1988 (in press).
5. Beryman D.J. "Elastic Properties of Composite and Porous Media", IICIP Lecture notes preprints, SMR/214-15, Trieste, 1987.
6. Engelman R., Jaegen Z., Eds."Fragmentation Form and Flow in Fractured Media", Am.Israel Phys.Soc., 1986, v.8.
7. Kjems J.K., Freltoft T. "Neutron and X-Ray Scattering from Aggregates", in: "Scaling Phenomena in Discordered Systems", (R.Dym and A.Skjeltorp, Eds.), Nato ASI Series B, 1986, v.133, p.133, Plenum Press, New York, J.K.Kjems, P.Schofield. "Neutron and X-Ray Studies of Interfaces", ibid, p.141.
8. Liu S.H. - Solid State Physics, 1986, v.39, p.207.
9. Teixeira J. "Experimental Methods for Studying Fractal Aggregates", in: "On Growth and Form", H.E.Skinley, Ed. 1986, p.145, Natinus Nijhoff Pbls., Boston.
10. Wong P.-Z. "Fractal Surfaces in Porous Media", in: the J.Banhavar, J.Koplik and K.W.Winkler, Eds., AIP Conference Proc.154, "Physics and Chemistry of Porous Media", 1987, p.305, AIP, New York.
11. Wong P.-Z., Howard J., Lin J.-S. - Phys.Rev.Lett., 1986, B57, p.637.
12. Bale H.D., Schmidt P.W. - Phys.Rev.Lett., 1984, v.53, p.596.
13. "Small Angle X-Ray Scattering", (O.Glatte, O.Kratky,Eds.) 1982, Acad.Press, London.
14. Katz A.J., Thompson A.H. - Phys.Rev.Lett., 1985, v.54, p.1325.
15. Pfefter P., Avnir D. - J.Chem.Phys., 1983,v.79, p.3558.
16. Farin D., Avnir D. - J.Phys.Chem., 1987, v.91, p.5517.
17. Vagov V.A. et al. - JINR preprint P14-83-998, Dubna,1983.
18. Anan'ev V.D. et al. - Atomnaya Energija, 1984,v.57,p.227.
19. Kinetics of Aggregation and Gelation (F.Family and D.P.Landau, Eds.), 1984, Amsterdam, North Holland.

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