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SURFACE ADSORPTION OF

Cs ¹³⁷ IONS ON QUARTZ CRYSTALS

By S. Antkiw, H. Waesche, and F. Senftle

Trace Elements Memorandum Report 862

UNITED STATES DEPARTMENT OF THE INTERIOR

GEOLOGICAL SURVEY



UNITED STATES
DEPARTMENT OF THE INTERIOR
GEOLOGICAL SURVEY
WASHINGTON 25, D. C.

AEC-488/5

January 13, 1955

Dr. T. H. Johnson, Director
Division of Research
U. S. Atomic Energy Commission
16th and Constitution Avenue, N. W.
Washington 25, D. C.

Dear Dr. Johnson:

Transmitted herewith is one copy of TEM-862, "Surface adsorption of Cs¹³⁷ ions on quartz crystals," by S. Antkiw, H. Waesche, and F. Senftle, December 1954.

We plan to submit this report for publication in *Geochimica et Cosmochimica Acta*, News and notes.

Sincerely yours,

for *John H. Eric*
W. H. Bradley
Chief Geologist

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Physics

This document consists of 9 pages,
Series A.

UNITED STATES DEPARTMENT OF THE INTERIOR

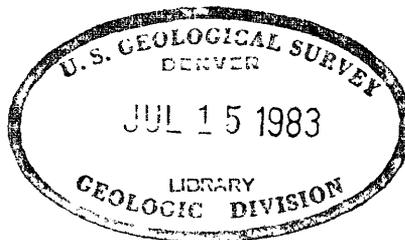
GEOLOGICAL SURVEY

SURFACE ADSORPTION OF Cs¹³⁷ IONS ON QUARTZ CRYSTALS*

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S. Antkiw, H. Waesche, and F. Senftle

December 1954



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*This report concerns work done on behalf of the Division of Research of the U. S. Atomic Energy Commission.

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SURFACE ADSORPTION OF Cs¹³⁷ IONS IN QUARTZ CRYSTALS

By

S. Antkiw, H. Waesche, and F. Senftle

ABSTRACT

Adsorption tests were made on four large synthetic and three natural quartz crystals to see if surface defects might be detected by subsequent autoradiography techniques. The adsorbent used was radioactive Cs¹³⁷ in a solution of Cs¹³⁷Cl. Natural quartz crystals adsorbed more cesium than the synthetic crystals. Certain surface defects were made evident by this method, but twinning features could not be detected.

INTRODUCTION

To determine if there is any relation between imperfections in quartz crystals caused by variations in crystal structure or in growth patterns and adsorption of ions on the crystal surface, a preliminary investigation was made of the adsorption of radioactive Cs¹³⁷ ions on quartz crystal faces from a solution of Cs¹³⁷Cl. Such an adsorptivity might be useful in detecting defective quartz crystals without destructive testing. Both natural and synthetic crystals were used in the investigation.

This study was undertaken as part of a program conducted by the Geological Survey on behalf of the Division of Research of the Atomic Energy Commission.

PROCEDURE

Each natural crystal was boiled in nitric acid for approximately 30 minutes to remove surface impurities. Both natural and synthetic crystals were then washed in benzene, alcohol, and de-ionized water. After drying the crystals were immersed in Cs^{137}Cl solution, the radioactivity of which was 1 millicurie or more, for periods ranging from 20 minutes to 1 hour. The synthetic crystals were immersed for the longer periods because adsorption was much less than with the natural crystals regardless of the time of contact with the solution.

Preliminary measurements, using a Geiger counter with a sensitive area of 0.08 mm^2 , showed that the resolution was not sufficient to determine surface differences in radioactivity. Autoradiographs made with two types of commercially available X-ray film gave good results. The films were kept in contact with the natural crystals for 18 hours and with most synthetic crystals for 120 hours. Normal photographic developing techniques were used.

RESULTS

Natural crystals

Crystal 4A (courtesy of Earl Ingerson, U. S. Geological Survey).-- Lines on a major rhombohedral face (r) indicate increased adsorption over the remainder of the surface. These lines seem to be surface manifestations of growth irregularities complicated by internal fractures and inclusions that may be parallel to regular crystallographic directions, such as s or x faces, not exhibited in the outer form of the crystal. An adjoining minor rhombohedral face (z) showed similar

lineations. It is interesting to note that, although there were visible patches of what appeared to be electrical twinning and well-developed oscillatory combination lines between the prism and rhombohedral face, no selective adsorption was evident on these crystallographic structures.

Crystal N1 (courtesy of Jane Titcomb, U. S. Geological Survey).-- Adsorption lines seem to be caused by oscillatory combination on a prism face. This is in contrast to what was observed on crystal 4A.

Crystal N3 (courtesy of David Gottfried, U. S. Geological Survey).-- A minor rhombohedral face (z) and a major rhombohedral face showed broad band lineations parallel to the intersection between the two faces. These lineations seem to be associated with a growth pattern. Dark spots due to surface pits are visible.

Synthetic crystals

Crystal B-3-5 (courtesy of D. R. Hale, Brush Laboratories Co.).--An artificially grown face approximating the minor rhombohedral face (z) shows regular and irregular banding with the regular banding parallel to the face boundaries.

Crystal B-5-4 Brazil twinned (courtesy of Warren Roberts, Signal Corps Engineering Laboratories, Fort Monmouth, N. J.).--Both prism faces show an irregular shading pattern with sharp well-defined oriented lines that coincide with what appear to be vicinal or modifying forms. Numerous spots correspond to pits on the surface that can be seen with a hand lens. In incident light there are faint growth lines but these produced no apparent effect on adsorption characteristics. An autoradiograph of a major rhombohedral face (r) produced an irregular shading

pattern that seemed to be unrelated to what appear to be growth spirals. A minor rhombohedral face (z), adjoining a major rhombohedral face (r), produced a distinct anomalous adsorption pattern at the center of the face which bore no relation to an elaborate pattern of growth lines visible in incident light.

Crystal R-518-B-9 (courtesy of Warren Roberts, Signal Corps Engineering Laboratories, Fort Monmouth, N. J.)--This synthetic crystal contained artificial inclusions of acmite and displayed no optical twinning. A rhombohedral face with marked spiral-type growth patterns produced variations in shading and spots suggesting a relation to the patterns. An identification number scratched on one rhombohedral face was reproduced on the autoradiograph in detail, but a prism face with an incipient vicinal face or other regularly distributed growth patterns produced no apparent results on the radiograph. However, the positions of minute pits and acmite inclusions were sharply defined. The thickest concentration of spots was in the vicinity of near-surface acmite inclusions.

Crystal S-13 (courtesy of A. C. Walker, Bell Telephone Laboratories, Summit, N. J.)--A synthetic crystal with electrical twinning shown by fluoride etching. A minor rhombohedral face (z) that had been etched to reveal twinning produced no distinctive pattern on the film to reflect the twinning. The film pattern did reproduce the fine-grained texture of an etched surface with spots that may have been caused by small selectively etched pits. Regular growth lines on the prism faces produced no effect on the film although surface pits and depressions produced numerous spots. A slight lineation in one series of spots coincided with surface defects along the boundary of the seed plate. A second

prism face produced no photographic pattern representative of growth lines or of seed plate although there were spots produced by surface pits.

CONCLUSIONS

In general it appears that adsorption of Cs¹³⁷ ions on quartz faces is much greater by natural than by synthetic crystals. This is caused in part by unidentified differences in the surface texture. These differences are related to differences in growing conditions and subsequent environment. The natural quartz crystals, because of more chance of growth irregularities and surface abrasion from geologic conditions and recent handling by man, would be expected to have greater surface roughness and consequently greater adsorption qualities. The synthetic crystals have been grown under essentially uniform conditions, free from abrasion or inclusions; also they have had relatively less handling by man.

One crystal that exhibited obvious electrical twinning after a fluoride etch showed no variation in the adsorption pattern. This may be readily explained by the fact that electrical twinning produces only differences in orientation of the etch pattern that are readily detected by reflected light but would not produce a difference in texture in either portion of the twin. Both portions of an electrically twinned (Dauphine) crystal have identical structures and would react identically to etch solutions. Thus it seems logical that radioactive ion adsorption could not be expected to distinguish electrical twinning.

In some crystals it was evident that what appear to be spiral growth patterns can be emphasized and possibly some significance may

be attached to this phenomenon.

The strong spot adsorption at the centers of a spiral seem to confirm the theory advanced by D. Hammond of the Signal Corps Engineering Laboratories that the centers would tend to be regular minute elongated cavities perpendicular to the direction of growth in a growth mechanism of this nature.^{1/}

A longer program of research along these lines might result in valuable information. Some correlation between crystal imperfections and adsorption has been demonstrated. It is evident that this method is not useful for determining electrical twinning in quartz crystals.

^{1/} Oral communication, Frequency Control Review of Technical Progress, April 12-14, 1954, Asbury Park, N. J.