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Zeolite Determination & Geothermometry Interpretation Associated with Volcanic Rocks in Oil Fields in Northwestern Mississippi

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Zeolite Determination & Geothermometry Interpretations Associated with Volcanic Rocks in Oil Fields in Northwestern Mississippi

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The Mississippi Mineral Resources Institute
University, Mississippi 38677

FINAL REPORT

ZEOLITE DETERMINATION & GEOTHERMOMETRY INTERPRETATIONS ASSOCIATED WITH BURIED VOLCANIC ROCKS IN OIL FIELDS IN NORTHWESTERN MISSISSIPPI

(A CONCLUDING STUDY)

MMRI Grant Number S5-ÖF

Submitted tas

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ABSTRACT

The project waS a detailed study to confirm the presence of zeolites and then determine what type of zeolite minerals are associated with the subsurface volcanic province in northwestern Mississippi» Results of such a a study will aid in making a much better interpretat ion of the past activity of volcanic events that produced the features in the subsurface» By knowing precisely what zeolite minerals are present and where they are located, a detailed thermal history of possible oil and gas traps associated with these igneous features can be proposed. Therefore the type and distribution of zeolites present in the rocks has been the goal of this research. The results of this study and similar work in the future, together with the concurrent MMRI LANDSAT and gravity research in the area, will provide a valuable tool for exploration and production of oil and gas prospects in this part of Mississippi. It will also provide a model for application to exploration in other parts of the state and region.

The study was restricted to a three-county area (Humphreys, Leflore, and Holmes) because of sample availability, presence of oil fields, and amount of time available to do the work. The most abundant zeolite mineral is analcite. The petrographic microscope and X-ray diffraction with the Gandolphi camera were the primary tools used to identify the minerals. Natrolite and chabazite are both suspected as minor mineral components in several locations. Other minerals such as celestite, ankerite, and clay (illite type), were found in the process of looking for zeolites. The conclusion of this study is that the abundant presence of analcimite indicates that the temperature regime associated with volcanism is relatively low, probably no higher than 120 - 130 degrees Centigrade. This is not enough heat to degrade hydrocarbons to a non-commercial state. The results from this preliminary study indicate that thermal contribution to the trapping system by past volcanic events in the area does not increase risk of successful oil well drilling.

ZEOLITE DETERMINATION & GEOTHERMOMETRY INTERPRETATIONS ASSOCIATED WITH BURIED VOLCANIC ROCKS IN OIL FIELDS IN NORTHWESTERN MISSISSIPPI

INTRODUCTION

A proposal was submitted to and funded by MMRI to study zeolites that are associated with volcanic and hypabyssal rocks in the subsurface of northwestern Mississippi» The determination of specific mineralogy of zeolites has been more difficult than anticipated. Developing techniques for obtaining conclusive information for ident ification and analysis of the fine grained volcanic rock, took a great deal of time and experimentation.

SCIENTIFIC DISCUSSION

The oroblem addressed in this oroject is the determination of the type and distribution of zeolites present in volcanic and other associated rocks in selected areas of northwestern Mississippi. Areas *of* special interest are those associated with oil field and/or potential hydrocarbon traps involving centers of volcanic activity.

The volcanic rocks in the area have been investigated by the principal investigator (see MMRI Final Reports, Sundeen, D. A», 1979, 19Ö0, 19Ö1, 1932). Previous work in the 15-county area □rövided the samples and thin sections for locating concentrât ions of zeolite mineralization (see Figure 1).

The presence of volcanic flows, plugs, and volcanicl asties has been documented in most of the subsurface in northwestern and west-central Mississippi at depths of 2,300 to 1ø, øøø feet. Rock types have been determined by the principal investigator (PI) and assistants under my supervision (see Bibliography for list of publications and completed Masters theses)«

Although the rocks have been located and identified, only a sketchy picture of how they are distributed, connected, and how the volcanic structures are shaped has been determined« Major gravity anomalies that are suspected to be the product of igneous rock structures are common in the area. The overlapping of extrusive igneous rocks coming from the vents associated with the gravity anomalies is a strong probability.

In previous studies done by the PI, zeolites (?) were noted in thin sections, but lack of time prevented any major effort to determine which varieties were present« These suspected zeolites occurred in phonolites, nephelinites, vesicular basalts, and volcaniclastics throughout the 15-county study area. Some zeolite minerals have been located and tentatively identified from selected locations (Crawford, J. L. , and Sundeen, D, Au-1934).

All thin sections and petrographic reports from previous work were available for study by the PI and research assistant (RA). This permitted the speedy selection and separation of samples for the detailed study of suspected zeolites. This concluding study attempted to determine what zeolites were present and how they were distributed throughout the 15-county area. However, this last year's effort spent most of the time looking for zeolite bearing rocks that were associated with a few oil fields and potential structural traps associated with large positive gravity anomalies in Humphreys, Leflore and Holmes count i es.

The details of tectonism during the Mesozoic era is unclear, but as the igneous history becomes more defined and better understood, a more concise picture of the Mississippi Embayment, the buried Ouachita front and its relation to the Appalachian tectonic front should emerge. The results of such studies (like that of zeolite minerals) will provide additional data for interpreting events associated with volcanism.

Previous studies in the area by the PI and assistants have been aimed at seeking out potential mineral resources. As an explorat ion aid, Mumpton (1961) states about zeolites thats

"Recent studies in Japan indicate that zeolite assemblages in altered tuffs can not only delineate the conditions of formation of certain ore deposits but also serve as exploration tools, especially in areas of thick overburden. Yoshida and Utada (1969) and Utada et al. (1974) noted that analcime rich aureoles surrounding Kuroko-type mineralization in Neogene sediments of the Green Tuff region are thickest in the vicinity of majoy ore deposits.

"Also, in Japan, Katayama et al (1974) attributed the concentrat ion of uranium to the presence of a heulandite-cl inopt il ite zeolite in tuffaceous sandstones of Miocene age near Tono, Gigu Prefecture. Oxidized uranium in ground water is presumed to have been adsorbed on the zeolite, which in some zones contains as much as 2.5* U."

Another aspect of the zeolite investigation involves the nuclear waste isolation technology industry. There is a strong affinity for the removal of such elements as radioactive cesium and strontium from contaminated wastes by the zeolite c1inooti1 ite. Once the capacity to absorb the waste is reached, the solid can be oackaged and buried. This and similar methods are used in many places throughout the industrialized world

(Canada, Great Britain, France, Bulgaria, Hungary, Mexico, Japan, Germany, USSR, and USA). For instance, a tuff rich in chabazite and phillipsite in the Eifel region of Germany (marketed as "FiItro—lit") is useful in removing Cs 137 from waste in streams. The zeolite-rich Neopolitan tuff (Naples, Italy) is used routinely to successfully remove radionuclides from cont aminated liquid waste at Gasacela, Italy.

Should nuclear waste be stored in Mississippi, a secondary industry may be developed in the state to produce zeolites, or zeolit ie tuff for waste packaging, for clean—UP in the event of a spill, for preparation of waste to be shipped from the Port Gibson nuclear power plant, or possibly for locating a deep subsurface storage site in the zeolite—bearing volcaniclast ics themselves.

EROELEM STATEMENT

LANDSAT st udy and development has been progressing in Mississippi. Successful implementat ion of this technology has been realized when applied to petroleum exploration in areas outside of our state. As a result, local interest for its appi icat ion to identify potential gas and oil prospects has been nenerated. The results of this study supplements a concurrent LNDSAT project in northwestern Mississippi.

Gravity data are being gathered and processed by others to determine the shape of suspected volcanic features in the subsurface. Gravi ty models help select the best prospects for drilling a wildcat we 11. For instance, if an old volcanic feat ure in a marine setting can be modelled to show a coralline limestone cas-rock can now buried under several thousands of feet of sediment, then this strucure can be high-graded to a preferred prospect. If zeolites (temperat ure-sensit i ve minerals) in the volcanic rock around this orospect appear to have a relatively low equilibrium temperature, that would indicate that the gas and oil has not been destroyed by volcanic heat from subsequent igneous events» This type of geological information would encourage investment in oil and gas exploration in Mississippi (Figures 2, 3).

RESEARCH OBJECTIVES

The research objectives were as follows:

(1) Find and report on the type, relative abundance, and distribution of zeolites found in volcanic and volcaniclastic rocks»

(2) Determine the thermal maxima associated with the zeolites. This requires both ident ification of the mineral type and also knowing the chemical composition« X-ray diffraction (XRD) and microprobe analysis are used to obtain this data.

(3) Integrate the information with concurrent LPNDSAT and gravity projects underway in other MMRI projects,

(4) Develop methodology and expertise for future work in zeolite studies for application in other areas and rock t y pes«

METHODOLOGY

Personnel

Mr. James Crawford ard Mrs. Cyrthia Fintou! (graduate students in the Geology department at USM), and Jonathon Lewis (an under graduate student at USM), along with the PI, have carried on the study of Mississippi zeolite minerals. The urdergraduate assistant helped me primarily in inventorying data, keeping base maps updated, providing assistance in sample preparation and data gathering when needed»

Equipment

Petrograph ie microscopes, re f r act ion index oils, SEM, EDAX, standard X-ray di ffractometer, Gandol ph i x-ray camera, and thin sect ioning facilities were available for use by the the Geology department at USM. A1so, m i croprobes at two other Geology Departments were available to use for detailed chemical analysis of about 10 selected represent at ive zeolites samples from the study area.

The Gandolphi is a special type of XRD recording device. It is a specially designed circular box that contains 35 mm film, the sample holder, has a small entry port for X-rays from a standard generator, and an exit tube with a fluorescent target used to align the sample in the X-ray beam (see Figure 4). The advantage to the Gandolphi camera is that a very small sample can he used. It does not have to be crushed to form a powder. Instead, the sample is mounted on a glass rod, centered in the camera with a centering microscope, and a motor is attached to spin the sample in the X—ray beam. Not only does the sample spin, but because of the manner in which it is mounted, it rotates the sample as well. This has the effect of giving one or two crystals an infinite number of orientations over a 4-hour exposure period. The reflections and their intensities are recorded on the film and measured after developing. The advantage to all of this is that minerals in volcanic rocks that have small mineral grains, especially in the matrix where the zeolites are most abundant, can be studied with XRD techniques.

Procedure

A summary of the procedure is presented in the list below:

(1) Reviewed data from previous reports from about 3øø wells in the 15-county area; the total area was reduced to a 3—county area (Holmes, Humphreys, and Leflore, Figure 1) due to a time shortage and equipment problems.

(2) Isolated and then determined zeolite mineral type using both the polarizing microscope and various x-ray techniques. The standard procedure described by Azaroff and Buerger (195Ö) in their classic text The Powder Method was used to read the film and convert the readings to d-spacings. A form was designed to record the values and automatically reduce them to a d—spacing. However, the final step was not completed, and a Hewlett-Packard HP-15 programmable calulator was used to incorporate 1«) the readings from the 114 mm camera, and 2.) the filtered Cu radiation wavelength to determine the reported d-spacing values.

(3) Selected 1® of the best and most representat ive samples for microprobe chemical analyses. (This data has yet to be

furnished and will not be in this peport.)

(4) Selected several known zeolites and ran a tiny representat ive fragment on the Gandolphi camera to confirm the cited capability. Also, a known mineral (quartz) and a blank (just the glass mounting rod and a glob of rubber cement), were run to be sure that no lines were added or deleted because of technical oversights.

PRELIMINARY RESULTS

Thin sections of volcanic rocks from Holmes, Humphreys and Leflore counties were examined (and are being re-examined on the basis of the results), and samples were identified for extraction of small amounts of minerals suspected to be zeolites. A number of cores from the Union Producing, #1 C. B. Box, well in Humphreys county were selected for detailed mineral study.

The mineral collection in the Geology department has a number of samples of known zeolites. They were sampled and run on the Gandolphi camera to double check the mineral label and to test the ability of the camera to record the major d-spacing lines diagnostic of their types. The results of the runs on the standards are given in Table 1. For the most part, there is a strong correlation between the d-spacings observed and the d-spacings given in the JCPDS Mineral Powder Diffraction File; Search Manual (Bayliss and others, 1980).

In addition to the standard zeolite minerals, the results of the quartz known and the blank are given in Table 1, also.

The unknown minerals studied to date had the morphology of fibrous natrolite and cubic analcite. However, they turned out to be celestite, a strontium sulfate, and ankerite, a calcium/iron/ magneium carbonate respectively. An altered feldpsar phenocryst was analyzed, and it turned out to be an illite type clay mineral. The clay was expected, but the celestite and ankerite came as a disappoint ing surprise. The results of the XRD study of these three minerals are given in Table 2.

About 20 samples are being processed. The best samples will be sent off to Virginia Tech for microprobe work. It is expected tahi the results will be available within three months. An addendum to this report will be furnished at that time.

It is expected that the zeolite—appearing minerals will be primarily analcite. It is possible that natrolite and chabazite will also be identified. The most intense characteristic ri-spacings of the more common zeolites are given in Table 3.

CONCLUSIONS

If this estimate of the presence of analcite holds up with the new information, then the prediction of the approximate upper temperature limit of 120 to 125 degrees Centigrade would be in order (Fig. 2). The presence of illite indicates that the maximum value may be from 123 degrees Centigrade (see overiac of analcite and illite in Figure 2).

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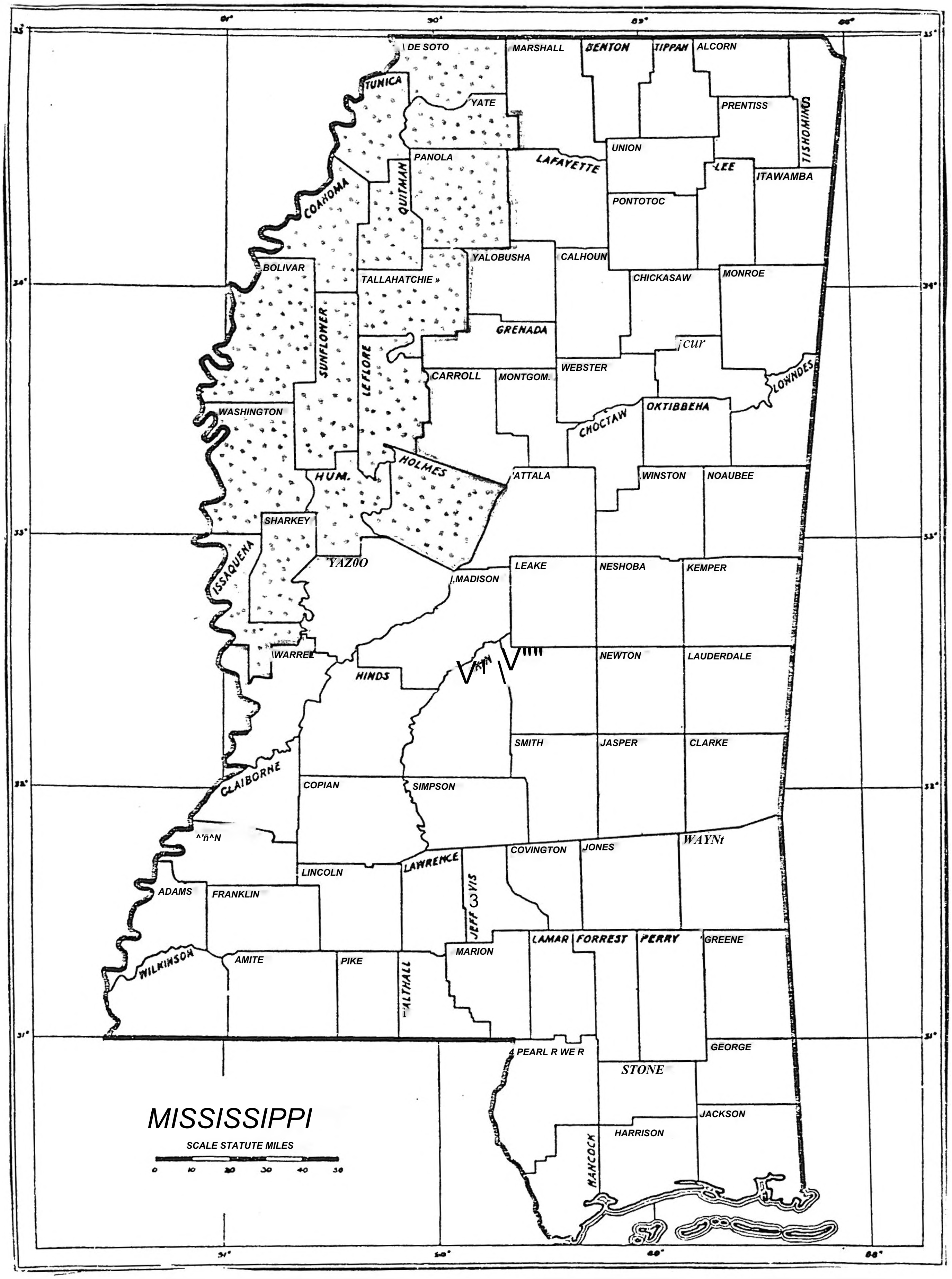


Figure 1 Map of a 15-county area in west-central & northwestern Mississippi where previous studies funded by MMRI have generated an extensive inventory of samples and thin sections.

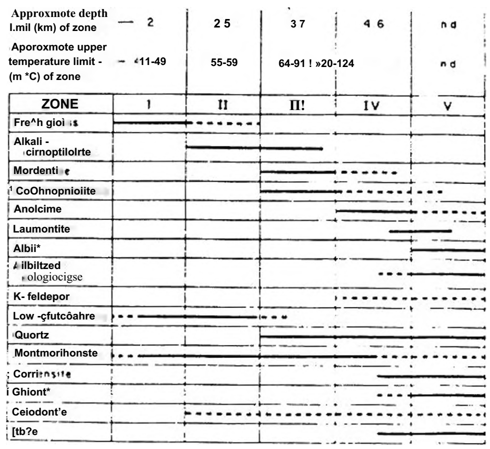


Figure 2. Stability ranges of authigenic minerals in the Niigata oil field (modified after Iijima and Utada, 1972). Dashed line denotes rare occurrence.

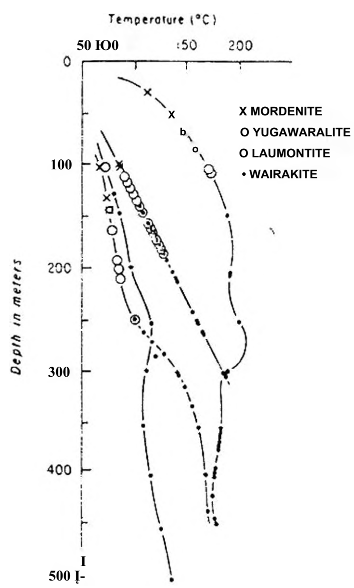
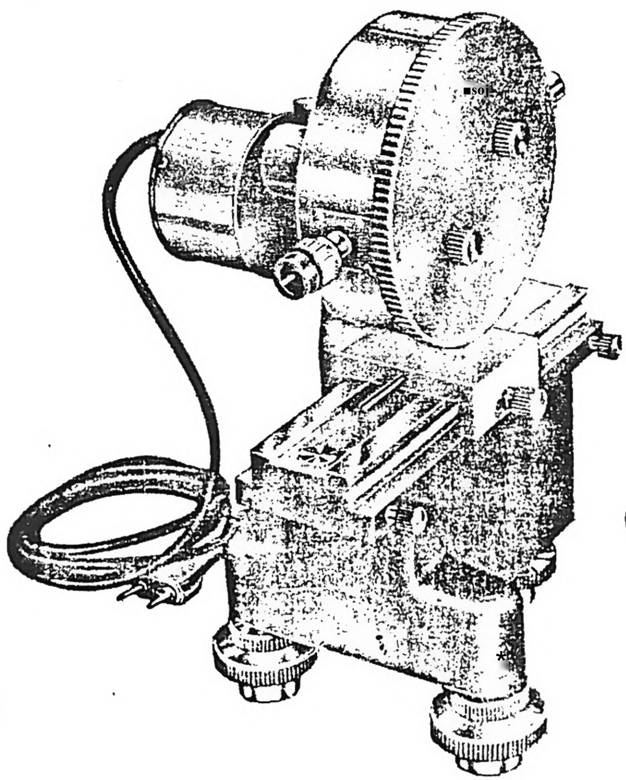


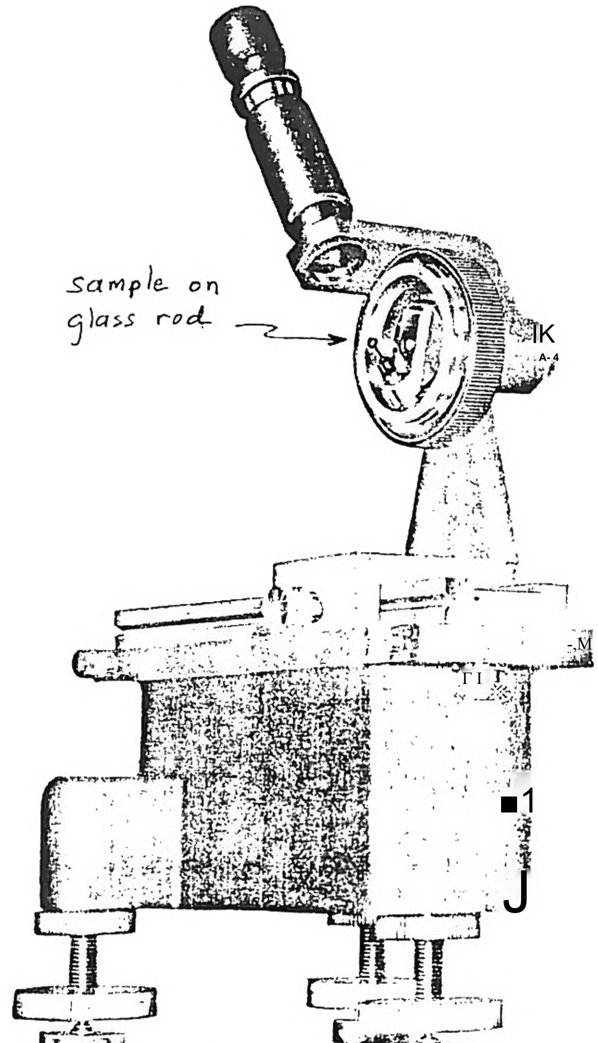
Figure 3. Geothermal gradients and zeolite distribut ions in the Katayama geothermal area, Onikobe, Japan. (From Seki, and others, 1929) \

SPECIAL FEATURES



A

- COMPLETE POWDER PATTERN FROM SINGLE CRYSTALS AS SMALL AS 30 MICRON or from powder
- CAN BE USED AS SINGLE CRYSTAL CAMERA or Debye-Scherrer
- CAMERA CAN BE USED TO STUDY ZONED CRYSTALS, RECORDING POWDER PATTERN FOR EACH ZONE
- POWDER PATTERNS CAN BE OBTAINED WITH-JTH GRINDING CRYSTAL SO CRYSTAL CAN BE STUDIED FURTHER
- MOUNTS ON ANY STANDARD TRACK OR OPTIONAL TRACK AVAILABLE
- CAN BE OPERATED IN AIR, VACUUM OR ATMOSPHERE
- PATTERNS GAIN IN SHARPNESS OF THE RECORDED REFLECTIONS BY USING VERY SMALL AND SPHERICAL CRYSTALS WHICH WILL BE ALSO AFFECTED LESS BY ABSORPTION ERRORS AND CYLINDRICAL SAMPLE EFFECTS



B

Figure 4. a.) The Gandolphi camera used in this study. It is the 114. & mm variety, the X-rays enter edge of the camera through the tubular oort which is inserted into the X-ray generator. The smaller cylinder with the attached cord is the motor that spins the sample. The camera and motor is mounted on a track that has three adjustable legs that are used to align the system so that the X—rays pass through the samóle. b.) H photograph of the microscope centering device used to align the sample in the camera holder.

TABLE i. D-SPACING DATA FOR STANDARDS RUN ON THE GANDOLPHI CAMERA

Standard Quartz	JCPDS File No- 5-0490	Standard Natrolite	JCPDS File No. 22-122 J 4-
4.71 (5)*	— —	6. 44 (1øø)	6* 53 (50)
4*25 (Gø)	4.26 (35)	5* 78 (3ø)	5. 90 (1øø)
3*71 (10)	— —	4.55 (1ø)	4*61 (25)
3*345 (100)	3.343 (100)	4. 32 (1ø)	4* 38 (50)
2*462 (20)	2.458 (12)	4. 09 (15)	4. 12 (12)
2« 280 (30)	2.282 (12)	— —	3. 17 (50)
2.240 (1ø)	2*237 (6)	[illegible] (3ø)	3. 11 (25)
2*132 (30)	2. 128 (9)	— —	2*914 (5)
1*984 (20)	1*980 (8)	2. 83 (1øø)	2* 851 (1Й)
1*822 (80)	1*817 (17)	2. 53 (1ø)	2. 58 (25)
1.672 (40)	1.672 (7)	2. 42 (1ø)	2* 425 (25)
1*541 (45)	1.541 (15)	2* 17 (5ø)	2. 187 (15)
1.380 (80)	1.382 (7)	— —	1. 881 (15)
— —	1*375 (11)	1.86 (2ø)	1. 807 (25)
		1* 79 (1ø)	1792 (5)
		1.77 (1ø)	1* 749 (10)
		1.72 (2ø)	— —

Standard Laumontite	JCPDS File No. 15-0278	Standard Laumontite (cont.)	JCPDS File No*
9* 31 (1øø)	9. 49 (1øø)	3. 038 (30)	3. 033 (25)
6» 9*5 (9ø)	6» 86 (35)	2* 894 (5)	2. 88 (14)
6« 1 1 (5)	6* 19 (Ep) +	2. 830 (5)	— —
5* 08 (5)	5* 052 (6p)	— —	S» 798 (2)
4* 758 (5)	4. 731 (2ø p)	2. 751 (5)	— —
4* 501 (5)	4. 500 (8o)	— —	2. 6E9 (4)
4*255 (1ø)	4. 314 (2)	2. 569 (1ø)	2. 575 (14)
4. 152 (5)	4. 158 (60)	2. 457 (1ø)	2. 463 (4)
4„ 049 (5)	— —	— —	2. 439 (14)
— —	3. 768 (2)	2. 359 (1ø)	2. 361 (12)
3* 865 ((5)	3* 667 (14)	2. 154 (5ø)	2. 153 (18)
3* 555 ((5)	3* Slø (3øp)	2. 069 (5)	2. 082 (2)
3*447 (5ø)	3*411 (8p)	[illegible] (1ø)	[illegible] 060 (2)
3. 290 (5)	3. 272 (2ø)	[illegible] (5)	1.955 (12)
[illegible] (3ø)	3. 205 (8)	1.835 (5)	1.887 (4)
3. 148 (15)	3. 152 (16)	1» 756 (5)	— —
		1.518 (25)	1.517 (?)

Standard
Blank (glass rod and wad of rubber cement)

no lines on the developed film

* (5) parenthesis indicates intensity of line; visual estimate for USM standard values

+- (2p) indicates that the sample was in a preferred orientation for the intensity readinn given

TABLE i. D-SPACING DATA FDR STANDARDS RUN ON THE DAMDDLPHI CAMERA
(coot in tied)

File No.

[illegible]

TABLE r. D—SPACINGS OF SEVERAL MINERALS FROM UNION PRODUCING CO., #1 C. B. BOX, WELL IN HUMPHREYS COUNTY. MISSISSIPPI

Standard Celestite *	JCPDS File No. 5—0593	Standard Ankerite*	JCPDS File No. 12-0088
—, .--	4. 23 (11) +	3. 70 (40)	3. ¯/0 (4)
3.75 (5)	3. 77 (35)	2. 91 (100)	2. 899 (100)
3-40 (100)	3.57 (2)	2. 69 ((5)	2. 685 (4)
3-29 (1ø©)	3. 295 (100)	2. 41 (40)	2- 411 (6)
3.. 16 (100)	3. 177 (59)	2. 20 (40)	2. 199 (6)
2.974 (Sø)	2. 972 (100)	2. 03 (40)	2« 02 (4)
2-716 (50)	2. 731 (63)	1.86 (5)	1.852 (21)
— —w	2. 674 (49)	1 « 82 (60)	i «812 (G)
[illegible]	2. 258 (18)	1,80 (60)	1.792 (6)
2. 143 (5)	2. 141 (25)	1.57 (5)	1.569 ((1)
2-056 (5ø)	2. 045 (55)	1.55 (30)	1,548 (1)
— ww.	2.041 (57)	i. 48 (5)	1.468 (1)
2-011 (3ø)	2. 006 (40)	1.40 (30)	1. 391 ((1)
—·—	i » 999 (46)	1.39 (20)	1.34 (<1)
í - 758 (20)	1.7 69 (17)		
1.694 (20)	1.691 (3)		
1-610 (2ø)	1.60 ‑L (15)		
1.487 (lø)	1 - 475 (16)		

Standard Illite 2m2**	JCPDS File No. 24—*0494	Standard Illite 2m2	JCPDS (cont.) File No. 24-Θ494
10.46 (100)	lø. 3 (100)	— -	2. 182 (20)
—·—	5. 06 (45)	2.569 (95)	2.583 (20)
4-459 (100)	4. 49 (65)	2.383 (30)	2. 402 (16)
— —	3» 92 (2'5)	2.176 (25)	2. 186 (8)
3-655 (70)	3. 68 (45)	1.983 (25)	2« 006 (35)
3.314 (65)	3. 35 (65)	1.646 (30)	1.668 (16)
→ —w	3.21 (30)	1.501 (80)	1.500 (35)
3.069 (60)	3. 07 (45)	1.296 (lø)	1.292 (12)
——	2. 86 (25)		

* from phonolite-appearing core at approximately 5,590 to 5,610 ft., sample #284

t~ (li) parenthesis indicates intensity of line? visual estimate for core-mineral values

♦# from altered phenocrysts in phonolite-appearing core taken at approx imately 5,610 to 5,630 ft., sample #290

TABLE 3. ZEOLITE MINERAL GROUP MAJOR D-SPACING VALUES*

Mineral	Composition	d-spacings+	JCPDS File No«
Analei me	NaAlSi2D6.HEO	3» 43 5« 60 LL» 93	19~11Bø
Chabazite	CaAlSi8024. 12H20	£« 93 4. 32 9. 35	19-0208
Cl inopt i 1 ite	(Na, ЮБ, (Si,Al)36072 L 20H2>0	3» 97 8. 99 3. 91	[illegible]
Harmot ome	Ba(A1ES i 6016). SHED	7« 13 3, 17 8« 13	25-0855
Heul and ite	CaAlESi7018. 6H20	3« 92 I. 96 8. 85	£1-0131
		8« 95 3. 98 7. 93	25-0144
Laumontite	CaAlESi4012)«4H20	4. 16 3. 51 9. 50	26-1047
Natrol ite	NaEA1ES i 301ø.EHEO	2« 85 5.89 2. 72	20-0759
		6.49 5. 90 4„ 15	19~1185
Phi 11i esite	LCa(A13SÍ5D16).6HE0	7. 18 7« 16 3a 21	26-1310
Scolecite	Ca(AlESi3O10)«3H20	A.04 E. 88 6. 59	26-1048
Stilbite	CaAl£Si70i8«7H£0	4. 06 4. 04 9. 11	24-0894
		9. 12 4. 06 4. 63	26-0584
		9« 04 4. 07 3. 04	18-1203
Thomsonite	NaCa2(A15Si502ø)«6Hc >0	2. 86 4. 64 2. 68	19-1344

* From Mineral powder diffraction file (Bayliss, and others, 1980)

+· d-spacings listed in decreasing order of intensity