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Origin of the Riley travertine as constrained by the clay mineralogy of acid- and EDTA-insoluble residues

by

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Introduction

The Riley travertine is an unusual and potentially economic limestone deposit of Plio-Pleistocene age in northwestern Socorro County, New Mexico (Fig. 1). This paper investigates the clay minerals present in the insoluble residues of the Riley travertine to constrain its origin.

The origin of the Riley travertine is controversial because of its highly varied morphology. Opinions vary widely and include playa-lacustrine deposition, pedogenesis (caliche), spring deposition (travertine), and pervasive secondary calcite formation (nonpedogenic calcrete). Previous work, covered in Barker (1983), which bears directly on this paper is summarized in Table 1. Earlier studies in the area of this report include Barker (1983), Chamberlin and others (1982), Massingill (1977), Kottlowski (1962), and Denny (1940, 1941). The origin most supported is that of caliche deposit (pedogenesis).

The clay-mineral assemblages of proposed depositional environments of the Riley travertine can be used to constrain the possible origins. After reviewing over 300 published and unpublished references on calcrete and caliche, Goudie (1972) states that the clay mineral fraction, most frequently contains sepiolite and palygorskite (attapulgite) but may also contain other clay minerals. Based on this and other work summarized in Table 2, the presence or absence of attapulgite and sepiolite along with their relative abundance, favors some depositional environments over others.

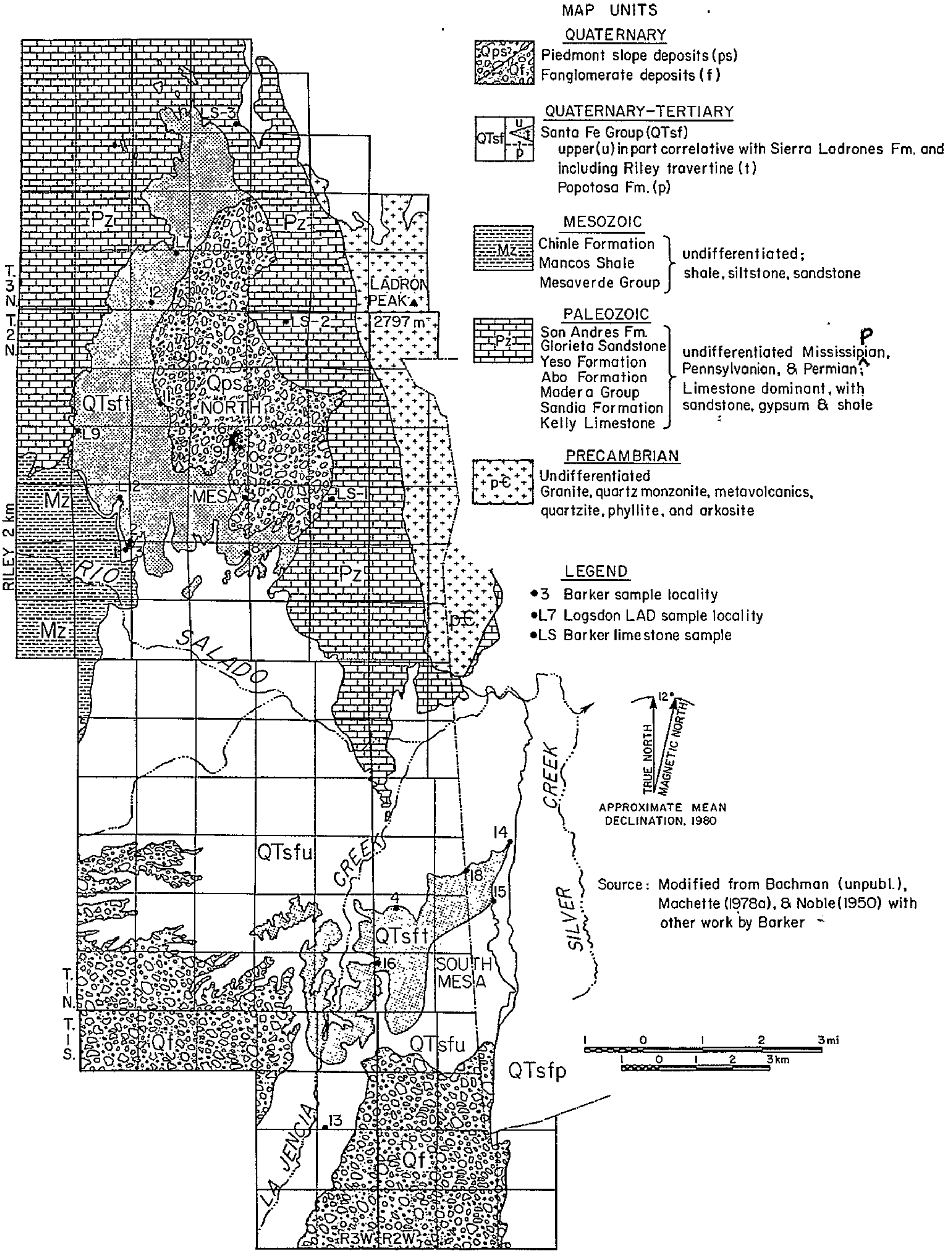
MAP UNITS
QUATERNARY
Qps? Qf
Piedmont slope deposits (ps)
Fanglomerate deposits (f)
QUATERNARY-TERTIARY
QTsf u t p
Santa Fe Group (QTsf)
upper (u) in part correlative with Sierra Ladrones Fm. and including Riley travertine (t)
Popotosa Fm. (p)
MESOZOIC
Mz
Chinle Formation
Mancos Shale
Mesaverde Group
undifferentiated; shale, siltstone, sandstone
PALEOZOIC
Pz
San Andres Fm.
Glorieta Sandstone
Yeso Formation
Abo Formation
Madera Group
Sandia Formation
Kelly Limestone
undifferentiated Mississipian, Pennsylvanian, & Permian;
P
Limestone dominant, with sandstone, gypsum & shale
PRECAMBRIAN
p€
Undifferentiated
Granite, quartz monzonite, metavolcanics, quartzite, phyllite, and arkosite
LEGEND
•3 Barker sample locality
•L7 Logsdon LAD sample locality
•LS Barker limestone sample
12°
TRUE NORTH
MAGNETIC NORTH
APPROXIMATE MEAN DECLINATION, 1980
Source: Modified from Bachman (unpubl.), Machette (1978a), & Noble (1950) with other work by Barker
0 1 2 3mi
1 0 1 2 3km
T. 3 N.
T. 2 N.
T. 1 N.
T. 1 S.
RILEY 2 km
Pz
Mz
QTsft
Qps
NORTH
MESA
LS-3
LS-2
LS-1
L7
L9
L12
LADRON PEAK
2797 m
p€
RIO
SALADO
QTsfu
CREEK
SILVER
CREEK
SOUTH MESA
QTsfp
Qf
LA JENCIA
R3W
R2W
1
2
3
4
5
6
7
8
9
11
12
13
14
15
16
18

Figure 1. Generalized geologic map of the Riley travertine and adjacent area.

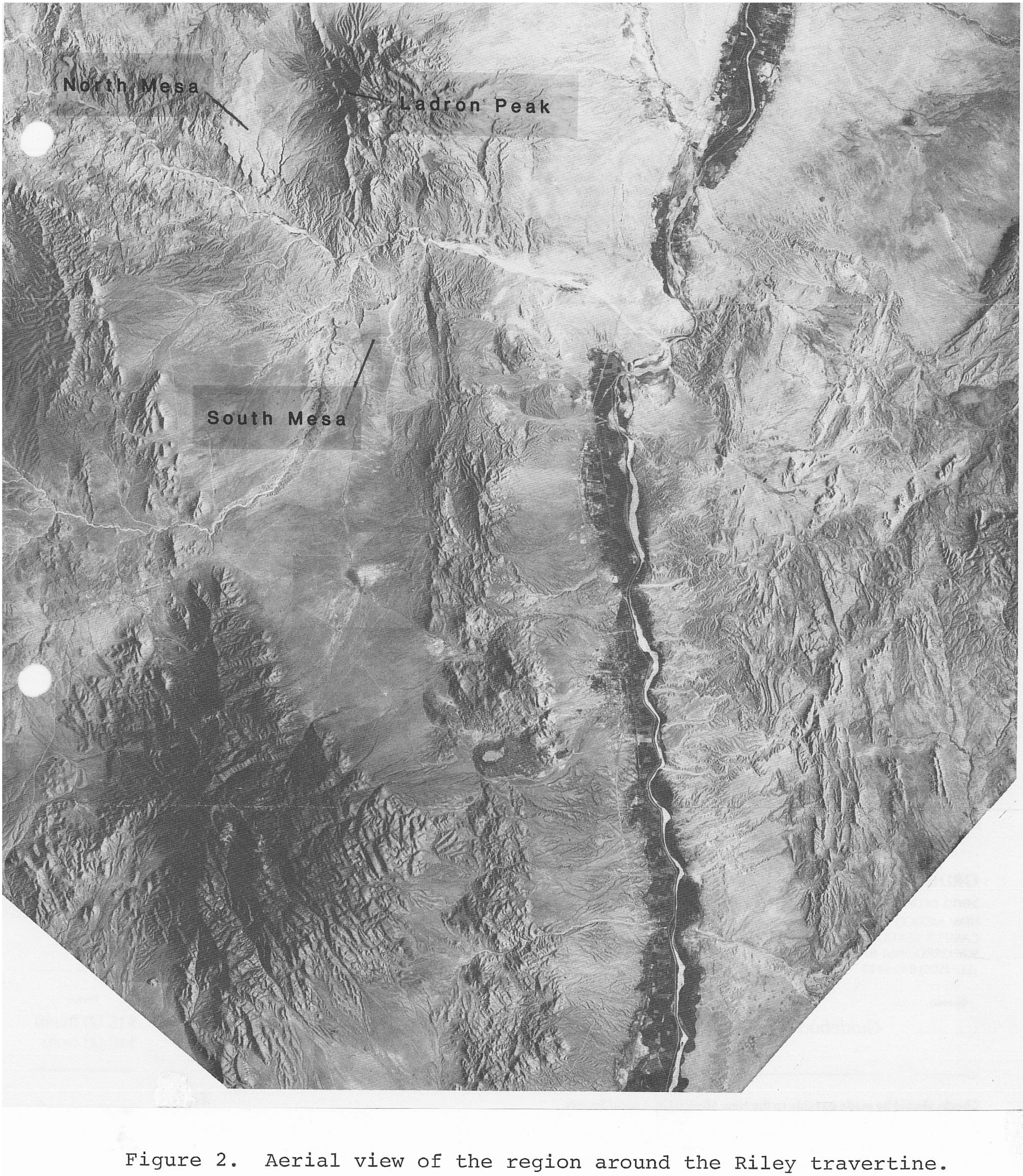
North Mesa
Ladron Peak
South Mesa

Figure 2. Aerial view of the region around the Riley travertine.

Source: NMGS Guidebook, 34th Field Conference, 1983, Socorro II

Worker (Publication date)	J.M. Barker (1983; and this report)	R.M. Chamberlin and others, (1982)	G.C. Massingill (1977)	F.E. Kottlowski (1962)	C.S. Denny (1940, 1941)
Nomenclature used in study	Riley travertine at north mesa (west of Ladron Mtns); Riley travertine at south mesa (west of Silver Creek)	travertine or high-calcium limestone	travertine or carbonate unit	Riley travertine	Caliche forming on Tio Bartolo surface at west slope Ladron Mtns. and Snake Ranch Flat
Portion Studied	All of both north and south mesas	about half of north mesa	limited area around manganese prospects on north mesa	All of both north and south mesas	All of both north and south mesas
Morphology of Limestone	laterally complex, including laminated, massive, massive vuggy, nodular, and reworked	crusted, banded, and fragmented	banded, porous-spongy or dense-structureless; some laminated, algal- or oncolite-like textures	massive bedded or laminated	fine-grained massive, nodular, or horizontally banded; locally abundant cavities
Analyses	clay minerals in insoluble residue: smectite, illite, kaolinite	large portions estimated to exceed 95% $CaCO_3$	dominantly $CaCO_3$ with some sand and silt	>99% $CaCO_3$ with some quartz silt	-------------------
Thickness	$\leq$ 15 m (surface) $\leq$ 25 m (subsurface)	1 to 8 m	$\leq$ 15 m	$\leq$ 6 m	$\leq$ 6 m
Age	1 - 3 m.y.	Plio-Pleistocene 1-3 m.y.	< 3.5 million years < late Pliocene	Cenozoic	Quaternary
Origin	complex lateral groundwater system with surface, spring, lacustrine, reworked, and subsurface pervasive-carbonate facies	springs at toes of limestone-rich alluvial fans and groundwater system flowing southwesterly of Ladrons	spring-fed lake (probably warm)	lacustrine limestone in a playa	calcite-cemented alluvium; calcite deposition in small fluvial pools; lime accumulation in B horizon by evaporation
Carbonate Source	Paleozoic limestone east, north, and west of north mesa; San Juan Basin contribution is possible	Paleozoic limestone fragments in piedmont slope deposits	-------------------------	Pennsylvanian limestone of Ladron Mtns. and limestone in Yeso and San Andres Fms. to the northwest	carbonate charged ephemeral streams from limestone region of Ladron Mountains

Table 1: Summary of major conclusions of prior workers on the Riley travertine.

Worker (Date)	Environment			Mode of Formation			Remarks
	Soil	Alkaline Lake Playa	Fresh-water Lake	Alt. of Precursor	Direct Precipitation	Clastic	
Khoury, *et al.* (1982)		S		S(?)	S		Mg(+), pH(+), evaporation (-)
Galan and Ferrero (1982)		S, A		A	A, S		Mg(+), SiO_2(+), pH(+); arid=S, wetter=A; S:A=inverse
Frye, *et al.* (1978)							reaffirmed A/S zones of Glass et al (1973), *S:A=inverse; many soils without A or S*
Post (1978)	S(?)	S			S		Mg(+), pH(+)
Frye, *et al.* (1974)	A	S	S	A(?)	A,S		Mg(+), SiO_2(+), pH(+), arid, hot
Glass, *et al.* (1973)	A	S		S,A?		A?	detrital A in post-Ogalla rocks; Mg(+), SiO_2(+), pH(+), montmorillonite alters to S
Goudie (1972)	A(+), S(-)				S,A		Summary of 300 papers prior to 1972; Mg(+), SiO_2(+), pH(+); montmorillonite alters to S
Papke (1972)		S			S		Mg(+), pH(+), evaporation(+)
McLean, *et al.* (1972)	A	S,A			S,A	S,A	Mg(+), SiO_2(+), pH(+), dessication; S & A in soil mostly reworked

Notes: + = major or dominant or high; - = minor or trace or moderate
? = association uncertain; supported by some evidence only;

Sepiolite = $Mg_3(S_{14}O_{11}) \cdot 11H_2O$
Attapulgite = $MgAl_2(S_{14}O_{10})\ (OH)_2 \cdot 4H_2$

Table 2: Summary of relationships among continental deposits of attapulgite (A) and sepiolite (S).

Geographic and geologic setting

The Riley travertine occurs in two main masses (north mesa and south mesa) centered approximately 6.5 km west and approximately 17 km south of the summit of Ladron Peak and east-southeast of Riley (Santa Rita), New Mexico (Fig. 2). The Riley travertine is intermittently exposed by local erosion of overlying Santa Fe Group sediments along mesa edges facing the Rio Salado.

The Riley travertine of north mesa underlies approximately 46 km^2 in T. 2 N., R. 3 W. and T. 3 N. R. 3 W. on the west flank of the Ladron Mountains. At south mesa, it underlies approximately 21 km^2 in T. 1 N., R. 2 W., T. 1 N., R. 3 W., T. 1 S., R. 2 W., T. 1 S., R. 3 W., and a small portion of the Sevilleta Game Refuge on the west side of the Silver Creek drainage.

Access to the study area is via graded roads from Magdalena (US-60) or from Bernardo (exit 175 on I-25). When dry, the Rio Salado provides secondary four-wheel-drive access to both north and south mesas. North mesa is approached most easily from the north on ranch roads bearing southeastward towards the western slope of the Ladron Mountains from the county road to Riley. The south mesa is reached most easily from the Hudgins Ranch road which intersects US-60 east of Magdalena. All of north mesa and most of south mesa are on the Riley 15-min quadrangle with the remainder on the Magdalena 15-min quadrangle. Preliminary 7.5-min quadrangles are available.

The Riley travertine is a relatively undeformed member of the Santa Fe Group (Barker, 1983) deposited between 1 and 3 m.y.

ago (Chamberlin and others, 1982). It descends in elevation from north mesa to south mesa and overlaps progressively younger (Paleozoic, Mesozoic, and Cenozoic) units to the south.

The Riley travertine ranges from massive to laminar with locally significant reworked, vuggy, algae-like, and fragmented portions. This varied morphology is interpreted by Barker (1983) as follows.

> The limestone is the result of a nonpedogenic process producing proximal (surface and subsurface) and distal (subsurface) secondary carbonate deposits related primarily to lateral groundwater flow. The carbonate-charged water is interpreted to have been generated in Paleozoic limestones on the west flank of the Ladron Mountains and the southeast flank of Sierra Lucero in the late Cenozoic. These waters flowed over and through alluvial fans and other sediments into and down the axis of an elongate basin or valley draining southward. This drainage merged with an east-trending valley which drained eastward near the present latitude of San Lorenzo Canyon and emptied into the ancestral Rio Grande. Proximal spring, lacustrine, and reworked carbonate deposits were formed at the surface. They are contemporaneous with pervasive and expansive subsurface secondary calcite cementation of pre-existing host sediments. This depositional system is analogous in part to the ground-water calcrete (nonpedogenic) described in Western Australia by several authors (see for example Carlisle and others, 1978).

This model should yield clay-mineral assemblages that result from the depositional environment of the host sedimentary rocks or sediments and, therefore, that are varied. In contrast, one mode of formation would tend towards a single clay-mineral assemblage. If the Riley travertine is a caliche, attapulgite should be dominant over other clays. If it is an alkaline lacustrine-playa deposit, sepiolite should be dominant. A spring, fresh-water lake, or pervasive secondary origin should yield detrital clays -- such as illite, smectite, and kaolinite, typical for an arid climate acting on a Paleozoic limestone substrate.

Sampling and experimental techniques

Seventeen samples of the Riley travertine were collected in March 1983. Preliminary data, including clay mineralogy of HCl (10%) insoluble fractions, are published in Barker (1983). Additional work was done in the fall of 1983 to generate more gently derived insoluble fractions. These samples were partially digested using very dilute acetic acid followed by warm EDTA solution. The clay-size fractions of the insoluble residues were then analyzed by X-ray diffraction (XRD) for clay and detrital mineralogy.

Samples of the Riley travertine were treated initially with dilute (0.25 M) acetic acid as described by Ostrom (1961). Because of the samples' high calcium carbonate content, this proved too slow. The samples were purged of acetic acid by washing and decanting with deionized water. A 0.2 M solution of EDTA was then used for digestion as described by Bodine and Fernalld (1973). This greatly sped up carbonate solution but at much greater cost in reagents. The EDTA procedure was modified slightly as described below.

Carbonate-solution procedures

Acetic-acid method--Samples of the Riley travertine (approximately 150-gr) were scrubbed and washed thoroughly in deionized water. Then, they were crushed for 5 min in a Buehler concentric-ring vibratory crusher yielding a very fine carbonate powder. Such a fine grind ultimately caused problems in both dissolving methods used, because much of the carbonate material begins as clay-size particles. These, plus the larger particles dissolved into the clay-size range just before particle extinction, yielding persistent clay-size carbonate residues on the XRD slides. This change from Ostrom's (1961) procedure is not recommended since clay-carbonate separation is not possible until all the carbonate is completely dissolved. I left coarser particles (1 cm +) to insure that carbonate was always present so the acid would be less likely to attack the clays. Ostrom's (1961) recommendation of a -60 mesh grind should be used, because the relatively coarse carbonate can be separated easily from the liberated clay-size material at any time during the dissolving process.

Acetic acid, mixed to 0.25 M concentration, was added to the samples, which were stirred periodically until reaction was complete. The spent acid was decanted, and a new charge of 0.25 M acetic acid added for as many iterations as needed. With materials as rich in carbonate as the Riley travertine, dozens of charges of acid would be needed at the 0.9-liter charge size utilized. Thus, an EDTA-based procedure was initiated part way through the sample-dissolving stage.

EDTA method--Chelation of carbonate by tetrasodium ethylenediamine tetracetic acid (EDTA) affords a method of carbonate solution that does not affect original clay mineralogy. The method described by Bodine and Fernalld (1973) was used. Based on their charts, a 0.2 M EDTA solution (75 gm technicalgrade disodium EDTA in 1 liter deionized water at pH 12.5) was applied to the ground carbonate partially digested by acetic acid. The solution was heated to 90° C for 60 to 90 min using a continuous magnetic stirrer. After settling and decanting, a new charge of EDTA was added until the carbonate was entirely chelated. The problems caused by the very fine grind as described above were also present in this procedure.

After dissolution, decanting, and deflocculation, using deionized water only, the clay fraction was separated from the coarser insoluble particles. Standard clay-mineralogy techniques were then used as follows.

Following deflocculation, the dispersed clay was left undisturbed for 10 min. Then, eyedropper charges of the suspension were collected carefully from the topmost surface and deposited on glass slides until they were fully covered. Four slides of each sample were prepared as described above and then allowed to air dry overnight. The oriented slides thus derived are not useable for quantitative work because of size fractionation in the suspension column during drying. The larger kaolinites settle out first and then are masked somewhat by later mantling by the slower-settling smaller clays such as smectite or illite.

The slides were run on a diffractometer at 2° 2θ/min from 38° to 2°θ2 . The slide was then glycolated at 60° C for 3 hrs and a second run was made as described above. The slides were then heated to approximately 300-330° C (some to 390° C) for 1 hr and run hot as described above, except the span was shortened to 15°-2° 2θ. Controlled-humidity and cation-saturation runs were not done.

Clay-mineral reactions during carbonate solution

Two problems possibly developed using the acetic-acid or EDTA digestion techniques. These are destruction of clays, such as illite or smectite, by excess acidity and the alteration of attapulgite-sepiolite by either excessively acid or basic conditions.

The work by Ostrom (1961) in proving his technique showed no alteration in acidic solutions (if less than 0.3 M) for randomly interstratified illite-montmorillonite, chlorite, illite, or kaolinite. He did not include attapulgite or sepiolite. Carroll (1970, pp. 43-44) states that attapulgite and sepiolite require alkaline conditions for survival and that they are decomposed by acid and won't survive below pH 7. Other workers suggest pH 3 as the threshold. In addition, Khoury, *et al.* (1982) predict that chlorite will form instead of attapulgite-sepiolite at high pH and high Mg and/or Al. This prediction is based on their interpretation of the work of Siffert (1962, *in* Khoury *et al.*, 1982), who found that sepiolite precipitates at pH 8.5, trioctohedral smectite (mixed-layer kerolite-stevensite of Khoury *et al.*, 1982) at pH 8.5-9, and talc plus trioctohedral smectite at pH above 9. The EDTA solution used has a pH of approximately 12.5, which is possibly high enough to alter sepiolite-attapulgite to mixed-layer kerolite or stevensite (chlorite) plus talc (Ebrl, *et al.*, 1982). The XRD data suggest that no such conversion occurred during digestion of the Riley travertine since neither kerolite, stevensite, or talc were detected.

Bodine and Fernalld (1973) evaluated the effects of EDTA treatment on clay minerals. They found no significant alteration occurred with treatment times under 4 hrs. They examined chlorite and illite (mixture), montmorillonite, and kaolinite. They did not determine effects on attapulgite-sepiolite. Glover (1961) implied that EDTA treatment was less destructive than acid treatment where clays were involved, but he studied no clays individually. Hill and Runnels (1960) made a similar suggestion.

The original digestion using 10% HCl (Barker, 1983) produced clay-size residues containing kaolinite, illite, and smectite in order of decreasing abundance (Table 3). Treatment with this concentrated a solution of HCl probably biased the clay data so a less chemically harsh dissolution technique was used for this study. The presence or absence of attapulgite or sepiolite is significant in the identification of depositional environment, and the HCl technique might have removed or altered them.

Clay-mineral analysis

The clay size fraction of the insoluble residues from eight samples of Riley travertine were analyzed by X-ray diffraction techniques. The samples were deflocculated by repeated rinsings with deionized water and 10-min centrifugation cycles. No deflocculating chemicals were used.

Standard oriented slides were prepared by sedimentation (Stokes Law) techniques with their inherent bias (Stokke and Carson, 1973; Gibbs, 1965, 1968). This bias precluded meaningful measurement of clay-mineral percentages, and many of the illite curves are masked by mixed-layer clays. Thus, the following analysis is based on the presence or absence of significant clays rather than on relative abundance.

The XRD analysis was done on a Rigaku D-Max. Settings were copper fine focus at 40 KV and 25 ma. Slits were 1° divergence, 1° scatter, 0.3° receiving, and 0.3° monochromator. Each sample was run untreated followed by a glycolated run and heated (300° C and/or 390° C) runs.

Results

The mineralogy of the clay fraction, based on number of occurrences in the samples and in decreasing order is as follows:

- quartz
- feldspar (Na-Ca-K combined)
- kaolinite
- illite
- mixed-layer illite smectite (random and ordered)
- rhodochrosite
- amphiboles
- zeolite (clinoptilolite)
- vermiculite (masked)
- chlorite (masked)
- smectite (difficult to identify as mashed)
- superlattice clay or ordered mixed-layer (vermiculite-illite)

This is the mineralogy derived from acetic-acid/EDTA insoluble residues. In contrast, the harsher HCl-derived insoluble residues have a much simpler mineralogy in their clay-size fraction, as shown below:

Sample	Quartz	Plagioclase	K-spar	Hb	Kaolinite	Illite	Calcium Smectite
RTB 4	+	0	0	0	+	0	tr
RTB 12	0	0	tr	tr	0	0	0
RTB 13	+	+	tr	0	0	0	0
RTB 14	+	–	–	0	+	tr	0
RTB 15	+	+	–	0	0	0	0

Symbol	Relative abundance
+	major
–	minor
0	absent
tr	trace

Cu fine focus
KV = 40, ma = 25
K-spar = potassium feldspar
Hb = hornblende

Source: Barker, 1983

Table 3. Qualitative X-ray diffraction analysis of the fine fraction (-230 mesh) of selected samples of the Riley travertine treated with 10% HCl. The clay peaks were very small except for kaolinite.

- quartz
- feldspar
- kaolinite
- illite
- amphibole
- smectite

The minerals described below are from the EDTA/acetic-acid procedure. Each mineral is described by characteristic and common peaks seen in the samples.

Quartz

Quartz is identified by its characteristic peak at approximately 26.7° 2 θ. A common peak also occurs at approximately 21° 2 θ with some variability.

Feldspar

The feldspars occur from 27.5° 2 θ to 28.1° 2 θ with some variation depending on potassium, calcium, and sodium content. The various feldspars were not differentiated.

Kaolinite

Kaolinite is found in 85% of the samples examined. Peaks around 12.4° 2 θ, 20.5°(+) 2 θ, and 24.9° 2 θ are typical. Kaolinite is a very stable clay so it is least affected by acid or EDTA techniques and, thus, is dominant in both suites of analyses.

Illite

Illite is as common as kaolinte (85% of samples), but its main peak at approximately 8.8° 2 θ is masked by the broad illite-smectite mixed-layer "bump". Illite in untreated slides is typically represented by a "shoulder" on the mixed-layer

Sample Number	Clay minerals							Other minerals					Remarks
	K	I	S	C	V	ML	SL	Q	F	A	Z	R	
4	+	+	?	+?	+?	+(nr)?	0	+	+	-	0	+	no heated run
5	-	-	?	0	+?	+(nr)?	0	+	+	+	0	0	
7	+	+	?	0	0	+(r)	0	+	+	-	0	+	
8	+	+	?	0	0	+(r)	0	+	+	0	+	0	
9	+	+	?	+	0	+(r)	0	+	+	0	+	tr	
11	+	+	0	0	0	0	+	-	tr	+	0	tr	vermiculite-illite superlatice
12	tr	0	0	0	0	0	0	+	tr	0	0	tr	virtually no clay minerals
13	0	tr	?	0	0	+(r)	0	+	+	0	0	+	

K = kaolinite
I = illite
S = smectite
C = chlorite
V = vermiculite
ML = mixed-layer illite-smectite (random = r, ordered = nr)
SL = superlattice vermiculite-illite (?)
Q = quartz A = amphibole R = rhodochrosite
F = feldspar Z = zeolite (probably clinoptilolite)

? cannot be differentiated
+ present
- trace
0 absent

Table 4. Qualitative X-ray diffraction analysis of the acetic-acid/EDTA insoluble residues of selected samples of the Riley travertine.

curve, which separates somewhat upon glycolation. The illite peak is greatly sharpened and enhanced by heating of slides because of recrystallization of the mixed-layer clay.

Mixed-layer Illite-Smectite

Mixed-layer clays occur in 70% of the samples as a broad bump between approximately 3° 2 θ and 9° 2 θ. This range varies and usually includes a masked illite peak and often a masked vermiculite-chlorite one as well. The mixed-layer clays are frequently random, but one possible instance of an ordered mixed-layer clay was observed in sample 4. However, this could also be interpreted as a vermiculite or chlorite peak. Sample 4 has no heated run because of slide disintegration; consequently, a definitive answer is not possible. The broad mixed-layer peak shifts to a lower 2 θ upon glycolation (lattice expands).

Rhodochrosite

Rhodochrosite ($MnCO_3$) is found in 85% of the slides, usually in trace amounts. It is recognized by a sharp peak at approximately 31.4° 2 θ. The Riley area is noted for high manganese values including a once-active mine at north mesa. The probable source rocks in the Paleozoic carbonates also have appreciable amounts of manganese (Table 5). Four samples with peaks at 31.4° 2 θ were analyzed for $MnCO_3$ (Table 6). Measurements range from a trace to 0.25% manganese. Given the abundance of manganese and the close relationship between calcium and manganese carbonates, the presence of rhodochrosite is not unusual. Rhodochrosite is soluble in HCl, so it did not appear in the hydrochloric-acid treated samples (addendum 1).

Table 5. Analyses of selected samples of Riley travertine and other carbonates.

Sample	Description & location[1]	HCl insoluble (%)	HCl soluble (%)	$CaCO_3$ % (titr.)	Calcium % (titr)	Magnesium % (AA)	Strontium ppm (AA)	Strontium ppm (XRF)	Manganese ppm (AA)	Cadmium ppm (AA)	Cobalt ppm (AA)	O^{18} SMOW	C^{13} PDB
RTB 1	basal, laminated NM	2.20	97.80	92.15	36.9	0.26	1300	1483	34	6	<30	+24.2	+6.8
2	upper massive NM	0.47	99.53	97.89	39.2	0.23	639	775	81	7	32	+23.7	+6.2
3	middle, mass. to lam. NM	14.47	85.53	87.66	35.1	0.27	583	807	53	6	<30	+23.7	+7.0
4	massive SM	16.27	83.73	79.16	31.7	0.39	278	490	35	6	<30	+23.2	+0.6
5	laminated NM	1.14	98.86					1087					
5a	laminated NM	0.96	99.04					1099					
6	laminated NM	2.03	97.97					933					
7	massive NM	5.74	94.26	92.40	37.0	0.23	528	710	117	5	<30		
8	massive NM	4.11	95.89	95.65	38.3	0.22	635	857	23	5	<30		
9	crudely laminated NM	6.32	93.68					1083					
10	travertine facies NM	8.26	91.74	91.64	39.1	0.30	757	1099	150	7	<30		
11	massive, some recrystall. NM	10.01	89.99	96.89	38.8	0.33	462	608	78	8	<30		
12	massive, some recrystall. NM	2.43	97.57	99.64	39.9	0.22	416	555	1123	5	32		
13	calcrete not Riley traverine	21.07	78.93					569					
14	massive SM	27.34	72.66	64.93	26.0	0.38	396	488	114	4	28		
15	massive, recryst. SM	29.04	70.96	83.66	33.6	0.38	318	331	84	6	35		
16	massive SM	4.58	95.42	93.40	37.4	0.34	<300	373	56	7	<30		
18	massive SM	12.39	87.61					233					
LAD 7	Chamberlin et al.1982 NM				>20	0.15	500						
9	Chamberlin et al.1982 NM				>20	0.3	1000						
12c	Chamberlin et al.1982 NM				20	0.2	700						
12d	Chamberlin et al.1982 NM				>20	0.5	1500						
MATB	travertine, Lucero Quarry	0.91	99.09	98.39	39.4	0.27	471	617	37	6	30		
LS 1	Madera Group Ls., Ladron Mtns.							759					
2	Madera Group Ls., Ladron Mtns.							1,339					
3	Madera Group Ls., Ladron Mtns.							759					
Kottlowski, 1962 Riley trav.			99.46	40.04	0.13								

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1) NM = north mesa; SM = south mesa

Source: Barker, 1983

Amphibole

I did not differentiate the various peaks from 10 to 11° 2θ but rather assigned them to the general class of amphiboles. Depending on composition, a range of peaks is possible, and the varied lithologies of provenance areas open possibilities beyond the scope of this paper.

Zeolites

A strong peak at 9.8° 2θ with a secondary peak at 22.3° 2θ indicates clinoptilolite. The presence of a zeolite in 25% of the samples is not unexpected, since these are very common sedimentary minerals in arid terranes. Zeolites form generally in alkaline ground-water conditions or in igneous rocks. Clinoptilolite is more indicative of a sedimentary origin but may be diagenetic on a small scale rather than representing large-scale alkaline conditions.

Vermiculite-Chlorite

Vermiculite (sample 5) or chlorite (sample 9) is indicated by a peak at 6.3-6.5° 2θ. Neither was affected by glycolation, but, in one instance, the peak disappeared upon heating (vermiculite) but did not in the other (chlorite).

Smectite

Smectite may be present as a distinct phase but is masked by the broad mixed-layer illite-smectite peak.

Super lattice Clay

One sample showed a broad peak at 3.8° 2θ and a multiple at 7.6° 2θ, which, when converted to d-spacing, yielded a clay most likely made up of vermiculite-illite. This clay did not expand much upon glycolation nor contract much upon heating (from 23° 2θ

Sample Number	Manganese Percent	Remarks
4	0.025-0.125	massive facies, south mesa
5	trace	laminated facies, north mesa
11	trace	
12	0.05-0.25	massive facies, some recrystallization, north mesa

Table 6. Semiquantitative X-ray fluorescence analysis of manganese content of Riley travertine samples with a significant peak at 31.5° 2θ (rhodochrosite).

to $20.5^{\circ}\ 2\theta$ to $22^{\circ}\ 2\theta$).

Discussion

The data for the HCl digestion are in Table 3, and the data for the acetic-acid/EDTA digestion are in Table 4. The XRD plots are in addendum 1 (HCl) and addendum 2 (acetic acid-EDTA). X-ray fluorescence (XRF) plots of selected samples for their manganese content are in addendum 3.

Glass and others (1973) and Frye and others (1974, 1978) studied the Ogallala Formation in eastern New Mexico. The general regional geology is similar to that of the Riley travertine area. Both are underlain by Permian and Triassic rocks, often with identical units. The clay minerals they assigned to a "normal" detrital assemblage from such basement rocks were smectite, illite, and kaolinite. This assemblage is basically the same as that found in the Riley travertine insoluble residues. Based on this association, the Riley travertine has only a detrital clay component.

Attapulgite and sepiolite were not detected in the Riley travertine. The data in Table 2 can be used to differentiate the occurrence of attapulgite and sepiolite. These two minerals tend to be mutually exclusive. However, they often occur together during a transition, and this mixture represents slightly varying conditions at the interface between the stability fields for each.

Universal requirements for both attapulgite and sepiolite are relatively dry or dessicating conditions. The chemistry of these minerals requires high silica, high Mg, and high (but restricted) pH. Table 5 shows the high Mg content of the regional carbonates. Ishphording (1973) has shown that attapulgite additionally requires high aluminum. Climatically, sepiolite occurs under drier conditions. Attapulgite has much greater resistance to weathering than sepiolite. Attapulgite is usually sedimentary, whereas sepiolite is sedimentary but also is common in igneous association. Since both require high magnesium and alkalinity, conditions may not have been correct. However, Glass and others (1973) and Frye and others (1974, 1978) found abundant attapulgite and sepiolite in certain facies dependent on environment. So attapulgite and sepiolite do occur in eastern New Mexico where source rocks and climate are very similar to northwestern Socorro County. Thus, the lack of attapulgite and sepiolite in the Riley traverinte must be related to factors other than lack of magnesium, low alkalinity, etc. since they formed in eastern New Mexico under similar conditions.

The variable seems to be the environment of deposition. Attapulgite is primarily associated with soils while sepiolite is more common in alkaline lakes or playas (Table 2). Apparently, these environments were not present during formation of the Riley travertine, which is thus neither a soil nor an alkaline lacustrine deposit. This conclusion is in harmony with recent work (Barker, 1983).

The main 2-θ peaks for attapulgite (A) and sepiolite (S) are as follows:

A	8.4*(10)	13.75(3)	19.86(4)**	27.61(3)**	35.19(3)
S	7.3*(10)	11.91(2)**	19.77(3)**	20.60(2)**	26.52(2)**

* key line ** usually masked in Riley samples

(relative intensity)

The 10-intensity peaks are masked by the broad mixed-layer illite zone. In addition, many of the secondary peaks are masked by various other clay and nonclay minerals. Thus, a small amount of attapulgite or sepiolite could be present and missed. However, the basis for assigning a pedogenic or alkaline lacustrine environment to the Riley travertine is based on attapulgite or sepiolite dominating the clay mineralogy. Minor amounts of attapulgite and sepiolite overwhelmed by illite, smectite, kaolinite, etc. is nondiagnostic. For these reasons, I conclude that the Riley travertine was not formed as a soil or as an alkaline lake-playa deposit.

The illite-smectite-kaolinite suite does not define other environments conclusively. Therefore, the Riley travertine could be a spring deposit or a pervasive secondary carbonate deposit. The detrital clays could be deposited in a travertine during its deposition either by wind or, as circumstances permit, by fluvial activity. In contrast, during pervasive carbonate deposition, the clays are an artifact of the depositional environment the host sediments represent. Carbonate crystallization can destroy some silicates (including clays), so the initial host clay mineralogy cannot be known with certainty.

Summary

The origin of the Riley travertine is constrained by the absence of attapulgite and sepiolite. These clay minerals are associated with soils (caliche-calcrete) and alkaline lakes, respectively, so the probability that these are the depositional environments for the Riley travertine is low.

The clay-mineral assemblage present is a typical detrital one for areas of New Mexico with Permian-Triassic bedrock. The vermiculite, chlorite, illite, mixed-layer illite-smectite, and kaolinite are not diagnostic and may represent either syngenetic minerals in a spring deposit or minerals representative of the host-rock depositional environment if a pervasive calcite origin is correct. The presence of vermiculite and chlorite is uncertain pending more detailed sampling.

Because of the preliminary nature of this report, some additional work must be done to confirm the conclusions reached. Additional work includes, but may not be limited to, the following:

1) Dissolve by EDTA a calcareous rock with attapulgite and sepiolite as a control for the above experiments.
2) Redissolve all the Riley travertine samples using EDTA alone to eliminate possible problems inherent in the acetic-acid procedure.
3) The clay-size fraction should be further sized and scanning-electron micrographs should be made of a fraction appropriate to detect acicular attapulgite and/or sepiolite.
4) A recent caliche from the Riley area should be analyzed for attapulgite and sepiolite to see if they are forming under present conditions. This could include secondary carbonate material from case-hardened portions of the

Riley travertine.

5) Drill cores of the Riley travertine are in hand, and deeper portions should be analyzed as described earlier to eliminate any overprint in clay mineralogy from collecting near-surface samples.
6) Undertake additional detailed geology including dating, mapping (geologic and facies), thin-section analysis, and detailed sampling.

Acknowledgments

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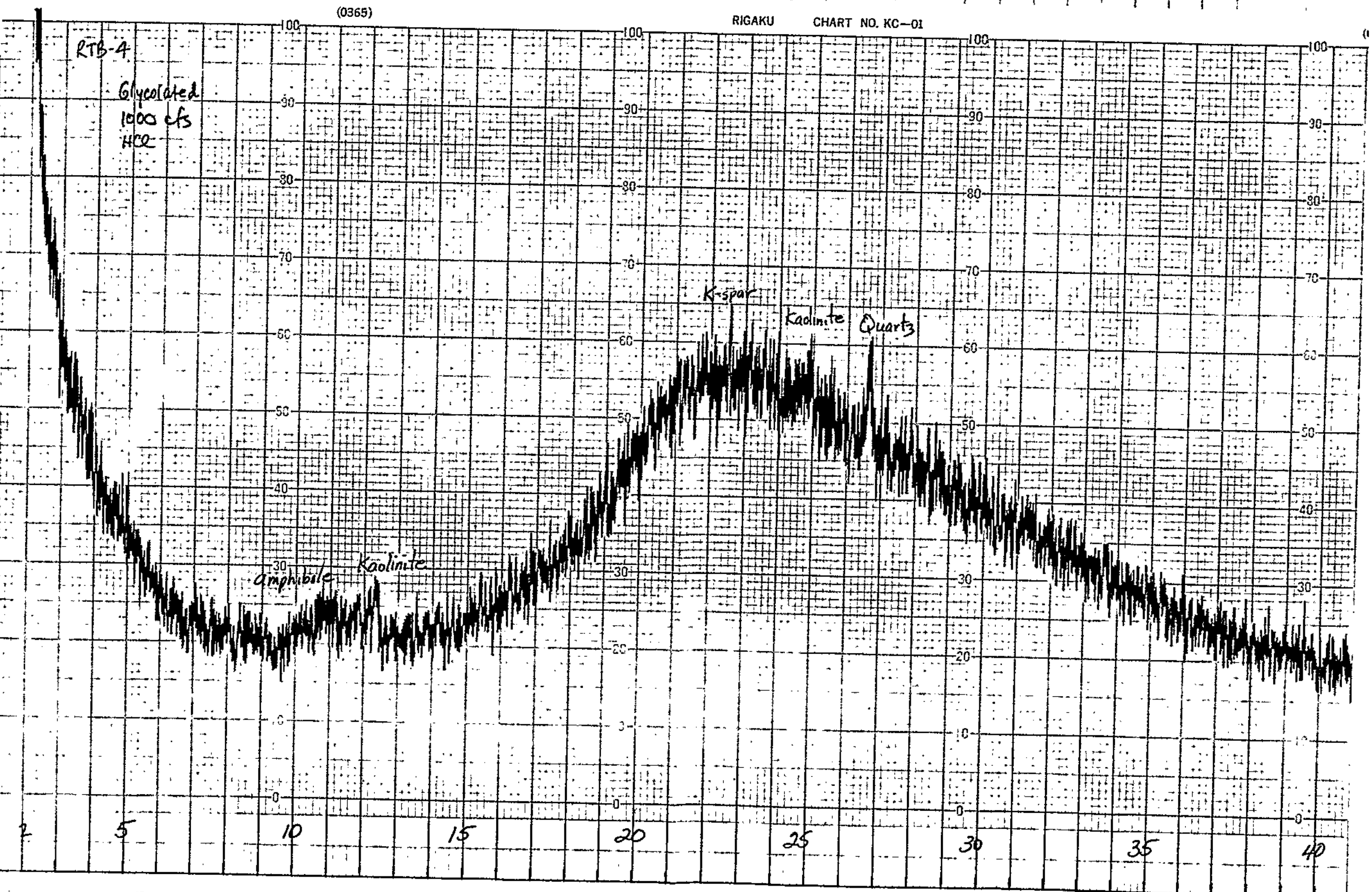
Addendum 1

XRD Data on HCl-derived Insoluble Residues of Riley Travertine Samples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Glycolated
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HCl
amphibole
Kaolinite
K-spar
Kaolinite
Quartz
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70
60
50
40
30
20
10
0
2
5
10
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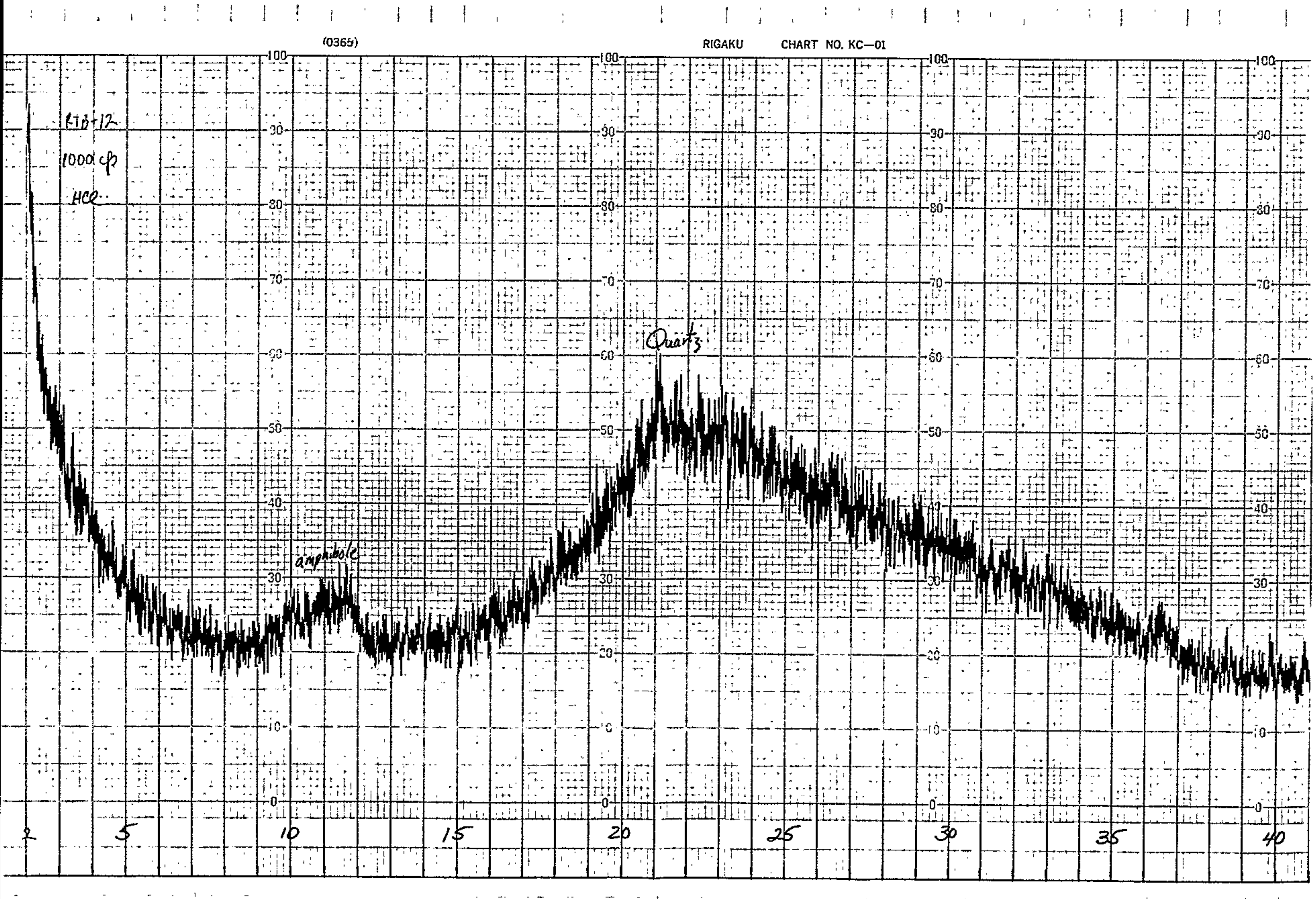
20
25
30
35
40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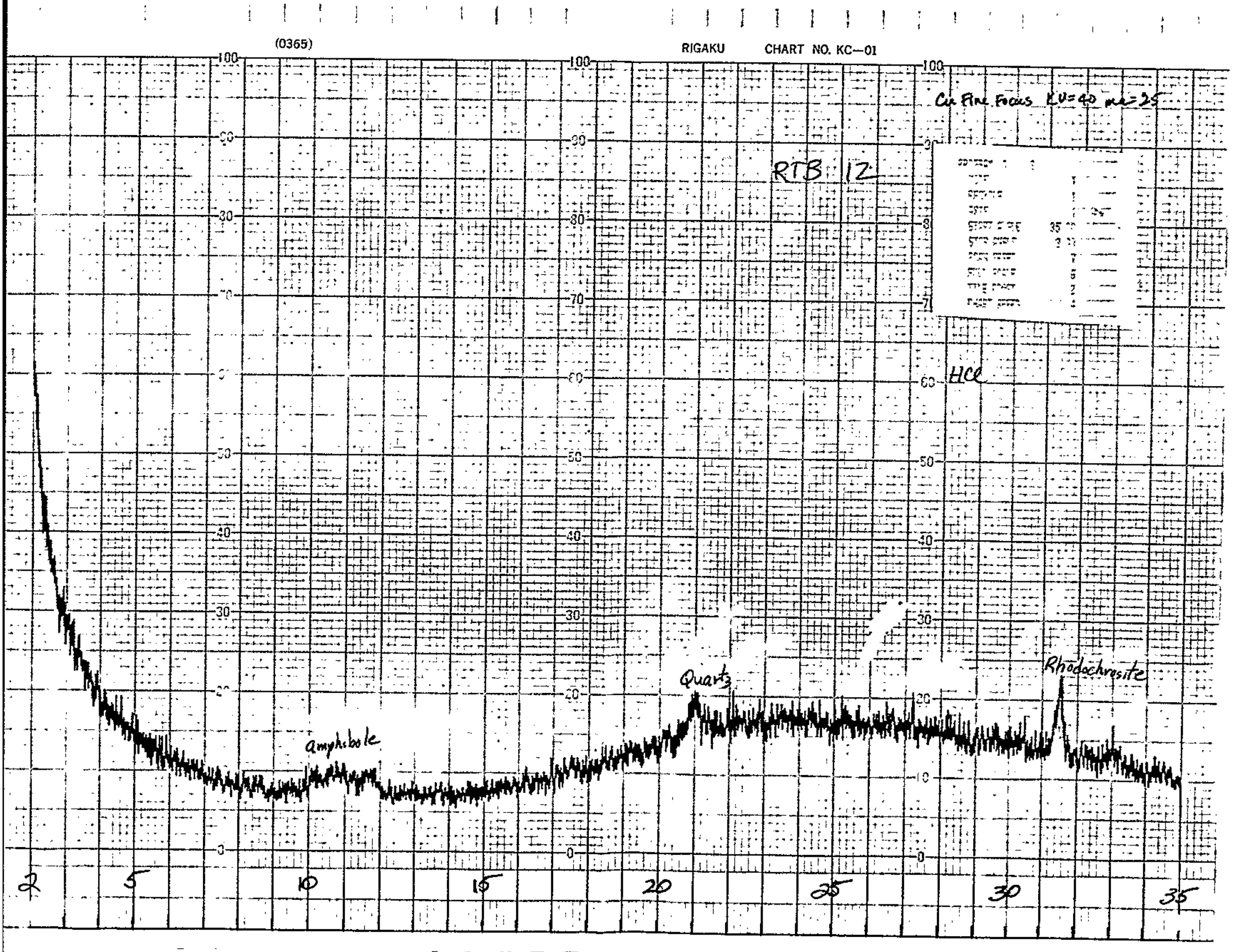
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RTB 12
HCl
amphibole
Quartz
Rhodochrosite
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70
60
50
40
30
20
10
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2
5
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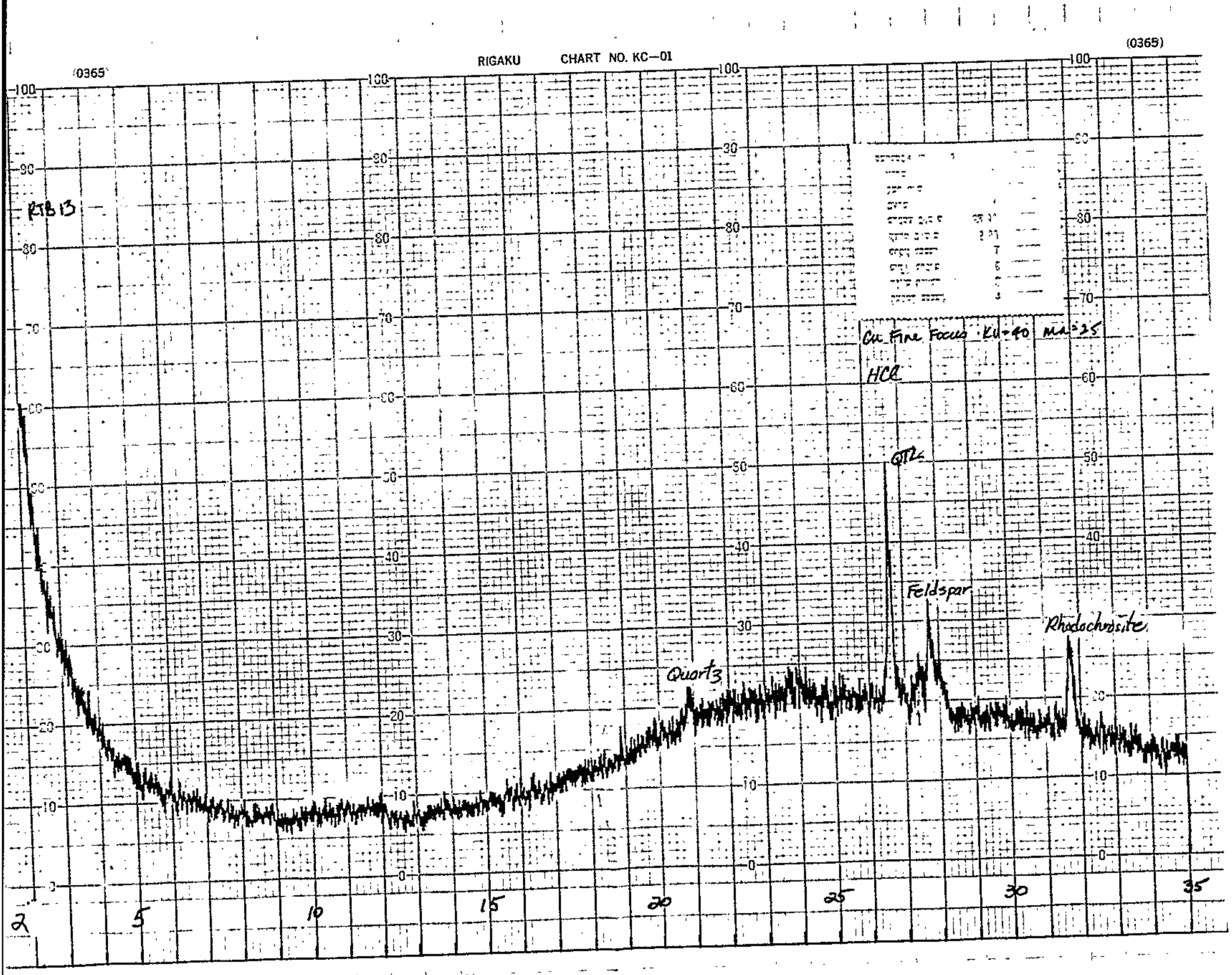
15
20
25
30
35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Feldspar
Rhodochrosite
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70
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2
5
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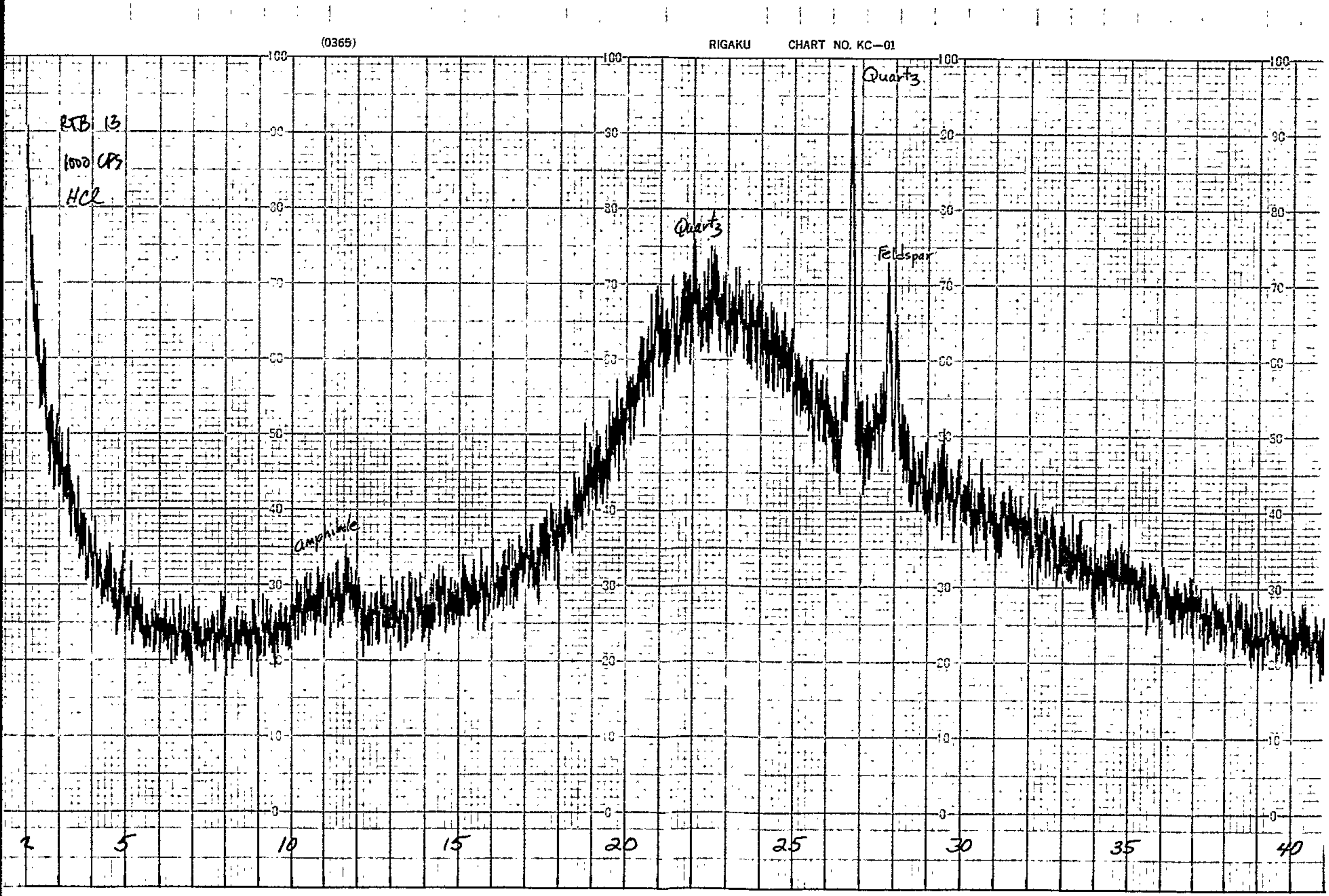
25
30
35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1000 CPS
HCl
Quartz
Quartz
Feldspar
amphibole
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20
25
30
35
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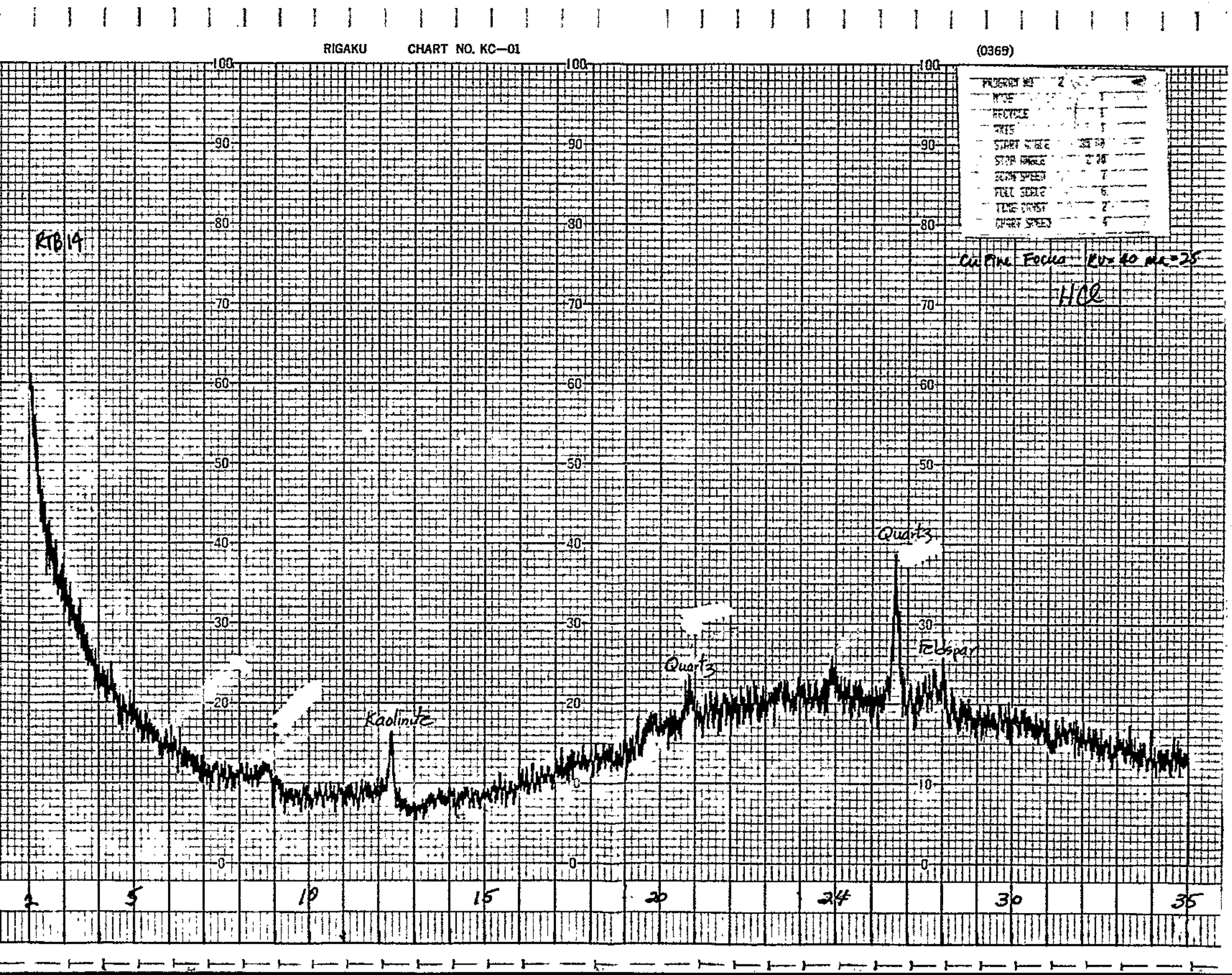
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STOP ANGLE
SCAN SPEED 1
FULL SCALE 6.
TIME CONST 2
CHART SPEED
Cu Fine Focus Kv= 40 ma=25
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RTB14
Kaolinite
Quartz
Quartz
Feldspar
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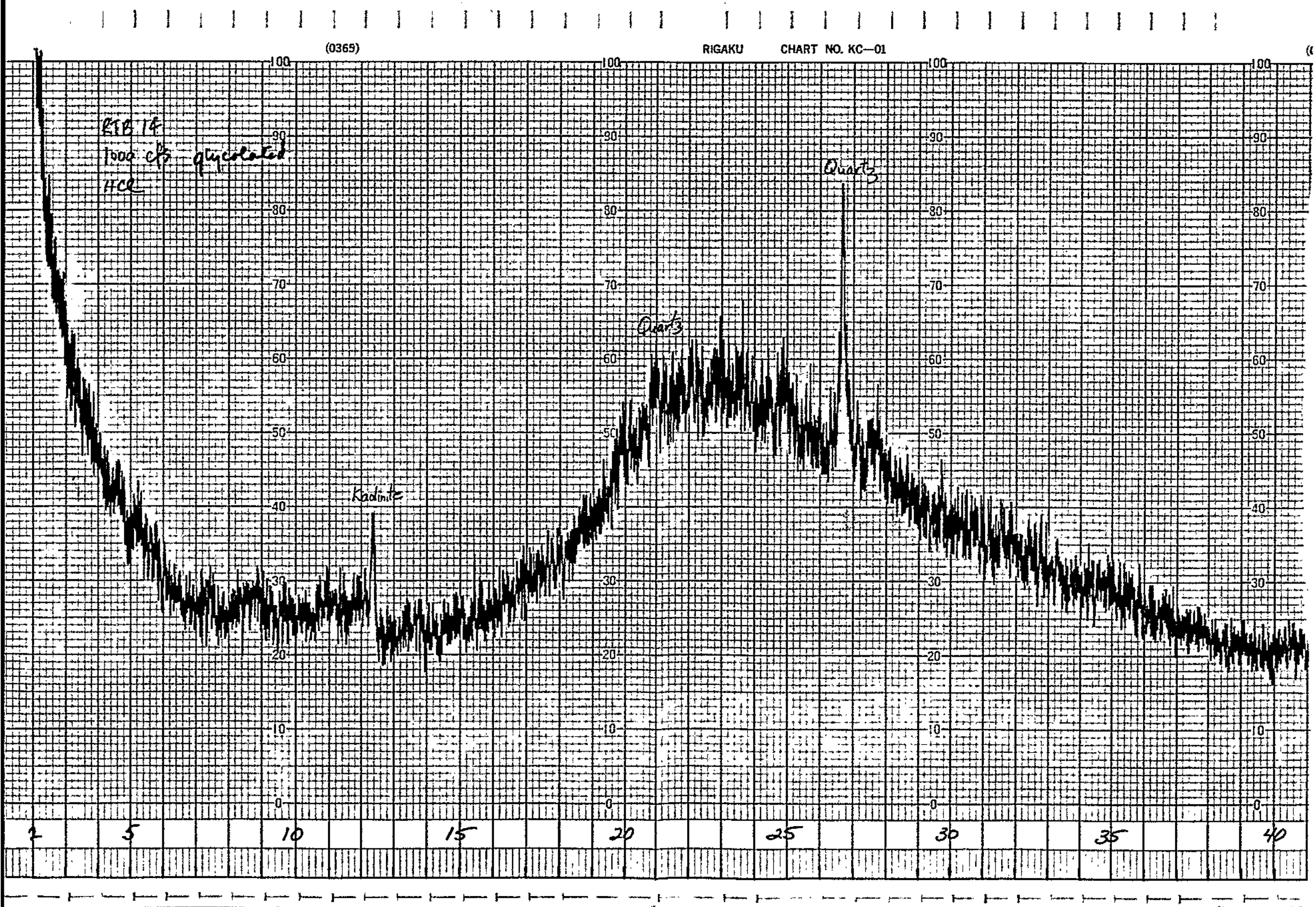
10
15
20
24
30
35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1000 cps glycolated
HCl
Kaolinite
Quartz
Quartz
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5
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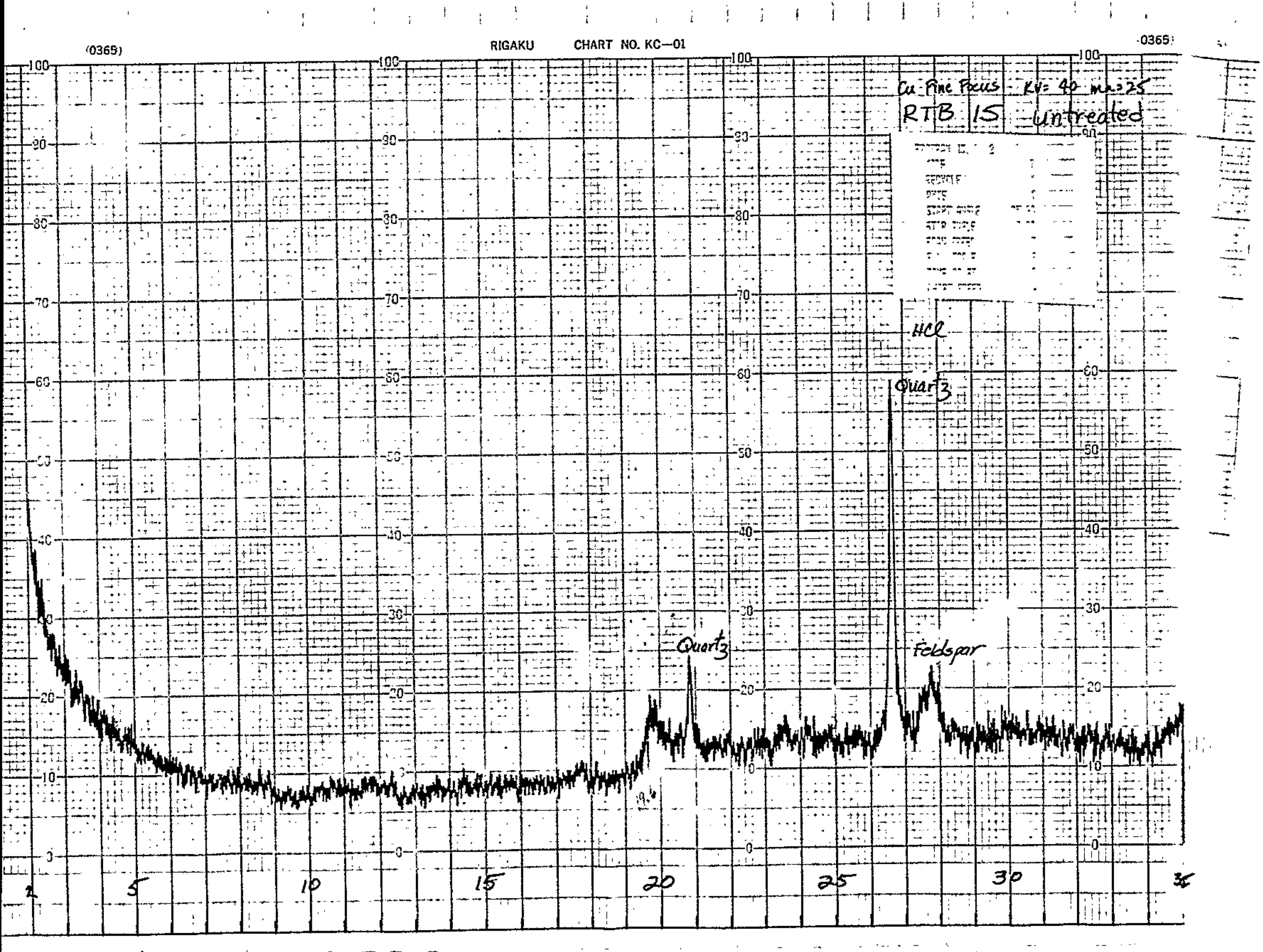
15
20
25
30
35
40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(0365)
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RTB 15 untreated
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90
80
70
60
50
40
30
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HCl
Quartz
Quartz
Feldspar
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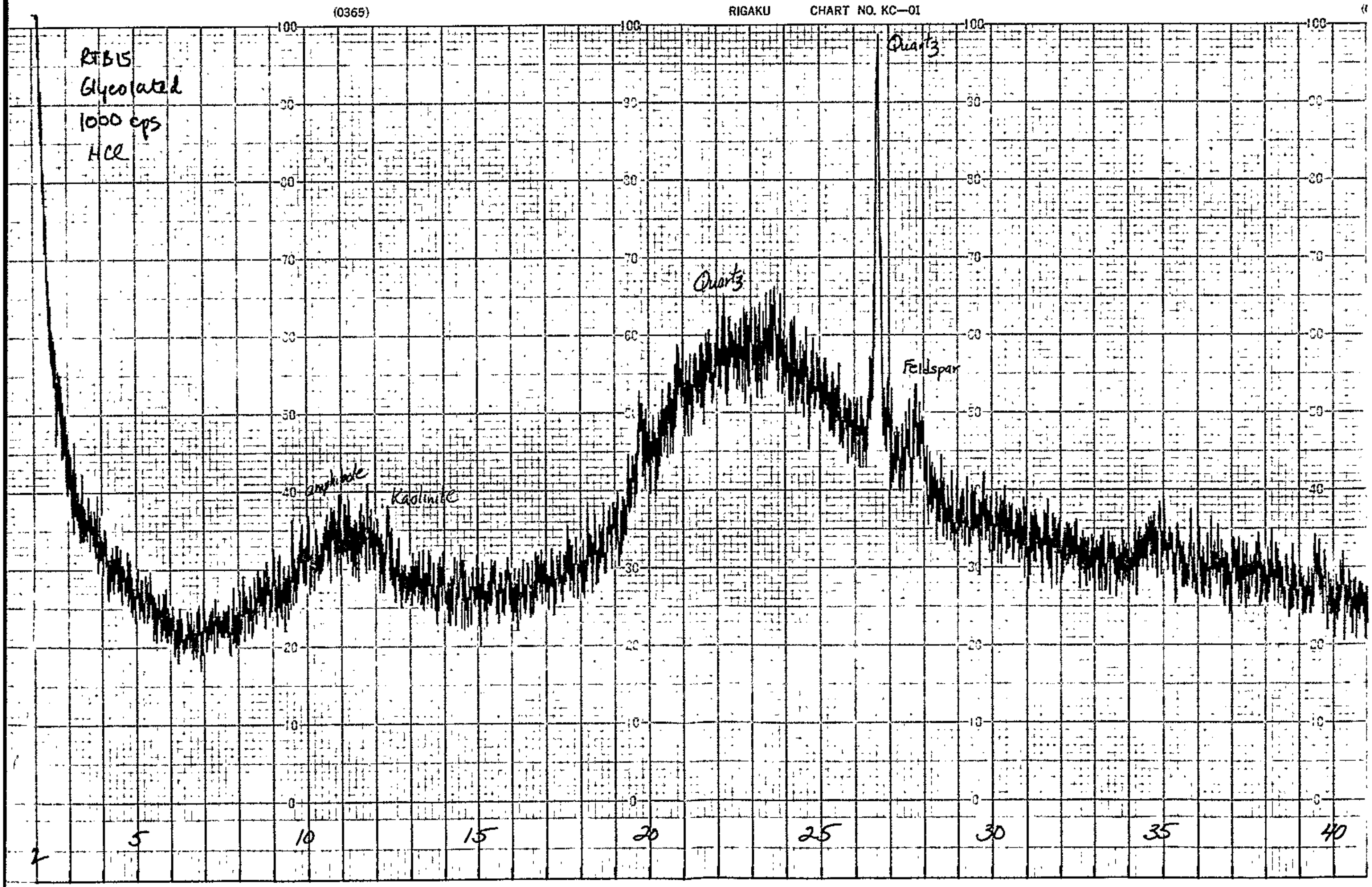
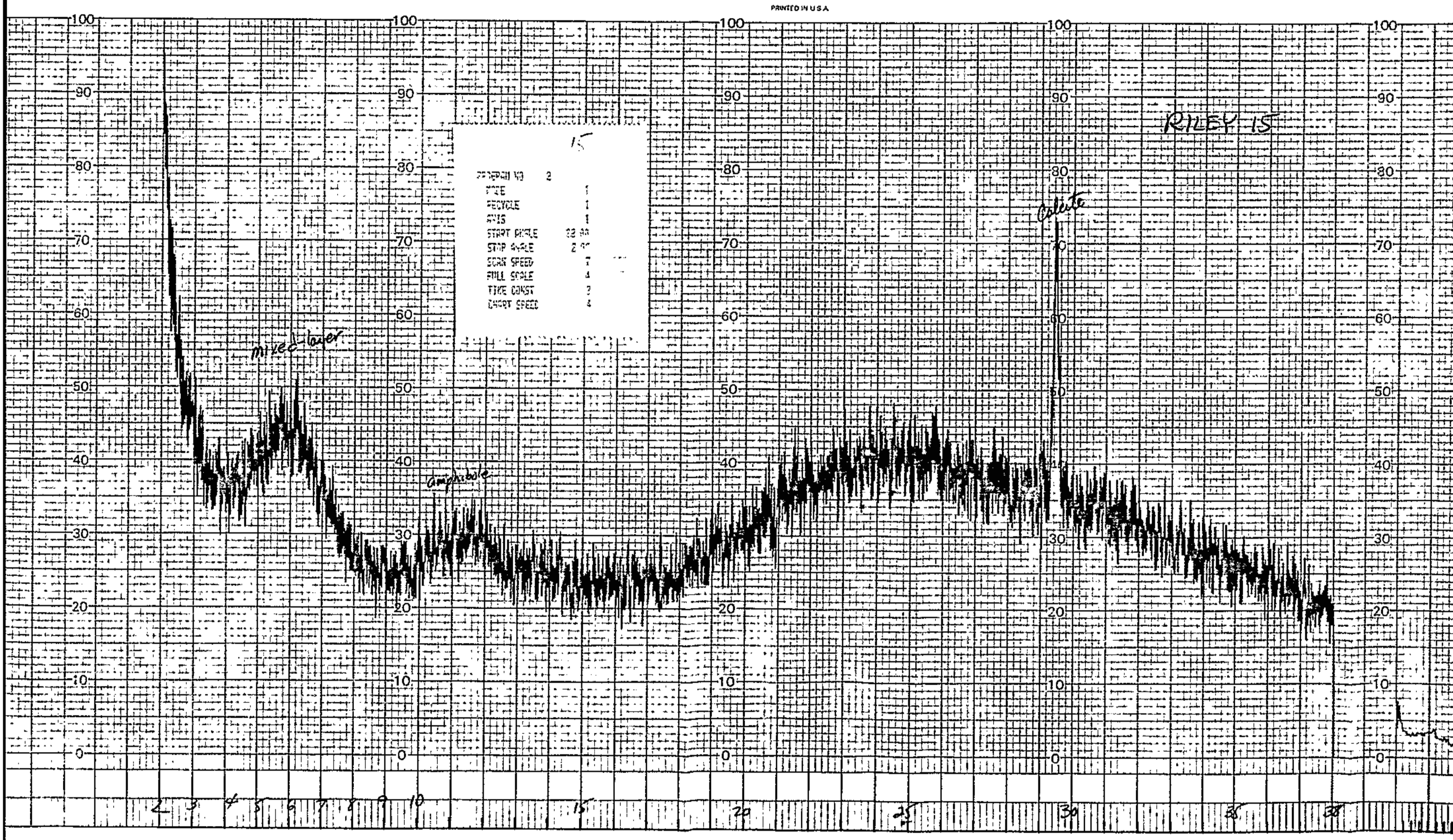
2
5
10
15
20
25
30
35



RTB15
Glycolated
1000 cps
HCl



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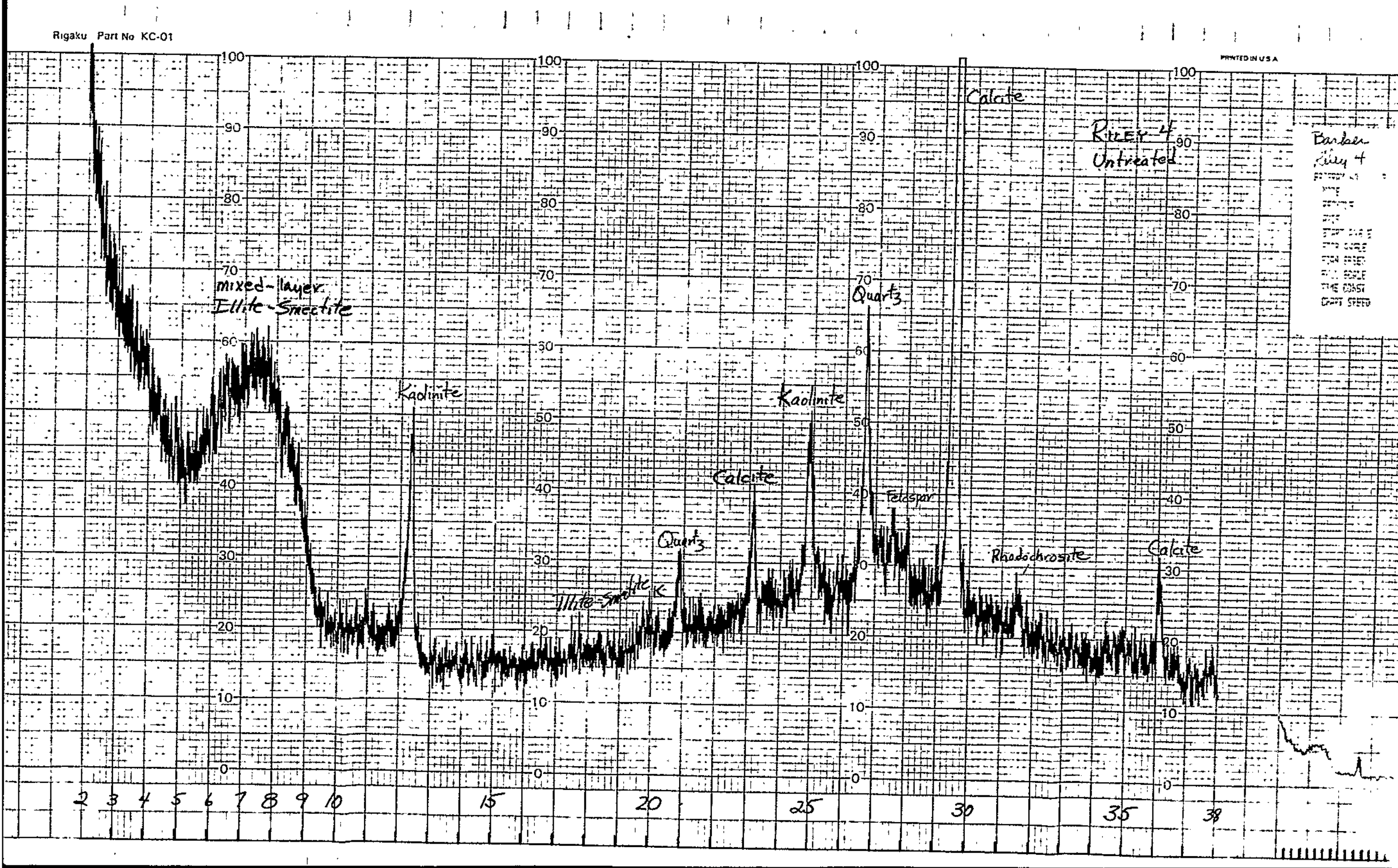
Addendum 2

XRD Data on Acetic Acid/EDTA - Derived Insoluble Residues of Riley Travertine Samples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Riley 4
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Barber
Riley 4
SCAN SPEED
FULL SCALE
TIME CONST
CHART SPEED
mixed-layer
Illite-Smectite
Kaolinite
Illite-Smectite
K
Quartz
Calcite
Kaolinite
Quartz
Feldspar
Calcite
Rhodochrosite
Calcite
100
90
80
70
60
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4
5
6
7
8
9
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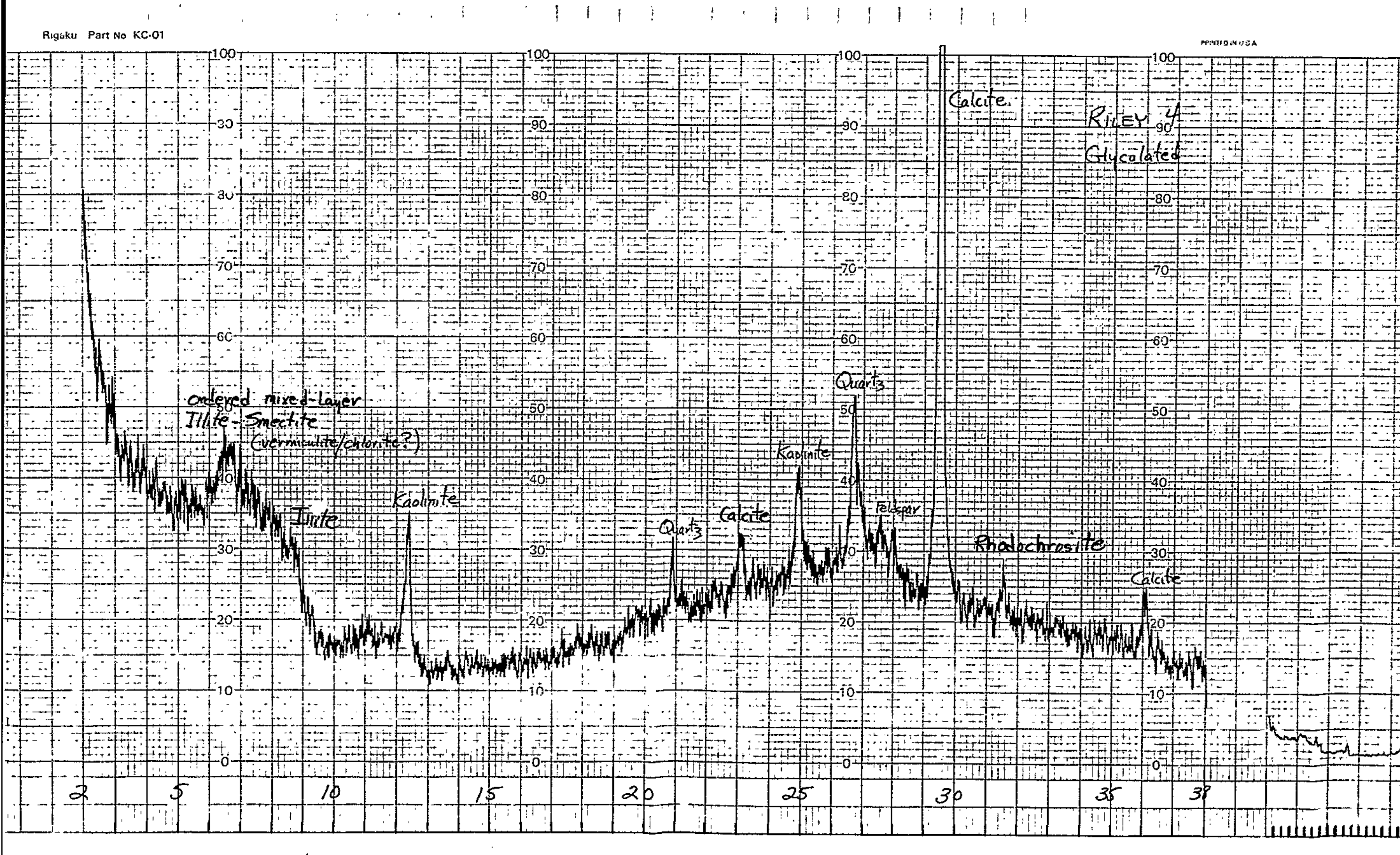
15
20
25
30
35
38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(vermiculite/chlorite?)
Illite
Kaolinite
Quartz
Calcite
Kaolinite
Quartz
Feldspar
Rhodochrosite
Calcite
100
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60
50
40
30
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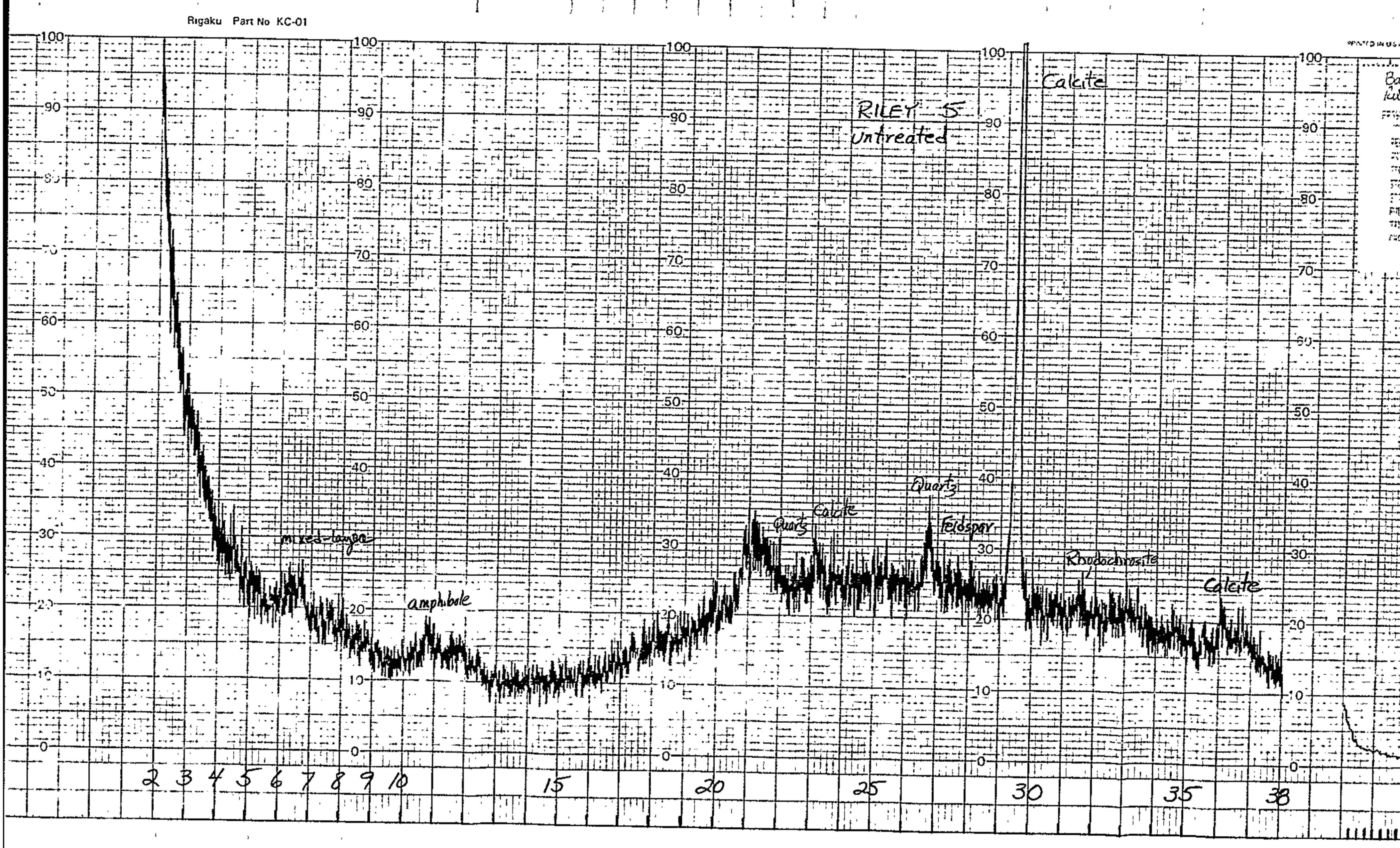
15
20
25
30
35
38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Untreated
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amphibole
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Quartz
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Calcite
100
90
80
70
60
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3
4
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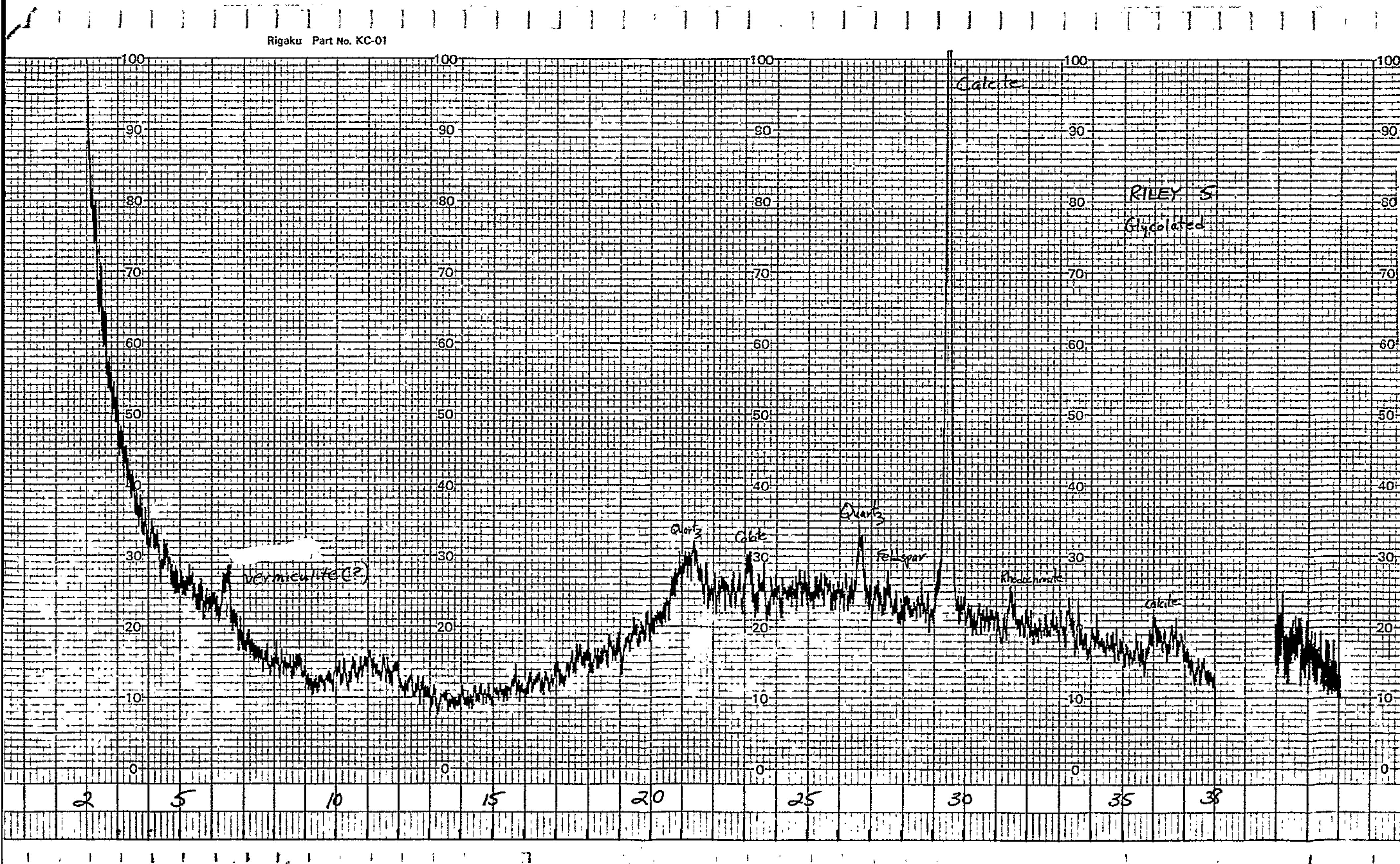
7
8
9
10
15
20
25
30
35
38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RILEY 5
Glycolated
Calcite
vermiculite (?)
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Calcite
Quartz
Feldspar
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Calcite
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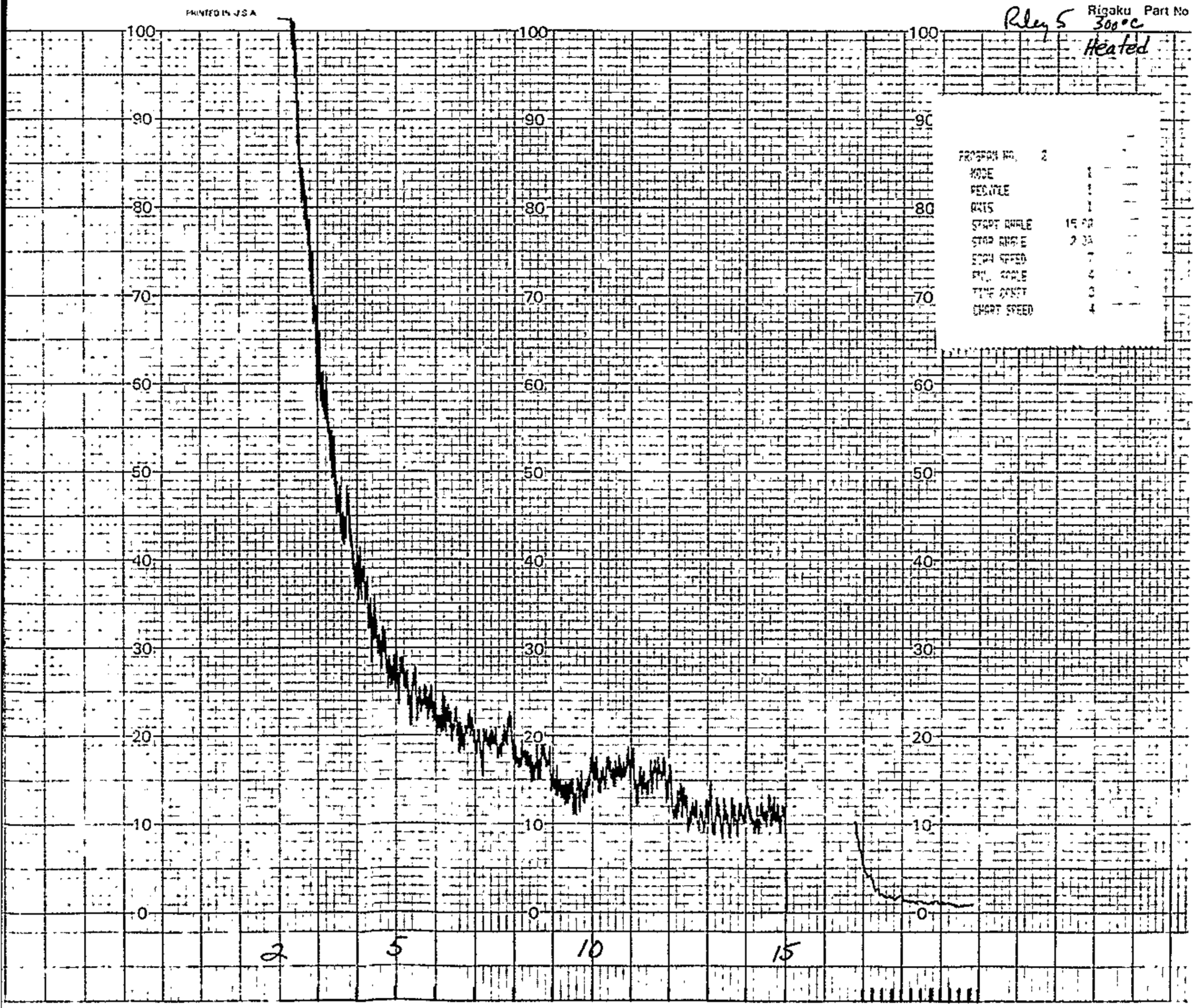
60
50
40
30
20
10
0
2
5
10
15
20
25
30
35
38



Riley 5 300°C Heated

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  STOP ANGLE        2.00
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  FULL SCALE           4
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  CHART SPEED          4
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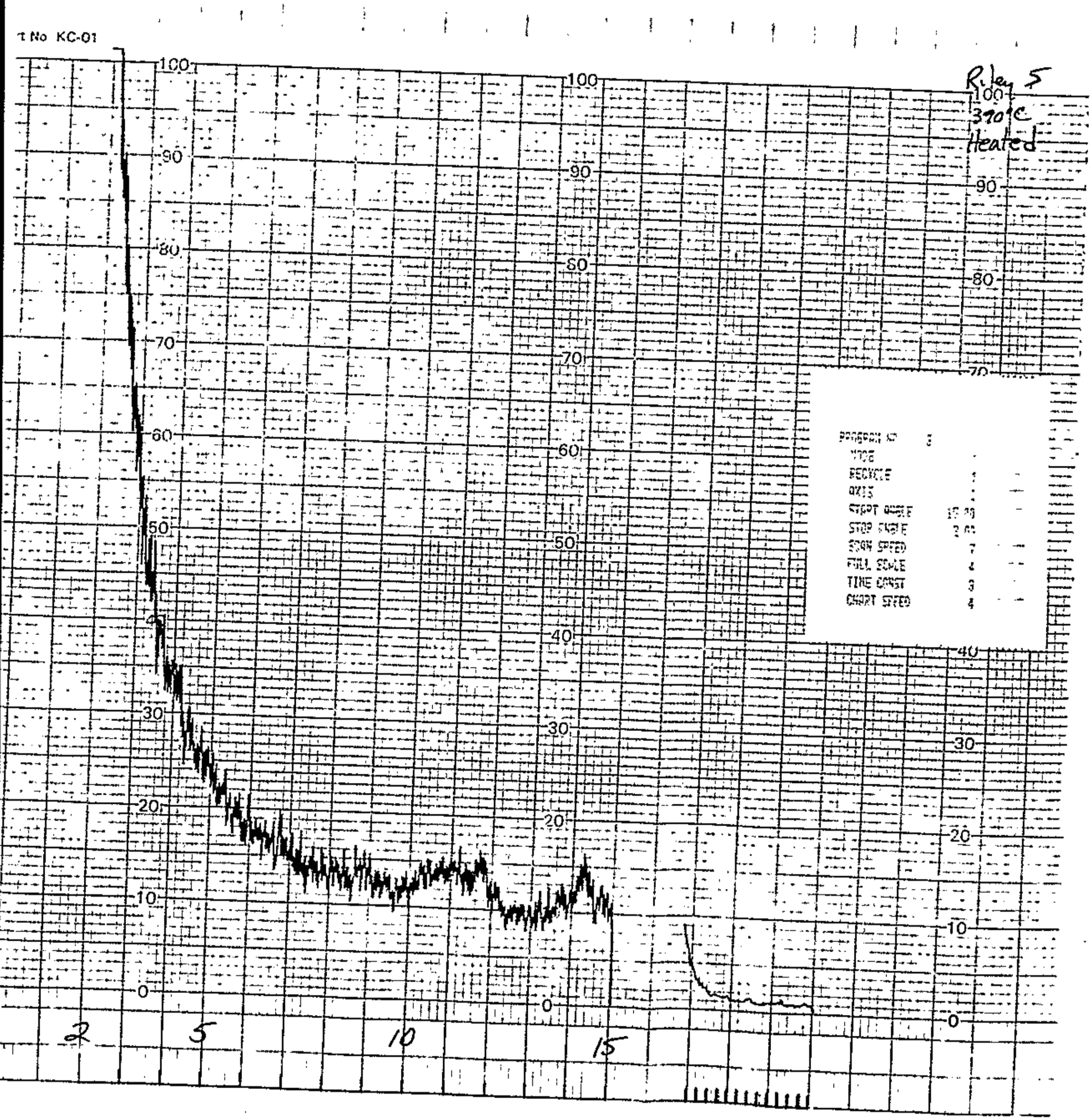

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  CHART SPEED          4
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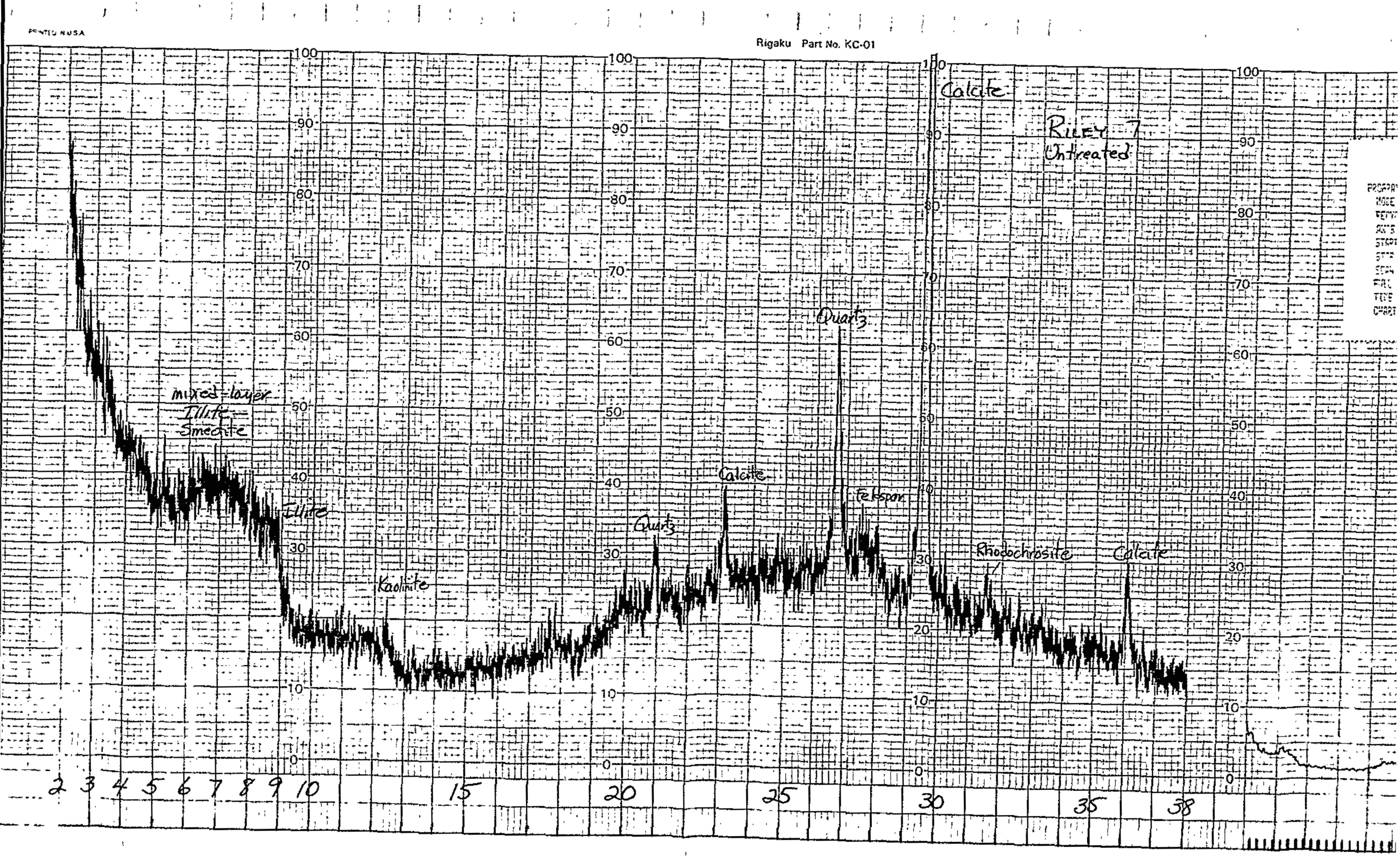
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Riley 7
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Quartz
mixed-layer
Illite-
Smectite
Illite
Calcite
Felspar
Quartz
Kaolinite
Rhodochrosite
Calcite
100
90
80
70
60
50
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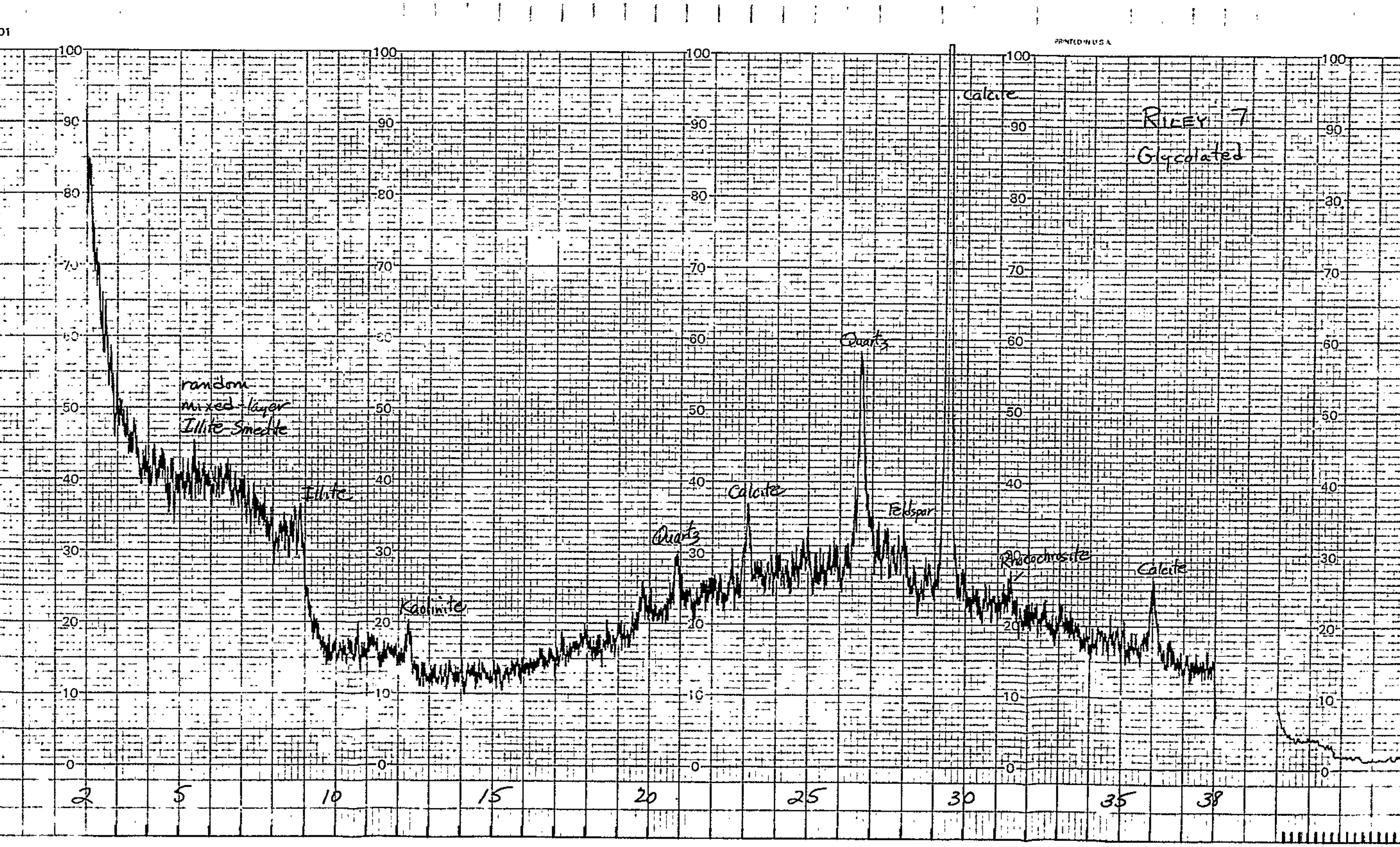
35
38


01
PRINTED IN U.S.A.
RILEY 7
Glycolated
100
90
80
70
60
50
40
30
20
10
0
random mixed-layer Illite-Smectite
Illite
Kaolinite
Quartz
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Feldspar
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2
5
10
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20
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38

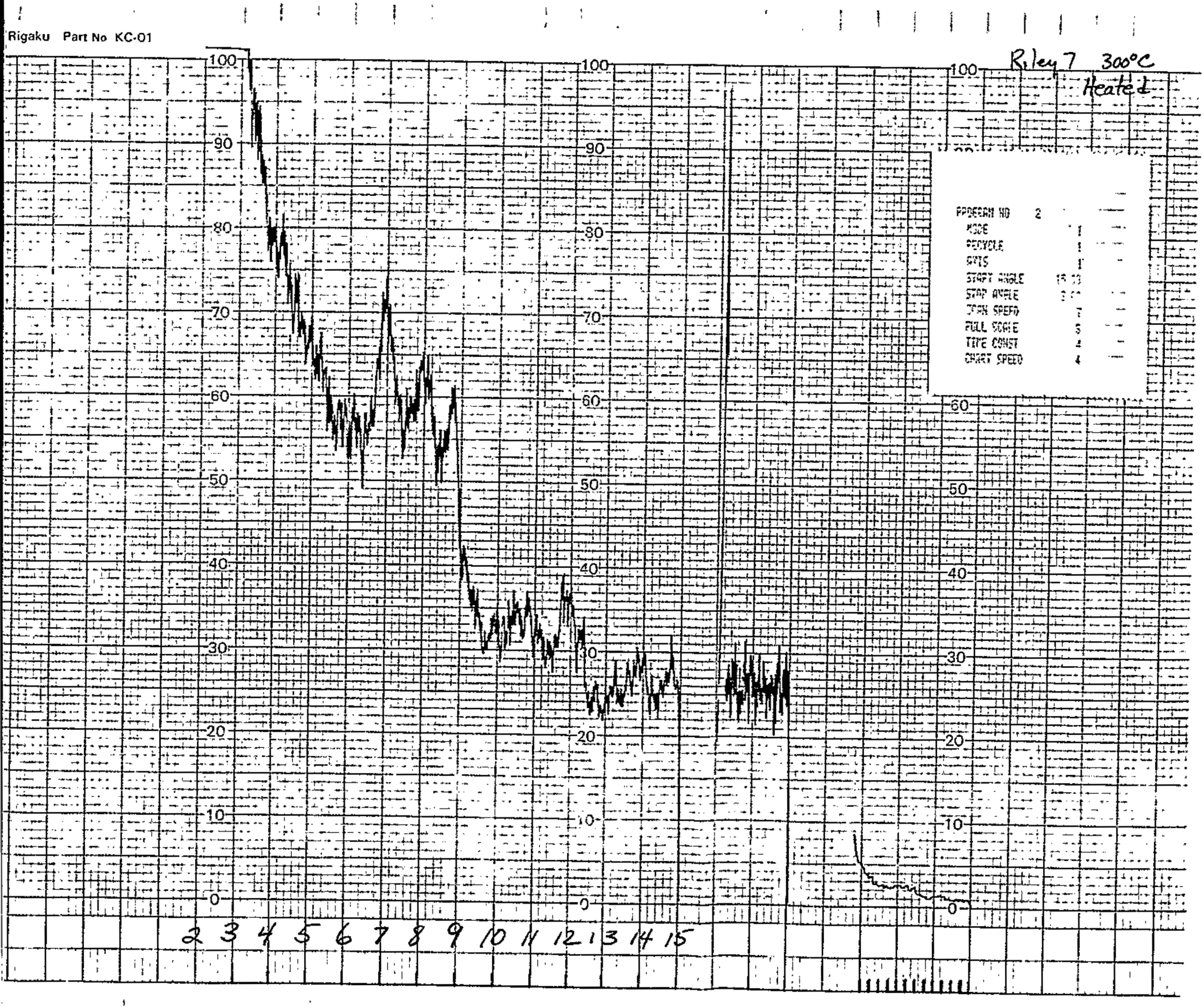

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  CHART SPEED       4
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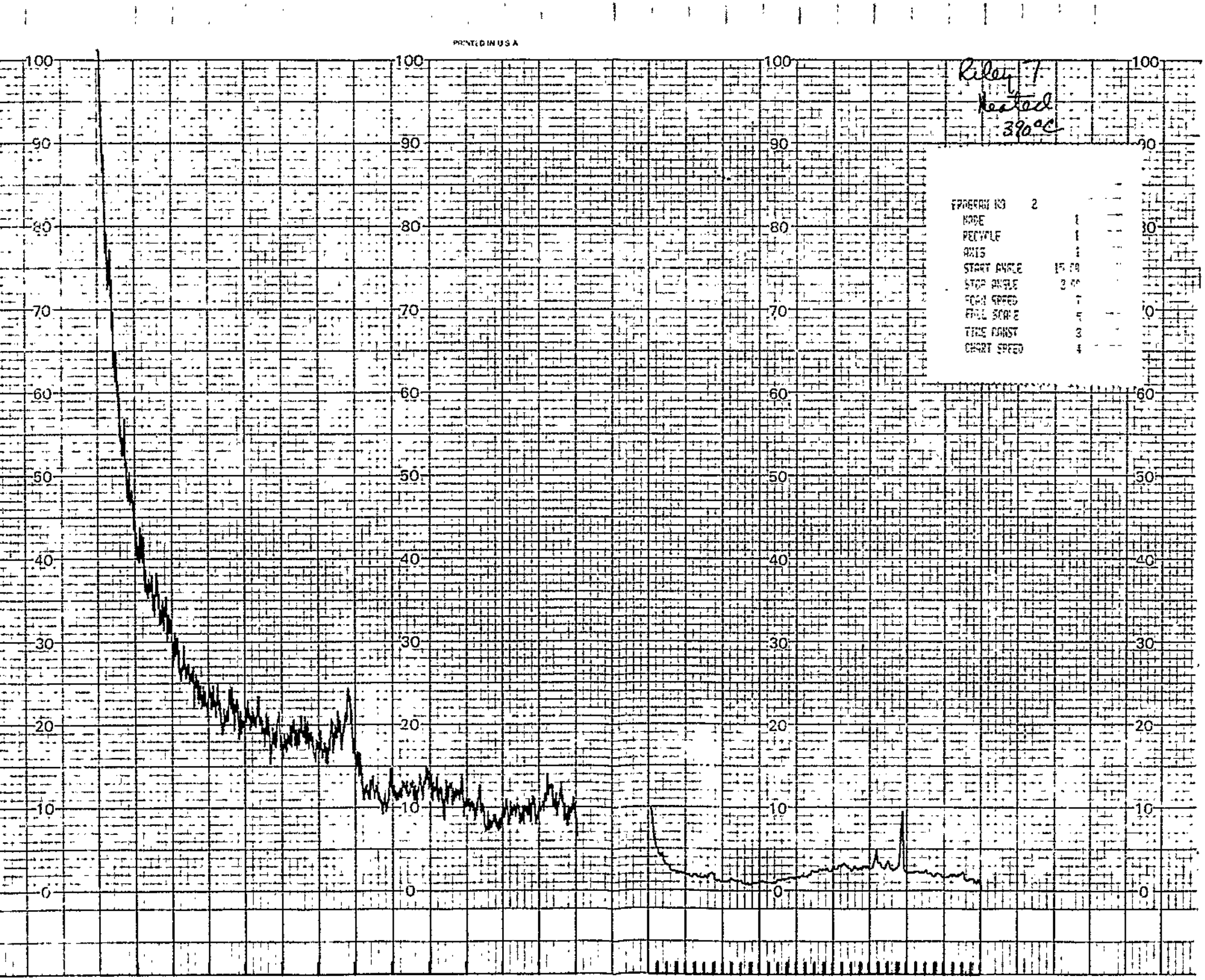

Riley 7
Heated
390°C

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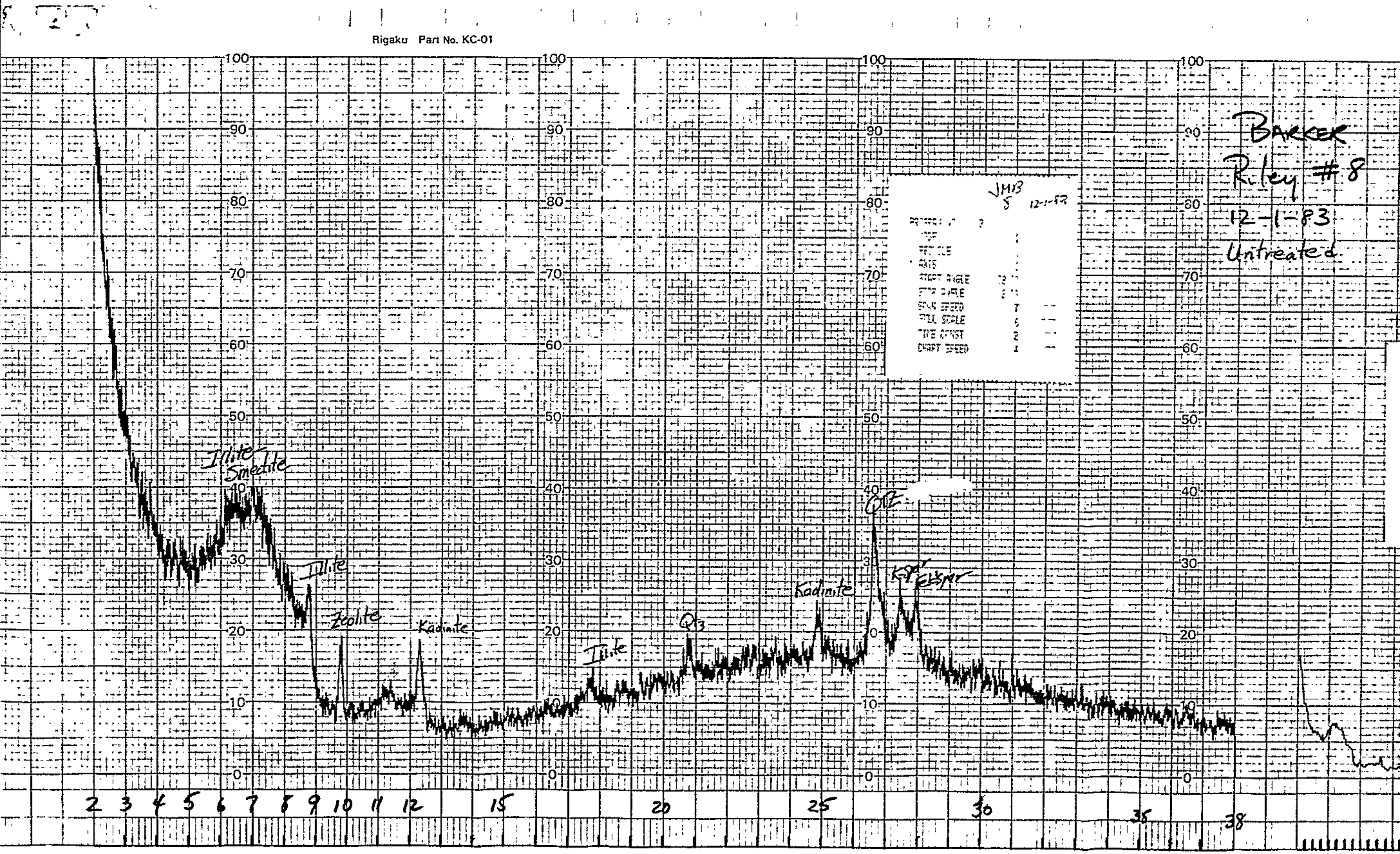
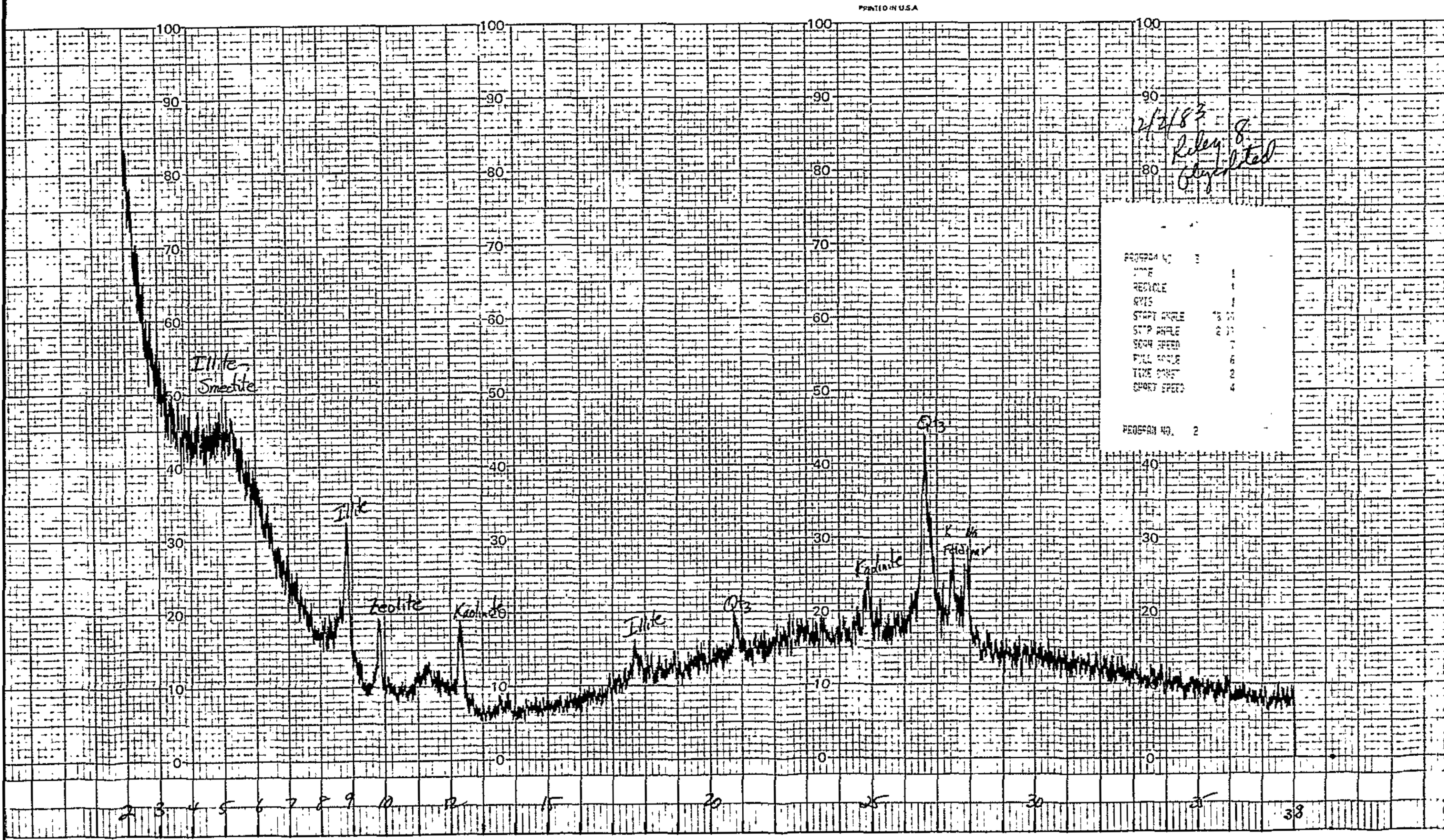
TIME CONST 3
CHART SPEED 4



Barker
Riley #8
12-1-83
Untreated



12/2/83
Riley 8
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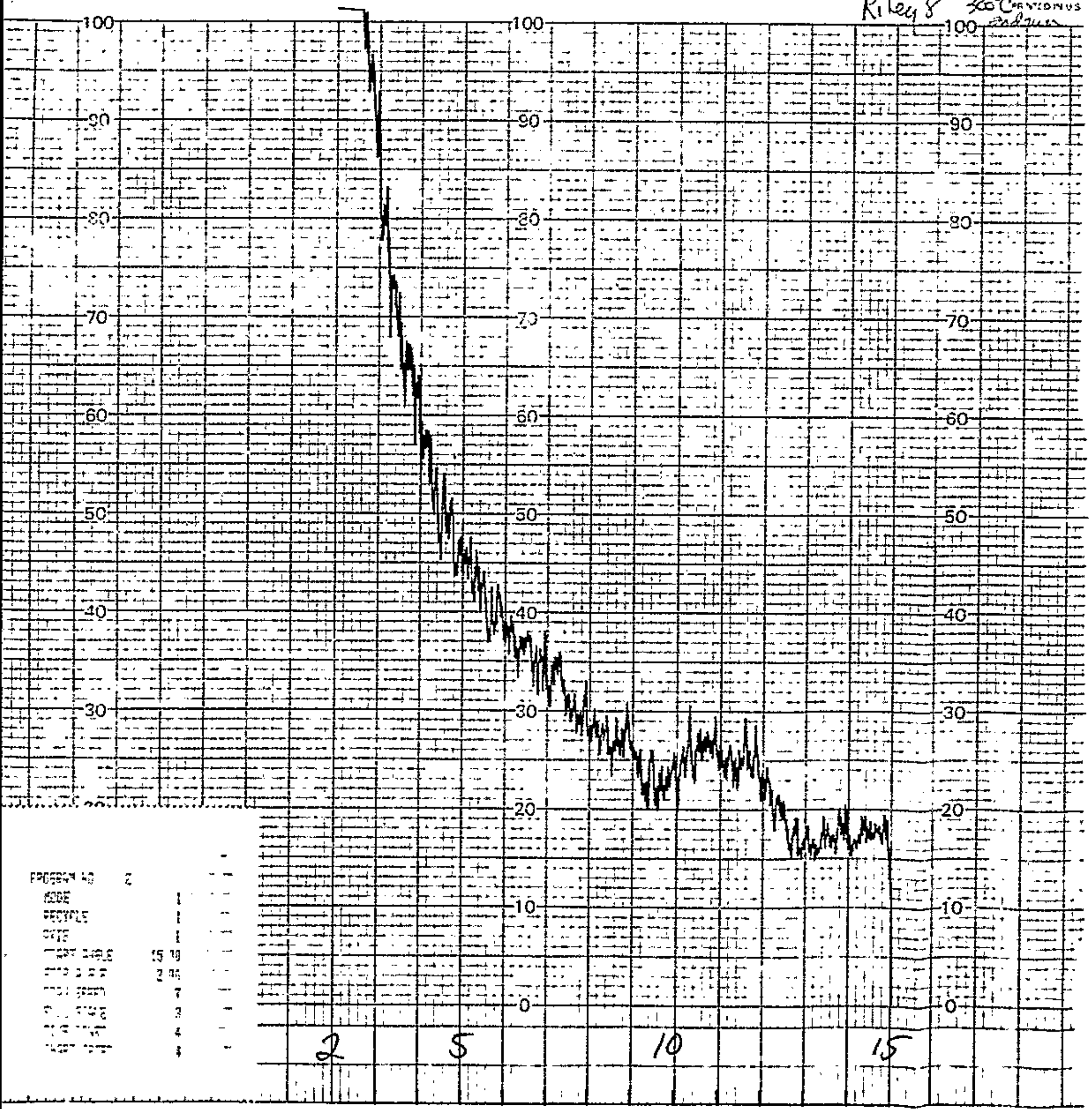
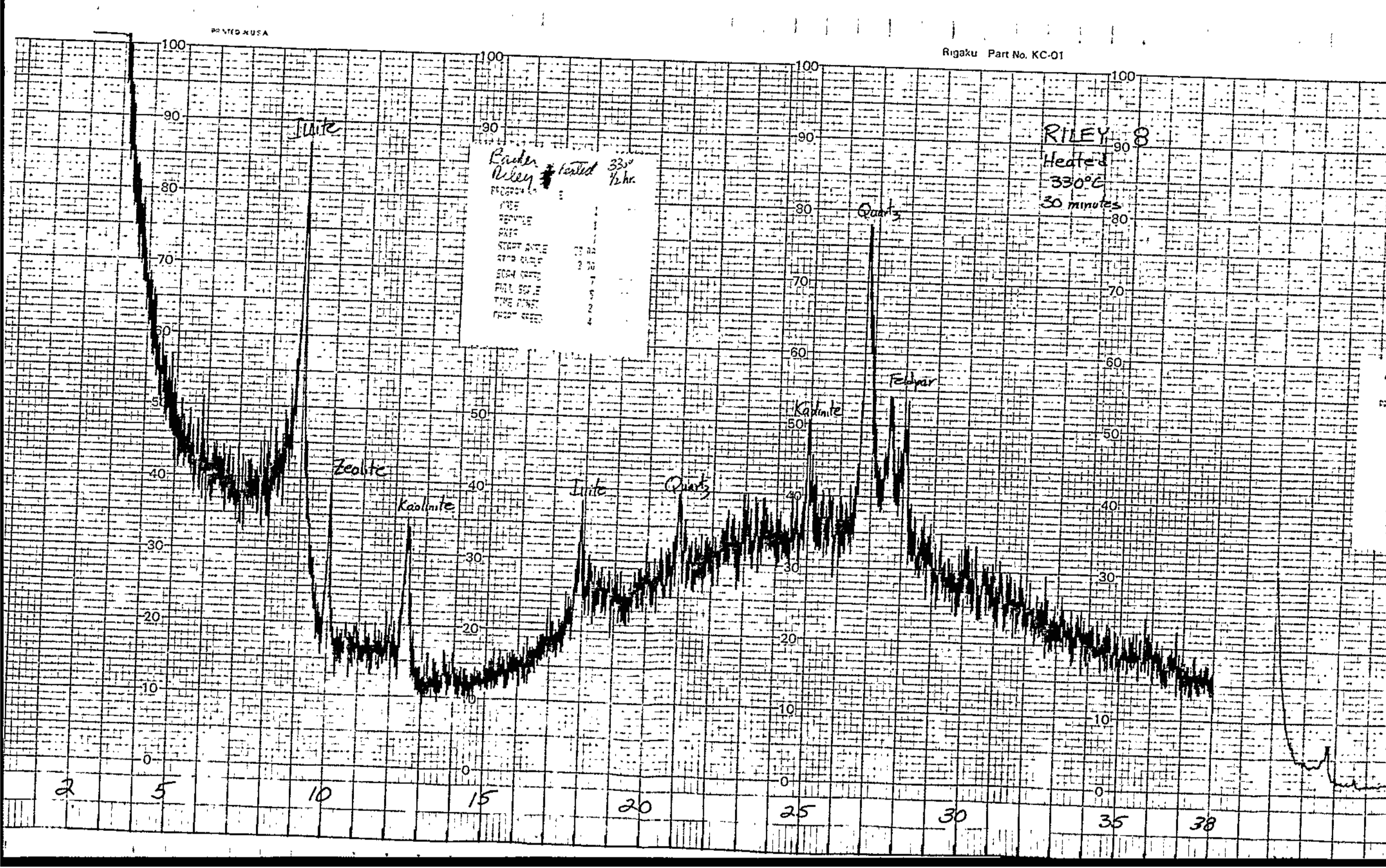
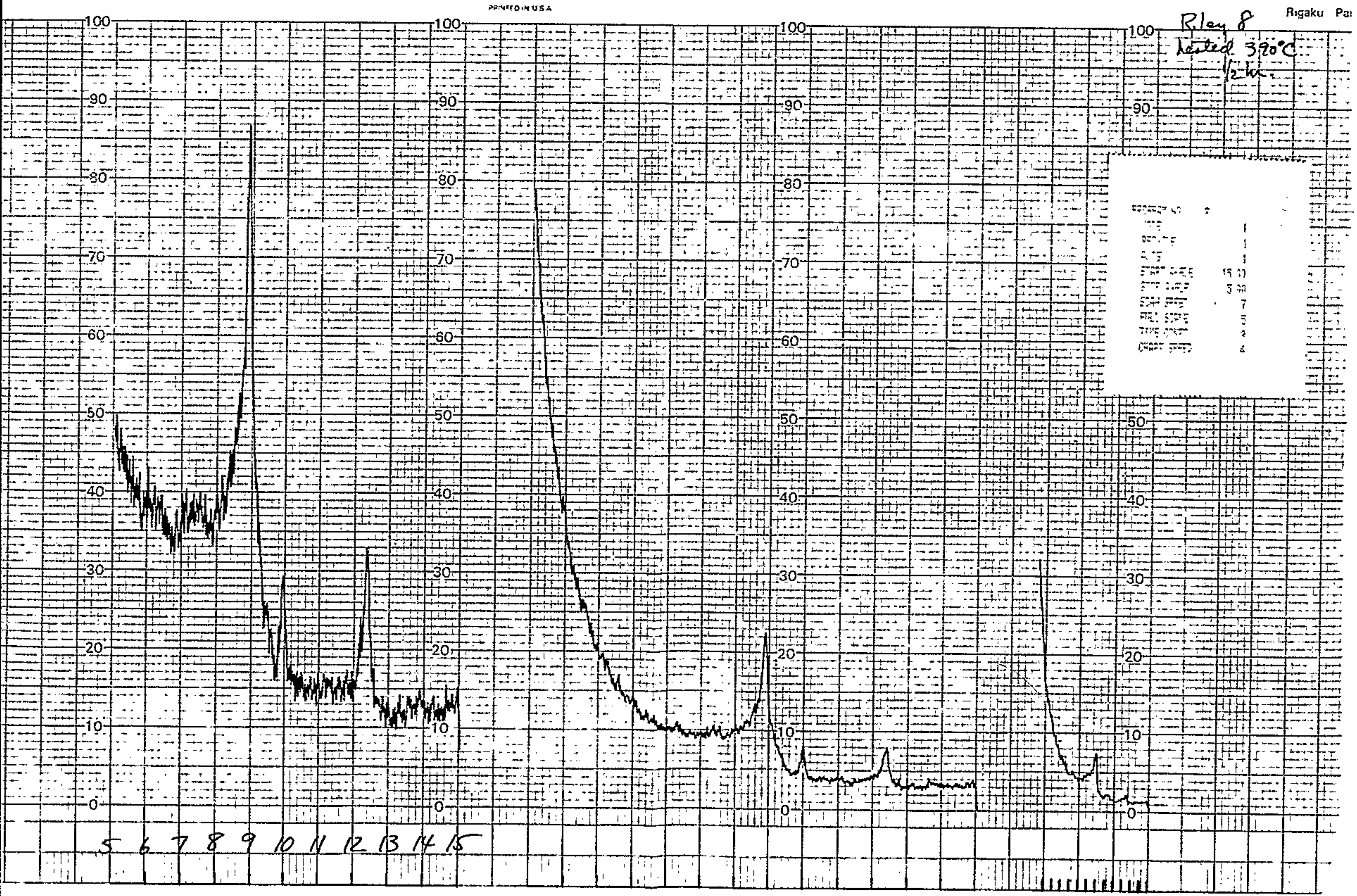
  CHART SPEED         4


PROGRAM NO.   2
```

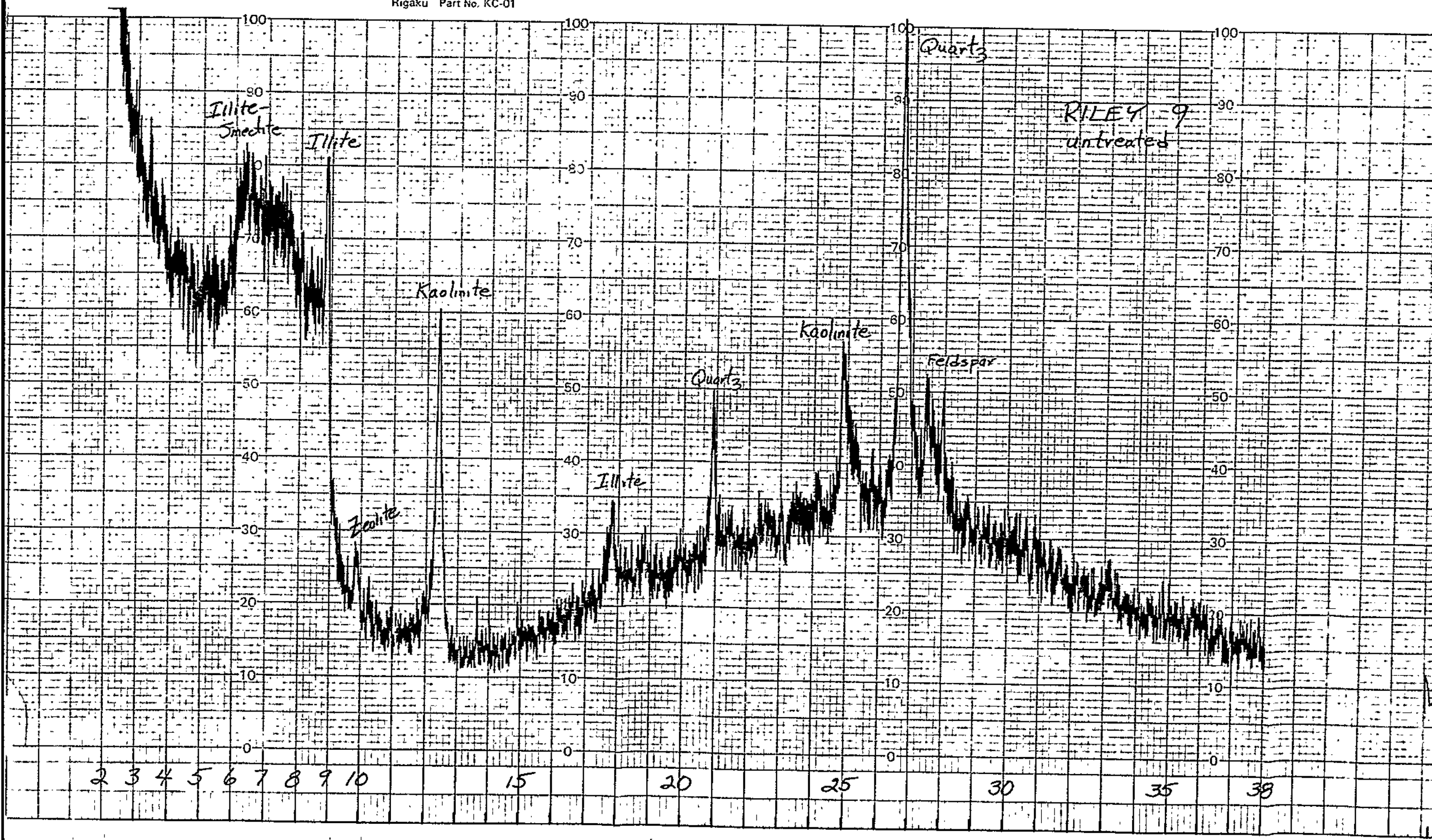


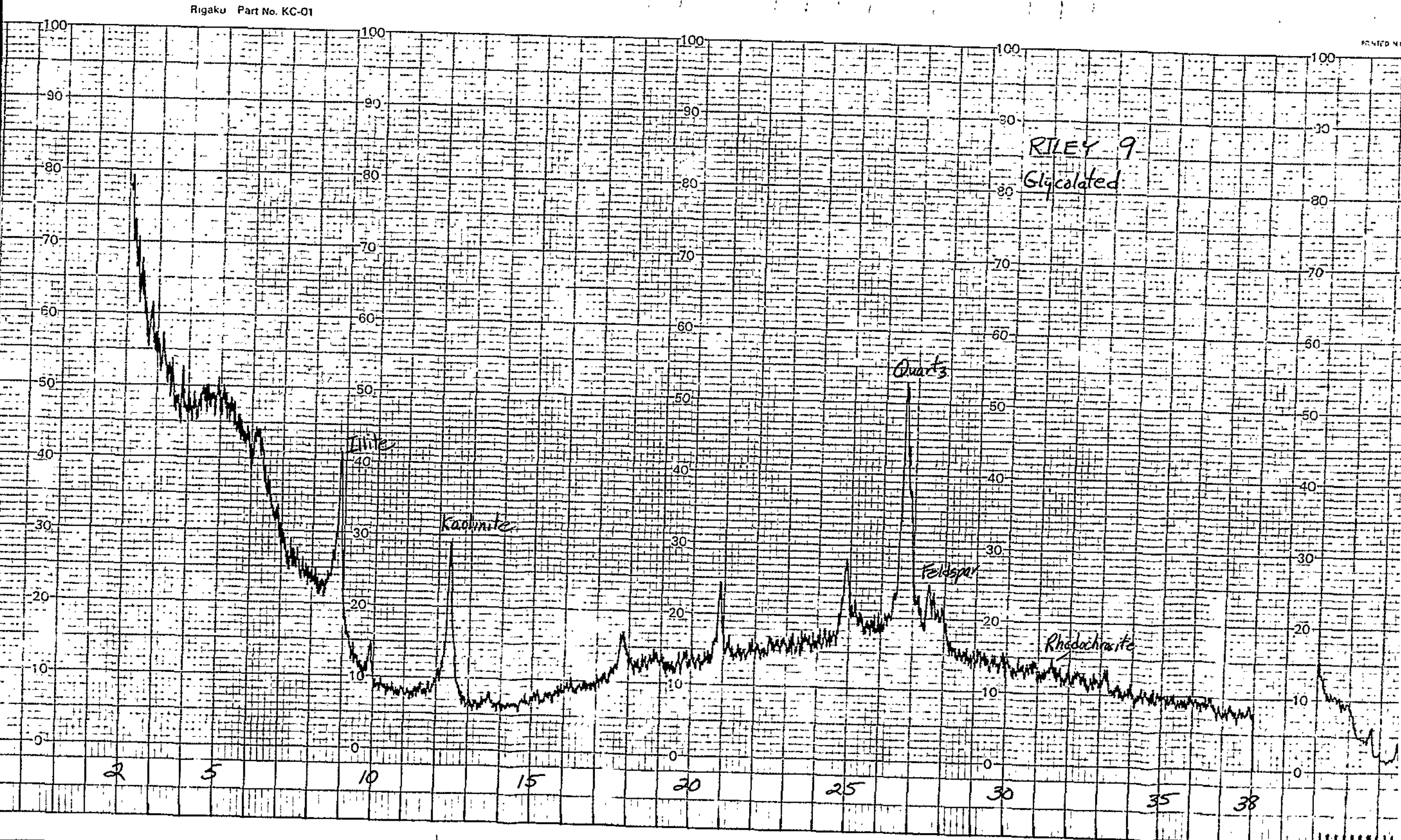
```
PROGRAM NO      2
  MODE                1
  RECYCLE             1
  RATE                1
  [illegible]     15 [illegible]
  [illegible]      2 [illegible]
  [illegible]         7
  [illegible]         3
  [illegible]         4
  [illegible]         4
```

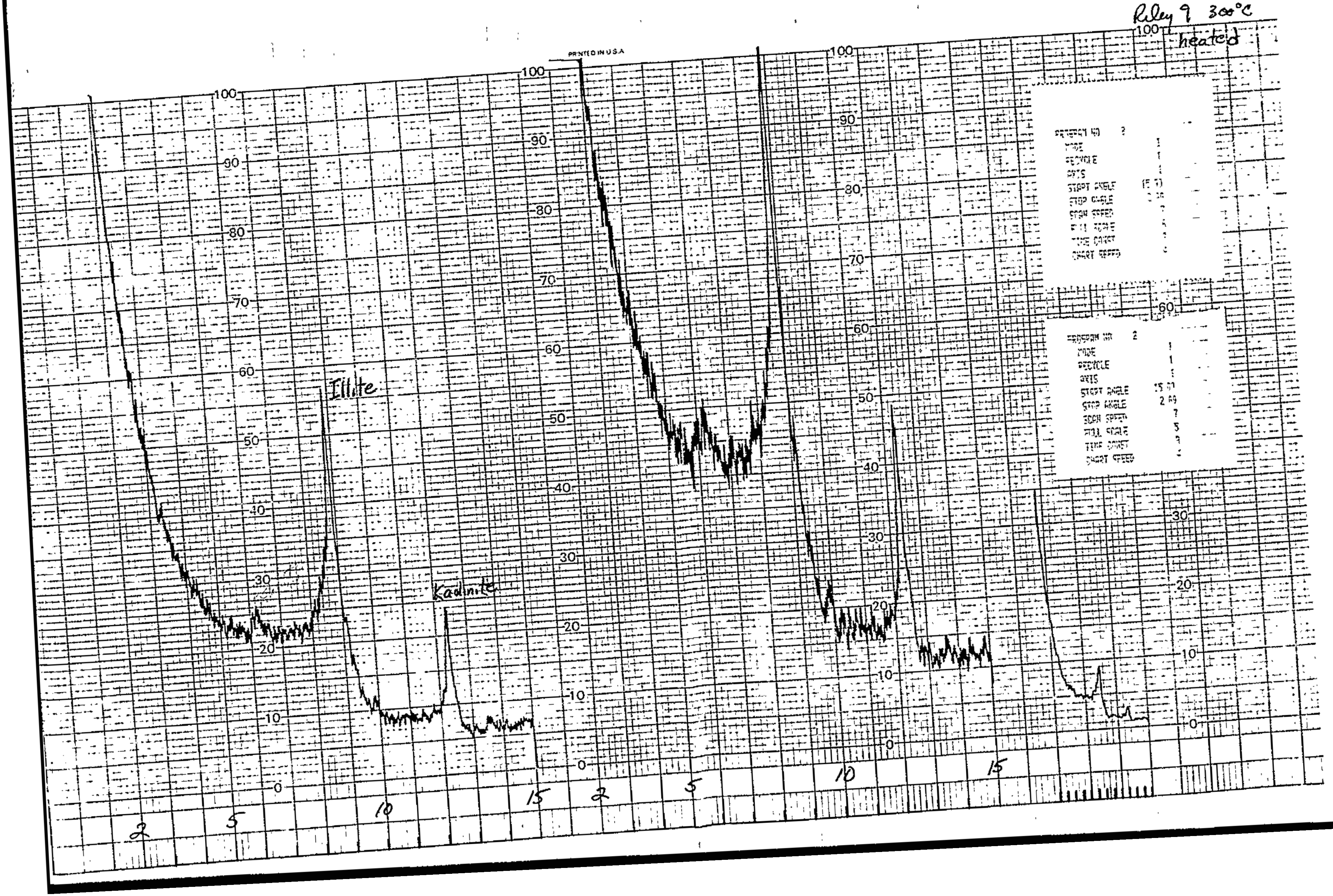

PRINTED IN U.S.A.
Rigaku Part No. KC-01
RILEY 8
Heated
330°C
30 minutes
Becker
Riley heated 330°
½ hr.
Illite
Zeolite
Kaolinite
Illite
Quartz
Kaolinite
Quartz
Feldspar
100
90
80
70
60
50
40
30
20
10
0
2
5
10
15
20
25
30
35
38

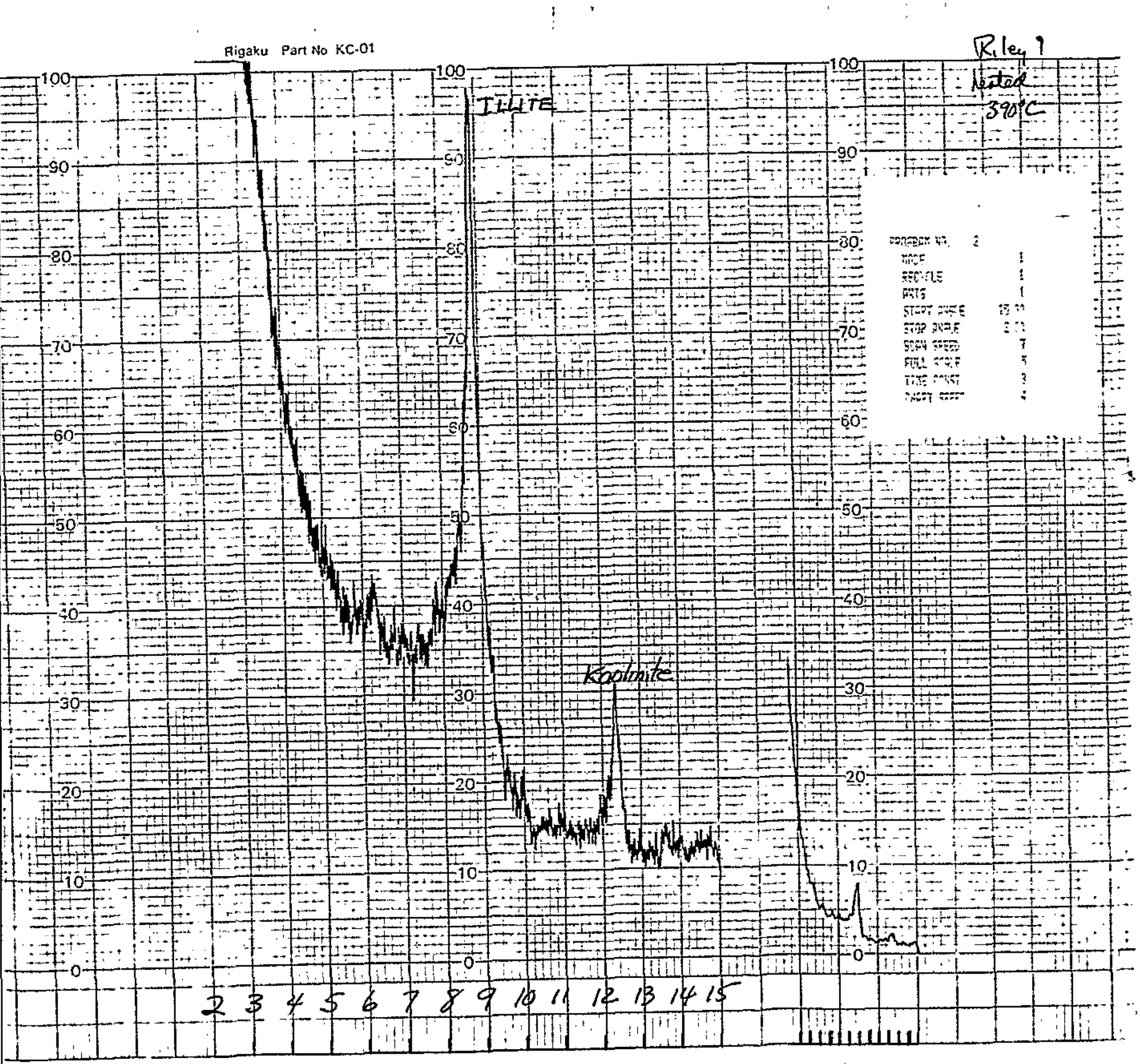


Riley 8
heated 390°C
1/2 hr.

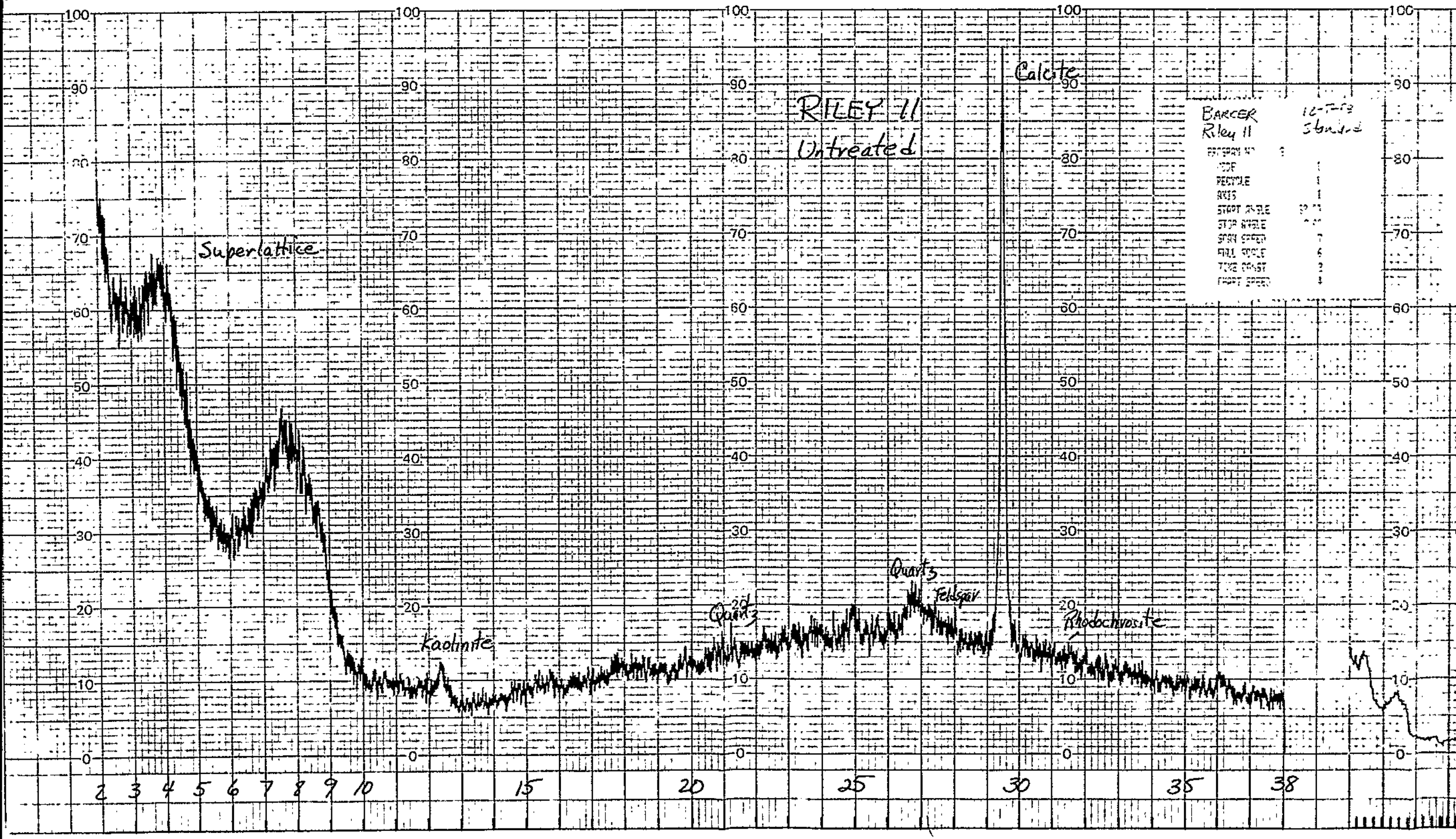

Rigaku Part No. KC-01
RILEY 9
untreated
Illite-
Smectite
Illite
Kaolinite
Zeolite
Illite
Quartz
Kaolinite
Quartz
Feldspar
100
90
80
70
60
50
40
30
20
10
0
2
3
4
5
6
7
8
9
10
15
20
25
30
35
38

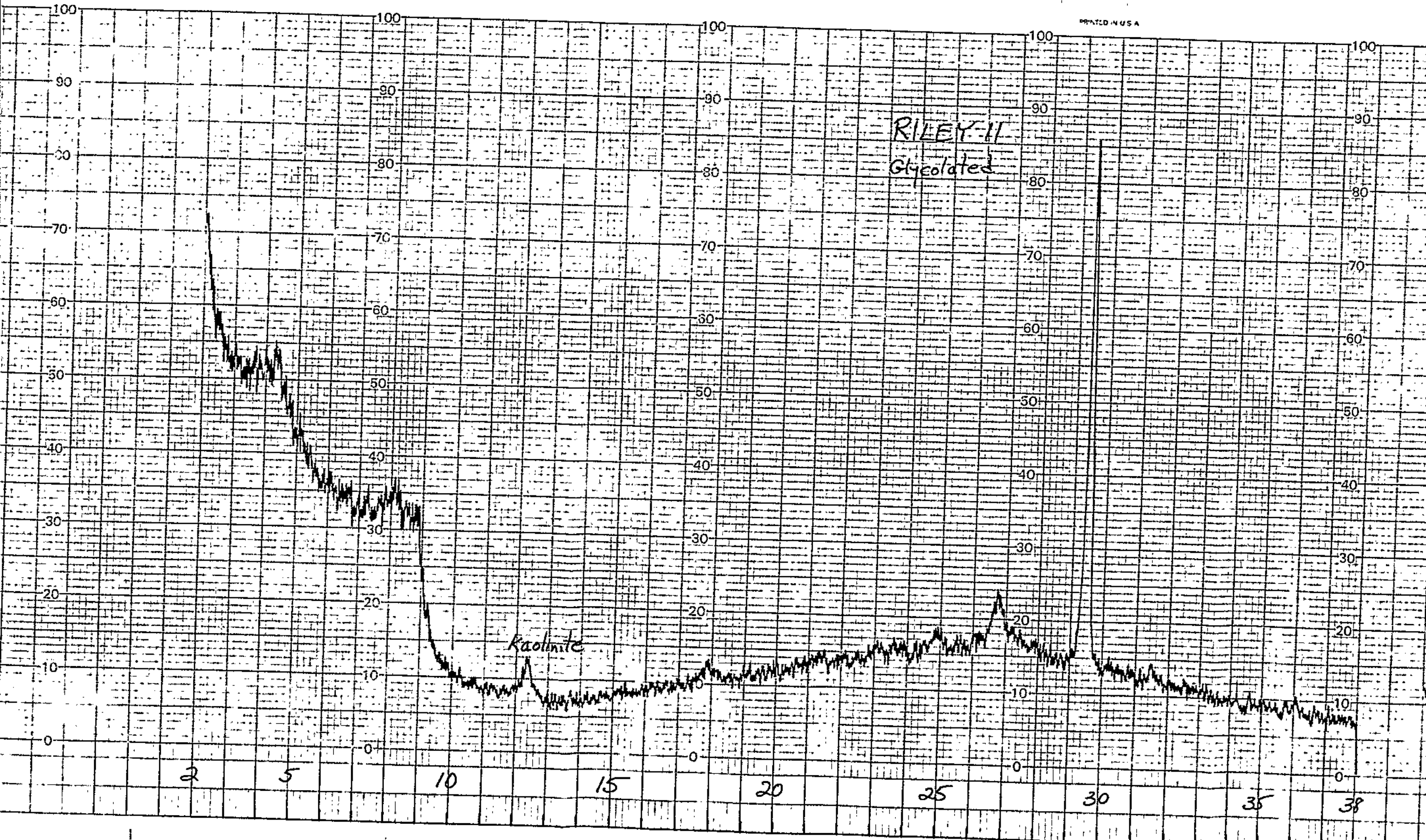

Rigaku Part No. KC-01
RILEY 9
Glycolated
Illite
Kaolinite
Quartz
Feldspar
Rhodochrosite
100
90
80
70
60
50
40
30
20
10
0
2
5
10
15
20
25
30
35
38

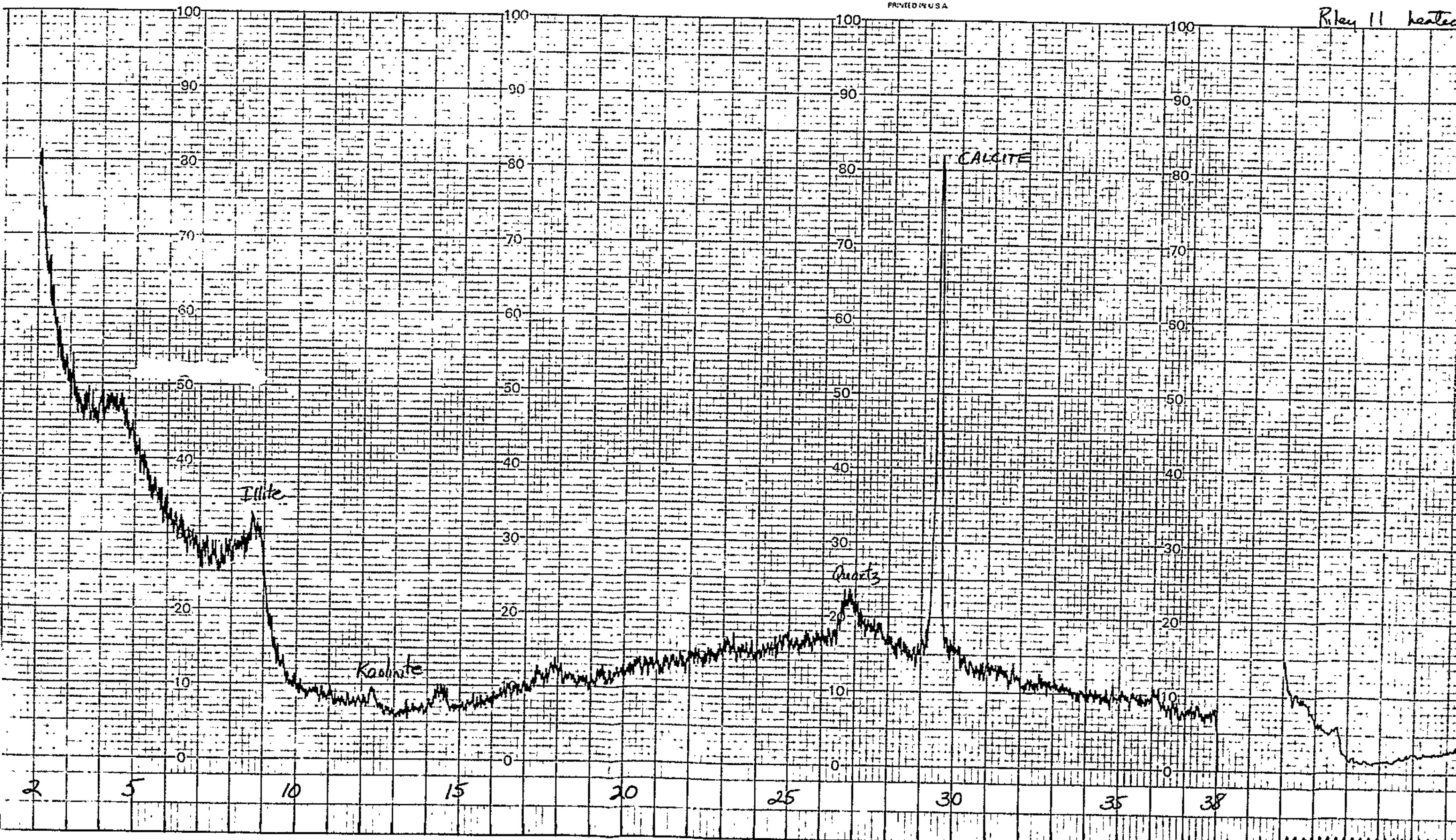

Riley 9 300°C
heated
Illite
Kaolinite
PRINTED IN U.S.A.
100
90
80
70
60
50
40
30
20
10
0
2
5
10
15
PROGRAM NO 2
MODE 1
RECYCLE 1
AXIS 1
START ANGLE 15.01
STOP ANGLE 2.49
SCAN SPEED 7
FULL SCALE 5
TIME CONST 3
CHART SPEED 2



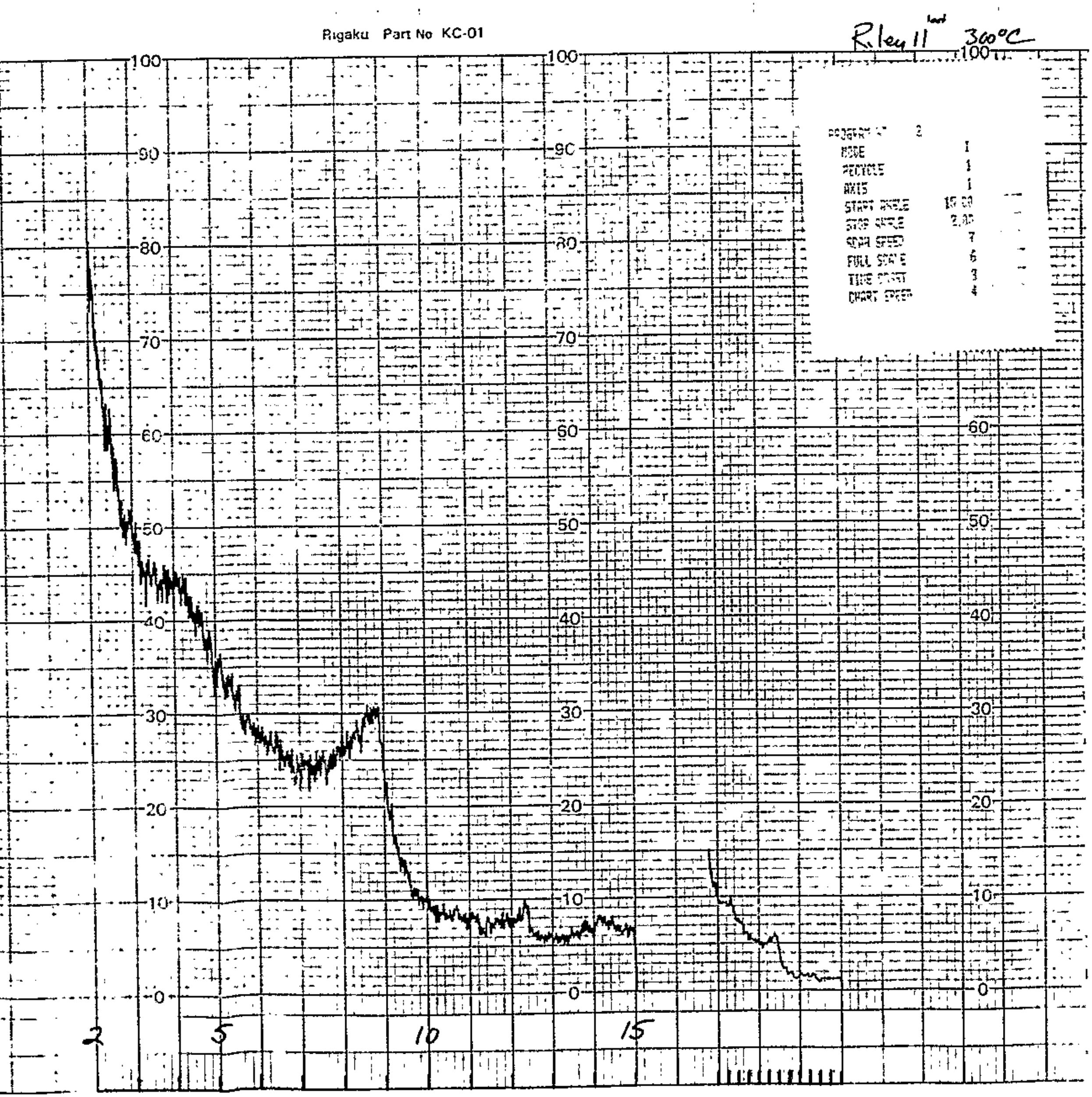
PROGRAM NO. 2
MODE 1
RECYCLE 1
PRTS 1
START ANGLE [illegible]
STOP ANGLE [illegible]
SCAN SPEED 7
FULL SCALE 5
TIME CONST 3
CHART SPEED 4


RILEY 11
Untreated
Calcite
Superlattice
Kaolinite
Quartz
Quartz
Feldspar
Rhodochrosite
BARCER
Riley 11
12-7-78
Standard
PROGRAM NO
MODE 1
RECYCLE 1
AXIS 1
START ANGLE
STOP ANGLE
SCAN SPEED 7
FULL SCALE 6
TIME CONST 2
CHART SPEED 4
PRINTED IN U.S.A.
100
90
80
70
60
50
40
30
20
10
0
2
3
4
5
6
7
8
9
10
15
20
25
30
35
38

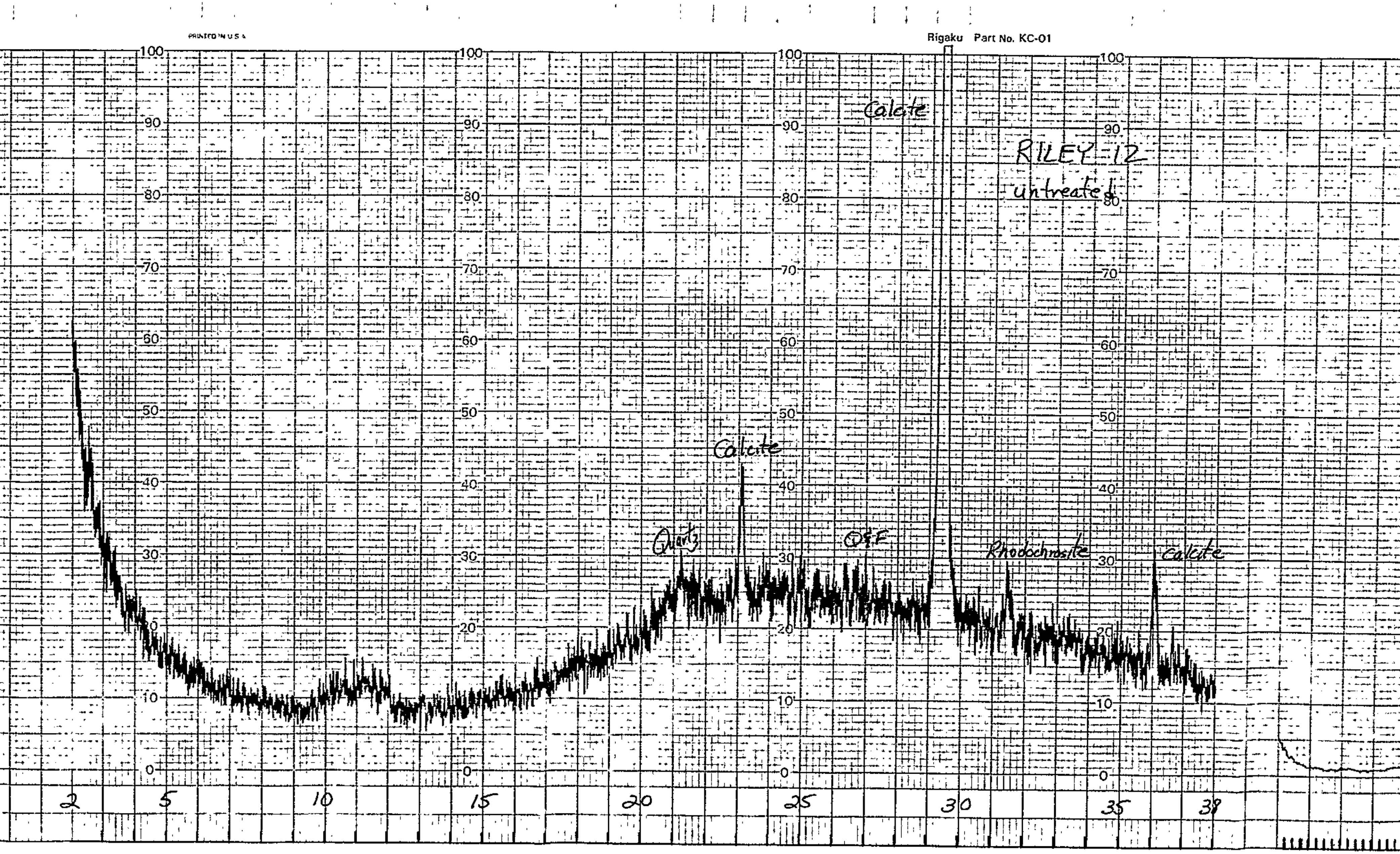

RILEY 11
Glycolated
Kaolinite
PRINTED IN U.S.A
100
90
80
70
60
50
40
30
20
10
0
2
5
10
15
20
25
30
35
38

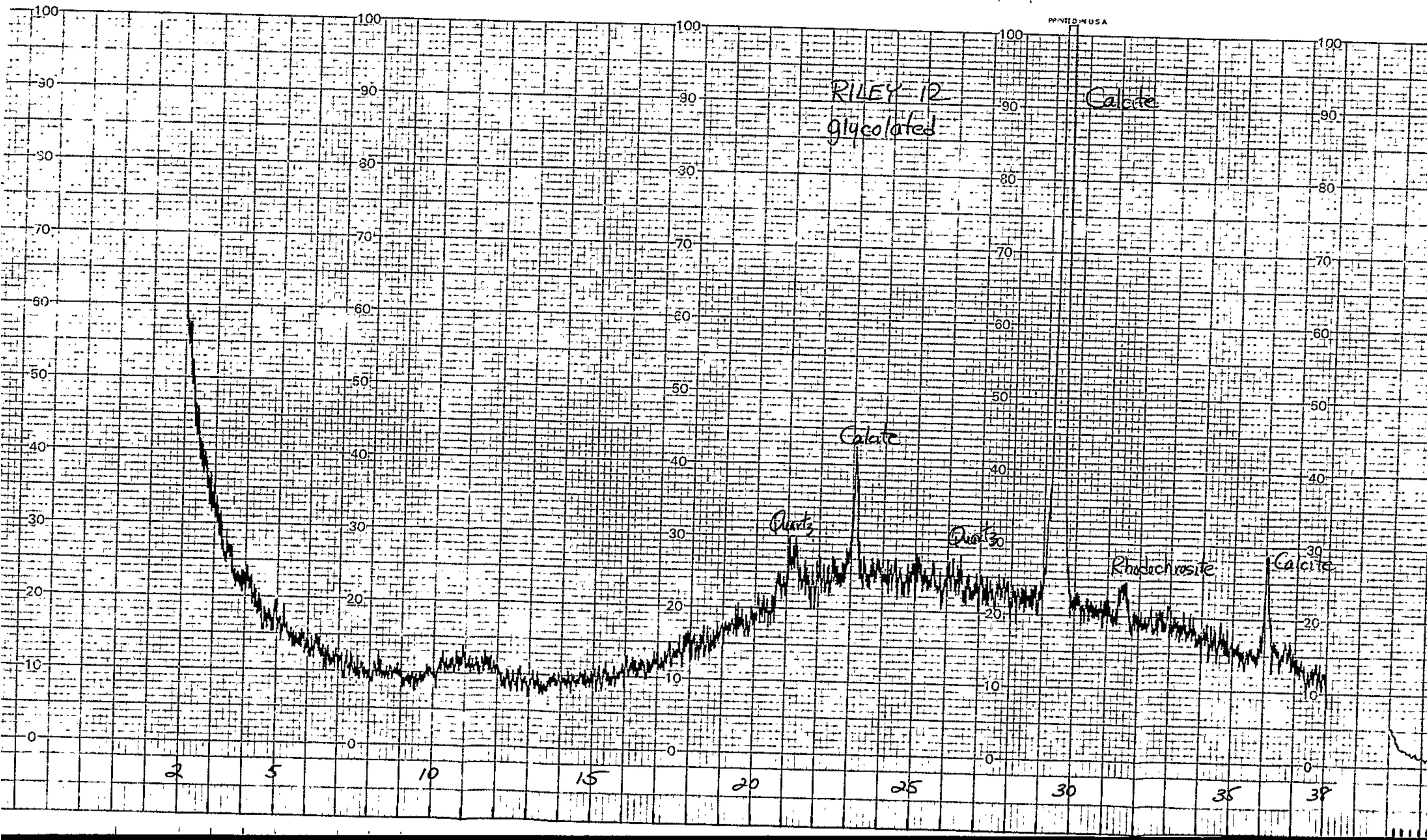

Riley 11 heated
PRINTED IN U.S.A.
100
90
80
70
60
50
40
30
20
10
0
CALCITE
Quartz
Illite
Kaolinite
2
5
10
15
20
25
30
35
38

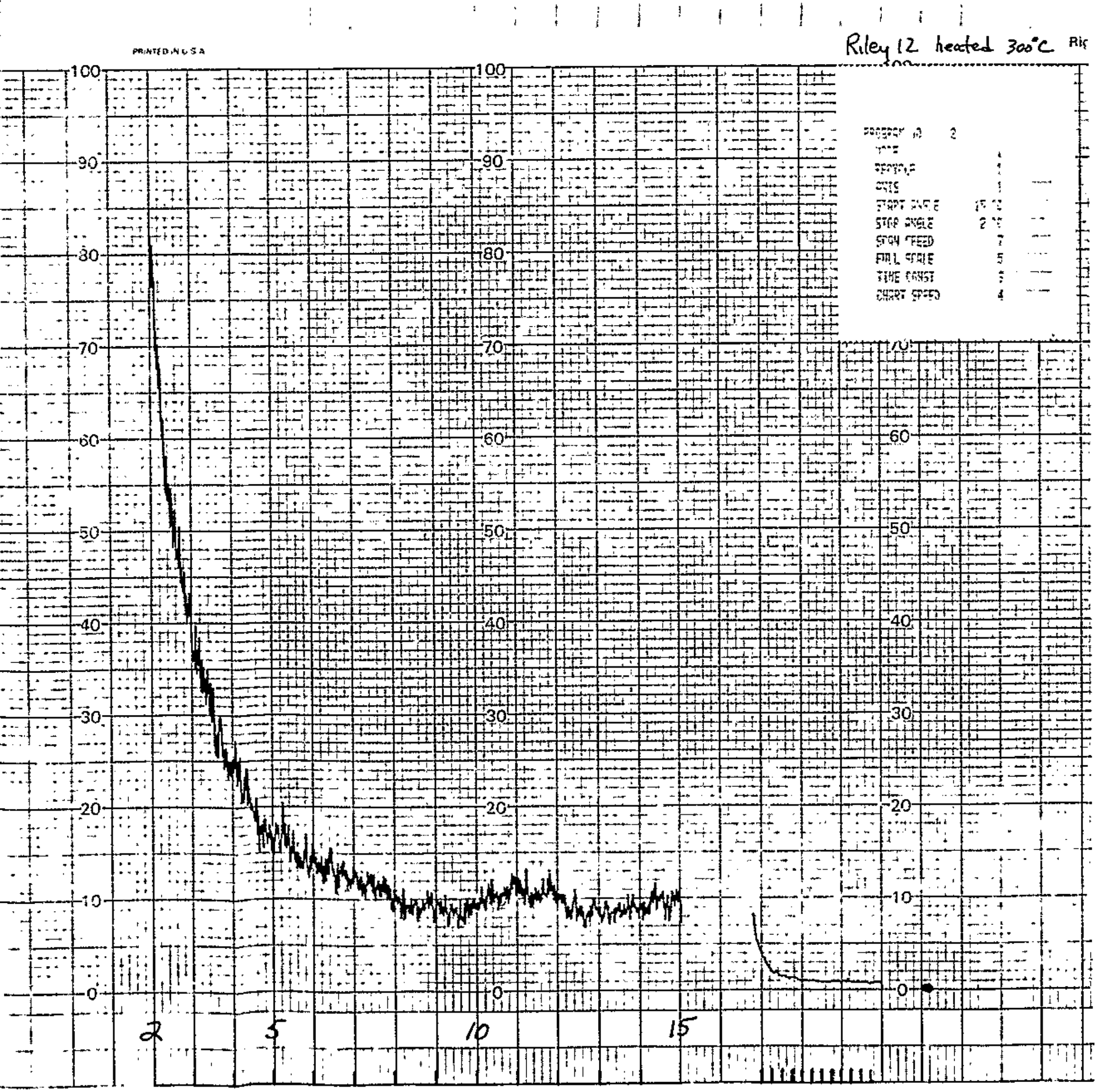
Riley 11 last 300°C



PROGRAM NO 2
MODE 1
RECYCLE 1
AXIS 1
START ANGLE 15.00
STOP ANGLE 2.00
SCAN SPEED 7
FULL SCALE 6
TIME CONST 3
CHART SPEED 4

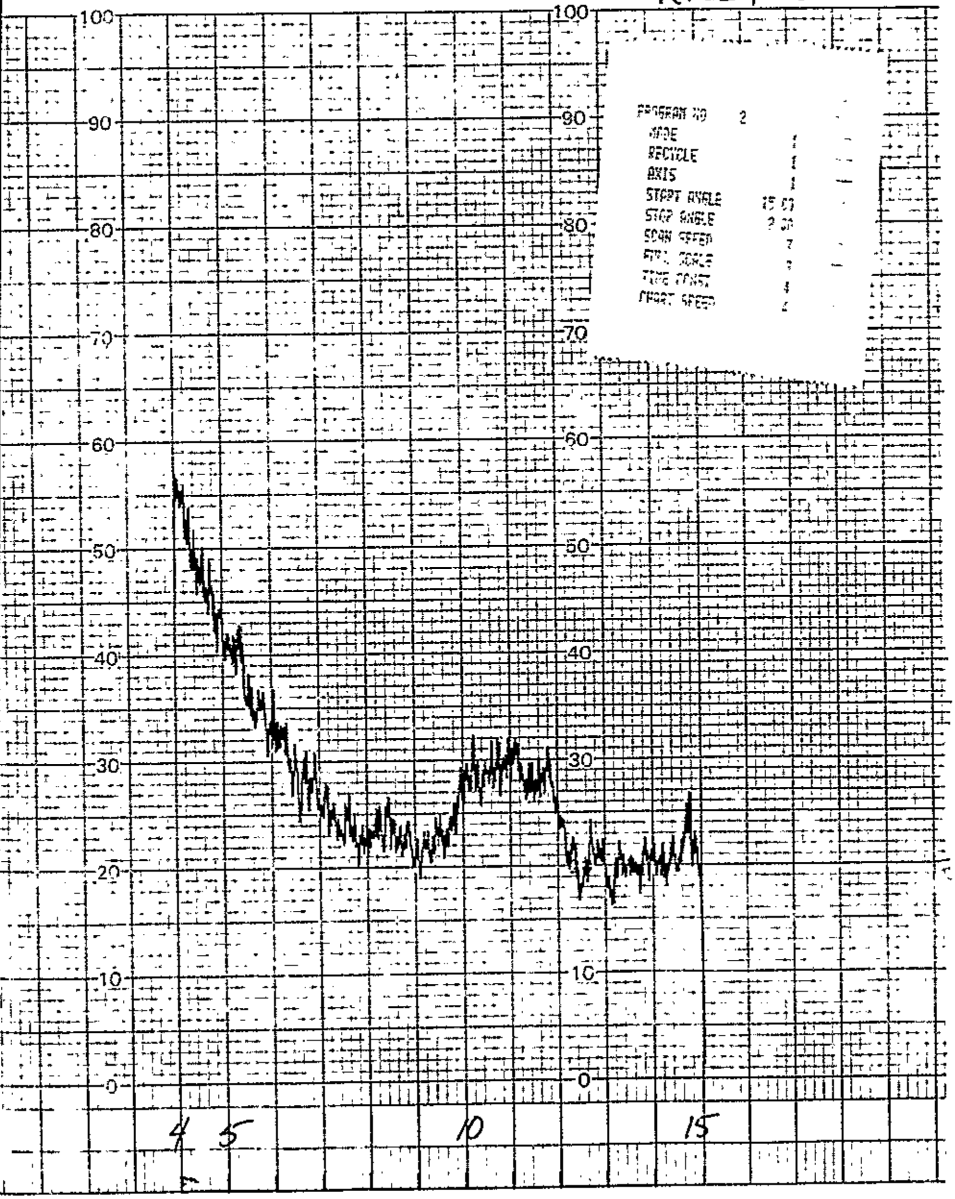

PRINTED IN U.S.A.
Rigaku Part No. KC-01
RILEY 12
untreated
Calcite
Calcite
Quartz
OFF
Rhodochrosite
Calcite
100
90
80
70
60
50
40
30
20
10
0
2
5
10
15
20
25
30
35
38


RILEY 12
glycolated
Calcite
Calcite
Quartz
Quartz
Rhodochrosite
Calcite
PRINTED IN U.S.A.
100
90
80
70
60
50
40
30
20
10
0
2
5
10
15
20
25
30
35
39



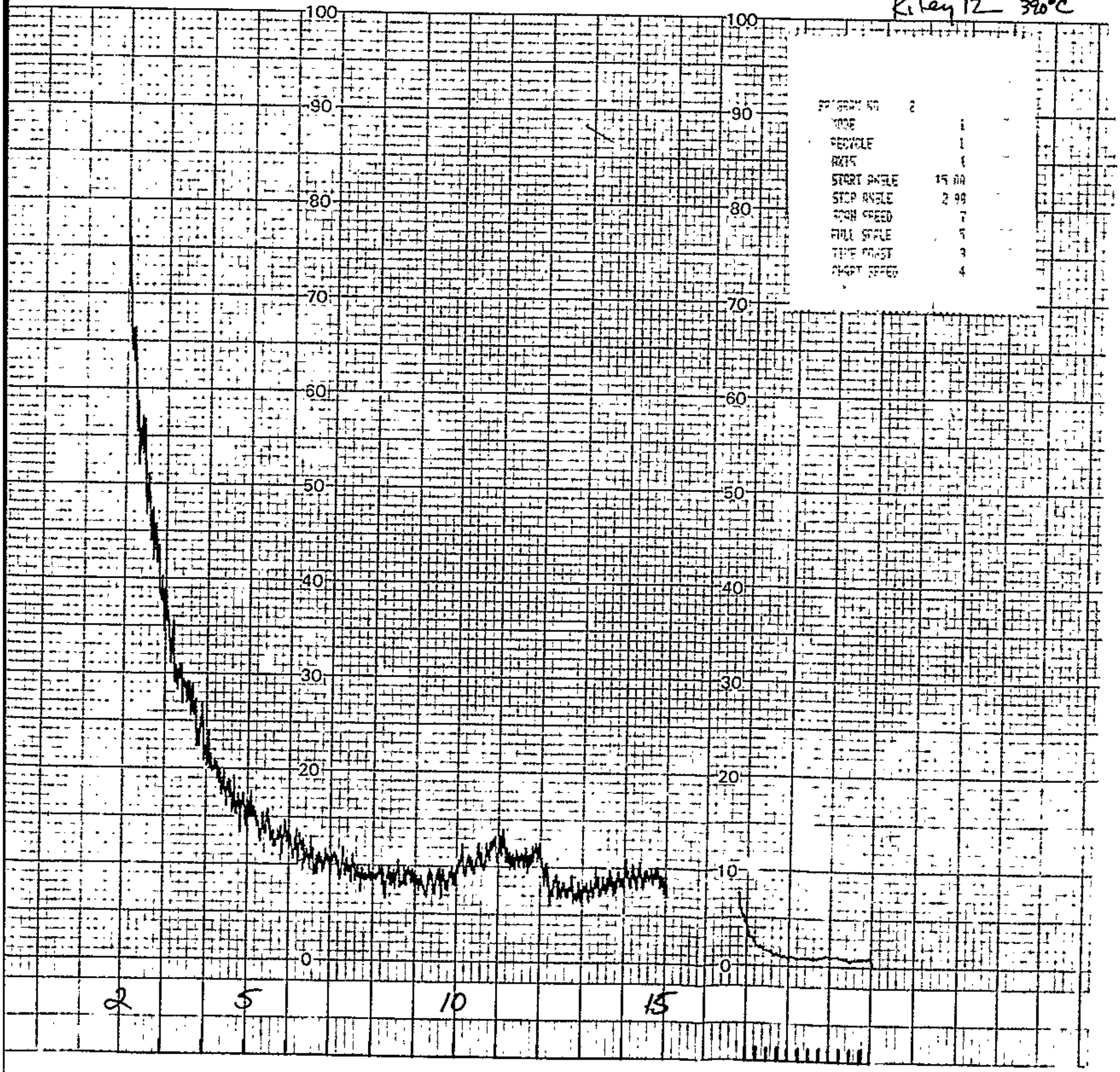
Riley 12 heated 300°C

RILEY 12 300°C



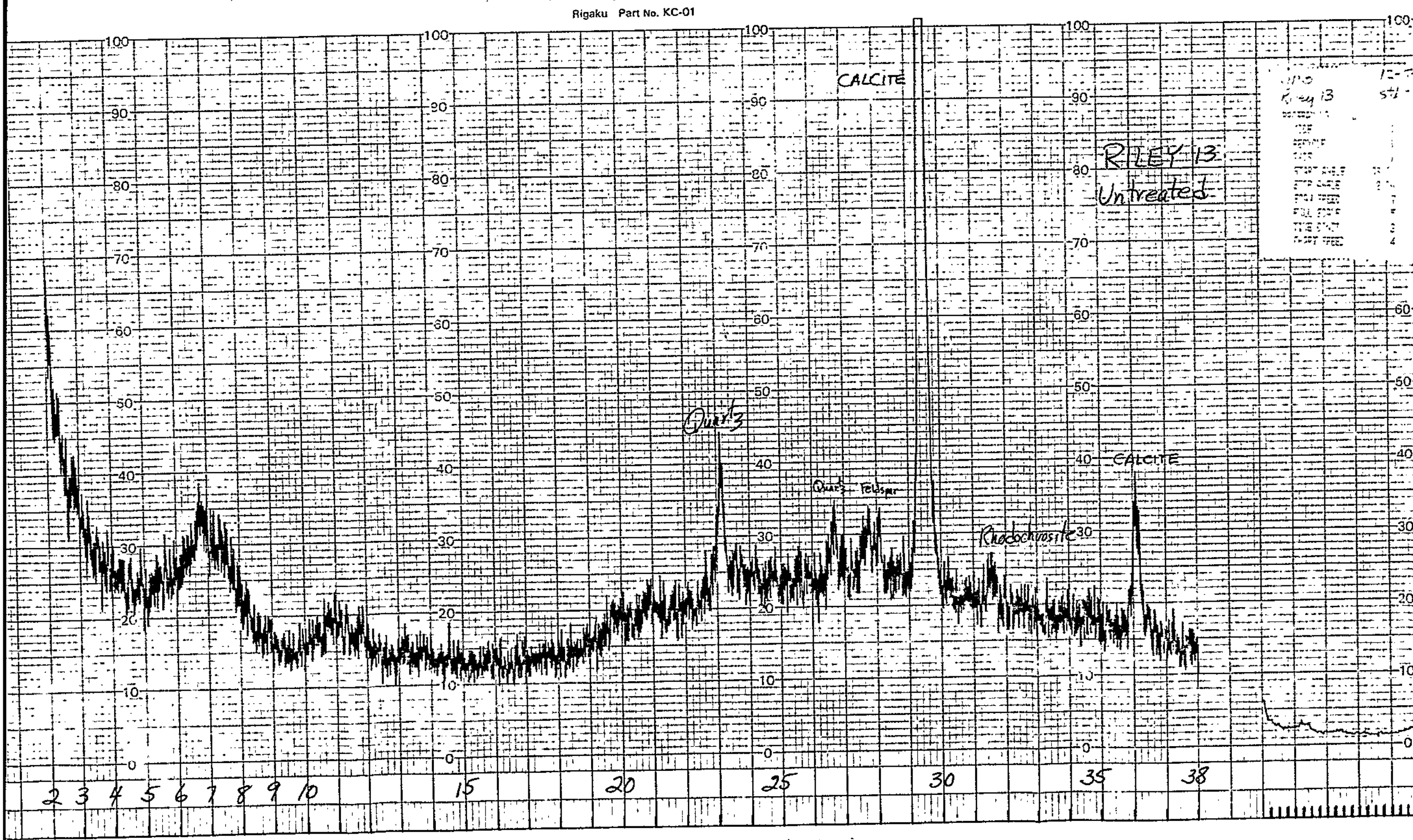
PROGRAM NO	2
MODE	1
RECYCLE	1
AXIS	1
START ANGLE	15.00
STOP ANGLE	2.00
SCAN SPEED	7
FULL SCALE	3
TIME CONST	4
CHART SPEED	4

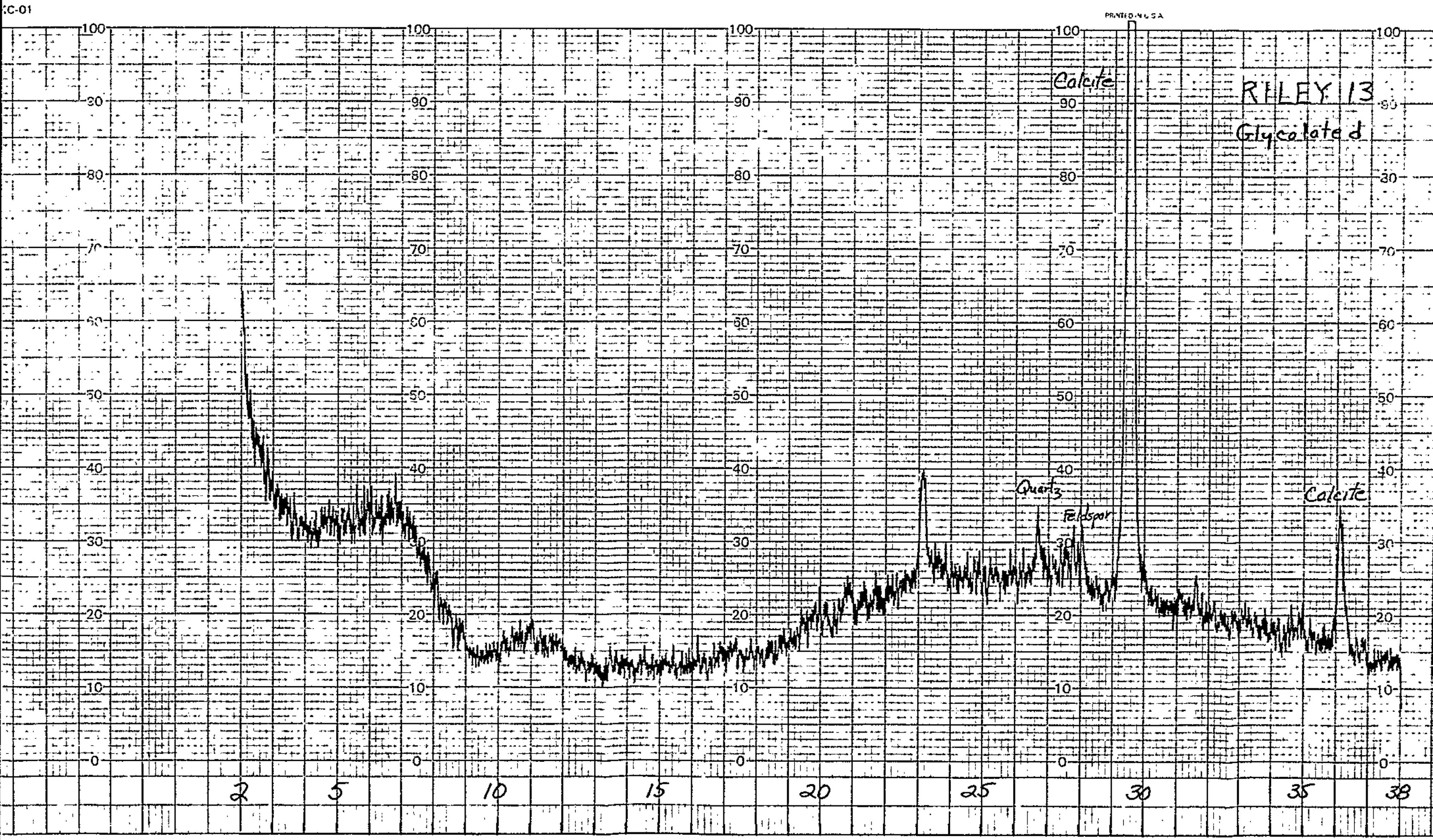
Riley 12 390°C

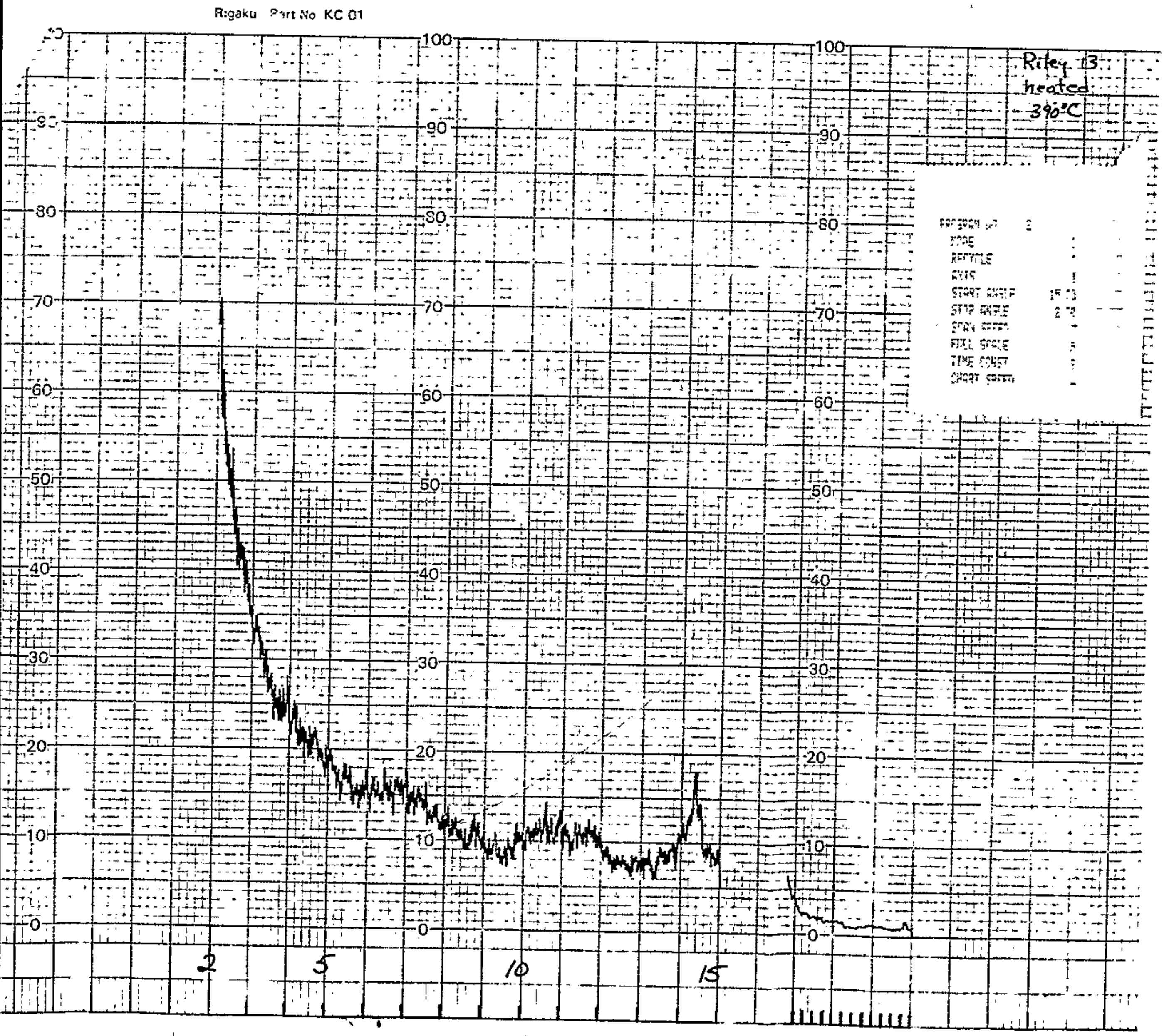


```
PROGRAM NO    2
  MODE              1
  RECYCLE           1
  AXIS              1
  START ANGLE   15.00
  STOP ANGLE     2.99
  SCAN SPEED        7
  FULL SCALE        5
  TIME CONST        3
  CHART SPEED       4
```

d 2
S= 17+7=23
10
V+I
C+S
C+V=

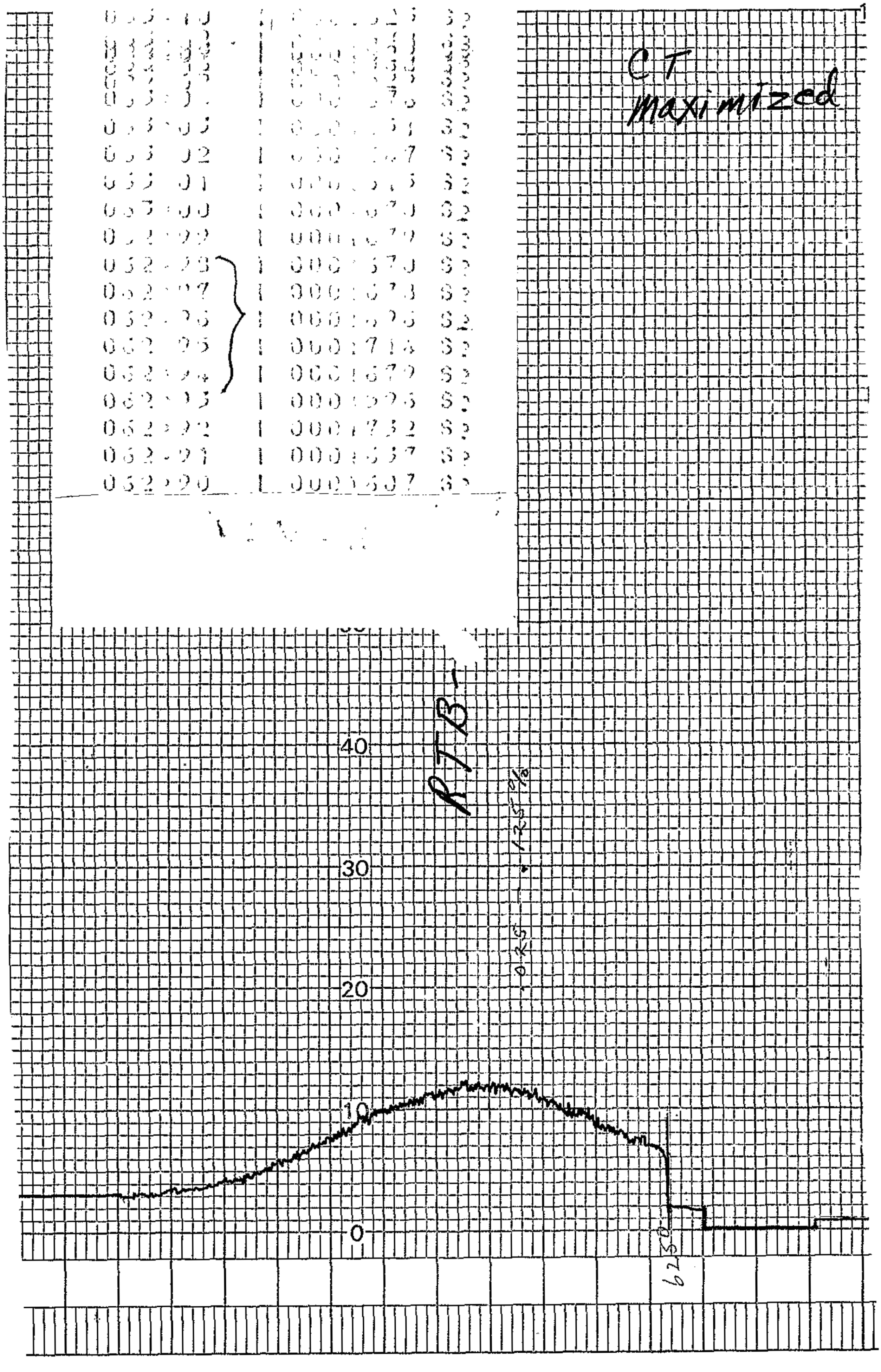



XC-01
PRINTED IN U.S.A.
RILEY 13
Glycolated
Calcite
Quartz
Feldspar
Calcite
100
90
80
70
60
50
40
30
20
10
0
2
5
10
15
20
25
30
35
38


Rigaku Part No KC 01
Riley 13
heated
390°C
PROGRAM NO 2
MODE
RECYCLE
AXIS
START ANGLE
STOP ANGLE
SCAN SPEED
FULL SCALE
TIME CONST
CHART SPEED
100
90
80
70
60
50
40
30
20
10
0
2
5
10
15

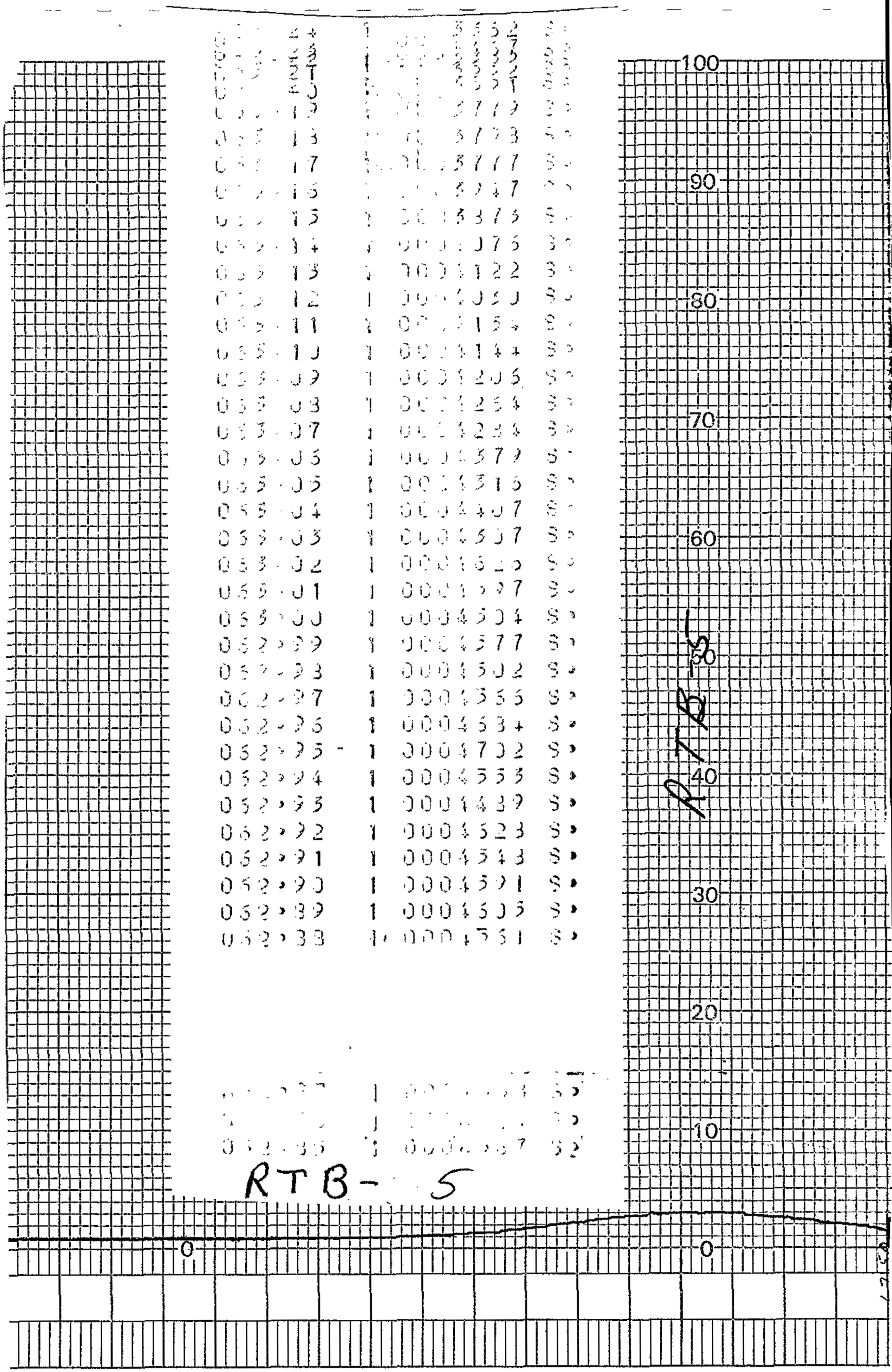
Addendum 3

XRF Data on Manganese Content of some Riley Travertine Samples



CT maximized

```
053:10   | [illegible]   S2
[illegible]
053:03   | [illegible]   S2
053:02   | [illegible]7  S2
053:01   | [illegible]5  S2
053:00   | 0001670   S2
052:99   | 0001679   S2
052:98   | 0001670   S2
052:97   | 0001673   S2
052:96   | 0001676   S2
052:95   | 0001714   S2
052:94   | 0001679   S2
052:93   | 0001596   S2
052:92   | 0001732   S2
052:91   | 0001637   S2
052:90   | 0001607   S2
```

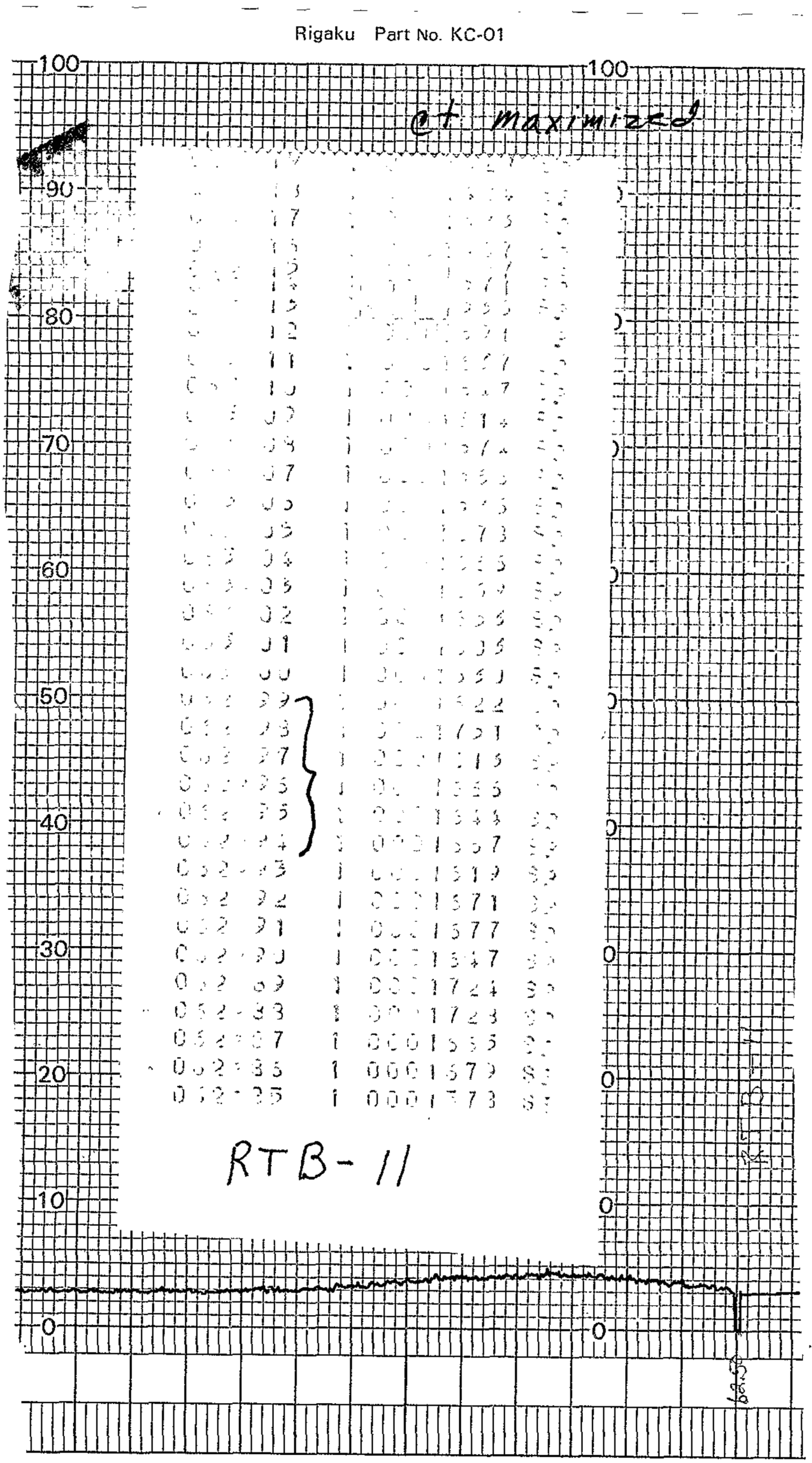


```
[illegible]   24   1  [illegible] 3552  S
[illegible]   23   1  [illegible] 3537  S
[illegible]   21   1  [illegible] 3532  S
[illegible]   20   1  [illegible] 3551  S
[illegible]   19   1  [illegible] 3779  S
[illegible]   13   1  [illegible] 3773  S
0 [illegible] 17   1  [illegible] 3777  S
0 [illegible] 16   1  [illegible] 3947  S
0 [illegible] 15   1  00[illegible]3375 S
0 5 3 . 1 4   1  0 0 0 4 0 7 5  S
0 5 3 . 1 3   1  0 0 0 4 1 2 2  S
0 5 3 . 1 2   1  0 0 0 4 0 5 0  S
0 5 3 . 1 1   1  0 0 0 4 1 5 4  S
0 5 3 . 1 0   1  0 0 0 4 1 4 4  S
0 5 3 . 0 9   1  0 0 0 4 2 0 5  S
0 5 3 . 0 8   1  0 0 0 4 2 5 4  S
0 5 3 . 0 7   1  0 0 0 4 2 3 4  S
0 5 3 . 0 6   1  0 0 0 4 3 7 9  S
0 5 3 . 0 5   1  0 0 0 4 3 1 6  S
0 5 3 . 0 4   1  0 0 0 4 4 0 7  S
0 5 3 . 0 3   1  0 0 0 4 5 0 7  S
0 5 3 . 0 2   1  0 0 0 4 6 2 0  S
0 5 3 . 0 1   1  0 0 0 4 5 9 7  S
0 5 3 . 0 0   1  0 0 0 4 5 0 4  S
0 5 2 . 9 9   1  0 0 0 4 5 7 7  S
0 5 2 . 9 8   1  0 0 0 4 5 0 2  S
0 5 2 . 9 7   1  0 0 0 4 5 5 5  S
0 5 2 . 9 6   1  0 0 0 4 5 3 4  S
0 5 2 . 9 5   1  0 0 0 4 7 0 2  S
0 5 2 . 9 4   1  0 0 0 4 5 5 3  S
0 5 2 . 9 3   1  0 0 0 4 4 3 9  S
0 5 2 . 9 2   1  0 0 0 4 5 2 3  S
0 5 2 . 9 1   1  0 0 0 4 5 4 3  S
0 5 2 . 9 0   1  0 0 0 4 5 9 1  S
0 5 2 . 8 9   1  0 0 0 4 5 0 5  S
0 5 2 . 8 8   1  0 0 0 4 5 5 1  S

[illegible]   1  [illegible]  S
[illegible]   1  [illegible]  S
0 5 2 . 8 5   1  0 0 0 4 [illegible] 7  S
```

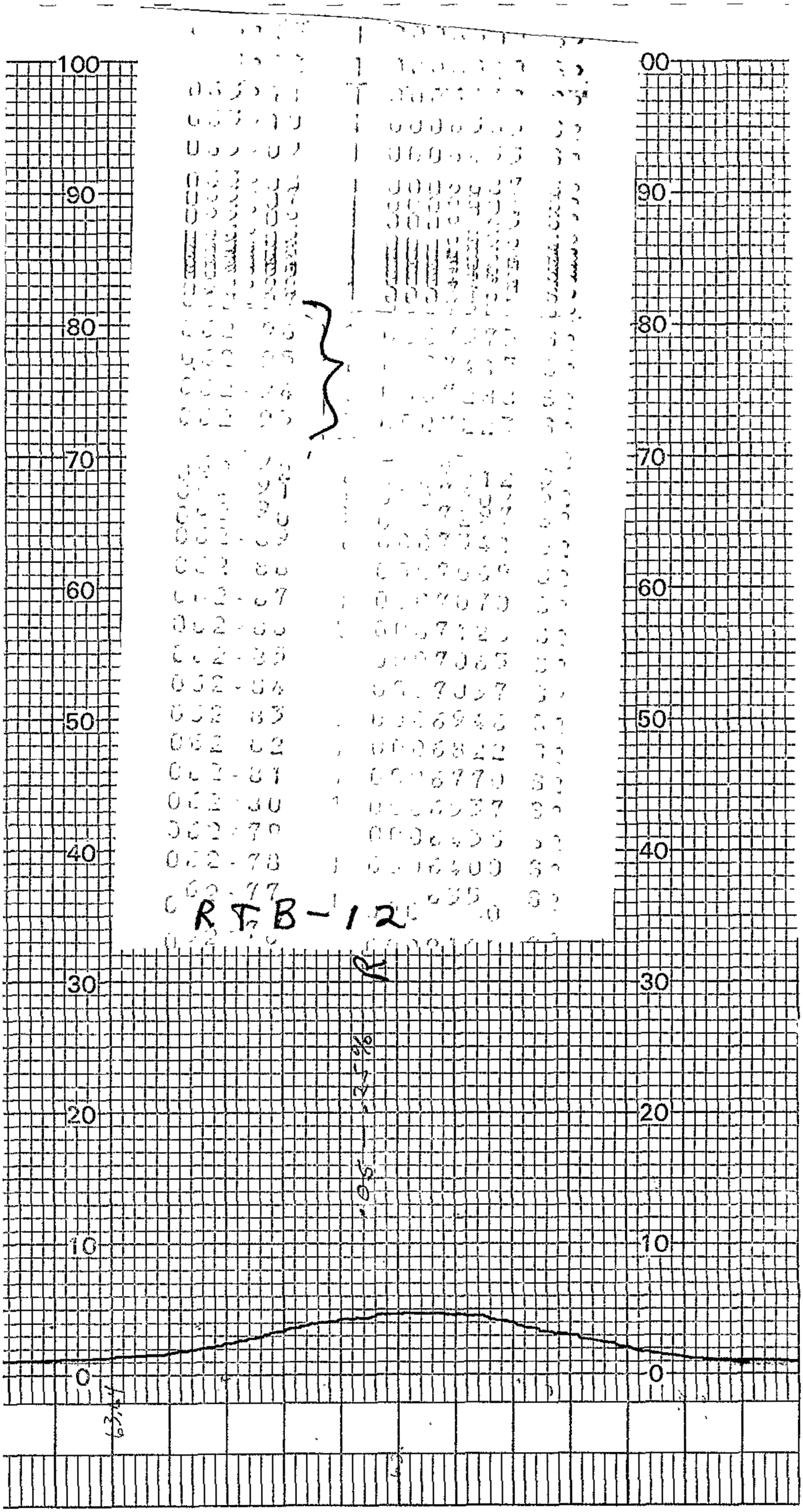
RTB- 5

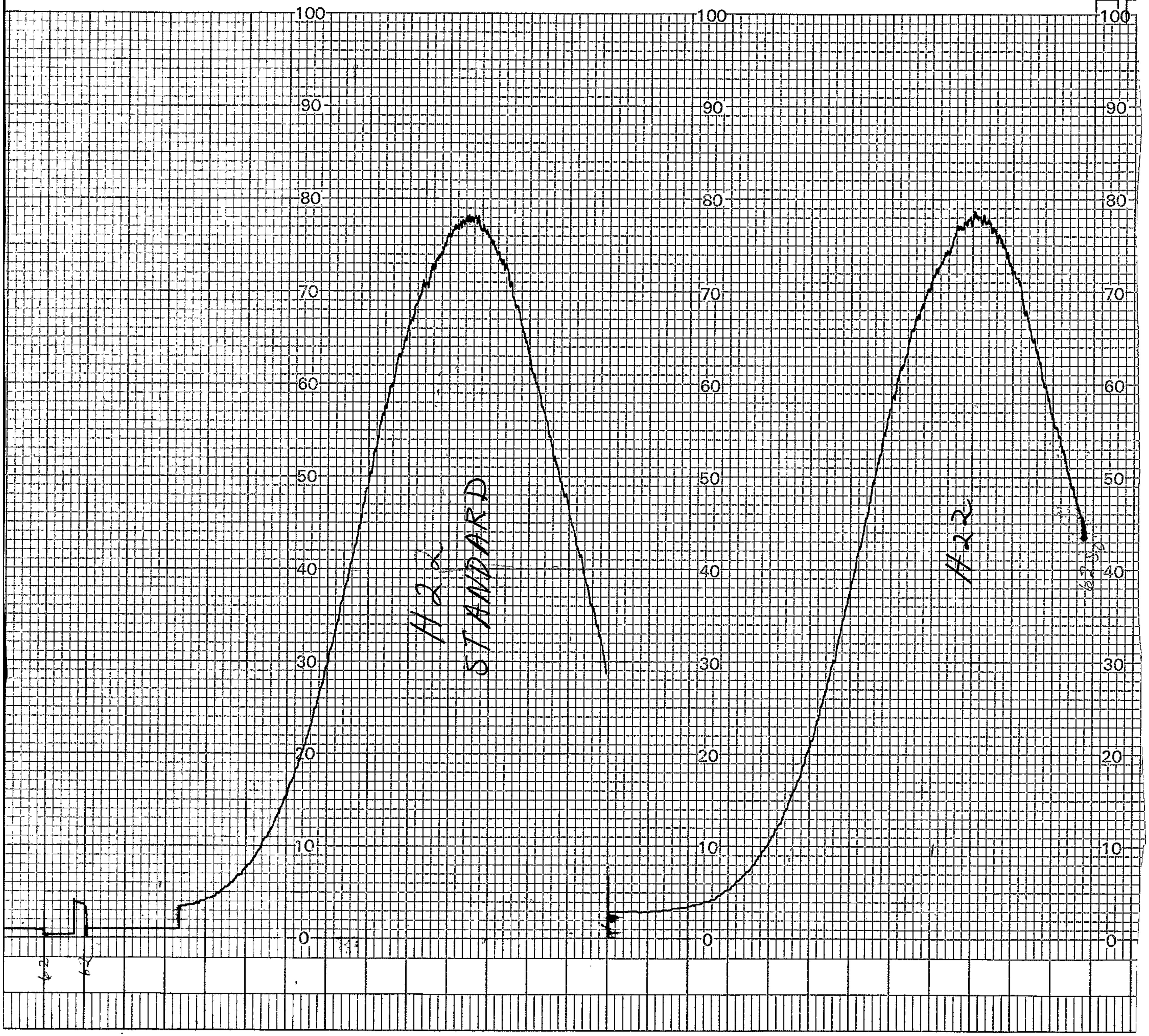
RTB-5



ct maximized

RTB-11


100
90
80
70
60
50
40
30
20
10
0
00
RTB-12
.05 — 25%

PRINTED IN U.S.A.