HYDROGEOCHEMISTRY AND OCCURRENCE OF SELENIUM IN THE GARBER-WELLINGTON AQUIFER, CENTRAL OKLAHOMA

By

KATHERINE KRETOW MCBRIDE

Bachelor of Science

Saint Lawrence University

Canton, New York

1978

Submitted to the Faculty of the Graduate College
of the Oklahoma State University
in partial fulfillment of the requirements
for the Degree of
MASTER OF SCIENCE
July, 1985

HYDROGEOCHEMISTRY AND OCCURRENCE OF SELENIUM IN THE GARBER-WELLINGTON AQUIFER, CENTRAL OKLAHOMA

Thesis Approved:

A Hounslow
Thesis Adviser

Wayne Pettyjohn

William Back

Norman N. Durham
Dean of Graduate College

PREFACE

The hydrogeochemistry of the Garber-Wellington Aquifer was studied to determine the types and extent of formation-water interactions occurring in the system and to define the geochemical mechanism responsible for the release of selenium into the ground water. It was determined that principal water types are calcium-magnesium-bicarbonate and sodium-bicarbonate. Selenium is present in the ground water in areas where the pH of the water is high, enabling oxidation of the selenite ion, which is normally found adsorbed, to selenate, which is mobile.

I wish to express my appreciation to my major adviser, Dr. Arthur Hounslow, for suggesting the study and for providing support and guidance throughout the course of my work. I would like to thank Drs. Wayne Pettyjohn and William Back for serving as committee members. Acknowledgement is also extended to the Oklahoma State University Water Resources Center, which provided funds for sample analysis, to the Garber-Wellington Association for use of their water quality data, to Ray Powers for his help with XRD, and to Cindy Patterson for compiling information from numerous sources. Special thanks also go to my typist, Kristi Girl, for doing an excellent job on the manuscript.

Completion of this work would not have been possible without the help of many friends, a list of whose names would fill an entire page. In the interest of brevity, I will mention only a few whose friendship and encouragement kept me going. Love and appreciation are extended to

Jennifer Richardson, Freddi Manni, and Mary Rafalowski for constant emotional support and countless good times. Thanks to David Back for his entertaining company and his chair. Thanks to Randall Ross for being my slave, and to Kelley Race for giving much needed shots in the arm. Recognition is extended to "Willies" for providing an escape from the drudgery and to the OSU Weightlifting Club for providing a physical outlet. Last but not least, thanks to Curt McCormick for showing up at the right time with a very good suggestion.

I would like to dedicate this thesis to Scott McBride and Mary Kretow, whose love and faith have helped more than they could ever know.

TABLE OF CONTENTS

Chapter Page

LIST OF TABLES

LIST OF FIGURES

Figure Page

CHAPTER I

INTRODUCTION

Statement of Purpose

The purpose of the study has been to examine the water quality of the Garber-Wellington Aquifer and describe its hydrogeochemistry. Particular attention has been given to the occurrence of selenium in the water, as it has been detected in several supply wells in concentrations greater than the potable water standard of 10 ug/l. The objectives of the study included determination of the mode of occurrence of selenium in the rocks and identification of the geochemical factors responsible for its release into the ground water system.

Location

The study area is located in central Oklahoma, where the Garber Sandstone and Wellington Formation yield usable quantities of water and form the Garber-Wellington Aquifer. This area encompasses all of Oklahoma and Cleveland Counties, the southern part of Logan County, and the western portions of Lincoln and Pottawatomie Counties (Figure 1). It is bounded by T19N, T6N, R4W, and R6E.

Scope

The physiography, geology, and hydrogeology of the study area are all well documented in the literature, therefore, background information

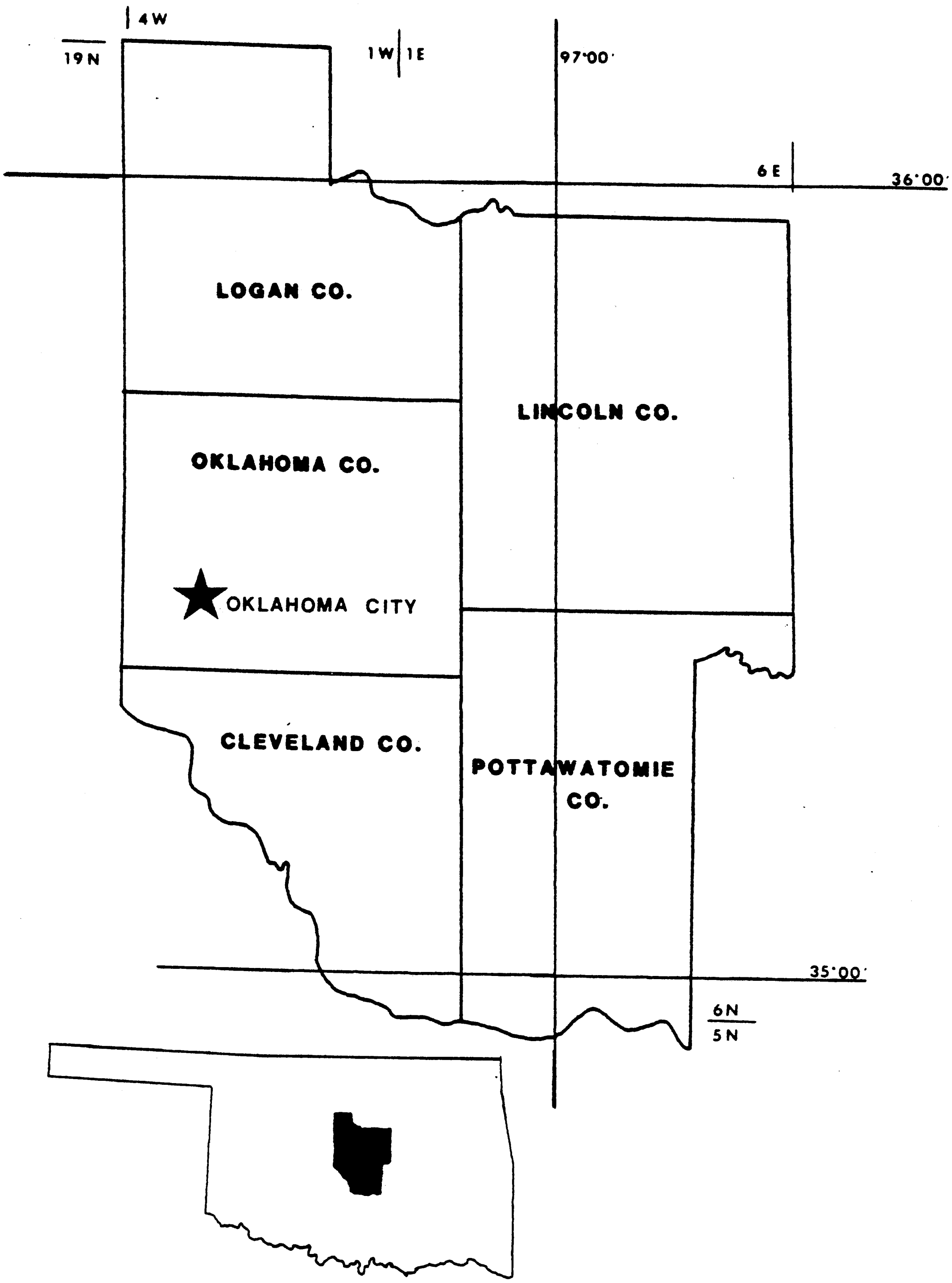


Figure 1. Location of the Study Area in Oklahoma

was collected from published sources. Water quality analyses were gathered principally from data bases compiled by the U.S. Geological Survey (WATSTOR), the Oklahoma Geological Survey, and the Garber-Wellington Association.

Lithologic samples were collected from the Garber Sandstone and Wellington Formation across their respective outcrop areas. Well cuttings were obtained from the Oklahoma Geological Survey Core and Sample Library. Analytical work on these samples was done using both Oklahoma State University facilities and private laboratories.

Where possible, all the data were analyzed using the Statistical Analysis System (SAS). Correlation and factor analysis programs were used extensively to determine data interrelationships and interdependencies. WATEQF, a hydrogeochemical modelling program developed by the U.S. Geological Survey, was used to examine the chemical equilibria of the system with respect to various mineral species.

CHAPTER II

PREVIOUS INVESTIGATIONS

Geology

The first study of the geology and water resources of Oklahoma was published by Gould in 1905. At that time, the Lower Permian strata in northcentral Oklahoma had not been subdivided and were known collectively as the Enid Formation. As described by Gould, "The . . . formation includes all of the rocks of the red beds formation from the base of the Permian to the lowermost gypsum ledges on the eastern slope of the Gypsum Hills" (Gould, 1905). In the study area the Enid is described as red clay shales with interbedded sandstone. Gould gives a brief description of the geography, geology, and water usage within the Enid Formation over its outcrop area.

Subdivision of the lower Permian strata in central Oklahoma was undertaken by Aurin, Officer, and Gould (1926), who correlated the Enid with formations in southern Kansas, and named six distinct geologic units occurring in this state. The Garber Sandstone and Wellington Formation were two of these. In the study area, the Wellington Formation (correlated with the formation of the same name in Kansas) is described as "Alternating beds of red shales and red sandstones" (Aurin et al., 1926) bounded by the Herington Limestone below and the lowest heavy sandstone of the Garber Formation above. The Garber Sandstone, described as "a series of red clay shales, red sandy shales and red sandstones," was further subdivided into a lower Lucien Shale member and an upper Hayward Sandstone member. The Garber is bounded above by the distinctive "blocky red clay shales of the Hennessey Formation."

In 1933, Patterson described in detail the lower Permian strata in Logan and Lincoln Counties, further subdividing the Wellington Formation into a lower Fallis Sandstone member and upper Iconium Shale member. This differentiation is based on the decreasing proportion of sandstone to shale progressing upward through the section. Patterson also noted the occurrence of dolomite within the Iconium member and suggested that both the Garber and Wellington were deposited under deltaic conditions.

Further summaries of the general geology and structure of the Garber Sandstone and Wellington Formation in the study area were published in Oklahoma Geological Survey Bulletin 40, by Anderson, Bale, and Travis in 1930. These reports were published by county as part of the series, "Oil and Gas in Oklahoma."

Merritt and Minton (1930) investigated the occurrence of dolomite in the Garber and Wellington. They found that carbonates occurred erratically throughout both formations in Cleveland, Logan, Oklahoma, and Pottawatomie counties and were most likely to be found in conglomeratic zones where the pebbles consist chiefly of dolomite. Hamm and Merritt (1944), in their work on barite in Oklahoma, noted an abundance of barite rosettes in the upper 100 feet of the Garber Formation throughout the central part of the state. Although not as prolific, rosettes were also found in upper zones of the Wellington Formation in this region. Olson (1967) and Simpson (1979) have described and summarized the lower Permian terrestrial vertebrate fauna in central Oklahoma outcrops. Garber and Wellington Formations.

Simpson concludes that the fossils reflect a progression from pond and marsh to stream environments, and are indicative of increasingly arid climatic conditions over the period of deposition.

Aside from the papers described above, no work has been done on the general geology or mineralogy of the Garber or Wellington within the study area. However, numerous papers have been written that examine the Wellington Formation elsewhere in Oklahoma. Shelton (1979), in his study of the geology and mineral resources of Noble County, Oklahoma, examined the petrography and sedimentology, and summarized the paleontology of the Permian strata exposed there. He subdivided the Wellington Formation into four unnamed units using three "key bed" sandstone sequences having lateral continuity through Noble county. He notes that the most striking characteristic of the Wellington in this area is the "facies change whereby lenticular sandstones are developed southward at the expense of red mudrock and thin dolomites". Raasch (1946) also studied the Wellington Formation in Noble County, recognizing the occurrence of fossiliferous beds in clayey carbonate sediments. These were noted to pinch out, however, with the change in rock composition described above, and do not occur in the present study area. Tasch (1964) has examined periodicity in the Wellington Formation in Kansas and northern Oklahoma. Using paleolimnologic and paleontologic data, he concludes that the Wellington was deposited under conditions alternating from "limited evaporitic to brackish to fresh." The environment of deposition is reconstructed as a coastal flat with relict puddles, ponds, and small lakes, which gradually freshened as the epeiric sea regressed.

Al Shaieb (1976) has studied the Uranium potential of tidal flat sandstones and siltstones in Oklahoma. He concluded that the Wellington Formation in Noble county was deposited under conditions similar to those found in western Oklahoma formations where Uranium mineralization has occurred. Cox and Al Shaieb looked at stratabound copper in the Lower Permian red beds in Grant County, Oklahoma. They discovered copper sulfide in several thin mineralized beds in the shallow subsurface, in the upper shale member of the Wellington Formation. The genesis of the deposits is attributed to upward migration of cuprous chloride-rich waters during diagenisis, and subsequent precipitation of copper. Shockey et al. (1974), discovered copper-silver solution fronts in sandstone paleochannels in the Wellington Formation at Paoli, Oklahoma. Jordan (1961) has mapped salt beds in the Wellington at depths of 812 to 928 feet below the surface in western Oklahoma. Culver and Gray (1966) have done a pedological study of the Wellington Formation in northern Oklahoma, and found that the predominant clay minerals in soils developed over the formation are illitic and chloritic with some interstratification of montmorillonitic clays.

Because the Garber and Wellington Formations show dramatic lateral variation in lithology, extrapolation of characteristics noted elsewhere is often not possible. As a primary example, the formations are capable of yielding usable quantities of water only within the study area.

Hydrogeology and Geochemistry

The first examination of water from the Permian redbeds in Oklahoma was published by Gould (1905). Water was chemically characterized as being hard or soft, based on the presence and amount of calcium and magnesium. Aquifer characterization was limited to measurements of depth to water and supply capabilities (gpm) of scattered wells. Records of wells and water quality data in northern Oklahoma and southern Logan Counties were compiled by Carr and Marcher (1977). Bingham and Moore (1975) studied the ground water resources of the Oklahoma City Quadrangle and published a hydrologic atlas of that area. Further studies of the hydrogeology of the Garber-Wellington aquifer were done by Wood and Burton (1968) for Cleveland and Oklahoma Counties, Carr and Marcher (1977) for southern Logan and northern Oklahoma Counties, and Wickersham (1979) for the southern part of the ground-water basin in Cleveland, southern Oklahoma, and parts of Pottawatomie County. Assessments of hydrologic properties of the aquifer were made in all of the above reports. An estimate of total fresh water stored in the Garber-Wellington was given by Wickersham (1979, for 1973) at greater than 50 million acre-feet. Estimates of total saturated thickness, transmissivity, storage coefficient, and yield were presented for each of the regions studied. Average recharge was given by Carr and Marcher and Wickersham as 10%, Wood and Burton as 5% of total precipitation. Additional work on recharge was done by Pettyjohn and Miller (1982), who based preliminary estimates of effective ground water recharge rates in central Oklahoma on data generated by a computerized stream hydrograph separation technique.

Chemical quality of the water has been investigated by several writers. Wood and Burton (1968) analyzed the major chemical constituents of 131 ground water samples from Cleveland and Oklahoma counties. They concluded that overall, water from the Garber-Wellington aquifer is potable, however, locally may be "hard, or high in sulfate, chloride, fluoride, nitrate, or dissolved solids." In addition, they found that the availability of potable water is controlled by the depth to the fresh water-salt water interface. Bingham and Moore (1975) studied the water resources of the Oklahoma City Quadrangle and found that the dissolved solids content of the Garber-Wellington aquifer was generally less than 500 mg/l, although locally it exceeded 1000 mg/l due to high sodium and bicarbonate content. Carr and Marcher (1975) sampled 28 wells for selected constituents in southern Logan and northern Oklahoma counties. They found that dissolved solids generally did not exceed 1000 mg/l except in areas where oil field activities artificially contaminated the aquifer. Wickersham (1979) summarized data collected by the Oklahoma Water Resources Board from the southern part of the ground water basin. Her results indicate that water quality varies with depth; the best quality is found at depths of 500 to 800 feet.

In an effort to evaluate the potential for Uranium mineralization in the Garber-Wellington aquifer, the Department of Energy contracted Union Carbide to perform a reconnaissance geochemical survey of the Oklahoma City Quadrangle. More than 200 wells tapping the aquifer were sampled for uranium and several other parameters. Based on the information collected, it was concluded that the Garber-Wellington is not a likely candidate for uranium mineralization. In response to concern expressed by municipalities dependent on the aquifer for potable supply that high levels of selenium, chromium, and uranium were contaminating municipal wells, Bloch, Gay and Dunbar (1981) reviewed and summarized the data collected during the Hydrogeochemical and Stream Sediment Reconnaissance Program. They found that concentrations of these three elements in water from most wells sampled met the U.S.

Environmental Protection Agency standards for drinking water. The exceptions were four wells in which the standard for chromium was exceeded, and eighteen wells in which the <u>proposed</u> standard for uranium was exceeded.

CHAPTER III

PHYSIOGRAPHY

Description

The physiography of Oklahoma has been described by Gould (1905), Snider (1917), and Fenneman (1922). The outcrop area of the Garber Sandstone and Wellington Formation is in the Central Lowland Physiographic Province of the United States (Fenneman, 1922). This region is further described by Fenneman as belonging to the Osage Plains and Tall Grass Prairie sections of the province. Gould and Snider classify the five-county study area as being part of the Flint-Sandstone Hills and Low Plains, and Sandstone Hills and Red Beds Plains physiographic regions of Oklahoma, respectively (Figure 2). The contact between the Sandstone Hills region and Red Beds Plains to the west is gradational, therefore the boundary between them is arbitrary. Gould interprets this boundary as a NNE-SSW trending line through central Logan, Oklahoma and Cleveland Counties, placing most of the study area in the Sandstone Hills region. Snider's interpretation puts the area primarily in the Red Beds Plains as he feels the change in physiography occurs further east in Lincoln and Pottawatomie Counties. The altitude of the region ranges from approximately 800 feet (east, southeast) to 1300 feet (west, northwest) above mean sea level.

The Sandstone Hills region is characterized by rolling topography indicative of alternating sandstone and shale beds which dip to the west

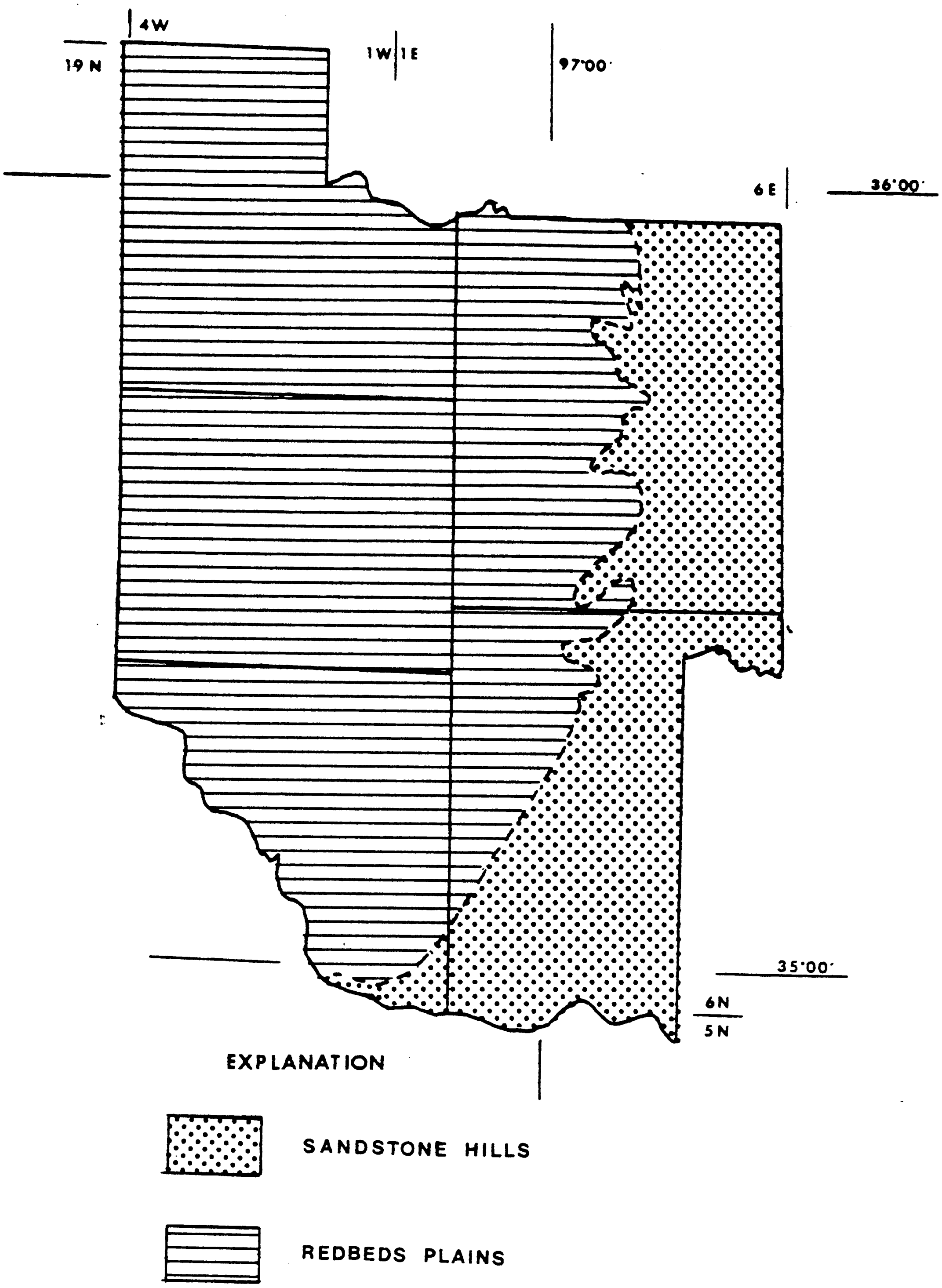


Figure 2. Physiographic Map of the Study Area
(After Snider, 1917)

and northwest. Land surface of this region is sharply undulating, with broad sandstone escarpments 300 to 400 feet high separating valleys formed by rapid weathering of less resistant shale (Snider, 1917). Geologically, the amount of sandstone cropping out decreases westward, until it occurs as thin seams in soft red shale beds. In this region the Hennesey Shale overlies the Garber-Wellington aquifer. With the reduction in sandstone, a less pronounced topography has been developed. The Red Beds Plains region consists of a rolling plain sloping primarily south of east where upland areas rarely rise greater than 100 feet above valley floors.

Drainage

The entire study area lies within the drainage basin of the Arkansas River. Principal watercourses include the Cimarron River in the far north and northeast, Canadian and Little Rivers in the south, and Deep Fork and the North Canadian River in the central part of the region (Figure 3). These major rivers are mature eastward-flowing streams characterized by broad, flat, sand-filled channels and wide flood plains. The average gradient is 3 to 4 feet per mile. Tributary streams generally flow northward or southward and exhibit dendritic to subtrellis drainage patterns (Snider, 1917). They have incised shallow, narrow channels into the prairie uplands.

The U.S. Geological survey operates 12 stream gaging stations on the principal rivers and their tributaries. Flow rates can fluctuate dramatically over the course of one year as channels are usually full during wet periods and can dry up almost entirely during long dry spells. Before extensive damming occurred, flash flooding was common

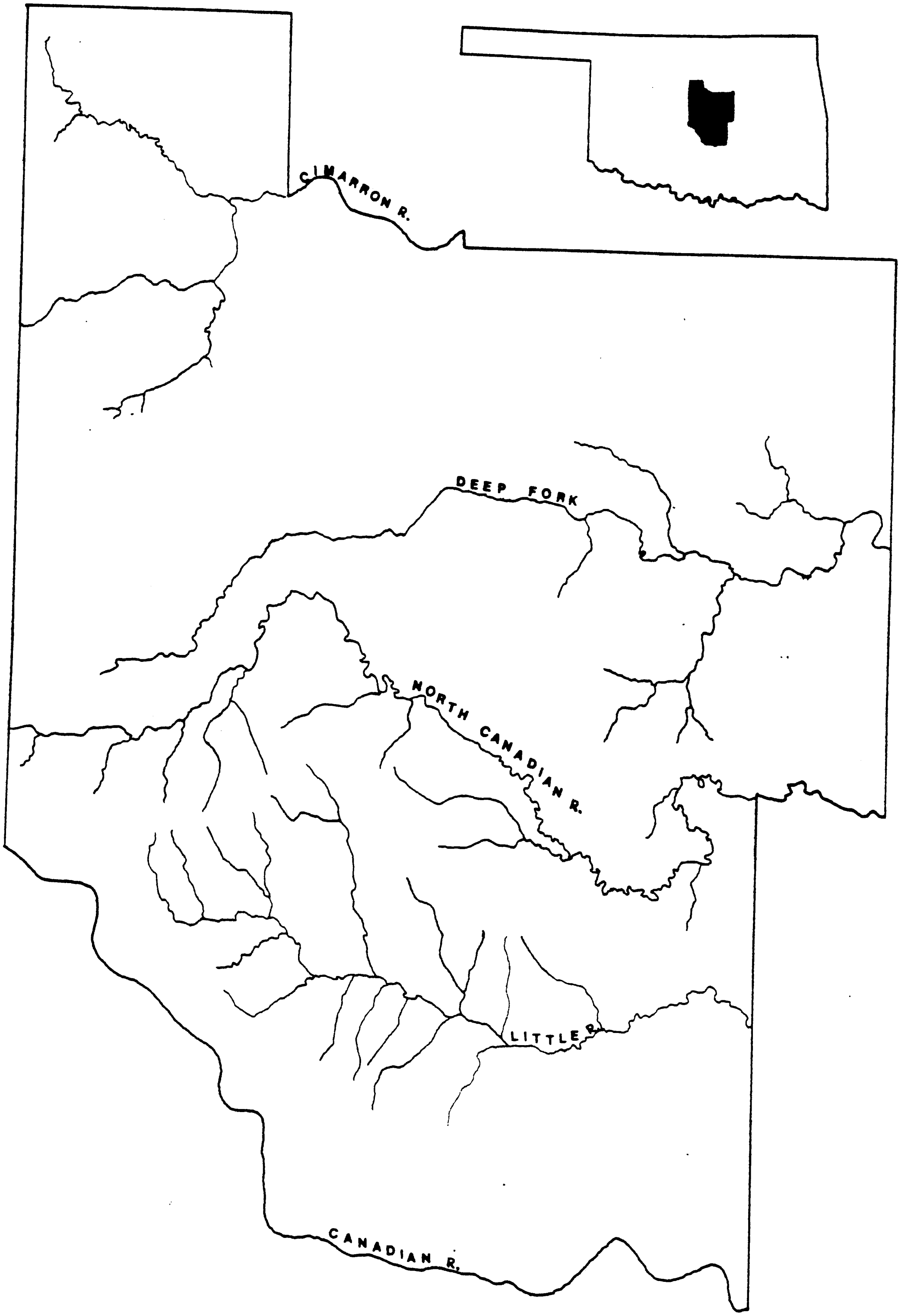


Figure 3. Principal Surface Water Courses

after heavy rainfall and due to snowmelt in the spring. However, numerous streams have been dammed throughout the study area to form reservoirs for water supply, and current flow rates are much more controlled.

Vegetation

Native vegetation is strongly influenced by both soil (and underlying rock) type and the availability of water, which vary considerably across the region. Precipitation decreases from east to west (Figure 4) while the percentage of clay in the soil generally increases in this direction. The sandy upland areas in the east are forested by post oak, scrub oak, blackjack oak, and hickory with an understory of grasses [Soil Conservation Service (SCS), 1977]. The shale valleys and western upland prairies are characterized by tall prairie grasses such as big bluestem, little bluestem, indiangrass, side-oats grama, and buffalograss (SCS, 1969).

Land Use

Much of the land overlying the Garber-Wellington aquifer has been cultivated and is used extensively for agriculture. Grazing livestock, primarily beef cattle, and growing small grains (alfalfa, sorghum, wheat, oats, and hay) are the primary enterprises (SCS, 1970). Numerous oil wells tapping formations beneath the aquifer are scattered across the five counties. Urban development is extensive in the Oklahoma City region and surrounding suburbs. The demand for water both agriculturally and domestically has risen steadily within the last 100 years [Oklahoma Water Resources Board (OWRB), 1980].

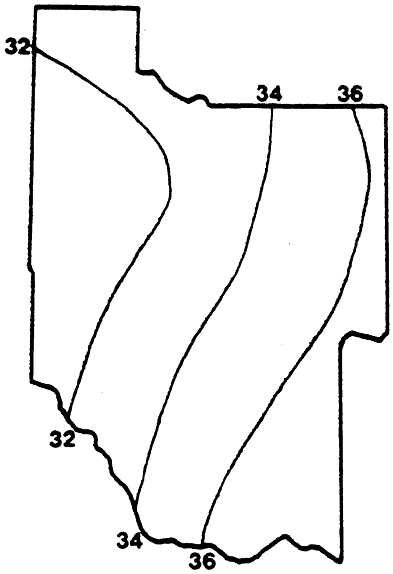


Figure 4. Average Annual Precipitation in Inches (OWRB, 1980)

Soils

The soils developed over the Garber Sandstone and Wellington Formation can be classified as residual as they strongly reflect the lithology of the underlying parent rock. Three main soil associations occur within the study area; they are distinguished principally by texture, drainage, and permeability (Figure 5). The characteristics of each, as described in Soil Surveys of Oklahoma (SCS, 1969), Lincoln (SCS, 1970), Logan (SCS, 1960), Cleveland (SCS, 1942), and Pottawatomie (SCS, 1977) Counties are described below.

1) Darnell - Stephenville and associated soils: occupy slopes and narrow ridge tops, are shallow (Darnell) and deep (Stephenville), gently to strongly sloping, permeable sandy loams that have developed on reddish sandstone in rolling to hilly wooded uplands. These soils are well to excessively drained, have a typically acid reaction and exhibit a leached, weathered profile.

2) Renfrow - Vernon and associated soils: occupy gently rolling plains, were developed under tall, bunch grasses (OWRB, 1980), are deep and shallow, nearly level to sloping, clayey and loamy soils on prairie uplands. These soils have developed over clay and shale or atop firm calcareous material (Vernon). They tend to have a neutral to alkaline reaction, are slowly to very slowly permeable and are excessively drained.

3) Zaneis - Chickasha and associated soils: deep, gently to moderately sloping loamy tall grass priarie soils that have developed over sandy and silty shale. They can be moderately to slowly permeable and have clay loam subsoils; Chichasha are darker brown and occur on more level surfaces.

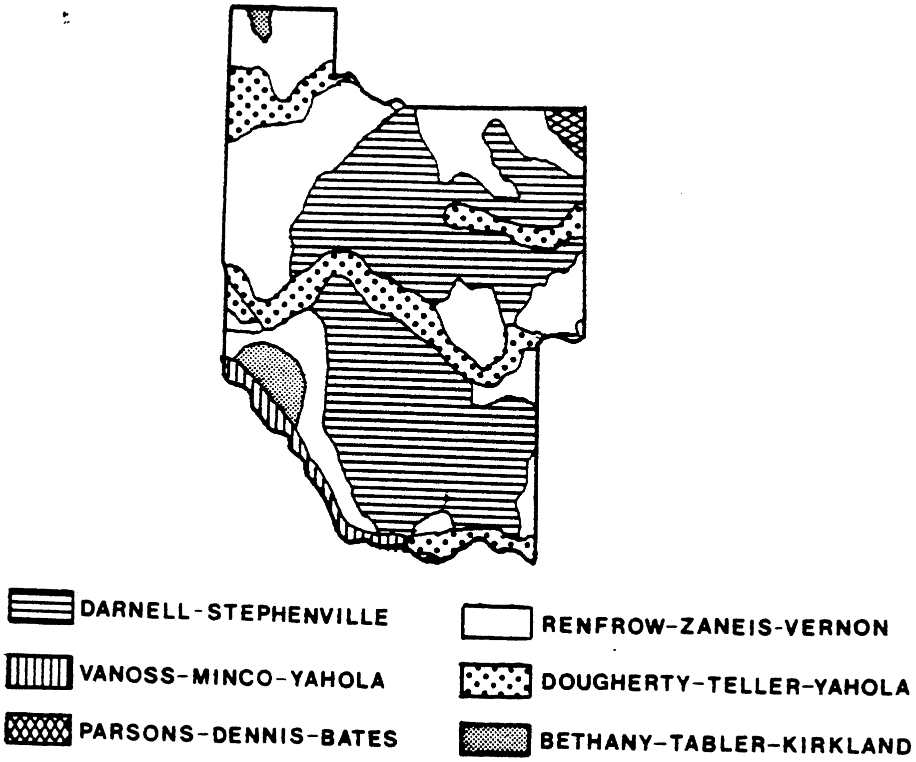


Figure 5. Principal Soil Associations (OWRB, 1980)

In general, soils in the central and eastern portion of the study area have higher permeability, lower runoff potential, and higher infiltration rates than those to the west (USDA, 1969). This occurs despite more pronounced topography because of the prevalence of sandstone in outcrops of both the Garber and Wellington in these areas.

According to the National Cooperative Soil Survey system of soil classification, the soils present fall into Orders Mollisol, Alfisol, and Inceptisol. Mollisols have well defined genetic horizons and generally develop under grasses, Alfisols are soils having clay-enriched B horizons and are high in base saturation, and Inceptisols are those that have formed on young but not recent land surfaces.

Climate

The climate of central Oklahoma is that of a temperate, continental region. It is characterized as subhumid (SCS, 1977), experiencing pronounced day to day changes in weather but only gradual seasonal changes (OWRB, 1971). Summers are generally hot and dry, winters are relatively short and mild. Average annual precipitation ranges from 30 inches in western Logan County to 38 inches in southeastern Pottawatomie County (Figure 4). Average annual snowfall ranges from 6 to 10 inches (Pettyjohn et al., 1983). May is the wettest month of the year (15% of precipitation); spring is the wettest season, having 33% of the total precipitation. Thunderstorms occur 50 to 60 days of the year and account for 50 to 60% of the annual rainfall (OWRB, 1980). Average annual evapotranspiration, calculated by subtracting streamflow from average annual precipitation, ranges from 28 to 32 inches from west to east across the study area (Pettyjohn, 1982). Various workers

(Wickersham, 1979; Wood and Burton, 1968; Pettyjohn et al., 1982) have estimated that 2.5 to 10% of the total precipitation recharges the Garber-Wellington aquifer.

The mean annual air temperature is 61-62°F (OWRB, data 1931-1960). Mean daily air temperature during January ranges from 32-36°F (NW-SE), and during July is approximately 82°F.

CHAPTER IV

GEOLOGY

Age

The exact age of the Wellington and Garber has been a source of disagreement due to the paucity of fossils associated with either formation. Dott, in 1941, using the newly standardized classification of the Permian system into Ochoa, Guadelupe, Leonard, and Wolfcamp Series, differentiated the two formations as being Leonardian in age. Havens (1977), while placing both formations in the Sumner Group, considered them to be lowermost Permian and does not use a Series classification. Shelton (1979), in his paper on the Geology and Water Resources of Noble County, states that the Oklahoma Geologic Survey currently considers the Wellington as the lowermost unit of the Cimarronian Series. Since it is clear that this problem has not yet been satisfactorily resolved, for the purposes of this study the Garber Sandstone and Wellington Formations will be considered early Permian in age (Figure 6).

Regional Setting and Structure

During late Pennsylvanian and early Permian time, regional stratigraphic patterns exhibited by rocks of the mid-continent were controlled largely by the tectonic behavior of the Anadarko Basin in central and western Oklahoma (Rascoe, 1962). At this time the north

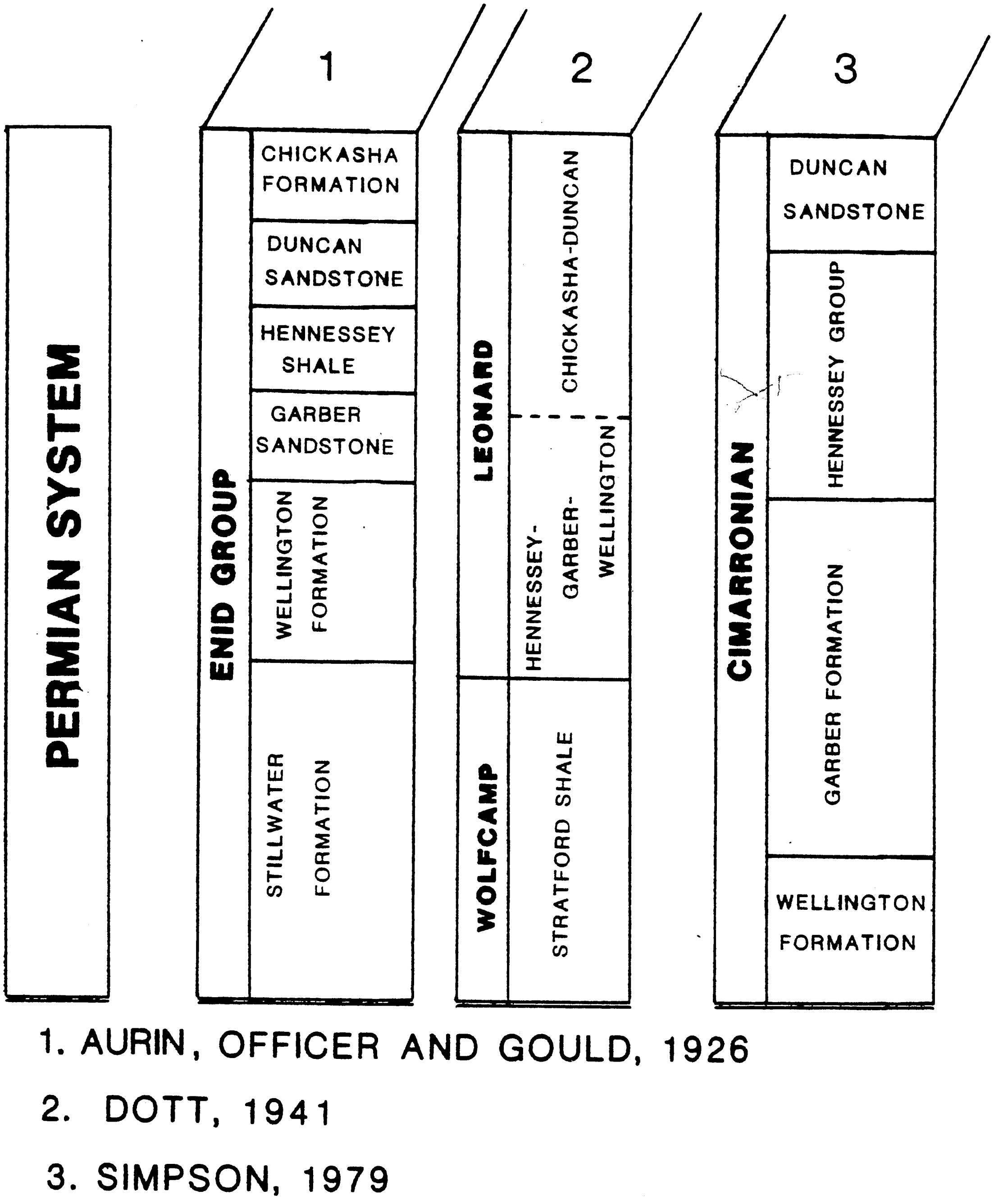


Figure 6. Stratigraphic Section of the Study Area

central region of the state consisted of a broad shelf or platform trending north-south along the basin's eastern margin. The entire area experienced continuous subsidence and deposition during the late Pennsylvanian. At the close of this period, extensive areas in southeastern Oklahoma, Arkansas, and northwestern Louisiana were uplifted causing a rapid shift of the sea westward into northwestern Oklahoma. This tectonism was coincident with cessation of subsidence of the basin and marked the beginning of a regressive phase of marine deposition. Rapid erosion of the uplifted areas ensued, resulting in northward and westward transport of large volumes of clastic sediment onto what had been the eastern shelf of the Anadarko basin (Anderson, 1941). Consequently, during the early Permian, this region was transformed into a wide alluvial plain. Thus Permian continental red bed sediments were deposited atop Pennsylvanian marine limestones.

Structurally, the Permian formations in north central Oklahoma form a gently westward-dipping homocline (Travis, 1930) (Figure 7). The formations become progressively younger to the west and are apparently conformable. The strike of these strata at the surface is slightly west of north and the beds have a normal westward dip of 30 to 40 feet per mile. Generally, the westward-dipping homocline is quite uniform, however, flexure of the Garber sandstone south of Oklahoma City has resulted in locally eastward-dipping sediments. The arching has been calculated to be in excess of 360 feet (Travis, 1930). This fold, known as the Oklahoma City anticline, has caused doming of the Garber Sandstone along its axis (Jacobsen and Reed,1949). A second structural anomaly associated with the fold is a subsurface fault, reflected in near surface sediments by a steepening of the dip of the east-tilting beds.

Depositional Environment

The depositional environments of the Wellington formation range from marine to nonmarine, progressing eastward from the Anadarko Basin. Within the study area the sediments are completely terrigenous, however, their basinward equivalents indicate a transition from evaporitic to brackish to fresh water environments. Tasch (1964) suggests a "coastal flat with relict puddles, ponds and small-scale lakes that gradually freshened as the epeiric sea regressed" (p. 481). Further westward the terrigenous deposits grade into their marine equivalents, with the position of the eastern margin of the sea dictating the region of contact between the marine and nonmarine strata. Consequently, two series of sediments were deposited contemporaneously; red-colored shale and sandstone on the alluvial plain, and a marine series of light-colored sandstones, blue-gray shales, limestones, and evaporites in the sea to the west. Rocks in the study area, specifically the Garber Sandstone and Wellington Formation, consist of the landward portion of these sediments.

The Garber Sandstone is everywhere a continental deposit. Sediment gradations and facies changes within the formation indicate deposition onto an eastward-prograding delta (Green, 1937). This idea is supported by wedging out of Garber sandstones to the north, west, and south. Anderson (1941) sites the presence of Amphibia, reptiles and land plants to conclude that both the Wellington and Garber were deposited in a nonmarine deltaic environment. It is generally accepted that a large deltaic system of westward and northwestward flowing streams carried sediment in from source areas in the Ouachitas and Ozarks to the east (MacLachlan, 1967). The resultant deposits consist of large lenses of sandstone which grade laterally and interfinger with red shales (Dott, 1941). (The overall picture is one of a complex fluvio-deltaic environment ~~which will~~ be used as a model for sediments in the present study area.)

Ham and Merritt (1944), on their work on barite in Oklahoma, concluded that the presence of barite rosettes and their distribution indicate that the Permian sediments were periodically inundated with marine waters rich in barium. "The lenticular distribution of the barite zones harmonizes with the nature of sea incursions on an oscillating shoreline. The sediments now containing the barite were not continually exposed to the sea water, but at a particular time certain portions of the strata were undoubtedly covered by local and temporary marine embayments" (Ham and Merritt, 1944). They then conclude that the environment of deposition was a broad delta on which was deposited both marine and nonmarine sediments; the marine phases being represented by dolomitic-clay intraformational conglomerates and dolomitic sandstones.

Classification

The lower Permian strata in north central Oklahoma were first described by Gould (1905), who referred to these rocks collectively as the Enid Formation. The Enid included "All of the rocks of the red beds formation from the base of the Permian to the lowermost gypsum ledges on the eastern slope of the gypsum hills". Lithologically, the rocks were described simply as red clay shales with interbedded sandstone.

Subdivision of the Enid Formation was undertaken by Aurin, Officer, and Gould (1926), who correlated the lower Permian red beds in Oklahoma with formations in Southern Kansas. Six distinct geologic units were recognized in this state. They were, in order of decreasing age, the Stillwater Formation, Wellington Formation, Garber Sandstone, Hennessey Shale, Duncan Sandstone, and Chickasha Formation. The Garber was further subdivided into a lower Lucien Shale member and an upper Hayward Sandstone member. Both these classifications are somewhat arbitrary, as the Stillwater Formation is absent over much of the present study area, and the Lucien-Hayward distinction is not readily recognized.

Patterson (1933) described in detail the lower Permian strata in Logan and Lincoln Counties, further subdividing the Wellington into a lower Fallis Sandstone member and an upper Iconium shale member. This distinction rests on the decreasing proportion of sandstone to shale progressing upward through the section. It too, is valid only locally, however, these units can be traced through the region under consideration.

Lithology

In the study area, the Wellington Formation consists of "An alternating, intergrading and interfingering succession of red shales and red, cross-bedded sandstones" (Dott, 1941). Its lower boundary has been described by Aurin, Officer, and Gould (1926) as the top of the Pennsylvanian Herington Limestone, however, this boundary is not everywhere clearly defined. The formation is bounded above by the base of the lowest heavy sandstone of the Garber, above. The belt of exposures of the Wellington includes central and western Lincoln County, western Pottawatomie County, the eastern third of Logan and Oklahoma Counties, and the northeast corner of Cleveland County. Its estimated thickness is 500 feet in Logan and Oklahoma Counties (Bale, 1928 and Travis, 1930), and 400 feet in Cleveland county (Figure 7). Two distinct members, an upper shale and a lower sandstone, can be traced through Logan and Lincoln Counties. Lithologically, sand in the Wellington is "Fine-grained, friable, micaceous, and cross-bedded. Dolomitic conglomerates often mark the base of the formation and occur throughout at shale to sandstone transition zones" (Patterson, 1933).

Conformably overlying the Wellington Formation, "the Garber Sandstone is an interstratified series of red clay shales, red sandy shales, and massive, cross-bedded red sandstones" (Aurin et al. 1926). It is bounded above by the Hennessey shale, and can be distinguished from this formation principally by textural variation. Two units are recognized in the Garber; the lower Lucien shale and upper Hayward sandstone. The Lucien is composed primarily of red fissile clay shales interstratified with thin seams of red sandstone. It is approximately 250 feet thick. The Hayward member consists of heavy ledges of massive red sandstone, "More or less lenticular, generally cross-bedded and not uncommonly conglomeratic, interstratified with beds of fissile shale and sandy shale (Aurin et al., 1926). It is approximately 350 feet thick. Barite rosettes are a common occurrence throughout the formation, but are particularly abundant at the base and top of the beds. The Garber Sandstone outcrops in eastern Cleveland, Oklahoma, and western Logan Counties.

It is important to note that the textural and mineralogic characteristics of both the Garber and Wellington change dramatically

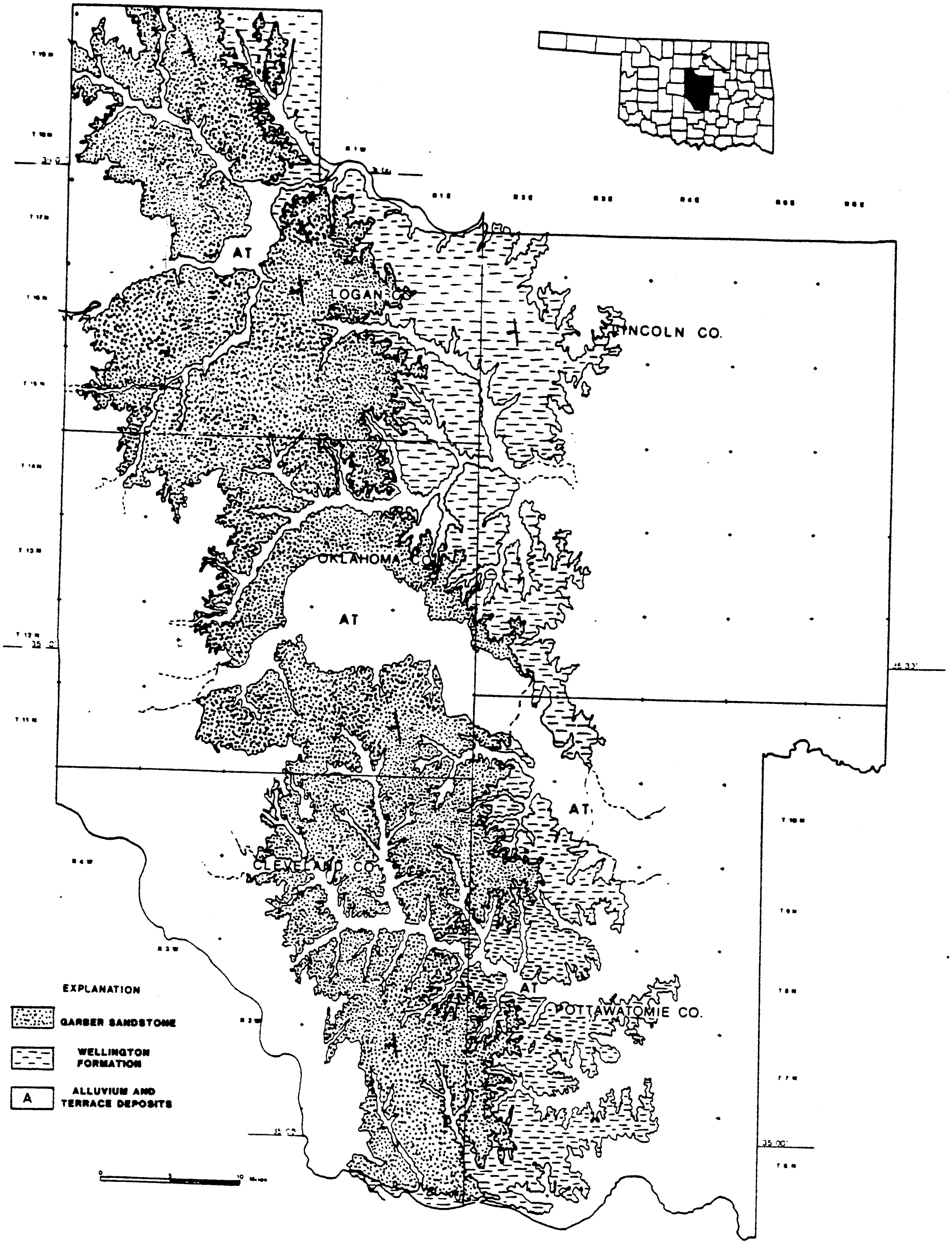


Figure 7. Outcrop Area of the Garber Sandstone and Wellington Formation in Central Oklahoma (Bingham and Moore, 1975)

over their areas of outcrop and in the subsurface. Generally, the percentage of sand in the Garber-Wellington decreases northward and southward from the Oklahoma/Cleveland county Lines. Thus, even though the formations extend northward into Kansas and south to the red river in Texas, the proportion of sandstone to shale decreases as the deposit grades into rocks consisting mainly of shale. Similarly, from east to west, the lithology of the Garber Wellington changes down-dip; sandstone grades into siltstone and shale near the Oklahoma/Canadian county line" (Wickersham, 1979).

CHAPTER V

HYDROGEOLOGY

Introduction

The Garber sandstone and Wellington Formation exhibit a gradational contact, are hydrologically interconnected, have similar water-bearing properties, and are thus considered a single aquifer. This aquifer is the most important source of ground water in central Oklahoma, specifically, in Logan, Lincoln, Oklahoma, Cleveland, and parts of Pottawatomie Counties. It is used for water supply by municipalities, institutions, industry, private domiciles and also for irrigation (Wickersham, 1979). It is estimated that over 50 million acre-feet of water are stored in the Garber-Wellington (Wickersham, 1979; Carr and Marcher, 1977) based on a specific yield of 0.20.

The aquifer consists of about 900 feet of interbedded, lenticular sandstone and shale, and is characterized by irregular lateral and vertical distribution of water-bearing zones. Because of its origin as a deltaic system with shifting channels and variable currents, the aquifer has a complex lithology, preventing correlation of beds over even short distances. "Sandstone comprises 35 to 75 percent of the aquifer and averages about 50 percent" (Carr and Marcher, 1977). The maximum thickness of individual sandstone beds is 40 feet, however, thicknesses of 5 to 10 feet are more common (Patterson, 1933). Shale beds can be as much as 50 feet thick, but most are less than 5 feet (Carr and Marcher, 1977).

Extent of Aquifer

The Garber Wellington provides an abundant supply of good quality water over the area extending from the Cimarron River south to the Canadian River, and westward from Lincoln and Pottawatomie Counties to the western border of Oklahoma County (Wickersham, 1979). This area encompasses approximately 2000 square miles. The aquifer crops out in the eastern portion of the study area and lies beneath rocks of the Hennessey Group in the west. Because of the lenticular nature of the sediments, water-bearing units cannot be traced for any great lateral distance through the aquifer.

Potable quality water can be obtained from the Garber Wellington from the top of the saturated zone to depths exceeding 1000 feet. The maximum depth is controlled by the position of the fresh water-salt water interface, which varies from about 100 feet below land surface in southeastern Cleveland and northwestern Logan counties to greater than 1000 feet near Midwest City and in southwestern Oklahoma County (Wood and Burton, 1968). The configuration of the base of fresh water (defined by Carr and Marcher to be water containing less than 1000 mg/l dissolved solids) is in some places structurally dependent. The lowest altitude of the interface is less than 200 feet above mean sea level, coinciding with the structural trough in the Midwest City area. The altitude rises rapidly to greater than 600 feet above mean sea level west of the trough, reflecting the structural high near the Oklahoma City well field (Carr and Marcher, 1977). The rise in the base of fresh water found at the western edge of the study area may be attributable to the increasing proportion of shale to sandstone in the formations (Wood and Burton, 1968).

The greatest thicknesses of sand are found in the region corresponding to the structural trough in Oklahoma County. Both north and south of this area, the sandstone lenses become thinner and the proportion of shale in the aquifer increases (Wickersham, 1979). Wells drilled to depths of 750-800 feet in the vicinity of Midwest City commonly encounter 200-300 feet of water-bearing sandstone, elsewhere only a few thin sandstone lenses may be penetrated (Bingham and Moore, 1975).

Recharge

Water in the Garber Wellington aquifer is derived principally from precipitation in the study area, and recharge occurs primarily as the result of downward percolation of rainwater. However, the rocks which form the deeper part of the aquifer crop out in the eastern portion of the study area, and down-dip migration may account for some water in these deeper sediments (Carr and Marcher, 1977). In addition to down-dip migration, two additional mechanisms are thought to be responsible for the occurrence of ground water in the confined portion of the aquifer. These are, leakage from adjacent units, and direct downward percolation through fractures in the shale (Pettyjohn and Miller, 1982). Overall, however, it is thought that much of the water in the basin infiltrates and travels at most a few miles before it is discharged to surface water or withdrawn (Wickersham, 1979).

Seasonally, recharge is greatest during late winter and early spring due to reduced evapotranspiration. Consequently, water levels are highest in March and April and decline consistently through the summer and late fall. During summer months rainfall of greater than one inch can produce a temporary rise in water levels (Bingham and Moore, 1975).

Natural recharge to the outcrop area of the aquifer is estimated to be approximately 130,000 acre-feet per year (Wickersham, 1979) or 15 million gallons per square mile annually (Wood and Burton, 1968). Great local variation occurs depending on the permeability and structure of the rocks at the surface. Average effective recharge rates are influenced by precipitation volume and patterns. Numerous estimates of the actual amount of water recharging the aquifer have been made. Wickersham (1979) and Carr and Marcher (1977) estimate that 10 percent, Bingham and Moore (1975) 5 percent to 9 percent, and Wood and Burton (1968) greater than 5 percent of annual precipitation is available for infiltration. Pettyjohn and Miller (1982), calculating recharge for wet-, dry-, and normal-water years, found great variation both spacially and with time. They proposed an overall average recharge rate of 2.1 inches per year for the unconfined portion of the aquifer. The above researchers all agree that no significant overpumpage is occurring in the Garber Wellington. Wickersham (1979) concludes that the aquifer is being under-utilized, based on maintenance of water levels despite increased pumping in recent years.

Discharge

In the study area ground-water discharges occur principally into surface water bodies. There is also evidence that water from the Garber-

Wellington discharges to alluvium on the floodplains of the major rivers (Carr and Marcher, 1977). Potentiometric surface maps constructed by Carr and Marcher and Wickersham for the shallow part of the aquifer indicate that principal directions of ground water movement are toward the Cimarron, North Canadian and Canadian Rivers and their tributaries. Generally, base flows in the larger streams are a result of ground water discharge, though these can be sustained or prolonged by effluent from sewage treatment plants and industrial waste (Bingham and Moore, 1975). Data on discharge points for water in the deeper part of the aquifer are not available.

Ground Water Flow Regimes

Flow regimes in the Garber Wellington are differentiated both laterally and with depth. The aquifer exists under water table (unconfined), semiconfined and artesian conditions over the study area. It is unconfined across its outcrop area in the east and confined where it is fully saturated and overlain by shales and siltstones of the Hennessey Group in the west. Limited water-level data indicate that the confining effects begin somewhere between the Garber-Hennessey contact (Wickersham, 1979) and four miles west of this point (Carr and Marcher, 1977). The flow regimes also vary with depth due to lithologic factors. The greater thickness and number of sandstone units in the deeper sediments facilitate higher well yeilds.

Flow in the upper aquifer has two main components; principal lateral movement from recharge to discharge areas, and secondary vertical movement. Downward movement occurs in recharge areas because the head decreases with depth. This movement may be restricted, however, because of the presence of intervening shale beds of low hydraulic conductivity. Concurrently, it may be promoted due to fracture systems in the shale. Upward movement occurs in discharge areas where the head in deeper wells is higher than in corresponding shallow wells.

Flow in the deeper part of the aquifer has not been conclusively defined because water levels in deep wells often represent composite heads. Consequently, determination of hydraulic gradient is made more difficult. It is generally believed that overall flow direction corresponds to the regional dip of the strata to the west (Bingham and Moore, 1975).

Hydrologic Properties

Hydraulic characteristics of the sandstone beds are dependent on the size, shape and sorting of the sand grains, and the type and amount of cement present. Most of the sand grains in the Garber Wellington are angular to subangular; as much as 10 percent may be subrounded (Carr and Marcher, 1977). Jacobsen and Reed (1944) found the average diameter to be 0.006 inches, which constitutes a fine sand. The aquifer sands are also well sorted, having sorting coefficients ranging from 1.12 to 1.62, with an average value of 1.26 (Carr and Marcher, 1977).

Transmissivities and storage coefficients have been calculated by several writers based on aquifer test data from the southeastern part of the study area in Oklahoma and Cleveland counties. Wood and Burton (1968) found that transmissivity ranges from 300 to 7000 gallons per day per foot (gpd/ft), and averages 5000 gpd/ft. Wickersham (1979) calculated average transmissivity to be 3300 gpd/ft. A storage coefficient for the confined portion of the aquifer was determined by

Wood and Burton to be 2.0 X 10^{-4} whereas Wickersham obtained an average specific yield of 0.20 for the unconfined sediments. Specific capacities of wells in the Garber Wellington range from 0.6 (Wood and Burton) to 2.3 (Wickersham) gallons per minute per foot (gpm/ft) of drawdown. Variability in specific capacity is not uncommonly a reflection of well design and construction and, therefore, is not a reliable indicator of the productivity of the aquifer.

Well Yields

Well yields within the Garber Wellington are highly variable across the study area. The variations are caused by differing hydrologic conditions, the thickness of the saturated material penetrated, and well-construction methods. In general, the highest yields are obtained where wells penetrate the entire aquifer and are screened opposite all significant water-bearing zones. High yielding wells tend to be concentrated along a north-south trending line just east of Oklahoma City, corresponding to the great thickness of sands associated with the structural depression in this area (Wickersham, 1979). Table I summarizes well-yield data published by several writers.

TABLE I

WELL YIELDS IN THE GARBER-WELLINGTON AQUIFER

Investigator	Location	Yield (gpm)	
		Shallow	Deep
Wood and Burton, 1968	southern		50-450 avg. 240
Bingham and Moore, 1975	central	25 (salt water 200-300 ft below surf.)	200-250
Carr and Marcher, 1977	northern	225	550
Wickersham, 1979	southern	150-450 avg. 250	
Pettyjohn and Miller, 1982	unconfined	70-475 avg. 245	

CHAPTER VI

GEOCHEMISTRY OF SELENIUM

Chemistry

Selenium occurs in Group VI A, Period IV of the Periodic table. Its atomic number is 34 and it has an atomic weight of 78.96. The arrangement of electrons (2, 8, 18, 6) allows classification as a metalloid, consequently it possesses both metallic and nonmetallic properties. Elemental selenium exists in several polymorphs, two monoclinic, one hexagonal and one amorphous. All varieties can exist at room temperature, however, only the hexagonal form is thermodynamically stable (Sindeeva, 1964). Seventeen isotopes are known, ranging in mass from 80 to 87, 6 of these are stable and the remainder are radioactive (Bagnall, 1966).

Depending on its oxidation state, selenium may act as either an oxidizing or reducing agent. It can exist in 4 valence states; -2, 0, 4, and 6. The elemental form is insoluble and not rapidly oxidized or reduced in natural, near-surface environments. In compounds with metals and hydrogen, selenium has a valence of -2 and forms ionic selenides or sulfoselenides. Heavy metal selenides are very insoluble; hydrogen selenide is a highly reactive gas that decomposes quickly in the presence of oxygen. When selenium is combined with oxygen its valence can be either +4 or +6 (selenite and selenate, respectively) forming both dioxides and trioxides. The inorganic selenites have an affinity for iron and aluminum sesquioxides, forming stable absorption complexes. When dissolved in water, selenium dioxide forms selenious acid (H_2SeO_3), a compound which behaves similarly to sulfurous acid. Salts of this acid are derived by neutralization by hydroxides and carbonates (Sindeeva, 1964). Under acid and reducing conditions selenites are reduced to elemental selenium. Alkaline and oxidizing conditions favor the formation of selenates, which are not readily complexed with iron or aluminum. Selenium is one of the dispersed or widely distributed elements in the earths crust.

Geochemical Cycle

Selenium enters the geochemical cycle as a constituent of magma, where its behavior parallels that of sulfur (Figure 8). During early magmatic stages, selenium containing sulfides of iron, cobalt, and nickel separate to form sulfide deposits. As magmatic crystallization continues, volatile constituents become concentrated in a residual fluid phase which eventually forms a supercritical aqueous solution (Shamberger, 1981). The volatiles are then able to separate from the magma by movement through joints and fractures. In a relatively closed system, sulfide ore bodies will form. However in an open system such as a volcano, sulfur and selenium escape into the atmosphere as gases. Several writers have suggested that this is a major mechanism for atmospheric enrichment of selenium. Table II presents a summary of the available data on selenium content of volcanic exhalations. The data suggest that the relative amounts of selenium injected into the atmosphere may vary widely both within and between volcanoes, depending

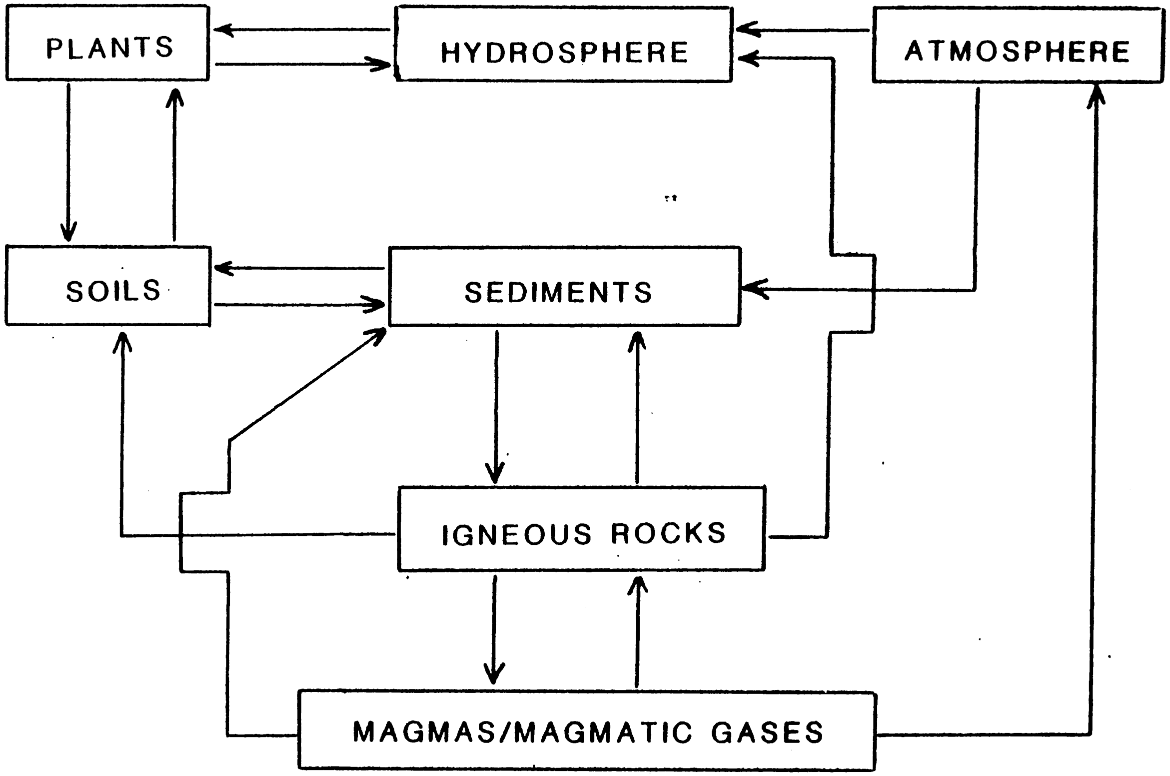


Figure 8. Geochemical Cycle of Selenium (After Shamberger, 1981)

TABLE II

SELENIUM IN VOLCANIC EMANATIONS

Location	Reference	Se Conc. (ppm)
Selenium in Volcanic Sulfur:		
Colorado	Byers (1935)	8350
Hawaii	Byers, et al. (1936)	1400,2200
West Indies	Byers, et al. (1936)	5
Hawaii	Lakin, et al. (1940)	4-1600
Mexico	Williams, et al. (1940)	0-10
Alaksa	Zies (1929)	1200
Japan	Suzuoki (1964)	15.5-404
Selenium in Fumarole Deposits:		
Iceland	Mroz and Zoller (1975)	265±260
Selenium in Fumarole Condensate:		
Kilauea Iki, Hawaii	White and Waring (1963)	12+

on magma composition and eruption characteristics. Mroz and Zoller (1975) found that the concentration of selenium was much higher in fumarole deposits and aerosols than in lava-ash samples. They also concluded that selenium (along with Zn, Sb, and Br) is volatilized out of the magma, possibly in the form of volatile halides.

Separation of selenium from sulfur in the exogenic environment occurs upon weathering of primary sulfide deposits. Selenides are rapidly oxidized to selenite, which is stable and can migrate until fixation by metal hydroxides and/or soil minerals occurs. Under similar conditions, sulfide will form sulfuric acid or the sulfate ion, both of which are very soluble and move easily into ground water systems. For this reason selenium is rarely found associated with sulfur in secondary sulfide and sulfate deposits (Vinogradov, 1959).

Eh-pH studies have shown that elemental selenium is the most stable form of the element over most of the range of natural, near-surface conditions (normal oxidation potential) (Leutwein, 1969) (Figure 9). At higher Eh values, selenium is oxidized to selenite; if the redox potential is very high, selenate will be formed. The existence of selenate is questioned by Fischer and Zemann (1969) who believe that the Eh values required for its formation are greater than that required to dissociate water. They conclude that selenate will form only if the environment is extremely hot, dry, alkaline, and strongly oxidizing. If weathering takes place under acid conditions (pH <4) selenium will be present in either the elemental or reduced (selenide) forms, both of which are relatively immobile (Dall'Aglio et al., 1978). Both selenites and selenates are readily reduced to elemental selenium and various selenides. The fixation of selenite can be nearly completely

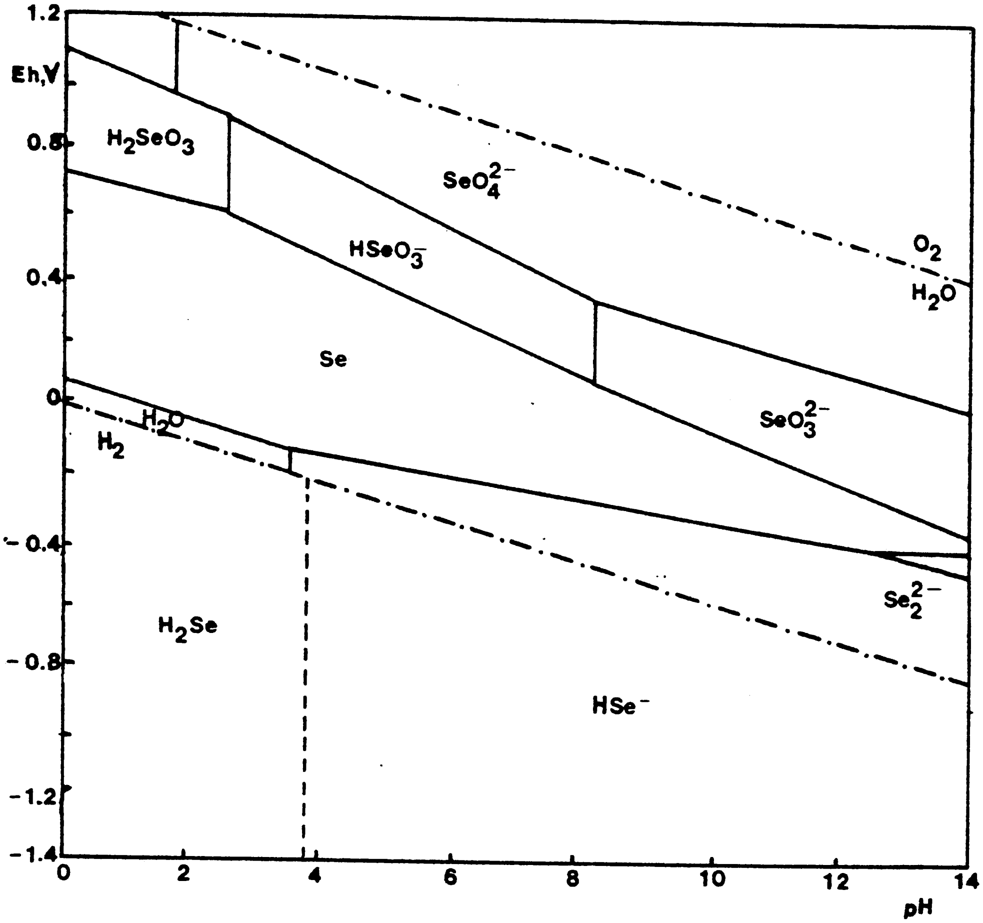


Figure 9. Thermodynamic Equilibria in the System H_2O-Se at Σ Se = 10^{-6} at 25°C, P = 1 atm. (Dyachkova and Khadokovskiy, 1968)

accomplished by adsorption onto precipitated iron hydroxides and oxides (Fischer et al., 1969; Rosenfeld and Beath, 1964). In aqueous systems, the degree to which this occurs is dependent on pH, the composition of the surrounding rocks, and hydrologic conditions.

Geologic Occurrence

Selenium is unevenly distributed in rocks near the earth's surface. Its crustal abundance has been estimated at 0.05 ppm (Krauskopf, 1965), although it is not commonly found in rock forming minerals. Volcanic gases, tuffs, and elemental sulfur have been found to contain selenium, suggesting that volcanism is strongly related to the occurrence of seleniferous strata. Under endogenic conditions, the element has strong chalcophile tendencies and it can substitute for sulfur in the structure of many common sulfide minerals (Sindeeva, 1964). The selenium content of igneous and metamorphic rocks is generally low, while that of sedimentary rocks is quite variable. Seleniferous limestones and shales in the western United States contain selenium in hundreds of parts per million (Beath, 1937). Table III presents the range in selenium content of several common rock types as found by various writers.

Sedimentary Occurrence

Rosenfeld and Beath (1964), in their study on the occurrence of selenium in various sedimentary rocks, found that its content varies both between and within beds of the same geologic formation. This variation can be related to the mineralogic and textural composition of the rock or due to the occurrence of relatively high secondary concentrations of selenium emplaced after deposition.

TABLE III

SELENIUM CONTENT OF VARIOUS ROCKS

Rock Type	Reference	Se Conc. (ppm)
Basalt	Brunfelt & Steinnes (1967)	0.093-0.123
Granite	Brunfelt & Steinnes (1967)	0.005
Granite	Wells (1965)	0.13-0.38
Salic Intrusives & Extrusives	Sindeeva (1964)	0.14
Mafic & Ultramafic Intrusives & Extrusives	Sindeeva (1964)	0.13
Alkalic Rocks	Sindeeva (1964)	0.10
Volcanic Ash	Williams, et al. (1940)	0.10
Basaltic Ash	Wells (1965)	0.61
Andesitic Ash	Wells (1965)	1.19
Bentonite & Gypsum	Byers, et al. (1938), Byer (1935)	1.0, 22.0
Gneiss	Wells (1965)	0.2-0.4
Schist	Wells (1965)	0.14-0.33
Limestone	Rosenfeld & Beath (1964)	0.1-6.0
Shale	Leutwein (1971)	0.1-5.0
Graywacke	Wells (1965)	0.17-0.72
Phosphate Rock	Rosenfeld & Beath (1964)	1.0-300
Uranium-Vanadium Ore	Rosenfeld & Beath (1964)	500-2600

Low levels of selenium have been found to occur in the sulfate minerals jarosite and barite (Faust and Aly, 1981). Jarosite ($KFe(SO_4)_2(OH)_6$) is an alteration product that occurs in thin seams along bedding, joint, and fracture surfaces in shale beds. Selenium is thought to substitute for sulfur in the structure (Rosenfeld and Beath, 1964). Selenium minerals have been observed in barite veins in associations formed under oxidizing conditions (D'Yachkova and Khodakovskiy, 1968).

During sedimentary processes, clay and iron-rich sediments tend to accumulate selenium through adsorption (Dall'Aglio, 1978). Fischer et al. (1974) found that selenium is accumulated in clay sediment, with the degree of enrichment dependent on the amount of oxide and hydroxide present in the sediment. This mechanism is thought to be responsible for selenium enrichment of shale in red beds.

The concentration of most trace metals is higher in shales than sandstones or limestones, but this concentration usually closely approximates the crustal abundance of the element (Krauskopf, 1965). Selenium is found to be concentrated in shales, however, its concentration greatly exceeds its crustal abundance. This is due to the fact that selenium is supplied to sediments by volcanic emanations as well as by erosion of existing selenium-rich deposits. Thus if chemical fixation occurs, its distribution can be widespread and dispersed.

Trelease and Beath (1949) found that limonitic concretions in the shales of the Niobrara Formation contain appreciable selenium. In addition, they noted that selenium tends to acuumulate in carbonaceous shales and, through leaching, may enrich adjacent sandstone beds. In soils, variable amounts of selenium can be found with sediments containing sulfides or pyrite (Rosenfeld and Beath, 1964). In acid soils selenium would be present as selenite, firmly bound to iron oxide colloids. Under alkaline conditions, further oxidation to selenate would occur, in which form selenium can enter the root system of plants (Faust and Aly, 1981).

Selenium in Aqueous Systems

Selenium can exist in all four of its oxidation states (-2, 0, 4, 6) in aqueous systems. The occurrence of soluble selenium compounds in some soils and rocks suggests that under certain conditions, natural waters are effective in leaching and transporting selenium (Faust and Aly, 1981). As mentioned above, adsorption is the primary process responsible for limiting the level of the element in water. Because these compounds onto which selenium can be adsorbed are common constituents of sediments, only a small fraction of the selenium present in sediments or soils is usually mobile (Rosenfeld and Beath, 1964).

Heavy metal selenides of copper, silver, lead, and mercury are insoluble and tend to precipitate. Iron selenites, principally $Fe_2(SeO_4)$ and $Fe(OH)_4SeO_3$, are also insoluble. Selenite salts of the alkalis and alkaline earths are soluble in most systems. However, oxidation potential and pH are the main controls over the mobility of selenium. At pH 8, the amount of adsorption is greatly reduced, above pH 11 no adsorption occurs. At low pH all selenium species become immobile because the they are is either precipitated or adsorbed (Dall'Aglio, 1978). Between pH 3.5 and 9.9, biselenite ion is the predominant ion found in water (Faust and Aly, 1981).

Under moderately reducing conditions, heavy metal selenides will precipitate and selenites are rapidly reduced to elemental selenium.

Under mildly oxidizing conditions, selenious acid species are predominant. The solubility of selenium compounds is summarized by Faust and Aly (1981, p. 375) as follows:

"Most selenite salts are less soluble than the corresponding selenates. The extremely low solubility of ferric selenite and the basic ferric selenite, which is found in dilute solutions of ferric chloride and sodium selenite, are important to the environmental cycling of selenium. Selenites also form stable adsorption complexes with ferric oxides of even lower solubility than the ferric selenates. Under certain conditions, selenite seems to be completely adsorbed by ferric hydroxide, and to a lesser extent by aluminum hydroxide, while selenate is not. The adsorption of the selenite was found to follow a Langmuirian isotherm, with the specific adsorption being higher in acid solutions and decreasing with an increase of pH value. Selenate appears to be the most significant form of selenium as far as environmental pollution is concerned because its stability at alkaline pH values, its solubility and ready availability to plants."

Stach (1978) found that in South Dakota ground waters, 90% of the selenium in solution was in the form of selenate. In addition, a significant correspondence was found to exist between elevated nitrate and selenium levels. He hypothesized that oxidizing conditions control the distribution of selenium and nitrate in shallow, unconfined aquifers.

CHAPTER VII

METHODS AND MATERIALS

Data Sources - Water Quality

Data on water quality in the Garber-Wellington were gathered from several sources. Analyses which reported concentrations of all major constituents were obtained primarily from Carr and Havens (1977) for northern Oklahoma and southern Logan Counties, and Wood and Burton (1968) for Cleveland and Oklahoma Counties. In addition, the U.S. Geological Survey WATSTOR data base contained three analyses not included in the above papers. Data generated during the Department of Energy's Hydrogeochemical and Stream Sediment Reconnaissance (HSSR) Program (as part of the National Uranium Research Evaluation (NURE) Program) for the Oklahoma City NTMS Quadrangle contained five analyses which reported concentrations of all major constituents except chlorides.

A total of 56 complete analyses, and 5 in which chloride concentration was estimated, were available for interpretation. Where numerous wells of similar depth were clustered in a small area, a limited number of representative analyses were used in data interpretation. Locations of the data points are noted on Figure 10. Appendix A contains copies of the raw water quality data.

Data used for analysis of trace element concentrations in water from the Garber-Wellington aquifer were obtained from the HSSR program, Oklahoma City quadrangle. A total of 195 wells were sampled during the

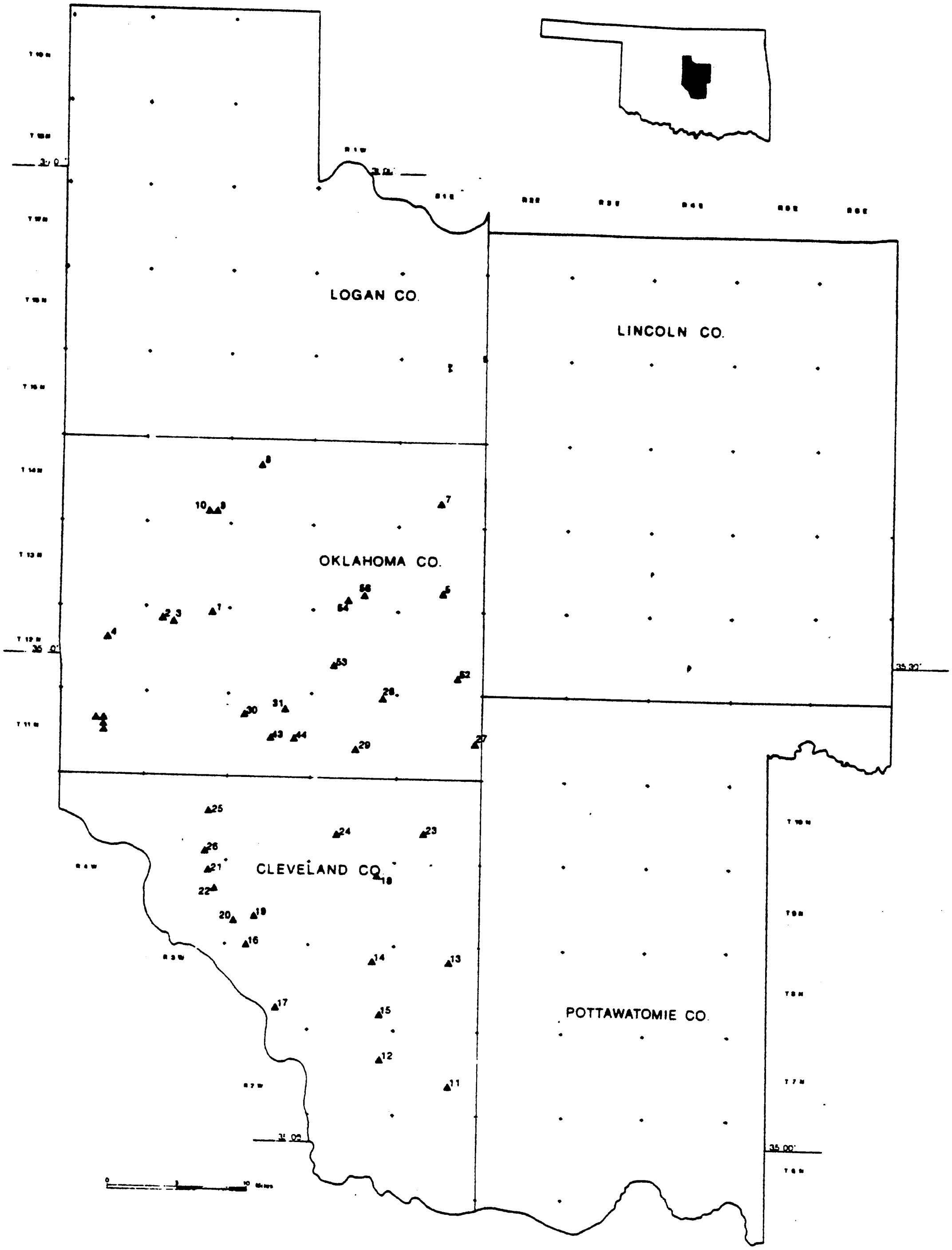


Figure 10. Data Points Used in Analysis of Major Constituents in the Garber-Wellington Aquifer

period from October 1977 to February, 1978 by the Oklahoma Geological Survey. Information on sampling and analytical procedures can be found in the HSSR report. Analyses of water from 89 wells were chosen for evaluation in this study, based on the occurrence of selenium greater than the 2 parts per billion (ppb) detection limit. Other parameters analyzed included: well depth, dissolved oxygen, alkalinity, pH, conductivity, aluminum, arsenic, boron, barium, calcium, chromium, copper, potassium, lithium, magnesium, manganese, molybdenum, sodium, niobium, silica, sulfate, strontium, thorium, uranium, vanadium, yttrium, and zinc. Additional data on the concentration of selenium in wells tapping the aquifer were obtained from records on file with the Oklahoma State Department of Health which were compiled by the Garber Wellington Association. Locations of sampling points used in data interpretation are noted on Figure 11. Appendix B contains copies of the raw water quality data used in trace element analysis.

Data Sources - Petrologic Analysis

Samples of formation material from the Garber Sandstone and Wellington Formation were obtained from outcrops in the study area and from well cuttings on loan from the Oklahoma Geological Survey Core and Sample Library. Sample locations are noted on Figure 12.

Methods of Data Evaluation - Water Quality

Primary components of water from the aquifer were analyzed graphically by means of a Piper Diagram (Piper, 1944). The FORTRAN IV version of WATEQ (Truesdell and Jones, 1974), WATEQF (Plummer et al., 1976), was used to calculate the equilibrium distribution of inorganic

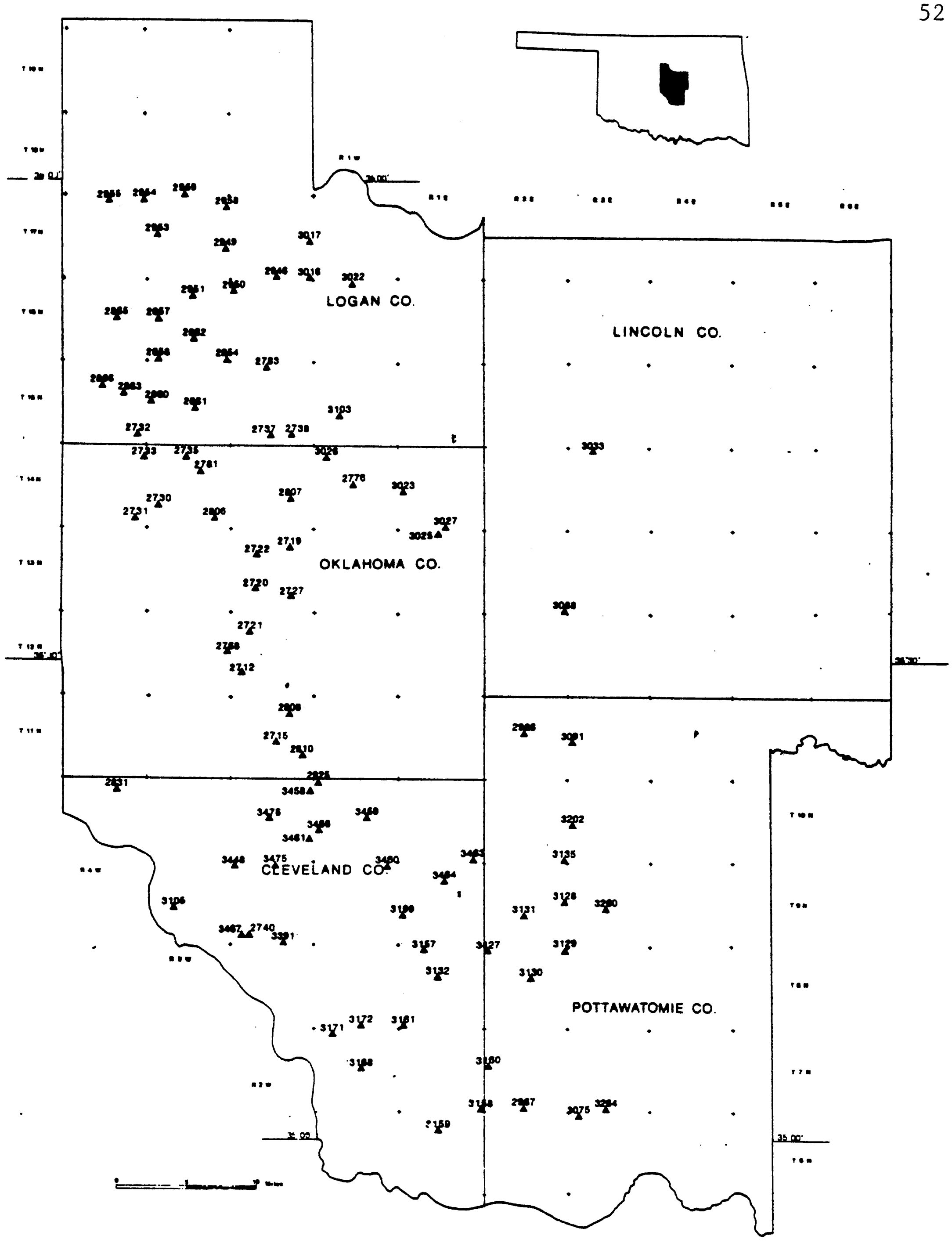


Figure 11. Data Points Used in Analysis of Trace Elements in the Garber-Wellington Aquifer

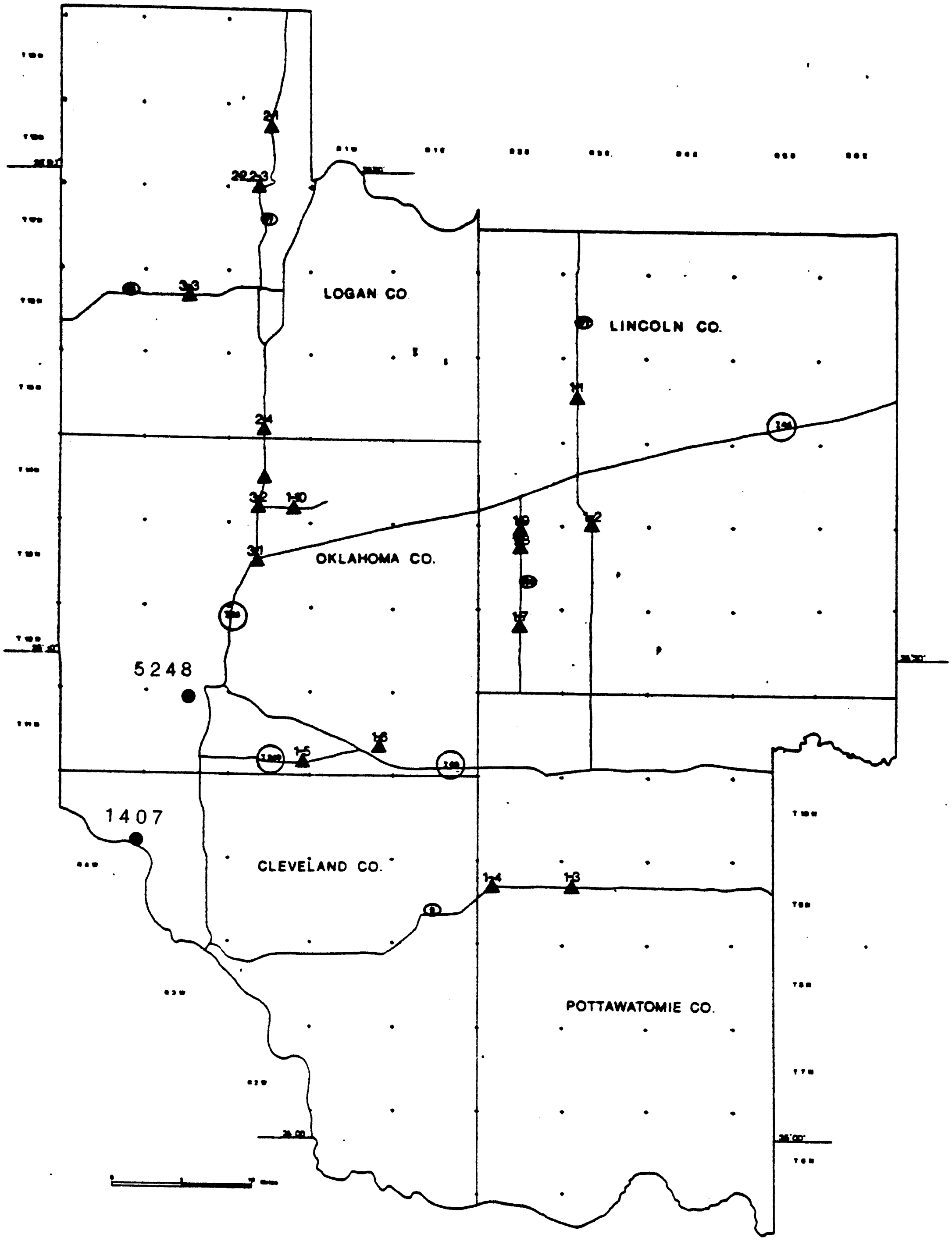


Figure 12. Location of Outcrop Sampling Locations and Wells From Which Cuttings Were Examined

aqueous species of major elements, and to determine the redox potentials of the water.

Both the major constituent and trace element data sets were statistically analyzed using Statistical Analysis Systems Institute (SAS) programs available on the Oklahoma State University VAX 11-780 computer system. The SAS procedure PROC CORR (determination of Pearson correlation coefficients) was used to obtain correlation matrices for both principal ion and trace element (NURE) data. The SAS procedure PROC FACTOR was used to perform principal components analysis of the correlation matrices output from PROC CORR. The number of factors extracted was determined using the criterion Mineigen = 1. Factors were extracted for both unrotated and VARIMAX rotated axes.

Factor analysis is a multivariate statistical procedure that defines factors within a data set which can be viewed as "causes" of the patterns they represent. Component factor analysis is concerned with patterning all of the variation within a set of variables, whether this variation is common or unique. The factors obtained delineate independent (uncorrelated) patterns. Factors associated with an unrotated matrix are extracted in order of the greatest degree of relationship within the data. In a rotated matrix, no significance is attached to the factor order, however, distinct clusters of relationships are more clearly delineated if they exist. The rotated factor patterns are those that will be discussed more thoroughly in the following chapters.

For a discussion of Factor Analysis and its applications to Geology, see Joreskog, et al., 1976. Hydrogeochemically, factor analysis can be used to study the interrelationships between chemical constituents and properties, and aid in the identification of geochemical processes occurring in a ground water system.

Methods of Evaluation - Petrology

Select rock samples from well cuttings and outcrops were analyzed to identify major mineralogic and trace element constituents. Specimens were chosen on the basis of variation in texture, color, and macroscopically identifiable lithologic characteristics (presence of carbonate and or gypsum). Gross mineralogy was determined at Oklahoma State University using a Nicolet L11 computerized Powder Diffraction System. Trace element content of the rocks was evaluated (qualitative, semi-quantitative) by X-Ray Fluorescence (XRF). Two sets of samples were analyzed by Fluo-X-Spec Laboratory in Denver, Colorado, and one set by CSMRI-Analytica, Inc., in Golden, Colorado. Sample preparation for all of the above analyses consisted of grinding rock samples to a powder in a SPEX mixing mill.

Four duplicate samples were sent to both labs as a check on quality control. The variation in results was extraordinarily high (>50% on many analyses) rendering the quantitative aspect of the data unreliable. Comparison of results on the duplicate samples is presented in Table IV. The findings do have qualitative merit, however, and are discussed in this light in Chapter VIII.

Analysis for selenium content of the rocks was done by Fluo-X-Spec and CSMRI-Analytica, using XRF. The detection limits for instruments at both labs are quite high (actual number varies with each sample, in the range of tens of parts per million), and the selenium content of many samples fell below these limits. Reproducibility was also a problem on

TABLE IV

COMPARISON OF X-RAY FLUORESCENCE DETERMINATIONS OF TRACE ELEMENT CONCENTRATIONS IN DUPLICATE ROCK SAMPLES*

Sample #/Lab	Cr	Ni	Cu	Zn	As	Pb	Sr	U
4B/1	***ND-27	62	94	100	15	200	240	140
4B/2	99	27	154	35	ND-20	13	85	ND-10
% Variation	>57%	39%	24%	48%	NA	88%	43%	>87%
5A/1	****30/74	29/29	88/88	75/27	62/ND-10	220/ND-10	160/150	ND-35/81
5A/2	192	14	17	23	ND-20	ND-10	175	ND-10
% Variation	73%/44%	35%	67%	53%/8%	>51%/0	>87%/0	4%/8%	NA/>78%
9A/1	60	200	30	170	17	440	340	ND-50
9A/2	130	50	12	59	<20	10	214	ND-10
% Variation	36.8%	60%	42.8%	48.4%	NA	95%	22.7%	NA
10/1	60	14	100	110	43	110	52	ND-34
10/2	41	ND-10	8	25	ND-20	<10	32	ND-10
% Variation	20%	>16%	85%	62%	>36%	>83%	24%	NA
11/1	ND-71/120	10/40	92/150	53/41	69/ND-10	1300/390	56/100	ND-170/270
11/2	26	ND-10	26	20	29	129	27	15
% Variation	NA	NA/>60%	56%/70%	45%/34%	41%/49%	82%/50%	35%/57%	NA/89%

*(all values in ppm)

**(variation calculated $\frac{A-B}{A+B}$ X 100)

***(ND - not detected at specified limit)

****first analysis 2-6-85/second analysis 2-26-85

LAB #1 is Fluo-X-Spec Laboratory - Denver, Colorado

LAB #2 is CSMRI - Analytica, Inc., Golden, Colorado those samples found initially to contain a substantial quantity of selenium. When duplicate samples were analyzed at a later date, all results showed the selenium content to be below detection limits (see Table V). In view of the unsatisfactory results obtained using the XRF technique, additional analysis for selenium was done at Oklahoma State University's Water Quality Research Lab using Atomic Absorption Spectroscopy. Sample preparation consisted of digestion of a specific volume of sample with concentrated nitric acid, followed by decanting, filtration, and evaporation of the leachate to a specified volume. Two duplicate samples were run as a check on quality control. Variation in these samples equalled 0.56% and 7.9%, respectively.

TABLE V

SELENIUM CONCENTRATIONS OF DUPLICATE ROCK SAMPLES AS DETERMINED BY X-RAY FLUORESCENCE

Sample #/ Lab	FX SPEC 1	FX SPEC 2	CSMRI 3	WQRL 4
4B	37	not done	ND-20	6.44
5A	130	ND-22	ND-20	6.49
10	66	not done	ND-20	1.77, 1.79
11	100	ND-40	ND-20	1.52, 1.28
1000 ppm Se Std.			678	
100 ppm Se Std.				100.8

CHAPTER VIII

PETROLOGIC ANALYSIS

Mineralogy

Nine subsurface and thirteen outcrop samples representing various lithologies occurring in the Garber Sandstone and Wellington Formation were powdered and analyzed using X-ray Diffractometry. The diffraction patterns were examined to identify major mineralogic constituents. Patterns corresponding to these lithologies are presented in Appendix C. Table VI provides a summary of the results obtained.

Sandstones

Sandstones of the Garber-Wellington vary with respect to texture, degree of induration, and color. They can be fine to coarse-grained, friable to indurated, and exhibit numerous colors in addition to the most common 'red bed' hues.

Red and buff massive, and yellow-orange laminated sandstones are generally friable and fine-grained. They contain quartz as the primary constituent and a minor amount of sodium (albite) and potassium (microcline) feldspar. Kaolinite is the principal clay mineral present. The colors are due to the occurrence of iron oxide cement and grain coatings, which, because of their poorly crystalline structure, do not appear on the diffraction patterns.

TABLE VI

MINERALOGIC CONSTITUENTS IN THE GARBER SANDSTONE AND WELLINGTON FORMATION

P - primary
S - secondary
M - minor
T - trace

	Lithology - Sample #											
	Gray Shale	Red Shale	Gray Sandy Shale	Gray Shaly Dolomitic Cgl.	Gray Sandy Shale	Ironstone Nodules	Red Sandstone	Red Dolomitic Iron-Rich Cgl.	Orange Sandstone	Sandy Iron-stone Layers	Sandy Iron-stone Layers	Barite Rosettes
Mineral	2-1A 2-1B	1-9A	2-3-LA	1-5A	1-4B	2-4-AX	1-3	3-2	1-10	1-11	2-3-BX	1-5D
Quartz	P	P	P	S	P	P	P	S	P	P	P	P
Dolomite			S	P				P				
Calcite	S											
Hematite		M				S		M		S	S	
Goethite								M			S	
Barite												P
Potassium Feldspar							M		M			
Sodium Feldspar	M	S	M	M					M			
Kaolinite	M	M	M	M	T-M		T-M		T			
Illite			M	M	M							
Montmorillonite												

White and gray-green sandstones occur in distinct reducing zones, most often as layers sandwiched between darker colored sandstones and shales. The white sandstones tend to be highly indurated, whereas the gray-green variety are often friable and occasionally interlaminated with red sandstone. Quartz is once again the primary constituent, however, dolomitic (and calcitic in one sample) cement is present in varying amounts. Albite and microcline occur as minor constituents; kaolinite is the only identifiable clay mineral present.

The origin of the carbonates in the reduced sandstones is unclear, however, several hypotheses are presented. Initially, the problem of a mechanism for the formation of localized reducing conditions must be addressed. It has been suggested by several authors that deposition of Garber Wellington sediments took place under arid climatic conditions. This environment might promote the formation of Gypsum beds or localized caliche deposits. Reducing conditions could have occurred within the gypsum as a result of the action of sulfate reducing bacteria, or below the caliche due to inhibition of movement of oxygenated waters downward through this zone. Sulfate reduction of the gypsum would release calcium and bicarbonate to the ground water system, which could then be used in the formation of calcite. Ground water rich in magnesium would then be required to alter the calcite to dolomite.

A discussion of the process by which layers of caliche prevent downward percolation of oxygenated waters, causing formation of localized reducing zones beneath them, is presented in Francis, et al. (1970). In this discussion, the reducing zones occur beneath dolomitic "cornstone" horizons in the Old Red Sandstone. A stratigraphic sequence similar to this is evident in the Garber-Wellington outcrops (where pebble conglomerates overly thin, gray-green leached zones), except that the conglomeratic zones have evidently been reworked. The shape and texture of the pebbles, however, indicates that their origin may have been as a calcrete deposit (Donovan, 1985, personal communication). Francis (1970) offers a possible explanation for the mineralogy by stating that the "cornstone" originally formed as calcite and was later altered to dolomite by the influx of magnesium-rich ground water. If reworking of the Garber-Wellington sediments involved mixing of marine and fresh waters, the dolomite could have formed as a result of lowered salinity and maintenance of a high Mg:Ca ratio (Tucker, 1981). If reworking took place in continental waters, algal decay might have contributed the required magnesium to the system.

Shale

Shales present in the Garber Wellington are similar to the sandstones discussed above in that they vary greatly in texture and color. Red shale is the most common lithology; it can be massive and blocky, or fissile and friable. Gray-green sandy shales occur as distinct bands or zones in otherwise darker colored rock, and indicate the past occurrence of localized reducing conditions.

Two samples of red shale were examined. The diffraction patterns indicate that quartz is the primary component of these rocks. Albite and microcline are the principal feldspars, present as minor constituents. Identifiable clays are kaolinite and illite. Hematite is also present in trace amounts.

The primary difference between the red and the light-colored shales (as determined by XRD) is the presence of dolomite and calcite in the latter. It is interesting to note that these two carbonates occur together in only one of the three samples examined. Kaolinite was identified in all three samples; illite occurs in two of the three. Albite is the only feldspar that could be identified. It is likely that the same mechanism controlling the occurrence of carbonates in the sandstones is responsible for their presence in the shales.

Conglomerates

Conglomeratic zones were noted in a number of outcrops in the study area. At site 2-3 (see Figure 12), two distinct horizons were identified and sampled. Over most of the outcrop, leached zones occurred directly beneath conglomeratic horizons, however, additional conglomerates occurred within massive red sandstone beds. The conglomerates are highly indurated, they range in color from gray to red and are often mottled in appearance. The clasts range in size from gravel to pebble, are subrounded to rounded, and account for a fair percentage of the total volume of the rock. The matrix consists of fine to medium-grained material similar in appearance to the clasts.

The principal mineralogic constituent of all conglomerates examined is dolomite. This differentiates these rocks from all other lithologies in the Garber Wellington in the study area. Quartz is secondary in abundance and appears to be only a matrix constituent. Calcite is present in minor quantities in two of the five samples. Albite is the sole feldspathic constituent; kaolinite and illite are the primary clay minerals present. One sample from outcrop 1-5 contains a minor amount of barite. This conglomeratic zone occurs proximal to a barite rosette horizon. The most highly indurated, layered conglomerate (3-2) contains numerous small iron nodules (discussed below); the diffraction pattern for this sample indicates the presence of both hematite and goethite.

Merritt and Minton (1930) proposed that the conglomerates in the Garber and Wellington are intraformational. They hypothesized that dolomitic beds were deposited, then disturbed for an extended period of time by wave action, giving the pebbles a degree of roundness. This material was then thought to have been redeposited, with finer particles acting as cement for the more coarse-grained pebbles. In this manner, they explain the occurrence of dolomite in the matrix of the rock as well as comprising the clasts. The cross-bedded character of the conglomeratic horizons is given as evidence that the sediments were subjected to wave action.

A second hypothesis which should be considered was discussed in the previous section. In summary, it is hypothesized here that caliche deposits, composed of either calcite or dolomite, formed in relatively stable areas as a result of arid climatic conditions. These sediments were then reworked and deposited as the conglomeratic horizons now visible in outcrop. If the caliche were originally calcitic, the sediments were most likely dolomitized during this period.

Gypsum

The only rocks which showed a positive result when stained for gypsum were located in subsurface cuttings at a depth of 280-350 feet. These fragments are white and chalky in appearance. X-ray diffraction patterns indicate that they consist primarily of quartz, kaolinite, gypsum, and microcline are present in small amounts.

Barite Rosettes

Numerous barite rosettes were collected from outcrop 1-5. The diffraction patterns for these sediments show the major constituents present are quartz and barite.

Ironstone Layers and Nodules

Ironstones are abundant locally at several outcrops, and are most often found associated with yellow-orange laminated sandstones. They take the form of hard, sandy layers up to 1 cm thick, and small, rounded, modular concretions up to 3 cm in diameter. Quartz, hematite and goethite are the principal mineralogic components of these rocks.

Chemistry

Trace Elements

Poor correlation between duplicate samples analyzed by two laboratories has resulted in anomalous results regarding the presence and amount of many trace elements in rocks of the Garber-Wellington. Because of these discrepancies it was not feasible to analyze the data using statistical correlation or factor analysis techniques. A qualitative summary of the trace element occurrence with respect to ligholog'y is presented below.

The mineralogic composition of Garber-Wellington rocks is relatively simple, the primary constituent is quartz, except in conglomeratic zones. Potassium and sodium-rich feldspars occur throughout in lesser amounts, and kaolinite and illite are present in most of the fine-grained strata. Carbonates dolomite and calcite are abundant locally, occurring in light-colored, leached zones as cement as well as comprising pebbles in the conglomerates. The presence of hematite and goethite is also ligholoigically controlled, it is predominant in ironstone layers and nodules, and in the red-colored shales. Iron oxide occurs as coating on the quartz grains, as cement, and as discrete grains of oxide mineral in all of the red sediments.

Both the iron and calcareous material, in addition to clays, are responsible for the occurrence of trace elements in the rocks. Hydrous iron and manganese oxides and aluminum hydroxides have high adsorption capacities and affinities for heavy metals, and have been found to contain Co, Ni, Cu, Zn, Pb, Ag, and Cd (Drever, 1982). Calcite and dolomite can incorporate substantial iron and manganese into the carbonate lattice, and to a lesser extent Zn, Pb, Co, Ni, Cd, Ba, and Sr (Bricker and Garrels, 1967). Adsorption of these elements is controlled largely by the Eh-pH states existing within the ground water system; under natural, unstressed conditions in the Garber-Wellington aquifer maximum adsorption would occur.

Analysis of a sample of red shale from the Wellington Formation indicated appreciable quantities of Ni, Cr, Sr, and Zn. Of these, only strontium is not commonly found in hydrolyzate sediments, although it can be adsorbed in minor quantities. The remaining elements are most likely tied up with the amorphous iron and hematite in the sample. Analysis of three samples of gray-green shale indicated above average values (based on abundance in shales) for Ti and V, Cu, Zn, and Pb in this rock type. Kaolinite is the predominent clay mineral in these rocks, and is most likely providing adsorption surfaces for the titanium and vanadium.

Elevated levels of copper and zinc may be the result of incorporation of these elements into the dolomite lattice.

Analysis of a red shaly conglomerate containing dolomite, quartz, hematite and goethite exhibited elevated levels of As, Mn, and U, and enrichment in Pb and Zn. The manganese is probably in the form of manganese oxide, and as such provides additional adsorption sites for the heavy metals. Manganese was also found to be elevated in a gray shaly conglomerate, along with Cr, S, Sr, and Ba. The barium and chromium ions might be in an adsorbed state; however, concurrence with high sulfur would indicate the presence of barite and possibly celestite in the rock. If present, these minerals occur in very small quantities, as neither was evident on the X-ray diffraction pattern for this sample.

Two sandstones, one red (massive) and one orange-yellow (laminated) were analyzed for trace metal content and showed no particular enrichment with respect to any element. This is probably a function of the reduced surface area available for adsorption. Barite rosettes were found to contain a significant amount of strontium, which can substitute for barium in the $BaSO_4$ lattice. The amount of strontium present as the mineral celestite is minor if present, as $SrSO_4$ was not represented on the X-ray diffraction pattern for this sample. Enrichment in Pb, Zn, U, and As was evidenced in two ironstones analyzed. Adsorption of these elements is not uncommon, given the Eh-pH conditions existing in the aquifer.

The source of the heavy metals in the Garber and Wellington Formations has not been conclusively determined. However, the generally dispersed occurrence, at moderate concentrations, of most of these elements renders it not unlikely that they were incorporated in minerals which comprised the source rocks for both formations. Although not areally extensive, numerous mineralized zones are associated with the Ouachita and Ozark Ranges, regions which are believed to be the source of Garber-Wellington sediments. Barium is thought to have been derived from inundation by marine water either contemporaneous with sediment deposition or at a later date (Ham and Merritt, 1944). The strontium may have had a marine origin also, and, if aragonite were the initial carbonate present, strontium would have been incorporated in its lattice. Later neomorphism of the aragonite to calcite would have released and mobilized the strontium, allowing for its adsorption onto clays in the sediments.

CHAPTER IX

HYDROGEOCHEMISTRY

Major Constituents

General Character of the Water

Water from the Garber-Wellington aquifer is suitable for potable supply, irrigation, and industrial uses. Based on the water quality data examined in this study, total dissolved solids content ranges from 96-1077 mg/l. It is generally less than 400 mg/l, except in areas where solution of halite has contributed high concentrations of sodium and chloride ions to the ground water. The mean conductivity is 635 umhos; conductivity values range from a low of 138 umhos to a high of 1830 umhos.

The pH of the water is quite variable, ranging from 6.1 to 9.4 over the study area. High pH values occur most often in the western and southwestern portions of the aquifer, where the water is under artesian conditions. The chemical characteristics of the water in this region are significantly different from those in the remainder of the aquifer.

Information on redox potential of the water was not readily available. However, data from the HSSR Program include values of dissolved oxygen throughout the aquifer. The concentrations range from 2.2 mg/l to 13 mg/l, with the mean of 89 analyses equal to 6.95 mg/l. These values are quite high for a ground water system and may reflect conditions in the wells rather than being indicative of the state of water in the aquifer. Excessive agitation of the water due to pumping could result in artificially high dissolved oxygen values.

Piper Diagram Analysis

A Piper plot of 56 complete analyses of water from the Garber-Wellington is presented in Figure 13. The two lower triangles represent relative percentages of cations and anions (meq/l), respectively. Points in the upper diamond translate each cation-anion pair into a single point representing the entire analysis.

Cations plot in two distinct regions and in the intermediate area between them. One region is characterized by a dominance of calcium and magnesium, and negligible amounts of sodium and potassium. The ratio of calcium to magnesium approaches 1:1, with calcium being slightly higher. The second region is characterized by a high percentage of sodium and potassium, with calcium and magnesium accounting for a minor percentage of the total cations. As can be seen on Figure 14, the two primary water types, if classified by cation content, are differentiated areally within the aquifer. Excessive sodium concentrations occur only in the west and southwest. Points plotting between these two clusters delineate two trends, one in which the $Ca^{++}:Mg^{++}$ ratio remains constant while the relative percentage of sodium increases, and a second in which the $Ca^{++}:Mg^{++}$ ratio increases with the increase in sodium.

The majority of points in the anionic triangle plot in the region where HCO_3^- ($+CO_3^{--}$) comprises >50% of the total. In numerous samples, HCO_3^- accounts for >90% of the anionic content of the water. Where bicarbonate represents <85% of the anions, chloride ranges from 5-55% and

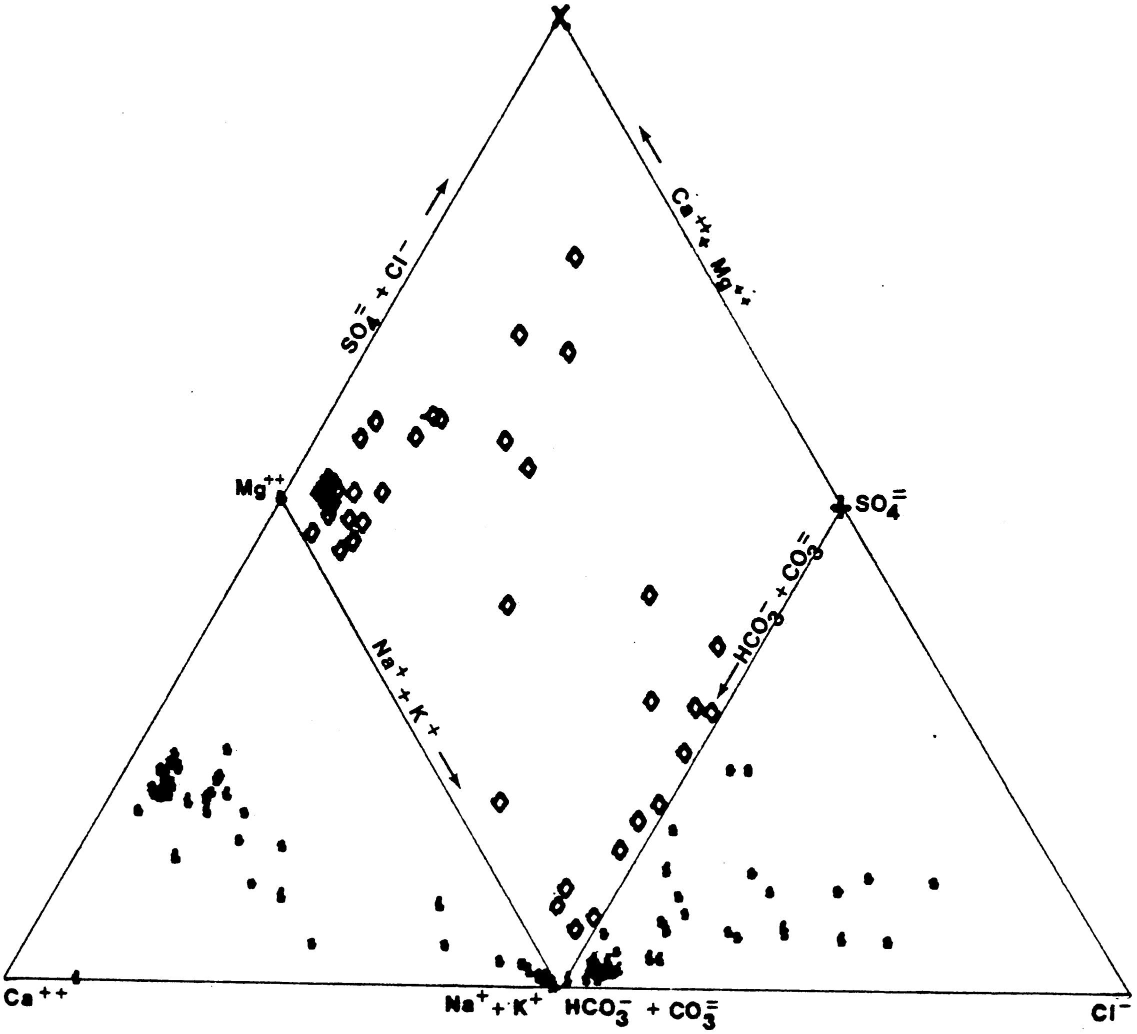


Figure 13. Piper Diagram Plot of Garber-Wellington Waters

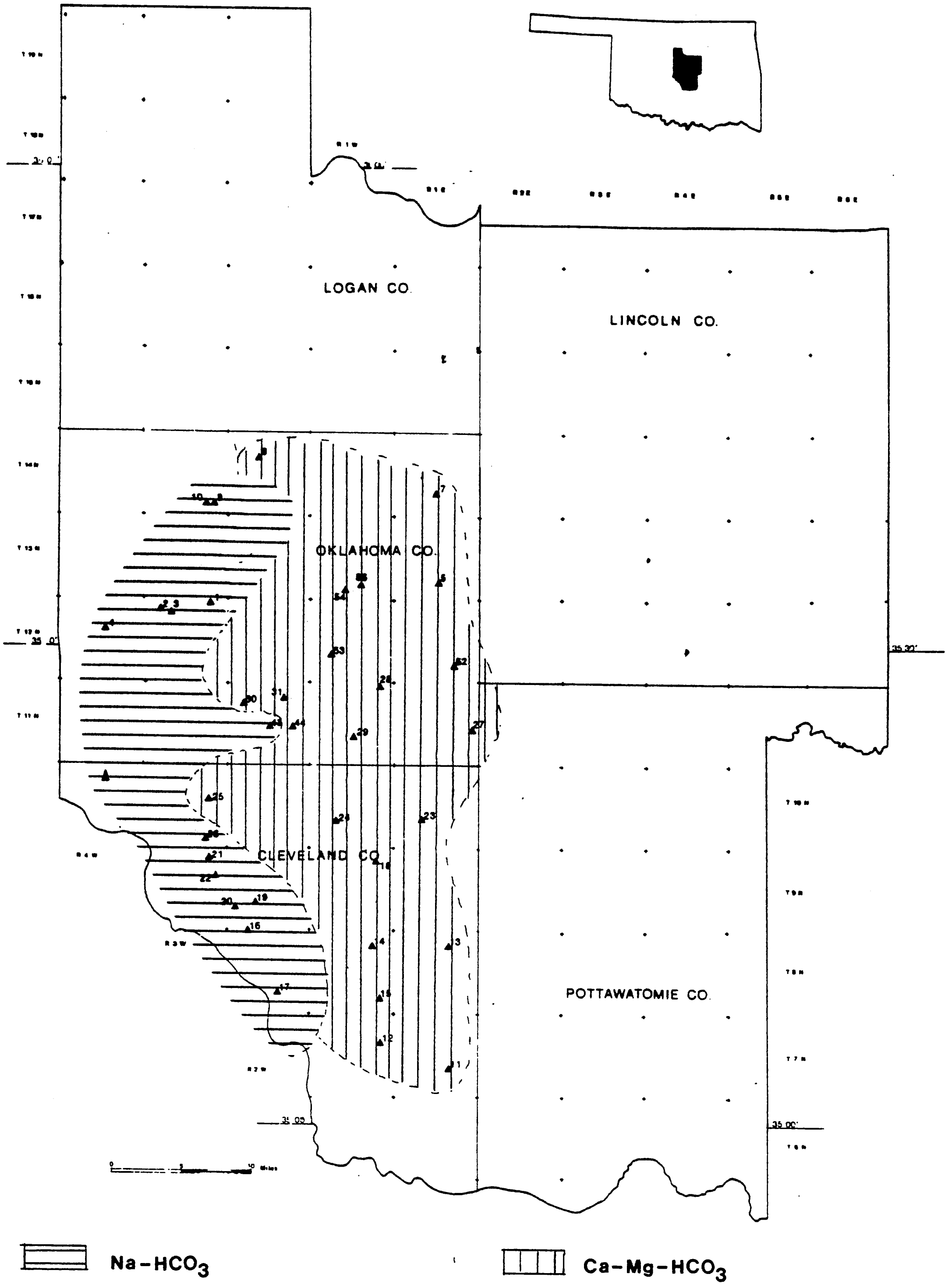


Figure 14. Areal Distribution of Sodium-Bicarbonate and Calcium-Magnesium-Bicarbonate Waters

sulfate generally accounts for 10-25%. Within this region, the percentage of chloride varies. Overall, chloride and sulfate never exceed 60% and 50%, repsectively, of the total anionic content.

In the central diamond, the primary cluster is indicative of water dominated by Ca^{++}-Mg^{++}-$\overline{HCO_3}$. The consistent, nearly 1:1 ratio of calcium to magnesium in this area suggests that dissolution of dolomite, which is present both as a cement in the leached zones as well as a primary constituent of conglomeratic horizons is occurring. A tail emanates from this cluster in the direction of increasing chloride and sodium content. These analyses may represent areas where dissolution of both sodium chloride and dolomite both contribute to the ionic make-up of the water. Elevated sulfate concentrations are also associated with waters intermediate in sodium content.

A second area of concentration exists along the lower right side of the diamond. Water analyses plotting here are characterized by predominant sodium in conjunction with bicarbonate, and minor sulfate. Waters represented by these points may be involved in cation exchange where sodium is substituting for calcium and magnesium subsequent to carbonate dissolution. This would infer the presence of sodic-rich clays in the sediments. One problem with this hypothesis is that montmorillonitic clays cannot be identified in XRD patterns of the outcrop samples. The only clays which appear to be present are kaolinite and illite. Therefore, a change in mineralogy of the subsurface strata must be assumed if cation exchange is taken to be the mechanism repsonsible for high sodium concentrations in the water.

The occurrence of appreciable sulfate and calcium in a few samples indicates that some gypsum is being dissolved. The percentage of sulfate is high where sodium is the dominant cation, which suggests a second hypothesis for the origin of the sodium-bicarbonate waters, specifically, the dissolution of sodium-bearing evaporite minerals. The occurrence of gypsum and halite in the subsurface indicates the presence of evaporites, at least locally. Bradley and Eugster (1969) have discussed the physical and chemical conditions necessary for precipitation of sodium carbonate and bicarbonate minerals in the Green River Formation of Wyoming. They believe that given a sodium-rich brine, the primary controls on the mineral species that will precipitate are the CO_3/HCO_3 ratio, temperature and the availability of CO_2. The carbon dioxide essential to the system is hypothesized to be derived from the atmosphere or is biogenic in origin. In the Garber-Wellington, the source of sodium may have been weathering of plagioclase feldspars, which are found associated with dolomite in the samples analyzed. If this hypothesis is correct, it would support the theory that carbonates in the formation have a fresh water origin, and lend evidence to the idea that the conglomerates are reworked, dolomitic calcretes.

Ionic Correlations and Factor Analysis

SAS linear correlation and component factor analysis programs were used to analyze major constituent relationships within the aquifer. Input data was obtained from both the complete analysis data set (#1) (well locations shown on Figure 10, raw data Appendix A) and the HSSR Program data set (#2) (well locations shown on Figure 11, raw data Appendix B), the latter of which includes some major constituents, but was used primarily as a trace element data base. A modified version of the correlation matrix for Data Set #1 is presented in Table VII. Only

TABLE VII

MODIFIED CORRELATION MATRIX OF MAJOR CONSTITUENTS IN THE AQUIFER (SAS, 1982)*

	pH	TDS	Cond.	Ca^{++}	Mg^{++}	Na^{+}	K^{+}	Cl^{-}	SO_4^{--}	HCO_3^{-}	SiO_2	CO_3^{--}	Depth	NO_3^{-}
pH														
TDS			0.99			0.85		0.84	0.76	0.65				
Conductivity						0.85		0.83	0.72	0.69				
Ca^{++}					0.92									
Mg^{++}														
Na^{+}								0.68	0.69			0.74		

*Only those values >0.65 or <-0.65 are shown, raw data is Data Set #1 those correlation coefficients >0.65 or <-0.65 are included. Factor analysis of this correlation matrix was done in order to extract significant factors. The printout for the "VARIMAX" (SAS, 1982) rotated matrix is presented in Table VIII.

Strong linear correlations were obtained for a number of parameters. The first factor relates TDS, conductivity, sodium, and chloride. It demonstrates that sodium and chloride are the principal ions affecting the conductivity and dissolved solids content of the water. Waters characterized by high sodium chloride are most likely either dissolving localized halite deposits or being affected by mixing with salt water at the base of the aquifer. The influence of either mechanism is minimal, however, because the highest chloride concentrations reported in the data were 325 mg/l. This factor accounts for 33% of the total variance in the system.

A second high correlation exists between calcium and magnesium, however, it is interesting to note that the correlation coefficients between the two data sets differ considerably. For data set #1 the value is 0.92 and for #2 is 0.79. Data set two covers a larger portion of the aquifer, extending further north and east (compare Figures 10 and 11). The discrepancy in values suggests that the correlation is somewhat regionally controlled. The strong relationship between these two variables is also demonstrated in factor analysis, where a high positive covariance between them defines the second factor. The elucidation of this relationship strengthens the hypothesis that dolomite dissolution is a major reaction in the geochemistry of the ground water system. Given the difference in correlation values between data sets, it appears that this reaction occurs to a greater extent in the western part of the

TABLE VIII

RESULTS OF FACTOR ANALYSIS - MAJOR CONSTITUENTS IN THE AQUIFER

	"VARIMAX " (SAS, 1982) Rotated Matrix			
	Factor 1	Factor 2	Factor 3	Factor 4
pH	0.35	-0.35	0.64	0.45
TDS	0.94	0.00	0.30	-0.07
Conductivity	0.92	0.02	0.31	-0.05
Ca^{++}	0.01	0.95	-0.10	-0.14
Mg^{++}	-0.02	0.96	0.05	-0.14
Na^{+}	0.78	-0.48	0.32	0.06
K^{+}	0.35	-0.10	0.06	-0.61
Cl^{-}	0.92	0.02	-0.07	-0.11
SO_4^{--}	0.63	-0.18	0.10	-0.12
HCO_3^{-}	0.46	0.29	0.78	0.18
SiO_2	0.06	0.08	0.03	-0.15
CO_3^{--}	0.36	-0.57	0.47	0.13
Depth	0.17	-0.20	0.06	0.75
NO_3^{-}	0.09	0.28	-0.05	-0.68
	Variance Explained by Each Factor			
	33.1%	22.5%	16.4%	15.5%

aquifer. This is most likely a function of sediment lithology, due to an increase in dolomitic horizons in this region. An additional point to note regarding Factor 2 is that sodium and carbonate are loaded onto it in a moderate negative covariance with calcium and magnesium. This lends further evidence to the hypothesis that cation exchange is responsible, in part, for the occurrence of high sodium concentrations in certain areas (Factor 2 accounts for 22.5% of the total variance in the system).

To further elucidate the different geochemical processes occurring in the system, data set #1 was subdivided into two subsets, 1A and 1B, and a factor analysis was run on each of these. Subset 1A consisted of those analyses representing Na^+-HCO_3^- waters and subset 1B, Ca^{++}-Mg^{++}-HCO_3^- waters. The primary difference between 1 and 1A occurs on the second factor, where the negative correlation between Ca^{++}-Mg^{++} and CO_3^{--} was observed in the sodium-bicarbonate waters. The striking difference between data sets 1 and 1A, and 1B and 2 was the emergence of sulfate as the principal variable loading on factor 1 in the latter. It indicates that dissolution of gypsum is contributing significantly to the ionic make-up of the water. An additional difference was noted in factor 2 of data set 1B, where the very strong Ca-Mg-HCO_3 loadings illustrate the dolomite dissolution component of the system.

The strong positive correlation between calcium and sulfate (0.92) found in data set #2 accounts for a large part of the variance, as it defines the principal Factor extracted from the correlation matrix (see Table IX). It suggests that either dissolution of gypsum is taking place to a greater extent than in those areas not covered by data set #1, or alternatively, that dissolution is occurring throughout the aquifer,

TABLE IX

VARIATION IN VARIMAX ROTATED FACTORS FOR $NA-HCO_3$ AND $CA-MG-HCO_3$ WATERS

Data Set 1	Data Set 1A	Data Set 1B	Data Set 2
Entire	$Na-HCO_3$ Water	$Ca-Mg-HCO_3$ Waters	HSSR
Factor 1:			
TDS .94	TDS .96	SO_4 .95	SO_4 .94
Cl .92	Cond .95	Cl .94	Ca .86
Cond .91	Na .94	Na .85	
Na .78	Cl .91	TDS .76	
	HCO_3 .82	Cond .74	
Factor 2:			
Mg .96	Mg .95	HCO_3 .96	
Ca .95	Ca .87	Mg .87	
CO_3 -.57	CO_3 -.88	Ca .78	
Na -.48			

and that in the western part of the study are its effect is being masked by cation exchange.

Factor 3 is marked by a moderately strong positive covariance between pH and bicarbonate. This relationship is explained by the effect that dissolution of carbonate rocks has on pH in natural waters. As the rock dissolves, CO_3^{--} ions go into solution and combine with H^+ ions to form HCO_3^-. This leaves an excess of OH^- ions in the system, which increases the pH. Factor 3 accounts for 16.4% of the variance in the system.

The fourth factor extracted relates potassium and nitrate in a positive covariance, and correlates these negatively with well depth. It is suspected that this relationship is due to the influence of fertilizers in the ground water. It reflects infiltration of water into the shallow aquifer that has leached soils to which fertilizer has been applied. Factor 4 accounts for 15.5% of the variance in the system.

Together, the four factors discussed above account for 87.5% of the total variance in the system as it is represented in data set #1.

Mineral Equilibria

Determination of the saturation state of the water with respect to various mineral species in the Garber-Wellington aquifer was accomplished using WATEQF (Plummer, et al., 1976), a computer program which calculates chemical equilibria in natural waters. Input data was restricted to data set #1 (major constituents), which covers only the western and southwestern portions of the aquifer. The effectiveness of the calculations was hampered by the lack of data on redox potential of the system, and accurate estimations on the amount of dissolved iron in the water. Nevertheless, determination of the equilibrium state of several mineral species was possible. Because the flow paths in the deeper aquifer are not known, effects of residence time and distance from recharge areas could not be considered in the evaluation. Figures 15, 16, and 17 define limits of saturation using Log IAP/KT (saturation index) values as calculated by WATEQF.

Figure 15 presents the state of saturation with respect to calcite. The region of supersaturation does not appear to correlate with any particular water type within the aquifer. the zone of saturation cuts acros areas of sodium, calcium-magnesium, and calcium-sulfate concentration.

Figure 16 illustrates the equilibrium conditions in the aquifer with rspect to dolomite. Slight oversaturation is evident primarily in the western (deepest) part of the aquifer, and near T14N, R1E, and occurs in both sodium and calcium-magnesium dominated waters. Slight undersaturation does occur in one area where gypsum dissolution has added Ca^{++} and SO_4^{--} ions to the system. Unfortunately, additional data points were not available in other localities where gypsum dissolution is occurring, precluding determination of the extent of this process on dolomite saturation of the water.

Given the situation described above, it is postulated that dedolomitization of Garber-Wellington sediments taking place in those areas which show saturation with respect to calcite and undersaturation with respect to dolomite. This occurs in the southern part of the aquifer (Figures 15 and 16) and, though the data is not available, possibly in Logan County where calcium sulfate is prevalent. "The process of dedolomitization consists of dolomite dissolution and

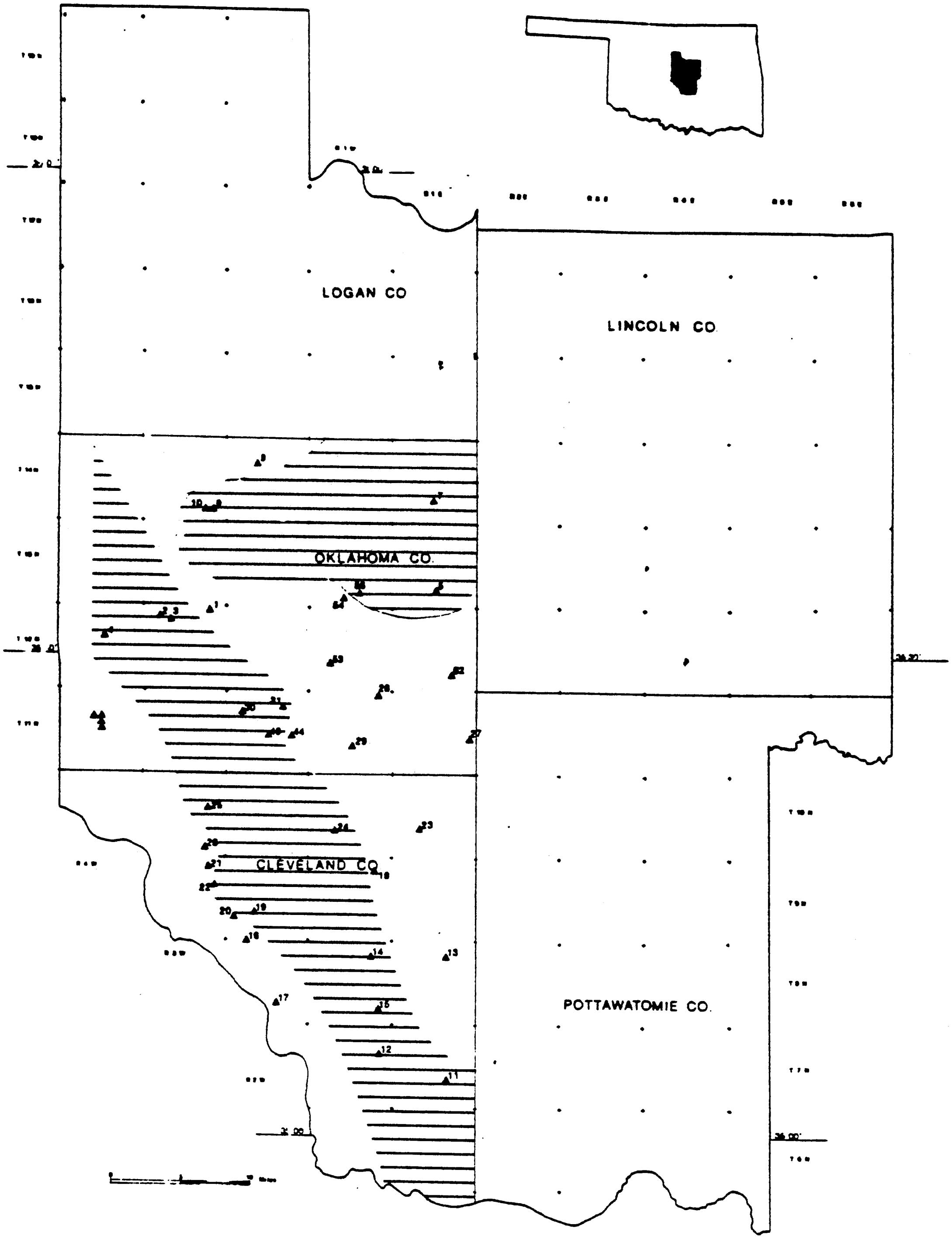


Figure 15. Saturation of the Aquifer With Respect to Calcite (Stippled Area)

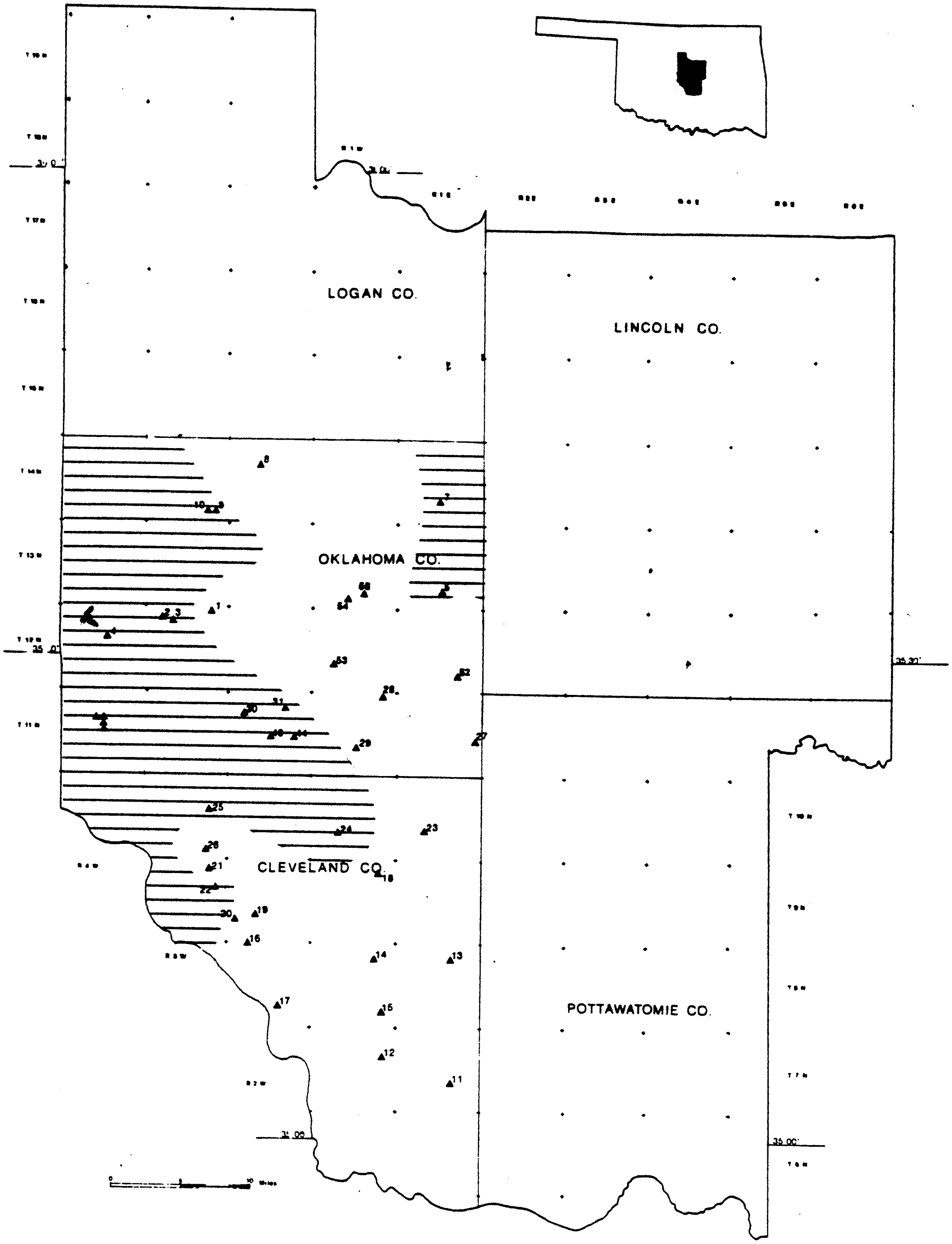


Figure 16. Saturation of the Aquifer With Respect to Dolomite

concurrent precipitation of calcite; it is driven by the dissolution of gypsum." (Back et al., 1983). Dedolomitization occurs when the $Ca^{++}:Mg^{++}$ ratio in carbonate-rich waters, which have been dissolving calcite, dolomite, and gypsum, becomes significantly greater than 1:1. In certain waters of the Garber-Wellington, gypsum dissolution is raising the $Ca^{++}:Mg^{++}$ ratio and forcing this process to occur. Back et al. (1983) conclude that it can be viewed mechanistically as follows:

A) dissolution of calcite,

$$H_2O + CO_{2(s)} + CaCO_3 \dashrightarrow Ca^{++}_{(c)} + 2HCO^{-}_{3(s,c)}$$

B) dissolution of dolomite,

$$2H_2O + 2CO_{2(s)} + CaMg(CO_3)_2 \dashrightarrow Ca^{++}_{(d)} + Mg^{++}_{(d)} + 4HCO^{-}_{3(s,d)}$$

C) dissolution of gypsum,

$$CaSO_4 \quad 2H_2O \dashrightarrow Ca^{++}_{(g)} + SO^{--}_{4(g)} + 2H_2O$$

where c, d, and g represent ions from calcite, dolomite, and gypsum, respectively; and s represents CO_2 from soil gas. When occurring simultaneously, $CaCO_3$ will precipitate as follows:

$$Ca^{++}_{(c)} + Ca^{++}_{(d)} + Ca^{++}_{(g)} + 6HCO^{-}_{3(c,d,s)} \dashrightarrow$$

$$3Ca_{(c,d,g)}CO_{3(c,d,s)} + 3HCO_3^{-} + 3H^{+}$$

where $SI_{(c,d)} \quad 0$.

Saturation indices of the principal clay minerals present in the rocks indicate that water in the entire aquifer (except for three wells) is supersaturated with respect to kaolinite, and all but the western most region is saturated with respect to illite (Figure 17). Highly variable

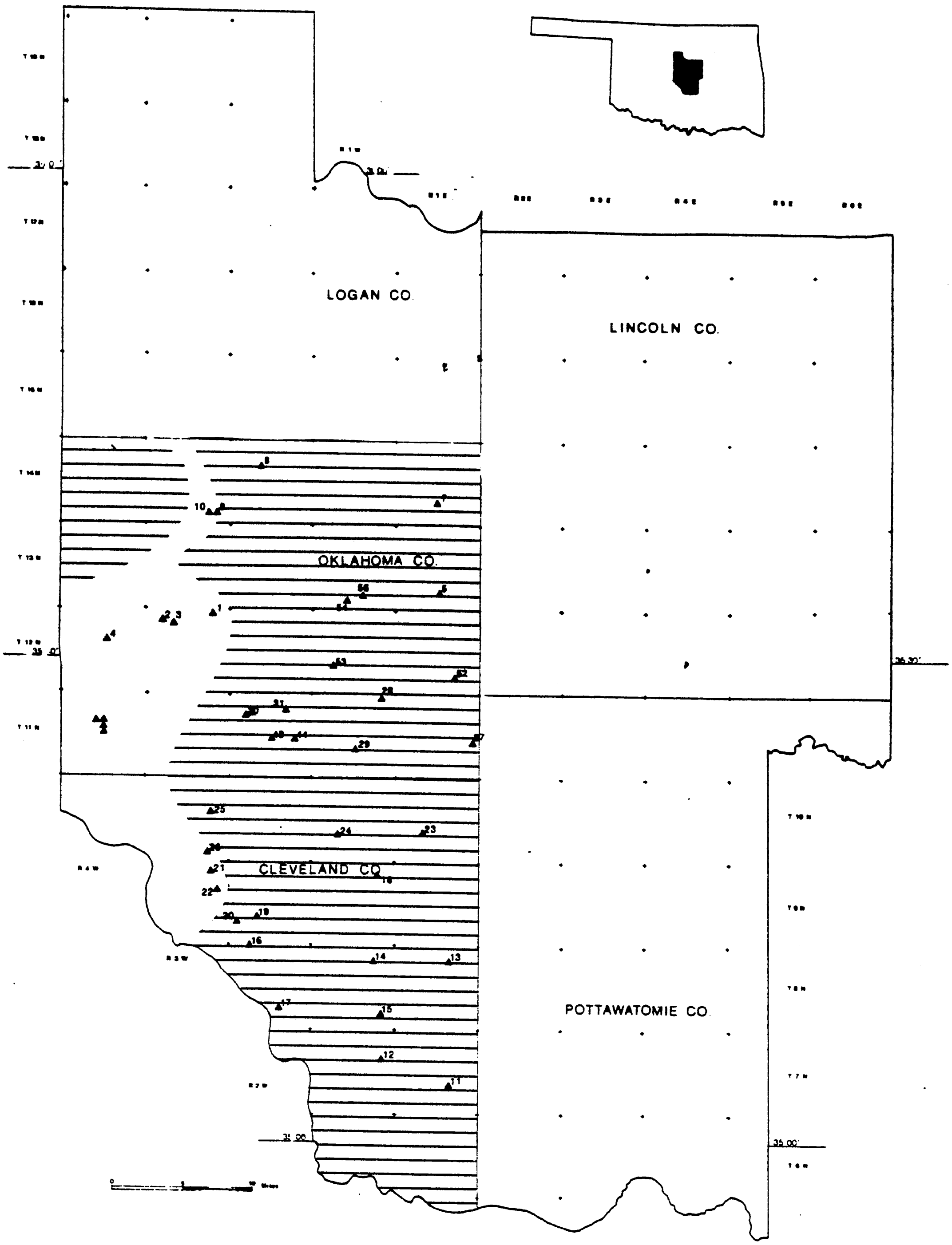


Figure 17. Saturation of the Aquifer With Respect to Illite

values for calcium and sodium montmorillonite suggest that these minerals have not reached equilibrium in the system. The same holds true for gypsum, as all saturation index values were negative.

Trace Elements

Trace element distributions and interrelationships were examined both areally within the aquifer, and statistically using SAS linear correlation and Factor Analysis programs. Input data was obtined from the HSSR Program data set, which also contains analyses of a few major constituents. The locations of the wells sampled are noted on Figure 11.

Distribution

Elevated levels of trace elements were found primarily in the western part of the study area. In addition, one area of concentration is in southwestern Pottawatomie County (see Appendix B for concentrations of various constituents by well). Three distinct water types have been defined based on trace element associations in conjunction with high concentrations of certain major constituents. These are plotted on Figure 18, and are differentiated as follows: 1) Ca-Mg-SO_4-HCO_3 with Nb, Th, U, Y, B, and occasionally Zn, Mn, and Li; 2) Na-HCO_3 with As, Cr, V, and Se; and 3) Ca-Mg-HCO_3 with Ba and Sr. The area in Pottawatomie County is also a Ca-Mg-HCO_3 water which shows sporadic elevated levels of several compounds with very little between-well correlation.

The first association of trace elements, occurring in a predominantly calcium sulfate water, contains levels of Niobium >10, Th >20, U >25, Li >50, Mn >30, B >1000, and Zn >500 ug/l. It is clear that

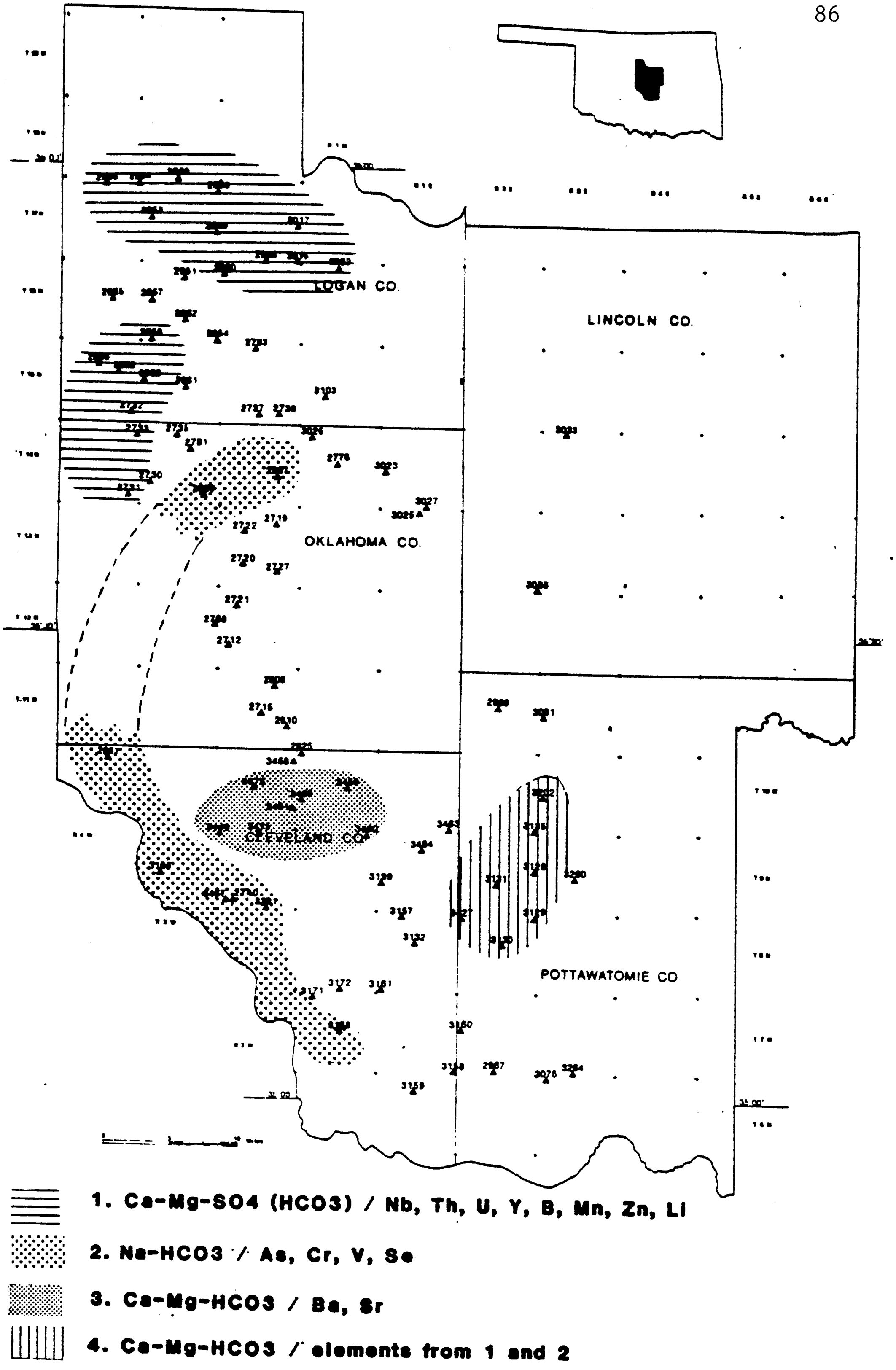


Figure 18. Trace Element Associations and Distribution Within the Aquifer

dissolution of gypsum is producing the ionic relationships observed in the water. Lithium, Niobium, and Boron are common trace constituents of evaporites. Zinc is often detected in waters emanating from gypsiferous strata. Yttrium occurs both in evaporite deposits and can substitute for calcium in the carbonate lattice. It is likely that these elements are entering the ground water system due to the dissolution of an evaporitic zone in the Garber-Wellington. A point which should be noted is that many of the trace elements found in this association have been detected in continental evaporite mineral sequences in the Green River Formation (Bradley and Eugster, 1969).

Waters in the second association are marked by predominance of sodium and bicarbonate ions. As discussed in a previous section, the geologic environment producing these waters has not been conclusively determined. The trace elements associated with the Na-HCO_3 waters are Arsenic >5, Chromium >40, and Vanadium >100 ug/l. In addition, it is in this region of the study area that the highest levels of selenium have been found in the ground water (by other sources).

Arsenic, Vanadium, and Chromium are enriched in the hydrolyzate sediments, specifically, adsorbed onto aluminum hydroxides (clays). Under most natural Eh-pH conditions in ground water, they would be tied up in the sediments and not released to the water. The desorption of these elements is accomplished primarily under high oxidizing conditions. Rankama and Sahama (1950) states that arsenic, vanadium, and chromium can all be oxidized to soluble complex anions which are readily mobile. This also holds true for sulfur, selenium, molybdenum, tungsten, and uranium. The appearance of several of these compounds in elevated levels in the ground water system suggests that high oxidizing conditions either exist naturally in the aquifer or have been artificially created surrounding the wells from which the samples were collected. As reported in this data set, dissolved oxygen content in the aquifer ranged from 2.3 to 13.0 mg/l. In addition, the pH of the water in this region (as found in those wells containing appreciable selenium) is quite high, ranging from 8.2 to 9.4. High pH also tends to decrease the amount of adsorption of trace elements in water.

The third water type, noted in Cleveland County, is marked by the occurrence of barium >700 and strontium >500 ug/l in Ca-Mg-HCO_3 water. Strontium and barium are highly mobile during weathering, and tend to migrate as bicarbonates, chlorides and occasionally, sulfates. The presence of strontium suggests that some of the carbonate in these sediments was originally aragonite. Upon polymorph inversion to calcite this element was expelled from the lattice and may have formed celestite. Celestite often occurs as an impurity in carbonate minerals, gypsum and anhydrite. The fourth water type noted on Figure 18 is also a calcium-magnesium-bicarbonate rich solution. The water exhibits slightly elevated levels of several trace elements that occur in both water types discussed above.

Factor Analysis

The first factor extracted (Table X) correlated well with the association of elements found in type 1 water, which were discussed above. Selenium is also loaded onto this factor (.68), for reasons which are not clear. It is possible that selenium is found in the gypsiferous sediments, though not likely, because its occurrence in evaporites is rare (Rankama, 1969). Levels of selenium above the

TABLE X

RESULTS OF FACTOR ANALYSIS - TRACE ELEMENTS IN THE AQUIFER

	"VARIMAX" (SAS, 1982) Rotated Matrix		
	Factor 1	Factor 2	Factor 3
D.O.	-0.41	-0.18	0.03
Alkalinity	-0.07	0.55	-0.19
pH	-0.36	0.54	0.32
Conductivity	0.18	0.03	0.53
U	0.34	0.64	0.12
SO_4	0.94	0.01	0.17
As	-0.06	0.93	-0.26
Se	0.68	0.00	-0.01
Al	-0.08	0.44	0.11
B	0.71	0.43	0.19
Ba	-0.21	-0.41	-0.26
Ca	0.86	-0.20	0.32
Cr	-0.24	0.80	0.14
Cu	0.11	-0.01	0.30
Li	0.76	0.14	-0.06
Mg	0.77	-0.26	0.23
Mn	0.06	-0.03	0.62
Mo	0.08	0.59	0.69
Na	0.46	0.68	0.19
Nb	0.71	-0.01	0.59

TABLE X (Continued)

	"VARIMAX" (SAS, 1982) Rotated Matrix		
	Factor 1	Factor 2	Factor 3
Th	0.63	0.20	0.77
V	0.03	0.90	0.04
Y	0.76	0.16	0.64
Zn	-0.02	-0.08	0.23
K	-0.15	-0.34	0.25
Sr	0.07	-0.13	0.09
Si	-0.39	-0.57	0.45
	Variance Explained by Each Factor		
	27.0%	23.5%	15.1%

potable water standard have not been detected in these waters, however, the highest concentration reported in the HSSR Report (7.7 ug/l) is in this region. This sample is proximal to other samples exhibiting elements of the second association, with which selenium can be grouped geochemically. This factor accounts for approximately 27% of the variance of the system.

The second factor, which relates arsenic, vanadium, chromium and sodium, is associated with the type 2 water described above. The occurrence of these elements in the ground water is attributed to high oxidizing conditions in the aquifer. This factor accounts for 24% of the variance within the data set.

The third factor shows a high positive covariance of Th, Mo, Y, and Mn. These four elements are not associated strongly with any of the waters discussed above. The loading of thorium and yttrium on this factor as opposed to Factor 1 may indicate that these elements are not found in the water due to the dissolution of gypsum or evaporites. In this case, the occurrence of yttrium would be a function of its tendency to remain partly in solution when adsorbed to clays, as its hydroxide is a stronger base than aluminum hydroxide (Rankama, 1969). Molybdenum does not occur in the Garber-Wellington in elevated concentrations. Manganese occurs in three wells (concentrations of 32, 86, 185 ug/l) associated with Ca-Mg-SO_4 water. Manganese generally goes into solution at low redox potentials and is precipitated at high ones. However, its solubility is increased in the presence of sulfates, which probably accounts for its presence in water which is dissolving gypsum. Factor three accounts for 15% of the variance in the system.

Taken together, the first three factors account for 66% of the variance in the system as represented by this data set. The validity of the fourth factor is questionable since it related depth and producing depth. In most of the wells tapping the Garber-Wellington, total depth is not an important factor, as screens have been set in numerous water-bearing zones throughout the saturated interval. In conclusion, when combining information on principal water types, the distribution of trace elements, and factor Analysis results, a good overall picture of the qualitative hydrogeochemical aspects of the system can be obtained. A possible reason for the factors accounting for only 66% of the variance in the data is that, because lithologies change laterally and vertically within each well, mixing of waters is occurring. The process described above affect each other physically and chemically, causing further interactions in an already complex system.

CHAPTER X

OCCURRENCE OF SELENIUM IN THE GARBER-WELLINGTON AQUIFER

Origin

The origin of selenium in seleniferous sedimentary rocks has been debated since the 1930's. Beath et al. (1935) and Trelease and Beath (1949) suggest that the selenium contained in the Cretaceous Pierre and Niobrara Formations is a primary constituent of the magmas introduced on the central Cordilleran land mass from which the rocks were derived. However, Byers et al. (1936, 1938) believed that these formations may have acquired their selenium content from gaseous emanations and dust which accompanied volcanic activity. They hypothesized that the selenium was present in the atmosphere as selenium dioxide or salts of selenious acid following volcanic eruptions. Davidson and Powers (1959), after studying the selenium content of some volcanic rocks from the western United States and Hawaii, conclude that their data support the hypothesis of Byers. This conclusion is based on results showing low levels of selenium in flow rocks, and higher values in tuff and ash beds (see Table III).

It is proposed here that the selenium in the Garber Wellington is present as a result of one of two processes. The first is that the element was deposited in the sediments directly as a result of weathering of sulfide ore bodies. The second is that it was introduced both during and after deposition, by infiltration of atmospheric, seleniferous precipitation; the result of the solution of selenium-rich dust and gasses from volcanic exhalations. Evidence to support the "sulfide ore" hypothesis is in the existence of numerous mineralized zones in the source rocks of the Ouachitas to the east. Scull (1959) has dated epithermal lead, zinc, and copper deposits in Arkansas as late Pennsylvanian, their formation being associated with the Ouachita orogeny. Weathering and erosion of these rocks during early Permian time would have provided a source of selenium to the Garber-Wellington sediments during deposition. Although this hypothesis is plausible, it does have certain drawbacks. Concentrations of selenium in these sediments are generally higher than in average (world-wide abundance) sandstones and shales. Even though the element is preferentially concentrated in the hydrolyzate sediments, it is still dispersed and ubiquitous within both formations. If the selenium were contained in weathering products of discrete ore bodies, one would expect to find that its occurrence was localized and highly concentrated in certain areas. In addition, it would be likely that elevated levels of lead, zinc, and copper might be associated with the selenium, as these elements all tend to form adsorption complexes with oxides and hydroxides in sediments. As discussed in Chapter 8, this is not the case. Therefore, it is more likely that primary weathering of sulfide ore bodies is not the mechanism responsible for emplacement of selenium in their Garber-Wellington.

The second hypothesis under consideration, that selenium-bearing volcanic dust and gas was transported aerially and entered the aquifer through infiltration of precipitation, appears to have no serious drawbacks. The origin of the volcanic gasses cannot be determined conclusively, however, several volcanic sources were in existence during and after deposition of the Garber-Wellington sediments. Volcanic activity is known to have occurred in the northwestern United States during Permian time. Beath et al. (1937) have shown that the Permian Phosphoria and Dinwoody Formations are seleniferous in places. The origin of the selenium is accepted as volcanic. Volcanism continued in this region from Permian to Cretaceous time, which would have allowed for a small but consistent supply of atmospheric selenium to sediments of the Garber-Wellington if atmospheric conditions were favorable. The fact that selenium was carried in a southeasterly direction from the Idaho-Oregon-Washington area and deposited in formations in Wyoming and Colorado would support the possibility of further movement southeast into the Oklahoma region.

A second source of volcanic selenium would have been to the east, in the Ouachita Mountains. However, volcanic activity did not begin in this region until Cretaceous time. Miser and Ross (1925) postulated the existence of volcanoes concealed by beds of late Cretaceous and Quaternary Ages. Scull (1959) mapped four volcanic centers occurring in mineralized and igneous areas in the Ouachita Mountains in Arkansas. Because the Permian Garber-Wellington sediments have been exposed at the surface since their deposition, it is not unlikely that infiltration of selenium-bearing waters occurred during Cretaceous time.

Distribution of selenium throughout Garber-Wellington rocks would have occurred as a result of movement of selenium-rich ground water through the aquifer. Fixation of the element in the sediments would then have occurred through adsorption onto hydrolyzates and oxidates such as iron and Manganese oxides. Although at first it might seem likely that the more permeable sediments would become enriched in selenium, this does not occur due to the paucity of adsorption sites in these sediments.

Possible Modes of Occurrence

A review of the distribution of selenium in sedimentary rocks has been presented in Chapter VI. Based on this information, it was determined that within the Garber-Wellington, selenium occurrence could be related to any one of several lithologies. A likely mode of occurrence, given that selenium is known to be somewhat enriched in the hydrolyzates (Rankama and Sahama, 1950), is in the form of the selenite ion (Se03), which would be firmly adsorbed onto iron hydroxides, or clays present most abundantly in the shales and to a lesser extent in the sandstones of either formation. In this state, the selenium would be highly immobile in the range of normal Eh-pH conditions in ground water.

A second possible mode of occurrence of selenium is as a substitute for sulfur in the sulfate minerals barite and jarosite. Two viable sources would be within barite-rich deposits in the Garber Sandstone, and/or along bedding, joint and fracture surfaces in the shale horizons of either formation. Jarosite is an alteration product of iron-bearing sulfide minerals that occurs along these surfaces in shale. It is commonly associated with limonite, goethite, and hematite, pyrite, kaolin clays, and secondary minerals of base metals. If the selenium were present in barite or jarosite, it would be relatively insoluble under ordinary near-surface ground water conditions.

Lastly, it was thought that selenium might be concentrated is the nodular ironstone concretions which were found at two sampling localities (1-10 and 2-4). Mineralogically, these concretions consist almost exclusively of quartz, hematite, and goethite and can be classed as oxidate sediments. Rankama and Sahama (1950) state that the degree of selenium enrichment in the oxidates is even higher than in the hydrolyzates. Trelease and Beath (1949) found that limonitic concretions in shales of the Niobrara Formation contain appreciable quantities of selenium.

Lithologic Associations

Table XI lists the concentrations of selenium and mineralogic constituents of representative lithologies occurring in the Garber Sandstone and Wellington Formation (see Figure 12 for sampling localities). The values range from a low of 1 ppm to a high of 16 ppm. The lowest values occur in a barite rosette (1-5D), two sandy ironstone layers (1-11, 2-3-BX), an orange-yellow laminated sandstone (1-10), and a red, dolomitic, iron-rich conglomerate (3-2). It can be seen by comparing constituents of the various rock types that a common factor among these samples is the absence of clay minerals. The crystalline iron minerals hematite and goethite range from being secondary constituents to absent in these rocks. Feldspars are recognized in only one of five samples, and the primary constituent is either quartz or calcite.

Those samples highest in selenium (2-1A, 1-9A, 2-3L-A) are shales, both red and green, which contain definite clay (kaolinite and illite) and sodium feldspar components. Hematite is present in only one sample, and carbonates occur in two of three. Three of the four samples in which the concentration of Selenium falls in the middle of the range have mineralogic characteristics similar to those at the upper end. In two of

TABLE XI

MINERALOGIC CHARACTERISTICS AND SELENIUM CONTENT OF GARBER-WELLINGTON ROCKS

P - primary S - secondary M - minor T - trace	Lithology - Sample #											
Mineral	Gray Shale 2-1A 2-1B	Red Shale 1-9A	Gray Sandy Shale 2-3-LA	Gray Shaly Dolomitic Cgl. 1-5A	Gray Sandy Shale 1-4B	Ironstone Nodules 2-4-AX	Red Sandstone 1-3	Red Dolomitic Iron-Rich Cgl. 3-2	Orange Sandstone 1-10	Sandy Iron-stone Layers 1-11	Sandy Iron-stone Layers 2-3-BX	Barite Rosettes 1-5D
Quartz	P	P	P	S	P	P	P	S	P	P	P	P
Dolomite			S	P				P				
Calcite	S											
Hematite		M				S		M		S	S	
Goethite								M			S	
Barite												P
Potassium Feldspar							M		M			
Sodium Feldspar	M	S	M	M					M			
Kaolinite	M	M	M	M	T-M		T-M		T			
Illite			M	M	M							
Montmorillonite												
Selenium (Content (ppm)	15.7 HIGH	12.8	9.1	6.5	6.4	6.1	4.5	2.0	1.78	1.58, 1.28	1.28	1.16 LOW

these, however, there is a greater proportion of sand (1-4B, 1-3) and less clay and feldspar, reducing the amount of surface area available for adsorption. Sample 2-4-AX is anomalous in that it contains virtually no clay, yet has a relatively high selenium content.

Judging by the results discussed above, it appears that concentration of selenium in rocks of the Garber-Wellington is largely controlled by the distribution of hydrolyzates in the sediments. This conclusion is in opposition to Drever (1982) who believes that in oxidizing environments, adsorption by iron and manganese oxides is generally much more important. Wells (1967), however, has found that highly weathered, strongly leached, clay-rich soils contain high amounts of selenium. Samples in this study having fine-grained texture and containing a significant amount of kaolin clays are those which also exhibit the greatest enrichment in selenium (except for 2-4-AX), which is in agreement with Wells' findings. In conclusion, although adsorption of selenium onto oxidate sediments is most likely occurring, it is not the primary process responsible for accumulation of this element in the sediments. Adsorption onto clays is much more prevalent and important in these rocks.

Geochemical Factors Controlling the Release of Selenium into the Aquifer

Selenium has been detected in concentrations exceeding the potable water standard of 10 ug/l in a number of wells tapping the aquifer. Figure 19 shows the location, depth, concentration of selenium, and pH in each of these wells. Elevated values occur primarily in the western and southwestern portions of the aquifer, where it is confined beneath rocks

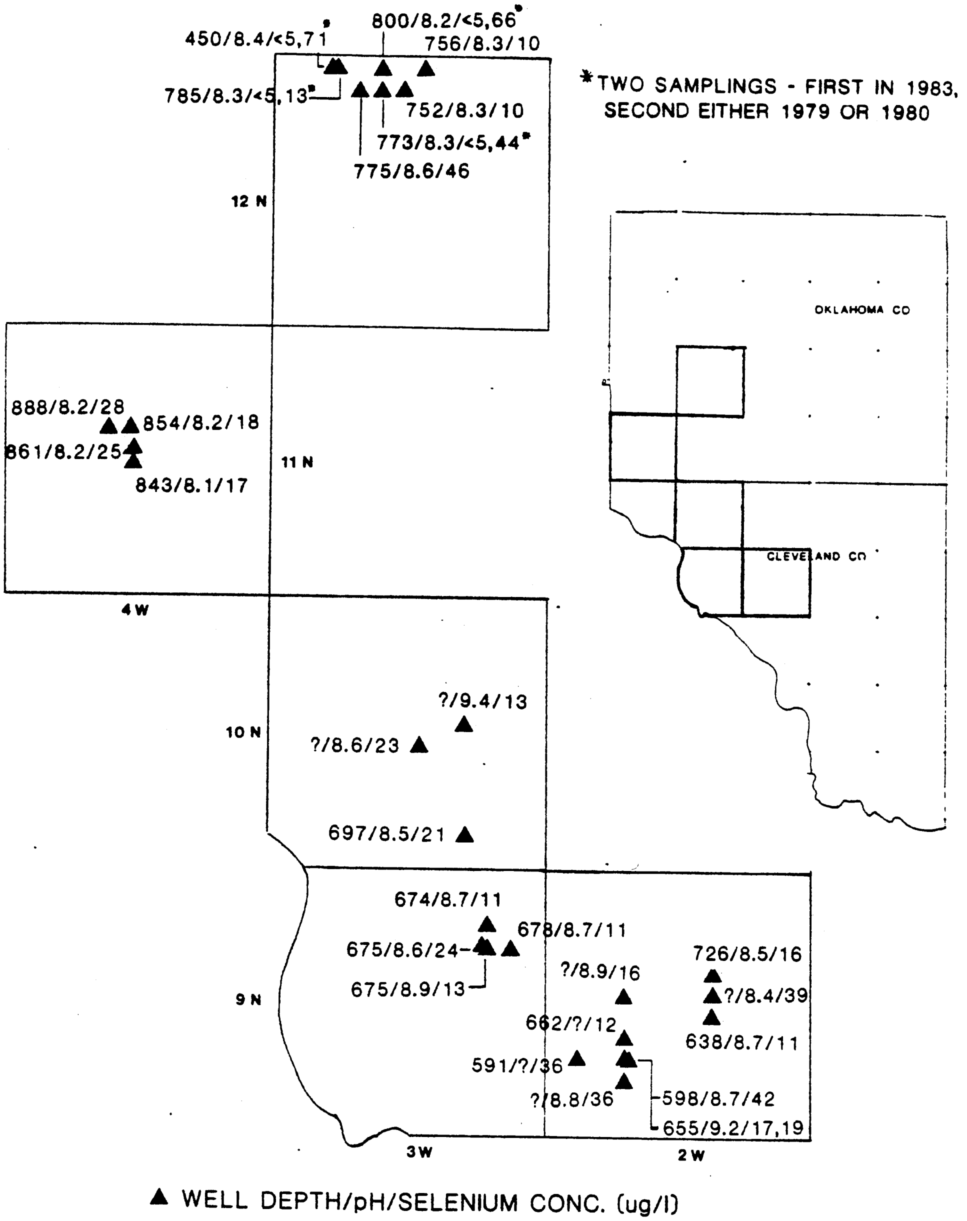


Figure 19. Location and Distribution of Wells Showing Elevated Levels of Selenium (10 ug/l)

of Hennessey Group. Depths of the wells ranges from 450 to 880 feet below land surface. They are all screened in numerous water-bearing zones, therefore, no conclusion can be made with regard to the existence of a zone of highly seleniferous strata. It should be noted that the two highest concentrations (71 ug/l and 66 ug/l) were present in the shallowest (450 ft), and one of the deepest (800 ft) wells, respectively. Both of these are located in T12N R3W. In addition, a second sampling of the water done three years subsequent to the initial sampling, indicated that in both wells the level had dropped to less than 5 ug/l. This most likely indicates that alteration of the geochemistry of the system is controlling the release of selenium into the aquifer.

Because selenium, under normal Eh-pH conditions in ground water, is firmly adsorbed onto hydroxides and oxides in the form of the selenite ion (SeO_3^{--}), it is unusual that high concentrations of this element have been detected in water of the Garber-Wellington aquifer. As stated previously, two factors controlling the amount of adsorption and desorption of many trace elements are the Eh and pH of the system. Alkaline and oxidizing conditions favor formation of the selenate ion (SeO_4) which is not readily complexed with iron or aluminum and is, therefore, mobile. As can be seen in Figure 19, the pH of the water is high (8.1-9.4) due to the presence of excessive bicarbonate. The Eh required for the formation of selenate decreases with increasing pH, and it can be seen from Figure 20 that at the given pH values, the Eh of the system need only be between .26 and .36 volts for selenate to form. It is therefore feasible that high pH values are indirectly responsible for the oxidation of selenite to selenate, and the subsequent release of selenium into the ground-water system. Further evidence of this is

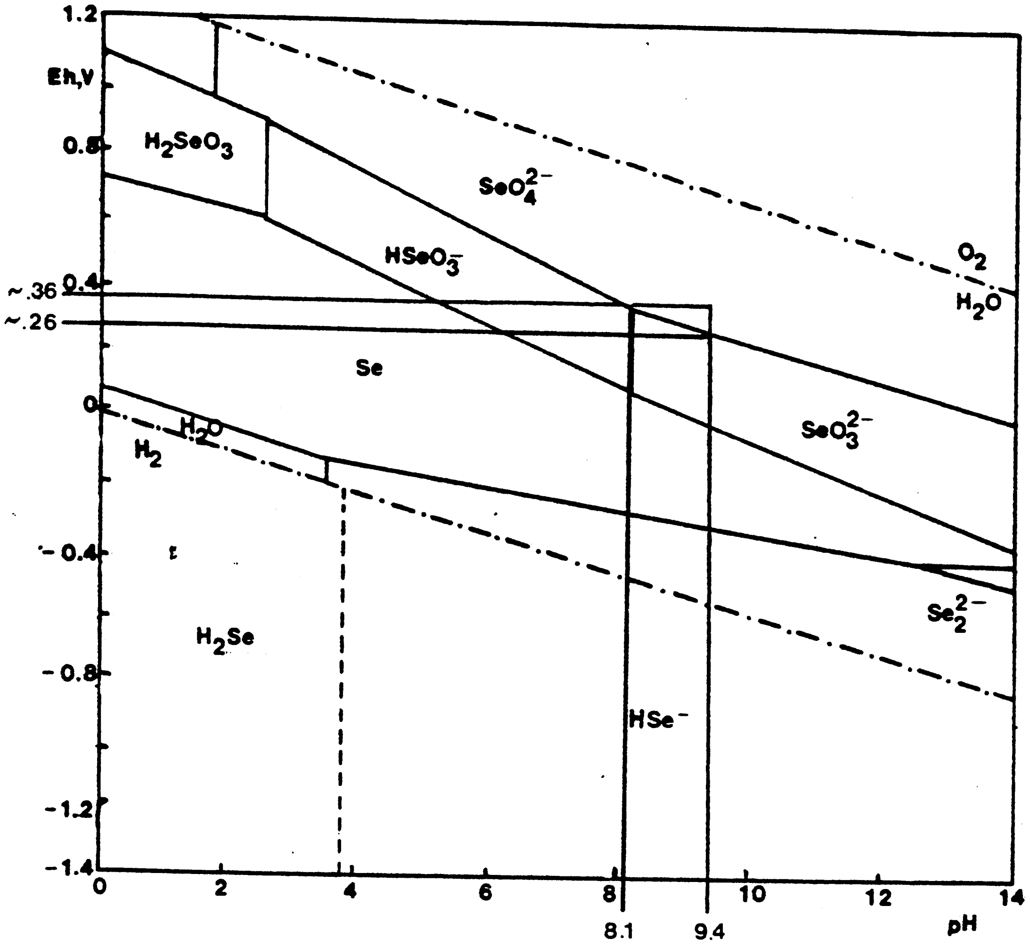


Figure 20. Eh-pH Diagram of Selenium, Indicating Species Present Given the Range of pH Values Found in Wells Containing Elevated Levels of Selenium

demonstrated by the association of selenium with elevated levels of chromium, arsenic, and vanadium in the water (Figure 15). These elements are also normally adsorbed onto aluminum hydroxides, but under high redox potential form soluble complex anions which are highly mobile.

CHAPTER XI

CONCLUSIONS

1) Sediments in the Garber Sandstone and Wellington Formation are composed predominantly of quartz, with dolomite and calcite occurring as secondary minerals in light-colored sandstones and shales. Dolomite also occurs as a primary constituent in pebble conglomerates that are thought to be reworked dolomitic calcretes.

2) The primary accessory minerals found in outcrop samples (as determined by XRD) are kaolinite, illite, albite, hematite, goethite, and barite (in barite rosettes). Gypsum is found only in subsurface well cuttings.

3) Occurrence of most trace elements in the rocks is believed to result from adsorption onto amorphous oxides, clays and calcareous material. However, some heavy metals are probably incorporated into the carbonate lattice.

4) Selenium occurs in the Garber-Wellington rocks as the selenite ion, which is generally immobile due to adsorption onto oxides and hydroxides. Selenium is distributed throughout the rocks, but was found to be concentrated in those sediments containing significant amounts of kaolinite and illite (6-16 ppm Se). Samples containing hematite and geothite were generally low in selenium (1-2 ppm). This indicates that selenium occurrence and accumulation is controlled by the distribution

and percentage of hydrolyzate sediments, and it is found adsorbed to these rather than to the oxidates, iron and manganese oxides.

5) Selenium in rocks of the Garber-Wellington most likely originated as a constituent of volcanic emanations, entering the sediments as a component of atmospheric precipitation. Possible sources include volcanic centers to the northwest, which were active from Permian through Cretaceous time, and volcanic centers to the east (Arkansas Ouachitas), active during Cretaceous time. A second possibility, believed less likely, is that the selenium was deposited directly, due to weathering of sulfide ore bodies in the rocks which were eroded to form Garber and Wellington sediments.

6) Water in the Garber-Wellington is generally either enriched in Ca-Mg-HCO_3 or Na-HCO_3. Intermediate waters are locally high in calcium sulfate or sodium chloride. The occurrence of calcium-magnesium-bicarbonate waters is attributed to dissolution of dolomite. Waters containing significant calcium sulfate are correlated with dissolution of gypsum. Mixing of Garber-Wellington water with brines located at the base of the aquifer is thought to be responsible for locally high sodium chloride concentrations.

7) The origin of the sodium bicarbonate water has not been conclusively determined. The most obvious mechanism causing this composition is sodium exchange with calcium and magnesium ions in the water. A decrease in calcium and magnesium concurrent with increased sodium content supports this hypothesis. However, sodium-bearing montmorillonitic clays were not identified in any of the surface samples collected. Therefore, a change in clay mineralogy in the subsurface must be assumed for cation exchange to be feasible.

A second possibility for the origin of this water is the dissolution of fresh-water, sodium-bearing evaporites. Evidence for this hypothesis follows:

A) Evaporites (gypsum) do occur in deeper Wellington sediments.

B) The presence of dolomitic calcretes indicates a continental source for the carbonates in the formation.

C) If cation exchange is assumed, and accounted for by equilibrating the amount of calcium and magnesium lost to the amount of sodium gained, there is still an excess of sodium in the water.

D) Trace elements associated with the Na-HCO_3 water are found as minor constituents in sodic evaporites in the Green River Formation in Wyoming.

However, to date no writers have even hinted at the occurrence of fresh water evaporites in the Wellington, and the evidence presented here is certainly not conclusive.

8) Results of equilibrium calculations indicate that water in the aquifer is saturated with respect to calcite, dolomite, illite, and kaolinite in several locations in the study area. The system was found to be subsaturated with respect to gypsum. Dedolomitization is occurring in certain parts of the aquifer, driven by dissolution of gypsum. Evidence of this process is given by supersaturation of the waters with respect to calcite and concomitant subsaturation with respect to dolomite.

9) Elevated levels of arsenic, vanadium and chromium in the sodium-bicarbonate rich waters are attributed to alkaline and oxidizing conditions. High pH values resulting from excessive bicarbonate

concentrations effectively lower the Eh necessary for oxidation of these elements to soluble ions.

10) Elevated concentrations of Th, Nb, Li, Mn, Zn, and B observed in calcium-sulfate dominated waters are thought to be caused by dissolution of gypsum.

11) Selenium is being released to the water in the form of the selenate ion, which is soluble and highly mobile. Oxidation of selenite, which is immobile due to adsorption onto clays and amorphous hydroxides, is occurring as a result of high alkaline and oxidizing conditions in the aquifer. Elevated pH values (caused by high bicarbonate concentrations) reduce the Eh needed for this reaction to occur. This mechanism is also responsible for the release of arsenic, chromium, and vanadium into the aquifer.

REFERENCES CITED

Al Shaieb, Z., 1976, Summary of the Stratigraphy, Sedimentology, and Mineralogy of Pennsylvanian and Permian Rocks of Oklahoma in Relation to Uranium Resource Potential: Report for ERDA, Contract # (05-1)-1641.

Anderson, G. E., 1941, Origin of Line of Color Change in Red Bed Deposition: Bulletin of the Geological Society of America, Vol. 52, pp. 211-218.

Aurin, F. L., Officer, H. G. and C. N. Gould, 1926, The Subdivision of the Enid Formation: AAPG Bulletin, Vol. 10, pp. 786-799.

Back, W., Hanshaw, B. B., Plummer, L. N., Rahn, P. H., Rightmire, C. T., and Ribin, M., 1983, Process and Rate of Dedolomitization: Mass Transfer and 14C Dating in a Regional Carbonate Aquifer: Geological Society of America Bulletin, Vol. 94, pp. 1415-1429.

Bagnall, K. W., 1966, *The Chemistry of Selenium, Tellurium and Polonium*: Elsevier, New York.

Bale, H. E., 1928, Logan County, in Oil and Gas in Oklahoma: Oklahoma Geological Survey Bulletin #40-GG.

Beath, O. A., 1937, The Occurrence of Selenium and Seleniferous Vegetation in Wyoming: U. of Wyoming Agu.-Sept. Sta. Bull. #221, Part 2, pp. 35-64.

Bingham, R. H. and Moore, R. L., 1975, Reconnaissance of the Water Resources of the Oklahoma City Quadrangle, Central Oklahoma: OKGS Hydrologic Atlas #4, 4 sheets, scale 1:250,000.

Bloch, S., Gay, C. D., and Dunbar, D. E., 1981, Uranium, Chromium, and Selenium Concentrations in Water From Garber-Wellington Aquifer (Permian), Central Oklahoma: Oklahoma Geological Survey Notes, Vol. 4, No. 3, June 1981.

Bloch, S., 1979, Application of WATEQF Computer Model (Runnells Version) to Interpretation of Hydrogeochemical Data from Clinton Quadrangle, West Central Oklahoma: Oklahoma Geol. Survey Notes.

Bradley, W. H. and Eugster, 1969, Geochemistry and Paleolimnology of the Trona Deposits and Associated Authigenic Minerals of the Green River Formation of Wyoming: U.S. Geological Survey Professional Paper 496-B, 71 pp.

Bricker, O. P. and Garrels, R. M., 1967, *Mineralogic Factors in Natural Water Equilibria in Chemical Hydrogeology*: W. Back and R. A. Freeze, Eds., Hutchinson Ross Publishing Co., Pennsylvania, 1983.

Brunfelt, A. O. E., and E. Steinnes, 1967, Determination of Selenium in Standard Rocks by Neutron Activation Analysis: Geochim. Cosmochim. Acta, Vol. 31, pp. 283-287.

Byers, H. G., 1935, Selenium Occurrence in Certain Soils of the United States With a Discussion of Related Topics: U.S. Dept. Agr. Tech. Bull. No. 482, pp. 1-47.

Byers, H. G., Williams, K. T., and Lakin, H. W., 1936, Selenium in Hawaii and its Probable Source in the United States: Ind. Eng. Chem. Vol. 28 pp. 281-283.

Byers, H. G., Miller, J. T., Williams, K. T., and Lakin, H. W., 1938, Selenium Occurrence in Certain Soils in the United States with a Discussion of Related Topics: Third Report: USDA Technical Bulletin #601, pp. 11-31.

Cannon, H. L., 1964, Geochemistry of Rocks and Related Soils and Vegetation in the Yellow Cat Area Grand County, Utah: U.S. Geological Survey Bulletin 1176, 54 pp.

Carr, J. E. and Havens, J. S., 1976, Records of Wells and Water Quality for the Garber-Wellington Aquifer, Northern Oklahoma and Southern Logan Counties: OKGS open file report 76-619, 32 pp.

Carr, J. E. and Marcher, M. V., 1977, A Preliminary Appraisal of the Garber-Wellington Aquifer in Southern Logan and Northern Oklahoma Counties, Oklahoma: USGS open file report 77-278, 23 pp.

Cox, R. and Al-Shaieb, Z., 1980, Stratabound Copper in Lower Permian Red Beds North Central Oklahoma: Oklahoma Geology Notes, Vol. 40, No. 5, pp. 191-192.

Culver, J. R. and Gray, F., 1966, A Pedological Study in the Wellington Formation: Proc. of the Okla. Acad. of Sci. for 1966, pp. 163-169.

Dall'Aglio, M., Ghiara, E., and Proietti, W., 1978, New Data on the Hydrogeochemistry of Selenium: "Rendiconti: -Societa Italiana di Mineralogia e Petrologia, Vol. 34, No. 2, pp. 591-604.

Davidson, D. F. and Powers, H. A., 1959, Selenium Content of Some Volcanic Rocks From Western United States and Hawaiian Islands: U.S. Geol. Survey Bull #1084-C, pp. 69-81.

Dott, R. H., 1954, Regional Stratigraphy of the Mid-Continent: AAPG Bulletin, Vol. 25, No. 9, pp. 1619-1685.

Drever, J. I., 1982, *The Geochemistry of Natural Waters*: Prentice-Hall, Inc., Englewood Cliffs, NJ.

Dyachkova, J. B. and Khodakovskiy, J. L., 1968, Thermodynamic Equilibria in the Systems S-H_2O, Se-H_2O and Te-H_2O in the 25°-300° Temperature Range and Their Geochemical Interpretations: Geokhimiya, Vol. 5, p. 1108.

Faust, S. D. and Aly, M. A., 1981, Chemistry of Natural Waters: Ann Arbor Science Publishers, Inc., Michigan.

Fenneman, N. M., 1922, Physiographic Provinces and Sections in Western Oklahoma and Adjacent Parts of Texas: U.S. Geological Survey Bulletin 730, pp. 115-139.

Fischer, R. and Zemann, J., 1969, Selenium: Chapter 34A, in Handbook of Geochemistry, K. W. Wedepohl, ed.: Springer-Verlag, Berlin.

Francis, E. H., Forsyth, I. H., Read, W. A., and Armstrong, M., 1970, The Geology of the Stirling District: Natural Environment Research Council - Institute of Geological Sciences, Her Majesty's Stationery Office, Edinourgh.

Gould, C. N., 1905, Geology and Water Resources of Oklahoma: U.S. Geological Survey Water Supply Paper #148, 178 pp.

Green, D. A., 1937, Major Division of Permian in Oklahoma and Southern Kansas: AAPG Bulletin, Vol. 21, No. 12, pp. 1515-1533.

Ham, W. E. and Merritt, C. A., 1944, Barite in Oklahoma: Oklahoma Geological Survey Circular #23.

Havens, J. S., 1977, Reconnaissance of the Water Resources of the Lawton Quadrangel, Southwestern Oklahoma: Oklahoma Geological Survey Hydrologic Atlas 6.

Howard, J. H., III, 1977, Geochemistry of Selenium: Formation of Ferroselite and Selenium Behavior in the icinity of Oxidizing Sulfide and Uranium Deposits: Geochim et Cosmochim Acta, Vol. 41, pp. 1665-1678.

Jacobsen, C. L., and Reed, E. W., 1949, Ground Water Supplies in the Oklahoma City Area, Oklahoma: Oklahoma Geological Survey Mineral Report #20.

Jordan, L., 1961, Salt in the Wellington Formation, Grant County, Oklahoma: Oklahoma Geology Notes, Vol. 21, No. 10, pp. 272-274.

Joreskog, K. G., Klovan, J. E., and Reyment, R. A., 1976, Geological Factor Analysis: Elsevier Scientific Publishing Company, Amsterdam.

Krauskopf, K. B., 1967, Introduction to Geochemistry: McGraw-Hill, Inc., New York, 719 pp.

Lakin, H. W. and Byers, H. G., 1941, Selenium Occurrence in Certain Soils in the United States, with a Discussion of Related Topics: Sixth Report, U.S. Dept. Agric. Tech. Bull. for 1941, p. 783.

Leutwein, F., 1969, Selenium: Chapter 34B-0, in *Handbook of Geochemistry*, K.H. Wedepohl, ed.: Springer-Verlag, Berlin.

Luttrell, G. W., 1959, Annotated Bibliography on the Geology of Selenium: U.S. Geological Survey Bulletin 1019-M.

MacLachlan, M. E., 1967, Paleotectonic Investigations of the Permian System in the United States. Chapter E -Oklahoma: U.S. Geological Survey Professional Paper 515-E.

Merritt, C. A. and Minton, J. W., 1930, The Dolomites of the Stillwater, Wellington, Garber, Hennessey and Duncan Formations: Okla. Acad. Sci., Vol. 10, pp. 69-72.

Miser, H. D. and Ross, S. C., 1925, Volcanic Rocks in the Upper Cretaceous of Southwestern Arkansas and Southeastern Oklahoma: American Jour. Sci., Vol. IX.

Moxon, A. L., Olson, O. E., and Searight, W. V., 1939, Selenium in Rocks, Soils and Plants: South Dakota Agricultural Expt. Sta. Technical Bull. #2.

Mroz, E. J. and Zoller, W. H., 1975, Composition of Atmospheric Particulate Matter from the Eruption of Heimacy, Iceland: Science, Vol. 190, pp. 461-463.

Oklahoma Water Resources Board (OWRB), 1980, Oklahoma Comprehensive Water Plan: Oklahoma Water Resources Board Publication #94.

Olson, E. C., 1967, Early Permian Vertebrates of Oklahoma: Oklahoma Geological Survey Circular #74, 111 pp.

Patterson, J. M., 1933, Permian of Logan and Lincoln Counties, Oklahoma: AAPG Bulletin, Vol. 17, No. 3, pp. 241-253.

Pettyjohn, W. A. and Miller, A., 1982, Preliminary Estimate of Effective Ground Water Recharge Rates in Central Oklahoma: Report presented to OWRB, November 1982.

Piper, A. M., 1944, A Graphic Procedure in the Geochemical Interpretation of Water Analyses: Am. Geophys. Union Trans. 25:914-923.

Plummer, L. N., Jones, B. F., and Truesdell, A. H., 1976, WATEQF - A FORTRAN IV Version of WATEQ, a Computer Program for Calculating Chemical Equilibrium of Natural Waters: U.S. Geol. Surv. Water Resources Investigations 76-113, 66 pp.

Raasch, G. O., 1946, The Wellington Formation in Oklahoma: Unpublished Ph.D. Dissertation, University of Wisconsin.

Rankama, K. and Sahama, T. G., 1950, *Geochemistry*: The University of Chicago Press, Chicago.

Rapp, G., 1972, Selenium: Element and Geochemistry, in The Encyclopedia of Geochemistry and Environmental Sciences, Rhodes W. Fairbridge, ed.: Van Nostrand Rheinhold Co., New York.

Rascoe, B., 1962, Regional Stratigraphic Analysis of Pennsylvanian and Permian Rocks in the West Midcontinent: Colorado, Kansas, Oklahoma, Texas: AAPG Bull., Vol. 46, pp. 1345-1370.

Renfro, A. R., 1974, Genesis of Evaporite Associated Stratiform Metalliferous Deposits -a Sabkha Process: Economic Geology, Vol. 69, pp. 33-45.

Rose, A. W., 1976, The Effect of Cuprous Chloride Complexes in the Origin of Red-Bed Copper and Related Deposits: Economic Geology, Vol. 71, pp. 1036-1048.

Rosenfeld, I. and Beath, O. A., 1964, Selenium, Geobotany, Biochemistry, Toxicity and Nutrition: Academic Press, Inc., New York.

Scull, B. J., 1959, The Age of Mineralization in the Ouachita Mountains of Arkansas and Oklahoma: in Geology of the Ouachita Mountains, A Symposium; L. M. Cline, W. J. Hilseweck, and D. E. Feray, Eds. Dallas Geological Society, Ardmore Geological Society.

Shamberger, R. J., 1981, Selenium in the Environment: The Science of the Total Environment, Vol. 17, pp. 59-74.

Shelton, J. W., 1979, Geology and Mineral Resources of Noble County, Oklahoma: Oklahoma Geological Survey Bulletin 128.

Shockey, P. N., Renfro, A. R., and Peterson, J. R., 1974, Copper-Silver Solution Fronts at Paoli, Oklahoma: Econ. Geol., Vol. 69, No. 2, pp. 266-268.

Simpson, L. C., 1979, Upper Gearyan and Lower Leonardian Terrestrial Vertebrate Faunas of Oklahoma: Oklahoma Geology Notes, Vol. 39, No. 1, pp. 3-19.

Sindeeva, N. D., 1964, Mineralogy and Types of Deposits of Selenium and Tellurium: Interscience Publishers, New York.

Snider, L. C., 1917, Geography of Oklahoma: OKGS Bulletin 27.

Soil Conservation Service (SCS), 1954, Soil Survey of Cleveland County, Oklahoma: U.S. Government Printing Office.

Soil Conservation Service, 1960, Soil Survey of Logan County, Oklahoma: U.S. Government Printing Office.

Soil Conservation Service, 1969, Soil Survey of Oklahoma County, Oklahoma: U.S. Government Printing Office.

Soil Conservation Service, 1970, Soil Survey of Lincoln County, Oklahoma: U.S. Government Printing Office.

Stach, R. L., 1978, Selenium in South Dakota Surface and Ground Water: South Dakota Water Resources Institute and South Dakota Geological Survey Completion Report, 68 pp.

Statistical Analysis System, 1982, SAS User's Guide--Basics: SAS Institute Inc., Cary, North Carolina.

Statistical Analysis System, 1982, SAS User's Guide--Statistics: SAS Institute, Inc., Cary, North Carolina.

Suzuoki, Tetsuro, 1964, A Geochemical Study of Selenium in Volcanic Exhalations and Sulfur Deposits: Bull. Chem. Soc. Japan, Vol. 37, No. 8, pp. 1200-1206.

Tasch, P., 1964, Periodicity in the Wellington Formation of Kansas and Oklahoma: Kansas Geological Survey Bulletin 169, Vol. 2, pp. 481-496.

Travis, A., 1930, Oklahoma County, in Oil and Gas in Oklahoma: OKGS Bull. 40-55, 32 pp.

Trelease, S. F. and Beath, O. A., 1949, "Selenium": New York, Published by the Authors, 292 pp.

Truesdell, A. H. and Jones, B. F., 1974, WATEQ, A Computer Program for Calculating Chemical Equilibria of Natural Waters: U.S. Geol. Survey Jour. Research, Vol. 2, pp. 233-248.

Tucker, M. E., 1981, Sedimentary Petrology, An Introduction: John Wiley & Sons, Toronto.

U.S. Department of Energy, 1978, Hydrogeochemical and Stream Sediment Reconnaissance Basic Data for Oklahoma City NTMS Quadrangel, Oklahoma: U.S. Department of Energy Report, prepared by Union Carbide Corp. for DOE National Uranium Resource Evaluation Program.

Vinogradov, A. P., 1959, The Geochemistry of Rare and Dispersed Elements in 'Soil', 2nd Ed. (Translated from Russion): Consultants Bureau, Inc. New York.

Wells, N., 1965, Selenium Content of Soil-Forming Rocks: New Zealand J. Geol. Geophys., Vol. 10, pp. 198-208.

White, D. E. and Waring, G. A., 1963, Data of Geochemistry, 6th Ed., Chapter K: USGS Prof. Paper 440-K.

Wickersham, G., 1979, Ground Water Resources in the Southern Part of the Garber-Wellington Ground Water Basin -Cleveland and Southern Oklahoma Counties and Parts of Pottawatomie County, Oklahoma: OWRB Hydrologic Investigation Pub. #86.

Williams, K. T., Lakin, H. W., and Byers, H. G., 1940, Selenium Occurrence in Certain Soils in the United States With a Discussion of Related Topics: 4th Report: U.S. Dept. Agr. Tech. Bull. #702, pp. 1-59.

Wood, P. R. and Burton, L. C., 1968, Ground Water Resources in Cleveland and Oklahoma Counties, Oklahoma: Oklahoma Geological Survey Circular 71, 67 pp.

Zies, E. C., 1929, Natl. Geog. Soc. Contrib. Papers, Katomai Ser., 1, #4, p. 79.

APPENDIXES

APPENDIX A

RAW-WATER QUALITY DATA - MAJOR CONSTITUENTS (DATA SET #1)

```
                                                        SAS                       13:54 SATURDAY, FEBRUARY 9, 1985   1

 OBS   ID    PH     TDS   COND      CA      MG      NA     K      CL     SO4  HCO3   SIO2  CO3  DEPTH       NO3

   1    1   8.0     280    440     4.5     2.9   102.0   2.0    10.0    13.0   270   12.0    0    750         .
   2    2   8.9     640   1030     3.8     2.7   247.0   2.2    50.0    65.0   445    8.5   32    816    1.3000
   3    3   8.7    1077   1830     3.8     1.2   413.0   4.4   296.0    93.0   436   12.0   35    810    0.9000
   4    4   7.8     738   1130    39.0    12.0   204.0   3.0    46.0   260.0   319   14.0    0    608    2.0000
   5    5   7.5     330    612    58.0    34.0    11.0   4.4     1.0     4.9   387   14.0    0    140    0.5000
   6    6   7.4     338    581    64.0    37.0    11.0   0.8    12.0    12.0   352   15.0    0    100   12.0000
   7    7   7.2     550    972    88.0    41.0    40.0   3.6    69.0    47.0   319   21.0    0    172   83.0000
   8    8   6.8     337    286    30.0    15.0     5.8   1.3    11.0    19.0   130   13.0    0     90    6.0000
   9    9   8.5     810   1350     3.5     1.6   311.0   2.2   166.0    85.0   411   12.0   23    741    1.5000
  10   10   8.2     699   1220    20.0     7.9   243.0   2.4   150.0    68.0   409   15.0    0    400    3.5000
  11   11   7.2     405    738    76.0    44.0    14.0   2.4    15.0    11.0   458   20.0    0    116    1.3000
  12   12   7.5     355    611    58.0    36.0    28.0   1.6    14.0     8.7   376   16.0    0    100    8.3000
  13   13   7.1     129    207    35.0     0.1     5.0   1.7     4.5     7.6   109   18.0    0     63    1.6000
  14   14   7.2     357    624    73.0    39.0     9.7   2.0    14.0     5.9   392   12.0    0     76    7.9000
  15   15   7.5     679   1190   100.0    58.0    58.0   2.4   104.0    58.0   430   16.0    0     69   62.0000
  16   16   7.9       .   1510    10.0     4.0   368.0   3.0    45.0   357.0   410   53.0   30    567    1.3000
  17   17   8.0     539    848     3.9     1.4   197.0   1.8    21.0   106.0   318   10.0   30    461    0.2000
  18   18   6.5     109    190    17.0     9.4     7.6   0.9     8.5     5.6    94   15.0    0    100    1.9000
  19   19   8.9     411    662     2.0     0.0   161.0   0.6     5.0    39.0   322   12.0   27    650    0.6000
  20   20   8.6     666   1060     2.0     0.8   244.0   1.4    14.0   175.0   342    9.6   43    591    1.0000
  21   21   8.4     363    584     2.0     1.5   146.0   1.0     7.2    17.0   340   10.0    9    679    1.4000
  22   22   8.7     326    524     5.0     3.4   122.0   1.0     5.8    14.0   308    9.0   10    635    1.2000
  23   23   7.1     200    349    29.0     8.1    20.0   9.1    21.0    31.0    88   10.0    0    100   28.0000
  24   24   7.5     370    672    72.0    45.0    12.0   2.4    11.0    16.0   425   14.0    0     72    1.2000
  25   25   7.6     296    540    44.0    36.0    22.0   2.0     8.0     4.9   359   18.0    0    501    0.8000
  26   26   8.5     387    621     2.7     1.4   155.0   1.1    10.0    15.0   354    9.4   13    704    2.2000
  27   27   6.7      96    138    12.0     1.5    17.0   1.0     7.5    11.0    63   10.0    0    132    0.6000
  28   28   7.1     359    616    48.0    20.0    35.0   1.1   114.0    63.0    80   11.0    0    100    0.1000
  29   29   7.4     166    297    38.0    14.0     4.5   1.0     7.5     5.7   175   12.0    0    121    0.8000
  30   30   7.8     240    424    48.0    22.0    11.0   0.8     6.0     7.4   268   20.0    0    325    1.1000
  31   31   7.8     192    362    35.0    18.0    15.0   1.6     7.5     6.7   224   11.0    0    793    0.7000
  32   32   7.6     222    407    45.0    24.0     7.1   1.6    10.0     6.6   246   10.0    0    800    2.0000
  33   33   7.8     210    384    42.0    21.0     9.1   1.4     7.8     6.7   237   10.0    0    800    0.4000
  34   34   7.5     220    416    48.0    22.0    10.0   1.4     8.5     8.1   254   12.0    0    938    0.7000
  35   35   7.6     228    420    49.0    22.0     8.9   1.5     8.2     7.4   261   12.0    0    884    0.5000
  36   36   7.5     224    422    49.0    23.0     9.7   1.8     8.5     6.3   262   12.0    0    837    0.8000
  37   37   7.6     218    398    46.0    21.0     8.2   1.5     9.0     6.1   247   12.0    0    665    0.7000
  38   38   7.6     231    418    45.0    21.0    15.0   1.4    11.0     7.7   256   12.0    0    829    0.7000
  39   39   7.6     205    394    44.0    22.0     7.2   1.8    12.0     6.3   233   11.0    0    780    1.5000
  40   40   7.8     220    399    42.0    24.0     8.7   2.2    12.0     6.4   238   11.0    0    740    1.8000
  41   41   8.2    1020   1790    14.0     7.0   377.0   3.0   325.0    84.0   387   10.0    0    920    2.2000
  42   42   7.8     193    364    32.0    21.0    15.0   2.2    12.0     7.2   214   12.0    0    755    2.4000
  43   43   8.2     195    336     9.6     7.3    58.0   1.6     5.8     6.8   204   10.0    0    792    1.4000
  44   44   7.6     225    414    48.0    22.0     8.4   1.5     7.8     6.3   256   12.0    0    669    0.7000
  45   45   7.6     225    415    50.0    22.0     7.6   1.3     9.2     6.8   258   12.0    0   1030    0.4000
  46   46   7.6     230    411    49.0    22.0     7.0   1.4     9.0     6.8   255   11.0    0   1070    0.7000
  47   47   7.6     225    404    48.0    22.0     6.2   1.4     9.5     6.5   250   11.0    0    800    1.3000
  48   48   7.6     232    504    50.0    22.0     8.7   1.7     9.0     7.1   259   11.0    0    790    0.5000
  49   49   7.7     226    422    49.0    23.0     9.4   1.3     8.5     6.6   265   12.0    0    770    0.8000
  50   50   7.6     233    438    52.0    23.0     9.6   1.4     7.8     7.4   273   12.0    0    764    0.7000
  51   51   7.5     235    433    49.0    23.0    10.0   1.5     8.5     8.0   271   12.0    0    664    0.8000
  52   52   6.4     211    364    29.0     7.7    32.0   2.2    30.0    30.0    99   14.0    0     62   18.0000
  53   53   6.1     284    469    35.0    19.0    26.0   1.1    48.0    34.0    85   22.0    0     72   55.0000
  54   54   6.8     246    435    49.0    24.0     8.9   1.0    24.0    13.0   224   14.0    0     76    1.7000

  55   55   7.3     564    896   112        31       41    1.4    37        84    388   21      0      .         .
  56   56   7.4     953   1600   120        58      139    2.0   260       189    346   14      0    240  0.100000
```

APPENDIX B

RAW-WATER QUALITY DATA - TRACE ELEMENTS (DATA SET #2)

```
                                                   SAS                                16:38 THURSDAY, MAY 2, 1985  1

OBS   FM     ID     DEP    PRDEP      DO    ALK    PH     CON          U    SO4         AS     SE     AL       B

  1   G    2712      89       89     2.3    384   7.1     740      1.510      9     8.8000    0.2     11     136
  2   G    2715     794      794     6.5    198   6.8     490      1.060      8          .    0.2      .      62
  3   G    2719     108       92     4.0    294   7.3    1050          .     17     0.7000    0.3      .      61
  4   G    2720      52       49     8.0    450   7.5    1600          .    120     1.4000    3.0      .      54
  5   G    2721     131      128     6.7    314   7.3     790      0.550     12     1.1000    0.2      .      44
  6   G    2722     114      108     5.5    292   7.1    1030      0.820      7     1.5000    0.3      .      46
  7   G    2727     400      360     6.0    191   7.5     840      0.760      .     1.0000    0.3      .      50
  8   G    2730     125      125     6.8    255   5.8     900     32.400     79     1.0000    0.3      .    1553
  9   G    2731     377      377     3.2    110   5.8     437     82.800   1260     0.5000    7.7     35    5161
 10   G    2732     125      125     2.4    234   6.7    2290     17.200   1085     1.2000    0.3     14    2000
 11   G    2733      92       29     7.0    263   7.4     690      1.870     44     2.1000    0.2      .     150
 12   G    2735       .        .     8.3    220   7.7     590      1.290     18     1.2000    0.3      .      86
 13   G    2737      49       49     7.6    200   7.7     710      0.200     23     0.9000    0.3      .      28
 14   G    2738     134       65     8.3    250   7.7     790      0.650     18     0.6000    0.3      .      32
 15   G    2740     164      164     7.1    265   8.0     870     12.200     80     8.4000    0.3    225    3394
 16   G    2768     630      630     7.5    434   7.0    1210      3.110     21     1.1000    0.2      .      92
 17   G    2776     118       91    12.0    390   6.9    1270      3.390      .          .    0.2     15     156
 18   G    2791     167      141     8.1    238   6.3     540      5.620     12     1.8000    0.2      .     234
 19   G    2793     430       39     8.0    240   7.5     950      1.010     17     0.7000    0.3      .      39
 20   G    2806     320      403     4.8    465   8.6    1410    146.000     78    27.0000    0.4      .    2428
 21   G    2807     197      197     4.0    324   7.8     760     53.900     19    21.0000    0.6      .    1084
 22   G    2808     656      656     8.1    194   6.4     650      0.600      7     0.5000    0.3     35      36
 23   G    2810     197       89     9.3    225   7.3     690          .      7     0.6000    5.0     13      79
 24   G    2831     551      551     2.5    316   6.7    1150     30.100     30     8.8000    0.8      .    1959
 25   G    2854     220      220     7.8    250   7.5     890      0.400     22     1.2000    0.3      .      71

OBS    BA       CA     CR     CU    CL      MG    MN    MO      NA    NB    TH     V    Y     ZN          K     SR    SI

  1   171     55.2      .      .    22    31.8     .     .    40.6     5    15     .    1     21          .      .     .
  2   390     42.2      8      .    14    23.2     .     .     9.0     .    10     9    1     18          .      .     .
  3    63     62.7      .      .    14    26.2     .    11    48.3     .     .     .    .    109          .      .     .
  4    28     95.0      .      2    11    91.8     .    11    84.8     .     .     .    1     32          .      .     .
  5   392     71.6      .      .     8    39.1     .     .    19.2     .     .     .    1      .          .      .     .
  6   662     74.5      .      .     6    40.6     3     .    14.4     .     .     .    1     29          .      .     .
  7   304     45.0      .      .    10    22.3     .     .    13.9     .     .     .    .      9          .      .     .
  8     7     75.3      5      3    20    40.1     2     9    69.9     .    16    13    1    142          .      .     .
  9     .    476.0     14      4    56   175.0     6    20   284.0    24     .    24    6      .          .      .     .
 10     6    319.0      .      .    42    75.1     2    12   152.0    12     .    21    3      6          .      .     .
 11    56     63.3      .      .     6    31.4     .     .    29.7     9     .     9    1      5          .      .     .
 12    45     58.1      .      3     6    18.8     2     .    42.9     .    16    11    1     87          .      .     .
 13    91     72.4      .      2     5    37.0     2     .    14.0     .     .     .    1      .          .      .     .
 14   330     76.6      .      .     7    36.3     .     .    21.4     9     .     .    1      8          .      .     .
 15    67     10.5      .      .    12     8.4     .    20   196.0     .     .    27    .      .          .      .     .
 16   259     28.6      .      .    10    54.4     .    13    51.5     .     .     6    .      .          .      .     .
 17   488     67.1      .      .     9    45.1     2     7    23.6     4     .     .    .     41          .      .     .
 18   238     36.5      6      2     7    18.2     .     5    38.1     .     .    20    1      .          .      .     .
 19   524     72.3      .      4     7    36.4     3     .    16.6     4    14     .    1    540          .      .     .
 20    40      4.0    116      2    12     1.5     .    94   362.0     .     .   376    .     17          .      .     .
 21   140     25.6     51      5     8    13.0     2     6   133.0     .     .   250    .     33          .      .     .
 22   437     47.1      .      8     8    18.4     .     .    10.0    11     .    12    .      6          .      .     .
 23   522     38.7      .      .     7    27.6     .     .    10.0     8     .     6    1    149          .      .     .
 24    16      5.1     41      .    17     1.3     2     5   326.0     .     .   181    .     60          .      .     .
 25   215     39.4      .      3     9    32.0     2     .    54.6     7    14     .    2    152          .      .     .
```

```
                                                     SAS                                  16:38 THURSDAY, MAY 2, 1985   2

OBS  FM   ID   DEP  PRDEP    DO   ALK   PH    CON        U   SO4       AS   SE   AL       B   BA

 26  G   2857  125    86    5.5   243  6.7    840    1.300    14  0.80000  0.2    .    65.0  498
 27  G   2858  128    98    6.0   224  7.1   1970    3.900   508  1.90000  0.2    .   287.0   54
 28  G   2860   85    85    7.0   241  7.1   2030   15.600   771  0.70000  0.5    .   919.0   19
 29  G   2861  200   200    2.3   239  7.3    750    1.000    18  1.20000  0.3   25    63.0  495
 30  G   2862  328   328    4.7   170  7.2    760    0.900    10  0.90000  0.2    .    49.0  513
 31  G   2863  164   164    2.5   101  7.5   3990   33.600  1364  0.50000  2.1   15  6946.0   30
 32  G   2865   36    36    7.5   285  7.8   1210    2.900    15  4.80000  0.2   23   144.0  284
 33  G   2866   66    66    7.3   374  7.6   1380    1.700    59        .  0.3    .   303.0  143
 34  G   2925  105   105   10.0   164  7.0    830    0.300     .  2.20000  0.3    .    33.0  706
 35  G   2946  230   230    9.4   308  7.9   1370  177.000    96  2.00000  0.3   25  3234.0   75
 36  G   2949   39    13    8.1    95  7.1    750        .    15        .  0.2    .    46.0  144
 37  G   2950  230   230    8.5   267  7.4    820    1.100     .  1.50000  0.4    .    94.0  342
 38  G   2951   43    20    9.1   240  7.7    830    1.100     7  0.50000  0.5   10    70.0  560
 39  G   2953  216    86    8.5   305  7.5    950    3.700    63  5.30000  0.4    .   200.0   49
 40  G   2954   89    23    8.4   164  7.8    830    0.300     6  0.70000  0.4    .    54.0  520
 41  G   2955   33    23    8.5   590  7.0   1960   12.900    15  0.60000  0.5    .   115.0  296
 42  G   2958  184   184    6.0   199  6.4    890    0.900    11        .  0.2    .    63.0  409
 43  G   2959   20    16    4.4   335  6.8    900    6.300     5        .  0.2   13   117.0  556
 44  W   2967   56    56    8.9   313  6.9    470    4.100    10  0.70000  0.2   10   148.0  286
 45  W   2986  112   112   11.0   205  7.7    543    2.600     7  0.50000  0.3    .   273.0   32
 46  G   3016  249   249    6.9   245  6.5   6300    9.600    12  1.20000  0.2    .   193.0  205
 47  G   3017  197    98    5.5   205  6.8   1560   16.400   568  2.50000  0.4    .   804.0  103
 48  G   3022  200   200    6.7   281  7.2    780   14.900    34  0.50000  0.6   12   495.0   65
 49  W   3023  220   220    4.2   446  6.4    760    8.400     7        .  0.3   11   259.0  459
 50  W   3025   89    23    8.7   322  6.9    650   14.100    24        .  0.2    .   190.0  274

OBS     CA  CR   CU   LI     MG   MN   MO     NA  NB   TH    V   Y    ZN        K    SR        SI

 26   36.3   .    2    3   21.9    3    .   27.5   .   25    5   2   208        .     .         .
 27  258.0   .    .   42   51.0    2    .   80.3  13   35   38   4    53        .     .         .
 28  267.0   .    .   29   60.8    3    .   99.6  12   22    5   4    45        .     .         .
 29   74.7   .   23    5   22.6    2    .   24.3   4   15    6   1    30        .     .         .
 30   79.1   .    7    5   24.3    3   12   23.7   .    .    .   .     7        .     .         .
 31  379.0   8  133   43  113.0   86   26  404.0  32   47   18   6   395        .     .         .
 32   65.3   .    5    6   55.7    3    .   54.7   8    .   19   1   105        .     .         .
 33   99.6   .    4   22   34.8    2    .  141.0   .   17    4   1    36        .     .         .
 34   32.0   .    2    6   23.7    3    .    8.3   .    .    .   1    51        .     .         .
 35   32.2   .    2   14   11.7    .   14  299.0   .    .   24   .   411        .     .         .
 36   32.3   .    7    6   10.5    .    .   17.6   5   11    .   1    77        .     .         .
 37   63.5   .    6    7   21.0    .    .   29.1  14   14   10   1   245        .     .         .
 38   80.8   .    3    5   20.7    .    .   18.0   4   17    5   2    96        .     .         .
 39   59.1   .    .   23   31.8    .   15   50.0   .    .   15   .   195        .     .         .
 40   53.7   .    .    3   12.2    .    .    8.3   .    .    4   1    59        .     .         .
 41   78.2   .    6   40   60.4    3    .  230.0  13   13   14   1    27        .     .         .
 42  103.0   .    2    5   32.9   32    .   23.4   7   29    .   2  1027        .     .         .
 43  104.0   .    4   12   36.7  185    .   35.0   .   26    .   2   566        .     .         .
 44   57.3   .    .   13   34.3    .    .   32.0   .    .   11   .   155  1.40000   589   6.00000
 45   11.4   5    .   20    5.5    .    9  102.0   .    .   18   .    33        .     .         .
 46   55.0   .    7   14   30.9    .    8   61.0   .    .    8   .    20        .     .         .
 47  225.0   4    .   15   51.2    2    .   67.1  19   37   51   4     .        .     .         .
 48   62.6   .    7   11   52.3    6    .   74.7  11   11   15   1    91        .     .         .
 49   44.9   .    3    7   54.7    2    .   24.5   6   13   12   1    16        .     .         .
 50   63.7   .    4   13   37.8    2    .   37.4   .   17    .   1   772        .     .         .
```

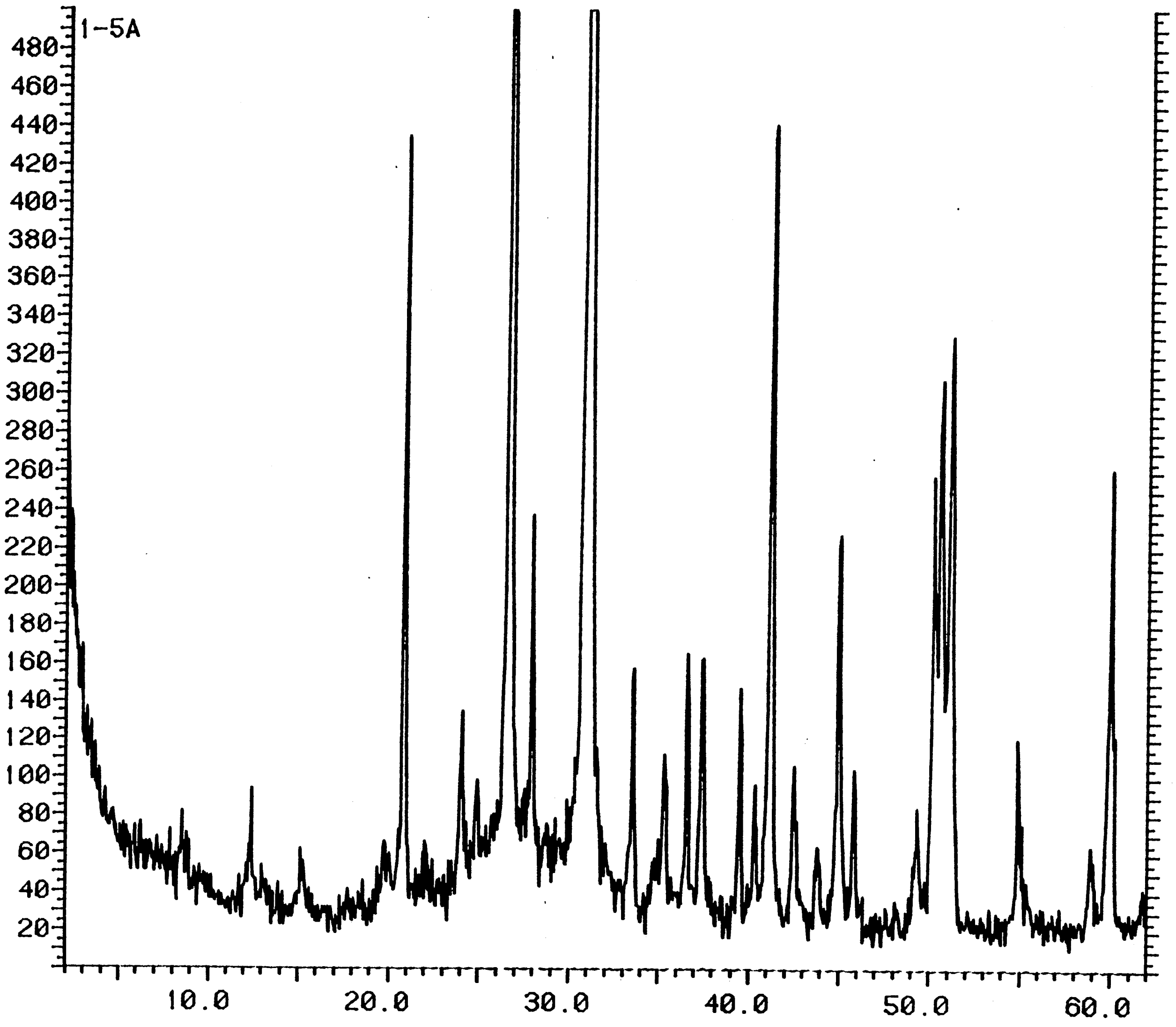
```
                                                   SAS                                  16:38 THURSDAY, MAY 2, 1985   3
OBS  FM   ID    DEP   PPDEF    DO   ALK   PH     CON          U   SO4        AS    SE   AL        B    BA

 51  W   3026   148     56   13.0   505   7.7    880     8.5000    12   2.00000   0.4    .   1261.0   271
 52  W   3027     .     15    8.0   255   7.5    460     2.5000    12   0.90000   0.3   19    133.0   507
 53  W   3032   207     66    7.0   330   6.2    640    23.1000     7         .   0.3   13    377.0   370
 54  W   3075   197    197    8.2   770   7.6   1780    12.3000   223         .   0.7   10   1699.0    25
 55  W   3078   164     66    9.1   227   7.7    940     1.2000     .         .   0.2    .    139.0   148
 56  W   3091    56     33    2.2   409   7.1    120    11.7000    76         .   0.3    .    165.0   136
 57  G   3103   220    151    6.0   278   6.7    470     0.6000     9         .   0.5   10     39.0   332
 58  G   3105   565      .    3.6   314   8.3    450    48.8000    24   4.90000   0.5    .   1751.0    71
 59  W   3127    92     85    7.3   278   8.3    490    11.7000    10   0.60000   0.3    .    670.0   132
 60  W   3128   184    151    9.6   360   7.2    490     6.0000    29         .   0.9    .     33.3   526
 61  W   3129   190    141    6.4   428   7.3    710     1.9000     .   0.80000   0.2    .    133.0   787
 62  W   3130    56      .    3.3   150   6.5    350          .     .         .   0.3    .    115.0   810
 63  W   3131    89     82   10.0    48   7.2    300          .    29         .   0.2    .     27.0    86
 64  G   3132    98     82    9.0   150   5.3    640          .     .         .   0.2    .     38.0   618
 65  W   3135   197    108    8.2   290   7.1   1250    97.6000    34   1.70000   0.5    .   1255.0   101
 66  G   3157   109    103    7.4   280   7.2    410     0.7000     9         .   0.2    .    109.0   597
 67  G   3156    56     56    7.8   260   7.0    350          .     9         .   0.3    .     67.0   381
 68  G   3159   102    102    9.3   310   7.1    470     2.1000    13   1.00000   0.5    .    111.0   228
 69  G   3160   216    171    7.7    60   6.4    290          .    18   0.90000   0.2    .     48.0   304
 70  G   3161   141    141    9.1   310   6.8    480     0.5000    12   1.70000   0.3   16     44.0   544
 71  G   3158   243    243   10.0   369   7.8    580    26.5000    19   5.80000   0.3    .   2429.0   119
 72  G   3171   102    102   10.0   354   7.2    520     1.7000    14   1.90000   0.3    .    117.0   324
 73  G   3172    92     92   10.0   302   7.2    410     0.9000    13         .   0.4   22     72.0   329
 74  G   3199   554    246    8.0   215   5.8    770     3.3000     7         .   0.4   15    166.0   379
 75  W   3202   121     89    7.6   375   7.2   1220    16.9000    42         .   0.5   28    486.0   227

OBS     CA   CR   CU   LI    MG   MN   MO     NA   NB   TH     V   Y     ZN       K     SR     SI

 51   12.5   13    .   17   8.6    .    .  223.0    .    .    91   .     99       .      .      .
 52   52.6    .    2    8  27.4    .    .   12.6    7    .    12   1     49       .      .      .
 53   60.4    .    .   26  33.5    .    .   38.7    .    .    13   1     22       .      .      .
 54   26.8    .    2   45  64.2   34    5  530.0    6    .     .   1     68       .      .      .
 55   47.5    .    .    9  26.1    .    4   11.7    4   16     5   1    260       .      .      .
 56  113.0    .    6   55  38.6    3    4   26.8    5   20     .   2    200       .      .      .
 57   66.5    .   13    7  33.7    2    .   11.0    6   23     4   2    137       .      .      .
 58    4.2   61    .   16   1.7    .   16  175.0    .    .   239   .     44       .      .      .
 59    3.2   51    .   11   5.4    .    .  152.0    .    .    16   .     82       .      .      .
 60   65.0    .    3   16  44.7    3    .   16.6   10   15    10   1    309       .      .      .
 61   83.0    .   33   16  47.4    2    .   19.0    6   22     9   1     69       .      .      .
 62   26.5    .    .    6  14.4   18    .   28.4    .    .     .   1   1680       .      .      .
 63   14.4    .  557   11   8.0    8    .   38.6    .    .     .   .    552       .      .      .
 64   25.0    .    .   14  15.1    .    7    9.4    .    .     .   .     21       .      .      .
 65   43.8   13    .   21  24.3    6    .  142.0    .    .    33   1     95       .      .      .
 66   52.6    .   26   14  27.0   46    4   11.9    .    .     .   .    110       .      .      .
 67   53.4    .    .   18  25.9    2    .   12.0   10    .     .   1     20       .      .      .
 68   55.6    4   11   19  32.5    4    .   39.1   11   23    12   1    555       .      .      .
 69   25.5    .    3   17  12.7    .    .   22.6    .    .     .   .    107       .      .      .
 70   56.0    .    .   12  39.6    .    .   12.7    .    .     .   .     27       .      .      .
 71   20.8   16    3   27  11.7    5    8  170.0   11    .   119   .    403       .      .      .
 72   54.4    .    5   31  26.9    .    5   72.2    .    .     4   .    812       .      .      .
 73   59.0    .    .   22  28.8    2    .   23.2    .    .     .   .   1421       .      .      .
 74   35.5    .    .    9  23.1    2    .   16.9    6    .     .   .    153       .      .      .
 75   65.0    .    .   34  45.3    2    4   84.3   13   11    14   1      8       .      .      .
```

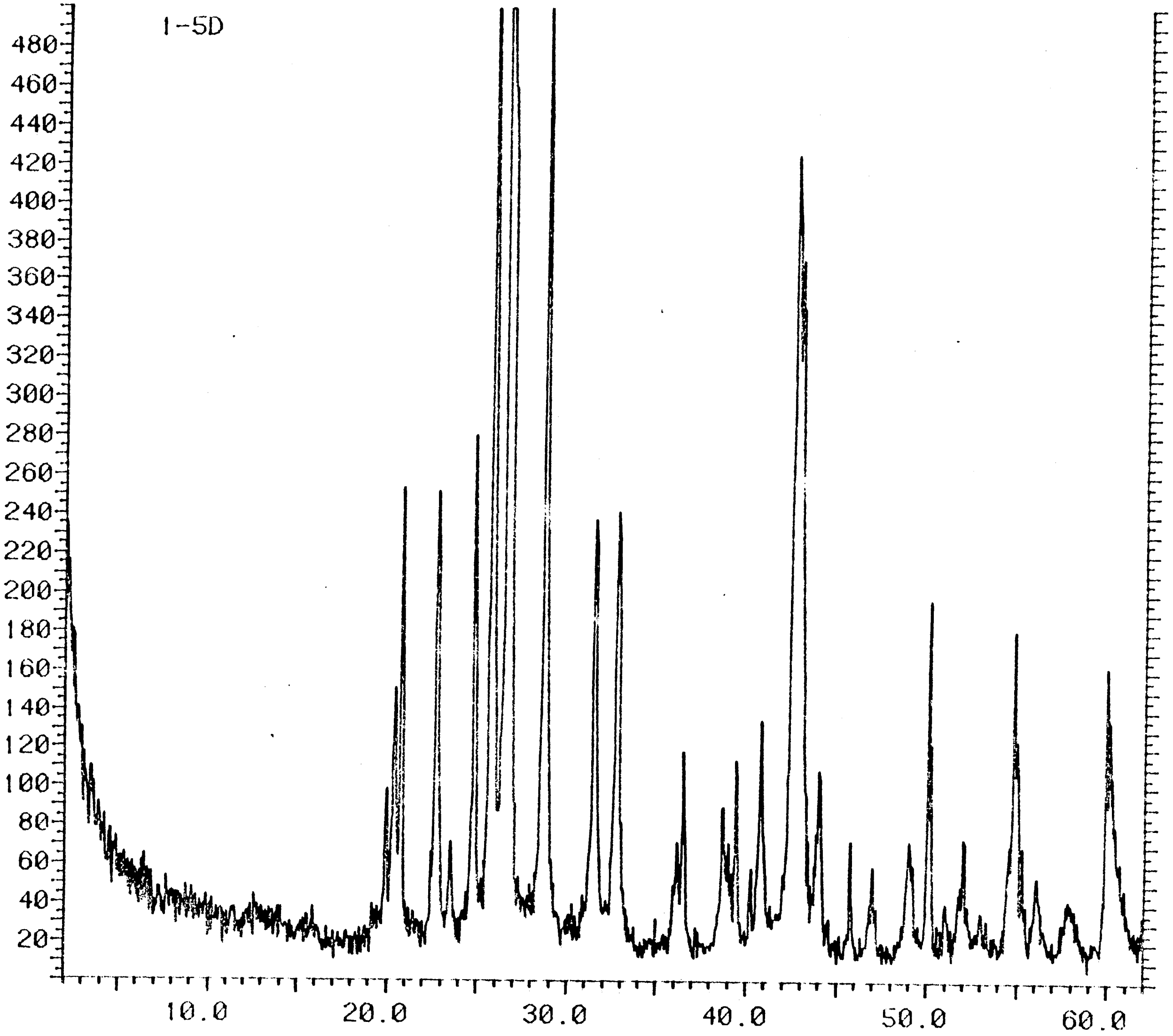
```
                                                            SAS                                     16:39 THURSDAY, MAY 2, 1985  4

OBS      FM      ID     DEP     PRDEP     DO     ALK     PH     CON          U     SO4          AS    SE     AL        B     BA

76       W      3260    121       36     6.8     260    7.2    1230       1.00     10            .    0.2    10       79    291
77       W      3264    154      154     6.4     360    7.3     600      11.70      7      0.60000    0.3    18     1119    475
78       C      3391    289      134     2.3     477    7.0    1002      29.80     22      9.50000    0.5     .     2762    195
79       G      3443    308      308     6.9     310    7.9    5800       0.40      .      1.50000    0.4     .      668    129
80       C      3453    164      164     6.3     250    6.9     460       0.47      5      0.70000    0.2    18       48    481
81       G      3459    174      174     6.6     100    7.0     290       0.22      .            .    0.2     .       32    711
82       G      3460    118      118     7.5     165    7.2     290       2.67      .            .    0.2     .      180    271
83       G      3461     86       32     7.8     210    6.9     350       0.42      .            .    0.2     .       32    999
84       G      3463    214      214     5.0     200    6.1     360       1.67      .            .    0.2     .       82    349
85       C      3464    181      181     6.3      72    6.6     270       0.02     14            .    0.3    14       36    238
86       C      3465    109      105     4.0     263    6.6     430       2.48      .            .    0.3     .       82    495
87       G      3467    141      141     6.5     140    7.0     310       0.36      .            .    0.3     .       33    623
88       C      3473    263      263     6.2     342    7.6    5600       1.47      7      0.60000    0.2    12      187     56
89       G      3475    220      220     5.2     252    7.1    1650       2.50      6      0.60000    0.2     .      177    861

OBS      CA      CR      CU      LI      MG      MN      MO        NA      NB      TH      V      Y      ZN          K       SR          SI

76      62.2      4       7      17     38.8     2       .        20.1      4      22      5      1     383          .        .           .
77      26.4      .       7      24     17.5     .       .       127.0      .      14      4      1     146          .        .           .
78       4.6      8       .      32      2.2     .      25       224.0      4       .     75      .      49    0.60000      158     3.90000
79      18.2     12       .      19     11.4     .       .       105.0      5       .      6      .     126    2.00000      531     6.20000
80      35.9      .       .      10     31.1     .       .        14.3      .       .      .      .      33    0.90000      127     7.20000
81      26.3      .     202       9     14.9     6       .         5.3      5       .      .      .     319    0.90000       68     7.40000
82      33.2     29       .       8     19.1     .       .        10.9      5       7      6      .     195    2.40000      375     3.80000
83      46.0      .      10       6     25.6     2       .         8.8     11      10      .      1     164    1.30000       95     6.30000
84      34.4      5       .      15     26.7     3       .         8.0      6       9     12      1       7    2.30000      257     4.30000
85      22.2      .       6      13     12.7     4       .        17.7      .       .      .      .      13    2.10000       82     9.10000
86      34.8      5       .      20     30.9     .       .         9.9      .      19      4      1      13    2.40000      315     3.80000
87      23.5      4      21       6     14.4     2       .         6.6      .       5      .      .       9    0.80000       76     6.70000
88       8.9      .       .      11     41.8     .       .        28.3      .       .      .      .       .    1.40000      126     7.70000
89      57.2      .       .      12     90.2     2       .        56.6      .       .      .      .       .    0.50000     1093     7.30000
```

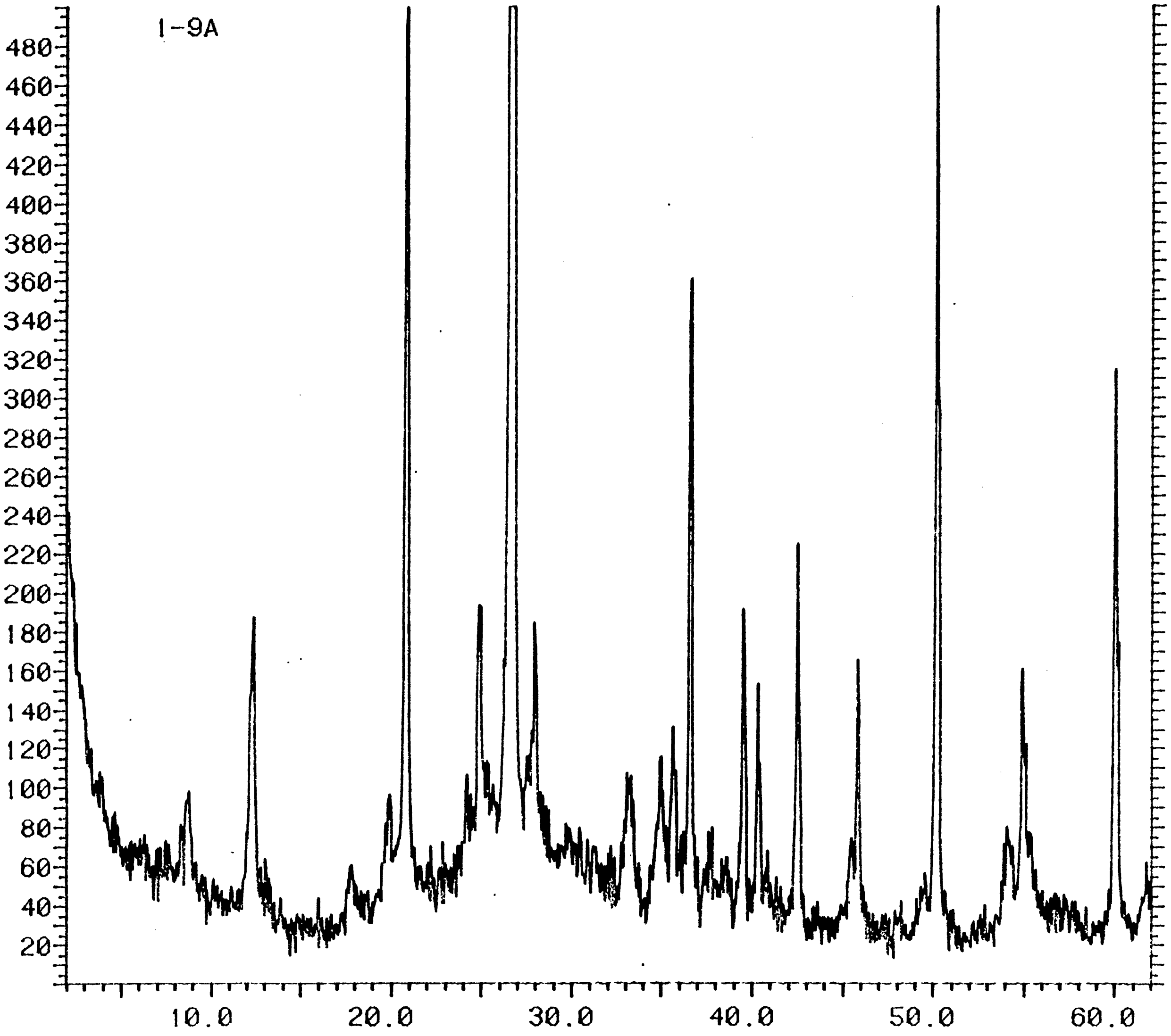
Cr cd Li

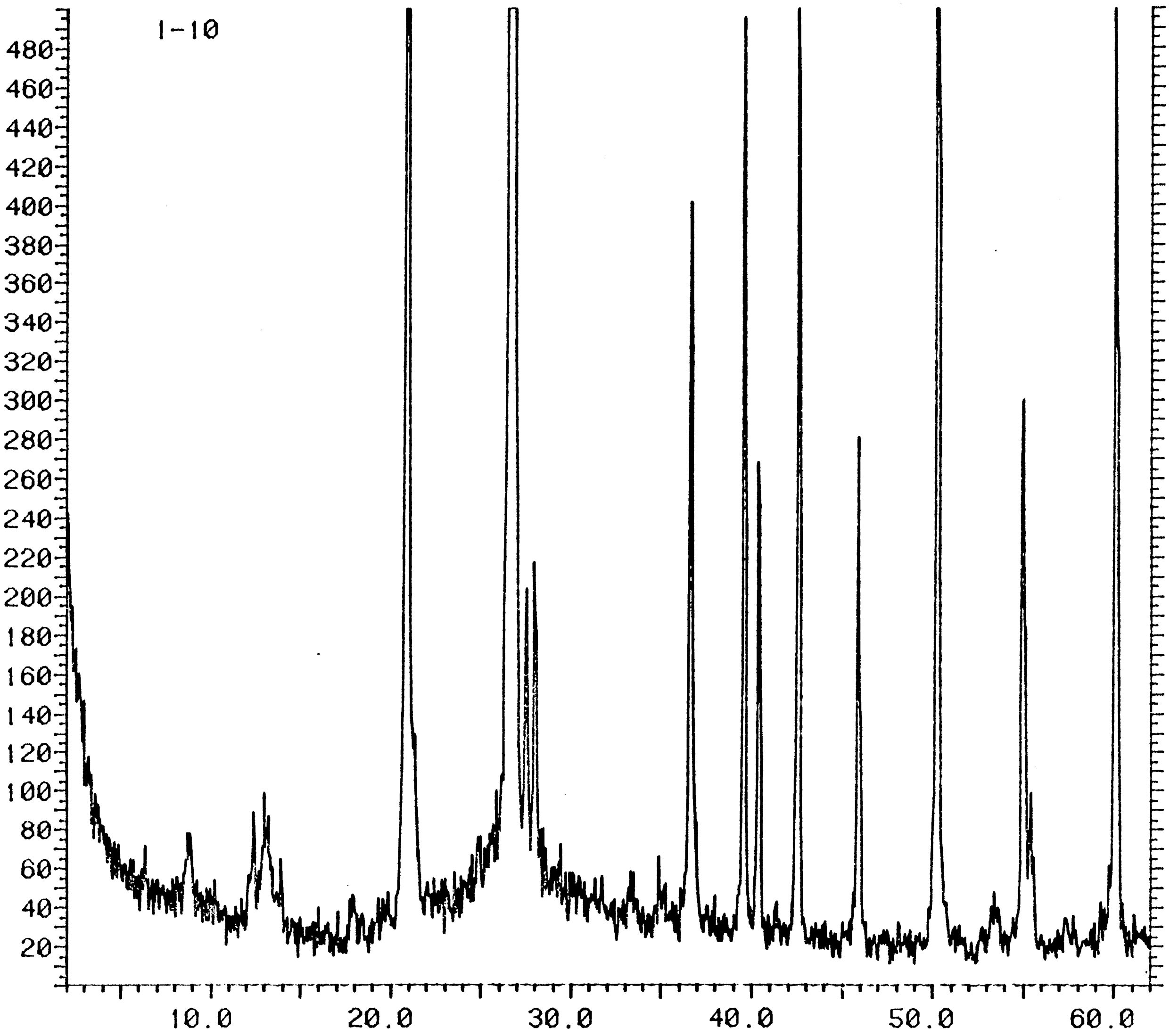
APPENDIX C

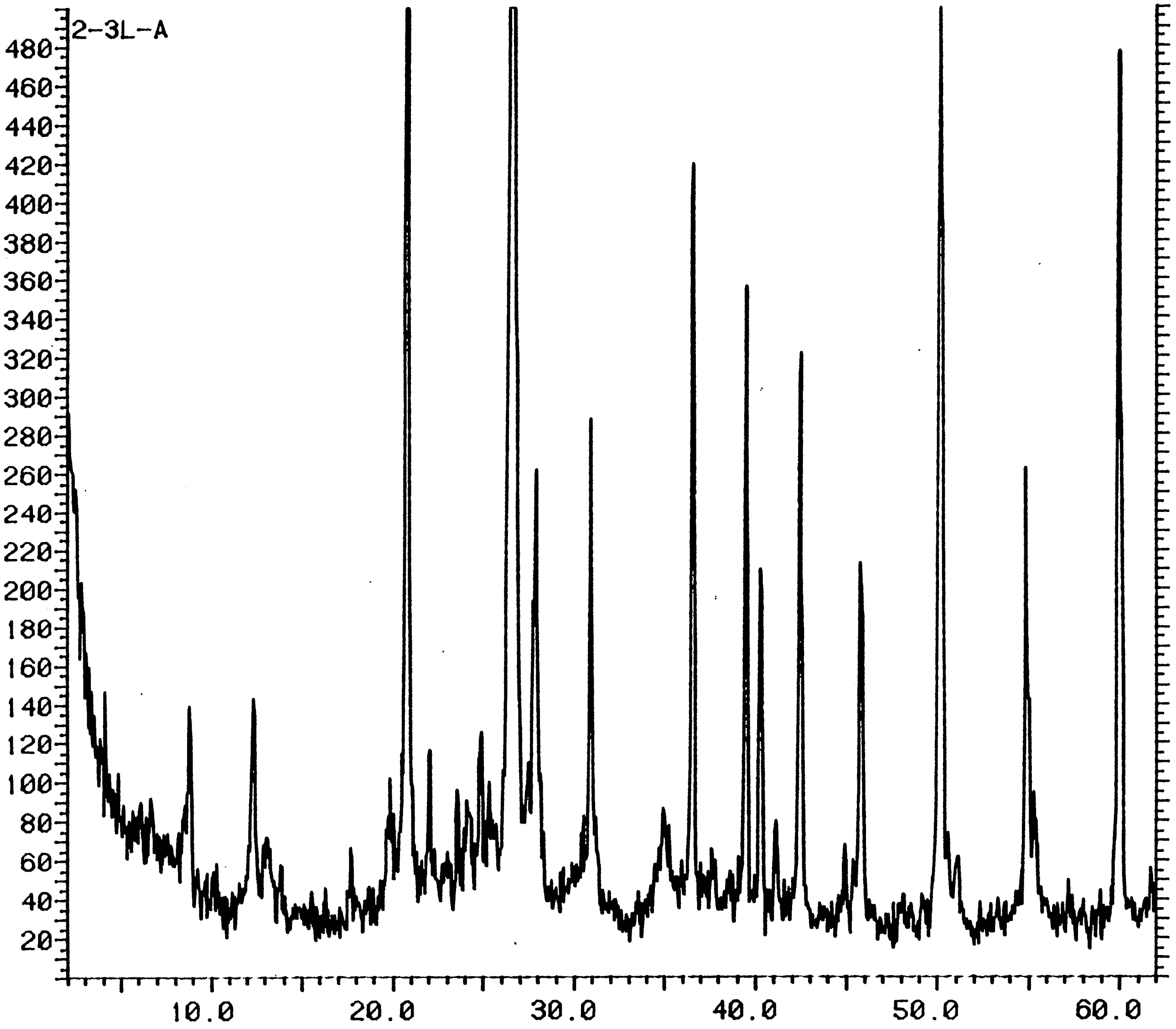
SELECTED X-RAY DIFFRACTION PATTERNS OF SAMPLES FROM THE GARBER SANDSTONE AND WELLINGTON FORMATIONS

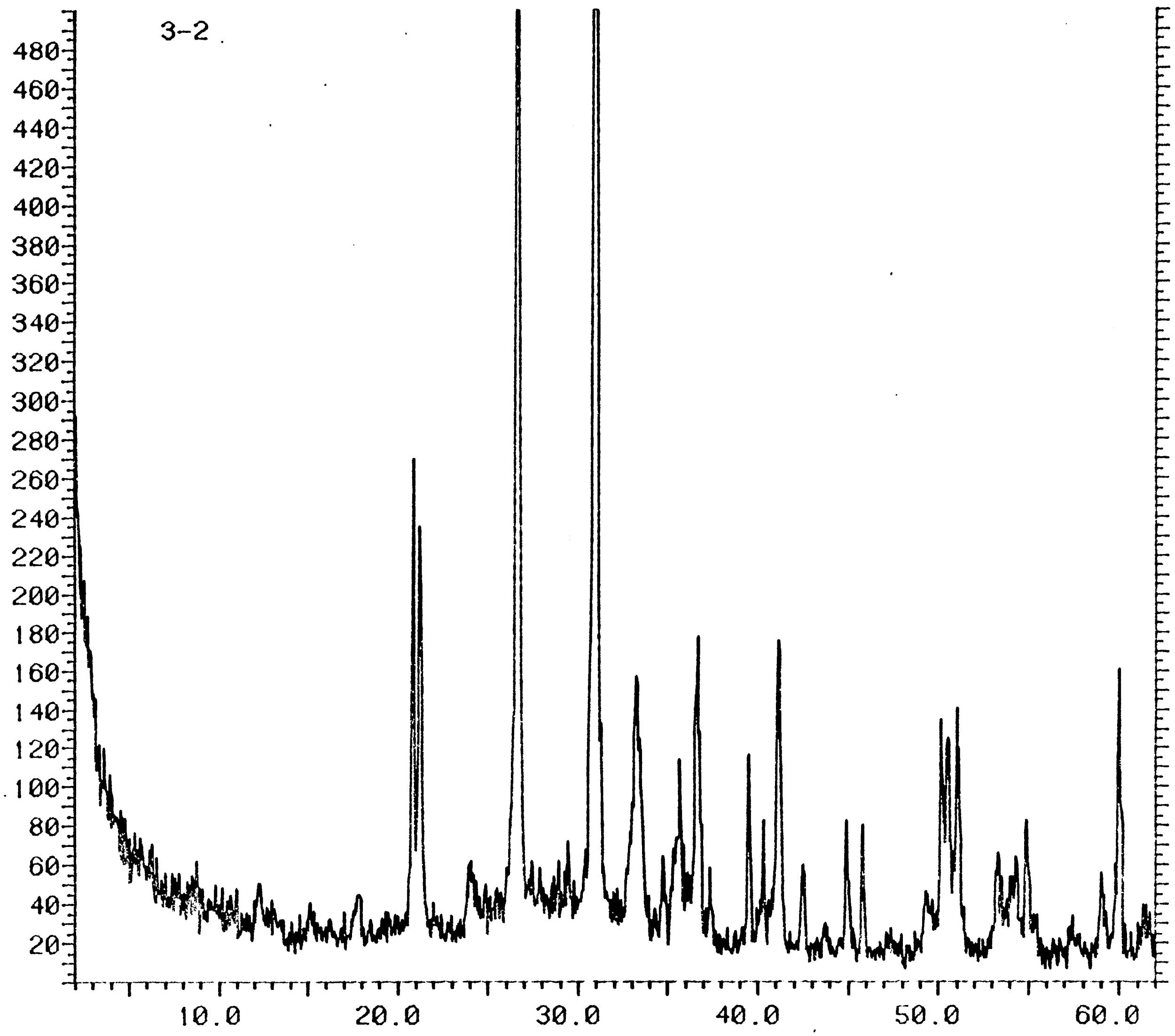

1-5A
480
460
440
420
400
380
360
340
320
300
280
260
240
220
200
180
160
140
120
100
80
60
40
20
10.0
20.0
30.0
40.0
50.0
60.0


1-5D
480
460
440
420
400
380
360
340
320
300
280
260
240
220
200
180
160
140
120
100
80
60
40
20
10.0
20.0
30.0
40.0
50.0
60.0


I-9A
480
460
440
420
400
380
360
340
320
300
280
260
240
220
200
180
160
140
120
100
80
60
40
20
10.0
20.0
30.0
40.0
50.0
60.0


1-10
480
460
440
420
400
380
360
340
320
300
280
260
240
220
200
180
160
140
120
100
80
60
40
20
10.0
20.0
30.0
40.0
50.0
60.0


2-3L-A
480
460
440
420
400
380
360
340
320
300
280
260
240
220
200
180
160
140
120
100
80
60
40
20
10.0
20.0
30.0
40.0
50.0
60.0


3-2
480
460
440
420
400
380
360
340
320
300
280
260
240
220
200
180
160
140
120
100
80
60
40
20
10.0
20.0
30.0
40.0
50.0
60.0

VITA

Katherine Kretow McBride

Candidate for the Degree of

Master of Science

Thesis: HYDROGEOCHEMISTRY AND OCCURRENCE OF SELENIUM IN THE GARBER-WELLINGTON AQUIFER, CENTRAL OKLAHOMA

Major Field: Geology

Biographical:

Personal Data: Born in Brooklyn, New York, September 5, 1956, the daughter of Paul and Mary Kretow.

Education: Graduated from Hunter College High School, New York City, New York, June 1974; received Bachelor of Science degree (cum laude) in Geology from Saint Lawrence University, Canton, New York, May 1978; completed requirements for the Master of Science degree at Oklahoma State University, July 1985.

Professional Experience: Hydrogeologist, New Jersey Department of Environmental Protection, Ground Water Pollution Analysis Unit, July 1979-June 1982; Hydrogeologist; Dan Raviv Associates, East Orange, New Jersey, July 1982-December 1982; Research Assistant, Department of Geology, (EPA Grant #OU6931-15), Oklahoma State University, January 1983-August 1984.

Professional Organizations: National Water Well Association
Association of Women Geoscientists