BARITE TRAVERTINE FROM SOUTHWESTERN

OKLAHOMA AND WEST -

CENTRAL COLORADO

By

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BARITE TRAVERTINE FROM SOUTHWESTERN OKLAHOMA

AND WEST - CENTRAL COLORADO

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PREFACE

This thesis evolved out of research work initiated in September 1984 which I undertook after my attention was drawn to the Zodletone deposits by Dr. Nowell Donovan. Since the emphasis of the study clearly included much geochemical work, Dr. Arthur Hounslow agreed to supervise my efforts. The nature of the springs and their barium - rich deposits allowed me to make a study which led naturally from the world of "classical" geology into the applied field of hydro-geology; the transition that I came to OSU to make. My enjoyment of the project parallels its importance in my development as a scientist.

My joint advisers, Drs. Donovan and Hounslow, have been extremely helpful to me throughout the course of my research at OSU. It is my hope that they will both find in these pages something of the excitement I feel at the geological directions I have inherited from them. Likewise Dr. Wayne Pettyjohn, who gave me invaluable advice on the hydrogeological aspects of this thesis, has made a profound impression on my geo - consciousness. To all three gentlemen I extend my warmest thanks.

Other people in the academic sphere who have helped

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me greatly in my study are Dr. David Francko in the OSU department of Botany (who taught me the identity of the biota in the spring samples), Dr. Gary Stewart of Geology (who gave fruitful advice on Oklahoma stratigraphy), John Ozga of the U.S. Bureau of Reclamation Grand Junction Projects Office (who supplied the streamflow data used in the aquifer evaluation in Chapter 3) and Bob Schuster at the U.S. Geological Survey in Lakewood, Colorado (who provided me with information on the Chipeta landslide).

During fieldwork in Oklahoma Steve and Cathy Bridges of Russellville, Arkansas, very kindly took me to the locality for the first time.

Fieldwork in Colorado was an event on both occasions. Clark Poore accompanied me on the first trip to Lazear (August 1985) and helped in driving; in hauling heavy water samples back to the trailhead at the Fish Hatchery and in checking my field observations. During my second visit to Lazear (October 1985) I was hosted by the Neal Ward and David Black Families at the Hotchkiss National Fish Hatchery, who gave me a very comfortable roof over my head and excellent hospitality. Jerry Pearson and his family took me to the Black Canyon of the Gunnison and made me feel really welcome in Hotchkiss. Sandy Wade, administrative assistant at the

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Springs have always commanded Man's fascination. Even though it is the purpose of this thesis to scientifically explain the nature and origins of two suites of springs, the conclusions I reach as to their genesis fill me with even more wonder at the Intelligence which causes springs to be. The mystery of the living Earth is celebrated for me by the music of spring water as it

trickles from its orifice. These years of study have filled me with a heightened awareness of the sanctity of Gods creation, and with excitement at the fact that I am myself caught up in that creation.

I therefore dedicate this thesis to many people, most of whom will never read it. The people to whom this thesis is dedicated are the many I have met who are happy to be alive and proud to be part of creation; these include: My parents, brother and sisters; Monika Bilger; Lance and Pat Henson of the Southern Cheyenne; Clark Poore; the Reynolds of Lazear; Angus and Melanie Spirit of Ulbster, Caithness, Scotland; the community of Osage Monastery, Sand Springs, Oklahoma; the struggling Dineh (Navajo) people of Big Mountain, Arizona; Fr. Tony Battle of Newcastle, England; the Little Brothers of Jesus in Detroit, Michigan and all who acknowledge that they are moved by the Spirit who moves all creation; the God of Jesus, of Mahatma Gandhi, of Martin Luther King Jr., of Oscar Romero. This thesis is dedicated to all those who share my dream of unity with the "force that drives the water through the rocks".

"The force that drives the water through the rocks

 Drives my red blood; that dries the mouthing streams

 Turns mine to wax.

 And I am dumb to mouth unto my veins

 How at the mountain spring the same mouth sucks."

<div style="text-align: right">Dylan Thomas.</div>

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CHAPTER I

INTRODUCTION

1.1 General Introduction.

In 1984   some   unusual   deposits of previously
undescribed barite   travertine   were   encountered by
Dr. R.N. Donovan in the course of geological mapping in
the vicinity of Zodletone   Mountain,   Kiowa   County,
Oklahoma. Dr. A.W. Hounslow later visited the locality
and, together with Dr. Donovan, suggested that an in
depth study of them ought to be made. Half of this
thesis is devoted to reporting the results of this
study. At the time the initial work at Zodletone was
undertaken it was believed these were the first deposits
of barite travertine to be discovered. An extensive
literature search eventually revealed   that several
occurrences of barite travertine were described in the
late nineteenth century and in the earlier years of this
century, albeit in rather obscure books and journals and
under names other than "barite travertine". The fruits
of this literature search form the substance of section
1.2 below. Only one occurrence had ever been noted in
the USA, however, and no attention had been paid to the

petrology or genesis of the deposit (Headden, 1905a). It was therefore resolved that a study of the nature and genesis of this deposit would also be desirable. Hence half of this thesis is dedicated to the deposits found at the Doughty Springs, Lazear, Colorado. As such the sum total of this thesis represents a complete study of both known occurrences of barite travertine in the USA.

To preserve some manageable order in this thesis it is divided into four segments. The first is this introduction, which includes details on previous work conducted on similar problems and a review of the geochemistry of barium. The second and third segments contain separate accounts of the deposits at Zodletone, Oklahoma, and Lazear, Colorado respectively. Reviews of the geology of these areas and of earlier work in the neighbourhoods are given in the appropriate segments. Finally, the fourth segment draws observations from both localities together for a joint discussion on the nature of barite travertine.

A note on semantics is probably justified here. The word "travertine" is an anglicised form of the Italian corruption of the Latin word "tiburtino" which was used in ancient times to describe calcium carbonate mineral deposits along the banks of the great Tiber River of Rome (Chafetz and Folk, 1984). Hence since the earliest

times the word "travertine" has had a specific attachment to <u>calcium carbonate</u> mineral deposits formed from springs and rivers. On the grounds of depositional environment or morphology, however, there is no way to distinguish the deposits described here from calcium carbonate travertines; their distinction is purely mineralogical and geochemical in nature. Hence, just as a turbidite is a turbidite whether it is siliciclastic or carbonate, it would seem logical to extend the use of the term travertine to all rock types of appropriate morphology and depositional environment, irrespective of mineralogy.

1.2 Previous Studies on Similar Occurrences.

Deposition of barite under vadose conditions from natural waters was first noted by Richardson in 1863 (Clowes, 1889b). He described the precipitation of barite in mine workings within the Carboniferous Coal Measures of north east England. Dunn (1877) chemically analysed the deposit and attendant water, and found strontium as well as barium in the barite deposit, but failed to find either in the ambient water. It was Clowes (1899b) who first realised that the deposit was formed by precipitation when a barium rich brine encountered a barium - free but sulphate - rich

water leaking into the mine workings from overlying aquifers. Dr. J.M. Jones of the University of Newcastle Upon Tyne, England, allowed the author access to samples of these deposits. They are termed "Sunday - Stone" locally, due to their daily layering, marked by six bands of black barite (full of inclusions of coal dust, incorporated during week days when mining was active) followed by a layer of creamy barite (relatively inclusion - free since it was formed on Sundays, when no mining occured and the air in the mine was relatively free of coal dust; J.M. Jones, personal communication, 1985). A similar occurrence was noted by Latterman in 1888 in a mine near Lautenthal, Hartz Mountains, Germany (Clarke, 1924, pp. 591 - 592).

Headden (1905a) mentions "baritic sinter" assoc-iated with the Doughty Springs, Colorado. His emphasis in the study afforded them was primarily on the chem-istry of the springs, but he did note that the barite sinter was conspicuously radioactive because of the radium contained in it. This deposit forms part of the subject of this thesis and hence details are omitted here.

While both of the springs considered in this thesis are cold or tepid in temperature, the most impressive deposits of barite travertine hitherto described are

associated with hot springs in volcanic environments. In 1907, Dr. Y. Okamoto discovered radioactive plumbiferous barite sinter around the hot springs (80 - 90 deg. C) at Hokuto, Taiwan (Okamoto, 1911). Hayakawa and Nakano (1912) noted that this deposit contained up to 41% of lead substituted for barium into the barite crystal lattice, and they determined that the species primarily responsible for the radioactivity of the travertine were ionium, polonium and radium. The name "Hokutolite" was proposed for this plumbiferous species of barite by Professor K. Jimbo (1913). Further notes on the Hokuto deposit may be found in the monograph of Ishizu (1915) who also described a similar occurrence at the Shibukuro Hot Spring (97 deg.C), on the flanks of Yakeyama volcano, Akita Prefecture, Japan. The plumbiferous barite at Shibukuro was also given the name "Hokutolite" by Suganuma (1928), who studied the chemistry of the deposit. Suganuma (1928) made the interesting observation that precipitation of the barite only occurs when the waters have cooled to around 40 deg.C, and that cyanophyceae (red algae) apparently play some role in the precipitation mechanism. Upon investigation of the mineralogy, Ohashi (1920) discarded the name "Hokutolite" on the grounds that the mineral is simply an isomorph of common barite (with lead substituting for

barium by as much as 7 - 27%).

Hot spring waters at Idaho Springs, Colorado, are involved in the deposition of barite as a cavity filling in alkali syenite. Barium is leached from the alkali syenite (which contains around 0.26 wt% Ba) by the hot water, and as the water cools the barium combines with sulphate in the water (present at concentrations between 317 and 392ppm) to form barite (Spur and Garrey, 1908, p. 165).

Small quantities of accessory barite have been noted in hot spring deposits at Yellowstone, Wyoming (White, 1955).

Vermiform, cylindrical, intertwined masses of quasi - stalactitic barite (about 1 cm in diameter) were described by Walker (1919) from a shallow (i.e. within 15m of the land surface) fluorite mine near Madoc, Ontario, Canada. Walker (1919) suggested that the peculiar form of the quasi - stalactitic barite could be explained by precipitation on the surfaces of plant roots which extended into the cavity where the deposits were found.

Quasi - stalactitic barite has also been noted in Derbyshire, England, since the 1830's when it was first used for ornamental purposes (Ford and Sarjeant, 1964). This barite is really of dominantly botryoidal

form, with an illusory impression of stalactitic form coming from many sections cut at oblique angles through elongate botryoids.

Truly stalactitic barite has only been described once before. A large cavity in a dyke cutting Carboniferous Coal Measures near Blyth, Northumberland, England was found to contain a ridge of massive white stalactitic barite, with a corresponding 1m x 0.3m ridge of stalagmitic barite beneath (Randall and Jones, 1966). Occurring in the same coalfield as the "Sunday - Stone" deposits mentioned above, these deposits are believed to have been formed by a similar mechanism of mixing of barium - rich water with sulphate - rich water.

Other reviews of the deposition of minerals other than carbonates by springs include the excellent early work of Lindgren (1919; pp.105 - 106 cover barite) and the detailed syntheses on thermal springs and their deposits by Blankenship and Bentall (1965) and White (1955).

Chafetz and Folk (1984) have provided an excellent up - to - date summary of work done on calcitic travertines, with special emphasis on the role of bacteria in their formation.

1.3 Barium Geochemistry.

Barium (Ba) is an "alkali earth metal" as it falls in Group IIA, (Period 6), of the periodic table and thus is chemically similar to calcium and strontium. With an atomic number of 56 and a mean relative atomic mass of 137.36 it is a fairly heavy metal; a fact which has many implications for its physico - chemical behaviour. Seven natural stable isotopes of Ba are known, but no natural radio - isotopes. Of these seven the four most abundant are 138 (71.66%), 137 (11.32%), 136 (7.81%) and 135 (6.59%) (Pilkey, 1972). Ba forms a divalent cation with an ionic radius of 1.35 angstroms (cf. 1.21 angstroms for strontium, 1.26 angstroms for lead and 1.08 angstroms for calcium; Krauskopf, 1979, pp. 547 - 548). Like the high atomic mass, this large ionic radius exerts a profound influence over the geochemical behaviour of Ba.

The cosmic abundances of Ba (relative to Si $= 10^6$) are: Sun -- 2.75; solar system -- 4.8 (Henderson, 1982). Mean terrestrial abundances are as follows (Hem, 1970; Henderson, 1982; Pilkey, 1972): Bulk Earth -- 5.3 ppm; continental crust -- 425 ppm; total crust (continental and oceanic) -- 390 ppm; lakes, rivers and

rock types: Igneous -- 595ppm; sandstone -- 193 ppm; shales -- 250 ppm; carbonates -- 30 ppm (Hem, 1970).

Ba forms more than a dozen minerals (Pilkey, 1972), most notably barite ($BaSO_4$; orthorhombic), witherite ($BaCO_3$; orthorhombic), and celsian ($BaAl2Si2O8$; mono-clinic -- a barium feldspar end - member of a solid solution series through to potassium feldspar). Barite, the main mineral discussed in this thesis, is by far the most common of all Ba minerals (Deer et al., 1966).

Goldschmidt (1954) presented the first review of the behaviour of Ba in the geochemical cycle. Since then, very little attempt has been made to weave into one the many existing threads of knowledge concerning the distribution and circulation of Ba in our world.

Movement of Ba from mantle to crust is governed almost entirely by the behaviour of Ba in igneous systems. The size, mass and low ionic potential (= atomic number / ionic radius; i.e. a measure of charge per unit surface area of an ion) of Ba render it incompatible with most silicate mineral structures. An exception to this behaviour exists with regard to the potassium rich silicates such as potassium feldspar (and to a lesser extent biotite mica). Ba can substitute for potassium in these minerals to a considerable extent, even going so far as to form a Ba - feldspar (celsian)

in solid solution with orthoclase (Goldschmidt, 1954; Deer et al., 1966; Rhodes, 1969). Hence during progress- ive crystallisation of a silicate magma (of basaltic composition, for example) Ba is strongly partitioned into the liquid phase during the early (high - temperature) stage of crystallisation (when calcic plagioclase, olivine and pyroxene are forming), but is differentially concentrated into the solid phases during later, lower temperature stages when biotite and potassium feldspar begin to form. When temperature drops below the mica - potassium feldspar range, Ba will once more be partitioned strongly into the liquid phase. Finally it will be accommodated, along with other strongly incompatible trace elements, into the more exotic minerals which are found in pegmatites and late - stage granites (e.g. lepidolite and zinnwaldite; Deer et al., 1966 pp.217 - 219; Hughes, 1982, pp. 222 - 223).

From the above considerations it would seem that granitic igneous rocks with an abundance of potassium feldspar and biotite amongst their minerals ought to be the most fertile source of barium for natural waters involved in rock weathering, and this is indeed the case (Bowen as quoted in Brook et al., 1980, p.263). When alkaline granitic rocks are weathered the Ba - bearing minerals are dissolved and Ba goes into solution. On

account of its low ionic potential, Ba tends to go into
solution as hydrated ions (Pilkey, 1972).

The two most common barium minerals, barite and
witherite, differ markedly in solubility character-
istics. Barite is highly insoluble in common mineral
acids and pure water (1 part barite will dissolve in
400000 parts pure water -- Ham and Merritt, 1944;
i.e. the solubility is about 2 mg/l -- Cowan and
Weintritt, 1976), and it has a solubility product of
about 10-10 (Hem, 1970). Witherite on the other hand is
considerably more soluble, behaving very much like
calcite (Millero et al., 1984). Thus a barium - bearing
water encountering another water containing moderate and
equivalent amounts of sulphate and carbonate will first
precipitate barite in abundance, leaving little (if
any) Ba in solution to precipitate as witherite
later. This illustration helps to explain the fact that
barite is far more abundant than witherite in nature.

As the salinity and/or temperature of water
increases a commensurate increase in the solubility (and
solubility product) of barite takes place (Templeton,
1960). For example, while only 2 - 3 mg/l of $BaSO_4$ can
be coaxed into solution in pure water at 25 deg.C,
40mg/l $BaSO_4$ will dissolve in 2M KCl at 50 deg.C. High
CO_2 fugacities and the presence of dissolved alkaline
carbonates also cause an incease in barite solubility,

but the presence of sodium and/or potassium chlorides remains the stronger control on barite solubility (Cowan and Weintritt, 1976). Pressure has recently been identified as a very important control on barite solubility (Dr. G. Atkinson [University of Oklahoma, Norman], 1986, personal communication). Dr. Atkinson has found that barium sulphate is 200% more soluble at 1000 atmospheres pressure than it is at 1 atmosphere (i.e. barite is much more soluble in deep brines than it is in surface waters).

Barium has been widely noted in natural waters (Puchelt, 1967). Amongst the highest concentrations recorded in ground water are those in brines of the Carboniferous Coal Measures of north east England, where Edmunds (1975) has recorded concentrations as high as 4180mg/l. These Ba - brines formerly emanated from surface springs prior to artificial lowering of the potentiometric surface in this century to facilitate subsurface mining. A study of ground water quality in the Upper Cretaceous Woodbine sandstone of the East Texas Basin revealed the presence of up to 50 mg/l of Ba in solution (Brooks, 1960). Highest concentrations of barium occur in the north west part of the basin -- i.e. the part nearest to the Wichita Mountains alkaline igneous province; an obvious primary source for the

barium. This source was overlooked by Brooks (1960) who suggested the barite veins in the Tri - State orefield of Oklahoma, Kansas and Missouri as a source for the barium, in defiance of our knowledge of barite solubility. This occurrence of Ba in ground water is of particular interest inasmuch as it reflects the high Ba content in the Zodletone waters which are on the opposite flank of the Wichita Mountains to the Woodbine waters.

Ba is frequently noted in the oil field brines of Oklahoma, and it is often involved in the precipitation of an highly insoluble barite scale when sulphate bearing waters are used to flush formations during secondary recovery operations (Cowan and Weintritt, 1976). Collins (1969) has found Ba concentrations of up to 600 mg/l in brines from deep Carboniferous aquifers in the Anadarko basin of Oklahoma.

Lacustrine Ba circulation has been discussed by Sholkovitz and Copland (1982) and Finlay et al. (1983), the latter including descriptions of active participation of freshwater protozoa in the system. Chow and Goldberg (1960) provided one of the earliest evaluations of marine Ba geochemistry, noting an increase in both Ba concentration and solubility product with increased depth (and decreased temperature). Hanor

(1969) noted the effects of aqueous complexing and interference by strontium on the saturation relations of barite in sea water. Biological participation in marine Ba cycling has long been suspected (Goldberg, 1965; Chester, 1965) on account of the coincidence between high oceanic Ba content and high organic productivity (Cronan, 1980), and because of the ubiquitous presence of organic matter in barite deposits of marine origin (cf. Cronan, 1980; Berkheiser, 1984; Revelle and Emery, 1951; and Shawe et al., 1969). Support for the idea of biological participation was recently furnished when barium was found to accumulate in the soft parts of certain marine invertebrates (Cronan, 1980).

Biological accumulation of Ba and barite has been more frequently observed amongst continental organisms. Suganuma (1928) led the way with his observations on the behaviour of red algae (cyanophyceae) at the Shibukuro Hot Springs, Japan, with respect to barite precipitation. Bowen and Dymond (1955) give a good review of the occurrence of Ba and Sr in plants and soils, and the inter - relation of concentrations in both, listing the alga <u>Chara vulgaris</u> as the most vigorous Ba accumulator of all the plants studied (containing up to 402 ppm Ba). Barite statoliths in

<u>Chara</u> <u>fragilis</u> were described by Schroter et al.,
(1975), and Desmid algae were shown to be Ba accum-
ulators by Brook et al. (1980). Phytoplankton play a
definite role in lacustrine Ba circulation according to
Sholkovitz and Copland (1982). Protozoan species with
intracellular barite crystals have been investigated by
Gooday and Nott (1982) and Finlay et al. (1983). Mann
and Fyfe (1984) found that certain fresh water green
algae will take Ba up from aqueous solution so enthusi-
astically that it will be enriched in their tissues at
factors of up to 200,000 times the concentration in the
ambient water. The paper by Gooday and Nott (1982)
includes an annotated bibliography on the occurrence of
Ba and alkaline earth sulphates in plants and animals.
Apart from a possible role in gravitropic responses in
phytoplankton, there is no known physiological use for
barite or Ba in plants (Finlay et al., 1983). Ba can act
as a general muscle stimulant in man, although ingestion
of excess soluble Ba salts (e.g. $BaCO_3$) can result in
the poisoning of the circulatory and nervous systems. Ba
does not substitute for Ca into bone. Accumulations of
insoluble Ba salts in the tissues can cause chronic
irreversible tissue damage. Because of this it is not
advisable to drink water containing any more than
about 1 ppm of Ba (Miller, 1962).

As noted above, Ba moves to the Earth's crust from the mantle primarily by way of inclusion in potassic phases of igneous rocks. Some may also come by way of hydrothermal processes (Sawkins, 1966; Barnes, 1979), although most hydrothermal deposits of barite (and witherite) were probably precipitated from water of meteoric origin (Dunham, 1970; Dozy, 1970; Solomon et al., 1971; Edmunds, 1975).

Sedimentary deposits of barium are almost exclusively baritic in mineralogy. They may be conveniently divided into primary deposits (formed by typical sedimentary processes) and secondary deposits (of diagenetic origin). Most primary barite deposits are strongly bedded, but this is a coincident veneer on the vast array of environments in which such deposits may be formed. Black, fine grained bedded barite, with abundant associated organic matter, occurs in sequences of eugeosynclinal pelagic sediments, occasionally interbedded with volcanics (Shawe et al., 1969; Berkheiser, 1984). Other primary deposits of barite are far more rare, but they include: Bedded detrital barite within terrestrial clastic sequences in the early Permian of Britain (Lewis, 1923) and Southern Africa (Reimer, 1978); barite and celestite of evaporitic origin in several localities (reviewed by de BrodtKorb

et al., 1982, who describe the deposits at Neuquen, Argentina); and finally barite travertine, the subject of this thesis (Headden, 1905; Ishizu, 1915; Younger et al., 1985).

Secondary sedimentary barite deposits include the various concretionary forms of barite, such as ocean floor nodules (Revelle and Emery, 1951) and the celebrated barite rosettes, which are to be found in the Permian of Oklahoma (Nichols, 1906; Ham and Merritt, 1944) as well as at Kharga, Egypt (Pogue, 1911) and in the Permian of Scotland (Donovan, R.N., personal communication, 1985). Diagenetic barite is also found: (i) As cements in sandstones and limestones (Clowes, 1889a; Ham and Merritt, 1944), and (ii) as residual deposits left behind after the weathering of carbonate host rocks (Ham and Merritt, 1944).

Barite has several uses to man (Brobst, 1970), the most important of which is as a weighting agent in well - drilling muds. It is also used in the manufacture of glass, rubber, paint, heavy printing papers, plastics, rope finishes, car clutch facings, brake linings, and linoleum. Medical x -ray photography, television engineering and industrial construction all rely to some degree on the availability of barite. Metallic barium does not occur naturally and hence must be

extracted from barite for inclusion into various barium chemicals (for which over 2000 specific industrial applications have been catalogued). Brobst (1970) reviewed the worldwide economic geology of barite, and updated information can be found in Ampian (1985). Extraction of barite from the crust currently amounts to about 7.9 million tonnes per year (8 x 109 kg/yr).

The geological occurrence of barite has been well summarised by Brobst (1980), and an index map and annotated bibliography of barite deposits in the USA have been prepared by Dean and Brobst (1955). Oklahoma barite deposits were first discussed by Nichols (1906), who studied the barite rosettes from the Permian redbeds. With the exception of Honess (1923), who described veins of hydrothermal barite in the Ouachita Mountains, all other work on barite in Oklahoma between 1906 and 1944 centred on the Permian rosettes (e.g. Meland, 1922; Shead, 1923; Gould, 1926; and Tarr, 1933). In 1944, a lengthy report on "Barite in Oklahoma" was published by the Oklahoma Geological Survey (Ham and Merritt, 1944). This report reviewed the petrology and geochemistry of all the known deposits of barite in the State at that time, including hydrothermal deposits, residual deposits, sandstone cements and rosettes. Apart from subsurface barite scale deposits in the

Anadarko Basin and beneath Payne County (Cowan and Weintritt, 1976, p.162), no other previously undescribed deposits of barite in Oklahoma were noted until 1984 when the deposits described in this thesis were discovered (Younger et al., 1985).

Colorado deposits of barite have been listed in the annotated bibliography of Dean and Brobst (1955), and four main deposits recognised. These deposits are all of gangue type and occur in association with base metal sulphide deposits, gold telluride deposits, fluorite and ferberite, and all are of veined structure. The barite deposits described here, and first mentioned by Headden (1905), along with the the dyke replacement deposits at Idaho springs (described by Spur and Garrey, 1908, and mentioned above in section 1.2), are the only other deposits which have been discovered in the state.

CHAPTER II

SPRING DEPOSITS NEAR ZODLETONE MOUNTAIN, KIOWA COUNTY, OKLAHOMA

2.1 -- Introduction to the Geography of the Zodletone Area

The mineral - forming springs discussed in this chapter flow at the north - eastern foot of Zodletone Mountain, a 503 M (1649 feet) scrub - covered eminence which rises some 76 M (250 feet) above the surrounding grassland plains of Kiowa County, southwestern Oklahoma (SW1/4, SW1/4, Sec.9, T6N, R14W; Figures 2.1, 2.2 and 2.4). In geological terms this locality lies at the southern perimeter of the Anadarko Basin, within the frontal fault zone of the Wichita Mountains Uplift.

Kiowa County has a dry - subhumid climate and (with a mean annual precipitation of 62.5 cm (25 inches), and a 10 - year low of 37.5 cm, or 15 inches) it is some-what susceptible to drought (Lamar, 1979; pp. 69 - 70). The mean annual maximum and minimum temperatures are 42oC (107oF) and -15oC(5oF) respectively. Record highs and lows are 47oC (117oF) and -24oC (-11oF)

Figure 2.1 -- Location of Zodletone barite springs.
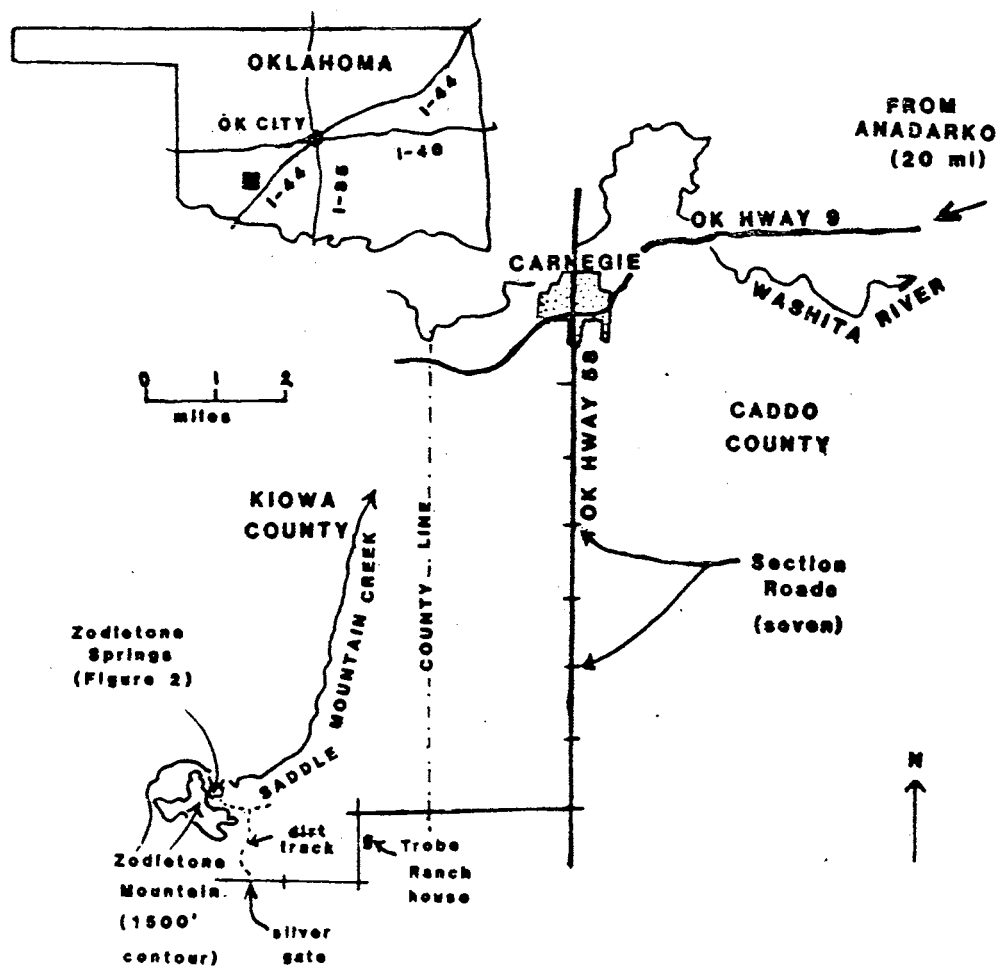
respectively. Mean relative humidity at 6 a.m. is 75 to 85% throughout the year, but for 6 p.m. it varies from 40% in spring and summer to 60% in winter. A distinct absence of clouds from the skies over long periods each year means that Kiowa County residents enjoy about 70% of each year's total possible sunshine. Mean annual evapotranspiration rates in Kiowa County are around 62 cm (25 inches) per year (Pettyjohn et al., 1983); an amount approximately equal to annual precipitation.

The Zodletone springs flow near the southern bank of Saddle Mountain Creek, and feed a small tributary brook of this stream, which is itself a tributary of the Washita River. Unfortunately none of the streams in the neighbourhood are gauged by state or federal agencies (Pettyjohn et al., 1983) but the map in Goke and Hollopeter (1930) represents these streams as being intermittent. "Zodletone" means "Stinking Creek" in the local Comanche language (Lance Henson, personal communication, 1986), alluding to the stench of H_2S gas which is liberated from the spring water. It is interesting to note that Saddle Mountain Creek flows into another creek called Stinking Creek some miles south of the confluence with the Washita River -- a fact of interest with regard to areal distribution of the aquifer from which the studied springs emerge.

Zodletone Mountain is somewhat remote from main centers of population. The nearest settlers are the Trobe family, whose ranch embraces the area studied (Figure 2.1). Mountain View and Carnegie are the nearest towns, lying some 11 Km (7 miles) to the northwest and 13 Km (8 miles) to the northeast of the springs respectively.

2.2 Previous Geological Studies
in the Vicinity of Zodletone.

Since previous studies on spring deposits of barite, and on barite in Oklahoma have already been reviewed (Sections 1.2 and 1.3) it only remains here to review previous work on the general geology in and around the Zodletone area before embarking upon more detailed descriptions and discussions. No previously published works discuss the locality described in this chapter (except an abstract by Younger et al., 1985). Much work has been done on surrounding districts which is of interest with regard to the nature of the formations encountered within the studied area.

Taff (1902) was the first to map and describe the geology of the Arbuckle and Wichita Mountains, and it was he who defined most of the formations mentioned in

this chapter. The Oklahoma Geological Survey (1917) were next to study Kiowa County geology as part of an assessment of the petroleum and gas resources of Oklahoma. In their report (Oklahoma Geological Survey, 1917, pp. 280 - 282), the location, topography, geology and structure of Kiowa County are briefly described, and the development of the Gotebo oil field is recounted.

Gould (1925) reviewed the stratigraphic nomenclature in contemporary use in Oklahoma.

Once more in pursuit of oil and gas, Sawyer (1930) laid Kiowa County to the pen on behalf of the Oklahoma Geological Survey, summarising stratigraphic knowledge to date and noting that granite had been encountered at depth during the drilling of several oil wells some distance to the north of Zodletone mountain.

Two governmental soil surveys of Kiowa County have been published; the first by Goke and Hollopeter (1930) and the second by Lamar (1979), and in addition to soil information they include useful climatological information.

Many other workers have added to the store of knowledge on local and regional geology, and a separate volume would be required to list them all. Several items of special interest include: (i) The collection of papers on southern Oklahoma petroleum geology edited by

Hicks et al. (1956), which includes much information on Anadarko Basin stratigraphy, (ii) Johnson and Denison's (1973) account of Wichita Mountains igneous geology (iii) the summary of Oklahoma geology by Johnson and Mankin (1975), (iv) the stratigraphic and structural syntheses in Ham's (1978) guidebook to the regional geology of the Arbuckle Mountains, (v) Machlachlan's (1964) excellent 75 - page review of the stratigraphy, structure, palaeogeography and development of the Anadarko Basin, and (vi) the guide to the geology of the eastern Wichita Mountains edited by Gilbert and Donovan (1982).

There are several other springs associated with the Arbuckle Group in southern Oklahoma, but all of these occur in relatively simple hydrogeological environments, where the Arbuckle Group forms outliers with suitable aquifer properties, with springs emerging at the edges of the outliers at geological contacts. Such springs are to be found in the Slick Hills (Havens, 1983) and the Arbuckle Mountains (Fairchild, 1984) where they are involved in the precipitation of calcite travertines (Emig, 1917).

Important hydrogeological work relevant to this study has been conducted by Collins (1969), who considered the geochemistry of Anadarko Basin brines, and
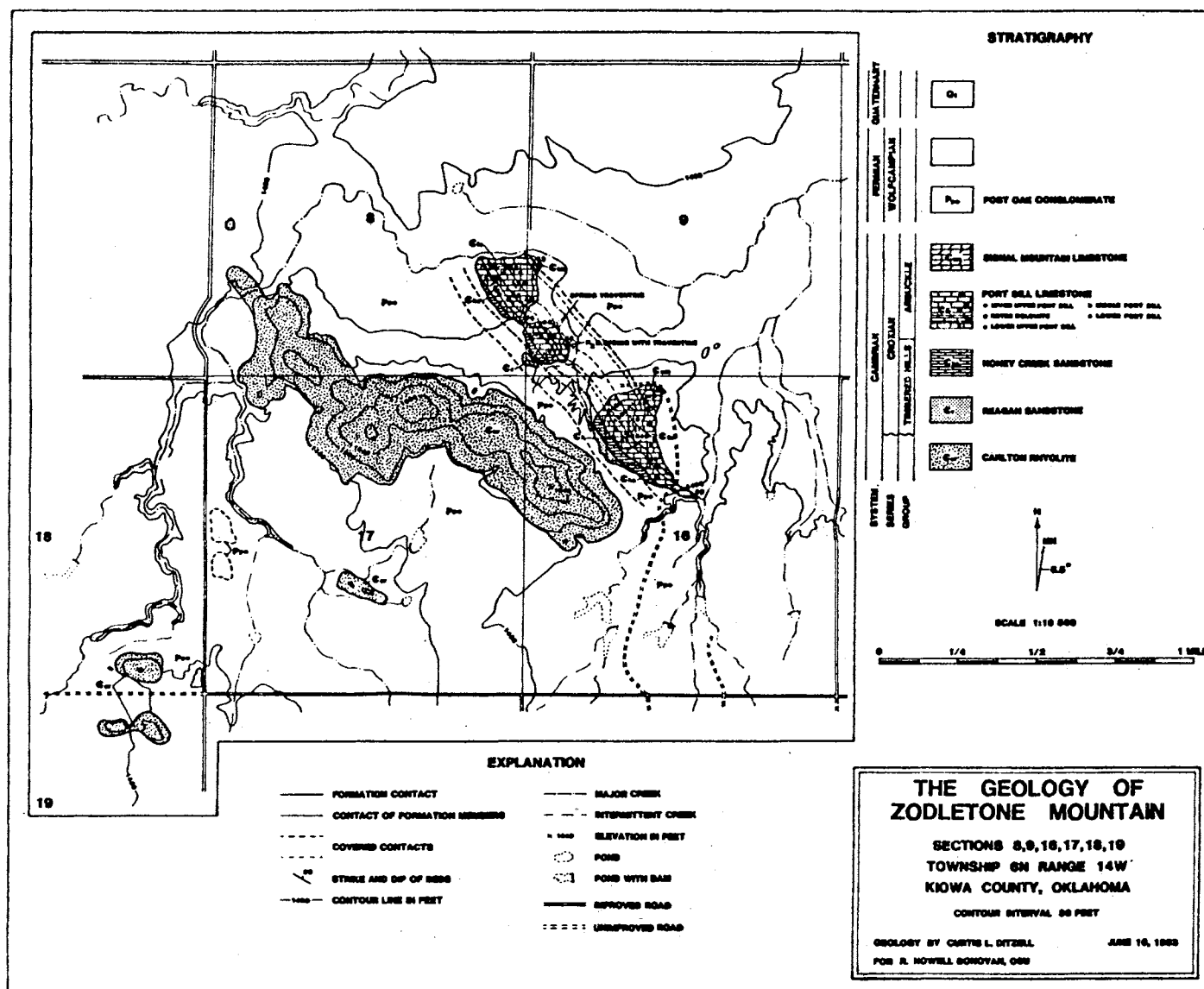
Figure 2.2 -- The geology of Zodletone Mountain.

Figure 2.3 -- Stratigraphic succession in the Slick Hills.

Period	Age	Group	Formation	Formal Justification of Boundary	Lithology	Average Thickness	Detrital Quartz	Chert	Dolomite	Glauconite	Massive Algal Boundstones	Abundant Body Fossils
Permian	Wolf-cambian		Post Oak	Calcretes; Calcite, barite, and hematite cements		120 m (400 ft)						
	Hen-nessey		West Spring Creek	Top not seen — Didymograptus protobifidus praecursor — Quartz sand		90 m (300 ft)						
Ordovician	Canadian	Arbuckle	Kindblade	Tritoechia / Orespira / Ceratopea { C. tennesseensis / C. keithi / C. capuliformis		300 m (1000 ft)						
			Cool Creek	Diaphelasma oklahomense / Leceanospira		300 m (1000 ft)						
				Thatcher Creek Member — Significant incoming of quartz sand								
			McKenzie Hill	Finkelnbergia		275 m (900 ft)						
			Signal Mountain	Missisquoia Zone / Symphysurina Zone — Massive bedding: medium gray / "Tombstone" bedding: dark gray		200 m (700 ft)						
Cambrian	Croixian	Timbered Hills	Honey Fort Sill Creek	Saukia Zone / Saratogia Zone — Thin-bedding: dark gray / Massive bedding: light gray		120 m (400 ft)						
			Reagan Sandstone	Ellipsia Zone / Saratogia Zone		60 m (200 ft)						
			Carlton Rhyolite			45 m (150 ft)						

Havens (1983) who made a reconnaissance survey of ground water in the Wichita Mountains area, including in his report (without comment) an analysis of the Zodletone spring water (identified solely by grid reference).

An unpublished geological map of Zodletone mountain was prepared by Mr. Curtis Ditzell of Oklahoma State University (Dr. R.N. Donovan, personal communication, 1985) and his observations are shown in Figure 2.2. The stratigraphic log for the area (Figure 2.3) is the work of two outstanding contributors to local geological knowledge; Donovan (1982) and Ragland (1983).

2.3 Field Geology of the Zodletone Springs Locality.

It must be stated that immediate impressions of the Zodletone springs locality on a first visit can be deceivingly disappointing: An ephemeral drainage channel in a copse of wood leading down to a tennis - court - sized area of bare soil with a large spring, surrounded by crumbling concrete walls, and several smaller springs feeding a small brooklet which winds down towards Saddle Mountain Creek, entering it as a small cataract (Figure 2.4). Along with the astringent smell of hydrogen sulphide gas, which bubbles up from the

spring waters continuously, the scene lacks the aesthetic appeal of the backdrop of verdant hills to the south. Nonetheless, perseverence reveals a number of extremely interesting features at this locality which allude to a fascinating story.

Apart from the quasi - mystical activity of the springs, which bubble away, lined with purple sulphur bacteria (Chromatiaceae), the first sign that the ground water is behaving in an unusual manner here is the soil alteration profile seen above some seeps which ooze out on the bank of Saddle Mountain Creek about 40m north east of the springs (Figure 2.4). Soil in contact with the oozing water is jet black, and as the soil is traced upwards it passes through a grey horizon, bedecked with

Figure 2.4 -- Sketch map of the Zodletone Springs locality
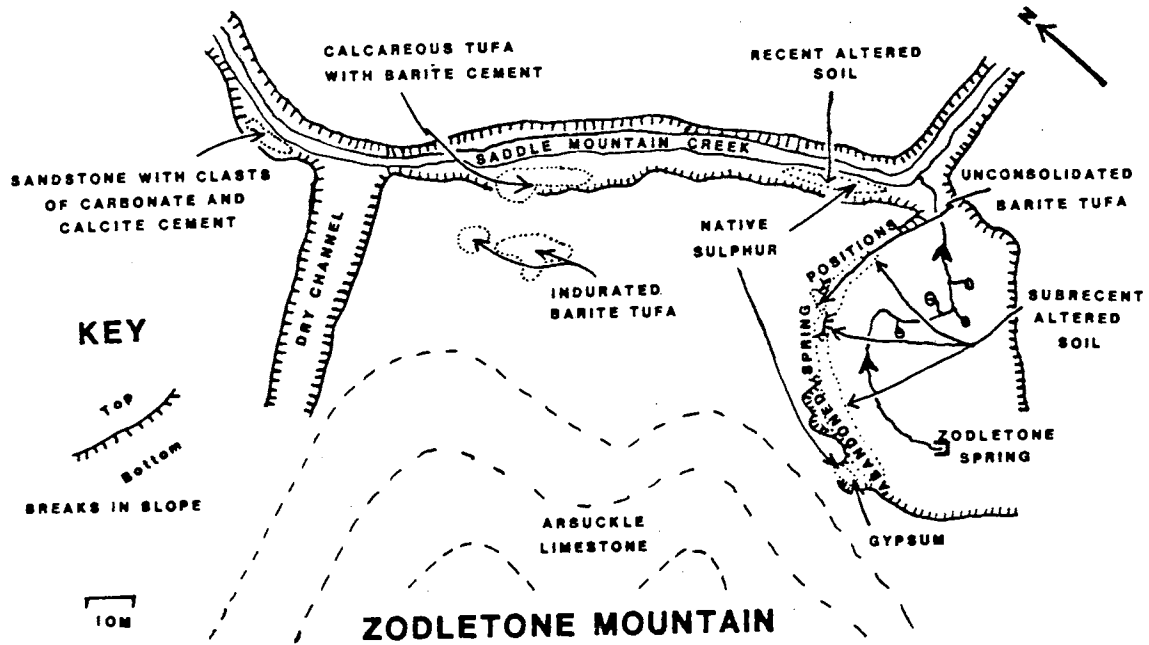
sulphur and alunogen (? - a white pastey sodium sulphate mineral) blooms, into a brown unaltered zone. Immediately east of this altered bank of soil the brooklet which drains the springs forms a small cataract (1.5m high) as it joins Saddle Mountain Creek. Plant debris (mostly leaves, twigs and branches) is incorporated into the wall of the cataract and is cemented strongly in place by calcite, which is being actively precipitated here.

Away from the banks of Saddle Mountain Creek, arranged at radii of 5 to 10m from the main spring (Figure 2.4) are a number of channel - like depressions cut into the 1.5m bluffs of soil which surround the spring. Abandoned drainage channels lead from these depressions towards the spring brooklet, attesting to the former activity of the depressions as spring discharge points. All of the depressions examined displayed dried soil alteration profiles very similar to the active profile on the bank of Saddle Mountain Creek which was described in the preceding paragraph. In several depressions the profile is crowned by a horizon which is packed with ghost - white tubules; clearly the remains of plant material (stems or roots) coated with some mineral (discovered to be barite during petrographic examination; Section 2.4.2). To the north west

of these bluffs are several exposures of indurated
travertine (Figure 2.4), some of which will fizz a
little when hydrochloric acid is applied to them (barite
- cemented calcareous travertines) and other, heavy ones
which show no tendency to fizz (mature barite travert-
ines). The petrography of these deposits is covered in
detail in Section 2.4.2 below.

2.4 Laboratory Studies on the Zodletone Occurrence.

Geochemical investigations of the water and
deposits from the Zodletone locality were supplemented
by petrological studies of the solid samples. This
section details these studies.

2.4.1 Hydrogeochemistry. Samples of the water from the
main spring were collected for study on 30th April 1985,
with pairs of duplicate samples being taken. One bottle
of each pair was acidified with concentrated nitric acid
to prevent removal of cations from solution by precip-
itation with carbonate or sulphate ions. The other
bottle in each pair was left unaltered to allow deter-
mination of anions to be performed. All bottles were
kept at or below their collection temperature in an ice

TABLE 2.1 -- Chemical Analyses of the Zodletone Spring Water.

(All concentrations in mg/L, conductivities in micro-siemens).

Constituent	DMZW - 1	ZT - 1	Havens (1983)
Ba	43.5	35.0	--
Ca	273.5	296.0	--
Fe	1.1	--	--
K	28.6	--	--
Li	1.1	--	--
Mg	149.0	144.0	--
Na	2500.	2550.	2900.(Na + K).
SiO_2	10.9	--	--
Sr	12.4	--	--
Cl	4910.	8800.*	5000.
SO_4	70.4	55.0	90.0
HCO_3	--	481.0	270.0
CO_3	--	0.0	0.0
NO_3 (N)	--	3.0	--
TDS	8001.	9926.	9160.
Hardness (Ca,Mg)	--	--	1300.
pH	7.4	7.7	8.2
Conductivity	>10000.	15040.	14800.
Temperature °C	22	22	22

Table 2.1 Continued.

Major constituents expressed in meq/L.

Sample	ZT - 1	DMZW - 1
Na + K	110.9	109.5
Ca	14.8	13.6
Mg	11.8	12.3
Cl	141.0	138.5
SO_4	1.1	1.5
HCO_3	7.9	
C.A.B.	4.2%	1.2%

- -

Notes on Table 2.1. ZT - 1 was jointly analysed by the Agronomy Soil and Water Testing Laboratory, OSU, and by the author. * The analysis for chloride conducted by agronomy is suspect, since the value given (8800) is much higher than the 5000 mg/L found in the other analyses (with which ZT - 1 agrees very closely in every other respect). If the meq/L value for 8800 mg/l Cl (i.e. 248) is used instead of that for 5000 mg/L (i.e. 141.05) to calculate the cation - anion balance an error of 30.2% is found. This reduces to only 4.2% when the 5000 mg/L concentration is assumed. C.A.B. = Cation - Anion Balance = [(Sum of cations - sum of anions)/sum of all ions]x100%.

- -

chest during the four hour car journey to Stillwater.

Results. Analysis of all samples was undertaken
(using the techniques outlined in the Appendix) within a
week of sample collection. The resultant analysis (ZT -
1) is given in Table 2.1 below. Two other analyses are
included for comparison in Table 2.1; those of Cindy
Patterson (DMZW -1, sampled 12th July 1984; OSU Geology
Department, Written Communication, 1984) and Havens
(1983). Conductivity, pH, temperature and alkalinity
(HCO_3) for all samples were determined in the field.
With the exception of alkalinity these same parameters
were also measured by Greg Lanham of the Oklahoma Water
Resources Board (Personal Communication, 1985) on 12th
July 1984. His results were as follows: pH = 7.0;
Temperature = 22 oC; Conductivity = 14000 microsiemens
and the discharge of the main spring = 3.14 gpm (by
flume).

Discussion. The analyses presented in the last few
pages represent all available data on the chemistry of
the Zodletone waters. If it is assumed that the water
at Zodletone today is identical to that which preci-
pitated the barite travertine complex in the past then
the it is logical to assess the current condition of the
water with respect to barite equilibria.

Barium geochemistry was reviewed fairly thoroughly

in Section 1.3 above. In that section it was noted that barite is highly insoluble in pure water, and that one of the primary controls on barite solubility is the salinity of the ambient water. Simple calculations of molarity reveal that the Zodletone water is an approximately 0.11 M solution of NaCl. In a solution of this salinity at 25 oC, the solubility of barite is 1.537 x 10-4 M/L (Cowan and Weintritt, 1976). Because dissolution of one mole of $BaSO_4$ yields one mole of Ba2+ and one mole of SO_{42-}, the solubility product of BaSO4 is equal to [Ba] x [SO_4], which is the same as the square of the solubility, i.e.

$$Ksp = (1.537 \times 10-4)2 = 2.36 \times 10-8.$$

When the ion activity product (IAP) of [Ba][SO_4] is calculated for DMZW - 1 and ZT - 1 (Table 2.1) values of 2.32 x 10-7 and 1.45 x 10-7 are respectively obtained. Saturation conditions are revealed by the Saturation Index, I_s = IAP / Ksp. Both samples reveal that the Zodletone water is theoretically supersaturated with respect to barite (I_s = 9.8 for DMZW - 1 and 6.14 for ZT - 1; supersaturation is realised when I_s > 1). Thus it would be no surprise to find barite being actively precipitated at Zodletone today, although precipitation may be supressed by the action of the Chromatiaceae bacteria which are continually reducing sulphate to

hydrogen sulphide in the spring orifice (and possibly in the subsurface). Aeration of the spring water would kill these bacteria and allow the sulphate activity to rise, with precipitation occurring as a result of the common ion effect. The water is aerated in two places as it enters Saddle Mountain Creek; firstly in the small cataract formed by the channel from the main spring, and, secondly, where water from the stream bank seeps trickle down the soil face. Calcite has been identified as a precipitate around twigs and branches in the cataract, and barite has been found as a white crust around the seeps on the stream bank (Section 2.4.2).

In order to better understand the possible genetic associations of the Zodletone water, the data in Table 2.1 were fed into two classification schemes; the Sulin classification of oilfield waters, (as described by Collins, 1975, who claims it is the most widely used classification scheme for oilfield waters, which is why it is used here) and the anion - cation facies classi-fication system of Morgan, Winner and Back (as described by Freeze and Cherry, 1979, p.252). Details of the classification systems are omitted here, since both are well described in the two widely available refer-ences just cited.

Table 2.2 shows the classification parameters which define the position of DMZW - 1 in the Sulin class-

Table 2.2 -- Sulin Classification Parameters for

Zodletone Spring Water

Parameter	Value
rNa	10.96
sNa	39.66
rCa	1.46
sCa	5.27
rCl	13.85
sCl	50.10
rSO_4	0.15
sSO_4	0.53
rMg	1.23
sMg	4.44
Total r	27.64
sNa/sCl	0.79
$(sNa - sCl)/sSO_4$	-19.70
$(sCl - sNa)/sMg$	2.35
Palmer Values	
a	39.66
b	9.71
d	50.63

- -

Explanation: r values = [ion] in (meq/L)/10; s values = r for each ion / Total r (i.e. the sum of all the r values).
meq/L, milliequivalents per litre = (mg/L of ion x valence of ion) / RAM of ion. Palmer values -- a = sNa, b = sCa + sMg, d = sCl + sSO_4.

ification scheme. By comparison with Table 8-II in Collins (1975), the Zodletone waters fall unequivocally into the Chloride Calcium Type, Chloride Group, Sodium Sub - Group, Class $S_{1}S_{2}$. Waters in this division of Sulin's classification constitute the Type and Group of waters most commonly associated with hydrocarbon occurrence. This is therefore strong evidence that the spring water at Zodletone is an oilfield brine which has found its way to the surface after a long history of subsurface migration. The implications of this for petroleum exploration are:

(i) The water has found a permeable "short - circuit" which leads from depth to the surface, and since water is more dense than hydrocarbons, it is likely that any hydrocarbons in the immediate vicinity of the foot of this "short - circuit" will have already escaped from the field ahead of the water. Hence drilling immediately beneath the springs is likely to be futile. (ii) The presence of barium in this water suggests that secondary recovery operations in oilfields near to Zodletone ought to be conducted with carbon dioxide (the presence of which increases barite solubility in water; Ham and Merritt, 1944) or else with water known to be free of sulphate ions. If sulphate is present in waterflooding waters it will precipitate barite upon encountering

barium, causing deposition of a porosity - reducing highly insoluble scale (Cowan and Weintritt, 1976). To test the hypothesis that the Zodletone waters are of an "oilfield" association, the BRIN database of Dwight's Energy Data Inc. (an Oklahoma City oil industry service company) was consulted. This database contains a vast compilation of chemical analyses of over 77000 oilfield water samples compiled from internal reports of oil companies (Charles Dunn, Dwight's Energy Data, Written Communication, 1984). All available analyses of brines from Kiowa County oil wells were examined, which turned out to be four wells near Hobart (Section 10, T7N, R17W). Table 2.3 gives the chemical analyses for these samples, with the DMZW - 1 analysis from Table 2.1 for comparison. Most of these deep waters are an order of magnitude greater than the Zodletone water in their concentrations of ions, with the exception of HCO_3, while the relative proportions of the components remain roughly the same. This suggests that the Zodletone water may be a diluted version of one of these deeper brines, and that the dilution, if it occurred, involved the agency of a groundwater containing some bicarbonate and a little sulphate (supplying these ions to waters which were previously deficient in them). It is reasonable that at least some mixing on these lines ought to occur,

Table 2.3 -- Analyses of Kiowa County Oil Field Brines
Compared with that of the Zodletone Water.

Sample	Depth (m)	Ca	Ba	Na	Cl	HCO_3	Mg
Zodletone	0	273	43	2500	4910	270	149
35009819	539	9285	2	64000	123090	61	2405
35009820	532	11312	104	60928	122080	41	2788
35007461	532	10100	93	54400	109000	37	2490
35007462	538	8780	2	57200	110000	55	2150

given the presence of Arbuckle limestones (a source for HCO_3) in the shallow subsurface near the springs. The presence of sulphate in the Zodletone waters (while it is totally absent in the deep waters) suggests that a reduction in Ba content from 104 in the subsurface to 43 at the spring may be effected by subsurface precipitation of barite as sulphate encounters the Ba in the deep water. Such subsurface precipitation would result in a loss of porosity and permeability through time -- a factor consistent with the reduction in the thickness and volume of deposits through time indicated by the field geology at Zodletone springs. Low sulphate activities are characteristic of Chloride Calcium Type waters, and Collins (1975) holds that this is due to (a) interactions between sulphate ions and the bituminous components of the rocks, or (b) sulphate reduction performed by purple sulphur bacteria (<u>Chromatiaceae</u>). The occurrence of these purple sulphur bacteria in the orifice of the main spring at Zodletone (Section 2.3) is recalled by this remark.

Figure 2.5 is a Piper diagram (plotted as described by Hem, 1970) with the Zodletone water plotted, along with the Doughty Springs (Colorado) waters for comparison. All data in Table 2.1 were converted into meq/L values before plotting, then the relative quantities of

Figure 2.5 -- Piper Diagram showing the Classification
of the Zodletone Water (with the Doughty Springs Water
for Comparison).

ZT - Zodletone
A1
A2 } Doughty
B

Mg, Ca and (Na + K) as percentages of the sum of all four cations were obtained and plotted in the lower left triangle. Cl, SO_4 and (CO_3 + HCO_3) were treated in a similar manner and plotted in the lower right triangle. Finally the intersection of the two vectors in the rhombic plot was located and plotted for the sample. According to the classification of ionic facies based on this diagram (Freeze and Cherry, 1979, p. 252) the Zodletone water is of the Sodium Chloride Type Facies.

2.4.2 Petrology of the Zodletone Deposits. The petrology

of the Zodletone occurrence was investigated in several ways. Optical methods involved the preparation and examination of thin sections and the inspection of grain mounts for fluid inclusions. Scanning Electron Microscopy (SEM) with an EDX facility was used to study the petrology of fine grained deposits. X - Ray diffraction analysis was used to glean information on the mineralogy of fine grained and unindurated samples unsuited to petrographic examination. Semi - quantitative X - Ray Fluorescence analysis of the solid samples was used to determine aspects of the geochemistry of the samples.

Petrography of the Zodletone deposits. The three facies of baritic spring deposits observed in the field (Section 2.3, Figures 2.4 and 2.6) are even more strongly distinguishable in thin section.

(i) Unconsolidated barite travertine.

The organic matter which is seen as tubules at outcrop looks brown and isotropic in thin section. Barite occurs as an isopachous coating (typically 0.1 - 0.2 mm thick) on the inner and outer surfaces of the tubules. Various textures analogous to those seen in calcitic travertines are seen in all three deposit types. Isopachous textures indicate precipitation under phreatic conditions (with pores 100% saturated with water). In several samples, preferential thickening and lack of crystal terminations suggested pendant textures, indicative of precipitation under vadose conditions (with both air and water present in the pores), although these textures are much more frequently and classically seen in the other types of deposit. Some cavities show drusy barite, and many of the fringes contain "growth lines", delineated by lines of inclusions of organic matter continuous through dozens of adjacent crystals. A final coat of micritic calcite is seen on the surface of some of the barite fringes.

Figure 2.6 -- Lithological Textures in the Zodletone Deposits seen in Thin Section.

2.6a -- Sketch of typical textures.

ORGANIC MATTER

PENDANT VADOSE BARITE

BARITE GROWTH CONTROLLED BY HIATI

LUMEN

ISOPACHOUS FRINGE OF BARITE
(PHREATIC GROWTH)

VEGETABLE MATTER

CALCITIC FLOWSTONE
(VADOSE GROWTH)

0   m m   3

ADVANCED BARITE GROWTH

Ct

CRYSTAL CLUSTER GROWING IN PHREATIC CONDITIONS

FORM CONTROLLED BY CRYSTAL GROWTH ESPECIALLY ON {110}

HIATI RECORDED BY MINOR PHASES OF CALCITE PRECIPITATION (Ct)

Figure 2.6b -- Cluster of euhedral barite in mature barite travertine. Good crystal terminations indicate phreatic conditions during growth. Crossed polars.

Figure 2.6c -- Detail on 2.6b showing organic matter delineating former growth limits of euhedra. Plane - polarised light.
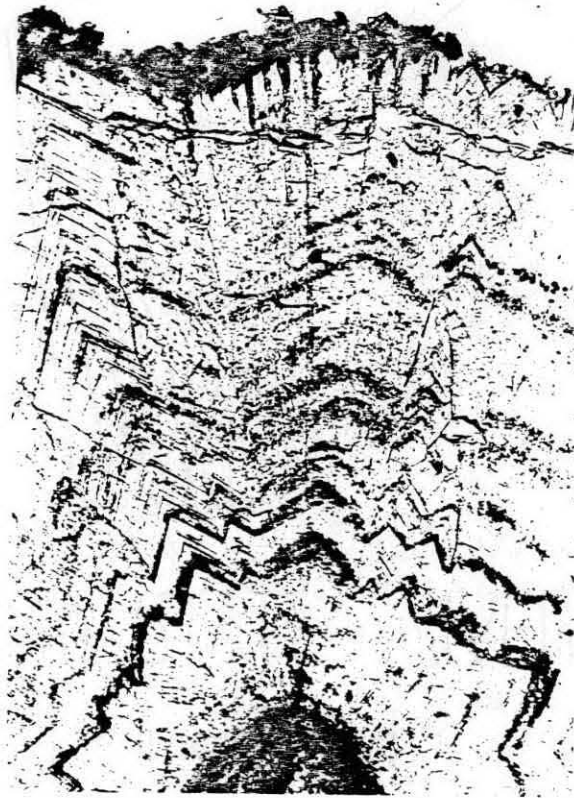
Figure 2.6d -- Chevron zoning in euhedral barite caused
by the dominant growth of {110} at the expense of {011}.
Crossed Polars.
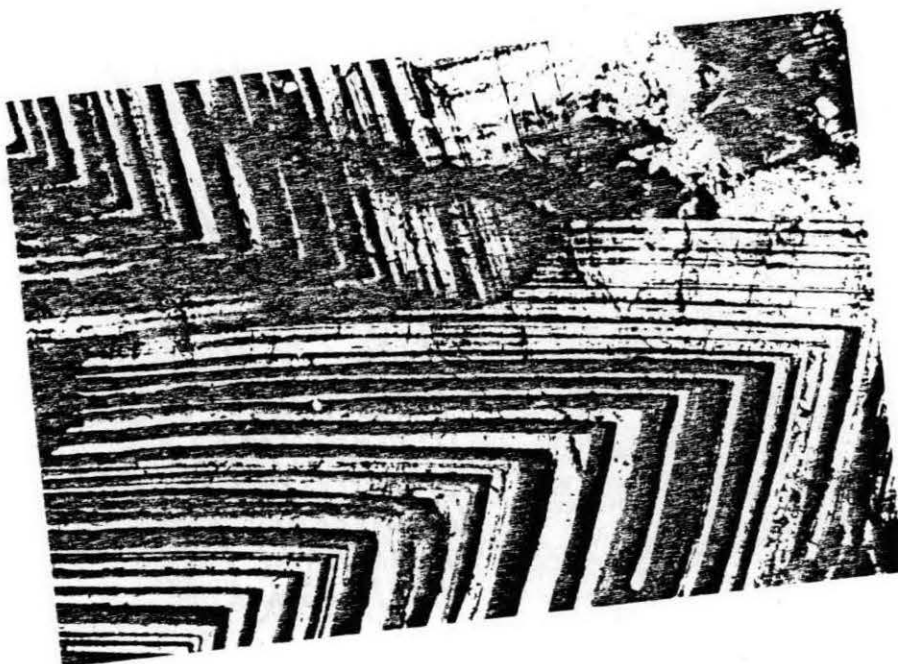
2.6e -- Vadose barite on vadose calcite in the barite cemented calcareous travertine. Crossed Polars.

Various signs of alteration are seen in the tubules themselves, including the presence of (<0.1mm diameter) quartz (a variety without strain extinction suggesting authigenic origin, although detrital influx from the nearby Reagan Sandstone outcrops can not be ruled out), micritisation, and the presence of barite needles within the organic matter, which is thus both host and victim of the mineralisation.

(ii) Barite - coated calcareous tufa.

Calcite occurs as the framework of this lithology in two ways:

(a) As laths of micrite replacing organic matter, and

(b) As stalactitic calcite coating these laths.

Both types have been involved in brecciation (both before and after the precipitation of   the second phase). The syn - depositional violence done to this deposit ceased before the precipitation of the as - yet undisturbed barite cement generations. Both vadose and phreatic - type textures are visible in this variety (Figure 2.6), although the latter are far more abundant than the   former. Phreatic barite in this deposit comprises 0.1 mm - thick acicular isopachous fringes. Vadose pendant textures are often present, and in some cases a "flowstone - like" texture in a calcite clast is mimicked by the texture of its barite coating. Abundant

plant remnants are visible in this rock, and as in the immature barite travertine many quartz crystals (this time up to 0.3 mm diameter) are present.

(iii) <u>Indurated mature barite travertine.</u>

This rock contains the coarsest and most beautifully developed barite crystals seen in any of these deposits. Most of the rock is composed of medium to coarse grained barite euhedra, arranged in strong (though locally buckled) laminae. A very distinctive chevron zoning (reflecting the preferential growth of the {110} faces at the expense of the {011} planes during development of these crystals), lamellar twinning, plumose habit and undulose extinction are characteristic of the barite in this rock, which displays first order grey - white interference colours. Outlines of plant tubules can still be discerned, although much of the organic matter has been replaced by a mat of barite needles, with minor micrite. Episodic crystal growth is implied by the conspicuous growth lines, which zig - zag their way across adjacent {110} faces, picked out by calcite and/or organic matter (Figure 2.6). Classic vadose textures are seen in this rock, in the form of concentrically zoned pendant barite.

Barite Crystallography. Examination of the thin
sections and of SEM images allowed some inferences to be
made about the nature of the barite crystals in the
Zodletone deposits. The usual form of a barite crystal
is shown in Figure 2.7a. The only way chevron zoning of
the type seen so frequently in the Zodletone deposits
would seem to be by the expansion of the {110} form
faces. To allow expansion of these faces, faces of the
{011} form (which dominate over the {110} during normal
crystal growth; Seager, 1959; Sweet, 1930; Seager, 1953)
must atrophy in the course of crystallisation. The
result of such a change in habit would be a crystal such
as that shown in Figure 2.7b. In Figure 2.7b the
relationship between the forms and the appearance of the
crystal (as seen in thin section; Figure 2.6d). Changes
in habit during growth of barite crystals, with result-
ant alterations of appearance like those just mentioned,
have been documented by Seager and Davidson (1952), but
the cause of the habit changes has not been explained.

Fluid Inclusion Check. Ten grain mounts prepared
from the mature barite travertine were inspected (under
the guidance of Dr. David London at the University of
Oklahoma Geology and Geophysics Department) in an
attempt to see if there was any prospect for determining
homogenization temperatures for the barite crystals.

Figure 2.7 -- Barite Crystallography in the Zodletone
Deposits: (a) Generalised Barite Crystal (after Deer et
al., 1966) (b) Sketch of Mature Zodletone Zoned Barite
Crystal Showing Relationship Between
Forms and Appearance.

(a) GENERALIZED VIEW OF A SIMPLE BARITE
CRYSTAL SHOWING POSSIBLE FORMS

CHEVRON ZONING FROM SUCCESSIVE
EDGES OF GROWTH ON {110}

STRIATIONS PARALLEL TO {010}
FORMED EARLY, DURING GROWTH OF O

FINE STRIATIONS PARALLEL IN {010}

TRACE OF PERFECT
{001} CLEAVAGE

(b) MATURE BARITE CRYSTAL SHOWING
RELATIONSHIP OF FORMS TO APPEARANCE
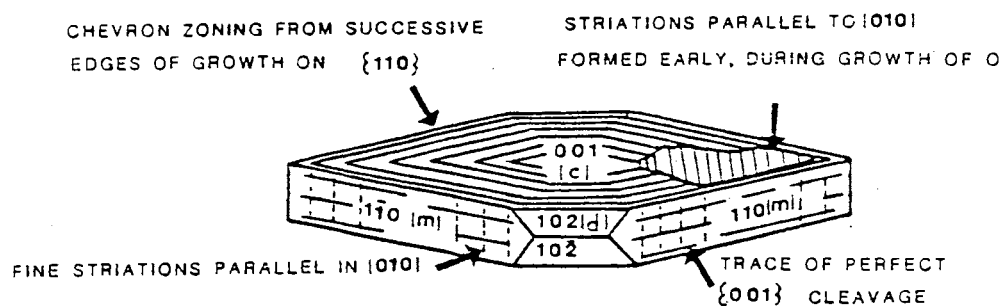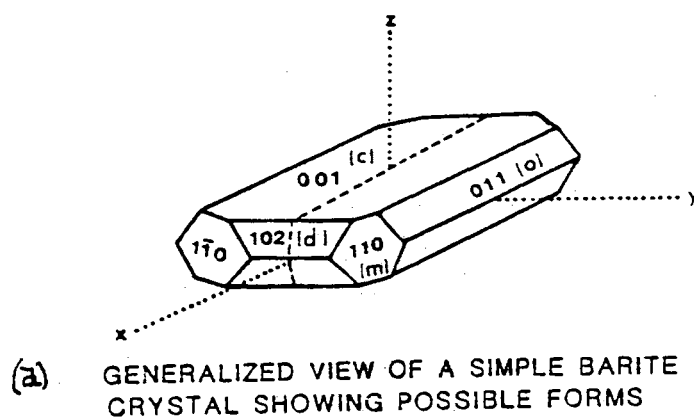
Such knowledge would have settled any doubts about whether the spring waters have ever been warmer than they are today. Unfortunately, the inclusions found were too few and too small to admit of useful scrutiny.

X - Ray Diffraction (XRD). Three samples from Zodletone (Z1, Z3 and Z4) were subjected to XRD analysis to determine mineralogy (see the Appendix). These were all samples of the white cement coating the branches and twigs which form the wall of the small cataract down which the runoff from the main spring falls to enter Saddle Mountain Creek (Figure 2.4). The d - spacings of the four strongest lines for each sample are given in Table 2.4 below. Tentative identifications of the minerals present are given. These are based on the data in the mineral powder diffraction data file (JCPDS, 1980).

- -

Table 2.4 -- XRD Results for Zodletone Samples.

Sample	d - spacings (4 strongest lines)	Mineral
Z1	3.040, 2.496, 2.097, 2.288	Calcite
Z3	3.040, 3.350, 2.100, 2.280	Calcite
Z4	3.354, 4.282, 2.461, 1.821	Low Quartz

- -

The cementing phases in the small waterfall at Zodletone are therefore calcite and low (alpha -) quartz. Low quartz is stable at atmospheric pressure below 573oC and is therefore the variety which is formed by springs, supporting a claim of primary origin for the quartz, although the inversion of high quartz to low precludes the use of this as sufficient evidence in itself.

<u>Scanning Electron Microscopy (SEM).</u> This was used to determine the mineralogy of one sample from Zodletone and to photograph several previously identified samples (see the Appendix). A sample of white, powdery sulphate from the seep line along the banks of Saddle Mountain Creek was analysed and determined to be barite. The morphology of the mineral was first identified and then its chemical composition was confirmed using the EDX facility. This was the first time present - day precipitation of barite at Zodletone was proven.

<u>X -Ray Fluorescence (XRF).</u> All elements with atomic numbers greater than 21 were checked for in three samples from Zodletone by Mr. M.L. Salmon at the Fluo - X - Spec laboratory, Denver, Colorado. Detection limits are listed in Appendix I. One sample of each of the three petrographically distinguished facies was analysed. Table 2.5 below lists the findings.

Table 2.5 -- Semi - Quantitative XRF Scan for

Elements with Atomic Numbers > 21 for Zodletone Samples.

Sample	Elements Present	Approximate Concentrations (ppm)
Unconsolidated	Cu	150
Barite	Zn	19
Travertine	Pb	380
	Fe	710
	Co	44
	Ni	18
	Ba	330,000
	Sr	8,000
	Ti	490
	Cm	190
Barite	Cu	88
Cemented	Zn	19
Calcareous	Pb	330
Tufa	Fe	710
	Ba	310,000
	Sr	7,900
Mature	Pb	670
Barite	Fe	360
Travertine	Ba	350,000
	Sr	5,000

Notes: If an element is not listed above it means either
(i) it has an atomic number < 21 and was not checked
for, or (ii) it was not present at a concentration above
the detection limit (Appendix I).

These XRF results show that as induration increases

so the complement of heavy metals falls. This is no

doubt due to the progressive elimination of unaltered

organic matter, which not only accomodates such ions as

Ni and Co as substitutes for Mg in chlorophyll but also

detains a wide variety of elements by surface adsorp-
tion. In the purer barite samples ("mature barite
travertine") the only ions detected other than Ba are
divalent cations compatible with the barite lattice. All
three samples are conspicuously radioactive; this
radioactivity is possibly due to decay of radiogenic
strontium and/or lead. In essence, the elemental
composition of these deposits is well within the bounds
of the predictable.

2.5 -- Discussion of the Origin of the Zodletone Water.

As outlined above ("Discussion" in Section 2.4.1),
all of the relevant geochemical and structural evidence
suggests that the spring water at Zodletone is invading
the shallow aquifer by leakage from deeper formations,
rising along a fault plane under confining pressure
(possibly aided by subsurface expansion of gases;
cf. Doughty Springs). The question raised by this model
is how the earlier evolution of the Zodletone water,
as a subsurface brine, gave it the character of a barium
- bearing brine suitable for precipitating the deposits
described above.

Barium migrates from the mantle into the geo-
chemical cycle near the Earth's surface by incorp-
oration in potassium feldspars, biotite and other K -

rich igneous minerals (Section 1.3; Rhodes, 1969). In the Wichita Igneous Province there are several alkalic rocks with high potassium feldspar contents. As would be expected some of these contain comparatively large amounts of Ba. One of these, the Carlton Rhyolite, contains up to 4251 ppm Ba in the Fort Sill section (Gilbert, 1982; p.15). Weathering of the potassium feldspar in such rocks would result in the production of a montmorillonite - dominated clay fraction during semi - arid periods of geological history, and in a kaolinite dominated fraction during humid periods. At neutral pH montmorillonite adsorbs Ba at about 70 meq/100g of clay while kaolinite can only bind about 10 meq/100g of clay (Grim, 1968). During the relatively dry Cambrian - Devonian period most of the sediments deposited in the Anadarko Basin where carbonate, but the Bois D'Arc and Haragan Formations of the Hunton Group both comprise argillaceous muds with skeletal fossil fragments (Ham, 1978, p.7). The clay fraction in both of these form-ations would have been montmorillonite - dominated at the time of deposition, and would therefore be carrying adsorbed Ba in all likelihood, which could be later released to saline ground waters by ion exchange. Carboniferous clastics were deposited during a humid interval of geological history, and hence their clay

fraction would be kaolinite - dominated, and would have little Ba in association with it. By contrast the overlying Permian clastics were deposited during a semi - arid epoch and thus had a montmorillonite - dominated clay mineralogy at the time of deposition, with Ba adsorbed in quantity. Contact of invading coastal waters (which were very rich in sulphate at the time, as the Blaine Gypsum attests) would result in precipitation of barite as the Ba and SO_4 met and mixed. Such would account for the origin of the celebrated sand - barite rosettes of Central Oklahoma, which occur in a zone roughly parallel to the Permian coastline (Ham and Merritt, 1944).

Some of the ground water in the Permian rocks could enter the underlying Carboniferous rocks by leakage. Collins (1969, p. 173) has found Ba in waters from Carboniferous rocks of the Anadarko Basin at concentrations up to 600 mg/L. Further leakage into the underlying Cambro - Ordovician carbonates could account for Ba rich waters in them. Ba enrichment in waters of these rocks could have occurred fairly early in their history as aragonite (present in ooids etc) inverted to calcite. Ba will fit into the orthorhombic aragonite lattice but not in the trigonal calcite lattice (Pingitore and Eastman, 1985). Any contribution to the

Zodletone waters from this source can only be affecting the modern spring composition if the rate of flow in the aquifer is <u>extremely</u> slow.

It would therefore seem that the barium content of the Zodletone waters is entirely explicable in terms of the geology of the Anadarko Basin. More detailed explanation of the evolution of the water is not relevant here, but can be expected to follow the general patterns for brine evolution described by Carpenter (1978).

2.6 -- Summary and Conclusions.

<u>Summary.</u> Barite travertine deposits occur at the north foot of Zodletone Mountain, Kiowa County, Oklahoma, where a suite of springs are discharging barium - rich (45 ppm) very saline (TDS = 9000) ground water. Pre - modern deposits of barite travertine (at abandoned spring positions to the west of the modern springs) are more extensive than the currently forming deposits, suggesting a waning of total spring discharge through time. This apparent waning could be (i) illusory, arising from a myopic view of the time over which precipitation of the pre - modern deposits occurred, or (ii) a function of genuine reduction in spring discharge due to lowering of permeability by sub - surface barite

precipitation.

Three principal types of barite travertine are recognised on petrographic grounds: (i) Unconsolidated barite travertine, (ii) Calcareous travertine with a barite cement, and (iii) Mature barite travertine.

Thermodynamic calculations demonstrate that the spring water at Zodletone today is saturated with respect to barite, and precipitation is apparently inorganic. Any stifling of barite precipitation is probably due to the sulphate reduction performed by purple sulphur bacteria (chromatiaceae) which can be seen in the main spring orifice, busily producing bubbles of H_2S gas.

The Zodletone water has the geochemical characterisics of an oilfield brine, and, according to its position in the Sulin classification of oilfield waters, it is of the type most often associated with hydrocarbon occurrence. In view of this, and in view of the anomalous quality of the spring water in comparison with other local ground waters, it appears that the Zodletone water has invaded the shallow aquifer from which it discharges by leakage from a deeper aquifer, under the influence of confining pressure. A possible focus for such leakage could be one or more fault planes of the Wichita Frontal Fault Zone, in which the springs lie.

The ultimate source for the barium in the spring water is the alkalic fraction of the Wichita Igneous Province. Barium is concentrated in potassium feldspars, biotite and other potassium bearing phases in igneous rocks. Weathering of rocks of appropriate mineralogy (e.g. the Carlton Rhyolite) through geological time would result in the transfer of Ba to sediments of the Anadarko basin in the various specific ways discussed above. Later contact of these sediments with deep, saline ground waters such as the Zodletone water could well result in Ba being taken into solution, to be precipitated later near the surface when sulphate is encountered, or when the solubility of $BaSO_4$ drops low enough for precipitation to commence (bearing in mind that barite is 200% more soluble at 1000 atmospheres pressure than it is at 1 atmosphere, the pressure at the Earth's surface).

Conclusions. This occurrence is possibly unique. Nowhere else in the world has barite been observed precipitating naturally from cool waters. The only other occasions on which precipitation of barite from such waters has been observed at all is in coal workings where Ba - brines have been artificially brought into contact with sulphate - rich ground waters. At the

Doughty Springs, Colorado, (Chapter 3), barium fixation is occurring through the agency of biota, and apparently not as inorganic barite precipitation.

The occurrence of this water, with its hydrocarbon - associated geochemical signature, in the Wichita Frontal Fault Zone suggests that exploration for oil and gas beneath the springs may prove fruitful. It must be noted that the water chemistry itself issues a "caveat" to any potential petroleum developers -- secondary recovery from wells in this area of Kiowa County should be performed with CO_2 (which increases barite solubility) or with water absolutely free of sulphate. Failure to do this is inviting barite scale precipitation if Zodletone waters are encountered at depth. While on the subject of the petroleum industry, it should be noted that barite is an important commodity in the drilling business because of its use as a weighting agent for drilling mud. It is my opinion that the barite deposits at Zodletone are too small to be economically exploitable, and that, even if they weren't, it would be a criminal act to destroy such a unique deposit of barite for the sake of short term profit.

A number of specific questions remain with regard to the petrology of the Zodletone deposit. Is the zoning

seen in the barite in thin section compositionally controlled, and if so, why? What causes the changes in habit seen in the Zodletone barite?

One broader question upon which reflection is required is whether this barite reflects subsurface development of a Mississippi Valley Type (MVT) lead - zinc ore deposit. A substantial deposit of sphalerite (ZnS) has been discovered in the Arbuckle Mountains, and west of it (i.e. between the Zodletone barite and the sphalerite) is an area of fluorite mineralisation (Dr. David London, Dept. of Geology, Okla. Univ., Norman, Personal Communication, 1986). This spatial distribution of the three minerals recalls the zoning seen in many MVT ore fields (e.g. in the Northern Pennine Orefield, Northern England, Solomon et al., 1971). Furthermore the fact that the barite at Zodletone is hosted on Palaeozoic limestone (the Arbuckle), the invariable host of MVT mineralisation can not be overlooked. Dozy (1970) postulated a genetic relation- ship between oilfield brines and MVT mineralising fluids (actually mentioning the Anadarko Basin by name, along with the McAlester Basin in relation to the MVT deposits in southwest Missouri).

The Zodletone occurrence is compared to the Doughty Springs (Colorado) occurrence in Chapter 4.

CHAPTER III

THE DOUGHTY SPRINGS, LAZEAR,
DELTA COUNTY, COLORADO

3.1 Introduction to the Geography of the Area

The Doughty Springs flow on the north bank of the
North Fork Gunnison River near Lazear, Delta County,
Colorado (NW1/4, NW1/4, Sec.11, T15S, R93W; Figure 3.1),
approximately 0.8 km (1 mile) east (upstream) of the
Main Unit of the Hotchkiss National Fish Hatchery and
1.6 km (1 mile) southwest (downstream) of the Chipeta
Unit of the Hatchery (which is currently in ruins after
devastation by a landslide in December 1981; Schuster
and Hurr, 1982). With Saddle Mountain and Mount Lambert
to the east and Grand Mesa to the north, the Doughty
Springs lie in a highland valley at 1585 M (5200 feet)
above mean sea level. The "Western Slopes" is the name
popularly given to the district of Colorado within which
the Doughty Springs lie, a district of semi - arid
sagebrush - covered mesas and river - cut canyons,
distinctly different from the glaciated mountain terrain

to the east.

The climate of Delta County typifies that of much of the western slopes district, with low precipitation, low humidity, abundant sunshine and widely ranging annual and diurnal temperatures (Cline et al., 1967). In parallel with the dominant air circulation, most winds blow from the west, but lose most of their moisture over the hills, leaving the North Fork Gunnison River Valley unvisited by rain for most of the year. Delta, the county seat some 34 km (21 miles) to the west of the springs, receives about 20 cm (8") of rain per year. Record highest and lowest temperatures are 41oC (106oF) and -33oC (-27oF) respectively but the mean annual maximum and minimum temperatures are a more moderate 37oC (99oF) and -22oC (-8oF) respectively.

Geologically, the Doughty Springs emanate from the Dakota Formation (Lower Cretaceous), one of several Mesozoic clastic formations outcropping in this area (Figure 3.2). Tectonically, this area forms part of the northern flank of the Uncompahgre Uplift, a structural positive which has been influential since at least Pennsylvanian times, separating the Paradox basin to the south - west from the Piceance Basin to the north - east (Curtis, 1960). Precambrian granitic rocks, such as the Pitts Meadow Granodiorite (Barker et al., 1976) form the

Figure 3.1 -- Location of the Doughty Springs.
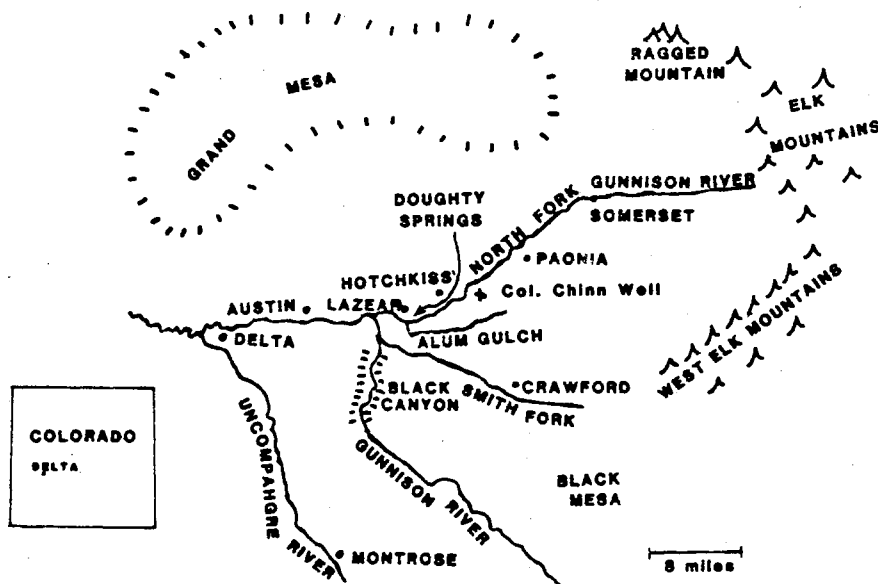
FIGURE 3.1 - LOCATION MAP FOR DOUGHTY SPRINGS

heart of the Uncompahgre uplift. As the Mesozoic clastic formations present around the springs are traced to the north - east they disappear beneath the Upper Cretaceous Mesaverde Formation (rich in coal, which is mined in eastern Delta County) and the Tertiary Green River and Uinta Formations, which contain some of the richest oil shale deposits discovered in the USA to date (Weeks, 1974). These rocks are all overlain by an irregularcoating of Pleistocene and Holocene outwash and other fluvial sediments (Hail, 1972a, 1972b; Junge, 1978a). Further discussion of the geology of the area is presented in later sections of this chapter.

Above and behind the springs lies the flat expanse of Rogers Mesa (Sec. 2, 3, 4 T15S, R93W; Sec. 32, 33, 34, 35, T14S, R93W). The first people to inhabit the Rogers Mesa area were Ute Indians, who regarded the Doughty Springs as sacred and used to leave trinkets in the large spring pools as prayer offerings (Headden, 1905a). After expropriation of the Ute in the late nineteenth century, the first person to settle on the land occupied by the Doughty Springs was the springs' namesake, Mr. Ray Doughty, who lived in the farm now owned by Mr. Carl James (NE1/4, NE1/4, NW1/4, Sec. 11, T15S, R93W), raising muskrats in pools north of the farm. Ray Doughty was in the habit of bathing in the

Figure 3.2 -- Geology of the Doughty Springs area.

QUATERNARY OUTWASH & ALLUVIUM [Q]

TERTIARY INTRUSIVES [Tip]

GREEN RIVER FORMATION [Tgr]

WASATCH FORMATION [Tw]

MESAVERDE FORMATION [Kmv]

MANCOS SHALE [Km]

DAKOTA FORMATION [Kdb]

JURASSIC FORMATIONS [J]

PRECAMBRIAN INTRUSIONS & METAMORPHICS

For full stratigraphic log see Figure 3.3

(Modified from Hall, 1972a, 1972b, and Hansen, 1968)

STREAMFLOW STATIONS (+)

S - Somerset
N - North Fork
G - Gunnison River
A - Alum Gulch
B - Austin
D - Delta

8 miles

"blue spring" (A2 spring in this account; the "bath tub" of Headden 1905a), in the belief that it was good for his arthritis (Mr. Jesse Reynolds, personal communication, 1985). Although the Doughty farm is now owned by Carl James, the strip of land occupied by the springs remains in possession of Ray Doughty's grandson, Tony Briggs of Craig, Colorado (Mr. Neal Ward, personal communication, 1985). Other houses on Rogers Mesa are widely scattered, with a small cluster around the Post Office/Store at the hamlet of Lazear. The nearest town of any size is Hotchkiss (Sec. 30, T14S, R93W).

3.2 Previous Related Studies in the Area.

First literary mention of the Doughty Springs was by Headden (1905a) who went on from a detailed description of the locality and water chemistry to describe deposits of alunogen at the site (Headden, 1905b) and to relate the existence of several notable springs in the surrounding area (Headden, 1909). Headden's (1905a, 1905b, 1909) papers make delightful reading, with the site descriptions (including the mentions of barite which spurred the present study) being rendered in charmingly grandiloquent Edwardian style. According to the bibliography of Colorado geology prepared by the

American Geological Institute (1976), Headden's (1905a) first paper is the first published work on Delta County geology.

Lee (1912) was the next to write on the local geology, preparing a report on the Somerset coal field of eastern Delta County. George et al. (1920) included summaries of the geochemistry of the Doughty Springs and the other springs listed by Headden (1909) in their summary of contemporaneous knowledge of Colorado mineral waters.

The first systematic study of the stratigraphic geology and water resources of part of Delta County was made by Weeks (1925). Apart from providing the first geological map for the district, Weeks (1925) recounted the abortive attempts to find oil by "wild cat" drilling near Austin. The well yielded no oil, but did evolve abundant gas (98% CO_2) and strongly mineralised water under artesian pressure.

Between the springs at Austin and the Doughty Springs lies an area of intense sulphur mineralisation known as the Gunnison Forks Sulphur Deposit, which was first described by Dings (1949) (and later by Sharps, 1965). Further scattered references to Delta County geology dealt with the coal district around Paonia (e.g. Johnson, 1952) and with the Mesozoic rocks of the

Figure 3.3 -- Stratigraphy of the Delta County area.

MAXIMUM THICKNESS (M)		
	Q	Quaternary sediments : Alluvium in valleys, outwash on hills (mostly from Grand Mesa)
	Tip	Intrusive porphyritic rocks, mostly rhyodacitic, as dikes, sills and laccoliths
	Tgr	Green River Formation: Calcareous siltstone, Shaley Marlstone and some oil shale.
530	Tw	Wasatch Formation: Varicoloured shale, sandstone and conglomerate
790	Kmv	Mesaverde Formation: Sandstones, shales and coals. Local lenses of conglomerate.
1330	Km	Mancos Shale Formation: Dark brown to grey shale. Juana Lopez Member is calc, sandstone.
80	Kdb	Dakota Sandstone Formation (includes "Burro Canyon Fm"). Indurated sandstone. Some shale.
150	Jm	Morrison Formation: shales with lenticular sands, silts and conglomerates.
70	Jw	Wanakah Formation: silty mudstones, cherty limestones, bedded gypsum and silty limestone.
34	Je	Entrada Sandstone Formation: Aeolian sandstone. Basal conglomerate has local provenance clasts.
	∧∧	REGIONAL UNCONFORMITY
	pCp	Pitts Meadow Granodiorite: Medium Gr. Plag. 45-55% Microcl. 2-18% Qz. 25-35% Bl. 5-15%
	pCm	Metamorphics: Include migmatitic gneiss, quartzitic gneiss, amphibolite and mica schist.

Periods (right margin): Quaternary, Tertiary, Cretaceous, Jurassic, PreCambrian

Adapted from Hansen (1968) and Hail (1972a, 1972b)

county (e.g. Young, 1959; Craig et al., 1955).

In the years 1968 through 1972 the first detailed geological maps of the area were published by the US Geological Survey (Hansen, 1968; Hail, 1972a, 1972b), and these maps remain the primary references on Delta County geology to the present day.

Cadigan and Felmlee (1975) and Cadigan et al. (1976) renewed interest in the Doughty Springs after a 70 year silence, inferring them to be late manifestations of a large extinct hydrothermal system in which the waters at Austin and the Colonel Chinn water well are also implicated.

Detailed mapping of the surficial geology of the North Fork Gunnison River valley was undertaken by Junge (1978a) who also investigated the geological hazard potential of the area (Junge, 1978b). Some of this potential was realised in December 1981 when a catastrophic landslide destroyed much of the Chipeta Unit of the Hotchkiss National Fish Hatchery (Schuster and Hurr, 1982).

During an assessment of the geothermal resources of Colorado, Pearl (1979) studied the Colonel Chinn Water Well (mentioned earlier by Headden, 1909; George et al., 1920 and Cadigan et al., 1976), concluding that it did not represent an economic resource.

Iorns et al. (1965) were first to describe the hydrology of the Gunnison River Basin in any detail. Pearl (1974) described ground water conditions in the Western Slopes area in general, while Brooks (1983) and Cox (1983) concentrated on the relationship between hydrology, coal mining, water quality and land subsidence in eastern Delta County. Most recently, a reconnaissance of ground water resources in the lower Gunnison River Basin was undertaken by Brooks and Ackerman (1985).

3.3 Field Geology of the Doughty Springs Area.

3.3.1 Introduction. The geological units exposed in the vicinity of the Doughty Springs are of two ages; Cretaceous and Quaternary. Deposits of both ages are significant aquifers, with the river - bank spring line in the Cretaceous rocks being paralleled by a cliff - top spring line at their contact with the overlying Quaternary outwash deposits.

Figure 3.3 summarises the stratigraphic sequence in the Delta County area. Of all the Mesozoic formations shown in the stratigraphic column, only two are to be found in close proximity to the Doughty Springs; namely the Dakota Sandstone Formation (Lower Cretaceous) and the Mancos Shale Formation (Upper Cretaceous). While the Mancos is apparently conformable on the Dakota, the Quaternary outwash deposits are unconformable on both.

3.3.2 The Cretaceous Rocks. Figure 3.4 is a graphic log of the Dakota Sandstone Formation, based on a section measured at the Doughty Springs. Although the boundary with the overlying Mancos ought to occur towards the top of this measured section it is grad- ational in character and therefore impossible to pinpoint unequivocally. As the Dakota is traced west

Figure 3.4 -- Graphic log of the Dakota Formation at the Doughty Springs.

REMARKS

Well bedded dull brown.

Silty shale , faun.
Massive , grey, with
some iron spots.
Weathers faun.

Dark grey with iron-stained
bedding planes.

Mottled grey , weathers brown.

Mottled grey .
Highly indurated.

Mottled grey with
orange iron spots.

Light grey, friable.

Grey and
iron stained,
weathers pale brown/faun.

clay silt   f   m   c
                sand
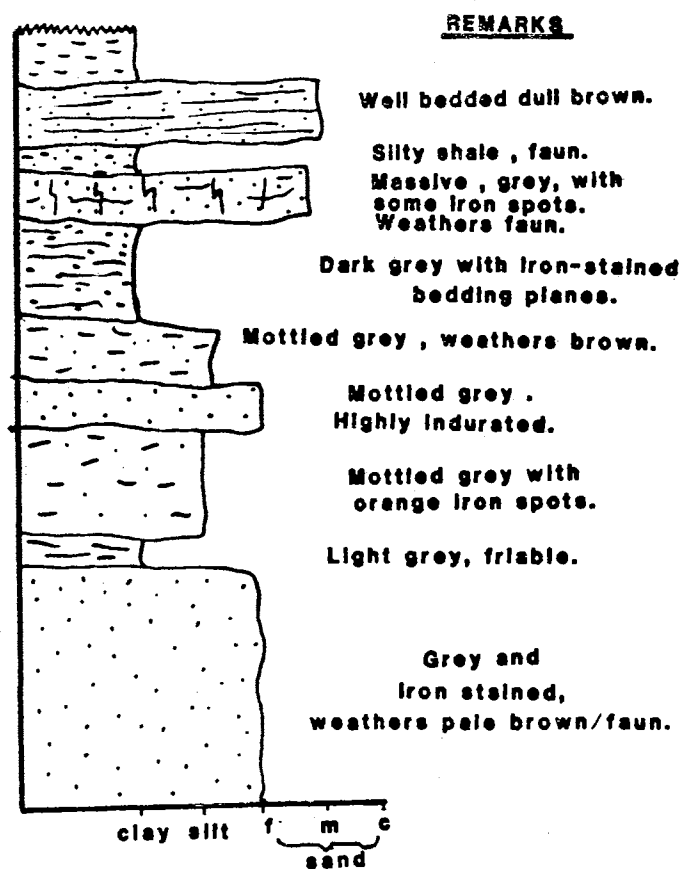
ward from the springs it is seen to become more sand - dominated.

Large, massive (? channel - fill) sand bodies occur near the Fish Hatchery as the number and thickness of shale breaks decrease. North of the Hatchery, on the stairway beside the Tommy Dowell Spring outlet, the ledge forming sandstone is a faun - grey, well - sorted, compositionally mature quartz arenite, with medium - sized subrounded grains. Carbonaceous smears are conspicuous in places. Cementation, which is reflected in friability, is extremely capricious -- here the sandstone will knock sparks off a geological hammer; there it will crumble in your hand. Iron staining is common. At this locality bedding dips to the northwest at about 14oN, with a strike of 055oN. Two conjugate sets of vertical joints are prominently developed here, with strikes of 004oN and 104oN. Joint spacings are on the order of 45 cm and joint apertures are typically 3 or 4 mm. Many of the joint faces are lined with fine grained white calcite which has a bubbly surface texture.

South of the North Fork Gunnison River, in Alum Gulch, basal channel - lag conglomerates (frequently alunitised) are found to underlie the channel sands. The uppermost sandstone horizon of the Dakota here contains

well preserved anastomosing wave - formed ripple marks. Large vertical fractures here trend 12°N and 104°N.

The Mancos Shale is very sparsely exposed. Where it is visible (e.g. south of Hotchkiss and the North Fork Gunnison River at NW1/4, NW1/4, Sec. 12 T15S, R93W) it is a blue - grey shale with three sets of joints. Two of these sets are conjugate and are spaced at around 8 cm. The third set bisects the angle between the first two and is spaced at about 20 cm.

3.3.3 The Quaternary Sediments. North of the North Fork Gunnison River the Cretaceous rocks are unconformably overlain by at least 18 M (60') of outwash deposits. These deposits are extremely variable in character. A small gravel pit northwest of the Doughty Springs (SW1/4, SW1/4, Sec. 2, T 15S, R 93W) contains well excavated sections through the outwash. Horizons of monomictic matrix - supported conglomerate, with clasts of vesicular lava (which can only have come from the mesa - capping lavas still visible in the distance atop Grand Mesa) and matrices of sand and gravel (in contrast to the clay matrices seen in equivalent conglomerates by the Tommy Dowell Spring), are interbedded with (0.6 - 1.0 M thick) lenses of sand,

silt or cohesive clay. Surficial efflorescent crusts of calcite can be seen on exposures of the outwash in the shallow railway cuttings east of Mr. Jesse Reynolds home (i.e. around NE1/4, SW1/4, SE1/4, Sec.3, T15S, R93W). On the steep access road immediately west of the Fish Hatchery, a 0.5 cm thick horizon of displacive fibrous gypsum, with fibres in vertical orientation (i.e. perpendicular to bedding), was found in a shaley member of the outwash about 1 M above the basal Dakota contact.

3.3.4 The Springs and their Deposits. Along the north bank of the North Fork Gunnison River east of the Hotchkiss National Fish Hatchery (SE1/4, SE1/4, T 15S, R 93W), the Dakota Sandstone cliffs are undergoing active erosion, and steep - faced coalesced talus cones have smoothed the angle between cliff and valley. Sulphur stains line many of the clasts in these talus slopes. A narrow strip of alluvial clay and sand, as yet un-impinged by landslide deposits, allows arough passage to be made along the river bank beneath the talus slopes. Amongst the reeds and rushes, which grow in abundance here, a few seeps of hydrogen sulphide - bearing water ooze out of the clay about 0.6 - 1 M above the high water stage of the river. This water is precipitating calcite crusts on the clay and plant material along the

seepage front.

As it is followed to the east, the apron of alluvium disappears beneath a thick landslide deposit, and further eastward progress can be made only by traversing the landslide talus. Irregular masses of native sulphur and white, brittle sulphate minerals occur as cavity linings (or cements) in this landslide deposit. Unlike the steep faced cones to the west, this landslide deposit is fairly flat topped and forms the first of two vegetation - free benches where springs are actively flowing today (Figure 3.5). This first bench is composed primarily of sandstone and shale clasts and other debris derived from the 40 M cliff above (in distinction from the second which is composed almost exclusively of travertine). It measures about 50 M long (E - W, parallel to cliff and river) by about 20 M wide (N - S, perpendicular to cliff and river). The lower part of the cliff here is composed of fine to medium grained, ripple - marked, cross - bedded, grey coloured, strongly jointed Dakota sandstone, with bedding dipping about 15o to the north (i.e. into the cliff). Joint faces in the sandstone are lined with native sulphur and a fine - grained, powdery, grey - black carbonaceous material. A number of seeps ooze out of the sediment in the eastern portion of the bench, many of them tributary

to the more substantial rivulet flowing from the spring which emanates from fractures at the foot of the cliff. The small channels are lined by white pastey alumino - sulphate deposits and native sulphur. Many surface pebbles have fringes of the white sulphate mineral also, as a surficial efflorescent crust (none of the mineral is found beneath the pebbles).

The first bench is separated from the second bench by a 20 M wide swampy zone of the landslide debris overgrown with grasses and reeds. Composed almost entirely of horizontal light grey travertine, the second bench measures about 120 M long (E - W) by 35 - 45 M wide (N - S), and rises about 6 M above the river surface. The edge of the travertine bench has already been substantially undermined by the river, into which large blocks of the bench material have fallen. Some collapsed blocks have been re - cemented to the bench by subsequent calcite precipitation.

Springs emanate from the inaccessible face of the bench on the river's brink and also at the back of the bench by the foot of the cliff. These cliff - foot springs appear to be the most active in terms of both discharge and mineral precipitation. Several notable springs emanate from fractures in the cliff in the eastern part of the bench, such as the A1 spring (Figure

Figure 3.5 -- Sketch Map of the Doughty Springs.
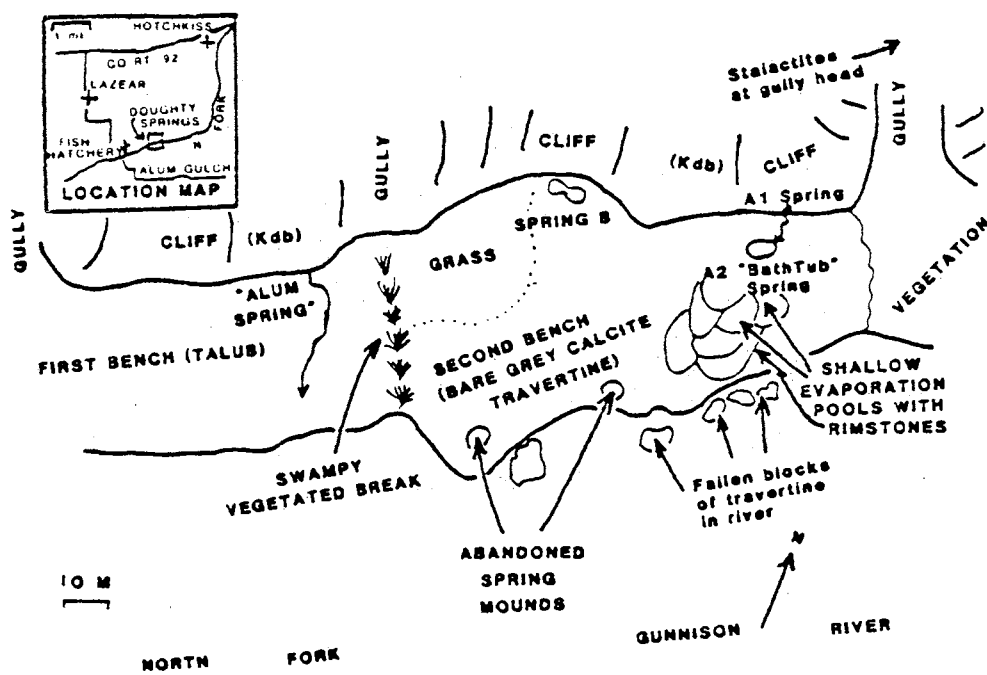
3.5), which has a discharge of 1.17 gpm (0.074 L/s).
Yellow algal blooms coat the orifice of this spring, and
these are clearly involved in the entrainment of mineral
precipitates. Water from the A1 spring discharges into
the "Bath Tub" (so named by Headden, 1905a). Water
samples from the "Bath Tub" are labelled as "A2" in this
report. This "Bath Tub" measures about 6 M long (para-
llel to the cliff) by 4 M wide and varies in depth from
0.45 M to 0.7 M. Suspended mineral particles in the
"Bath Tub" water impart a milky - blue hue to its
water. These   suspended   mineral   particles must be
precipitating in - situ since the A1 water is clear and
no agitation occurs where the A1 water flows into the
pool. Occasional overspills of the pool have resulted in
shallow sheet floods spreading over the surface of the
travertine bench to form terracettes of travertine as
mineral precipitation occurs. Well developed rimstones
mark the perimeters of these terracettes. Hydrochloric
acid caused the rimstones and all other components of
the bench to fizz, with the evolution of CO_2 gas,
implying that the precipitates are dominantly carbonate
minerals (in all likelihood calcite; but possibly
barytocalcite or even witherite).

To the west of these springs, at a distance of 60
or 70 M, is another small suite of springs which emanate

from fractures in the cliff as well as from cauldrons in the ground. Semi - solid light grey muddy precipitates line these springs (designated the letter B in this report; Figure 3.5).

Radioactivity of the second bench, as measured with a small hand - held geiger counter varied from a mean reading of 0.5 mR/hr (microRads per hour) at the edge of the Bath Tub spring to a mean of 0.08 mR/hr at the edge of the bench nearest the river.

Beyond the main bench to the east, there are a few small seeps and one main spring, which lies immediately west of the creek below the James farm (i.e. NE1/4, NW1/4, Sec.11, T 15S, R 93W). The orifice of this main spring contains a fireplace - like array of fused ribbed stalactites and stalagmites.

Fractures in the Dakota Sandstone Formation are very striking in the vicinity of the Doughty Springs, and two prominent gullies reflect large fractures (which do not appear to displace the strata) at the easterly and westerly limits of the second spring bench. At the head of the eastern gully is an overhanging bench of uppermost Dakota Sandstone bearing three remarkable arrays of stalactites and stalagmites. Two of these arrays are cloaked entirely in thick green moss, but one set remains unclothed. It is mostly composed of buff -

yellow calcite with a coral - like reticulate texture, attesting to the role of plants in its construction), but it has a thin surface coating of knobbly barite. Water from the cliff top spring line (i.e. not Doughty - type water, as demonstrated by its low conductivity of 900 microsiemens) cascades over these stalactites and stalagmites continually. Three partially fused stalactites are draped over the edge of the sandstone overhang, suspending 1 M down towards the three corresponding stalactites, which stand 0.7 M proud of the surface of the underlying sandstone ledge.

3.3.5 Other Relevant Features of Interest in the District. South of the river, opposite the Doughty Springs, travertine deposits are noticeably lacking. Small patches of white alteration can be seen upon close inspection of the sandstone in the cliffs above the river, but no H_2S bearing water is present. Small patches of efflorescent calcite surround dessication cracks in the soil near the mouth of Alum Gulch, recalling the calcite patches on and around the Quaternary outwash perched aquifer north of the river.

In Alum Gulch itself there are abundant signs of pre - modern alteration of the Dakota lithologies by "Doughty Type" waters. Several large sections of the cliffs on both sides of the creek are alunitised, with

white powdery minerals replacing clastic material. Most of this alteration is concentrated along a few large fractures, dying down as it is traced into the rock body away from fractures and bedding planes. It is possible to find individual clasts in some conglomeratic horizons which are half replaced, half virgin. Matrix sediment is usually totally replaced by alunite. Alunitisation is most intense in the lower half of the main sandstone body but is not restricted to it. Tiny green flecks observed in the white altered patches from place to place may be malachite.

White powdery surface efflorescences are seen in various other localities south of the river; notably by an abandoned stream channel (at NW1/4, SE1/4, NE1/4, Sec. 11, T15S, R93W) and on thin soil overlying the Mancos Shale (at NW1/4, NW1/4, Sec. 12, T15S, R93W). At these two localities the white powder will not effervesce when HCl is applied to them, and since they do not taste salty they would seem to be neither NaCl or $CaCO_3$. It is suspected that they are alkali sulphates. Both have abundant blades of selenitic gypsum associated with them.

By Colorado Highway 92 near Lawhead gulch (SW1/4, Sec. 26, T14S, R94W) a topographic hollow containing pools of water and white surficial calcite indicates a

shallow water table bounding calcium carbonate - bearing waters (like the $CaCO_3$ precipitating waters in the Tommy Dowell Spring and the other springs of the alluvial aquifer.

The river bank west of the hatchery shows evidence of the action of "Doughty Type" waters, with sulphur blooms and aluminium sulphate patches on the soil and in the cliff - forming sandstones. These sandstones (near the gulch at SE1/4, SW1/4, Sec.3, T15S, R93W) hosted an interesting array of quasi - stalactitic quartz, which has apparently formed between separated bedding planes.

3.4 A Hydrogeological Survey of Rogers Mesa and Vicinity.

Because of the close proximity of the Quaternary outwash aquifer to the Dakota sandstone aquifer which transmits the water to the Doughty Springs, a brief appraisal of the outwash aquifer on Rogers Mesa was attempted in order that possible interactions between the two aquifers might be better understood. This appraisal was undertaken largely by interviewing residents of the Mesa who own wells completed in the outwash.

Prior to settlement of Rogers Mesa by white

American people in the late nineteenth century, arable farming was not practiced on the Mesa, and after the arrival of the first white settlers agriculture was still impossible without irrigation. The father of Mr. Jesse Reynolds (now, at 73, one of the oldest lifetime residents of the Mesa) dug the first irrigation channel to conduct water from Leroux Creek (Sec. 22, T14S, R93W) to Rogers Mesa (J. Reynolds, 1985, personal communication). Leroux Creek typically dried up by mid - July each year, however, and so a more perenially reliable source of irrigation water was sought, eventually resulting in the construction of the Fire Mountain Canal to conduct water from Paonia Reservoir which lies some 20 km to the east. Domestic water supplies on Rogers Mesa come from two sources; all of those people living south of the Section 3 road receive water from a large municipal well 0.8 km north of the Lazear Post Office and about 100 m west of the road; everyone else on the Mesa is linked onto the system of the Rogers Mesa Domestic Water Company who abstract water from Leroux Creek about 10 km upstream from the water treatment plant and distribute it to 280 domestic fawcetts on the Mesa (Mr. Don Johnson, Rogers Mesa Domestic Water Company, Personal Communication, 1985).

Other wells on the Mesa are privately owned and

used mostly for horticultural irrigation. Mr. Dewey Blees has a well on his property (3203 Highway 92; at the common corner of sections 26 and 34, T14S, R93W) which reaches bedrock at 42.7 m (140 feet) and has a mean depth to static water level of 21.6 m (71 ft). At construction it had a specific capacity (Sc) of 10 gpm/ft of drawdown (suggesting that the transmissivity, T, of the aquifer at this point is on the order of 20000 gpd/ft, using the simple rule of thumb T $\approx$ Sc x 2000 of Dr. W.A. Pettyjohn, personal communication, 1986). A complete chemical analysis of the water obtained from this well shortly after completion was undertaken by the U.S. Geological Survey, and Mr. Blees provided a copy of their results to help this study (Section 3.4).

East of the Blees home, at the North Fork Nursery, (SE1/4, SW1/4, Sec. 26, T14S, R93W) an irrigation well was drilled which encountered bedrock at 36.6 m (120 feet) and static water level at 24.4 m (80 feet) (Mr. K. Anderson, Delta Drilling Company, Personal Communication, 1985).

Mr. Wayne Andrews has a well by his home just north of Lazear (at NE1/4, NE1/4, Sec. 4, T15S, R93W) in which mean depth to water is about 7.6 m (25 ft). Just south of Lazear is another small well in which the depth to water is reputed to be 12 m (40 feet).

Further chemical analyses of water from the outwash aquifer were furnished by Mr. Neal Ward (Manager of the Fish Hatchery). These are analyses of the water emanating from the Tommy Dowell Spring which is the source of water for the Hatchery (Section 3.4).

A small test well about 150 m east of the Hatchery buildings, which was drilled during preliminary investigations of the suitability of the site as a location for the Hatchery, held water at a depth of 2.667 m (8.75 ft). A period of relatively low flow in the North Fork Gunnison River, which runs only 15 m to the south of the well (and about 4.6 m lower than it), was selected as a suitable time for determining the quality of the water in this well which is an indication of the quality of ground water runoff to the river. After bailing the well for half an hour, the conductivity values of the water stabilised at 3200 micro - siemens. At the same time, the conductivity of the water in the North Fork Gunnison River was measured and a mean value of 980 micro - siemens was obtained. This strongly supports the notion that the ground water runoff into the north side of the North Fork Gunnison River (near the Fish Hatchery as well as at the Doughty Springs) is of Doughty Type (Section 3.5).

3.5 Laboratory Investigations.

3.5.1 Hydrogeochemistry. Two approaches were used in the laboratory evaluation of the hydrogeochemistry of the aquifer system which gives rise to the Doughty Springs; chemical analysis of water samples from the A1, A2 and B springs (using the techniques itemised in The Appendix) and scrutiny of temporal streamflow and quality data from unpublished records of the U.S. Bureau of Reclamation for various streams in the area (Figure 3.2).

Results. Table 3.1 summarises the chemical data obtained for the analysed samples. All data are given in both mg/L and meq/L, to allow their manipulation in various calculations and to allow them to be plotted on the Piper Diagrams (Figures 2.5 and 3.7). Published data are available for the chemistry of the Doughty Springs, although there is some locational ambiguity.

Discussion. Delineation of the aquifer responsible for the waters of peculiar chemistry in the Delta County area can be approached by an analysis of stream flow and quality records. During periods of low stream discharge most of the water in a stream channel will be ground water runoff (base flow). Hence a scrutiny of stream quality during low - flow periods can provide much information on the quality of local ground water

Table 3.1 -- Chemical Analyses of the Doughty Springs Waters.

Suite 1 -- Sampled 19th August, 1985.

		mg/L			meq/L	
Sample	A1	A2	B	A1	A2	B
Na	1000	1000	1200	43.5	43.5	52.2
K	36	38	35	0.92	0.98	0.89
Ca	200	100	220	9.98	4.99	10.98
Mg	14	29	28	1.15	2.38	2.30
Ba	1.4	2.1	2.1	0.02	0.03	0.03
Sr	3.0	3.0	3.1	0.07	0.07	0.07
Cl	670	670	800	18.9	18.9	22.6
SO_4	130	140	98	2.7	2.9	2.04
Alk.*	2349	2188	2480	38.5	35.9	40.65
TDS	3040	3050	3300			
Condy. *	3400	3500	3750			
pH *	6.6	7.0	6.8			
TOC *	17.5	21.5	20.0			

- -

C.A.B.				21%	5.3%	0.84%

Table 3.1 Continued.
Suite 2 -- Sampled 3rd October 1985.

mg/L

Sample	A1	A2	B	C
Na	871.8	908.2	921.5	145.2
K	36.0	38.4	34.8	17.1
Cu	0.004	0.010	0.018	0.007
Ba	0.369	0.484	0.621	0.157
Cl	637.2	675.1	787.6	41.58
SO_4	134.0	125.2	143.9	368.0
Alk. *	1067.8	2221.1	2410.3	683.4
Cond. *	4650	5000	5600	1600
ToC *	15	16	17	17
pH *	6.9	7.0	6.9	7.1

- -

Notes on Table 3.1

Suite 1 samples were analysed at the laboratory of the
Colorado Department of Health in Denver, Colorado. Suite
2 samples were analysed in the Water Quality Research
Lab (Zoology Department, OSU) for cations and the water
Lab (Geology Department, OSU) for anions by the author.
All parameters marked thus " * " were determined in the
field. Conductivity values are in microsiemens. C is a
sample of water from the cliff top stalactite locality,
and represents water from the perched outwash aquifer.
C.A.B. = cation - anion balance =[(sum of cations - sum
of anions)/sum of all ions] x 100 %. All quantities used
in C.A.B. determination are in meq/L. Cond. = Cond-
uctivity. Alk. = Alkalinity as HCO_3.

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(U.S. EPA, 1985).

Figure 3.2 shows the geology in the district around the Doughty Springs as well as the location of 6 stream gauging/quality sampling stations operated by the Grand Junction Projects Office of the U.S. Bureau of Reclamation. Unpublished data on discharge and water quality for these stations were made available by Mr. John Ozga of the U.S. Bureau of Reclamation. Isolation of low - flow quality data from the records provided reveals that the quality of water in the North Fork Gunnison River and Alum Gulch deteriorates rapidly as the streams cross the boundary between the Mancos Shale and the underlying Dakota Sandstone. North and east of the Doughty Springs, where the Dakota disappears beneath the Mancos, the Dakota is effectively a confined aquifer. The springs emanate very close to the point where the Dakota is first unconfined. Table 3.2 summarises the data on low flow and quality for the six stations studied for the years 1978 and 1981 through 1983. Low flows in the autumn were selected since the other low flow period (winter) is influenced by freezing of the river water. Extra details on the quality - runoff relations for each station are included in Table 3.2 for reference.

At Somerset, which sits at the contact between the

Table 3.2 -- Runoff - Quality Relations for the Gunnison River Valley in Delta County.

(See Figure 3.2 for station locations)

Date Station	Oct '78 cfs	TDS	Oct '81 cfs	TDS	Sep '82 cfs	TDS	Oct '83 cfs	TDS
Somerset	85	107	94	87	218	76	30	93
Alum Gulch	2	1848*	3	1979*	1.7	2736	8.2	2608
N. Fork	95	1425	80	1089	191	1224	400	1189
Gunnison	700	188	1150	141			510	104
Austin	580	421	1500	424	900	396	2000	311
Delta	650	706	1160	611	1180	624	1460	454

	Max. TDS (ppm)	Discharge at max. TDS	Discharge Min.	Max.	Mean
Somerset	167	750	30	3800	509
North Fork	2409	120	43	3660	453
Gunnison R.	1560	173	2.6	32050	1225
Austin	1150	950	60	13550	1727
Delta	1995	720	100	10000	1882
Alum Gulch	4670	0.1	0.1	35	6

- -

Notes
TDS = Total dissolved solids, in parts per million (ppm). All discharges in cubic feet per second (cfs).
* -- estimated from conductivity by the relation TDS $\cong$ 0.66 x conductivity.
- -

Mancos Shale and the overlying Mesaverde Formation (Junge 1978a), the total dissolved solids (TDS) content of the water never exceeds 167 ppm. In the North Fork Gunnison River, the water in the stream near the confluence with the Gunnison proper has a maximum TDS of 2409 mg/L -- showing a dramatic increase in mineral content as it flows over the Dakota. Where the extreme reach of Alum Gulch crosses the boundary between the Mancos onto the Dakota, the maximum TDS content of the stream (which contains little water at this point and thus reflects the quality of water in the Dakota fairly faithfully) is 4670 ppm, coincidentally at the lowest flow (0.10 cfs). Water in the Gunnison River just above the confluence with the North Fork has a mean TDS at low - flow of around 150 ppm, representing the chemical composition of ground water in the Morrison, Wanakah and Entrada Formations which underlie the Dakota.

These relationships clearly show that the Dakota Formation contains ground water of anomalous quality when compared to the other aquifers in the area. This implies reasonably effective isolation of the Dakota waters from the waters in the over- and underlying formations; in other words the Mancos Shale and the Morrison Formation function as fairly effective aqui-tards. This result is hardly surprising when the distribution of mineral springs in the North Fork

Gunnison River Valley is recalled; all lie within the outcrop of the Dakota and all evidence for their existence vanishes as the boundary with the Mancos is crossed. The direction of water movement in the Dakota is obviously from north to south, since all the spring activity is restricted to the north bank of the North Fork and Gunnison Rivers.

Alunitisation in the lower reaches of Alum Gulch opposite the Fish Hatchery attests that Doughty Type water once flowed through the sandstone there, although it clearly no longer does. On the other hand in the upper reaches of Alum Gulch where the Dakota emerges from beneath the Mancos for the first time (i.e. no Dakota is exposed in the river valley in a line extended to the north - parallel to flow in the aquifer - from this point) the ground water runoff is distinctly mineralised. South of the river (in Section 14 T 14S, R92W) the Colonel Chinn water well, which is drilled through the Mancos into the Dakota, encounters warm (42°C) mineralised water with a chemistry similar to the Doughty Springs (Table 3.3). Pearl (1979) erroneously attributes the source of water in the Dakota at this point to infiltration "at the outcrop area along the Smith Fork"; this is clearly absurd since the Smith Fork represents a focus of ground water discharge.

Table 3.3 -- Major Element Analyses of Water from the
Perched Aquifer (Tommy Dowell Spring) and from the
Dakota at Depth (Colonel Chinn Well) (in mg/L).

Ion	Tommy Dowell Spg.	Colonel Chinn Well
Ca	180	110
Mg	51	32
Na	89	570
K	--	41
Ba		4
Cl	6	400
SO_4	199	58
HCO_3	356	764
CO_3	0	0

- -

Notes : The Tommy Dowell Spring emerges from the perched
Quaternary Alluvium Aquifer and supplies the Hotchkiss
National Fish Hatchery, 0.8 Km west of the Doughty
Springs. The analysis given here is courtesy of Mr. Neal
Ward, Manager of the Hatchery. The Colonel Chinn Well
yields artesian water from the Dakota at 42 deg. C. This
analysis is from Bliss (1983).

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Rather, the water in the Dakota where it is confined beneath the Mancos south of the river has passed from north to south beneath the North Fork Gunnison River (in hydraulic isolation from the river). Similarly the mineralised water discharging from the Dakota into upper Alum Gulch (NW1/4, Sec. 13 T 15S, R93W) has passed beneath the North Fork Gunnison River confined beneath the Mancos (Figure 3.6a). Wherever the North Fork Gunnison has breached the Mancos to expose the Dakota, as at the Doughty Springs, the water migrating from the north discharges into the river as base flow and further movement of the mineralised water to the south of the river is forestalled by the imposition of this ground water divide (Figure 3.6b). Hence when erosion by the North Fork Gunnison River finally broke through the Mancos shale near the current location of the Fish Hatchery the water which had previously been alunitising the Dakota in what is now Alum Gulch was diverted into the North Fork Gunnison River as base flow. Hence the North Fork has been operating as a giant "switch" in this area over the last several hundred thousand years, gradually limiting the extent of Doughty Type waters as it pierces through the confining Mancos to tap them for base flow.

There can be no doubt that leakage is occurring

Figure 3.6 -- Schematic Cross Sections Showing the
Flow Patterns in the Dakota Formation with Respect
to the Mancos Shale and the Gunnison River: (a) Before
Mancos is Breached by River; (b) after Mancos is
Breached by the River.
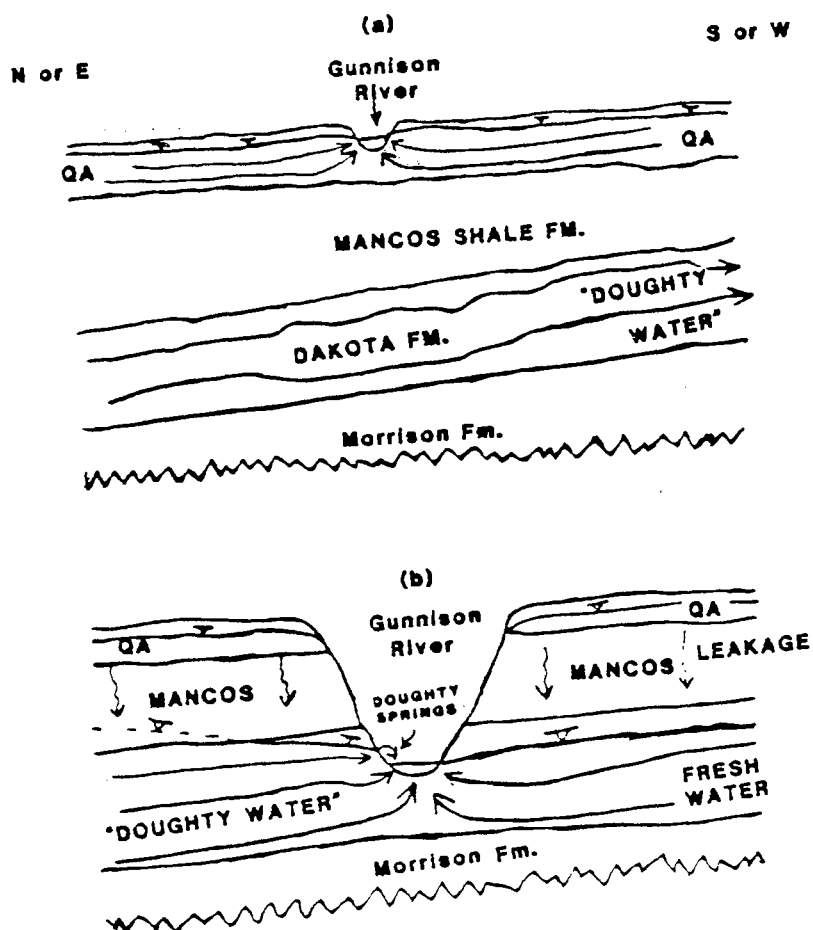
through the Mancos into the Dakota, given the fractured nature of the former as observed at NW1/4 Sec. 12 T 15S R 93W (Section 3.3.2), and the lowering of the potentiometric surface in the Dakota near the discharge focus along the North Fork Gunnison River. How extensive is this leakage? The Piper plot (Figure 3.7) shows no mixing trend characteristics between the water in the outwash aquifer (which would be the source of leakage) and the Doughty water, suggesting that any contributions to the water in the Dakota from downward leakage are very low. But if mixing is assumed, so that the Doughty Springs water is a resultant mixture of water from the outwash and some deeper water, mixing equations given in U.S. EPA (1985) can be used to work out the proportions of each water contributed to the final mixture. These equations can be written as:

$$Q = Q_p + Q_m \ . \ . \ . \ (i)$$

and $\qquad\qquad QC = C_m Q_m + C_p Q_p \ . \ . \ . \ . \ (ii)$

Where:

Q = discharge of Doughty Springs,

Q_p = component of discharge originating as leakage from perched aquifer,

Q_m = component of discharge originating as deep mineralised water,

C = Conductivity of Doughty Springs water,

Cp = Conductivity of water in perched aquifer,

Cm = Conductivity of deep mineralised water.

If the water in the Colonel Chinn water well is assumed to represent the deep mineralised water, then Cm = 3560 (Cadigan et al., 1976), Cp = 1017 (Tommy Dowell Spring; Neal Ward, Personal communication, 1985) and C = 3400. Hence:

$$3560Qm + 1017Qp = 3400(Qm + Qp)$$

thus $$Qp = 0.067Qm.$$

Now $Qp + Qm = Q$ (100%). Therefore $Qp = 6.3\%$ and $Qm = 93.7\%$ of the total water. In other words the perched aquifer can not be contributing more than 6.3% of the total water emanating from the Doughty Springs. If the Colonel Chinn water is representative of the water at depth, this sets a limit on the contribution made by leakage to the spring water.

Thermodynamic calculations on the water from the Doughty Springs show that A1, A2 and B are all super - saturated with respect to barite. Samples A1, A2 and B are all 0.02M solutions of NaCl, and in such a solution at 25oC the solubility product (Ksp) of $BaSO_4$ is approximately 2.1×10^{-9} (by interpolation in the data of Cowan and Weintritt, 1976). The saturation index (IAP/Ksp; where IAP stands for ion activity product -- in this case [Ba] [SO_4], with activities in mol/L) for

the three waters is shown in Table 3.4 below, along with the same ratio calculated for other waters in the Delta County area (using the analyses for the Colonel Chinn well and Austin Springs given in Cadigan et al., 1976). Note that the Austin Spring Water is a 0.12M solution of NaCl and hence a solubility product of 2.36 x 10-8 is used in the determination of the saturation index for the Austin sample. The results show that saturation with respect to barite is restricted to the Doughty Springs amongst the waters of the area.

When the analyses of the spring waters (Table 3.1) are plotted on a Piper diagram (Figure 3.7) they are seen to fall in the field of the "sodium - potassium - bicarbonate facies" as defined by the Morgan, Winner and Back (Freeze and Cherry, 1979, p. 252). This distinguishes them quite readily from the "sodium - potassium - chloride facies" waters at Zodletone (Figure 2.5). Since the dominant anion is bicarbonate rather than chloride, it would perhaps make more sense to review the thermodynamic stability of barite in the system Ba - SO_4 - H2O - Na - HCO3 rather than in the NaCl solutions considered above. While barite solubility is known to be enhanced by the presence of bicarbonate in solution (Ham and Merritt, 1944; p.8) the only published attempt to quantify this behaviour (Davis and

Figure 3.7 -- Piper Diagram Showing the Nature of the
Doughty Springs Waters Relative to Perched Aquifer
Waters.

T - Tommy Dowell Spring
(perched aquifer).

A1 ⎫
A2 ⎬ Doughty
B ⎭

% of total (meq/L)
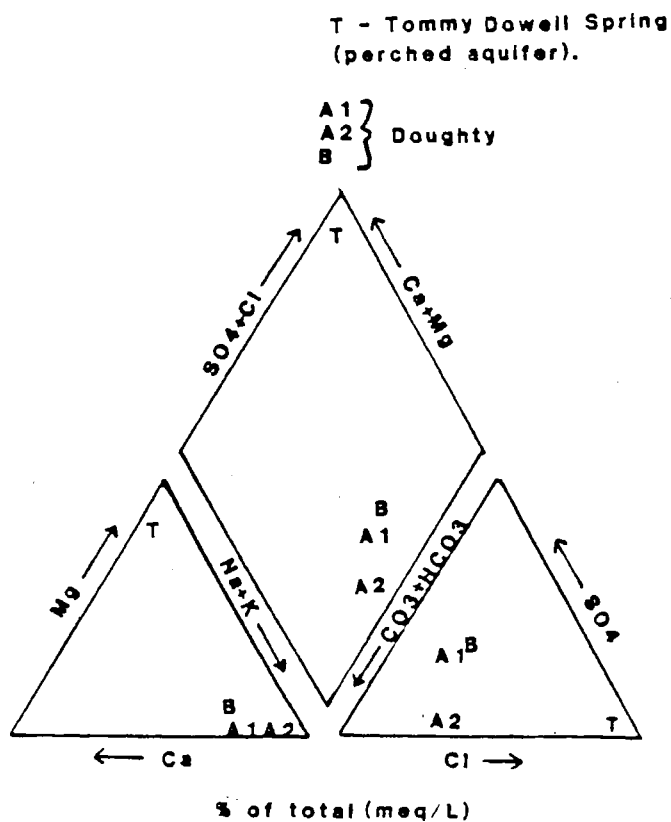
Collins, 1971) was hindered by the removal of Ba from solution by precipitation with CO_3^{2-}, which forms by dissociation of bicarbonate ions. Hence data on the effect of bicarbonate ions on barite equilibria are not available as they are for the effects of NaCl molality.

Using a simple routine devised by Dr. A.W. Hounslow (Personal Communication, 1985; the scheme is based on the work of Garrels and Mackenzie, 1967) it is possible to investigate possible evolution paths for the Doughty water in terms of the mineral weathering reactions in which it may have been involved. To do this, meq/L concentrations of various major chemical species are compared in an established order (SiO_2 is converted to millimoles per litre for the process by division of the mg/L concentration by 60, the relative molecular mass of SiO_2). For all three spring samples the same results were found:

Na > Cl . . . This, along with the relatively low TDS, suggests that there has been little or no contact with evaporites.

Ca > SO_4

HCO_3 > 10 x SiO_2 . . . This suggests that carbonate weathering has dominated the evolution of this water rather than siliciclastic weathering

Table 3.4 -- Saturation Indices (IAP/Ksp) for Delta

County Mineral Waters with Respect to $BaSO_4$

Sample	IAP $[Ba][SO_4]$ (moles/L)	IAP/Ksp
A1	1.33×10^{-8}	6.3*
A2	2.3×10^{-8}	10.9*
B	1.6×10^{-8}	7.4*
Austin	2.3×10^{-9}	0.0099
Chinn	1.7×10^{-8}	0.74
A1C	2.5×10^{-8}	11.9

- -

Notes : Austin, Chinn and A1C were calculated from analyses given in Cadigan et al. (1976). A1C is an analysis of the A1 spring water. * means that these are minimum values because they assume $25^{o}C$ whereas the springs are at $16^{o}C$, at which temperature $BaSO_4$ is even less soluble than it is at $25^{o}C$. A1, A2 and B were calculated from the data in Table 3.1.

$(SiO_2$ value 17 mg/L = 0.28 mmoles/L from Cadigan et al., 1976, p. 24, sample DEL6).

This inferred role of carbonate minerals in the evolution of the Doughty waters begs the question of which formations in the possible recharge areas contain suitable minerals in significant quantities. Inspection of geological maps (Hail, 1972b), stratigraphic columns (e.g. Figure 3.3) and sedimentological descriptions for the area north and east of the springs (i.e. the Piceance Creek Basin and its periphery) reveals that the Mancos shale locally contains a calcareous sand/shale member (the Juana Lopez Member) and that the Green River Formation (Eocene) is largely "calcareous siltstone and shaley marlstone" (Hail, 1972b). Recharge to the Dakota by leakage through these formations would inevitably lead to the infiltrating water gaining the signature of a carbonate type water. Discussion on the recharge of the Dakota in this region is reserved for Section 3.6.

3.5.2 Biota Identification. Samples of algae and other biota were taken from the A1, A2 and B springs as well as from the B outlet brook and from one of the evaporating pools of water retained behind a teracette on the second bench surface. Dr. David A. Francko of the OSU department of Botany inspected the samples and

taught the author the distinguishing features of the various flora present. Two of the samples were scanned for elements with atomic numbers greater than 21 by X - Ray Fluorescence (Section 3.5.3), and their Ba contents are noted here to allow discussion in an appropriate place.

Results

A1 Spring

No macroflora present. Microflora occurs as a pale yellow coating on the cliff wall beneath the spring orifice. Under the microscope the microflora is distinguishable as a monoculture of Oscillatoria (?) sp., which is present as small unsheathed algal cells (about 2 um in diameter). The white coating on the algae does not effervesce with HCl and is thus not a carbonate. Bulk sample Ba content = 78000.

A2 Spring

Macroflora is Chara sp., a green alga, which has nodular calcite precipitates on its vascular components. Complex microflora. Includes three species of blue - green algae; Spirulina sp., Oscillatoria sp., and Anabeana sp., none of which precipitate calcite. In addition several varieties of diatoms are present (including ?Navicula sp. and Pinularia sp.).

B Spring

Mud from the spring orifice has a microflora only, which consists of abundant microflagellate (?green) algae (3 - 5 um in diameter), abundant protozoans and a few diatoms (<u>Navicula</u> sp.). One filament of <u>Spirulina</u> was observed. Ba content of total sample = 170000 ppm.

B outlet brook

<u>Chara</u> sp. dominates the macroflora. Mats of <u>Spirulina</u> are also abundant. The microflora includes diatoms (<u>Navicula</u> sp. and <u>Cymbella</u> sp.), microflagellate green algae, bacteria and protozoans.

Evaporating Pool

The microflora in this pool is very similar to that in the "Bath Tub" (A2) from which it is replenished with water. Diatoms (<u>Pinularia</u> sp. and <u>Navicula</u> sp.) are extremely abundant.

<u>Discussion.</u> Literature dealing with biological accumulation of barium and barite was reviewed in Section 1.3. It was noted there that the most vigorous barium accumulator amongst more than 50 plants from alkaline earth - rich soils studied by Bowen and Dymond

(1955) was the green alga <u>Chara</u> <u>vulgaris</u>. Algae of the same genus (<u>C. fragilis</u>) have been found to contain statoliths of barite (Schroter et al., 1975). Thus it was with no little excitement that the discovery of <u>Chara</u> sp. as the dominating member of the macroflora in the "Bath Tub" (A2) and in the B outlet brook was greeted. Charophyta have played a role in rock - building since at least late Devonian times (Johnson, 1954) with the forerunners of modern <u>Chara</u> sp. first appearing in Pennsylvanian times. Ironically enough, the finest body of fossilised <u>Chara</u> is a unit of the Morrison Formation (i.e. the formation which immediately underlies the Dakota) known as the Chara Limestone, which outcrops near Perry Park, Colorado. Scholl and Taft (1964) described the role played by algae (mostly blue - green) in the formation of calcareous tufa at Mono Lake, California, and Suganuma (1928) discussed how cyanophyceae algae might be implicated in the formation of the plumbiferous barite travertine at Akita, Japan. No reference to the role of <u>Chara</u> in the formation of travertine appears to have been made, but the fact that <u>Chara</u> is a barium / barite accumulator "par excellence" amongst algae makes its presence in the Doughty Springs very interesting. Freshwater protozoans, such as are found in the B spring and outlet, have been found to

accumulate barium in two English lakes (Finlay et al., 1983). Perhaps similar behaviour accounts for the fact that the B orifice mud contains 17 wt% (170000ppm) barium. The 7.8 wt% Ba noted for the A1 algal mush suggests that <u>Oscillatoria</u> sp. is also accumulating barium. Concentration factors for barium for samples A1 and B over the spring water content are 55,714 and 80,950 respectively -- which compare extremely favourably with the concentration factors of up to 200,000 for Ba uptake from solution reported for the freshwater green algae <u>Ankistrodesmus</u> sp. and <u>Selenastrum</u> by Mann and Fyfe (1984).

3.5.3 Petrology of the Doughty Deposits. Petrographic

and geochemical studies were made on the various solid samples collected at the Doughty Springs. Thin sections were prepared by the Mineral Optics Laboratory, Winchester, MA. X - ray diffraction analyses were run in the geology department, OSU. Geochemical analysis was restricted to semi - quantitative x - ray fluoroscopy to determine all elements with atomic numbers greater than 21. These various laboratory techniques are reviewed in some more detail in the Appendix.

Petrography

None of the thin sections from the Doughty samples revealed any barite textures comparable to the beautifully developed textures seen in the Zodletone samples (Section 2.4.2). Indeed only three of the thin sections contain barite, and even then it is in very small quantities. The brief descriptions which follow show that the studied samples are remarkable more for what they don't contain than for what they do.

Sample 24a -- travertine from the rim of the A2 "Bath Tub" spring.

This sample consists almost entirely of organic matter altered into carbonate (presumably calcite, although aragonite or even barytocalcite can not be ruled out on petrographic grounds alone). Most of the carbonate is micritic but sparry varieties (<0.5 mm in diameter) occur around the perimeters of large pores. Barite is very sparse in the rock, occurring as tiny spherules (about 0.2mm in diameter), plugging pores, and as mats of needley crystals (up to about 0.3 mm in length), replacing vascular plant material along with acicular calcite. Undulose extinction is characteristic of this barite, but no chevron zoning is visible (in contradistinction to the Zodletone barite; Section

2.4.2). Barite can not account for more than 1 or 2% of the rock. Quartz grains are thinly scattered throughout the sample, the result of detrital influx from the cliffs of Dakota sandstone behind the springs.

Sample 31 -- Stalagmitic deposits from the cliff top behind the springs.

This consists of micritised plant roots and stems cemented by drusy sparite. Barite is present as a 0.25mm thick surface coating on the stalagmite. Extremely fine grained, only the birefringence of the barite serves to distinguish it from the micrite. A former growth face on the speleothem is demarcated by a layer of iron oxide staining. A second surficial coat of barite marks this face also, although its development is more sporadic than it is on the present outer surface. The vascular material in this sample is considerably more slender than that seen in sample 24a, with tubule walls rarely exceeding 0.2mm in diameter. It is unusual to see plant material play such a central role in speleothem growth. The only other component of this deposit is a little detrital quartz.

Sample 30 -- A1 spring orifice indurated travertine

Similar in many respects to the two samples just described, this rock is composed mostly of micritic

calcite after organic matter with patches of drusy sparite cement. The organic matter in this rock is generally less bulky than that seen in 31 and 24a -- which is in accordance with the descriptions of the biotic assemblages for each spring in Section .2 above. Detrital quartz is present as usual. Barite occurs as small patches (displaying pseudo - uniaxial "interference figure - like" undulose extinction) intimately associated with surface organic matter, of which it appears to be an alteration product. Individual crystals measure < 0.3mm in diameter.

Sample 3 -- Indurated tufa from an abandoned spring position 10M east of second bench.

Completely micritic, this rock contains well preserved diatoms.

Sample 10 -- Dakota sandstone from Tommy Dowell Spring.

Compositionally and texturally supermature quartz arenite. Well rounded grains about 0.5mm in diameter with ubiquitous development of syntaxial overgrowths.

Sample 13 -- Pseudo - stalactitic quartz from gulch west of hatchery.

Identical to Sample 10, save for the presence of an extremely fine micrite generation as a final cement on the grains. Suggests that the stalactitic shape is a

coincidental erosional form rather than a depositional texture.

X - Ray Diffraction Results.

Five samples form the Doughty Springs were analysed by XRD. Table 3.5 gives the results. As usual, reference should be made to the Appendix for the method. Mineral identification is based on data in JCPDS (1980).

- -

Table 3.5 -- XRD Results for Samples from the Doughty Springs.

Sample	d spacings for strongest lines	Mineral Identification.
1	3.03, 1.87, 2.28, 1.91	Calcite
7	3.03, 1.91, 2.28, 2.49	Calcite
11	4.24, 3.65, 2.90	Gypsum ? (Tamarugite ?)
20	7.62, 3.80, 3.34, 4.29	Quartz + Gypsum? (Brushite ?)
15	8.30, 4.61, 5.48	Gypsum + Montmorill- onite? (Sauconite ?)

- -

Discussion

Samples 1 and 7 are from the A1 spring orifice and the edge of the travertine bench respectively and hence it is not surprising that they are both calcite.

Sample 11 is from the gulch 1/2 mile west of the

Hatchery (SW1/4, Sec. 3, T15S, R93W). It was supposed to be alunite or alunogen at the time of collection because of its white powdery nature (which resembles the nature of both of these minerals found elsewhere in the area). The diffraction pattern, however, indicates it to be Tamarugite. Palache et al. (1951) note that Tamarugite is a monoclinic mineral with a chemical formula of $[NaAl(SO_4)_2.6H2O]$. This formula is similar to those of alunogen $[Al_2(SO4)_3.18H2O]$ and alunite $[KAl3(SO4)2(OH)6]$ with the major difference being in the presence of sodium rather than potassium and in the extent of hydration. Tamarugite is typically formed "under arid conditions by the oxidation of sulphide in aluminous and alkali - rich environments" (Palache et al., 1951; pp. 466 - 467), and has been noted to occur with alums in a sulphur cave at Miseno, near Naples, Italy. It is a dehydration product of Soda Alum. It thus seems that Tamarugite might be reasonably expected to occur in the setting in which it was found; the absence of spring water at the present time from the locality where it was collected might have given it a chance to form as an alteration product of a sodic alum precursor. It must be stressed that such an identification is not unequivocal since the diffraction pattern could well be a distorted gypsum pattern.

Sample 20 is another white powdery mineral from a selenite - bearing patch occurring on thin soil over-lying the Mancos Shale south of the river at SW1/4, NW1/4, Sec. 12, T15S, R93W. The XRD signature suggests a mixture of gypsum and quartz, or else the mineral brushite [$CaHPO_4.2H_2O$]. The paragenesis of this mono-clinic mineral is generally as efflorescences and cavity linings associated with phosphate deposits (Palache et al., 1951; pp. 704 - 705). If this mineral is indeed brushite (a point on which independent confirmation is required) the source of phosphate is probably from fertilisers used on the farms up hill from here, which would contribute phosphate to the ground water. Calcium occurs as the sulphate (selenitic gypsum) in fractures in the Mancos Shale in many places in Delta County (Weeks, 1925; p. 23) -- an obvious source of readily mobilised calcium for ground water in the Mancos Shale.

Sample 15 has the XRD pattern of Sauconite, which is a zinc - rich smectite (montmorillonite). Its chemical formula is $(Zn, Mg)_3(Si, Al)_4O_{10}OH_2.XH_2O$. Deer et al. (1966) note that smectites such as sauconite have been found as hydrothermal alteration products around metalliferous veins or deposits, and by hot springs and geysers. In its position as a cement for the first bench talus, in close association with the Doughty Springs,

sample 15 is a very interesting occurrence of this clay (if the identification is valid). SEM analysis of Sample 15 produced further interesting results which suggest that the XRD signature here may be a composite signature from copiapite and gypsum.

Scanning Electron Microscopy (SEM)

The procedure used is briefly reviewed in the Appendix. Four samples from the Doughty Springs were analysed optically and chemically using this method.

Sample 15 -- Cement from First Bench Talus.

This is the sample which gave a "sauconite" signature under XRD analysis. When viewed under the SEM (up to 750x magnification was used) it is seen to be composed of several different crystal types, notably a suite of "stobby" crystals and a suite of platey / needly crystals. Both share a chemistry dominated by S, Fe, Al, Mg, and Mn (in decreasing order of abundance). Obviously some sort of iron magnesium sulphate, comparison of the appearance and XRF signature of the sample with those in Welton's (1984) SEM Petrology Atlas suggested that the mineral is in fact copiapite [(Fe, Mg)$Fe_{43+}(SO_4)_6(OH)_2.20H_2O$; Triclinic]. Palache et al. (1951) mention that copiapite has a paragenetic association with alunogen and other sulphates, often

forming as an alteration product of sulphides such as pyrite. It is mentioned as occurring in association with hydrothermal springs at Steamboat Springs, Nevada, and at Sulfur Bank Hot Springs in Lake County, California. Barite occurs in small quantities within Sample 15 (proven by XRF), as surficial crusts.

Sample 30 -- A1 orifice travertine

Much of this deposit was seen to comprise unaltered biota, including diatoms and algae. All had a chemistry dominated by Cu, Zn, Ca and Fe, which are presumably combined as carbonates to some extent judging from the readiness with which this sample fizzes under treatment with hydrochloric acid. Gypsum and quartz were also identified.

Sample 24a -- travertine from the edge of the Bath Tub.

This sample was very uniform in texture and mineralogy -- a reticulate mass of calcite. Some of the calcite crystals have a surface coating of MnO.

Sample 13 -- Pseudo - stalactitic quartz from gulch west of hatchery.

This sample was inspected to see if any species besides the quartz seen in thin section could be identified. The result is that nothing except quartz was identified.

X -Ray Fluorescence (XRF)

Ten samples from the Doughty Springs and environs were analysed by semi - quantitative XRF (the Appendix), for all elements with atomic numbers greater than 21, at the Fluo - X - Spec Laboratory in Denver, Colorado. Table 3.6 below summarises the results.

Table 3.6 -- XRF Scan of Doughty Springs Samples for all

Elements with Atomic Numbers > 21.

(All values in ppm)

Sample	11	14	15	20
Element				
Cu	85	80	270	18
Zn	590	18	630	*
Pb	*	*	100	*
I	*	58	*	*
Fe	3700	21000	100000	2000
Co	200	*	*	*
Ni	850	55	190	*
Rb	*	68	*	*
Ba	*	900	*	330
Sr	16	1500	87	1400
Ti	510	520	170	*
Zr	*	400	78	*
V	*	*	85	*
Cr	160	66	180	*
Mo	21	*	38	*
Mn	3600	260	740	*
Y	62	23	27	*

Table 3.6 Continued.

Sample	26	28	30	24a
Element				
Cu	*	90	340	*
Zn	*	30	42	42
Fe	1200	1400	4000	1400
Ni	*	44	70	*
Rb	43	47	*	*
Ba	240000	3300	21000	52000
Sr	4100	4600	5400	4500
Ti	1100	*	*	*
Cr	*	120	*	*
Mo	*	20	*	*
Mn	580	1400	1400	1900
Y	*	66	*	*

Table 3.6 Continued.

Sample	A1	B
Element		
Cu	69	200
Zn	*	17
Pb	100	200
Fe	1800	4300
Ni	42	32
Rb	*	94
Ba	78000	170000
Sr	2200	2600
Mn	120	350

Notes: * -- means not present above the detection limits (see the Appendix). Sample identities:
11 - White powder mineral from gulch west of hatchery.
14 - Carbonate crust from seepage face west of first bench. 15 -- Cement from first bench talus.
20 -- White crust from sth. of river (NE1/4, SE1/4, NE1/4, Sec. 11, T15S, R93W). 26 -- Solid deposits from B spring orifice. 28 -- Wet rimstone from bench top.
30 -- A1 spring orifice travertine. 24a -- Travertine from edge of Bath Tub (A2) spring. A1 -- algally entrained minerals from spring orifice. B -- Semi - solid sample of light grey protozoan mud from orifice of spring B.

3.6 Discussion of Results.

The meaning of the Al and B results in terms of bioaccumulation of Ba was discussed above in Section 3.5.2, where it was noted that <u>Oscillatoria</u> sp. in the Al spring has concentrated Ba up to 57,714 X the ambient water concentration and that freshwater protozoa in the B spring have even exceeded this amount of concentration, with a 80,950 X concentration factor for Ba over water. Other concentration factors include 180,000 for Fe; 10,000 for Pb; and 733 for Sr (Al spring). The range of Ba concentrations for the Doughty deposits is as follows: 2.1 wt% (Al spring orifice travertine); 5.2 wt% (edge of bath tub); 7.8 wt% (Al algal mush); 17 wt% (B algal mud) and 24 wt% (indurated B spring orifice deposits). When these samples are treated with HCl, however, they effervesce merrily, implying that the barium they contain is combined as carbonates rather than as sulphates. In other words the mineralogy of these barium deposits at the Doughty is not barite, but barytocalcite (a monoclinic Ba - Ca carbonate) or alstonite (an orthorhombic Ba - Ca carbopnate, apparently in solid solution series with witherite ($BaCO_3$) and aragonite ($CaCO_3$) which are both orthorhombic. Palache et al. (1951, p. 219) say that they consider alstonite a "double salt" with witherite and aragonite

on crystallographic and thermodynamic grounds, but Deer et al. (1962, p.320) state without any qualification that ". . . alstonite .. is a distinct species and not an isomorphous mixture of aragonite and witherite". All analyses of barytocalcite fix its Ba concentration at 50 - 52% (Palache et al., 1951) and there are no monoclinic $BaCO_3$ or $CaCO3$ with which it could enter into solid solution. It would therefore seem that the mineralogy in the B spring at least ought to be orthorhombic -- i.e. that the carbonate which contains up to 24 wt% Ba is an aragonitic alstonite, which would incidentally occupy positions in the solid solution series never before observed.

Further aspects of the geochemistry of these solid samples will be discussed in the following section, in which the genesis of the Doughty waters is considered.

Origin of the Doughty waters. Due to the mythology surrounding springs it almost seems blasphemous to attempt to rationalise their occurrence. Any trepidation at adopting the role of iconoclast dissipates fairly rapidly when it becomes apparent, as in this case, that the springs are loathe to bare their souls to rational analysis.

With the exception of tiny amounts of volcanogenic water, all ground water begins its term in the sub-

surface as recharge -- infiltrating surface waters, ultimately originating as rainfall. It is therefore reasonable to pose the question "where does the Doughty water recharge?". In answering this question it is easiest to begin by stating where it does not recharge. To determine this it is necessary to ascertain the boundaries of the ground water basin. The field relations at the springs demonstrate that the waters discharging there flow from the north and north - east in the Dakota Sandstone. Immediately north and north - east of the springs, however, the Dakota disappears beneath the Mancos shale, which in turn disappears beneath the Mesaverde Formation and the other Mesozoic and Cenozoic formations shown on Figure 3.3. Due north, the formations enter a synclinal structural trough known as the Piceance Creek Basin. This basin is not a topographic basin, however; it is overlain by the bulk of Grand Mesa, the most spacious table top mountain in the United States. The disposition of ground water basins generally conforms to the disposition of surface water basins on a regional scale. Topographic divides are surface watrer divides, and therefore usually ground water divides also (particularly where shallow infiltrating ground water is concerned). Hence the boundaries of the basin in which the Doughty waters arose can be easily picked off a

topographic map of western Colorado. When the boundaries of the basin so defined are compared with a geological map (Burbank et al., 1935) it is found that the nearest points at which the Dakota re - emerges from the sub - surface are already beyond the boundaries of the ground water basin in which the Doughty waters formed (Figure 3.8). Hence any recharge to the Dakota within this basin must come from leakage through the overlying formations.

Is there any geochemical evidence as to which formations the water passed through on its way to the Dakota? As mentioned in the discussion in Section .1 the chemistry of the Doughty waters suggests that their geochemical evolution has been influenced more by weathering of carbonate rocks than by weathering of silicate rocks (igneous or siliciclastic). Stratigraphic considerations led to the conclusion that suitable candidates for the carbonate - bearing rocks are the Juana Lopez Member of the Mancos Shale (calcareous sandy siltstone) and the Green River Formation (calcareous siltstone and shaley marlstone), were the Doughty water to recharge by leakage through these formations.

Cadigan et al. (1976) noted the predominance of CO_2 and H_2S gases in the Delta County spring waters, and suggested that expansion of these gases in the subsurface provides some of the energy responsible for the

migration of the Doughty waters to the surface. Indeed at Austin there is a cold water geyser (which erupts for 20 - minute periods several times a day) which is driven by the accumulation of pressure due to exsolution of CO_2 in the subsurface (Cadigan et al., 1976, p.8). Theories on the genesis of CO_2 in the subsurface have been reviewed in detail by Farmer (1965), who identified five main theories which may be sub - divided into two categories; organic and inorganic. Organic theories include (i) the decay of organic matter and (ii) the oxidation of hydrocarbons by mineralised waters, while inorganic theories embrace (iii) solution of carbonates by ground water (iv) igneous emanations, and (v) metamorphism of carbonates. Of these five theories, only the last two are apparently beyond the pale as far as evolution of the Doughty waters is concerned, since no igneous intrusion or metamorphism has occurred in this region since the Tertiary. What of the remaining three? Genesis of carbon dioxide by anaerobic oxidation of organic matter by bacteria usually results in the evolution of methane as well as CO_2 (Farmer, 1965, p. 379) and it therefore seems unlikely that this source has made a very substantial contribution to the CO_2 complement of the Doughty water.

If the Doughty waters have percolated through the
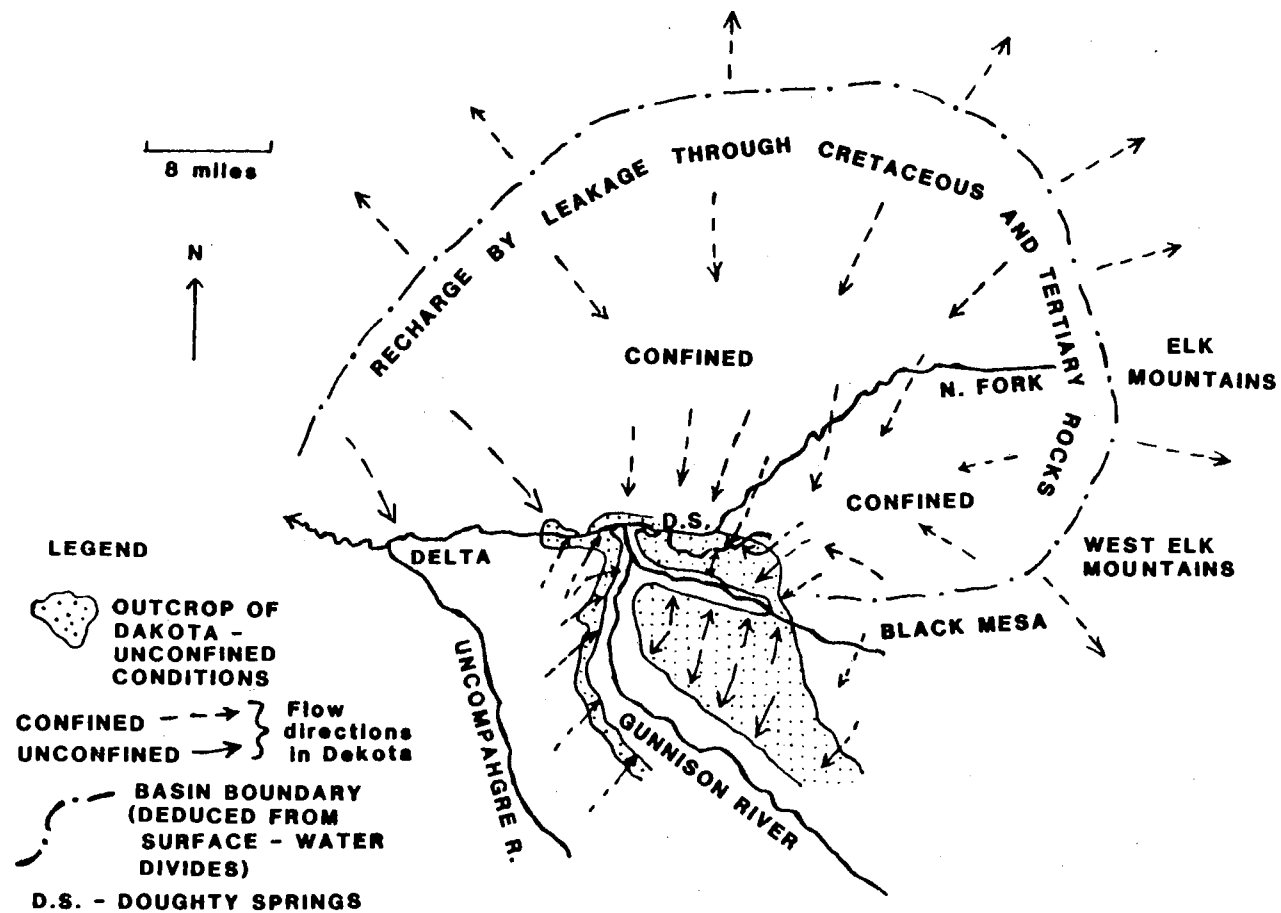
FIGURE 3.8 - GROUND WATER BASIN BOUNDARIES AND FLOW DIRECTIONS IN DAKOTA SANDSTONE AQUIFER

Green River Formation (which contains some of the richest oil shale deposits in North America) the potential for CO_2 generation by oxidation of hydrocarbons is great. This could occur according to the equation:

$$CnHm + x(SO_{42-}) \longrightarrow n(CO2) + m/2(H2S)$$
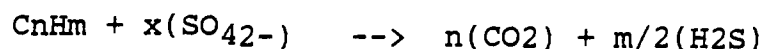
This reaction would also reduce the sulphate activity in the water, allowing it to take more barium into solution than would otherwise be possible. It also has the advantage of explaining the origin of H_2S simultaneously. Hydrocarbons residual after oxidation by ground waters are generally enriched in tars -- i.e. viscous bitumens such as occur in oil shales (Farmer, 1965, p.379). Hence the retention of hydrocarbons in the Green River Formation may to some extent be governed by the increase in viscosity contingent upon oxidation by sulphate - bearing ground waters.

The theory of CO_2 genesis by solution of carbonates is not elaborated upon by Farmer (1965). Another related theory was developed recently by Wood (1985) who envisaged CO_2 production by bacterial oxidation of organic carbon carried deep into the vadose zone by infiltrating ground water. An area of high CO_2 concentration at depth would result, and when infiltrating ground water encounters this it will become subsaturated

with respect to carbonate minerals. Dissolution of subsequently encountered carbonate mionerals would follow. (This hypothesis, incidentally, explains why caves form deep in the vadose zone in carbonate terrains rather than from the surface down).

Genesis of CO_2 in the system producing the Doughty water by oxidation of hydrocarbons would similarly result in subsaturation of the water with respect to carbonate minerals, encouraging the dissolution of carbonates (which are inferred, on geochemical grounds, to be governing evolution of the Doughty water; Section 3.5.1).

Further evidence supporting the case that the Doughty water has had contact with hydrocarbons, such as those in the Green River Formation and the coaly lower part of the Mesaverde Formation, is the trace element content of the spring deposits (Table 3.6; discussion part in Section 3.5.3). In lieu of igneous interactions (apparently precluded by the low silica content of the waters) the presence of the following elements in the deposits bespeak contact of the parent waters with organic matter:

Vanadium (85 ppm in sample 15).

Nickel (850 ppm in sample 11; 55 ppm in sample 14; 190 ppm in sample 15; 44 ppm in sample 28; 70 ppm in sample

30; 42 ppm in the A1 algal mush; 32 ppm in the B spring protozoan mud).

Molybdenum (20 ppm in sample 28; 38 ppm in sample 15; 21 ppm in sample 11).

The relatively high concentrations of these three particular elements in bituminous matter has been known for a long time (Goldschmidt, 1958, p. 495). They occur naturally in petro - porphyrins, substituting for Fe and Mg (e.g. replacing Mg as the bridgeing ion in the chlorophyll molecule and its geochemical derivatives. V/Ni ratios are often used in geochemical studies of oils for such tasks as relative dating of different crudes; V complexes are far less stable than Ni complexes, and hence V/Ni will be smaller in older oils than it will be in younger oils; Tissot and Welte, 1978, pp. 363 - 365).

From the foregoing discussion it would seem that there are several features of the geochemistry of the Doughty waters and their deposits which support the idea (first proposed above on structural/stratigraphic grounds) that all recharge to the leaky confined Dakota aquifer (which supplies water to the Doughty Springs) occurs as leakage through the overlying Mancos, Mesaverde and Green River Formations. The full impact that leakage through confining layers can have on the

regional water budget of a leaky confined aquifer has only begun to be appreciated since the early 1960s. Leakage from overlying Pennsylvanian and Permian beds is now thought to account for almost all of the production from wells in the Madison Limestone in the Midwest area of Wyoming. This is only one of numerous examples (reviewed by Bredehoeft, Back and Hanshaw, 1982) of behaviour analogous to that postulated here for the Dakota system.

Accounting for the small amount of barium in the water is really no problem; it is not present at concentrations in excess of those which can be explained in terms of barite solubility in pure water. Having said this, however, it is unlikely that barite released the barium found in this water. It is far more likely that this comes from the gradual dissolution of potassic feldspars (prime hosts for juvenile barium from the mantle; Section 1.3) which have been deposited in the arkosic sandstones of the area (e.g. the Rollins Member of the Mesaverde Formation; Weeks, 1925) upon release from the Pitt's Meadow Granodiorite by weathering. The Pitt's Meadow Granodiorite contains 614 ppm barium on average (Barker et al., 1976). Radium, the element chiefly responsible for the radioactivity of the springs (Headden, 1905a), follows barium very closely throughout

the geochemical cycle (Langmuir and Riese, 1985; Chow and Goldberg, 1960) and hence its presence in the waters probably reflects a common source.

3.7 Summary and Conclusions.

Summary. The Doughty Springs near Lazear, Delta County, Colorado, yield cool ($16^{o}C$) sodium - bicarbonate waters which are involved in the precipitation of travertine. This travertine is unusual in that, in addition to calcite, it contains considerable quantities (up to 24 wt%) of barium, which occurs as the sulphate (barite) and also apparently as calcic carbonate minerals. What is most surprising is the small concentration of barium in the waters (< 2.1 mg/L) which produce deposits so rich in the element. This apparent anomaly is explicable by the active participation of protozoans and algae (_Oscillatoria_ sp.) in barium accumulation from the water. Thermodynamic calculations suggest that the water is saturated with respect to $BaSO_4$, so that some inorganic precipitation must also be occurring. A number of rare minerals have been tentatively identified in association with the springs including copiapite and sauconite.

The Doughty Springs emerge from the Dakota Sandstone, which supplies a whole suite of mineral springs

along the North Fork Gunnison River and the north bank of the Gunnison River below the confluence with the North Fork between Lazear and Austin. North and east of the Doughty Springs, i.e. in the direction from whence the spring - feeding water is coming, the Dakota rapidly disappears beneath the Mancos Shale (which is in turn overlain by three more formations, all conformable; the Mesaverde, Wasatch and Green River Formations). The Mancos acts as an hydraulically confining layer on the Dakota. Recharge to the Dakota seemingly occurs by leakage through the four overlying formations; the structure of the sedimentary basin, the dimensions of the ground water basin and the chemistry of the spring waters and their deposits all suppport the contention that the recharging water made contact with the organic - rich Green River and / or Mesaverde Formations during infiltration. Discharge from the Dakota at the springs is a result of up - dip (but down - hydraulic - gradient) migration of the Doughty type waters towards the low potential boundary which is the North Fork Gunnison River. This migration is aided by expansion of gases (H_2S and CO_2) in the subsurface waters.

Conclusions. The Doughty Springs represent a very rare occurrence; deposition of barite and barium carbonates from moderately saline (TDS < 3000 mg/L)

waters in which the dominant ion is bicarbonate. In a solution of such relatively low ionic strength it is rare indeed to find barite in solution, and even more rare to find precipitation of barium salts taking place above ground. Active biological participation in the accumulation of barium in the spring deposits exemplifies once again the close association between barium (particularly as barite) and organic matter noted by many authors (e.g. Berkheiser, 1984; Cronan, 1980; Revelle and Emery, 1951; Finlay et al., 1983).

Hydrogeochemical analysis of the spring system appears to be a good tool to use in elucidating the hydrogeology of the ground water basin which spawned it. Confining bed properties can be qualitatively inferred for a large area on the strength of careful study of one discharge area. While the inferences presented here concerning the hydrogeology of the basin ought to be applied with caution, they have at least pinpointed some aspects worthy of more detailed study.

A comparison of the Doughty barium travertine occurrence with the Zodletone (Oklahoma) occurrence follows in Chapter 4.

CHAPTER IV

DISCUSSION AND CONCLUSIONS --

A Comparison of the Zodletone (Oklahoma)
and Doughty Springs (Colorado)
Barium Travertine Occurrences.

The two localities described in Chapters 2 and 3
are the only two sites in North America where spring
deposits of barite are known to occur, and represent
about 50% of the known world occurrences of barite
travertine (the other two localities being in Taiwan and
Japan; Ishizu, 1915).

Two coincidences between the two localities
concern their structural setting. Both occur at the edge
of sedimentary basins adjacent to uplifts of ancient
igneous basement rocks -- Zodletone fringes the Anadarko
Basin, peripheral to the Wichita Uplift igneous prov-
ince; the Doughty Springs fringe the Piceance Creek
Basin, peripheral to the Uncompahgre Uplift which has
the Pitt's Meadow Granodiorite at its core. The second
structural coincidence linking the two occurrences is
that they both occur along the edges of a Palaeozoic
rift system (recently identified by Larson et al., 1985)

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which extends from Colorado to Oklahoma and which
governed the development of the Anadarko Basin and the
Uncompahgre Uplift. These locational facts may prove
useful in future exploration for barite deposits.

Both spring systems come from aquifers which seem
to have been recharged by leakage through confining
beds, which influenced the chemical development of both
waters. Water chemistry differs quite markedly between
the sites, however (Figure 2.5), with the Zodletone
anions being dominated by chloride while the Doughty
water has bicarbonate for its dominant anion. Both share
sodium as the dominant cation. The Zodletone water is
much more saline than the Doughty water (9000 mg/L TDS
at Zodletone vs. 2500 mg/L TDS at Doughty).

Mineralogically the two localities are quite
different with zoned barite dominating at Zodletone
while calcite dominates at the Doughty Springs, with
barite present only as an accessory and most of the
barium incorporated into carbonates.

Depositional differences are quite marked between
the two springs. Barite precipitation occurring at
Zodletone today is clearly inorganic, suggesting that
the organic matter in the older deposits is purely
accidental, providing only a framework to the waters for
a passive coating process. Precipitation at the Doughty

Springs is apparently effected mostly by active biol-
ogical fixation of barium from the water by protozoans
and algae (Oscillatoria sp.).

The ultimate origin for the barium in both cases is
traceable to weathering of granitic rocks containing
abundant potassium feldspar.

Conclusions.

The two occurrences of barium travertine outlined
in this thesis display nuances of character and genesis
illustrative of various important facets of barium
geochemistry, including the effect of water salinity on
barite solubility and the role of biota in accumulating
barium for incorporation into minerals. Consideration of
the chemical evolution of the waters sheds some light on
the regional hydrogeology of the aquifer systems through
which they flow.

More specific conclusions for the Zodletone
locality include:
(i) The geochemistry of the Zodletone waters suggests a
genetic association with hydrocarbons. Hence petroleum
exploration in the vicinity of Zodletone may be war-
ranted.
(ii) Any attempts at secondary recovery from oil wells
in the vicinity of Zodletone ought to be undertaken with

fluids free of sulphate to avoid barite scale precip-
itation from contact with Zodletone type waters in the
subsurface.

(iii) The geology of this occurrence, when viewed
against the local backdrop, suggests that a Mississippi
Valley Type ore body may lie in the subsurface of the
Wichita Frontal Fault Zone.

(iv) Aspects of the petrology of the deposits of the
Zodletone deposits remain enigmatic -- the origin of
zoning and habit changes during crystal growth for
example. Is zoning compositionally controlled ?

The Doughty Springs have a number of features
worthy of special comment:

(i) The dominant mineralogy, even in barium rich parts
of the deposits, is always a calcium carbonate, showing
that Ba is present here in carbonates rather than
sulphates for the most part. This is contrary to the
reports of previous workers in the area (Headden, 1905a;
Cadigan et al., 1976) none of whom mention having done
any petrographical work on samples from the site. It
seems that they assumed that barium (found in chemical
analyses) was present as barite without checking.

(ii) The chemistry of the springs and their deposits
suggests that the waters had contact with hydrocarbons
during their evolution, implying that recharge to the

Dakota aquifer (from which they flow) is recharged via leakage through the overlying Mesaverde and Green River Formations, an implication supported by hydrogeological evidence.

(iii) The observation of the agency of biota in constructing the barium - rich travertine at the Doughty Springs represents the first time such a role has been proven in barium - rich spring deposits.

Both springs are examples of a very rare natural occurrence, and since they differ from each other in several important ways it is fair to say that each locality has a character unique in North America, and probably the world, amongst the geological features discovered to date. Nowhere in the world save at these two sites may cool waters (16 - 22oC) be observed precipitating barite and barium carbonate travertine.

It is hoped that the work contained in this thesis may provide a good foundation for further studies on the geology, petrology and geochemistry of barium and its compounds.

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APPENDIX

ANALYTICAL METHODS USED IN THIS STUDY.

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APPENDIX

ANALYTICAL METHODS USED IN THIS STUDY.

Chemical Methods.

(i) Water Samples

Chemical analysis of water samples involves making measurements in the field and in the laboratory. For all water analyses, the following measurements were made in the field:

pH and conductivity -- These were both measured using a hand - held portable meter.

Temperature -- Measured using a thermometer which was immersed in the spring orifices for five to ten minutes until the readings stabilised.

Alkalinity -- determined by titration using a portable hand - held "Hach" digital titrator. The volume of acid used (in ml) is calculated from the endpoint digits on the titrator using the relation:

Volume (ml of acid) = digits / 800.

2N hydrochloric acid was used for the titrations, and 50 ml of sample were titrated each time. Alkalinity (in

mg/L as HCO_3-) was then calculated using the relation:

Alkalinity =

[(vol. of acid X conc. of acid) X 1000/sample vol.] X

61.02

Field Sampling -- Duplicate samples were taken for each spring according to the standard procedures given by the U.S. EPA (1979). Separate samples were taken for anion and cation determinations. The anion samples were kept on ice and the cation samples were acidified to reduce the alteration of the water chemistry by precipitation of ionic species. All samples were analysed within a month of collection, and most within a week.

Laboratory analysis of the water samples was undertaken using spectrophotometric and volumetric techniques. For cation determinations atomic absorption spectroscopy was used. The specific techniques used in the anion determinations ($Cl-$ and SO_42-) are related below.

Atomic absorption spectroscopy (AAS) is a widely used technique, which has been described in some detail by U.S. EPA (1979) and Van Loon (1980). The fundamentals of an AAS system may be summarised as follows: Resonance radiation is produced by the excitation of a metallic element in a light source. This radiation is character-

istic of the element in the source and corresponds to the element which is under investigation. Leaving the light source, this radiation is passed through a sample

"cell" (as often as not a flame) in which ground state atoms of the element of interest are present, thanks to atomization of the sample. These ground state atoms absorb incident resonance radiation (since it exists at an energy level found within the element) and hence the radiation beam leaving the sample cell is of somewhat subdued intensity compared with the incident beam. After passing through the monochromator, which isolates the desired resonance line for the element of interest from among the many present, the beam falls on the photomultiplier, generating an electrical signal. This electrical signal is processed with respect to the intensity of the incident beam, and an electronic output is generated which is proportional to the amount of absorption performed by the analyte atoms in the sample cell. An approximately linear relationship between absorbance and elemental concentration exists, allowing quantitative determinations to be made (Van Loon, 1980, p.12).

Sulphate determinations were made according to the spectrophotometric method advocated by the U.S. EPA (1979) in which the sulphate ions are converted to

barium sulphate (practically insoluble) by addition of barium under controlled conditions. The increased turbidity of the solution arising from this reaction is measured using a spectrophotometer (operating at around

420 nm) and the SO_4^{2-} concentration determined by comparison of the absorbance reading with values on a standard curve prepared from measurements on standard sulphate solutions.

Chloride determinations were made by titration of an acidified sample with mercuric nitrate in the presence of a mixed diphenylcarbazone / bromophenol blue indicator. The endpoint is signalled by the formation of a blue - violet diphenyl carbazone - mercury complex (U.S. EPA, 1979).

(ii) Solid Samples.

X - Ray Fluorescence (XRF) Spectroscopy was used to scan the solid samples for every element with an atomic number greater than 21. This was done at the Fluo - X - Spec Laboratory in Denver, Colorado. An energy - dispersive X -ray (EDX) unit built into the Scanning Electron Microscope (SEM) used in petrological studies (see below) performs XRF analyses at a microscopic level. Bombardment of an element with X - ray photons induces emission (the so - called "fluorescence") of secondary X - Rays which have wavelengths characteristic

of the element in question. Intensity of the emitted energy is related to elemental concentration, although thickness and bulk sample composition produce interfering effects. Further details on the technique may be found in Reeves and Brooks (1978, pp. 232 - 249).

Mineralogical methods

Apart from straightforward thin section study, two main laboratory methods were used in mineralogical analysis during this study; namely scanning electron microscopy and X - ray diffractometry.

Scanning Electron Microscopy (SEM) in its application to petrology has been well described by Welton (1984, pp. 1 - 7). A tungsten wire is heated until it begins to thermionically emit electrons. These electrons are focused onto the solid sample, which has been coated in graphite and mounted in the SEM vacuum chamber. Secondary electrons and X - rays (as well as other radiation forms) are emitted from the sample surface in response to the excitation from the impinging electron beam. SEM imagery is constructed from the secondary electron distribution and XRF analysis is performed by the EDX unit on the X - rays. Hence the morphology and chemistry of an extremely small area of a sample may be obtained in a matter of minutes.

X - Ray Diffractometry (XRD) depends on the

diffraction of X - ray beams by the evenly - spaced array of equivalent points in a crystal lattice. The spacings of the planes defined by these points can be determined from the behaviour of these X - rays, which can in turn be used to define the unique signature of each individual mineral. XRD analysis remains one of the most powerful techniques available for mineral identification. Battey (1972) has summarised the theory and practice of the technique. Identification of minerals during this study was accomplished by comparison of data obtained from the samples with standard data in JCPDS (1980).

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