γ

DOE/ID/12524--T1

DE86 014383

DOE/ID/12524
Distribution Category:
UC66a

Received by OSTI

AUG 1 8 1986

DOE/ID/12524--T1

GEOCHEMISTRY, ISOTOPIC COMPOSITION AND ORIGIN OF FLUIDS EMANATING FROM MUD VOLCANOES IN THE COPPER RIVER BASIN, ALASKA

Final Report

R. J. Motyka
Alaska Div. of Geological & Geophysical Surveys
Juneau, Alaska
D. B. Hawkins
Institute of Water Resources
University of Alaska
Fairbanks, Alaska
R. J. Poreda
Scripps Institute of Oceanography
University of California
La Jolla, California
A. Jeffries
Global Geochemistry Corporation
Canoga Park, California

May 1986

Prepared for the U.S. Department of Energy
Idaho Operations Office, Idaho Falls, ID
Under Contract Number DE-FG07-84ID12524
Sponsored by the Office of the Assistant Secretary for
Conservation and Renewable Energy
Office of Renewable Energy
Washington D.C.

MASTER

DISCLAIMER

CONTENTS

ABSTRACT

Two compositionally different groups of mud volcanoes exist in the Copper River Basin: the Tolsona group which discharges Na-Ca rich, HCO_3-SO_4 poor saline waters accompanied by small amounts of gas, composed predominately of CH_4 and N_2; and the Klawasi group which discharges Ca poor, Na-HCO_3 rich saline waters accompanied by enormous amounts of CO_2. The saline waters appear to be derived from an overpressured zone in Lower Cretaceous deposits. The Tolsona-type water chemistry and isotopic composition could have been produced through the following processes: dilution of original interstitial seawaters with paleo-meteoric waters, possibly during a period of uplift in the mid-Cretaceous; loss of HCO_3 and SO_4 and modification of other constituent concentrations by shale-membrane filtration; further depletion of Mg, K, HCO_3, and SO_4, and enrichment in Ca and Sr through dolomatization, hydrolysis, and clay-forming processes; and leaching of B, I, Li, and SiO_2 from marine sediments.

Compared to the Tolsona waters, the Klawasi waters are strongly enriched in Li, Na, K, Mg, HCO_3, SO_4, B, SiO_2 and $\delta^{18}O$ and strongly depleted in Ca, Sr and D. The Klawasi waters also contain high concentrations of arsenic (10 to 48 ppm), several orders of magnitude more than any of the Tolsona waters (< 10 ppb). The differences in fluid chemistry between Klawasi and Tolosona can be explained as the result of the interaction of fluids derived from a magmatic intrusion and contact decarbonation of limestone beds underlying the Klawasi area with overlying Tolsona-type formation waters. Evidence for a magma-decarbonation influence on the Klawasi system include: 1) the high $^3He/^4He$ ratios at Klawasi (4.1), 2) the $\delta^{13}C$ compositions of CO_2 (-4.8 to -3.1 per mil) and HCO_3 (+1.6 to +3.1 per mil), 3) consistency with large volumes of CO_2 and HCO_3, and with the Klawasi water chemistry, 4) the high concentrations of As, and 5) chemical geothermometery. The proportion of metamorphic to magmatic CO_2 is estimated to be $\approx$ 40 to 50 per cent. Interaction of the CO_2 with the formation waters results in carbonic acid hydrolysis and decomposition of clays and other silicates and aluminosilicates and saturation with respect to $CaCO_3$. The resulting waters emanating at the surface would be rich in SiO_2, alkali metals, HCO_3, CO_2, and depleted in Ca and Sr. Differences in isotopic compositions between Klawasi and Tolsona-type waters can be partially attributed to mineral-water isotope exchange processes and perhaps also to mixing with magmatic or metamorphic water.

Application of geothermometers to the Klawasi waters remains problematic because of fluid-fluid and fluid-mineral reaction rates but reservoir temperatures of 100 to 125°C appear to be indicated. The moderate reservoir temperatures

and low spring temperatures (20°C) indicate the intrusive must be relatively deep-seated with little or no hydrothermal circulation between the overlying formation waters and the intrusive. The Chitistone limestone may be the source of contact metamorphic CO_2 which would place the depth of the intrusive at 2.5 to 3.0 km. The Taral fault could be acting as a zone of weakness for the intrusion and also be the avenue of ascent for magmatic and contact metamorphic CO_2 gases.

The most likely sources for the Copper River Basin methanes are coal and lignite beds in mid- to lower Cretaceous formations underlying the basin. The $\delta^{13}C$ of CH_4 from the Lower Klawasi vents is particularly heavy (-18 per mil), which suggests a mantle component in the Klawasi methane.

1. INTRODUCTION

Two compositionally different groups of mud volcanoes and saline springs exist in the Copper River Basin: the Tolsona group which discharges sodium and calcium-rich and bicarbonate and sulfate-poor saline waters accompanied by small amounts of methane and nitrogen rich gases; and the Klawasi group which discharges calcium-poor, sodium and bicarbonate-rich saline waters accompanied by enormous amounts of carbon dioxide gas. The sources of the saline spring waters and gases, the origins of the fluid constituents, and the causes of the differences in fluid chemistries are the subjects of this paper.

The Copper River Basin is a poorly drained, intermontane sedimentary basin, located in southcentral Alaska (fig. 1 and 2). The Tolsona group of mud volcanoes, Tolsona 1 and 2, Nickel Creek and Copper Center, are located in the western part of the basin and are typified by broad, shallow edifices of accretionary mud, 3 to 20 m in height, which feebly discharge saline waters. In contrast, Upper and Lower Klawasi and Shrub mud volcanoes, which comprise the Klawasi group and are located west of Mt. Drum, a large Quaternary andesitic volcano, are much larger edifices, 50 to 100 m in height, and vigoruosly emit carbon dioxide-charged saline waters.

Previous Work

The origins and striking differences in chemistries of gases and brines emanating from the mud volcanoes and mineral springs located in the Copper River Basin have long interested and puzzled investigators. Nichols and Yehle (1961a) concluded that the waters of the two mud volcano groups were related chemically and that the high salinity resulted from evaporation of glacial lakes followed by subsequent concentration through permafrost formation. Grantz and others, 1962, discounted the role of evaporation and permafrost on the grounds that the composition of waters resulting from such processes is incompatible with the observed waters in that evaporite waters should contain high concentrations of sulfates which are not seen in the mud volcano waters. Instead, Grantz and others suggested that the saline waters emerging at the surface of the basin probably originate from Cretaceous or older marine sediments which underlie the basin. They did not speculate on how these formation waters attained their particular chemistries.

Grantz and others did present several different hypotheses to explain the differences in fluid chemistries between the two groups of mud volcanoes. They considered the probability for discharge of two totally unrelated kinds of saline waters in close proximity to be slight and that more likely the Klawasi waters were Tolsona-type waters modified by mixing and reacting with CO2-rich fluids derived from a sedimentary, metamorphic, or volcanic source. They had insufficient data to conclusively select one of the possibilities over the others but based on the proximity of the Klawasi group to large Quaternary andesitic volcanoes, Grantz and others speculated the more likely sources to be volcanic, or alternately, from contact metamorphism with an igneous intrusive.

Based on the analyses of $\delta^{13}C$ in carbon dioxide and methane, Reitsima (1979) concluded that the carbon dioxide-rich gases of the Klawasi group originated from the dissolution of limestone by moisture, heat, and acidity of volcanic gases, and that the methane rich gases of the Tolsona group were formed by the thermal decomposition of coaly materials.

Recent geophysical investigations by Wescott and Turner (1985) added credence to the possibility of an intrusive body underlying the Klawasi group. They suggested that anomolies in gravity and magnetic surveys could be explained by the presence of a small, relatively shallow igneous intrusion.

Hawkins and Motyka (1984) examined the relationship of the mud volcano and saline spring waters to regional ground water and found that simple seawater - ground water - meteoric water mixing models were incompatible with the stable isotope compositions of the Copper River basin waters. They further suggested that membrane filtration processes and fluid-mineral interactions could have significantly modified the original connate water compositions.

Present Study

The impetus for the present study arose from investigations of the state's geothermal resource potential. Casual application of commonly used fluid chemical geothermometers to waters emanating from the Klawasi group of mud volcanoes led some resource analysts to believe a hydrothermal resource might underlie the area. Closer examination of fluid chemistries showed up several ambiguities in terms of interpreting the geothermometers and that proper evaluation of the area's geothermal potential required a much better understanding of the nature and origin of the brines and gases emanating from the basin's mud volcanoes and mineral springs.

In this study we distinguish between formation water, the water currently present in the sedimentary formations underlying the basin, and connate water, the water which was

initially entrapped in the interstices of the sedimentary rocks at the time of their deposition. The origins of the sedimentary formation waters in the Copper River Basin and their unique chemical compositions, which differ substantially from seawater, and the processes which could give rise to the striking differences in fluid chemistries observed at the two groups of mud volcanoes have not been considered in any detail by previous investigators.
The geothermal study was therefore broadened to include these objectives to help decipher whether or not a geothermal resource underlies the Klawasi area and to also determine the source(s) of the copius amounts of carbon dioxide emanating from the Klawasi group and the sources of methane emanating from both groups of mud volcanoes.

New data obtained through this study to help meet these objectives include: 1) geochemical compositions of water and gas samples obtained from all mud volcanoes and saline springs in the Copper River Basin; 2) arsenic concentrations in the water samples (arsenic analyses had not been done in any previous study); 3) oxygen 18/16 ratios in the basin's brines, groundwaters, and surface meteoric waters and in selected carbonates; 4) hydrogen/deuterium ratios in the various basin waters; 5) carbon 13/12 ratios in carbon dioxide and methane gases, in bicarbonates and in selected carbonates; and 6) helium-3/4 ratios in gases emanating from the mud volcanoes and saline springs. Drawing on analogies to oil-field brines studied elsewhere in the world, these data were then interpreted within the geologic-tectonic framework of the Copper River basin, isotopic exchange and mixing processes, fluid-fluid and fluid-mineral interactions, and ultra-membrane filtration processes.

Summary of Results

We believe the results of our study strongly indicate a recently emplaced igneous intrusion is causing deep-seated metamorphic decarbonation of limestone beds beneath the Klawasi group of mud volcanoes. Copius amounts of CO_2 gas from the intrusive and from contact metamorphic reactions flow upward under pressure into overlying Jurassic and Cretaceous marine sandstones and shales where the gases interact with Tolsona-type formation waters. Formation of carbonic acid results in hydrolysis and acid decomposition of clays and other silicates and aluminosilicates causing an increase in dissolved alkali metals and silica. Continued interaction buffers the waters to neutral pH, the waters become saturated with respect to $CaCO_3$, resulting in precipitation of calcite and consequent depletion of calcium in the waters. The resulting waters emanating at the surface of the Klawasi mud volcanoes are rich in alkali metals, bicarbonate, CO_2 gas, and depleted in Ca.

Our primary evidence for the existence of the intrusive and contact-metamorphic decarbonation process is: 1) the high helium-3/4 ratios obtained for the Klawasi gases which reflect a strong magmatic influence on the Klawasi system; 2) the rate of CO_2 production which appears consistent only with a magmatic or magmatic-contact metamorphic source; 3) the carbon-13/12 signatures which point to a limestone decarbonation process as the source of much of the carbon dioxide gas; and 4) the extremely elevated concentrations of arsenic found in the Klawasi brines (43 ppm vs < 0.01 ppm in Tolsona brines).

Application of geothermometers to the Klawasi waters remains problematic because of the fluid-fluid and fluid-mineral reactions involved but a reservoir temperature of 100 to 125°C appears to be indicated. Such moderate reservoir temperatures and low spring temperatures (20°C) indicate the intrusive must be relatively deep-seated with little or no hydrothermal circulation occuring between the overlying connate waters and the intrusive.

The formation waters themselves probably originated as connate seawater entrapped in Cretaceous and perhaps Jurassic marine sediments that was subsequently diluted with meteoric water during a Late Jurassic or mid-Cretaceous period of regional uplift. The present Tolsona-type chemistry could be produced through mixing and dilution of the entrapped seawaters with paleo-meteoric waters, further modified by shale-membrane filtration and fluid-mineral interactions. Differences in isotopic compositions between Klawasi and Tolsona-type waters can be partially attributed to mineral-water isotope exchange processes and perhaps mixing with a magmatic or deep-metamorphic water component.

REGIONAL GEOLOGY

Setting

The Copper River Basin lies in south-central Alaska (fig. 1). It is an intermontane sedimentary basin which covers 14,000 sq. km. and is surrounded by 1,500 to 5,000 m peaks of the Alaska Range and the Talkeetna, Chugach, and Wrangell Mountains. The basin is divided into two physiographic subunits (Nichols and Yehle, 1961a). The Copper-Sustina Lowland lies between 600 and 900 m and is situated in the northern and western parts of the basin. The Copper River Trough is a flat to gently sloping lacustrine plain extending in an arc along the north, west, and south sides of the Wrangell Mountains. Drainage from the basin is restricted almost entirely to the Copper River which has incised a deep canyon through the Chugach Range to the south.

Rocks bordering the basin range in age from Late Paleozoic to Tertiary. They consist largely of schist, greenstone, greywacke, slate, shale, and sandstone, locally associated with minor amounts of altered limestone, tuffaceous beds, and basalt flows and are intruded by a wide variety of igneous rocks (Nichols and Yehle, 1961a). Large areas of the Wrangell and Talkeetna Mountains and local areas of the Chugach Mountains are underlain by considerable thicknesses of basaltic and andesitic lava flows. In the trough, bedrock exposures are few and except for one greenstone exposure and a few scattered limestone outcrops, only Pleistocene deposits, including a few exposures of near surface lava and debris flows, are exposed.

Basin Stratigraphy

Figure 2 shows a stratigraphic cross-section of Copper Basin Basin generalized from Church and others (1969) and Ehm (1983). Basin stratigraphy is based on logs of ten oil and gas exploration wells drilled to depths of 850 to 2,680 m and by inference from bedrock outcrops in adjacent mountains. Depth to the Permian/Pennsylvanian basement, which is presumed to underlie the basin, is inferred from proprietary seismic and gravity studies by various oil exploration companies (Ehm, 1983).

The uppermost unit in the basin consists of undifferentiated Quaternary and Tertiary deposits which, at least in the the southwest part of the basin (perhaps including the Tolsona group of mud volcanoes), contain semi-consolidated Tertiary sandstones and conglomerates with a few lignitic beds (Miller and others, 1959; Nichols and Yehle, 1961a). These beds unconformably overlie the Upper Cretaceous Matanuska Formation which consists of marine shales with occasional fine-grained sandstones. The log from at least one well (located northeast of Gulkana) reported traces of coal and thin lignitic beds scattered through the mid-portion of this formation.

In the central part of the basin, the wells intersect the basal portion of the Matanuska Formation - fine-grained marine sandstones with minor interbedded shales. An unconformity separates the Matanuska Formation from underlying Lower Cretaceous Kennicott, and possibly Nelchina Formations - marine shales with minor quartzose sandstone beds. These formations unconformably overlie Upper Jurassic Naknek and Chitina Formations - marine tuffaceous sandstones and shales - and the Middle Jurasic Tuxedni Formation, consisting of marine shales and interbedded sandstones.

The basal portion of the Matanuska Formation and the Lower Cretaceous and Upper and Middle Jurasic formations are not present at either Amoco-Ahtna drill site in the northeastern portion of the basin. Both wells did bottom in the Lower

Jurassic Talkeetna Formation which consists primarily of basaltic and andestic flows, tuffs, volcanic breccias, and volcanic sandstones.

Rocks of the Talkeetna Formation record an Early Jurassic magmatic arc volcanic pulse that affected much of southwestern Alaska (Moore and Connelly, 1977). The Naknek and Matanuska Formations are forearc basin deposits related to two later pulses of magmatic arc volcanism.

Tectonostratigraphic Terrane Correlations

The Lower Jurassic through Lower Cretaceous rock formations that underlie much of the Copper River Basin are part of the Peninsular Tectonostratigraphic terrane as defined by Jones and Siberling (1979). Fragments of this terrane are scattered as far west as the end of the Alaska Peninsula.

The Wrangell volcanoes and probably the eastern-most part of the Copper River Basin are underlain by an allochthonous terrain of Paleozoic and Mesozoic carbonates, fine clastics and pillow basalts, fragments of which extend discontinously along the Pacific margin to at least as far south as Vancouver Island. This well-known stratigraphic assemblage has been named Wrangellia by Jones and others (1977). Wrangellia is thought to have arrived in its present position by the late Mesozoic (Jones and others, 1977) with suturing to the North American plate estimated to have occurred in the late Early Cretaceous (Winkler and others, 1981).

The Talkeetna Formation contrasts markedly with coeval rocks in the Wrangell Mountains, which are not volcanogenic indicating the Peninsular and Wrangellia terranes were probably not juxtaposed until Middle Jurassic (Winkler and others, 1981). The boundary between the two terranes, which appears to be the Taral fault, is hidden by Quaternary-Tertiary deposits in the eastern Copper River Basin (Winkler and others, 1981; Jones and others, 1984). Northward projection of the fault's trend from where it surfaces southeast of the basin suggests the boundary between the terranes may lie in the vicinty of the Klawasi group of mud volcanoes.

Late-Tertiary - Quartenary Wrangell Mountain Volcanism

The massive late-Tertiary - Quaternary andesitic volcanoes on the eastern border of the basin are among the largest andesitic volcanic edifices in the world. Mt. Drum, Mt Sanford, and Mt. Wrangell, have been largely built over the past one million years (Nye, 1983). The construction of these large, closely spaced volcanoes over the relatively short time span indicated by the radiometric ages suggests that the rate of edifice production in the Wrangells is about five times greater than that reported for other circum-Pacific volcanoes. Large quantities of heat must have been transported into the upper crust during the extrusion of these magmas and it is probable that much of this heat is still retained in shallow magma chambers.

Mt. Drum, located directly east of the Klawasi group of mud volcanoes, erupted as recently as 200,000 years bp (Richter and others, 1979) and is thought to still house a shallow crystallizing magma chamber (Smith and Shaw, 1979). Mt. Wrangell, southeast of the basin, is the only volcano currently active in the Wrangell Mountains, having had several mild eruptions during the early decades of this century. The volcano is capped by a 5 x 3 km diameter ice-filled summit caldera that is thought to have formed in the late Pleistocene or early Holocene. Three hydrothermally active craters, one of which has superheated fumaroles, lie along the rim of the caldera and indicate large amounts of residual heat still remain in the magma chamber (Motyka, 1983).

Quaternary Geology

The Copper River Basin is blanketed by Quaternary glacial, alluvial, and lacustrine deposits which in places probably exceeds 300 m in thickness (Mendenhall, 1905). Andestic lava flows and tuffs and thick volcaniclastic debris flows are interbedded wtih Pleistocene deposits in the eastern and southeastern parts of the basin (Richter and others, 1979; Yehle and Nichols, 1980; Winkler and others, 1981).

During the early Pleistocene, glaciers from the surrounding mountains repeatedly invaded the basin, at times covering the entire basin floor (Nichols and Yehle, 1961a). During later glaciations, ice may have covered all but small areas of the basin, but during the last major glaciation large areas were ice-free. At various times ice advances dammed the Copper River to form extensive proglacial lakes. Strandlines suggest lake levels reached as high as 850 m. Following retreat of the glaciers and drainage of the lake (before 9,000 yr bp), permafrost began to form in lacustrine and glacial deposits (Ferrians and others, 1983). Present-day permafrost lies about 0.5 m below the surface and is on the order of 30 to 60 ft thick.

MUD VOLCANOES

General

In general the term "mud volcano" has been applied to eruptions or surface extrusion of watery mud or clay which almost invariably is accompanied by methane gas, and which commonly tends to build up a solid mud or clay deposit around its orifice, often conical or volcano-like in shape (Hedberg, 1974). Mud volcanoes are found in many parts of the world, generally in areas of Cenozoic or late Mesozoic sediments, and commonly asssociated with thick, rapidly deposited succession of Tertiary and Upper Cretaceous sedimentary beds. The mud emanating from these volcanoes, which is a mixture of clay and salt water, is believed to be kept in a state of a slurry by the churning action of the accompanying gases. The source of mud volcano effluents have been commonly traced to substantial subsurface layers of overpressured mud or shale. Mud volcanoes also commonly appear related to fractures, faults, or sharp folding.

The activity of a mud volcano is usually mild but there are many instances of explosive eruptions where large masses of rock have been blown out and scattered over the adjacent area (Sokolov and others, 1969). Such eruptions suggest periodic buildup and release of pressure from the formation of gases.

Location and Description

The mud volcanoes and mineral springs in the Copper River Basin have been described in detail by Nichols and Yehle (1961a; 1961b) and Grantz and others, (1962). A comparison of certain physical characteristics of the mud volcanoes is reproduced in figure 3. Mud and silt brought up by the saline spring waters and deposited in outflow channels appears to be the principal means by which these cones have been built.

Shrub and Upper Klawasi cones lie at similar elevations (900 m) on outwash fans built by glacial streams from the west slopes of Mt. Drum. Both cones are elliptical in plan and drumlinoid in profile, and are covered with glacial drift. In contrast, Lower Klawasi cone is lower in elevation (550 m), nearly symmetrical, and has no traces of glacial drift or glacial-lacustrine deposits.

Shrub volcano is presently dormant although it issued small amounts of saline water and carbon dioxide gas as recently as 1973 (I. Barnes, U.S. Geological Survey, pers. comm.). Upper Klawasi experienced a sharp increase in discharge of both gas and water sometime between 1941 and 1954 (Nichols and Yehle, 1961a). Water temperature at Upper Klawasi has dropped since then, measuring 31°C in 1954 and 1960 vs 17°C in 1981 and 19°C in 1985. Water temperatures appear to have also dropped slightly at Lower Klawasi, measuring 28°C in 1956 but 20 to 22°C in 1960, 1981, and 1985. Upper and Lower Klawasi, and Shrub before it went dormant, all discharged carbon dioxide gas and Na-Cl-HCO_3 rich waters.

Water discharge measured 110 lpm in 1982 at both Upper and Lower Klawasi craters, indicating discharge has increased since 1960 (cf. table 3).

Cones of the Tolsona group are all much smaller in size compared to the Klawasi group, all lie below nearby strandlines of Pleistocene glacial lakes and are covered with probable glacio-lacustrine deposits. Nickel Creek cone appears to have been modified by glacial activity while the shield-like shape of the other cones of the Tolsona group, and also Lower Klawasi, indicate the general form of these cones developed after the melting of glaciers. Springs from the Tolsona group (excepting Shephard mud volcano which is dormant) emit small amounts of methane gas and cool (2 - 10°C), Na-Ca-Cl rich waters, with rates of discharge less than one lpm.

Waters from the Copper Center mineral spring have the highest chloride concentration of any of the spring waters in the basin. The spring waters emanate from a low mound of silt and mud and the site appears to be developing into an incipient mud volcano cone. The spring discharges Na-Ca-Cl rich waters at a rate of about 35 lpm accompanied by minor amounts of methane and nitrogen-rich gas.

Elevated chloride concentrations were found in several river waters, suggesting saline waters reach the surface over a fairly broad area of the Copper River Basin (Grantz and others, 1962). In addition numerous water wells in the Glenn Allen area are high in chlorides indicating some shallow aquifers are being contaminated with saline waters.

METHODS

Sampling Procedure

Samples of waters and gases from Copper River Basin mud volcano and other mineral spring sites were collected on three separate occasions during the course of this study. The broadest specrtum of samples were obtained during June of 1982, and included samples from each mineral spring, from selected water wells, and from representative streams and cold springs. Additional samples were collected from Upper and Lower Klawasi, Nickel Creek, and Copper Center in September, 1981 and from Upper and Lower Klawasi in July, 1985.

Spring waters samples were collected as close to the issuing vent as possible; domestic wellwaters were collected as close to the wellhead as possible and always before entering any purification system. The samples were filtered through 0.45 micron filters. The sample suite normally consisted of one liter each of filtered untreated and filtered acidified

(HCl) waters; 100 ml 1:10 and 1:5 diluted samples for silica determinations; and 30 ml samples for oxygen-18 and deuterium isotopic analyses. Raw untreated samples were collected for field determinations of HCO_3, pH, NH_3, and H_2S. In 1982, one liter samples of raw waters were collected from Upper and Lower Klawasi and treated with 30 ml of ammoniacal $SrCl_2$ saturated solution to force precipitation of bicarbonate and carbonate as $SrCO_3$. The precipitate was subsequently used for determining the carbon-13 composition of the bicarbonate-carbonate species in the waters. At Upper and Lower Klawasi, one liter of filtered water was collected and treated with formaldehyde for later determination of oxygen-18 composition of the sulfate species.

Gases were collected by immersing a plastic funnel in the pool of spring waters. The funnel was placed over a train of bubbles and connected to an evacuated gas collecting flask with tygon tubing. The gas sample was taken by allowing the gases to displace water in the funnel, purging the sampling line of air, then collecting the gas in the evacuated flask. Samples were normally collected in 50 to 100 cc flasks constructed from helium-impermeable Corning 1720 glass. At the Klawasi mud volcano sites, where carbon dioxide was known to be the predominate gas, 300 cc evacuated flasks charged with 50 to 100 cc of 4 N sodium hydroxide solution were also used for gas collection. Carbon dioxide, sulfur, and ammonia gases are absorbed by the sodium hydroxide allowing trace gases to concentrate in the head space of the flask.

In 1982 and again in 1985 we were able to sample gases from fumaroles at the hydrothermally active North Crater, located at the 4,270 m summit of nearby Mt. Wrangell volcano. These samples provide chemical and isotopic compositional comparisons to what could be presumed to be a magmatic - volcanic component to Copper River mud volcano gases. Sampling procedure was similar to that described above except that rather than using a funnel, heat resistant tubing was inserted down the fumarole vent to obtain a flow of gases.

Analyses Procedures

Water: pH and HCO_3, NH_3, and H_2S concentrations were determined in the field following methods described in Presser and Barnes (1974). The remaining constituents were analyzed at the DGGS water laboratory in Fairbanks. Major, minor and trace cation concentrations were determined using a Perkin-Elmer atomic absorption spectrometer following standard procedures outlined in Skougstad and others (1979) and in the Perkin-Elmer reference manual. Sulfates were determined by the titrimetric (thorin) method; fluorides by specific ion electrode; Cl by Mohr titration; bromide by hypochloride oxidation and titration; and boron by colormetric carminic acid method. Silica concentrations were determined by the molybdate blue method.

Gases: Gases collected in uncharged flasks and unabsorbed gases collected in the sodium-hydroxide charged flasks were analyzed on dual-column gas chromatographs using both argon and helium carrier gases. The chromatographic analyses of gases collected in 1982 were performed at the U.S. Geological Survey, Menlo Park, California; gases collected in 1985 were analyzed at the Global Geochemistry Corporation. For samples collected in sodium-hydroxide charged flasks, the total moles of gases not absorbed in solution were determined by measuring the gas pressures and the head space volumes in the flasks. CO_2 and H_2S molar concentrations in the solution were determined by titration and by gravimetric means respectively, follwing procedures outlined in Sheppard and Giggenbach (1984). Ammonia was analyzed by specific ion electrode method. Adjustments were made for head space gases dissolved in the solution using Henry's Law. Moles of each constituent collected were then determined and the mole percent of each constituent calculated. Where required a correction was made for air contamination by using the ratio of oxygen in the sample to oxygen in air. The gas concentrations in mole percent were then recalculated on an air-free basis.

Isotopes: Stable isotope compositions of the water samples ($^{18}O/^{16}O$ and D/H) were analyzed under contract by the Stable Isotope Laboratory at Southern Methodist University, Dallas, Texas. Procedures followed are outlined in Viglino and others (1985).

The $^{18}O/^{16}O$ composition of sulfate species was analyzed in cooperation with C. Janik of the U.S. Geological Survey, Menlo Park, California. Procedures followed are discussed in Nehring and others (1977).

Analyses of Carbon 13/12 ratios in CO_2 gas in the 1981 and 1982 samples were performed at the Stable Isotope Laboratory at Southern Methodist University and at the U.S. Geological Survey, Menlo Park, California. The CO_2 absorbed in sodium-hydroxide was first gravimetrically precipitated as $SrCO_3$ using $SrCl_2$. The $SrCO_3$ precipitate was then reacted with phosphoric acid to release the CO_2 gas. The U.S. Geological Survey also performed the analses of carbon 13/12 ratios in the $SrCO_3$ precipitated from the 1982 Klawasi waters and of limestones obtained from drill cuttings from the AHTNA-AMOCO 1A well.

Carbon 13/12 ratios in CO_2 and methane gases collected in 1985 were analyzed at Global Geochemistry Corporation.

Helium 3/4 ratios in the sampled gases were analyzed at the Stable Isotope Laboratory at the Scripps Institute of Oceanography, La Jolla, California. The procedures followed for gas extraction, measurement of absolute helium amounts, mass spectrometer measurement of $^3He/^4He$ ratios, and application of He/Ne correction for air contamination are described in Lupton and Craig (1975), Torgersen and others (1982), and Poreda (1983).

RESULTS

The results of our geochemical and isotopic analyses of water and gases from the Copper River Basin mud volcanoes and saline springs are presented in tables 1, 2, and 3. Our analyses of wellwaters and river waters are given in Appendix A, and a compilation of all previous analyses of saline spring waters and gases are provided in Appendix B.

Compared to the Tolsona waters, the Klawasi waters are strongly enriched in alkali metals (Li, Na, K), Mg, HCO_3, SO_4, B, and SiO_2, and strongly depleted in Ca and Sr (table 1; fig. 4). The Klawasi waters also contain high concentrations of arsenic (10 to 48 ppm), several orders of magnitude more than any of the Tolsona waters (< 10 ppb).

The Tolsona and Klawasi mud volcano waters plot as easily recognizable and distinctly separate fields on both cation and anion trilateral diagrams (figs. 5 and 6). The percentage anion composition of most of the saline wellwaters and the more-dilute saline springs show close affinities with the Tolsona group while the percentage cation compositions of these more-dilute waters plot on a mixing trend between Tolsona waters and low chloride meteoric and ground waters.

The stable isotopic compositions (per mil $\delta^{18}O$ and δD) of saline spring waters, wellwaters, and meteoric waters in the basin are plotted on fig. 7. Included on the graph are unpublished data for Klawasi and Tolsona water samples obtained and analyzed by I. Barnes in 1973 (U.S. Geological Survey, pers. comm.; cf. Appendix B). We make three observations regarding the mud volcano spring waters: (1) they are strongly enriched with respect to the heavier isotopes when compared to modern-day meteoric waters; (2) the Klawasi waters are enriched in $\delta^{18}O$ and both the Tolsona waters and more so the Klawasi waters are depleted in deuterium with respect to standard mean ocean water (SMOW); and (3) the Tolsona and Klawasi waters plot in distinctly separate fields.

Gases emanating from the Klawasi group are almost entirely CO_2 with minor amounts of N_2 and CH_4 and trace amounts of Ar and He. In contrast, the Tolsona gases are composed of roughly equal amounts CH_4 and N_2 with only trace amounts of CO_2 but significant concentrations of He. Trace amounts of H_2 were found in several of the Copper River Basin gas samples.

Although the proportion of CH_4 in the gases emanating from the Klawasi mud volcanoes is much smaller than at the Tolsona group, the overall rate of gas discharge is so much greater at Klawasi that the absolute rate of discharge of CH_4 is probably similar to and perhaps even greater than at the Tolsona group.

We preface our discussion of these and other results by examining the evidence which points to over-pressured zones in the Cretaceous marine sediments as the probable source of the brines emanating from the basin's mud volcanoes. We next briefly review the process of shale-membrane ultrafiltration before proceeding to examine the possible origins of these sedimentary brines, their chemical constituents, isotopic compositions, and causes of the differences between the two groups of mud volcanoes.

SOURCE OF SALINE SPRING WATERS

The saline spring waters, at least in the vicinity of the Tolsona mud volcanoes, appear to be derived from an overpressured zone in Lower Cretaceous deposits. Saline waters, accompanied by tars and methane, were produced from an overpressured zone in the Pan-Am Moose Creek well which is located near the Tolsona mud volcanoes (fig. 2). The zone occurs in two quartzose sandstone units at 1680 to 1830 m below the surface, in the lower part of the Lower Cretaceous section of the well. The chemical composition of the Pan-Am Moose Creek waters reported by Foresman (1970) bear marked similarities to the chemistry of the Tolsona mud volcano waters (Appendix B; fig. 5 and 6).

A suite of Upper Cretaceous fossil fragments found in outflow deposits at both the Klawasi and the Tolsona mud volcanoes were also found in the Upper Cretaceous sections of the Pan-Am and the Aledo wells (Grantz and others, 1962; Foresman, 1970). Apparently the fossils were brought to the surface by movement of mud and water from the overpressured zone in Lower Cretaceous sediments through overlying younger strata. Although the Klawasi waters differ markedly in many respects to the Tolsona waters, the presence of Upper Cretaceous fossils in the Klawasi outflow muds indicate the Klawasi waters are probably also primarily derived from an overpressured zone in strata underlying the Matanuska Formation.

Overpressured zones appear to be lacking at most other wells in the basin. The Lower Cretaceous formations, the zone of overpressuring at the Pan-Am well, are missing at both Amoco-Ahtna wells. Methane gas and flow of saline waters with a reported chloride concentration of 8400 ppm were produced from a depth of 2,165 m from Jurassic sediments at Amoco-Ahtna 1. However, the flow quickly died out giving no indication of overpressuring.

Methane and saline water flows (Cl ≈ 8500 ppm) were obtained from the Matanuska Formation at depths of 640 to 700 m at Amoco-Ahtna 1A. The increase in mud weight required by the drillers to stem the flow suggest these waters are being subjected to pressures substantially above hydrostatic. The proximity of the Copper River saline seep to the well site suggest these spring waters are derived wholly or in part from this apparent zone of overpressuring.

ORIGIN OF BRINES

The association of the saline waters with marine sediments argues strongly that at least a portion of the water is connate in origin, i.e., seawater entrapped at time of deposition. Dissolution of evaporites is unlikely to have contributed to the brine chemistry since no evaporite beds were reported in any of the wells or in any of the formations that underlie the basin. The saline spring waters have nearly identical bromide to chloride ratios, and very similar iodide to chloride ratios (table 1; fig. 4). The similarity in the ratios of these conservative constituents indicate the various spring waters are ultimately related to the same or very similar parent water(s). Furthermore, acquisition (or depletion) of halides in the water by evaporite or other mineral dissolution or (deposition) is unlikely to have produced such similarities in halide ratios. Thus, the only other obvious source for the halides is seawater. If so, the original interstitial seawater must have undergone substantial modification to account for the present chemical and isotopic compositions (figs. 4 and 7).

Major differences in formation brine vs seawater chemical and isotopic compositions have been documented at many other marine sedimentary basins and various processes have been advanced to account for the differences. Degens and others (1964) attributed the differences in oxygen isotope ratios to mixing of meteoric waters wtih original marine interstitial solutions. Clayton and others, (1966) based on studies of salinities and isotopic compositions of oil-field brines from the Illinois, Michigan, and Alberta basins and the Gulf Coast, concluded that virtually all the original interstitial water was lost during compaction and subsequent flushing by fresh water, and that the present formation water is of predominately local meteoric origin that has been isotopically shifted through oxygen isotope exchange between the water and the reservoir rocks. Hitchon and Friedman (1969) and Hitchon and others (1971) attributed variations in chemical and isotopic compositions to a combination of the two previous processes and also concluded that formation waters can be further chemically modified by diagenetic processes, redistribution of dissolved solids by movement of fresh water through a basin, and selective depletion and concentration of constituents by shale membrane ultrafiltration processes. White and others (1973), in a study of thermal and mineral waters of nonmeteoric origin in the California Coast Ranges, agreed with Hitchon and Friedman's interpretation, and suggested that in some cases waters of metamorphic origin may also contribute to the formation waters.

Given the wide variety of potentially applicable modifying processes and the complexity of some of these mechanisms it would be impossible within the the framework of our limited data base to trace in detail the lineage of the Copper River Basin formation brines. However, there is sufficient evidence to indicate that nearly all of the above mentioned processes have played a part in establishing the chemical and isotopic composition of these brines. Before proceeding to a closer examination of Tolsona- and Klawasi type waters we first breifly review the process of shale-membrane ultrafiltration.

ULTRAFILTRATION

Several investigators have suggested that certain features of formation brines could be explained if shales behaved as semipermeable membranes, allowing water molecules to escape but retarding or preventing migration of dissolved species (White, 1965; Hitchon and Friedman, 1969; Hitchon and others, 1971)). Ultrafiltration and the relative retardation by geologic membranes of cations and anions was subsequently experimentally verified by Kharaka and Berry (1973) and Hanshaw and Coplen (1973). A comprehensive review and treatment of ultrafiltration by clay membranes has been given by Graf (1982).

Briefly, the semipermeable membrane properties of shales result from charge deficiencies on the surfaces and edges of the clay particles. The pore walls of the shale have a net negative charge because of the substitution of lower-charge cations for framework Al^{3+} and Si^{4+} in clay minerals. If the pores are small enough so that the charge in their walls is felt throughout the pore, anions will be repelled by the surface and will be unable to pass through the pore. Cations will be attracted to the charged surface of the clays, partially balancing the negative charge and thus enabling other cations to pass through the pore. Build up of cations at the pore exit and the need to preserve overall electrical neutrality in the solution tends to impede further cation flow. Diffuse flow toward equilibrium solution will also counteract to some degree the previous retardation mechanisms.

Some charged species pass more easily than others through the clay membrane. Factors controlling the mobility of ions include selective adsorption or repulsion by the membrane and the relative velocities of dissolved species during flow of fluid (Hanor, 1979). Cations more strongly attracted to exchange sites on clays should be more strongly retarded. Ions of large hydration radii should show greater hydraulic drag and slower flow rates. For slow flow rates, hydraulic drag is secondary, and theory favors passage of small , monovalent cations, Li > Na > K and the retardation of large, divalent cations, Mg < Ca < Sr. Uncharged species, eg., H_2O, H_2CO_3, H_2S, and $NaHCO_3$, should pass easily through the micropores as should nearly neutral complexes such as $NaSO_4^-$.

Kharaka and Berry (1973) found that the retardation of monovalent and of divalent cations in clay membranes followed the general sequence described above. At pressure gradients characteristic of subsurface conditions, calcium should be strongly retarded with respect to sodium; chloride and sulfate are more strongly retarded than bicarbonate. Kharaka and Berry also found that the efficiency of the ultrafiltration process increases with increased cation exchange capacity of the clay minerals, with increased compaction pressure, with decrease in salinity of input solution and slightly with decreasing temperature.

Hanshaw and Coplen (1973) experimentally verified the existence of minor membrane fractionation effects for the stable isotopes of hydrogen and oxygen postulated by Hitchon and Friedman (1969). Distilled water and 0.01 N NaCl solution were forced to flow at ambient temperature under a pressure of 100 bars through a montmorillonite disc having a 35 per cent porosity. The ultrafiltrates in both cases were slightly depleted in D by 2.5 per mil and ^{18}O by 0.8 per mil relative to the residual solution.

Graf (1982) has distinguished between the roles of chemical osmosis, osmotic pressures, and reverse chemical osmosis. In nature, chemical osmosis produces an overpressuring on the high-salinity side of the shale membrane, i.e., a fluid pressure greater than that which would exist if the fluid column had an uninterrupted connection to the surface through macro-channels. It is reverse chemical osmosis that has been invoked to help explain observed subsurface distributions of chemical compositions. The operation of reverse chemical osmosis requires that some process generate a hydraulic pressure gradient sufficient to drive upward against osmotic gradients through compacted shale membranes. As flow of water continues and membrane filtration of charged species takes place, deeper waters become progressively concentrated and selectively enriched in those anions and cations which are discriminated against by the membranes.

Calculations by Graf indicate that sedimentary basin overpressuring is more than adequate to overcome chemical osmosis and drive reverse chemical osmosis in sedimentary sequences. Overpressuring occurs when the escape of fluids from a compacting sediment cannot keep pace with increasing overburden and internal pressures. The interstitial fluid then not only supports the normal hydrostatic pressure corresponding to its depth but also additional pressures exerted by the overlying rocks.

The most commonly discussed mechanisms for generating overpressures are (1) rapid sedimentation, (2) lateral tectonic compression, (3) thermal expansion of water (aquathermal pressuring), (4) dehydration of gypsum and/or clay minerals, and (5) gas generation. The first mechanism is normally the greatest contributor to the development of overpressuring in sedimentary basins and is certainly operative in the Copper River Basin where the accumulation of Quaternary, Tertiary and Upper Cretaceous sediments in the central part of the basin ranges from 1500 to 2000 m in thickness. Lateral tectonic compression is likely to be another contributing factor to overpressuring in the Copper River Basin. The basin lies in a region which for the past several million years has been undergoing crustal forshortening due to the compressive tectonic stresses being exerted by the motion and subduction of the North Pacific Plate beneath the North American Plate. Thus overpressuring in the basin may have existed for some time, driving reverse chemical osmosis for millions of years. An additional factor which would have increased the lithostatic pressure in the recent past is the loading of glacier ice and large proglacial lakes that existed in the basin during the last major glacial advance (Grantz and others, 1962).

Mechanisms 3, 4 and 5 can only be very minor contributors to overpressuring at the Tolsona group. The bottom hole temperature which measured ≈ 54°C at 2,680 m in the Pan-Am well, indicates a geothermal gradient that is at or slightly below the world average thermal gradient. Dehydration of gypsum appears to be an unlikely contributor as no gypsum or anhydrite beds were reported in the well logs. Dehydration of clay minerals also appears to be unlikely contributor because mica dehydration usually does not begin until $T \geq 100°C$. The amount of gas emanating from the Tolsona group appears too minor for gas formation to be a significant contributor to overpressuring.

However, the large amounts of carbon dioxide gas emanating from the Klawasi group suggest that gas pressures there can be a significant factor. Also, results of this study discussed later, indicate the reservoir temperatures at Klawasi group may be substantially higher then at the Tolsona area so that thermal expansion of water may be an important process contributing to overpressuring at Klawasi. These additional overpressuring mechanisms could intensify membrane filtration and could also explain the much greater rate of water discharge and larger mud volcano edifices at Klawasi compared to Tolsona.

TOLSONA-TYPE WATER CHEMISTRY

Isotopic Compositon and Evidence for Dilution

The Tolsona and Klawasi waters are isotopically similar to many other oil-field brines (cf. Taylor, 1979). However, the isotopic compositions of brines for most other basins fall on distinctive linear trends characteristic of the specific basin. Such trends have been taken as evidence that the brines in a specific basin are related to each other with the linear trends indicative of meteoric - formation water mixing (White and others, 1973; Hitchon and Friedman, 1969; Clayton and others, 1966). No linear trend is evident between the Tolsona and Klawasi waters despite their geographical proximity to each other, nor do the data sets within either group show any obvious mixing trend with present-day meteoric waters. Signs of any apparent mixing trends with present-day meteoric waters are also lacking on plots of both $\delta^{18}O$ vs Cl or δD vs Cl although arguments can be made for possible mixing with a much heavier, perhaps paleo-meteoric water (figs. 8 and 9).

At the Copper River Basin the chloride concentrations in the mud volcano waters range from 8,600 to 14,400 ppm compared to 18,000 ppm for seawater which indicates the original interstitial seawater must have been diluted. Diluton prior to entrapment seems unlikely given the wide range of chloride concentrations and the short distance between sites. The similarity in chloride concentration between the brine produced from the overpressured zone in the Pan-Am well and the Tolsona waters argues against any contamination of the brine upon ascent before emerging as springs. In any event, isotopic evidence indicates that modern meteoric waters cannot be the diluting agent as no simple mixing trends exist between seawater (SMOW), the mud volcano waters, and present-day meteoric water (figs. 7, 8, and 9). Consequently, the original interstitial seawaters probably became diluted after entrapment but apparently during an epoch when the local meteoric water was isotopically much heavier than today. This is most likely to have occurred during a period of regional uplift, such as must have occurred during the Late Jurassic or mid-Cretaceous, during which time circulation of fresh water would have had the opportunity to mix with, dilute, and possibly flush the interstitial brines.

The stable isotope composition of the Tolsona waters could be explained by simple dilution of original interstitial seawaters with paleo-meteoric waters and a shift in ^{18}O through isotopic exchange with reservoir rocks. If fractionation by shale-membrane filtration is assumed to be negligible and Copper Center mineral spring is excluded, a mixing line from SMOW through Tolsona waters on the plot of δD vs Cl (fig. 8) gives an estimated δD composition of the diluting water of -35 per mil; the corresponding $\delta^{18}O$ would be -5.5 per mil. Fractionation by membrane filtration tends to concentrate the heavier isotopes in the residue although the effect is considered minor (Coplen and Hanshaw, 1973; Hitchon and Friedman, 1969). Thus, the paleo-meteoric diluting water may have been slightly lighter or heavier than the above estimate depending on whether the Tolsona water sampled is the filtrate or residue. Evidence presented later suggests that modification of the Tolsona water by membrane filtration is equivocal and that, if anything, the water is the product of an intermediate stage of filtration.

Assuming dilution only, the resulting mixed water would have had a $\delta^{18}O$ value of about -4 per mil compared to 0 per mil for the Tolsona mud volcano waters. The isotopic shift could have been produced through exchange of ^{18}O with marine carbonates and possibly also shales in the sedimentary formations. Marine carbonates are characteristically highly enriched in ^{18}O. For example, a limestone sample from Ahtna-Amoco well 1A has a $\delta^{18}O$ value of +25 per mil(see table 4). The average for marine pelagic sediments is +19 per mil (Savin and Epstein, 1970). The magnitude of the isotopic shift is temperature dependent with increased shifts favored by higher reservoir temperatures. The lack of a similar shift in ^{18}O at Nickel Creek is puzzling but may indicate a lack of carbonates or that reservoir temperatures there are too low to allow exchange to occur.

The isotopic compositions of some of the more dilute saline springs such as the Tazlina mineral spring and some of the well waters that are high in chloride could be derived from mixtures of meteoric waters with either Tolsona or Klawasi type waters. Water from the Copper River saline seep appears to lie on a trend between present-day meteoric waters and seawater (figs. 8 and 9). If the seep brines are being mostly derived from from the middle of the Matanuska Formation as suggested by the neighboring well, the $\delta^{18}O$ and

δD vs Cl trends suggest that the waters in this zone are mostly modern meteoric waters.

Although the Copper Center mineral spring water has an isotopic composition nearly identical to Tolsona waters, it is more saline and more concentrated in Ca then the Tolsona waters (table 1; fig. 4). It is possible that membrane filtration has selectively concentrated Cl, Ca, and other constituents at Copper Center but without significantly affecting isotopic composition thereby explaining the apparent shift from the Tolsona mixing line on the δD vs Cl diagram. However, the Copper Center water does lie on an apparent linear trend between seawater and the Klawasi waters, suggestive of mixing with a meteoric end member considerably lighter than estimated for the Tolsona waters. If such mixing did occur, the difference in ^{18}O composition between Copper Center and Klawasi could be reconciled if the Klawasi waters are presumed to have been more strongly shifted through isotopic exchange processes. However, the existance of two such compositionally different meteoric mixing end members seems improbable given the short distance between sites and the former explanation is preferred.

In conclusion, although there is strong evidence that dilution has modified original connate waters, the degree of flushing and the proportion of original seawater remaining is difficult to estimate because of complications arising from the uncertainties in the efficiency of ultrafiltration processes, isotope exchange, and isotope fractionation.

Membrane Filtration

We wish now to examine what effect, if any, membrane filtration has had on the Tolsona water chemistry and, if we can distinguish whether the waters are 1) an ultrafiltrate, i.e., the end result of multi-step up-section filtration; 2) the residue left behind from long-term filtration ; or 3) some intermediate between the two end products.

Concentration of surface discharge at spring vents indicates that flow of fluids from the overpressured zone is primarily, if not totally, by way of macro-porositic channels. Thus, membrane filtration is unlikely to have affected fluids during their ascent from the overpressured zone as evidenced by the similarity between chemistries of fluids from the Tolsona springs and the Pan-Am well. The spring water chemistry, then, is probably representative of formation waters in the overpressured quartzose sandstone beds.

Compared to seawater, the Tolsona waters are depleted in Na, K, Mg, HCO_3, SO_4, Cl and Br and slightly to highly enriched in Li, Ca, Sr, I, SiO_2, and B. As discussed above, paleo-meteoric waters have probably diluted the original interstitial seawaters and can account for some of the apparent depletions. In an attempt to isolate and compare compositional changes caused by processes other than dilution, ionic concentrations were ratioed to chloride (figure 10). Chloride was chosen because its concentration is unlikely to have been altered by precipitation or dissolution of halite or other chloride minerals and because this ion is among the most efficiently retained in the residual pore fluids by membrane filtration. Leaching of Cl from sedimentary rocks, which have an averge chloride content of 100 to 200 ppm, can at best introduce only minor amounts of additional chloride.

The nearly identical Br/Cl ratio in the Copper River Basin brines has already been noted. The ratio is lower than in seawater (0.0025 vs 0.0036) indicating there has been a net depletion of Br, assuming addition of Cl from other sources can be ruled out. Whatever processes are involved, these processes appear to have been uniform across the basin to account for the similarities in Br/Cl ratios. Results of ultrafiltration experiments indicate that shale-membrane filtration retention efficiency for Br should be similar to or slightly better than that for chloride (Kharaka and Berry, 1973) thus suggesting the Tolsona water is a filtrate end member.

Regarding the remaining ionic species, the enrichments and depletions relative to seawater corresponding to what would be expected for the residue end of an ultrafiltration process include depletion of HCO_3 and SO_4 relative to Cl and Br and enrichment of the divalent cations Ca and Sr relative to the monovalent cations Na and K. However, the order of depletion relative to seawater of the monovalent cations, $K < Na < Li$, is the reverse of what would be expected for a residual water and more in line with a filtrate end-member as are the enrichments of I and B relative to Cl and Br. In addition, the concentrations of Ca, Sr, Li, I, and B are much greater than in seawater, and far in excess of comparable concentrations of Cl relative to seawater, indicating some process other than membrane filtration must be introducing these ions into the formation solutions. The large depletions in Mg also seem much greater than can reasonably be accounted for by selective filtration.

The Tolsona water thus appears to be of a more intermediate type, but closer to a residual water. Furthermore, filtration processes can only explain a portion of the Tolsona chemistry and other mechanisms must have also been instrumental in modifying the waters.

Rock leaching

The enrichment in iodine compared to seawater can be explained by decomposition of marine plants contained in the sedimentary rocks (White, 1965). A large proportion of the boron enrichment is also probably derived from the marine sediments themselves. Boron has been shown to be selectively adsorbed on clay particles during seawater circulation through both near-shore and deep sea pelagic marine sediments (Palmer and others, 1985). The average concentration of boron in shales is 100 ppm (Krauskopf, 1979). Li is also enriched in shales (60 ppm) compared to other rocks and seawater, and leaching of Li by the pore solutions could account for the increased Li. The SiO_2 concentration in the Tolsona-type waters is about what would be expected if silica in the solution is in equilibrium with quartz.

Fluid - Mineral Interactions

One chemical process which would be effective in increasing the Ca and Sr concentrations in the water while at the same time removing Mg is dolomitization:

$$2CaCO_3 + Mg^{2+} = CaMg(CO_3)_2 + Ca^{2+}$$

However, compared to relative seawater concentrations, the increase in Ca corresponding to the decrease in Mg through dolomization is insufficient by itself to balance the excess Ca. For example, based on the relative ratio of Cl concentration, the original diluted interstitial seawater at Tolsona 2A would have had Ca and Mg concentrations of 210 and 650 mg/l respectively compared to 1620 and 40 mg/l respectively in the water now. Dolomitization can only account for at most 610 mg/l of added Ca leaving the source of the remaining half of the Ca unexplained.

Another reaction which would release Ca^{++} into the formation waters is the hydrolysis of marine carbonaes:

$$CaCO_3 + H_2O = Ca^{++} + HCO_3^- + OH^-$$

If the Ca^{++}ions are retained but HCO_3^- and OH^- lost through selective membrane filtration then additional carbonate may be dissolved resulting in a net accumulation of Ca in the residual foramtion waters.

The Ca ions released by the dolomitization and hydrolysis processes, combined with the original seawater Ca could have become concentrated through selective retention during filtration. If so, then retention efficiency for Ca is much greater than for Cl. The high concentration of Ca would then indicate the Tolsona waters are closer to the residue of the filtration spectrum. If so then the depletion in K with respect to seawater remains problematic. One possible mechanism for removal of K (and also Mg) is the formation of clay minerals such as glauconite. Even if new clays are not formed out of dissolved substances, the preponderance of illite in marine shales suggests that K^+ takes part in alteration of other clay minerals (Krauskopf, 1979).

To summarize, the Tolsona-type water chemistry could have been produced through the following processes: dilution of original interstitial seawaters with paleo-meteoric waters, possibly during a period of uplift in the Late Jurassic or mid-Cretaceous; loss of HCO_3 and SO_4 and modification of other constituent concentrations by shale-membrane filtration; further depletion of Mg, K, HCO_3, and SO_4, and enrichment in Ca and Sr through dolomatization, hydrolysis, and clay-forming processes; and leaching of B, I, Li, and SiO_2 from marine sediments. The isotopic compositions could have been produced by simple dilution with paleo-meteoric waters followed by a positive shift in ^{18}O through isotopic exchange with marine carbonates and other sediments. Enrichments in heavier isotopes may also have been caused by ultrafiltration fractionation but the effects of this process are thought to be slight (Hitchon and Friedman, 1969; Coplen and Hanshaw, 1973).

KLAWASI-TYPE CHEMISTRY

In this section we present arguments that the differences in fluid chemistry between Klawasi and Tolosona are primarily a result of the interaction of fluids derived from a magmatic intrusion and contact decarbonation of limestone beds underlying the Klawasi area. Evidence for a magma-decarbonation influence on the Klawasi system include: 1) the high $^3He/^4He$ ratios at Klawasi, 2) the ^{13}C compositions of the CO_2 gas and bicarbonate, 3) consistency with large volumes of CO_2 gas and with the Klawasi water chemistry, 4) the high concentrations of As, and 5) chemical geothermometers which indicate reservoir temperatures at Klawasi are substantially above those at Tolsona.

Helium-3

Samples of gases obtained from each major saline spring vent and also from fumaroles at the summit of Mt. Wrangell have been analyzed for ^3He content and the results are presented in table 3 and on fig. 2. Enrichments in ^3He with respect to atmospheric levels have been correlated with magmatic activity on a worldwide basis with the excess ^3He thought to be derived from the mantle (Craig and Lupton, 1981). The R/R_a values ($^3He/^4He$ ratio of sample vs air) of 6.0 and 6.1 for Mt. Wrangell fall within the range of values of 5 to 8 found at volcanic vents in the Aleutian Arc and at convergent margin volcanic arc settings elsewhere in the world (Poreda, 1983; Motyka and others, 1985; Craig and others, 1978). The Mt. Wrangell gas samples were obtained from the North Crater which contains sevaral superheated fumaroles that are discharing CO_2- and SO_2-rich gases. These gases are thought to be directly derived from a crystallizing body of magma underlying the North Crater (Motyka, 1983) and the R/R_a values are therefore probably representative of magmatic helium in the western Wrangell Mountains.

Although the R/R_a values for gases from sites in the Copper River Basin are all lower than that from Mt. Wrangell, those for the Klawasi group are still substantially above atmospheric. The highest values are at Lower Klawasi (4.0 - 4.1) with progressively lower values towards Tolsona (1.0) and Nickel Creek (0.75).

The high value for R/R_a at Lower Klawasi indicates a more direct connection to magmatic sources with little or no crustal contamination. The lower values at the other sites indicate a greater crustal influence of radiogenic ^4He which is derived through decay of U and Th. However, even the near-atmospheric values found at the Tolsona group are substantially above what would be expected for a sedimentary basin of this age. For example, sedimentary basins in Alberta have R/R_a ratios of 0.02 (M. Kennedy, U. of California, Berkeley, pers. comm.).

The apparent ^3He gradient, decreasing outward from Lower Klawasi, would suggest that the focus of any magmatic activity underlies Lower Klawasi. Helium is highly mobile and the magmatic helium may be diffusing outwards and mixing with crustal radiogenic ^4He to produce the values found at the surrounding sites.

CO_2 and Fluid - Mineral Interactions

Dissolution of carbonates within the sedimentary beds containing the Klawasi formation water cannot explain the extremely high concentration of HCO_3, the enormous quantities of CO_2 gas, accompanied by the simultaneous near depletion of Ca and Sr. Although dissolution of reservoir calcite would liberate CO_2 and HCO_3 it would also substantially increase the Ca concentration, in excess of 5,000 mg/l just to balance the HCO_3 found in the surface spring waters. The reverse is found in the Klawasi waters and therefore some external agent must be introducing the CO_2 into the reservoir waters.

Many of the differences in fluid chemistry that exist between Klawasi and Tolsona can be explained by assuming a small magma body has intruded deep-seated limestone beds underlying the Klawasi area. In the simplest model, silica-rich solutions from the magma invade and interact with the contact limestone beds to form Wollastonite and release CO_2 gas:

$$CaCO_3 + SiO_2 = CaSiO_2 + CO_2(g)$$

The reaction is dependent on the partial pressure of CO_2 with high PCO_2 inhibiting formation of wollastonite . If the system is more open so that CO_2 is free to escape, eg. via faults and fractures, the process can take place at relatively low temperatures, T≈400 to 500 C (Krauskopf, 1979). More complex reactions involving impure limestones and dolomites have been reviewed by Kerrick (1974) and generally follow the same pattern.

Under our model, the large quantities of CO_2 degassing from the magma, together with CO_2 produced by decarbonation reactions escape via fractures or fault zones, possibly the Taral fault, and invade formation waters in the overlying marine sediments resulting in the formation of carbonic acid:

$$H_2O + CO_2(g) = H_2CO_3 \; (H+ + HCO_3-)$$

The carbonic acid causes hydrolysis of silicates and clays. A simple example for silicates is fosterite:

$$Mg_2SiO_4 + 4H_2CO_3 = 2Mg{+}{+} + 4HCO_3- + H_4SiO_4$$

and a general reaction for clays, is given by:

$$\text{clay} + H_2CO_3 = (Na+,\ K+) + \text{aluminum silicate} + H_4SiO_4 + HCO_3-$$

Thus hydrolysis reactions would increase alkalis, silica and HCO_3 concentrations in the water. Breakdown of marine clays might also facilitate release of boron which had been adsorbed on the clay particles, increasing its concentration in the formation water.

The hydrolysis reactions will quickly buffer the system and the pH will increase. Despite the probable high partial pressures of CO_2 within the reservoir, which would tend to increase calcite solubility, the high initial concentration of calcium in the formation water results in the water becoming quickly saturated with respect to calcium carbonate and precipitation will occur. Figure 11, taken from Holland and Malinin (1979), shows the solubility surface for calcite as a function of PCO_2 and temperature for the system $CaCO_3$-CO_2-H_2O. Application of chemical geothermometers, discussed later, suggests formation water reservoir temperatures lie between 100 and 125°C. The solubility of calcite increases with salinity, and for molar concentrations representative of Klawasi (≈ 0.3 to 0.4) the $CaCO_3$ solubility for the temperature range 100 to 125 °C would be approximately 1.5

to 2.0 greater than for pure water. For CO_2 partial pressures of 30 to 50 atm calcite saturation would then range from 900 to 2,000 mg/l. The equivalent Ca concentrations are 360 to 800 mg/l, substantially below Ca concentrations in nearby Copper Center mineral spring waters.

Although the solubility of calcium carbonate increases with decreasing temperature, the rapid drop in PCO_2 as CO_2 exsolves upon ascent of the fluids controls calcite solubility and calcite will continue to precipitate from solution resulting in almost complete depletion of Ca (and Sr) in the surface spring waters. The surface spring waters are in fact saturated with respect to calcite and travertine has been deposited in the outflow channels.

The preceding model is consistent with the observed differences in water chemistry between Klawasi and Tolsona (fig. 4 and 10). If the formation waters at Klawasi were originally similar to Tolsona-type waters then the above reactions would have caused enrichments in Li, Na, K, Mg, , SiO_2, and B, sharp increases in HCO_3 and CO_2 gas, and sharp depletions in Ca and Sr. The increased SO_4 and perhaps also some of the B may have been derived from H_2S and B gases escaping with the CO_2 gases from the metamorphic contact zone.

As discussed previously, thermal expansion of waters and the large infusion of CO_2 gas could both be enhancing filtration processes at Klawasi. Many of the relative depletions and enrichments of ions in the Klawasi waters are consistent with the pattern expected for an ultrafitrate end member, although the relative enrichments of the monovalent cations are in reversed order for an ultrafiltrate.

Arsenic

Arsenic is highly concentrated in the Klawasi waters (10 to 48 ppm), several orders of magnitude greater than the Tolsona waters (0.001 to 0.008 ppm) or seawater (0.004 ppm). Reported concentrations of As in oil-field brines, sedimentary formation waters, and almost all other natural waters are generally either below detection or in trace amounts (< 0.05 ppm) (White and others, 1963). Concentrations of As for saline hot spring waters which are probably derived from sedimentary formations in the Wilbur mining district of the eastern California Coast Range, are reported to be 0.5 to 0.9 ppm (J. Thompson, USGS, pers. comm.) but a large fraction of the spring fluids are thought to be derived from a geothermal reservoir with an estimated temperature of 230 °C (Thompson, 1979). In fact, hot spring and well waters in geothermal areas commonly have concentrations of As ranging from 1 to several ppm. For example, As concentrations in Yellowstone hot springs range from 0.2 to 3.6 ppm and 2 to 3 ppm at Steamboat Springs, Nevada (Stauffer and Thompson, 1984); 4.5 ppm at Waireki and 5.7 ppm at Broadlands (Ellis, 1973); 10 to 12 ppm at the Makushin geothermal area (Motyka and others, 1985). Extremely elevated concentrations of As, comparable to that found at Lower Klawasi, have been reported for El Tatio, Chile, 47 ppm (Cusicanqui and others, 1976); Kizildere, Turkey, 39 ppm (Ellis, 1973); and the Lassen geothermal area, 27 ppm (Thompson and others, 1985). What all these areas have in common are that are associated with hydrothermal systems with estimated reservoir temperatures of 200 °C or higher.

Available thermodynamic data suggest the solubility of As increases sharply with increasing temperature and pH and laboratory experiments suggest that As levels in most geothermal waters can be attributed to a rock-leaching (Stauffer and Thompson, 1984). Arsenic occurs in trace amounts in most rocks and soils, averaging 2 ppm in igneous rocks, 10 ppm in shales, and 1 ppm in sandstones and carbonates (Krauskopf, 1979). Onishi and Sandell (1955) found that silicic volcanic rocks and especially volcanic glasses (As > 12 ppm) have elevated As concentrations. Stauffer and Thompson (1984) concluded that at least 30 to 50 per cent of the As in the Yellowstone hot spring waters was derived by leaching of rhyolitic tuffs in the reservoir.

The origins of extremely elevated concentrations of As are still uncertain. Thompson and others (1985) argued that sources other than rock-water interaction were required to explain the elevated As concentrations at Lassen. In view of the sedimentary reservoir rocks at Klawasi it seems improbable that the high arsenic concentrations there can be attributed solely to rock-leaching.

A magmatic source for As in geothermal systems remains controversial. There is scant information on arsenic in volcanic gases but Greenland and Aruscavage (1986) reported molar concentrations of 1.7 to 4.5 ppm in eruptive gases from Kilauea volcano. Arsenic is a highly volatile metal and apparently is concentrated in fumarolic emissions from some volcanic systems as evidenced by the deposition of orpiment and realgar around high temperature vents (Zies, 1929).

Other possible sources for at least some of the arsenic are volcanic formations that may underlie the Klawasi area. The situation is complicated by the uncertainty in the location of the Taral fault, the apparent boundary between the Wrangellia and Peninsular terranes. The mid- to upper Triassic Nikolai Greenstone, one of the key units that defines Wrangellia, consists primarily of altered tholeiitic basalts. This formation, whose aggregate thickness is on the order of 3,000 m, is extensively exposed along both the southern and northern borders of the Wrangell Mountains (MacKevett, 1978; Richter, 1976) and was the source of ore for the McCarhty and Kennicott copper mines. Tholeiitic basalts usually have very low concentrations of As and are therefore unlikely to be the source of the Klawasi As. However, arsenopyrite, the principal ore of arsenic, is commonly associated with copper deposits and arsenic may have been concentrated along with the copper during secondary deposition in the interstial fractures of the pillow lavas. If the Nikolai Greenstone does underlie the Klawasi area, hot fluids could be remobilizing arsenic within this formation and introducing it into the overlying sedimentary formation waters.

The Lower Jurasic Talkeetna Formation, which is associated with the Peninsular Terrane, is another potential source of arsenic. The formation, which consists of magmatic arc related volcanic rocks, is reported to have a large proportion of silicic flows (R. Forbes, pers. comm., 1986).

In any event, all these processes for explaining large concentrations of As in water involve elevated temperatures. Thus, whatever the source of the arsenic, the high concentrations in the Klawasi waters clearly implies some high temperature regime most exist beneath Klawasi.

$\delta^{13}C$ - CO_2

The carbon-13 composition of CO_2 gas emanating from the Klawasi vents help constraint possible origins of CO_2. Potential sources of CO_2 in the Copper River Basin include (1) oxidation of reduced carbon (methane, coal, and other organic material contained in sedimentary rocks and recharge water), (2) decarbonation reactions involving the destruction of calcite to form calc-silicate minerals, (3) dissolution reactions in which calcite is leached from the sedimentary rocks in the aquifer, (4) primary CO_2 from a magmatic source, and (5) atmospheric CO2 dissolved in groundwater recharge. Carbon of different $\delta^{13}C$ values may be contributed by each of these sources.

Figure 12 compares carbon isotope composition of CO_2 from the Klawasi springs with available data for carbon-13 in other carbon components in the Copper River Basin. The $\delta^{13}C$ ranges of carbon-bearing materials reported by Craig (1963), and Ohmoto and Rye (1979) are also shown. The range of carbon-13 in CO_2 from the Klawasi springs ($\delta^{13}C$ = -3.1 to -4.8) rules out any major contribution from source (1). Atmospheric CO_2 ($\delta^{13}C$ = -7 per mil) seems an improbable source given the large quantities of CO_2 at Klawasi, the very low concentration of CO_2 in air and the He\Ne and CO_2\Ar ratios in the Klawasi gases which indicate nearly negligilble atmospheric gas contamination. For the reasons discussed above, dissolution of aquifer calcite (3) is also unlikely to be a major source of the CO_2.

The range of $\delta^{13}C$ - CO_2 does overlap the low end of the range for marine carbonates and the high end of magmatic CO_2 which indicates the CO_2 is a mixture of gases derived from a magmatic source and from decarbonation of marine carbonates. However, the exact proportion of the CO_2 coming from each of these sources is difficult to estimate because of complicating exchange reactions which occur during the formation and ascent of the CO_2 gas.

Formation of bicarbonate, precipitaion of calcite, and exchange reactions between CO_2 and other carbon bearing species in the Klawasi system would all tend to deplete carbon-13 in the coexisting CO_2. Equilibrium fractionation between dissolved bicarbonate and carbon dioxide gas is zero for T = 125°C with ^{13}C becoming increasingly more depleted in the coexisting CO_2 as the temperature decreases (Friedman and O'Neil, 1977). The HCO_3 being discharged from the Klawasi vents has $\delta^{13}C$ ranging from +1.6 to +3.1 per mil and is enriched in carbon-13 with respect to the CO_2 gas by 6 to 7 per mil, indicating fractionation has occurred between the two species during the ascent and cooling of the fluids (fig. 12; tables 1 and 3).

No measurement could be made of the rate of gas discharge but judging from the state of ebulation observed at both Klawasi craters, flow rates must be in excess of several liters per second (lps). One mole of gas at surface conditions is approximately 22 liters in volume so that the molar rate of gas discharge would be about 0.5 to 1 mole per second. The rate of water discharge is ≈ 2 lps so for a HCO3 concentration of ≈ 8100 ppm (121 mmol/l), the rate of bicarbonate discharge is ≈ 0.240 mole per second and the relative molar proportion of CO2 to HCO3 being discharged is then about 2 to 4. Thus, accounting for the fractionation between CO_2 and HCO_3 during ascent of the fluids indicates that reservoir CO_2 had a $\delta^{13}C$ composition at least 1 to 2 per mil heavier than the surface spring CO_2.

The formation and precipitation of calcite would also deplete the ^{13}C in the coexisting CO_2 for temperatures less than 190°C, with the magnitude of the equilibrium fractionation increasing to 10 per mil for T = 25°C (Friedmen and O'Neil, 1977). Isotope exchange between CO_2 and carbonaceous sediments which are highly depleted in ^{13}C could have caused additional depletion of ^{13}C in CO_2.

Based on these preceding arguments, the CO_2 entering the reservoir water would presumably have a $\delta^{13}C$ composition ≥ -3 per mil. The CO_2 in gases evolving from fumaroles at Mt. Wrangell have $\delta^{13}C$ of -6.5 to -6.7 and serves as a tag for the probable composition of any magmatic component to the Klawasi gases. If the CO_2 gas generated during the decarbonation process is kinetically removed, the $\delta^{13}C$ of the gas should be similar to the original carbonate. Complications arise because of evidence that CO_2 liberated during contact metamorphism of carbonate rocks becomes isotopically enriched with respect to the coexisting calcite (Shieh and Taylor, 1969). At temp ≥ 250 C equilibrium fractionation between CO_2 and $CaCO_3$ remains fairly constant at ≈ +2 to +3 per mil (Friedman and O'Neil, 1977). Thus the liberated CO_2 could have a $\delta^{13}C$ composition ranging from zero to +2 to +3 per mil greater than the carbonate source rock.

The isotopic composition of some carbonates found in the Copper River area are given in table 4. The carbonates in the Ahtna-Amoco well and the Nelchina Limestone are probably too shallow to be the source of the metamorphic CO_2. A more likely candidate is the Upper Triassic Chitistone limestone which is extensively exposed along the west and south flanks of the Wrangell Mountains and has an aggregate thickness of up to 1100 m (MacKevett, 1978; Winkler and others, 1981). The Chitistone Limestone overlies the Nikolai Greenstone and is considered to be part of Wrangellia. Other potential canditates are Permian limestones and marbles which underlie the Nikolai Greenstone. Permian limestones are also part of the Peninsular terrane and are thought to underlie most of the western Copper River Basin. No $\delta^{13}C$ values have been reported for either of these Permian units but Keith and Weber (1964) report that the majority of Permian limestones found elsewhere in the world average +1 ± 2 per mil.

If we assume the source carbonate rock has a $\delta^{13}C$ of ≈ +2.5, then the contact metamorphic CO_2 would have a $\delta^{13}C$ of +2.5 to +5.0 depending on the degree of fractionation with the residual carbonate rock. If we further assume that the magmatic CO_2 has a $\delta^{13}C$ of -6.5 and that the mixed CO_2 entering the formation water reservoir has a $\delta^{13}C$ of -2.0, the proportion of metamorphic to magmatic CO_2 would be on the order of 40 to 50 per cent.

Water Isotopic Composition

Compared to both Tolsona waters and SMOW, the Klawasi waters are enriched in ^{18}O by +1 to +4 per mil and highly depleted in deuterium, by -15 to -20 per mil with respect to Tolsona and -33 to -46 per mil with respect to SMOW (table 1; fig. 7). The apparent enrichment in ^{18}O could be due to increased isotopic exchange reactions between the Klawasi water and the reservoir silicates and carbonates, particularly if, as we shall argue later, the Klawasi reservoir waters are substantially warmer than the Tolsona reservoirs. The shift in deuterium is harder to explain by exchange reactions. The only minerals in marine sediments containing hydrogen are clays and, although clays tend to be highly depleted in D compared to SMOW (-50 to -80 per mil depending on the clay; Savin and Epstein, 1970), the hydrogen content of clays is so small that isotopic exchange is unlikely to have significantly affected water composition.

One other process which could have depleted D in the Klawasi waters is shale-membrane ultrafiltration. As discussed earlier, the relative enrichment-depletion order of the cation and anion constituents of the Klawasi waters is roughly consistent with what would be expected as an ultrafiltrate end-member. The D content in an ultrafiltrate would be expected to be depleted with respect to the residue. However, the process should also cause a corresponding depletion in ^{18}O, by as much as -6.5 per mil if we apply the results of experiments performed by Coplen and Hanshaw (1973), contrasted to the enrichment in ^{18}O seen in the Klawasi water.

The possibility of mixing of seawater with a paleo-meteoric water having an isotopic composition distinctly different from that at Tolsona has already been discussed and considered unlikely.

Two other potential candidates for a mixing end member are metamorphic and primary magmatic waters. The ranges of isotopic compositions of such waters have been estimated by Taylor (1979) and are plotted on fig. 7. The mixing of a Tolsona-type water with either or both of these components could have produced the Klawasi water isotopic composition.

RESERVOIR TEMPERATURES

Bottom hole temperatures reported for older oil and gas exploration wells are often difficult to interpret because of the disruption and contamination of the reservoir by circulation of drilling fluids, and because usually the method of measurement used and the time lapse between cessation of drilling and temperature measurement are unspecified. However, such measurements are commonly the only direct information available on reservoir temperatures, as is the case at Copper River Basin. Table 5 gives the depth and bottom hole temperatures obtained from driller's logs for wells in the basin along with the calculated equivalent linear temperature gradient. These temperatures and gradients are not particularly unusual (they are similar or below the world-wide average), but the slightly higher temperature and gradient at Ahtna-Amoco 1A compared to equivalent depths at nearby deeper wells hints at the possibility that temperature gradients may be increasing going eastward towards the Klawasi group.

The Klawasi spring waters are warmer than the Tolsona waters which could reflect differences in reservoir temperatures between the two groups. However, the difference in vent temperatures could be also be ascribed to the difference in flow rates. The much lower rate of flow at Tolsona would result in greater conductive heat losses as the fluids ascend, particularly during passage through the permafrost table, than at Klawasi.

Chemical and isotopic geothermometers are commonly used for estimating reservoir tempertatures in hydrothermal systems where no direct temperature data is available. Geothermometers are based on temperature sensitive reactions in hydrothermal fluids that may control the absolute amount of an element (e.g., silica), relative concentrations of elements (e.g., cations), or fractionation of isotopes. However, for geothermometers to accurately reflect subsurface temperatures several conditions must be met: 1) constituents involved in the temperature dependent reactions must be sufficiently abundant to permit saturation; 2) water-rock equilibrium occurs at depth; 3) re-equilibration must be negligible as the fluids ascend to the surface; and 4) the fluids coming from depth must not mix with shallow ground water. Stable isotope compositions of the mud volcano mineral spring waters indicate condition 4) is probably met. The validity of the remaining conditions will be examined on a case by case basis. In particular, geothermometers must be applied with considerable caution for the Klawasi system because of interpretational ambiguities arising from the CO_2 induced fluid - mineral interactions which we believe are occurring in the reservoir waters.

Table 6 gives the results of those geothermometers which we feel have the best applicability to the Copper River Basin mud volcanoes. We present our rationale for selecting these geothermometers and dismissing others.

<u>SiO_2</u>: The origin and application of the silica geothermometer has been extensively reviewed by Fournier (1977; 1981) and by Arnorsson (1983). The solubilities of all the various silica phases increase with increasing temperature with amorphous silica having the highest solubility and quartz the least. The silica geothermometers most commonly applied to hydrothermal systems are the quartz and chalcedony geothermometers. Hydrothermal waters are usually supersaturated with respect to amorphous silica and precipitation of silica can occur during the ascent and cooling of the fluid so silica temperatures are commonly interpreted as minimum temperatures. A more difficult problem is judging which silica phase is controlling silica solubility in the reservoir. Arnorsson (1983) considers the formation of quartz or chalcedony to be determined by the rate of silica dissolution from the primary constituents of

the rock, and the kinetics of precipitation. Release of silica into solution at relatively high rates results in the more soluble silica mineral, chalcedony, becomimg the controlling phase, at least at temperatures ≤ 180°C. On the other hand, for low rates of leaching, quartz may form at relatively lower temperatures.

For the Tolsona group, where the rate of leaching has probably been very slow, quartz may be the controlling phase and the corresponding temperature estimates for the Tolsona and Copper Center mud volcanoes are 55 to 57°C, which is in close agreement with the bottom hole temperature measured in nearby wells. The lower silica temperatures at the Nickel Creek site implies a correspondingly lower reservoir temperature there. Because of the probable rapid release of silica by hydrolysis reactions, the chalcedony conductive geothermometer appears to be the more likely controlling phase for the Klawasi group. These temperature estimates range from 101 to 132°C for Lower Klawasi and Shrub, and from 61 to 88°C for Upper Klawasi.

Na/K: The soduim-potassium cation geothermometer is based on an empirically derived relationship between Na/K and temperature. The equation used in calculating the Na/K geothermometer temperatures in table 5 was determined by Fournier (1981) to be the best fit for well water data points above 80°C. Data points below 80°C were not included because of the lack of correlation between Na/K and temperature at these lower temperatures.

Despite being beyond the apparent range of applicability, the Na/K temperatures for the Tolsona group appear reasonably congruent with, but generally less than the quartz temperatures. The Na/K temperatures for the Lower Klawasi are very similar to the chalcedony temperatures but are substantially higher than chalcedony temperatures for Shrub and Lower Klawasi waters. Rock dissolution would increase Na and K concentrations in roughly equal amounts, thus the Na/K would tend to decrease as a result of hydrolyses reactions. If the water does not re-equilibrate, the Na/K geothermometer would tend to provide an overestimate of deep temperatures and this may explain the difference between the Na/K and chalcedony geothermometers. Alternatively, the Shrub and Upper Klawasi waters may be equilibrating with quartz rather than chalcedony.

Na-K-Ca: The Na-K-Ca geothermometer of Fournier and Truesdell (1973) was developed specifically to deal with calcium-rich waters that give anomously high calculated temperatures by the Na/K method, particularly at lower temperatures. However, this geothermometer cannot be accurately applied to the Klawasi group because of the probable disequilibrium removal of the Ca^{++} ion by calcite precipitation both in the reservoir and during the ascent of the fluids. The loss of aqueous Ca^{++} would result in Na-K-Ca temperatures that are too high. In fact, the calculated Na-K-Ca temperatures for the Klawasi group, which range from 155 to 194°C, are much higher than temperatures derived from most of the other geothermometers. Application of the Mg correction for magnesium-rich waters suggested by Fournier and Potter makes matters worse because it provides anomously low temperatures, generally less than vent temperatures.

In contrast, the Na-K-Ca temperatures for the Tolsona mud volcanoes are in general agreement with the other geothermomters though slightly higher than the corresponding quartz and Na/K temperatures. Congruency between the Na-K-Ca geothermometer and other geothermometers is not as good for Copper Center or Nickel Creek, though the Nickel Creek values agree well with the quartz and Na/K temperatures.

Na/Li: Thermal waters are often enriched in Li as well as other alkalis, which lead Foullic and Michard (1981) to propose a new geothermometer based on empirical relationships between the molar ratio of Na/Li and temperature. However, application of this geothermometer by at least two other investigators has given anomously high, discordant results compared to other temperature estimates (Sheppard and Lyon, 1984; Hutsinpiller and Parry, 1985). Such is also the case for the Klawasi group and the Tolsona group, where this Na/Li geothermometer gave temperature estimates ranging from 183 to 261°C, and 92 to 190°C, respectively. Because of the inconclusiveness regarding the application of this geothermometer, the Na/Li temperatures are not used.

K/Mg: Giggenbach and others (1983) recently proposed a K-Mg geothermometer based on an empirical relationship between K/Mg and temperature, valid for rock-water equilibration temperatures from 50 to 300°C. The geothermometer was found useful in situations when Na and Ca do not equilibrate rapidly enough and provided good correspondence between K/Mg temperatures and silica temperatures for Himalayan geothermal discharges. Reasonable concordance between silica and K/Mg geothermometers was also found for geothermal fluids of the Orakeiko Field, New Zealand (Sheppard and Lyon, 1984). Application of the Giggenbach geothermometer to the Klawasi group gives reasonable to good correspondence with chalcedony and Na/K geothermometers. The K/Mg temperatures for the Tolsona mud volcano waters are generally similar to the Na-K-Ca and Mg/Li temperatures but are higher than the corresponding Na/K and quartz temperatures.

Mg/Li: Kharaka and Mariner (Mariner, pers. comm., USGS, 1985) recently derived a Mg-Li geothermometer based on an empirical relationship between $\sqrt{Mg}/Li$ and temperature, using data specifically restricted to sedimentary-type environments. Application of this geothermometer to the Copper River Basin mud volcanoes gives gives reasonable to good correspondence with other geothermometers for the Klawasi group and for the Tolsona mud volcanoes but provides significantly higher temperature estimates for the Copper Center and Nickel Creek springs.

$\underline{\delta^{18}O,\ SO_4 - H_2O}$: The sulfate-water oxygen isotope geothermometer has found increasing acceptance as a reliable indicator of deep geothermal reservoir temperatures. A summary of previous experimental work leading to the development of this geothermometer and detailed explanation of its application can be found in McKenzie and Truesdell (1977). The equation for the equilibrium fractionation between dissolved sulfate and water suggested by McKenzie and Truesdell is:

$$1000 \ln \alpha = 2.88\ (10^6/T^2) - 4.1$$

where

$$\alpha = \frac{1000 + \delta^{18}O\ (SO_4)}{1000 + \delta^{18}O\ (H_2O)}$$

and T is in °K.

Experimental studies by Chiba and Sakai (1985) on the fractionation of ^{18}O between H_2O and SO_4 showed the equilibration time to be strongly dependent on both pH and temperature. For near neutral waters at 250 to 300°C, the equilibration half time is on the order of a few days to several weeks. In contrast, the extropolated half time of this reaction to oceanic temperature and pH conditions is about 10^9 years. Unless the reservoir waters are extremely acidic ($pH \leq 3.5$), the equilibration half time for temperatures of 100 to 125°C are on the order of several hundred to thousands of years. The advantages of using the $\delta^{18}O$, $SO_4 - H_2O$ geothermometer for hydrothermal systems are readily apparent for once equilibrium is attained at high temperature, little re-equilibration is likely to occur during movement of the water to the surface.

Unfortunately, interpretation of this geothermometer becomes clouded when the waters of interest are likely to have a seawater component or contain constituents of seawater origin. In such cases, it becomes unclear whether the calculated fractionation temperatures reflect relict seawater compositions or re-equilibration in a high temperature reservoir. In fact, using the average seawater composition for $\delta^{18}O$ in H_2O and SO_4, the geothermometer gives a seawater temperature estimate of about 200°C.

Two water samples collected from Klawasi springs, one from Lower Klawasi in 1981, the other from Upper Klawasi in 1982, were analyzed for $\delta^{18}O$ composition of the sulfate species. The results of the analyses and the calculation of the corresponding geothermometer temperatures are given in table 7. The temperature estimates are substantially above most of the the other geothermometer temperatures, particularly at Upper Klawasi, indicating that either the isotopic compositions were fixed in a much hotter part of the reservoir, or more probably reflect the influence of marine sulfates. The sulfate concentrations in the Klawasi waters are substantially above those in the Tolsona waters which suggests that some sulfates having a marine origin are being dissolved during hydrolyses reactions at Klawasi. Reported values of $\delta^{18}O$ in marine sulfates range from +7.2 to +9.8 with the majority of the samples near that of seawater sulfate of +9.5 (Longinelli and Craig, 1967). The $\delta^{18}O$ compositions of the Klawasi water sulfate species bracket the seawater value.

An alternate potential source of the sulfates in the Klawasi waters are sulfer gases that may accompany the CO_2 gas and react with the reservoir waters. A further complication is that if the apparent shift in $\delta^{18}O$ of Klawasi waters with respect to Tolsona waters occurred after the H_2O-SO_4 isotope fractionation had been already established, the geothermometer would give erroneously high temperatures.

<u>Summary of Geothermomtry</u>: We disregard the high temperatures given by the Na-K-Ca geothermometers for the Klawasi waters because of the probable disequilibrium depletion of Ca^{++} ions through calcite precipitation. We also discount the high temperatures given by the Na/Li geothermometer of Foullic and Michard because of evidence from other hydrothermal systems that this geothermometer gives disconcordant high temperature estimates. Interpretation of the sulfate-water oxygen isotope geothermometer remains problematic because of uncertainties regarding the source of the sulfates and the probability that some of the formation water and ionic species have a seawater origin. We also note that reservoir temperatures exceeding 200°C seem inconsistent with the relatively high rate of discharge (110 lpm) and relatively low temperature of the mineral springs (20°).

Based on the concordance of the remaining geothermometers as given in table 6 we estimate the Klawasi reservoir temperatures to be in the range of 100 to 125°C, and the reservoir temperatures at Tolsona to be similar to bottom hole temperature measurements in nearby wells, 50 to 60°C. Despite the uncertainties in estimating reservoir temperatures, it appears clear that reservoirs underlying Klawasi are substantially warmer than those at Tolsona.

DEPTH OF INTRUSION

Wescott and Turner(1985) reported a gravity high in the region between Lower and Upper Klawasi mud volcanoes. Gravity modelling showed the anomaly to be consistent with a small, relatively shallow (900 to 1500 m deep) plug or dike-like intrusive. However, Wescott (pers. comm., 1986) reported that the availible gravity data are insufficient to fully constraint the depth of the modelled intrusive and that, in fact, based on proprietary gravity data from Amoco, the anomoly may actually have a greater width, which would place the intrusive deeper. A deeper level for the proposed intrusive would be more consistent with the estimated formation water reservoir temperatures and the low surface spring temperatures.

The relatively low reservoir temperature would also indicate that little or no hydrothermal convection is occurring between the underlying intrusive and the saline formation waters in the overpressured zone. The pressure of CO_2 gas escaping from the intrusive and zone of contact decarbonation may be high enough to prevent the overlying water from entering the fracture system. Alternatively, the intrusive may be too young for any appreciable convection to have become established as yet.

Depth to basement rocks underlying the Klawasi group is not known but if we extrapolate from Ahtna-Amoco 1A it is likely to be on the order of 1700 m. This consistent with gravity models derived by Wescott and Turner(1985) and with Ehm's (1983) Oil and Gas basins map of Alaska. If the Chitistone limestone is the source of contact metamorphic CO_2 (and the Nikolai Greenstone the source of As) then depth of intrusive would be on the order of 2.5 to 3.0 km. The Taral fault could be acting as a zone of weakness for the intrusion and could also be the avenue of ascent for magmatic and contact metamorphic CO_2 gases.

SOURCE OF METHANE

The $\delta^{13}C$ compositions of the Copper River Basin methanes help constrain their possible origins (table 3; fig. 12). The carbon isotopic compositions of natural gas methanes span a broad range of values (-76 to -21 per mil; Deines, 1980). Based on similarities in $\delta^{13}C$ compositions, natural gas methanes with light isotopic compositions (-70 to -60 per mil) are thought to be the product of bacterial processes in recent sediments while isotopically heavy methanes ($\approx$ -25 per mil) are thought to have been generated during coalification processes.

Although methanes associated with petroleum span a broad range of values, the methanes from the majority of oil fields have $\delta^{13}C$ of less than -35 per mil, suggesting that methanes with intermediate isotopic composition might be related to petroleum maturation processes (Deines, 1981). At the Cook Inlet oil and gas fields, the closest producing petroleum province to the Copper River Basin, $\delta^{13}C$ for methane ranges from -62 to -44 per mil with the majority of the samples falling between -60 to -58 per mil (Claypool and others, 1980). The Cook Inlet oil and associated gas are thought to have migrated from Middle Jurassic Tuxedni Group sedimentary rocks into overlying Tertiary reservoir rocks (Magoon and Claypool, 1977). The Tuxedni Group also underlies the western part of the Copper River Basin, so would be the likely source of any petroleum associated methanes in the basin.

The $\delta^{13}C$ compositions of the mud volcano methanes range from -33.4 at Tolsona 1 to -17.9 per mil at Lower Klawasi. The methanes from the Tazlina mineral spring and the Copper River seep are considerably lighter at -43.6 and -76.7. We agree with Reitsima (1979) that the most likely source for the Tolsona and most if not all of the Klawasi methane are coal and lignite beds in the mid and lower Cretaceous formations underlying the basin. The range of $\delta^{13}C$ compositions of lignite and coal is -21 to -28 per mil (Deines, 1980). Reitsima (1979) reported a $\delta^{13}C$ value of -21.4 per mil for an outcrop sample of Lower Cretaceous Nelchina Formation coal from the west side of Copper River Basin. The Nelchina Formation underlies the Tolsona mud volcanoes. Mid-Cretaceous outcrops on the flanks of Mt. Drum, east of the Klawasi group, were reported to contain lignite and fossil wood fragmants (Richter and others, 1979). Fragments of coal and lignite were also reported in drill cuttings from the Upper Cretaceous Matanuska Formation intersected by wells in the central part of the basin. Thus ample supplies of coal and lignite appear to present in the basin to account for the generation of methane.

Experimental results indicate the CO_2 gas produced during the coalification process has a $\delta^{13}C$ composition similar to the original material whereas the co-produced CH_4 is isotopically lighter by several per mil (Deines, 1980). With increasing reaction time the $\delta^{13}C$ of the CH_4 approaches that of the originating coal.

The $\delta^{13}C$ values of the Tolsona and Klawasi group methanes thus appear consistent with methanes produced during coalification processes. Methane from the Copper River seep appears more consistent microbial origins while methane from the Tazlina mineral spring could be a mixture of coalification generated methane with microbial methane.

The $\delta^{13}C$ of CH_4 from the Lower Klawasi vents is particularly heavy (-18 per mil), which suggests the possibility of a mantle component in the Klawasi methane. Welhan (1981) reported values ranging from -15 to -20 per mil for $\delta^{13}C$ in methanes thought to be derived from the mantle from locations on the East Pacific Rise and in Yellowstone National Park. The proportion of mantle methane in the Lower Klawasi gases could be substantial given the -22 to -30 per mil value of the methane at the other mud volcanoes.

Fractionation of the ^{13}C isotope between CO_2 and CH_4 has been suggested as a geothermometer based on the assumption the gases achieve isotopic equilibrium (Craig, 1953; Bottinga, 1969). However, application of this geothermometer is questionable, particularly for temperatures below 400°C, where experimental and theoretical investigations indicate ^{13}C equilibration requires residence times on the order of tens of thousands of years (Sackett and Chung, 1979; Giggenbach, 1982). If a major portion of the methane at Lower Klawasi is magmatc in origin and isotopic equilibrium was achieved between the magmatic CO_2 and CH_4, and the CO_2 generated from contact metamorphism, the difference in values of $\delta^{13}C$ between CO_2 and CH_4 indicates fractionation equilibrium temperature was greater than 500°C.

NOBLE AND OTHER GASES

The gases emanating from both the Klawasi and the Tolsona mud volcanoes contain significant amounts of N_2 and, except at Upper Klawasi, helium is also present in amounts far in excess of what can be attributed atmospheric sources. High concentrations of both helium and nitrogen are often found in association with natural gas occurrences and it is commonly presumed these gases have migrated upward from underlying rocks into natural gas reservoirs. Three main sources have been proposed for nitrogen: atmospheric nitrogen, release from organic compounds incorporated in the sediments due to bacterial activity, release from deep-seated magmatic processes (Deines, 1980). The N_2/Ar ratio at Upper Klawasi is similar to that in air-saturated water (=38) indicating an atmospheric origin for these gases. The N_2/Ar ratio at the remaining vents is much greater than in either air-saturated water or atmospheric air (=82), indicating sources other than atmospheric are contributing nitrogen at these locations.

Pereira and Adams (1982) considered that most helium concentrations in natural gas occurrences could be explained by accumulation of radiogenic helium in sediments. Radiogenic ^4He from decay of uranium and thorium is a probable source for some of the excess helium at the Copper River Basin but the $^3He/^4He$ ratios indicate the mantle must also be a source for some of the helium. Similar conclusions were obtained by Urabe and others (1985) in their study of noble gases asssociated with natural gases in the forearc basins of Japan. They also suggested that some of the excess nitrogen found in Japanese forearc natural gases may have a mantle origin and may also have been derived from sediments associated with the subducted slab underlying the arc.

The lower concentrations of He, CH_4, and N_2 at Upper Klawasi compared to the other Copper River Basin vents may due to the lack of a suitable natural gas trap underlying this location. Upper Klawasi lies at the eastern edge of the basin and the sedimentary formations underlying this mud volcano are probably much thinner than at the other sites.

Trace amounts of H_2 gas were detected in several of the samples. The H_2 gas may have originated from reactions involving oxidation of CH_4 such as,

$$CH_4 + 2H_2O = CO_2 + 4H_2$$

or from the breakdown of ammonia,

$$2NH_3 = N_2 + 3H_2 .$$

The minor amount of H_2S gas reported in table 2 for Lower Klawasi spring, 6-16-82, is suspect because no other gas sample contained even trace amounts of H_2S. It is possible some spring water may have been sucked up into the sodium hydroxide charged flask used for collection. The sulfate in the contaminating water would cause an erroneous indication of sulfur gas during analysis of the sodium hydroxide supernate.

SUMMARY AND CONCLUSIONS

We believe the results of our study strongly indicate a recently emplaced igneous intrusion is causing deep-seated metamorphic decarbonation of limestone beds beneath the Klawasi group of mud volcanoes. Copius amounts of CO_2 gas from the intrusive and from contact metamorphic reactions flow upward under pressure into overlying Jurassic and Cretaceous marine sandstones and shales where the gases interact with Tolsona-type formation waters. Formation of carbonic acid results in hydrolysis and acid decomposition of clays and other silicates and aluminosilicates causing an increase in dissolved alkali metals and silica. Continued interaction buffers the waters to neutral pH, the waters quickly become saturated with respect to $CaCO_3$, resulting in precipitation of calcite and consequent depletion of calcium in the waters. The resulting waters emanating at the surface of the Klawasi mud volcanoes are rich in alkali metals, bicarbonate, CO_2 gas, and depleted in Ca.

Our primary evidence for the existence of the intrusive and contact-metamorphic decarbonation process is: 1)the high helium-3/4 ratios obtained for the Klawasi gases which reflect a strong magmatic influence on the Klawasi system; 2) the rate of CO_2 production which appears consistent only with a magmatic or magmatic-contact metamorphic source; 3) the carbon-13/12 signatures which point to a limestone decarbonation process as the source of much of the carbon dioxide gas; and 4) the extremely elevated concentrations of arsenic found in the Klawasi brines (43 ppm vs < 0.01 ppm in Tolsona brines).

The formation waters themselves probably originated as connate seawater entrapped in Cretaceous and perhaps Jurassic marine sediments that was subsequently diluted with meteoric during a Late Jurassic or mid-Cretaceous period of regional uplift. The present Tolsona-type chemistry could have been produced through mixing and dilution of the entrapped seawaters with paleo-meteoric waters, further modified by shale-membrane filtration, dolomitization, hydrolysis of carbonates, clay-forming processes, and rock leaching. The isotopic compositions could have been produced by simple dilution with paleo-meteoric waters followed by a positive shift in ^{18}O through isotopic exchange with marine carbonates and other sediments. Enrichments in heavier isotopes may also have been caused by ultrafiltration fractionation. Differences in isotopic compositions between Klawasi and Tolsona-type waters can be partially attributed to mineral-water isotope exchange processes and perhaps also to mixing with a magmatic or metamorphic water component.

The saline spring waters appear to be derived from an overpressured zone in Lower Cretaceous deposits. The accumulation of Quaternary, Tertiary and Upper Cretaceous sediments in the central part of the basin, which ranges from 1500 to 2000 m in thickness, is probably the primary mechanism generating the overpressuring. Lateral tectonic compression is likely to be another contributing factor to overpressuring in the Copper River Basin as the basin lies in a region which for the past several million years has been undergoing crustal forshortening due to the compressive tectonic stresses being exerted by the motion and subduction of the North Pacific Plate beneath the North American Plate. The thermal expansion of water and CO_2 gas pressures may be important processes contributing to overpressuring at Klawasi. These additional overpressuring mechanisms could intensify membrane filtration and could also explain the much greater rate of water discharge and larger mud volcano edifices at Klawasi compared to Tolsona.

If we assume the source carbonate rock has a $\delta^{13}C$ of ≈ +2.5, then the contact-metamorphic CO_2 being generated under Klawasi would have a $\delta^{13}C$ of +2.5 to +5.0 depending on the degree of fractionation with the residual carbonate rock. If we further assume that the magmatic CO_2 has a $\delta^{13}C$ of -6.5 and that the mixed CO_2 entering the formation water reservoir has a $\delta^{13}C$ of -2.0, the proportion of metamorphic to magmatic CO_2 would be on the order of 40 to 50 per cent.

We agree with Reitsima (1979) that the most likely source for the Tolsona and most, if not all, of the Klawasi methane are coal and lignite beds in the mid and lower Cretaceous formations underlying the basin. However, the $\delta^{13}C$ of CH_4 from the Lower Klawasi vents is particularly heavy (-18 per mil), which suggests the possibility of a mantle component in the Klawasi methane.

The gases emanating from both the Klawasi and the Tolsona mud volcanoes contain significant amounts of N_2 and, except at Upper Klawasi, helium is also present in amounts far in excess of what can be attributed atmospheric sources. The $^3He/^4He$ ratios indicate the mantle must be a source for some of the helium. Similar conclusions were obtained by Urabe and others (1985) in their study of noble gases asssociated with natural gases in the forearc basins of Japan. They also suggested that some of the excess nitrogen found in Japanese forearc natural gases may have a mantle origin and may also have been derived from sediments associated with the subducted slab underlying the arc.

We discount the high temperatures given by the Na-K-Ca geothermometers for the Klawasi waters because of the probable disequilibrium depletion of Ca^{++} ions through calcite precipitation. We also discount the high temperatures given by the Na/Li geothermometer of Foullic and Michard because of evidence from other hydrothermal systems that this geothermometer gives disconcordant high temperature estimates. Interpretation of the sulfate-water oxygen isotope geothermometer remains problematic because of uncertainties regarding the source of the sulfates and the probability that some of the formation water and ionic species have a seawater origin.

Based on the concordance of the remaining geothermometers we estimate the Klawasi reservoir temperatures to be in the range of 100 to 125°C, and the reservoir temperatures at Tolsona to be similar to bottom hole temperature measurements in nearby wells, 50 to 60°C. Despite the uncertainties in estimating reservoir temperatures, it appears clear that reservoirs underlying Klawasi are substantially warmer than those at Tolsona.

The relatively low reservoir temperatures indicate the intrusive is deep-seated and that little or no hydrothermal convection is occurring between the underlying intrusive and the saline formation waters in the overpressured zone. The pressure of CO_2 gas escaping from the intrusive and zone of contact decarbonation may be high enough to prevent the overlying water from entering the fracture system. Alternatively, the intrusive may be too young for any appreciable convection to have become established as yet.

If the Chitistone limestone is the source of contact metamorphic CO_2 (and the Nikolai Greenstone the source of As) then depth of intrusive would be on the order of 2.5 to 3.0 km. The Taral fault, which is thought to be the boundary between the Peninsular and Wrangellia tectonostratagraphic terranes, could be acting as a zone of weakness for the intrusion and could also be the avenue of ascent for magmatic and contact metamorphic CO_2 gases.

ACKNOWLEDGEMENTS

We wish to acknowledge the valuable field, office, and laboratory assistance of the following individuals: M. A. Moorman, S. A. Liss, G. LaRoche, J. Romick, M. Sturm, D. Solie, and E. Fogels.

We also wish to acknowledge C. Janik, W. Evans, and M. Stallard of the U.S. Geological Survey, Menlo Park for their cooperation in performing analyses of gas and isotope compositions.

This work was performed under grants from the U.S. Department of Energy and funding from the state of Alaska.

REFERENCES

Arnorsson, S., 1983, Chemical equilibria in Icelandic geothermal systems-Implications for chemical geothermometry investigations: Geothermics, v. 12, p. 119-128.

Beikman, H.M., 1974, Preliminary geologic map of the southeast quadrant of Alaska, 1:1,000,000 : U. S. Geological Survey Misc. Field Studies Map MF 612, 2 sheets.

Bottinga, Y., 1969, Calculated fractionation factors for carbon and hydrogen isotope exchange in the system calcite-carbon dioxide-graphite-methane-hydrogen-water vapor: Geochimica et Cosmochimica Acta, v. 33, p. 49-64.

Chiba, Hitoshi, and Sakai, Hitoshi, 1985, Oxygen isotope exchange rate between dissolved sulfate and water at hydrothermal temperatures: Geochimica et Cosmochimica Acta, v. 49, p. 993-1000.

Church, R.E., Crick, R.W., and Lian, E.B., 1969, Stratigraphic correlation sections of the Copper River Basin, Alaska: Alaska Geological Society, Anchorage, Alaska, 2 Plates.

Claypool, G.E., Threlkeld, C.N., and Magoon, L.B., 1980, Biogenic and thermogenic origins of natural gas in Cook Inlet Basin, Alaska: The American Association of Petroleum Geologists Bulletin, v. 64, 9 p. 1131-1139.

Clayton, R.N., Friedman, I., Graf, D.L., Mayeda, T.K., Meents, W.F., and Shimp, N.F., 1966, The origin of saline formation waters - I. Isotopic composition: Journal of Geophysical Research, v. 71, p. 3869-3882.

Coplen, T.B., and Hanshaw, B.B., 1973, Ultrafiltration by a compact clay membrane; I. Oxygen and hydrogen isotopic fractionation, Geochimica et Cosmochimica Acta, v. 37, p. 2295-2310.

Craig H., Lupton, J.E., and Horibe, Y., 1978, A mantle helium component in Circum-Pacific volcanic gases: Hakone, the Marianas, and Mount Lassen: in Terrestrial Rare Gases (ed. E.C. Alexander and M. Ozima), Cent. Acad. Publ. Japan.

Craig, H., 1953, The geochemistry of the stable carbon isotopes: Geochimica et Cosmochimica Acta, v. 3, p. 53-92.

Craig, H., 1963, The isotopic geochemistry of water and carbon in geothermal areas: in Tongiorgi, E., ed., Nuclear geology in geothermal areas, Spoleto, 1963: Pisa, Italy, Consiglio Nationale Delle Ricerche, Laboratorio di Geologia Nucleare, p. 17-53.

Craig, H., and Lupton, J.E., 1981, Helium-3 and mantle volatiles in the ocean and oceanic crust: in The Oceanic Lithosphere, Vol. 7, The Sea, John Wiley and Sons, 1981, p. 391-428.

Cusicanqui, H., Mahon, W.A.J., and Ellis, A.J., 1976, The geochemistry of the El Tatio geothermal field, northern Chile: in Proc. Second United Nations Symposium on the Development and Use of Geothermal Resources, San Francisco, 1975, p. 703-712.

Degens, E.T., Hunt, J.M., Reuter, J.H., and Reed, W.E., 1964, Data on the distribution of amino acids and oxygen isotopes in petroleum brine waters of various geologic ages: Sedimentology, v. 3, p. 199-225.

Deines, Peter, 1980, The isotopic composition of reduced organic carbon: in Fritz, P., and Fontes, J.C., eds., Handbook of Environmental Isotope Geochemistry, Elsevier Scientific Publishing Company, New York, p. 329-406.

Ehm, Arlen, 1983, Oil and Gas Basins Map of Alaska: Alaska Division of Geological and Geophysical Surveys Special Report 32.

Ellis, A.J., 1973, Chemical processes in hydrothermal systems - a review: Int. Symp. Hydrogeochemistry and Biogeochemistry, Japan, 1970, p. 1-26.

Ferrians, O.J., Nichols, D.R., and Williams, J.R., 1983, Copper River Basin, in Pewe, T.R., and Reyes, R.D., eds., Richardson and Glenn Highway, Alaska, Guidebook to Permafrost and Quatenary Geology, Guidebook 1, Alaska Division of Geological & Geophysical Surveys, p. 137-175.

Foresman, J.B., 1970, Mud Volcanoes and abnormal pressure, Copper River basin, Alaska: M.S. Thesis, University of Tulsa, Oklahoma, 39 pp.

Fouillac, C., and Michard, G., 1981, Sodium/lithium ratio in water applied to Geothermometry of Geothermal Resevoirs: Geothermics, v. 10, p. 55-70.

Fournier, R.O., 1977, Chemical geothermometers and mixing models for geothermal systems: Geothermics, v. 5, p. 41-50.

Fournier, R.O., 1981, Application of water chemistry to geothermal exploration and reservoir engineering, in Ryback, L., and Muffler, L.P.J., eds., Geothermal Systems: Principles and Case Histories: New York, Wiley and Sons, p. 109-144.

Fournier, R.O., and Truesdell, A.H., 1973, An empirical Na-K-Ca geothermometer for natural waters: Geochimica et Cosmochimica Acta, v. 37, p. 1255-1275.

Friedman, I, and O'Neil, J.R., 1977, Compilation of stable isotope fractionation factors of geochemical interest: in Fleischer, M., ed., Data of Geochemistry, U.S. Geological Survey Professional Paper, 440-KK, 12 p.

Giggenbach, W.F., 1982, Carbon-13 exchange between CO_2 and CH_4 under geologic conditions: Geochimica et Cosmochimica Acta, v. 46, p. 159-165.

Giggenbach, W.F., Gonfiantini, R., Jangi, B.L., and Truesdell, A.H., 1983, Isotopic and chemical composition of Parbati Valley geothermal discharges, Northwest Himalaya, India: Geothermics, v. 12, p. 199-222.

Graf, D.L., 1982, Chemical osmosis, reverse chemical osmosis, and the origin of subsurface brines: Geochimica et Cosmochimica Acta, v. 46, p. 1431-1448.

Grantz, Arthur, White, D.C., Whitehead, H.C., and Tagg, A.R., 1962, Saline Springs, Copper River Lowland, Alaska: American Association of Petroleum Geologists Bulletin, v. 46, no. 11, p. 1890-2002.

Greenland, L.P., and Aruscavage, Philip, 1986, Volcanic emissions of Se, Te, and As from Kilauea Volcano, Hawaii: Journal of Volcanology and Geothermal Research, v. 27, p. 195-201.

Hanor, J.S., 1979, The sedimentary genesis of hydrothermal fluids, in Barnes, H.L., ed., Geochemistry of Hydrothermal Ore Deposits, 2nd Edition, New York: John Wiley & Sons, p. 137-172.

Hanshaw, B.B., and Coplen, T.B., 1973, Ultrafiltration of a compacted clay membrane - II. Sodium ion exclusion at various ionic strengths: Geochimica et Cosmochimica Acta, v. 37, p. 2311-2327.

Hawkins, D.B., and Motyka, R.J., 1984, Multivariant statistical analysis and chemical mass balance analysis of waters of the Copper River Basin, Alaska: in Wallick, E., and Hitchon, B., eds., Proceedings of the

1st Annual Canadian-American conference on Hydrogeology, Banff, Alberta, (in press).

Hedberg, H.D., 1974, Relation of methane generation to undercompacted shales, shale diapirs, and mud volcanoes: The American Association of Petroleum Geologists Bulletin, v. 58, p. 661-673.

Hitchon, B., Billings, G.K., and Klovan, J.E., 1971, Geochemistry and origin of formation waters in the western Canada sedimentary basin III. Factors controlling the chemical composition: Geochimica et Cosmochimica Acta, v. 35, p. 567-598.

Hitchon, Brian, and Friedman, Irving, 1969, Geochemistry and origin of formation Waters in the western Canada sedimentary basin - I. Stable isotopes of hydrogen and oxygen: Geochimica et Cosmochimica Acta, v. 33, p. 1321-1349.

Holland, H.D., and Malinin, S.D., 1979, The Solubility and Ocurrence of Non-Ore Minerals, in Barnes, H.L., ed., Geochemistry of Hydrothermal Ore Deposits, 2nd Edition, New York: John Wiley & Sons, p. 461-508.

Hutsinpiller, Amy, and Parry, W.T., 1985, Geochemistry and geothermometry of spring water from the Blackfoot Resevoir region, southeastern Idaho: Journal of Volcanology and Geothermal Research, v. 26, p. 275-296.

Jones, D.L., Silberling, N.J., and Hillhouse, J., 1977, Wrangellia - a displaced terrain in northwestern North America: Canadian Journal of Earth Science, v. 14, p. 2565-2577.

Jones, D.L., and Silberling, N.J., 1979, Mesozoic stratigraphy -- the key to tectonic analysis of southern and central Alaska: U.S. Geological Survey Open-file Report 79-1200, 37p.

Jones, D.L., Silberling, N.J., Coney, P.J., and Plafker, George, 1984, Lithotectonic terrane map of Alaska (west of the 141st Meridian): in Lithotectonic terrane maps of the North American Cordillera, N.J. Silbering and D.L. Jones, eds., U.S. Geological Survey Open-file Report 84-523, Map Sheet A and p. A1-A10.

Keith, M.L., and Weber, J.N., 1964, Carbon and oxygen isotopic composition of selected limestones and fossils: Geochimica et Cosmochimica Acta, v. 28, p. 1787-1816.

Kerrick, D.M., 1974, Review of metamorphic mixed-volatile (H_2O-CO_2) Equilibria: American Mineralogist, v. 59, p. 729-762.

Kharaka, Y.K., and Berry, F.A.F., 1973, Simultaneous flow of water and solutes through geologic membranes, I. Experimental investigation: Geochimica et Cosmochimica Acta, v.37, p. 2577-2603.

Krauskopf, K.B., 1979, Introduction to Geochemistry: Second edition, McGraw-Hill Book Company, New York, 617 p.

Longinelli, A., and Craig, H., 1967, Oxygen-18 variations in sulfate ions in sea water and saline lakes: Science, v. 156, p. 56-59.

Lupton, J.E., and Craig, H., 1975, excess ^{3}He in oceanic basalts: Evidence for terrestrial primordial helium: Earth and Planetary Sciences Letters, v. 26, p. 133-139.

MacKevett, E.M., Jr., 1978, Geologic map of the McCarthy quadrangle, Alaska: U.S. Geologic Survey Misc. Invest. Series Map I-1032, scale 1:250,000.

Magoon, L.B., and Claypool, G.E., 1977, Origin of Cook Inlet Oil: Alaska Geological Society, Symposium Proceedings, 1977, p. G1-G17.

McKenzie, W.F., and Truesdell, A.H., 1977, Geothermal reservoir temperatures estimated from the oxygen isotope compositions of dissolved sulfate and water from hot springs and shallow drillholes: Geothermics, v. 5, p. 51-61.

Mendenhall, W.C., 1905, Geology of the central Copper River region, Alaska: U.S. Geological Survey Proffessional Paper 41, 133 p.

Miller, D.J., Payne, T.G., and Gryc, George, 1959, Geology of possible petroleum provinces in Alaska: U.S. Geological Survey Bulletin 1094, 131 p.

Moore, J.C., and Connelly, William, 1977, Mesozoic tectonics of the southern Alaska margin, in Talwani, Manik, ed., Problems in the evolution of island arcs, deep sea trenches, and back-arc basins (Ewing Volume): Journal of Geophysical Research, Special Volume, p. 71-82.

Motyka, R.J., 1983, Increases and Fluctuations in Thermal Activity at Mount Wrangell, Alaska: University of Alaska, Fairbanks, Ph.D. Thesis, 349 p.

Motyka, R. J., Queen, L. D., Janik, C. J., Sheppard, D. S., Poreda, R. J., and Liss, S. A., 1985, Fluid geochemistry and fluid-mineral equilibria in test wells and thermal gradient holes at the Makushin Geothermal Area, Unalaska Island, Alaska: Final report submitted to the Alaska Power Authority, under RSA #RS08-8227, Unalaska Geothermal Drilling. 155 p.

Nehring, N. L., Bowen, P. A., and Truesdell, A. H., 1977, Techniques for the conversion to carbon dioxide of oxygen from dissolved sulfate in thermal waters: Geothermics, v. 5, p. 63-66.

Nichols, D. R., and Yehle, L. A., 1961a, Mud volcanoes in the Copper River basin, Alaska, in Raasch, G. D., and Yehle, L. A., eds., Geology of the Arctic: Toronto, University of Toronto Press, v. 2, p. 1063-1087.

Nichols, D. R., and Yehle, L. A., 1961b, Analyses of gas and water from two mineral springs in the Copper River Basin, Alaska, in Short papers in the Geologic and hydrologic sciences 1961: U. S. Geological Survey Proffessional Paper 424-D, p. D191-D194.

Nye, C. J., 1983, Petrology and geochemistry of Okmok and Wrangell Volcanoes, Alaska: U. C. Santa Cruz Ph. D. thesis, 208 p.

Ohmoto, Hiroshi, and Rye, R. O., 1979, Isotopes of sulfur and carbon, in Barnes, H. L., ed., Geochemistry of Hydrothermal Ore Deposits, 2nd Edition, New York: John Wiley & Sons, p. 509-567.

Onishi, H., and Sandell, E. B., 1955, Geochemistry of arsenic: Geochimica et Cosmochimica Acta, v. 7, p. 1-33.

Palmer, M. R., Spivack, A. J., and Edmond, J. M., 1985, abs., EOS, Transactions, American Geophysical Union, v. 66, p. 916.

Pereira, E. B., and Adams, J. A. S., 1982, Helium production in natural gas resevoirs: Geophysical Research Letters, v. 9, p. 87-90.

Poreda, R. J., 1983, Helium, neon, water and carbon in volcanic rocks and gases: University of California, San Diego, Ph. D. thesis, 215 p.

Presser, T. S., and Barnes, Ivan, 1974, Special techniques for determining chemical properties of geothermal waters: U. S. Geological Survey Water Resources Investigation Report, 22-74, 11 p.

Reitsema, R.H., 1979, Gases of the mud volcanoes in the Copper River Basin, Alaska: Geochimica et Cosmochimica Acta, v. 43, p. 183-187.

Richter, D.H., 1976, Geologic map of the Nasbena quadrangle, Alaska: U.S. Geologic Survey Misc. Invest. Series Map I-932, scale 1:250,000.

Richter, D.H., Smith, R.L., Yehle, L.A., and Miller, T.P., 1979, Geologic map of the Gulkana A-2 Quadrangle, Alaska: U.S. Geological Survey Geologic Map GQ 1520, scale 1:63,360.

Sackett, W.M., and Chung, H.M., 1979, Experimental confirmation of the lack of carbon isotope exchange between methane and carbon oxides at high temperatures: Geochimica et Cosmochimica Acta, v. 43, p. 273-276.

Savin, S.M., and Epstein S., 1970, The oxygen and hydrogen isotope geochemistry of clay minerals: Geochimica et Cosmochimica Acta, v. 34, p. 43-64.

Sheppard, D.S., and Giggenbach, W.F., 1985, Methods for the analysis of geothermal and volcanic waters and gases, Chemistry Division, Department of Scientific and Industrial Research, New Zealand, Report No. C.D. 2364, 78 p.

Sheppard, D.S., and Lyon, G.L., 1984, Geothermal fluid chemistry of the Orakeikorako Field, New Zeland: Journal of Volcanology and Geothermal Research, no. 22, p. 329-349.

Shieh, Y.N., and Taylor, H.P., Jr., 1969, Oxygen and carbon isotope studies of contact metamorphism of carbonate rocks: Journal of Petrology, v. 10, part 2, p. 307-331.

Skougstad, M.W., Fishman, M.J., Friedman, M.J., Erdmann, D.E., and Duncan, S.S., 1979, Methods for determination of inorganic substances in water and fluvial sediments: U.S. Geological Survey Techniques of Water-Resource Investigations, book 5, Cap. A1, 626 p.

Smith, R.L., and Shaw, H.R., 1979, Igneous-related geothermal systems, in Muffler, L.J.P., ed., Assesment of geothermal resources of the United States, 1978: U.S. Geological Survey Circular 790, p. 12-17.

Sokolov, V.A., Buniat-Zade, Z.A., Goedekian, A.A., and Dadashev, F.G., 1969, The origin of gases of mud volcanoes and the regularities of their powerful eruptions: in Advances in Organic Geochemistry, 1968: Pergamon Press, p. 473-484.

Stauffer, R.E., and Thompson, J.M., 1984, Arsenic and antimony in geothermal waters of Yellowstone National Park, Wyoming, USA: Geochimica et Cosmochimica Acta, v. 48, p. 2547-2561.

Taylor, H.P., 1979, Oxygen and hydrogen isotope relationships in hydrothermal mineral deposits, in Barnes, H.L., ed., Geochemistry of Hydrothermal Ore Deposits, 2nd Edition, New York: John Wiley & Sons, p. 236-277.

Thompson, J.M., 1979, A reevaluation of geothermal potential of the Wilbur Hot Springs area, California: U.S. Geological Survey, Geothermal Resources Council, Transactions, v. 3, p. 729-731.

Thompson, J.M., Keith, T.E.C., and Consul, J.J., 1985, Water chemistry and mineralogy of Morgan and Growler Hot Springs, Lassen KGRA, California: U.S. Geological Survey, Geothermal Resources Council, Transactions, v. 9, part I, p. 357-362.

Torgersen, T., Lupton, J.E., Sheppard, D.S., and Giggenbach, W.F., 1982, Helium isotope variations in the thermal areas of New Zealand: Journal of Volcanology and Geothermal Research, v. 12, p. 283-298.

Urabe, Akiko, Tominaga, Takeshi, Nakamura, Yuji, and Wakita, Hiroshi, 1985, Chemical compositions of natural gases in Japan: Geochemical Journal, v. 19, p. 11-25.

Viglino, J.A., Harmon, R.S., Borthwick, J., Nehring, N.L., Motyka, R.J., White, L.D., and Johnson, D.A., 1985, Stable-isotope evidence for a magmatic component in fumarole condensates from Augustine Volcano, Cook Inlet, Alaska, USA: Chemical Geology, v. 49, p. 141-157.

Welhan, J.A., 1981, Carbon and hydrogen gases in hydrothermal systems: the search for a mantle source: University of California, San Diego, Ph. D. thesis, 182 p.

Wescott, E.M., and Turner, D.L., 1985, editors, Geothermal Energy Resource Investigations in the Eastern Copper River Basin, Alaska, University of Alaska, Geophysical Institute Report UAG R-302, 158 pp., 8 pl.

White, D.E., 1965, Saline Waters of sedimentary rocks, in Young, A., and Galley, J.E., eds., Fluids in Subsurface Environments, American Association of Petroleum Geologists, p. 343-366.

White, D.E., Barnes, Ivan, and O'Neil, J.R., 1973, Thermal and mineral waters of nonmeteoric origin, California Coast Ranges: Geological Society of America Bulletin, v. 84, p. 547-560.

White, D.E., Hem, J.D., and Waring, G.A., 1963, Chemical composition of subsurface waters: U.S. Geological Survey Proffessional Paper, 440F, 67 p.

Winkler, G.R., Silberman, M.L., Grantz, Arthur, Miller, R.J., and Mackevett, E.M., Jr., 1981, Folio of the Valdez Quadrangle, Alaska: U.S. Geological Survey Open File Report, 80-898-A

Yehle, L.A., and Nichols, D.R., 1980, Reconnaissance map and description of the Chetaslina volcanic debris flow (new name) SW Copper River Basin and adjacent areas, Southcentral Alaska, U.S. Geological Survey, Map MF-1209.

Zies, E.G., 1929, The Valley of 10,000 Smokes: The fumarolic incrustations and their bearing on ore deposition. II. The acid gases contributed to the sea during volcanic activity: Nat. Geogr. Soc. Contr. Tech. Papers, Katmai Ser. 4, p. 1-79.

TABLES

Table 1. Water chemistry, Copper River Basin mud volcanoes and mineral springs. Units are mg/l unless otherwise noted. nd = not done; tr = trace.

No	Site Name	Sample Date	T, °C	pH	Na	K	Ca	Mg	Li	Sr	NH_4	As	Cs
1	Upper Klawasi CL	7-19-85	19	7.0	9115	207	105	571	9.3	1.9	nd	10.1	0.04
2		6-17-82	17	nd	10810	230	5	425	8.8	nd	13	nd	nd
3		8-21-81	13	7.2	10095	223	165	395	9.0	0.3	nd	nd	nd
4	Lower Klawasi CL	7-19-85	22	7.5	10705	280	50	177	6.6	12.9	nd	42.9	0.14
5		6-16-82	20	7.2	11235	299	84	140	6.0	1.9	10	48.2	nd
6		8-22-81	20	nd	10820	275	50	141	6.2	1.8	nd	nd	nd
7	Lower Klawasi spr	6-16-82	14	6.8	9450	240	142	252	6.8	4.0	14	nd	nd
8	Copper Center spr	8-23-81	20	8.1	6300	36	3240	6	1.8	13.9	nd	0.008	nd
9	Tolsona 2 (A)	6-13-82	10	7.4	4375	17	1630	41	0.7	24.7	15	tr	nd
10	Tolsona 1 (B)	6-13-82	2	7.2	4360	17	1665	36	0.7	nd	nd	nd	nd
11	Nickel Creek MV	6-19-82	10	8.0	2658	8	2215	11	1.2	nd	3	0.002	nd
12		8-26-81	7	8.1	2560	11	2720	9	1.5	17.2	nd	<0.001	nd
13	Copper River Spr	6-14-82	3	6.7	1517	17	2150	366	0.6	22.1	5	<0.001	nd
14	Tazlina River Spr	6-14-82	5	7.7	645	5	299	31	0.1	4.2	6	0.007	nd

Table 1. Continued

No	HCO_3	SO_4	F	Cl	Br	I	SiO_2	B	TDS	$\delta^{18}O$	δD	$\delta^{13}C$ HCO_3	Br/Cl
1	10144	479	0.5	10696	24	10.0	40	130	26498.3	nd	nd	nd	0.0004
2	nd	510	0.4	10800	28	6.1	68	138	-	nd	nd	1.6	0.0026
3	9268	640	0.1	10892	27	7.4	42	146	27207.3	1.9	-37	nd	0.0025
4	8059	676	0.4	12343	25	12.9	112	195	28774.4	nd	nd	nd	0.0004
5	8164	647	0.4	12000	29	6.3	138	174	28790.2	2.5	-35	2.7	0.0024
6	nd	660	0.1	12140	29	7.9	121	184	-	2.5	-34	nd	0.0024
7	8103	584	0.3	10700	26	5.5	85	152	25649.6	0.7	-46	3.1	0.0024
8	88	6	0.5	14370	37	10.8	17	84	24165.4	0.3	-18	nd	0.0025
9	51	42	1.2	9540	22	5.8	16	31	15762.0	-0.1	-17	nd	0.0023
10	nd	42	1.3	9470	nd	nd	16	31	-	0.2	-18	nd	-
11	44	116	0.9	8570	21	6.1	9	11	13651.0	-3.7	-19	nd	0.0025
12	99	120	0.1	8620	21	6.3	9	10	14153.4	-2.3	-12	nd	0.0024
13	361	39	0.4	7070	19	2.1	41	5	11409.2	-15.9	-132	nd	0.0027
14	341	3	0.3	1500	3	0.5	29	2	2690.7	-18.7	-150	nd	0.0020

Table 2. Copper River Basin air-corrected gas analyses, this study, in mole per cent.

Location	Date sampled	RO_2	CO_2	H_2S	H_2	CH_4	He	N_2	Ar	N_2/Ar
Upper Klawasi CL	7-19-85	0.005	98.8	-	-	0.04	0.0001	1.27	0.039	33
Upper Klawasi CL	8-21-81	0.19	98.5	*	tr	0.14	0.0001	1.34	0.058	23
Lower Klawasi spr	7-19-85	0.002	98.0	-	-	0.28	0.0029	1.63	0.004	406
Lower Klawasi spr	6-16-82	0.089	97.6	(0.16)[a]	-	0.42	-	1.86	0.004	424
Lower Klawasi spr	6-16-82	0.002	98.4	-	-	0.31	-	1.54	-	-
Copper Center spr	7-19-85	0.016	0.071	-	-	49.3	0.0021	50.6	0.15	343
Copper Center spr	8-23-81	0.012	tr	*	0.05	57.4	0.0056	42.4	0.13	322
Nickel Creek MV	7-20-85	0.21	0.054	-	-	45.9	0.031	54.1	(0.012)[b]	-
Nickel Creek MV	8-26-81	0.13	tr	*	0.04	60.6	0.10	39.2	0.091	430
Tazlina spr	7-20-85	0.005	0.050	-	-	58.3	0.018	41.6	0.096	433
Tolsona 2	7-20-85	0.028	0.10	-	-	68.9	0.023	30.9	0.15	208
Tolsona 2	8-27-81	0.006	tr	*	tr	72.3	0.079	27.6	0.085	324
Tolsona 1	7-20-85	0.008	0.090	-	-	68.7	0.040	29.6	0.083	356
Copper River spr	7-20-85	0.080	2.02	-	-	24.9	0.074	73.1	0.44	165

RO_2 = ratio of oxygen in sample to oxygen in air.
tr = trace.
\- = below detection.
* = reported as CO_2 + H_2S.

[a] Suspect analysis because of possible sulfate contamination from spring waters.

[b] Suspect argon analysis.

Table 3. Isotopic analyses in per mil, Copper River Basin gases. All carbon and nitrogen isotopic analyses performed at Global Geochemistry Corporation unless otherwise noted. All helium isotope analyses performed at Scripps Institute of Oceanography.

Location	Date sampled	^{13}C-CO$_2$[1]	^{13}C-CH$_4$[1]	^{15}N-N$_2$[2]	^{3}He/^{4}He R/R$_a$[3]
Mt. Wrangell	7-18-85	-6.5	-	-	6.0
Mt. Wrangell	6-13-82	-6.7[4]	-	-	6.1
Upper Klawasi CL	7-19-85	-4.8	-23.4	-3.5	3.3
Upper Klawasi CL	8-21-81	-4.3	-	-	2.6
Lower Klawasi CL	8-22-81	-3.1	-	-	4.0
Lower Klawasi spr	7-19-85	-4.1	-17.9	-	4.1
Lower Klawasi spr	6-16-82	-4.6[4]	-18.1[5]	-	-
Lower Klawasi spr	6-16-82	-4.1[4]	-	-	-
Copper Center spr	7-19-85	-	-28.0	+1.6	2.7
Copper Center spr	8-23-81	-	-	-	2.6
Nickel Creek MV	7-20-85	-	-22.1	-0.7	0.75
Nickel Creek MV	8-26-81	-	-22.9	-	0.76
Tazlina spr	7-20-85	-	-43.6	-1.8	0.95
Tolsona 2	7-20-85	-	-28.4	-1.6	0.96
Tolsona 2	8-27-81	-	-28.8	-	1.0
Tolsona 1	7-20-85	-	-33.4	-1.1	0.97
Copper River spr	7-20-85	-	-76.7	-0.7	1.25

[1] With respect to PDB.

[2] With respect to atmosphere.

[3] R/R$_a$ = ratio in sample over ratio in air.

[4] U.S. Geological Survey, Menlo Park, W. Evans and D. White analysts.

[5] U.S. Geological Survey, Menlo Park, M. Stallard, analyst.

Table 4. Isotopic composition of selected carbonates, per mil.

Amoco-Ahtna well 1A:

Depth, m	$\delta^{13}C^1$ PDB	$\delta^{18}O^1$ SMOW	$\delta^{13}C^2$ PDB	$\delta^{18}O^2$ SMOW
713	-9.6	26	-10.6	24
983	-4.9	25	-5.0	25
1,535	-0.8	4	-1.1	6

Limestone formations in vicinity of Copper River Basin from Reitsima (1979):

Formation	$\delta^{13}C$ PDB
Nelchina	-0.3
(L. Cretaceous)	1.7
	1.8
Chitistone	2.9
(Triassic)	2.3

---

[1] U.S. Geological Survey, Menlo Park, T. Presser and D. White, analysts.

[2] Stable Isotope Laboratory, Southern Methodist University, J. Borthwick, analyst.

Table 5. Bottom hole temperatures for oil & gas wells in Copper River Basin.

WELL	DEPTH, m	T, °C	ΔT/ΔZ, °C/km
Tanawe Lake #1	2048	40	20
Tazlina #1	2693	47	18
Pan/Am Moose Creek	2429	54	22
Ahtna-Amoco #1	2420	59	24
Ahtna-Amoco #1A	1700	48	28
Salmon Berry Lake #1	2412	52	22
Rainbow Fed #1	914	28	31
Rainbow Fed #2	852	27	32

Table 6. Geothermometry applied to Copper River Basin mud volcano spring waters. Temperatures in °C.

Site and sample date	Qz[1]	Chal[2]	Na-K[3]	Na-Ca-K[4]	K-Mg[5]	Mg-Li[6]
Shrub MV						
1973	148	122	137	-	112	118
Klawasi - Upper, C. L.						
7-19-85	92	61	116	-	92	101
6-17-82	117	88	112	-	99	104
8-21-81	94	63	115	-	99	105
1973	105	75	119	-	105	105
Klawasi - Lower, C. L.						
7-19-85	144	118	124	-	117	108
6-16-82	156	132	125	-	122	108
8-22-81	148	123	122	-	120	109
1973	157	133	127	-	121	107
Klawasi - Lower, spr						
6-16-82	128	101	122	-	107	104
Copper Center, min spr.						
8-23-81	57	25	53	75	107	120
Tolsona 2 (A)						
6-13-82	55	23	40	62	64	68
1973	-	-	41	61	65	62
Tolsona 1 (B)						
6-13-82	55	23	40	62	65	69
1973	-	-	50	78	64	43
Nickel Creek MV						
6-19-82	36	3	30	31	61	100
8-26-81	34	1	43	36	71	108

Geothermometry formulas, all concentrations in mg/kg:

1) $T°C = 1309/(5.19 - \log SiO_2) - 273.15$; ref.: Fournier, 1981.
2) $T°C = 1032/(4.69 - \log SiO_2) - 273.15$; ref.: Fournier, 1981.
3) $T°C = 1217/(\log(Na/K) + 1.483) - 273.15$; ref.: Fournier, 1981.
4) $T°C = 1647/(\log(Na/K) + \beta[\log(\sqrt{Ca}/Na) + 2.06] + 2.47) - 273.15$; ref.: Fournier, 1981.
5) $T°C = 4410/[13.95 - \log(K^2/Mg)] - 273.15$; ref.: Giggenbach and others, 1983.
6) $T°C = 2200/(\log(\sqrt{Mg}/Li) + 5.47) - 273.15$; ref.: Kharaka and Mariner (Mariner, pers comm, 1985).

Table 7. Sulfate-water oxygen isotope geothermometer temperatures (°C) for Klawasi mud vocanoes.

Site	$\delta^{18}O-SO_4$ SMOW	$\delta^{18}O-H_2O$ SMOW	Geothermometer Temperature
Lower Klawasi, 1981	+11.0	+2.5	205
Upper Klawasi, 1982	+7.5	+1.9	272

C. Janik, U.S. Geolological Survey, Menlo Park, CA, and R. Motyka, Alaska Division of Geological and Geophysical Surveys, analysts.

FIGURES

Figure 1. Geologic map of the Copper River Basin, Alaska, generalized from Beikman (1974) and Winkler and others (1981).

Figure 2. Location map of Copper River Basin mud volcanoes, mineral springs, and oil and gas exploration wells. Stratagraphic cross-section generalized from Church and others (1969) and Ehm (1983). Helium isotope ratios are ^{3}He/^{4}He in air over atmospheric ratio. Sites displaying two values were sampled on separate occasions.

Figure 3. Comparison between certain physical characteristics of mud volcanoes, Copper River Basin, Alaska, taken from Nichols and Yehle, 1961a.

Figure 4. Comparison of water compositions of Copper River Basin mud volcanoes and seawater. Kl = Klawasi group; CC = Copper Center; Tol = Tolsona; NC = Nickel Creek; and Sea = seawater.

Figure 5. Trilateral cation diagram in relative reactive percentages for waters from Copper River Basin mud volcanoes, mineral springs, saline wells, and oil and gas well.

Figure 6. Trilateral anion diagram in relative reactive percentages for waters from Copper River Basin mud volcanoes, mineral springs, saline wells, and oil and gas well.

Figure 7. Stable isotope composition of waters from the Copper River Basin. Symbols: + = Tolsona group; □ = Klawasi group; ◇ = mineral springs; X = domestic wells; Δ = cold springs and rivers. Craig's meteoric water line and standard mean ocean water (SMOW) shown for comparison. Fields for metamorphic and primary magmatic waters were taken from Taylor (1979).

Figure 8. Deuterium vs chloride concentration in Copper River Basin waters. Identifying symbols defined in caption for fig. 7.

Figure 9. Oxygen-18 vs chloride concentration in Copper River Basin waters. Identifying symbols defined in caption for fig. 7.

Figure 10. Comparison of water compositions of Copper River Basin mud volcanoes and seawater with concentrations ratioed to chloride concentrations. Kl = Klawasi group; CC = Copper Center; Tol = Tolsona; NC = Nickel Creek; and Sea = seawater.

Figure 11. The solubility surface of calcite in the system $CaCO_3$-CO_2-H_2O between 50° and 300° C and between 0 and 70 atm CO_2. Taken from Holland and Malinin (1979).

Figure 12. Carbon-13 compositions of carbon species from the Copper River Basin. Carbon-13 compositions of natural materials shown for comparison.

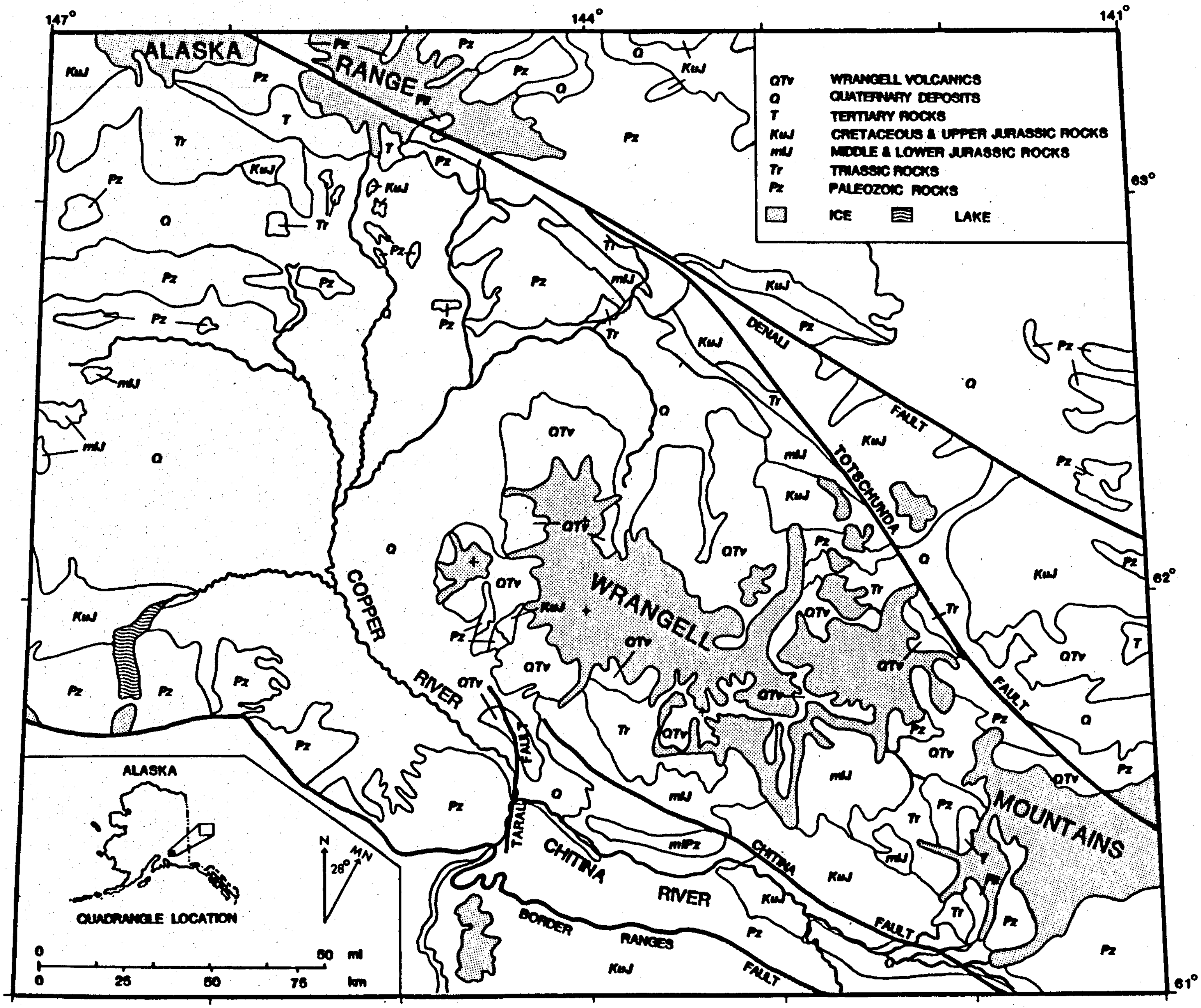

147°
144°
141°
63°
62°
61°
QTv WRANGELL VOLCANICS
Q QUATERNARY DEPOSITS
T TERTIARY ROCKS
KuJ CRETACEOUS & UPPER JURASSIC ROCKS
mlJ MIDDLE & LOWER JURASSIC ROCKS
Tr TRIASSIC ROCKS
Pz PALEOZOIC ROCKS
ICE
LAKE
ALASKA RANGE
DENALI FAULT
TOTSCHUNDA FAULT
WRANGELL MOUNTAINS
COPPER RIVER
TARAL FAULT
CHITINA RIVER
CHITINA FAULT
BORDER RANGES FAULT
mlPz
ALASKA
QUADRANGLE LOCATION
N
MN
28°
0
50 mi
0
25
50
75
km

Fig. 1

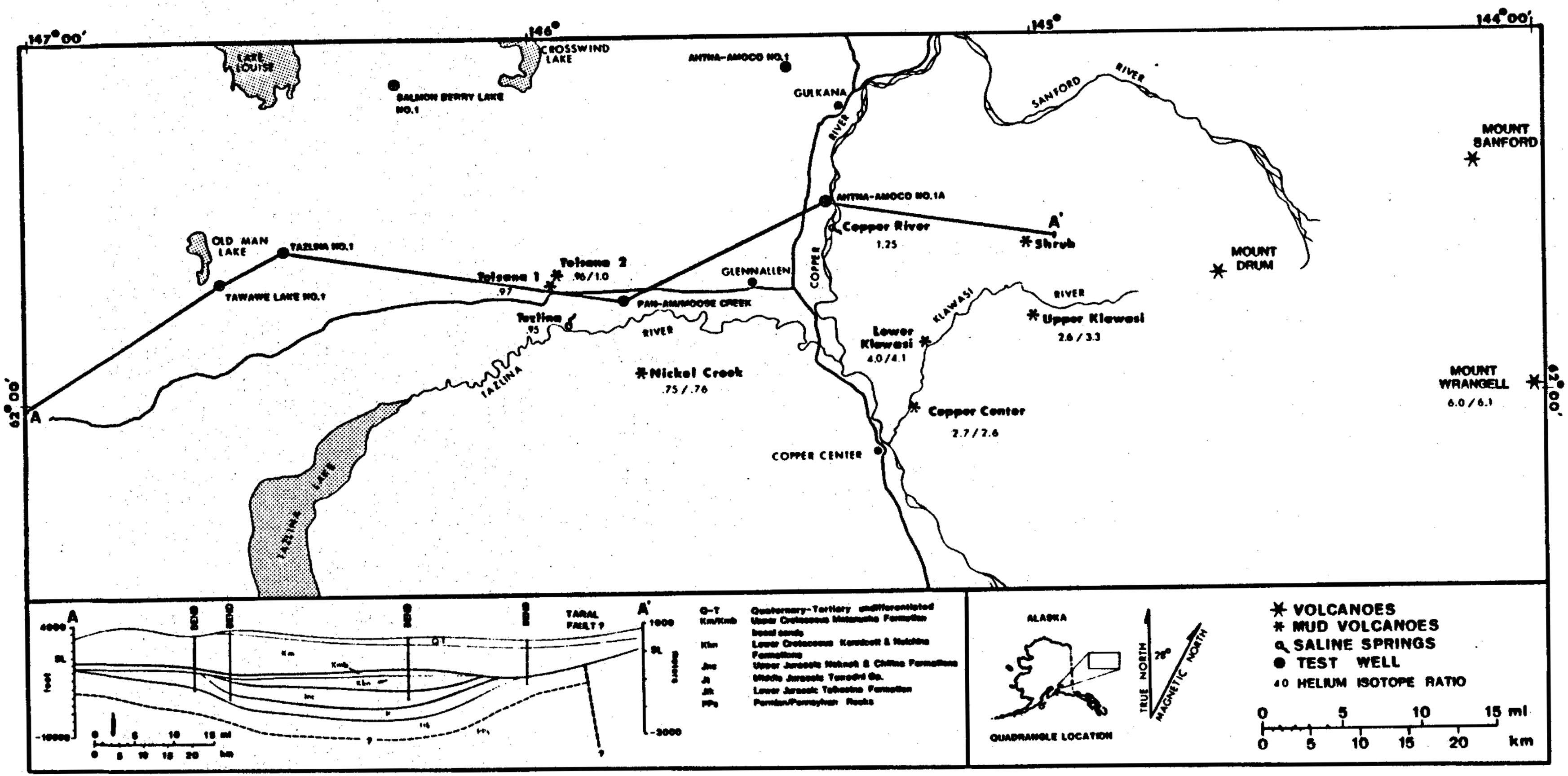
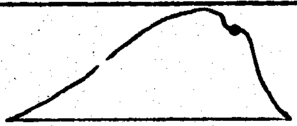
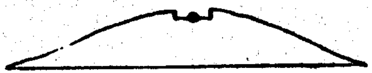
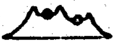
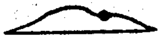

147° 00'
146°
145°
144° 00'
62° 00'
LAKE LOUISE
CROSSWIND LAKE
SALMON BERRY LAKE NO.1
ANTHA-AMOCO NO.1
GULKANA
SANFORD RIVER
COPPER RIVER
AMTHA-AMOCO NO.1A
Copper River
1.25
A'
Shrub
MOUNT SANFORD
MOUNT DRUM
OLD MAN LAKE
TAZLINA NO.1
TAWAWE LAKE NO.1
Tolsona 1
.97
Tolsona 2
.96/1.0
GLENNALLEN
PAN-AM/MOOSE CREEK
Tazlina
.95
TAZLINA RIVER
KLAWASI RIVER
Lower Klawasi
4.0/4.1
Upper Klawasi
2.6/3.3
Nickel Creek
.75/.76
Copper Center
2.7/2.6
COPPER CENTER
MOUNT WRANGELL
6.0/6.1
A
TAZLINA LAKE
A
A'
4000
SL
feet
-10000
TARAL FAULT ?
1000
SL
meters
-3000
Q-T
Km
Kmb
Kln
Jnc
0 5 10 15 mi
0 5 10 15 20 km
Q-T Quaternary-Tertiary undifferentiated
Km/Kmb Upper Cretaceous Matanuska Formation basal sands
Kln Lower Cretaceous Kennicott & Nelchina Formations
Jnc Upper Jurassic Naknek & Chitina Formations
Jt Middle Jurassic Tuxedni Gp.
Jlt Lower Jurassic Talkeetna Formation
PPs Permian/Pennsylvan Rocks
ALASKA
QUADRANGLE LOCATION
TRUE NORTH
MAGNETIC NORTH
28°
VOLCANOES
MUD VOLCANOES
SALINE SPRINGS
TEST WELL
4.0 HELIUM ISOTOPE RATIO
0 5 10 15 mi
0 5 10 15 20 km

Fig. 2

COMPARISON BETWEEN CERTAIN PHYSICAL CHARACTERISTICS OF MUD VOLCANOES, COPPER RIVER BASIN, ALASKA

	Mud Volcano	Diagrammatic cross-section N S	Approximate dimension * of cone		Alt. * of crest	Approx. * diam. of "crater"	Surf. water temp., °F.	Est. water disch., gpm.
			Base	Hgt.				
Drum Group	Shrub		3600 4200	310	2950	120	54	< 1/4
	Upper Klawasi		4200 6700	300	3017	150	86.5	2-5
	Lower Klawasi		6000 8200	150	1875	175	82	5-10
Tolsona Group	Nickel Creek		800 1000	60	2025	150	cold	< 1/4
	Shepard		1300 1600	25	2172	15	——	——
	Tolsona No. 1		600 900	25	2045	30	38-55	< 1/4
	Tolsona No. 2		2000 2300	40	2085	150	40-60	< 1/4

* =in feet, ● = active spring, ○ =inactive spring.

Fig. 3

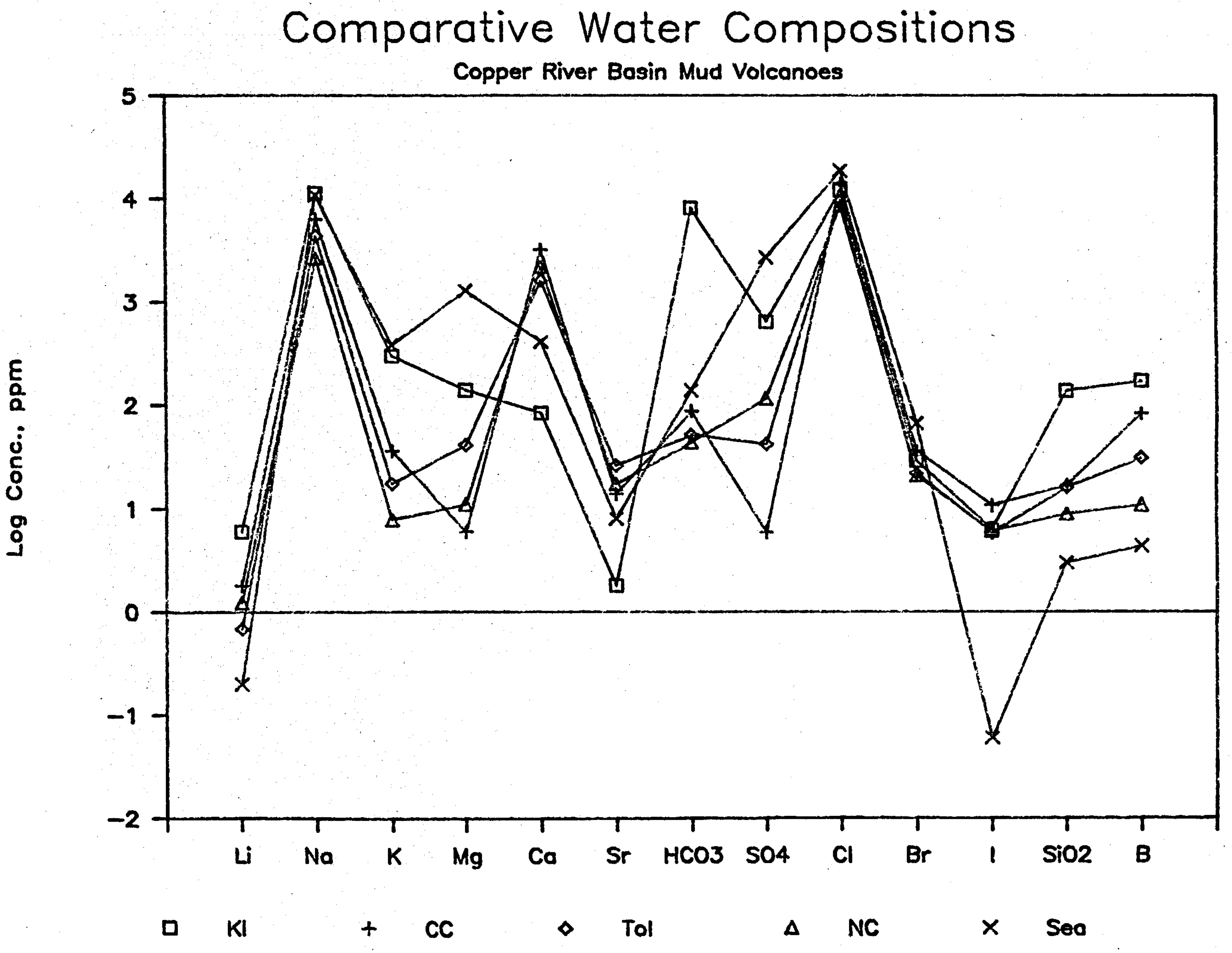
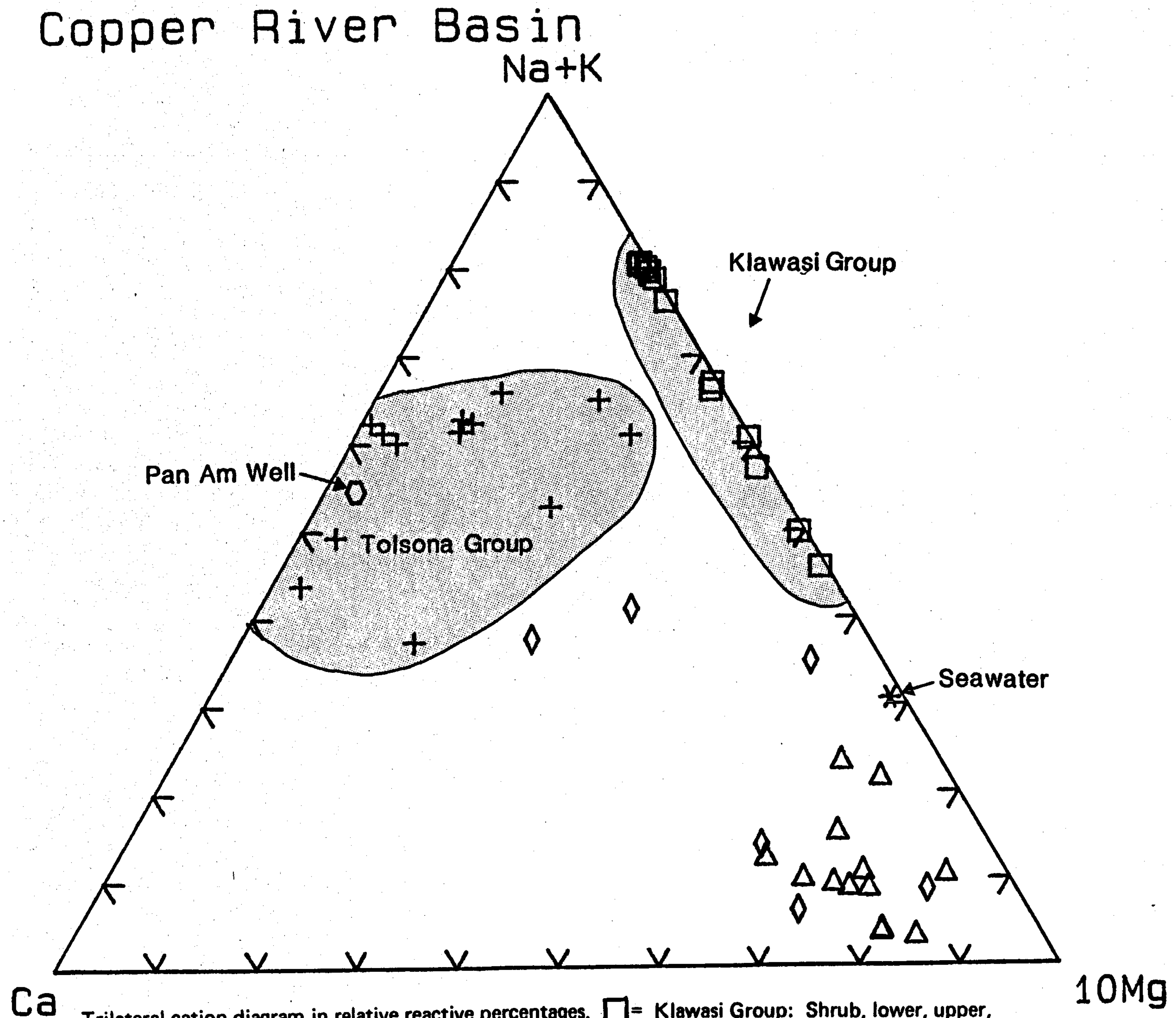

Comparative Water Compositions
Copper River Basin Mud Volcanoes
Log Conc., ppm
5
4
3
2
1
0
−1
−2
Li
Na
K
Mg
Ca
Sr
HCO3
SO4
Cl
Br
I
SiO2
B
□ Kl
+ CC
◇ Tol
△ NC
× Sea

Fig. 4

Fig. 5



Trilateral cation diagram in relative reactive percentages. □ = Klawasi Group: Shrub, lower, upper, + = Tolsona Group: Copper River, Tolsona 1 & 2, Nickel Creek; ◊ = Saline springs; △ = Saline wells; ⬡ = Pan-Am Moose drill hole; ✳ = Seawater.

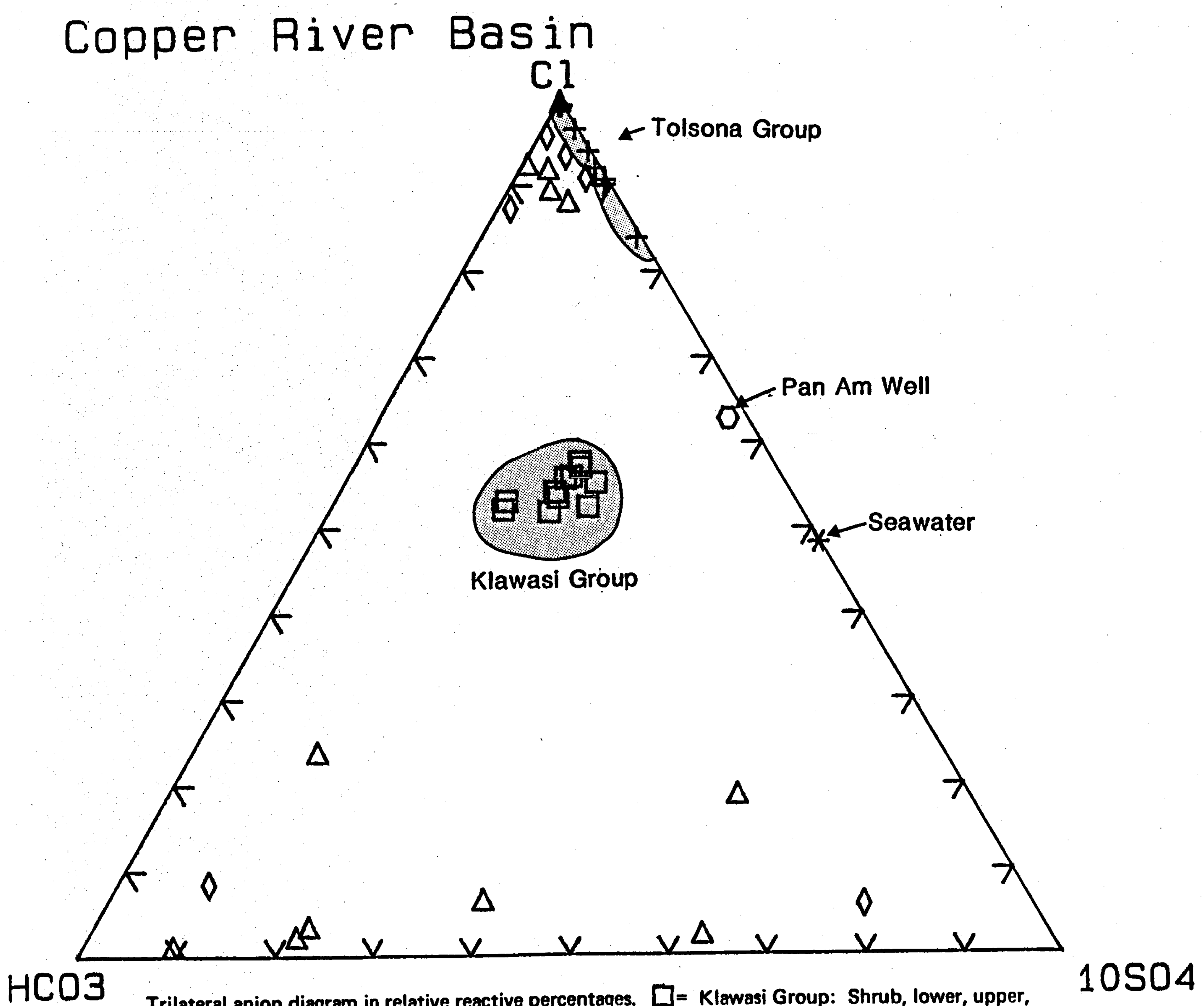


Fig. 6

Trilateral anion diagram in relative reactive percentages. □= Klawasi Group: Shrub, lower, upper, += Tolsona Group: Copper River, Tolsona 1 & 2, Nickel Creek; ◊= Saline springs; △= Saline wells; ⬡= Pan-Am Moose drill hole; ✳= Seawater.

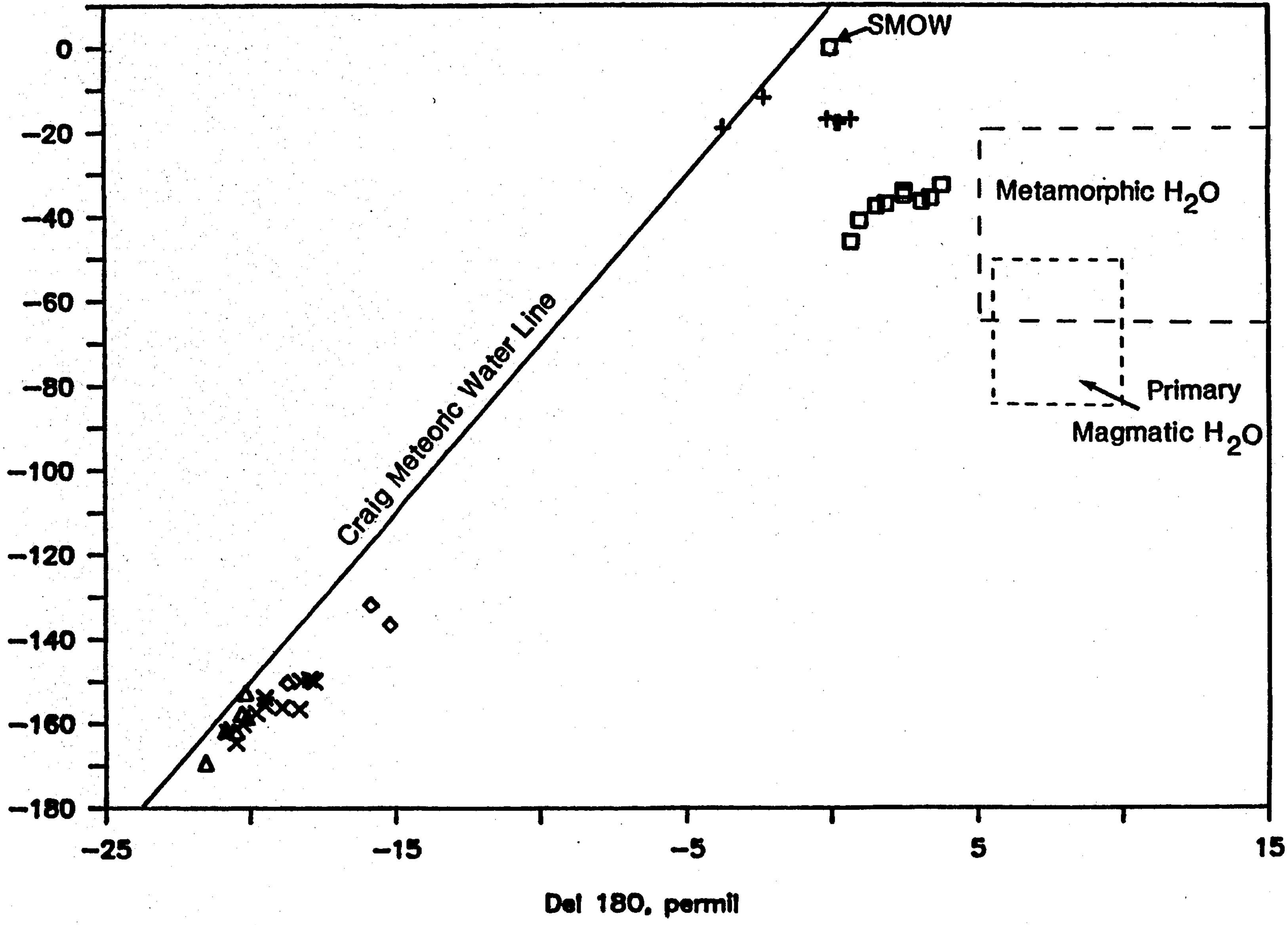

SMOW
Metamorphic H_2O
Primary
Magmatic H_2O
Craig Meteoric Water Line
Del D, permil
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
Del 18O, permil
-25
-15
-5
5
15

Fig. 7

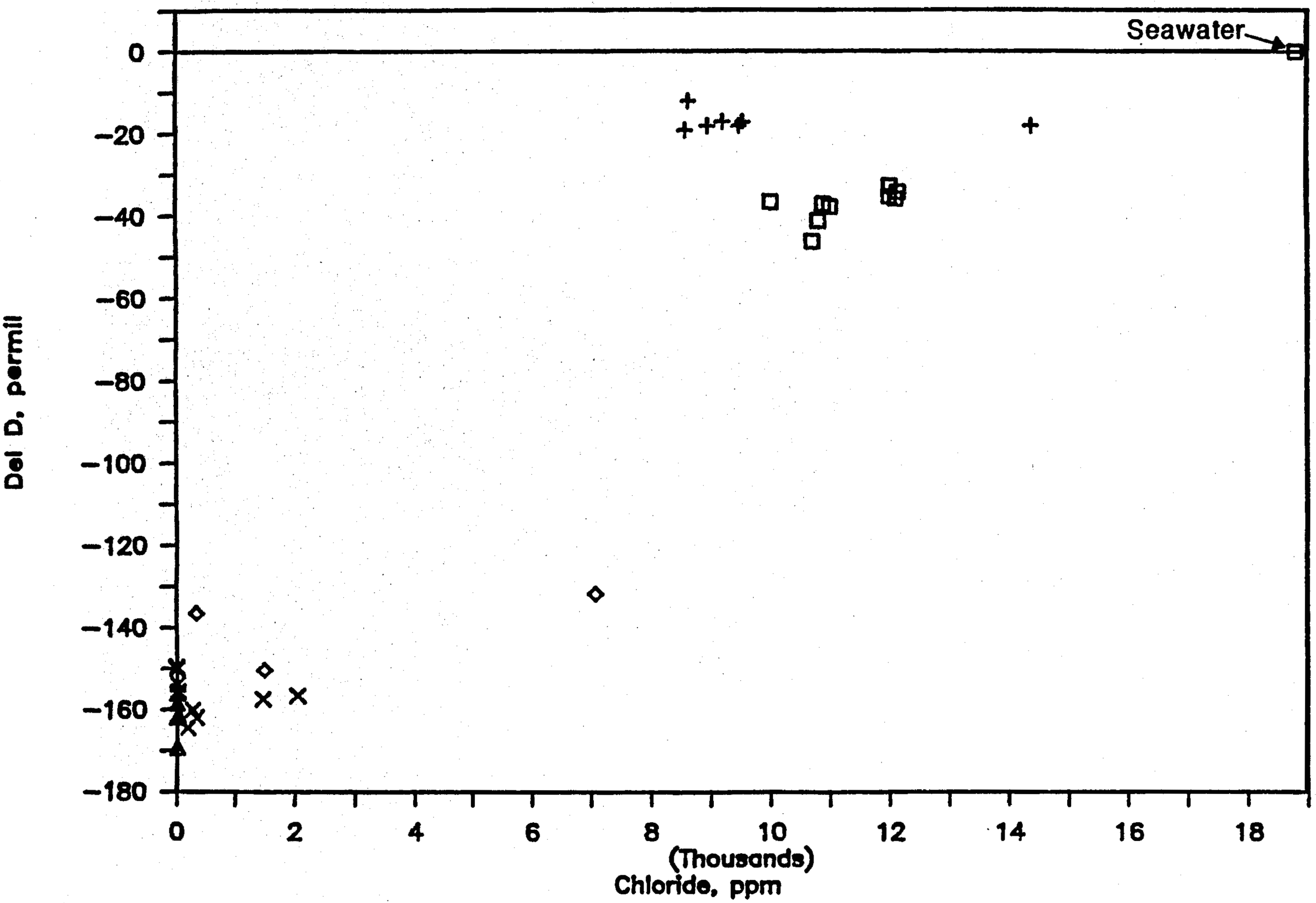
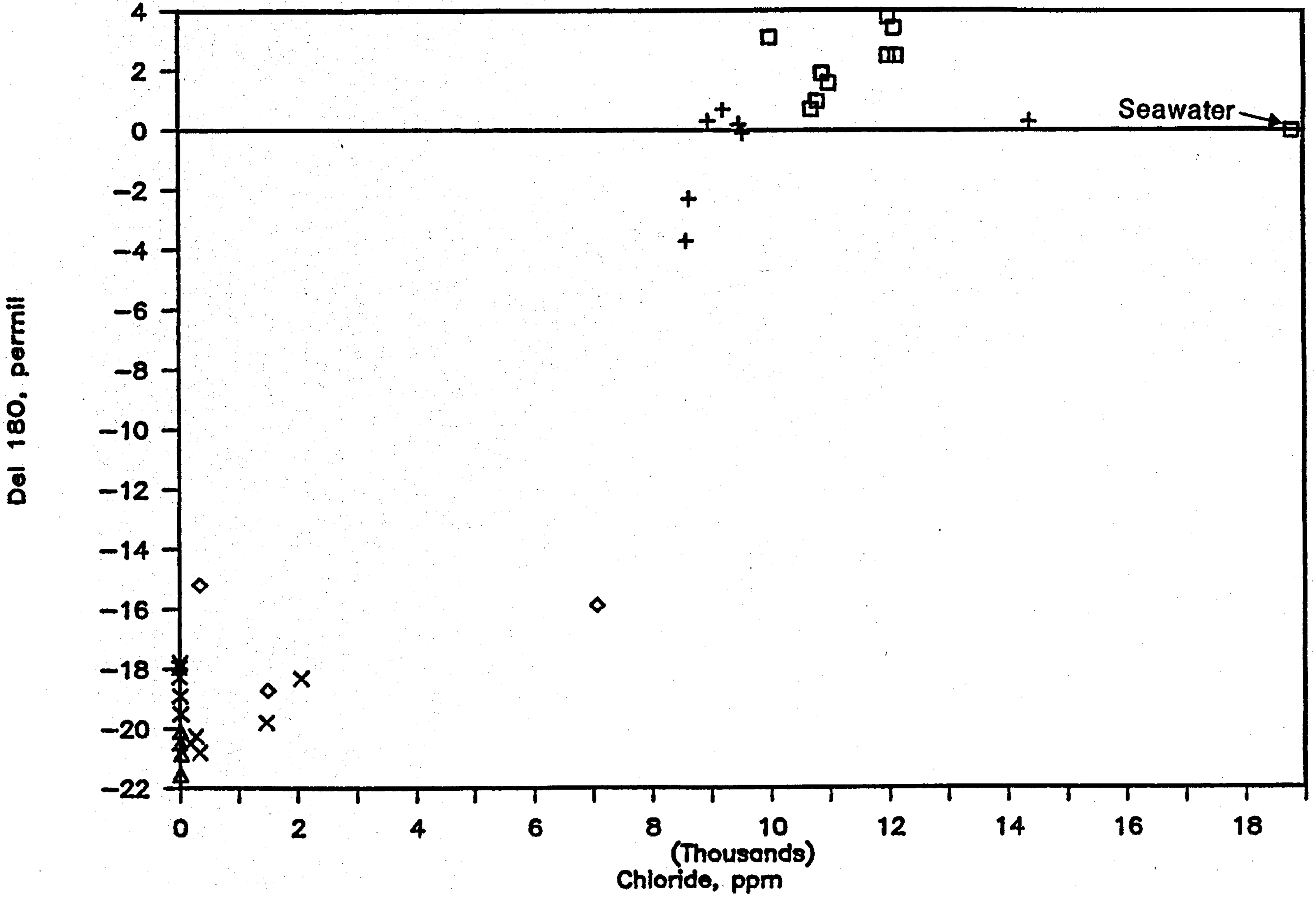

Seawater
Del D, permil
0
−20
−40
−60
−80
−100
−120
−140
−160
−180
0
2
4
6
8
10
12
14
16
18
(Thousands)
Chloride, ppm

Fig. 8

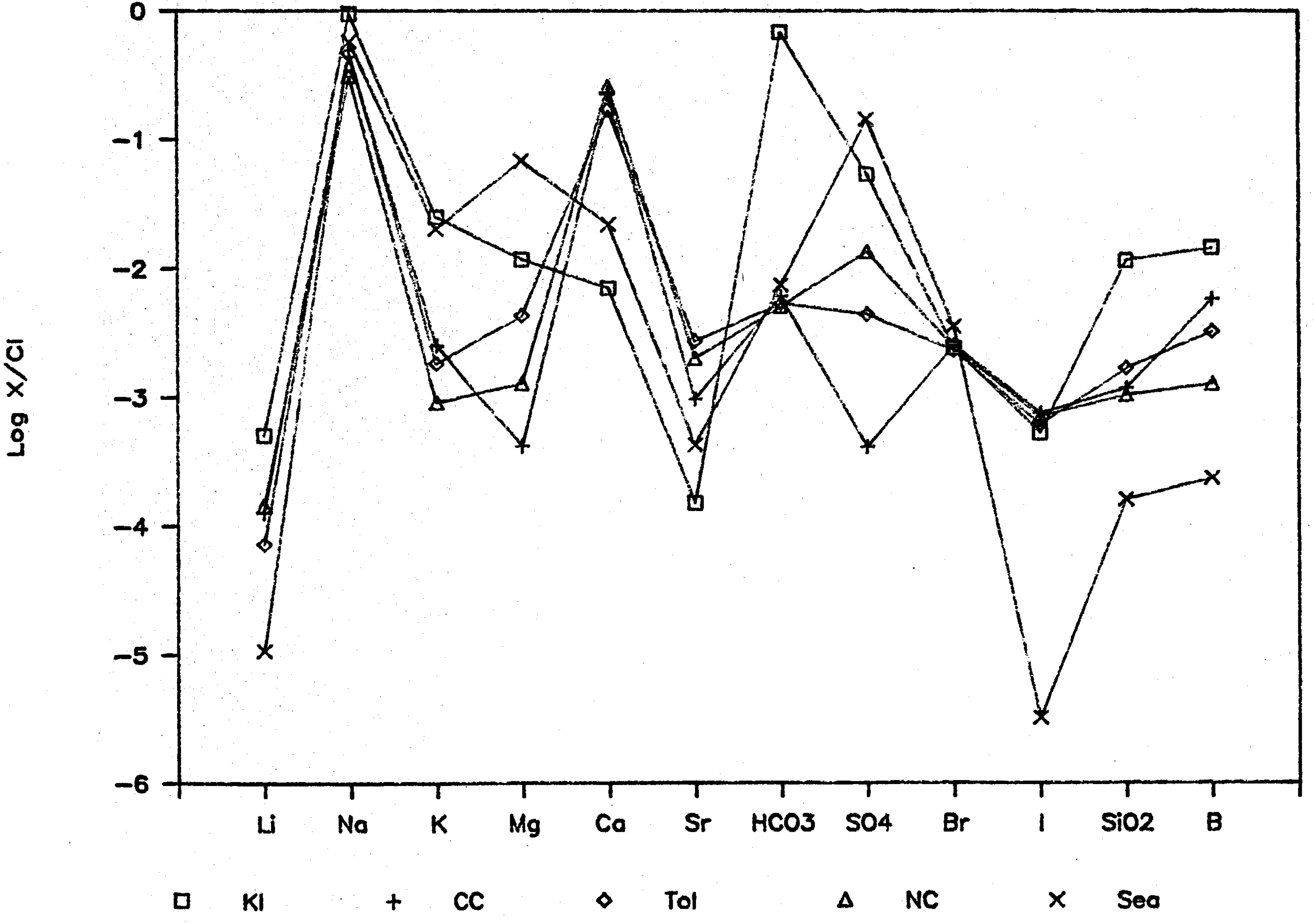
Fig. 9



Del 18O, permil
4
2
0
−2
−4
−6
−8
−10
−12
−14
−16
−18
−20
−22
Seawater
0
2
4
6
8
10
12
14
16
18
(Thousands)
Chloride, ppm

Comparative Water Compositions

Copper River Basin Mud Volcanoes



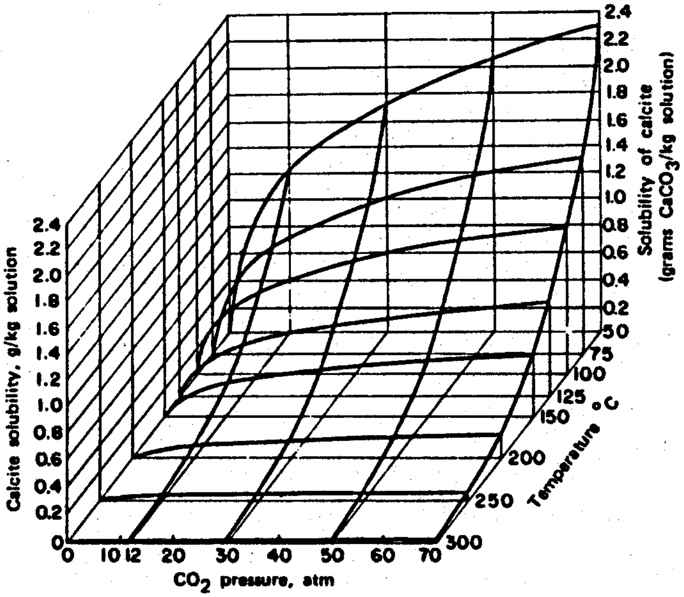

Calcite solubility, g/kg solution
0
0.2
0.4
0.6
0.8
1.0
1.2
1.4
1.6
1.8
2.0
2.2
2.4
Solubility of calcite
(grams $CaCO_3$/kg solution)
50
75
100
125
150
200
250
300
Temperature °C
0
10
12
20
30
40
50
60
70
CO_2 pressure, atm

Fig. 11

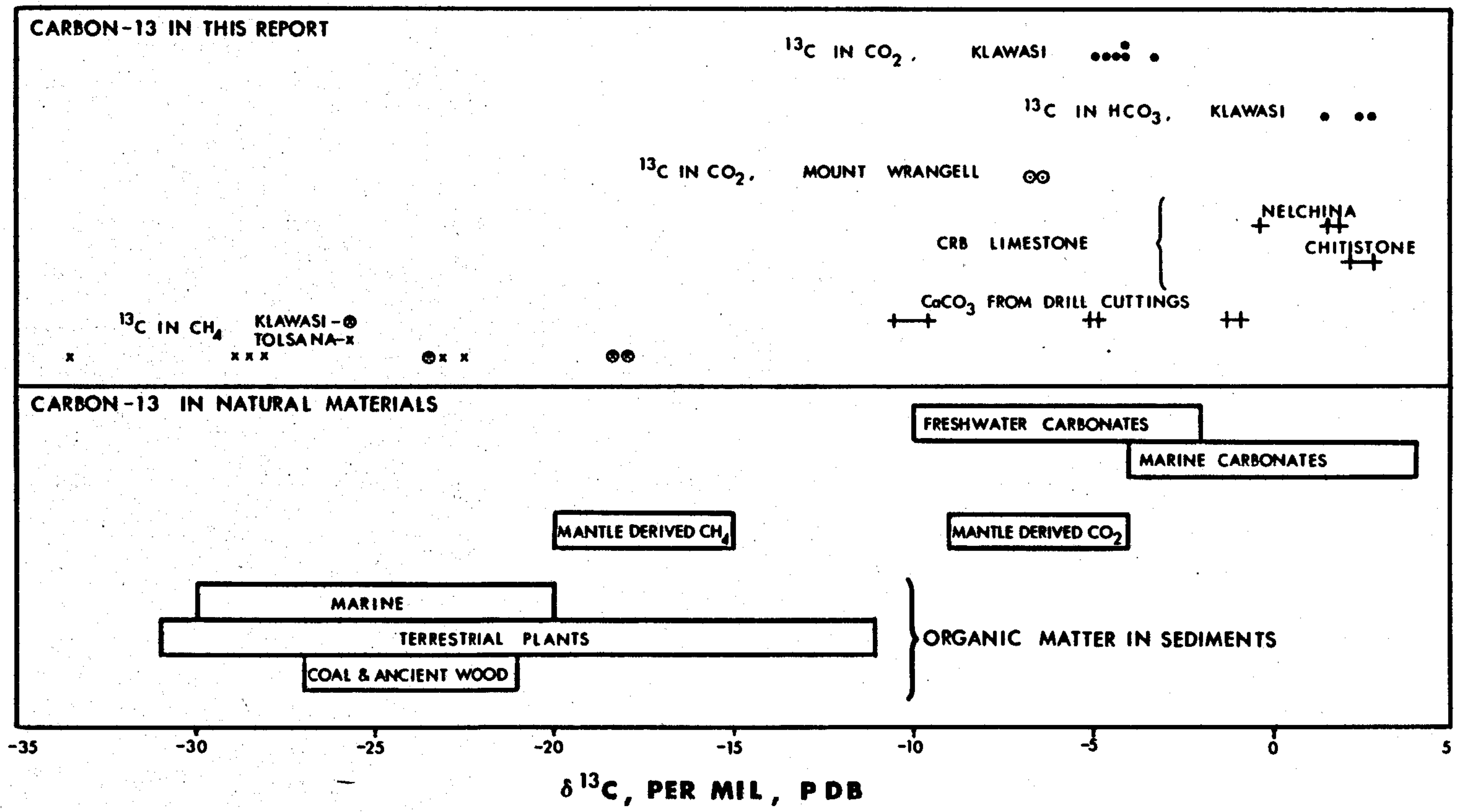

CARBON-13 IN THIS REPORT
13C IN CO2, KLAWASI
13C IN HCO3, KLAWASI
13C IN CO2, MOUNT WRANGELL
CRB LIMESTONE
NELCHINA
CHITISTONE
CaCO3 FROM DRILL CUTTINGS
13C IN CH4
KLAWASI-⊗
TOLSANA-x
CARBON-13 IN NATURAL MATERIALS
FRESHWATER CARBONATES
MARINE CARBONATES
MANTLE DERIVED CH4
MANTLE DERIVED CO2
MARINE
TERRESTRIAL PLANTS
COAL & ANCIENT WOOD
ORGANIC MATTER IN SEDIMENTS
-35
-30
-25
-20
-15
-10
-5
0
5
δ13C, PER MIL, PDB

Fig. 12

APPENDIX A

Water Chemistry, Copper River Basin Cold Springs, Domestic Water Wells, and River Waters.

Table A1. Water chemistry, Copper River Basin cold springs, domestic water wells, and river waters. Units are mg/l unless otherwise noted. nd = not done; tr = trace.

No	Site Name	Sample Date	T, °C	pH	Na	K	Ca	Mg	Li	Sr	NH_4	As	Cs
	Cold springs:												
1	Mendeltna Spr	6-15-82	10	7.2	11	1	43	6	<0.01	nd	nd	nd	nd
2	St. Anne Lake Spr	6-15-82	2	7.6	5	2	26	6	<0.01	nd	nd	nd	nd
	Domestic wells:												
3	Ahtna	6-22-82	4	6.9	82	4.3	140	35	0.05	nd	1.0	<0.001	nd
4	Bishop	6-21-82	8	7.3	12	3.2	49	15	0.01	nd	2.2	<0.001	nd
5	Copperville	6-18-82	14	7.4	564	13.8	469	139	0.12	5.9	5.7	0.003	nd
6	Ellis	6-18-82	2	7.2	129	9.5	69	57	0.01	nd	2.8	nd	nd
7	Eaton, Silver Spr	6-18-82	1	6.9	471	6.7	136	84	0.44	nd	2.0	<0.001	nd
8	Fisher 1	6-19-82	5	7.5	21	0.2	31	10	<0.01	nd	nd	nd	nd
9	Fisher 2	6-19-82	12	6.3	5	0.7	17	7	<0.01	nd	nd	nd	nd
10	Gulkana Motel	6-24-82			100	6.8	17	9	<0.01	nd	nd	nd	nd
11	Park's Place	6-19-82	16	7.3	11	3.1	46	14	0.01	nd	nd	nd	nd
12	Tazlina Wayside	6-21-82	3	7.6	330	7.9	386	124	0.06	4.2	5.2	<0.001	nd
13	Cache Store	6-21-82	6	nd	143	3.6	93	21	nd	nd	nd	nd	nd
	River Water:												
14	Klawasi River 1	6-17-82	16	6.6	5	0.7	5	3	<0.01	nd	nd	0.001	nd
15	Klawasi River 2	6-16-82	10	7.7	24	0.2	31	10	0.02	0.04	nd	nd	nd
16	Tazlina River		nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
17	Klutina River		nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd

Table A1. Continued

No	HCO_3	SO_4	F	Cl	Br	I	SiO_2	B	TDS	$\delta^{18}O$	δD	$\delta^{13}C$-HCO_3	Br/Cl
1	162	15	0.1	5	nd	nd	11	1	171.8	-20.1	-158	nd	-
2	99	14	0.1	8	nd	nd	17	1	127.2	-21.5	-169	nd	-
3	398	77	0.3	181	nd	nd	29	<0.5	745.2	-20.5	-164	nd	-
4	282	2	0.2	2	nd	nd	32	<0.5	256.2	-18.0	-150	nd	-
5	210	9	0.4	2050	5.5	1.3	41	1.3	3403.3	-18.3	-157	nd	0.0027
6	737	102	0.6	25	nd	nd	23	<0.5	781.0	-19.5	-155	nd	-
7	1517	24	0.4	326	0.9	0.4	49	4.5	1851.7	-20.8	-162	-6.3	0.0028
8	185	10	0.2	12	nd	nd	24	<0.5	198.8	-19.5	-154	nd	-
9	106	2	0.1	2	nd	nd	9	<0.5	93.8	-18.3	-150	nd	-
10	nd	8	0.7	8	nd	6.0	34	<0.5	-	-18.9	-156	nd	-
11	257	6	0.2	6	nd	nd	30	<0.5	241.9	-17.8	-150	nd	-
12	202	1	0.4	1470	4.3	0.6	30	<0.5	2458.8	-19.8	-157	nd	0.0029
13	nd	9	0.5	268	nd	nd	39	0.8	-	-20.3	-160	nd	-
14	32	<1	0.1	<5	nd	nd	22	<0.5	51.9	-20.5	-162	nd	-
15	156	19	0.2	22	nd	nd	24	<0.5	206.7	-20.9	-161	nd	-
16	nd	nd	nd	nd	nd	nd	nd	nd	-	-20.3	-158	nd	-
17	nd	nd	nd	nd	nd	nd	nd	nd	-	-20.2	-153	nd	-

APPENDIX B

Copper River Basin Water and Gas Chemistry, Previous Studies.

Table B1. Water chemistry, previous studies, Copper River Basin mud volcanoes, mineral springs, and saline domestic wells, All units are in mg/l unless otherwise noted.

No	Site Name	Date	T, °C	pH	Na	K	Ca	Mg	Li	Sr	NH_4
1	Shrub MV	1973	-	7.2	10000	330	21	350	13.0	-	-
2		7-13-60	-	8.2	-	-	12	272	-	-	-
3		8-11-56	12	8.2	9390	275	94	502	-	-	11
4	Upper Klawasi CL	1973	-	7.1	10000	240	7	300	7.9	-	-
5		7-13-60	31	7.5	9490	232	63	248	9.1	-	1
6	Lower Klawasi CL	1973	-	7.6	10500	290	18	150	5.8	-	-
7		7-13-60	20	7.7	10000	271	31	136	6.9	8.0	7
8		9-07-56	28	7.7	10400	433	119	130	-	-	-
9	Copper Center spr	8-07-60	17	8.0	5960	55	3060	24	-	-	-
10		7-13-60	-	8.1	5910	33	3040	14	-	-	-
11	Tolsona 2 (A)	1973	-	6.8	4200	17	1700	37	0.5	-	-
12		7-25-60	10	6.6	3970	19	1150	39	2.0	26.0	6
13		7-14-58	10	6.3	4000	26	1580	94	0.0	-	-
14	Tolsona 1 (B)	1973	-	7.5	4750	25	820	86	0.3	-	-
15		9-21-56	8	7.1	4660	60	787	111	-	-	6
16	Nickel Creek MV	6-19-58	-	6.8	2600	24	2760	65	8.0	-	-
17	Copper River Spr	5-26-55	-		670	-	2080	392	-	-	-
18	Spr east of Gakona	1973	18	8.5	2200	140	400	200	1.2	-	-
19	Spr near Gakona	9-23-58	-	7.8	100	8	91	52	-	-	6
20	Tazlina River Spr	8-07-60	4	7.3	1170	11	909	48	-	-	6
21	Pan Am Moose Cr well	1963	(60?)	-	3871	-	2603	12	-	-	-
22	Seawater				10770	380	412	1290	0.2	8.0	-
23	Moose Lake spr	11-52	-		-	-	7600	-	-	-	-
	Saline wells, previous studies										
24	502', Glen HW	10-25-59	-	8	767	27	290	118	-	-	-
25	321', Rich. HW	8-06-51	-		429	-	693	118	-	-	-
26	433', Gulk Air	1945	-	7	2630	82	4780	984	-	-	-
27	354', Gulk Air	12-28-54	-	7	1150	44	1900	520	-	-	-

1) I. Barnes, U.S. Geological Survey data files, pers. comm., 1980.
2) Grantz and others, 1962.
3) Nichols and Yehle, 1961a; 1961b.
4) Foresman, 1970.
5) Krauskopf, 1979.
6) U.S. Geological Survey, Alaska water chemistry data files, Anchorage, Alaska.

Table B1. Continued

No	HCO_3	SO_4	F	Cl	Br	I	SiO_2	B	TDS	δ^{18}O	δD	Reference
1	9920	460	0.2	10000	-	-	120	170	26351	3.1	-36	1
2	9670	650	-	10300	-	-	-	-	15998	-	-	2
3	7350	-	0.4	12000	-	-	65	120	26078	-	-	3
4	7730	740	0.4	11000	-	-	53	140	26296	1.6, 1.0	-38, -41	1
5	8281	614	0.6	10800	22	6.2	34	173	25773	-	-	2
6	7190	750	0.3	12000	-	-	140	190	27586	3.8, 3.4	-33, -36	1
7	7230	664	0.3	12100	29	6.8	123	169	27114	-	-	2
8	7290	666	-	12500	-	-	132	-	27971	-	-	3
9	124	4	1.7	14400	-	-	24	-	23590	-	-	3
10	65	9	-	14500	-	-	18	-	23556	-	-	2
11	57	75	1.0	9200	-	-	6	34	15299	0.7	-17	1
12	46	-	1.3	8790	20	4.4	9	30	14090	-	-	2
13	48	6	-	9450	-	-	7	-	15186	-	-	3
14	97	98	0.3	8950	-	-	-	18	14795	0.3	-18	1
15	143	-	0.3	8870	17	3.7	16	35	14636	-	-	3
16	90	230	0.4	9100	17	2.2	9	-	14860	-	-	3
17	226	60	-	5680	-	-	-	-	8993	-	-	3
18	5720	50	0.9	340	-	-	16	100	6266	-15.2	-137	1
19	458	161	-	90	-	-	-	-	734	-	-	2
20	216	4	0.3	3400	-	-	24	-	5678	-	-	3
21	525	742	-	9752	-	-	-	-	17239	-	-	4
22	140	2715	1.3	18800	67	0.1	3	4	34520	0.0	0	5
23	16	-	-	15000	-	-	-	-	22608	-	-	2
24	201	20	-	1900	-	-	22	-	3243	-	-	6
25	290	15	-	2300	-	-	47	-	3745	-	-	6
26	84	5	-	15400	-	-	-	-	23922	-	-	6
27	53	-	-	6470	-	-	19	-	10129	-	-	6

Table B2. Copper River Basin gas analyses, previous studies, mole per cent.

Location	Date sampled	CO_2	H_2S	H_2	CH_4	He	N_2	Ar	Reference
Shrub MV	8-11-56	99.3	-	-	-	tr	0.6	tr	1 & 3
Upper Klawasi MV	6-18-58	98.9	-	-	0.1	tr	1.1	tr	1 & 3
Upper Klawasi MV	6-74	99.6	-	-	0.37	0.010	0.4	nr	4
Lower Klawasi CL	6-17-58	96.4	-	-	tr	tr	3.4	0.2	1 & 3
Lower Klawasi CL	6-74	99.5	-	-	0.2	0.026	-	nr	4
Copper Center spr	8-07-60	0.1	-	-	44.6	tr	55	0.1	2 & 3
Nickel Creek MV	6-19-58	0.4	-	tr	54.4	0.1	44.9	0.1	1 & 3
Nickel Creek MV	6-74	-	-	0.014	54.9	0.18	45	nr	4
Tazlina spr	8-08-60	0.9	-	0.1	58.2	0.1	40.4	0.2	2 & 3
Tolsona 2 MV	7-14-58	0.4	-	-	69.4	0.1	30	0.1	1 & 3
Tolsona 2 MV	6-74	0.36	-	-	70.6	0.10	28.1	nr	4
Tolsona 1 MV	9-07-57	0.2	-	-	66.9	0.1	32.6	0.1	3
Tolsona 1 MV	6-74	0.37	-	-	69.2	0.061	30.5	nr	4
Moose Lake spr	11-09-52	0.2	-	-	48.6	0.1	50.6	0.1	1 & 3

1. Nichols and Yehle, 1961a.
2. Nichols and Yehle, 1961b.
3. Grantz and others, 1962.
4. Reitsima, 1979.

tr = trace
nr = not reported
\- = below detection