ORIGINS OF SALTS IN THE DRY VALLEYS OF VICTORIA LAND, ANTARCTICA, BY ^{36}Cl TRACING

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ABSTRACT

The Dry Valleys of southern Victoria Land, Antarctica contain numerous saline lakes. The source of salt to these lakes has been debated for over 20 years. The main sources hypothesized in the literature are sea water, meteoric deposition, weathering by-products, and ground water.

Chlorine-36 was used to trace the origins of salts in six Dry Valleys lakes. Chlorine-36 signatures were first determined for the various potential sources. Simple mixing models were then employed to determine the origins of the salts and where possible to quantify their relative contributions.

It was determined that Lake Vanda has received its chloride from both deep ground water and the Onyx River. Don Juan Pond has received nearly all its chloride from ground water. Lakes Bonney and Fryxell have received chloride from more than one source, however, insufficient data were collected to identify the sources. Lakes Hoare and Vida appear to have received all their chloride from meteoric deposition transported by glacial meltwater.

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INTRODUCTION

Most of the Antarctic continent is covered with glacial ice and snow, however, there are a few areas which are free of ice. These ice-free areas have been termed 'dry' as they are polar deserts characterized by extreme aridity (mean annual precipitation between 10 and 20 mm) and cold (mean annual temp. -20°C).

The ice-free area of Southern Victoria Land is situated in the Trans-antarctic Mountains west of McMurdo Sound, Ross Sea (Figure 1). Three east-west trending glacial valleys comprise the area: Victoria Valley, Wright Valley and Taylor Valley. These valleys contain both fresh and saline lakes and ponds. The lakes are characterized by high salt concentrations and high evaporation and sublimation rates. The lakes and ponds in the Dry Valleys may be classified into three categories (Cartwright and Harris, 1981): 1)'glacial' lakes and ponds, supplied primarily by meltwaters from glaciers and snowfields; 2)'ground water' lakes and ponds, supplied primarily by either shallow ground water only or both shallow and deep ground water; and 3)'mixed' lakes and ponds, supplied primarily by glacial meltwater but also receiving ground waters.

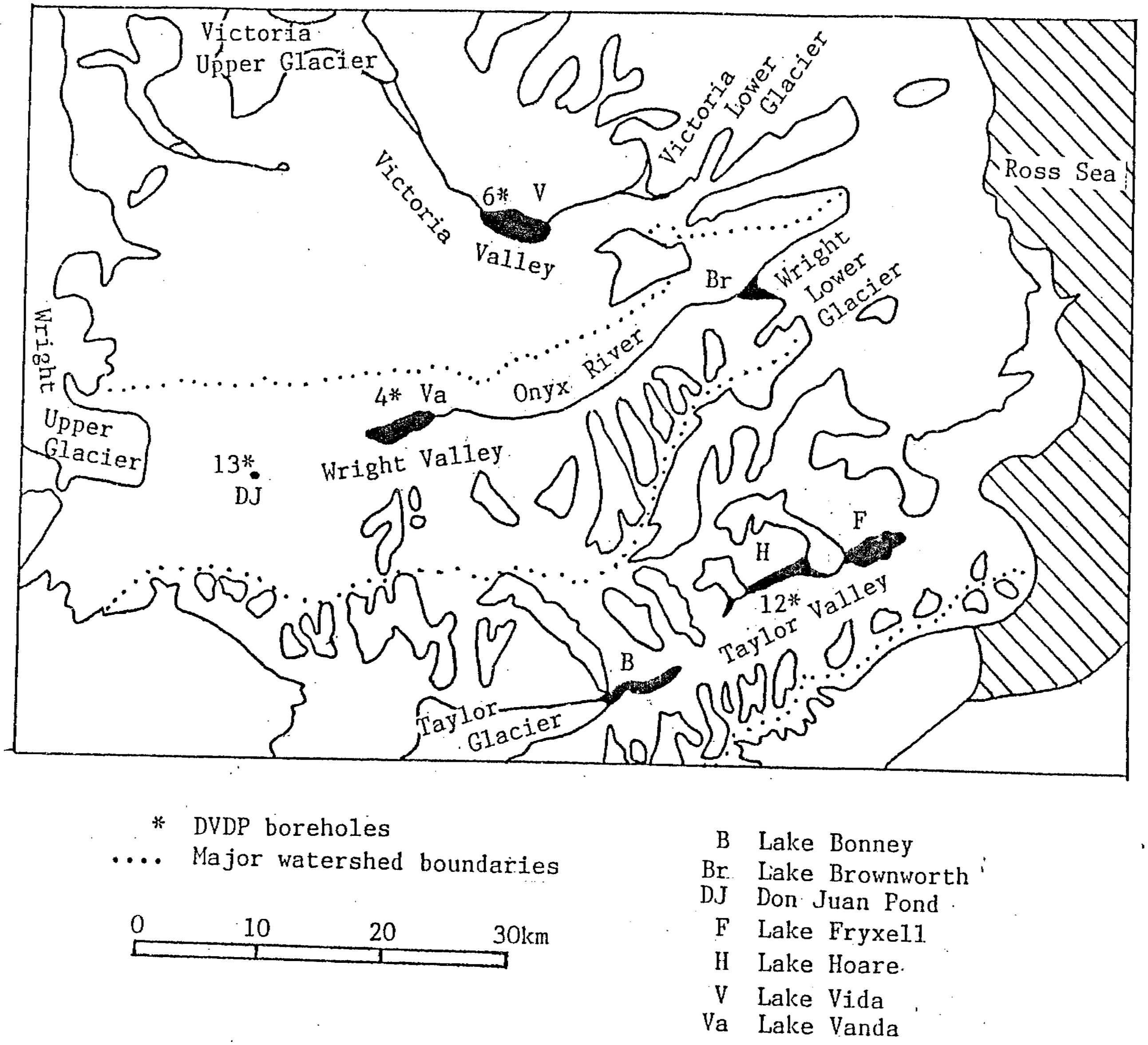

Figure 1. Map of the Dry Valleys of Southern Victoria Land.

(adapted from Cartwright and Harris, 1981)

The lake geochemistry of the Dry Valleys of Southern Victoria Land has been studied for over 20 years. Yet the origin of the salts in the lakes is still disputed. Various hypotheses have been offered to explain the presence of high salt concentrations in the lake waters. Among these are thermal springs, trapped sea water, dry atmospheric fallout, local weathering, and ground water.

A number of geochemical approaches have been used to explain the salt concentrations. The most widely employed approach has been the analysis of dissolved major elements (Angino and Armitage, 1963; Nakaya and Nishimura, 1977; Torii et al., 1977). The source of the salts is hypothesized and then geochemical processes are examined which could modify the source waters to the present lake water. These geochemical processes include evaporation, precipitation and ion exchange with sediments. Analysis of minor and trace elements has also been employed in a similar manner (Boswell et al., 1967; Masuda and Nishimura, 1982; Lyons et al., 1985).

Stable isotope ratios of oxygen, hydrogen, carbon and sulfur have greatly aided in the investigation of the origin of both salt and water in the lakes (Ragotzkie and Likens, 1964; Nakai et al., 1975; Matsubaya et al., 1979). However, oxygen and hydrogen isotopes are subject to fractionation by evaporation in such an arid environment as the Dry Valleys. Carbon and sulfur are affected by biological activity resulting in precipitation, vaporization and fixation. The most unambiguous tracer used to date has been the radioisotope strontium-87 (Jones and Faure, 1967). However, strontium is a minor constituent of the lake waters and may not reflect the origin of major ions. In addition, strontium is not particularly conservative.

The purpose of this study was to directly trace the origins of salts in the lakes of the Dry Valleys and to test the major hypotheses presented in the literature. Three conditions had to be met by the tracer. First, the tracer must be a major constituent of the lake salts. Second, it must be conservative. Third, the tracer must provide a distinctive signature for each possible source. Chlorine-36 met all these requirements.

GENERAL DESCRIPTION OF LAKES IN THE DRY VALLEYS

The Dry Valleys of Southern Victoria Land are situated west of McMurdo Sound which is part of the Ross Sea. The area is divided into three east-west trending glacial valleys (Figure 1). These valleys, in order from north to south, are Victoria Valley, Wright Valley and Taylor Valley. Both fresh and saline lakes are found in these valleys. The most studied lakes are Lake Vanda and Don Juan Pond in Wright Valley and Lakes Bonney and Fryxell in Taylor Valley. Less studied are Lake Hoare in Taylor Valley and Lake Vida in Victoria Valley.

Lake Vanda is located in the topographically lowest part of Wright Valley, approximately 50 km from the Ross Sea. The lake is 5.6 km long, 1.5 km wide, and 68.8 m at its deepest point (Nelson and Wilson, 1972). Lake Vanda is perennially covered with 3-4 meters of ice except for a narrow moat that forms near the shore during the warmest weeks of the austral summer. Water is supplied to the lake during this six- to eight-week period by the Onyx River (Green and Canfield, 1984). The Onyx River is a dilute meltwater stream that originates from the Wright Lower Glacier. Tributary streams contribute approximately 10% of the river water (Chinn, 1981). The drainage area is characterized by igneous and metamorphic rocks, dolerite sills, and weakly developed soils (Cameron, 1971). Lake Vanda is meromictic, i.e. the lake does not undergo complete circulation and the main water mass does not mix with a lower portion. The deeper water is perennially stagnant (monimolimnion) and the upper water layer periodically circulates (mixolimnion). A steep salinity gradient separates the two, termed a chemocline. Lake Vanda is both chemically and thermally stratified. The water temperature increases gradually with depth and reaches a maximum value of 24.5-25.7^{o}C at the bottom despite a mean annual air temperature of -20^{o}C (Nakai et al., 1975). Lake Vanda has no outlet. Evaporation and sublimation are the only mechanisms by which water leaves the basin.

Don Juan Pond is located in the south fork of Wright Valley about 9 km west of Lake Vanda. It is situated in the center of a playa at the bottom of a narrow canyon. The pond is small and shallow, approximately 300 m long, 100 m wide and 10 cm deep (Yamagata et al., 1967). In midsummer, meltwater is supplied to the pond from a moraine containing ice lenses on the west edge of the basin. Don Juan Pond is extremely saline and is nearly saturated with calcium chloride. The salt concentration is so high that even during the Antarctic winter when the air temperatures drop below -50^{o}C, the pond remains completely or at least partially unfrozen. The floor of the basin is a discharge zone for an underlying confined dolerite aquifer (Harris and Cartwright, 1981). The ground water is currently transporting salts into the basin. Large deposits of salts are found in and around Don Juan Pond. These salts are principally halite and antarcticite ($CaCl_2 \cdot 6H_2O$) which is usually found only in winter. Salts may be being transported out of the basin by wind. Don Juan Pond has no outlet.

Lake Bonney is located approximately 16.5 km west of the Ross Sea in Taylor Valley. The lake is divided into two lobes that differ in water and sediment composition (Hendy et al., 1977). The west lobe is 2.6 km long, 0.8 km wide and 35 m deep (Torii and Yamagata, 1981). It is connected to the larger eastern lobe through a channel 36 m wide and 9.5 m deep (Angino, 1964). The east lobe is 4.8 km long, 0.8 km wide and 33 m deep (Torii and Yamagata, 1981). Lake Bonney is perennially covered with 3-4 meters of ice (Weand et al., 1975) except for a narrow moat that forms near the shore during a 4- to 6-week period in the austral summer. Glacial meltwater enters the lake at this time from the LaCroix, Matterhorn, Sollas, Hughes, Calkin, Rhone and Taylor Glaciers. Both lobes of Lake Bonney are meromictic. The chloride concentration of the bottom waters of the east lobe is over twice that of the bottom waters of the west lobe (Hendy et al., 1977). The bottom water of the east lobe is nearly saturated with sodium chloride (Hoare et al., 1964). Lake Bonney is both chemically and thermally stratified. Maximum temperatures of $7^{\circ}C$ and $1.3^{\circ}C$ occur in the eastern and western lobes respectively despite a mean annual air temperature of $-20^{\circ}C$. Lake Bonney has no outlet. Evaporation and sublimation are the only mechanisms by which water leaves the basin.

Lake Fryxell is located about 10 km east of Lake Bonney in the Taylor Valley. It is situated in the center of a wide, shallow basin. The lake is approximately 5 km long, 2 km wide and 19 m deep (Torii and Yamagata, 1981; Lawrence and Hendy, 1985). Between 3.8 and 4.5 m of ice permanently cap Lake Fryxell. The lake is fed primarily by meltwater from Canada and Commonwealth Glaciers during the austral summer when a moat forms along the lake periphery. Lake Fryxell is chemically and thermally stratified and has no outlet.

Lake Hoare is located between Lakes Bonney and Fryxell in Taylor Valley, just west of Canada Glacier. The lake is 3.5 km long, 0.5 km wide and 31 m deep (Parker et al., 1980). A permanent ice cover averaging 5.5 meters caps the lake. Lake Hoare receives glacial meltwaters from the north through shallow ice-free moat areas along the lake periphery. Unlike the lakes described above, Lake Hoare is not saline nor chemically or thermally stratified (Parker et al., 1980).

Lake Vida is located about 37 km west of the Ross Sea in Victoria Valley. It is about 3.8 km long and 1.5 km wide (Armitage and House, 1962). Thickness of ice in the lake is not known. The lake may be entirely frozen (Calkin and Bull, 1967) or it may have saline bottom waters at the lake's center (McGinnis et al., 1973). Principal inflows to Lake Vida are meltwater streams from Victoria Lower and Victoria Upper Glaciers.

HISTORICAL SURVEY OF RELATED RESEARCH

Lake Vanda

Lake Vanda was first studied during the Antarctic summer of 1960-61 by Armitage and House (1962). The purpose of the study was to investigate the biology of zooplankton in Lakes Vanda and Bonney and to make a general survey of their limnological conditions. When no zooplankton were collected from either lake, Armitage and House changed their emphasis to the physical and chemical characteristics of the lakes. Two corings were made through the ice of Lake Vanda. Temperature, chlorinity and conductivity profiles were measured. Lake Vanda was found to be both chemically and thermally stratified. The mixolimmnion was identified to be above 55m; the monimolimnion below 60m; with a sharp chemocline between 55-60m. Armitage and House (1962) suggested evaporation or salting-out during freezing to explain the deep saline layer. They considered the most likely source of heat to be either thermal springs or a high geothermal gradient.

Angino and Armitage (1962) further investigated the origin of the monimolimnion and the lake's source of heat. Cation concentrations of the monimolimnion lead Angino and Armitage (1962) to conclude that the waters of Lake Vanda are primarily of fresh water origin with the present high Cl^- concentrations due to freezing. They reaffirmed the geothermal origin of the temperature profile in Lake Vanda, favoring the high geothermal gradient explanation over thermal springs.

Wilson and Wellman (1962) investigated the heat balance of Lake Vanda. Temperature profiles were taken at twelve locations at 5 ft intervals. In addition, a geothermal gradient probe was driven 2 ft into the bottom of the lake. They found that heat was being conducted downward from the lake. Wilson and Wellman (1962) considered five possible sources of heat for Lake Vanda: 1) biological activity; 2) chemical heating; 3) hot springs; 4) abnormally high geothermal gradient; and 5) radiant energy from the Sun. They eliminated the first four sources and concluded that the only possible source of heat to the lake was radiant energy from the Sun.

The geology of the Lake Vanda area was investigated by Nichols (1963). He found that the level of Lake Vanda had once been approximately 185 ft higher than the present level. Nichols (1962) also observed that the only inflow to Lake Vanda was via the Onyx River which he suggested supplies over 80% of the lake water. No surface outlet was observed.

Wilson (1964) attempted to explain the origin of the salt concentration gradient in Lake Vanda utilizing the geology of Nichols (1963). He suggested that some time in the past the Onyx River did not supply sufficient water to Lake Vanda to maintain its high water level. Evaporation concentrated the chemical constituents into a few feet of remaining brine. Later, the Onyx River began to provide an increased volume of fresh water to the lake which flowed on top of the denser brine. Upward diffusion of calcium chloride has been occurring since this time. Wilson (1964) then calculated the time required for the present concentration profile to be produced by the diffusion process. He concluded that the climatic change occurred approximately 1200 years ago. Nakaya et al (1979) independently calculated a similar time estimate of 800-1200 years assuming diffusion in the water column and ion exchange with sediments.

The heat balance of Lake Vanda was re-examined by Ragotzkie and Likens (1964). Three thermal probes were emplaced in the lake sediment. Two indicated an increasing geothermal gradient with depth. Ragotzkie and Likens (1964) concluded that the lake is receiving heat from two sources - solar radiation and conduction from the lake bottom. No advection of heat from either surface or subsurface sources was observed. Hoare (1968) later conclusively determined that heat from the bottom of the lake is only a minor contributor to the heat distribution in the lake. Solar energy is the primary heat source (Hoare, 1968) as suggested by Wilson and Wellman (1962).

Water samples for deuterium analysis were collected from several depths within Lake Vanda (Ragotzkie and Friedman, 1965). The measured deuterium content was low, supporting the theory that the ionic composition of the deep saline layer is derived from evaporation of fresh water and not sea water. The deuterium values from Lake Vanda are lower than the value for the only observable input, namely the Onyx River, indicating another source of water to Lake Vanda. Ragotzkie and Friedman (1965) attributed the source of the lower deuterium values to stream water that may once have flowed along an old stream bed located between Lake Vanda and Upper Wright Glacier.

Craig (1966) questioned Ragotzkie and Friedman's (1965) interpretation of the deuterium data. He pointed out that changes in the D/H ratio occur as a result of evaporation and equilibration with atmospheric water vapor. Craig (1966) concluded that the deuterium data could not be used to determine the source of the saline water in Lake Vanda. Based on other data he held that the water is of marine origin.

A trace element survey of Lake Vanda waters was conducted to address the source of the salts. Boswell, Brooks and Wilson (1967) found that the relative concentrations of major elements in Lake Vanda differ significantly from sea water. They concluded that either sea water has been extensively chemically altered or sea water is not the source.

Jones and Faure (1967) were the first to use unstable isotopes as a tracer in Lake Vanda. They considered five sources of salt: 1)hot springs; 2)leaching of evaporite beds in sedimentary rocks of Wright Valley; 3)wind-transported marine salts; 4)trapped sea water; and 5)chemical weathering of bedrock and soil. On the basis of $^{87}Sr/^{86}Sr$ ratios, they concluded that Sr in Lake Vanda is derived from chemical weathering of bedrock in Wright Valley and transported to the lake by the Onyx River.

Eleven months of hydrological data were collected in 1968-69. Cutfield (1974) found that a water balance of inflow, surface ablation, precipitation and changes in lake level indicated that there must be another source of water to Lake Vanda. Cutfield (1974) suggested possible subterranean seepage as the unidentified source.

Nakai et al. (1975) investigated the possible sources of both the water and salts in Lake Vanda using stable isotopes: ^{13}C, ^{18}O and ^{34}S. They concluded that the present lake water is from a fresh water source, such as glacial melt water, but that the sulfate in the lake water has a marine origin. They suggested that Lake Vanda was originally a fjord that was isolated from the ocean. Evaporation reduced the sea water to salt deposits. Later flooding with glacial melt water occurred. This sequence is interpreted to have occurred twice before Wright Lower

Glacier was formed. The lake has been flooded with melt water since.

The salt distribution in Lake Vanda was modelled by Toth and Lerman (1975) assuming molecular diffusion as the only mode of mixing. They were able to simulate the salt distribution assuming an age of stratification of 1000 yrs and concluded that extensive intermittent mixing has not occurred in Lake Vanda. The computed curve deviated from the actual data most significantly in the bottom three meters of the lake.

Torii et al. (1979) examined the processes of saline water formation utilizing data from three DVDP cores from Wright Valley, water chemistry and a reconnaissance in the Labyrinth and Pearse Valley. They found that continental ice and snow were similar to sea water in composition. In a cold, arid climate, the meltwater composition would be expected to approach that of sea water. Any further alterations would be the same regardless of whether the original water source was meltwater or sea water. They concluded that the concentration of salt in the lakes of the Dry Valleys could be the same whether the original water body was glacial melt water or trapped sea water (Torii et al, 1979; Torii and Yamagata, 1981). They ascribed the origin of the salts in Lake Vanda to a combination of sea water, sea spray and rock weathering (Torri et al , 1979).

Wilson (1979) measured 6.4 ± 0.4 tritium units in a water sample collected from the bottom of Lake Vanda. If the bottom of Lake Vanda has been out of contact with the atmosphere for 800-1200 years, tritium levels should by unmeasurable. Wilson (1979;1981) suggested that brine flows along the top of the frozen water table, enters the lake, and interfingers to the appropriate density layer. The shallow briny ground water was interpreted by Wilson (1979; 1981) to be the product of a deliquescent separation process working on salts derived from evaporated snow water. Additional salt is leached from subsurface materials during ground water transport. Wilson suggested that the saline ground water inflow into Lake Vanda may be another mechanism for chemical stratification. Diffusion calculations to determine lake 'age' would then have to be used with caution. Green and Canfield (1984) suggest that either the measured tritium value is erroneously high or that there is another mode of entry for tritium to the lake.

Fluid-level measurements made during the drilling of DVDP 4A in Lake Vanda indicated that ground water flows upward from crystalline bedrock, through a sand and gravel unit, into the lake (Cartwright and Harris, 1981). Cartwright and Harris (1981) estimated that 20,000 m^3 of deep ground water enter Lake Vanda each year. The addition of deep ground water would not preclude upward diffusion of salts through the lake, although it may increase the rate of diffusion (Cartwright and Harris, 1981). Cartwright and

Harris (1981) also observed " a few small, shallow ground water flows on the northern shore". They considered shallow ground water to be a minor contributor to Lake Vanda.

Green and Canfield (1984) considered the estimate of deep ground water discharge of 20,000 m^3 into Lake Vanda excessive. They employed a mixing model with two end members - the waters of the Onyx River and deep ground water. They found that mixing 3570 years of present-day Onyx River inflows and deep $CaCl_2$ ground water adequately predicted observed levels of Ca, HCO_3, K, and SO_4. Mg was not well predicted. Green and Canfield (1984) concluded that the composition of the deep saline layer in Lake Vanda is the result of mixing Onyx River inflows with $CaCl_2$ ground water.

In summary, five sources of salt have been proposed for Lake Vanda: 1)hot springs; 2)trapped sea water; 3)atmospheric salt; 4)chemical weathering by-products transported by the Onyx River; and 5)ground water. After 20 years of research four sources are still considered feasible origins of the salts in Lake Vanda: trapped sea water; atmospheric salts; weathering by-products; and ground water.

Don Juan Pond

Don Juan Pond was discovered in October 1961 during a helicopter reconnaissance (Meyer et al., 1962). The pond was subsequently studied because it remains unfrozen while other lakes and ponds in the Dry Valleys are frozen. Meyer et al. (1962) observed that the valley surrounding Don Juan Pond was composed of metasediments intruded by dolerites and granites. Moraines block both ends of the valley, enclosing the basin. Ancient beach lines were identified 10 m above the present water level on the north side of the valley. Meyer et al. (1962) observed two sources of water to Don Juan Pond: drainage from the western moraine and snowfall. Neither source contributes significant volumes of water to the pond. Chemical analysis of pond water indicated a salinity 13.7 times that of sea water. Total dissolved solids were 474,000 ppm and the chloride concentration 212,000 ppm (Meyer et al., 1962). Two deuterium determinations were made on the pond water. The pond water was found to be lighter with respect to deuterium than water from McMurdo Sound (Meyer et al., 1962). Meyer et al. (1962) suggested that the high salt concentration may be due to weathering of the surrounding rocks coupled with increases in concentration through evaporation.

McGinnis et al. (1972) employed geophysical techniques to identify frozen and unfrozen ground in Antarctica. Among the sites investigated was Don Juan Pond. Two Schlumgerger soundings were conducted on the moraine west of the pond. These soundings were interpreted as indicating an ice-cored moraine lying on unfrozen glacial drift and basement. Seismic refraction profiles indicated that the basement may be faulted or have a highly irregular surface. Water was observed flowing from the ice-cored moraine on the west edge of the basin after 2 days of 10°C air temperatures. McGinnis et al. (1972) also noted the presence of $CaCl_2$ and NaCl deposits covering the beach area around the pond.

Mudrey et al. (1973) examined the chemistry of Don Juan Pond to explain the chemical evolution of the pond water. They determined that the water chemistry cannot be explained by mixing fresh, marine "or any other normal waters". Evaporation was identified as the mechanism responsible for the observed chemistry. Based on water chemistry, inferred mineralogy, and mass balance models for evaporation, Mudrey et al. (1973) concluded that the sources of water and salts to Don Juan Pond are meltwater streams similar in composition to the ones presently supplying the pond. They also concluded that sea water could not have been a significant source for Don Juan Pond.

In 1973, a hole was drilled at Don Juan Pond as part of the Dry Valley Drilling Project (DVDP) (Cartwright et al., 1974). An upward pressure gradient caused ground water to flow from the borehole into the pond. Drilling was stopped and the hole plugged due to increasing ground water pressure with depth. Cartwright et al. (1974) concluded that Don Juan Pond is the discharge zone for a ground water flow system. A second borehole was drilled in 1975 (McGinnis, 1979). Fractured Ferrar dolerite was identified as the aquifer.

A mass balance study of Don Juan Pond was conducted during the austral summer of 1975-76 (Harris et al., 1979). It was determined that the chemical variation of the pond water is controlled by hydrologic factors and temperature. Harris et al. (1979) identified three sources of water to the pond: snowfall; unconfined ground water resulting from summer melting in the permafrost layer and contributing to stream flow; and confined, saline ground water. Water is lost from the basin through evaporation and sublimation.

Wilson (1979; 1981) has suggested that shallow ground water resulting from a deliquescent separation process on salts from meltwater is the major contributor of salt to Don Juan Pond. Salt leached from subsurface materials during ground water transport was considered another significant source. No quantitative study was conducted to test this hypothesis.

Harris and Cartwright (1981) examined the physical hydrology of Don Juan Pond during the austral summers between 1973 and 1976. They observed that precipitation is an insignificant source of water to the pond. The majority of water is supplied by the underlying Ferrar dolerite (approximately 70% in 1975-76). The Ferrar dolerite is a confined highly fractured aquifer with an estimated porosity at the bedrock/sediment interface of over 20%. The waters of the aquifer are highly saline. Harris and Cartwright (1981) calculated that between 35 and 60 m^2/day of deep ground water discharge into the pond. Harris and Cartwright (1981) noted that the surface of the water table around Don Juan Pond sloped gently toward the pond. They estimated that approximately 0.5 m^2/day of shallow grond water discharges to the pond. The shallow ground water discharge is approximately 0.8-1.4% of the total ground water input to the pond. The only other source of water to the pond is intermittent, freshwater streams which derive their waters from melting within the permafrost zone. Calculations of salt input to the pond indicate that either: 1) the discharge of deep saline ground water is a comparatively recent phenomena; 2) the volume of ground water discharge has varied over time; or 3) salt has been carried out of the basin - perhaps by wind transport.

Tomiyama et al. (1983) investigated the sources of chemical constituents in the salts of Don Juan basin. They examined water soluble salts in seven sediment cores, ground water and pond water. They concluded that sea water, sea spray, weathered rock material and glacial meltwater are not sufficient to explain the chemistry of Don Juan basin. Ground water is identified as an important source for the salts.

In summary, three sources of water and salt have been identified for Don Juan Pond: stream water, shallow ground water and deep ground water. Ground water is suggested as the main source of the salts.

Lake Bonney

Lake Bonney was first studied during the Antarctic summer of 1960-61 by Armitage and House (1962). One core was made through the ice near the middle of the lake. Temperature, chlorinity and conductivity profiles were measured. Lake Bonney was found to be both chemically and thermally stratified. The monimolimnion had SO_4/Cl and Mg/Ca ratios that indicated a possible sea water origin (Armitage and House, 1962). The mostly likely source of heat was considered to be either thermal springs or a high geothermal gradient.

Angino and Armitage (1962) further investigated the geochemistry of Lake Bonney. Temperature profiles for Lakes Bonney and Vanda differed, indicating that the same processes were not at work in both lakes. An examination of the water chemistry lead Angino and Armitage (1962) to suggest that the monimolimnion of Lake Bonney had either a sea-water origin or had been influenced by salt-water contamination. A thermal water origin was not ruled out. They also hypotesized that Lake Bonney may be a remanent of an earlier Glacial Lake Llano, from which the salts have been concentrated by extensive evaporation or prolonged freezing.

A close examination of the chemistry of Lake Bonney revealed that the eastern and western lobes differed in water chemistry and sediments (Angino et al., 1964). The monimolimnion (below 12 m) of the western lobe was interpreted to be derived from entrapped sea water that was subsequently altered and concentrated. The chemical and temperature data collected from the eastern lobe was suggestive of an inflow of thermal water (Angino et al., 1964). The ionic content of the upper waters in both lobes was interpreted as reflecting the flushing of soil salts by inflowing waters.

Hoare et al. (1964) drilled a total of 15 holes through the ice of both lobes of Lake Bonney. Water temperatures were measured at 5 ft intervals. They ruled out hot springs or a high geothermal gradient as major sources of heat based on the positions of maximum temperature and the small deviations from the average temperature at any depth. A simulation of the temperature profile assuming only solar radiation adequately reproduced the measured temperature depth profile. Solar radiation was identified as the main heat source for the observed temperature profiles.

A trace element survey of Lake Bonney waters was conducted to address the source of the salts. Boswell, Brooks and Wilson (1967) found that trace-element ratios for Lake Bonney closely resembled those of sea water. They concluded that there is evidence for a sea water origin.

The salt distribution in Lake Bonney was modelled assuming molecular diffusion as the only mode of mixing (Toth and Lerman, 1975). Toth and Lerman (1975) were able to simulate the salt distribution assuming an age of stratification of 60 years. The value of the diffusion coefficient required to simulate the chloride profile was somewhat higher than the diffusion coefficient of dissolved chloride in water at or below room temperature. Toth and Lerman (1975) suggested that other transport mechanisms may contribute to the salt-migration process, however, they considered these unidentified sources to be insignificant contributors of chloride.

Surface flow to Lake Bonney was observed from Sollas, LaCroix, Matterhorn, Hughes, Calkin, Rhone and Taylor Glaciers during the austral summer of 1973-74 (Weand et al., 1975). Meltwater from Taylor Glacier provided approximately 74% of the total surface inflow to the lake. Total inflow from the glacial meltwater streams was not sufficient to explain the observed increase in lake level. Weand et al. (1975) attributed 59% of the increase in lake volume to ground water.

Measurements of major-ion concentrations, ^{18}O and ^{14}C content of Lake Bonney waters were made to interpret the geochemical history of the lake (Hendy et al., 1977). Hendy et al. (1977) suggested that Bonney basin was flooded with sea water 100,000-300,0000 yr ago. Prior to 15,000 yr ago the west lobe was evaporated to near dryness. About 15,000 yr ago the west lobe began filling with glacial meltwater supplied principally from Taylor Glacier. With time, water from the west lobe overflowed into the east lobe, forming the bottom waters of the east lobe between 1800-4600 yr ago. Inflow was reduced and water evaporated in the east lobe, concentrating the salts. About 400-750 yr ago, the water level in the west lobe rose again, spilling into the east lobe. More recently, saline water began flowing into the east lobe as Taylor Glacier advanced into the west lobe, reducing its volume. Based on this historical reconstruction, Hendy et al. (1977) concluded that the salts in Lake Bonney are derived from sea water which was subsequently modified by the leaching of soils, precipitation of minerals and the addition of salts from atmospheric aerosols via runoff into the lake. Variations of this reconstruction of Lake Bonney's evolution is supported by Matsubaya et al. (1979) and Torii and Yamagata (1981).

In summary, the evolution of Lake Bonney is complex and uncertain. There are four possible sources of salts in Lake Bonney: 1) trapped sea water; 2) weathering of soil salts;

3) atmospheric aerosols; and 4) ground water.

Lake Fryxell

Water samples, including melted ice core, were collected from Lake Fryxell by Angino et al. (1962). Three chemically distinct layers were identified. The salt concentration of the layers ranged from 1/35 to 1/5 that of sea water. Four possible sources of the salts were presented: 1) ocean spray; 2) weathering by-products; 3) relict sea water; and 4) thermal springs. Angino et al. (1962) considered sea water to be the most unlikely source, favoring a thermal-spring source. They concluded that no one origin for the lake was satisfactory.

Hoare et al. (1965) investigated the source of heat to Lake Fryxell. They concluded that solar radiation was the sole source of heat. No evidence for thermal springs was observed.

A trace-element survey of Lake Fryxell waters suggested the possibility that the lake may have contained sea water in the past (Boswell et al., 1967). However, the data were not considered conclusive.

McGinnis et al. (1972) conducted a geophysical survey along the shores of Lake Fryxell and on the lake ice. They determined that permafrost was present within 10 m of the surface on the moraine near the lake. Beneath the confining permafrost lies unfrozen sands and gravels saturated with low salinity water. McGinnis et al. (1972) also determined that the ground beneath the lake was not frozen.

Lawrence and Hendy (1985) examined water and sediment cores from Lake Fryxell. They suggested that Lake Fryxell was much larger about 20,000 yr ago. Retreat of glacial ice from the basin resulted in a diminished lake volume due to evaporation and reduced meltwater inflow about 10,000 yr ago. Readvancing glaciers resulted in an increase in Lake Fryxell water volume. Evaporitic salts diffused upward to form the present stratification. Based on this reconstruction, Lawrence and Hendy (1985) suggested that the salt concentrations are the product of modified glacial meltwaters.

At present, it appears that the sources of salts to Lake Fryxell are wind-blown aerosols and weathering by-products transported by glacial meltwater (Lawrence and Hendy, 1985).

Lake Hoare

The third year of the Project ECOLS (Ecosystem Comparisons of Oasis Lakes and Soils) conducted by Virginia Polytechnic Institute and State University concentrated on Lake Hoare. The lake was found to contain freshwater. It was neither chemically, thermally or biologically stratified

(Parker et al., 1980). The ice cover averaged 5.5 m thick. No attempt was made to determine the sources of water to Lake Hoare. However, an important biologically mediated output mechanism for select chemical constituents was discovered. It was observed that benthic algal mats moved upward through the ice cover eventually to be blown away. Salts and nutrients are lost from the lake by this mechanism (Parker et al., 1980).

Stuiver et al. (1981) utilized oxygen isotope ratios of permafrost waters from DVDP core 12 (Lake Hoare) to reconstruct the history of Lake Hoare. They suggested that a deep, solar-heated lake (Lake Washburn) existed in Taylor Valley between 20,000 yr ago and 12,000 yr ago. Permafrost that had formed prior to the ancient lake was melted and lake water drained downward through the unfrozen sediments. After the lake was drained, freezing of the sediments began from the top down. Lake Hoare now lies on the permafrost surface.

In summary, only one source has been postulated for the waters of Lake Hoare, glacial meltwater.

Lake Vida

Lake Vida was first studied by Armitage and House (1962). They unsuccessfully attempted to core through the lake ice. Numerous pressure domes characteristic of ice frozen to the ground were observed. Armitage and House (1962) concluded that there may be little or no liquid water in Lake Vida.

A geophysical survey of Lake Vida indicated that a confining permafrost layer surrounds the lake (McGinnis et al., 1972). Along the western end of Lake Vida the lake is frozen to the bottom where it lies on frozen glacial debris. The lake deepens from 20 m near the west to 40 m near the lake center. Unfrozen, saline water or lake sediment lying underneath the lake occurs beneath the lake's center.

According to Cartwright and Harris (1981), Lake Vida receives glacial meltwater from Victoria Lower and Victoria Upper Glaciers. Groundwater flows in frozen ground near Lake Vida have been documented, but no evidence indicates that the lake receives any groundwater discharge.

At present, glacial meltwaters appear to be the only source of water to Lake Vida.

Present Study

The purpose of the present study is to trace the origins of the salts in the Dry Valley lakes. The radioisotope chlorine-36 has been chosen as the tracer. A unique ^{36}Cl signature will be identified for each potential source of salt. Simple mixing models will be employed to identify the sources of salt to each lake and to quantify, where possible, the contributions of each source to the salt concentrations. The results of this study will then be used to test the various hypotheses discussed above.

CHLORINE-36 AS A TRACER

Naturally-occurring isotopes have been used in hydrologic investigations since the early 1950's. Most commonly employed are the stable isotopes deuterium and oxygen-18 and the radioactive isotopes carbon-14 and tritium. Stable isotopes have principally been employed as tracers to identify source(s) of water. Radioisotopes have generally been used to date ground water. In recent years, radioisotopes have been used as tracers as well.

Interpretation of isotopic data can be complicated by the processes of fractionation and decay. Fractionation is the process by which the original isotope content of a fluid/material is altered as a result of a phase change, chemical reactions or biological processes. Decay of radioisotopes occurs over time as a function of the isotope's half-life. Another more recent complication is the anthropogenic enrichment of isotope concentrations due to atmospheric testing of thermonuclear bombs. The 'bomb pulse' produced in the late 1950's and early 1960's has served as a powerful tracer for some studies.

An ideal hydrologic tracer must meet three conditions. First, the isotope should be of an element that is both abundant in and representative of the system being studied. Second, the tracer should provide a unique signature for each source. Third, the tracer should be conservative -- little affected by fractionation.

Chlorine-36 is a powerful hydrologic tracing tool which meets the above criteria. Chloride is a common major element that is highly soluble in water. For studies of recent events, the $^{36}Cl/Cl$ ratio of a substance is essentially constant due to its long half-life (301,000 years). Chloride does not participate in redox reactions and is among the least sorbed ions on solid surfaces (Bentley et al., in press).

Natural production of ^{36}Cl may be classified into three categories: meteoric, epigene and hypogene. In addition, ^{36}Cl was anthropogenically produced in the 1950's during atmospheric weapons testing. Meteoric ^{36}Cl is produced in the atmosphere by cosmic ray spallation of ^{40}Ar and neutron activation of ^{36}Ar. Production occurs in both the troposphere (40%) and the stratosphere (60%). Stable chloride derived from sea spray mixes with the atmospherically produced ^{36}Cl before 'falling out'. Fallout varies with latitude, the heaviest fallout occurring in the mid-latitudes of both hemispheres. Fallout also decreases exponentially from coastal areas toward continental interiors. The average ratio of ^{36}Cl to chloride ($^{36}Cl/Cl$) in atmospheric fallout is dependent on latitude and distance from the coast. The meteoric ratio will remain constant despite evaporation (Bentley et al., in press).

Epigene ^{36}Cl is produced at the earth's surface primarily by cosmic-ray spallation of K and Ca and neutron activation of ^{35}Cl. When chloride is exposed at the earth's surface, ^{36}Cl begins to build up increasing the ^{36}Cl/Cl ratio. When ^{36}Cl decay equals the production rate, a secular equilibrium is reached. Secular equilibrium is dependent on altitude and chemical composition of the surrounding materials (Bentley et al., in press).

Hypogene ^{36}Cl is produced at depth (below 30 m) primarily by neutron activation of ^{35}Cl. The neutrons are provided by decay of U and Th series elements as most cosmic rays are attenuated in the upper few meters of the earth's crust. The secular equilibrium ratio is dependent of chemical composition of the rock and U, Th concentrations (Bentley et al., in press).

'Bomb ^{36}Cl' was produced anthropogenically by neutron activation of seawater chloride during atmospheric nuclear weapons testing. Fallout from 1953 to 1965 was augmented in ^{36}Cl, increasing ^{36}Cl/Cl ratios about 2 to 3 orders of magnitude above natural meteoric fallout levels (Phillips et al., 1984).

Analysis of Chlorine-36

Natural levels of ^{36}Cl/Cl range between 1.36×10^{-16} to 1.36×10^{-10}. Chlorine-36 was initially measured in screen-wall counters. This technique had a sensitiviy of 1 x 10^{-12}. The application of liquid scintillation in the 1960's increased the sensitivity to about 5 x 10^{-13}. Improvements to the liquid scintillation technique increased sensitivity slightly. However, many natural levels still could not be detected, limiting the applications of ^{36}Cl. Tandem accelerator mass spectrometry (TAMS) expanded the scope of ^{36}Cl application by providing a sensitivity of 5 x 10^{-16} atoms $^{36}Cl/Cl$ (Elmore et al., 1979). TAMS is capable of measuring all natural levels of $^{36}Cl/Cl$ with the exception of marine salts. This mass spectrometric approach radically departed from the direct counting procedures used previously. High sensitivity and small sample size are two notable advantages of this technique.

EXPERIMENTAL PROCEDURE

Sample Collection

A total of 24 samples for ^{36}Cl analysis were collected in the Dry Valleys during the austral summer of 1984-85 (Figure 2; Table 1). Five water samples were collected from Lake Vanda at depths of 5, 15, 30, 45, and 62m. Two water samples were collected from the Onyx River: one at its headwaters near Lake Brownworth and one at the confluence with Lake Vanda. Two water samples were collected from Don Juan basin: one from the pond and one from a surface flow to the pond. Three water samples were collected from Bonney basin: one from the lake surface, one from the saline discharge of Taylor Glacier and one from the meltwater of Taylor and Rhone Glaciers. Three water samples were collected from Fryxell basin: one from the lake surface, one from meltwater of Commonwealth Glacier and one from a shallow puddle near the lake shore. One water sample was collected from both Lake Hoare and Lake Vida. One soil sample was collected from a moraine of Lower Wright Glacier. Three soil samples were collected from the slopes of Don Juan basin at heights of 5, 20, and 100m above the pond. Two salt samples were collected from Don Juan basin: one from the shore of the pond and one from the Don Juan playa. One rock sample was collected from a moraine near Commonwealth Glacier.

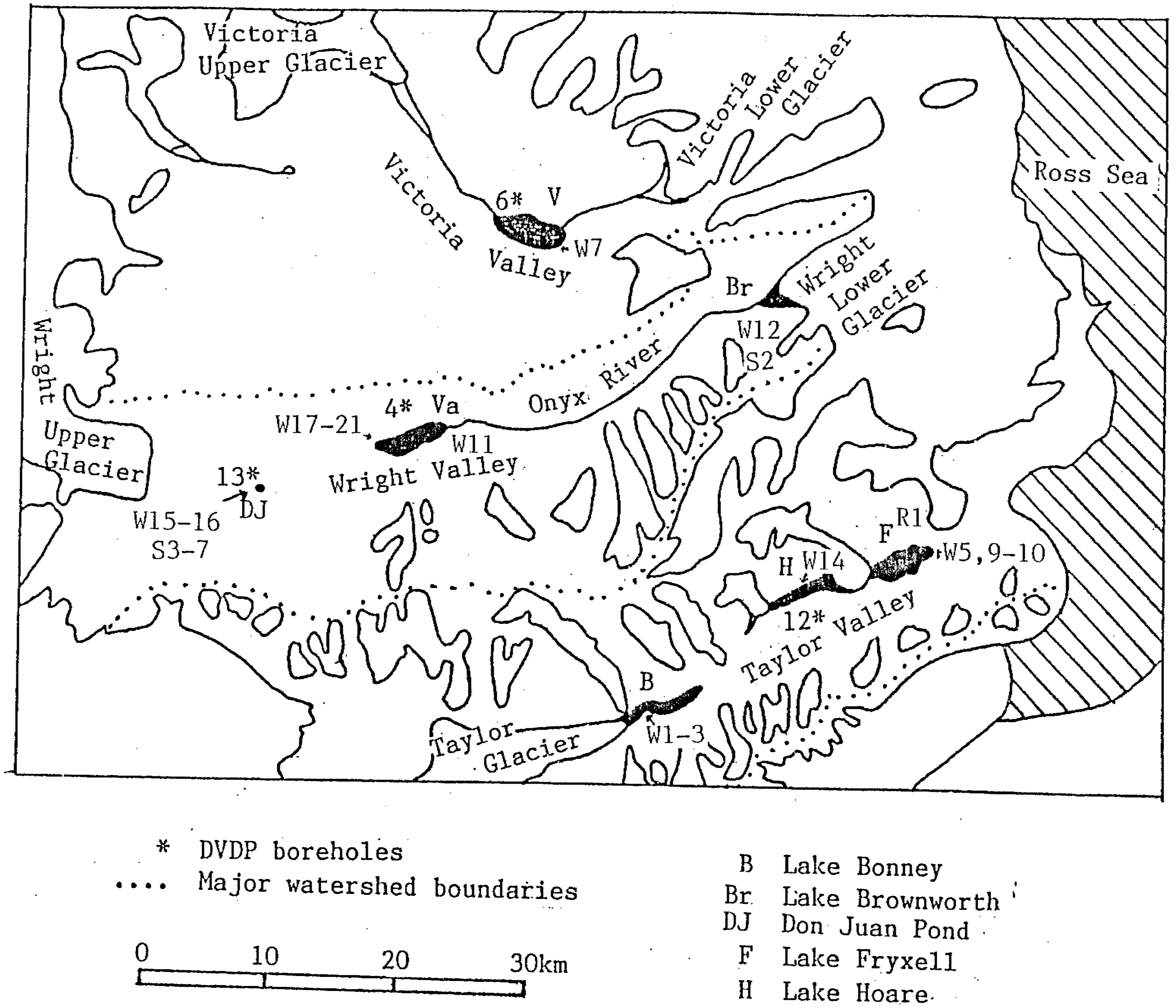

Figure 2. Sample locations (W=water, S=soil or salt, R=rock). (adapted from Cartwright and Harris, 1981)

Table 1. Sample locations in the Dry Valleys

Sample No.	Location description
DVW-1	Combined discharges of Taylor and Rhone Glaciers into Lake Bonney about 100m above inflow point
2	Red saline discharge from Taylor Glacier
3	Lake Bonney, sampled by bucket about 10m offshore and 300m from Taylor Glacier on North shore
4	Lake Hoare, sampled about 100m South of Hoare Hut by bucket from shore
5	Lake Fryxell, sampled from small peninsula on North shore about 1km from Canada Glacier
7	Lake Vida, collected from South shore about 3km east of Victoria River inflow
9	Snowmelt from a snowbank seep about 2km North of the East end of Lake Fryxell
10	Runoff from Commonwealth Glacier, collected on ion exchange resin from meltwater stream west of glacier
11	Onyx River at Vanda inflow, collected on ion exchange resin
12	Onyx River at Lake Brownworth outflow, collected on ion exchange resin
14	Lake Hoare, sample collected on ion exchange resin
15	Small stream flowing from South side of rock

	glacier West of Don Juan Pond toward the pond
16	Brine from center of Don Juan Pond about 10m Southeast of stilling well
17-21	Lake Vanda depth profile samples
17	5m
18	15m
19	30m
20	45m
21	62m
DVS-2	Soil salt from moraine near lower Wright Glacier
3	Salt sample from center of Don JUan Pond playa about 3m from DVW-16, large white crystals collected from small dried pool around a rock
4	Salt from South edge of Don Juan Pond about 25m from edge of playa directly south of DVS-3
5	Soil salt collected on slope about 20m above Don Juan Pond directly South of DVS-4
6	Soil salt collected from surface of a large boulder within seepage area about 100m above Don Juan Pond
7	Soil salt from within granitic pebbles about 2cm below soil surface on North shore of Don Juan Pond about 5m above pond
DVR-1	Granitic rock from moraine in front of Commonwealth Glacier

In addition, five soil samples were obtained from Scott Wilson of the University of Wisconsin-Madison to date the exposure time using ^{36}Cl build-up. As discussed above ^{36}Cl begins to build-up when chloride is exposed at the earth's surface. Ages for these samples have been established by K/Ar, ^{14}C and U/Th techniques. Four samples were from moraines in Wright Valley; one was from a moraine in Taylor Valley.

Collection of Chloride as AgCl

Analysis of ^{36}Cl by TAMS requires that the chloride be in the form AgCl. Water samples with concentrations in excess of 20 mg/L were acidified and then precipitated by the addition of excess $AgNO_3$ (Appendix I). Water with lower chloride concentrations were passed through an anion exchange resin to concentrate the chloride prior to acidification and precipitation as AgCl (Appendix II). One water sample with a low chloride content was precipitated with dead carrier (salt with no measurable ^{36}Cl) due to the small volume of the sample. Salt samples were dissolved in distilled, deionized water prior to acidification and precipitation as AgCl. Soil samples were leached with distilled, deionized water to remove the salts. The leachate was then acidified and chloride precipitated as AgCl. The rock sample was ground and powdered prior to fusion in sodium hydroxide. The fusion cake was then dissolved in distilled, deionized water and nitric acid. Excess $AgNo_3$ was added to the solution to precipitate AgCl.

Laboratory Preparation of AgCl Samples

Prior to analysis by TAMS, the AgCl samples were purified of ^{36}S. Sulfur-36 is an interferring isobar in the ^{36}Cl mass spectrometry. Purification involves repeated dissolution and reprecipitation of the AgCl (Appendix I).

Analysis of Chloride Content

Aliquots of the water samples were analysed for chloride concentrations. The technique employed was mercuric nitrate titration (U.S. Environmental Protection Agency, 1979).

Tritium Analysis

Seven water samples were analyzed for tritium content by the electrolytic enrichment method at the University of Waterloo. The purpose of this analysis was to identify whether the thermonuclear testing during the 1950's enhanced isotope ratios. Jouzel et al. (1982) estimated a mean 'pre-bomb' value of 11.3 TU for a coastal site in Antarctica and 32 TU at the South Pole. Bomb-enhanced values ranged from 100 TU near the coast to over 600 TU at the South Pole.

RESULTS AND DISCUSSION

Results

Chloride concentrations, $^{36}Cl/Cl$ ratios and tritium levels are presented in Tables 2-4. The raw $^{36}Cl/Cl$ data were reduced by the method of Elmore et al. (1984) (Appendix III). One sample was corrected for the addition of dead carrier.

Table 2. Chloride concentrations and $^{36}Cl/Cl$ ratios of samples collected for this study.

Sample No.	Location	Sample type	Cl^- mg/L	$^{36}Cl/10^{15}Cl$	Analy. uncert ($^{36}Cl/10^{15}Cl$)
	Lk Vanda				
W-17	5m	water	186.5	167	19
W-18	15m	"	310.8	110	14
W-19	30m	"	466.3	84	12
W-20	45m	"	777.2	62	11
W-21	62m	"	58884	38.4	8.6
	Onyx R.				
W-12	L Brownworth	"	--	529	28
W-11	Lk Vanda	"	--	641	34
	Don Juan b.				
W-16	pond	"	212940	23.0	5.2
W-15	inflow	"	186.5	1110	110
S-4	pond	salt		25.1	7.5
S-3	playa	"		33.1	7.2
S-7	5m, N	soil		60	14
S-5	20m, S	"		34	17
S-6	100m, S	"		19	16
W-3	Lk Bonney	water	21.8	159	12
W-1	inflow	"	8.2	427	21
W-2	sal. dis.	"	32777	9.5	4.6
W-5	Lk Fryxell	"	29.6	178	13

W-10	inflow	"	11.1	989	62
W-9	puddle	"	18.8	828	54
W-14	Lk Hoare	"	10-15*	1660	180
W-7	Lk Vida	"	2.5	1350	77
S-2	Moraine,TV	soil		1150	101
R-1	Moraine,TV	rock		251	22

* Hach kit determination

Table 3. Chlorine-36 ratios for soil samples

Sample No.	Age yrs	Location	^{36}Cl/10^{15}Cl	Anal. uncert (^{36}Cl/10^{15}Cl)
38	>2.89 MA	Marr Gl., TV	409	19
122	17-21000	Trilogy Moraine,TV	464	47
128	300000	"C" Moraine, WV	611	40
134	145-185000	Loop Moraine, WV	653	58
165	210000	Alpine IIb Mor,WV	572	24

Table 4. Tritium values

Sample No.	Location	TU
	Lake Vanda	
W-17	5m	<0.8
W-18	15m	<0.8
W-19	30m	<0.8
W-20	45m	<0.8
W-21	62m	<0.8
W-15	Don Juan Pond inflow	57
W-9	Lake Fryxell meltwater	1.1

Discussion of Data

The $^{36}Cl/Cl$ ratios of the lake, meltwater and soil samples are plotted in Figure 3. The $^{36}Cl/Cl$ ratios range from 23×10^{-15} to 1660×10^{-15}. Various samples may be grouped together according to ratio magnitude. Don Juan Pond has the lowest ratio (23×10^{-15}), which is an order of magnitude lower than any other measured ratio, with the exception of the Taylor saline discharge. For this reason Don Juan Pond is placed in its own group. Cartwright and Harris (1981) classified the pond as a ground-water lake. The surface water of Lakes Vanda, Bonney and Fryxell have ratios between 150 and 180×10^{-15}. These lakes have been grouped together. Cartwright and Harris (1981) classified Lakes Vanda and Bonney as mixed lakes. It is suggested here that Lake Fryxell may also be a mixed lake. Lakes Hoare and Vida have very high ratios which are interpreted as being bomb-^{36}Cl enhanced. Cartwright and Harris (1981) classified these lakes as glacial lakes.

The moraine salts have ratios that range between 409 and 653×10^{-15}. Two of the meltwater samples have ratios that also fall in this range (W-1, W-12). One anomalously high soil value (S-2) and two meltwater values (W-10, W-15) are attributed to bomb enrichment. Tritium levels for one of the water samples support the bomb enrichment. A value of 57 TU was determined for the inflow to Don Juan Pond. This value is high even if the water originated from the

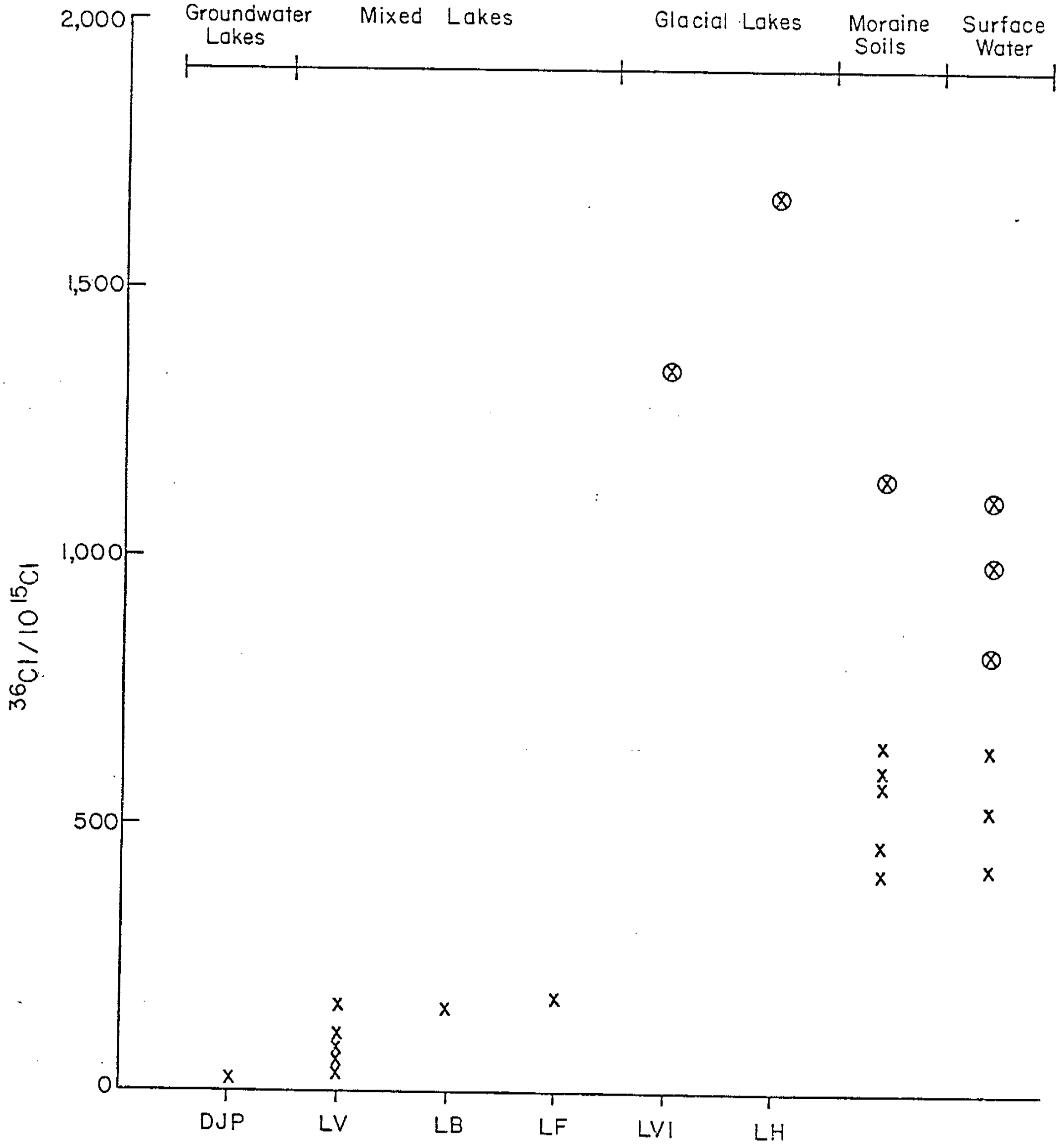

Figure 3. ^{36}Cl/Cl ratios for lake, surface water and soil samples (DJP=Don Juan Pond, LV=Lake Vanda, LB=Lake Bonney, LF=Lake Fryxell, LVI=Lake Vida, LH=Lake Hoare).

polar plateau.

Chlorine-36 signatures. Four sources of salt to the lakes of the Dry Valleys are presently considered:trapped sea water, atmospheric salts, weathering by-products and ground water. A unique $^{36}Cl/Cl$ ratio for each source is necessary in order to trace the origin of the salts.

Sea water. The $^{36}Cl/Cl$ ratio of sea water is less than 10^{-15} (Phillips et al., 1984). For practical purposes sea water is considered "dead" (0×10^{-15}).

Atmospheric salts. Samples of fresh snow were not available at the time of this study for $^{36}Cl/Cl$ determination. One sample of snowmelt (W-9) was collected in an attempt to sample the last year's snow fall. The tritium value for this sample was low however, indicating that the snow was old. Glacial meltwater is simply meteoric water which has been transported as ice. Ratios for meltwater should therefore reflect the meteoric ratio of the accumulation zone. The tritium levels detected in some of the meltwaters indicate that bomb ^{36}Cl has enhanced the atmospheric ratios in some areas. Thus an attempt was made to define the background meteoric ratio by examining buried soil salts. No correlation between soil age and $^{36}Cl/Cl$ ratio was observed. A direct correlation between age and ^{36}Cl build-up was expected. The lack of such correlation indicates that the soil salts are in equilibrium with atmospheric chloride. Equilibrium would occur if the salts were repeatedly melted and refrozen. The values of the soil salts clustered between 400 and 650 x 10^{-15}. The background meteoric ratio was thus assumed to be 400-650 x 10^{-15}. Meltwater with values greater than 827 x 10^{-15} (W-9) is assumed to be influenced by bomb-^{36}Cl.

Weathering by-products. Variation would be expected in the ratios of weathering by-products due to length of exposure and chemical composition. However only one rock sample was analyzed for ^{36}Cl. The ratio of 251 x 10^{-15} is considered representative of the order of magnitude of weathering by-products. Additional samples would need to be analyzed to determine a range of values.

Ground water. Samples of ground water were not available at the time of this study. However, the ^{36}Cl/Cl ratio of the deep ground water can be calculated by the method of Bentley et al. (in press), assuming that the ground water has resided in the aquifer long enough that secular equilibrium is reached. Inputs to the calculation include chemical composition of the aquifer material, U/Th concentrations, porosity and the chloride content of pore water. Two bedrock units are of concern in the Dry Valleys: the Ferrar dolerite and the granitic basement. The secular equilibrium for the Ferrar dolerite was calculated using the chemical analyses of Gunn (1966) and Compston et al. (1968). A porosity of 1% and a chloride concentration of 138,000 ppm (Harris and Cartwright, 1981) were used. The secular equilibrium was calculated to be 13.55 x 10^{-15} (Appendix IV). Chemical analyses of the granitic basement in Taylor and Wright Valleys were not available at the time of this writing. However, analyses of the Vida Granite in Victoria Valley were available (Vocke and Hanson, 1981; McGinnis et al., 1981). A porosity of 1% and a chloride concentration of 129,700 ppm (Cartwright and Harris, 1981) were used. The secular equilibrium ratio for the granitic basement was 21 x 10^{-15} (Appendix V). Bentley et al. (in press) calculated a ratio of 30 x 10^{-15} for a typical granite.

Shallow ground water would be expected to have ratios similar to meteoric chloride.

Lake Vanda. A plot of $^{36}Cl/Cl$ vs 1/Cl for the five Lake Vanda samples is presented in Figure 4. The data points plotted along a straight line with a correlation coefficient of 0.998. The linear relationship indicates that the observed ^{36}Cl and Cl^- distributions are the result of a two-component mixing process. The correlation with depth also indicates that one source is located at the bottom of Lake Vanda and the other at the surface. Figure 4 shows that the bottom end member is extremely saline and has a $^{36}Cl/Cl$ ratio of approximately 34 x 10^{-15}. This ^{36}Cl signature is too high to be sea water and is similar to the value calculated for ground water in the granitic basement. The upper end member is characterized by low chloride and

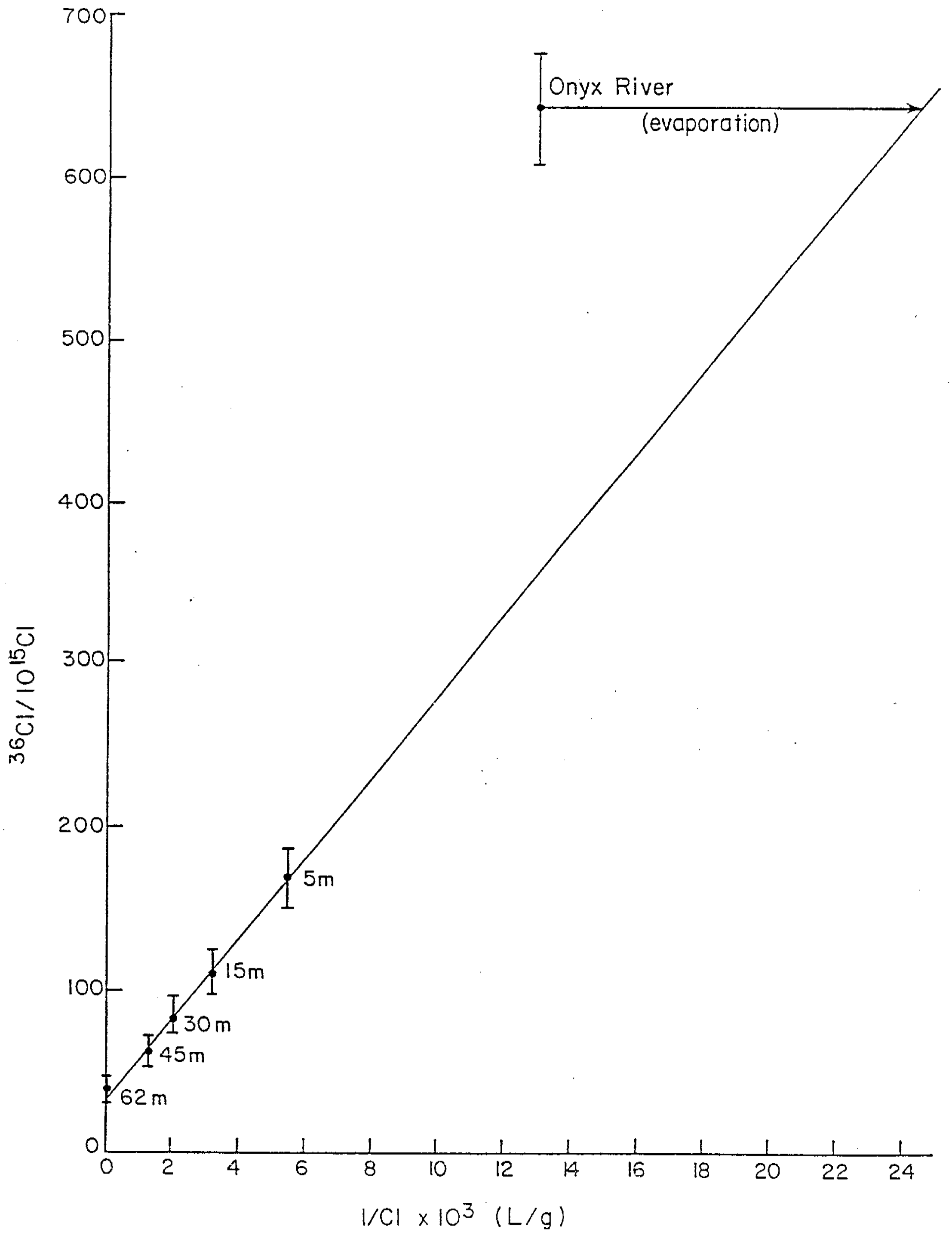

Figure 4. Plot of Lake Vanda depth profile data. The mixing line has a correlation coefficient of 0.998.

high ^{36}Cl. This is consistent with the origin being the Onyx River. Evaporation of Onyx River water on the order of 3-5x yields a chloride concentration and ratio that plots on the mixing line (40 mg/L and 641 x 10^{-15} ^{36}Cl/Cl, respectively). This rate of evaporation is common in the arid Dry Valleys. The contribution of water volume, ^{36}Cl concentration and chloride content to Lake Vanda from each source was calculated for the five sample depths using ground water and concentrated Onyx River water as the two end members. The equations used are presented in Appendix VI. The results of the calculations are presented in Table 5.

Table 5. Relative contribution of water volume, ^{36}Cl content and chloride content to Lake Vanda.

	Vol. %		Cl-36		Chloride	
Depth	GW	Onyx R.	GW	Onyx R.	GW	Onyx R.
5m	0.1	99.9	14.8	85.2	76.4	23.6
15m	0.2	99.8	25.8	74.2	86.7	13.3
30m	0.3	99.7	34.3	65.7	90.7	9.3
45m	0.5	99.5	46.6	53.4	94.2	5.8
62m	50.6	49.4	99.4	0.6	100	0.0

It is clear from the table that the Onyx River has contributed over 99% of the water volume to Lake Vanda's mixolimnion and approximately 50% to the monimolimnion. However, ground water has been the main source of chloride to both layers.

The chloride transported by the Onyx River may have two sources: atmospheric aerosols and weathering by-products. Two water samples were collected from the Onyx River. One sample was taken at the outlet of Lake Brownworth, the meltwater lake formed below Lower Wright Glacier. The $^{36}Cl/Cl$ ratio of 529×10^{-15} is well within the range expected for meteoric chloride. The second water sample was taken at the inflow to Lake Vanda. The measured ratio is 641×10^{-15}, still within the meteoric chloride range and slightly higher than the upstream value. There is no evidence that the $^{36}Cl/Cl$ ratio has significantly changed with the input of runoff between the two Onyx River sampling locations. This suggests that the primary source of chloride to the Onyx River is atmospheric aerosols.

The data indicate that there are two sources of chloride to Lake Vanda. Deep ground water is the primary source and the Onyx River is the secondary source.

Dating Upper Lake Vanda. An age for the mixolimnion of Lake Vanda was calculated assuming that time is equal to the total volume of inflow over time divided by the inflow rate from the Onyx River:

$$T = \frac{V}{Q}$$

The total inflow water volume is equal to the present volume in the lake divided by a residual fraction, f. The residual fraction is calculated as the residual chloride concentration divided by the original concentration raised to the power, 1/(e-1):

$$f = \frac{mr}{mo}^{(1/(e-1))}$$

'e' is the efficiency of chloride removal from the lake's surface. It is equal to the chloride concentration lost from the lake surface divided by the chloride concentration at the lake surface:

$$e = \frac{m_{loss}}{m_{lake}}$$

Combining and rearranging yields the equation:

$$T = \frac{V}{Q} = \frac{v}{Q \frac{mr}{mo}^{(1/(e-1))}}$$

where: T = time in years
V = total inflow over time, m^3
Q = discharge rate of Onyx River, 10^6 m^3/yr (Green and Canfield, 1984)
v = volume of water in Lake Vanda, 191 x 10^6 m^3/yr (from Nelson and Wilson, 1972)
mr= chloride concentration of surface lake water, 40 mg/l taken from mixing line
mo= chloride concentration of Onyx River, 8 mg/L (Green and Canfield, 1984)
e = efficiency of chloride removal

The age was calculated using two different values for efficiency, 0 and 0.1, assuming that chloride removal from the lake surface is relatively inefficient. The calculated age is between 955 years (e=0) and 1142 years (e=0.1). This age range is consistent with the 800-1200 years of Wilson (1964) and Nakaya et al. (1979). This implies that ground water inflow does not significantly impact the diffusion processes in the lake, in support of Toth and Lerman's (1975) conclusions.

Don Juan Pond. Two water and five soil salt samples were collected from Don Juan basin. One water sample was taken from the pond and the other from surface inflow to the pond. The $^{36}Cl/Cl$ ratios are 23×10^{-15} and 1110×10^{-15}, respectively. The high ratio of 1110×10^{-15} is interpreted as being augmented by bomb-^{36}Cl based on the tritium level of 57. As discussed above, the average pre-bomb tritium level for Antarctica ranges between 11.3 and 32. The value of 57 is considerable higher than even the background level for the South Pole. A background meteoric ratio of 525×10^{-15} is assumed. The low ratio for the pond water indicates a source of chloride with a low ratio $<23 \times 10^{-15}$, in addition to the meltwater source. The only ^{36}Cl signatures with ratios this low, besides sea water, are deep ground waters from either the Ferrar dolerite (13.55×10^{-15}) or the granitic basement (21×10^{-15}). A mixing model with two end members was employed to determine the percent water volume, ^{36}Cl content and chloride content contributed to Don Juan Pond by ground water and meltwater. The percentages were calculated using Ferrar dolerite-meltwater and granitic basement-meltwater systems. To take into account the effects of evaporation, only one-third of the present chloride concentration in the pond was used in the calculation (Cartwright and Harris, 1981). The results of the calculations are presented in Table 6.

Table 6. Relative contributions of water volume, ^{36}Cl content and chloride content to Don Juan Pond.

	Vol. %		Cl-36		Chloride	
System	GW	inflow	GW	inflow	GW	inflow
dol.-mltwtr	86.8	13.2	99.2	0.8	99.98	0.02
gran.-mltwtr	54.9	45.1	97.3	2.7	99.9	0.01

The mixing model indicates that the source of ground water does not significantly affect the origin of the salts. Whether the ground water comes from the Ferrar dolerite or the granitic basement, at least 99.9% of the chloride comes from the ground water input. The ground water source does affect, however, the volume of water contributed to the pond.

The $^{36}Cl/Cl$ ratios for soil salts on the hillslopes near Don Juan Pond are significantly lower than the ratios for all the other measured soil salts in this study. This suggests that the soil salts near Don Juan Pond have resulted from a different source than the other salts with higher ratios. The Don Juan Pond salts have ratios similar to the pond water. Deep ground water is the most likely source of these low ratio salts. Since these salts were collected from above the highest paleoshore, they indicate that playa salts have been transported great distances and possibly out of the basin by wind. One soil sample was collected at 5m, half-way between the present pond level and the highest paleoshore. This sample had a ratio of 60 x 10^{-15}, similar to the pond and playa salts. The similar value indicates that ground water contributed significant amounts of chloride to the pond at the time this salt was deposited. The value suggests that either there has been some fluctuation in the ground water discharge over time as the salt ratio is 3x that of the present pond water or it contains a larger proportion of meteoric/bomb ^{36}Cl.

Lake Bonney. Three water samples were collected from Bonney basin. One sample was collected from the saline discharge of Taylor Glacier; one from a meltwater stream from Taylor and Rhone Glaciers; and one from the lake itself. The measured ratios were 9.5, 427 and 159 x 10^{-15}, respectively. The ^{36}Cl/Cl ratio for Lake Bonney is lower than that for the meltwater inflow indicating another source(s) of chloride input to the lake. Without collecting depth samples for a profile, the other source(s) of chloride to Lake Bonney cannot be determined. Profiling both lobes would be beneficial to the interpretation of the origin of salts in Lake Bonney.

Lake Fryxell. Three water samples were collected from the Lake Fryxell area. One sample was taken from the lake itself. Two water samples were taken from inflowing surface water. The surface inflows may have been influenced by bomb Cl-36 as they have slightly higher ^{36}Cl/Cl ratios than the soil salts and some of the other inflows. The ^{36}Cl/CL ratio for Lake Fryxell is lower than that for the meltwater inflows and the average background ratio level of 400-650 x 10^{-15}. This indicates that another source(s) of chloride contributes to Lake Fryxell. Without collecting depth samples for a profile, the other source(s) of chloride to Lake Fryxell cannot be determined. Profiling the lake would be beneficial to the interpretation of the origin of salts in Lake Fryxell.

Lakes Hoare and Vida. One water sample was analyzed from each lake. Both lakes had high ratios indicating enhanced from bomb ^{36}Cl.

Comparison of Data with Origin Hypotheses

Lake Vanda. Four sources of salt are currently hypothesized for Lake Vanda: trapped sea water; atmospheric salts; weathering by-products; and ground water. The present study conclusively shows that trapped sea water is not a source of chloride. The two end members of the mixing model have ^{36}Cl/Cl ratios greater than sea water. Jones and Faure (1967) concluded that strontium in Lake Vanda was derived from weathering by-products. The present study suggests that weathering by-products do not contribute significant volumes of chloride to the Onyx River or Lake Vanda. Green and Canfield (1984) concluded that the Onyx River is the major source of water to Lake Vanda, but that ground water is the major source of chloride. The ^{36}Cl data support their conclusions. Wilson (1979; 1981) suggested shallow ground water as a main source of salt to Lake Vanda. The ^{36}Cl data does not support this hypothesis. The depth profile indicates two sources, one from the lake bottom and the other from the lake surface. The Onyx River is the observable surface source and the ground water source has a ratio approximately 34 x 10^{-15}. Clearly, shallow ground water is not a significant source to the Lake Vanda system. The age calculated for upper Lake Vanda is consistent with that calculated by Wilson (1964) and Nakaya et al. (1979). It is concluded that Lake Vanda was once much larger than at present. Reduced inflow and evaporation at some early time served to concentrate the salts in the lake, resulting in a thin layer of brine. Between 950 and 1150 years ago, an increase in surface flow to Lake Vanda occurred. The inflowing surface water did not mix with the lower brine, resulting in a meromictic lake. Salts have been diffusing upward from the briny layer since this time.

Don Juan Pond. Three sources of salt to Don Juan Pond have been identified in the literature: deep ground water, shallow ground water and meltwater. Only two sources have been confirmed by this study: deep ground water and melwater. Wilson's (1979; 1981) contention that shallow ground water contributes significant quantities of salt to Don Juan Pond is not supported by the ^{36}Cl/Cl data. Shallow ground water would be expected to have a ratio similar to meteoric ^{36}Cl. The main source to the pond must have a ratio less than 23 x 10^{-15}.

Lake Bonney. Four possible sources of salts have been presented for Lake Bonney in the literature: 1) trapped sea water; 2) weathering by-products; 3) atmospheric aerosols; and 4) ground water. The low ^{36}Cl/Cl ratio of surface lake water indicates that either sea water, ground water or both are contributing chloride to Lake Bonney, in addition to meltwaters. At present there is insufficient data to identify the origin of salts in Lake Bonney.

Lake Fryxell. Two sources of salt have been proposed in the literature for Lake Fryxell; atmospheric aerosols and weathering by-products. The low ^{36}Cl/Cl ratio of Lake Fryxell surface water indicates that atmospheric aerosols and weathering by-products are not the only sources of chloride. Both postulated sources have ^{36}Cl signatures larger than the ratio of the lake water. Only two known sources could lower the meltwater ratio: ground water or sea water. At present there is insufficient data to identify the origin of salts in Lake Fryxell.

Lakes Hoare and Vida. Glacial meltwater has been postulated as the sole source of salts to Lakes Hoare and Vida. Data collected during this study suggest that glacial meltwater is the primary if not sole source of chloride, due to the very high ratios. Additional sampling would better define these systems.

SUGGESTIONS FOR FUTURE RESEARCH

1)Collect depth profile samples for Lake Fryxell and both lobes of Lake Bonney to identify sources of chloride.

2)Collect deep ground water samples from DVDP 13 and DVDP 4 (archived) for ^{36}Cl/Cl signatures.

3)Collect sample of fresh snow fall for meteoric ^{36}Cl/Cl signature.

4)Collect ice core from at least one glacier to identify bomb pulse.

SUMMARY

There are two sources of chloride to Lake Vanda: ground water and Onyx River water. The primary source of chloride is deep ground water. The age of the mixolimnion is calculated to be between 955 and 1142 years.

Don Juan Pond recieves chloride from two sources: deep ground water and meltwater. Deep ground water has contributed over 99.9% of the chloride in the pond. Salts are presently being transported from the playa by wind.

Lake Bonney receives salt from more than one source, however there is insufficient data at this time to determine the source(s) other than meltwater. Sea water, ground water or both are probably contributing to the salt concentration.

Lake Fryxell receives salt from more than one source. It is suggested that either sea water or ground water may be contributing to the salt content of the lake, in addition to meltwater.

Lakes Hoare and Vida appear to be receiving the majority if not all their salt from meltwater.

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APPENDIX I: AgCl Purification Procedure

Equipment for AgCl Purification Procedure

fume hood
low temperature oven
hot plate
vacuum pump
1000ml Erlenmeyer filtering flask
glass test tubes, 25x200mm
beakers, 200ml and 400ml
watch glasses
stirring rods
300ml millipore filter funnels
filter paper, 0.45 micron (to fit filter funnel, eg. 47 mm)
laboratory squeeze bottles containing: a)distilled deionized (DD) water, b)dilute HNO3, c)dilute NH4OH, and d)reagent grade NH4OH
amber glass sample bottles(30-60ml) - or small glass vials, if wrapped to keep out light
parafilm
disposable polyethylene gloves
plastic forceps
distilled water
distilled-deionized water
chemicals:
    barium nitrate
    ammonium hydroxide (reagent grade)
    nitric acid (reagent grade)
    silver nitrate
    NaCl (table salt for blank or carrier)

AgCl Purification Procedure

Purification of Chlorine-36 samples prior to analysis in the tandem-accelerator mass spectrometer is necessary to reduce the sulfur content of the samples. Sulfur-36 ions follow along a similar path as Chlorine-36 ions in the accelerator, thus hindering Chlorine-36 analysis.

Care must be taken during the purification process to avoid contamination. Samples should be covered whenever possible, even when in the filter funnels. The entire process is conducted in a laboratory fume hood. Disposable poly gloves should be worn during the entire process, and all equipment should be washed and treated each time it is used. Laboratory squeeze bottles of distilled deionized (DD) water, dilute HNO_3, and dilute NH_4OH are useful for treating equipment. Glass- and plasticware should first be washed with laboratory soap and water, and rinsed with distilled water. Next it should be rinsed with dilute HNO_3 followed by DD water, then rinsed with dilute NH_4OH followed by several rinses with DD water.

1)Add reagent grade $AgNO_3$ in an amount sufficient to precipitate at least 200mg AgCl. Let stand for 24 hours in the dark.

2)Decant and discard the supernatant. Filter the AgCl precipitate to near dryness in a filter funnel, with 0.45 micron filter paper, using a vacuum pump. Wash the precipitate thoroughly, in the filter funnel, with DD water and discard solution.

3)Transfer the filter funnel to an armed flask with a 25x200mm test tube inside(lower and raise test tube into and out of the flask with treated plastic forceps). Dissolve the precipitate by adding 25-50ml reagent grade NH_4OH to the filter funnel. Allow sufficient time for the precipitate to dissolve and gravity filter. Only if necessary, gently draw the solution into the test tube with the vacuum pump. Use a squeeze bottle of reagent grade NH_4OH to rinse and dissolve any precipitate that may stick to the sides of the funnel. Remove filter funnel and discard used filter with any remaining precipitate.

4)Transfer solution from test tube to a treated 200ml beaker. Carefully add 1ml $Ba(NO_3)_2$ to solution in beaker, as sputtering may occur. Cover beaker with parafilm and allow to sit overnight. (To make the $Ba(NO_3)_2$ solution, place a good amount of solid $Ba(CO_3)_2$ in a flask. Add sufficient HNO_3 to dissolve some of the $Ba(CO_3)_2$, but leave some in solid form in the bottom of the flask. When using the $Ba(NO_3)_2$ solution, draw off the liquid from the top).

5)Filter solution into a test tube and transfer solution to a treated 400ml beaker(more efficient during evaporation process). Discard used filter paper.

6)Lay a glass stirring rod across the top of the beaker and cover with a chemical watch glass(concave side up). Evaporate the NH_4OH and reprecipitate the AgCl by heating the beaker at $50^{0}C-65^{0}C$ for 1-1/2 to 3 hours. Add small amounts of DD water(from squeeze bottle) during the heating process to buoy up the precipitate and prevent it from sticking to the bottom of the beaker.

7)Using DD water, rinse the precipitate from the beaker into the filter apparatus. Wash the precipitate thoroughly with DD water and filter it to near dryness.

8)Transfer filter funnel to an armed flask with a test tube set up. Redissolve the AgCl precipitate by adding 25-50ml reagent grade NH_4OH to the filter funnel. Again allow sufficient time for the precipitate to dissolve and gravity filter. Only if necessary, draw solution into test tube with the vacuum pump. Use a squeeze bottle of reagent grade NH_4OH to rinse and dissolve any precipitate that may stick to the sides of the funnel. Remove the filter funnel and discard used filter paper.

9)Transfer solution to a 400ml beaker and repeat steps 6 and 7. If sulfur contamination is a concern(ie. solution has color) or a known problem, repeat step 9. During final filtering process, try to "gather" precipitate from filter funnel sides onto the micropore filter using DD water.

10)Crumple and then flatten a blue filter-cover paper(found between the individual 0.45 micron filters), and lay it on a treated watch glass(concave up). Usin g treated forceps, place the filter paper with the AgCl precipitate on top of the blue filter-cover paper. Place the watch glass in an oven allowing the precipitate to dry overnight at 45^{o}C(if time is of the essence, a drying time of 1-2 hours at 65^{o}C should be sufficient).

11)Weigh a treated and dried sample bottle. Transfer the dry powder sample to the dark-glass sample bottle, reweigh to obtain sample weight. Wrap parafilm around the bottle cap. Label, date, and store in a dark location.

APPENDIX II: Anion-exchange Resin Procedure

CHLORINE-36 SAMPLING -- Extraction of chloride from fresh water using anion-exchange resin

Materials - 20-50 mesh Dowex 1-X8, Cl^- form
PVC columns, 3 cm diameter, 25 cm long, with screw-on endcaps and metal nipples
$NaNO_3$ or HNO_3, NaAc, $AgNO_3$

Resin preparation

1. Resin initially in Cl^- form. Elute with 2M $NaNO_3$ (AR grade) or 2M HNO_3 until no Cl^- is detected in the eluant when tested with a solution of $AgNO_3$. The flowrate should be about 0.4 ml/min/cm^2 bed per recommendation in BioRad catalog (p. 12). Takes about 5 or more bed volumes of NO_3^- solution.
2. Rinse with distilled deionized water until the pH returns to normal (pH 5-6).
3. Elute resin with 2M NaAc. Check for Cl^- in eluant by $AgNO_3$ test. Check for NO_3^- in eluant, e.g. by Hach kit-Cd reduction method. Residual NO_3^- on resin will reduce efficiency of Cl^- capture but otherwise is not of concern.
4. Rinse with distilled H_2O. Pack columns or store resin in bottles for packing of columns in field.

Column preparation

1. With one end capped and plugged, fill PVC column partially with distilled water. Add saturated glass wool plug, tamp into place. Minimize presence of entrapped air as much as possible (affects flowrate in field).
2. Slurry into column about 30 cm^3 of resin. At 1.4 meq/cm^3, this amount should be adequate to collect the desired quantity of Cl^-. (Note: you can probably make do with much less resin.)
3. Add saturated glass wool plug to top of resin, fill column with distilled H_2O and screw on top endcap.

Field operation

1. Collect sufficient sample to contain at least 200 mg Cl^-. Store in container such as a carboy with a stopcock outlet.
2. Connect flexible tubing to stopcock outlet, fill tubing with sample water by opening stopcock, then connect resin column to end of tubing.
3. Set up column so that it flows up through column to maximize exchange efficiency. Flow rate should be on order of 3 ml/min/cm^2 bed cross-section. For a column of 3 cm diameter, this rate is about 1.2 l/hr. (Note: this is a conservative estimate of the rate. I got nearly complete recovery of Cl^- from the samples at this flowrate, so you could probably go faster and monitor the outlet with $AgNO_3$ to judge efficiency.)
4. The flow may slow considerably if the sample degases in the tubing or in the column. In that case, let the air bubbles out and re-start the flow.

Sample Preparation

1. Slurry resin from column into buret containing small glass wool plug on bottom.
2. Elute resin with 2M $NaNO_3$ until Cl^- content of eluant is negligible. Takes about four bed volumes. Resin volume will decrease by about 20%.
3. Add sufficient $AgNO_3$ solution to eluant to precipitate at least 200 mg AgCl. Let sit overnight.
4. Filter out precipitate. Purify by normal procedure.

JF-M
6/8/84

APPENDIX III: Calculation of $^{36}Cl/Cl$ ratio for Ferrar Dolerite

```
                                                      PROGRAM CHLOR

C      THIS PROGRAM CALCULATES THE SECULAR EQUILIBRIUM OF 36CL/CL

C      THE DIMENSIONS OF THE INITIALED ARRAYS ARE DEPENDENT
C      ON THE INPUT DATA AND MUST BE RE-DIMENSIONED FOR NEW DATA

       REAL AV,ACL,PN,RS,CL,NW,NS,NHW,NHS,CHEM(1,18),MOLE(18),RB,
       1S(18),SSN(1),CACO(1),CM(1,18),SN(1,18),AB,SNS(1),SFU(1),
       1ANU(1),ANTH(1),SUTH(1),RSE(1),SRSE,R(1),SR,SDEV,MEAN,CCL

       INTEGER I,J,N

C      THE DATA SETS THAT ARE INITIALIZED TO ZERO NEED TO BE
C      RE-DIMENSIONED TO USE THIS PROGRAM

       DATA SSN,SNS,SFU,ANU,ANTH,SUTH,RSE,R/8*0.0/
       DATA SN,CM/36*0.0/

C      THE CHEM ARRAY IS THE CHEMICAL ANALYSIS RESULTS OF
C      18 PARAMETERS:SIO2,TIO2,AL2O3,FE2O3+FEO,MGO,CACO3+CAO,
C      NA2O,K2O,LI,RB,SR,MN,U,TH,SM,GD,B; RESPECTIVELY. THE OXIDES
C      ARE IN WT. %  AND THE ELEMENTS ARE IN PPM.  WHEN FILLING
C      THE ARRAY LIST ALL SIO2 FIRST, THEN ALL TIO2, ETC.

       DATA CHEM/53.75,0.70,14.23,9.74,6.64,10.6,1.83,0.81,0,
       131,125,0,1.6,3.8,0,0,0,0/

C      THE MOLE ARRAY DOES NOT NEED TO BE CHANGED FOR FUTURE
C      PROGRAMS IF YOU ARE STILL USING THE 18 PARAMETERS LISTED
C      ABOVE. THIS ARRAY IS THE CONVERSION FACTORS FROM WT. %
C      AND PPM TO MOLES/100G.

       DATA MOLE/6.009E1,79.9,50.98,77.18,40.31,78.085,30.99,
       147.1,6.94E4,85.47E4,87.62E4,54.94E4,238.03E4,232.04E4,
       1150.35E4,157.25E4,10.81E4,1.0/

C      THE ARRAY CACO IS A LISTING OF THE CACO3 VALUES IN WT. %.
C      IT WILL NEED TO BE RE-INITIALIZED WITH EVERY CHANGE OF INPUT.

       DATA CACO/0.0/

C      THE ARRAY S IS THE THERMAL CROSS-SECTION FOR EACH OF
C      THE 18 PARAMETERS LISTED ABOVE. THE ARRAY NEED NOT BE
C      RE-INITIALIZED.

       DATA S/0.1638E-24,6.4205E-24,0.232E-24,2.5133E-24,
       10.0625E-24,0.4546E-24,0.400E-24,2.1459E-24,
       171E-24,0.07310E-24,0.0862E-24,13.3E-24,0.0,0.0,
       15746.7687E-24,48815.982E-24,760E-24,0.0265E-24/
```

```
C     AVOGADRO'S NUMBER
      AV=6.022E23
C     THERMAL CROSS-SECTION
      ACL=43.0E-24
C     POROSITY
      PN=0.01

C     SPECIFIC WEIGHT OF ROCK MATERIAL
      RS=2.965
C     CHLORIDE CONCENTRATION IN G CL/KG WATER
      CL=138

      RB=(1-PN)*RS
      CCL=CL/34.45
      NW=0.7577*(PN/RB)*CCL*AV

C     NS IS N35WS35CL AND NEEDED FOR RSE EQUATION
      NS=NW*ACL

      NHW=(PN/((1-PN)*2.65))*100*AV

C     NHS IS NH2OWSH AND NEEDED FOR RSE EQUATION
      NHS=NHW*(0.386E-24)

C     THE DO LOOP CALCULATES SUM(MOLES-BARNES/100G)
      I=1
              DO 11 J=1,18
                      IF (J.EQ.18) THEN
                      CHEM(I,18)=(CM(I,1)*2)+(CM(I,2)*2)+(CM(I,3)*3/2)
     1+(CM(I,4)*4/3)+CM(I,5)+CM(I,6)*2+CM(I,7)/2+CM(I,18)/2
                      CM(I,18)=CHEM(I,18)/MOLE(18)
                      SN(I,18)=CM(I,18)*S(18)
                      SSN(I)=SSN(I)+SN(I,18)
                      AB=SSN(I)*AV
                      SNS(I)=AB*960.0/100
                      ELSE
                      CM(I,J)=CHEM(I,J)/MOLE(J)
                      SN(I,J)=CM(I,J)*S(J)
                      SSN(I)=SN(I,J)+SSN(I)
                      END IF
11            CONTINUE

C     THIS PART OF THE DO LOOP CALCULATES PHI-N IN N/KG
              SFU(I)=0.4764*CHEM(I,13)*1000
              ANU(I)=(CHEM(I,13)/100)*(13.8*CM(I,7)*22.99
     1+5.4*CM(I,5)*24.31+5.0*CM(I,3)*26.98+0.61*CHEM(I,1)+0.24*
     1CACO(I))*1000
              ANTH(I)=(CHEM(I,14)/100)*(6.0*CM(I,7)*22.99
     1+2.45*CM(I,5)*24.31+2.88*CM(I,3)*26.98+0.27*CHEM(I,1)+0.10*
     1CACO(I))*1000
              SUTH(I)=SFU(I)+ANU(I)+ANTH(I)
              D=((2.236E-6)*(SNS(I)+NS+NHS))

C     RSE IS THE SECULAR EQUILIBRIUM OF CL-35 FOR EACH SAMPLE
              RSE(I)=(0.7577*SUTH(I)*ACL)/D

      WRITE(3,*) 'POROSITY=', PN
      WRITE(3,*) 'RSE=', RSE

      WRITE(5,*) RSE

      STOP
      END
```

APPENDIX IV: Calculation of ^{36}Cl/Cl ratio for Granitic Basement

```
                                                  PROGRAM CHLOR

C        THIS PROGRAM CALCULATES THE SECULAR EQUILIBRIUM OF 36CL/CL

C        THE DIMENSIONS OF THE INITIALED ARRAYS ARE DEPENDENT
C        ON THE INPUT DATA AND MUST BE RE-DIMENSIONED FOR NEW DATA

         REAL AV,ACL,PN,RS,CL,NW,NS,NHW,NHS,CHEM(1,18),MOLE(18),RB,
         1S(18),SSN(1),CACO(1),CM(1,18),SN(1,18),AB,SNS(1),SFU(1),
         1ANU(1),ANTH(1),SUTH(1),RSE(1),SRSE,R(1),SR,SDEV,MEAN,CCL

         INTEGER I,J,N

C        THE DATA SETS THAT ARE INITIALIZED TO ZERO NEED TO BE
C        RE-DIMENSIONED TO USE THIS PROGRAM

         DATA SSN,SNS,SFU,ANU,ANTH,SUTH,RSE,R/8*0.0/
         DATA SN,CM/36*0.0/

C        THE CHEM ARRAY IS THE CHEMICAL ANALYSIS RESULTS OF
C        18 PARAMETERS:SIO2,TIO2,AL2O3,FE2O3+FEO,MGO,CACO3+CAO,
C        NA2O,K2O,LI,RB,SR,MN,U,TH,SM,GD,B; RESPECTIVELY. THE OXIDES
C        ARE IN WT. %  AND THE ELEMENTS ARE IN PPM.  WHEN FILLING
C        THE ARRAY LIST ALL SIO2 FIRST, THEN ALL TIO2, ETC.

         DATA CHEM/71.1,0.17,14.1,1.77,0.2,1.37,3.42,4.74,0,
         1207,149,0,2.8,11,3.72,2.88,0,0/

C        THE MOLE ARRAY DOES NOT NEED TO BE CHANGED FOR FUTURE
C        PROGRAMS IF YOU ARE STILL USING THE 18 PARAMETERS LISTED
C        ABOVE. THIS ARRAY IS THE CONVERSION FACTORS FROM WT. %
C        AND PPM TO MOLES/100G.

         DATA MOLE/6.009E1,79.9,50.98,77.18,40.31,78.085,30.99,
         147.1,6.94E4,85.47E4,87.62E4,54.94E4,238.03E4,232.04E4,
         1150.35E4,157.25E4,10.81E4,1.0/

C        THE ARRAY CACO IS A LISTING OF THE CACO3 VALUES IN WT. %.
C        IT WILL NEED TO BE RE-INITIALIZED WITH EVERY CHANGE OF INPUT.

         DATA CACO/0.0/

C        THE ARRAY S IS THE THERMAL CROSS-SECTION FOR EACH OF
C        THE 18 PARAMETERS LISTED ABOVE. THE ARRAY NEED NOT BE
C        RE-INITIALIZED.

         DATA S/0.1638E-24,6.4205E-24,0.232E-24,2.5133E-24,
         10.0625E-24,0.4546E-24,0.400E-24,2.1459E-24,
         171E-24,0.07310E-24,0.0862E-24,13.3E-24,0.0,0.0,
         15746.7687E-24,48815.982E-24,760E-24,0.0265E-24/
```

```
C       AVOGADRO'S NUMBER
        AV=6.022E23
C       THERMAL CROSS-SECTION
        ACL=43.0E-24
C       POROSITY
        PN=0.01

C       SPECIFIC WEIGHT OF ROCK MATERIAL
        RS=2.965
C       CHLORIDE CONCENTRATION IN G CL/KG WATER
        CL=129.7

        RB=(1-PN)*RS
        CCL=CL/34.45
        NW=0.7577*(PN/RB)*CCL*AV

C       NS IS N35WS35CL AND NEEDED FOR RSE EQUATION
        NS=NW*ACL

        NHW=(PN/((1-PN)*2.65))*100*AV

C       NHS IS NH2OWSH AND NEEDED FOR RSE EQUATION
        NHS=NHW*(0.386E-24)

C       THE DO LOOP CALCULATES SUM(MOLES-BARNES/100G)
        I=1
                DO 11 J=1,18
                        IF (J.EQ.18) THEN
                        CHEM(I,18)=(CM(I,1)*2)+(CM(I,2)*2)+(CM(I,3)*3/2)
        1+(CM(I,4)*4/3)+CM(I,5)+CM(I,6)*2+CM(I,7)/2+CM(I,18)/2
                        CM(I,18)=CHEM(I,18)/MOLE(18)
                        SN(I,18)=CM(I,18)*S(18)
                        SSN(I)=SSN(I)+SN(I,18)
                        AB=SSN(I)*AV
                        SNS(I)=AB*960.0/100
                        ELSE
                        CM(I,J)=CHEM(I,J)/MOLE(J)
                        SN(I,J)=CM(I,J)*S(J)
                        SSN(I)=SN(I,J)+SSN(I)
                        END IF
11              CONTINUE

C       THIS PART OF THE DO LOOP CALCULATES PHI-N IN N/KG
                SFU(I)=0.4764*CHEM(I,13)*1000
                ANU(I)=(CHEM(I,13)/100)*(13.8*CM(I,7)*22.99
        1+5.4*CM(I,5)*24.31+5.0*CM(I,3)*26.98+0.61*CHEM(I,1)+0.24*
        1CACO(I))*1000
                ANTH(I)=(CHEM(I,14)/100)*(6.0*CM(I,7)*22.99
        1+2.45*CM(I,5)*24.31+2.88*CM(I,3)*26.98+0.27*CHEM(I,1)+0.10*
        1CACO(I))*1000
                SUTH(I)=SFU(I)+ANU(I)+ANTH(I)
                D=((2.236E-6)*(SNS(I)+NS+NHS))

C       RSE IS THE SECULAR EQUILIBRIUM OF CL-35 FOR EACH SAMPLE
                RSE(I)=(0.7577*SUTH(I)*ACL)/D

        WRITE(3,*) 'POROSITY=', PN
        WRITE(3,*) 'RSE=', RSE

        WRITE(5,*) RSE

        STOP
        END
```

APPENDIX V: Program to Reduce Raw $^{36}Cl/Cl$ Data

```
0       REM This Program Reduces Chlorine-36 Data
1      DATA S201, 3, 421.5, 29.73, 428.0, 30.19, 410.2, 28.93
2      DATA 203, 6, 2.96, 4.44, 3.80, 5.70, 5.84, 3.50, 2.98, 2.77, 3.39, 3.16.
, 1
3      DATA S201, 1, 549.8, 38.78
4      DATA 202, 2, 1164, 81.92, 1126, 79.29
5      DATA 205, 2, 30.48, 6.99, 28.56, 6.09
6      DATA 206, 2, 40.49, 9.05, 41.85, 9.13
7      DATA S204, 2, 521.0, 36.75, 425.5, 29.94
8      DATA 207, 1, 41.29, 16.51
9      DATA S204, 2, 501.3, 35.36, 604.5, 42.53
10     DATA 208, 2, 38.04, 8.97, 26.40, 6.82
11     DATA 209, 2, 45.78, 9.34, 21.85, 4.13
12     DATA S211, 2, 401.9, 28.28, 478.1, 33.72
13     DATA 210, 3, 45.23, 7.54, 83.99, 10.42, 57.95, 9.80
14     DATA S211, 1, 420.3, 29.50
15     DATA S215, 2, 269.6, 19.11, 443.0, 31.25
16     DATA 212, 2, 115.3, 13.78, 125.7, 13.25
17     DATA 213, 2, 79.28, 10.41, 80.88, 10.62
18     DATA 214, 2, 67.96, 10.49, 63.96, 9.53
19     DATA S215, 2, 392.3, 27.67, 338.2, 23.85
20     DATA 217, 2, 43.06, 7.86, 48.87, 8.38
21     DATA 218, 2, 34.12, 7.12, 27.79, 6.22
22     DATA 216, 3, 6.06, 3.64, 12.32, 4.31, 5.25, 2.76
23     DATA S215, 4, 287.9, 20.26, 306.3, 21.55, 365.8, 25.80, 294.0, 20.74
24     DATA S501, 3, 356.8, 25.05, 412.3, 28.93, 380.6, 26.84
25     DATA 502, 3, 283.0, 19.91, 300.0, 21.16, 279.0, 19.68
26     DATA 504, 2, 104.0, 12.52, 120.0, 13.34
27     DATA S503, 2, 352.8, 24.82, 329.0, 23.15
28     DATA 505, 2, 421.1, 29.63, 443.5, 31.28
29     DATA 506, 2, 408.9, 28.84, 379.6, 26.78
30     DATA S511, 2, 379.3, 26.62, 367.2, 25.90
31     DATA 507, 3, 2.85, 2.65, 9.08, 3.89, 7.70, 3.64
32     DATA S511, 3, 317.0, 22.25, 290.2, 20.42, 348.9, 24.55
33     DATA 502. 2, 305.5, 21.55, 316.0, 22.23
34     DATA S503, 3, 307.3, 21.62, 287.2, 20.26, 384.6, 27.06
35     DATA 504, 2, 101.4, 11.00, 125.1, 11.93
36     DATA 505, 2, 515.1, 36.24, 443.8, 31.30
37     DATA 506, 2, 370.8, 26.03, 322.1, 22.61
38     DATA S501, 3, 337.8, 23.83, 313.4, 21.95, 359.5, 25.36
39     DATA S506, 2, 327.2, 23.02, 386.1, 27.16
40     DATA D502, 6, 503.0, 35.39, 519.9, 36.67, 611.9, 42.84, 498.7, 35.18, 601.
3, 42.31, 565.7, 37.97
41     DATA S501, 2, 336.7, 23.75, 359.6, 25.37
42     DATA D503, 3, 534.5, 37.51, 529.8, 37.37, 620.2, 41.17
43     DATA D507, 2, 659.0, 46.25, 676.3, 47.01
44     DATA S501, 3, 310.8, 21.92, 365.6, 25.79, 309.2, 21.81
45     DATA D504, 3, 291.1, 21.18, 379.4, 26.76, 334.0, 23.56
46     DATA D505, 3, 483.1, 33.99, 409.6, 28.82, 506.6, 35.64
47     DATA S506, 2. 378.8, 26.72, 355.1. 24.92
```

```
48    DATA D510, 2, 8.63, 4.54, 7.66, 4.03
49    DATA S506, 3, 384.1, 27.09, 599.2, 42.26, 428.6, 30.15
50    DATA S609, 4, 492.1, 34.63, 464.7, 32.61, 395.9, 27.85, 369.2, 25.97
51    DATA 611, 3, 162.2, 16.39, 159.9, 15.84, 147.0, 13.83
52    DATA S601, 3, 477.5, 33.68, 492.5, 34.56, 398.7, 28.12
53    DATA S603, 2, 477.1, 33.65, 483.0, 34.07
54    DATA 610, 2, 557.0, 39.29, 619.0, 43.66
55    DATA S614, 4, 550.9, 38.85, 457.3, 32.26, 434.5, 30.65, 441.8, 31.16
56    DATA S614, 2, 491.2, 34.65, 429.2, 30.28
57    DATA S701, 3, 462.8, 29.94, 451.2, 27.21, 457.7, 25.91
58    DATA 704, 2, 631.0, 35.11, 572.3, 30.86
59    DATA 707, 2, 1199, 59.68, 950.0, 47.92
60    DATA S710, 3, 389.8, 22.03, 453.4, 24.52, 380.5, 21.86
61    DATA 706, 3, 1698, 56.81, 1549, 530.5, 1478, 455.7
62    DATA S701, 2, 487.3, 33.71, 551.3, 31.94
63    DATA S701, 3, 460.1, 32.38, 428.5, 29.02, 399.5, 27.84
64    DATA 708, 2, 1320, 392.2, 1413, 396.9
65    DATA 707, 2, 1099, 57.3, 981.7, 45.72
66    DATA 704, 2, 487.8, 25.57, 489.5, 24.32
67    DATA S701, 2, 526.5, 35.49, 496.2, 34.92
68    DATA 704, 3, 608.0, 32.5, 532.8, 29.11, 570.7, 29.71
69    DATA S701, 3, 537.3, 34.61, 450.0, 31.74, 527.7, 37.22
70    DATA 708, 2, 1470, 500.6, 1555, 479.4
71    DATA S709, 2, 564.9, 38.89, 502.8, 33.1
72    DATA S809, 3, 298.6, 21.06, 312.7, 21.68, 336.2, 21.31
73    DATA 814, 3, 256.2, 18.07, 262.6, 18.43, 270.5, 18.94
74    DATA S815, 3, 258.2, 18.21, 302.0, 21.2, 303.9, 21.17
75    DATA S809, 3, 280.7, 19.70, 314.4, 21.96, 303.6, 21.36
76    DATA 814, 2, 238.4, 16.81, 255.8, 18.04
77    DATA S815, 2, 330.8, 23.28, 288.0, 20.31
2000  PRINT "DATA REDUCTION FOR WHEEL #, MONTH YEAR"
2010  LPRINT "DATA REDUCTION FOR WHEEL #, MONTH YEAR"
2020  LPRINT ""
2030  LPRINT ""
2040  DIM UC(100), RC(100), RM(100), US(100), RJN(100), UJN(100), RS(100), RU(1
0), UU(100), L$(100), RNS(100)
2050  PRINT "SAMPLE #", "RUN #", "WEIGHTED MEAN RATIO", "UNCERTAINTY"
2060  LPRINT "SAMPLE #", "RUN #", "WEIGHTED MEAN RATIO", "UNCERTAINTY"
2070  LPRINT ""
2080  PRINT "NUMBER OF SEQUENCES INPUT"
2090  INPUT M
2100  FOR J=1 TO M
2110  READ L$(J)
2120  READ N
2130  A=0
2140  AA=0
2150  B=0
2160  BB=0
2170  C=0
2180  CC=0
2190  FOR I=1 TO N
2200  READ RC(I), UC
2210  A=RC(I)*((UC)^-2)
2220  AA=AA+A
2230  B=(UC)^-2
2240  BB=BB+B
2250  NEXT I
2260  RM(J)=AA/BB
2270  UI=BB^-.5
2280  FOR K=1 TO N
2290  C=(RC(K)-RM(J))^2
2300  CC=CC+C
2310  NEXT K
2320  IF N=1, THEN UE=0 ELSE UE=ABS(CC/(N*(N-1)))^.5
2330  IF UI>UE, THEN US(J)=UI ELSE US(J)=UE
2340  LPRINT ""
```

```
2350  PRINT ""
2360  PRINT L$(J), J, RM(J), US(J)
2370  LPRINT L$(J), J, "        "RM(J)"      ", US(J)
2380  RS(J)=RM(J)
2390  NEXT J
2400  RS(A)=RM(A)
2410  PRINT "REMOVE BLANK, Y=1 N=0".
2420  INPUT AB
2430  IF AB=0, THEN GOTO 2570
2440  PRINT "VALUE OF BLANK TO BE REMOVED"
2450  INPUT NN
2460  PRINT "VALUE OF BLANK UNCERTAINTY"
2470  INPUT BU
2480  PRINT "REMOVE BLANK FROM WHICH RUN NUMBER"
2490  INPUT X
2500  RS(X)=RS(X)-NN
2510  US(X)=(US(X)^2+BU^2)^.5
2520  PRINT RS(X), US(X)
2530  PRINT "REMOVE SAME BLANK, Y=1 N=0"
2540  INPUT MM
2550  IF MM=1 THEN GOTO 2480
2560  IF MM=0 THEN GOTO 2410
2570  PRINT "NORMALIZE SEQUENCE TO STANDARDS, Y=1 N=0"
2580  INPUT MN
2590  IF MN=0 THEN GOTO 2820
2600  PRINT "RUN NUMBER OF STANDARD MEASURED BEFORE UNKNOWN"
2610  INPUT F
2620  PRINT "RUN NUMBER OF STANDARD MEASURED AFTER UNKNOWN"
2630  INPUT G
2640  PRINT "TRUE STANDARD RATIO"
2650  INPUT H
2660  KF=(RS(F)/H)
2670  KG=(RS(G)/H)
2680  UJF=(ABS((US(F)/RS(F))^2)^.5)*KF
2690  UJG=(ABS((US(G)/RS(G))^2)^.5)*KG
2700  PRINT "RUN NUMBER OF UNKNOWN"
2710  INPUT P
2720  RNS(P)=((KF*UJF^-2)+(KG*UJG^-2))/(UJF^-2+UJG^-2)
2730  UIN=(UJF^-2+UJG^-2)^-.5
2740  UEX=(ABS(((KF-RNS(P))^2+(KG-RNS(P))^2)/2))^.5
2750  IF UIN>UEX, THEN UK=UIN ELSE UK=UEX
2760  RJN(P)=RS(P)/RNS(P)
2770  UJN(P)=(ABS((US(P)/RS(P))^2+(UK/RNS(P))^2)^.5)*RJN(P)
2780  PRINT L$(P), P, RJN(P), UJN(P)
2790  PRINT "NORMALIZE ANOTHER SEQUENCE TO SAME STANDARDS, Y=1 N=0"
2800  INPUT Y
2810  IF Y=1, THEN GOTO 2700 ELSE GOTO 2570
2820  LPRINT ""
2830  LPRINT ""
2840  LPRINT "SAMPLE #", " R", "   U"
2850  LPRINT ""
2860  PRINT "CALCULATE WEIGHTED MEAN OF NORMALIZED RATIOS, Y=1 N=0"
2870  INPUT YN
2880  IF YN=0, THEN GOTO 3260
2890  AX=0
2900  AAX=0
2910  BX=0
2920  BBX=0
2930  CX=0
2940  CCX=0
2950  PRINT "RUN NUMBER OF SEQUENCE TO BE WEIGHTED"
2960  INPUT QQ
2970  AX=RJN(QQ)*((UJN(QQ))^-2)
2980  BX=(UJN(QQ))^-2
2990  AAX=AAX+AX
3000  BBX=BBX+BX
```

```
3010  PRINT "ANOTHER SEQUENCE FOR THE SAME SAMPLE. Y=1 N=0"
3020  INPUT QR
3030  IF QR=1, THEN GOTO 2950   -
3040  RU(QQ)=AAX/BBX
3050  UUI=BBX^-.5
3060  PRINT "CALCULATE UNCERTAINTY OF NORMALIZED RATIOS. Y=1 N=0"
3070  INPUT QP
3080  IF QP=0, THEN GOTO 3260
3090  PRINT "RUN NUMBER OF SEQUENCE FOR UNCERTAINTY CALCULATION"
3100  INPUT QT
3110  CX=(RJN(QT)-RU(QT))^2
3120  CCX=CCX+CX
3130  PRINT "ANOTHER SEQUENCE FOR THE SAME SAMPLE, Y=1 N=0"
3140  INPUT QU
3150  IF QU=1, THEN GOTO 3090
3160  PRINT "NUMBER OF RUNS INPUT FOR THIS SAMPLE"
3170  INPUT TH
3180  IF TH=1, THEN UUE=0 ELSE UE=ABS(CCX/(TH*(TH-1)))^.5
3190  IF UUI>UUE, THEN UU(QQ)=UUI ELSE UU(QQ)=UUE
3200  PRINT L$(QQ), RU(QQ), UU(QQ)
3210  LPRINT L$(QQ), RU(QQ), UU(QQ)
3220  LPRINT ""
3230  PRINT "ANOTHER SAMPLE TO BE REDUCED, Y=1 N=0"
3240  INPUT ZZ
3250  IF ZZ=1, THEN GOTO 2960
3260  END
```

APPENDIX VI: Mixing Model Equations

MIXING MODEL EQUATIONS

Contribution of water volume from each source:

$$R_LCl^- = R_1Cl^-(x) + R_2Cl^-(1-x)$$

rearranging,

$$x_1 = \frac{R_LCl^-_L + R_2Cl^-_2}{R_1Cl^-_1 + R_2Cl^-_2}$$

where: x = fraction of water contributed to lake
$\underline{R}$ = $^{36}Cl/Cl$ ratio
Cl^- = chloride concentration in mg/L
L = Lake water

1,2 = identify end member.

Contribution of ^{36}Cl from each source:

$$y_1 = \frac{R_1Cl^-(x)}{R_1Cl^-_1(x) + R_2Cl^-_2(1-x)}$$

where: y = fraction of ^{36}Cl contributed to lake.

Contribution of chloride from each source:

$$z_1 = \frac{Cl^-_1}{Cl^-_1(x) + Cl^-_2(1-x)}$$

where: z = fraction of chloride contributed.