

APPLICATION OF CHLORIDE STABLE
ISOTOPE ANALYSIS TO HYDROGEOLOGY

Ron Kaufmann, Harold Bentley, Stanley Davis, and Austin Long (University of Arizona, Tucson)

Introduction

Anomalous concentrations of chloride in groundwater have been found in many geologic settings. In deep aquifer systems, chloride concentrations ten times sea water have been reported. In shallow systems, chloride concentrations are generally observed to increase with depth (White, 1965). Chloride in groundwater is believed to come mostly from six sources: chlorides introduced directly from volcanic emanations, chlorides leached from small amounts of brine present in micropores in igneous rocks, chlorides released from minerals by weathering or diagenetic processes, direct dissolution of halite, sea water entrapped in sediments, and chlorides from the surface transported downward by meteoric water. Occurrence of chloride in unusual concentrations in aquifers may indicate nearby igneous activity, dissolution of aquifer material, presence of trapped sea water, cross formational solute movement, or concentration within the aquifer by ion filtration. Of these five processes, three are rarely suggested to explain chloride occurrence within a specific aquifer. Igneous activity is not a likely chloride source unless there is direct evidence of such. In old aquifers, most soluble components are thought to have already been removed so dissolution of halite is not usually considered as a process that contributes chloride to groundwater. Sea water is only considered a direct contributor of chloride if the overall chemistry of the groundwater appears to have evolved from marine water. As a result, occurrence of unusual chloride concentrations in a specific aquifer are most often attributed to either cross formational solute movement (both movement of water with solutes or movement of solutes alone) or ion filtration. These two processes are difficult to distinguish because the chloride itself has not been thought to provide direct evidence of its origin. This paper proposes that the distribution of stable chloride isotopes in groundwater may be applied to understanding some groundwater systems, and in particular in helping to distinguish the effects of ion filtration and cross formational solute movement.

Theory of Stable Chloride Isotope Fractionation

Previous research indicated that chloride isotope distribution does not vary significantly in natural systems. Hoering and Parker (1960) studied stable chloride (masses 35 and 37) in samples from more than 30 natural materials including halite, sea water, oil field brines, meteorites, and various rock types. Of all the terrestrial samples they analyzed, only two samples, well field brines from the Muddy J formation of Oklahoma, were "significantly" different from the laboratory standard. The Muddy J samples were isotopically lighter by less than 1.0 per mil. The apparent lack of chloride isotope fractionation is not surprising. J. Hoefs, in his book Stable Isotope Geochemistry (1980), says that fractionation of isotopes of light elements is likely to occur as a result of equilibrium reactions in which the elements are in different phases or oxidation states, or during bacterially catalyzed reactions. Chloride would not be expected to fractionate because chloride is rarely in equilibrium between phases, is mostly in one oxidation state, and is not selectively used during bacterial reactions. Still there is the mystery of why the Muddy J samples contained fractionated chloride.

Chloride isotope fractionation does occur when chloride diffuses, but the effect is apparently quite small. Kendall (1928) tried to separate chloride mass 35 from 37 by having chloride diffuse down a tube under an electrostatic potential. He found no fractionation of chloride isotopes. Madorsky and Straus (1947) succeeded in separating chloride isotopes by using counter current migration. They also had a NaCl electrolyte solution migrate along a sand-packed tube under an electrical potential. However, in their experiment, the electrolyte solution flowed in a direction opposite to that of the diffusing chloride ions. The rate of flow was sufficient to reduce the net transport of chloride to zero. During the experiment, more mobile chloride 35 migrated towards the cathode while chloride 37 was carried towards the anode by the flow of the solution. Madorsky and Straus reduced the chloride 37 to 35 ratio at the cathode from an initial value of 0.3205 at the beginning of the experiment to 0.2392 at the end.

Two geologic processes analogous to counter current migration are ion filtration of groundwater and diffusion of solutes between aquifers due to concentration gradients. In an aquifer which is confined by compacted clay or shale under a large hydraulic head gradient, water may be forced out of the aquifer through the confining layers. If the boundary of the confining layer is electrostatically charged by clay minerals, only uncharged water molecules will leave the aquifer unhampered. Charged particles will not pass into the confining layer as readily and are concentrated in the aquifer. This process, referred to as salt filtration or ion filtration, may have produced some of the saturated brines in deep aquifers and other anomalies at shallow depths. Clays in the confining layer may play a similar retarding role when solutes diffuse out of an aquifer due to concentration gradients. Diffusion of solutes from one aquifer to another may also have produced some anomalies.

Phillips (1982) suggested an equation to describe the influence that ion filtration and cross formation solute movement may have on the distribution of chloride isotopes in groundwater. The counter current model is applied to the boundary between the aquifer and confining layer. The negative charge of the clays at the boundary is a barrier to chloride anion diffusion out of the aquifer. Impetus to cross the boundary is provided either by a hydraulic or concentration gradient. When these two opposing forces are in equilibrium, only a portion of the chloride crosses the boundary. Because of its larger ionic mobility, chloride 35 is more efficiently repelled by the boundary charge so the chloride crossing the boundary is isotopically heavier. The resultant distribution of chloride isotopes in the aquifer can be described by an equation in the form of the Rayleigh distillation equation.

$$\frac{R_{ri}}{R_0} = (f^a - 1) \times 10^3$$

R_{ri} indicates ratio (Cl-37/Cl-35) of residual chloride left in the aquifer at time i .

R_0 indicates the initial isotopic ratio of the aquifer (time = 0).

f indicates the fraction of chloride remaining in the aquifer at time i .

a indicates a fractionation factor defined as follows in terms of membrane filtering efficiency (E) and ionic mobility ($U_{total}, U_{35}, U_{37}$).

$$a = \frac{(U_{35} - U_{37})(1 - E)}{U_{total} - U_{35}}$$

The equations above are independent of whether ion filtration or cross formational solute movement is occurring. The equations predict that where diffusion of chloride is occurring out of an aquifer, the chloride remaining behind in the aquifer will become isotopically lighter. Conversely, chloride diffusing out of one aquifer into another will make the chloride of the receiving aquifer isotopically heavier. Knowledge of potentiometric head and concentration gradients linked with chloride isotope information can indicate if the diffusion of chloride is caused by ion filtration or cross formational solute movement. In light of Phillips' theory, the chloride isotope ratios in the Muddy J samples would suggest that chloride ions are diffusing out of the Muddy J, possibly during the formation of the brine.

Applications to Hydrologic Studies

For our study, we wanted to know if the counter current theory could be applied to understanding real groundwater systems. The first step was to develop an analytic method for chloride isotope analysis, in this case we chose mass spectrometry of methyl chloride gas. The laboratory method is described in detail by Taylor and Grimsrud (1969), and is summarized as follows:

1. Chloride is quantitatively precipitated as AgCl from a water sample.
2. The AgCl precipitated from the groundwater sample is reacted with excess methyl iodide in an evacuated tube for two (2) days at 70°C.
3. The resultant methyl chloride is separated from the unreacted methyl iodide gas by gas chromatography.
4. Methyl chloride is analyzed by positive ion mass spectrometry.

Commercially produced methyl chloride gas was used as a reference gas during spectrometric measurements. A value of the stable chloride ratio was determined for sea water from three Pacific ocean samples. Chloride ratio results of our study are reported with respect to this value of sea water.

The groundwater samples used in our study came from a Louisiana salt dome area and the Milk River aquifer in Alberta, Canada. These two areas represent two different problems in the geochemical interpretation of chloride occurrence in groundwater; chloride origin and chloride concentration mechanism in aquifers.

Chloride origin

In the vicinity of Louisiana salt domes, samples of groundwater have high chloride concentrations. The question is whether the chloride comes from dissolution of salt domes or from some other source. Samples of salt and fluid from the Weeks Island and Avery Island salt domes were collected by J. Fabryka-Martin of the University of Arizona along with well field brines near the domes.

Six well field samples were taken from Tertiary sandstone beds at depths between 3,000 and 12,000 feet. These sandstones are slightly tilted by regional structural activity. The salt domes are intruded into the tertiary rock layers. Chloride concentrations of the well field samples range from 70,000 mg/l to 90,000 mg/l. Sampled wells were adjacent to or above the salt domes.

Four samples of salt solution from within the domes (two from each of the domes) were obtained along with one salt sample from the Weeks Island dome. Chloride concentration in the dome solutions varied among samples from about 185,000 mg/l to 230,000 mg/l. Results of the stable chloride analysis for both well field and dome samples are shown in Table 1.

Table 1. Results of Stable Chloride Analyses of the Louisiana Samples, Including Chloride Ratio Results, Number of Analyses per Sample, and Chloride Concentrations

Sample	Cl Concentration** (mg/l)	Cl Isotope Ratio* (per mil)	Number of Analyses
Avery Island Dome Brines			
AV-2A	189,744	+0.1	1
AV-7706/18	228,330	+0.3	1
Weeks Island Dome Brines			
WI-IGE	201,426	+0.1	1
WIMP	194,700	+0.3	1
Weeks Island Salt Well Field Brines			
Gulf PC-3	89,562	-0.2	
WC-W122	82,836	(0.0)-(-.05)	2
WC-W141	70,800	(0.0)-(-0.26)	3
WC-W155	78,588	(-0.13)-(-0.58)	3
WC-W245	81,420	-0.14	1

* All measurements are with respect to sea water. Ranges indicate where multiple analyses were performed.

** Analyses of chloride concentration provided by J. Martin, University of Arizona.

Table 1 indicates that samples from within the dome are .1 to .3 per mil heavier than sea water, while those outside the dome are as much as .58 per mil lighter. Though the difference between the two sample groups is not large (reaching a maximum of 0.88 per mil), the consistency of the results suggests that the difference is significant.

That the chloride ratio value of sea water seems to divide dome chloride from well field chloride may not be accidental. Chloride from both the dome and well field probably came from sea water originally. The difference between the two groups may be that the well field water has been concentrated

by ion filtration, while dome solutions have not. Removal of a fraction of the well field chloride by an ion filtration process would be expected to produce isotopically lighter chloride within the aquifer.

A couple of additional observations may be made about the Louisiana area chloride isotope results. First, chloride of the well field brines probably did not come from the domes. This observation is consistent with a recent study concerning strontium in the Louisiana well fields and salt domes. Pushkar (1983) looked at strontium 87/86 ratio as we looked at the chloride isotope ratio and concluded that strontium in the well field did not originate from the salt domes. Second, while ion filtration may explain fractionation of well field chloride, apparently some other mechanism has caused the dome chloride to be isotopically heavier than sea water. This other mechanism, though unknown, may be associated with equilibrium processes during salt deposition, or time variations in the isotopic ratio of the marine chloride.

Concentration Mechanisms in Aquifers

The second area for which chloride ratio analysis was performed presents a more complex problem than the Louisiana study area. The Milk River aquifer of Alberta, Canada is a sandstone aquifer that outcrops near the U.S.-Canadian border. The aquifer dips to a depth of 1000 feet about 60 miles into Canada. A thick layer of glacial sediments overlies the Milk River. Approximately 1350 feet of shale separate the Milk River from an underlying aquifer, the Bow Island sandstone. Chloride concentration in the Milk River aquifer varies from near zero at the outcrop to 1295 mg/l or more in the deeper portions of the aquifer 60 miles north of the recharge zone. Similar increases are noted for other major ions (Swanick, 1982). Chloride concentration in the Bow Island is as high as 14,000 mg/l (Schwartz et al., 1981). Potentiometric maps of the Milk River and Bow Island indicate that the head gradient is toward the Bow Island (Swanick, 1982).

The unresolved question associated with the Milk River aquifer is whether increased concentration of dissolved constituents in groundwater is due to ion filtration or cross formational solute movement. Hitchon, et al., 1971, examined the ion chemistry of the Milk River aquifer and several other west Canada aquifers and concluded that ion filtration controlled groundwater chemistry in the area. Schwartz and Muelenbachs (1979) reviewed ion chemistry and hydrogen and oxygen isotope distribution in the Milk River, and concluded that mixing of incoming and connate water from adjacent shale beds was responsible for the aquifer chemistry. Phillips (1980) reviewed the same isotope data from the Milk River and suggested that ion filtration could have caused the observed isotope distribution. Bentley, et.al. (1983) concluded from radioactive Cl-36 data that ion filtration is the dominant mechanism for chloride concentration.

To help resolve the question of concentration mechanisms in the Milk River aquifer, we measured chloride stable isotope ratios of six samples from the aquifer. Table 2 contains the results of those measurements.

Table 2. Results of Stable Chloride Analyses of the Milk River, Including Chloride Ratio Results, Number of Analyses per Sample, and Chloride Concentrations

Sample	Cl Concentration** (mg/l)	Cl Isotope Ratio* (per mil)	Number of Analyses
1	627	(-0.31)-(-0.38)	2
17	1093	+0.8	1
43	420	+0.6	1
11	356	+0.7	1

* All measurements are with respect to sea water. Ranges indicate where multiple analyses were performed.

** Chloride concentrations are from Swanick, 1982.

Sample 1 is from the northwestern corner of the study area. Sample 17 is located about 50 miles directly east of sample 1. Sample 11 is midway between samples 1 and 17. These three samples are 60

miles north of the intake area for the aquifer. Sample 43 is located about 20 miles south of sample 11.

Table 2 indicates that all the samples except sample 1 have a chloride isotope ratio of about +0.7 per mil. Sample 1 has a value that is about 1.0 per mil lighter (-0.38 per mil).

A relevant interpretation of the stable chloride ratio results can be made by assuming the chloride at the point of recharge is the same as sea water (0.0 per mil). Using the counter current fractionation model, sample 1 would indicate fractionation during outflow of chloride from the aquifer. The other samples indicate inflow of chloride, possibly from confining layers, perhaps ultimately from the Bow Island. It is not difficult to envision chloride coming from the Bow Island since the concentration in the Bow Island is much greater than in the Milk River. Although the present potentiometric head is higher in the Milk River than the Bow Island, it is possible for chloride to diffuse upward against the hydraulic head. Approximations of these two processes using the darcy velocity equation and Fick's First Law with suitable variables for the Milk River situation indicate that the velocity of the water movement vertically is on the same order of magnitude as the rate of diffusion (about 10^{-11} m/s) upward from the Bow Island. Then the only question is why would the west side of the study area have chloride that was isotopically lighter than the east side. This situation might occur if the west side possessed a potentiometric head which was larger than the east side and sufficient to stop diffusion of chloride into the Milk River. Indeed the west side of the area has a potentiometric head gradient between the two aquifers that is twice the head gradient in the east. In other words, it is possible that water is leaving the Milk River by ion filtration throughout the area but on the east side, flow is sufficiently slow that chloride can diffuse into the Milk River from the Bow Island. Interestingly, this interpretation reconciles Phillips' and Bentley's conclusions with Schwartz' and Muelenbachs' interpretation, in that both ion filtration and cross formational solute movement is suggested to be occurring. Before the chloride isotope interpretation can be accepted for the Milk River aquifer, more work must be done to clearly establish a link between laboratory experiments and actual field situations.

Summary and Final Discussion

Anomalous occurrences of the chloride in groundwater are often attributed to ion filtration or cross formation solute movement. Evaluation of isotopic and ion chemistry has not always been able to distinguish the influence of these two mechanisms. Analysis of stable isotopes of chloride has the potential to differentiate the influence of the two mechanisms. Counter current theory, based on laboratory experiments, suggests that groundwater chloride will be fractionated during diffusion through clay or shale confining layers. The direction of movement (either into or out of an aquifer) of chloride will be indicated by the chloride isotopes ratios.

Utility of this counter current fractionation theory was tested by determining the isotopic distribution of chloride in aquifers in Louisiana and Alberta, Canada. In Louisiana, the chloride isotope results were used to determine whether chloride in brines from wells was contributed by dissolution of nearby salt domes. The results suggest that the chloride in brine from wells had been made lighter by ion filtration than the salt dome chloride, and probably did not originate from the dome. In Alberta, Canada, chloride analysis was used to determine whether ion filtration or cross formational solute movement influenced chloride concentration in the Milk River aquifer. Analysis results suggested that both processes may be involved in the concentration of chloride in the aquifer, though the processes were not operating uniformly throughout the aquifer.

The results of this study indicate that chloride isotopes are fractionated in natural systems and that the fractionation may aid in understanding the origin of chloride and diffusion processes in groundwater. More specifically, chloride isotopes, in conjunction with other information, may allow researchers to distinguish the influences of ion filtration from those of cross formational solute movement. In addition, several general comments should be noted concerning the use of stable chloride isotope analysis for interpreting the groundwater systems. Some of the advantages of chloride isotope analysis are as follows:

1. Accurate isotope measurements are not difficult to obtain.
2. Chloride isotope distribution is probably not influenced by mechanisms other than counter current fractionation.
3. Other information used when interpreting chloride isotope analysis results, such as potential head and concentration gradients, is not difficult to obtain.

Though chloride isotope analysis can become a powerful tool for hydrogeologic research, considerable work needs to be done before there is complete confidence in interpreting the results.

Laboratory experiments which more closely describe diffusion processes in natural systems should be done and chloride ratios evaluated from such experiments. This would help close the gap between the original counter current experiments and natural systems. Also, other chlorine fractionation mechanisms such as those associated with hydrothermal and precipitation processes should be investigated to provide a better understanding of natural processes which could affect isotopic ratios of chlorine.

References Cited

- Bentley, H., F. Phillips, and S. Davis, 1983. ^{36}Cl in the terrestrial environment. In: Handbook of Environmental Isotope Geochemistry VII, Fontes and Fritz, editors, Elsevier (in press).
- Hoefs, J., 1980. Stable Isotope Geochemistry, 2nd Edition, Springer-Verlag, Berlin, New York: 21-22.
- Hitchon, B., G. Billings, and J. Klovan, 1971. Geochemistry and origin of formation waters in the western Canada sedimentary basin III. Factors controlling chemical composition. *Geochim. Cosmochim. Acta.* 35: 567-598.
- Hoering, T., and P. Parker, 1960. The geochemistry of the stable isotopes of chlorine. *Geochim. Cosmochim. Acta.* 23:186-199.
- Kendall, J., 1928. Separations by the ionic migration method. *Science.* 67:163-170.
- Madorsky, S., and S. Straus, 1947. Concentration of isotopes of chlorine by the counter current electromigration method. *J. Research NBS.* 38:185-189.
- Phillips, F., 1982. Letter to R. Kaufmann dated March 16, 1982. Re: revisions to possible effects of ion filtration on isotopic groundwater dating, and other groundwater tracing techniques.
- Phillips, F., 1980. Possible effects of ion filtration on isotopic groundwater dating, and other groundwater tracing techniques. Unpublished paper.
- Pushkar, P., 1983. Strontium isotopic analyses of anhydrite and other mineral phases of the Vacherie salt dome, Louisiana. In: GSA Abstracts With Programs. No. 20271. 15(1):38.
- Schwartz, F., and K. Muelenbachs, 1979. Isotope and ion geochemistry of groundwaters in the Milk River aquifer, Alberta, *Water Resources Research.* 15(2):259-268.
- Schwartz, F., K. Muelenbachs, and D. Chorley, 1981. Flow system controls of the chemical evolution of groundwater. *Development in Water Sciences:* 225-243.
- Swanick, G., 1982. The Hydrochemistry and Age of the Water in the Milk River Aquifer, Unpublished Masters Thesis, University of Arizona.
- Taylor, J., and I. Grimsrud, 1969. Chlorine isotopic ratios by negative ion mass spectrometry. *Anal. Chem.* 41(6):805-810.