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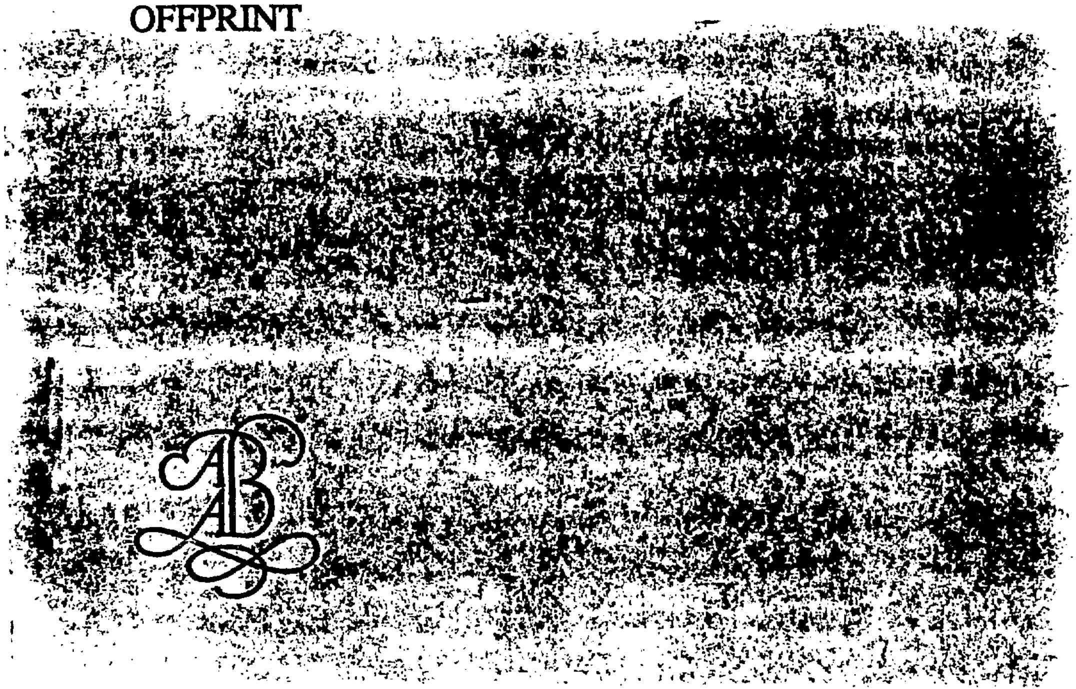

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A preliminary study of the chemistry of pore water extracted from tuff by one-dimensional compression

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ABSTRACT: A specially designed and fabricated one-dimensional compression cell is being used to extract water from nonwelded and densely welded tuffs having degrees of saturation greater than 16 and 37 percent respectively. Chemical analyses of pore water obtained at increasing pressures are used to evaluate possible changes in chemistry caused by compression. The extracted pore water varies from a calcium chloride type to a sodium bicarbonate type. The mean concentration of dissolved ions generally decreases during compression. The relative abundance of the major cations varies little with increasing pressure. The relative abundance of the major anions varies moderately with increasing pressure. Possible causes of the pore-water-chemistry changes include: 1) dilution of pore water by low ionic strength adsorbed water from zeolites and clays; 2) dissolution reactions caused by the increase in dissolved carbon dioxide concentrations that may result from pressurization; 3) membrane filtration by zeolites and clays; and 4) ion exchange with the zeolites and clays.

1 INTRODUCTION

The U.S. Department of Energy is studying Yucca Mountain, Nevada, as a potential site for a high-level radioactive waste repository. An evaluation of the hydrologic system in the unsaturated tuff at Yucca Mountain by the U.S. Geological Survey (USGS), includes a hydrochemical study to assess characteristics of the system, such as traveltime, flowpaths, recharge and source relations, and reaction chemistry of the unsaturated tuff. The objectives of this research are: (1) to develop a viable technique for extracting pore water from cores of unsaturated, nonwelded and densely welded tuffs by compression, and (2) to investigate the effects of the extraction method on the original pore-water composition. This paper describes and presents preliminary results of an evaluation of the changes in pore-water chemistry due to one-dimensional compression of pore water by extraction.

Cores used in the study were collected from drill holes UE-25 UZ #4, UE-25 UZ #5, and USW UZ-13 located on Yucca Mountain and from the U12g tunnel complex (G-tunnel) at Rainier Mesa, Nevada (Figure 1). These sample sites are located on or near the Nevada Test Site (NTS), which is about 110 kilometers northwest of Las Vegas, Nevada. Several additional cores were obtained from a site (Apache Leap) near Superior, Arizona.

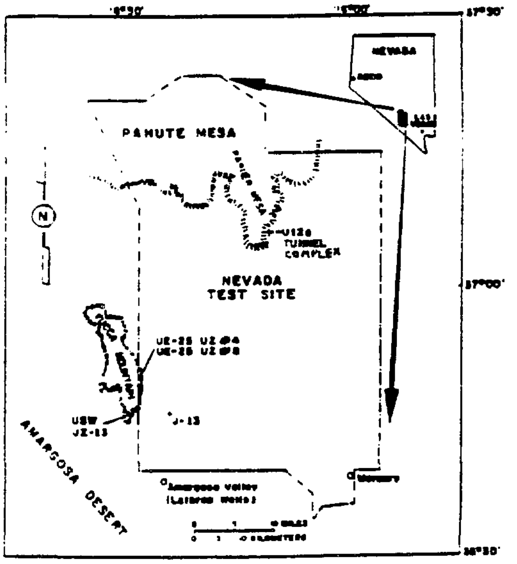

Figure 1. Location of sample sites on and near the Nevada Test Site, and nearby geographic features in southern Nevada.

Pore water and gases were extracted from welded and nonwelded tuff samples at various pressures up to 830 megapascals during compression. Pore water was analyzed for major ions, specific conductance, and pH. Gas samples were analyzed for carbon dioxide, methane, and sulfur hexafluoride.

2 PORE-WATER AND PORE-GAS EXTRACTION METHODS

The one-dimensional compression system used in this study, designed and built by the USGS and the U.S. Bureau of Reclamation (Mower and others, 1990; Figure 2), is made of heat-treated 4340-alloy steel and age-hardened Monel K500 nickel alloy. The rock sample is wrapped in a teflon sheet and confined in the sample sleeve. The drainage plates have holes for pore-water and pore-gas extraction that are connected by nylon tubing to syringes for water and gas collection. The cell has a maximum compressive stress rating of 552 megapascals and can accommodate cores up to 110 millimeters in length and 61 mm in diameter. A second-generation cell made principally of C250 maraging steel that has a maximum compressive stress rating of 830 megapascals was also used for compression in this study. The design of this cell is similar to the original one-dimensional cell (Figure 2).

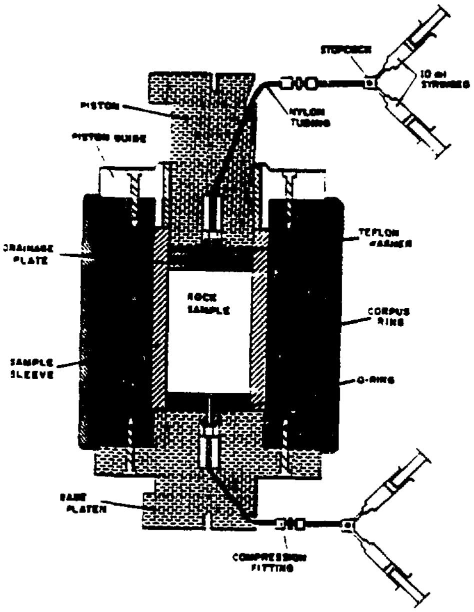

Figure 2. Schematic diagram of one-dimensional compression cell used in this study

Axial stress is applied to the core by a load frame that has a capacity of 915 megapascals. Pore water and gas are collected in syringes as the core is compacted by the load. At the maximum axial stress, when water expulsion ceases and the core stops compacting, additional pore water often can be extracted by injecting nitrogen gas into the pore space. Pore water was filtered through a 0.45 micron filter and stored in polyethylene bottles prior to analysis for dissolved ions. Pore gas was stored in glass syringes prior to analyses. Temperature measurements were made during several compression tests using a chromel-alumel thermocouple.

Water has been extracted at pressures ranging from 34 to 828 megapascals from nonwelded cores having a degree of saturation as low as 16.2 percent, and from welded cores having a degree of saturation as low as 37.3 percent. The nonwelded cores yielded an average of 24 milliliters of water and 39 milliliters of gas. The welded core yielded an average of 6 milliliters of water and 15 milliliters of gas.

3 PORE-WATER AND PORE-GAS CHEMISTRY

Analyses of dissolved ionic species were performed on 449 water samples collected from 83 core samples. Gas samples were collected from each of the 83 cores.

Water analyses included determination of calcium, magnesium, sodium, potassium, bicarbonate, chloride, sulfate, silica, nitrate, pH, and specific conductance (SC). Water analyses were performed using ion-specific electrodes, ion chromatography (IC), atomic absorption (AA), and colorimetric methods. A 3-milliliter water sample is required for a complete analysis. Gas analyses were performed by USGS personnel using gas chromatography (GC) methods for carbon dioxide, methane, and sulfur hexafluoride determinations. A 3 milliliter gas sample is required for a complete analysis.

Table 1 lists average chemical compositions of water for each of the four representative tuffs. To obtain sufficient water for chemical analyses at various pressure levels from low moisture content welded cores, an artificial pore water having an ionic composition shown in table 1 was imbibed under a vacuum into 6 densely welded cores from the Grouse Canyon Member of the Belted Range Tuff to produce saturations of at least 98 percent.

Pore water extracted from nonwelded Paintbrush Tuff core samples is a calcium chloride type with a mean pH of 6.4 and a mean SC of 890 microsiemens per centimeter. Pore water extracted from a nonwelded geologic unit (Tunnel Bed 5) is a sodium bicarbonate type with a mean pH of 7.4 and a mean SC of 670 microsiemens per centimeter. Pore water extracted from a densely welded geologic unit (Grouse Canyon Member of the Belted Range Tuff) in G-Tunnel is a sodium chloride type with a mean pH of 6.5 and a mean SC of 610 microsiemens per centimeter. Pore water extracted from cores from a partially welded geologic unit (Apache Leap Tuff) is a calcium sodium chloride type with a mean pH of 6.8 and a mean SC of 410 microsiemens per centimeter. Carbon dioxide concentrations in the collected gas samples averaged 0.1 percent and ranged from 0.01 to 1.3 percent of the gas composition.

Table 1. Average chemical compositions for four representative tuff waters and an artificial pore water.

[SC, microsiemens per cm; Ca, calcium; Mg, magnesium; Na, sodium; HCO_3, bicarbonate; SO_4, sulfate; Cl, chloride; SiO_2, aqueous silica; which are reported in milligrams per liter; NA, not analyzed]

	Water Source				
	NWPT[1]	NWTS[2]	DWGC[3]	PWAL[4]	APW[5]
No. of Samples	83	314	21	9	8
Gas CO_2 (%)	0.22	0.07	NA	NA	NA
SC	890	670	610	410	640
pH	6.4	7.4	6.5	6.8	4.0
Ca	93	6.7	22	46	41
Mg	19	0.9	2.3	12	1.3
Na	42	120	100	43	66
HCO_3	61	150	72	81	30
SO_4	120	88	92	48	130
Cl	150	23	93	90	95
SiO_2	74	56	45	62	2.0

1 - nonwelded, Paintbrush Tuff
2 - nonwelded, Tunnel Bed 5
3 - densely welded, Grouse Canyon
4 - partially welded, Apache Leap
5 - artificial pore water

The mineralogy of the four tuffs was analyzed and the results are shown in table 2. The data in the table indicates that the nonwelded rocks are composed primarily of clinoptilolite (a zeolite), with lesser amounts of clays and sanidine. The welded rock is composed primarily of sanidine, quartz, albite, and clays. The partially welded rock from Arizona is composed primarily of albite, with lesser amounts of sanidine, quartz, and cristobalite. Cation-exchange capacities are about twice as high in the samples from nonwelded Tunnel Bed 5 as in the nonwelded Paintbrush Tuff and cation-exchange capacities of samples from the densely welded tuff of the Grouse Canyon Member are minimal.

Table 2. Mineralogical composition of tuff samples.

[Mineral content in percent by volume; --, not found; NA, not analyzed; mineralogical analyses by Crystal Research Laboratory[1]]

	Tuff			
	NWPT[2]	NWTS[3]	DWGC[4]	PWAL[5]
Cation exchange capacity	91	175	4.3	NA
Sanidine	3.9	12	48	16
Albite	1.1	--	14	45
Quartz	1.7	1.4	27	15
Christobalite	5.2	--	--	15
Chalcedony	4.5	7.8	--	4.0
Clinoptilolite	66	67	0.6	--
Ferric Illite	4.3	11	9.8	--
Illite/Montmorillonite	10	--	0.3	--
Biotite	1.5	--	--	4.0

1 - any use of firm names is for descriptive purposes only and does not imply endorsement by the U.S. Government
2 - nonwelded, Paintbrush Tuff
3 - nonwelded, Tunnel Bed 5
4 - densely welded, Grouse Canyon
5 - partially welded, Apache Leap

The water analyses were evaluated by using the computer program WATEQF (Plummer and others, 1976), a FORTRAN program that models thermodynamic speciation of inorganic ions and complex species in solution. The use of the saturation-index data from WATEQF, a knowledge of the phases known to occur in a system, and geochemical intuition can determine whether a specific mineral phase would dissolve or precipitate and whether ion exchange or other reactions could be occurring. Average saturation indices for the minerals most prevalent in the four tuffs are shown in table 3. Saturation indices greater than zero indicate super saturation.

Table 3. Average saturation indices determined by the computer program WATEQF

[--, indicates mineral not important to specific tuff type]

	Tuff			
	NWPT[1]	NWTS[2]	DWGC[3]	PWAL[4]
Albite[*]	--	1.4	-1.1	0.0
Chalcedony	0.6	0.6	--	0.4
Christobalite[**]	0.7	0.7	0.3	0.5
Illite	5.5	5.0	2.9	--
Montmorillonite	6.9	--	--	--
Quartz	1.1	1.1	0.7	0.9

[*] Sanidine saturation indices are not calculated in WATEQF but are assumed to be similar to or slightly less than those for Albite.
[**] Christobalite saturation indices were calculated using log KT values from Ball and Nordstrom (1991).
An aluminum concentration of 0.1 mg/l was input into WATEQF and was estimated from published information about groundwater chemistry at the Nevada Test Site.
Potassium concentrations obtained from water analyses were suspect and were not used in the calculation of saturation indices.
1 - Nonwelded, Paintbrush Tuff
2 - Nonwelded, Tunnel Bed 5
3 - Densely Welded, Grouse Canyon
4 - Partially Welded, Apache Leap

4 INTERPRETATION

Possible causes of pore-water chemistry changes that occur as a function of increasing pressure during compression are discussed below.

Dilution by compression of clays and zeolites and release of ion-deficient, previously-bound water (van Olphen, 1963) would result in progressively decreasing ion concentrations. Figure 3 demonstrates ion concentrations for a nonwelded tuff sample are consistent with this mechanism. The volume of ion-deficient bound water required to produce the observed ion concentration decreases were calculated to represent about 5 to 33 percent of the available bound water in the zeolites.

The interaction of pore-water with carbon dioxide gas contained in unfilled pore space would form a weak carbonic acid solution that could cause pH or alkalinity changes and dissolve minerals. The total moles of carbon in the gas phase were calculated using mean carbon dioxide concentrations and mean milliliters of gas collected. The total moles of carbon in the aqueous phase were calculated using mean bicarbonate concentration and the mean total milliliters of water available. Calculated amounts (1.2×10^{-6} moles in gas and 1.1×10^{-4} moles in water) indicate that the gas phase could be an important component of the chemistry of these waters. Dissolution of minerals due to carbon dioxide dissolving into solution or due to the creation of fresh surfaces by the compression process could cause increases in calcium, magnesium, sodium, potassium, and silica. No significant increases in any of these constituents are seen as a result of compression (Figure 3). Thus, if dissolution is occurring, it is being counteracted by another mechanism.

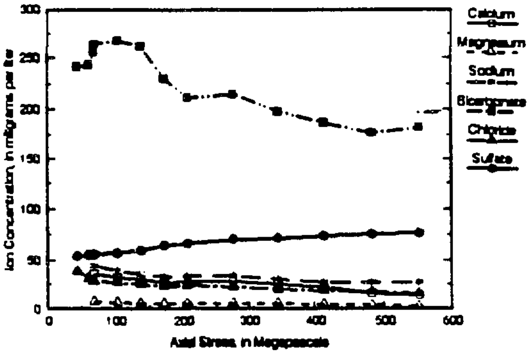

Fig. 3. Changes in major ion concentrations in nonwelded tuff with increasing applied pressure

Precipitation of minerals due to changes in saturation states of the pore water because of other reactions occurring during compression would decrease ion concentrations. The saturation indices indicate supersaturation with respect to all relevant rock minerals. However, the kinetics for the formation of these minerals would probably preclude their precipitation during compression.

Membrane filtration of ions may occur as they flow through a semipermeable membrane (Bredehoeft and others, 1963). The compressed clay and zeolite minerals may act as a semipermeable membrane causing a decrease in ion concentration and a change in the relative proportions of ions. Preferential adsorption of sodium was shown by Hanshaw (1964) and Hanshaw and Coplen (1973). Some selectivity for anions has been shown but is less defined. Decreases in cations are observed in water from the nonwelded Tunnel Bed 5 tuff and nonwelded Paintbrush Tuff core samples, with sodium having the greatest decrease (Figure 3).

Ion exchange reactions, involving both cations and anions in the pore water from the rock matrix and from the clay and zeolites, would be reflected in total ion concentrations as well as in the relati proportions of ions. Changes in the rel tive ion proportions would be indicated increases in sodium relative to calciu and bicarbonate and sulfate relative chloride. In the artificially saturat densely welded Grouse Canyon tuff, t change in chemistry between the artifici pore water and the final compressed wat indicates an increase in sodium and decrease in calcium (Figure 4).

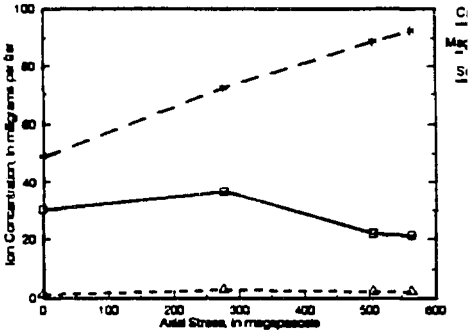

Fig. 4. Changes in major cation concentrations in artificia saturated Grouse Canyon Tuffs with increasing applied pr

Evaporation of pore water due to lo storage periods would cause drying to occ systematically from the outside of the co inward toward the center, leaving behi the dissolved salts. The initial wat removed from the core would dissolve the salts, causing increased concentratio that would *subsequently* decrease as ado tional water samples were collected. T relative proportions of ions would rema constant. Although the data are consiste with this mechanism, figure 5 indicat very little correlation between the leng of time sealed and decreases in SC w compression. Thus, dilution by adsor water seems more likely than slow accumu tion of salts due to evaporation.

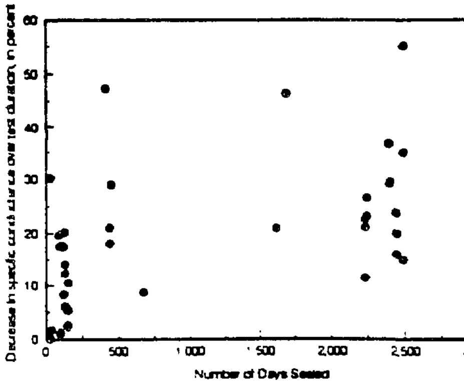

Fig. 5. Relation between number of days sealed and the c in specific conductance of extracted water from all t

As a result of the compression process, Temperature and pressure changes could result in ion concentration changes. Temperatures inside the compression cell and of extracted water changed little during compression. Although the rock core is being subjected to 830 megapascals during compression, the amount of pressure acting on the gas and water in the rock probably is much less because the extraction routes are open to the air. Therefore, the major effect of the pressure is probably to cause gas to be dissolved into the pore water. Thus, the effects of pressure are probably limited to the carbonate system, as described previously.

Hydraulic drag effects caused by the movement of dissolved ions passing through the electric double layers near clay and zeolite surfaces would retard larger, divalent ions relative to smaller, univalent ions (Kharaka and Berry, 1973). Relative concentration effects caused by the mixing of clay- and zeolite-adsorbed waters and pore water can result in an ion concentration increase during compression of the core (Appelo, 1977). Although these mechanisms are possible, and are at least partly supported by the data, their impact is seen as minor.

5 CONCLUSIONS

The mechanisms responsible for changes in ion concentrations due to compression that appear most probable for the tuffs considered include: dilution by zeolite-adsorbed water, dissolution of carbon dioxide gas into the pore water during compression, and membrane-filtration and ion-exchange effects caused by the presence of the clays and zeolites. Planned further investigations of the mechanisms include: 1) analysis of pore water from different pressure levels for oxygen 18/16 and deuterium/hydrogen isotope ratios to aid in determining if the dilution of pore water by zeolite-adsorbed water and the membrane-filtration effects are occurring; 2) analyses of aluminum, iron, and other trace elements to better determine the effects of possible mineral dissolution; 3) analyses of carbon dioxide concentrations in water and carbon-14 ages of both the pore water and gas to better determine the carbonate system effects; 4) the use of various geochemical models, including possibly PHREEQE (Parkhurst and others, 1980) and NETPATH (Plummer and others, 1991); and 5) rock analysis to gain further information concerning the effects of compression on mineral surface areas.

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