

TRITIUM CONTENT OF CLAY MINERALS

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Abstract—The presence, percentage, origins, and rate of formation of clay minerals have been important components in studies involving the geochemical and structural composition of waste-rock piles. The objective of the present study was to investigate the use of tritium as an indicator of the origin of clay minerals within such piles. Tritium values in pore water, interlayer water, and structural hydroxyl sites of clay minerals were examined to evaluate the origins of clay minerals within waste-rock piles located near Questa, New Mexico. Five clay minerals were identified: kaolinite, chlorite, illite, smectite, and mixed-layer illite-smectite, along with the hydrous sulfate minerals gypsum and jarosite. Analysis of waters derived from clay minerals was achieved by thermal reaction of dry-sieved bulk material obtained from the Questa site. In all Questa samples, the low-temperature water derived from pore-water and interlayer sites, as well as the intermediate-temperature water derived from interlayer cation sites occupied by hydronium and structural hydroxyl ions, show tritium values at or near modern levels for precipitation. Pore water and interlayer water ranged from 5.31 to 12.19 tritium units (TU) and interlayer hydronium and structurally derived water ranged from 3.92 to 7.93 TU. Tritium levels for local precipitation ranged from ~4 to 8 TU. One tritium unit (TU) represents one molecule of $^3\text{H}^1\text{HO}$ in 10^{18} molecules of $^1\text{H}^1\text{HO}$. The elevated levels of tritium in structural sites can be accounted for by thermal incorporation of significant amounts of hydronium ions in interlayer cation sites for illite and mixed-layer clays, both common at the Questa site. In low-pH environments, such as those found within Questa waste-rock piles (typically pH ~3), the hydronium ion is an abundant species in the rock-pile pore-water system.

Key Words—Formation Age, Hydronium, Interlayer Water, Isotopic, Tritium, Slope Stability, Structural Hydroxyl.

INTRODUCTION

The tritium content of structural hydroxyl sites and interlayer water in clay minerals may be used to determine the timing of clay formation and the interaction of clay minerals with water in the post-nuclear testing era. The use of tritium as a tracer in the environment was facilitated by the onset of above-ground nuclear testing that was conducted in the 1950s and 1960s. As a result of these tests, a large amount of tritium was introduced into the atmosphere, reaching its highest values in the early to mid 1960s. The large 1960s peak became known as the ‘bomb peak’. Spikes in the 1960s were typically >1000 TU but were different in the northern and southern hemispheres due to the heavy bias on nuclear testing by both the United States and the former Soviet Union (Begemann and Libby, 1957). Tritium serves as a very useful conservative tracer and is typically measured in tritium units (TU), which represents one molecule of $^3\text{H}^1\text{HO}$ in 10^{18} molecules of $^1\text{H}^1\text{HO}$ (Solomon, 2000). The presence or absence of tritium in the structural hydroxyl sites in clay minerals may indicate the time of formation of the clay minerals to pre- or post-1960s. Due to the timing of emplacement

of waste-rock piles at Questa during the 1970s, any newly formed clay minerals within the waste-rock piles should yield significant tritium values from the structural hydroxyl sites.

A common problem faced in open-pit mass mining is the eventual long-term stability of the waste-rock piles produced by dumping overburden. In some cases, the slope of waste-rock piles can be very steep and can become susceptible to slope failure producing a hazard when in close proximity to infrastructure. The presence, percentage, and rate of formation of clay minerals are integral to the calculation of slope stability because lithologic units within a slope that contain large amounts of clay minerals tend to form failure surfaces. The first objective of this study was to use tritium as an indicator of the origin of clay minerals within a waste-rock pile – were they actively forming or original, pre-mining clay minerals?

Conventional measurements of low-level tritium require ~1 L of water that is electrolytically enriched before gas proportional or liquid scintillation counting. The present study used the helium-3 in-growth method (Clarke *et al.*, 1976) which provided a detection limit of ~0.5 TU with as little as 29 mL of water.

Site description

The Questa molybdenum mine operated by Chevron Mining, Inc., is located ~8 km east of the town of Questa, New Mexico (Figure 1). The mine property is located on the north side of Red River Canyon where

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Figure 1. Location of the Questa, New Mexico, study area.

nine waste-rock piles are present. Underground and open-pit mining have been practiced on this site since 1919 with most open-pit mass mining starting in 1965 and completed by 1983 (Schilling, 1990; McLemore *et al.*, 2009a).

The Questa Climax-type porphyry molybdenum deposit occurs within the Tertiary-age Latir volcanic field. The molybdenum mineralization is genetically and spatially related to granitic to aplitic plutons, which intruded the southern boundary of the Questa Caldera. Minerals that comprise the mine-waste piles that are the subject of this study consist of hydrothermally formed minerals formed along with the molybdenum mineralization, minerals that resulted from pre-mining weathering of the deposit, and minerals that formed during weathering of the waste piles. Hydrothermal minerals associated with the formation of the deposit have been summarized by Cline and Bodnar (1994), Klemm *et al.*

(2008), McLemore (2009), McLemore *et al.* (2009a, 2009b), and references therein. The alteration-product minerals are similar to other Climax-type deposits and consist of multiple-alteration minerals assemblages. Regional-scale propylitic alteration of the volcanic rocks that surround the deposit has led to the formation of chlorite, epidote, calcite, pyrite, and clay minerals. Minerals which have resulted from potassic alteration include K-feldspar, phlogopitic biotite, and illite; followed by quartz-illite-pyrite veins; argillic and advanced argillic alteration has resulted in the formation of chlorite, smectite, kaolinite, calcite, epidote, quartz, and pyrite. Some of the jarosite, gypsum, and clay minerals are also related to pre-mining supergene alteration of the deposit and adjacent host rocks. Post-mining weathering-product minerals include jarosite and gypsum which resulted from acidic, sulfate-bearing solutions from sulfide oxidation.

Previous work

Weathering and hydrothermal alteration can produce clay minerals. A conventional method to differentiate between the two primary types of clay deposits is the use of the stable isotopes deuterium and oxygen-18. Equations for isotopic fractionation between water and clay minerals have been established experimentally for most clay minerals (Savin and Epstein, 1970). The fractionation factors for clay minerals and water are temperature dependent, resulting in fields of probable isotopic signature of clay formation at any given temperature. The isotopic signature of any clay mineral is obtained by cross-plotting δD and $\delta^{18}O$ data obtained from oxygen and hydrogen structural sites in clay minerals. In most cases, experiments used to obtain equations for isotopic fractionation of clay minerals in water were conducted at standard temperature (25°C) and neutral pH. However, temperature within the Questa rock piles can reach 75°C and pH has been observed as low as 2.8 (McLemore *et al.*, 2009a; Reiter, 2009).

The results of the $\delta^{18}O$ and δD data, the geochemistry of water discharging from the toe of the Goat Hill North rock pile at Questa, and natural analogs adjacent to the mine site in the form of alteration scars led to the conclusion that no active formation of clays is occurring at the Questa Mine site (Graf, 2008; Donahue *et al.*, 2007). The second objective of this study was to validate conclusions made by previous studies using the tritium content of structural water in clay minerals.

Waters obtained from Straight Creek, a tributary drainage 5 km upstream of the Questa Mine Site, bore a δD signature of -86.56 to -133.61% . In contrast, the δD signature for adjacent groundwater monitoring wells was -92.12 to -100.06% (Naus *et al.*, 2005). Tritium data gathered from the same wells ranged from 6.64 ± 0.10 to 10.79 ± 0.15 TU. Wells within the monitoring group ranged in depth from ~ 30 – 60 m below the surface, with one well at 128 m below the surface. Groundwater ages, obtained by use of chlorofluorocarbons (CFC) and $^3He/^3H$ dating techniques ranged from 10 to 45 y (from CFCs) and from 0 to 22 y (from $^3He/^3H$) (Naus *et al.*, 2006). Most of the shallow groundwater samples obtained from a geographically adjacent Straight Creek location are <50 y old; therefore, similar isotopic signatures should be expected for pore water in shallow locations at the Questa Mine Site.

Thermal dehydroxylation of clay minerals

Generally, clay minerals undergo four types of thermal reaction: low-temperature reactions below 400°C, intermediate-temperature reactions from 400 to 750°C, high-temperature reactions at $>750^\circ C$, and oxidation reactions (Newman, 1987). For the purpose of the present study, the first two reactions were considered for extraction of water contained in clay minerals. Low-temperature reactions involve the removal of any residual pore, adsorbed, or

interlayer water in the form of molecular water (nH_2O). Intermediate reactions involve the dehydroxylation of clay minerals

Clay-mineral thermal behavior varies from mineral to mineral. In order to maximize the volume yield, water was collected from 20 to 345°C and was considered to represent pore, adsorbed, or interlayer water. Water collected from 350 to 800°C was considered to be structural in origin. Analysis of water derived from structural hydroxyl sites in clay minerals for the ratio between deuterium/hydrogen typically involves a small sample given that modern techniques for δD analysis require <5 mL of water. In many cases, where deuterium analysis is the only interest, water is converted to hydrogen gas using uranium or the zinc reduction method, again requiring a small amount of liquid water for accurate results (Savin and Epstein, 1970; Hyeong and Capuano, 2004). Significant contamination occurs when waters occupying adsorbed and interlayer sites in clay minerals are not fully removed before advancing thermal dehydroxylation (Savin and Epstein, 1970). Samples that were contaminated tended to yield intermediate values between modern stable isotope values and expected values depending on the sample. The water that occupies the adsorbed and interlayer sites in clay minerals can exchange completely with atmospheric water vapor or pore water within a few hours (Savin and Epstein, 1970). Deuterium occupies the same sites as tritium within clay minerals and so the same potential for contamination by isotopically exchanged pore water and interlayer water exists during extraction.

METHODS

Sample collection

Samples were collected from five sites from the Chevron Mining, Inc. site near Questa, New Mexico within Universal Transverse Mercator (UTM) zone 13S. Site 1 (DBF3) is located south of the main administrative building for the mine at 452369mE 4059919mN and consists of an inactive debris flow associated with mass wasting-type weathering that occurred before mining activity began in the area (Ayakwah, 2009). Site 2 (SSW3) is located at mid-elevation on the southern end of Sugar Shack West waste-rock pile at 453682mE 4060534mN. Site 3 (SSW7) is located on the top of Sugar Shack West waste-rock pile at 453975mE 4060822mN. Site 4 (SPR3) is located at mid-elevation on the Spring Gulch waste-rock pile at 455255mE 4060534mN. Site 5 (QPS3) is located near an alteration scar high on the north wall of the abandoned open pit mine at 454146mE 4062285mN. A sample (QPS-GYP) of gypsum that occurs in extensive amounts in veins adjacent to the alteration scar at 454107mE 4062831mN was collected to verify the method of extraction to be used on the bulk clay samples (Figure 2). Three precipitation samples were collected at various locations on Sugar

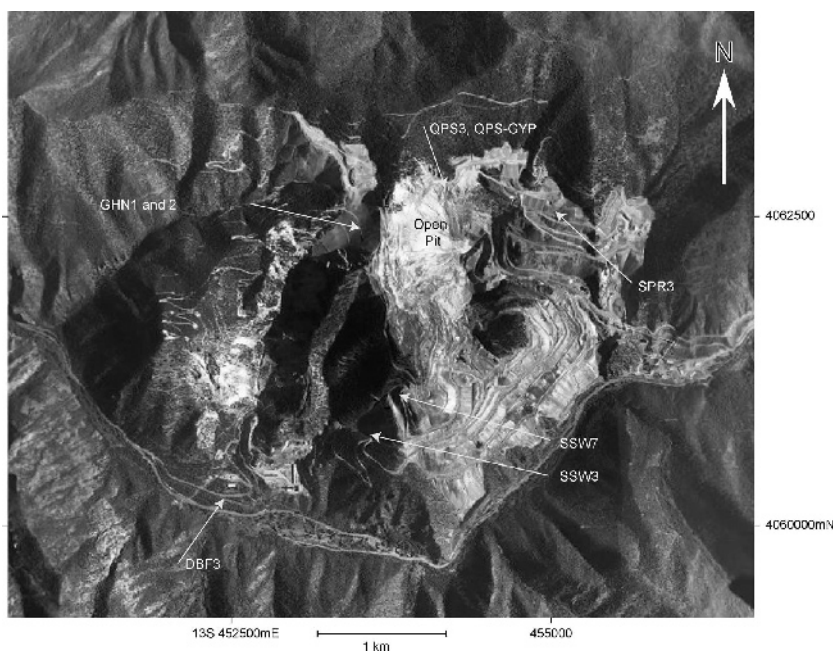


Figure 2. Locations of collection sites for bulk clay material at the Questa Mine site.

Shack South rock pile to identify the tritium signature of precipitation and give an estimate of probable near-surface pore water tritium values (Table 1).

In order to relate this study to work done previously on the Questa Rock Pile Weathering and Stability Project (QRPWASP, 2008), samples collected in a like manner from Goat Hill North (GHN) rock pile were utilized. The Goat Hill North samples obtained from New Mexico Institute of Mining and Technology (NMT) were collected in 22 L buckets during the reclamation of GHN when active trenching was occurring. After $6.35\ \mu\text{m}$ sieving of the raw material, sub-samples were combined to obtain enough water for tritium analysis. Combination of units was determined based on the location of the sample in relation to depth of trenching, resulting in two composite samples: GHN1 and GHN2 (Figure 2).

In addition to collection of samples in Questa, two shale samples of Carboniferous age were collected from sites in Utah. The samples were collected from excavated pits, and were near enough to the original ground surface to contain modern pore water, but minimal weathering products. Samples meeting this criterion exhibit the strongest contrast between tritiated pore-water sites and

non-tritiated structural sites. These samples can be used to evaluate effectively any contamination produced in collection intervals during thermal reaction of clay minerals. FMP-1 was collected from the Long Trail Shale (Mississippian in age) located near Five Mile Pass on the border of Utah and Tooele Counties near state route 73 in a recently excavated clay pit at UTM zone 12T 398757mE 4455150mN. Sample JR-1 was collected from Manning Canyon Shale (of Mississippian–Pennsylvanian age) located on the east side of the Lake Mountains in Utah County just south of Pelican Point, Utah Lake, west of state route 68 in a recently excavated clay pit at UTM zone 12T 424587mE 4452553mN.

The raw samples from Questa contained $\sim 3\text{--}5\ \text{wt.}\%$ clay ($< 2\ \mu\text{m}$ particle-size fraction). Each of the five bulk clay samples from Questa was sieved in the field to $< 6.35\ \mu\text{m}$ to increase the ratio of clay minerals to bulk. In the case of the shale samples, FMP-1 and JR-1, collected in Utah, the percentage of clay minerals was expected to be 30% or more, and thus bulk material was used. To minimize the presence of any clay minerals formed by recent active weathering, each of the Utah samples was collected at least 0.5–1.0 m below land

Table 1. Precipitation tritium values from Questa, New Mexico, USA.

Sample	Collection date	Tritium (TU)	1σ error (TU)
SSS-UTM-0013	5 February 2007	5.57	0.45
SSS-UTM-0015	5 February 2007	4.60	0.35
SSS-UTM-0017	5 February 2007	4.63	0.60

surface. In both the Questa and Utah samples, material was placed in a 22.5 L plastic bucket and sealed with a rubber o-ring. Isolation from the atmosphere upon collection prevented further exchange of pore, adsorbed, and interlayer water with atmospheric water after the initial collection.

Pore-water extraction

Separate 6.35 μm sieved bulk samples DBF3, SSW3, SSW7, SPR3, QPS-GYP, and QPS3 from Questa were placed in 2 L stainless steel cylinders. The headspace of atmosphere above the samples in cylinders was purged with dry nitrogen to limit isotopic exchange with the atmosphere. Each cylinder was placed under vacuum equal to 0.26664 Pa. After stabilization, liquid nitrogen (LN) was placed on an inline glass trap and the sample was isolated from the source of vacuum to prevent any 'blow-by' water vapor being lost to the vacuum pump. At this point the cylinder was heated to a temperature of 105°C using collar heaters, for 6 to 8 h, effectively cryodistilling the pore waters from the samples and trapping them in the LN-cooled glass trap. Cryodistillation under a sealed vacuum utilizing a LN trap limits any fractionization of water as this method traps all gases with freezing points greater than LN temperature. Cryodistilling was considered complete when the system registered <13 Pa at 105°C.

Dry sieving and sample preparation

Samples DBF3, SSW3, SSW7, SPR3, QPS3, GHN1, and GHN2 collected from Questa were dried in an oven at 90°C for ~48 h. After cooling, samples were dry sieved on a motorized agitator to 177 μm using a No. 80 mesh, yielding at least 1 kg of material, and placed in plastic sample bags. Shale samples collected from Utah were crushed and sieved to 177 μm , yielding at least 2 kg of material, and placed in plastic sample bags. All samples were funneled into quartz glass tubes of ~2 L volume capable of withstanding heat in excess of 1000°C. A total of 1–1.5 kg of 177 μm material was used for each site. All samples were mixed with 2 to 3 moles of cupric oxide to ensure that any sulfide minerals contained in the samples were oxidized, preventing the formation of hydrogen sulfide gas and free hydrogen gas.

Residual pore, adsorbed, interlayer, and structural water extraction

A known amount of sample was placed in a quartz glass tube and then loaded into a Lindberg tube furnace capable of being heated to 1000°C. The tube was then placed under vacuum until an inline Baritron pressure gauge registered 0.66661 Pa. Liquid nitrogen was placed around an inline glass trap of known mass and stepwise heating, begun at 200°C, was increased by 50°C every hour until 345°C was reached. In the case of samples from Questa, the combination of sulfide minerals and

cupric oxide reagent caused significant degassing of oxygen, carbon dioxide, and sulfur dioxide. The result of this degassing required that the vacuum pump be open to the sample for the duration of the thermal reaction. The consequence of having the vacuum pump open to the sample is the loss of any 'blow by' condensable gases that are not collected by the LN trap including some water vapor. An improvement in design would utilize a capillary between the quartz tube and the vacuum pump that would limit the amount of 'blow by' water vapor lost from the system. When the temperature reached 345°C the sample was isolated from the rest of the line and the vacuum pump, and the glass trap was removed from the system and sealed with rubber caps. The glass trap was then placed in a fume hood and connected to a flow of dry nitrogen to purge the headspace of the trap while the water, carbon dioxide, and sulfur dioxide melted/sublimed. When the melt/sublimation was complete, the trap was weighed and the mass recorded. Meanwhile, the bulk clay material was stepwise heated in the tube furnace from 345°C, increasing by 100°C hourly, to 800°C, and the previous collection procedure was repeated. In all cases, when higher temperatures were reached, the production of gases accelerated and most of the gases produced were trapped at LN temperature. The trap and pump assembly were mounted within a ventilation hood for safety purposes.

At the completion of the thermal reaction, the dehydroxylated sample was cooled for >72 h and was weighed and the dry mass of the bulk clay material recorded.

Extraction, degassing, and the ^3He in-growth method

Liquid water collected during the 0–345°C and the 345–800°C heating intervals were then extracted from the glass trap into separate stainless steel spherical flasks under vacuum for tritium analysis using the helium-3 in-growth method (Clarke *et al.*, 1976). Water was delivered to the flasks using a septum and stainless steel needle. As the water exited a needle into the flask, some was vaporized by high vacuum and was substantially degassed beyond its already distilled state. The flask was then agitated for a period of 1 h under vacuum to completely degas the sample of both ^3He and ^4He . Given the total volume of water degassed, a helium in-growth period of ~6 months was needed to provide results with an error of ± 0.5 TU. During this holding period, some tritium in the sample decayed to ^3He and was subsequently analyzed on a magnetic sector-field mass spectrometer at the University of Utah Noble Gas Laboratory. Because of the small volume of water yield in most of the clay samples, 1 σ error is larger than when a typical 500 mL sample is used.

Chemical and mineralogical methods

Separates of 177 μm dry sieved material from DBR3, SSW3, SSW7, SPR3, QPS3, GHN1, and GHN2 were

analyzed for major oxides by means of X-ray fluorescence (XRF) and sulfur and carbon analyses conducted using a Leco furnace by ALS Chemex (Reno, Nevada, USA). Analytical accuracy and laboratory procedures conformed to international standards ISO 9001:2000 and ISO 17025:2005. Analyses were accurate to the significant figures reported.

The <2 μm size fraction of each sample was extracted from the <177 μm sieved fraction by centrifuging. X-ray diffraction patterns were obtained from oriented smears on glass slides, following air drying, solvation with ethylene glycol at 60°C for 12 h, and heating to 350°C for 1 h, using a Rigaku D2200 V Diffractometer with Cu anode X-ray tube. The step size was 0.02°2 θ with a counting time of 1.2 s per step. Instrument alignment at low 2 θ angles was checked routinely with National Institute of Standards and Technology standard reference material 675 fluorophlogopite. The modal mineralogy was estimated by a least-squares fit of mineralogy, mineral chemistry, and whole-rock chemistry using MODECALC computer software (Parry *et al.*, 1980).

Thermogravimetric analysis

A 10–20 mg separate of the 177 μm dry sieved material from each of samples DBF3, SSW3, SSW7, SPR3, GHN1, and GHN2 was prepared for analysis of total water loss for the thermal reaction range 20–1000°C on a thermogravimetric analysis (TGA) system. The 177 μm separate from QPS3 was an undried sample. In this case, the oven volume was purged with dry nitrogen gas to prevent oxidation of sulfide minerals in samples during the thermal reaction. A thermal curve was produced by heating samples at 10°C/min for the 20–1000°C interval. The derivative of the weight *vs.* temperature curve was computed and plotted to identify thermal intervals where mass loss was most significant.

RESULTS

Verification of methodology by dehydration of gypsum

The sample QPS-GYP, consisting of vein gypsum collected adjacent to QPS3, yielded 150.70 mL of water from 898.30 g of gypsum. The sample was collected at exposed outcrops at the surface, and had been exposed to meteoric water for thousands of years. The water of hydration in gypsum yielded a tritium value of 0.60±0.31 TU (Figure 2, Table 2), a value which falls outside of the range of tritium in precipitation for the area, and verifies that the tritium identity of water derived within mineral structures is preserved by the method of vacuum cryodistillation.

Pore water and precipitation samples

Pore water collected from DBF3, SSW3, SSW7, SPR3, and QPS3 by cryodistillation yielded a range of 0.025–0.065 mL/g of water. Tritium values for the pore water ranged from 5.78 to 7.93 ± ~0.50 TU (Table 3). By

Table 2. Dehydration and tritium values from water in gypsum collected from Questa, New Mexico, USA.

Sample	Mass of gypsum (g)	Mass of $\text{CaSO}_4 - 1/2\text{H}_2\text{O}$ (g)	Mass of waters of hydration (g)	Gravimetric fraction of water in sample	Expected gravimetric fraction of water in $\text{CaSO}_4 - 2\text{H}_2\text{O}$	Waters of hydration tritium (TU)	1 σ error
QPS-GYP	898.30	747.60	150.70	0.17	0.20	0.60	0.31

comparison, precipitation within the last 10 y ranges from 5 to 15 TU and tritium from recent studies conducted by the US Geological Survey in Straight Creek drainage have yielded values of 6.64 to $10.79 \pm \sim 0.10$ TU for groundwater from wells (Naus *et al.*, 2005). Pore-water tritium analyzed from the five sites on the Chevron Mining, Inc. property near Questa fell within the expected values for shallow pore water derived from recent precipitation. Collected precipitation samples SSS-VTM-0013, -0015, and -0017 yielded tritium values ranging from 4.60 to $5.57 \pm \sim 0.50$ TU (Table 1).

Pore, adsorbed, and interlayer water collected over the 0–345°C thermal reaction of samples from Utah (FMP-1 and JR-1) was dominated by the tritium signal produced from pore water due to the fact that these two samples were not baked in an oven at 90°C to remove the majority of the pore water. FMP-1 and JR-1 yielded 0.078 mL/g and 0.029 mL/g of water, respectively, from pore, adsorbed, and interlayer water sites and tritium values of 7.96 ± 0.81 and 6.45 ± 0.44 TU, respectively (Figure 3, Table 4). Pore-water tritium analyzed from Five Mile Pass, Utah, and Jack Rabbit Pit, Utah, USA fell within expected values for shallow pore water derived from recent precipitation.

Residual pore, adsorbed, interlayer, and structural water samples

Samples SSW3, SSW7, QPS3, GHN1, and GHN2 collected at the Questa site, yielded 0.013–0.021 mL/g of water from pore, adsorbed, and interlayer sites, and 0.022–0.026 mL/g of water from structural sites. The

small volume of water derived from the pore, adsorbed, and interlayer sites was used to verify the results produced from the pore-water samples. Pore, adsorbed, and interlayer water yielded tritium values ranging from 5.31 to $12.19 \pm \sim 1.50$ TU. The increase in error is due to smaller than normal analysis volumes (25 mL) used in the present study (Figure 3) (Table 3). Replicating the accuracy of larger-volume samples would require an in-growth time in excess of 8 months. While the results of the small-volume samples broadened the range of tritium occupying pore spaces, the range still falls within expected values for shallow pore water derived from recent precipitation.

Samples DBF3, SSW3, SSW7, SPR3, QPS3, GHN1, and GHN2 yielded 0.022–0.045 mL/g of water from the interlayer ion sites and structural sites in clay minerals. Tritium values from the interlayer ion sites and structural sites ranged from 3.92 to 7.23 TU with errors ranging from ± 0.37 to 1.46 TU depending on the volume of water processed (Figure 3, Table 3). The Utah samples, FMP-1 and JR-1, yielded 0.043 mL/g of water from the structural sites in clay minerals. Structural sites for FMP-1 were not analyzed due to the large amounts of ammonia produced by ammonium illite in the sample. Structural sites for JR-1 yielded a tritium value of 1.35 ± 0.48 TU (Figure 3, Table 3).

Chemistry and mineralogy results

Minerals present in the Questa samples include primary igneous minerals, minerals that resulted from hydrothermal alteration of the host igneous rocks, and weathering-product minerals (McLemore *et al.*, 2009b).

Table 3. Dehydration and dehydroxylation of bulk clay samples from Questa, New Mexico, and Utah.

Sample	Mass of wet bulk (g)	PWAIL water (cm ³) ^c	STRUC water (cm ³) ^d	Mass of de-hydroxylated bulk (g)	Clay mineral fraction normalized to kaolinite	PWAIL water tritium (TU)	1 σ error (TU)	STRUC water tritium (TU)	1 σ error (TU)
DBF3 partial ^{b,f}	932.10	60.58	42.05	829.47	0.54	7.93	0.59	5.94	0.57
SSW3 partial ^{b,f}	999.80	39.32	30.51	929.97	0.35	7.15	0.44	4.96	0.61
SSW7 partial ^{b,f}	998.00	32.87	35.36	929.77	0.41	6.12	0.40	6.80	0.43
SPR3 partial ^{b,f}	911.20	41.07	23.68	846.45	0.30	7.95	0.57	7.04	0.64
QPS3 partial ^{b,f}	1150.10	28.58	39.41	1082.11	0.39	5.78	0.28	5.60	0.30
GHN1 full ^a	905.90	19.35	21.84	864.71	0.27	11.42	1.20	4.86	1.37
GHN2 full ^a	836.50	11.03	18.56	806.91	0.25	12.19	1.07	6.07	1.46
SSW3 full ^a	1092.80	14.16	26.12	1052.52	0.27	9.98	1.02	7.23	0.75
SSW7 full ^a	1063.40	18.14	26.14	1019.12	0.28	12.02	1.04	3.92	0.55
QPS3 full ^a	1091.30	15.04	28.22	1048.04	0.29	5.31	1.43	6.21	0.60
JR1 full ^a	1428.30	42.04	61.34	1324.94	0.49	7.96	0.81	1.35	0.48
FMP1 full ^a	1502.90	117.47	64.15	1321.28	0.51	6.45	0.44	ND ^e	ND ^e

^a full = samples using a 345–800°C structural water window.

^b partial = Samples using a 200–800°C structural water window.

^c PWAIL = pore, adsorbed, and interlayer water.

^d STRUC = water derived from structural hydroxyl sites in clay minerals.

^e ND = no data.

^f PWAIL in these samples refers to porewater only.

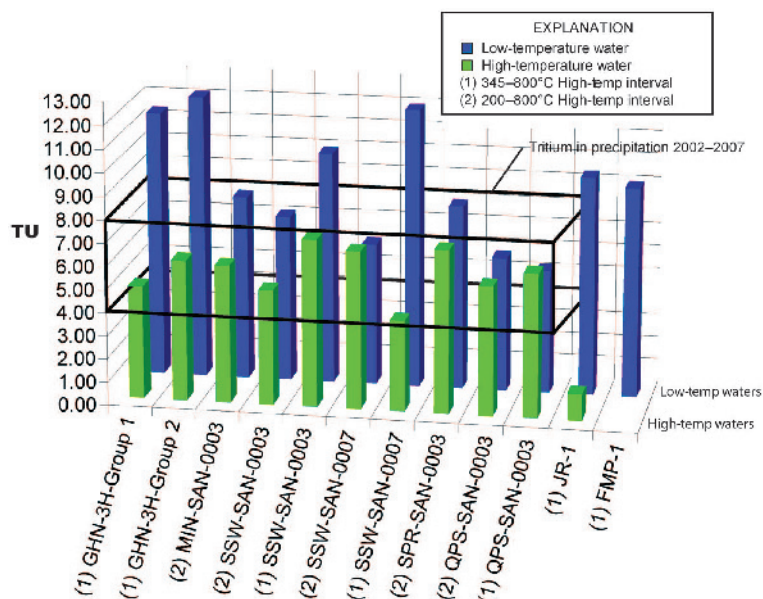


Figure 3. Tritium derived from pore, adsorbed, interlayer, and structural water from Questa, New Mexico, and Utah, USA. The high-temperature waters include pore water, adsorbed water, and some interlayer water. The low-temperature waters include structural water and some interlayer water.

Bulk-chemistry results (Table 4) include C from calcite and S from sulfide and sulfate minerals. Weight loss on ignition (LOI), measured following ignition to 1010°C of the samples dried at 110°C, included C, S, and H₂O.

X-ray diffraction (XRD) analysis of samples from Questa revealed that five common clay mineral species are present throughout the site: kaolinite, chlorite, illite, smectite, and mixed-layer illite-smectite (I-S) clay minerals (Figure 4). The clay size fraction also contains jarosite (Figure 4). Mineral abundances (Table 4) are: (Illite + I-S) 5–9%, smectite 3–7%, kaolinite 7–21%, chlorite 4–10%, jarosite 7–15%, and gypsum 5–11%. The samples also contained feldspars and quartz (Table 4). The chemical composition, XRD analysis, and mineralogy of samples from Utah revealed that clay minerals in FMP-1 are R3 I-S (61%) and kaolinite (3%) and the clay minerals in JR-1 are R1 I-S (rectorite) (15%), R>3 I-S (27%), and pyrophyllite (49%) (Table 4, Figure 4).

Thermogravimetric analysis

In all Questa samples other than QPS3, the derivative curve of the thermal reaction curve showed significant losses of mass at 100–110°C and for all samples at 500–600°C. A less pronounced peak was observed in the 350–450°C interval (Figure 5). Mass lost during the 100–110°C interval represented pore water. Mass lost during the 500–600°C interval represented dehydroxylation of clay minerals. The mass lost during 350–450°C interval lies within the thermal interval known for thermal reaction of interlayer hydronium (Loucks, 1991). Noise in the initial heating (0–200°C)

of the QPS3 was probably a result of evaporation of a substantial amounts of pore water in the undried sample.

Interlayer hydronium contamination mass balance

In acid solutions, hydrogen ions occur in the form of hydronium (H₃O⁺) that may substitute for K⁺ in potassium minerals such as jarosite and illite. Loucks (1991) established that H₂O bound in interlayer sites makes up a substantial proportion of structural water in most hydrothermal muscovite samples. Heating these minerals releases hygroscopic surface water below 110°C, interlayer molecular H₂O, and hydronium in the 200–500°C range and structural dehydroxylation at 600–700°C. Exchange of hydrogen isotopes with water released at 110°C takes place in hours, exchange with interlayer hydronium takes place in 6–12 weeks, and exchange with structural OH could not be detected in the experiments for up to 2 y (Moum and Rosenqvist, 1958). Minerals formed by hydrothermal alteration or weathering (illite, jarosite) and which contain hydronium could exchange hydrogen isotopes in the interlayer sites at the temperature range that exists within the mine-waste piles.

At low pH, hydronium ions can constitute a large fraction of the exchangeable interlayer cations. Using data obtained from the thermogravimetric analysis, a mass balance was calculated for the total influence of hydronium ions on the tritium results. For the thermal interval 345–800°C, two subintervals were calculated in terms of total mass. The interval containing the thermal reaction of hydronium ions from interlayer sites in clay minerals was assigned to 345–500°C. The interval containing the

Table 4. Bulk chemical analysis (wt.%) and *MODECALC*-estimated mineral abundance (wt.%) of 200 µm dry sieved separate.

Sample	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	Na ₂ O	K ₂ O	Cr ₂ O ₃	TiO ₂	MnO	P ₂ O ₅	SrO	BaO	LOI	Total	C	S
DBF3	62.22	14.89	6.22	0.14	0.89	0.54	4.2	<0.01	0.69	0.03	0.231	0.02	0.12	8.89	99.08	0.64	0.93
SSW3	54.88	13.64	6.58	3.93	2.26	1.68	3.09	0.01	0.72	0.08	0.316	0.06	0.09	10.85	98.19	0.05	2.5
SSW7	47.82	14.32	7.85	4.41	1.24	0.53	3.85	0.01	0.63	0.09	0.316	0.04	0.1	14.2	95.41	0.08	3.94
SPR3	53.79	13.4	8.86	4	3.71	2.08	2.59	0.02	0.82	0.17	0.398	0.08	0.09	8.22	98.22	0.07	1.48
QPS3	52.74	13.79	8.33	3.48	1.25	0.74	3.43	0.01	0.65	0.03	0.372	0.05	0.1	11.15	96.12	0.07	3.05
GHN1	48.76	14.9	8.87	5.05	2.28	1.33	2.23	0.01	0.69	0.38	0.361	0.04	0.08	11.4	96.39	0.05	2.35
GHN2	46.65	13.6	12.59	4.56	2.31	1.28	2.18	0.01	0.79	0.33	0.571	0.04	0.07	13.25	98.24	0.06	2.62

K-feldspar	Quartz	Andesine	Chlorite	Sericite (I-S and illite)	Kaolinite	Smectite	Jarosite	Gypsum	Pyrophyllite	I-S
DBF3	14	4	4	6	21	7	8	NP	NP	NP
SSW3	11	15	10	7	9	3	8	9	NP	NP
SSW7	14	6	5	9	12	3	13	11	NP	NP
SPR3	8	17	17	6	7	3	7	5	NP	NP
QPS3	12	8	5	9	10	3	13	8	NP	NP
GHN1	6	13	11	6	15	4	10	9	NP	NP
GHN2	3	11	11	5	16	3	15	8	NP	NP
JR1	NP	NP	NP	27	NP	NP	NP	NP	49	15
FMP1	NP	NP	NP	61	3	NP	NP	NP	NP	NP

NP = not present. Samples may also contain pyrite, apatite, epidote, hornblende, and other minerals not modeled.

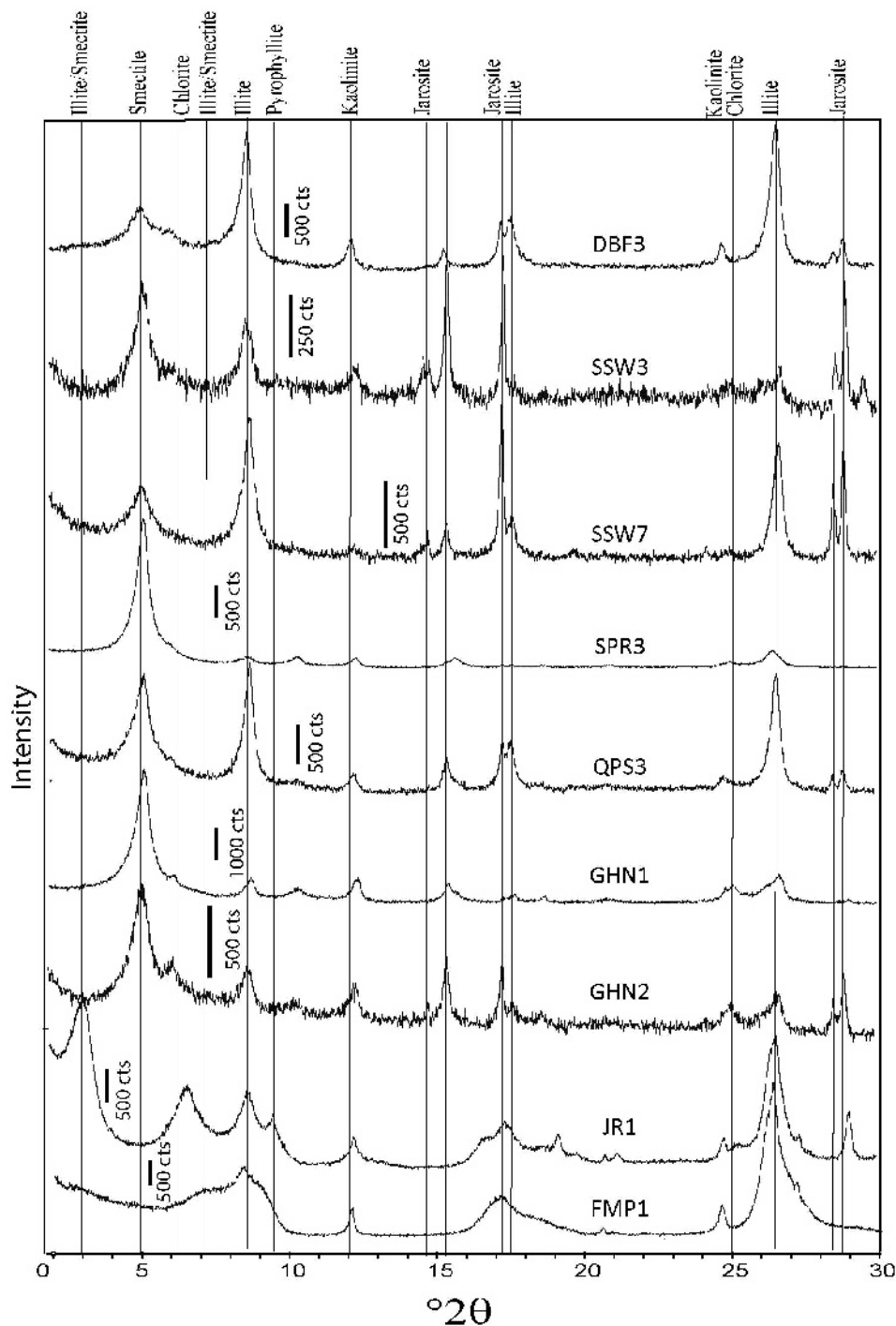


Figure 4. XRD patterns for the <2 μm clay size fraction extracted from the <200 mesh sieved samples by a series of centrifugation steps. The diffraction traces are for samples glycolated at 60°C for 12 h.

thermal reaction of structural water in clay minerals was assigned to 500–800°C. The lower interval yielded 30–40% of the total mass lost for the 345–800°C interval, while the higher interval yielded 60–70% of the total mass for the 345–800°C interval (Table 5).

DISCUSSION

Accuracy of results from low-volume tritium samples

Typically, water samples analyzed for tritium at the University of Utah Noble Gas Laboratory use 250 or

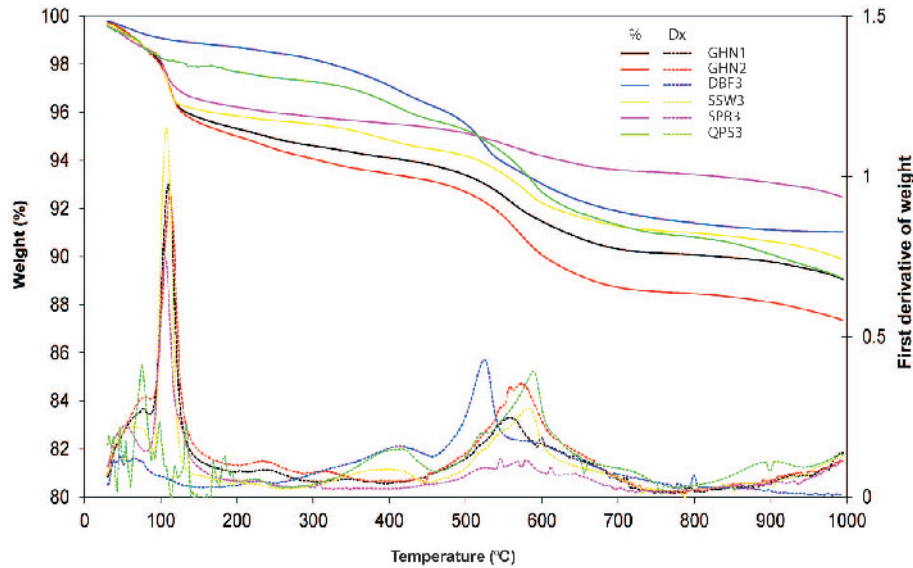


Figure 5. TGA (upper curves) and DTGA (lower curves) analyses of samples from Questa, New Mexico.

500 mL of water in the ^3He in-growth method. Typical in-growth periods for 250 and 500 mL samples are 2 months and 1 month, respectively. Decreasing the volume results in an increase in in-growth time to attain similar accuracy due to the presence of fewer ^3H atoms by volume, thus producing less ^3He in a given time period. In order to verify the accuracy of low-volume samples, a series of standards was extracted using similar volumes of water and analyzed simultaneously with samples from this study. Four standards were selected to represent the expected tritium values in this study: University of Utah Noble Gas Lab-produced standards at 0.00 TU and 2.37 TU, and International Atomic Energy Agency (IAEA, 2006) standards at 0.00 TU and 24.95 TU. The lab-produced standards were prepared by diluting a National Bureau of Standards (NBS) standard containing 2.009 Bq/g tritium with tritium-free water. The results yielded by analysis of these standards supported an analytical error of no

more than 1 TU for the clay samples, which is sufficient accuracy to distinguish samples that are tritium-free from samples that contain significant amounts of tritium in post 1960s water.

Separation of low- and high-temperature thermal reactions

Clay minerals in samples collected near Questa and in Utah include a range of clay species and abundances. A varied release of structural hydroxyls from various clay minerals was expected. In order to reduce contamination of water derived from structural water, the mineral with the highest thermal reaction temperature for adsorbed and interlayer water, or in this case, waters of hydration, was selected as a thermal threshold. Jarosite in the Questa samples released its hydration water at the highest temperature among the species present. Hydronium jarosite loses both its structural water and its hydration water at between 262 and 385°C (Frost *et al.*, 2006.) The water derived from loss of hydrogen ions in the hydronium-occupied potassium site occurred at 557°C. The clay minerals included in this study lost pore, adsorbed, and interlayer water by 400°C, where dehydroxylation began to occur (Newman, 1987). Conventional methodology used in stable isotope studies of clay minerals typically utilize a >200°C threshold for structural water (Savin and Epstein, 1970; Hyeong, 2004). Because samples used in this study contain minerals other than pure clay minerals, a 345°C threshold was used. The rationale for using 345°C as a dividing temperature resulted from the need to minimize the contamination potential from jarosite, while obtaining enough high-temperature water to conduct reliable tritium analyses. Jarosite comprised an average of

Table 5. Mass balance for hydronium interlayer sites.

Site	Low-temp/high-temp (%)	Tritium concentration of low-temp water required to produce study results (TU)
DBF3	44/56	13.50
SSW3	30/70	21.20
SPR3	39/61	18.05
QPS3	31/69	19.01
GHN1	23/77	21.13
GHN2	20/80	30.35

10.6% of the total sample weight and did not contaminate significantly the results for structural water from Questa. Ideally, a much larger sample would be used, on the order of 5 kg of bulk material, and a 560°C threshold for structural water would be used.

Verification of separation of waters from thermal reaction

To evaluate if contamination occurred for the chosen low-/high-temperature water intervals, samples were collected from a second site independent of the Questa study. The characteristics of the second site required that the sample contained clay minerals that formed prior to possible exposure to tritiated waters, were near enough to the surface to have been exposed to modern meteoric waters either directly or by percolation, and had not undergone any significant weathering. These criteria ensured that the clay minerals retained their isotopic signature of formation and were in interlayer contact with modern meteoric water. The Utah shale sites were chosen based on these criteria and were collected from recent mining pits that would be unlikely to show any weathering products but have pore water of modern origin. Collection sites from both clay pits represent lithology that would have been at least 20 m below the surface 30 y ago. In both cases extra care was taken to collect after additional hand excavation to minimize the amount of any weathering products. The results of analysis on FMP-1 and JR-1 yielded a pore, adsorbed, and interlayer water tritium signature that fell in an expected modern precipitation at 6.45–7.96 TU and a structural water tritium signature that suggests water dominated by pre-1960s formation at 1.35 TU (Figure 3). More importantly, these results verify that the use of a 345–800°C window for structural water effectively separates low-temperature thermal reactions from high in terms of dehydroxylation for the relatively neutral pH environment from which the Utah samples were collected.

Origins of clay minerals on the Questa site

Based on the results in Figure 3, significant amounts of tritium were observed in the high-temperature water, or water derived from the structural sites and interlayer cation sites. For comparison with stable isotopes, both the deuterium and tritium atoms occupy the same sites within a clay-mineral structure; therefore, they should yield similar results. If the clay minerals found on the Questa site are indeed weathering products, the deuterium results should be similar to average deuterium values found in a modern precipitation. The results of the stable isotopes study on clay minerals at the Questa site yielded δD values ranging from –65 to –95‰, a study which concludes that the clay minerals found in the rock piles on the Questa site are hydrothermal in origin (Graf, 2008; Donahue *et al.*, 2007; Donahue *et al.*, 2009). This range falls within a range of δD values in surface and groundwater found in a study conducted by

the US Geological Survey in 2005 and similar to average meteoric water for the region (Naus *et al.*, 2005). The water collected for deuterium analysis included thermal intervals below 200°C, thus including substantial amounts of pore water, and all water on interlayer and adsorbed sites. Given the low-pH environment and the probable hydronium ion exchange for potassium sites in illite, conclusions made by stable isotopes based on deuterium values were probably inaccurate.

Other work at Questa has concluded that significant weathering is not occurring within the waste-rock piles. Petrographic observation of many sites at Questa suggested that new fringing clays were not occurring on silicate minerals, and so no new clays are forming (Dunbar *et al.*, 2008). Analysis of natural analogs (in the form of alteration scars) in the area, where abundant clay minerals exist from initial hydrothermal alteration where pH is very low, showed no new formation of clay minerals by weathering processes (Graf, 2008). The alteration scars reflect an environment very close to the conditions observed within waste-rock piles at the Questa area. Analysis of a spring that discharged at the toe of Goat Hill North Rock Pile showed a geochemical regime that is not ideal for the formation of clay minerals, but rather is more likely to dissolve clay minerals due to the low-pH waters (from the oxidation of sulfide minerals and subsequent acid formation within the rock pile) (M. Logsdon, pers. comm., 2010). Although this is true for areas where oxygen and water saturation are plentiful, it may not be true for the entire waste-rock pile. The water at the toe of Goat Hill North may not represent the hydrologic chemistry of all pore water within the rock pile; rather, it may only represent some preferential flow within the rock pile. Logsdon (pers. comm., 2010) stated: “There is substantial evidence, from Questa rock piles and other rock piles, that there are zones of preferential flow, both upward of air and downward of water.” In addition, Logsdon (pers. comm., 2010) observed that the stable isotope signature of water that discharged from the toe of Goat Hill North resembles non-evaporated meteoric water, or water that has passed quickly through the rock pile by preferential flow. Areas of anoxic conditions within the rock pile where clay formation is geochemically feasible is a possibility.

Potential contamination sources

The only potential hydrous mineral that may contribute to elevated tritium in the high-temperature water is jarosite. The results of the bulk chemical composition analysis yielded an average mineral abundance of 10.6% jarosite in samples used for tritium analysis (Table 4). The water reacted from this percentage of the sample above 345°C contributed to the elevated levels of tritium in the high-temperature water, but at a diminished level and does not explain the observed high tritium values.

Pore water in the Questa rock pile has a low pH and may exchange hydronium for potassium in illite and

jarosite. All of the samples collected from Questa for the tritium study contained a significant amount of illite in the <177 μm dry-sieved separate. The chemical composition and structural orientation of the aluminosilicate layers in illite result in the tritium being especially susceptible to interlayer potassium exchange with hydronium (Loucks, 1991). Up to 30% of the water yielded by the total thermal reaction to dehydroxylate the illite structure can be assigned to interlayer hydronium (Loucks, 1991). If a 0 TU tritium signature is assigned to all water collected above 500°C in the thermal reaction, the tritium signature necessary to produce the observed result for the 345–800°C interval ranges from 15 to 30 TU, by mass balance calculation (Figure 5, Table 5). Decay-corrected water with this isotopic signature at the time of collection in 2007 represents meteoric waters from the mid-1960s to the late 1970s (Figure 6). The 1970s through the early 1980s were years of the most active period of open-pit mining at Questa, correlating to the inception time of chemical alteration within waste-rock piles after emplacement. Interlayer hydronium replaces interlayer K and becomes isotopically unique like structural hydroxyl, in that the interlayer ionic site does not exchange at low temperature.

CONCLUSIONS

The results of tritium derived from structural hydroxyl sites in clay minerals on the Questa site can be represented by a conceptual model. Originally, before any open-pit mining occurred, hydrothermally formed clay minerals at the Questa site were at depth in unsaturated environments that were anoxic and at neutral pH. During the 1970s and 1980s the Questa open-pit mining operation excavated a large amount of ore

material including hydrothermal clay minerals. Waste rock from the open-pit mining operation was disposed of in areas adjacent to the open pit, eventually forming the waste-rock piles observed in 2007. The environment near the surface of the waste-rock piles became more acidic as exposure to meteoric water and oxygen increased. Conditions within the rock piles resulted in very low-pH pore waters with abundant sulfide oxidation and acid production. During this period, clay-mineral interlayer potassium exchanged readily with abundant hydronium ions in solution; thus the isotopic signature of the hydronium in solution reflects the isotopic signature of the meteoric water at the time of potassium-hydronium replacement.

By taking the most extreme case, where all water collected above 500°C is assigned 0.00 TU, the water collected from 345–500°C must be at most 15–30 TU. These values coincide with the period when hydronium would be replacing potassium in illite mineral structures (Figure 6). Given this result, the majority of the clay minerals with the Questa rock piles are probably hydrothermal in origin and not new weathering products. The elevated tritium in the high-temperature interval can be explained by interlayer hydronium contamination, but may be the result of a combination of contamination, possible exchange, and small fractions of new weathered clays existing in anoxic portions of the rock piles.

Most importantly, the results of the present study revealed that when examining the isotopic characteristics of clay minerals in low-pH environments, a new methodology must be adopted. Accurate examination of structurally bound hydrogen in clay minerals at low pH requires that only water collected from 500°C and above be considered when identifying the isotopic signature of formation. In addition (and as mentioned by Loucks, 1991), the hydronium interval interlayer water collected from 300–500°C in a low-pH environment clay mineral may provide information about the recent history of the clay. In this case, the hydronium in water probably revealed the timing of the excavation and subsequent interlayer exchange of the potassium for hydronium ion.

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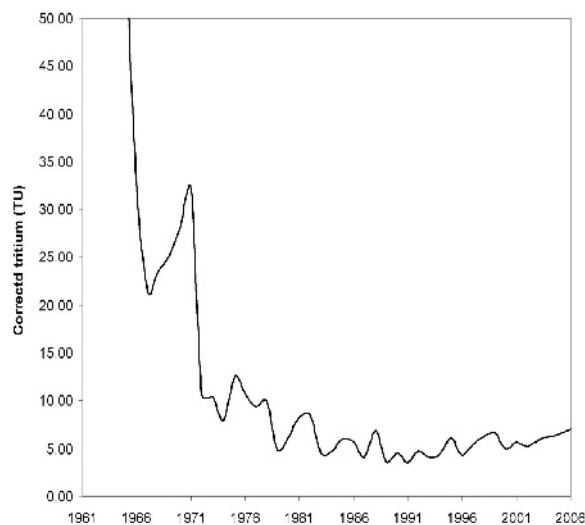


Figure 6. Decay-corrected tritium curve for precipitation in Albuquerque, New Mexico, in 2007.

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