Mineralogy of suspended sediment in three karst springs

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Abstract Springs in karstic carbonate rocks frequently carry a sediment load as well as a dissolved load. Analysis of morphology and mineralogy of suspended sediment from three contrasting karst springs reveals a suite of clastic particles that reflect both source areas and processes that take place within the aquifer. Nolte Spring in Lancaster County, Pennsylvania discharges sediment of apparently precipitated calcite indicating that at some point in the aquifer or vadose zone, water exceeds saturation with respect to calcite. Sediment morphologies and chemical conditions in the aquifer point to two different scenarios for this precipitation. The other two springs, Arch Spring in Blair County, Pennsylvania and Bushkill Spring in Northampton County, Pennsylvania, show no evidence of calcite precipitation. Arch Spring discharges mainly layer silicates while Bushkill Spring discharges mainly silica.
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Introduction

Springs draining from carbonate aquifers frequently carry a load of suspended sediments that varies with discharge and other factors. Karst springs often become turbid or completely muddy during storm flow. Sediment fluxes in karst aquifers are clearly episodic. Sediments move mostly during storm flow and fluxes decrease to a low background of small particles during base flow. There has been a good deal of recent interest in the clastic sediments discharged from karst springs because of their importance when the springs are used as water supplies and for the role of clastic particles in contaminant transport.

Much of the literature on clastic sediments in karst drainage basins is concerned with the sedimentary deposits found in caves. In active stream caves, these represent sediments in transit, i.e. sediments carried a certain distance during a previous storm and held in storage waiting for a storm of sufficient magnitude to move them again. When the conduit system is drained, the sediments in residence at the time are trapped in the dry cave where they can be examined and interpreted. A variety of facies have been recognized, ranging from laminated clays to boulder piles (Bosch and White 2004). Cave sediments are of interest, both intrinsically in terms of transport mechanisms, and as archives of paleoclimatic information. However, the sediment piles observed in caves are mostly much coarser material than the small size particle fraction that is easily mobilized and carried from the aquifer to the spring orifice during ordinary storms. These fine-grained suspended sediments are less well studied and are the subject of interest in the present paper.

The conduit system of a karst aquifer acts as both mixing and storage chamber for clastic sediments. Fluxes of sediment are input from sinking streams, from soil piping from sinkhole drains, from soil washdown from the epikarst, and as the residual insoluble fraction remaining after dissolution of the limestone. Materials from these varied sources are mixed in the conduit system, differentiated according to density and particle size, and transported when the storm flows through the aquifer reach necessary thresholds. Most easily moved are the fine-grained, uncompacted sediments and these often appear at springs during low to moderate flows. Coarser materials appear at springs only when flows exceed thresholds and are observed only during exceptional storms (Herman et al., 2005).

Most of the literature concerning suspended sediments discharged from springs is quite recent and deals with the mechanisms of sediment transport (e.g. Mahler and Lynch 1999; Amraoui et al. 2003; Massei et al. 2003; Peterson and Wicks 2003; Dogwiler and Wicks 2004). Only a few papers address the question of the actual mineralogical content of the suspended sediment (Drysdale et al. 2001; Lynch et al. 2004; Mahler et al. 2004). It has been demonstrated that bacteria (Mahler et al. 2000) and heavy metals (Vesper and White 2003) are carried through karst aquifer systems attached to small sediment particles. Particle mineralogy, composition, and surface morphology would seem to be useful as a possible source of information about internal processes within the aquifer.

The present paper reports sediment particle characterization from three springs in Pennsylvania, shown and described in Figure 1. The three springs investigated were selected to represent different hydrologic settings in terms of the type of recharge and the characteristics of the aquifer feeding the springs. A discussion of storm variation in specific conductance related to sediment transport is being published elsewhere (Toran et al. 2006).

Spring Descriptions

Arch Spring is the downstream outlet of a master conduit system that drains Sinking Valley, Blair County, Pennsylvania. It is the headwater of the lower portion of Sinking Run, which drains into the Juniata River, a tributary of the Susquehanna River. The master conduit can be accessed through Tytoona Cave with an entrance in a collapse sink 1.2 km upstream from the spring, although much of the conduit lies upstream from the collapse sink. Cave divers have explored almost the entire length of conduit between the cave and the spring. The discharge is on the order of 250 – 400 L/s at baseflow. The spring and master conduit are developed in the Grazier member of the Hatter Formation, a lower unit of the Ordovician Black River Group (Rones, 1969). Below this limestone unit, the carbonate sequence consists mainly of dolomite (Fig. 1). The recharge reaching the spring is from mountain runoff that sinks where the Reedsville Shale contacts the limestones and from direct infiltration through the limestone soils of the carbonate valley uplands.

Nolte Spring is located in West Earl Township, Lancaster County, Pennsylvania. It is approximately 4.5 meters in elevation above and 200 meters upstream from Conestoga Creek, the base-level surface drainage for the area. Conestoga Creek is part of the Susquehanna River drainage. The spring orifices are two 15-cm diameter solutionally-widened fractures located in a chamber beneath the pumping station for the West Earl Township Water Authority. The spring was at one time used as a public water supply, but that usage was discontinued because of increased turbidity following storms.

The base flow discharge is about 25 L/s. The bedrock at the spring is the Ordovician Epler Formation, the middle unit of the Beekmantown Group of mixed limestones and dolomites. The catchment area for the spring is a carbonate rock upland with numerous sinkholes but little evidence for allogenic recharge. Most water entering the aquifer must percolate through a soil cover.

Bushkill Spring in Northampton County, Pennsylvania, discharges from a sequence of small openings along bedding planes just above stream level on Bushkill Creek about 12 km upstream from the creek's confluence with the Delaware River. There are multiple discharge points but no distinct solutionally-widened conduit at the surface. The orifice chosen for measurement was about 5 cm wide and had a base flow discharge on the order of one L/s. The spring orifices are close to the contact between the Ordovician Epler and Rickenbach Formations, both consisting of interbedded limestone and dolomite. The recharge area is a carbonate upland that includes an athletic field that has been plagued with sinkholes, but a hydraulic connection between the sinkholes and the spring has not been determined. Although an integrated conduit system has not been demonstrated, the drainage basin is small and flow paths are short.

Sediment Sampling and Analytical Methods

During site visits to each spring, samples were collected for suspended sediment analysis, major cation and anion analysis, and alkalinity titration. Site visits were spaced from two weeks to one month apart depending on the time of year and storm frequency, and the sampling period continued from July 2002 to August 2004 at Bushkill and Nolte Springs and December 2003 to December 2005 at Arch Spring. In addition to monthly samples, ISCO™ automatic samplers placed at each of the springs collected water samples when triggered by a rise in water level. The sampler took 24 samples spaced at pre-set intervals. The intervals were selected based on the typical storm duration at a spring.

The samples collected for water chemistry were filtered in the field and refrigerated until analysis by ion chromatography and by titration for alkalinity. The pH and temperature of samples were recorded in the field. The stormwater samples and one set of monthly samples were filtered in the laboratory to remove suspended sediments from the water for analysis. The samples were filtered sequentially on 5 μm and 0.45 μm mixed-cellulose or cellulose nitrate membrane filters. Because sediment concentrations were low during storms at Nolte Spring, much of the information on Nolte is based on monthly samples. The other springs generally showed higher suspended sediment concentrations during storms.

A scanning electron microscope (SEM) with energy dispersive X-ray spectroscopy (EDX) was used to examine filtered sediments from the three springs. The SEM was useful for surveying the filtered sediment and investigating questions of morphology, while the EDX determined the chemical composition of various target grains of sediment. The combination of morphology and bulk chemistry allowed identification of most mineral grains to a low degree of specificity. X-ray diffraction (XRD) to determine mineralogy of crystalline phases was used on the few samples for which there was adequate crystalline sediment for analysis.

While composition results for filtered sediment have provided insight into spring behavior, attempts to determine sediment size distributions have to date not been particularly successful. Clumping of sediment, particularly clay-rich sediment, on the 5.0 μm filters prevented the use of different-sized filters for sizing, and the irregular shape of most particles made other sizing methods impractical.

Mineralogy and Composition of Suspended Sediments

Arch Spring

Some representative images of Arch Spring sediment, shown in Figure 2, display a range of morphologies with fossil fragments and some coarse-grained minerals easily visible. However, the bulk of the material was fine-grained even at the SEM scale in low vacuum mode so that morphologies and bulk composition of individual particles could not be determined. EDX analysis showed silicon and aluminum to be the dominant components with concentrations of potassium and iron appearing in some samples. Figure 2-i features a sample taken on the recessing limb of the hydrograph following a minor storm, while Figure 2-ii depicts a sample taken on the recession limb following a larger storm and at the beginning of one of the largest storms collected. Figure 2-iii is from the same storm as Figure 2-ii, but the water level had already risen 20 cm illustrating that, regardless of discharge at the spring and timing in relation to a storm event, clay minerals and silica are the most common particles at Arch Spring. The presence of potassium indicates that illite or possibly muscovite is likely present although the characteristic micaceous morphology was not apparent. Iron-rich grains may be iron oxyhydroxides. One flake of a calcium-rich grain was detected in a storm sample from September 1, 2003 (Figure 2-iii). This appeared to be biologically precipitated calcite, but was unique among the Arch Spring samples investigated and therefore not a common component.

The water from Arch Spring over the course of this study and in a previous study (Shuster and White 1971) consistently remained well below saturation with respect to calcite and dolomite, as the saturation indices of calcite (SI_C) and dolomite (SI_D) were negative and CO_2 partial pressure (P_{CO2}) was high. Tytoona Cave upstream of Arch Spring was also undersaturated. The silicate-dominated sediment discharged from Arch Spring was consistent with the relatively low specific conductance (from about 80 μS/cm to 260 μS/cm) and low SI_C of the water (-1.01 to -0.76).

Nolte Spring

The sediments from Nolte Spring were surprising in that they contained substantial amounts of calcite as shown in Figure 3. Because of the substantial variation in calcite morphology in monthly samples, further data on temporal variation in Nolte spring geochemistry are also presented. Representative examples of the calcite morphologies observed with SEM are shown in Figure 4, and discussed further below.

In a few samples, the quantity of sediment was sufficient to allow mineral identification by XRD. The X-ray pattern of a July 9, 2003 sample revealed calcite almost exclusively (Figure 3-i). Other samples, like one taken September 15, 2003 (Figure 3-ii), consisted of a mix of quartz, calcite, muscovite, and chlorite. Siliciclastics predominated in some samples (Figure 3-iii), but sediment concentrations of the calcite-rich samples were generally higher than those of the siliciclastic samples as illustrated in Figure 5. It was more difficult to assign a specific mineral composition to samples with sparse sediment and no calcite. In these samples, individual particles were indistinguishable (Figure 3-ii), or there were only a few small particles with indistinct morphology on which to base the determination (Figure 3-iii).

Variations in sediment concentration through time at Nolte Spring are shown in Figure 5. Monthly samples had higher concentrations of sediment than storm samples even when the monthly samples were collected shortly before the storm. For example, the September 22, 2002 storm samples had less than 1 mg/L of sediment, even though the stage was the lowest of the monitoring period and the baseflow sediment concentration was about 30 mg/L prior to the storm. Although the spring had lower sediment concentration during storms, the sediment flux (sediment concentration multiplied by the discharge) was higher overall (Tancredi 2004).

There was little evidence of a seasonal effect on sediment concentration or type. During the fall of 2002 and the summer of 2003, though hydrologic conditions were very different, there were high concentrations of calcite observed in the sediment (Figure 5). During the remainder of the sampling period, the sediment was either dominantly siliciclastics in the form of clay and silt, or a mix of calcite and siliciclastics.

Bushkill Spring

Representative particle morphologies and analyses from Bushkill Spring are presented in Figure 6. Most samples from Bushkill Spring contained silica (presumably quartz) as the dominant phase. Although the concentration and flux of sediment varied substantially with stage and discharge in the spring, silica predominated through a variety of hydrologic conditions. Figure 6-iii shows a sample taken during very low stage, when the spring had likely been dry just a few days earlier. Based on examination with an optical microscope, the sediment morphology and composition of low stage samples were not substantially different from storm samples taken March 30, 2003 and October 15, 2003, when the water was quite high in the spring (Rillstone and Toran 2004). Water in the Bushkill Spring was consistently below saturation with respect to calcite (SI_C ranged from 0 to –1.6, with a mean of –0.4), and as expected, calcite was not seen in the samples. The drainage to the spring at Bushkill was probably below saturation throughout its extent making it a substantially different spring from Nolte Spring in spite of its geologic similarity.

Origin of Calcite in the Nolte Samples

Because the discovery of calcite particles in the Nolte Spring suspended sediment was completely unexpected, some additional discussion is required. The SI_C at Nolte generally remained below saturation, with the only values over saturation occurring in the drought of 2002, making the origin of much of the precipitated calcite a puzzle. Chemical conditions in the aquifer must be more complicated than indicated by water chemistry at the spring mouth.

Our samples showed sediment being flushed out the spring in both base flow and high flow conditions. The average flow rate at the spring was 25 L/s, but over the seasons shown in Fig. 5, the flux varied from only 0.1 L/s (September 2002 drought) to slightly over 40 L/s (March 2003). There was no seasonal variation in sediment type or amount. This implies a continuous sediment source or else the system would have been flushed clean over time. The soil and regolith in the epikarst provides the only available continuous source of siliciclastic particles. The bedrock probably does not provide a continuous source of carbonate sediments because calcite, rather than a mix of calcite and dolomite, is the material observed in the spring water, while both are present in the bedrock. This suggests that contemporary precipitation of calcite is occurring in other parts of the spring's feeder system where more saturated conditions prevail.

The variation in calcite morphologies observed in Nolte Spring sediment (Figure 4) point to at least two distinct origins for the particles. The popcorn structures and nodules of calcite observed in some of the samples suggest precipitation from either supersaturated water in a fracture or in the vadose zone. For example, prisms in the sample collected on October 17, 2002 (Figure 4-v) appear to be joined at the base, as if they had grown together. Although the aspect ratio of these crystals' long and short axes is 3:1 and too low to be termed acicular, the fabric of the calcite prisms is similar to that of needle-like acicular calcite, which forms in the vadose zone of arid or semi-arid climates (Fitzpatrick 1993; Scholle and Ulmer-Scholle 2003). A sample collected on September 18, 2003 (Figure 4-ii) has a popcorn texture, which may indicate precipitation during condensation of water also likely in the vadose zone (Gonzalez et al. 1992).

Other calcite morphologies, such as rhombs with dissolution pits, flakes, and other chipped or etched grains, indicate that these may have been precipitated in a pool or quiet environment. Such sediment grains offer clues not just to their precipitation history, but also to their transport history. A suspended sediment sample collected on July 9, 2003 contained equant crystals and nodules, as well as shell-shaped particles and thin crusts, some of which were chipped or looked like they had been broken off a larger area (Figure 4-i). A calcite rhomb showed a chipped edge and dissolution pits in a storm sample from June 3, 2003 (Figure 4-vi). Etch pits and other evidence of re-dissolution are consistent with transport to the spring mouth in undersaturated conditions. The variety in calcite grain morphology implies that the chemical saturation state of calcite changes along the flow path. Undersaturated water emerging from the spring mouth does not imply that such conditions exist throughout the aquifer.

The geochemistry at the spring mouth suggests different geochemical and hydrologic conditions during particular times in the sampling period. The P_{CO2} and SI_C conditions at the Nolte Spring mouth fell into three categories: low P_{CO2} with high SI_C, intermediate P_{CO2} and SI_C, and high P_{CO2} with low SI_C as shown in Figure 7. Low P_{CO2} with high SI_C occurred during the drought of 2002 in summer and fall; intermediate P_{CO2} and SI_C occurred from mid-fall 2002 to spring 2003; and high P_{CO2} with low SI_C occurred during the growing season in the summer and early fall of 2003, which was unusually wet for those seasons. Two sets of chemical conditions prevailed when the sediment discharged from the spring was primarily calcite: low P_{CO2} with high SI_C and high P_{CO2} with low SI_C. During periods of intermediate P_{CO2} and SI_C, sediment was mainly clay and other siliciclastics which were expected for such chemical conditions. As such only the low P_{CO2} with high SI_C and high P_{CO2} with low SI_C groups will be discussed in this section

Calcite During the 2002 Drought (low P_{CO2} with high SI_C)

Precipitation at the spring mouth or in dewatered fractures during the 2002 drought might explain calcite in the spring samples. At Nolte Spring, the low stage during the drought of 2002 may have caused the larger fractures and the conduits that are usually phreatic to drain, allowing dissolved CO_2 in groundwater to escape into air-filled spaces. This would lower the P_{CO2}, which would in turn cause the SI_C to increase (Figure

7). The following reaction for calcite dissolution would be driven to the right allowing for precipitation at the spring:

$$Ca^{2+} + 2\,HCO_3^- \rightarrow CaCO_3 + CO_2 + H_2O \qquad [1]$$

Between site visits (two to four weeks), a calcium carbonate crust sometimes developed on the automatic sampler's water level sensor, indicating that the air-water interface where CO_2 outgassing can occur results in saturated conditions and precipitation at the spring mouth.

Some calcite morphologies observed during the drought suggest that vadose growth at the soil/bedrock interface may also have accounted for the presence of calcite in the spring. Although the overlying soils are generally well-leached, the carbonate at the soil/bedrock interface could have dissolved and re-precipitated. The drought may have caused supersaturated conditions sufficient for calcite to form, become disarticulated, and be transported into the aquifer by storm water.

Calcite in the 2003 Growing Season (high P_{CO2} with low SI_C)

Calcite precipitation at the spring mouth cannot account for the calcite in spring samples from summer and early fall 2003. The SI_C values calculated during this time were the lowest of the entire monitoring period, ranging from -0.75 to -0.52 in the samples from July 9, 2003 to October 15, 2003, compared to values from -0.43 to 0.33 during the remainder of the monitoring period. P_{CO2} values were the highest of the monitoring period, ranging up to an order of magnitude higher than the P_{CO2} measured one year earlier (during the drought). These values indicate that water in the spring would have been aggressive toward calcite. During the 2003 growing season, CO_2 was accumulating in the karst aquifer, instead of out-gassing. This drives equation 2 to the right, which would have decreased the pH and caused calcite dissolution, making precipitation at or near the spring mouth highly unlikely.

$$CO_2 + H_2O \rightarrow H^+ + HCO_3^- \qquad [2]$$

Calcite precipitated at an earlier time seems a much more likely source for this sediment. The calcite grains would have been transported to the spring from elsewhere in the system during the growing season of 2003. The transport time to the spring would have to be faster than the time required for dissolution of these dislodged particles; given the small capture zone of this spring (on the order of several km^2, Tancredi 2004) transport of remnant calcite would be possible. However, the flow rate can only be measured at the spring mouth, so the fast flow rates are only inferred from the presence of calcite during undersaturated conditions. Because the seasonal highs and lows in flow rate do not create a trend in sediment concentration or type (Fig. 5), the flow rate at the mouth cannot be used to predict the presence of sediment or calcite in particular.

Similarly, the geochemical conditions at the spring mouth cannot predict the presence calcite in spring mouth sediments. The growing season sediments were not expected to contain calcite (and note the June 2003 sample does not). Instead, the suspended sediment delivered to the mouth and the morphology of the calcite present provides clues to conditions further back in the system, perhaps all the way back to the recharge area.

Conclusions

The suspended sediments flushed from the three karst springs had distinctly different mineral compositions despite their relatively similar geologic settings. The sediment from Arch Spring, with recharge reflecting a large component of mountain runoff, was mainly fine-grained layer silicates. Nolte Spring, with recharge mainly by dispersed infiltration through thick soils, discharged suspended sediment containing large fractions of calcite but not dolomite. Much of the calcite was recovered from spring water that was undersaturated with respect to calcite. Bushkill spring, also with dispersed recharge on a limestone upland, discharged sediment that was dominantly silica.

These results are consistent with the presented mixing and fractionation model for clastic sediment transport through karst aquifers. Although the sediment mineralogy reflects the available material in the recharge area, these materials are injected and mixed within the aquifer. Moderate storms, such as those that occurred during the present investigation skimmed off only the very fine-grained fraction of the injected sediment load. As confirmed by direct observation of the sediment in the Tytoona Cave conduit in the Arch Spring feeder system, the coarser material remains in storage in the conduit awaiting rare high intensity storms.

Morphological evidence suggests that the anomalous calcite particles in Nolte Spring sediments were precipitated *in situ* somewhere in the active karst drainage system. The chemistry requires CO_2 degassing from water that had previously been brought to near saturation at a high CO_2 partial pressure – likely the soil/bedrock interface at times and a quiescent pool at others. The precipitation was followed by flushing of the particles into the main flow path. The transport of the particles through the karst conduit system must have been sufficiently rapid so as to bring the particles to the spring before they dissolved in the undersaturated water of the main flow system.

This study provides detailed mineralogy of the most readily transported fraction of the clastic sediment load revealing material with composition dependent on source area, on mixing within the aquifer, and on transport mechanisms. A further result is that a clastic carbonate fraction may appear depending on the saturation state of water along the flow path within the aquifer.

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Figures

Figure 1. Geology of the spring basins. Arch Spring has a combination of carbonate and non-carbonate units in the Sinking Run watershed (outline shown on geologic map). The units represented are from oldest to youngest 1) Stonehenge Limestone, 2) Bellefonte Dolomite, 3) Limestones of the Trenton and Black River Groups, 4) Reedsville Shale, 5) Bald Eagle Sandstone, and 6) Juniata formation. Nolte Spring has carbonate Epler and Stonehenge formations in the recharge area; the sandstones and shales of the Cocalico and Onetelaunee are outside the capture area. Bushkill Spring has the smallest capture area, draining limestones of the Epler formation and dolomites of the Rickenbach formation.

Figure 2. SEM images and EDX spectra from three Arch Spring storm samples. From top: i) August 31, 2003; ii) September 1, 2003, 2:56am; and iii) September 1, 2003, 11:56am. All three samples showed predominantly layered silicates based on EDX analysis, but the 9/1/03, 11:56am, sample had a particle of calcium-rich sediment. The EDX spectrum shown in 2i covers the entire area pictured; in 2ii, the spectrum targeted the largest mass visible in the bottom center of the image; the spectrum in 2iii covers the area of the single calcite grain, which incorporates some of the sediment resting on and around the grain. The arrow in Figure 2ii points to a diatom skeletal fragment representative of fragments common in the Arch Spring samples. In Figure 2iii, the arrow marks the rim of the calcite particle dominating the micrograph.

Figure 3. SEM images and EDX spectra from three Nolte Spring monthly samples. From top: i) July 9, 2003; ii) September 15, 2003; and iii) May 29, 2003. The 7/9/03 sample had the highest sediment concentration of the monitoring period, and the EDX spectrum over the area shown in the image has a high calcium peak, indicating that most

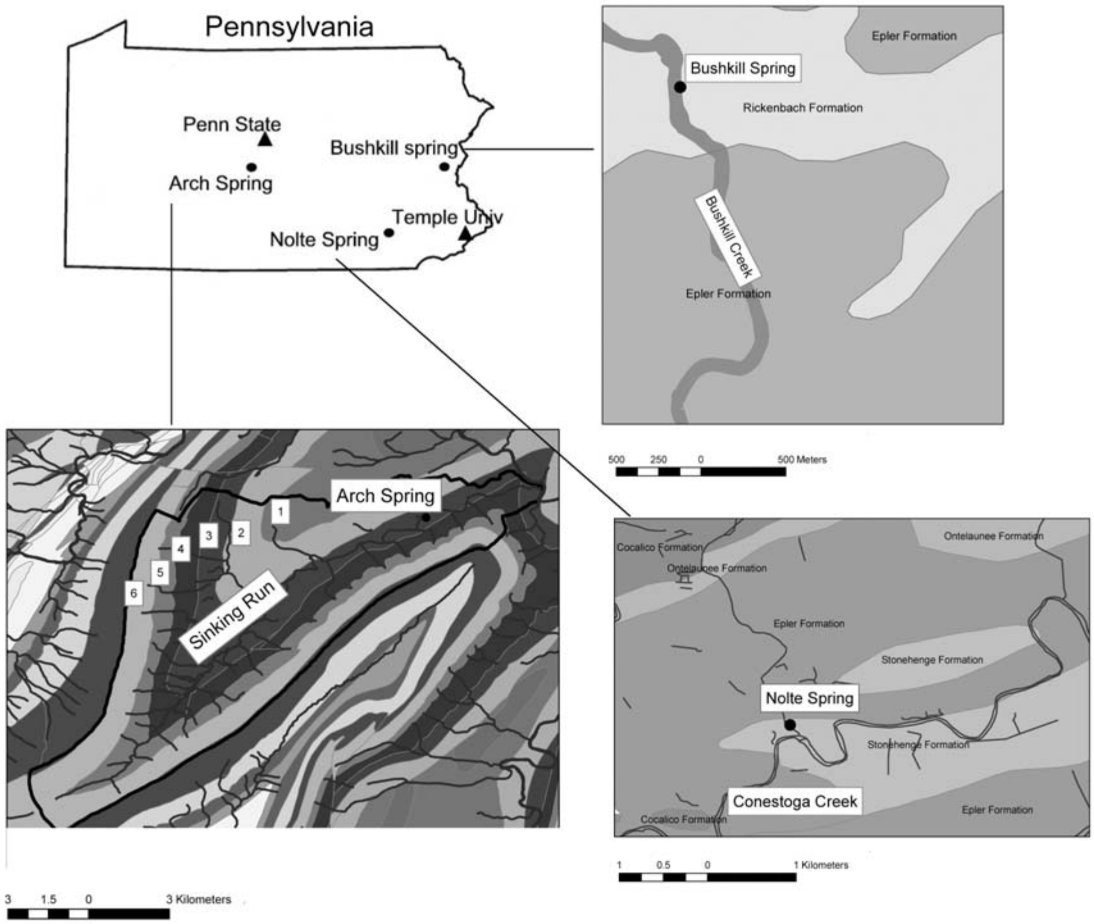
of the particles in the image are composed of calcite. The 9/15/03 sample was classified as a mixture of calcite and clay, and XRD indicated the presence of quartz, calcite, muscovite, and chlorite on this sample. The particle from May 29, 2003 was siliciclastic**.** Most samples primarily composed of siliciclastics had small amounts of sediment, so XRD could not be used to identify the mineralogy.

Figure 4. Morphologies of calcite from Nolte Spring observed with SEM. Micrographs of samples collected on the following dates: i) July 9, 2003; ii) September 18, 2003; iii) August 15, 2003; iv) March 7, 2003 (storm sample) v) October 17, 2002; and vi) June 3, 2003 (storm sample). The morphology of the July 9, 2003 sample suggests that calcite was broken off from a precipitation site and transported to Nolte Spring. The prismatic calcite grains in the October 17, 2002 sample appear to have grown together (v). Popcorn (ii), flakes (iii), and pitted crystals (vi) are also present.

Figure 5. Sediment concentration and mineralogy for monthly samples from Nolte Spring for September 2002 through December 2003. Data points marked with a symbol for mineralogy were analyzed with SEM/EDX. Samples with high concentrations of sediment had some calcite. Calcite was observed in the samples from early fall 2002 and summer 2003, whereas mostly siliciclastics were observed during the winter and spring 2003 seasons. After December 2003, sediment concentrations of samples collected were generally less than 5 mg/L, and no further SEM/EDX analyses were conducted to identify sediment composition.

Figure 6. SEM images and EDX spectra from three Bushkill Spring samples. From top: i) May 8, 2003; ii) November 6, 2002; and iii) May 4, 2003. The samples all showed sliciclastics with silica predominating. Pictured here are fine-grained siliciclastics from the storm sample of 5/8/03 (i), a quartz grain with conchoidal fracture from the 11/6/02 storm sample (ii), and a collection of diatoms from the 5/4/03 monthly sample. Diatoms were very common in the Bushkill Spring samples, but it is possible that their source was Bushkill Creek flowing past the spring rather than the spring itself. It was not possible to rule out stream contributions due to sampling constraints.

Figure 7. Geochemistry and mineralogy of Nolte Spring for September 2002 through December 2003. Mineralogy of samples collected concurrent with the geochemistry samples are marked on the SI_C data points, which are below saturation except for fall 2002. Calcite precipitation when P_{CO2} was low may have been driven by CO_2 outgassing. Calcite precipitation when P_{CO2} was high may have occurred under different geochemical conditions elsewhere in the system, followed by rapid transport to the spring. A sample from 10/17/02 also showed mostly calcite, but was not used for geochemical modeling and is not plotted here. After December 2003, sediment concentrations of samples collected were generally less than 5 mg/L, and no further SEM/EDX analyses were conducted to identify sediment composition.



Spring	Type of Aquifer	Area of Basin
Arch	Master conduit	~50 km^2
Nolte	Fracture and enlarged fracture	~1-2 km^2
Bushkill	Fracture	Multiple outlets make basin indeterminate

Figure 1. Geology of the spring basins. Arch Spring has a combination of carbonate and non-carbonate units in the Sinking Run watershed (outline shown on geologic map). The units represented are from oldest to youngest 1) Stonehenge Limestone, 2) Bellefonte Dolomite, 3) Limestones of the Trenton and Black River Groups, 4) Reedsville Shale, 5) Bald Eagle Sandstone, and 6) Juniata formation. Nolte Spring has carbonate Epler and Stonehenge formations in the recharge area; the sandstones and shales of the Cocalico and Onetelaunee are outside the capture area. Bushkill Spring has the smallest capture area, draining limestones of the Epler formation and dolomites of the Rickenbach formation.

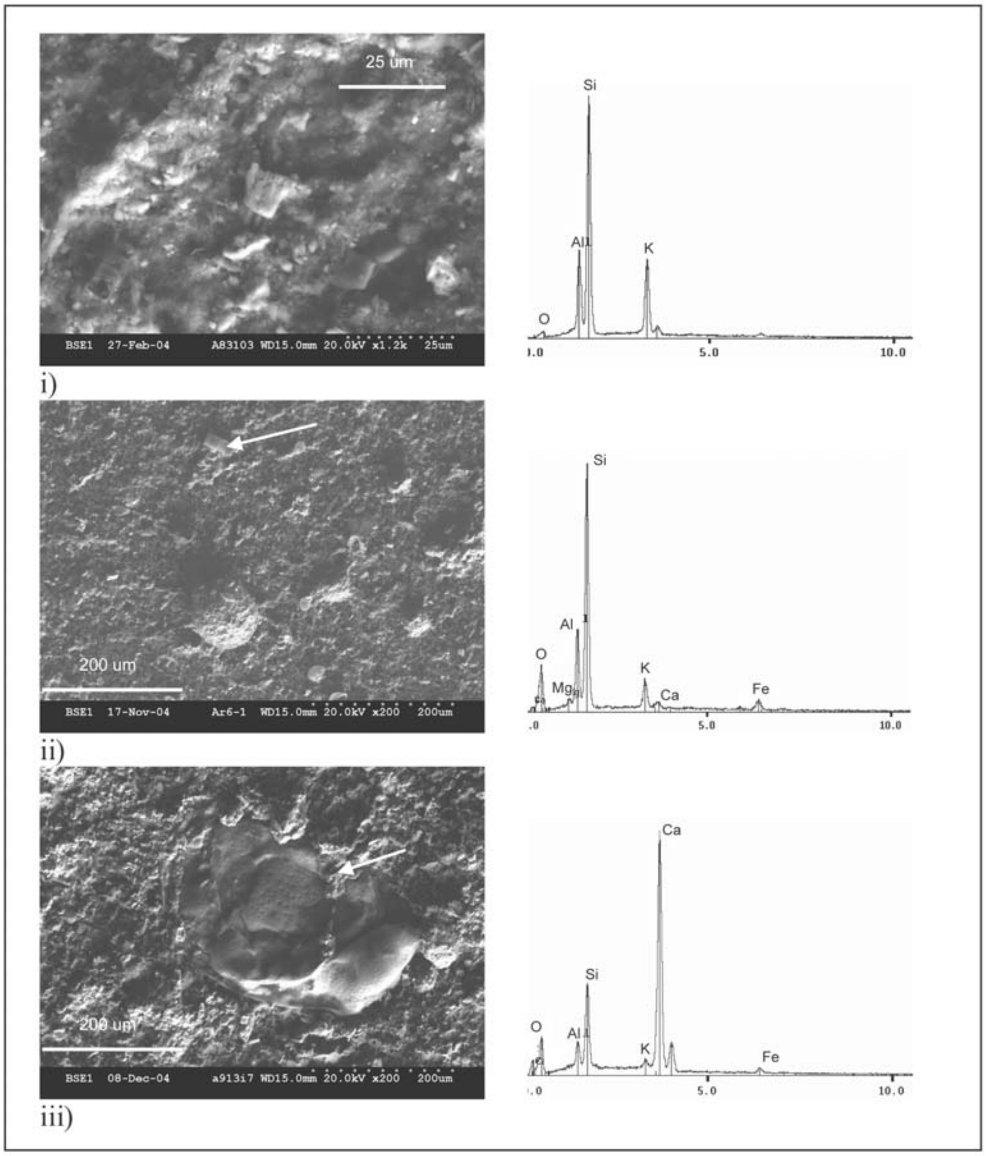


Figure 2. SEM images and EDX spectra from three Arch Spring storm samples. From top: i) August 31, 2003; ii) September 1, 2003, 2:56am; and iii) September 1, 2003, 11:56am. All three samples showed predominantly layered silicates based on EDX analysis, but the 9/1/03, 11:56am, sample had a particle of calcium-rich sediment. The EDX spectrum shown in 2i covers the entire area pictured; in 2ii, the spectrum targeted the largest mass visible in the bottom center of the image; the spectrum in 2iii covers the area of the single calcite grain, which incorporates some of the sediment resting on and around the grain. The arrow in Figure 2ii points to a diatom skeletal fragment representative of fragments common in the Arch Spring samples. In Figure 2iii, the arrow marks the rim of the calcite particle dominating the micrograph.

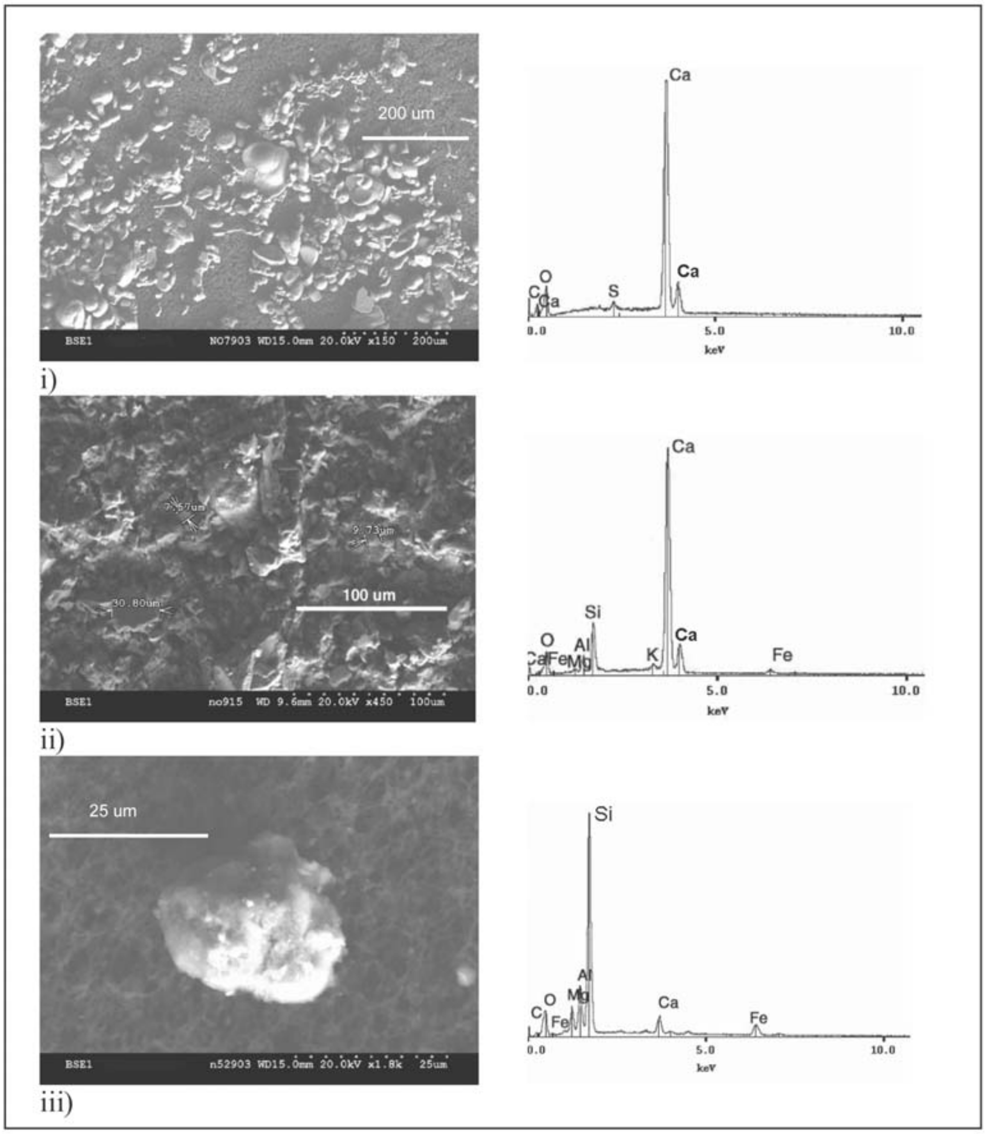


Figure 3. SEM images and EDX spectra from three Nolte Spring monthly samples. From top: i) July 9, 2003; ii) September 15, 2003; and iii) May 29, 2003. The 7/9/03 sample had the highest sediment concentration of the monitoring period, and the EDX spectrum over the area shown in the image has a high calcium peak, indicating that most of the particles in the image are composed of calcite. The 9/15/03 sample was classified as a mixture of calcite and clay, and XRD indicated the presence of quartz, calcite, muscovite, and chlorite on this sample. The particle from May 29, 2003 was siliciclastic**.** Most samples primarily composed of siliciclastics had small amounts of sediment, so XRD could not be used to identify the mineralogy.

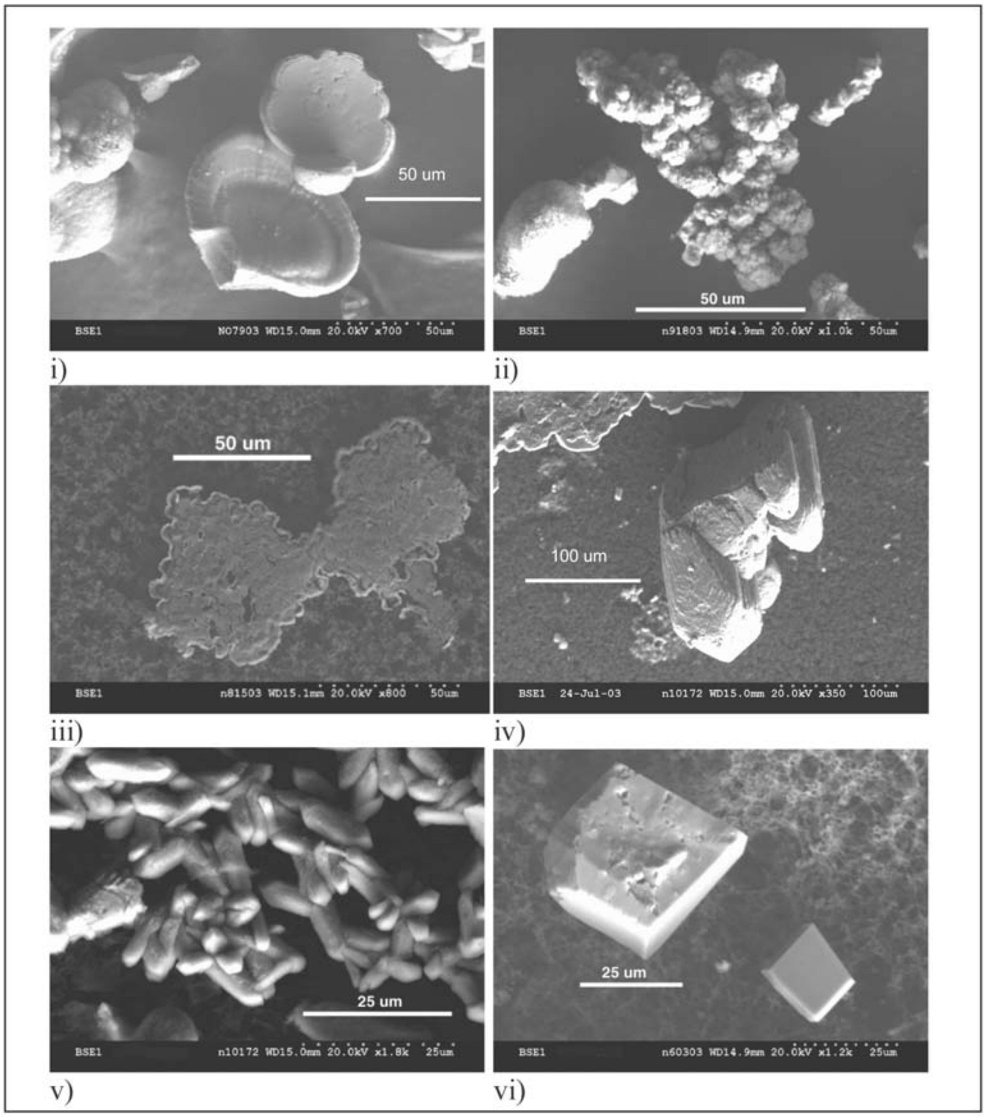


Figure 4. Morphologies of calcite from Nolte Spring observed with SEM. Micrographs of samples collected on the following dates: i) July 9, 2003; ii) September 18, 2003; iii) August 15, 2003; iv) March 7, 2003 (storm sample) v) October 17, 2002; and vi) June 3, 2003 (storm sample). The morphology of the July 9, 2003 sample suggests that calcite was broken off from a precipitation site and transported to Nolte Spring. The prismatic calcite grains in the October 17, 2002 sample appear to have grown together (v). Popcorn (ii), flakes (iii), and pitted crystals (vi) are also present.

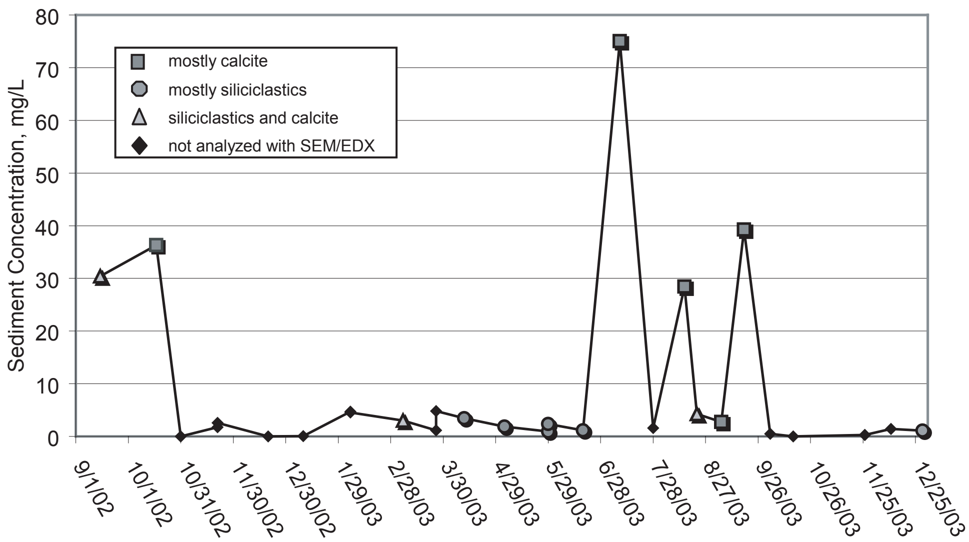


Figure 5. Sediment concentration and mineralogy for monthly samples from Nolte Spring for September 2002 through December 2003. Data points marked with a symbol for mineralogy were analyzed with SEM/EDX. Samples with high concentrations of sediment had some calcite. Calcite was observed in the samples from early fall 2002 and summer 2003, whereas mostly siliciclastics were observed during the winter and spring 2003 seasons. After December 2003, sediment concentrations of samples collected were generally less than 5 mg/L, and no further SEM/EDX analyses were conducted to identify sediment composition.

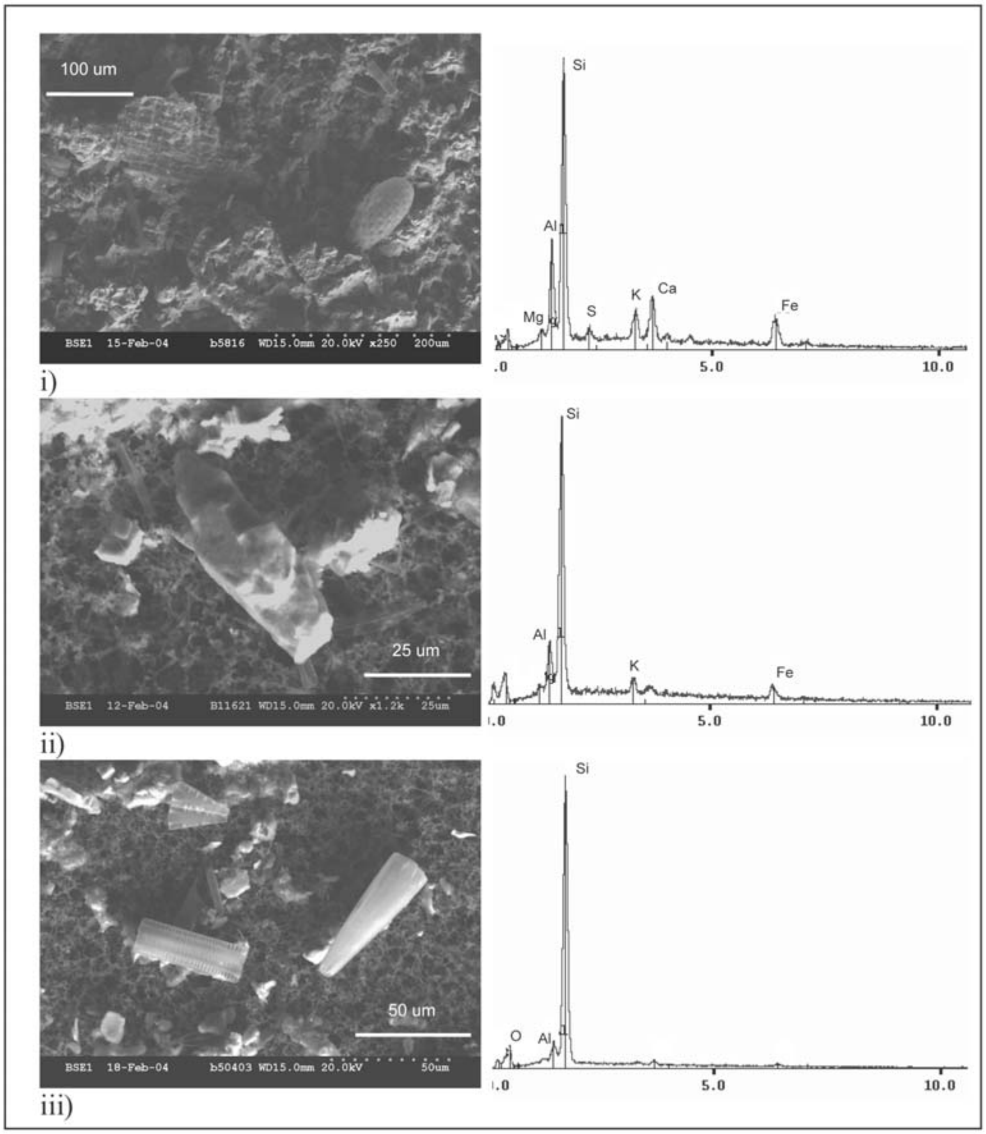


Figure 6. SEM images and EDX spectra from three Bushkill Spring samples. From top: i) May 8, 2003; ii) November 6, 2002; and iii) May 4, 2003. The samples all showed sliciclastics with silica predominating. Pictured here are fine-grained siliciclastics from the storm sample of 5/8/03 (i), a quartz grain with conchoidal fracture from the 11/6/02 storm sample (ii), and a collection of diatoms from the 5/4/03 monthly sample. Diatoms were very common in the Bushkill Spring samples, but it is possible that their source was Bushkill Creek flowing past the spring rather than the spring itself. It was not possible to rule out stream contributions due to sampling constraints.

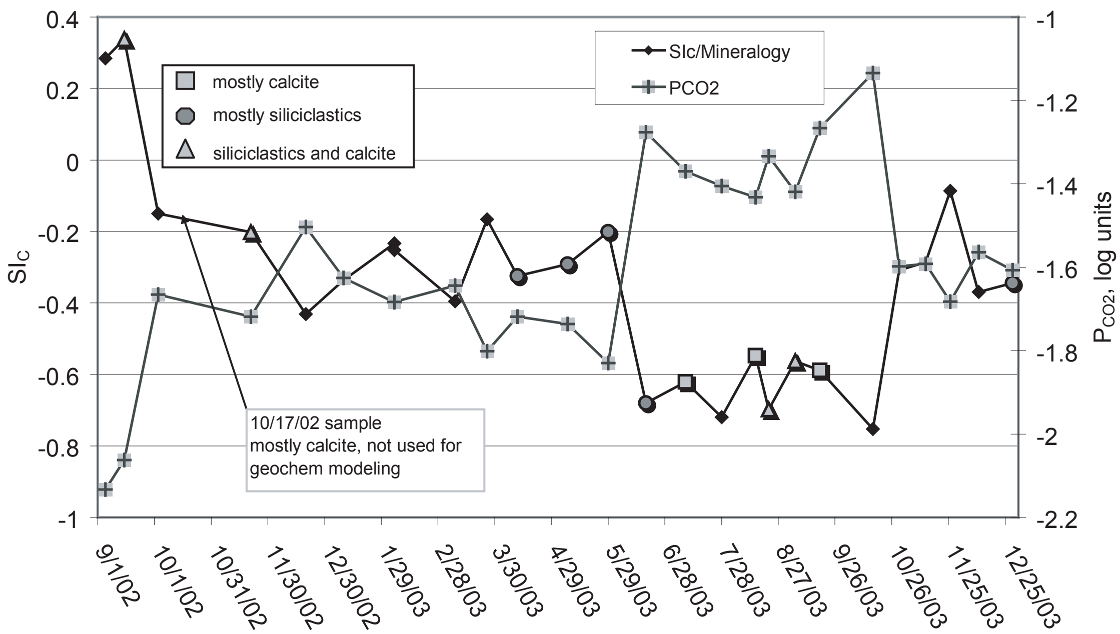


Figure 7. Geochemistry and mineralogy of Nolte Spring for September 2002 through December 2003. Mineralogy of samples collected concurrent with the geochemistry samples are marked on the SI_C data points, which are below saturation except for fall 2002. Calcite precipitation when P_{CO2} was low may have been driven by CO_2 outgassing. Calcite precipitation when P_{CO2} was high may have occurred under different geochemical conditions elsewhere in the system, followed by rapid transport to the spring. A sample from 10/17/02 also showed mostly calcite, but was not used for geochemical modeling and is not plotted here. After December 2003, sediment concentrations of samples collected were generally less than 5 mg/L, and no further SEM/EDX analyses were conducted to identify sediment composition.