Weathering rates in alpine catchments of central Colorado, USA

Richard B. Wanty, Philip L. Verplanck, Carleton Bern, Carma SanJuan, Ed H. deWitt, Terry L. Klein, David Fey, Travis S. Schmidt, Stanley E. Church

U.S. Geological Survey, MS 964d Denver Federal Center, Denver, CO 80225 USA (rwanty@usgs.gov)

ABSTRACT: Streams were sampled in central Colorado, USA, to provide a geochemical baseline and evaluate the regional effect of catchment lithology on stream-water chemistry. Drainage from abandoned historical mines, as well as the natural weathering of hydrothermally altered rocks, causes some streams to have low pH and high concentrations of metals and sulfate (acid-rock drainage, or ARD). In the absence of these effects, weathering of some lithologic groups has subtle but important influences on water chemistry. In the presence of ARD, greater concentrations of alkali metals and alkaline earths are observed, but their contribution to the total element load is diminished as Fe, Al, and SO_4 constitute a greater proportion of the total load below pH5. In the absence of ARD, drainages from certain highly weatherable lithologic groups have greater chemical weathering rates. Median chemical weathering rates for all sites was 11,500 kg a^{-1} km^{-2}. In the absence of ARD, median weathering rate was 5,400 kg a^{-1} km^{-2}, which is lower than published rates in wetter climates.

1 INTRODUCTION

From 2004 to 2007, stream-water samples were collected in central Colorado, USA. First- and second-order streams were sampled to link water quality with catchment lithology, and to test the hypothesis that water-rock interaction processes in headwater streams are a first-order control on overall water quality (Wanty et al., 2007; 2009). This study also will provide geochemical baseline information.

The sample sites are at high elevation; from 1,800 to 3,560 meters. Maximum elevations at the top of some catchments exceeded 4200 m. Climate is temperate continental, with generally >50 cm of precipitation per year that occurs as snow in winter or as rain between June and August. Vegetation ranges from deciduous cover at lower elevations and in riparian zones, to conifer forests, and to open tundra at the highest elevations.

Soil cover is thin to nonexistent, especially in catchments with steeper slopes. The area has been glaciated repeatedly, most recently ending approximately 10^4 years ago. The combination of steep slopes and recent glaciation contributes to the paucity of soil cover. Above treeline, fresh rock is continually exposed due to the physical action of freeze/thaw cycles and other mechanical weathering mechanisms, which may accelerate weathering rates (Mast et al., 1990; Meyer et al., 2009).

The Colorado Mineral Belt (CMB) lies within the study area (Figure 1). Thousands of historical mines occur within the CMB; many of them produce acidic metal-rich drainage. Mining represents the primary land-disturbing activity in any of the catchments studied. The CMB is also an area of high background concentrations of dissolved metals that are liberated by the weathering of pyrite and other sulfide minerals. Regional hydrothermal alteration has added pyrite and other sulfide-bearing minerals to the rocks, which, when exposed to the weathering environment, may produce acid rock drainage (ARD). For this study, samples were grouped as being from mined, prospected, or unmined settings, based on whether historical mining or prospecting operations took place in their respective catchments. Catchments that are classified as mined or prospected also may have a component of natural acid drainage that adds solutes in addition to what may have been contributed from anthropogenic activities.

In this alpine environment, weathering reactions involving silicate minerals might be expected to occur slowly, because of the low average annual temperatures (usually <5° C), and relatively low precipitation (Mast et al., 1990; Drever and Zobrist, 1992; White and Blum, 1995). In comparison to world average rivers, most of the samples collected for this study have low total dissolved solids (TDS) and low Na concentrations relative to Ca (Gibbs, 1970). However, the presence of regional hydrothermal alteration and generation of ARD appears to accelerate weathering rates and alter weathering mechanisms. This study demonstrates the effects of ARD on weathering rates and mechanisms for alpine catchments in Colorado. We also compared weathering rates for the catchments without hydrothermal alteration or historical mining to similar catchments in the USA and elsewhere (Mast et al., 1990; Drever and Zobrist, 1992; Jansen et al., 2010). Here we use the term ‘weathering rate’ to describe the area-normalized annual solute flux from a catchment.

In contrast to previous studies of chemical weathering, this study allows for comparison of a large number of catchments, representing a variety of catchment lithologies, but with relatively little variation in climate. Each catchment was sampled at only one point, so this study lacks the detailed information common to most other studies, but the strength of this work lies in the large number and well-characterized lithologic variety of catchments, thus allowing comparison of weathering rates based on lithology, as well as the presence or absence of hydrothermal mineralization and alteration.

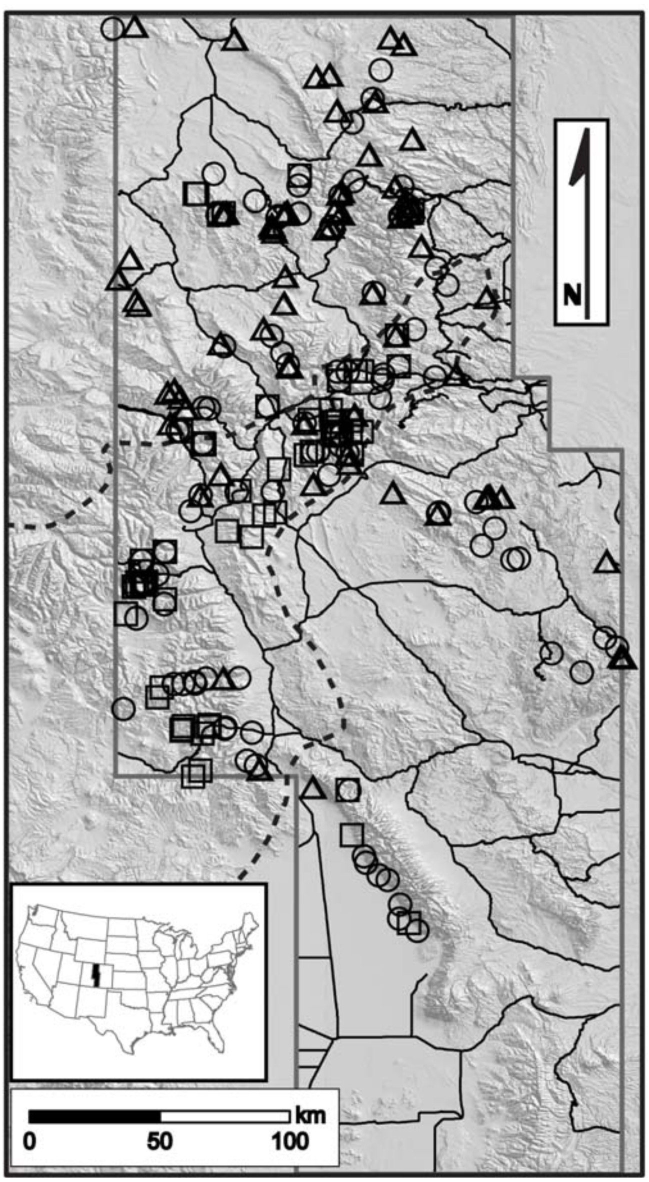

Figure 1- Study area in central Colorado, USA. Symbols represent bulk weathering rates, in kg a^{-1} km^{-2}: Δ <5,000; ○ 5,000-20,000; □ >20,000. Dashed line shows Colorado Mineral Belt.

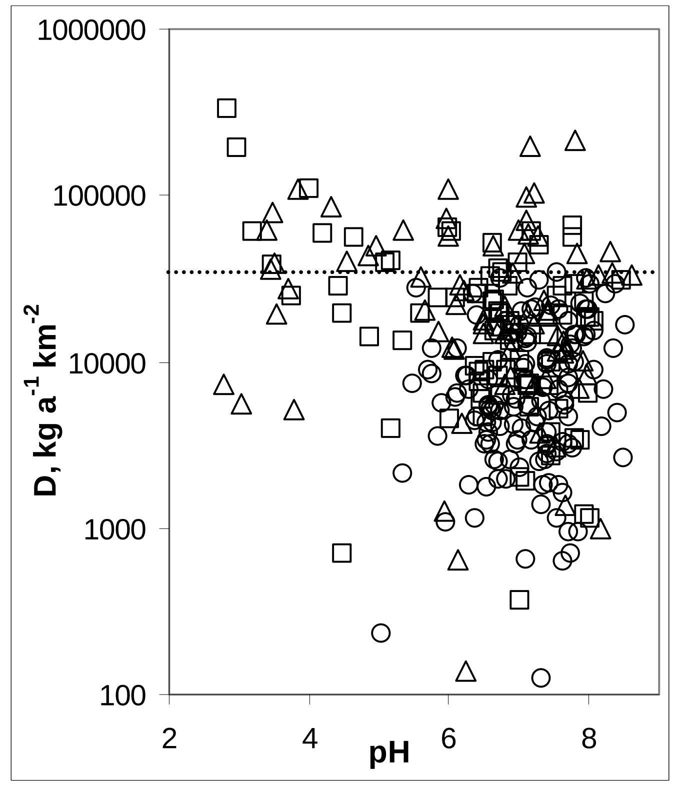

Figure 2- Annualized weathering rates, *D*, normalized to catchment area. Δ- catchments with historical mining; □- catchments with prospects but no mines; ○- unmined catchments. Dotted line represents the maximum D value for unmined catchments.

2 METHODS

Samples were collected according to the procedures in Wanty et al. (2007; 2009), in mid to late summer to avoid effects of spring and early summer snowmelt. We also avoided sampling after storm events. Samples were filtered on-site through a 0.45 µm filter, and acidified with ultrapure HNO_3 to pH~1. Major and trace cations were analyzed by ICP-MS and ICP-AES, and anions were analyzed by ion chromatography. Stream flow (discharge) was measured with a pygmy meter (Rantz et al., 1982).

Sample locations were combined with digital elevation models to generate catchment boundaries specific to each sample location. These boundaries were combined with digital lithologic maps to quantify the proportion of the area of each catchment that is underlain by each rock type. Annualized bulk weathering rates, *D*, were calculated for each catchment according to the formula:

$$D = (\text{TDS} * \text{discharge}) / \text{catchment area} \qquad (1)$$

with appropriate conversion factors to express *D* in units of kg a^{-1} km^{-2}. Calculating *D* with this formula assumes that a single sampling point is representative of an entire, average year. This assumption is certainly poor, but provides a means of comparing all of our studied catchments on an area-normalized basis. This calculation also allows comparison to other published studies that report annualized weathering rates. All samples were collected in a similar flow regime (after runoff, no storm events), so there is a degree of uniformity to the samples and limited bias should be introduced by this calculation.

3 RESULTS AND DISCUSSION

Calculated values of D for all catchments ranged from 120 to 327,000 kg a^{-1} km^{-2}, with a median value of 11,500 kg a^{-1} km^{-2}. For comparison, Harmon et al. (2009) compiled values ranging from 16,000 to $>10^6$ kg a^{-1} km^{-2} for large river basins throughout the world. Jansen et al. (2010) calculated an average dissolved silica load of 2680 kg SiO_2 a^{-1} km^{-2} for relatively large river basins in the USA, compared to an average for this study of 1500 kg SiO_2 a^{-1} km^{-2} for unmined catchments with no hydrothermal alteration. For both of these comparisons, our weathering rates and silica loads are somewhat lower, possibly reflecting the lower temperatures and precipitation of the catchments we studied.

For this study, many of the highest values of D were found in waters with low pH, or in those catchments with historical mining or prospecting (Figure 2). Weathering rates from unmined, unmineralized catchments were generally in the lower 50th percentile of the entire population of samples ($D <$ 11,500 kg a^{-1} km^{-2}); the maximum value of D for unmined catchments was 34,000 kg a^{-1} km^{-2}, shown by the dotted line in figure 2. At low pH, the importance of weathering of sulfide minerals such as pyrite is indicated, based on increased contributions of Fe and SO_4 to total weathering loads. Annualized loads of Al also increase dramatically as pH decreases. Other elements typically found in sulfide ore deposits, such as Zn, Cd, Cu, and Pb, also increase with decreasing pH, as is typically found in ARD-affected streams. The increased proportion of Al in low-pH samples is likely due to increased weathering rates of aluminosilicate minerals, but also due to the increased solubility of Al-bearing secondary minerals such as kaolinite and gibbsite. PHREEQC (Parkhurst and Appelo, 1999) was used to evaluate the saturation state of the samples with respect to primary and secondary minerals. For all samples with pH values less than about 4, major secondary aluminosilicates (gibbsite, diaspore, kaolinite, etc.) are undersaturated. Thus, in the low-pH environment, aluminosilicates appear to weather more rapidly, and the formation of secondary Al phases is inhibited. These two processes combine to increase Al loads at lower pH.

3.1 *Role of catchment lithology*

Of the 227 unique catchments sampled in this study, 97 were classified as unmined. Compared to the mined catchments, the unmined ones have lower total weathering loads, with a median value approximately half that of the entire population (5,400 kg a^{-1} km^{-2}). For these catchments, in the absence of the perturbations imposed by ARD-related processes, it is possible to evaluate lithologic effects on weathering rates.

Lithologic classifications for the study area are described in Wanty et al. (2009). In general, igneous, metamorphic, and sedimentary groups are subdivided by rock composition (silica-poor, intermediate, and silica-rich) and for the sedimentary groups, additional subdivisions exist for presence/absence of carbonates and evaporates. More than 200 geologic formations of various ages were grouped into 17 lithologic compositional classifications. Of these 17, 4 lithologic groups are represented by more than 5 samples; these are shown in figure 3. In the figure, Minturn Formation is shown as a fifth group, a subunit of sandstone-dominated catchments.

The Minturn Formation contains minor amounts of calcite, dolomite, and gypsum (Tweto and Lovering, 1977), and the weathering of these minerals appears to dominate the chemistry of streams draining catchments containing Minturn Fm. In figure 3, all samples with Ca/Na >10 were collected from catchments that contain at least a small amount of Minturn Fm., even though in some cases <10% of the area of the catchment was underlain by Minturn Fm. These streams also had high sulfate loads. These results suggest a much greater reactivity for some mineral constituents of the Minturn Fm., most likely the carbonate minerals and gypsum. Thus, the water chemistry is dominated by a relatively small percentage of more reactive minerals. Saturation indexes for the carbonates are near 0 (equilibrium) and gypsum SI values were significantly <0, but greater than the gypsum SI values for catchments with no Minturn Fm. Mast et al. (1990) arrived at a similar conclusion for a catchment dominated by felsic plutonic rocks that contained minor amounts of calcite. In that case, <1% of calcite in the rock contributed ~40% of the cation load to the main trunk stream in the catchment. Mast et al. (1990) attributed this result to the role of mechanical weathering in their granitic catchment, as it continually brings fresh, more-reactive minerals to the surface.

In catchments containing Minturn Fm., mechanical weathering may contribute to solute loads. Continual exposure of fresh rock to the surficial weathering environment is caused by physical weathering mechanisms such as freeze-thaw cycles, landslides, and rock glaciers on steep slopes. When considering mined and prospected catchments, the role of mechanical weathering also is important, as exposure of fresh hydrothermally altered rock may contribute additional solute loads by the weathering of sulfide-bearing minerals, production of ARD, lowering the solution pH, and increased weathering rates of aluminosilicate minerals.

4 SUMMARY

Streams draining alpine catchments in Colorado were sampled to evaluate chemical weathering rates. Catchments were at high elevation and within similar climate zones, so the primary effects of lithologic variations, presence or absence of hydrothermal alteration and presence or absence of historical mines could be examined. Catchments with historical mines or prospects generally had greater weathering rates, independent of lithologic variations. In these catchments, the relative contribution of natural vs. anthropogenic solute loads to the total weathering load is difficult or impossible to quantify, and would require much more detailed study of each individual catchment (cf. Borrok et al., 2009).

In the absence of historical mining activity or regional hydrothermal alteration, lithologic effects on weathering behavior were observed. The most distinctive of these effects was observed in catchments containing outcrops of Minturn Formation, a sandstone unit that contains minor amounts of calcite, dolomite, and gypsum. The presence of these highly reactive minerals imparted greater loads of Ca, sulfate, and alkalinity compared to streams draining unmined catchments in other lithologies. This was observed even in catchments with <10% of their total surface area covered by Minturn Fm.

Although the weathering rates calculated in this study are limited by the assumption that a single sample point can be used to calculate annual weathering rates, the results compare favorably with other published studies. In general, rates calculated for this study are lower than for other published studies, but considering the low average annual temperatures and precipitation of the Colorado catchments, this result was expected.

REFERENCES

Borrok, D.M., Wanty, R.B., Ridley, W.I., Lamothe, P.J., Kimball, B., Verplanck, P.L., Runkel, R. (2009) Investigating metal fluxes in a mountain watershed using iron and zinc isotopes. Applied Geochemistry 24, 1270-1277.

Drever, J.I., Zobrist, J., 1992. Chemical weathering of silicate rocks as a function of elevation in the southern Swiss Alps. Geochimica et Cosmochimica Acta 56, 3209-3216.

Gibbs, R.J., 1970. Mechanisms controlling world water chemistry. Science 170, 1088-1090.

Harmon, R.S., Lyons, W.B., Long, D.T., Ogden, F.L., Mitasova, H., Gardner, C.B., Welch, K.A., Witherow, R.A., 2009. Geochemistry of four tropical montane watersheds, Central Panama. Applied Geochemistry 24, 624-640.

Jansen, N., Hartmann, J., Lauerwald, R., Durr, H.H., Kempe, S., Loos, S., Middelkoop, H., 2010. Dissolved silica mobilization in the conterminous USA. Chemical Geology 270, 90-109.

Mast, M.A., Drever, J.I., Baron, J., 1990. Chemical weathering in the Loch Vale Watershed, Rocky Mountain National Park, Colorado. Water Resources Research 26, 2971-2978.

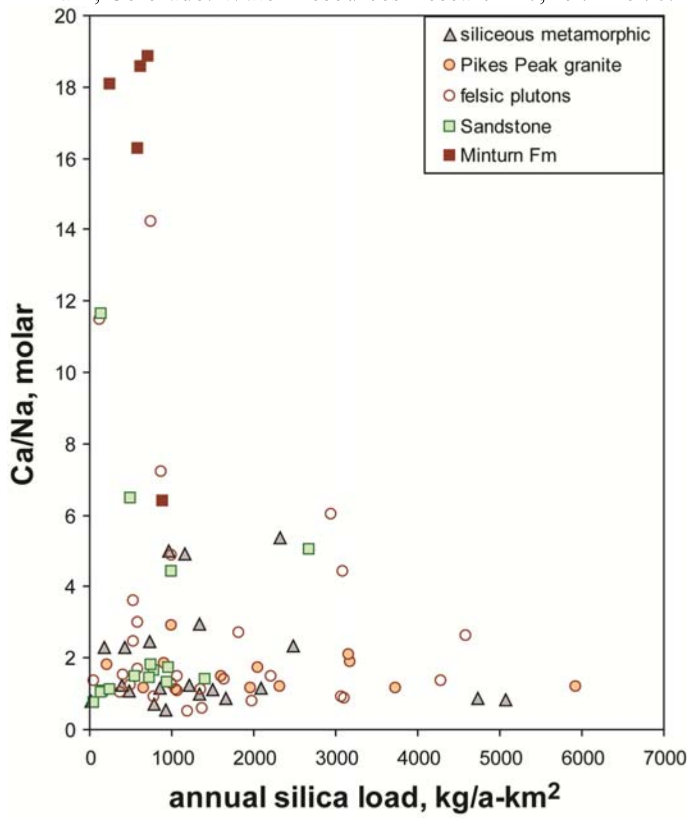

Figure 3- Ca/Na ratio and silica loads for unmined catchments, separated by dominant catchment lithology.

Meyer, H., Strauss, H., Hetzel, R., 2009. The role of supergene sulphuric acid during weathering in small river catchments in low mountain ranges of Central Europe: Implications for calculating the atmospheric CO_2 budget. Chemical Geology 268, 41-51.

Parkhurst, D.L., Appelo, C.A.J., 1999. User's guide to PHREEQC (Version 2)- A computer program for speciation, batch-reaction, one-dimensional transport, and inverse geochemical calculations. U.S. Geol. Survey Water-Resources Investigations Report 99-4259.

Rantz, S.E., et al. (1982) Measurement and computation of stream flow. U.S. Geol. Survey Water-Supply Paper 2175.

Tweto, O., Lovering, T.S., 1977. Geology of the Minturn 15-minute quadrangle, Eagle and Summit counties, Colorado. U.S. Geol. Survey Profesisonal Paper 956.

Wanty, R.B., Verplanck, P.L., Fey, D.L., Church, S.E., San Juan, C.A., and Swigert, V.A., 2007. Geochemistry of surface water in alpine catchments in central Colorado, USA: An example of sampling scale versus detail. In, Bullen, T.D., and Wang, Y. (eds.), Proceedings of the 12th International Symposium on Water-Rock Interaction, Taylor and Francis, London, 453-456.

Wanty, R.B., Verplanck, P.L., SanJuan, C.A., Church, S.E., Schmidt, T.S., Fey, D.L., DeWitt, E.H., Klein, T.L., 2009. Geochemistry of surface water in alpine catchments in central Colorado, USA: Resolving host-rock effects at different spatial scales. Applied Geochemistry 24, 600-610.

White, A.F., Blum, A.E., 1995. Effects of climate on chemical weathering in watersheds. Geochimica et Cosmochimica Acta 59, 1729-1747.