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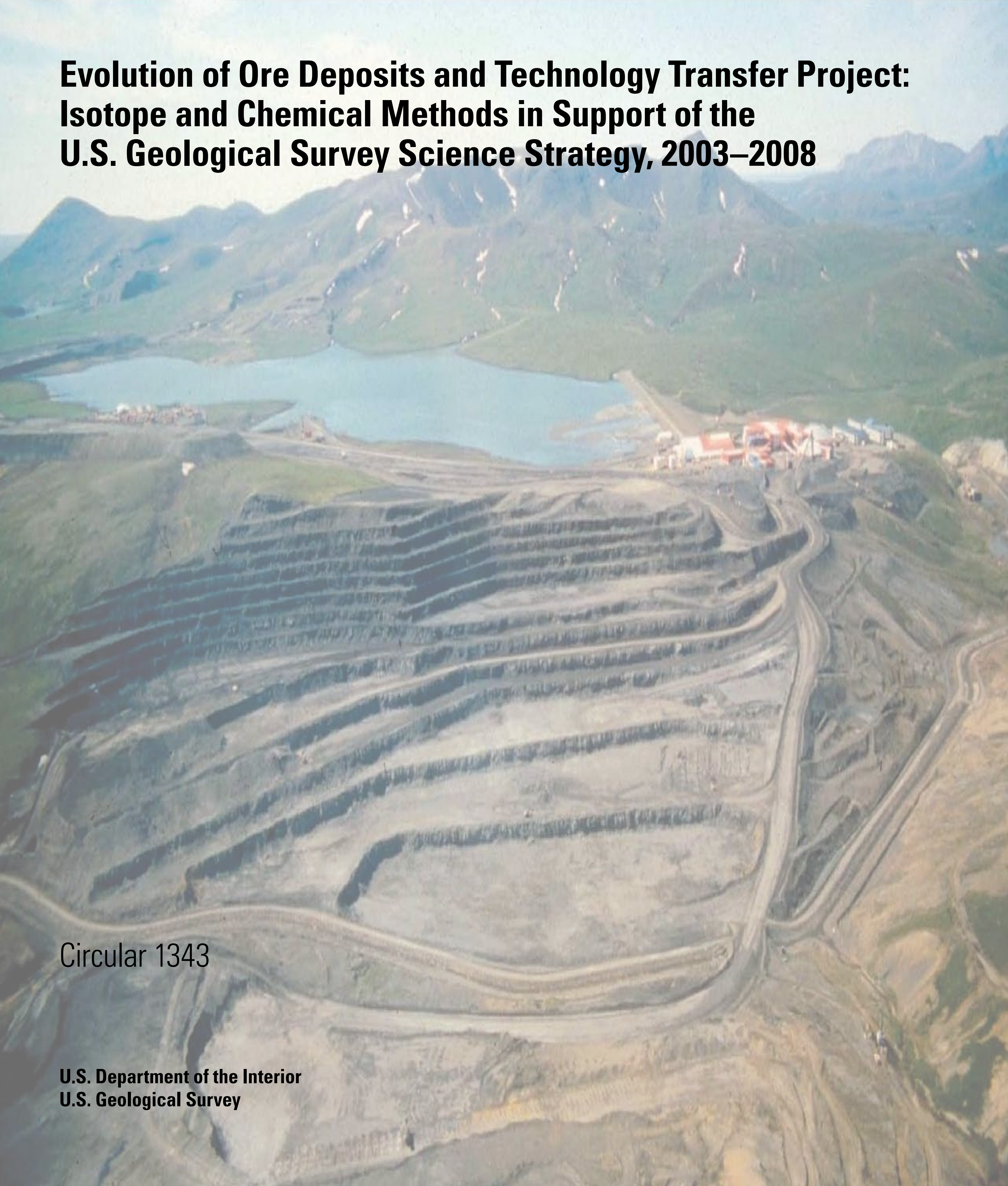

Evolution of Ore Deposits and Technology Transfer Project: Isotope and Chemical Methods in Support of the U.S. Geological Survey Science Strategy, 2003–2008

Circular 1343

U.S. Department of the Interior
U.S. Geological Survey

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By Robert O. Rye, Craig A. Johnson, Gary P. Landis, Albert H. Hofstra,
Poul Emsbo, Craig A. Stricker, Andrew G. Hunt, and Brian G. Rusk

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Conversion Factors and Datums

Multiply	By	To obtain
	Length	
inch (in.)	25,400	micron (m)
inch (in.)	2.54	centimeter (cm)
inch (in.)	25.4	millimeter (mm)
foot (ft)	0.3048	meter (m)
mile (mi)	1.609	kilometer (km)
	Area	
acre	0.4047	hectare (ha)
acre	0.004047	square kilometer (km^2)
square mile (mi^2)	259.0	hectare (ha)
square mile (mi^2)	2.590	square kilometer (km^2)
	Volume	
gallon (gal)	3.785	liter (L)
cubic inch (in^3)	16.39	cubic centimeter (cm^3)
cubic inch (in^3)	0.01639	liter (L)
cubic mile (mi^3)	4.168	cubic kilometer (km^3)
	Mass	
ounce, avoirdupois (oz)	28,350	milligram (mg)
ounce, avoirdupois (oz)	28.35	gram (g)
pound, avoirdupois (lb)	0.4536	kilogram (kg)
ton, short (2,000 lb)	0.9072	metric ton
	Pressure	
atmosphere, standard (atm)	0.1013	megapascal (MPa)
bar	0.100	megapascal (MPa)
	Concentration	
parts per billion, by weight (ppb)	0.001	milligrams per kilogram (mg/kg)
parts per million, by weight (ppm)	1	milligrams per kilogram (mg/kg)
per mil (‰)	1	atoms per thousand atoms

Temperature in degrees Celsius (°C) may be converted to degrees Fahrenheit (°F) as follows:

$$°F=(1.8\times°C)+32$$

Temperature in degrees Fahrenheit (°F) may be converted to degrees Celsius (°C) as follows:

$$°C=(°F-32)/1$$

Evolution of Ore Deposits and Technology Transfer Project: Isotope and Chemical Methods in Support of the U.S. Geological Survey Science Strategy, 2003–2008

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Introduction

Principal functions of the U.S. Geological Survey (USGS) Mineral Resources Program are providing assessments of the location, quantity, and quality of undiscovered mineral deposits, and predicting the environmental impacts of exploration and mine development. The mineral and environmental assessments of domestic deposits are used by planners and decisionmakers to improve the stewardship of public lands and public resources. Assessments of undiscovered mineral deposits on a global scale reveal the potential availability of minerals to the United States and to other countries that manufacture goods imported to the United States. These resources are of fundamental relevance to national and international economic and security policy in our globalized world economy.

Performing mineral and environmental assessments requires that predictions be made of the likelihood of undiscovered deposits. The predictions are based on geologic and geoenvironmental models that are constructed for the diverse types of mineral deposits from detailed descriptions of actual deposits and detailed understanding of the processes that formed them. Over the past three decades the understanding of ore-forming processes has benefited greatly from the integration of laboratory-based geochemical tools with field observations and other data sources. Under the aegis of the Evolution of Ore Deposits and Technology Transfer Project (referred to hereinafter as the Project), a 5-year effort that terminated in 2008, the Mineral Resources Program provided state-of-the-art analytical capabilities to support applications of several related geochemical tools to ore-deposit-related studies.

In addition to advancing the understanding of the Nation's mineral resources, the Project also transferred geochemical technology and expertise to other high-priority investigations in the biological, hydrological, and geological sciences within the six science directions laid out by the USGS Science Strategy Team in their 2007 publication "Facing tomorrow's challenges: USGS science in the coming decade." Briefly stated, the six science directions are:

- Understanding ecosystems and prediction ecosystem change: ensuring the Nation's economic and environmental future
- The role of environment and wildlife in human health: a system that identifies environmental risk to public health in America
- A water census of the United States: quantifying, forecasting, and securing freshwater for America's future
- A national hazards, risk, and resilience assessment program: ensuring the long-term health and wealth of the Nation
- Climate variability and change: clarifying the record and assessing consequences
- Energy and minerals for America's future: providing a scientific foundation for resource security, environmental health, economic viability, and land management.

The rationale for the technology transfer stems from the recommendation of the USGS Science Strategy Team that,

> " . . . the USGS leverage its talents and skills to undertake comprehensive and integrated studies that examine the Earth as a system including atmosphere, biosphere, hydrosphere, and lithosphere."
>
> Facing tomorrow's challenges: USGS science in the coming decade

The analytical capabilities and scientific approaches developed within the Project have wide applicability within Earth-system science. For this reason the Project laboratories represent a valuable catalyst for interdisciplinary collaborations of the type that should be formed in the coming years for the United States to meet its natural-resource and natural-science information needs.

This circular presents an overview of the Project. Descriptions of the Project laboratories are given first including descriptions of the types of chemical or isotopic measurements that are made and the utility of the measurements.

This is followed by summaries of selected studies that were carried out by the Project scientists. The studies are grouped by science direction. Virtually all of them were collaborations with USGS colleagues or with scientists from other governmental agencies, academia, or the private sector. For the sake of brevity, individual collaborators are not named in the study descriptions. However, cooperating organizations are listed in a separate section, and the individual scientists appear as lead or junior authors on Project publications, which are listed in the final section.

Descriptions of Project Laboratories

Project laboratories employ commercially-available analytical instruments that are modified by Project scientists to meet specific research needs. The laboratories are supervised and operated by experienced scientists with strong backgrounds in their fields of specialization. An emphasis is placed on developing new conceptual approaches and on integrating information from multiple types of geochemical analysis in order to maximize the insight into complex natural systems. The development of new instrumentation, new analytical methods, and new conceptual approaches has led to groundbreaking research results in several scientific areas. The high level of innovation within the Project is recognized worldwide and has attracted graduate student volunteers, post-doctoral fellows, and visiting professors working on studies that support USGS science goals. The Project has also recruited several young scientists through the Mendenhall Fellow program, which represents an important vehicle for renewing and strengthening the USGS research staff.

Stable Isotope Laboratory

The elements that are studied in the field of stable isotope geochemistry—carbon, hydrogen, nitrogen, oxygen, and

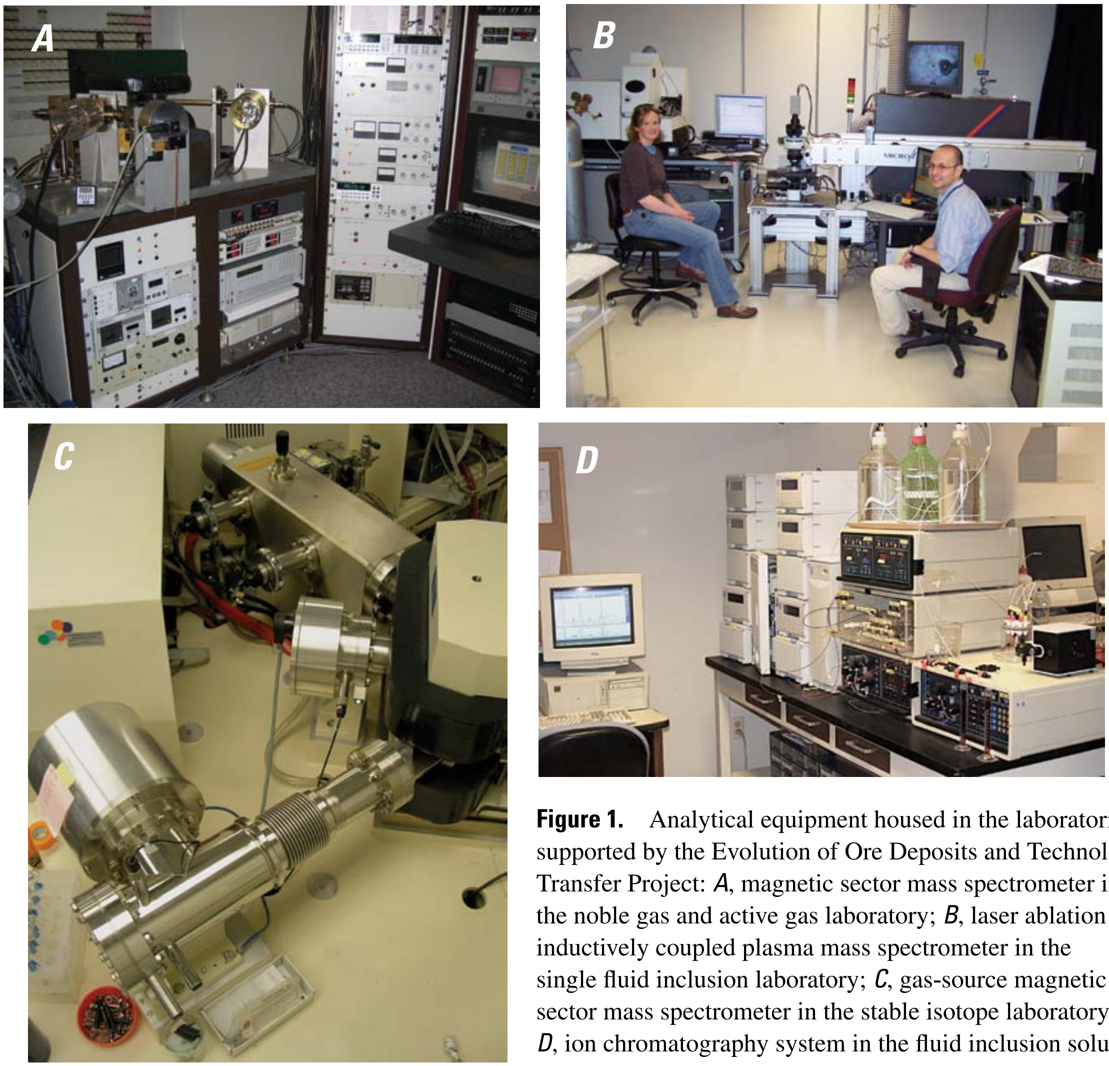

Figure 1. Analytical equipment housed in the laboratories supported by the Evolution of Ore Deposits and Technology Transfer Project: *A*, magnetic sector mass spectrometer in the noble gas and active gas laboratory; *B*, laser ablation inductively coupled plasma mass spectrometer in the single fluid inclusion laboratory; *C*, gas-source magnetic sector mass spectrometer in the stable isotope laboratory; *D*, ion chromatography system in the fluid inclusion solute chemistry laboratory.

sulfur—are abundant in many minerals and rocks; they are also the main building blocks of common geologic fluids (such as surface waters, groundwaters, high temperature fluids, and hydrocarbons) and biological compounds. Thus, in addition to being a useful tool for studying the Earth's lithosphere, stable isotope geochemistry is also useful for studying the hydrosphere and biosphere.

The stable isotope laboratory provides analyses of the isotopes of carbon, hydrogen, nitrogen, oxygen, and sulfur in a variety of solid, liquid, and gaseous samples. The laboratory contains five gas-source mass spectrometers and the equipment necessary to quantitatively convert the elements of interest into gaseous form prior to isotopic measurements. The present-day facility is the descendant of the laboratory established by the original USGS Branch of Isotope Geology, which was founded in the 1950s when the field was in its infancy. As a consequence of its long and robust history, the laboratory staff has at its disposal an exceptionally broad array of analytical capabilities and a wealth of accumulated experience in isotope applications. In contrast to most other stable isotope laboratories in academic institutions or in the private sector, the Project stable isotope laboratory offers a broader array of analytical capabilities and more extensive experience from which scientists can draw for new or innovative applications.

The development of new analytical techniques for novel scientific applications is ongoing in the laboratory. Recent analytical accomplishments are (1) the isotopic analysis of trace sulfur in biological and inorganic samples for application to ecosystem studies and mineral resource assessments, and (2) implementation of a method to analyze the minor isotope ^{17}O for application to studies of atmospherically deposited sulfate in Earth surface environments.

Noble Gas and Active Gas Laboratory

The concentrations and isotopic compositions of the noble gases are useful for tracing the movement of fluids within the earth-atmosphere system. Either alone or in combination with active-gas concentration measurements, the data allow sources of fluid constituents to be identified, and allow fluid-rock interactions to be characterized. Noble and active gas measurements can be insightful in diverse investigations. Examples of recent applications include (1) characterization of ore-forming fluids and ore-forming processes, (2) assignment of ages and time scales to geomorphic processes, (3) assessment of the age, flow rates, and recharge of groundwater resources, (4) monitoring of volcanic eruptions and associated hazards, and (5) determination of water budgets for wetland ecosystems.

The noble gas and active gas laboratory provides analyses of the concentrations and isotopic compositions of the noble gases helium, neon, argon, krypton, and xenon and the concentrations of the active gases hydrogen, methane, carbon dioxide, nitrogen, sulfur dioxide, and hydrogen sulfide in solid, liquid, and gaseous samples. Analyses can be obtained for virtually any geologic material using a custom-designed combination of high resolution static sector and quadrupole mass spectrometers with an automated ultrahigh vacuum sample inlet manifold. Active gas concentrations are calculated from quadrupole mass spectral data, whereas noble gas concentrations and isotopes are determined using both the quadrupole and sector mass spectrometers through the use of electron multiplier and ion counting techniques. The inlet manifold is equipped with getters and cryogenic traps to isolate and purify analyte gases. Other features of the inlet include calibrated gas pipettes, a high-temperature low-blank tantalum furnace and sample dispenser, a fluid inclusion multisample drop loader with tube furnace, a capillary jet separator, and numerous pass-through traps.

Fluid Inclusion Solute Chemistry Laboratory

Data on fluid inclusion solutes can reveal the sources of ore constituents and can help unravel ore-forming processes, both of which are important for developing scientifically robust geologic and geoenvironmental models for mineral deposits. The techniques can also be useful in studies of geologic environments unrelated to ore formation because fluid inclusions form in may different settings. Wherever they occur, the inclusions provide a valuable record of fluid composition, fluid and solute sources, and fluid-rock interactions along subsurface flow paths.

The fluid inclusion solute chemistry laboratory provides analyses of the concentrations of a suite of key anions and cations in tiny amounts of water liberated from inclusions in minerals. The centerpiece of the laboratory is a custom-designed ion chromatography system that measures the following chemical constituents: F^-, Cl^-, Br^-, I^-, NO_3^-, CO_3^{-2}, PO_4^{-3}, HS^-, SO_3^{-2}, SO_4^{-2}, $S_2O_3^{-2}$, SeO_4^{-2}, C_1–C_4 organic acids, Li^+, Na^+, NH_4^+, K^+, Rb^+, Cs^+, Fe^{+2}, Mg^{+2}, Ca^{+2}, Sr^{+2}, and Ba^{+2}.

Single Fluid Inclusion Laboratory

The analysis of single fluid inclusions within minerals takes advantage of recent developments in laser and mass spectrometer technology that are being used in only a few laboratories around the world. Inclusions in hydrothermal minerals can preserve remnants of the fluids that formed mineral deposits; the same analytical techniques can also be used to study inclusions in igneous quartz crystals that contain quenched silicate melts. The data that have been collected to date, in other laboratories as well as the USGS laboratory, have greatly advanced the understanding of the chemical characteristics of ore-forming fluids and have helped constrain the amounts of fluid required for the formation of deposits of significant size.

The single fluid inclusion laboratory provides measurements of metal concentrations in the inclusions. Analysis is performed using a petrographic microscope–laser ablation–inductively coupled plasma–mass spectrometer system. Inclusions as small as 10 microns diameter are identified using the petrographic microscope. They are exposed and ablated using the laser, and the ablated material is introduced to an inductively coupled plasma–mass spectrometer where between 20 and 40 different elements are measured.

Summaries of Selected Studies

Understanding Ecosystems and Predicting Ecosystem Change

Grizzly Bears in the Greater Yellowstone Ecosystem

Issue

The grizzly bear population (*Ursus arctos horribilis*) within the Greater Yellowstone Ecosystem (GYE) was listed as threatened under the Endangered Species Act from 1975 to 2007 due to concern over loss of habitat and high mortality resulting from conflicts with humans. Despite the recent increase in numbers, GYE bears remain vulnerable for many reasons, including isolation from other populations and predicted reductions in important food resources. The Interagency Grizzly Bear Study Team, a group of scientists that includes representatives from USGS, National Park Service, U.S. Fish and Wildlife Service, USDA Forest Service, Bureau of Land Management, and wildlife agencies of Idaho, Montana, Wyoming, Washington, British Columbia, and Alberta, was created to monitor long-term population status and habitats of GYE grizzly bears. An important goal of the recovery plan was to provide a scientific basis for habitat protection by conducting research on habitat use and nutritional ecology.

Objectives

Grizzly bear population viability depends in part upon the availability and acquisition of high quality food resources. Bear diets are known to vary seasonally and interannually, but they have traditionally been difficult to quantify, particularly over the long term and in the larger framework of ecosystem change.

Project scientists studied the nutritional ecology of GYE grizzly bears to improve the understanding of the foraging habits and potential nutritional constraints imposed on population recovery. The study, which included the dissertation project of a doctoral student at Washington State University, was coordinated by the Interagency Grizzly Bear Study Team. The overall objectives were to develop diet-composition estimates, confirm the nutritional importance of specific forage items, and constrain the amount of fish consumption from Yellowstone Lake and surrounding tributaries, all of which would aid in future management of the population. In designing the studies, scientists hoped to exploit chemical and isotopic methods that, if fruitful, could be employed as long-term monitoring tools to better understand the demography and ecology of GYE grizzly bears and offer opportunities for adaptive management in the face of changes to the ecosystem.

Background

In principle, animal diets can be inferred by comparing the isotopic compositions or trace element contents of potential food sources with the tissues of the animal. For GYE grizzly bears, potential food sources include bison and elk meat, cutthroat trout, army cutworm moths, white bark pine nuts, and vascular plants. In using the isotopic approach, it is important to calibrate the isotopic fractionations—or the vital effects involved in the synthesis of a particular tissue. For these studies the calibrations were determined at the Washington State University Bear Center by performing controlled feeding experiments using captive grizzly bears.

Results

The isotopic compositions of carbon, nitrogen, and sulfur were found to vary significantly among food resources in the GYE. In particular, pine nuts were identified as an important, lipid-rich food resource and grizzly bear diet estimates were shown to correlate with mast (crop) size. In addition, the mercury content of fish from Yellowstone Lake was found to be high due to the natural flow of mercury-bearing hydrothermal waters into the lake. Thus, mercury in bear tissues served as a fingerprint of this particular food source. Additionally, a second set of controlled feeding studies was employed to

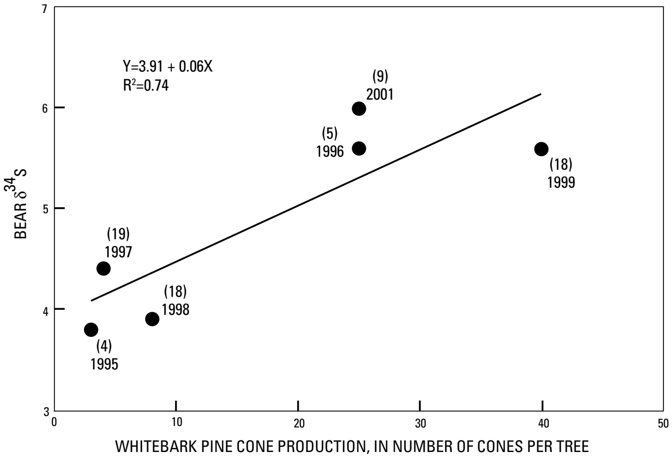

Figure 2. Sulfur isotopic composition of GYE grizzly bear hair relative to white bark pine nut mast crop. (Modified after Felicetti and others, 2003, Use of sulfur and nitrogen stable isotopes to determine the importance of whitebark pine nuts to Yellowstone grizzly bears: Canadian Journal of Zoology, v. 81, p. 763–770).

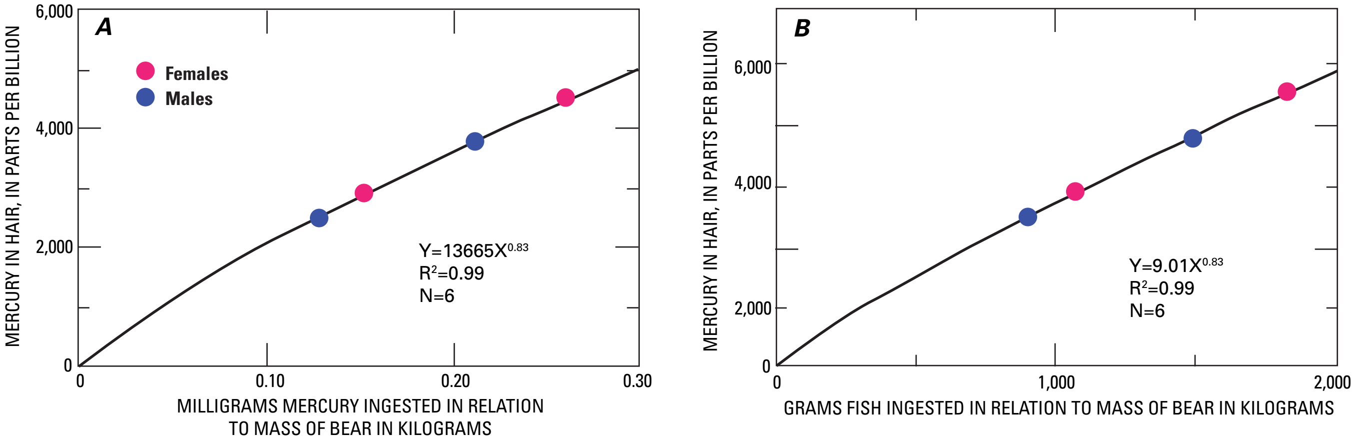

Figure 3. Relationships between mercury intake, concentration of mercury in hair, and Yellowstone Lake cutthroat-trout consumption for six captive grizzly bears. (Modified after Felicetti and others, 2004, Use of naturally-occurring mercury to determine the importance of cutthroat trout to Yellowstone grizzly bears: Canadian Journal of Zoology, v. 82, p. 493–501).

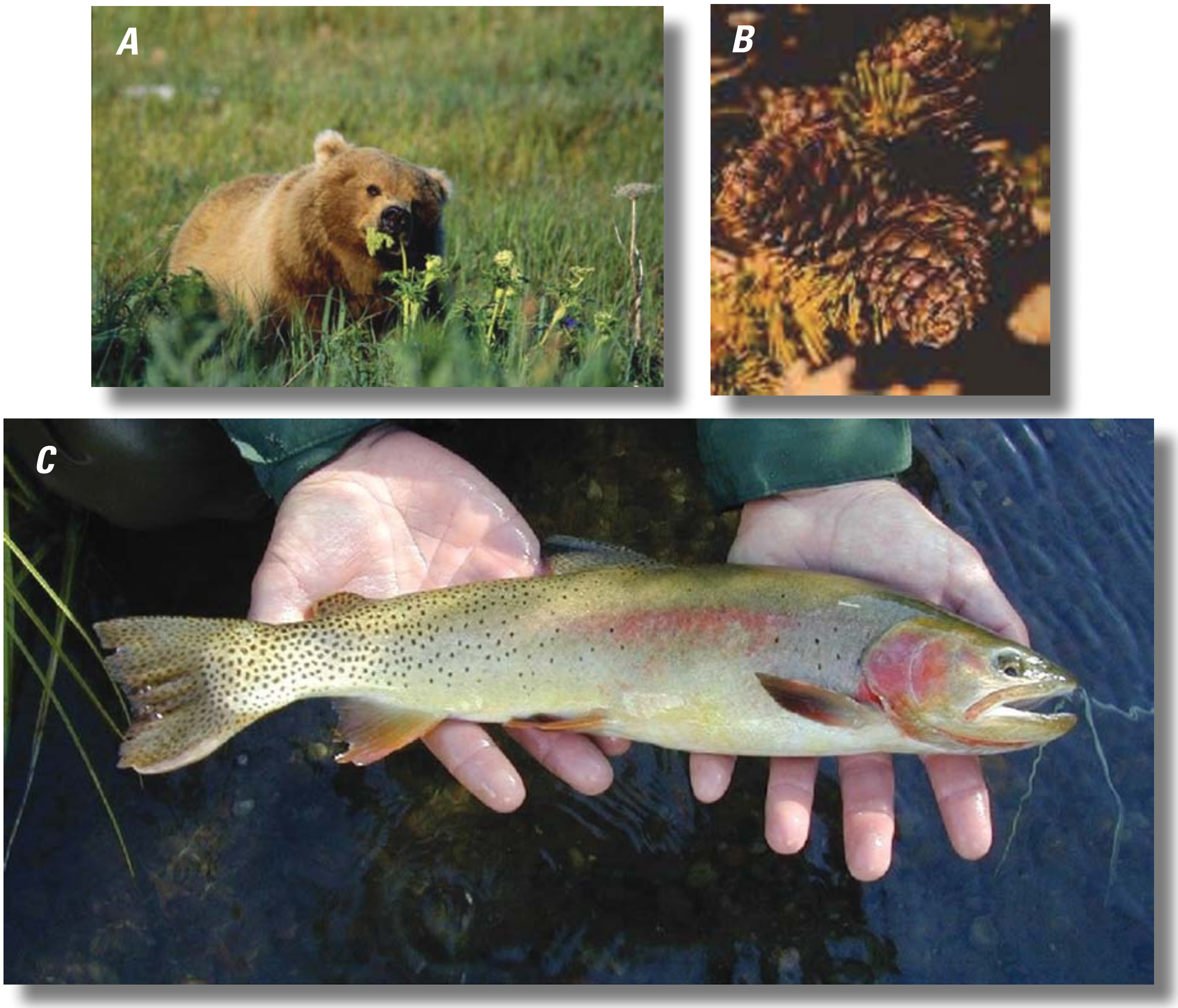

Figure 4. (*A*) Grizzly bear eating cow parsnip in Yellowstone National Park, photograph courtesy of Karyn Rode. Other important food sources for bears in the Greater Yellowstone Ecosystem include nut-bearing cones from white bark pine trees (*B*), photograph courtesy of Charles Schwartz, and cutthroat trout (*C*), photograph courtesy of USDA Forest Service.

calibrate mercury accumulation in bear hair as a function of cutthroat trout consumption. Using hair samples from GYE grizzly bears known to frequent the Yellowstone Lake area, it was shown that male GYE grizzly bears consumed about five times more trout than female bears.

Conclusions

White bark pine nuts, which bears obtain by raiding squirrel caches, are important for the survivability and reproductive success of female grizzly bears, but availability is constrained by mast crop. As a result, the spread of blister rust, a blight that has damaged white bark pine through much of its range in the northern Rocky Mountain region, has the potential to negatively impact the viability of the GYE grizzly bear population.

Mercury is subject to biomagnification; it was observed in high concentrations in the hair of male grizzly bears that consumed cutthroat trout from Yellowstone Lake. The novel combination of stable isotopes and a biomagnifying trace metal has for the first time made it possible to quantify the amount consumed of a particular dietary resource, which should prove helpful to managers. Additionally, isotopic and geochemical markers appear to have great promise as monitoring tools that can be employed in the GYE grizzly bear recovery plan.

Biogeochemical Perspectives on Prairie Wetland Food Webs

Issue

The Northern Great Plains is a mosaic of grasslands and pothole wetlands. The pothole wetlands, which are relict features of the last glaciation, are known to influence water quality, mitigate flooding, provide for groundwater recharge, and furnish critical habitat for wildlife, particularly migratory waterfowl. Habitat quality is maintained by the characteristic wet-dry cycle of this environment, whereby wetland hydroperiod is dynamic at the annual and decadal scales. Dry-down and sediment oxidation followed by reflooding appears to be very important for nutrient regeneration and for sustaining high levels of aquatic productivity. Hydrologic and biogeochemical linkages between discrete wetlands are an important feature of the prairie landscape, but the linkages are not well understood, especially with regard to aquatic food webs. An improved understanding of the ways in which individual prairie wetlands interact with adjacent wetlands and with the surrounding terrestrial landscape would aid in land management decisionmaking, particularly as it relates to the availability of high quality aquatic habitat for migratory waterfowl throughout the Northern Great Plains.

Objectives

The goal of this work was to characterize the seasonal dynamics of pothole-wetland sulfur biogeochemistry within the fabric of a prairie landscape. Sulfur has multiple oxidation states and is subject to a variety of geochemical transformations that can be explored in great detail using sulfur isotope techniques. The objectives of the project focused on better understanding surface water/groundwater hydrochemical interactions within a small prairie wetland subcatchment and the extent to which aquatic food webs integrate landscape-scale biogeochemical processes. The research was conducted as part of a Mendenhall Postdoctoral Fellowship under the supervision of senior scientists from the Geologic and Biological Resources Disciplines.

Background

The study was conducted in a highly instrumented subcatchment (about 65 hectares) located in eastern South Dakota, which consisted of four wetlands along a hydrologic gradient corresponding to approximately six meters of total relief. Surface water, groundwater, and wetland biota were collected during the growing seasons of 2002 and 2003. The sulfur isotopic composition was measured in all samples and used in combination with sulfur geochemistry to assess important biogeochemical processes, surface water–groundwater interactions, and sources of sulfur to aquatic food webs. Sulfur is a redox sensitive element that spans a wide range of oxidation states and offers a novel tracer for wetland biogeochemical processes such as bacterially mediated sulfate reduction, sulfide oxidation, and food-web relationships.

Results and Conclusions

Groundwater geochemistry evolves rapidly along the predominant flow path (from higher elevation portions of the watershed to lower elevation portions), with higher salinities lower in the landscape. High salinities derive, in part, from the oxidation of sulfides in glacial tills which produces secondary sulfate with distinctive depleted sulfur isotopic compositions. The groundwater salinities are highly diagnostic of wetland hydrologic function in that lower salinity waters reflect areas of groundwater recharge. Surface waters exhibited a similar downgradient salinity pattern, but were more dilute. Surface water sulfur isotopic compositions ranged more widely than groundwater compositions, which suggests that oxidation and reduction processes exerted a strong influence on the dissolved sulfur pool. Higher salinity surface waters generally had isotopically more depleted sulfate, but the isotopic compositions were not related in a simple way to position in the landscape. Wetland primary and secondary consumers (snail and dragonfly, respectively) were isotopically depleted relative to

Figure 5. Aerial photo of study catchment in eastern South Dakota. Arrow denotes the predominant groundwater flow direction along approximately six meters of total relief. Four discrete wetlands are shown: semipermanent (SP) wetlands are located at groundwater discharge sites in lowlands, whereas seasonal (S) wetlands are located at groundwater recharge sites in uplands.

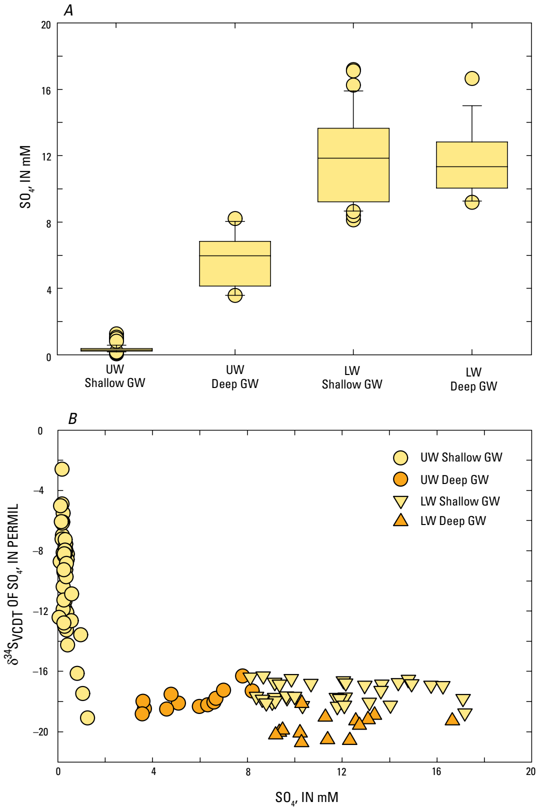

Figure 6. (*A*) Box and whisker plot of groundwater sulfate concentrations indicating a general increase in salinity along the hydrologic flow path. (*B*) Sulfur isotopic compositions of groundwater sulfate showing that different locations and depths along the flow path are isotopically distinct. UW corresponds to upper watershed, LW corresponds to lower watershed.

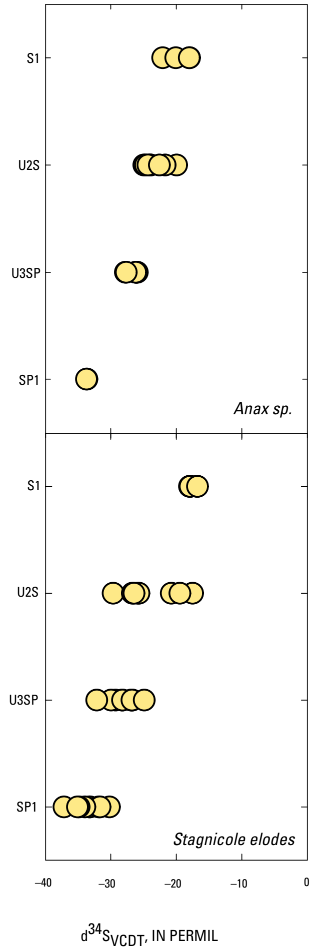

Figure 7. Consumer (*Stagnicola elodes* or snail and *Anax* species or dragonfly) sulfur isotopic compositions vary systematically with position in the landscape. Both consumers show an isotopic depletion down hydrologic gradient (from S1 to SP1), which suggests that consumers integrate aspects of wetland and landscape biogeochemistry. There is a strong negative correlation between wetland sulfate concentration and sulfur isotopic composition of consumers.

source waters (surface and groundwater), which suggests that secondary sulfate is the predominant sulfur source for wetland food webs. Consumer isotopic patterns closely tracked salinity patterns and were spatially distinct within the subcatchment. The study demonstrated that sulfate reduction and transient oxidation caused by water-level fluctuations, in combination with limited shallow groundwater contributions, impart unique food-web sulfur isotope signatures in prairie wetland landscapes. Further, the focus on sulfur biogeochemistry has provided a more detailed understanding of the way in which hydroperiod influences nutrient regeneration in wetland soils, particularly redox-sensitive elements.

Nutritional Stress as a Possible Cause for Declines in the Western Stock Steller Sea Lion

Issue

The western stock of the Steller sea lion (*Eumetopias jubatus*), which ranges from the Gulf of Alaska to the Kuril Islands, has declined in recent decades and is currently listed under the Endangered Species Act. The decline is thought to reflect, at least in part, decreased juvenile survival rates. Decreased survival may reflect an inability of adult females to deliver adequate milk to large late-lactation pups, or an inability of newly weaned pups and juveniles to acquire sufficient food while foraging. Potentially, the effects of nutritional stress might be expressed in shorter nursing times, changes in times of weaning, and changes in foraging behavior by young. Improvements in underwater capture techniques have aided researchers in studying sea lions younger than three years, but the capture of adult females remains difficult and is currently prohibited under U.S. Marine Mammal Protection Act permits. It is critical to develop a more detailed understanding of Steller sea lion diets so that scientifically sound fishery-management policies can be developed.

Figure 8. Free-ranging Steller sea lions in coastal waters of the North Pacific Ocean, photograph courtesy of Lorrie Rea. Research on these animals was undertaken under Marine Mammal Protection Act permit #358–1888 and Alaska Department of Fish and Game Animal Care and Use Committee assurance #06–07.

Figure 9. Vibrissae being removed from a captured juvenile Steller sea lion, photograph courtesy of Lorrie Rea. Research on this animal was undertaken under Marine Mammal Protection Act permit #358–1888 and Alaska Department of Fish and Game Animal Care and Use Committee assurance #06–07.

Objectives

Project scientists, in collaboration with Alaska Department of Fish and Game and the National Oceanic and Atmospheric Administration, employed stable isotope techniques to study the nutritional ecology of wild free-ranging Steller sea lions. Vital isotope effects were first assessed through paired comparisons of pup vibrissae roots (whiskers; most recent growth) with blood serum and fresh milk (pumped from stomachs). Vibrissae collected from juveniles were used to develop isotopic chronologies that, after adjustment for vital effects, could be used to reconstruct dietary histories and evaluate the role of nutritional stress on population declines.

Background

Vibrissae were collected from pups and juveniles throughout the range of the Western stock (Prince William Sound, southeast Alaska, Aleutian Islands). The vibrissae were sectioned into discrete intervals and the stable carbon and nitrogen isotopic compositions measured. Steller sea lion pups are born with developed vibrissae, so the tips (first growth) represent in-utero growth that reflects the maternal diet. Subsequent vibrissae growth reflects the milk diet during periods of nursing, followed by a transition (weaning) to independent foraging on whole prey items. Changes in carbon and nitrogen isotope values in the vibrissae chronologies reflect the seasonal availability of dietary resources, the general location of foraging (inshore and offshore), and dietary composition

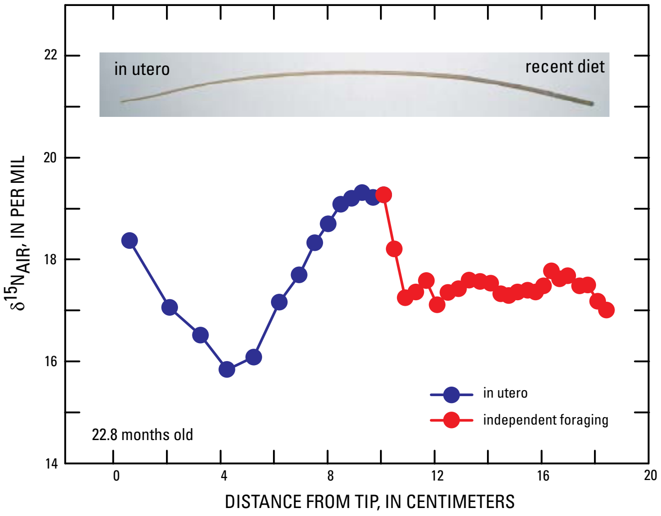

Figure 10. Vibrissae chronology for a 22.8 month old juvenile from southeast Alaska. Changes in isotopic composition correspond to seasonal maternal diet shifts (in utero) and the nutritionally independent juvenile. Weaning is likely indicated by the abrupt decrease in nitrogen isotope value at about 10 cm distance from tip, which suggest a drop in trophic level. This research was undertaken under Marine Mammal Protection Act permit #358–1888 and Alaska Department of Fish and Game Animal Care and Use Committee assurance #06–07.

(milk versus whole prey). Additionally, the time frame in which juveniles are weaned can potentially be inferred from decreases in nitrogen isotope values, a reflection of trophic level. Project scientists will use these data to contrast the nutritional ecology of discrete Western stock populations and evaluate the role of nutritional stress on recent declines.

Results and Conclusions

Isotopic discrimination during vibrissae growth was determined empirically by parallel analysis of pup vibrissae and fresh milk pumped from their stomachs. Vibrissae $\delta^{13}C$ and $\delta^{15}N$ values are higher than the corresponding milk values by 2.0 and 2.5 per mil, respectively. After accounting for this offset, pup vibrissae data can be used to infer the diet of the lactating female at the time of milk production. Strong seasonal changes in the isotopic profiles of pups from southeast Alaska suggest that adult females switch to a higher trophic level diet once they leave the breeding rookeries on the outer coast for inshore haul out locations. Seasonal fluctuations were also evident in Prince William Sound animals. Independent foraging by pups is marked by a change in trophic level following weaning. Continuing work is allowing for an assessment of the nutritional-stress hypothesis for population declines.

Nutritional Ecology of Denali Wolves

Issue

Nutrition is known to be a critical control of the demographics and sustainability of natural free-ranging wildlife populations, but the nutritional ecology of many important species is poorly understood because it is notoriously difficult to study. Throughout North America, wolves (*Canis lupus*) have been assumed to be obligate predators of ungulates (moose, caribou, Dall sheep) with other prey playing little or no role in wolf-population dynamics. This assumption has been difficult to verify using traditional diet assessment methods such as visual tracking or scat analysis. For management purposes, especially in locations where wolf control measures have been adopted, it is important to evaluate potential nonungulate food sources so that the understanding of wolf ecology can be improved.

Objectives

In collaboration with the USGS Biological Resources Discipline and the National Park Service, stable isotope techniques were used to derive diet estimates of free-ranging wolves in Denali National Park and Preserve (DNPP) in central Alaska. Of particular interest was the dietary importance of spawning Pacific salmon because salmon are a high quality food resource that could subsidize wolf diets during winter when other foods are less available. In coastal settings, wolf populations are known to utilize seasonally available salmon as a dietary resource, but marine food subsidies to central Alaska wolves have not been considered in assessing the nutritional ecology of these animals.

Background

The free-ranging wolves of DNPP have been intensively studied for decades by BRD and NPS scientists. In a collaboration with Project scientists, carbon and nitrogen isotope ratios were measured on bone collagen from 73 wolves that had been radiocollared during the time period 1986–2002, and on potential diet items that were available to wolves within their home ranges. Using previously published values for vital isotope effects associated with collagen synthesis, wolf diets were estimated and comparisons made among the various DNPP packs in the context of available dietary resources.

Results and Conclusions

Ungulates comprised the majority of DNPP wolf diets. However, wolves from home range locations with access to salmon showed clear differences in their bone collagen isotopes consistent with utilization of salmon as a dietary resource. From an energetics perspective, the fall runs of chum and Coho salmon were comparable to the ungulate biomass in the Northwestern flats (region 1 in fig. 12). The fact that wolf density in this area exceeds the predicted density based

Figure 11. Fitting a radio collar to an anesthetized wolf in Denali National Park and Preserve, photograph courtesy of Layne Adams.

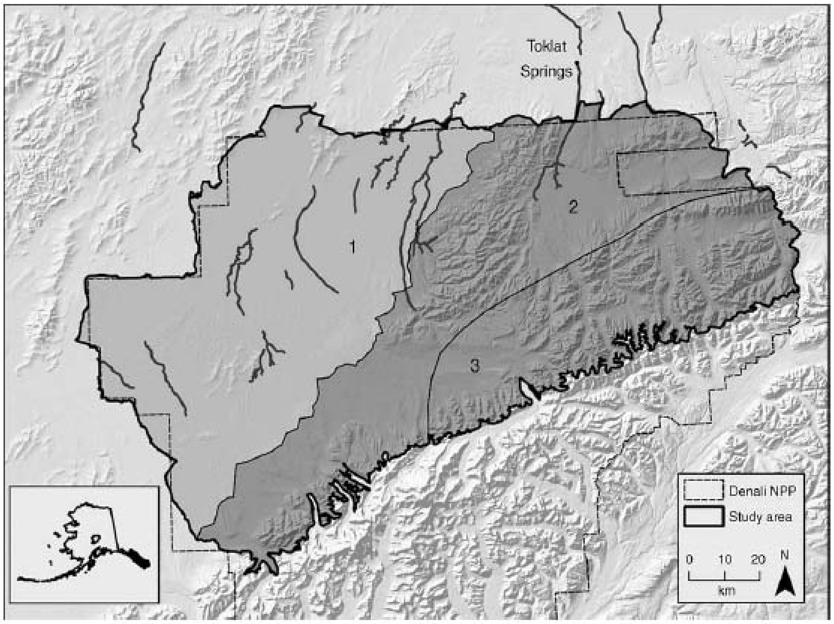

Figure 12. The study area within Denali National Park and Preserve was divided into three regions on the basis of ungulate abundance and access to spawning Pacific salmon. Region 1 offered ready access to salmon and low ungulate densities; region 2 offered some access to salmon and moderate ungulate densities; region 3 offered no access to salmon and moderate ungulate densities.

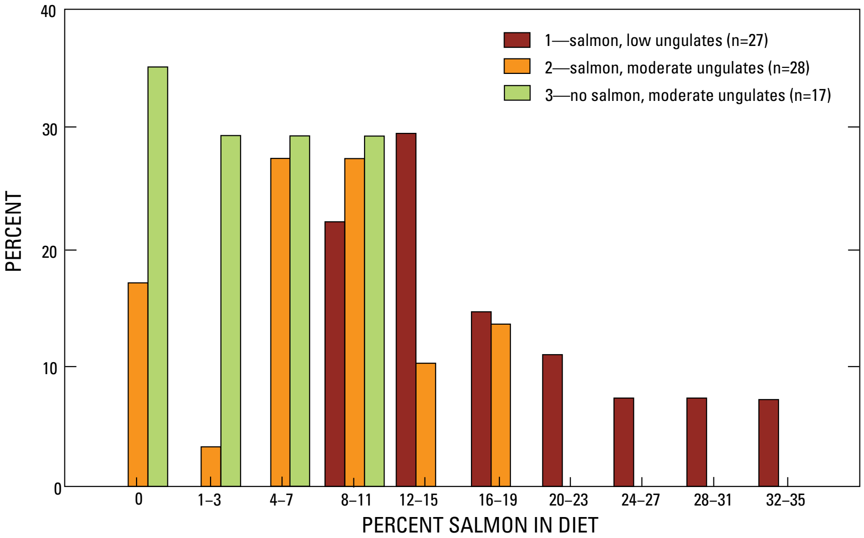

Figure 13. Estimates of the proportion of salmon in wolf diets for each of the three regions within the Denali National Park and Preserve study area. Region 1 wolves had the greatest proportion of dietary salmon.

solely on ungulate biomass is consistent with a contribution of salmon to wolf diets that is comparable to the contributions that have been estimated for wolves in coastal settings in southeast Alaska. The wolf abundance in the Northwestern flats of DNPP was probably enhanced by the nutritional subsidy provided by salmon. The greater wolf abundance in the area may also indicate that moose densities are depressed through increased predation.

The Role of Environment and Wildlife in Human Health

Anthropogenic Sulfate in Natural Waters

Issue

Sulfate (SO_4^{2-}) is present at significant concentrations in many surface waters and groundwaters. Its origin can be either natural—principally rock weathering and natural sulfate in precipitation—or pollutive. Elevated sulfate can be a consequence or indicator of processes that adversely affect water quality and the environment. These include acidification of surface waters, buildup of salts in associated soils which can stunt vegetation and lower crop yields, and point- or diffuse-source pollution. At many localities it is difficult to determine the source of abundant sulfate, so whether water quality reflects natural process or pollution can be uncertain, particularly where pollution sources are suspected but not proven.

Objectives

Isotopic techniques have been utilized to determine the sources of dissolved sulfate in natural waters, the chemical pathways by which sulfate was produced, and the importance of natural attenuation. The methods, which rely on the combined measurements of the isotopic composition of sulfur and oxygen, have been applied to several sites where water quality is of concern. These include sites affected by mine drainage, sites where soils are rich in evaporative salts, alpine streams that are highly sensitive to acid precipitation, and a fly-ash disposal site where groundwaters are monitored for evidence of elemental mobility from the ash. In each of the studies, the isotope tools are being used to identify the source of dissolved sulfate and the chemical reactions or physical processes controlling its mobility.

Background

Both sulfur and oxygen have multiple stable isotopes that can be measured and used to constrain the sulfate source. For example, low $\delta^{34}S$ values suggest that sulfate was produced by oxidation of either bacterial H_2S or minerals that formed from bacterial H_2S, whereas high $\delta^{34}S$ values can indicate weathering of sulfate minerals in sedimentary bedrock. Low $\delta^{18}O$ values implicate the weathering of sulfide minerals by meteoric water, whereas high $\delta^{18}O$ values suggest either weathering of sulfate minerals of sedimentary origin or the deposition of atmospheric sulfate. Conclusive evidence for atmospheric sulfate can be found in measurements of $\delta^{17}O$. Source attribution arguments are strongest where isotopic analyses can be obtained for the potential sources of sulfate and an isotopic match can be demonstrated between source and water.

Results

Studies have been carried out at sites ranging from alpine settings in the Rocky Mountains to semiarid settings in eastern Colorado. Major findings include the following:

- Excess ^{17}O appears to be characteristic of atmospheric sulfate deposited in alpine snow; measurements of this parameter may be useful in identifying atmospherically derived sulfate and tracking its movement through alpine soils.

- Coal-mine spoils along the Front Range in northern Colorado drain sulfate that is high in $\delta^{34}S$ (fig. 14A) relative to the background sulfate in local soils, salts, and surface waters, which suggests that sulfur isotopes might be useful in monitoring environmental effects of past coal mining activity.

- Saline soils along the Front Range contain sulfate with $\delta^{34}S$ values that are predominantly negative irrespective of whether the δ-values in the underlying bedrock are negative or positive (the marine Pierre Shale and the nonmarine Laramie Formation, respectively; figs. 14B, C); this suggests that the salts are not anthropogenic but rather reflect deposition of wind-blown sediment that originated in upwind Pierre Shale outcrops in the northwestern portion of the area.

- At fly-ash disposal sites sulfur isotopic measurements of sulfate in surrounding groundwaters—which can be obtained from monitoring wells—can be a very sensitive indicator of the leaching of ash constituents to local groundwater.

Conclusions

Isotopic tools for studying the source and fate of sulfate have wide application in investigations of processes influencing surface and groundwater quality.

Cyanide in Leach Wastes at Gold Mines

Issue

At most gold mines, the ores are processed using a dilute solution of cyanide (CN^-). Cyanide can be toxic to wildlife and humans, so its use is closely regulated. At some mines, the ore-processing solutions are released through permitted

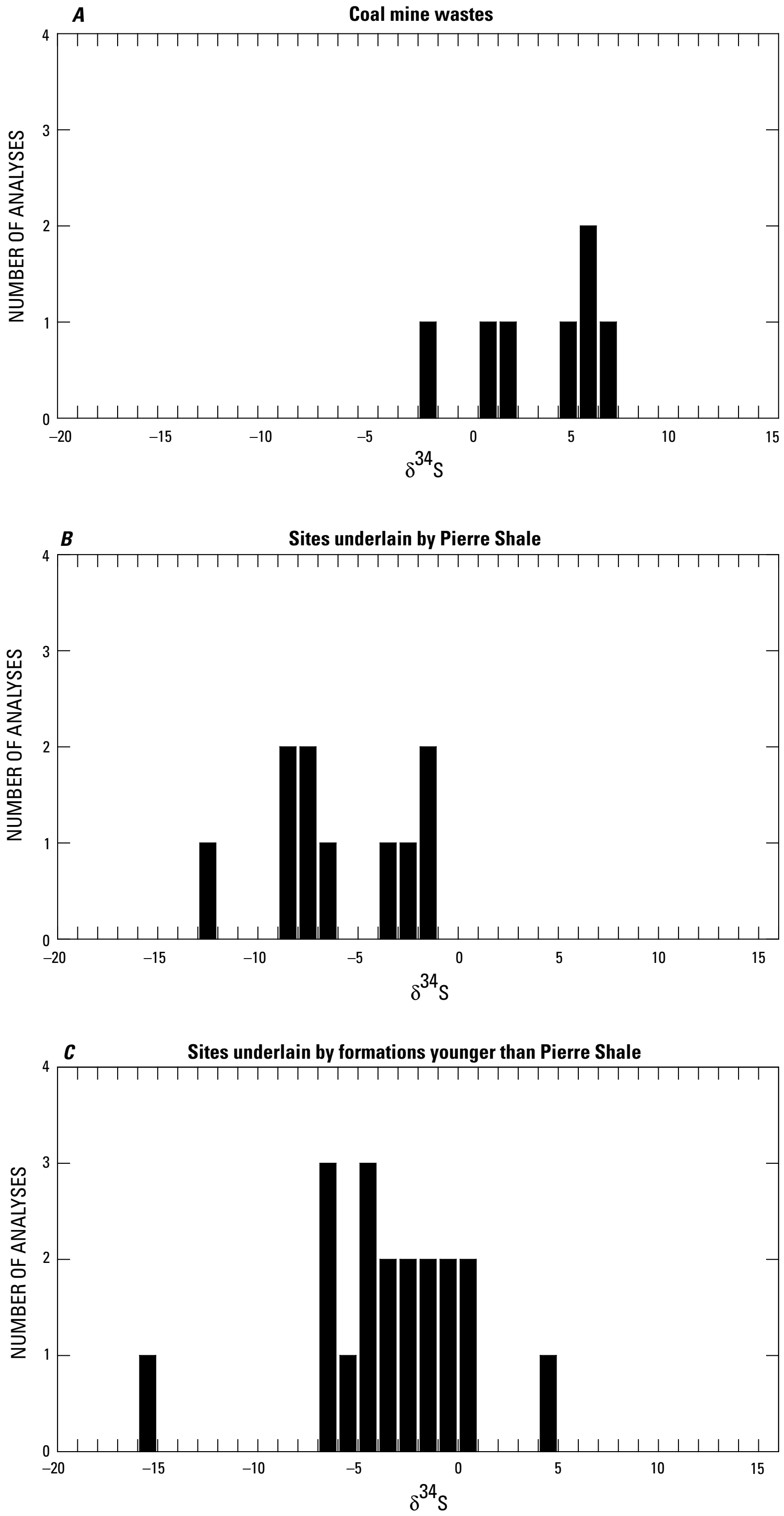

Figure 14. Sulfur isotopic compositions of sulfate in salts, soils, and coal mine wastes from Front Range sites north of Denver. On average, coal mine wastes (*A*) are isotopically distinct from background salt and soil in the area (*B, C*), which suggests that sulfur isotope analyses may be useful as tracers of water pollution related to coal mining. (Data from Otton and others, 2005, Origin of saline soils in the Front Range area north of Denver, Colorado: U.S. Geological Survey Professional Paper 1698, p. 73–87)

discharges following detoxification. Occasionally they are released unintentionally through accidental spills or unintended seepage from ore heaps or tailings. The released solutions typically contain a variety of metal-cyanide complexes that form during leaching of the mined rock by reaction of the CN^- anion with metal-containing minerals. Toxicity varies greatly among the different metal-cyanide complexes; the cyanocomplexes of zinc, for example, are significantly more toxic to aquatic life than the cyanocomplexes of copper. As a consequence of the varying toxicities, it is difficult to assess the environmental significance of cyanide in released process solutions without a complete chemical characterization of the solution, or an accurate prediction of cyanide speciation.

Objectives

To better assess the environmental significance of solution releases at ore-processing operations at gold mines, cyanide was studied at active and inactive operations in the southwestern United States in collaboration with mining company metallurgists, and at sites where leach solutions had been released to the environment in collaboration with environmental and U.S. EPA scientists. The objectives of the work were to improve the understanding of cyanide chemical speciation in leach solutions and to examine the environmental controls on cyanide persistence. Complete chemical analyses of water samples were carried out using specially developed analytical techniques, and stable carbon and nitrogen isotope analyses were made of the dissolved cyanide. In addition, toxicity tests were carried out in collaboration with biologists at the USGS Columbia Environmental Research Center to examine the tolerance of fish and fresh water crustaceans for metal-cyanide complexes that had not been previously recognized in gold leach effluents.

Background

At modern gold mines, the gold is leached either by mixing cyanide solutions and crushed ore in vats or by pumping cyanide solutions onto ore heaps and allowing the solutions to percolate through to underlying drains. In both methods, the solutions are then recovered, stripped of their gold, and reused in subsequent leach cycles after cyanide and other reagents are added as necessary. In the arid southwestern United States, which is where the majority of United States gold mines are located, the recycling of process solutions is typically complete and there is no net discharge from the ore-processing operation. The cyanide complexes that form during the leach process can be determined by comparing chemical analyses of fresh cyanide solutions and with chemical analyses of metal-carrying cyanide solutions exiting vats or ore heaps. The same types of chemical analyses applied to solution storage ponds or subsurface seepage will give insights on the persistence of specific cyanide species. Stable carbon and nitrogen isotope measurements can in principle give information on mechanisms by which cyanide is lost from process solutions.

Results

- Carbon and nitrogen isotopic compositions of cyanide do not change through the leaching process which suggests that the quantities of cyanide released to the atmosphere from gold-leach operations is minor. The measurements also reveal that industrial cyanide sources can differ greatly in their carbon isotopic compositions. Thus, carbon isotopes may be useful as a forensic tool at sites where the source of cyanide pollution must be determined.

- Cyanide combines with iron during leaching to produce low-toxicity chemical complexes. However, these complexes can revert to higher-toxicity free cyanide as a consequence of photolytic dissociation of the complexes where process solutions are sunlight-exposed.

- Significant amounts of cyanide can combine with cobalt during leaching even at mines where cobalt is present in the ores at trace levels. Where process solutions are not sunlight exposed—as in seepage to the subsurface—cobalt-cyanide complexes tend to be long-lived and may be the most persistent cyanide species. However, where the solutions are sunlight-exposed, the complexes can revert to higher-toxicity free cyanide, much like iron-cyanide complexes.

- Cobalt-cyanide complexes are not especially toxic to fish but, where effluents are exposed to sunlight, photolytic dissociation can produce free cyanide resulting in higher toxicity.

Conclusions

Although it is present at no more than trace concentrations in most gold ores, cobalt may be the ultimate control on cyanide persistence in ore-processing wastes at many gold mines. Cyanide combines with cobalt to form a strong chemical complex that will persist unless it is exposed to sunlight. Monitoring cyanide-cobalt complexes during the remediation stage and taking specific steps to degrade them would likely reduce the potential for negative environmental consequences resulting from cyanide use at gold-leach operations.

A Water Census of the United States

Geochemical Reconnaissance of the Arbuckle-Simpson Aquifer, South-Central Oklahoma

Issue

In 2002, the Central Oklahoma Water Resource Authority, which consists primarily of communities in Canadian County, offered to purchase water from the Arbuckle-Simpson aquifer, to drill production wells, and to build an 88-mile

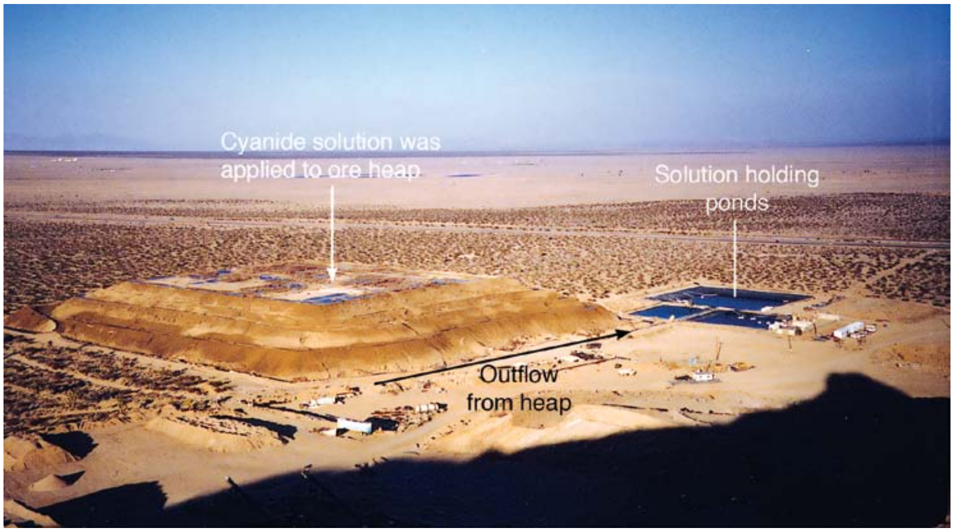

Figure 15. Heap leach operation at the Standard Hill gold mine near Mohave, CA. Leaching of the ore heap was halted several years ago after the mine was exhausted of ore. The heap was subsequently remediated by rinsing with clean groundwater. Photograph courtesy of David Grimes.

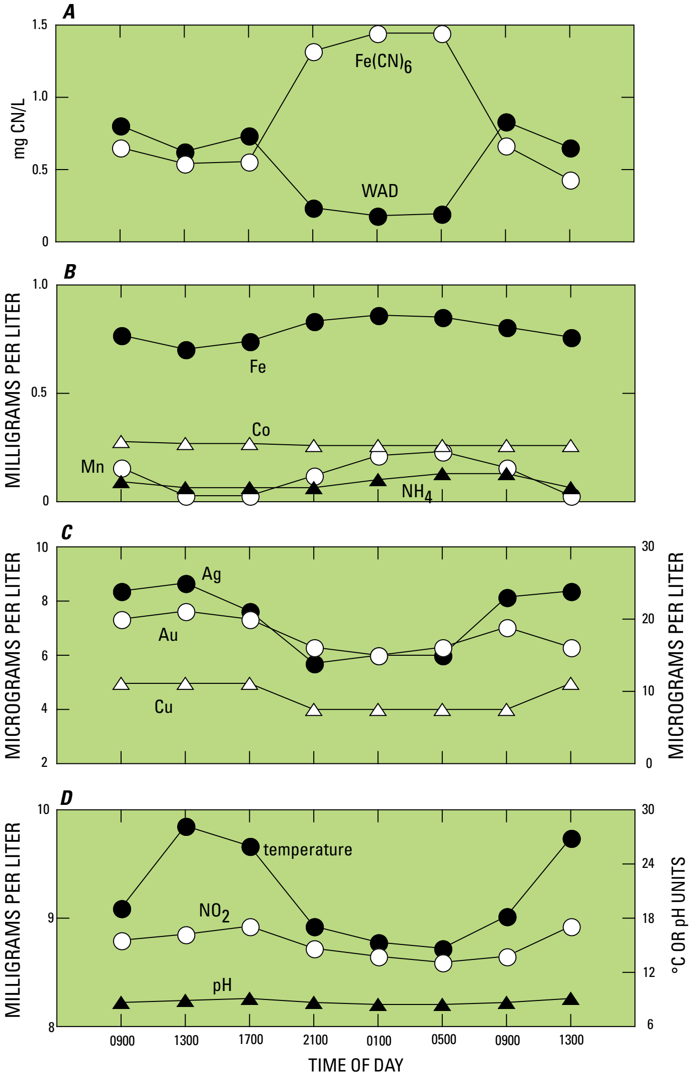

Figure 16. Diurnal cycles in chemical constituents of heap effluent passing through a sunlight-exposed channel at Standard Hill: *A*, Iron-complexed cyanide and WAD cyanide (which includes both free cyanide and cyanide contained in weak complexes with zinc, copper, silver, and other metals); *B*, Total dissolved iron, cobalt, manganese, and ammonium; *C*, Total dissolved silver and gold (concentrations on right axis) and copper (concentrations on left axis); *D*, Nitrite, solution temperature, and solution pH. The data suggest that iron-cyanide complexes dissociate in sunlight to produce free cyanide, increasing the concentration of WAD cyanide, and free iron, which precipitates as oxyhydroxides decreasing the concentration of dissolved iron. The free cyanide produced during daylight hours liberates silver, gold, and copper from channel sediment as cyanocomplexes.

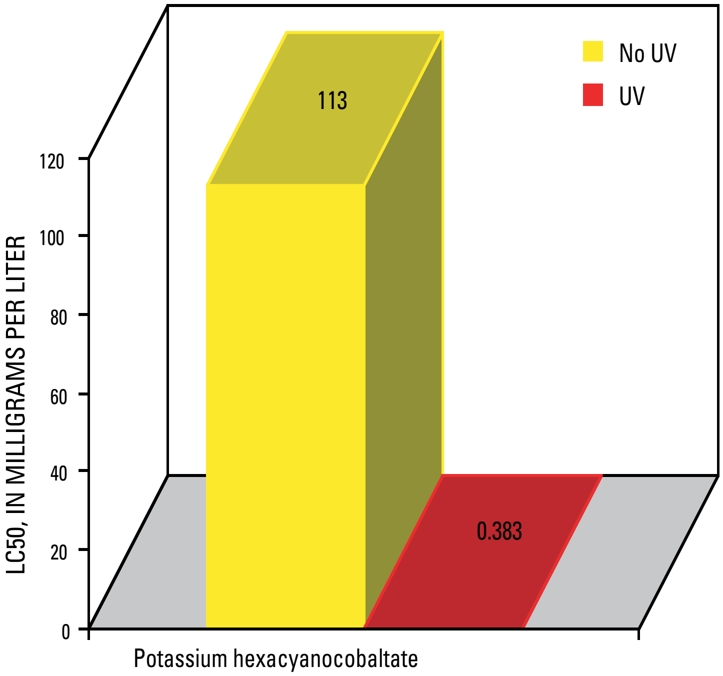

Figure 17. The results of toxicity experiments in which juvenile rainbow trout were exposed to cobalt-complexed cyanide. The toxicity was two orders of magnitude higher in sunlight-simulating ultraviolet light (UV) than in darkness (no UV) reflecting the tendancy of cobalt-cyanide complexes to produce high-toxicity free cyanide by photodissociation. LC50 is the concentration at which mortality was 50 percent after 90 hours. (Data from Little and others, 2007, Toxicity of cobalt-complexed cyanide to *Oncorhynchus mykiss*, *Daphnia magna*, and *Ceriodaphnia dubia*: Environmental Science and Pollution Research, v. 14, p. 333–337).

pipeline to transport the water to Canadian County. In the State of Oklahoma, groundwater is the property of the owner of land surface rights. Thus, the withdrawal and transport of water by the Central Oklahoma Water Resource Authority would be considered a permissible use by the State of Oklahoma. However, local residents, citizen groups, and the National Park Service were concerned that large withdrawals from the Arbuckle-Simpson aquifer would reduce flow in rivers and springs and cause groundwater levels to decline jeopardizing water supplies, recreational opportunities, and aquatic habitat.

Objectives

In response to these concerns, the Oklahoma Senate passed Senate Bill 288, which imposed a moratorium on the issuance of temporary groundwater permits for the use of municipal or public water supplies outside the boundaries of any county that overlies a “sensitive sole source groundwater basin.” The Arbuckle-Simpson aquifer is the only aquifer in Oklahoma classified as sole source. The Oklahoma Water Resources Board, in cooperation with the U.S. Bureau of Reclamation, the USGS, Oklahoma State University, and the University of Oklahoma, initiated a comprehensive multiyear investigation of Arbuckle-Simpson aquifer in south central Oklahoma to evaluate possible consequences of new large water withdrawals.

Background

A geochemical reconnaissance of the Arbuckle-Simpson aquifer was initiated in 2004 to characterize the groundwater quality at the aquifer scale, to determine the chemical evolution of groundwater as it flows from areas of recharge to areas of discharge in streams and springs, and to determine water residence times. Characterization of aquifer-scale groundwater quality was accomplished by (1) collecting 36 water samples from 32 wells and springs distributed across the aquifer for analysis of major ions, trace elements, isotopes of oxygen and hydrogen, dissolved gases, and age-dating tracers; and (2) compiling descriptive statistics using the results of the water analyses.

Results

The chemistry results show that the fresh waters within the aquifer are well suited for public water supplies. Carbon-14, tritium, and dissolved-gas data were used to calculate groundwater ages, recharge temperatures, and mixing relationships for the aquifer. Data from multiple age-dating techniques indicate that all but two sampled waters represent recharge to the aquifer since 1950. The two exceptions are sites where carbon-14 results gave recharge ages of 33,000 and 9,000 years. These wells produce water from the confined portion of the aquifer and are not representative of the fresh-water portion. The fact that most of the sampled groundwater was modern (less than 55 years old) indicates that water is moving quickly from recharge areas to discharge to streams and springs.

Figure 18. Photograph of historic Vendome Well in the Chickasaw National Recreation Area, which is fed by water from the Arbuckle-Simpson aquifer.

Conclusions

The results of the investigation show that drinking-water quality is good within the aquifer. The young ages of the groundwaters are advantageous for development of the aquifer as a public water supply because they suggest that replenishment is relatively rapid. Older, poorer quality (more saline) waters exist in the system, but these appear to be easily defined spatially and may not pose problems for future development. Although the geochemical investigation is encouraging for the development of the aquifer, further evaluations will be needed to determine the size of the fresh-water resource and the withdrawal rate that can be sustained without depleting the resource.

Noble Gas Geochemistry of the Edwards Aquifer, South-Central Texas

Issue

The Edwards-Trinity area in south-central Texas hosts a rapidly growing population, a broad array of land uses, and a great diversity of plant and animal species. The area can be considered as an ecosystem comprising the Edwards aquifer and its catchment area. One of the most productive carbonate aquifers in the world, the Edwards aquifer is the sole source of water for more than 1.5 million people living within the city of San Antonio. In addition to supplying domestic water needs, the aquifer provides nearly all the water that supports industry, military installations, and irrigation in the area. The water needs of San Antonio potentially compete with the needs of farmers and ranchers west of the city. Furthermore, withdrawals by the city may threaten the artesian flows that are responsible for the largest springs in the southwestern United States, which supply water to downstream municipal and agricultural users, sustain habitat for endangered species, and support tourism-based local economies. The Edwards aquifer also harbors diverse aquatic communities both above and below the land surface. Some 90 species, one-half of which are subterranean, are unique to the region.

Objectives

The Edwards aquifer stores large quantities of water, but only limited amounts can be withdrawn without causing spring flows to be reduced. Digital hydrologic models are being developed by the USGS to assist managers in optimizing water use. Groundwater, surface water, geological, and biological models are being constructed to assess the effects of water withdrawals on the entire ecosystem. To help attain balance between sustainable water withdrawal from the aquifer and public- and federally-mandated water needs, Project scientists are conducting multidisciplinary studies in cooperation with the Edwards Aquifer Authority, San Antonio Water Systems, and the USGS National Mapping Program to gather input data for the models so that regulators have access to the appropriate information on which to base water use decisions.

Background

Project geochemical investigations are addressing groundwater flow issues in the aquifer and the nature of the interface between the fresh-water zone and a zone of saline water that is down-dip of the fresh-water zone. Although the fresh-water/saline-water interface has been located, little is known about the nature of flow across or along it. Of critical importance is the question of whether increased utilization of fresh water would cause infiltration of saline waters and degradation of the quality of the fresh water resource.

Results

A series of investigations using helium-3/tritium age dating have shown that the fresh-water zone of the Edwards aquifer is composed primarily of modern recharge. The work, which was spearheaded by a Mendenhall Fellow, has demonstrated that the waters become progressively older toward an arbitrary threshold defined as 1,000 milligrams total dissolved solids per liter that separates usable waters from down-dip saline waters. Below this threshold, the saline waters are much greater than 50 years old, possibly reaching ages of thousands to tens of thousands years, and may have multiple origins that involve input from, or interaction with, hydrocarbon reservoirs in the area. Noble gas results suggest that hydrocarbons associated with the saline waters range from natural gas to light or heavy crude oil. However, the hydrocarbon-associated waters are only marginally saline which suggests that they are mixtures of a fresh water end member and a hydrocarbon-related brine.

Figure 19. Scientists collect water from a well in south-central Texas that is fed by the Edwards aquifer.

Figure 20. Scientist uses a portable geophysical logging system to collect data at a well penetrating the Edwards aquifer.

Conclusions

The saline-water zone that has been identified in the Edwards aquifer represents a transition from fresh waters to deeper connate brines that are not tapped by existing monitoring wells. The transition zone is composed of mixtures of submodern waters and connate brine that is hydraulically connected in some way to the fresh-water zone. The nature of the hydraulic connection remains unclear.

A National Hazards, Risk, and Resilience Assessment Program

Landslide Hazards at Mount Rainier Related to Hydrothermal Alteration

Issue

Hydrothermally altered rocks are present on many active volcanoes in the High Cascades in the northwestern United States. The alteration can result in weakened volcanic edifices that are susceptible to failure and catastrophic landslides. About 5,600 years ago, a portion of the Mount Rainier edifice collapsed to produce the Osceola Mudflow, which traveled more than 120 kilometers and covered an area of about 550 square kilometers. A similar mudflow occurring today would have catastrophic consequences because the Osceola deposits extend, at least, to the Seattle suburb of Kent and the Port of Tacoma on Commencement Bay. Hydrothermal alteration of active volcanoes is a manifestation of the same processes that produced ore deposits at older equivalents of the High Cascades volcanoes. Assessing the possibility of future landslides and the mineral potential of older volcanoes elsewhere requires an understanding of the fundamental parameters of the alteration process, including depth, duration, temperature, and sources of altering fluids.

Objectives

In collaboration with scientists from the USGS Volcano Hazards Program and with the support of the National Park Service, Project scientists developed an integrated geologic and hydrologic model in which underlying magmas degas through a Mount Rainier-like hydrologic structure—with some probability of ore formation—to create landslide-prone material through alteration of near-surface rocks. Mount Rainier was chosen as a natural laboratory because this volcano is well understood from previous studies, because its summit is accessible for sampling, and because there have been numerous potentially dangerous debris flows, some which carried fragments of wall rock from the interior of the volcano to the surface where they can be sampled for mineralogical and geochemical study.

Background

Hydrothermal alteration has waxed and waned over the 500,000-year growth history of the Mount Rainier edifice. Multiple debris flows have erupted in the last 10,000 years. The three cubic-kilometer Osceola Mudflow contains the highest temperature and deepest-formed hydrothermal minerals exposed on the volcano, including pyrophyllite, topaz, and magmatic hydrothermal alunite. In contrast, the Paradise lahar, which formed by collapse of the summit or near-summit at about the same time as the Osceola Mudflow, contains only smectite, pyrite, and other minerals characteristic of lower temperature, near surface, steam-heated and fumarolic alteration environments. A series of younger debris flows permitted sampling of alteration products from a range of depths and temperatures to complete sampling of the pre-Osceola alteration geometry. The pre-Osceola Mudflow alteration geometry is thought to have consisted of a narrow feeder zone with intense magmatic-hydrothermal alteration near the conduit of the volcano grading outward to weak smectite-pyrite alteration, developed chiefly in porous breccias, that extends a kilometer or more from the edifice axis.

Results

The mineralogy and stable isotopic compositions of samples from outcrops and clasts in Holocene debris flows revealed three distinct hypogene argillic/advanced argillic hydrothermal environments: magmatic-hydrothermal, steam-heated, and magmatic steam (fumarolic). Minor supergene alteration was apparent in samples from all three environments. The edifice is capped by a steam-heated alteration zone, which resulted mainly from condensation of fumarolic vapor and oxidation of H_2S to corrosive sulfuric acid in the unsaturated zone above the water table. Frequent eruptions of lava supplied hot magmatic fluids that altered the upper portion of the volcano. Despite the long and complex history of Mount Rainier, intensely altered collapse-prone rocks are restricted to the volcano's conduit and present-day summit, and to nearby zones on the upper east and west flanks of the volcano. This spatial distribution is a consequence of the fact that the reactive components responsible for alteration were carried by ascending magmatic fluids. Hydrothermal alteration was most intense within breccias, because they were the most permeable and porous lithologies.

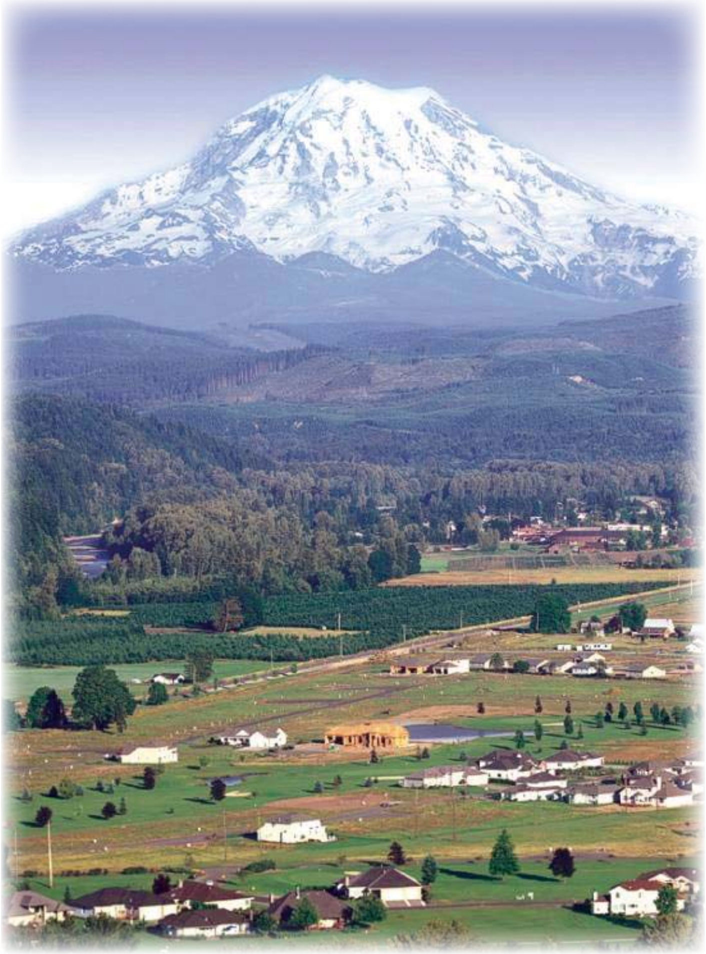

Figure 21. Mount Rainier volcano, located about 100 kilometers southeast of downtown Seattle. The farms and residential development shown in the foreground cover the Osceola Mudflow, which formed during a catastrophic eruption 5,600 years ago and buried an area of about 550 square kilometers. Photograph courtesy of USGS Cascades Volcano Observatory.

Conclusions

Hydrothermal mineral assemblages at Mount Rainier, and their distributions, can be understood within the framework of hydrothermal processes and environments that has been developed from studies of ore deposits that formed in analogous settings. Volcanoes with abundant near-conduit upper-edifice breccias are prone to alteration and have associated collapse potential, whereas volcanoes that are breccia-poor and have

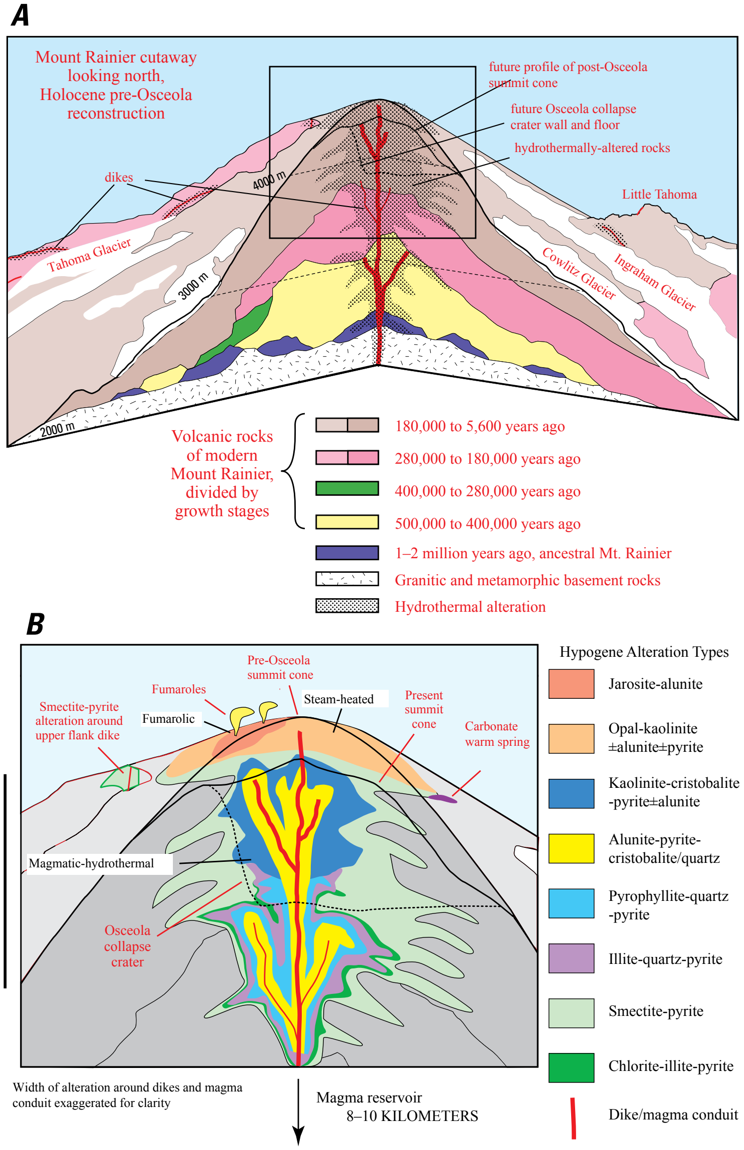

Figure 22. Cutaway sections of Mount Rainier showing a model of eruptive units (A) and hydrothermal alteration types (B) prior to eruption of the Osceola Mudflow 5,600 years ago. The upper part of the pre-Osceola hydrothermal system was dominated by steam-heated and fumarolic alteration; deeper parts were dominated by magmatic-hydrothermal alteration around the central magma conduit. (Modified after John and others, 2008, Characteristics, extent and origin of hydrothermal alteration at Mount Rainier volcano, Cascade arc, USA—Implications for debris-flow hazards and mineral deposits: Journal of Volcanology and Geothermal Research, v. 175, p. 289–314).

massive domes are less prone to alteration and collapse. The hydrothermal assemblages and isotopic compositions observed at Mount Rainier are similar to the assemblages and compositions found in high-sulfidation epithermal gold-silver deposits and in rocks overlying porphyry copper deposits. However, the great depth of the Mount Rainier magma reservoirs (4–10 kilometers), the absence of massive domes, and the sparse nature of the alteration in the debris flows are signs that economic mineral deposits are unlikely to be present at depth.

Fault Slip Rates of the West Salton Detachment System: Input to Earthquake Hazard Assessment

Issue

In areas of active uplift, earthquake hazard assessment requires quantitative information on the timing of fault movements. Whereas geologic mapping can give the timing of faulting and other events on a relative basis, geochronologic studies are required to determine absolute ages and obtain quantitative information on timing. A relatively new technique—cosmic ray exposure dating—can provide the necessary quantitative information when the study design is guided by careful mapping and by an understanding of the role of faulting in the development of geomorphic surfaces.

Objectives

On the west side of the Salton Trough, which is part of the San Andreas fault system, a normal fault places upper Neogene Zosel sequence sedimentary rocks against crystalline rocks of the Santa Rosa Mountains. This locality provided an opportunity for fruitful collaboration between Project scientists and geologists from the USGS National Cooperative Geologic Mapping Program. From about 6 million years ago to about 1.1 million years ago, the uplifted crystalline rocks shed sediments into the Zosel basin. Conglomerates within the Zosel sequence contain distinctive clasts composed of hornblende tonalite, the only exposed source for which lies 24 kilometers away across the Clark strand of the San Jacinto Fault. Sediment deposition in the Zosel basin ended with the onset of right-slip motion along the Clark strand. The exposure age of the tonalite boulders on the surface of the Zosel sequence would reveal the time required for the 24 kilometers of displacement along the San Jacinto Fault.

Background

Cosmic particles strike the outer atmosphere and produce a cascade of neutrons and muons that cause nuclear transformations when they impact the earth's surface. The transformations generate isotopes of helium (^{3}He) and neon (^{21}Ne) at rates that vary with atmospheric density, magnetic field strength, latitude, altitude, rock density, and burial depth. By measuring the number of cosmogenic ^{3}He or ^{21}Ne nuclides contained within a mineral and dividing by the calibrated nuclide production rate, one can determine the length of time that the mineral has been exposed at the earth's surface. The technique is feasible for exposures up to 10^7 years.

Results

Helium-3 and ^{21}Ne measurements made with a special high resolution mass spectrometer yielded cosmogenic nuclide abundances of 10^6 and 10^8 atoms per gram, respectively. The boulders of hornblende tonalite on the surface of the Zosel sequence have exposure ages of 1.1 to 1.3 Ma, and indicate, with 24 km of right-slip offset, an average slip rate of 20 millimeters per year along the San Jacinto Fault during this time period.

Conclusions

The average slip rate of 20 millimeters per year calculated for this active section of the San Andreas Fault system is geologically relatively fast. Slip rates are important input parameters for models that forecast the buildup and release of strain along this geologically hazardous corridor.

Climate Variability and Change

Lake Studies in Support of Global Change Program

Issue

The arid western United States is highly susceptible to drought. Water has always been a precious commodity in the West and, with population on the rise, the demand for water has never been greater. The recreation industry relies on water in the form of streams and snowpack, and the agricultural industry uses large amounts of water to grow food crops. Historical records of climate change usually extend back in time only about 100 years. Such short-term records probably do not provide adequate information on the frequency and intensity of future droughts.

Objectives

Project scientists teamed with members of the USGS National Research Program Arid Regions Climate Project and with scientists from Lawrence Livermore National Laboratory, University of Nevada, and University of Southern California to create an 8,000-year lake-based sediment record of climate change for the Sierra Nevada and eastern Great Basin of the western United States. Project scientists were primarily responsible for measuring oxygen-isotope values of carbonate minerals that had been deposited in the cores over the past 8,000 years.

Background

The Truckee River drains the northern Sierra Nevada and flows into the hydrologically closed Pyramid Lake, Nevada. Pyramid Lake is the home of the Pyramid Lake Paiute tribe which have lived around the lake for several centuries. Because the lake is hydrologically closed, water leaves the lake solely by evaporation; thus, the height of the lake surface is a simple function of how much water enters the lake from the Truckee River and how much water leaves the lake during evaporation. To obtain a record of past changes in lake size, sediment cores totaling about 11 m in depth were taken from the deep (105 meters) waters of Pyramid Lake. The carbonate minerals precipitate from near-surface waters of the lake during the warm season, recording the oxygen-isotope values of the lake over time. Simply put, if the lake rises because Truckee River input exceeds evaporative output, the stable oxygen isotope value of Pyramid Lake water decreases, and the reverse.

Results

The oxygen-isotope data indicate that major changes in the size of Pyramid Lake occurred about every 150 years during the past 8,000 years. During the past 3,000 years, drought durations ranged from 20 to 100 years with intervals between droughts ranging from 80 to 230 years. Many of these droughts lasted much longer than the major droughts we have observed during the past 100 years. The data also demonstrated that a millennial-scale drought occurred between 6,500 and 3,800 years ago, causing Lake Tahoe to shrink to the point that it did not overflow to the Truckee River. This implies that it was at least 30 percent drier during this 2,700 year period than during the past 100 years.

Conclusions

The record of past changes in the hydrologic balance of Pyramid Lake shows that many long-lasting and intense droughts occurred in the far West during the past several thousand years and that our historical records are too short to convey the severity of droughts that could occur in the future.

Figure 23. Outwash fans flanking the Pinto Mountains in Joshua Tree National Monument are examples of geomorphic surfaces that can be dated using cosmogenic nuclides. Potential target minerals include quartz in granitoid clasts and olivine in basalt clasts.

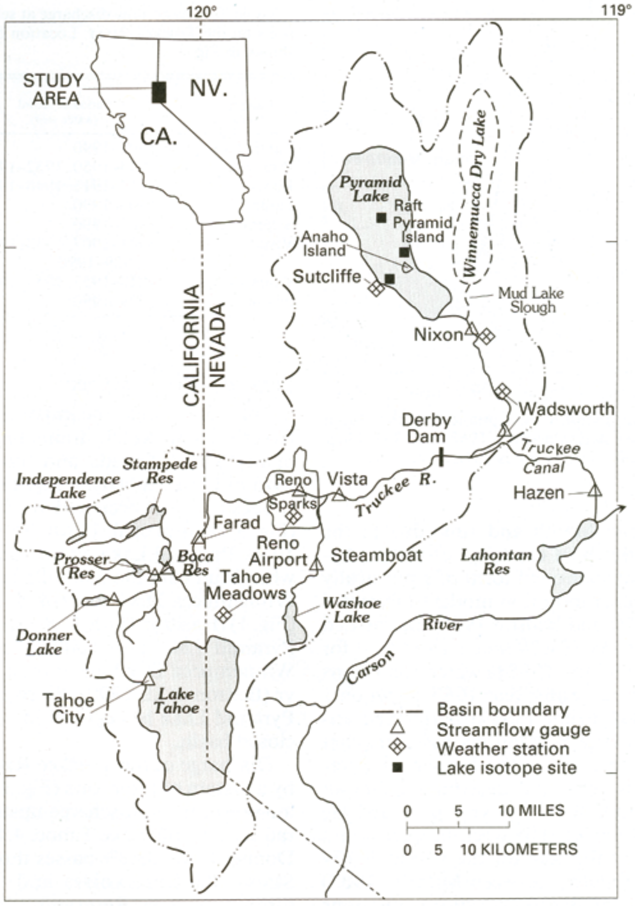

Figure 24. The Lake Tahoe–Truckee River–Pyramid Lake system.

Figure 25. Pyramid Lake and the Pyramid. The white band along the shore is composed of calcium carbonate that precipitated from the lake when its level was at or near its overflow point to the Winnemucca Lake subbasin.

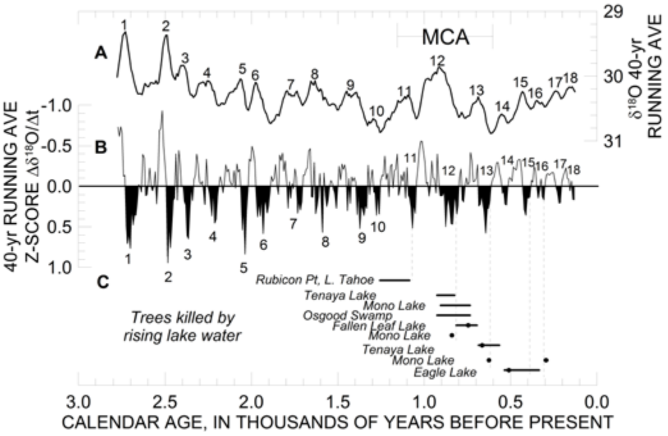

Figure 26. Forty-year running average of stable isotope and tree-ring data over the last 3,000 years showing trees killed by rising water after previous droughts. MCA is the time interval of the Medieval Climatic Anomaly. Z-score is a normalized change in $\delta^{18}O$ per unit time; positive values correspond to hydrologic droughts.

Brown Bears in the Kuskokwim Mountains, Southwest Alaska

Issue

The possible effects of climate variability on wildlife populations is a topic of intense current interest. Of particular importance—but challenging to determine—are the potential impacts on the availability of foods that sustain wildlife populations. Brown bear (*Ursus arctos*) are known to range in feeding behavior from herbivorous diets to diets heavily subsidized by high quality protein. Changes in the availability of protein can influence body mass, litter size, and population productivity. An improved understanding of the impact of climate variability on the availability of dietary resources would greatly benefit land and wildlife managers.

Objectives

The goal of this research was to assess the importance of spawning Pacific salmon, which represents a high quality seasonal protein resource, to a brown bear population located in interior Alaska. Radio-collared female bears in the Kuskokwim Mountains of southwest Alaska were studied from 1992 to 2002 during which time returns of spawning salmon underwent an abrupt decline. The study site is located far enough from the coast to be on the fringe of salmon availability. Of particular interest was how the salmon run decline during the second half of the study influenced population-level changes in nutritional ecology and demography.

Background

Hair samples collected from female brown bears during mark-recapture efforts were analyzed for carbon, nitrogen, and sulfur isotope values. Dietary composition was estimated for individual animals by comparing the stable isotope values of hairs to potential dietary resources, after corrections for vital isotope effects. Inter-annual changes in the nutritional ecology of the bear population were related to the availability of dietary resources, particularly spawning Pacific salmon, and evaluated in the context of demographic responses during the period of study.

Results and Conclusions

Salmon was a major component of bear diets throughout the study period, but the proportion of salmon relative to other foods mirrored declines in spawning salmon returns, as measured by an escapement index commonly used by fisheries managers. The commercial salmon catch and spawner return numbers are known to be closely linked to sea-surface temperatures in the Pacific Ocean, which are reflected in the Pacific Decadal Oscillation (PDO) climate index. Positive PDO phases reflect cooler surface waters, which result in higher ocean survival rates and higher spawner returns in British Columbia and Alaska. The post-1996 years were characterized by negative PDO phases, higher sea-surface temperatures, and sharp declines in salmon returns. The declines in salmon returns also corresponded with declines in the growth rate of the brown bear population. The results of the study demonstrate that the health of the Kuskokwim Mountain brown bear population is in part dependent upon access to high quality, seasonally available protein, such as salmon. Furthermore, a tentative connection has emerged between bear population viability and regional climate and ocean conditions, both of which will be sensitive to global climate change.

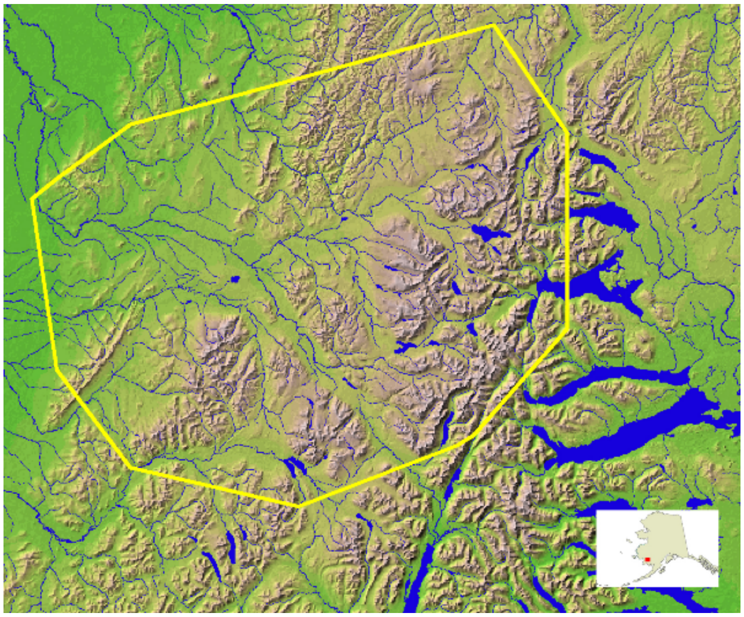

Figure 27. Study area within the Kuskokwim Mountains of southwest Alaska. Illustration courtesy of Gail Collins and Steven Kovach.

Figure 28. Brown bear anesthetized during the Kuskokwim Mountains capture operation, photograph courtesy of Gail Collins and Steven Kovach.

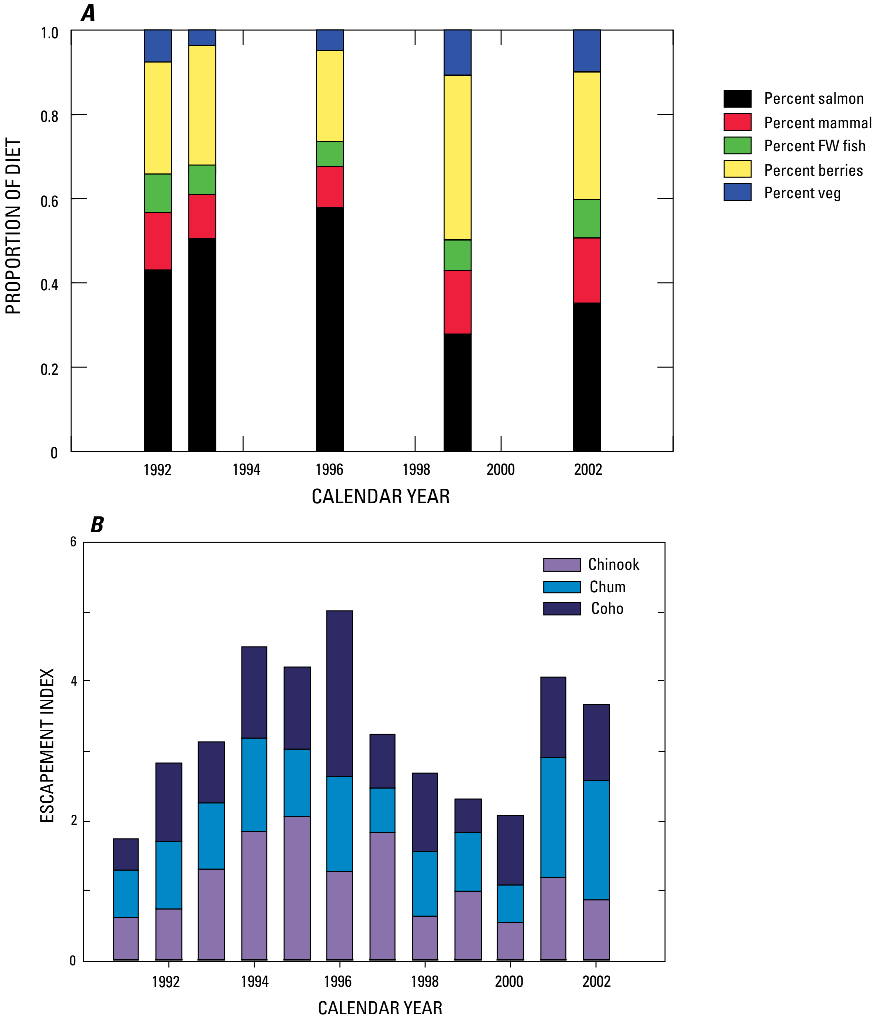

Figure 29. (*A*) Diet estimates for female brown bears in the Kuskokwim Mountains, southwest Alaska expressed as annual averages. Before 1996 Pacific salmon accounted for 40–60 percent of brown bear diets, whereas after 1996 salmon dropped to less than 40 percent. (*B*) The fisheries escapement index, which reflects salmon returns, also shows a decline after 1996. This has been attributed to anomalous conditions in the Pacific Ocean that impaired salmon survival.

Colorado Alpine Glaciation and Climate History

Issue

Establishing the areal extent and timing of Quaternary glacial cycles is critical to improving the understanding of Earth's climate system and the reliability of forecasts of climate change. In alpine environments such as the Rocky Mountains, the primary record of glacial advances and retreats are the geologic deposits contained in glacial end moraines and lateral moraines.

Objective

To address the timing of alpine glacial maxima (maximum glacial advance) in Colorado, exposure ages were obtained for Pinedale and pre-Pinedale moraines in the Middle Boulder Creek, North Saint Vrain, and Roaring Fork drainages in the north-central part of the state. Samples were collected from the tops of large granite and quartz monzonite boulders on the moraine crests. Quartz was separated from the rocks for analysis of the nuclides ^{21}Ne, ^{10}Be, and ^{36}Cl. Exposure ages of the boulders were calculated using nuclide production rates making corrections for latitude, altitude, magnetic field intensity, and shielding from snow.

Background

In Colorado, widely recognized alpine glacial advances include the Pinedale, pre-Pinedale, and much older Bull Lake events (elsewhere in the western United States other names are used for these events). The glaciers are estimated to have been 10–20 kilometers long and 180–350 meters thick and to have terminated at elevations between 2,500 and 2,700 meters. The advancing ice formed moraines from transported debris that was deposited where the glaciers melted. Large moraines, with debris ranging from rock flour to large boulders, are found where the ends of glaciers remained at the same positions for long periods of time. For moraines that were not destroyed by later advances of ice, the bombardment of exposed rocks by cosmic rays provides a means of determining the age of the moraine surface. Cosmic rays striking the outer atmosphere produce a cascade of neutrons and muons that impact rocks at the earth's surface with sufficient energy to cause nuclear transformations. Isotopes of helium (^{3}He) and neon (^{21}Ne) are produced at rates that depend on atmospheric density, magnetic field strength, altitude, latitude, and burial depth which provides for shielding of the target rock from cosmic radiation. Measuring the abundance of cosmogenic ^{3}He or ^{21}Ne in a target mineral by ion counting mass spectrometry and dividing by the calibrated production rate yields the length of time that a mineral has been exposed at the earth's surface. The cosmogenic nuclides ^{10}Be and ^{36}Cl are measured by different techniques, but they can be used in analogous ways to determine exposure ages.

Results

Chlorine-36 and ^{10}Be exposure ages of Pinedale moraine surfaces ranged from 16.5 to 20.9 thousand years suggesting minimal erosion of moraine material for the past 20 thousand years in the Colorado Rocky Mountains. This is in agreement with other published results for pre-Pinedale or Bull Lake moraines of 100–122 thousand years and with results for Pinedale moraines of 15.1–19.9 thousand years. Shielding of small boulders by snow would have significantly decreased the rate of cosmogenic nuclides production leading to erroneously young ages if this effect is not accounted for. Snow shielding is difficult to estimate precisely, but it cannot be ignored. Neon-21 exposure age results are considerably older, which may reflect complex inheritance from prior exposures. These histories are not easy to decipher, and they are the subject of ongoing research.

Conclusions

Developing accurate corrections for snow shielding will be critical to obtaining accurate exposure ages for Colorado moraines and matching the ages to other western United States, continent-wide, or global glacial histories. The age of the pre-Pinedale middle-Pleistocene glacial advance remains uncertain.

Figure 30. Geologist samples boulders along the crests of Pinedale terminal moraines in the Roaring Fork drainage, North Park, Colorado.

Energy and Minerals for America's Future

Spar Lake Copper-Silver Deposit, Montana: Ore-Forming Processes Revealed in Fluid Inclusion Gas Analyses

Issue

Sediment-hosted stratiform copper deposits form where subsurface brines migrate through oxidized clastic sediments, where they acquire copper and other metals, and then through reduced zones in the subsurface where the metals precipitate. Although the process is understood in general terms, for many important deposits the nature of the reduced zone is poorly understood and the specific chemical reactions leading to ore formation are uncertain.

Objectives

At the Spar Lake copper-silver deposit in northwest Montana, ores and associated rocks contain cements and overgowths of ankerite, feldspar, and quartz with abundant fluid inclusions. Textural evidence suggests that the inclusions contain remnants of the solutions that transported copper and other metals to the site of ore formation. The objective of the study was to analyze the inclusions for noble gases, active gases, noble gas isotopes, and carbon and oxygen stable isotopes to determine physicochemical characteristics of the ore-forming environment and to identify the chemical reactions that led to ore formation.

Background

Spar Lake is an important deposit that lies within Proterozoic sedimentary rocks of the Belt Supergroup. The deposit is of the sediment-hosted stratiform type which, along with larger examples in central Europe and central Africa, represent the second-ranking source of global copper production after porphyry type deposits. To provide the most accurate assessments of domestic and global copper resources, it is important to improve the understanding of the geological environment in which Spar Lake formed and the processes that led to ore formation.

Results

Several samples showed very high fluid inclusion methane concentrations; one sample, from the fringe of the deposit, had perhaps the highest methane ever reported from any ore deposit. The high methane concentrations, together with spatial zoning of sulfide minerals within the orebody, suggest that H_2S, which is a critical ingredient for sulfide ore formation, was produced from dissolved sulfate by reaction with methane (and hydrogen) in natural gas pockets. The methane/carbon-dioxide ratio varies systematically across the deposit with the lowest values corresponding to high grade chalcocite-bearing ore and the highest values corresponding to chalcopyrite-bearing fringes of the deposit. The temperature and log fO_2 of ore formation—determined from phase equilibria—decreased from 200° to 160°C and –46 to –55, respectively, as the methane/carbon-dioxide ratio increased. The Spar Lake inclusion gases are low in hydrogen sulfide in comparison to fluid inclusion gases at other metal sulfide deposits, probably reflecting the oxidized nature of the metal-carrying solutions. Both the molecular hydrogen concentrations, which were 0.7–58 mole percent, and the hydrogen sulfide/sulfur-dioxide ratios changed along with the methane/carbon-dioxide ratio. Helium isotope data suggest mixing of crustal and atmospheric helium with little or no mantle or magmatic input.

Carbon and oxygen isotopic compositions of carbonate minerals support the interpretation that sulfate was reduced to hydrogen sulfide by reaction with methane. Manganiferous and ferroan calcite are common as cements in the fringes of the orebody. The minerals are characterized by low $\delta^{13}C$ values—commonly –10 to –18 per mil—which suggest carbon derivation predominantly from organic compounds. Within the orebody, ankerite occurs with chalcocite or chalcopyrite. The ankerite has somewhat higher $\delta^{13}C$ values consistent with a greater abundance of metalliferous brine and lesser methane than on the fringes of the deposit.

Conclusions

The coincidence of methane-rich fluid inclusions and low $\delta^{13}C$ carbonates in the sandstone wall rocks of the chalcocite-rich orebody is evidence that oxidized, metal-transporting brines reacted with reduced pore fluids within a natural gas reservoir to form the ores. Future assessments of copper resources should consider the possibility that natural gas reservoirs may play an important role in the formation of sediment-hosted stratiform-type deposits.

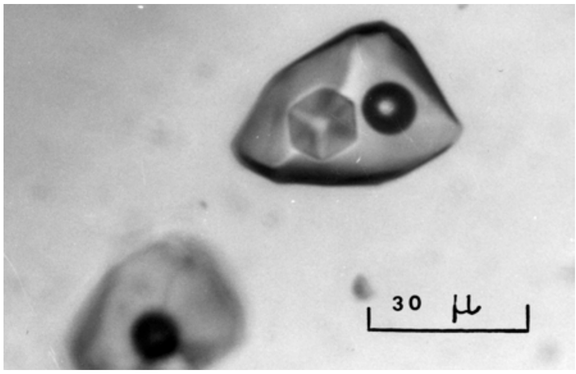

Figure 31. Microscopic inclusions similar to those that were analyzed in studies of the Spar Lake copper-silver deposit in Montana. The inclusion consists of a solid crystal, a vapor bubble, and a water-rich fluid. Chemical analysis of the vapor bubbles in many samples revealed the map-view spatial patterns shown in figure 32.

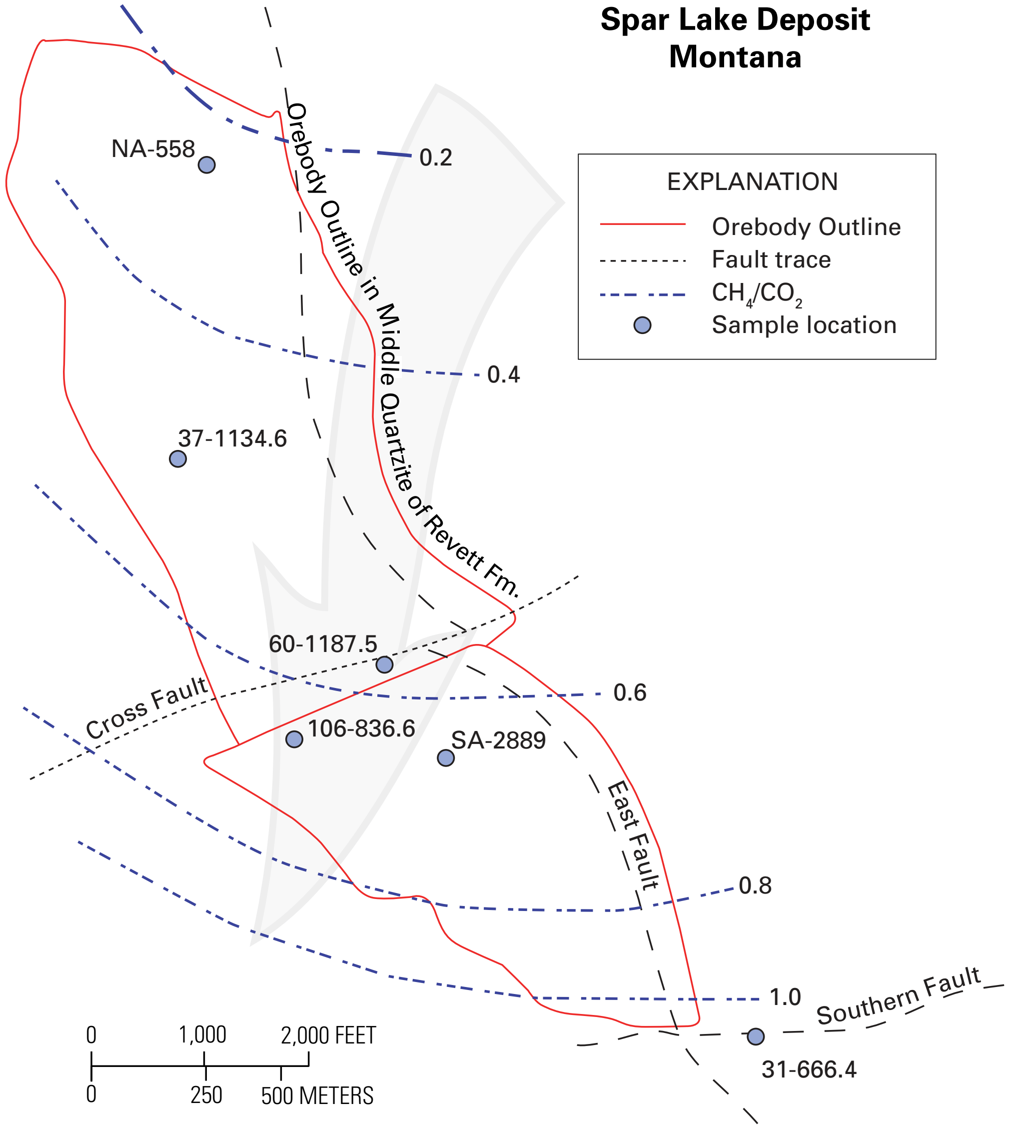

Figure 32. Map view of the outline of the Spar Lake copper-silver deposit (in red) and contours of the methane/carbon-dioxide ratio in inclusion gases. The patterns are evidence that the ores formed where oxidized metalliferous brines encountered a reduced natural gas reservoir.

Chemical Analysis of Fluid Inclusions in Hydrothermal Minerals

Issue

Hot aqueous fluids are essential components of the systems that form many ore types. The fluids scavenge metals from source rocks or source magmas and then transport them to sites where they precipitate to form mineral deposits. Identification of the fluid source is fundamental to reconstructing the environments of ore formation and constructing realistic models of ore-forming systems.

Objectives

The objective of this study was to survey solute concentrations in fluid inclusions from numerous examples of particular deposit types to search for patterns that would help identify fluid sources. Initially, the target was sediment-hosted base-metal deposits of the sedex and Mississippi Valley types. The insights gained were powerful. Subsequently, the method was extended to other deposit types including orogenic gold deposits, Carlin-type gold deposits, metamorphic zinc-lead-silver vein deposits, porphyry deposits, volcanogenic massive sulfide deposits, iron oxide-copper-gold deposits, and sediment-hosted stratiform copper deposits.

Background

Traditionally, stable isotopic analyses of hydrogen and oxygen have been used to determine the sources of ore-forming fluids. However, in systems where integrated water-to-rock ratios are low, both parameters can be shifted from their original values. An alternative method for determining fluid sources is chemical analysis of a diverse suite of solutes. Solute-concentration data can in some cases allow reconstruction of the geologic settings in which the fluids resided prior to their entrainment in an ore-forming system. Chemical analysis of ore-forming fluids requires analytical procedures targeted to the liquids contained in tiny fluid inclusions within hydrothermal minerals. The dual ion chromatography apparatus in the Project fluid inclusion chemistry laboratory was designed specifically for this application.

Results

A survey of numerous sediment-hosted base metal deposits on four different continents revealed similarities in the relative abundances of sodium, chloride, and bromide. These relations indicate that the fluids responsible for most Mississippi Valley-type and sedex-type ore deposits were seawater that had been evaporated to varying degrees. The evaporation was important for ore formation because it increased the salinity of the waters, which enhanced their ability to transport metals. Deposits of the Ozark Uplift in the mid-continent region of the United States showed somewhat different systematics consistent with salinity increases by dissolution of preexisting evaporite deposits. Among the other deposit types that were surveyed, sediment-hosted stratiform copper deposits also showed evidence that the ore-forming fluids were evaporated seawater. In at least some cases, the extent of evaporation was greater than for Mississippi Valley-type or sedex-type deposits, great enough that the seawater reached saturation in potassium salts.

The other deposit types that were studied showed a wide variety of sodium-chloride-bromide systematics. Orogenic gold deposits in Alaska, Canada, and Australia displayed extremely broad concentration ranges for the three solutes that do not uniquely implicate a specific fluid source. Many porphyry deposits, including examples in Utah, Colorado, and Bolivia, showed distinctive and closely similar compositions, which suggests that there is a distinctive chemical fingerprint for magmatic fluids. The analyses obtained in these studies may provide more specific insights on ore genesis as the understanding of sodium-chloride-bromide systematics continues to improve.

Conclusions

Chemical analyses of fluid inclusions in hydrothermal minerals have revealed general patterns that are common to many sediment-hosted base metal deposits and sediment-hosted stratiform copper deposits. The patterns suggest that the ore-forming fluids for these deposit types were evaporated seawater. Thus, ore formation was associated with arid coastal sedimentary environments, perhaps at low paleolatitudes. This association would be important to include in ore-deposit models to make the best possible forecasts of undiscovered resources of base metals and copper.

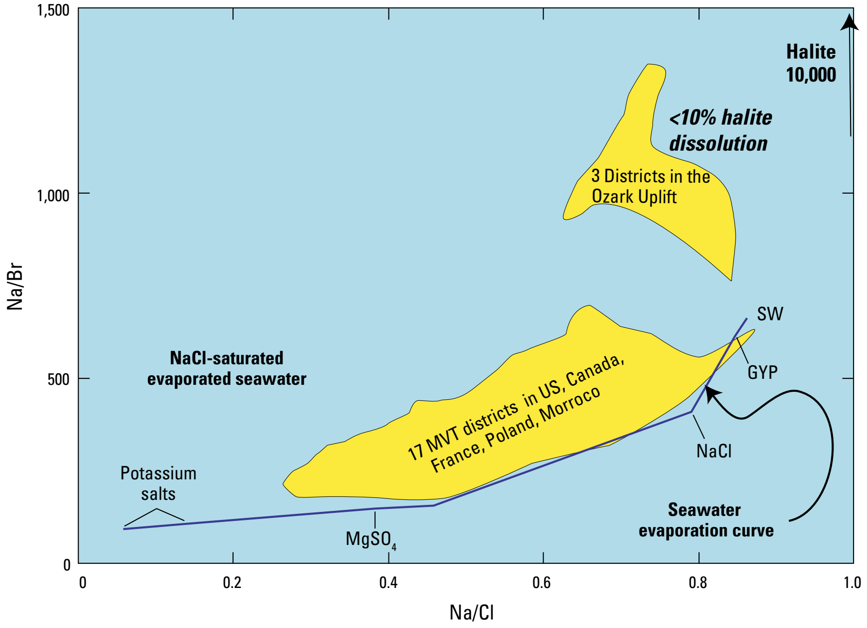

Figure 33. Sodium-chloride-bromide systematics for fluid inclusions from 20 Mississippi Valley-type deposits on three continents compared with the evaporation trajectory for seawater (SW). The seawater trajectory is marked with the first appearance of the different precipitate minerals: GYP, gypsum; NaCl, halite; $MgSO_4$, thenardite; potassium salts, sylvite and other potassium minerals. For 17 of the 20 deposits, the data suggest that the ore-forming fluid was evaporated seawater.

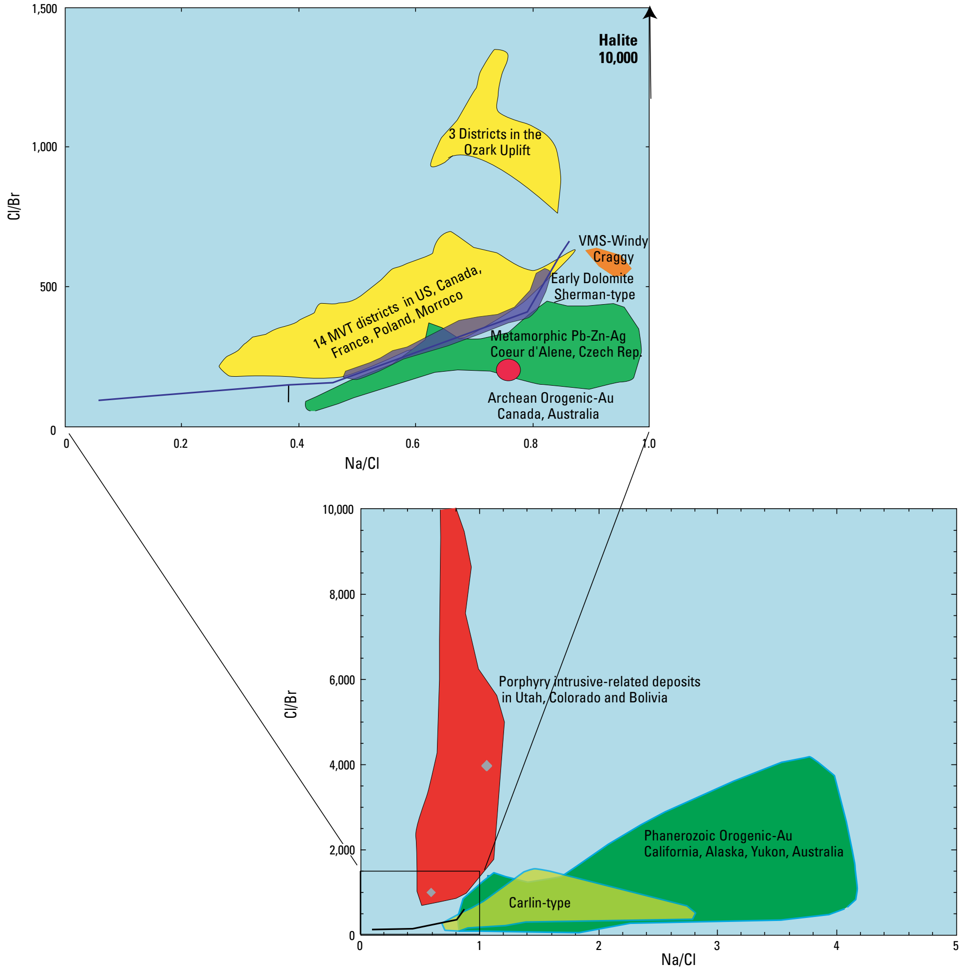

Figure 34. Sodium-chloride-bromide systematics for fluid inclusions from a variety of different deposit types in relation to the evaporation trajectory for seawater.

Natural Destruction of a Replacement Alunite Deposit at Big Rock Candy Mountain, Marysvale, Utah

Issue

Predictions of the environmental consequences of mining require discrimination between primary hydrothermal processes and minerals and secondary supergene (near surface) processes and minerals. Natural supergene processes are accelerated by open-pit mine excavation; their potential for negative environmental consequences depends to a large extent on the nature of the primary ore-deposit mineralogy. Improving predictions of the environmental consequences of mining will require an improved understanding of connections between primary mineralogy and supergene alteration processes. Locations where unmined mineral deposits are exposed to extensive natural weathering are ideal natural laboratories for studying this topic.

Objectives

Big Rock Candy Mountain in west-central Utah is a prominent occurrence of hydrothermally altered volcanic rocks whose primary mineralogy is a replacement alunite deposit lying above a pyrite-bearing dacite. At the present time, the alunite is not of economic interest. However, alunite- and pyrite-altered rocks are widely excavated elsewhere as parts of mining operations that exploit underlying precious metal or copper deposits. The Big Rock Candy Mountain rocks have been exposed by down cutting of the Sevier River. Supergene alteration has resulted in a prominent yellow, brown, and white hill slope, beneath which is Lemonade Spring. The locality has long been a tourist attraction for motorists visiting the nearby Marysvale mining district on their way to Zion and Bryce Canyon National Parks.

The objective of this study was to integrate mineralogical, remote sensing, stable isotope, and argon geochronology data to improve the understanding of the relationship between hypogene alunite-pyrite and supergene mineral assemblages at an unmined but intensely altered area.

Background

Big Rock Candy Mountain is a dissected erosional remnant that exposes a fossil hydrothermal system and replacement alunite deposit like others that occur in the nearby Marysvale volcanic field. A pyrite-bearing propylitic mineral assemblage at the base of the mountain grades into an alunite and minor barite assemblage at higher elevations. A capping assemblage of jarosite, hematite, and silica is inferred from erosional remnants. Laterally, the alunite grades into kaolinite, then dickite, and then a propylitic assemblage. The deposit is thought to have formed near the paleo ground surface above the upwelling limb of a hydrothermal convection cell where hot fluids erupted violently leading to the deposition of silica and the oxidation of hydrogen sulfide by incorporation of atmospheric oxygen. The sulfuric acid reacted with host rocks to form alunite and kaolinite below the water table, and jarosite, hematite, and silica above it. Below the zone of atmospheric oxygen incorporation, dacites were propylitized and sulfidized. Big Rock Candy Mountain was covered by sand and gravel deposits until regional uplift caused the rocks to be exposed by down-cutting action of the Sevier River.

Results and Conclusions

Stable isotope data indicate that hypogene alunite and barite are being dissolved and the resulting sulfate is either being precipitated as gypsum or being removed from the mineral deposit by modern surface and shallow groundwaters. The data also indicate that pyrite in the underlying dacites is being oxidized. Pyrite dissolution acidifies waters giving rise to compositions like those that emerge today from Lemonade Spring. Chemical reactions between acid waters and host rocks are forming supergene natrojarosite, kaolinite, and gypsum.

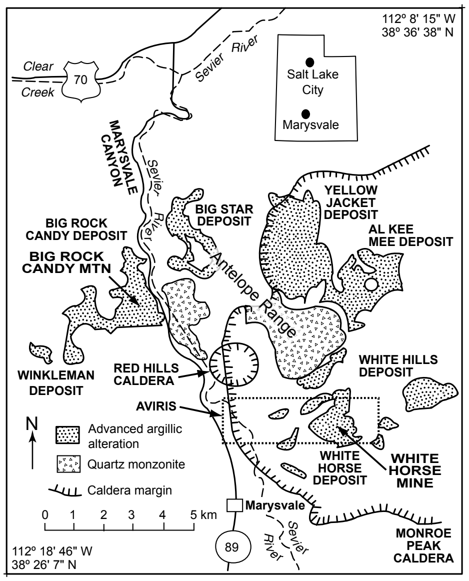

Figure 35. Map showing the location of Big Rock Candy Mountain within the Marysvale, UT mining district. (Taken from Cunningham and others, 2005, Origin and natural destruction of a hydrothermal replacement alunite deposit at Big Rock Candy Mountain, Utah—Mineralogy, spectroscopic remote sensing, stable isotope, and argon age: Chemical Geology, v. 215, p. 317–338).

^{40}Ar/^{39}Ar geochronology results indicate an age of 21.3 Ma for the formation of alunite, similar to other replacement alunite deposits in the Marysvale district. However, the age spectra also reveal a thermal event at 6.6 Ma, which probably reflects the tectonic activity that uplifted the region and initiated down cutting by the Sevier River. The same 6.6 Ma event is evident in the age spectra for supergene natrojarosite, which suggests that the secondary mineral assemblages observed today at Big Rock Candy Mountain are the accumulated products of about 6 million years of natural supergene alteration.

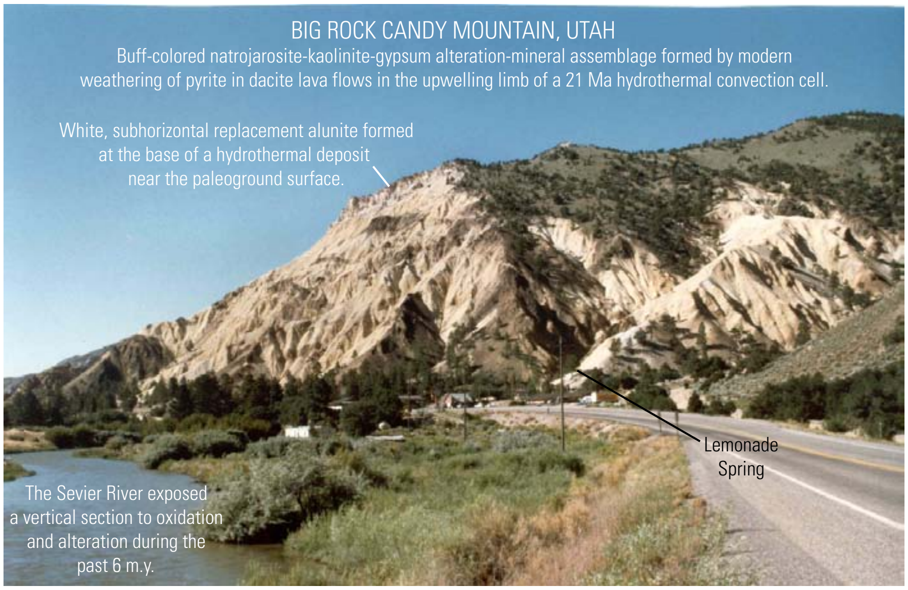

Figure 36. Big Rock Candy Mountain, UT is a prominent center of hydrothermally altered and weathered andesitic to dacitic lava flows, volcanic breccias, and tuffs. The buff color is due to the presence of natrojarosite and kaolinite, which are forming as a consequence of surficial oxidation of hydrothermal pyrite. A white, flat-lying alunite layer crops out at the top of the hill. View is looking south along U.S. Highway 89. (Taken from Cunningham and others, 2005, Origin and natural destruction of a hydrothermal replacement alunite deposit at Big Rock Candy Mountain, Utah—mineralogy, spectroscopic remote sensing, stable isotope, and argon age: Chemical Geology, v. 215, p. 317–338).

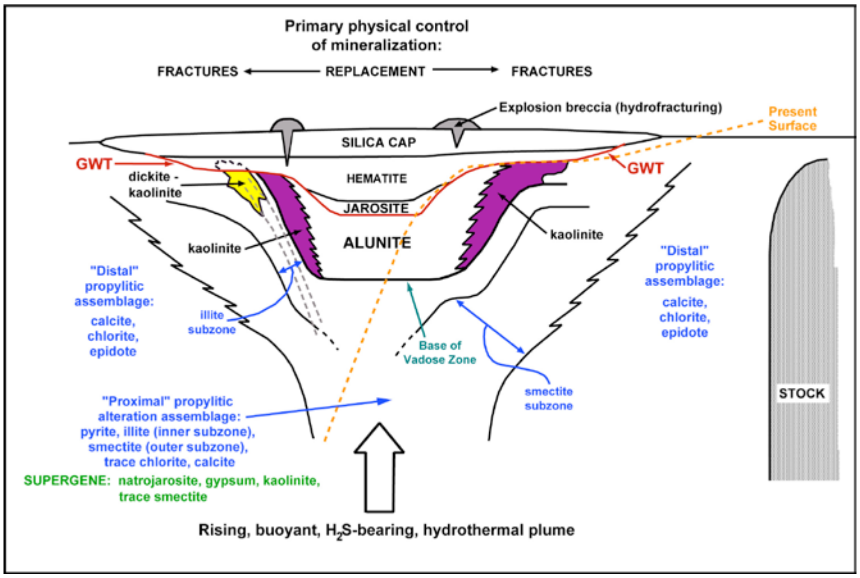

Figure 37. Genetic model of steam-heated, replacement alunite deposits showing the distribution of alteration minerals, proximity to the paleosurface and paleowater table, and location of the present-day surface of supergene alteration (fine dashed line, which corresponds to the hill slope shown in fig. 36). (Taken from Cunningham and others, 2005, Origin and natural destruction of a hydrothermal replacement alunite deposit at Big Rock Candy Mountain, Utah—Mineralogy, spectroscopic remote sensing, stable isotope, and argon age: Chemical Geology, v. 215, p. 317–338).

Coarse Banded Alunite as an Indicator of Ore-Forming Magmatic Hydrothermal Processes

Issue

Studies over the past 20 years have shown alunite to be a useful guide to undiscovered mineral deposits. In addition to being easily recognized in the field, the mineral can be mapped remotely using advanced spaceborne thermal emission/reflection radiometry or airborne visible/infrared imaging spectroscopy. The geologic and stable isotopic characteristics of alunite are also useful indicators of the conditions of formation of enargite-gold-silver and porphyry copper-molybdenum mineralization. However, there is a gap in the understanding of alunite geology related to the origin of coarse-banded occurrences. One of the best examples of this alunite type is the deposit at Alunite Ridge in west-central Utah.

Objectives

Isotope and geochemical investigations were carried out to determine the genesis and history of the hydrothermal system that gave rise to coarse banded alunite at Alunite Ridge. The results were integrated with geologic data that had been collected in previous studies and with the results of a recent airborne visible/infrared imaging spectroscopy survey. Of particular interest was the possible significance of this type of alunite as an indicator of underlying metal deposits.

Background

The formation of alunite requires sulfate, which can be derived from oxidation of pyrite, from near-earth's-surface oxidation of hot H_2S, or from the disproportionation of SO_2 degassed from magmas. Alunite with sulfate from these three sources is referred to, respectively, as supergene, steam-heated, and magmatic hydrothermal. Magmatic hydrothermal alunite can be associated with epithermal copper-gold-silver mineralization, as at Summitville, Colorado; Goldfield, Nevada; El Indio, Chile; Tombo, Peru; and Pierina, Peru. Magmatic hydrothermal alunite can also be associated with porphyry-type mineralization, as at the newly discovered, large Oyu Tolgoi deposit in Mongolia. At Alunite Ridge, alunite occurs with a distinctive coarse-banded texture in veins up to 20 meters wide. The texture is thought to reflect mineral precipitation from magmatic hydrothermal fluids that ascended especially rapidly. No metal enrichments have been recognized at Alunite Ridge, but the locality is surrounded by numerous gold and silver mines and prospects.

Results and Conclusions

Stable isotope data, noble gas isotope data, fluid inclusion active gas analyses, and mineral chemistry data have shown that over the life of the hydrothermal system, fluids were derived from multiple sources beginning with basalt derived from the mantle and ending with rhyolite presumably derived from melting of crust. The geologic setting and the geochemical data—particularly the elevated fluorine and tantalum contents of the alunite—suggest that Alunite Ridge may be an expression of an underlying Climax-type porphyry system. This finding highlights the potential utility of coarse banded alunite as a mineral assessment tool.

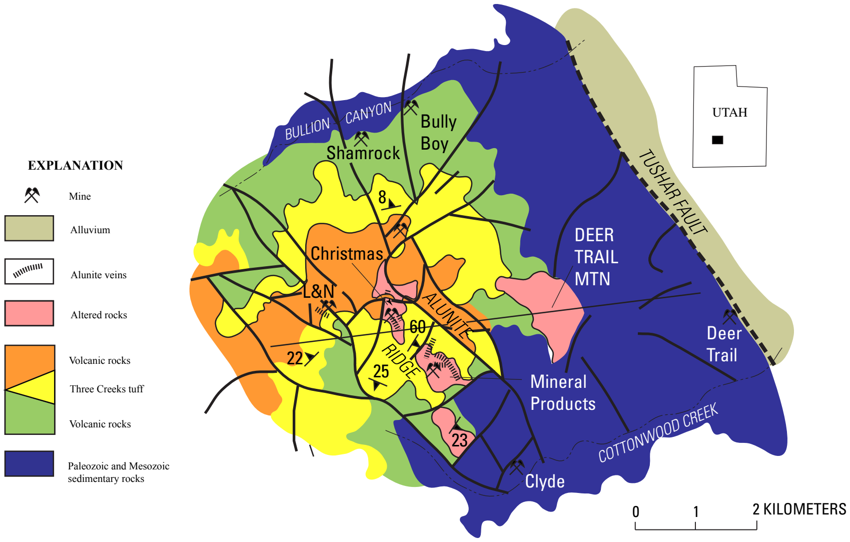

Figure 38. Geologic map of Alunite Ridge, which is located in the Marysvale district in west-central Utah. (Modified after Cunningham and others, 1984, Origins and exploration significance of replacement and vein-type alunite deposits in the Marysvale volcanic field, west central Utah: Economic Geology, v. 79, p. 50–71.).

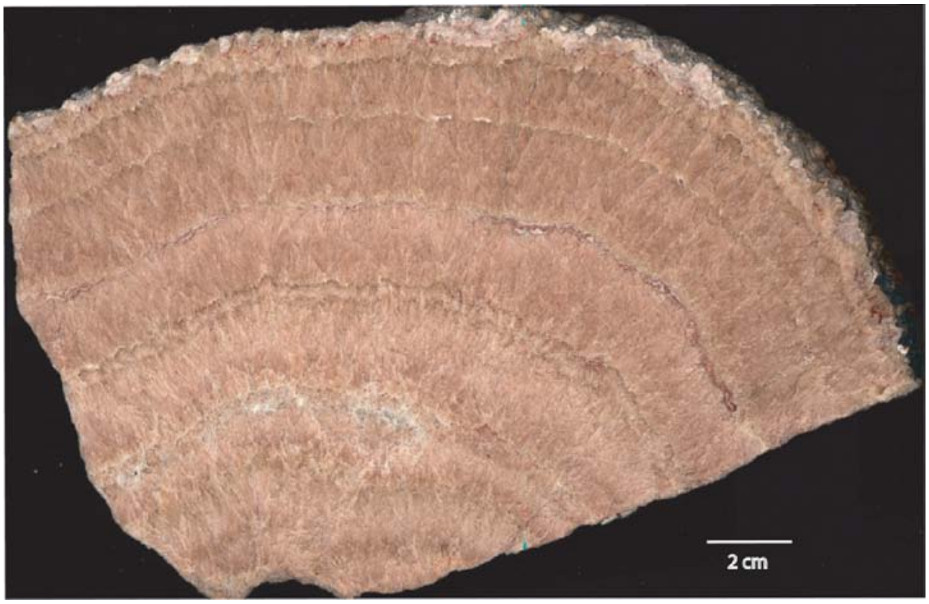

Figure 39. Coarse-banded alunite. Individual bands can be shown from stable isotope and trace element data to have resulted from single bursts of magmatic fluid.

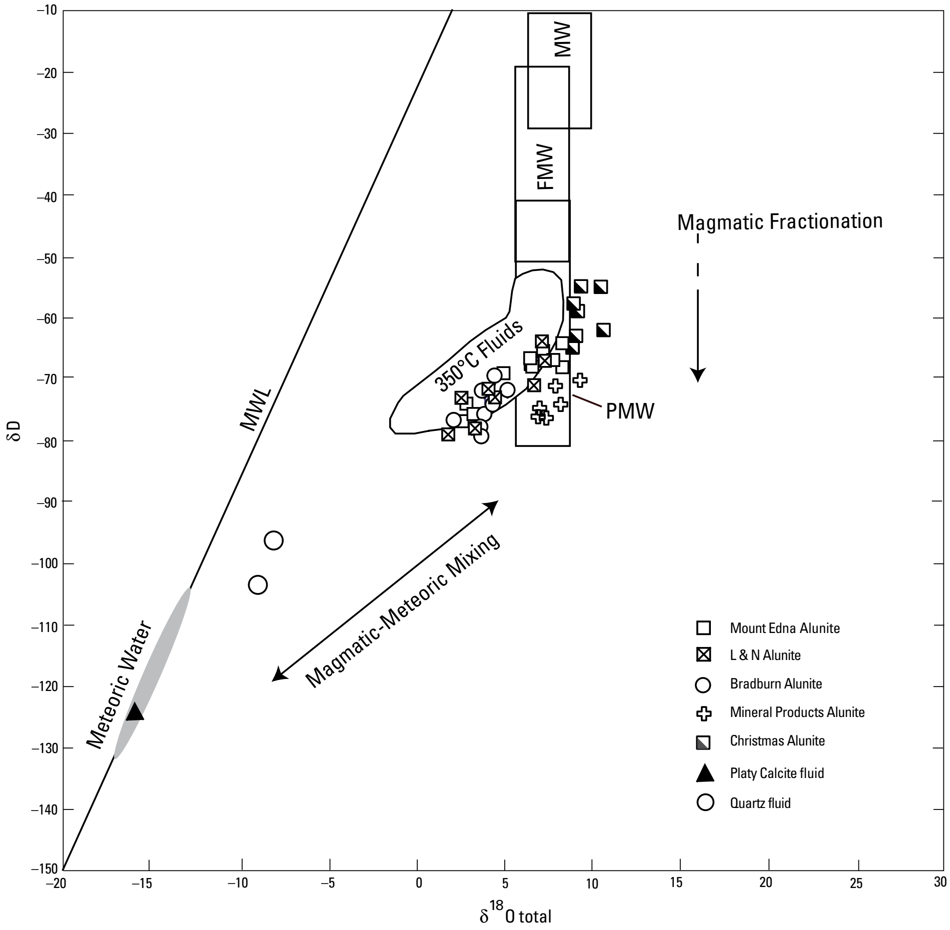

Figure 40. Hydrogen and oxygen isotope data for coarse-banded alunite from Alunite Ridge and field of calculated compositions of water in parent fluid showing two trends that reflect mixing of magmatic and meteoric water (sloped arrow) and deuterium depletion due to loss of vapor from magmatic fluid (vertical arrow). Also shown is the composition of water in early calcite and quartz fluids. These fluid compositions define a range of meteoric water compositions (shaded) that mixed with alunite magmatic fluids. MWL (meteoric water line), PMW (primary magmatic water), FMW (felsic magmatic water).

High Grade Deposits of Zinc and Lead in the Western Brooks Range of Alaska

Issue

More than half of the world's resources of zinc and lead reside in mineral deposits that formed in sedimentary environments on or below the floors of ancient seas. Within the United States, the most important example of this deposit type is found at the Red Dog mine in the western Brooks Range of Alaska (fig. 41). The Red Dog mine, which ranks first in the world in the production of zinc concentrate, accounts for 77 percent of domestic zinc production and about 30 percent of domestic lead production. Demand for these two metals has been strong in recent years and, consequently, exploration and mine development for these commodities have accelerated worldwide. Mine development and governmental oversight of mining activity rely heavily on geologic and geoenvironmental models of the deposit types being sought and exploited. The exposures at the Red Dog mine present a valuable opportunity to improve the existing models for this important deposit type.

Objectives

Stable isotope studies were carried out on the Red Dog ores and related rocks in collaboration with mining industry geologists in order to develop a comprehensive geologic model for the ore deposits in the area. The expectation is that the model will be used to (1) increase future discovery rates in the Brooks Range and other geologically similar areas, (2) improve the accuracy of mineral endowment estimates for the Brooks Range and other similar regions, and (3) support mineral assessment efforts for lands within the National Petroleum Reserve–Alaska, which includes a portion of the central Brooks Range.

Background

The Red Dog ores lie within carbonaceous shales that were deposited about 340 million years ago in a basin one tenth the size of the present day Gulf of Mexico. Numerous other zinc showings have been identified near Red Dog; these lie either at the same stratigraphic horizon as Red Dog or 70–100 meters lower in the stratigraphy. Thus, at some point in the history of the basin or perhaps at two points (corresponding to the two different stratigraphic horizons), large quantities of zinc and lead were transported to a 400 square kilometer area of the basin floor. The upper metalliferous horizon is unusual in that it also contains massive deposits of barite—a barium sulfate mineral—that were emplaced just prior to the zinc and lead minerals. Massive barite deposits are found farther east in the Brooks Range (fig. 42), as well as elsewhere in the world, but the Brooks Range barite deposits dwarf all but a few other occurrences. A key question in understanding the genesis of the zinc-lead ores is the nature of the link between the barite and the metals.

Results

Stable isotope analyses indicate that barite formation was accompanied by bacterial reduction of seawater sulfate to form hydrogen sulfide (fig. 43), which is an essential ingredient in the formation of zinc-lead ores. Thus, the barite forming event may have prepared sea-bottom environments for ore formation by causing reduced sulfur to accumulate prior of the arrival of the metal-bearing fluid. Zinc-lead ore formation also utilized hydrogen sulfide produced at higher temperature by reductive dissolution of barite. The isotopic variations within the barite deposits are identical to the variations that have been observed in authigenic barite deposits that have been found on the modern sea floor where low temperature, methane-bearing fluids emerge from sedimentary successions on the continental margins.

Conclusions

At Red Dog, ore formation was preceded by an event in which fluids were transported upward into shallowly buried sediments and then onto the sea floor. The fluids, which carried barium and possibly methane, prepared the site for zinc-lead ore formation by converting seawater sulfate to hydrogen sulfide, and by forming a vent-covering blanket of massive barite. These effects made for an especially efficient trap for the zinc and lead and, once the ores were formed, helped preserve them from destruction by seawater oxidation. Evidence for early venting of barium and methane should be considered as a favorable indication of the existence of zinc and lead deposits in unexplored marine sedimentary sequences.

Figure 41. View of the Red Dog mine in the western Brooks Range of Alaska. The mine currently ranks first in the world in the production of zinc concentrate. Zinc showings are abundant elsewhere in the region, which suggests that the district represents a zinc endowment of global significance. Photograph courtesy of Karen Kelley.

Figure 42. Gray ridge receding into the background is the Longview barite deposit in the Cutaway Basin of the central Brooks Range. This deposit is geologically and geochemically similar to massive barite deposits that are associated with high grade zinc-lead mineralization in the western Brooks Range.

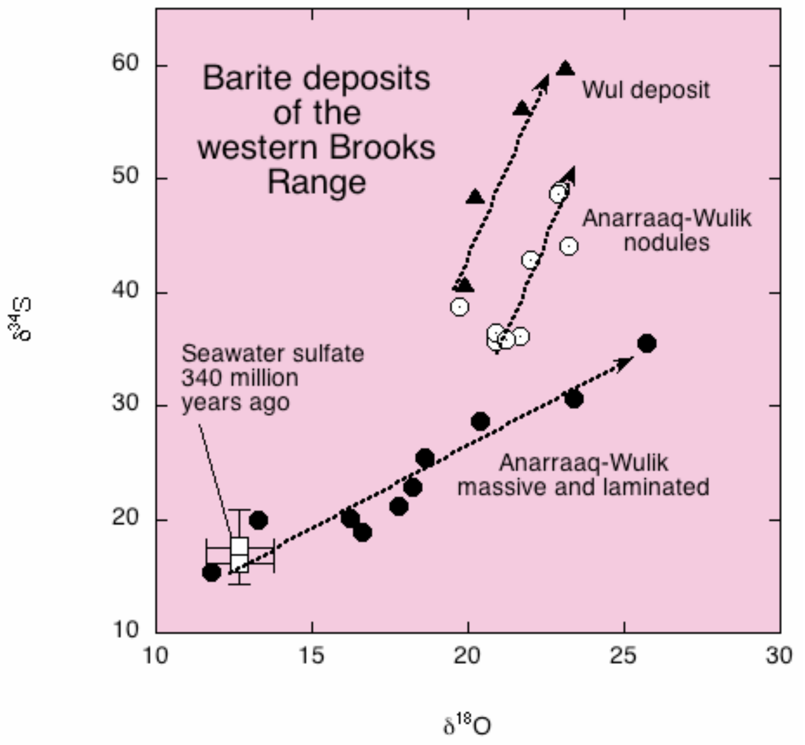

Figure 43. Sulfur and oxygen isotopic compositions of barite from deposits in the western Brooks Range. The barite—which is a barium sulfate mineral—formed from seawater sulfate within the Kuna Basin about 340 million years ago. The northeastward excursions on the plot, which are highlighted by arrows, suggest that barite formed at the same time that sulfate was being reduced to hydrogen sulfide.

Metal Precipitation in the Giant Porphyry Copper-Molybdenum Deposit at Butte, Montana

Issue

Porphyry type deposits are of considerable economic importance because they account for over 50 percent of the world's supply of copper and over 70 percent of the world's supply of molybdenum, and are a significant source of gold. Important parameters in geologic models of porphyry deposits are the quantities of magma and magma-derived fluid that are required to form deposits large enough to be economic. These parameters could potentially be determined from analyses of the metal contents of ore-forming fluids that were trapped as inclusions in hydrothermal quartz associated with the ore deposits.

Objectives

The copper-molybdenum deposit at Butte in southwestern Montana (fig. 44) has been studied for over a century. Consequently, its geology is well known. For this study, which was spearheaded by a Mendenhall Fellow, fluid inclusions were characterized using microthermometry, laser Raman spectroscopy, and laser ablation-inductively coupled plasma mass spectrometry. The data yielded information on inclusion filling temperatures, salinities, densities, carbon dioxide contents, and solute contents. In addition, quartz or sulfide samples were crushed or thermally decrepitated so that inclusion liquids and gases could be analyzed by ion chromatography, quadrupole mass spectrometry, and magnetic sector mass spectrometry. The resulting data yielded information on gas species, solutes, and hydrogen, helium, and carbon isotopic compositions.

Background

Porphyry copper deposits form at shallow levels in the earth's crust in regions characterized by tectonic convergence and subduction. The deposit-forming hydrothermal systems develop where crystallizing magmas of felsic to intermediate composition exsolve aqueous fluids at the same time that porphyritic dikes penetrate the overlying rocks. The exsolved fluids migrate upward through fractured wall rocks. As temperature and confining pressure decline, the fluids form veins and alteration envelopes containing sulfide minerals of copper, molybdenum, and other metals.

For most porphyry copper deposits, the mineralizing magmas rise to within 1–4 kilometers of the earth's surface. At these crustal levels, confining pressures are low enough that the exsolving fluids unmix to form separate brine and vapor phases. Fluid inclusions in growing minerals trap brine and vapor in varying proportions that do not reflect the original composition of the exsolving fluid. At Butte, the deposit is unusual because it formed at a depth of 6–9 kilometers. The greater confining pressures at this depth prevented the unmixing of fluids as they exsolved from magmas. Consequently, in the deeper part of the Butte deposit, hydrothermal quartz hosts fluid inclusions that contain the original single-phase fluid.

By studying fluid inclusions in paragenetically early veins in the core of the Butte deposit and younger veins toward the fringes of the deposit, the physical and chemical evolution of the hydrothermal system can be documented in time and space. Thus, the Butte deposit represents a valuable natural laboratory for determining the chemical and isotopic characteristics of the fluids responsible for one of the largest porphyry copper deposits in the world, and the physical and chemical triggers for metal precipitation as the fluids migrated away from their source intrusion and interacted with wall rocks.

Results

Quartz veins in the deeper parts of the Butte deposit, below most of the copper ore and within and below the highest grade molybdenum ore, have thin rims of potassium feldspar or exhibit host rock biotite alteration along the vein margins. Aqueous-carbonic inclusions within the veins have 30–70 volume percent vapor and chalcopyrite daughter crystals. Analyses of the inclusions suggest that the veins formed at 575–650°C and 200–250 MPa from an aqueous fluid containing 2–5 weight percent NaCl equivalent and 2–8 mole percent CO_2. The fluids had Na/Cl mole ratios of 0.9–1.5 and Cl/Br mole ratios of 1,400–3,000. The Cl/Br values are within the ranges displayed by other magmatic ore deposits. The Na/Cl values are higher than other magmatic deposits, which suggests that anions such as HCO_3^- and HSO_4^- may have complexed some of the copper and enhanced its transport. Samples from shallower levels in the deposit show evidence for unmixing of brine and vapor-rich fluids. Chlorine/Br values are the same as at deep levels, but Na/Cl values are 0.6–0.8, which suggests that chlorine was the main copper-complexing anion. In paragenetically later pyritic veins with sericite alteration, sulfide-hosted fluid inclusions show high $^3He/^4He$ ratios that indicate fluid provenance, at least partly, from mantle-derived magma. Hydrogen and carbon isotope data indicate that H_2O and CO_2 in the inclusions are dominantly magmatic. Although rocks in the deeper portions of the deposit are low in copper, analyses of individual fluid inclusions show high concentrations of copper (up to 1 weight percent) and slightly elevated concentrations of iron, manganese, and iron.

The Butte deposit contains an estimated 37.3 million metric tons of copper. If, as the new analyses would suggest, the ore-forming fluids carried copper at an average concentration of 5,000 milligrams per liter, then 7.46 billion metric tons of fluid would have been required to deliver the entire copper inventory of the deposit. The volume of magma that would have been required to exsolve this volume of fluid is about 100 cubic kilometers (calculated assuming an initial water content of 3 weight percent and a magma density of 2.5 grams per cubic centimeter, fig. 47). While large, this volume of magma is dwarfed by the volumes erupted in large volcanic events, which can reach 5,000 cubic kilometers. It follows from the mass balance considerations that the copper concentration in the Butte magma prior to fluid exsolution would have been about 150 milligrams per kilogram. This value matches the copper concentrations that have been reported for melt inclusions associated with other porphyry copper deposits.

Conclusions

Building on previous work, our new results suggest that the entire suite of vein and alteration types observed at Butte, as well as the distribution of the ore metals, reflect cooling and unloading of a fluid exsolved from a crustal magma as well as reactions between the fluid and wall rocks. However, a variety of observations, including the presence of mantle derived helium in paragenetically late pyrite, suggest that mantle sources contributed to the volatile budget throughout the lifetime of the hydrothermal system.

Retrospective

Overall, the Project laboratories—and the geochemical approaches that they provide—proved to be highly effective in developing basic science in support of mineral and geoenvironmental assessments, and in catalyzing interdisciplinary studies relevant to the current science priorities of the USGS. The Project accomplishments included contributions to the core mission of the Mineral Resources Program as well as contributions to the other science directions outlined by the USGS Science Strategy Team: ecosystems, environment, water, hazards, and climate. Key factors that fostered interdisciplinary collaborations were the multiplicity of methods and approaches that are associated with the Project, the commitment of the Mineral Resources Program to maintain the laboratories as highly capable state-of-the-art facilities, and the willingness of Project scientists to apply their geochemical expertise to scientific problems that lie outside their traditional areas of research.

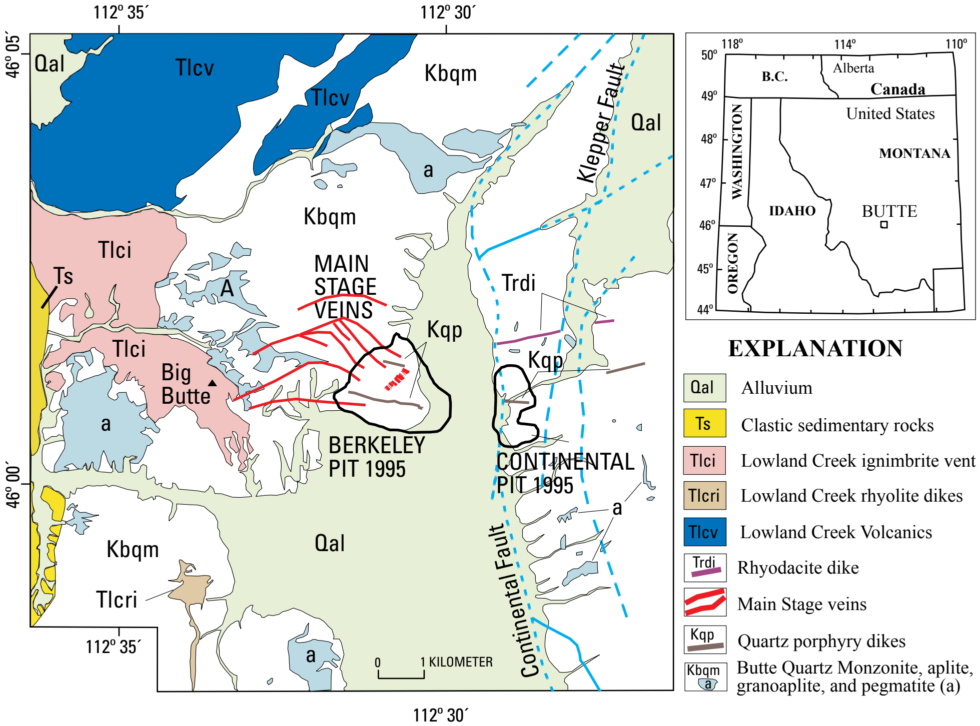

Figure 44. Map showing the location and geologic setting of the Butte district in Montana. The porphyry copper deposit lies within the Butte Quartz Monzonite and related aplites, granoaplites, and pegmatites. (Modified after Rusk and others, 2008, Fluid inclusion evidence for magmatic-hydrothermal fluid evolution in the porphyry copper-molybdenum deposit at Butte, Montana: Economic Geology, v. 103, p. 307–334).

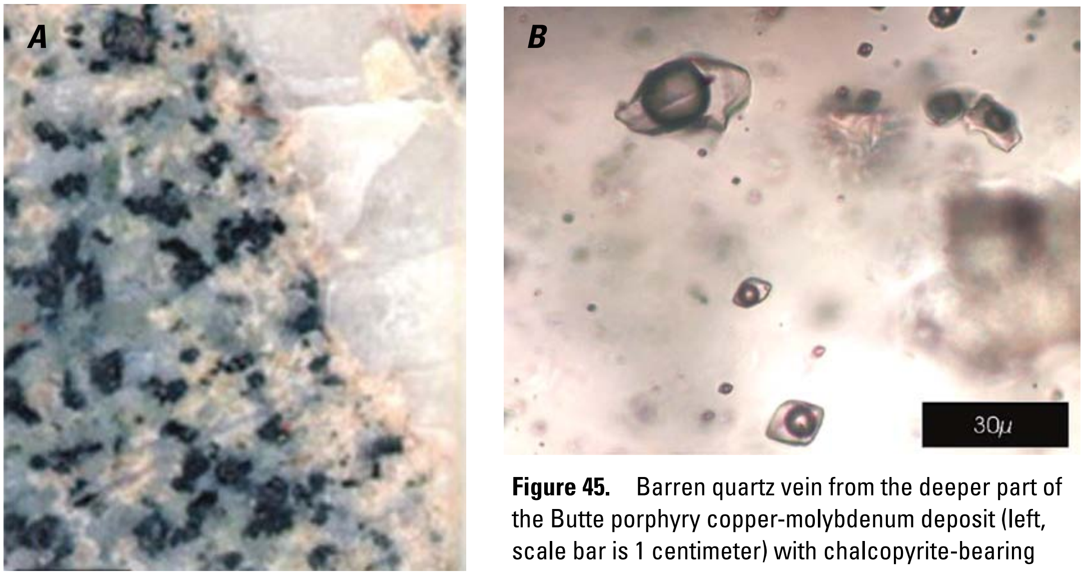

Figure 45. Barren quartz vein from the deeper part of the Butte porphyry copper-molybdenum deposit (left, scale bar is 1 centimeter) with chalcopyrite-bearing fluid inclusions (above).

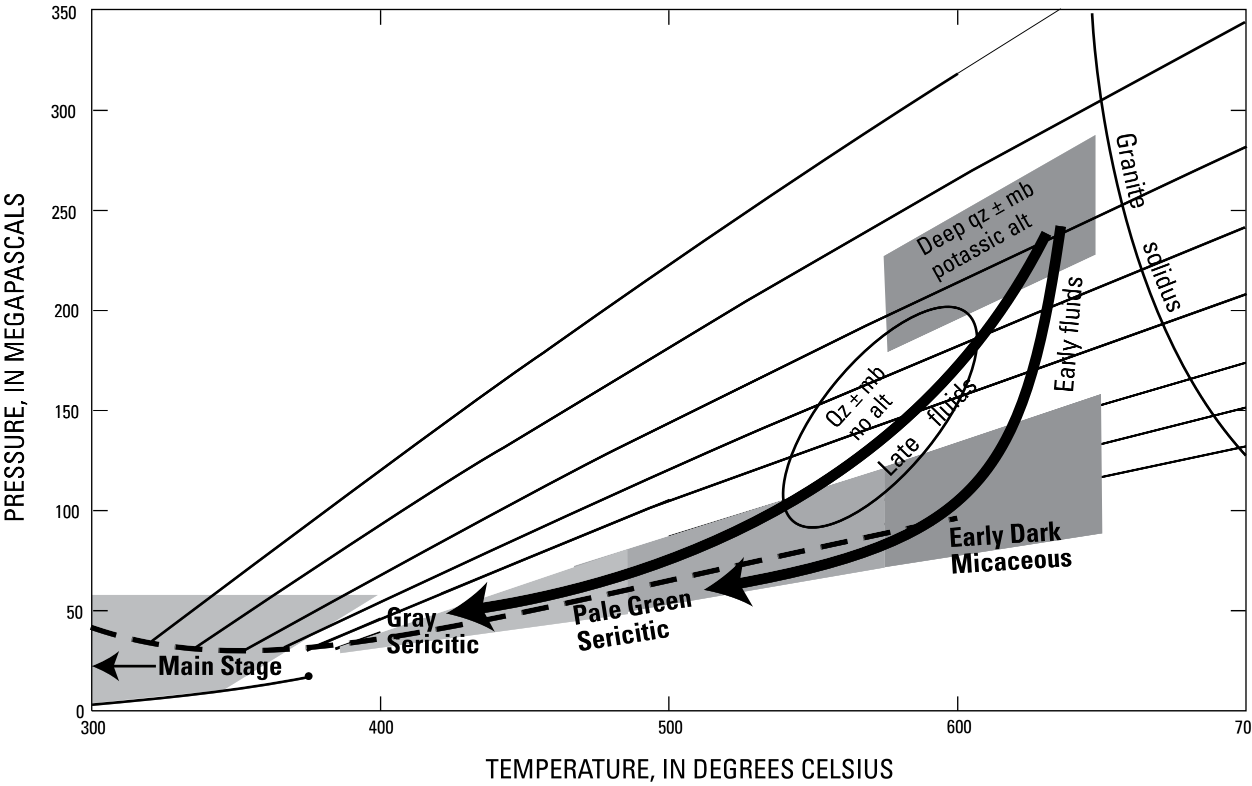

Figure 46. Pressure-temperature diagram showing isochores for a fluid with 4 weight percent NaCl and 5 mole percent CO_2 and the formation conditions of Butte veins. Most deep, quartz-rich veins with early dark micaceous or potassium feldspar alteration formed at pressures of 200–250 MPa and temperatures of 575–650°C. Cooling and unloading of the fluid resulted in changes in the stable mineral assemblages: pale green sericitic alteration, gray sericitic alteration, and main stage mineralization. Dashed curve indicates the limits of the miscibility gap in the system H_2O–CO_2–NaCl. (Modified after Rusk and others, 2008, Fluid inclusion evidence for magmatic-hydrothermal fluid evolution in the porphyry copper-molybdenum deposit at Butte, Montana: Economic Geology, v. 103, p. 307–334).

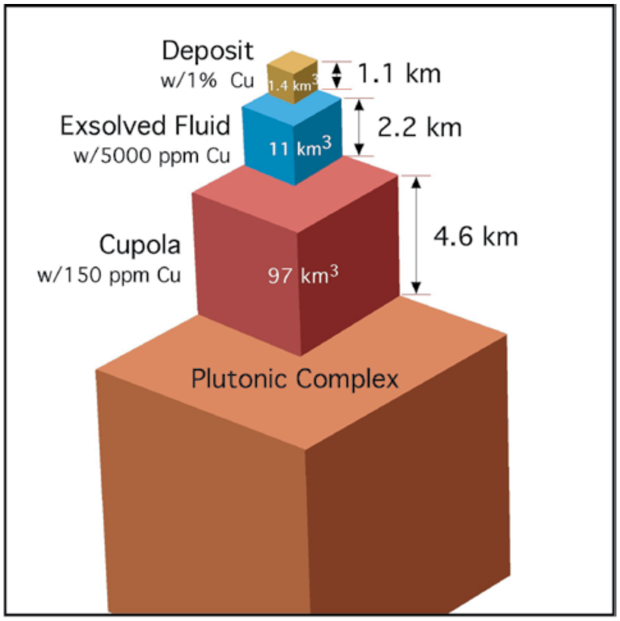

Figure 47. Diagram showing the volumes of magma, exsolved fluid, and ore that are inferred for the Butte ore-forming system.

Cooperators

Alaska Department of Fish and Game
Barrick Gold Corporation
Bureau of Land Management
Dalhousie University, Halifax, Nova Scotia, Canada
Edwards Aquifer Authority, San Antonio, Tex.
Getchell Gold Corporation
Idaho Geological Survey
Interagency Grizzly Bear Study Team
National Park Service
New Mexico Bureau of Geology and Mineral Resources
Newmont Gold Company
National Oceanic and Atmospheric Administration
Oklahoma Water Resources Board
On-Stream Resource Managers
Oregon State University
Paul Scherrer Institut of Particle Physics, Zurich, Switzerland
Pinson Mining Company
San Antonio Water Systems, San Antonio, Tex.
Shell Oil Company
South Dakota State University
Teck Cominco Limited
The RETEC Group, Incorporated
U.S. EPA Region 6
University of Oregon
USGS Alaska Science Center
USGS Columbia Environmental Research Center
USGS Fort Collins Science Center
USGS National Cooperative Geologic Mapping Program
USGS National Research Program—Chlorofluorocarbon Laboratory, Reston, Va.
USGS Northern Rocky Mountain Science Center
USGS Patuxent Wildlife Research Center
USGS Salton Sea Science Office
USGS Volcano Hazards Program
USGS Water Science Center, San Antonio, Tex.
USGS Water Science Center, Oklahoma City, Okla.
Washington State University Bear Center

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