

Stable Isotope Evidence for Magmatic Fluids in the Pueblo Viejo Epithermal Acid Sulfate Au-Ag Deposit, Dominican Republic

TORSTEN W. VENNEMANN, JOHN L. MUNTEAN, STEPHEN E. KESLER, JAMES R. O'NEIL,

Department of Geological Sciences, University of Michigan, Ann Arbor, Michigan 48109-1063

JOHN W. VALLEY,

Department of Geology, University of Wisconsin, Madison, Wisconsin 53706

AND NORMAN RUSSELL*

Rosario Dominicana S.A., Apartado Postal 944, Santo Domingo, Dominican Republic

Abstract

Stable isotope (H, C, O, and S) systematics of the Pueblo Viejo acid sulfate system, the world's largest bulk mineable acid sulfate gold deposit, were investigated to determine the importance of magmatic fluids in hydrothermal systems of this type. Mineralization at Pueblo Viejo is hosted by a maar-diatreme system that cuts sedimentary rocks and spilites of the Late Cretaceous Los Ranchos Formation. The deposit is characterized by two stages of advanced argillic alteration: stage I fluids produced deep alunite + quartz and shallower kaolinite + quartz, both associated with disseminated pyrite; stage II fluids overprinted stage I and produced deep pyrophyllite + diasporite and an overlying silica cap. An increase in temperature from stage I (~250°C) to stage II (~250°–300°C) is indicated by mineral stabilities and sulfur isotope thermometry of coexisting sulfide-sulfate pairs. Stage I quartz-alunite-kaolinite-pyrite alteration and associated disseminated Au-Ag mineralization are interpreted to have precipitated in equilibrium with magmatic discharge fluids ($\delta D = -35$ to -15‰ ; $\delta^{18}O = 6.5$ to 11‰) that experienced only minor ($\leq 25\%$) dilution by meteoric water ($\delta D = -30\text{‰}$; $\delta^{18}O = -5\text{‰}$). Stage II advanced argillic alteration resulted from a renewed influx of essentially pure magmatic discharge fluid. The shallow silica cap generated during stage II resulted from significant ground-water dilution of magmatic fluids.

Circulation of conductively heated seawater adjacent to the acid sulfate system caused deposition of a carbonate-sulfate zone that sealed the acid sulfate mineralization from ground-water and seawater infiltration. It is possible that the regional greenschist facies alteration of Los Ranchos Formation rocks was also related to such seawater circulation.

These results suggest that the dominant proportion of metals and fluids in acid sulfate systems are derived from bulk condensates of magmatic vapors. Relatively small ($\leq 25\%$) proportions of nonmagmatic fluids, that is, fluids from meteoric or seawater sources, may, however, have been important in causing precipitation of the ore components.

Introduction

ADVANCED argillic alteration typical of acid sulfate Au-Ag ore deposits, and of presently active and extinct hydrothermal systems, requires extremely acidic conditions (Knight, 1977; Hayba et al., 1985; Heald et al., 1987). Calculations by Brimhall and Ghorso (1983) and Stoffregen (1989) indicate that such fluids can be generated by the addition of about 1 mole percent of combined SO_2 , H_2S , HCl , and HF to water. As these species are readily generated by

andesitic to rhyolitic magmas, it is frequently proposed that advanced argillic alteration develops where these gases invade ground-water systems (e.g., Giggenbach, 1975, 1987; Bethke, 1984; Rye et al., 1992), presumably in the form of magmatic vapor plumes (Henley and McNabb, 1978). In addition, magmatically exsolved vapors contain significant quantities of base and precious metals (Symonds et al., 1987; Quisefit et al., 1989), which may contribute to the mineralization in acid sulfate deposits. High-temperature solfataric and fumarolic emissions of active subduction-related volcanoes have average combined SO_2 - H_2S - HCl - HF contents that vary be-

* Present address: American-Pacific Honduras, Apartado Postal 342, San Pedro Sula, Honduras.

tween 0.3 and 6 mole percent where the balance is largely made up by 80 to 95 mole percent H_2O and 3 to 15 mole percent CO_2 (Giggenbach, 1975; Rose et al., 1986; Quisefit et al., 1989). Thus, even if the acid constituents are diluted to the required minimum of ~ 1 percent by ground water, magmatic hydrothermal systems still contain a significant proportion of magmatic water condensate. This raises the question of whether meteoric water is a necessary requirement for the condensation of magmatic volatiles and metals in magmatic epithermal systems (e.g., Hedenquist and Aoki, 1991) or whether the mineralization can also form at depth, simply as reaction products from an interaction of bulk magmatic vapor condensates with suitable wall rocks. In this paper, we report the results of a detailed stable isotope study undertaken with the specific aim of determining the relative importance of various geologic reservoirs as sources for the H, C, O, and S in the Pueblo Viejo acid sulfate gold-silver deposit. We were particularly interested in determining the role of magmatic fluids in the system. Pueblo Viejo is the largest such deposit in the world, with particularly intense and pervasive advanced argillic alteration (Muntean et al., 1990). It is thus likely that a significant amount of magmatic fluid is required to produce this system, that is, if magmatic fluids are indeed important in the genesis of acid sulfate deposits.

Geologic Background

The Pueblo Viejo Au-Ag deposits are hosted by the Early Cretaceous Los Ranchos Formation, one of sev-

eral bimodal volcanic piles at the base of the Greater Antilles in central Hispanola (Kesler et al., 1981; Russell et al., 1981; Fig. 1). The Los Ranchos Formation comprises locally pillowed spilites (Cotui Member), keratophyre and quartz-keratophyre, tuffs and intrusions (Quita Sueño Member) at the base, overlain by volcanoclastic rocks and water-lain sedimentary units (Meladito Member), and massive spilites of the Platanal and Naviza Members (Kesler et al., 1991). The Meladito and Platanal Members are cut by a maar-diatreme complex (Pueblo Viejo Member), consisting of breccias and upward-fining carbonaceous strata that contain near-marine terrestrial fossils, as well as large silicified cobbles that appear to be diatreme fragments (Russell and Kesler, 1991). Lower greenschist facies metamorphic conditions for the Los Ranchos Formation are indicated by replacement of the magmatic pyroxene-plagioclase feldspar assemblage by metamorphic albite, quartz, chlorite, epidote, calcite, and clay minerals. Strontium isotope ratios of amygdaloidal calcite in spilitic rocks are similar to those of Cretaceous seawater, suggesting that these minerals formed through submarine hydrothermal metamorphism (Kesler et al., 1991).

The Pueblo Viejo deposits make up the largest bulk mineable acid sulfate Au-Ag district in the world (Kesler et al., 1981; Russell et al., 1986). Unlike other acid sulfate epithermal deposits in which most ore is hosted by veins, approximately 60 percent of the precious metal at Pueblo Viejo occurs as early, disseminated ore, while the remainder occurs in late-

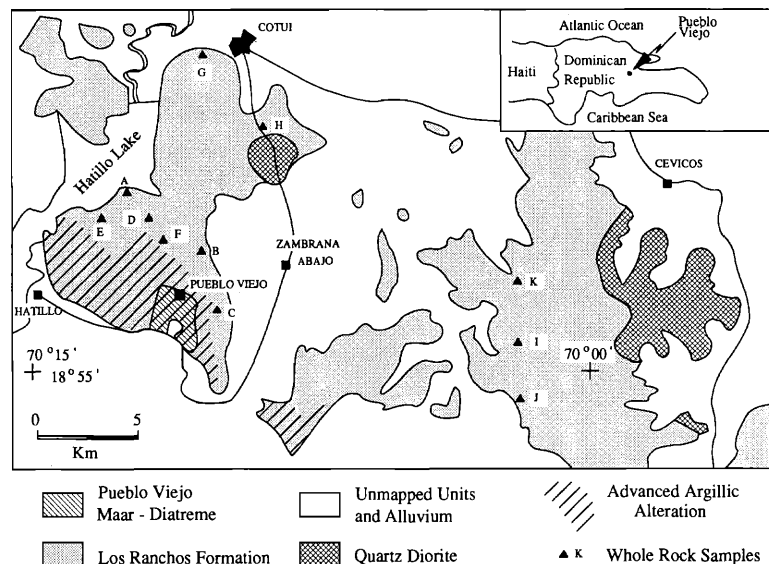


FIG. 1. Location of the Pueblo Viejo district relative to the Los Ranchos Formation, Dominican Republic.

stage base and precious metal-bearing veins (Kettler, 1989; Muntean et al., 1990). Geologic relations indicate that the mineralization is related to hydrothermal processes that were contemporaneous with the formation of the maar-diatreme complex. This complex, in turn, developed during the close of volcanism and is of probable explosive volcanic origin (Kesler et al., 1981, 1991; Muntean et al., 1990). Mineralization occurs in a number of funnel-shaped acid sulfate orebodies, the two largest of which are the Moore and Monte Negro orebodies (Russell et al., 1981). The throats of these funnels are largely confined to the spilitic rocks of the Platanal Member and the orebodies flare upward into overlying spilite-clast conglomerates and carbonaceous sedimentary strata (Kesler et al., 1981; Russell et al., 1981). Muntean et al. (1990) have shown that these deposits record two stages of advanced argillic alteration and associated precious metal mineralization which overprint the regional greenschist facies alteration of the spilites in the Monte Negro orebody.

Stage I is characterized by deep alunite-pyrite-quartz-rutile and shallow kaolinite-pyrite-quartz-rutile zones. Coexisting alunite and pyrite in this stage provide critical evidence for the presence of dissolved sulfate and sulfide in the mineralizing solutions. Gold is confined to inclusions in pyrite (Muntean et al., 1990; Kettler et al., 1992). Temperatures of less than 260°C and a pH of between 2 and 3 have been estimated for stage I mineralization from phase equilibria and sulfur isotope thermometry of coexisting pyrite-alunite (Muntean et al., 1990).

Stage II alteration, characterized by pyrophyllite \pm diaspore and high-level caps of massive silicification, overprinted and replaced stage I alteration to varying degrees. In deeper parts of the system, diaspore replaces alunite whereas pyrophyllite forms veinlets and patches that cut alunite, quartz, and pyrite (Muntean et al., 1990). In shallower parts of the system stage II overprinting is characterized by monomineralic pyrophyllite veinlets that cut a quartz-rich matrix and coalesce at kaolinite patches where pyrophyllite has replaced kaolinite to varying degrees. In places, early stage I quartz-kaolinite is completely overprinted by pyrophyllite, leaving some zones in which pyrite and rutile are the only remaining stage I minerals. Coexistence of pyrophyllite and diaspore suggests temperatures in excess of 285°C and a pH of 1 to 1.5 (Knight, 1977; Hemley et al., 1980). Massive silica was deposited at temperatures of \sim 220°C during stage II in the relict kaolinite zone above areas of massive pyrophyllite. Textures in the zone of massive silicification suggest that the microcrystalline quartz formed by recrystallization of chalcedony, opal, and amorphous silica (Muntean et al., 1990). Whereas little additional wall-rock pyrite appears to have been

deposited during stage II pyrophyllite formation, gold-bearing sulfide veins cut stage I assemblages and are interpreted to be contemporaneous with stage II. Sulfides include pyrite, enargite, and sphalerite which occur together with minor native sulfur, barite, and quartz. Common zonation from predominantly pyrite on the outside to enargite and/or sphalerite and barite in the center of the veins suggests that enargite, sphalerite, and barite are paragenetically late. Quartz occurs in interstices between sulfide grains and in vein centers. The veins rarely contain pyrophyllite. It is likely that stage II veins formed in response to hydrofracturing of the high-level silica cap (Muntean et al., 1990).

Analytic Procedures

All minerals analyzed for their stable isotope compositions were handpicked from drill cores or surface samples. For sample localities of drill cores please refer to Muntean et al. (1990) and Kettler et al. (1992). Surface sample localities are given in Figure 2. Alunite was purified by heat flow treatment of

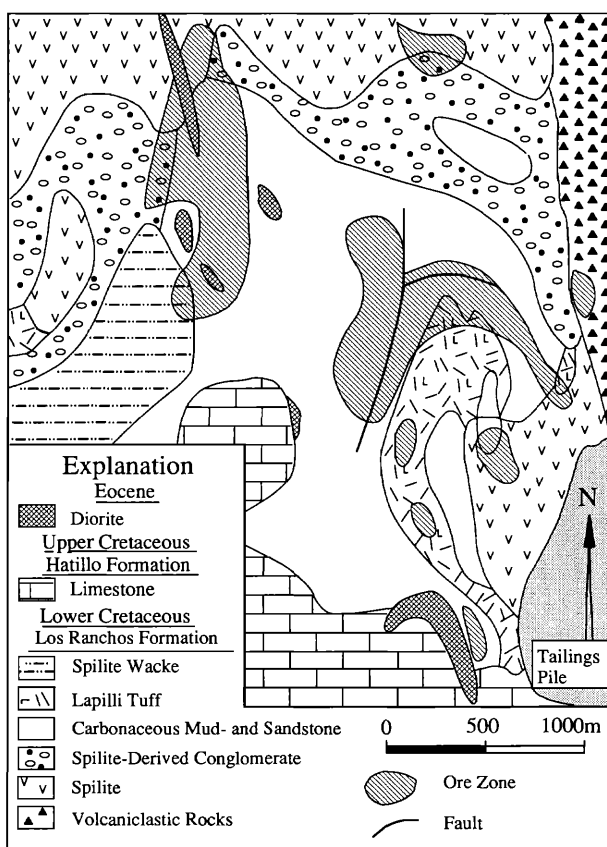


FIG. 2. Sketch map of the general geology of the Pueblo Viejo district, including surface projections of the ore zones.

alunite-silicate mixtures. Except where indicated otherwise, mineral separates were better than 95 percent pure or, in the case of sulfides, better than 90 percent pure (balance made up of silicates). After separation, all minerals were crushed until finer than 75 μm , washed in distilled H_2O , and dried at 110°C. Whole rocks were crushed to finer than 50 μm and analyzed directly. All analyses were performed in the stable isotope laboratory of the University of Michigan, except for some initial oxygen isotope analyses of quartz, pyrophyllite, and alunite, which were performed at the University of Wisconsin and the U.S. Geological Survey in Menlo Park.

Hydrogen from hydrous minerals and whole rocks was extracted according to the method described by Vennemann and O'Neil (in press) and analyzed for isotopic composition with a Finnigan Mat Delta-S mass spectrometer. The water content of minerals and whole rocks was determined as part of the extraction procedure given by Vennemann and O'Neil (in press) to a precision of ± 0.1 wt percent.

Oxygen was extracted from minerals and whole rocks according to the standard method described by Clayton and Mayeda (1963). Oxygen isotope compositions of both total alunite and sulfate extracted from the alunite were determined according to the method of Pickthorn and O'Neil (1985). By stoichiometric mass balance, the isotopic composition of hydroxyl oxygen was then calculated. All extracted oxygen was converted to CO_2 by reaction with a heated graphite rod in the presence of a Pt catalyst. After determining the amount of CO_2 , it was analyzed for $^{18}\text{O}/^{16}\text{O}$ ratio.

Carbon and oxygen isotope ratios of carbonates were determined according to the method described by McCrea (1950) using 100 percent orthophosphoric acid to extract CO_2 from calcite at 25°C and a CO_2 -acid fractionation factor of 1.01025 (modified from Sharma and Clayton, 1965). Carbonate content was determined as part of the orthophosphoric acid technique and measured as yields of CO_2 . Extracted CO_2 was analyzed on a Finnigan Mat Delta-S mass spectrometer.

Sulfur isotope ratios of sulfides were determined on SO_2 by combusting the sulfide with cuprous oxide at 1,000°C for 10 min. For sulfates, sample powders were mixed with a flux of sodium-metaphosphate ($(\text{NaPO}_3)_x \cdot \text{Na}_2\text{O}$) and combusted in the presence of native copper at 1,000°C for 20 min to produce SO_2 . Yields of SO_2 were commonly 98 ± 4 percent. Isotopic ratios of SO_2 were measured using a VG 602E mass spectrometer.

Fluid inclusions in quartz were decrepitated thermally at temperatures of less than 450°C and the δD and $\delta^{18}\text{O}$ values of the liberated water were analyzed according to the method described by Kishima and

Sakai (1980), except that zinc was used as reductant for D/H measurements of water. Amounts of CO_2 , CH_4 , and other gases were generally very small (≤ 5 mole %), and their contribution to the δD and $\delta^{18}\text{O}$ values was ignored.

All isotopic ratios are reported in δ notation relative to V-SMOW (Vienna standard mean ocean water) for hydrogen and oxygen, PDB (Peedee belemnite) for carbon, and CDT (Canyon Diablo troilite) for sulfur. Analytic accuracy was monitored using NBS-28 (quartz; $\delta^{18}\text{O} = 9.6\text{‰}$) for silicate oxygen, NBS-30 (biotite; $\delta\text{D} = -64\text{‰}$) for hydrogen, NBS-19 (limestone; $\delta^{13}\text{C} = 2.0\text{‰}$, $\delta^{18}\text{O} = 28.5\text{‰}$) for carbonates, and NBS-123 (sphalerite; $\delta^{34}\text{S} = 17.1\text{‰}$) for sulfur. Precision, as determined from replicate analyses of standards and samples, is better than ± 2 per mil for δD values, 0.1 per mil for $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values of minerals, and 0.3 per mil for $\delta^{34}\text{S}$ and $\delta^{18}\text{O}$ values of whole rocks.

Sulfur Isotope Composition of Sulfides and Sulfates

Stable isotope analyses of sulfides and sulfates made in this study, together with those reported by Kesler et al. (1981), are given in Table 1 and summarized in Figure 3. Additional $\delta^{34}\text{S}$ values of diagenetic, framboidal premineralization pyrite as well as nonframboidal Au-mineralized pyrite from the upper part of the Moore orebody at Pueblo Viejo are reported by Kettler et al. (1992). The range in $\delta^{34}\text{S}$ values of nonframboidal pyrite analyzed by Kettler et al. (1992) is identical to that reported in this study.

The analyzed sulfides have been distinguished as vein and bulk sulfides, the latter generally occurring as disseminated ore. However, the range of $\delta^{34}\text{S}$ values of vein and disseminated sulfides for both pyrite and sphalerite is similar and a mean of -5.2 per mil ($1\sigma = 2.2\text{‰}$; $n = 18$) is obtained for the total population of sulfides. Indistinguishable $\delta^{34}\text{S}$ values observed for sulfides within spilitic and carbonaceous sedimentary rocks are indicative of a common origin for the sulfur in these rocks with little or no influence of the host rocks on $\delta^{34}\text{S}$ values. Two samples of native sulfur have $\delta^{34}\text{S}$ values of -3.6 and -8.4 per mil, values expected from the equilibrium fractionations at temperatures of 150° to 250°C (Ohmoto and Rye, 1979). In one case where sphalerite and pyrite were analyzed from the same sample, disequilibrium is suggested by the large fractionation between them corresponding to temperatures of less than 100°C (Ohmoto and Rye, 1979). In contrast, temperatures of between 180° and 230°C for stage I are indicated by coexisting alunite-pyrite pairs and 200° to 260°C for stage II barite-sphalerite pairs (Table 1; Ohmoto and Rye, 1979). These temperatures are in good agreement with those predicted from stage I and II mineral assemblages (Muntean et al., 1990).

TABLE 1. Sulfur Isotope Compositions of Sulfides and Sulfates

Locality	Sample	Wall rock	Mineral	Stage	$\delta^{34}\text{S}$ (‰)	Temp. (°C)	Source
Monte Negro	DDH195- 63	C. sediment.	Pyrite-V	II	-4.3	180	(1)
	- 73	Spilite	Pyrite-V	II	-5.5		(1)
	-246	Spilite	Pyrite-V	I	-9.5		(1)
			Alunite-V	I	20.0		(1)
	-229	Spilite	Alunite-V	I	18.9		(1)
	DDH206-187	Spilite	Pyrite-V	II	-6.7		(1)
	DDH216- 22	C. sediment.	Sphalerite-V	II	-3.1		(1)
	DDH229- 84	Spilite	Sphalerite-V	II	-4.8	260	(1)
	-164	Spilite	Sphalerite-V	II	-5.0		(1)
			Barite-V	II	19.5		(1)
	DDH235- 53	C. sediment.	Sphalerite-V	II	-3.7		(1)
	- 67	C. sediment.	Sphalerite-V	II	-3.8		(1)
	Tunnel 12-5	C. sediment.	Pyrite-B	I	-6.0		(2)
Moore	RD-72-22	C. sediment.	Pyrite-V	II	-6.8	90	(2)
			Sphalerite-V	II	-9.1		(2)
	DDH92- 46	C. sediment.	Sphalerite-V	II	-10.1	200	(2)
			Barite-V	II	18.8		(2)
	DDH98- 23	C. sediment.	Barite-V	II	20.0	230	(2)
	DDH100- 16	C. sediment.	Pyrite-B	I	-8.0		(2)
	DDH101- 21	C. sediment.	Pyrite-B	I	-3.5		(2)
	DDH112- 15	C. sediment.	Pyrite-B	I	-3.8		(2)
	DDH159-176	C. sediment.	Pyrite-V	II	-2.9		(1)
	DDH165-166	C. sediment.	Sphalerite-V	II	-2.7		(1)
	DDH170-176	C. sediment.	Alunite-V	I	20.4		(1)
	DDH177-205	Spilite	Pyrite-V	I	-3.6		(2)
			Alunite-V	I	21.6		(2)
	DDH182-154	C. sediment.	Native S-V	II	-8.4		(1)
	DDH240-164	C. sediment.	Native S-V	II	-3.6		(1)

Samples with prefix DDH are from drill core, all others are surface samples; C. sediment. = carbonaceous sedimentary rock; B = bulk-rock separate; V = vein samples; (1) = this study; (2) = Kesler et al. (1981)

Hydrogen and Oxygen Isotope Compositions of Silicates, Whole Rocks, and Fluid Inclusions

Stable isotope analyses of quartz, sericite, alunite, kaolinite, and pyrophyllite are given in Table 2. Ad-

ditional $\delta^{18}\text{O}$ values of vein quartz together with δD values of fluid inclusion water in the quartz are given in Table 3. The distribution of $\delta^{18}\text{O}$ values for quartz and for pyrophyllite and kaolinite are illustrated in Figures 4 and 5. Stable isotope analyses of whole rocks are given in Table 4.

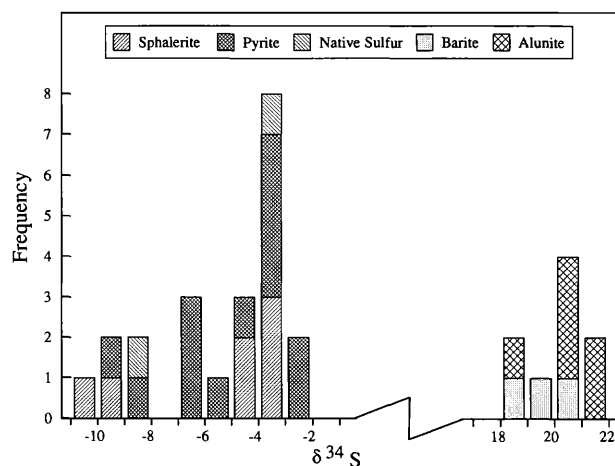


FIG. 3. Histogram of the $\delta^{34}\text{S}$ values of sulfides, sulfates, and native sulfur given in Table 1.

Alteration minerals and fluid inclusions

Quartz samples are divided into two groups representing the two stages of mineralization: stage I quartz from the alunite-quartz zone and stage II quartz from stage II generation veins. Bulk jasperoidal quartz separated from the silicified cap in the upper parts of the system represents mixtures of quartz deposited during stages I and II together with any prestage I quartz. Stage I and II quartz have mean $\delta^{18}\text{O}$ values of 13.5 per mil ($n = 5$; $1\sigma = 0.7\text{‰}$) and 14.3 per mil ($n = 16$; $1\sigma = 1.0\text{‰}$), respectively, suggesting a subtle increase in $\delta^{18}\text{O}$ values with time. Bulk quartz separates have somewhat lower values (mean = 12.3‰; $n = 6$; $1\sigma = 0.7\text{‰}$) compared to stage I and II quartz. Both the bulk separates and vein separates of pyrophyllite have similar $\delta^{18}\text{O}$ values. Pyrophyllite is ~1 per mil heavier than stage I kaolin-

TABLE 2. Oxygen and Hydrogen Isotope Compositions of Silicates and Sulfates

Locality	Sample	Wall rock	Mineral	Stage	$\delta^{18}\text{O}$ (‰)	δD (‰)	H_2O (wt %)
Monte Negro	DDH194- 55	Conglomerate	Quartz-B	I + II	11.7		
	- 98	Conglomerate	Kaolinite-quartz	I	11.4	-47	7.1
	DDH195- 8	C. sediment.	Pyrophyllite-V	II	13.0	-43	5.5
	-187	Spilite	Pyrophyllite-V	II	11.8	-38	4.7
	-229.7	Spilite	Alunite	I	7.9 ^T	-35	11.6
					13.3 ^S		
	-229.7	Spilite	Quartz	I	14.1		
	-236.5	Spilite	Quartz-V	II	14.4		
	-246.9	Spilite	Alunite	I	7.8 ^T	-33	10.2
					13.8 ^S		
	-246.9	Spilite	Quartz	I	13.4		
	-248	Spilite	Alunite	I	6.5 ^T		
	-248	Spilite	Quartz	I	13.6		
	-252	Spilite	Alunite	I	6.1 ^T		
	-252	Spilite	Quartz	I	14.1		
	DDH197- 38	Conglomerate	Quartz-B	I + II	12.3		
	- 58	Spilite	Quartz-B	I + II	12.2		
	- 98	Spilite	Quartz-B	I + II	11.4		
	DDH206- 28.3	C. sediment.	Pyrophyllite-V	II	11.8	-39	4.8
	- 83	Spilite	Quartz-B	I + II	13.2		
	DDH206-113	Spilite	Pyrophyllite	II	11.8	-36	4.9
	-122	Spilite	Quartz-B	I + II	12.7		
	-142	Spilite	Pyrophyllite	II	11.9	-36	4.9
	-202	Spilite	Pyrophyllite	II	12.0	-35	4.6
	-214.3	Spilite	Pyrophyllite	II	12.6	-38	4.6
	-219	Spilite	Pyrophyllite	II	12.5		
	-233.8	Spilite	Pyrophyllite-V	II	12.7	-36	4.7
	-252.1	Spilite	Quartz-V	II	14.6		
	-260.5	Spilite	Quartz-V	II	14.5		
	-302	Spilite	Pyrophyllite	II	11.4	-36	4.7
	DDH208- 28	C. sediment.	Kaolinite-quartz	I	13.5	-41	7.1
	DDH225- 60	Agglomerate	Quartz-V	II	14.5		
	MN-1-A	C. sediment.	Quartz-V	II	13.1		
	MN-1-C	C. sediment.	Quartz-V	II	14.0		
	S7-2	Arenite	Quartz-V	II	15.4		
Moore	DDH92- 175	C. sediment.	Pyrophyllite	II		-41	3.5
	DDH170-176	Spilite	Alunite	I	12.7 ^S	-31	11.3
	DDH176- 20	C. sediment.	Pyrophyllite-kaolinite	I + II		-44	10.5
	-270 m	Spilite	Alunite	I	5.4 ^T	-32	10.2
	-270 m	Spilite	Quartz	I	12.4		
	DDH177-205B	Spilite	Alunite	I	6.5 ^T	-42	9.2
	DDH222- 46.5	C. sediment	Pyrophyllite	II		-47	4.2
	DDH240- 95.5	C. sediment	Pyrophyllite	II		-41	5.6
	-136	C. sediment.	Kaolinite-V	I	10.9	-35	13.2
	DDH242-134.8	C. sediment.	Pyrophyllite-kaolinite	I + II		-40	7.9
	DDH243-197.3	Conglomerate	Quartz-V	II	13.3		
	East Mejita S23AB	Conglomerate	Kaolinite	I	10.3	-36	13.0
	La Cuaba DDH258- 60.5	Spilite	Quartz-V	I + II	12.1		
		Spilite	Sericite-V	I + II	8.6		

Samples with prefix DDH are from drill core, all others are surface samples; C. sediment. = carbonaceous sedimentary rock; B = bulk-rock separate; V = vein separate; alunite $\delta^{18}\text{O}$ analyses: ^T = bulk $\delta^{18}\text{O}$ by fluorination, ^S = sulfate $\delta^{18}\text{O}$ from alunite reprecipitated as barite

ite, which may be an equilibrium relation (pyrophyllite contains a higher SiO_2 component). There is no significant difference between the δD values of pyrophyllite and kaolinite, both having a range in δD values from -47 to -35 per mil. A similar range in δD values was also found for alunite (-42 to -31‰). Fluid inclusion waters extracted from stage II quartz

have a somewhat larger range of δD values (-53 to -25‰; Table 3).

By comparison with experimentally determined fractionation factors for coexisting quartz-alunite ($\delta^{18}\text{O}_{\text{SO}_4}$) and quartz-muscovite at temperatures of $\sim 250^\circ$ to 300°C (O'Neil and Taylor, 1969; Matsu-hisa et al., 1979; Stoffregen et al., 1989; also see be-

TABLE 3. Hydrogen and Oxygen Isotope Compositions of Fluid Inclusions and Host Quartz from Stage II Veins

Locality	Sample	Wall rock	Mineral	Quartz $\delta^{18}\text{O}$ (‰)	Fluid inclusions δD (‰)
Monte Negro	DDH185-295	Spilite	Quartz	14.7	-33
	DDH232- 63.9	Spilite	Quartz	13.4	-44
	DDH235- 53	C. sediment.	Quartz	14.1	-53
Moore	DDH176-156.3	C. sediment.	Quartz	15.2	-25
	-179.5	C. sediment.	Quartz	15.1	-31
	DDH191-130	C. sediment.	Quartz	14.8	-29
	DDH241-188	C. sediment.	Quartz	15.2	-35

Samples with prefix DDH are from drill core, all others are surface samples; C. sediment. = carbonaceous sedimentary rock

low), these mineral pairs may have approached oxygen isotope equilibrium in the Pueblo Viejo system. However, oxygen isotope fractionations calculated from average quartz and pyrophyllite $\delta^{18}\text{O}$ values in stage II veins do not correspond to temperatures of $\sim 300^\circ\text{C}$. This observation suggests that the extrapolated muscovite- H_2O oxygen isotope equilibration curve of O'Neil and Taylor (1969), which was used as an estimate for pyrophyllite- H_2O fractionations, is not applicable, that these phases are not cogenetic, or that one or both minerals exchanged oxygen with an external reservoir after their precipitation.

Wall-rock compositions

Spilites and keratophyres, the most abundant wall-rock types in the acid sulfate system, have major element compositions similar to those of basaltic and dacitic rocks, respectively. Hydrogen and oxygen isotope compositions of spilitic whole rocks analyzed from Pueblo Viejo (Table 4) are similar to those of

low-temperature ($\pm 200^\circ\text{C}$), seawater-dominated, hydrothermally altered basaltic rocks (e.g., Muehlenbachs and Clayton, 1972; Spooner et al., 1974; Stakes and O'Neil, 1982; Kyser and O'Neil, 1984). Figure 6 illustrates that, in general, there is a good correlation between H_2O abundance and $\delta^{18}\text{O}$ values of the spilitic whole rocks. Extrapolating the trend in Figure 6 to water contents common for fresh basaltic rocks (~ 0.9 wt %; Manson, 1967) gives $\delta^{18}\text{O}$ values similar to those of fresh basaltic rocks ($\sim 5.7 \pm 0.5$ ‰; e.g., Kyser et al., 1982), suggesting that hydration was accompanied by an ^{18}O enrichment, as would be expected from low-temperature hydrothermal seawater alteration (Muehlenbachs and Clayton, 1972).

The δD and $\delta^{18}\text{O}$ values of rocks affected by advanced argillic and argillic alteration are similar to or slightly higher (more positive) than those of the spilitic rocks of the Los Ranchos Formation that were unaffected by this alteration (Table 4; Fig. 6). Furthermore, no correlation can be observed between

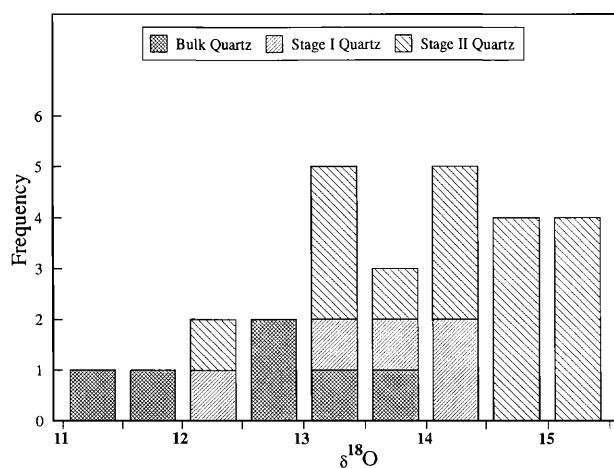


FIG. 4. Histogram of the $\delta^{18}\text{O}$ values of quartz from advanced argillic alteration zones in the Pueblo Viejo district.

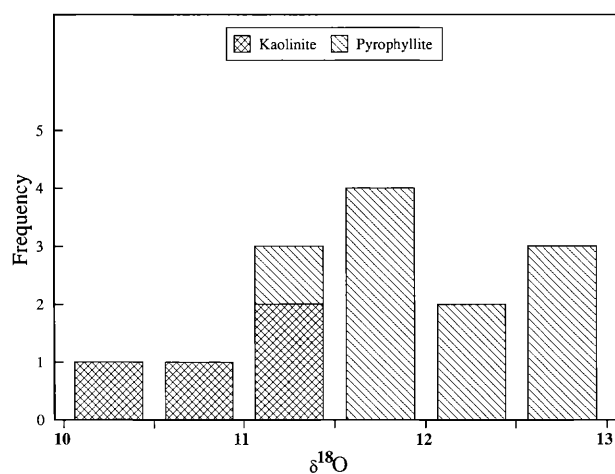


FIG. 5. Histogram of the $\delta^{18}\text{O}$ values of kaolinite and pyrophyllite from advanced argillic alteration zones in the Pueblo Viejo district.

TABLE 4. Hydrogen and Oxygen Isotope Composition of Whole Rocks

Locality	Sample	Alteration	Distance from diatreme (km)	$\delta^{18}\text{O}$ (‰)	δD (‰)	H_2O (wt %)
Platanal, spilites	RD-72-119 (A)	Greenschist	1.6	11.8	-56	3.95
	RD-73-204 (B)	Greenschist	0.3	9.9	-54	4.06
	RD-73-239 (C)	Greenschist	0.3	10.8	-55	3.38
	RD-73-383 (D)	Greenschist	0.5	9.2	-64	3.62
	RD-73-511 (E)	Greenschist	0.9	8.6	-51	2.36
	RD-73-538 (F)	Greenschist	0.1	8.2	-63	3.10
Cotui, spilites	RD-73-429 (G)	Greenschist	9.0	7.0	-53	2.14
	RD-73-595 (H)	Greenschist	7.0	7.2	-64	2.08
Naviza, spilites and keratophyre	RD-83-30 (I)	Greenschist	8.0	9.9	-54	3.66
	RD-83-184 (J)	Greenschist	8.0	11.7	-56	3.23
	RD-83-22 (K)	Greenschist	8.0	12.7	-66	1.65
Monte Negro, spilites	DDH203-116	Advanced argillic	0	10.4	-50	3.67
	DDH219-80	Advanced argillic	0	11.2	-50	4.07
	DDH106-306	Argillic	0	10.3	-49	5.29

Samples with prefix DDH are from drill core, all others are surface samples; letters in parentheses indicate sample localities in Figure 1

the distance from diatreme and the $\delta^{18}\text{O}$ value of the whole rock.

Carbon and Oxygen Isotope Composition of Carbonates

Calcite is present largely as replacements of plagioclase phenocrysts and in amygdulites, where it is part of the regional low-grade metamorphic alteration assemblage within spilitic rocks (Kesler et al., 1981, 1991). Calcite is also concentrated within spilitic rocks and veins along the margins of the main acid sulfate alteration zones (Kesler et al., 1981). It is absent from the funnel-shaped zones of advanced argillic alteration. The stable isotope compositions of calcite from veins and whole rocks at Pueblo Viejo (Table 5) have thus been plotted in Figure 7A as two distinct groups:

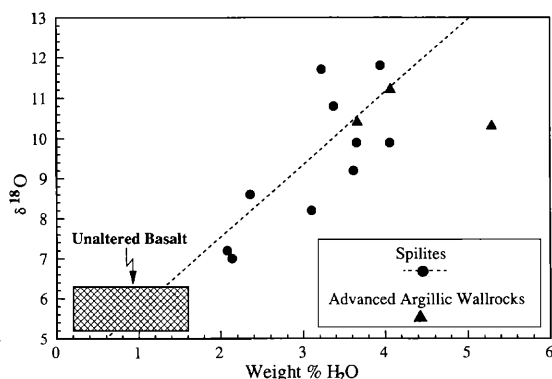


FIG. 6. Variation in $\delta^{18}\text{O}$ values with water content of the greenschist facies spilites of the Los Ranchos Formation and advanced argillic altered wall rocks in the Pueblo Viejo district.

Group A samples include pure calcite separates from veins and whole-rock samples of spilites occurring just outside ($\sim 1\text{--}5\text{ m}$) the zone of advanced argillic alteration. They have a very restricted range of carbon and oxygen isotope composition (-2.7 ± 2.3 and $12.0 \pm 0.4\text{‰}$, respectively) and their $\delta^{18}\text{O}$ values differ markedly from those of Cretaceous marine calcites (Fig. 7A), confirming that they formed or were influenced by hydrothermal or metamorphic processes.

Group B samples include calcite from the Los Ranchos Formation farther from the advanced argillic alteration zones. Their $\delta^{13}\text{C}$ values are similar to or slightly higher than those of the group A calcites and compare well with those observed for Cretaceous marine carbonates (excluding RD-72-119; see below). Their $\delta^{18}\text{O}$ values are generally higher than those of the group A carbonates and range from approximately 24 per mil in spilites seven or more kilometers away from areas of advanced argillic alteration, to values of around 13 per mil in spilites adjacent to the diatreme (Fig. 7B).

The steady decrease in $\delta^{18}\text{O}$ value of the regional group B calcites from values similar to those of Cretaceous marine calcites to values similar to those of the group A calcites is paralleled by an increase in the amount of carbonate (Table 5). Rocks just outside the zone of advanced argillic alteration have carbonate contents one to three orders of magnitude higher than those of the regional spilites well away from the advanced argillic alteration. No correlation is observed between the $\delta^{18}\text{O}$ values of silicates and carbonates.

Unlike $\delta^{18}\text{O}$, $\delta^{13}\text{C}$ values of carbonates do not vary significantly with distance from the zones of ad-

TABLE 5. Carbon and Oxygen Isotope Composition of Carbonates

Locality	Sample	Host rock	Type	Distance from diatreme ¹ (km)	CaCO ₃ (wt %)	$\delta^{13}\text{C}_{\text{PDB}}$ (‰)	$\delta^{18}\text{O}_{\text{SMOW}}$ (‰)
Monte Negro	DDH196-148	Spilite	Vein	0.001	80.2	-2.7	12.3
	DDH197-128	Spilite	Whole rock	0.001	11.4	-3.6	12.0
	DDH203-96	Spilite	Whole rock	0.001	3.3	-2.9	11.7
	DDH206-306	Spilite	Whole rock	0.001	9.2	-4.9	11.8
	DDH219-80	Spilite	Vein	0.001	78.1	-1.1	11.7
Moore	DDH243-197	Conglomerate	Vein	0.001	101.7	-1.7	12.4
	DDH243-197	Conglomerate	Whole rock	0.001	15.5	-1.5	12.3
Platanal rocks	RD-73-538 (F)	Spilite	Whole rock	0.1	0.3	-2.5	13.4
	RD-73-383 (D)	Spilite	Whole rock	0.5	0.2	0.3	14.7
	RD-73-511 (E)	Spilite	Whole rock	0.9	0.1	0.4	15.2
	RD-72-119 (A)	Spilite	Whole rock	1.6	0.3	-23.8	17.2
	RD-73-595 (H)	Spilite	Whole rock	7.0	0.1	-2.4	19.5
Naviza rocks	RD-30-22 (K)	Keratophyre	Whole rock	8.0	0.1	-2.1	20.1
	RD-83-30 (I)	Spilite	Whole rock	8.0	0.1	-0.7	23.7
	RD-83-184 (J)	Spilite	Whole rock	8.0	0.1	-2.6	24.3

Samples with prefix DDH are from drill core, all others are surface samples; letters in parentheses indicate sample localities in Figure 1

¹ For drill core samples distance is measured from zone of advanced argillic alteration

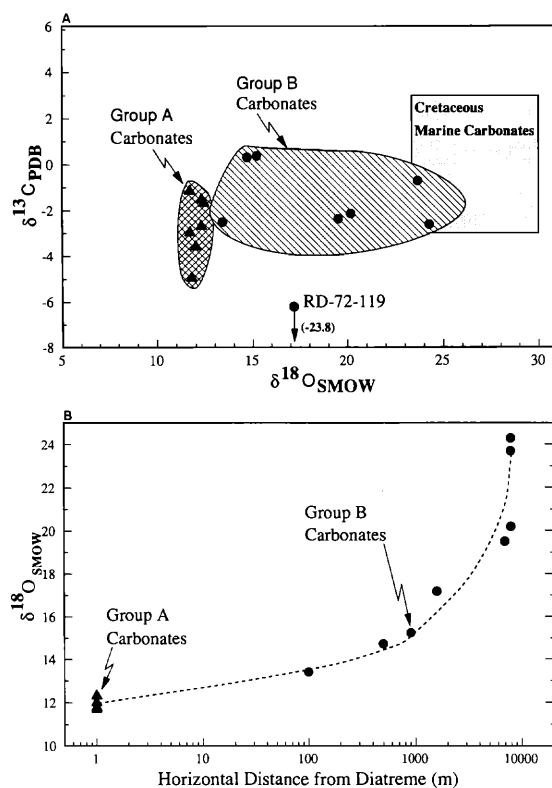


FIG. 7. A. Plot of $\delta^{13}\text{C}$ vs. $\delta^{18}\text{O}$ for the group A and B carbonates analyzed from veins and spilite whole rocks of the Pueblo Viejo district and Los Ranchos Formation, respectively. Field representing $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values of Cretaceous marine carbonates after Veizer and Hoefs (1976). B. Variation in $\delta^{18}\text{O}$ values of group A (Pueblo Viejo district) and B (Los Ranchos Formation) carbonates with horizontal distance from zones of advanced argillic alteration in the Pueblo Viejo acid sulfate system.

vanced argillic alteration. However, compared to the regional group B carbonates which have a $\delta^{13}\text{C}$ range of -2.6 to +0.4 per mil (excluding sample RD-72-119), the group A carbonates sampled from just outside the diatreme have $\delta^{13}\text{C}$ values that extend to somewhat lower values (range -5.0 to -1.1 per mil), even though there is considerable overlap in values between these two groups (Fig. 7A).

Sample RD-72-119 (Table 5), which has one of the lightest carbon isotope compositions ever reported for calcite, comes from spilites that directly overlie sediments of the Meladito Member which is rich in organic material. This calcite is similar in chemical composition and petrographic character to calcite seen elsewhere in the Los Ranchos Formation, and its composition indicates remobilization of organic carbon during the hydrothermal alteration of the Los Ranchos Formation.

Constraints on the Source of Advanced Argillic Alteration Fluids

If the advanced argillic alteration minerals and associated ores in the Pueblo Viejo acid sulfate system precipitated in chemical equilibrium with their parental fluid and did not experience subsequent isotopic exchange, their isotopic signatures should reflect those of the parental fluids. On the basis of regional geologic features (Kesler et al., 1991), fluids that may have been important in the formation of the Pueblo Viejo acid sulfate system include magmatic fluids and vapors and meteoric fluids and Cretaceous seawater, each of which has a distinct isotopic signature (e.g., Sheppard, 1986; Giggenbach, 1992). Recognition of any of these fluids depends critically on the degree of

stable isotope exchange between the original fluid and the wall rocks traversed during hydrothermal fluid flow. This, in turn, is a complex function of temperature, mode of fluid flow, water/rock ratios, and distance traversed by the fluid.

Sulfides and sulfates

Likely sources of sulfur in the Pueblo Viejo acid sulfate system include iron sulfides in Los Ranchos Formation spilites, direct magmatic-volcanic sulfur, and Cretaceous seawater sulfur (Kesler et al., 1981). It is unlikely, however, that seawater sulfate solutions could have produced the acidic conditions required for the advanced argillic alteration of the spilitic rocks (e.g., Seyfried and Mottl, 1982; Bowers et al., 1985) without an introduction of magmatic SO_2 and H_2S (Brimhall and Ghiorso, 1983; Bethke, 1984). However, only small amounts of SO_2 (<1%) need to be added to an aqueous solution in order to lower the pH to ~ 1 . Hence, it may be difficult to detect such small amounts of additional sulfur if the aqueous fluid is dominated by seawater, that is, by seawater sulfate.

The $\delta^{34}\text{S}$ values for total sulfur from magmatic sources such as volcanic rocks and/or magmatic intrusions should be approximately 0 per mil (Ohmoto, 1972), whereas those for total sulfur from Cretaceous seawater sulfate should be around 15 per mil (Holser and Kaplan, 1966). In Figure 8, the $\delta^{34}\text{S}$ values for sulfate (SO_4^{2-}) and sulfide (H_2S) were calculated from fractionation factors given in Ohmoto and Rye (1979) as a function of the aqueous sulfide/sul-

fate concentration ratio ($X_{\text{H}_2\text{S}}/X_{\text{SO}_4^{2-}}$) in fluids where the sulfur is of magmatic or Cretaceous seawater origin at temperatures of 200° and 300°C. Note that at the expected temperature and pH conditions a number of additional aqueous sulfur species (e.g., HSO_4^- , NaSO_4^- , KSO_4^- , CaSO_4 , MgSO_4 , and HS^-), besides H_2S and SO_4^{2-} , can become quantitatively significant. However, at 200° to 300°C the fractionation factor between H_2S and HS^- is small, whereas that between all sulfate species is essentially zero (Ohmoto and Rye, 1979). Thus, for the purposes of this discussion, we can approximate the total $\delta^{34}\text{S}$ value by $\delta^{34}\text{S}_{\text{TS}} = \delta^{34}\text{S}_{\text{H}_2\text{S}} \times X_{\text{H}_2\text{S}} + \delta^{34}\text{S}_{\text{SO}_4^{2-}} \times X_{\text{SO}_4^{2-}}$. The shaded areas between the 200° and 300° curves represent the range in $\delta^{34}\text{S}$ values of dissolved H_2S and SO_4^{2-} in equilibrium with the Pueblo Viejo sulfides and sulfates (Table 1; Ohmoto and Rye, 1979). It is evident from Figure 8 that magmatic fluids may represent the source of sulfur for aqueous sulfide/sulfate ratios larger than 1, whereas Cretaceous seawater may be the dominant sulfur source for ratios less than 0.3. Thus, if the sulfide/sulfate ratios can be determined independently, it should be possible to determine the dominant source of sulfur.

From phase equilibria, Muntean et al. (1990) estimated the average molar aqueous sulfide/sulfate ratios to be about 3 and 35, respectively, for stage I and II fluids and furthermore suggested that stage I disseminated sulfide precipitation occurred in response to wall-rock sulfidation at a molar sulfide/sulfate consumption of 7:1 (table 5, Muntean et al., 1990). The

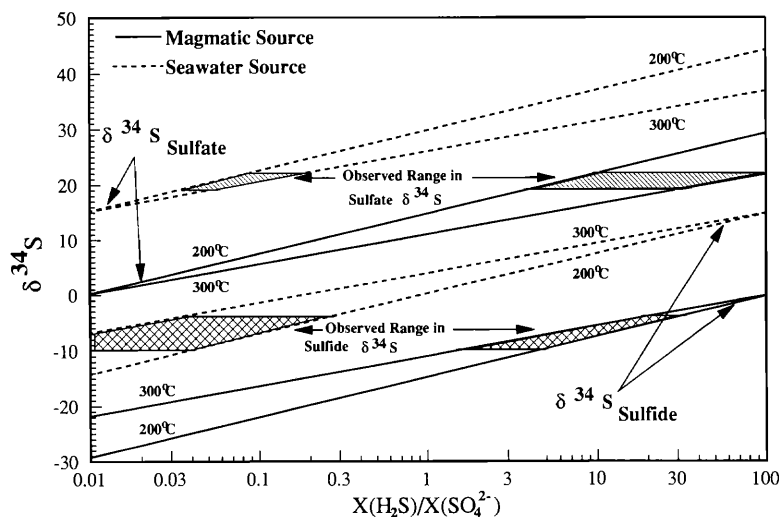


FIG. 8. Variation in $\delta^{34}\text{S}$ values of sulfides and sulfates precipitating from aqueous fluids containing variable proportions of the sulfide (H_2S) and sulfate (SO_4^{2-}). Both magmatic and seawater solutions with $\delta^{34}\text{S}_{\text{total}}$ values of 0 and 15 per mil, respectively, are considered at temperatures of 200° to 300°C. The range in $\delta^{34}\text{S}$ values measured from coexisting sulfides and sulfates in the Pueblo Viejo acid sulfate system are indicated by the shaded fields. Fractionation factors between aqueous sulfur species and precipitated minerals are from Ohmoto and Rye (1979).

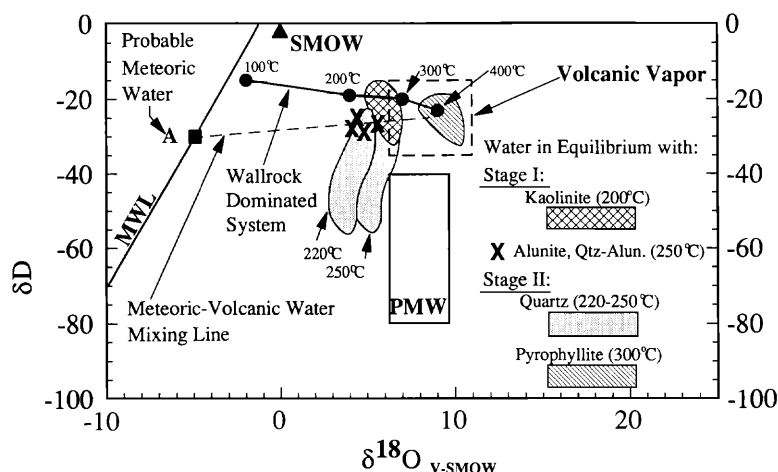


FIG. 9. The δD and $\delta^{18}O$ values of waters calculated to be in isotopic equilibrium with the advanced argillic alteration minerals of the Pueblo Viejo acid sulfate system (shaded fields) and an average spilitic wall rock of the Los Ranchos Formation (curve labeled "Wallrock Dominated System"). Note that owing to the relatively wide scatter in δD and $\delta^{18}O$ values of the Los Ranchos Formation rocks, the line depicting water in equilibrium with these rocks at temperatures of 100° to 400°C only represents a trendline to a much broader range in δD and $\delta^{18}O$ values. For stage II quartz the δD values were estimated from bulk fluid inclusion water, whereas for a coexisting quartz-alunite pair from stage I, the δD value of alunite but the $\delta^{18}O$ value of quartz were used. Also shown for reference purposes are the meteoric water line (MWL), δD and $\delta^{18}O$ values of standard mean ocean water (SMOW), primary magmatic waters (PMW), and volcanic vapors. Also shown is a mixing line between the δD and $\delta^{18}O$ values of meteoric water at the time of alteration and average volcanic water vapor. See text for more discussion.

$\delta^{34}S$ values of Pueblo Viejo sulfides and coexisting sulfates are thus consistent with a history of precipitation from fluids containing sulfur of magmatic origin. The observed range in $\delta^{34}S$ values (Fig. 3) can be produced best by decreasing aqueous sulfide/sulfate ratios during mineralization.

Furthermore, the alunite-sulfide and barite-sulfide fractionations record temperatures consistent with phase equilibria, suggesting attainment and preservation of sulfate-sulfide S isotope equilibria. Owing to the slow rates of sulfur isotope exchange between aqueous sulfate and sulfide (Ohmoto and Lasaga, 1982), retention of isotopic equilibrium among coexisting sulfate-sulfide pairs is commonly observed for magmatic hydrothermal acid sulfate systems but not necessarily for supergene nor steamheated acid sulfate systems (Rye et al., 1992).

Silicates, whole rocks, and fluid inclusions

The δD and $\delta^{18}O$ values of water in equilibrium with the silicates, sulfates, and whole rocks are summarized in Figure 9. For reference purposes, the δD and $\delta^{18}O$ values of meteoric water, seawater, the primary magmatic water field, and volcanic vapors have also been plotted. The δD and $\delta^{18}O$ values of waters calculated to be in equilibrium with these phases were obtained as follows.

Whole rocks: For the purpose of the calculation,

spilitic whole rocks are considered to consist of 25 percent albite, 25 percent chlorite, 15 percent epidote, 10 percent pyroxene, 10 percent sericite (muscovite), 7 percent quartz, and 3 percent magnetite, a mineral assemblage typical for greenschist facies metamorphic conditions. Given the modal abundance and the experimentally determined D/H and $^{18}O/^{16}O$ mineral-water fractionation factors for these minerals (O'Neil and Taylor, 1969; Wenner and Taylor, 1971; Suzuoki and Epstein, 1976; Matsuhisa et al., 1979; Graham et al., 1980; Matthews et al., 1983), it is possible to calculate average spilite-water fractionations at various temperatures. Hence, the isotopic composition of H_2O in equilibrium with an average spilite of $\delta D = 60$ and $\delta^{18}O = 10$ per mil can be computed at various temperatures. Note that it is commonly necessary to extrapolate calibrations for experimentally determined fractionation factors, as such calibrations have been determined only for temperatures in excess of 400°C. The curve, labeled "Wallrock Dominated System" in Figure 9 depicts water in equilibrium with the Los Ranchos Formation spilites at temperatures of 100° to 400°C. Inasmuch as mineral modes in the whole rocks are variable, δD and $\delta^{18}O$ values may vary significantly and the line depicting a wall-rock-dominated system only represents a trendline to a much broader area of possible fluid δD and $\delta^{18}O$ compositions.

Stage I alteration: Temperatures for stage I alteration were estimated to be 200°C for shallow kaolinite and 250°C for deeper quartz-alunite assemblages, as deduced from phase equilibria and sulfur isotope thermometry of coexisting alunite-pyrite (Muntean et al., 1990). Whereas the D/H fractionation between kaolinite and water of Marumo et al. (1980), as determined from a natural system, agrees well with that estimated from the experiments of Liu and Epstein (1984) at 300°C, considerable discrepancy exists between the two calibrations at temperatures of 200°C ($1,000 \cdot \ln \alpha_{\text{kaolinite-water}} = -15$ and $+7$, respectively). Structural analyses of the clay minerals in the natural system of Marumo et al. (1980) suggested fluid-mineral equilibrium. However, only partial D/H exchange occurred between kaolinite and water at 200°C in the experimental system of Liu and Epstein (1984) and fractionation factors were obtained by extrapolation, adding considerable uncertainty to the final value. The δD values of water in equilibrium with kaolinite are thus calculated from the D/H fractionation factors of Marumo et al. (1980). For $\delta^{18}O$ values of water in equilibrium with kaolinite, the experimental $^{18}O/^{16}O$ calibration of Kulla and Anderson (1978) was used. For the D/H ratios of water in equilibrium with stage I alunite, fractionations of Stoffregen et al. (1989) were used at a temperature of 250°C. Alunite $\delta^{18}O$ values given in Table 1 are separated into $\delta^{18}O$ values of total alunite and $\delta^{18}O$ values of the sulfate radical as determined from reprecipitated barite analyses (e.g., Pickthorn and O'Neil, 1985). In Figure 9 only the sulfate $\delta^{18}O$ values of alunite are used, except for one sample where the $\delta^{18}O$ value of coexisting quartz and the δD value of the alunite are used. Detailed work by Rye et al. (1992) has demonstrated that the oxygen isotope composition of the sulfate in alunite is commonly preserved. This is not true for the hydroxyl group, which readily exchanges oxygen with fluids during retrograde cooling and is therefore not useful for fluid $\delta^{18}O$ predictions, unless the alunite is of supergene origin (Rye et al., 1992). For reasons outlined below, a supergene origin for the Pueblo Viejo alunites is considered unlikely. Samples for which the $^{18}O/^{16}O$ ratios of quartz and those of the sulfate radical in coexisting alunite were determined; such compositions are observed to approach equilibrium at temperatures of $\sim 250^\circ\text{C}$ (Matsuhisa et al., 1979; Stoffregen et al., 1989), validating the combined use of quartz $\delta^{18}O$ and alunite δD values.

Stage II alteration: The $\delta^{18}O$ values of water in equilibrium with stage II quartz was determined from the $^{18}O/^{16}O$ calibrations of Matsuhisa et al. (1979), whereas for δD the values obtained from fluid inclusion waters are used. Temperatures are estimated at 220° to 250°C based on barite-sphalerite thermome-

try in stage II veins and temperature estimates of 220°C for the overlying silica cap. Somewhat higher temperatures, however, are indicated by coexisting quartz-calcite from the sample DDH243-197.3 where a fractionation of ~ 1 per mil suggests a temperature of $\sim 400^\circ\text{C}$ (Clayton et al., 1989). For pyrophyllite, considered to have precipitated at temperatures of $\sim 300^\circ\text{C}$, several assumptions were made—the D/H kaolinite-water fractionation of Liu and Epstein (1984), and the $^{18}O/^{16}O$ muscovite-water fractionation of O'Neil and Taylor (1969) are applicable; and the $^{18}O/^{16}O$ muscovite-water fractionation curve may also be extrapolated to temperatures lower than 400°C (lowest limit of calibration temperature used by O'Neil and Taylor, 1969). The similarity in $\delta^{18}O$ values of naturally coexisting muscovite and pyrophyllite (e.g., Sheppard and Taylor, 1974), together with their overall structural and chemical similarity, suggests that the muscovite-water fractionation curve, at least at temperatures between 400° to 650°C, may provide a good estimate for pyrophyllite-water oxygen isotope fractionation.

Calculated δD and $\delta^{18}O$ values of waters in isotopic equilibrium with the silicates are outlined relative to those of volcanic vapors, primary magmatic water, the meteoric water line, and seawater in Figure 9. Primary magmatic water (PMW; $\delta D = -40$ to -80‰ ; $\delta^{18}O = 6$ to 9.5‰) has been defined on the basis of isotopic data for a wide range of igneous rocks (e.g., Taylor, 1974; Boettcher and O'Neil, 1980; Kyser and O'Neil, 1984). In contrast, high-temperature volcanic vapor discharging directly from subduction-related magmas has δD values that are 20 to 40 per mil higher than those of the primary magmatic water (e.g., Matsubaya et al., 1975; Sakai and Matsubaya, 1977; Viglino et al., 1985; Matsuhisa, 1991). Recent research has demonstrated that this apparent enrichment in deuterium can be attributed to isotopic fractionation associated with the degassing of a magma during crystallization (Nabelek et al., 1983; Taylor et al., 1983; Dobson et al., 1989; Taylor, 1991). As acid sulfate alteration is a common product of modern subduction-related volcanic activity (e.g., Henley, 1985), it is likely that such alteration records the passage of vapors and fluids, including H_2O as well as SO_2 , which have been released from a magma.

Interpretation: A point of critical importance to the interpretation of these data is the general absence of significantly large δD and $\delta^{18}O$ value differences between the spilitic rocks of the Los Ranchos Formation and the wall rocks of the acid sulfate system. This is surprising in view of the large chemical changes that were accompanied by the advanced argillic alteration (Muntean et al., 1990). Such large changes in the chemical composition of the rocks require extensive fluid-rock interaction and large fluid/rock ratios.

Muntean et al. (1990) suggested fluid/rock ratios of between 100 to 1,000, based on the mobility of Si, Al, Fe, and Au in hydrothermal solutions. The most likely explanation for the striking similarity between the δD and $\delta^{18}O$ values of the regional spilites and the hydrothermally altered equivalents is that the acid sulfate fluids were similar in isotopic composition to fluids that are in equilibrium with the spilites. Under such conditions, it is practically impossible to quantify the fluid/rock ratios using stable isotope data. The alternative explanation that the advanced argillic alteration formed under conditions of small fluid/rock ratios contradicts concepts of hydrothermal alteration and is not consistent with the large changes in bulk-rock chemistry for the Pueblo Viejo system. It is also possible that the regional greenschist facies alteration and the advanced argillic alteration are genetically linked to a common fluid, although this interpretation is not supported by the overall geologic relations (Kesler et al., 1991).

At temperatures of 250° to 400°C, the good overlap between δD and $\delta^{18}O$ values of fluids in equilibrium with the wall rocks (average given by the "Wallrock Dominated System" in Fig. 9) and the box approximating isotopic composition of volcanic vapors underlines the importance of magmatic H_2O in the Pueblo Viejo acid sulfate system. This conclusion appears to be in general agreement with predictions of hydrogen and oxygen isotope compositions of the fluid, based on the advanced argillic alteration minerals.

Both stage I alunite and kaolinite have δD and $\delta^{18}O$ values consistent with precipitation from fluids dominated by volcanic discharges, although their tendency toward somewhat lower $\delta^{18}O$ values might imply a dilution of such fluids by ~25 percent meteoric water (Fig. 9). Likely δD values for meteoric water range from about -30 to -3 per mil based on the probable proximity to seawater as dictated by the general geology and fossil record of the Los Ranchos Formation rocks (Kesler et al., 1991), paleolatitude data for the Greater Antilles in the Central Hispanola (W. D. MacDonald, pers. commun., 1988), and stable isotope analyses of supergene clays from Puerto Rican Tertiary rocks (Sheppard et al., 1969). Meteoric water A in Figure 9 thus represents a best minimum estimate.

For stage II quartz the bulk of the data is consistent with precipitation from fluids similar to those for stage I alunite and kaolinite, although the subtle enrichment of stage II vein quartz in ^{18}O relative to stage I quartz may reflect less dilution of magmatic discharge fluids by local meteoric water. In contrast, the low $\delta^{18}O$ values of the bulk quartz relative to stage I and II quartz reflect significantly higher proportions of meteoric water in the shallow parts of the

system. The reason for the low δD value of inclusion water extracted from sample DDH235-53 is unclear. The small increase in $\delta^{18}O$ values of stage II pyrophyllite relative to stage I kaolinite at similar δD values is best explained by a second influx of magmatic fluids which have been less diluted by local meteoric water. This is clearly demonstrated by fluids calculated to be in equilibrium with stage II pyrophyllite (Fig. 9). In agreement with the observations by Marumo et al. (1980), little or no variations are expected in the δD values of the hydrous minerals at the temperature interval estimated between stage I and II alteration.

Carbonates

The decrease in $\delta^{18}O$ values of the calcites, paralleled by an increase in the carbonate content from the regional samples toward samples adjacent to the zone of advanced argillic alteration (Fig. 7B), indicates a genetic link between the advanced argillic alteration and the precipitation of the carbonates. Such a genetic link could have involved a common parental fluid for both the advanced argillic alteration and calcite precipitation or, alternatively, reflect a temperature gradient produced by the heat source responsible for the advanced argillic alteration with little or no commonality in fluid composition.

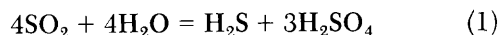
The best explanation for the combined strontium, carbon, and oxygen isotope compositions of the calcites is precipitation from circulating seawater which is conductively heated by the acid sulfate system. Regional group B carbonates with a $\delta^{18}O$ value of ~24 per mil are thus precipitated from seawater heated to ~80°C, whereas the carbonates adjacent to the diatreme (~12‰) precipitated at temperatures of ~170° to 200°C. Increasing carbonate content from regional amounts of ~0.1 wt percent carbonate to ~10 wt percent adjacent to the zone of advanced argillic alteration would reflect the retrograde solubility of calcite (Fein and Walther, 1987). In addition, such increased precipitation of calcites with increasing fluid temperature may effectively isolate the acid sulfate system from adjacent circulating seawater.

As an alternative explanation it can be considered that advanced argillic alteration and carbonate precipitation are related to a common parental fluid with carbonates precipitating as a result of an increase in fluid pH caused by continued reaction with surrounding wall rocks. If this is the case, the $\delta^{18}O$ values of calcites could be explained by precipitation from an isotopically homogeneous fluid of $\delta^{18}O = \sim 6$ per mil at temperatures of between 300° (group A) and 100°C (group B), respectively (O'Neil et al., 1969). The essentially constant $\delta^{13}C$ values of the group B calcites with decreasing temperature could

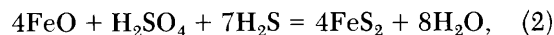
then reflect carbon isotope fractionation controlled by a solution in which the bicarbonate ion (HCO_3^-) is the dominant carbon species (e.g., Matsuhisa et al., 1980). However, such a model fails to explain the strontium isotope composition of calcites. The hint at lower $\delta^{13}\text{C}$ values for group A calcites relative to the regional group B calcites could reflect a minor addition of magmatic (-7 to -5%) or organic carbon (-25%).

Discussion and Conclusions

Geologic relations indicate that the Pueblo Viejo acid sulfate Au-Ag deposit was closely associated with an early Cretaceous maar-diatreme complex of probable explosive volcanic origin (Kesler et al., 1981, 1991; Muntean et al., 1990). The H, O, and S isotope compositions of advanced argillic alteration and ore minerals in the Pueblo Viejo system complement such interpretations as they are consistent with precipitation from fluids (vapors or liquids) discharged from subduction-related shallow magma bodies. Based on chemical analyses of volcanic vapors (e.g., Giggenbach, 1975; Rose et al., 1986; Quisefit et al., 1989), SO_2 exsolved from the magma is thus suggested as the main agent for acidification and the dominant source of sulfur to the system. Simple calculations for the Pueblo Viejo deposit indicate that about 13×10^6 tons of sulfur are required to produce the estimated 130 million metric tons of sulfide ore grading about 8 wt percent sulfur in the form of FeS_2 (Kesler et al., 1981; Muntean et al., 1990). Typical volcanic discharge rates of SO_2 are estimated at ~ 250 t/day, as measured from active volcanic emissions of White Island, New Zealand, and Momotombo, Nicaragua (Giggenbach, 1975; Rose et al., 1986; and Quisefant et al., 1989, respectively). According to Giggenbach (1987), relatively fast ascent rates permit only a small proportion of the SO_2 released by the magma to be available for reaction with the wall rock traversed by the discharged fluids. Thus, assuming that about 10 percent of the discharged SO_2 is extracted and allowed to react with the wall rocks via a combination of the following reactions:



and



even the 30 Mt of sulfide ore would correspond to only 2.9 kyr of volcanic activity. Complementary amounts of magma required to produce the necessary flux of SO_2 would be about 48 km^3 , assuming typical sulfur contents of the magma at 1,000 ppm and complete exsolution (Gill, 1981). Only 1 percent of the degassed SO_2 taken up by the wall rocks would increase the time of volcanic activity and the required

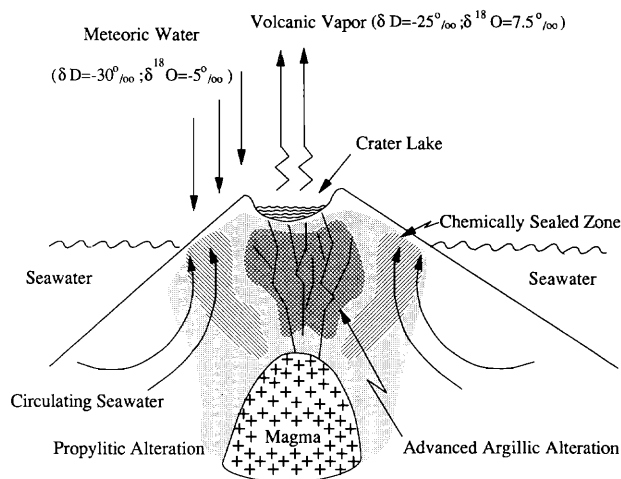


FIG. 10. Schematic cross section depicting a likely geologic setting for the formation of the Pueblo Viejo acid sulfate system.

amount of magma by a factor of 10 to 29 kyr and 480 km^3 ($\sim 1 \text{ km}^3/60 \text{ yr}$), both of which are still well within limits suggested for active hydrothermal systems and volcanic vents (White et al., 1971; Henley and Ellis, 1983). By comparison, Houghton and Nairn (1989) estimated that in order to maintain the long-term convective heat output and SO_2 flux of 400 t/day for White Island, New Zealand, about 1 km^3 is required every 30 to 250 y. Trace metal distribution in marine sediments around White Island, moreover, indicates that volcanic-hydrothermal activity has been maintained at similar levels for at least the last 10 kyr (Houghton and Nairn, 1989). It is also interesting to note that water vapor discharge for White Island has been estimated at 10,000 to 20,000 t/day which, over a period of 2.9 to 29 kyr would correspond to fluid/rock mass ratios of 130 to 1,300. These values are similar to those estimated by Muntean et al. (1990), based on combined silica, alumina, and gold solubility in acidic solutions of this kind.

It is concluded (Fig. 10) that the acid sulfate alteration and related Au-Ag mineralization at Pueblo Viejo formed in response to the release of magmatic vapors from a subjacent magma and the direct condensation and reaction of such vapors with the Fe-rich wall rocks. It appears that dilution of the magmatic fluids by meteoric water was limited to less than 25 percent during stage I mineralization and was largely nonexistent during deep stage II mineralization. The fact that the second stage of mineralization exhibits evidence for less dilution by meteoric water than the first stage, suggests that it was fed by a second pulse of magma. Meteoric fluids may, however, have been dominant during the generation of the shallow silica cap of stage II. It follows that the gold, copper, arsenic, tellurium, and other elements at

Pueblo Viejo (Kesler et al., 1981) must have been derived largely from a magmatic source (Henley, 1985; Muntean et al., 1990). Although the contribution of nonmagmatic fluids is small, such fluids may have been important in causing the precipitation of metal sulfides and acid sulfate alteration minerals during stage I mineralization. Two factors that could have contributed to profoundly limiting the amount of meteoric and/or seawater in the Pueblo Viejo system include: (1) a possible marine or near-marine geologic setting where the circulation of conductively heated seawater resulted in chemical sealing caused by the retrograde solubility of calcite (and anhydrite²), such as has been inferred in other areas of hydrothermal activity (White et al., 1971; Henley and Ellis, 1983; Houghton and Nairn, 1989); and (2) the development of the deposit deep in the hydrothermal system and close to the magma as suggested by the advanced argillic alteration style and stable isotope systematics, together with the presence of large amounts of disseminated mineralization and late-stage enargite, which are all reminiscent of porphyry-type lithocap environments (e.g., Sheppard et al., 1969; Larson, 1987; Rye et al., 1992). It is possible that the regional greenschist facies alteration of Los Ranchos Formation rocks was also related to seawater circulation driven by an impact of magmatic heat.

Similar interpretations may also apply to other acid sulfate systems such as the Rodalquilar deposit in Spain (A. Arribas, pers. commun., 1991) and the Summitville deposit in Colorado (Rye et al., 1992), where detailed stable isotope work indicates fluids similar to those at Pueblo Viejo, although other acid sulfate deposits such as those in the Nansatsu district of Japan appear to have experienced more dilution by meteoric water (Hedenquist et al., 1988).

Acknowledgments

The authors would like to thank W. J. Pickthorn and A. Arribas for assistance with the alunite analysis. Further appreciation is extended to A. Arribas for some fruitful discussion. We also acknowledge the constructive comments by three *Economic Geology* reviewers. The research was supported by National Science Foundation grant EAR-8607021 to SEK and Phillip Meyers. TWV also acknowledges the support of a Foundation for Research Development (South Africa) post-doctoral bursary.

February 6, June 29, 1992

REFERENCES

- Bethke, P. M., 1984, Controls on base and precious metal mineralization in deeper epithermal environments: U. S. Geol. Survey Open File Rept. 84-890, 40 p.
- Boettcher, A. L., and O'Neil, J. R., 1980, Stable isotope, chemical and petrographic studies of high-pressure amphiboles and micas: Evidence for metasomatism in the mantle source regions of alkali basalts and kimberlites: *Am. Jour. Sci.*, v. 280-A, p. 549-621.
- Bowers, T. S., von Damm, K. L., and Edmond, J. M., 1985, Chemical evolution of mid-ocean ridge hot springs: *Geochim. et Cosmochim. Acta*, v. 49, p. 2239-2252.
- Brimhall, G. H., Jr., and Ghiorso, M. S., 1983, Origin and ore-forming consequences of the advanced argillic alteration process in hypogene environments by magmatic gas contamination of meteoric fluids: *ECON. GEOL.*, v. 78, p. 73-90.
- Clayton, R. N., and Mayeda, T. K., 1963, The use of bromine pentafluorine in the extraction of oxygen from oxides and silicates for isotopic analysis: *Geochim. et Cosmochim. Acta*, v. 27, p. 43-52.
- Clayton, R. N., Goldsmith, J. R., and Mayeda, T., 1989, Oxygen isotope fractionation in quartz, albite, anorthite and calcite: *Geochim. et Cosmochim. Acta*, v. 53, p. 725-733.
- Dobson, P. F., Epstein, S., and Stolper, E. M., 1989, Hydrogen isotope fractionation between coexisting vapor and silicate glasses and melts at low pressure: *Geochim. et Cosmochim. Acta*, v. 53, p. 2723-2730.
- Fein, J. B., and Walther, J. V., 1987, Calcite solubility in supercritical CO₂-H₂O fluids: *Geochim. et Cosmochim. Acta*, v. 51, p. 1665-1673.
- Giggenbach, W. F., 1975, Variations in the carbon, sulfur, and chlorine contents of volcanic gas discharges from White Island, New Zealand: *Bull. Volcanology*, v. 39, p. 15-27.
- 1987, Redox processes governing the chemistry of fumarolic gas discharges from White Island, New Zealand: *Appl. Geochemistry*, v. 2, p. 143-161.
- 1992, Isotopic shifts in waters from geothermal and volcanic systems along convergent plate boundaries and the origin of "andesitic" water: *Earth Planet. Sci. Letters*.
- Gill, J. B., 1981, *Orogenic andesites and plate tectonics*: Berlin, Springer Verlag, 390 p.
- Graham, C. M., Sheppard, S. M. F., and Heaton, T. H. E., 1980, Experimental hydrogen isotope studies—I. Systematics of hydrogen isotope fractionation in the systems epidote-H₂O, zoisite-H₂O and Al(OH)-H₂O: *Geochim. et Cosmochim. Acta*, v. 44, p. 353-364.
- Hayba, D. O., Bethke, P. M., Heald, P. W., and Foley, N. K., 1985, Geologic, mineralogic, and geochemical characteristics of volcanic-hosted epithermal precious-metal deposits: *Rev. Econ. Geology*, v. 2, p. 129-167.
- Heald, P., Foley, N. K., and Hayba, D. O., 1987, Comparative anatomy of volcanic-hosted epithermal deposits: Acid-sulfate and adularia-sericite types: *ECON. GEOL.*, v. 82, p. 1-26.
- Hedenquist, J. W., and Aoki, M., 1991, Meteoric interaction with magmatic discharges in Japan and the significance for mineralization: *Geology*, v. 19, p. 1041-1044.
- Hedenquist, J. W., Matsuhisa, Y., Izawa, E., Marumo, K., Aoki, M., and Sasaki, A., 1988, Epithermal gold mineralization of acid-leached rocks in the Nansatsu district of southern Kyushu, Japan: *Geol. Soc. Australia Abstracts*, no. 22, p. 183-190.
- Hemley, J. J., Montoya, J. W., Marinenko, J. W., and Luce, R. W., 1980, Equilibria in the system Al₂O₃-SiO₂-H₂O and some general implications for alteration/mineralization processes: *ECON. GEOL.*, v. 75, p. 210-228.
- Henley, R. W., 1985, The geothermal framework for epithermal deposits: *Rev. Econ. Geology*, v. 2, p. 1-24.
- Henley, R. W., and Ellis, A. J., 1983, Geothermal systems ancient and modern: A geochemical review: *Earth-Sci. Rev.*, v. 19, p. 1-50.
- Henley, R. W., and McNabb, A., 1978, Magmatic vapor plumes and ground-water interaction in porphyry copper emplacement: *ECON. GEOL.*, v. 73, p. 1-20.
- Holser, W. T., and Kaplan, I. R., 1966, Isotope geochemistry of sedimentary sulfates: *Chem. Geology*, v. 1, p. 93-135.
- Houghton, B. F., and Nairn, I. A., 1989, The strombolian and

- phreatomagmatic eruptions of White Island volcano, 1976–1982: New Zealand Geol. Survey Bull. 32, p. 127–136.
- Kesler, S. E., Russell, N., Seaward, M., Rivera, J., McCurdy, K., Cumming, G. L., and Sutter, J. F., 1981, Geology and geochemistry of sulfide mineralization underlying the Pueblo Viejo gold-silver oxide deposit, Dominican Republic: *ECON. GEOL.*, v. 76, p. 1096–1117.
- Kesler, S. E., Russell, N., Polanco, J., McCurdy, K., and Cumming, G. L., 1991, Geologic and tectonic development of the North American-Caribbean plate boundary in Hispaniola: *Geol. Soc. America Spec. Paper* 262, p. 187–202.
- Kettler, R. M., 1989, Interactions between organic matter and hydrothermal systems: Unpub. Ph.D. thesis, Univ. Michigan, 272 p.
- Kettler, R. M., Rye, R. O., Kesler, S. E., Meyers, P. A., Polanco, J., and Russell, N., 1992, Gold deposition by sulfidation of ferrous Fe in the lacustrine sediments of the Pueblo Viejo district: The effect of Fe-C-S diagenesis on later hydrothermal mineralization in a maar-diatreme complex: *Chem. Geology*, v. 99, p. 29–50.
- Kishima, N., and Sakai, H., 1980, Oxygen-18 and deuterium determination on a single water sample of a few milligrams: *Anal. Chemistry*, v. 52, p. 356–358.
- Knight, J. E., 1977, A thermochemical study of alunite, enargite, luzonite, and tennantite deposits: *ECON. GEOL.*, v. 72, p. 1321–1336.
- Kulla, J. B., and Anderson, T. F., 1978, Experimental oxygen isotope fractionation between kaolinite and water: *U. S. Geol. Survey Open-File Rept.* 78–701, p. 234–236.
- Kyser, T. K., and O'Neil, J. R., 1984, Hydrogen isotope systematics of submarine basalts: *Geochim. et Cosmochim. Acta*, v. 48, p. 2123–2133.
- Kyser, T. K., O'Neil, J. R., and Carmichael, I. S. E., 1982, Genetic relations among basic lavas and ultramafic nodules: Evidence from oxygen isotope compositions: *Contr. Mineralogy Petrology*, v. 81, p. 88–102.
- Larson, P. B., 1987, Stable isotope and fluid inclusion investigation of epithermal vein and porphyry molybdenum mineralization in the Rico mining district, Colorado: *ECON. GEOL.*, v. 82, p. 2141–2157.
- Liu, K., and Epstein, S., 1984, The hydrogen isotope fractionation between kaolinite and water: *Isotope Geosci.*, v. 2, p. 335–350.
- Manson, V., 1967, Geochemistry of basaltic rocks: Major elements, in Hess, H. H., and Poldervaart, A., eds., *Basalts*: New York, John Wiley Sons, v. 1, p. 215–270.
- Marumo, K., Nagasawa, K., and Kuroda, Y., 1980, Mineralogy and hydrogen isotope geochemistry of clay minerals in the Ohnuma geothermal area, northeastern Japan: *Earth Planet. Sci. Letters*, v. 47, p. 255–262.
- Matsubaya, O., Ueda, A., Kusakabe, M., Matsuhisa, Y., Sakai, H., and Sasaki, A., 1975, An isotopic study of the volcanoes and the hot springs in Satsuma Iwojima and some areas in Kyushu: *Japan Geol. Survey Bull.*, v. 26, p. 375–392.
- Matsuhisa, Y., 1991, Origin of magmatic waters in subduction zones: Stable isotope constraints: *Japan Geol. Survey Rept.* 279, p. 104–109.
- Matsuhisa, Y., Goldsmith, J. R., and Clayton, R. N., 1979, Oxygen isotopic fractionation in the system quartz-albite-anorthite and water: *Geochim. et Cosmochim. Acta*, v. 43, p. 1131–1140.
- Matsuhisa, Y., Morishita, Y., and Sato, T., 1985, Oxygen and carbon isotope variations in gold-bearing hydrothermal veins in the Kushikino mining area, southern Kyushu, Japan: *ECON. GEOL.*, v. 80, p. 283–293.
- Matthews, A., Goldsmith, J. R., and Clayton, R. N., 1983, Oxygen isotope fractionations between zoisite and water: *Geochim. et Cosmochim. Acta*, v. 47, p. 645–654.
- McCrea, J. M., 1950, On the isotopic chemistry of carbonates and a paleotemperature scale: *Jour. Chem. Physics*, v. 18, p. 849–857.
- Muehlenbachs, K., and Clayton, R. N., 1972, Oxygen isotope studies of fresh and weathered submarine basalts: *Canadian Jour. Earth Sci.*, v. 9, p. 172–184.
- Muntean, J. L., Kesler, S. E., Russell, N., and Polanco, J., 1990, Evolution of the Monte Negro acid sulfate Au-Ag deposit, Pueblo Viejo, Dominican Republic: Important factors in grade development: *ECON. GEOL.*, v. 85, p. 1738–1758.
- Nabelek, P. I., O'Neil, J. R., and Papike, J. J., 1983, Vapor phase exsolution as a controlling factor in hydrogen isotope variations in granitic rocks: The Notch Peak granite stock, Utah: *Earth Planet. Sci. Letters*, v. 66, p. 137–150.
- Ohmoto, H., 1972, Systematics of sulfur and carbon isotopes in hydrothermal ore deposits: *ECON. GEOL.*, v. 67, p. 661–579.
- Ohmoto, H., and Lasaga, A. C., 1982, Kinetics of reactions between aqueous sulfates and sulfides in hydrothermal systems: *Geochim. et Cosmochim. Acta*, v. 46, p. 1727–1745.
- Ohmoto, H., and Rye, R. O., 1979, Isotopes of sulfur and carbon, in Barnes, H. L., ed., *Geochemistry of hydrothermal ore deposits*, 2nd ed: New York, Wiley Intersci., p. 509–567.
- O'Neil, J. R., and Taylor, H. P., 1969, Oxygen isotope equilibrium between muscovite and water. *Jour. Geophys. Research*, v. 74, p. 6012–6022.
- O'Neil, J. R., Clayton, R. N., and Mayeda, T. K., 1969, Oxygen isotope fractionation in divalent metal carbonates: *Jour. Chem. Physics*, v. 51, p. 5547–5558.
- Pickthorn, W. J., and O'Neil, J. R., 1985, $^{18}\text{O}/^{16}\text{O}$ relations in alunite mineral: Potential single mineral thermometer [abs.]: *Geol. Soc. America Abstracts with Programs*, v. 17, p. 686.
- Quisefit, J. P., Toutain, J. P., Bergametti, G., Javoy, M., Cheynet, B., and Person, A., 1989, Evolution versus cooling of gaseous volcanic emissions from Momotombo volcano, Nicaragua: Thermochemical model and observations: *Geochim. et Cosmochim. Acta*, v. 53, p. 2591–2608.
- Rose, W. I., Chuan, R. L., Giggenbach, W. F., Kyle, P. R., and Symonds, R. B., 1986, Rates of sulfur dioxide and particle emission from White Island volcano, New Zealand, and an estimate of the total flux of major gaseous species: *Bull. Volcanology*, v. 48, p. 181–188.
- Russell, N., and Kesler, S. E., 1991, Geology of the maar-diatreme complex hosting precious metal mineralization at Pueblo Viejo, Dominican Republic: *Geol. Soc. America Spec. Paper* 262, p. 203–216.
- Russell, N., Seaward, M., Rivera, J., McCurdy, K., Kesler, S. E., and Cloke, P. L., 1981, Geology and geochemistry of the Pueblo Viejo gold-silver deposit, Dominican Republic: *Inst. Mining Metallurgy Trans.*, v. 90, sec. B, p. 153–162.
- Russell, N., Polanco, J., and Kesler, S. E., 1986, Geology of the Monte Negro gold-silver deposit, Pueblo Viejo district, Dominican Republic, in MacDonald, A. J., ed., *Gold '86: Willowdale, Ontario, Konsult Internat.*, p. 497–503.
- Rye, R. O., Bethke, P. M., and Wasserman, M. D., 1992, The stable isotope geochemistry of acid-sulfate alteration: *ECON. GEOL.*, v. 87, p. 225–262.
- Sakai, H., and Matsubaya, O., 1977, Stable isotopic studies of Japanese geothermal systems: *Geothermics*, v. 2, p. 71–80.
- Seyfried, W. E., Jr., and Mottl, M. J., 1982, Hydrothermal alteration of basalt by seawater under seawater dominated conditions: *Geochim. et Cosmochim. Acta*, v. 3, p. 985–1002.
- Sharma, T., and Clayton, R. N., 1965, Measurement of $\text{O}^{18}/\text{O}^{16}$ ratios of total oxygen of carbonates: *Geochim. et Cosmochim. Acta*, v. 29, p. 1347–1353.
- Sheppard, S. M. F., 1986, Characterization and isotopic variation in natural waters: *Rev. Mineralogy*, v. 16, p. 165–184.
- Sheppard, S. M. F., and Taylor, H. P., 1974, Hydrogen and oxygen isotope evidence for the origins of water in the Boulder batholith and the Butte ore deposits, Montana: *ECON. GEOL.*, v. 69, p. 926–946.
- Sheppard, S. M. F., Nielsen, R. L., and Taylor, H. P., 1969, Oxygen

- and hydrogen isotope ratios of clay minerals from porphyry copper deposits: *ECON. GEOL.*, v. 64, p. 755-777.
- Spooner, E. T. C., Beckinsale, R. D., Fyfe, W. S., and Smewing, J. D., 1974, ^{18}O enriched ophiolitic metabasic rocks from E. Liguria (Italy), Pindos (Greece), and Troodos (Cyprus): *Contr. Mineralogy Petrology*, v. 47, p. 41-62.
- Stakes, D. S., and O'Neil, J. R., 1982, Mineralogy and stable isotope geochemistry of hydrothermally altered oceanic rocks: *Earth Planet. Sci. Letters*, v. 57, p. 285-304.
- Stoffregen, R. E., 1989, Genesis of acid-sulfate alteration and Au-Cu-Ag mineralization at Summitville, Colorado: Unpub. Ph.D. dissert., Univ. California, Berkeley, 205 p.
- Stoffregen, R. E., Rye, R. O., and Wasserman, D. M., 1989, Experimental determination of ^{18}O (sulfate-site) and D fractionations between alunite and water at 250° to 450°C [abs.]: *Geol. Soc. America Abstracts with Programs*, v. 22, p. A162.
- Suzuoki, T., and Epstein, S., 1976, Hydrogen isotope fractionation between OH-bearing minerals and water. *Geochim. et Cosmochim. Acta*, v. 40, p. 1229-1240.
- Symonds, R. B., Rose, W. I., Reed, M. H., Lichte, F. E., and Finnegan, D. L., 1987, Volatilization, transport and sublimation of metallic and non-metallic elements in high temperature gases at Merapi volcano, Indonesia: *Geochim. et Cosmochim. Acta*, v. 51, p. 2083-2101.
- Taylor, B. E., 1991, Degassing of H_2O from rhyolite magma during eruption and shallow intrusion, and the isotopic composition of magmatic water in hydrothermal systems: *Japan Geol. Survey Rept.* 279, p. 190-194.
- Taylor, B. E., Eichelberger, J. C., and Westrich, H. R., 1983, Hydrogen isotopic evidence of rhyolitic magma degassing during shallow intrusion and eruption: *Nature*, v. 306, p. 541-545.
- Taylor, H. P., 1974, The application of oxygen and hydrogen isotope studies to problems of hydrothermal alteration and ore deposition: *ECON. GEOL.*, v. 69, p. 843-883.
- Veizer, J., and Hoefs, J., 1976, The nature of $\text{O}^{18}/\text{O}^{16}$ and $\text{C}^{13}/\text{C}^{12}$ secular trends in sedimentary carbonate rocks: *Geochim. et Cosmochim. Acta*, v. 40, p. 1387-1395.
- Vennemann, T. W., and O'Neil, J. R., 1992, A simple and inexpensive method of hydrogen isotope and water analyses of minerals and rocks based on zinc reagent: *Chem. Geology*, v. 102, (in press).
- Vigilino, J. A., Harmon, R. S., Borthwick, J., Nehring, N. L., Motyka, R. J., White, L. D., and Johnston, D. A., 1985, Stable isotope evidence for a magmatic component in fumarole condensates from Augustine volcano, Cook Inlet, Alaska, USA: *Chem. Geology*, v. 49, p. 141-157.
- Wenner, D. B., and Taylor, H. P., 1971, Temperature of serpentinization of ultramafic rocks based on $^{18}\text{O}/^{16}\text{O}$ fractionation between coexisting serpentine and magnetite: *Contr. Mineralogy Petrology*, v. 32, p. 165-184.
- White, D. E., Muffler, J. P., and Truesdell, A. H., 1971, Vapor-dominated hydrothermal systems compared with hot-water systems: *ECON. GEOL.*, v. 66, p. 75-97.