



Preliminary mineralogic and stable isotope studies of altered summit and flank rocks and Osceola Mudflow deposits on Mount Rainier, Washington

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Abstract

About 5600 years ago part of Mount Rainier's edifice collapsed with the resultant Osceola Mudflow traveling more than 120 km and covering an area of at least 505 km². Mineralogic and stable isotope studies were conducted on altered rocks from outcrops near the summit and east flank of the volcano and samples of clasts and matrix from the Osceola Mudflow. Results of these analyses are used to constrain processes responsible for pre-collapse alteration and provide insight into the role of alteration in edifice instability prior to the Osceola collapse event.

Jarosite, pyrite, alunite, and kaolinite occur in hydrothermally altered rock exposed in summit scarps formed by edifice collapse events and in altered rock within the east-west structural zone (EWSZ) of the volcano's east flank. Deposits of the Osceola Mudflow contain clasts of variably altered and unaltered andesite within a clay-rich matrix. Minerals detected in samples from the edifice are also present in many of the clasts. The matrix includes abundant smectite, kaolinite and variably abundant jarosite.

Hydrothermal fluid compositions calculated from hydrogen and oxygen isotope data of alunite, and smectite on Mount Rainier reflect mixing of magmatic and meteoric waters. The range in the δD values of modern meteoric water on the volcano (-85 to -155‰) reflect the influence of elevation on the δD of precipitation. The $\delta^{34}S$ and $\delta^{18}O_{SO_4}$ values of alunite, gypsum and jarosite are distinct but together range from 1.7 to 17.6‰ and -12.3 to 15.0‰, respectively; both parameters increase from jarosite to gypsum to alunite. The variations in sulfur isotope composition are attributed to the varying contributions of disproportionation of magmatic SO_2 , the supergene oxidation of hydrothermal pyrite and possible oxidation of H_2S to the parent aqueous sulfate. The $\delta^{18}O_{SO_4}$ values of jarosite are the lowest recorded for the mineral, consistent with a supergene origin.

The mineralogy and isotope composition of alteration minerals define two and possibly three environments of alteration. At deeper levels magmatic vapor, H_2S , SO_2 and other gases from venting magmas migrated upward and condensed into the meteoric water. Disproportionation of SO_2 into aqueous sulfate and H_2S resulted in acid-sulfate (alunite + kaolinite + pyrite) and related argillic and propylitic alteration envelopes in a *magmatic hydrothermal* environment. At shallow levels H_2S reacted with andesite to form pyrite that is associated with smectite along fractures on both the flanks and upper edifice. It is not clear to what extent H_2S was oxidized by atmospheric O_2 to form aqueous sulfate in a *steam-heated* environment. Near the ground surface, pyrite is oxidized by atmospheric oxygen resulting in soluble iron- and aluminum-hydroxysulfates. These supergene hydroxysulfates, which may also form around fumaroles from the oxidation of H_2S , are subject to continuous solution and redeposition.

Introduction

In 1985, Nevado del Ruiz volcano (Colombia) had a very small eruption near its summit. This eruption triggered a mudflow that resulted in more than 22,000 deaths (Lopez and Williams, 1993; Voight, 1990; 1996). More recently, a relatively small portion of Casita volcano (Nicaragua) suddenly collapsed along an area of hydrothermally altered rock, leading to the largest single cause of death during 1998's Hurricane Mitch (van Wyk de Vries and others, 2000; Sheridan and others, 1999). The realization that catastrophic edifice collapse can occur without an attendant eruption coupled with the knowledge that edifice collapse at some volcanoes is directly related to hydrothermal alteration emphasizes the need for increased understanding of the geologic

and geochemical causes of alteration at volcanoes. This realization has become especially evident at Mount Rainier, where frequent and far-reaching debris flows and debris avalanches constitute the greatest volcanic hazard in the Cascade Range (Figure 1, Crandell and Mullineaux, 1967; Hoblitt and others, 1998). Because of these hazards, Mount Rainier was designated a Decade Volcano and a science plan for its study was issued by the U.S. National Research Council (1994) in conjunction with the United Nations International Decade for Natural Disaster Reduction (UN Resolution 42/169/1987).

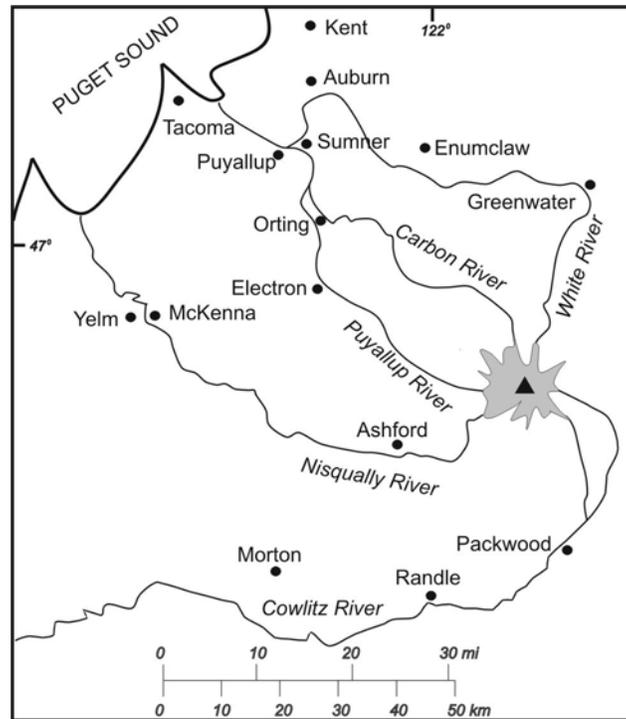


Figure 1. Index location map of Mount Rainier (gray) and surrounding communities.

For more than 100 years, geologists have noted that Mount Rainier must have been much higher in its geologically recent past (Russell, 1898). Massive collapse of this former summit material transformed into the Osceola Mudflow and Paradise Lahar about 5600 years before present (Crandell and Waldron, 1956; Crandell, 1963; Crandell, 1971). The Osceola is one of the largest ($> 3.8 \text{ km}^3$) and farthest traveled ($> 120 \text{ km}$) mudflows in the world (Crandell and Waldron, 1956; Crandell and Mullineaux, 1967; Crandell, 1973; Dragovich and others, 1994; Vallance and Scott, 1997). The mudflow filled valleys of the White River system north and northeast of the volcano to depths of more than 100 m before spreading into the Puget Lowland where it covered an area of at least 505 km^2 , including sites now occupied by towns such as Orting, Sumner, Puyallup, Fife, Auburn, Kent, Enumclaw, and Buckley (Crandell, 1963; Crandell, 1971; Dragovich and others, 1994). The Osceola is one of at least six lahars that have been documented to have traveled from Mount Rainier into the Puget Lowlands in the past 6800 years (Scott and others, 1995). In this paper the mineralogy and stable isotope geochemistry of alteration minerals in the matrix and small clasts of some of the Osceola Mudflow

deposits are compared with alteration minerals remaining on the flanks and summit of the present volcanic edifice. These observations are used to make preliminary reconstruction of the hydrothermal environments and conditions that produced the alteration of the edifice prior to collapse.

Geologic framework

Detailed geologic mapping and radiometric age dating indicate that the present Quaternary edifice of Mount Rainier began to form on Tertiary bedrock at about 500 ka (Sisson and Lanphere, 1999). Edifice construction occurred during two extended periods of magmatic activity, each lasting about 100 kyr, between about 500 and 420 ka and 280 and 180 ka (Sisson and Lanphere, 1999). Most units were deposited as flows, either massive or brecciated, with occasional interbedded tephra layers and most units were erupted from the same central vent occupied by the present summit cone, which is currently covered by an extensive glacial mantle. Unaltered Mount Rainier lavas are mostly geochemically uniform, plagioclase-phyric, two-pyroxene, magnetite-bearing andesites (Coombs, 1936; Fiske and others, 1963).

Mount Rainier's summit cone represents partial rebuilding of a formerly higher summit that was present prior to collapse and onset of the Osceola Mudflow (Crandell, 1976). The current cone is at least 300 m high, 2 km wide, and consists of two overlapping craters, aligned east-west. Both craters are snow-free along their rims and flanks, contain caves beneath their central ice caps, and are hydrothermally altered. The alteration of these cones has been described in Zimbelman and others (2000). The snow-free zones and snow caves are related to active fumaroles. Some of the fumaroles attain near-boiling-point temperatures and show large spikes of CO₂ and traces of H₂S but no SO₂ (Zimbelman and others, 2000). The large amounts of CO₂ indicate the gas chemistry of the fumaroles is influenced by mild degassing of the underlying magma (Zimbelman and others, 2000).

Below the summit cone, scarps formed by the Osceola collapse are exposed in only a few places, including Liberty Cap, Russell Cliffs, and Gibraltar Rock. In other areas, glaciers, post-collapse lava flows, or the post-collapse summit cone cover the Osceola scarp. Accessible summit scarps, such as Sunset Amphitheater, that are related to later collapse events, contain alteration minerals that can be considered to be representative of the type of alteration present on the summit prior to the Osceola collapse (e.g., Crandell, 1971; Scott and others, 1995).

The east flank of the volcano was partially denuded during the Osceola collapse event and has subsequently been partially covered by glaciers and post-Osceola volcanic flows and deposits. Where the Osceola collapse surface is exposed, two types of alteration are recognized: (1) widespread oxidation, silicification and argillization of thick block-and-ash flow units, and (2) more localized, acid-sulfate, advanced argillic, and argillic alteration of the block-and-ash flow and other units adjacent to dikes and fractures. The former has not been studied but is believed to be related to interactions of cooling volcanic units with ambient ground water and volcanic gases shortly after emplacement. The latter alteration is a result of episodic processes that began with the introduction of H₂S-rich volcanic gases along fractures during magma-degassing episodes.

Methods

Sampling

The locations of samples from the summit scarps, flanks and Osceola mudflow are shown in Figure 2. Samples representative of alteration near the summit of Mount Rainier were collected at Sunset Amphitheater and Liberty Cap. Alteration on the eastern flanks of the volcano was represented by samples collected at Glacier Basin and Little Tahoma Peak. The Osceola deposits were sampled at four sites described by Crandell (1969; 1971) and Pringle and others (1994). In the area of the Osceola source material, samples 9822, 9823, 9827, and 9828 are from thin veneers (few cm thick) of the mudflow preserved along ridge tops in the Steamboat Prow and Glacier Basin areas. Seven kilometers downstream samples 9806 to 9819 were spaced at approximately 5 m vertical intervals, from bottom to top, through a relatively thick stratigraphic section (> 20 m) deposited in the Inter Fork drainage upstream of the White River Campground. The sampled outcrop is steep and some of samples, particularly those near the base, may represent slough. Distal samples 9801, 9802, and 9803 were collected 25 km downstream from the source in a gravel pit near The Dalles campground along the White River.

Mineralogy

The mineralogy of altered rocks from the edifice and Osceola is summarized in Table 1. Most alteration phases are very fine grained and identification was by X-ray diffraction (XRD) analyses of bulk rock and mineral separates. Clay sized material separated from some samples was used to prepare oriented mounts that were analyzed by XRD as air-dried, saturated with ethylene glycol, and after heating at 550° C for one hour. A scanning electron microscopy (SEM) equipped with an energy dispersive x-ray spectrometer provided information on the chemical composition of some alteration phases.

Stable Isotopes

Sulfur, oxygen, and hydrogen isotope data were obtained by standard techniques using both conventional and continuous flow mass spectrometer systems. Stable isotope data for minerals from altered rocks on a summit scarp (Sunset Amphitheater), an old erosion surface (Steamboat Prow), east flank (Glacier Basin), and the three sites containing the Osceola Mudflow are summarized in Table 2 and Figures 3-5. Alunite and jarosite were largely separated and processed according to techniques described in Wasserman and others (1992). Sulfate in jarosite from the matrix of the Osceola mudflow was also extracted by first removing soluble sulfates with water and then heating the matrix in 2 N Na₂CO₃ overnight. This extraction precipitates the iron as ferric hydroxide and leaves sulfate in solution which was titrated to pH 3.5 and sulfate was precipitated by adding a barium chloride solution. Soluble sulfates were water leached and precipitated as BaSO₄ with barium chloride. The isotopic composition of water in smectite-forming fluids were calculated from δD and $\delta^{18}O$ data on smectite assuming a formation temperature of 100-175°C and the equations of Gilg and Sheppard,

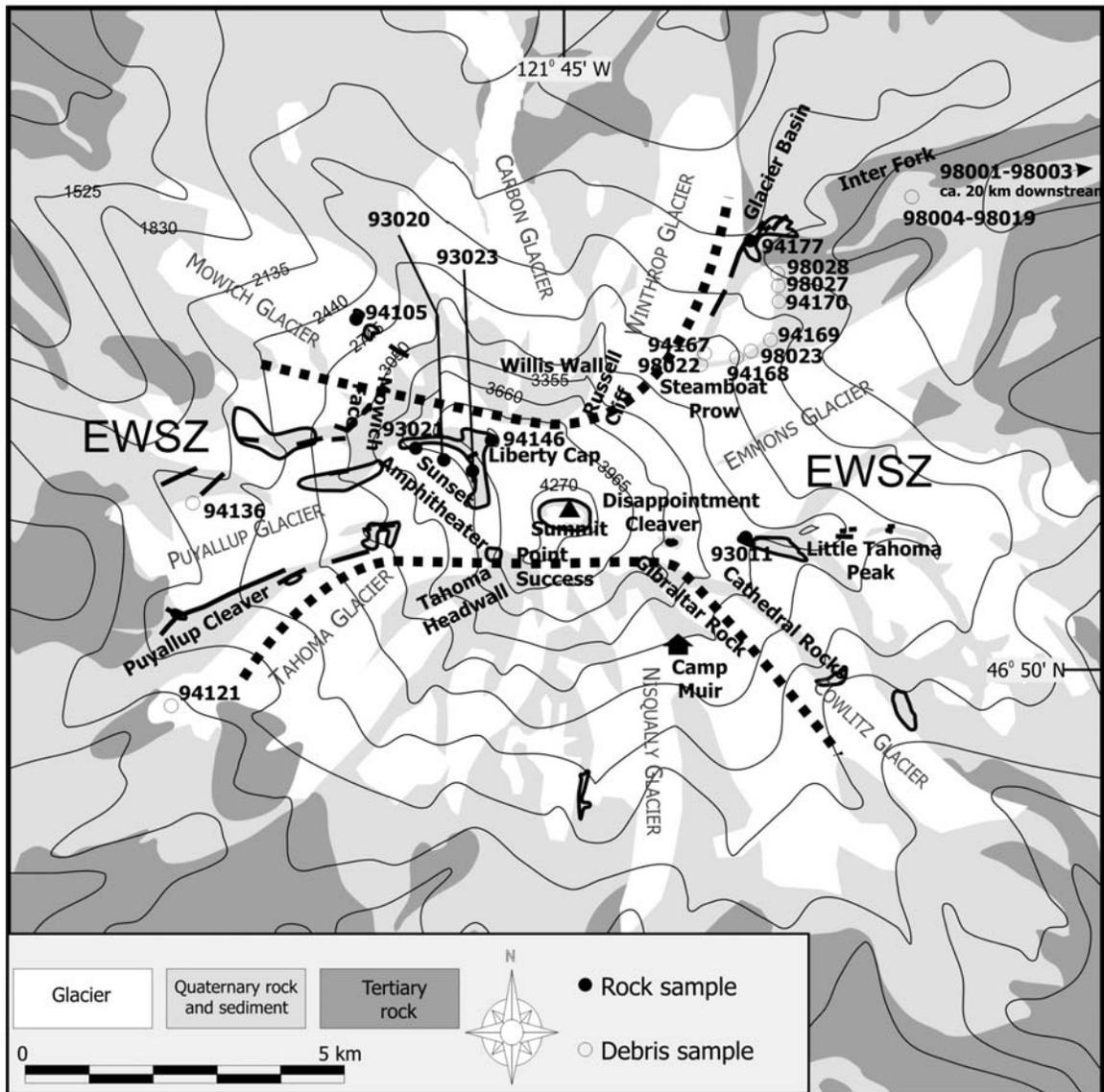


Figure 2. Map of central part of Mount Rainier volcano, including: sample locations (rocks, solid circles; debris deposits, open circles); generalized geology, including Tertiary rocks (dark gray), Quaternary rocks and deposits (light gray), glaciers (white), dikes (heavy black, solid lines), hydrothermally altered rocks (heavy black polygons), and east-west structural zone (heavy black, dashed lines; EWSZ). Distribution of dikes (Sisson and others, 2001).

Table 1. Results of X-ray diffraction analysis of bulk rock samples. Shaded areas indicate phase was detected. (Smec., smectite; Kaol., kaolinite; Anhy., anhydrite)

Location	Sample	Type	Smec.	Kaol.	Silica	Alunite	Jarosite	Gypsum	Anhy.	Other
SUMMIT										
Little Tahoma Peak	93011a	Rock outcrop	■	■	■					
Little Tahoma Peak	93011b	Rock outcrop	■							
Sunset Amphitheater	93020a	Rock outcrop	■					■		
Sunset Amphitheater	93021a	Rock outcrop	■	■				■		
Sunset Amphitheater	93023b	Rock outcrop	■		■	■	■	■		
Liberty Cap	94146c	Rock outcrop	■	■		■		■	■	
Liberty Cap	94146b	Rock outcrop	■	■		■		■		
Liberty Cap	94146c	Rock outcrop	■	■				■		
FLANK										
Mowich Glacier	94105a	Rock outcrop	■	■	■	■				potash alum, quenstedtite
Glacier Basin	94170a	Rock outcrop	■	■	■	■				
OSCEOLA MUDFLOW										
Steamboat Prow	94167a	Debris flow	■	■	■					
Steamboat Prow	94167b	Debris flow		■		■		■		
Steamboat Prow	94168	Debris flow	■			■				
Steamboat Prow	94169c	Debris flow	■	■	■					
Steamboat Prow	98022a	Debris flow	■	■	■					copiapite
Steamboat Prow	98023a	Debris flow	■		■					
Glacier Basin	94170a	Debris flow	■		■					
Glacier Basin	94170b	Debris flow	■	■	■	■				
Glacier Basin	98027a	Debris flow	■	■	■					
Glacier Basin	98028a	Debris flow	■	■	■					copiapite
Inter Fork	9806a	Debris flow	■	■	■					
Inter Fork	9807a	Debris flow	■	■	■		■			
Inter Fork	9808a	Debris flow	■	■	■					
Inter Fork	9809a	Debris flow	■	■	■		■			
Inter Fork	9810a	Debris flow	■	■	■					

Table 2. Summary of stable isotope data on alteration minerals from Mt. Rainier edifice and flank localities and Osceola Mudflow deposits. (soluble – refers to phases extracted by water).

Location	Number	Mineral	$\delta^{34}\text{S}$	$\delta^{18}\text{O}_{\text{SO}_4}$	$\delta^{18}\text{O}$	δD
EDIFICE SUMMIT						
Sunset Amphitheater	21B	Alunite	7.5	9.5		-121
Sunset Amphitheater	20	Gypsum	7.1	4.2		
Sunset Amphitheater	23A	Jarosite	3.1	-9.0		
Sunset Amphitheater	23B	Jarosite	3.3	-4.3		-146
Sunset Amphitheater	24A	Jarosite	1.3			
Sunset Amphitheater	24D	Jarosite	-1.2			
Sunset Amphitheater	24B	Smectite			8.4	-137
Puyallup River	124	Gypsum	10.7	7.3		
Camp Muir	03AH	Smectite			3.7	-131
Summit	182	Smectite			-2.3	-136
Summit	FNK-1	Gypsum	6.9	-1.6		
Mowich Face	114	Smectite			8.5	-111
FLANKS						
Steamboat Prow	169A	Alunite	17.3	15.0		-85
Steamboat Prow	169C	Jarosite	1.5	-12.3		-135
Steamboat Prow	170B	Jarosite	2.2	-10.8		-174
Steamboat Prow	167	Gypsum	7.5			
Steamboat Prow	196	Gypsum	3.6	-4.0		
Steamboat Prow	167B	Smectite			13.9	-121
Little Tahoma Peak	101	Smectite			9.2	
Little Tahoma Peak	11B	Smectite			8.5	-148
Glacier Basin	27B	Smectite			-5.8	-177
Glacier Basin	173	Smectite			7.9	-77
Glacier Basin	174	Smectite			7.7	-73
Glacier Basin	175B	Smectite			7.4	-119
Glacier Basin	MRVB17	Jarosite	4.6			
Glacier Basin	MRVB15	Jarosite	2.7			
Takaloo Rock	130	Smectite			10.7	-114

Table 2. (continued).

Location	Number	Mineral	$\delta^{34}\text{S}$	$\delta^{18}\text{O}_{\text{SO}_4}$	$\delta^{18}\text{O}$	δD
OSCEOLA MUDFLOW						
Steamboat Prow	MR9822	Jarosite	4.0			
Glacier Basin	MR9828	Jarosite	3.3			
Inter Fork	MR9806	Jarosite	6.2*	-5.0		
Inter Fork	MR9806	Soluble	1.7	-3.9		
Inter Fork	MR9807	Jarosite	5.9			
Inter Fork	MR9807	Soluble	0.6			
Inter Fork	MR9808	Jarosite	6.5			
Inter Fork	MR9808	Soluble	1.7			
Inter Fork	MR9808	Pyrite	-0.5			
Inter Fork	MR9809	Jarosite	5.6			
Inter Fork	MR9810	Jarosite	5.2			
Inter Fork	MR9810	Pyrite	0.9			
Inter Fork	MR9816	Jarosite	7.5*	-8.2		
Inter Fork	MR9817	Jarosite	5.0			
Dalles Campground	MR9801	Jarosite	3.8			
Dalles Campground	MR9803	Jarosite	5.1			
Dalles Campground	MR9803	Soluble	3.7	-0.9		

* probably contains alunite

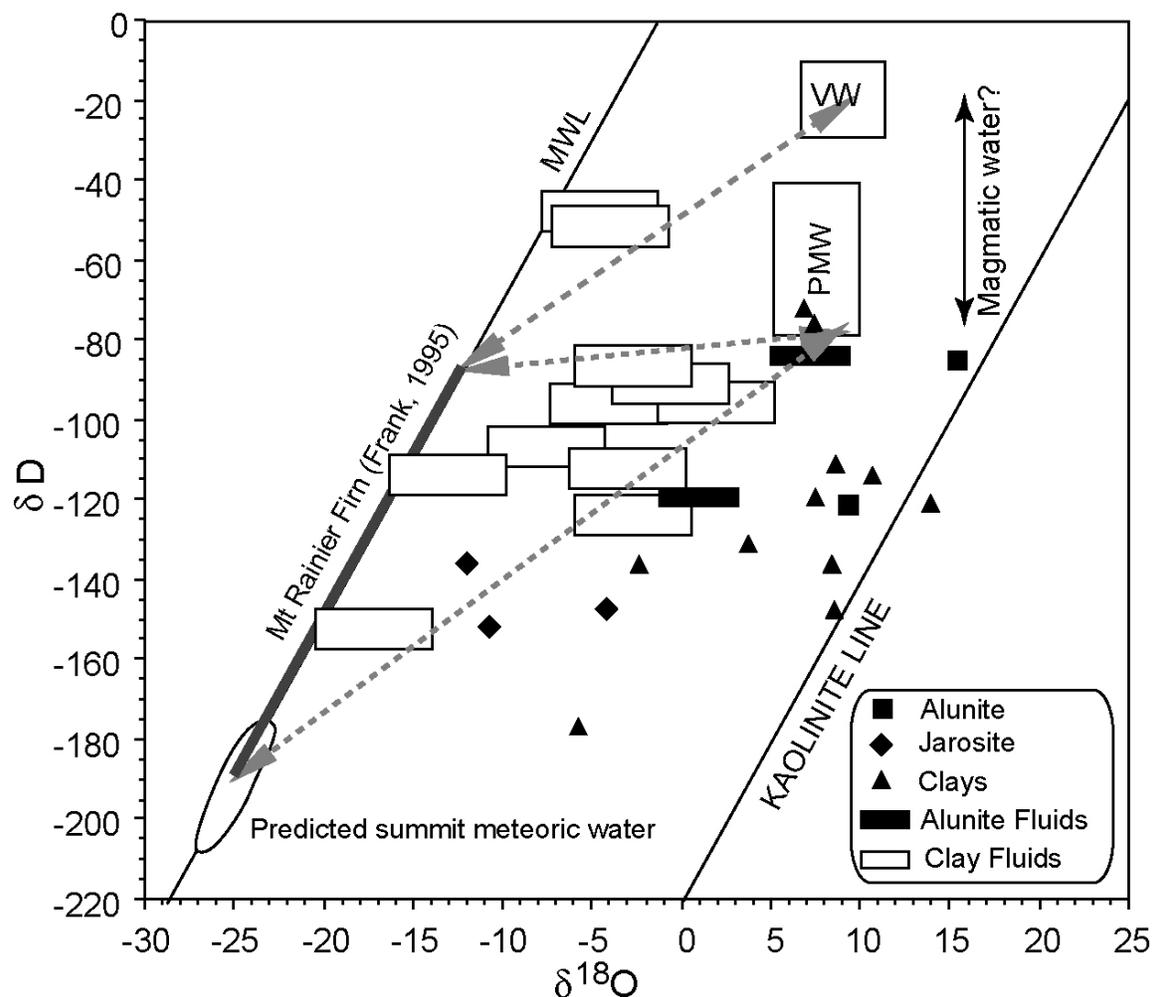


Figure 3. Summary of δD and $\delta^{18}O_{SO_4}$ data for alunite and jarosite and δD and $\delta^{18}O$ data for undifferentiated clays (kaolinite and smectite). Also shown are calculated range of δD and $\delta^{18}O_{H_2O}$ values for clay fluids assuming a temperature of 100-175°C and using equation of Sheppard and Gilg (1996) and for alunite fluids assuming a temperature of 200-300°C and using equation of Stoffregen and others (1994). Low $\delta^{18}O_{SO_4}$ values for jarosite require a supergene origin (Rye and Alpers, 1997). The $\delta^{18}O_{H_2O}$ values of supergene jarosite fluids cannot be calculated because the $\delta^{18}O_{OH}$ values of jarosite could not be determined. Also shown is the range of values for firm on Mount Rainier (Frank, 1995) and possible mixing trends with magmatic water (dashed faded arrows). References are the primary magmatic water (PMW; Taylor, 1979) and volcanic water (VW; Giggenbach, 1997), meteoric water line (Craig, 1961) and kaolinite (Savin and Epstein, 1970). The starting δD_{H_2O} values of magmatic fluids in a degassing volcano can vary considerably due to hydrogen isotope fractionation between melt and fluid and Rayleigh distillation effects during the exsolution of fluids from different batches of magma (Taylor, 1986).

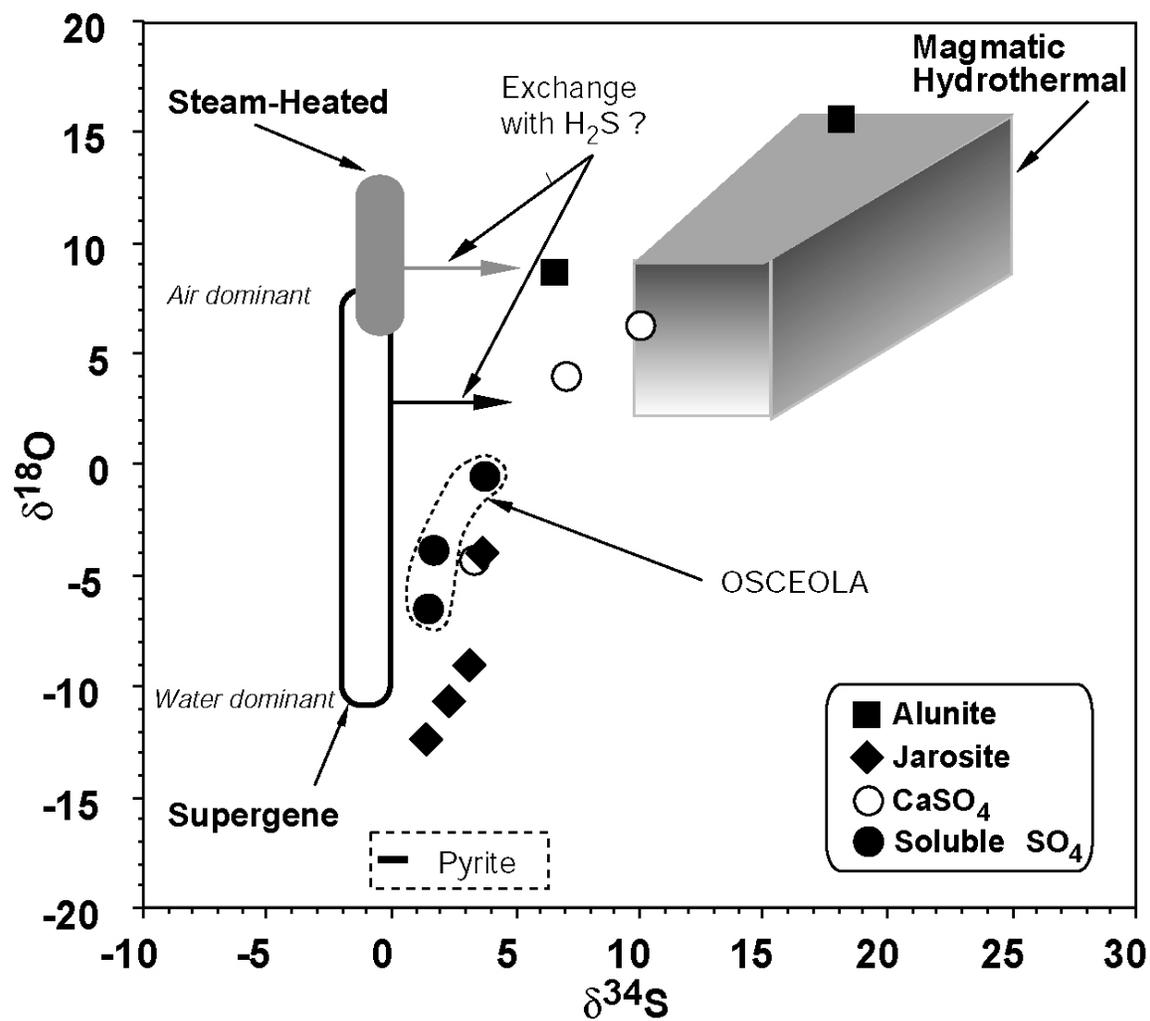


Figure 4. Summary of $\delta^{34}\text{S}$ and $\delta^{18}\text{O}_{\text{SO}_4}$ data of alunite, jarosite and gypsum from Mount Rainier summit scarps and jarosite and soluble Fe-Al hydroxysulfate from Osceola mudflow deposits. Also shown are fields of values expected for *magmatic hydrothermal* alunite for a fluid having a $\delta^{34}\text{S}_{\Sigma\text{S}}$ of 0 ‰ and a $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ of 6‰ and for *steam-heated* or *supergene* alunite or jarosite for a fluid having the $\delta^{18}\text{O}_{\text{SO}_4}$ of its parent aqueous sulfate controlled by the $\delta^{18}\text{O}$ of air or the $\delta^{18}\text{O}$ of meteoric water (See Rye and others, 1992; Rye and Alpers, 1997, for details). The general trend indicates parent aqueous sulfate was derived largely from the supergene oxidation of pyrite and the disproportionation of SO_2 from magmatic sources. Over time and space *magmatic hydrothermal*, *steam-heated* and *supergene* oxidation processes have probably overlapped as shown in Figure 6.

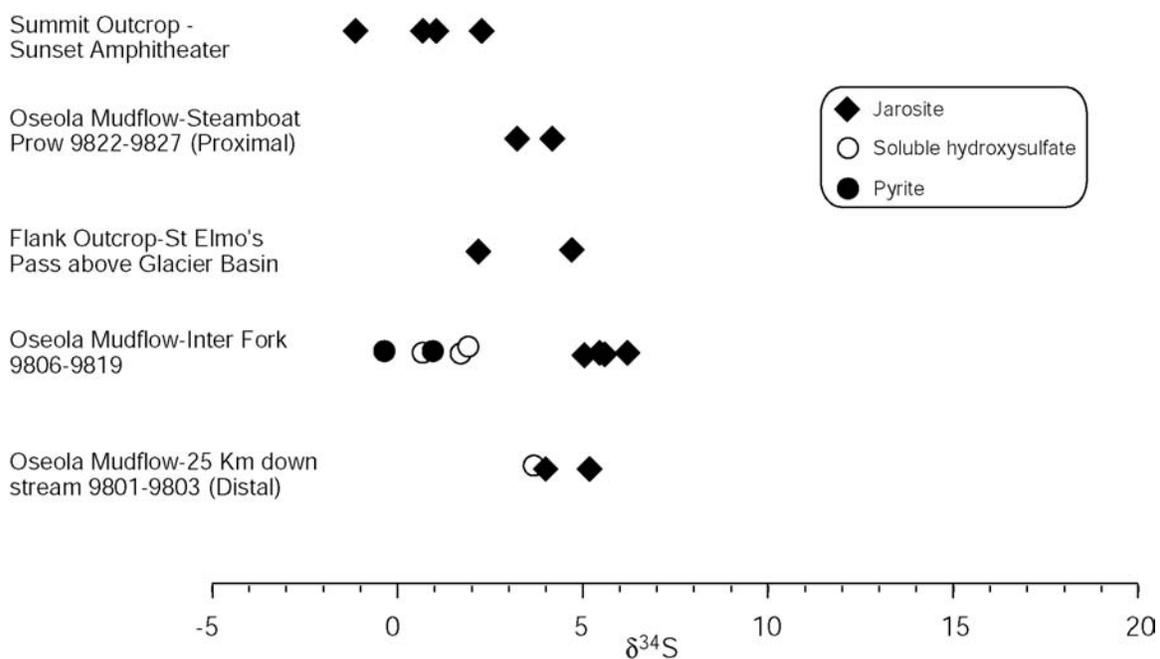


Figure 5. Summary of $\delta^{34}\text{S}$ data of jarosite from summit scarp, flank and, four Osceola mudflow deposits arranged by elevation. Also shown is data from the soluble sulfate in the largest Osceola deposit (Inter Fork). This difference of the $\delta^{34}\text{S}$ values for jarosite and soluble sulfate in the Inter Fork deposit indicates that they do not share a common origin. The difference in $\delta^{34}\text{S}$ values for jarosite for different Osceola deposits probably reflects the different degrees of exchange between streaming H_2S and aqueous sulfate formed from oxidation of H_2S prior to the precipitation of jarosite on the pre-collapse edifice.

1996); the composition of the alunite-forming fluids was calculated from δD and $\delta^{18}O_{SO_4}$ data on alunite assuming a formation temperature of 200-300° C and the equations of Stoffregen and others (1994).

Results

Mineralogy

Rocks in the uppermost parts of the pre-Osceola cone, such as Liberty Cap and Sunset Amphitheater, are partly to pervasively replaced by fine-grained smectite \pm kaolinite. Locally, alunite/natroalunite \pm kaolinite occur. Pyrite is rarely visible but traces are detected by XRD of samples from Sunset Amphitheater and other summit sites (Zimbelman, 1996). Patches and veinlets of jarosite/natrojarosite + smectite are also present along fractures in the summit scarps. Minor amounts of isomorphous analogs to alunite and jarosite, such as ammoniojarosite, florencite, and zunyite may be present based on the bulk-sample XRD. Highly soluble iron and aluminum hydrosulfate and hydrophosphate minerals, typically observed in acid mine drainage (e.g., Bigham and Nordstrom, 2000), were also detected by XRD. These include alunogen, metaalunogen, basaluminite, crandallite and salammoniac. Some of the phases likely are related to the oxidation of pyrite, but others may have formed as fumarolic precipitates.

The coarsest grains identified in the massive replacement alteration at Sunset Amphitheater are 10-micrometer, compositionally zoned alunite crystals. Semiquantitative analysis of these crystals in a polished thin section using a SEM defined micron-scale zoning of S, P, Na, Ca, K, and Fe. (Zimbelman, 1996). These crystals contain a Na-rich core (ca. 10 μm), surrounded by a more potassic zone that is then successively rimmed by a thin (ca. 1 μm) zone rich in Ca and P, and an outer Na-rich zone (ca. 2 μm) that lacks P. Surrounding these zoned sulfate crystals is a poorly-crystalline, interstitial Fe-sulfate rich in sodium.

Anhydrite/gypsum occurs as veins up to 2 meters thick in the summit scarp at Sunset Amphitheater. These constitute the only coarse-grained alteration minerals observed (Zimbelman (1996). Euhedral barite grains (0.5 to 1.5 mm), which occur in fracture-filling gypsum \pm anhydrite contain fluid inclusions that are generally 1 to 10 μm in size and are irregularly distributed (not aligned along fractures). Populations of primary fluid inclusions contain both vapor-rich and liquid-rich inclusions suggesting that boiling may have been important during their trapping. As described by Zimbelman (1996) fluid inclusion trapping temperatures vary between 204° and 266° C, salinities of liquid-rich inclusions are relatively high, ranging from 5.7 to >24.6 equivalent wt.% NaCl. The low eutectic temperatures (< -35° to -45° C) require salts other than NaCl or KCl in the trapped fluids (Crawford, 1981). Halite-bearing fluid inclusions typical of magmatic brines have not been identified. The low eutectics are likely related to $CaCl_2$ as would be consistent with the presence of gypsum and anhydrite in the veins.

Large areas of relatively unaltered volcanic units exposed on the flanks of the volcano have been locally oxidized and (or) vapor phase altered, presumably during emplacement. This alteration imparts a distinct orangish/reddish color to the outcrops. Bruce (1998) and Zimbelman (1996) noted widespread, but discontinuous, local alteration of the matrix in block-and-ash flow units in the lower parts of the volcano where smectite, locally present as veins, is the main alteration mineral. XRD analyses detected silica phases including cristobalite, tridymite, opal and quartz. Secondary iron oxide minerals include hematite, goethite, and maghemite. Smectite is the most prominent alteration mineral in volcanic rocks along dikes at Glacier Basin on the east

flank. Jarosite at Glacier Basin is limited to a relatively small area that includes both the block and ash units and the radial dike. Hydrothermal alteration minerals at Little Tahoma Peak also include jarosite and smectite with less common kaolin clays. Traces of soluble sulfates, including basaluminite, occur locally. Hydrothermally altered rocks in isolated areas lower on the volcano's west flank contain jarosite, smectite, and kaolinite.

The clay-sized fraction of the Osceola Mudflow ranges between about 2 and 15% and averages about 7% (Crandell, 1971; Scott and others, 1995; Franz and Voight, 1995). One of the notable features of the clay-sized fraction of the Osceola Mudflow is the widespread presence of a few percent jarosite, resulting in a characteristic ochre color to some of the deposits. Morphologically, jarosite occurs as dipyramids and elongate prisms, 0.5 to 1 μm thick. Alunite was not detected in the matrix of the Osceola deposits by XRD. Preliminary studies of small clasts indicate that about 30 percent contain pyrite. Alunite, dickite, and barite, are also present in some clasts.

Osceola Mudflow deposits from the Inter Fork deposit display systematic changes in water extractable phases with depth. Water slurried with the samples (50g solid/300 mL water) had increasing concentrations of dissolved sulfate and total dissolved solids and decreasing pH (6.4 to 3.5) from the upper to the lower samples. These trends are best explained by increasing contents of soluble aluminum and iron sulfates that were not sufficiently abundant to be detected by bulk sample XRD. Their isotopic composition (described below) is consistent with *in situ* oxidation of pyrite. Their abundance in stratigraphically lower samples, which may represent slough, could be a product of migration of aqueous sulfate in the deposit.

Stable isotopes

Alunite, jarosite, and clay minerals from all locations, display a large range in δD and $\delta^{18}\text{O}$ values (Figure 3). This range is attributed to mixing of magmatic and meteoric waters that have variously exchanged oxygen isotopes with wall rocks. Details of fluid history are difficult to determine, because hydrogen isotopes in fine-grained clay minerals probably are susceptible to retrograde exchange with later fluids in volcanic environments (O'Neil and Karaka, 1976) and the relationship between the alteration along faults and block and ash units is not currently understood. The isotope composition of the fluids that formed alunite is consistent with the largest relative content of magmatic water. In contrast, jarosite formed from fluids that contained predominantly meteoric water as indicated by the $\delta^{18}\text{O}_{\text{SO}_4}$ values that are the lowest recorded anywhere for jarosite (Rye and Alpers, 1997). Smectite formed from fluids that were a mixture of magmatic and meteoric water. The large range for calculated water compositions reflects the uncertainty in formation temperatures.

The range of δD values observed by Frank (1995) for firn and precipitation on Mount Rainier defines a $-65\text{‰}/\text{km}$ gradient for modern precipitation on Mount Rainier. The projected δD in Figure 3 for the isotopically lightest meteoric water component that formed the alteration phases is close to that observed for glacial ice on the summit today. The presumed range of $\delta\text{D}_{\text{H}_2\text{O}}$ of magmatic water may reflect isotope variations during degassing of magma (Taylor, 1986).

Bruce (1998) found that δD values of hydrothermal smectite along a well exposed dike from St Elmo's Pass to Steamboat Prow at Glacier Basin range from about -75 to -145‰ , whereas $\delta^{18}\text{O}$ values are much more uniform, from about 5.7 to 7.9 ‰ . The $\delta^{18}\text{O}$

values indicate low water:rock ratios that buffered $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ values of fluids. The δD values do not correlate with elevation but become larger (less negative) away from the dike. The range of δD values is consistent with alteration by meteoric water that originated from a range of elevations on the volcano above Glacier Basin.

The $\delta^{34}\text{S}$ and $\delta^{18}\text{O}$ values of alunite, gypsum and jarosite are summarized in Figure 4. The data in Figure 4 can be compared with characteristic isotope values for alunite and jarosite that form in *magmatic hydrothermal*, *steam-heated*, and *supergene* acid-sulfate environments from a given fluid composition, as discussed by Rye and others (1992) and Rye and Alpers (1997). The $\delta^{34}\text{S}$ values of all sulfate minerals range from 1.7 to 17.3‰. The largest value is for alunite at Steamboat Prow and the lowest is for jarosite at Sunset Amphitheater. The $\delta^{18}\text{O}_{\text{SO}_4}$ values of all sulfates range from -12.3 to 15‰ and show a positive correlation with $\delta^{34}\text{S}$ values. Alunite with the largest $\delta^{34}\text{S}$ and $\delta^{18}\text{O}_{\text{SO}_4}$ values also has the least negative δD value, a combination that requires a magmatic-hydrothermal origin in which H_2SO_4 that formed the alunite was derived from the disproportionation of magmatic SO_2 at a temperature less than 400°C (Rye and others, 1992). In contrast, jarosite has the lowest $\delta^{34}\text{S}$ and $\delta^{18}\text{O}_{\text{SO}_4}$ values consistent with parent aqueous sulfate formation largely from the oxidation of pyrite (Rye and Alpers, 1997). The $\delta^{34}\text{S}$ values of jarosite from the upper edifice range from 1.5 to 3.3‰; $\delta^{34}\text{S}$ values from the flanks at Glacier Basin range from 2.7 to 4.6‰; values of jarosite from the Osceola deposits range from 3.3 to 6.5‰. The distal samples are 3.8 and 5.0‰; proximal samples from the mudflow deposits at different elevations are 3.3 and 4.0 ‰; the jarosite in the Inter Fork ranges from 5.0 to 6.5 ‰. The $\delta^{18}\text{O}_{\text{SO}_4}$ values for four samples of upper edifice jarosite range from -4.3 to -12.3‰, while the $\delta^{18}\text{O}_{\text{SO}_4}$ values of two samples of Osceola jarosite range are -6.9 and -8.2‰. Vein anhydrite/ gypsum have intermediate $\delta^{18}\text{O}$ and $\delta^{34}\text{S}$ values that display a good correlation, as do the $\delta^{18}\text{O}$ and $\delta^{34}\text{S}$ values for the soluble sulfates from the Osceola deposits (Figure. 3).

Sulfur isotope data for jarosite, soluble sulfates and pyrite from the Osceola Mudflow deposits are further compared in Figure 5. The $\delta^{34}\text{S}$ values for jarosite for all of the Osceola deposits range from 3.3 to 6.5 ‰ with a spatial variation for individual deposits. These values are greater than those in altered rock at Sunset Amphitheater (1.0 to 3.3‰) but overlap with values for altered rock near St Elmo's Pass (2.5 to 4.7‰). The distinct sulfur isotope composition of the soluble sulfates (near 1.0 ‰) and jarosite (3.3 to 6.5‰) in the Osceola preclude the soluble sulfates being precursors to jarosite. Pyrite from small clasts in the Osceola deposits has $\delta^{34}\text{S}$ values of about 1 ‰.

Discussion

Two types of hydrothermal alteration are recognized on Mount Rainier (Zimbelman, 1996): 1) alteration of block and ash units on the flanks of the volcano that presumably occurred during and shortly after their eruption, and 2) alteration resulting from the introduction of acid volcanic gases into the meteoric water in fractured rocks on the summit and along lower flanks, within the EWSZ. The latter alteration was sampled in place on the summit and flanks of the volcano and also in the Osceola debris flow, which was derived from presumably altered summit rock that collapsed. Different types of alteration are the result of the range of physical and chemical conditions present in volcanoes and these conditions are inferred from the mineralogic and stable isotope data (Rye and others, 1992).

Stratovolcano hydrothermal model

According to Moran and others (2000) a magma chamber underlies Mount Rainier at a depth of about 5-6 km. Fluids degassed from the chamber produced hydrothermal alteration that is schematically described in Figure 6. Further discussion of the model leading to Figure 6 is presented in Rye (in press). The general features of this model have been developed from the study of ore deposits that formed in stratovolcanoes (or in silicic domes in continental terranes) and are based on the work of many people (e.g., Henley and Ellis, 1983; Rye and others 1992; Rye, 1993; Hedenquist and Lowenstern, 1994; Fournier, 1999). A fundamental spatial reference in this model is the brittle-ductile transition that occurs above a crystallizing magma at about 400 °C. Below this transition, rocks behave quasiplastically and brittle fracturing is restricted, penetration by meteoric water is minimized, and lithostatic pressures dominate. Above the transition, meteoric water can be present in open fractures and interact with a condensing magmatic vapor phase from degassing magmas. Because of the depth of the magmas and possible equilibration of magmatic fluids with crystalline calc-alkaline crystalline rocks below the brittle-ductile transition, condensing vapor fluids will typically have H₂S/SO₂ ratios >1 (Rye, 1993; in press). During times of high volcanic gas flux fluids may be more SO₂ rich. (Heald and others, 1963;). Residual saline liquids from boiling of magmatic fluids may become the source of Cu±Mo±Au porphyry mineralization at higher levels. As the vapor plume condenses beginning at about 400 °C, SO₂ disproportionates according to the reaction $4\text{SO}_2 + 4\text{H}_2\text{O} = 3\text{H}_2\text{SO}_4 + \text{H}_2\text{S}$. The H₂SO₄ leads to extreme base leaching and the formation of various zoned silica + alunite + kaolinite + pyrite assemblage and argillic and propylitic envelopes in a *magmatic hydrothermal* environment. The H₂S in these fluids normally reacts with iron in the rocks to produce pyrite with excess H₂S either venting to the surface or being oxidized by reaction with atmospheric oxygen. The H₂S, released by a magma or the boiling of deeper fluids, may be oxidized by atmospheric oxygen in *steam-heated* environment. Where atmospheric oxygen is unavailable in *magmatic hydrothermal* or *steam-heated* environment H₂S may form pyrite by the sulfidation of andesites such as at Marysvale, Utah (Cunningham and others, 1984; Cunningham and others, in press). Alunite often forms in *steam-heated* environments, but jarosite may develop instead of alunite under exceptionally low pH and high Fe³⁺ activity conditions (Stoffregen, 1993; Rye and Alpers, 1997). Pyrite is susceptible to oxidation when exposed to atmospheric oxygen in a *supergene* environment. The acid-sulfate alteration produced by oxidation of pyrite in a *supergene* environment can be isotopically and texturally similar to that produced by the oxidation of H₂S in a *steam-heated* environment (Rye and others, 1992).

Mount Rainier meteoric water hydrothermal system

Previous work (Frank, 1995; Zimbelman and others, 2000) identified an active meteoric water hydrothermal system on Mount Rainier in which water from glacial melt recharges underlying fractures at the summit edifice and is discharged at flanks and base

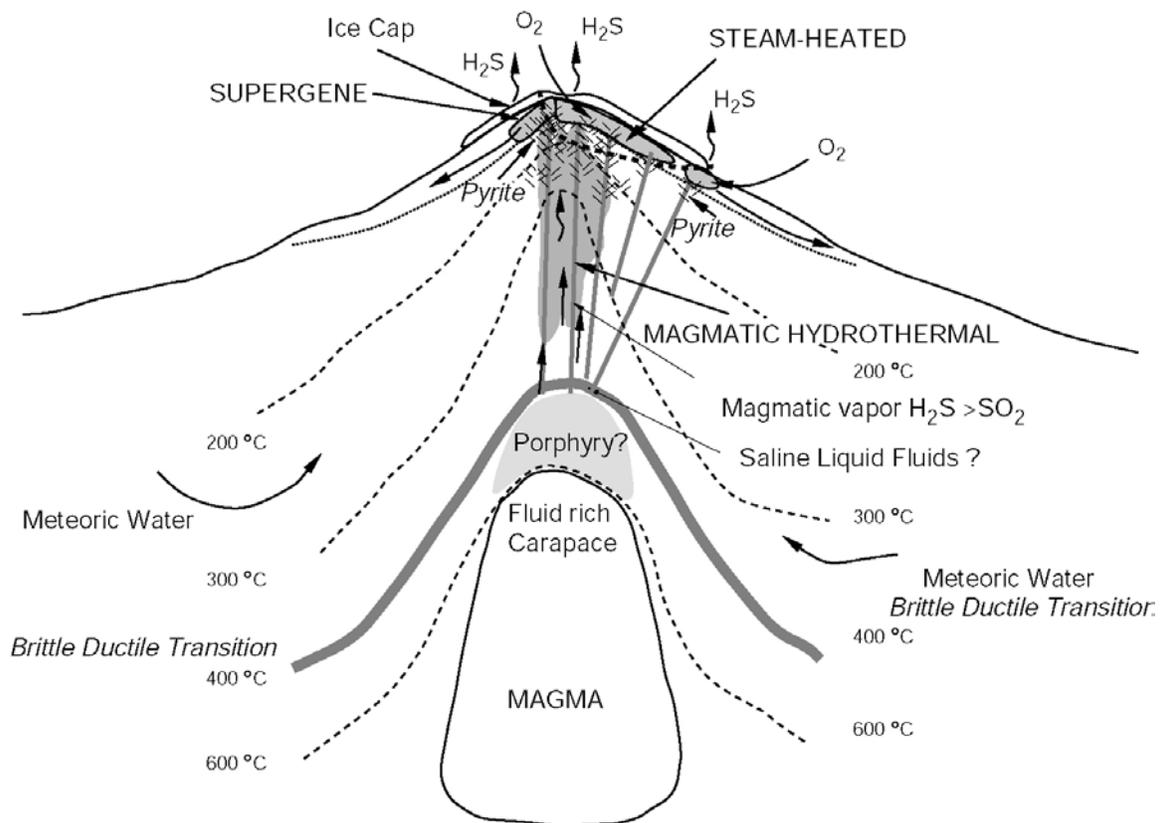


Figure 6. Schematic model of hydrothermal system on Mount Rainier (showing glacier cover) based on general models for such systems in stratovolcanoes. Model is modified from Henley and Ellis (1983); Rye and others (1992); Rye (1993); Rye (in press). *Magmatic hydrothermal* (grey), *steam-heated* and *supergene* environments (grey-black outline) are shown as overlapping but are normally separate at a given point in time. Diagonal cross pattern represents pyrite-rich areas which can occur 1) coexisting with alunite in the *magmatic hydrothermal* alteration, 2) in the surrounding intermediate argillic and propylitic alteration, or 3) below the unoxidized zone of a *steam-heated* environment. Also shown schematically relative to the *magmatic hydrothermal* and *steam-heated* acid-sulfate and *supergene* environments is approximate location of Osceola edifice collapse surface. Diagram is unscaled but Moran and others (2000) suggest that it is 5-6 km to the active magma underlying Mount Rainier.

of the volcano. The system has a deep water table. This meteoric water “scrubs” (Symonds and others 2001) volcanic gases such as SO₂, HF, and HCl and also serves as a source of H₂S to overlying vadose or shallow vapor dominated zones as proposed by Ingebritsen and Sorey (1988). Gases in active fumaroles in summit cones contain spikes of CO₂ up to 10,000 ppm and traces of H₂S but no SO₂ (Zimbelman and others, 2000). These fumaroles have been more active in the past, possibly with higher SO₂ contents, as indicated by the occurrence of alunite-type minerals, such as miamiite, on the surface near the dormant vents (Zimbelman and others, 2000).

The positive correlation between $\delta^{34}\text{S}$ and $\delta^{18}\text{O}$ values for all sulfate minerals including soluble sulfates in the Osceola deposits (Figure 4) is similar to relationships observed for sulfate minerals in many hydrothermal ore deposits (Seal and others, 2000). A similar correlation is observed for all sulfate minerals at all Cascade volcanoes studied to date (Zimbelman and others, in press). At a fundamental level the correlation reflects the mixing of isotopically heavy sulfate derived from magmatic fluids with isotopically light sulfate derived from the shallow oxidation of H₂S or pyrite (Rye and others, 1992; Seal and others, 2000; Rye in press). However, as shown in Figure 4 the possibility of sulfur isotope exchange between aqueous sulfate and H₂S prior to precipitation of sulfate minerals may complicate detailed interpretation of the isotope data.

Magmatic hydrothermal environment

The mineralogic and stable isotope data on summit and flank alunites require that a *magmatic hydrothermal* environment has been active at Mount Rainier. The alunite in an outcrop of altered rock at Steamboat Prow exposed in an old erosion surface has sulfur, oxygen and hydrogen isotope signatures (Figures 3 and 4) characteristic of the *magmatic hydrothermal* environment (Rye and others, 1992). The alteration is at least 200 ka years old (Sisson and Lanphere, 1999). Pyrite was not recovered at Steamboat Prow. Pyrite in the Osceola has an average $\delta^{34}\text{S}$ value of about 1 ‰. The sulfur isotope fractionation (17 ‰) between alunite and pyrite gives a calculated (Ohmoto and Lasaga, 1982) equilibrium temperature of 360 °C, typical of *magmatic hydrothermal* alteration (Rye and others, 1992). Alunite from near the present summit at Sunset Amphitheater has intermediate $\delta^{34}\text{S}$ and $\delta^{18}\text{O}$ values similar to those observed in other Cascade volcanoes (Zimbelman and others, in press). Isotope equilibrium involving aqueous sulfur species in hydrothermal fluids is kinetically inhibited at low temperatures, even in low pH fluids (Ohmoto and Lasaga, 1982). These intermediate isotope values are consistent with aqueous sulfate that formed during the disproportionation of magmatic SO₂ that was scrubbed out (Symonds and others, 2001) by low temperature meteoric water. This scrubbing appears to be going on today as the fumaroles on the present summit contain no SO₂ and only traces of H₂S (Zimbelman and others, 2000).

The fact that the alunite at the Sunset Amphitheater has a *magmatic hydrothermal* origin is supported by the presence of: (1) zunyite, a phosphate alunite analog, and florencite, a fluorine-rich alunite analog, (2) micron-scale, compositionally zoned alunites with highly variable K, Na and P contents, and (3) veins of anhydrite/gypsum containing barite crystals. Barite and anhydrite readily precipitate by mixing (Holland and Malinin, 1979), and it is likely that they precipitated as saline fluids mixed with meteoric water containing sulfate from the shallow oxidation of H₂S or pyrite. Hydrothermal pyrite was detected in only a few samples from the summit scraps (Zimbelman, 1996), because it quickly oxidizes to aqueous sulfate believed to form jarosite that is abundant along fractures. Pyrite detected in clasts from the Osceola Mudflow presumably came from

deeper within the mountain, beyond zones of extensive oxidation. This pyrite is likely the intermediate argillic or propylitic fringe of a *magmatic hydrothermal* environment.

Steam-heated environment

Jarosite + smectite is a characteristic of the matrix of the Osceola Mudflow deposits. Presumably, this assemblage was derived from original pyrite + smectite hydrothermal alteration. Acid-sulfate alteration in a classical *steam-heated* environment results from the oxidation of H₂S derived from the magma or deeper boiling fluids and typically results in formation of alunite + kaolinite (Rye and others, 1992). To what extent the pyrite + smectite alteration should be considered part of the low temperature intermediate argillic or propylitic fringe of a *magmatic hydrothermal* environment or the unoxidized part of a *steam-heated* environment is not clear.

Jarosite in the Osceola Mudflow has $\delta^{34}\text{S}$ values different from pyrite in clasts and from pyrite currently exposed on a summit scarp (Sunset Amphitheater). Therefore, jarosite in the Osceola did not form from the simple *in situ* oxidation of pyrite in the clasts or from pyrite near the current summit. The large range of $\delta^{34}\text{S}$ values could reflect variations in the $\delta^{34}\text{S}$ of magmatic H₂S over time (Taylor, 1986) or, more likely, exchange of aqueous sulfate that formed from the oxidation of pyrite with volcanic H₂S before the precipitation of jarosite. Such exchange between aqueous sulfate and H₂S has been interpreted to be relatively common in studies of the *steam-heated* environment (Ebert and Rye, 1997).

Supergene environment

Disseminated soluble iron and aluminum sulfates in the Osceola are attributed to the oxidation of pyrite. This interpretation is supported by the fact that the $\delta^{34}\text{S}$ values of the soluble sulfates are similar to those of the pyrite preserved in clasts (Figure 4, Table 1). The soluble Fe and Al hydroxysulfates that are observed in both the Osceola deposits and on summit scarps typically form in very low pH environments, which could include alteration zones resulting from surficial oxidation of pyrite. These sulfates are typically observed in acid-mine waters where they go through many cycles of solution and re-deposition (Bigam and Nordstrom, 2000). An active stratovolcano offers a unique environment where both supergene oxidation of pyrite and oxidation of H₂S could simultaneously occur at a given place.

Jarosite + smectite alteration is recognized on the flanks of the volcano at Glacier Basin below St Elmo's Pass. This occurrence is a circular -shaped alteration zone that includes both the block and ash units and a dike along the EWSZ. It probably represents the trace of a hydrothermal plume. The ochre colored zone is easily visible from Glacier Basin campground. The well-defined columnar jointing in the dike indicates that the dike was probably intruded underneath a glacier and that the hydrothermal plume that produced the circular alteration was close (probably within 50 meters, T.W. Sisson, personal communication, 2000) of the rock paleosurface. Within a zone of smectite alteration, the dike contains fine-grained pyrite. SEM examination and isotope analyses indicate that jarosite in the area is supergene and formed from aqueous sulfate derived from the oxidation of pyrite.

Hydrothermal alteration and edifice failure

As shown in Figure 6, *magmatic hydrothermal*, *steam-heated* and *supergene* acid-sulfate environments were developed on Mount Rainier prior to Osceola edifice collapse.

The deep-seated *magmatic hydrothermal* environment can be sampled only because of exposure by deep erosion at Steamboat Prow and edifice collapse at Sunset Amphitheater. The extent to which the *magmatic hydrothermal* environment is developing at depth on the volcano today is unknown.

Judging from the presence of pyrite and soluble hydroxysulfates observed in samples from summit scarps (Zimbelman, 1996), the supergene oxidation of pyrite and attendant jarosite precipitation in rocks containing smectite is occurring near the summit. The soluble sulfates may also form as sublimates around fumaroles and from the evaporation of acid waters. These sulfates should be quickly flushed from the rocks when they are exposed to dilute surface waters. Their presence in old altered rocks may imply the presence of ongoing pyrite oxidation. Recent acid-sulfate alteration is observed in the rocks in snow caves and on flank fumaroles (Zimbelman and others, 2000). Judging from mineral assemblages around dormant fumaroles, fluid flow appears to have been more vigorous in the past (probably immediately after the formation of the summit cones) than at present.

The spatial and isotopic relationships suggest that during edifice collapse the rock broke up along fractures containing supergene jarosite, such as observed today on summit scarps. The preservation of a unique range of $\delta^{34}\text{S}$ values for jarosite in the individual Osceola deposits (Figure 5) indicates that a crude edifice stratigraphy may be preserved in the proximal deposits, perhaps similar to that preserved in the proximal deposits of the 1980 eruption of Mount St. Helens (Glicken and others, 1980; Glicken, 1996).

Jarosite, regardless of origin, forms above the water table (Stoffregen, 1993; Rye and Alpers, 1997) whereas alunite forms at or below the water table (Rye and others, 1992). Alteration was localized along the EWSZ flank fractures and probably in the permeable core of the pre-Osceola portion of the edifice. Within the large wedge of rock defined by these fractures basal zones of volcanic rock are variously altered to smectite. Areas at Mount Rainier which contain large volumes of such altered rock have been the source to many post-Osceola collapse events, especially from the amphitheater directly west of Liberty Cap, but not the north, Willis Wall, side where altered rock is generally lacking. The area containing such alteration was largely removed during the Osceola collapse on the eastside of the volcano (Finn and others, 2001). However, a smaller area containing similar jarosite + smectite bearing rocks remains on the west-side of the volcano (Finn and others, 2001). As recently modeled by Reid and others (2001), this area represents the most likely source of future edifice failure.

Conclusions

Geologic, mineralogic and stable isotope data of Osceola Mudflow deposits, summit scarp and flank outcrops on Mount Rainier can constrain the processes leading to the alteration on the edifice of Mount Rainier prior to collapse 5600 years ago. Probably the most important feature in the development of the conditions that led to the Osceola edifice collapse and subsequent Osceola Mudflow on Mount Rainier was the EWSZ fracture system, which bisects the volcano through its summit. This fracture system has apparently existed for most of the volcano's history, ca. >500 ka, and has served as a conduit for magmas whose eruption built the volcanic edifice during two major periods (Sisson and Lanphere, 1999). It has also served as the plumbing system for meteoric water that was recharged at the summit from glacial melt and discharged at various levels along the flank of the volcano (Frank, 1995). Just as it does today, the fracture system on Mount Rainier focused acid gases from degassing magmas. The meteoric water fluids in

this fracture system served as a sink for acid volcanic gases such as H₂S, SO₂, HF and HCl at deeper levels and, after modification of gas chemistry, a source of H₂S to shallow levels. The introduction of magmatic gases into this system led to the development of a *magmatic hydrothermal* environment that involved the disproportionation of SO₂ to produce acid-sulfate alteration at depth. Reaction of H₂S with reduced iron in the andesite at shallow levels led to the formation of pyrite. The extent of oxidation of H₂S and the formation of a *steam-heated* environment at shallow levels is not clear.

Judging from the amount of pyrite+ smectite alteration in small clasts in the Osceola Mudflow deposits and jarosite + smectite alteration and soluble Fe and Al hydroxysulfates in summit scarps, the sulfidation of andesite related to hydrothermal processes appears to have been substantial. In the hydrothermal environment of an active stratovolcano, where wet and dry periods will be common (Symonds, 2001), this pyrite is susceptible to supergene oxidation with attendant acid-sulfate alteration.

Volcanic degassing led to formation of extensive hydrothermal pyrite and extensive alteration of rocks in the volcano's upper edifice and along EWSZ fractures. These structural zones may have been strengthened by the intrusion of dikes, many of which are relatively unaltered. However, altered rocks adjacent to these structures may have provided structurally weakened zones that localized collapse of triangular wedges of relatively stronger rock with possible local basal altered zones. The ages and relative role of *magmatic hydrothermal*, *steam-heated*, and *supergene* acid-sulfate alteration in edifice collapse needs to be assessed from further studies of debris flows from Mount Rainier.

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