ZINC ENRICHMENT IN THE PHREATIC ASHES OF MT. ST. HELENS, APRIL 1980

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ABSTRACT

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Micrometer-size condensate particles consisting of zincite (ZnO) with possibly minor zinc silicate occur in the phreatic ashes of Mt. St. Helens that were deposited in early April 1980. Zincite probably results from the reaction between steam, air and magmatic zinc halide. Thermodynamic calculations indicate that oxidation of zinc halide proceeds under the prevailing conditions in the eruption cloud. The zinc enrichment in the phreatic ashes adds evidence to the hypothesis that magmatic vapors were involved in the phreatic eruptions. It appears as if zinc is released from the magma already in the earliest stages of volcanism; monitoring of zinc in fumaroles and hot springs could possibly be helpful in the prediction of volcanic activity.

INTRODUCTION

In March 1980 Mt. St. Helens became active after a long dormant period. The volcanic activity started with phreatic eruptions, short explosions producing white steam clouds, followed by dark ash clouds (T.J. Casadevall, pers. commun., 1980; Cadle and Heidt, 1981). These eruptions were caused by the presence of a shallow magma reservoir, which induced snow melting. The melt water seeped down, became superheated, and phreatic explosions resulted. Although the eruption clouds consisted primarily of phreatic steam, indications are that a magmatic component was present (Cahill et al., 1980; Stoiber et al., 1980; Cadle and Heidt, 1981). Most of the material composing the phreatic ashes was derived from a hornblende—hypersthene dacitic dome, which formed the top of Mt. St. Helens before the climactic eruption on May 18, 1980 (Crandell et al., 1975). Bleached and altered rocks in the summit area had been noticed by Phillips (1941), and also could be observed after the snow had partially melted in spring 1980. Analyses of the summit rocks showed no enrichment in zinc (T.A. Cahill, pers. commun., 1980).

The present authors made a detailed study of a composite phreatic ash sample, deposited from several explosions on April 7 and 8, 1980. Particles with a remarkable fibrous morphology overgrowing silicate particles were found to be rich in zinc. Their morphology and composition was used to develop a model which accounts for their formation.

METHODS OF INVESTIGATION

The morphology and composition of the zinc-bearing particles were investigated with a scanning electron microscope (SEM) equipped with an energy dispersive X-ray spectrometer (EDS). We employed analytical procedures that permit the quantitative analysis of individual microparticles with diameters between 0.1 and 10 μm (Aden and Buseck, 1979; Aden, 1981).

Before analysis the ashes were dispersed ultrasonically in ethanol. A droplet of the dispersion was placed on a carbon planchet. This planchet was carbon-coated, and one half was also coated with gold/palladium for SEM imaging. Analyses were made at an accelerating voltage of 15 kV, micrographs at 25 kV.

Bulk analyses for zinc were performed with an atomic absorption spectrometer (AAS). Mercury analyses were performed with a thin gold-film analyzer (McNerney et al., 1972).

RESULTS

Morphology

The zinc-bearing particles consist of radiating fibers, platelets and aggregates, as shown in Figs. 1 and 2. Most single fibers have diameters between 0.1 and 0.4 μm. Small silicate particles are present between the fibers (Fig. 2). This morphology imposes constraints on the time of growth of the fibers. It is most unlikely that the aggregates could have survived a violent phreatic eruption. The growth of the aggregates postdates the fragmentation, since the zinc-bearing particles overgrow single ash grains (Fig. 1). The sizes and shapes of the particles suggest that the fibers grew out of a vapor phase in the eruption cloud. The hypothesis of growth in the eruption cloud is supported by the presence of similar zinc-bearing particles in phreatic ashes sampled about three miles northeast of the crater; thus, the distribution in combination with the observed textures can not be explained by a post-depositional origin as a result of fumarolic activity.

Composition

Representative analyses of the zinc-bearing particles are given in Table 1. Zinc was the main component of the fibrous particles (ZnO > 70 wt.%),

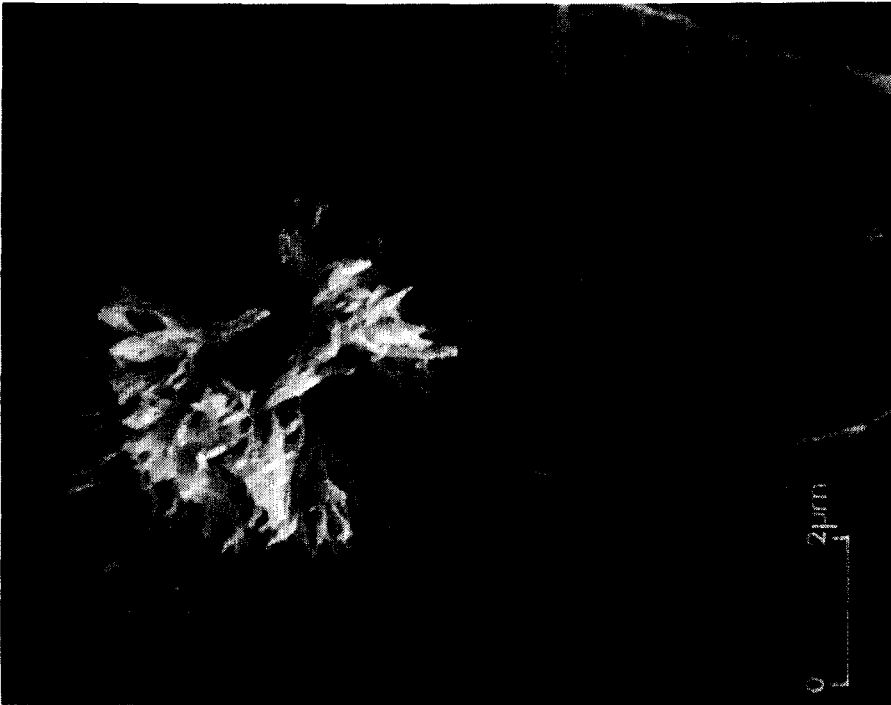Fig. 2. Zincite fibers with adhering small silicate grains.

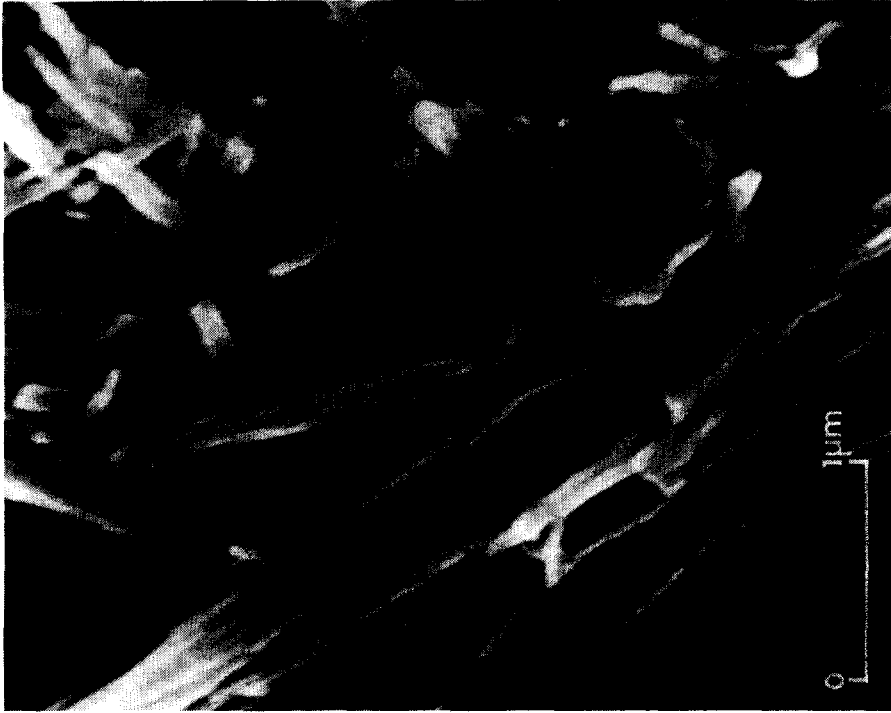Fig. 1. Aggregate of zincite fibers overgrowing a silicate particle.

TABLE 1

Analyses of 10 zinc-bearing particles, presented as wt.% (the correction procedures recalculate the total to 100%)

	1	2	3	4	5	6	7	8	9	10	11*
ZnO	80.4	83.0	86.1	78.6	83.2	73.9	77.7	75.2	73.2	80.4	72.9
Fe_2O_3	1.9	1.2	0.8	1.0	—	—	2.4	0.6	1.6	—	—
CuO	1.4	1.5	1.0	0.5	—	2.3	9.0	1.5	3.8	4.8	—
CdO	6.0	—	—	1.3	—	—	—	1.1	—	—	—
SiO_2	10.2	9.8	7.1	11.8	10.0	13.0	—	9.5	8.7	5.5	27.1
Al_2O_3	—	—	2.0	3.4	3.7	—	—	2.2	—	—	—
CaO	—	—	0.5	0.9	—	2.5	—	0.7	—	4.8	—
Cl_2	—	4.6	2.0	2.5	2.0	8.3	11.9	8.0	12.8	3.5	—
SO_3	—	—	—	—	1.2	—	—	1.2	—	—	—

*Hemimorphite particle analysis.

but a number of other elements were commonly observed, e.g. silica, aluminum, chlorine, copper and iron. None of these elements were found in all the analyses, and atomic ratios of the elements and zinc appear to vary randomly. We conclude that the analyses represent more than one compound, consistent with the presence of the small grains between the fibers (Fig. 2). The small grains turned out to be rich in silica and aluminum. Separate analyses of the small grains and the fibers proved to be almost impossible because of the small particle size and the intimate intergrowth of the fibers and the small ash grains (except for fiber analysis no. 7, Table 1). Furthermore, chlorine and sulfur were not only found in the zinc-rich particles but also in rock and mineral fragments in the ashes. The chlorine and sulfur are probably present in acid droplets, coating all particles in the ash (see e.g. Rose, 1977; Thomas et al., 1982). Iron commonly occurs in zincite (Palache et al., 1944), and cadmium and copper are common in the later Mt. St. Helens volcanic aerosols (Thomas et al., 1982).

The fibers showed a bright green cathodoluminescence under the electron-beam, which is typical of zincite and smithsonite. Four minerals or mineral combinations have compositions consistent with the EDS analyses: zincite (ZnO), willemite (Zn_2SiO_4), hemimorphite ($Zn_4Si_2O_7.(OH)_2.H_2O$), and smithsonite ($ZnCO_3$). We favor an identification of the zinc-bearing particles in our samples as zincite (or possibly a hydrated form). Wavelength dispersive analysis (WDS) of the particles showed no carbon, whereas we could detect carbon in standard smithsonite particles of a comparable size with our equipment. Therefore we conclude that the mineral is not smithsonite. We also excluded willemite and hemimorphite as the main constituents of the fibers because these minerals contain less zinc and more silica than the fibers (see hemimorphite analysis in Table 1, no. 11). The persistent occurrence of silica in the analyses, however, suggests that minor willemite or hemimorphite may be present. The association of these minerals and zincite is common. Zinc hydroxide, $Zn(OH)_2$, which is unknown as a mineral, can have a platy or acicular habit. However, it is a low-temperature phase (dehydration occurs at 140°C) and it does not precipitate from even a slightly acid solution. We kept the Mt. St. Helens material at 200°C for three days, and the morphology of the aggregates remained completely unchanged. Therefore we discard zinc hydroxide as a possible phase. The fibrous morphology and the fiber dimensions of the mineral are consistent with some occurrences of zincite (Gmelin, 1956).

Quantitative analysis of the accompanying silicate grains showed the majority to be plagioclase, with minor hornblende, hypersthene and potassium feldspar. Some grains of plagioclase contained up to 1.5 wt.% ZnO. Bright green cathodoluminescent spots were visible on the silicate grains under the electron beam, suggesting a separate zinc-rich phase. The low partition coefficient of zinc between plagioclase and acidic melts makes it highly unlikely that appreciable zinc is present within the plagioclase (Antipin et al., 1980).

Bulk analyses of the phreatic ashes from the top of Mt. St. Helens showed 220 ppm zinc, which is about three times the average value for Cascadian dacites (Wedepohl, 1978). Analyses for mercury were made to determine the possible enrichment of the ashes with this volatile element, which has an electron configuration similar to zinc. Mercury contents of the zinc-rich sample were about 14 ppb (background), but more distal ashes contained up to 50 ppb mercury.

OCCURRENCES AND STABILITY OF ZINCITE, WILLEMITE AND HEMIMORPHITE

The best known occurrence of these zinc minerals is in the ore deposits of Franklin and Sterling Hill in New Jersey (Frondel, 1972). Ramdohr (1969) refers to a pneumatolytic occurrence of zincite that formed from sphalerite. Lacroix (1904, p. 635) describes an interesting occurrence of zincite and willemite in the volcanic environment. During the 1902 blast of Mt. Pelée (Martinique) zincite and willemite formed where zinc nails in barrels were in contact with partially molten andesitic building stones in the houses of St. Pierre. Zincite is also observed in industrial plumes, where it usually has an elongated morphology (e.g. Bradley et al., 1981).

Experiments in the $Zn-SiO_2-H_2O$ system were carried out by Roy and Mumpton (1956). Their results show a low temperature limit of $500°K$ for the formation of willemite (at lower temperatures, hemimorphite becomes the stable phase), and a wide stability field for zincite. Harker and Hutta (1956) studied the reaction of smithsonite to zincite; at $550°K$ several hundred bars of CO_2 pressure are needed to form smithsonite. For industrial reasons (semiconductor research) crystal growth studies of zincite have been undertaken and acicular textures are often produced (e.g. Laudise et al., 1964).

ZINC IN THE VOLCANIC ENVIRONMENT

Zinc enrichments have been observed in fumarolic incrustations in many areas, e.g. the Valley of Ten Thousand Smokes (Zies, 1929), Vulcano (Bernauer, 1936), Santiaguito (Stoiber and Rose, 1974) and Kilauea (Naughton et al., 1974; 1976). We sampled incrustations of high temperature fumaroles on radial cracks in the crater floor of Mt. St. Helens during early September 1980. These incrustations contain about 1 weight percent zinc (Varekamp and Buseck, 1982). Mizutani (1970) described fumaroles from Showashinzan volcano in Japan with high zinc and copper concentrations in high temperature vents ($T > 400°C$), with low pH and chlorine-rich vapors.

Zinc is commonly found in leachates from ashes (Taylor and Stoiber, 1973; Rose et al., 1978). Wollenberg et al. (1979) found high zinc concentrations (2400 ppm) in the run-off of a small crater lake on Mount Hood (Oregon).

In areas distant from industrial pollution (e.g. Bermuda, South Pole), zinc and other volatile elements are strongly enriched in small aerosol particles. The size range of these particles suggests that a volatile phase is critical in their formation. Volcanism has been mentioned as a possible source (Zoller et al., 1974; Duce et al., 1976; Boutron, 1980; Boutron and Martin, 1980). Small aerosol particles in volcanic plumes are enriched in zinc, e.g. from the Etna (Buat-Menard and Arnold, 1978), from Heimaey (Mroz and Zoller, 1975), and from Augustine volcano (Lepel et al., 1978).

Analyses of particles from the clouds of the climactic 18 May eruption of Mt. St. Helens show strongly variable enrichments in zinc (Cahill et al., 1980; T.A. Cahill, pers. commun., 1980). Our preliminary analytical data on small aerosol particles collected in the gas plume of Mt. St. Helens in September 1980 indicate also enrichment in zinc, copper and cadmium (Thomas et al., 1982).

These studies show that zinc is commonly released by volcanoes, but no information is given on the mineral in which the zinc resides. Zies (1929) reported zinc to be present in magnetite; Naughton et al. (1976) predicted the presence of zincite on thermodynamical grounds but did not find it in incrustations. Mizutani (1970) supposed that vaporous zinc and copper chlorides react with H_2S to form a sulphide phase, but he could not detect sphalerite in the deposits.

MODELLING OF ZINCITE FORMATION

We used a simplified method to simulate the formation of zincite in a phreatic eruption cloud (Table 2). Zinc is probably carried to the surface in a magmatic gas phase. It is commonly supposed, and for copper observed, that heavy metals are transported as halides in a magmatic gas (Zies, 1929; Krauskopf, 1957; Murata, 1960; Naughton et al., 1976). $ZnCl_2$ and $ZnBr_2$ are the most likely species for zinc. These two species have similar thermodynamic properties. Some fumarolic incrustations sampled in the crater of Mt. St. Helens in September 1980 were found to be enriched in bromine, but for simplicity we consider $ZnCl_2$ only in our further discussion.

We constructed a phase diagram for zinc compounds in the pCl_2, pS_2 and pO_2 space from thermodynamical data (Robie et al., 1978). Data

TABLE 2

Conditions during three stages in the evolution of a magmatic gas (data after Carmichael et al., 1974; Volkov and Ruzaykin, 1975; Naughton et al., 1976; Casadevall et al., 1980)

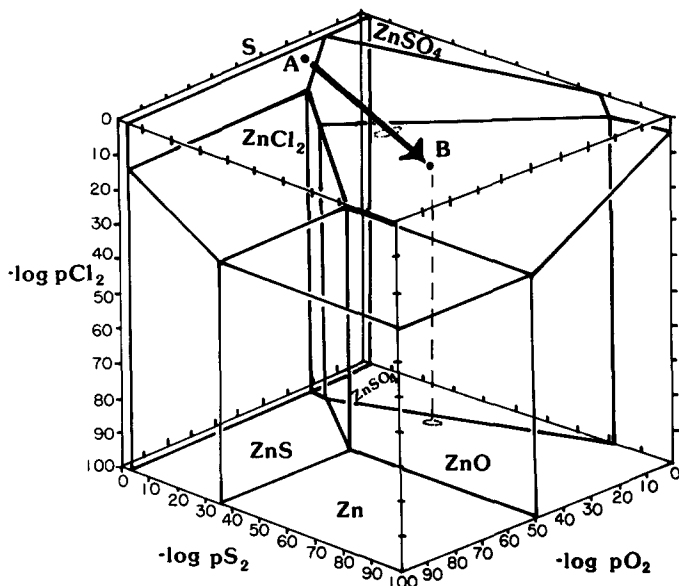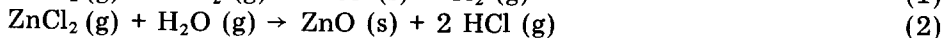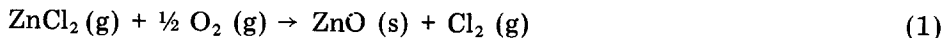|	T(K)	pO_2	pCl_2	pS_2
I. Magmatic conditions	1100	10^{-11} to 10^{-15}	10^{-2}	10^{-4}
II. Cooled to 600 K	600	10^{-25} to 10^{-30}	10^{-2} to 10^{-6}	10^{-7}
III. Dilution	600	ambient	very small	very small

Fig. 3. Phase diagram for zinc-bearing phases at about 600°K, P_{tot} = 1 bar, pCO_2 = 0 (calculated for $ZnCl_{2,vapor}$ in equilibrium with $ZnCl_{2,solid}$). Note that the $ZnCl_2$-volume forms the "roof" of the diagram.

are available for $ZnCl_2$ only at 298°K, but higher-temperature free-energy data could be calculated since the C_p function is given by Pascal (1962). The diagram (Fig. 3) was constructed for about 600 K, a realistic temperature in view of the temperature of zinc-rich fumaroles, as well as the experimental data on zincite stability.

When a magmatic gas leaves the magma with its load of metals, it starts to cool and equilibria shift accordingly (Heald et al., 1963). The magmatic gas phase, cooled to about 600°K, plots as point A in Fig. 3 in the $ZnCl_2$ volume (stage II, Table 2). Mixing with phreatic steam dilutes the gas, and its composition moves towards point B in Fig. 3. During the eruption further dilution and a strong increase in pO_2 result in the crystallization of zincite according to the reactions:

$$ZnCl_2 \text{ (g)} + \tfrac{1}{2} O_2 \text{ (g)} \rightarrow ZnO \text{ (s)} + Cl_2 \text{ (g)} \tag{1}$$
$$ZnCl_2 \text{ (g)} + H_2O \text{ (g)} \rightarrow ZnO \text{ (s)} + 2 HCl \text{ (g)} \tag{2}$$

We consider gas—gas reactions at elevated temperatures [reactions (1) and (2)] responsible for the zincite formation. A possible subsequent reaction is:

$$2 ZnO \text{ (s)} + SiO_2 \text{ (aq?)} \rightarrow Zn_2SiO_4 \text{ (s)} \tag{3}$$
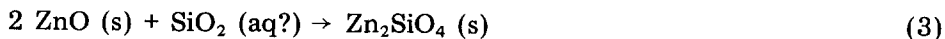
The latter compound may be converted to hemimorphite at lower temperatures. The gas—gas reactions (1) and (2) are kinetically more

favorable than gas—solid reactions at lower temperatures. Therefore the conversion of ZnO to other compounds will hardly occur within the eruption plume or shortly after deposition. In the long run, however, the likelihood of ZnO preservation is rather small, since the reaction:

$$ZnO \text{ (s)} + CO_2 \text{ (g)} \rightarrow ZnCO_3 \text{ (s)} \tag{4}$$

proceeds at ambient temperatures at a $pCO_2 = 10^{-2.9}$, which is only slightly higher than the normal atmospheric value.

CONCLUSIONS

The phreatic ashes of Mt. St. Helens from eruptions prior to the climactic eruption on May 18, 1980, are enriched in zinc. Ample evidence from the literature shows that zinc is common in magmatic emanations. We regard the zinc enrichment in the phreatic ashes as an indication for the involvement of a magmatic gas phase in these early Mt. St. Helens eruptions; evidence for recycled older zinc deposits on Mt. St. Helens is lacking. Zinc is partitioned strongly from a melt into a halide-rich gas phase (Holland, 1972). The value of the partition coefficient, which probably varies with the composition of the melt, is relatively large at melt compositions as found at Mt. St. Helens. It should be noticed that strong zinc enrichments were reported in vapor condensates from Santiaguito, a volcano with a melt composition similar to Mt. St. Helens (Stoiber and Rose, 1974).

Leachate analyses from the May 18, 1980, climactic eruption of Mt. St. Helens by Fruchter et al. (1981) showed low zinc concentrations, and bulk analyses of the ashes from this eruption showed zinc concentrations equal to background. A magma releases zinc already before an eruption. Emissions of zinc and possibly other trace elements are likely precursors to volcanic eruptions. Mercury, another volatile metal, was not enriched in the proximal phreatic ashes. Studies by Varekamp and Buseck (1980, 1981) indicate that mercury was mainly present as elemental mercury vapor in the Mt. St. Helens gas plume and does not condense on particles. This is in agreement with observations by Siegel and Siegel (1978) on Hawaiian volcanoes and data from coal-fired power plant outlets (Lindberg, 1980).

In conclusion:

(1) Zinc was released from Mt. St. Helens during the early stages of volcanic activity in 1980.

(2) A magmatic gas phase which carried zinc as zinc halides was involved in the phreatic eruptions.

(3) Zinc is present in the Mt. St. Helens phreatic ashes as zincite, possibly with minor willemite or hemimorphite. These minerals have not been identified before in volcanic sublimates.

(4) Zincite formed as a result of cooling, dilution and oxidation of a magmatic gas.

(5) Monitoring of zinc in fumaroles may be useful for eruption prediction and monitoring.

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