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Sulfate Minerals in Snake River Plain Volcanoes

Abstract

Various species of sulfate minerals are found within the vent complexes of Holocene lava fields of the Snake River basalt province, Idaho. The identification of the minerals was surprisingly difficult owing to reversible hydration reactions which occurred spontaneously with minor changes in temperature and humidity. Those minerals identified include various hydrous sulfates of Na, Mg, Ca, and Fe. The locations of the deposits suggest a fumarolic origin; however, known phase stabilities of the sulfates prohibit high temperatures of formation. A hybrid origin with ground water reworking originally fumarolic deposits is suggested for these occurrences.

Introduction

Extensive deposits of various sulfate minerals have been found in a number of Holocene lava fields within the Snake River Plain basalt province in Idaho (Fig. 1). The sulfate minerals (gypsum, mirabilite, bassanite, thenardite, bloedite, epsomite and jarosite) were found in various combinations in sheltered areas in the flows, mostly in vent craters and lava tubes.

The first such deposit reported was from Craters of the Moon lava field (Stearns, 1963; Peck, 1974), where massive encrustations of mirabilite + gypsum and powdery deposits of jarosite were encountered at Crystal Pit, a spatter cone. Similar deposits were later found at Hell's Half Acre lava field in conjunction with other investigations (Karlo, 1977). The existence of these deposits was somewhat surprising, since evidence of fumarolic activity is generally lacking in Snake River Plain volcanoes. Subsequent but by no means exhaustive collections were made at each of the major Holocene lava fields, and they form the basis of this report.

An interesting aspect of these deposits is the inordinant difficulty involved in identifying the minerals present. Standard X-ray techniques for identification give aberrant results in that the X-ray patterns produced are often unrepeatable. These difficulties are attributed to hydration-dehydration reactions resulting from minor changes in ambient temperature and/or humidity.

Occurrences

The sulfates occur either as encrustations or as powdery deposits. Encrustations of compact masses of micro-crystals were found lining the walls and ceilings of lava tubes and other cavities at Hell's Half Acre, Wapi, and Shoshone lava fields (Fig. 1). These

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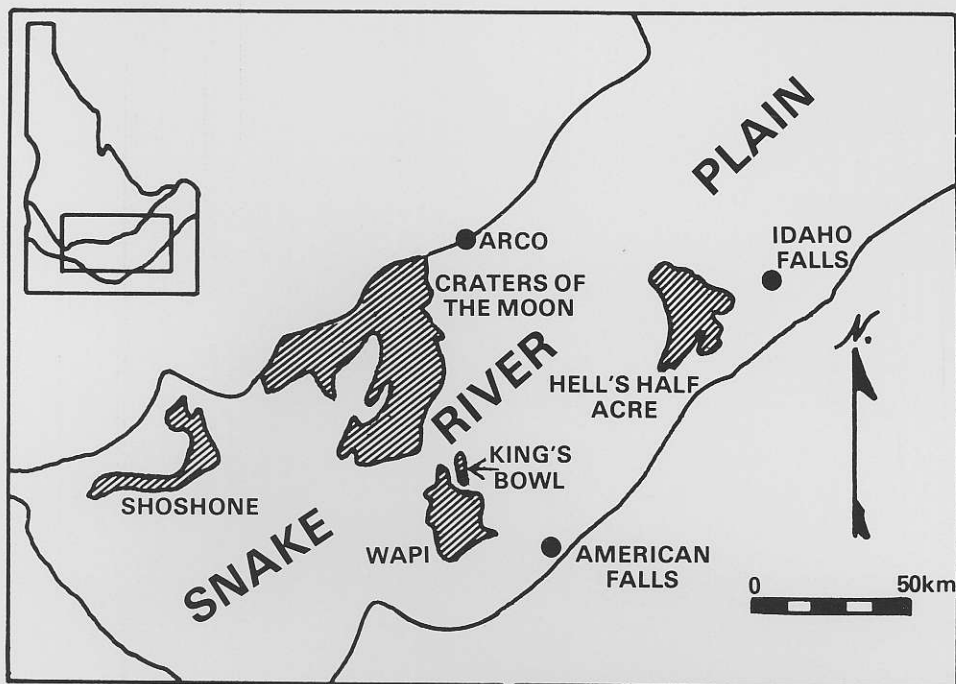


Figure 1. Locations of Holocene lava fields within the Snake River Plain, Idaho, from which sulfate minerals have been collected.

crusts vary considerably in thickness and extent; the most massive is 15 cm thick. Surfaces of the crusts are either globular, which is the original mode of occurrence, or, more commonly, rough with dissolution pits in areas affected by groundwater. The crusts were invariably found to be mixtures of gypsum + bassanite in contrast with the mirabilite + gypsum crusts reported from Craters of the Moon (Peck, 1974).

Powdery deposits were found at or near the vent areas of all the lava fields, and occur as layers on cavity floors, as fracture fillings, or less commonly as vesicle fillings. The layer deposits are typically discontinuous, show no stratification, and are 2-6 cm thick. All the powders are completely disaggregated and can easily be blown from their resting places. The powders are extremely fine-grained, with no crystal shapes discernible through a petrographic microscope. The minerals identified in the powders from each of the lava fields are: bloedite + thenardite, and bloedite + epsomite at Hell's Half Acre; thenardite and jarosite at King's Bowl, thenardite at Craters of the Moon; epsomite at Shoshone; and bloedite + epsomite at Wapi.

Identification

No effort was made to ensure that samples would not undergo phase changes prior to analysis owing to changes in temperature or humidity. All sample localities, while sheltered, were nevertheless freely exposed to the atmosphere, and any phase changes occurring subsequent to sampling would undoubtedly have occurred in the original environment.

The minerals were identified by X-ray diffraction and differential thermal analysis.

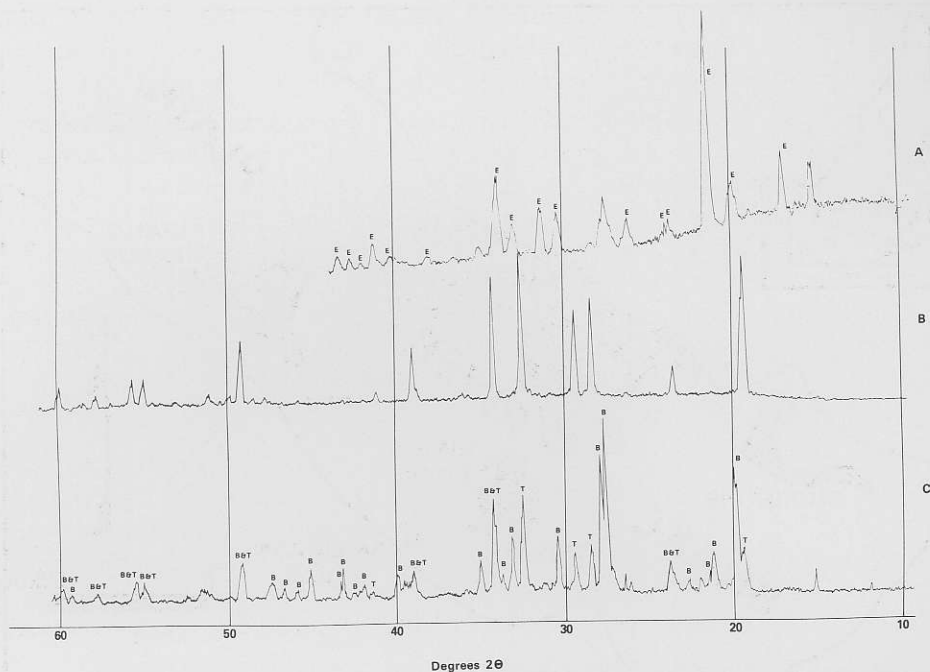


Figure 2. Representative X-ray powder diffraction patterns of sulfate deposits from Snake River Plain volcanoes. A. Epsomite (labelled E) from Pillar Butte, with unlabelled peaks representing a phase or phases which resulted from partial dehydration of the sample; B. Thenardite from King's Bowl; and C. Bloedites (B) and thenardite (T) from Hell's Half Acre.

X-ray diffraction powder analyses were done on a Phillips Norelco X-ray generator and chart recorder, with a goniometer speed of $1^\circ/\text{min.}$, coupled with a chart speed of $\frac{1}{2}$ in./min. The samples were prepared by settling the powders on a glass slide, using acetone as the wetting agent. Representative X-ray patterns are shown in Figure 2. Differential thermal analyses were also performed on selected samples, courtesy of Mettler Laboratories. The DTA results supported our X-ray identification of the sulfate phases.

Interpretation of X-ray patterns for samples containing epsomite was challenging since the epsomite readily undergoes hydration transition to hexahydrate (and vice versa) with minor fluctuations of room temperature or atmospheric humidity. Since the transitions rarely went to completion, various unidentified partial hydration stages occurred with the principal epsomite or hexahydrate phases. In several instances, the hydration states of the minerals apparently changed during the diffraction run, giving some highly puzzling patterns. Figure 2a shows a typical result for pure epsomite with some unlabelled, spurious peaks appearing in an otherwise simple pattern. Similar results were found with mixtures containing thenardite which formed small quantities of mirabilite on hydration. As an aid to identification, difficult samples were partially dehydrated by baking at 70°C for 24 hours, after which all erratic behavior disappeared. Baked unknowns were found to be simple mixtures containing the monohydrate form kieserite ($\text{MgSO}_4 \cdot \text{H}_2\text{O}$).

A similar circumstance was reported by Mitchell (1978). He found that pure

epsomite ($\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$) progressively changed to hexahydrate ($\text{MgSO}_4 \cdot 6\text{H}_2\text{O}$) and starkeyite ($\text{MgSO}_4 \cdot \text{H}_2\text{O}$) on dehydration at room temperature. Likewise, hydration of starkeyite produced a progressive change back to epsomite.

The degree of crystallinity varied for the different minerals examined. Thenardite appeared to have the highest crystallinity, giving clear X-ray diffraction patterns with peaks readily identifiable down to intensities of 4 percent of the principal (100) peak. Epsomite and bloedite did not appear quite as well formed. They yielded broader, less intense peaks, with the peaks predicted for the shorter d-spacings absent or ill-defined. Jarosite commonly gave poorly defined patterns with only the principal peaks present, or in some samples, showed only the broad bulge pattern associated with amorphous material, not an uncommon characteristic of this mineral.

Origin

Peck (1974) hypothesized that the Crystal Pit deposits at Craters of the Moon were formed by groundwater leaching of the basalts followed by subsequent deposition when the water entered open cavities. Peck discounted the role of fumarolic activity since mirabilite has been reported elsewhere from non-volcanic environments. However, the extreme youth of these lava flows, 2000-4000 yrs. B.P. (Prinz, 1970; M. Kuntz, U.S.G.S., pers. comm.), and the generally arid climate of southern Idaho are not in accord with this leaching hypothesis.

Stearns (1963) suggested that the sulfates were fumarolic in origin, which seems a more likely hypothesis; but mineralogic data do not fully support this. Jarosite precipitates at a temperature of about 110°C (Fairchild, 1933), which is well in the range of fumarolic activity. However, in the system $\text{Na-Mg-SO}_4\text{-H}_2\text{O}$, bloedite forms in equilibrium with epsomite and mirabilite between 20.6°C and 70°C at 1 atm. (Doelter, 1926), and the transition of mirabilite to thenardite in the $\text{Na}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ system occurs at approximately 32°C (Hill and Wills, 1938). These minerals appear to have formed within temperature ranges well below that expected for fumarolic deposits.

Peck (1974) may have been correct in stressing the role of groundwater, but its primary role in the Snake River Plain is more likely one of erosion (solution) rather than deposition. The sulfates are commonly present in the youngest flows but are absent from the older flows which have had longer exposure to groundwater. Although the deposits are extensive, they are not ubiquitous and are notably lacking in the wettest portions of lava caves. Further, the crust deposits show clear evidence of dissolution. Of the identified minerals, thenardite, epsomite and bloedite are soluble in water, and all of the minerals found are soluble in acidic solutions. None of the environments where the sulfates occur are fully protected from infiltrating water, and it is probable that the sulfate deposits are steadily diminishing in extent due to solution, rather than being actively deposited.

A "compromise" hypothesis seems most likely: an original series of deposits were fumarolic in origin, and the Jarosite powders and gypsum + bassanite crusts are the only remaining examples of this primary deposition. More soluble minerals were affected by groundwater and underwent solution, leaching, transport, and redeposition to varying degrees and in various combinations. The sulfates of Na and Mg are thus secondary minerals formed by reworking of the primary fumarolic deposits.

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