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Volatile Metal Deposits on Lunar Soils - Relation to Volcanism

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Volatile metal deposits on lunar soils — relation to volcanism*

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Abstract—Parallel leaching and volatilization experiments conducted on lunar samples and similar experiments on sphalerite do not supply the information needed to resolve the question of the chemical nature of ^{204}Pb, Zn, Bi and Tl deposits on lunar soil surfaces. It is proposed that in Apollo 17 mare and terra soils the fractions of ^{204}Pb, Zn and Tl that are insoluble under mild, hot pH 5 HNO_3, leaching conditions and involatile at 600°C were originally surface deposits which became immobilized by migration into the silicate substrate or by chemisorption. Only Bi is predominantly indigenous. The implication is also that the soils over their respective times of evolution were exposed to heavy metal vapors or that an episodic exposure occurred after they had evolved.

A sequence of events is proposed to account for orange 74220 and black 74001 glasses by lava fountaining and for soil 74241 as tephra from an explosive volcanic eruption.

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INTRODUCTION

WE SHALL EXAMINE HOW THE VOLATILE METALS ^{204}Pb, Zn, Tl and Bi are present on and in lunar soils, possible modes of transport, and their source(s). Most of the discussion will be confined to Apollo 17 samples since we have more data for these. A number of interelement correlations in soils from this relatively isolated site have been noted (Duncan *et al.*, 1974; Allen *et al.*, 1975). This is the site of the orange glass and we shall further elaborate on its relation to volcanism. We concur with a number of investigators concerning a volcanic source for this glass but we also propose that grey soil 74241 is volcanic tephra and that sequential eruptions could account for these ejecta as well as black glass 74001.

New data on Apollo 14, 15, 16 and 17 samples are given in Tables 1 and 2. Included in Table 2 are all of our volatization data and also the data for 74220 for easy reference. Some trends and interpretations, noted previously, were discussed briefly in the LSC VIII Abstract (Allen *et al.*, 1977), but will not be treated in this paper. These topics included heavy metal extraction during agglutimate formation, the roles of volatile rich 74220 and 66095 in understanding the source(s) of volatiles and rock weathering.

EXPERIMENTAL

We use fast and slow neutron activation analyses to measure the concentrations of ^{204}Pb, Zn, Tl and Bi in lunar samples and ESR to determine submicron metal which is a measure of the surface exposure of soil grains.

After irradiation, samples are leached with hot pH 5 HNO_3 for 10-15 minutes to remove water soluble surface deposits and salts. Since macro amounts of carriers of all the elements except Bi are present, it is assumed that not only solubility but also ion exchange between tracer and carriers play roles in removing surface deposits.

An effort was made to identify how the heavy metals were transported and the nature of their chemical form(s) as surface deposits. Leaching and volatilization steps were performed on aliquants of the same sample activated in a given irradiation. The volatilizations were made in vacuum at 600° and 1200°C. Leach and volatilization experiments paralleling those done on lunar samples were also attempted on a pulverized sphalerite sample. It was hoped that the results would provide clues for interpreting the lunar sample data.

Samples selected for the parallel leaching and volatilization experiments were monomict soil breccia 14047 and grey soil 74241. In the latter sample there appears to be a systematic factor of two difference in the concentrations determined in the leaching and volatilization experiments for the residual and 1200°C fractions for all four elements. Since the same monitor was used and the same irradiation, the only possible experimental source of error would be sample weight. A check of the amount allocated by the curator and the amounts used or still in our possession indicates that this is not the problem. The only possible conclusion is that the two aliquants were different and the average values are used for discussions.

The 250-500 μm sized agglutimate fraction from 75081 is a sample from the Meinschein (1976) 75081-consortium effort and was measured to test the interelement relationships which we attribute to the agglutimate formation process (Allen *et al.*, 1975b).

Interpretation of basaltic soil data at the Apollo 17 site requires that the basalts themselves be measured in order to resolve element concentrations and relations associated with soil formation and maturation processes. Samples 74275 and 75075 were selected for this purpose.

With the exception of 67455, the Apollo 16 breccias were measured in experiments designed to study Ru, Os and Hg (Jovanovic and Reed, 1977), hence only long-lived Zn and Tl were measured. Breccia 67455 was also selected for comparison with its fillet sample 67460 as a contribution to the Chao (1977) consortium.

The Apollo 15 soil breccias were the only Apollo 15 samples of which we had the 200-400 mg needed for ^{240}Pb measurements. Sample 15465 was measured as a part of a glass-breccia study.

Unless otherwise indicated, the uncertainties in the results were $\leq$ 10%. It is assumed that the errors are primarily counting statistical. Occasionally the capriciousness of the airlines in handling radioactive shipments caused some of our 52-hr ^{203}Pb counting data to be very uncertain because of decay.

RESULTS

Sphalerite experiment

An approach to resolving whether halides or sulfides are the surface deposits was attempted by subjecting a split sample of pulverized sphalerite-pyrrhotite mineral to the same leaching and volatilization procedures applied to lunar samples. The sphalerite was determined to have a composition of Fe/Zn $\sim$ 3; it was thus probably a solid solution of ZnS in FeS. The results are given in Table 3. In the leach experiment only 0.7% Zn dissolved in hot pH 5 HNO_3 and < 1.5% in 30 min in 4 N HCl; Fe, however, was leached and the residue approached a stoichiometry of Fe/Zn $\approx$ 1. Only 0.02% of the Zn volatilized at 600° but 98% at 1200°C. This experiment suggests that Zn, when present as sulfide, is very inert when in association with FeS. Fe-FeS eutectics may be present in lunar soil surface deposits as a result of the mechanism suggested by Allen *et al.*, 1974). This involved reaction -- as a result of micrometeorite impact, heating and melting -- of metallic Fe atoms, formed by atomic hydrogen reduction of ferrosilicates, with sulfur on surfaces. The source of the sulfur and the volatile metals, as well, was assumed to be fumarolic.

Lunar analog

In general we consider ^{204}Pb, Zn, Bi and Tl, but for comparison with the sphalerite results we will restrict the discussion to Zn. Using 74241 as an example, we note that 6% of the Zn is leached with pH 5 HNO_3. In general 2-10% of the Zn found in lunar samples is soluble. This may have been *all* the Zn present on the surfaces of the grains (see later). Under the leaching conditions, it appears that surficial Zn is dissolved in the lunar case but macro amounts of ZnS are insoluble. At 600°C about the same amount of Zn volatilized as in the case of sphalerite (0.03 vs. 0.02%, respectively), Based on volatility then, it appears that Zn could be present as the sulfide, whereas the leach results suggest that this may not necessarily be the case. However, if Zn is present as a soluble salt and this is a halide, its volatility would be expected to be between that of Bi and Pb, this is not the case (Table 4).

Metal volatility vs. leachability

The results of the comparison of pH 5 leached and residue vs. 600°C and 1200°C volatilized metals are given in Table 2. The concentrations in the leached residue and the 1200°C volatilized fractions tend to correspond and are always > 90% of the total metal in the sample. The concentrations in the leach are taken as the true surface deposits, see discussion below. Since no Bi carrier was present during leaching, the Bi_ℓ concentration may be a lower limit. Appreciable fractions of the leachable Pb and Bi are volatile; this is not the case for Zn and Tl. Possible experimental causes for the low relative volatilities of Tl and Zn are: Failure to transfer volatile material through the manifold to the traps or chemical alteration of the deposit in heating to 600°C; for instance, eutectic formation or thermal decomposition to yield the metal.

Possible explanations for these results assuming that they are not artifacts of the experimental procedure are:

1. The metals are deposited as sulfides.

At 1200°C the volatilities are in the order PbS > Bi(metal) > ZnS > ?Tl(metal)? The metals result from thermal decomposition of the sulfides at temperatures < 1200°C. If the 600°C volatilities are in the same order then the experimental results:

PbS, Bi_2S_3 → soluble *and* volatile

ZnS, Tl_2S → soluble, *not* volatile

are consistent with the available vapor pressure data, although we have no data on the vapor pressure of Bi_2S_3 at 600°C.

2. The metals are deposited as chlorides.

The order of volatility of the metal chlorides is $BiCl_3 > ZnCl_2 > Tl > PbCl_2$. In the experiments only Bi and Pb volatilized; an explanation is:

$PbCl_2$, $BiCl_3$ (simple cpds) → soluble and volatile

$ZnCl_2$, TlCl (double salts, solid solns) → soluble, suppressed volatility.

Both (1) and (2) have been considered by Meyer and Butler (1976). These authors also suggested the possible presence of mixed salts in Zn rich deposits observed by SEM-EDA to account for nonstoichiometry of Zn as a sulfide. Wasson *et al.*, (1976) have considered thermochemical and vapor pressure rationalizations to account for the surface deposited metals.

We propose another process which may account for the behavior of the surface deposits which we measure, as well as the much larger amounts of metals leached in the 4N HCl and dilute HF treatments by Wasson *et al.*, (1976). This process will also be proposed to explain other results discussed in the next section.

3. The metal ions migrate into the surface or are chemisorbed.

Pb, Bi are base metals	weakly bound or weakly chemisorbed	volatilized at 600°C and dissolved with weak HNO_3
Zn, Tl have lithophile affinities	substitutionally bound or strongly chemisorbed	retained at 600°C but dissolved with weak HNO_3

We suggest that metals migrating into the lattice or chemisorbed are volatilized according to their lithophilic tendencies. The larger amounts removed with strong acid is due to deeper penetration into and dissolving action on the silicate substrates.

We conclude that the nature of the surface deposits remains obscure.

74220 - 74241 comparison

In this and succeeding sections we examine the surface deposited metals in a suite of Apollo 17 soils, with special emphasis in this section on orange glass 74220 and overlying grey reference soil 74241. We shall examine the samples from the point of view of the relative amounts of ^{204}Pb, Zn, Bi and Tl they contain, hence that were present in the vapors that deposited on surfaces, and the times at which the deposition(s) occurred.

It can be seen in Table 5 that the intermetallic ratios of the leach and residue of metals in the two soils are very similar except for $^{204}Pb_{\ell}$ depletion in 74241. The inference is that both samples tapped the same reservior of volatiles. The concentrations of ^{204}Pb, Zn and Tl in 74241 in the residue after leaching or 600°C volatilization average about 45% of those in 74220, Table 6. Neither sample is enriched in Bi. The 74220 sample is > 95% orange and black glass, whereas 74241 has 1-4% of this glass but 30% basalt and 18% ropy glass (Heiken, 1974) based on the 90-500 μm grain size fractions. Even if there is a higher percentage of 74220 glass in the finer fractions of 74241, it could not constitute 40% of the sample. Lithophile and atmophile element concentrations are about the same on the surfaces and inside the two samples, Table 7.

The inferences of these experimental results are that (1) 74220 glasses do not provide 74241 volatiles [also see Schonfeld (1974)], (2) both samples acquired metal and atmophile volatile elements equally efficiently and (3) they were exposed to the same reservior of volatiles.

These observations may be geochemical evidence for a number of volcanic events and their relationships in type and time. In this context we will include black glass 74001 from below the orange glass taken in a drive tube. In this sample the glass is devitrified and contains composite spheres not present in vitreous 74220 glass (Heiken *et al.*, 1974). Three types of volcanic events may be envisioned and are depicted in Fig. 1.

1. Tephra ejection by explosive release of fragment charged vapor. Wall rock fragments (basalts, breccias?) and melts (ropy glass) make up the ejecta. The volatiles had been contained by a plugged conduit through which basaltic magmas had flooded the surface. The ropy glass was derived from original crustal material which underlays the maria. The relatively high viscosity (Uhlman *et al.*, 1974) of anorthositic rich crustal material accounts for this elongated twisted glassy material. The basaltic fragments are solidified mare basalts already at the surface. Crustal anorthositic material melted by ascending basaltic magma would tend to rise to the top of the magma in a conduit or in a secondary magma chamber which may have developed behind the plug. This anorthositic material would be the initial ejecta along with entrained wall rock fragments.

2. Fire fountaining of two types. Both involved basaltic magmas derived from the subcrustal regions from which mare basalts arose.

A. The eruption responsible for 74220 was the more energetic, possibly explosive, propelling a jet that rose high enough so that droplets formed and cooled through the glass transition temperature range of 960-900°K rapidly enough to avoid devitrification (Uhlman *et al.*, 1974). Turbulence in the rapidly rising jet was low hence collisions were not significant before droplet solidification had occurred.

B. Lava fountaining of less intensity and of longer duration could account for 74001. The composite spheres could be the result of collisions in flight, possibly by recycling in the plume as suggested by McKay and Heiken (1973) or to turbulence in the jet. The devitrification occurred either because of slow cooling, less than 10°K/sec based on Uhlman's *et al.*, (1974) data on the orange glass, while in flight or later while buried in a hot blanket (Haggerty, 1974).

If the strata in which these various samples were found had been inverted by the Shorty crater impact, the order of events could have been in the order discussed above and could have involved a single or possibly 2 or 3 volcanic vents. The opposite sequence of events is also possible with a steady effusive venting becoming more sporadic and explosive as the conduit or vent constricted; eventually after complete constriction the tephra erupted explosively.

Volatile metal behavior based on all Apollo 17 soils

We shall examine all the Apollo 17 soils that we have measured for insights into volatile metal behavior on and in soil grains. The percent metal leached compared with the concentration remaining after leaching is approximately constant within 50% for ^{204}Pb, Zn and Tl, Fig. 2a, b, c. Bi is the exception; inverse relationships are observed, one for basaltic and the other for terra samples, Fig. 2d. The percent Tl leached in 74220 and 74241 are the most striking exceptions, Fig. 2c.

An interpretation of this trend follows:

1. The residual metal is inherited. It migrates into the surface or becomes chemisorbed and is no longer labile under our mild leaching conditions.

Since most samples, regardless of their total residual metal content, appear to have similar percentages of readily labile metal (Bi excepted) some sort of equilibrium partitioning between surface and subsurface "interior", must have prevailed.

2. The Bi trends may be explained by the presence of a fixed amount of Bi on surfaces and variable indigenous amounts in the interior of the grams. Most of the Bi is not inherited by migration from the surface. We have reported previously that Bi is correlated with P_2O_5 (Allen *et al.*, 1975) and this is in the residual liquids from magma crystallization. The Bi deposits were different in the mare and front regions.

3. The relative amounts of Pb:Zn:Tl available for surface deposits remained approximately constant over the times the samples evolved. The samples are of various maturities and must also have been derived from rocks comminuted at different times.

We conclude that:

1. Most of the metals found in Apollo 17 soil samples were originally surface deposits which entered the substrate and became retentively held depending upon their lithophile characters and/or ionic radii. Thus Zn and Tl penetrate more deeply and/or were more strongly surface bound than Pb or Bi. The low relative volatilities of Zn and Tl are due to this effect. The higher concentrations leached by stronger acids may thus be accounted for.

2. Soil samples evolved over an extended period of time. Since the relative concentrations of metals was approximately constant a single source

of vapors is implied. The vapors must have been released over a time span comparable to that of soil evolution. Alternatively, the soils evolved to essentially their present states prior to the volcanic event, possibly related to 74220 and 74241, which provided a single exposure to vapors.

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Table 1. Primordial Pb, Bi, Tl, Zn and submicron metal in lunar samples*

Sample	^{204}Pb (ppb)		Bi (ppb)		Tl (ppb)		Zn (ppm)		Submicron Metal[††] (%)
	r[†]	ℓ[†]	r	ℓ	r	ℓ	r	ℓ	
Rocks									
15465,47 breccia					2.2	0.79	13	1	
15465,47 glass					1.8	2.5	5.3	0.47	
15505,17 soil breccia	2.4±0.7	≤0.43	≤5.2	2.5	0.59	0.3	11	0.33	0.41
15515,15 clod	2.1±0.4	0.15±0.10	<7.8	2.6	0.41	0.2	11	0.77	0.57
61016,131 breccia					44	2.1	0.66	0.21	
67455,76 breccia	1.7±1.3	nd	0.20	0.13±0.03	0.012	0.020	2.6	0.06	
74275,61 basalt	2.6±2.1	0.3 ± 0.7	0.12	0.07	0.12	0.44	1.2	0.15	<0.001
75075,24 basalt	0.8±0.7	0.2 ± 0.3	0.79	0.24	0.063	0.015	2.2	0.06	<0.001
Soil									
67460,5	≤4	0.8 ± 0.4	nd	nd	1.3	0.73	11	0.88	0.045
75081,9032[a] agglutinate fraction 2500-500 μm	4.4±1.6	2.6 ± 1.1	1.1	0.22±0.06	0.80	0.085	24	1.7	

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*Counting statistical errors are 10% or less or as indicated; [†]r = residue after hot pH 5 HNO_3 leach; ℓ = leach solution.

[††]Additional submicron metal results are given in footnote a, Table 2; [a]W. Meinschein consortium sample; nd = not detected.

Table 2. Concentrations of heavy metals in volatile, leach and residue fractions*

Sample	Experiment Leaching Volatilization	^{204}Pb(ppm) r†/s†	^{204}Pb(ppm) 1200°C	^{204}Pb(ppm) ℓ†/600°C	Bi(ppb) r/s	Bi(ppb) 1200°C	Bi(ppb) ℓ/600°C	Tl(ppb) r/s	Tl(ppb) 1200°C	Tl(ppb) ℓ/600°C	Zn(ppm) r/s	Zn(ppm) 1200°C	Zn(ppm) ℓ/600°C
14047,43[a]	leached	7.1±0.9		0.58±0.05	<1.9		0.05	22		0.85	20		0.57
	volatilized	---	7.7	<0.68	---	1.6	0.02	7.2	16	0.02	0.22	11	0.01
65015,32	volatilized							1.3	---	---	0.68	0.005	0.01[c]
68415,26	volatilized							3.8	---	---	0.47	0.002	0.008[c]
68815,107	leached							18		0.43	4.4		0.19
	leached	3.2±1.7		<0.09				24		6.0	1.4		0.13
	volatilized							11	---	---	1.3	0.037	0.010[c]
74241,18[a]	leached	5.9		0.4 ± 0.3	0.73		0.06	3.6		3.4	43		2.8
	volatilized	---	15	0.8 ± 0.5	---	1.5±0.2	0.03	--	15	0.17	---	76	0.024
74220,111[b]	leached	36		3.9	0.54		0.18	15		5.4	135		5.6
15101,44[b]	leached	3.2±1.5		3.3 ± 1									
<74 m	volatilized	3.8±1.5[d]		2.9 ± 1[c]									
15101,44[b]	leached	2.5±0.6		1.1 ± 0.7									
>74 m	volatilized	3.2±0.1[d]		1.3 ± 0.5[c]									

*Counting statistical errors are 10% or less or as indicated; †r = residue after hot pH 5 HNO_3 leach; ℓ = leach solutions; s = residue after volatilization at 1200°C; [a]Submicron metal in 14047 = 0.60 wt%, and 74241 = 0.088 wt%; [b]Reported in Allen *et al.*, 1973; [c]Volatilized at 450°C; [d]Residue after volatilization at 450°C.

Table 3. Extraction of Zn and Fe from FeS-ZnS mineral by leaching and volatilization experiments*

	Leached			Volatilized		
Element	pH 5 HNO_3 15 min, ∿100°C	4 N HCl 30 sec	4 HCl 30 min	600°C 1 hr	1200°C 1 hr	Residue
Zn%	0.68	0.16	1.2	0.02	98	1.6
Fe%	2.5	13	44	0.0	2.2	38

*The Fe:Zn was determined to be 3:1 in the sphalerite-pyrrhotite mineral from Peabody mine used in these experiments.

Table 4. Comparison of the leachability and volatility of heavy elements in lunar samples*

Sample	Element	Leached % pH 5 HNO_3 15 min, ∿100°C	Volatilized, % 600°C 1 hr
14047,43	^{204}Pb	8	8
	Bi	8	1
	Tl	4	∿0
	Zn	3	∿0
74241,8	^{204}Pb	6	5
	Bi	8	2
	Tl	49	1
	Zn	6	∿0

*Data are from Table 2.

Table 5. Interelement ratios in orange soil, 74220, and gray reference soil, 74241*

	74220 residue	74220 leach	74241 residue	74241 leach
Pb/Tl	2.4	0.72	1.6	∿0.12
Pb/Zn(10^{-3})	0.27	0.7	0.14	∿0.14
Tl/Zn(10^{-3})	0.11	0.96	0.08	1.2

*Data are from Table 2.

Table 6. Concentration ratios of heavy elements in 74220 and 74241 residue after hot pH 5 HNO_3 leach or 600°C volatilization*

Element		74241/74220
Pb(ppb)		11/36 = 0.31
Bi(ppb)		1.1/0.54 = 2
Tl(ppb)		9.3/15 = 0.62
Zn(ppm)		60/135 = 0.44
	Average (-Bi)	0.45

*Data are from Table 2. The average concentrations are used for 74241; see experimental section.

Table 7. Lithophile and atmophile element concentrations in 74220 and 74241 in hot water leach solution and residue after leaching*

74220 / 74241	F* ppm	Cl ppm	Br ppb	I ppb	Li ppm	U ppm
leach	36 / --	49,21 / 32	1200,300 / 380	14,13 / 13	-----	-----
residue	25 / --	23,82 / 27	380,120 / 420	-----	9.7,11 / 13	0.17,0.17 / 0.14

*Data from Jovanovic and Reed (1974). Total F in 74241 is approximately twice that in 74220.

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FIGURE CAPTIONS

Fig. 1. Eruption sequence postulated to account for three types of volcanic ejecta. I. A conduit through which mare-filling basaltic magma flowed to the surface is plugged. A possible magma chamber at a crust-subcrustal interface is suggested. Lower density, higher viscosity crustal melts float on basalt magma. II. Explosive eruption ejects anorthositic melt as ropy glass and entrained basalt and breccia fragments. III. Low viscosity, high velocity jet rises in a narrow cone to high altitudes, chilling glass spheres before they arrive at the surface. IV. Steady lower intensity lava fountaining causes mixing and recycling of glass spheres leading to composites. Up to three separate conduits could have been involved.

Fig. 2. The heavy metals leached by pH 5 HNO_3 is constant within 50% for ^{204}Pb, Zn and Tl irrespective of the total amount in the soil or the mode and time of evolution of the soil. The Bi results suggest a constant amount of surficial metal and varying amounts of metal in the bulk sample.

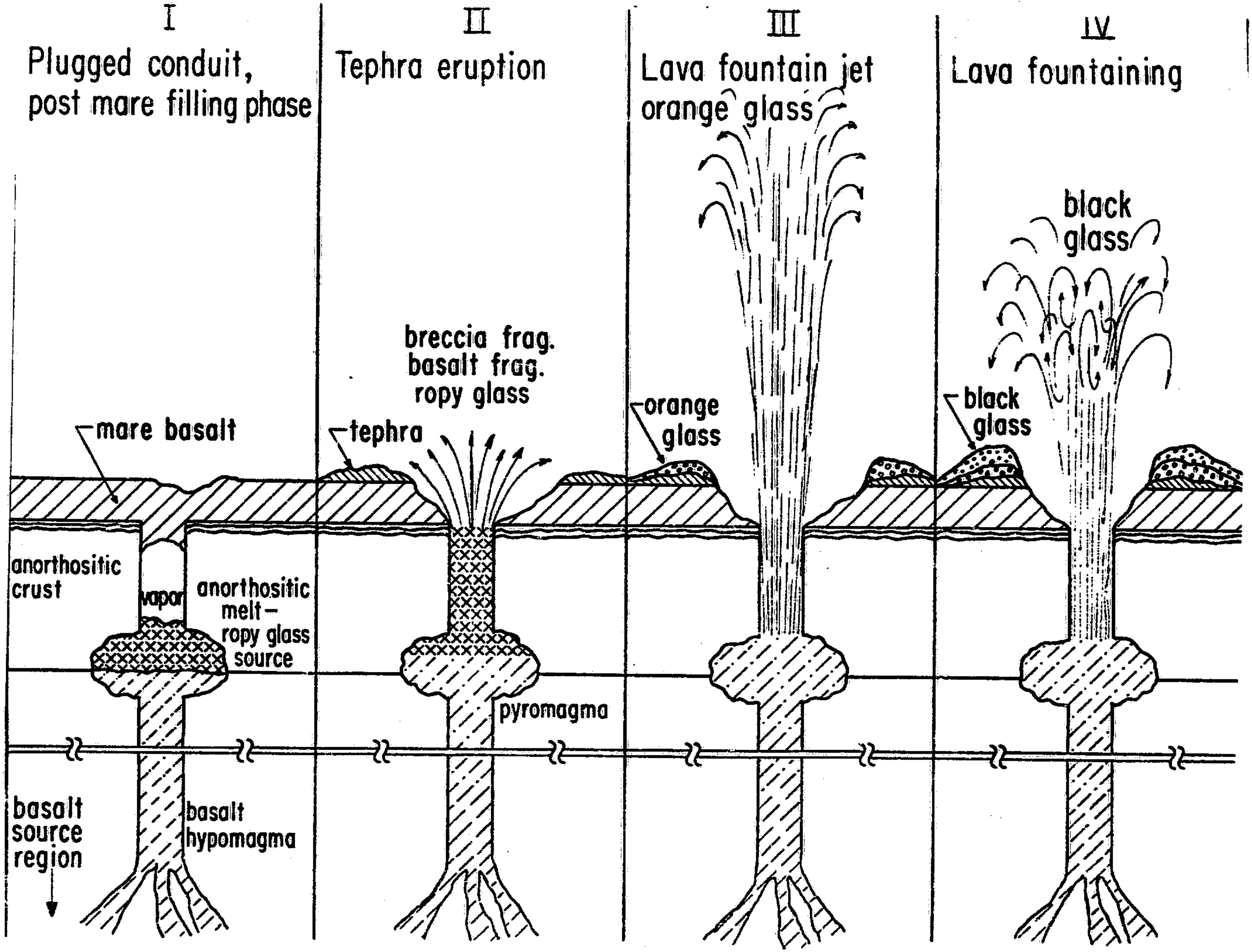
I
Plugged conduit, post mare filling phase
II
Tephra eruption
III
Lava fountain jet orange glass
IV
Lava fountaining
mare basalt
tephra
breccia frag.
basalt frag.
ropy glass
orange glass
black glass
black glass
anorthositic crust
vapor
anorthositic melt — ropy glass source
pyromagma
basalt source region
basalt hypomagma

Fig. 1

PERCENT METAL IN pH5 HNO$_3$ LEACH VS METAL IN RESIDUUM