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SOLFATARIC ALTERATION PRODUCTS OF ANDESITIC LAVAS IN THE CRATER OF COTOPAXI VOLCANO, ECUADOR

Abstract. The paper deals with the results of geochemical-mineralogical study of alteration products of andesitic lavas by solfataras, active in the crater of Cotopaxi volcano. Final products, occurring at solfatara vent, are *opalites*, consisting of opal-cristobalite with sulphur admixture and trace amounts of alunite and barite. *Alunitized andesites* are less altered rocks in which relict primary components are accompanied by secondary opal-cristobalite, alunite and traces of gypsum. Sulphur, opal-cristobalite, gypsum and alunite occur as incrustations or fissure fillings in surrounding rocks. Distribution and behaviour of major and minor elements and conditions governing various solfataric alteration processes are discussed.

GENERAL GEOLOGICAL DATA

Cotopaxi (5897 m), one of the highest active volcanoes in the world, represents a typical stratovolcano of almost ideal conic shape with summit crater. In historical times many eruptions of importance were observed, the most violent being those in 1744, 1768 and 1877. The last lava flow from central crater was noted in 1942 (Hantke, Parodi 1966). In 1972, during the investigations led by Czechoslovak-Polish geological expedition *Cotopaxi 72*, the volcano was in a state of dormancy, though numerous exhalations in crater itself and its vicinity took place. Nevertheless, the upper part of the cone, above 4600—4800 m, including crater, was covered with snow and ice, leaving only small exposures of rocks on vertical walls and in the places heated by volcanic gases.

Summit of Cotopaxi display fairly complicated geological structure (Fig. 1). Elliptical somma encircles small nested internal cone formed after 1903. This somma is a relict of the great, partly breached crater,

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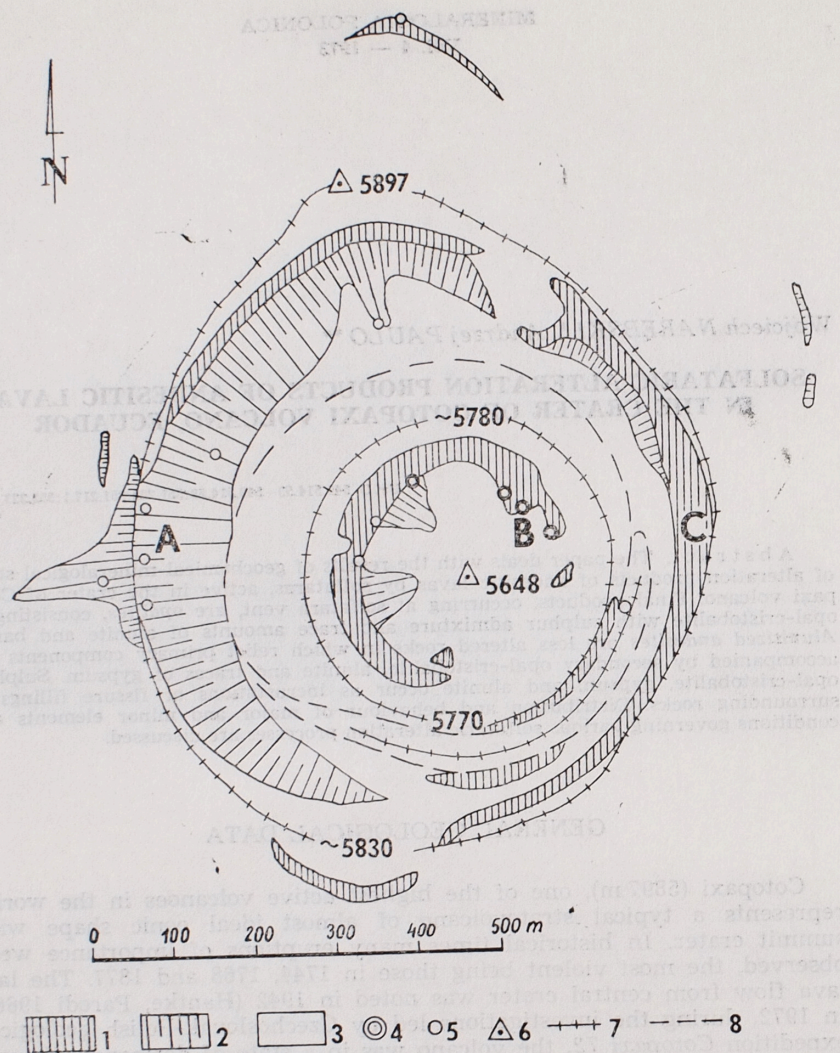** Institute of Mineralogy and Mineral Deposits, Academy of Mining and Metallurgy, Cracow (Kraków).

Fig. 1. Schematic map of the crater of Cotopaxi

1 — lavas and tuffs forming steep walls, *2* — tephra and talus debris, *3* — snow and ice cover, *4* — solfatara vents of permanent activity in August—September 1972, *5* — short-living exhalations, *6* — altitudes in metres according to Mapa Fisico del Ecuador 1 : 50 000 (1963), other altitudes measured by Czechoslovakian-Polish expedition, *7* — ridges, *8* — depression axes

observed in the period 1877—1903 by Wolff (1926), Whymper (1892), Meyer (1970) and others. In 1972, the new crater, in nested cone, was about 350 m in diameter and 120—130 m in depth. Judging from Hantke's description (*l. cit.*) it persisted in this form for nearly 30 years. In upper

part of this crater, on vertical walls, there outcrop tuffs and tephra layers, about 60 m thick (Phot. 1). Below, andesitic lavas occur, being partly covered with slopy rock debris.

At the foot of northern wall and in September also in the west part, solfataric streams carrying H_2O, H_2S (+ probably sulphur oxides) and CO_2 were emanating. Temperature of solfatara gases in *B* point (Fig. 1), situated more than 100 m below crater's margin, measured on 2 September 1972, amounted to 80—81°C. Apart from these exhalations, a week stream of steam and CO_2 (?), with temperature 9—10°C was observed within shallow throat in the centre of crater. Moreover, abundant sublimates of native sulphur occured at the western and particularly at the northern crateric wall.

Grab sampling of rocks *, occurring close to solfatara vent, allowed to discover their large-scale alterations in the range of about 20 m from the throat. Altered rocks in question display zonal distribution (Fig. 2).

General observations were also carried out on the slopes of somma in the *A* and *C* regions (Fig. 1). In the former one there prevails loose pyroclastic material but some fragments of preserved young lava flows are observed too. In the first days of August 1972 emanations of odourless gases, the temperature of which did not exceed 40°C, were observed here, whilst on September 2, 1972 no traces of exhalations were found in this place that was covered with fresh snow. On the surface of lapillae and small tephra blocks there occur delicate incrustations of sulphur and gypsum crystals. Moreover, alteration phenomena of pyroclastic material into opal substance are observed. Nevertheless, because of slope sliding of rocky material, it is very difficult to determine the zonality of alteration processes.

In the *C* region andesitic flows are exposed, showing no symptoms of these phenomena, except of some oxidation, marked by reddish colouration.

In this paper, comparison of petrographic, mineral and chemical composition of collected samples is referred to the structurally closest and commonest variety of andesites of the youngest generation, represented by sample 314.

METHODS OF EXAMINATION

All the collected samples were first investigated microscopically in thin sections. Subsequently, several selected specimens were examined by means of chemical and spectrochemical analyses for major and minor elements respectively. The former were determined by fusing with soda according to a scheme proposed by Narębski (1962). Thus, silica was estimated after classical acid separation using gravimetric method, Fe, Al, Ca, and Mg by complexometric titration, Ti, Mn and P photocolorimetrically and alkalis by flame photometry.

Trace elements of the iron group were determined by Dr. N. Bakun-

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* Sampling within crater was carried out by J. Dobrzyński and B. Mlčoch, at somma by A. Paulo.

-Czubarow using DFS-13 grating spectrograph and following analytical lines: V — 3183.98 Å, Cr — 3014.91 Å, Ni — 3050.82 and 3414.76 Å and Co — 3453.505 Å. Sr, Ba, Rb and Li contents were estimated by Dr. Z. Wichrowski also by means of DFS-13 spectrograph using 4607.33, 4934.09, 7800.23 and 6103.64 lines respectively.

Mineral composition of fresh andesites was determined essentially by microscopic method, whilst that of altered ones, displaying obscured and fine-grained textures, by X-ray, infrared spectroscopic and thermal methods using URS-50-I X-ray diffractometer, Zeiss UR-10 spectrophotometer, and Paulik-Erdey derivatograph, registering simultaneously DTA, TG and DTG curves.

UNALTERED ANDESITES

Lavas of young Cotopaxi cone display considerable petrographic variability. Detailed study on these rocks will be published later.

Older lava flows consist predominantly of massive pyroxene andesites showing porphyric texture and pilitic or pilotaxitic texture of the matrix. Large (2—4 mm) phenocrysts of plagioclases, ortho- and clino-pyroxenes are fairly abundant. Plagioclases (labradorite-andesine) often display zoning and composite twinning. Accessory magnetite, haematite and ilme-

Table 1

Chemical composition of andesites and their altered equivalents from Cotopaxi (in weight per cents)

Sample No.	314	351	343	345	344
Region (Fig. 1)	Out of crater	C	B	B	B
SiO_2	55,80	54,80	57,60	53,60	81,20
TiO_2	0,86	0,94	0,85	0,90	0,99
Al_2O_3	16,50	17,00	16,70	15,10	2,00
Fe_2O_3	3,29	6,78	6,05	5,45	0,72
FeO	4,35	1,72	1,80	1,21	0,09
MnO	0,11	0,11	0,09	0,064	0,006
MgO	3,22	3,37	3,36	2,51	0,13
CaO	7,03	7,02	6,43	2,43	0,07
Na_2O	4,05	3,68	3,74	2,43	0,07
K_2O	1,31	1,40	1,19	1,18	0,82
P_2O_5	0,35	0,26	0,31	0,32	0,10
H_2O	2,10	2,60	1,75	7,30	10,20
SO_3	—	—	—	7,73	—
S	—	—	—	—	3,20
Total	99,67	99,68	99,87	100,22	99,89

analyst: W. Narębski

nite are associated with pyroxenes. These andesites are from dark grey to reddish in colour. Some lavas contain frequent xenoliths of leucocratic rocks (andesite-dacites?).

Younger lava flows generally consist of porous and vesicular rocks containing more or less glass. Phenocrysts are represented by plagioclases (labradorite, less common andesine), ortho- and clino-pyroxenes and, in some rocks, olivine. These rocks are from black and dark grey to reddish in colour. Xenoliths of quartzites and various andesites were found to occur in black lavas.

Unit weight of unaltered andesites depending on porosity varies from 1.1 up to 2.65 g/cm^3 in massive rocks.

From geochemical viewpoint samples of fresh lavas resemble closely latite-andesites of Northern Chile (Siegers *et al.* 1969). This refers both to major and minor element contents (Tab. 1 and 2 — samples 314, 351

Table 2

Trace element contents in andesites and their alteration products from Cotopaxi (in ppm)

Sample No.	314	351	343	345	344
V	270	140	210	66	< 5
Cr	38	14	70	20	160
Ni	32	18	11	3	< 2
Co	41	22	21	6	< 1

analyst: N. Bakun-Czubarow

Sample No.	314	351	343	345	344
Sr	630	800	580	220	20
Ba	640	630	520	335	400
Rb	32	31	37	35	< 10
Li	47	27	21	5	< 5

analyst: Z. Wichrowski

and 343 — the two latter representing oxidizied rocks). However, because of rather normal potassium content these lavas can be preliminarily classified as andesites (Dickinson 1968). Further investigations of larger number of samples selected from those collected by the Czechoslovak-Polish expedition from the whole volcanic cone will allow to name these rocks more precisely.

ALTERED ROCKS

Distinct alteration of andesitic rocks are observed in the vicinity of solfatara vent. However, because of abundant sulphur incrustations and inaccessibility of outcrops, detailed observations of these phenomena are

very difficult. On the ground of grab sampling we can say that alteration zone is at least 20 m wide. Incrustations of native sulphur cover the walls of fissures, through which solfataras exhalate. Further outwards there occur subsequently: opalites, alunitized andesites and slightly altered andesites with gypsum veinlets (Fig. 2).
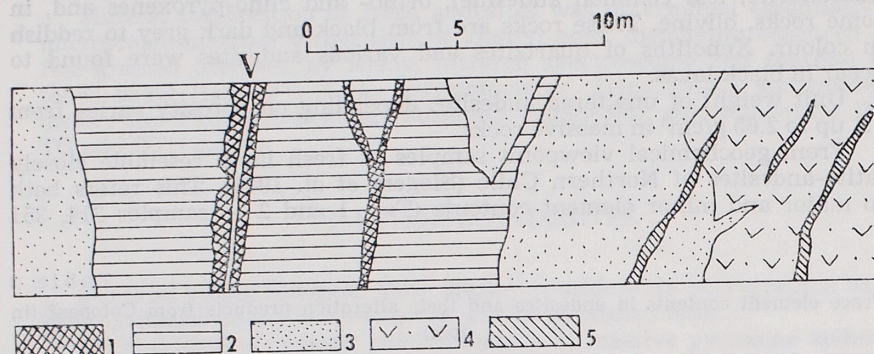
Fig. 2. Scheme of zonality in altered rocks around solfatara vent (region *B* on Fig. 1)
1 — sulphur, *2* — opalite, *3* — alunitized andesites, *4* — oxidized, slightly altered andesite, *5* — gypsum, *V* — solfatara vent

OPALITES

These opal rocks are white and porous, showing very low unit weight (1.17 g/cm^3) and locally containing sulphur aggregates. At the walls of fissures they easily disintegrate to form powder. In thin section we observe preserved vesicular structure of primary andesite, though some irregular pores can be due to leaching of constituents. Relics of primary porphyric texture are also observed.

Chief mineral component of the rock in question is opal, accompanied (within pseudomorphs after feldspar) by small amounts of native sulphur and cristobalite, and, locally, by alunite microlites. These components display zonal distribution, following zonal structure of primary plagioclases. Moreover, larger platy alunite and barite crystals occur sporadically on the margins of pores. Titanium oxide (anatase) occurs as very fine grains, 0.005—0.02 mm in size, dispersed irregularly within opal matrix.

X-ray diffractometer pattern of this rock display a characteristic broad band in the range 5—3 Å and the main reflections of low cristobalite (4.04, 3.13, 2.85, 2.48 Å) and sulphur (3.86, 3.20 Å) accompanied by weak lines of alunite (4.95, 2.96 Å). This indicates that this rock is composed mainly of opal-cristobalite, the idealized structure of which is based on stacking sequence of SiO$_4$ tetrahedral layers ABCABC (Frondel 1962). On heating opal substance loses nearly whole water at 180°C (Fig. 5) and its structure becomes gradually more ordered. At 400°C there disappear the lines of alpha-sulphur (which burns at about 360°C — Fig. 5). Finally, the substance is transformed into high-cristobalite, the strongest reflec-
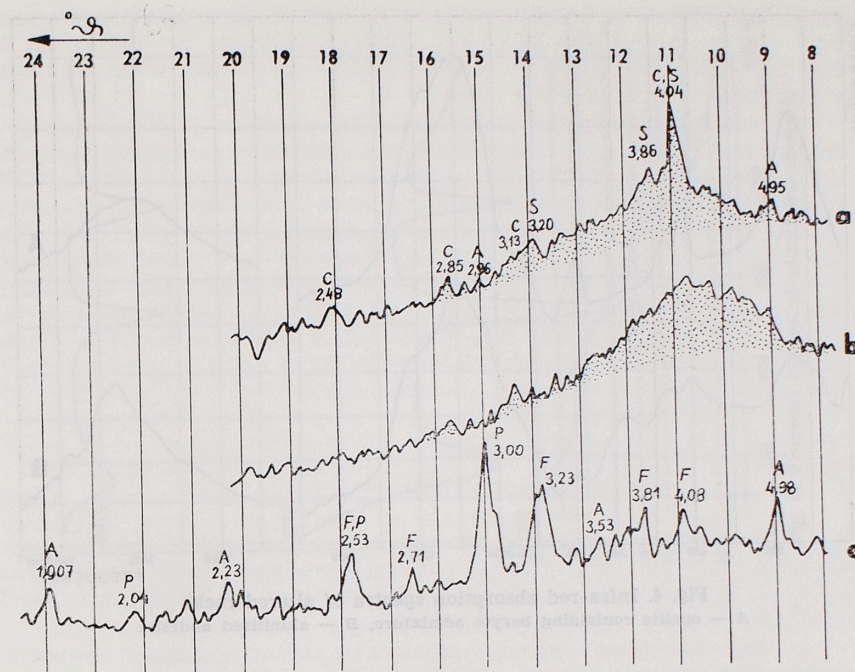
Fig. 3. X-ray diffractometer patterns of altered rocks (CuKα radiation)
a — opalite, *b* — opal from veinlet, *c* — alunitized andesite. Peaks: *A* — alunite, *C* — cristobalite, *F* — feldspar, *P* — pyroxene, *S* — sulphur

tions of which (4.15 and 2.53 Å) were found on X-ray diffractometer pattern of the sample heated to 900°C.

Taking into account the origin and chemical composition of the rock in question, its cristobalitic nature is well justified. Numerous experiments have shown that cristobalite is easily formed in hydrous and alkali-rich environment (Taylor and Lin 1941, Wyart 1943, Papailhau 1957). It should be remembered that this modification of silica show comparatively open structure, enabling substitution of Al for Si and introduction of equically number of Na or K atoms into lattice cavities. Therefore chemical composition of natural cristobalites generally departs from 100 per cent SiO$_2$ and the analyses always show the presence of Al, Na, K, Ca and of other elements in their crystal lattice. Most probably, this is also the case with opal-cristobalite in question, since the number of Al atoms in it corresponds approximately to the sum of charges introduced by Na$^+$, K$^+$ and Ca^{2+} ions (Tab. 3, sample 344).

Infrared absorption curve of opalite containing higher barite admixture is presented in Figure 4. The presence of this mineral was confirmed by X-ray diffractometer pattern of sample heated and evaporated with HF to get rid sulphur and silica, in which the following barite lines were identified: 3.48, 3.37, 3.06, 2.81, 2.70, and 2.09 Å. Increased amount of
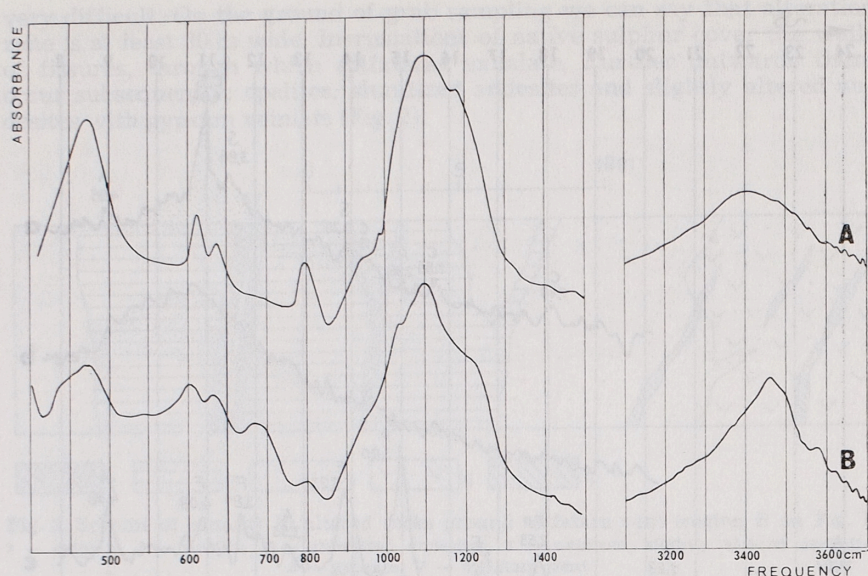
Fig. 4. Infra-red absorption spectra of altered rocks
A — opalite containing baryte admixture, *B* — alunitized andesite

barium in opalite was also determined by spectrochemical analysis (Tab. 2). Very interesting is high concentration of Cr in this strongly altered rocks what can be explained by some crystallochemical similarity of $[CrO_4]$ and $[SO_4]$ complexes.

ALUNITIZED ANDESITES

These rocks are pinkish-grey in colour and distinguish by numerous white spots and scarce vacuoles. Their unit weight is 1.86 g/cm³. Alunitized andesites display relict porphyric texture. Hardly recognizable matrix shows hialopilitic texture. Plagioclase phenocrysts are partly replaced by opal and sometimes by gypsum. Replacement was not complete and operated within some parts of grains, thus making their zoning more distinct. On the other hand, pyroxene phenocrysts exhibit only weak alteration phenomena. Primary vacuoles are partly filled with microcrystalline alunite aggregates. The role of alunite in filling pseudomorphs after feldspars is rather subordinate.

Because of rather obscured microscope picture of this rock, its mineralogical examination was greatly facilitated by applying instrumental technique. Since the alteration products are hydrated and anisodesmic compounds, the most useful here were found to be thermal and infrared absorption methods, supplemented by X-ray analysis (Figs. 3, 4 and 6).

As follow from these as well as from chemical and microscopic data, the new minerals formed are: opal-cristobalite, a little gypsum and fairly
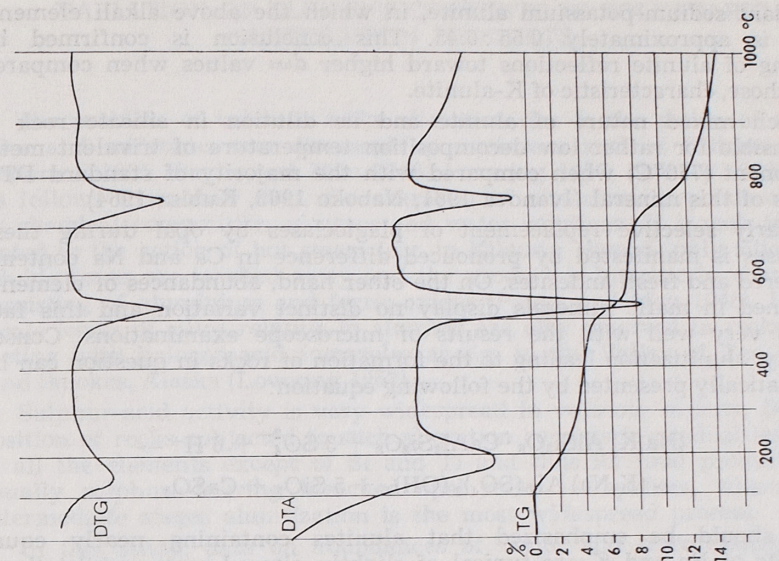
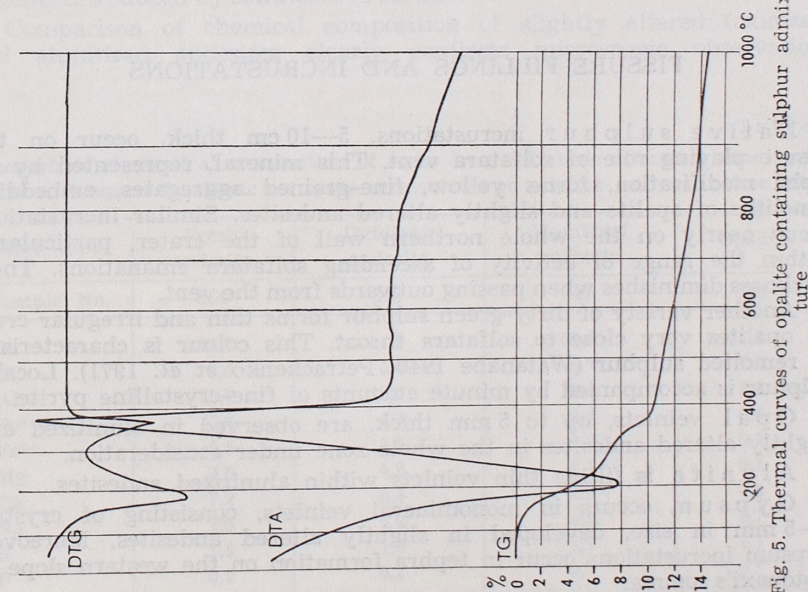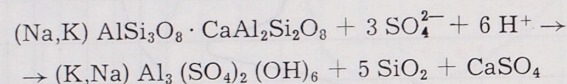Fig. 6. Thermal curves of alunitized andesite

Fig. 5. Thermal curves of opalite containing sulphur admixture

abundant sodium-potassium alunite, in which the above alkali elements ratio is approximately 0.55 : 0.45. This conclusion is confirmed by shifting of alunite reflections toward higher d_{hkl} values when compared with those, characteristic of K-alunite.

Such mixed nature of alunite and its dilution in silicate rock is responsible for rather low decomposition temperature of trivalent metal component (760°C) when compared with the majority of standard DTA curves of this mineral (Ivanova 1961, Naboko 1963, Kubisz 1964).

Nearly selective replacement of plagioclases by opal during these processes is manifested by pronouced difference in Ca and Na contents in altered and fresh andesites. On the other hand, abundances of elements contained in mafic minerals display no distinct variation and this fact agrees very well with the results of microscope examinations. Consequently, alunitization leading to the formation of rocks in question can be schematically presented by the following equation:

$$(Na,K)\, AlSi_3O_8 \cdot CaAl_2Si_2O_8 + 3\, SO_4^{2-} + 6\, H^+ \rightarrow$$
$$\rightarrow (K,Na)\, Al_3\, (SO_4)_2\, (OH)_6 + 5\, SiO_2 + CaSO_4$$

It should be emphasized that alunites containing nearly equal amounts of Na and K are typical of slightly altered rocks, whilst these minerals formed at later stages and precipitated in fissures are nearly purely potassic in character (Sidorov 1967).

As regards trace element contents we observe distinct impoverishment of alunitized andesites in V, Ni, Sr, Ba and Li (Tab. 2).

FISSURE FILLINGS AND INCRUSTATIONS

N a t i v e   s u l p h u r incrustations, 5—10 cm thick, occur on the fissure playing role of solfatara vent. This mineral, represented by its alpha modification, forms yellow, fine-grained aggregates, embedding xenoliths of opalite and slightly altered andesites. Similar incrustations occur nearly on the whole northern wall of the crater, particularly within the range of activity of ascending solfatara emanations. Their thickness diminishes when passing outwards from the vent.

Another variety of dirty-green sulphur forms thin and irregular crust on opalites very close to solfatara throat. This colour is characteristic of remolted sulphur (Watanabe 1940, Petrachenko *et al.* 1971). Locally sulphur is accompanied by minute amounts of fine-crystalline pyrite.

O p a l veinlets, up to 5 mm thick, are observed in alunitized and slightly altered andesites in the whole zone under consideration.

A l u n i t e is filling thin veinlets within alunitized andesites.

G y p s u m occurs in monomineral veinlets, consisting of crystals 2—5 mm in size, developed in slightly altered andesites. Moreover, gypsum incrustations occur in tephra formation on the western slope of Cotopaxi's somma.

VARIATION OF ELEMENT CONTENTS IN SOLFATARIC ALTERATION PRODUCTS

The problem of volcanic rocks alteration due to the action of fumaroles and solfataras was discussed by numerous authors (Rittma 1934, Anderson 1935, Payne and Mau 1946, Lovering 1957, Naboko 1963 etc.). As follows from their data, the character of alterations depends chiefly on chemical composition of gases and water solutions. If a rock is subjected to the action of hot steam (e.g. in Kilauea, Hawaii) only silica and soluble bases are leached away and the product is lateritic in character, consisting of aluminium and ferric oxides (Payne and Mau 1946). Large-scale losses of silica relative to alumina are also observed in rocks contacting with halogen-acid fumaroles as e.g. in the Valley of Ten Thousand Smokes, Alaska (Lovering 1957).

Sulphur-acid activity is very widespread in volcanic regions. Decomposition of rocks subjected to such alteration consists in gradual leaching of all the elements except of Si and Ti and thus its final products are usually sulphure-bearing bleached opal rocks — opalites, whereas at intermediate stages alunitization is the most widespread process.

In this study, data on abundances of major and trace elements in various solfataric alteration products of andesitic lavas at Cotopaxi were obtained which can contribute to our knowledge of their geochemical behaviour during processes under consideration. Such geochemical comparison is much more adequate if we present the contents of major elements in atomic percents after excluding water and sulphur as components introduced by solfataras (Tab. 3).

Comparison of chemical composition of slightly altered (oxidized) and alunitized andesites clearly confirms microscopic observations

Table 3

Comparison of chemical composition of rocks from solfataric alteration zone in the crater of Cotopaxi (in atomic per cents, recalculated on sulphur- and water-free basis)

Rock type	Fresh andesite	Oxidized andesite	Alunitized andesite	Opalite
Sample No.	314	343	345	344
Si	53,7	54,8	59,6	93,3
Ti	0,6	0,6	0,7	0,9
Al	18,7	18,9	19,8	2,8
Fe^{3+}	2,4	4,3	4,5	0,6
Fe^{2+}	3,5	1,5	1,2	0,1
Mg	4,6	4,8	4,1	0,1
Ca	7,2	6,5	2,9	0,3
Na	7,5	6,9	5,2	0,7
K	1,6	1,5	1,7	1,1
P	0,2	0,2	0,3	0,1

showing that solfataric agents are attacking first of all and nearly selectively feldspars and rock matrix, whereas mafic components remain rather unchanged. There is, however, distinct difference in behaviour of calcium and alkalis liberated from plagioclases during their decomposition. Large-scale impoverishment of alunitized rocks in calcium indicates that this element is leached from parent rock by sulphatic solutions and precipitated as gypsum more distant from solfatara vent. Analytical data clearly confirm entirely different geochemical behaviour of the remaining plagioclase components — Al, Na and K. Constancy of abundances of aluminium and potassium and negligible loss of sodium is due to fixation of these elements in the form of alunite, which, contrary to gypsum, is not soluble in acid solutions and fills vacuoles within the rock subjected to solfataric alteration.

Among trace elements the sequence of their leaching is as follows: $Li > Sr > Ba > Rb$. As already mentioned, limited mobility of barium is due to its fixation as insoluble barite, whilst the behaviour of rubidium can be explained by its close crystallochemical affinity to potassium. Under solfataric conditions strontium seems to follow calcium and to concentrate in gypsum veins.

Complete decomposition of all minerals during opalization process results in leaching out nearly all the major components except Si and Ti which are not soluble in sulphur-acid solutions. Some negligible part of Al and alkalis left is incorporated into open opal-cristobalite lattice and contained in scarce alunite relics.

CONDITIONS OF SOLFATARIC ALTERATION PROCESSES

On the ground of this study, field observations and by comparing them with other authors data, it is possible to reconstruct general conditions of alteration of the rocks in question. As already explained, nearly purel siliceous alteration products — opalites — were formed at Cotopaxi around solfataric throat due to direct action of hot sulphur-acid gases and very agressive solutions. At early stage of fumarolic activity these gases could also contain HCl vapours and thus react very strongly with surrounding rocks, leaching the majority of chemical elements. As follows from analyses of Soviet vulcanologists (Naboko 1963, Sidorov 1967) they are fairly concentrated (4—6 grams per litre) and show very low pH (1.3—1.6).

Another alteration products studied — alunitized andesites — were most probably subjected to the action of colder solutions slightly neutralized (to pH = 3—5) by alkalis leached from rocks situated closer to solfatara vents. Contrary to opalitic zone, in alunitic one metasomatism consists in some enrichment (impregnation) of leached components.

Similar zonal sequence of metasomatic alteration was observed e.g. in sulphur deposits of Japan (Mukayiama 1959) and Kamchatka (Borisov et al. 1971). In these volcanic areas, outer kaolinization and saponitization zones were described. It is possible that such zones can also occur at Cotopaxi, outside the sampled zone.

One of important factors, influencing and favouring development of alunitization process, could be the presence of ice, actually covering the vast majority of Cotopaxi's crater. Such cover prevents dilution of volcanogenic solutions by atmospheric waters and, because of cooling effect, can limitate their activity. Simultaneously, no atmospheric precipitates can fall in these open places, where hot emanations operate. Because of such convenient conditions the most important and often coupled alteration processes — alunitization and opalitization — could strongly develop in the crater of Cotopaxi during relatively short period of 30 years that passed since its last effusion.

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PRODUKTY SOLFATAROWYCH PRZEOBRAŻEŃ LAW ANDEZYTOWYCH W KRATERZE WULKANU COTOPAXI (EKWADOR)

Streszczenie

W pracy omówiono wyniki badań geochemiczno-mineralogicznych produktów przeobrażeń law andezytowych przez solfatary czynne w dolnej części krateru jednego z najwyższych czynnych wulkanów świata, Cotopaxi (5897 m). Badania przeprowadzono metodami mikroskopowymi, chemicznymi, spektralnymi oraz przy pomocy analizy rentgenowskiej, spektrofotometrycznej w podczerwieni oraz termicznej.

Wśród skał przeobrażonych wyróżniono dwie główne odmiany: opality i andezyty załunitowane. Pierwsze z nich, występujące w pobliżu ujścia solfatary, złożone są niemal wyłącznie (do 95%) z opalu-krystalitu z domieszką siarki, alunitu i barytu. Załunitowane andezyty, odsłaniające się dalej od solfatary, obok reliktów minerałów pierwotnych zawierają głównie Na—K ałunit i opal-krystalit. W tej strefie pirokseny wykazują znacznie większą odporność niż plagioklazy.

Podczas gdy opality są produktem prawie całkowitego wyługowania wszystkich składników z wyjątkiem Si i Ti, skały załunitowane powstały przez impregnację pęcherzyków pogazowych siarczanem Al, K, Na — pierwiastków odprowadzonych z pierwszej strefy. Wapń jest przenoszony poza obydwie wymienione strefy i stabilizowany w postaci gipsu. Na podstawie przeprowadzonych badań ustalono następujący szereg ruchliwości śladowych alkaliów i ziem alkalicznych w omawianym środowisku: Li > Sr > Rb > Ba. Wśród pierwiastków śladowych grupy żelaza Cr wykazuje najmniejszą ruchliwość a nawet koncentruje się w opalicie.

Przemiany w pierwszej strefie zachodziły pod działaniem gorących i silnie kwaśnych roztworów gazowo-wodnych (przy pH około 1,5), które ulegały, wskutek ługowania składników zasadowych, nieznacznej alkali-

zacji (pH = 3—5), umożliwiającej wytrącanie ałunitu. Powstanie stężonych i silnie kwaśnych roztworów było możliwe w specyficznych warunkach panujących aktualnie w kraterze, przy ograniczonym dostępie wód meteorycznych, powodowanym pokrywą lodową i odparowywaniem opadów w strumieniach gorących emanacji.

Badania wulkanu Cotopaxi przeprowadziła Czechosłowacko-Polska wyprawa Cotopaxi 72 latem 1972, a opracowane próbki pobrali J. Dobrzyński, B. Mlčoch i A. Paulo.

OBJAŚNIENIA FIGUR

Fig. 1. Schematyczna mapa krateru Cotopaxi
  1 — lawy i tufy tworzące strome ściany, 2 — tefra i osypiska zboczowe, 3 — pokrywa śnieżna i lodowa, 4 — ujście solfatar stale aktywnych w okresie sierpień–wrzesień 1972, 5 — krótkotrwałe ekshalacje, 6 — wysokości w metrach, na podstawie Mapa Fisico del Ecuador 1 : 50 000 (1963), pozostałe wysokości wg pomiarów wyprawy czechosłowacko-polskiej, 7 — grzbiety górskie, 8 — osie depresji

Fig. 2. Schemat zonalności skał przeobrażonych dokoła solfatary
  1 — siarka, 2 — opalit, 3 — załunityzowany andezyt, 4 — słabo zmieniony, utleniony andezyt, 5 — gips, V — ujście solfatary

Fig. 3. Dyfraktogramy skał przeobrażonych (promieniowanie CuKα)
  a — opalit, b — opał z żyłki, c — załunityzowany andezyt. Refleksy: A — ałunit, C — krystalit, F — skaleń, P — piroksen, S — siarka

Fig. 4. Spektrogramy absorpcyjne w podczerwieni skał przeobrażonych
  A — opalit z domieszką barytu, B — załunityzowany andezyt

Fig. 5. Derywatogramy opalitu z domieszką siarki

Fig. 6. Derywatogramy załunityzowanego andezytu

Войцех НАРЕМБСКИ, Анджей ПАУЛО

ПРОДУКТЫ СОЛЬФАТАРНЫХ ИЗМЕНЕНИЙ АНДЕЗИТОВЫХ ЛАВ В КРАТЕРЕ ВУЛКАНА КОТОПАХИ (ЭКВАДОР)

Резюме

В работе представлены результаты геохимического и минералогического изучения продуктов преображения андезитовых лав сольфатарами, действующими в нижней части кратера одного из высочайших действующих вулканов мира — Котопахи (5897 м). Исследования проводились методами микроскопического, химического, спектрального, рентгенового, ик-спектроскопического и термического анализов.

Среди измененных пород различаются две разновидности: опалиты и алунитизированные андезиты. Первые из них, распространенные вблизи устья сольфатары, состоят почти исключительно (до 95%) из опала-кристобалита с примесью серы, алунита и барита. Алунитизированные андезиты, залегающие на некотором расстоянии от сольфатары, кроме реликтов первичных минералов, содержат, в основном, натрий-калиевый алунит и опал-кристобалит. В этой зоне пироксены характеризуются намного большей устойчивостью чем плагиоклазы. Опалиты представляют продукт почти полного выщелачивания всех компонентов, кроме кремния и титана, а алунитизированные породы образовались

в результате заполнения пузыристых пустот минералом Al, K, Na — элементов, выщелоченных из первой зоны. Кальций удаляется за пределы обеих зон и концентрируется в виде гипса. По данным проведенных анализов определена последовательность рассеянных элементов по их подвижности в рассматриваемой среде: $Li > Sr > Rb > Ba$. Среди элементов группы железа хром характеризуется наименьшей подвижностью, он даже концентрируется в опалите.

Изменения в первой зоне происходили под влиянием горячих, сильно кислых газогидротермальных растворов (при pH около 1), которые обогащались основными компонентами и превращались в более щелочные растворы (pH = 3—5), которые способствовали выпадению алунита. Образование сильно концентрированных и сильно кислых растворов было возможно в очень специфических условиях, какие наблюдаются в кратере в настоящее время, при ограниченном доступе метеорных вод.

Фиг. 1. Схематическая карта кратера вулкана Котопахи
 1 — лавы и туфы, образующие крутые стенки, *2* — пепел и склоновые осыпи, *3* — снежный и ледовый покров, *4* — устья сольфатар, действующих постоянно в период август — сентябрь 1972 г., *5* — кратковременные эксгаляции, *6* — отметки в метрах, по физической карте Эквадора 1 : 50 000 (1963), остальные отметки по данным измерений Чехословацко-Польской экспедиции, *7* — горные хребты, *8* — оси долин

Фиг. 2. Схема зональности измененных пород вокруг сольфатары
 1 — сера, *2* — опалит, *3* — алунитизированный андезит, *4* — мало измененный, окисленный андезит, *5* — гипс, *V* — устье сольфатары

Фиг. 3. Дифрактограммы измененных пород (излучение CuK_α)
 a — опалит, *b* — опал из прожилка, *c* — алунитизированный андезит. Пики: *A* — алунит *C* — кристобалит, *F* — полевой шпат, *P* — пироксен, *S* — сера

Фиг. 4. ИК-спектрограммы поглощения измененных пород
 A — опалит с примесью барита, *B* — алунитизированный андезит

Фиг. 5. Дериватограммы опалита с примесью серы

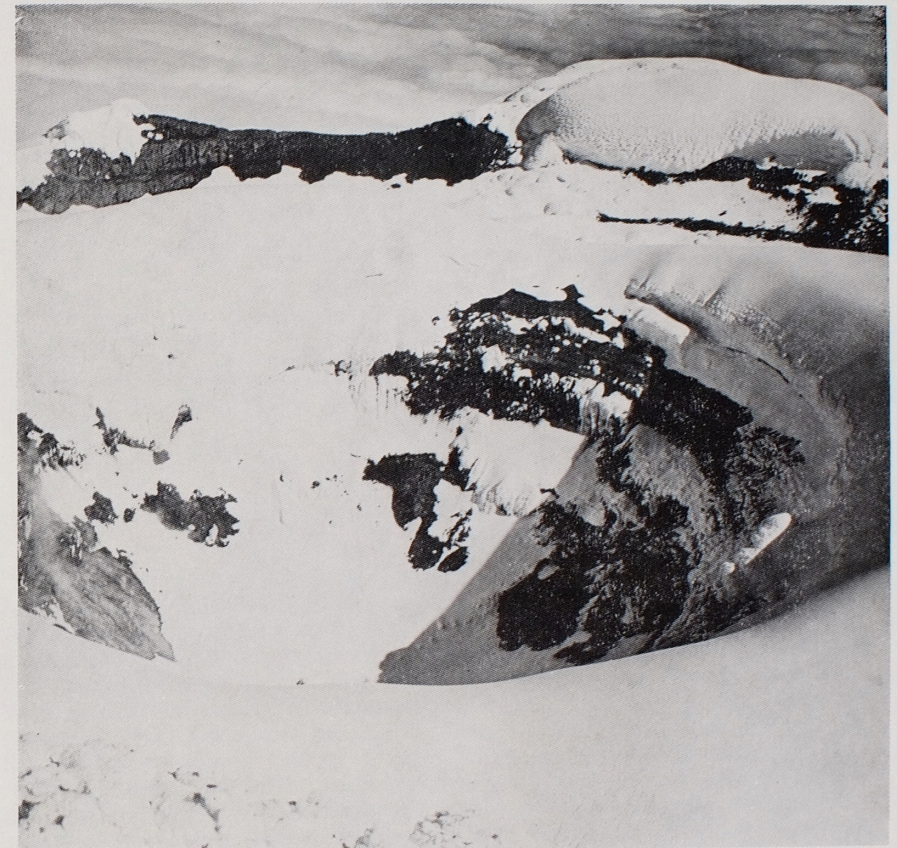Фиг. 6. Дериватограммы алунитизированного андезита

PLATE I (PLANSZA I, ТАБЛИЦА I)

Phot. 1. Crater of Cotopaxi viewed from summit towards the south. Crater rim and vast part of the interior covered with snow. At the left clouds of solfatara vapours above altered andesites. In the background fragment of somma with snowy southern summit (approx. 5830 m)

Photo: *J. Dobrzyński*

Krater Cotopaxi widziany z wierzchołka ku południowi. Brzeg krateru i znaczna część wnętrza pokryte śniegiem. Po lewej obłoki solfatarowe ponad przeobrażonymi andezytami. Na dalszym planie fragment sommy wraz z ośnieżonym południowym wierzchołkiem (około 5830 m)

Вид на кратер вулкана Котопахи с вершины, в южном направлении. Край кратера и значительная часть полости покрыты снегом. Слева сольфатаровые облака над измененными андезитами. На заднем плане часть двойникового вулкана с заснеженной южной вершиной (около 5830 m)

Phot. 1

Wojciech NARĘBSKI, Andrzej PAULO — Solfataric alteration products of andesitic lavas in the crater of Cotopaxi volcano, Ecuador